United States
Environmental Protection
Agency

Air Pollution Training Institute
MD 20
Environmental Research Center
Research Triangle Park, NC 27711

EPA 450/2-82-004
July 1983

Air

APTI
Correspondence Course 434
Introduction to Ambient Air Monitoring

Guidebook
Second Edition

Technical Content:
B. M. Ray

Instructional Design:
M. M. Peterson

Northrop Services, Inc.
P.O. Box 12313
Research Triangle Park, NC 27709

Under Contract No.
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EPA Project Officer
R. E. Townsend

United States Environmental Protection Agency
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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Air

APTI
Correspondence Course 434

Introduction to Ambient Air Monitoring

Guidebook

Prepared By:

ICES Ltd.
180 Providence Road, Suite 1A
Chapel Hill, NC 27514

Under Contract No. 68D60059

United States Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Notice

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Table of Contents

Course Introduction

Overview of Course

Course Description

This training course is a 50-hour correspondence course about ambient air quality monitoring. This course introduces terms used in air monitoring and presents practical information about the monitoring process. Theoretical monitoring concepts are also described. Course topics include the following:

- ambient air monitoring objectives
- ambient air sampling train design
- basic gas properties
- air movers and air measuring devices
- statistical techniques pertaining to air monitoring
- ambient sampling of particulate matter
- manual sampling of ambient gaseous pollutants
- calibration gas preparation
- reference methods and reference measurement principles for the criteria pollutants
- continuous air quality monitors
- air quality monitoring network design.

Course Goal

To familiarize you with general information about the reference methods and reference method principles for the criteria pollutants, continuous air quality monitors, air quality monitoring network design, and statistical techniques pertaining to ambient air monitoring. This course will also familiarize you with detailed information concerning basic gas properties, particulate matter sampling, manual sampling of ambient gaseous pollutants, and calibration of air quality monitors.

Course Objectives

Upon completion of this course, you should be able to

1. identify at least six objectives of ambient air quality monitoring.
2. describe and correct for the effects of temperature and pressure on measured air volumes.
3. recognize at least seven air movers and at least 13 air measuring devices used in atmospheric sampling.
4. identify at least six inertial collection devices, optimum inertial sampling conditions, at least five inertial sampling sources of error, and two applications of the inertial sampling of particulate matter.
5. identify considerations for the operation, maintenance, and calibration of high volume samplers and identify and describe how to minimize potential sources of error in high volume sampling.
6. describe how at least four filtration mechanisms are affected by filter and sampling conditions and identify the advantages and disadvantages of cellulose, glass fiber, and membrane filters.
7. describe the principles and relevant equipment for PM_{10} and $PM_{2.5}$ sampling.
8. recognize and describe the effects of at least five sampling conditions on the collection efficiencies of liquid absorbers.
9. identify and describe the effects of at least four sampling conditions on the adsorption of gaseous pollutants.
10. identify optimum conditions for preparing calibration gases using bags, permeation tubes, single dilution systems, and double dilution systems and calculate the concentrations of these gases.
11. recall advantages and disadvantages of at least six absorbents used in the preparation of zero air or the removal of water vapor from a gas stream.
12. identify the reference methods and reference measurement principles for the criteria pollutants.
13. recall advantages and disadvantages of coulometric, amperometric, second derivative spectroscopic, flame photometric, fluorescence, chemiluminescence, ultraviolet photometric, and nondispersive infrared air quality monitors.
14. identify major considerations in designing the sensor and data systems of an ambient air quality monitoring network.
15. recall requirements unique to PM monitoring within network design and site selection.
16. interpret and construct statistical graphs for analyzing ambient air monitoring data.

Sequence, Lesson Titles, and Trainee Involvement Time

Lesson number	Lesson title	Trainee involvement time (hours)
Part A		
A-1	Introduction to Atmospheric Sampling and Basic Properties of Gases	7
A-2	Air Movers and Air Measuring Instruments	7
A-3	Particulate Matter Sampling	8
A-4	Introduction to Pertinent Statistical Techniques for Air Monitoring	7
Part B		
B-1	Manual Sampling of Gaseous Pollutants	7
B-2	Preparation of Calibration Gases	7
B-3	Introduction to the Reference Methods and Reference Measurement Principles for the Criteria Pollutants, Continuous Air Quality Monitors, and Design of Air Quality Monitoring Networks	7

Requirements for Successful Completion of this Course

In order to receive 5.0 Continuing Education Units (CEUs) and a certificate of course completion, you must achieve a final course grade of 70 (out of 100).

Use of Course Materials

Necessary Materials

- *APTI Correspondence Course 434 Introduction to Ambient Air Monitoring Guidebook Second Edition*
- EPA 450/2-80-004, *APTI Course 435 Atmospheric Sampling: Student Manual, Third Edition*
- pencil or pen
- calculator (recommended)

Use of this Guidebook

Relationship Between Guidebook and Assigned Reading Materials

This guidebook directs your progress through the reference text *APTI Course 435 Atmospheric Sampling: Student Manual, Third Edition.*

Description of Guidebook Sections

This guidebook contains reading assignment sections which correspond to lessons of the course.

Each section contains the following:

- reading assignment
- reading assignment topics
- section's learning goal and objectives
- reading guidance
- review exercise

Please ***do not*** write in this guidebook.

Instructions for Completing the Quizzes and Examinations

- You should have received, along with this guidebook, a separate ***sealed*** envelope containing two quizzes and an examination.
- You must arrange to have someone serve as your test supervisor.
- You must give the ***sealed*** envelope containing the quizzes and examination to your test supervisor.
- At designated times during the course, under the supervision of your test supervisor, complete the quizzes and the final exam.

- After you have completed each quiz or exam, your test supervisor must sign a statement on the quiz/exam answer sheet certifying that the quiz/exam was administered in accordance with the specified test instructions.
- After signing the quiz/exam answer sheet, your test supervisor must mail the quiz/exam and its answer sheet to the following address:

  Air Pollution Training Institute
  Education and Outreach Group
  MD 17
  Research Triangle Park, NC 27711
- After completing a quiz, continue with the course. Do ***not*** wait for quiz results.
- Quiz/exam and course grade results will be mailed to you.

If you have questions, contact:

Air Pollution Training Institute
Education and Outreach Group
MD 17
Research Triangle Park, NC 27711

Part A

Section A-1

Introduction to Atmospheric Sampling and Basic Properties of Gases

Reading Assignment

Pages 1-1 through 2-34 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Objectives of air monitoring
- Sampling train design
- Temperature and pressure measurement
- Ideal Gas Law
- Gas density and viscosity
- Units of measurement
- Air monitoring terminology

Learning Goal and Objectives

Learning Goal

The purpose of this section is to familiarize you with objectives of air monitoring, air monitoring terminology, sampling train design, and basic properties of gases.

Learning Objectives

At the end of this section, you should be able to:

1. state the purposes of primary and secondary National Ambient Air Quality Standards (NAAQS) and identify the pollutants for which NAAQS have been established.
2. identify at least six objectives of ambient air quality monitoring.
3. identify the locations of sampling train components in a typical sampling train.
4. identify four temperature scales used in atmospheric sampling and convert temperatures from one scale to another.
5. define pressure terms used in atmospheric sampling.
6. describe pressure measuring devices used in ambient air quality monitoring.
7. explain the effects of temperature and pressure on sampled air volumes.

8. correct sampled air volumes to EPA's Standard Temperature and Pressure (STP) conditions for ambient air monitoring.
9. define the following gas characteristics: density, viscosity, molar volume, specific gravity, and Reynold's number.
10. report values commonly measured in ambient air sampling using their appropriate reporting units.
11. convert between pollutant concentrations expressed in parts per million (ppm) and those expressed in micrograms per cubic meter ($\mu g/m^3$).

Reading Guidance

- Refer often to the equations, example calculations, and figures of the assigned reading material as you progress through the assignment.
- When you have finished the reading assignment, complete the review exercise for Section A-1. It begins on the following page.
- After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
- For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment indicated on the answers page.
- After you have reviewed your incorrect answers (if any), proceed to Section A-2 of this guidebook.

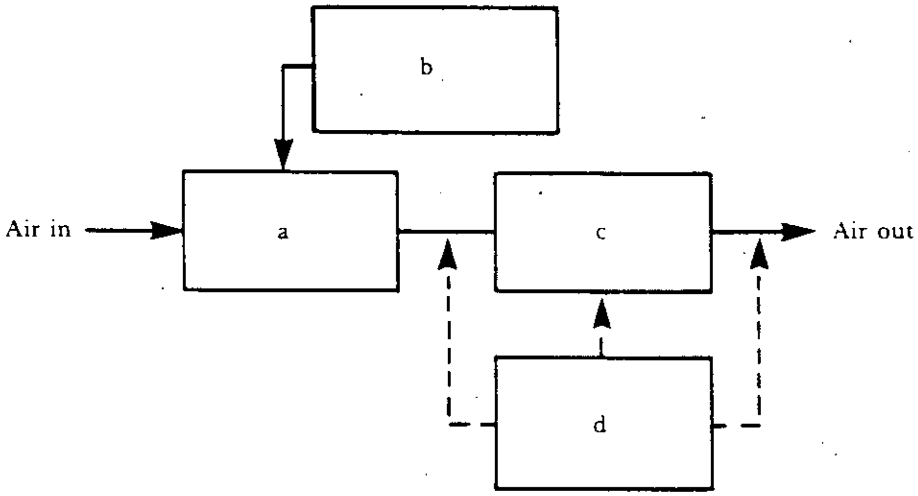
Review Exercise

Now that you've completed the assignment for Section A-1, please answer the following questions. These will help you determine whether or not you are mastering the material. Please do not write in this guidebook.

1. National Ambient Air Quality Standards (NAAQS) have been established for which of the following?
   a. sulfur dioxide
   b. total suspended particulate matter
   c. mercury
   d. both a and c, above
   e. both a and b, above
2. Which of the following has no NAAQS?
   a. nitric oxide
   b. nitrogen dioxide
   c. lead
   d. ozone
3. Primary NAAQS are established to protect public ____(?)____.
   a. health
   b. welfare
   c. health and welfare
   d. none of the above
4. Secondary NAAQS are established to protect public ____(?)____.
   a. health
   b. welfare
   c. health and welfare
   d. none of the above
5. True or False? State implementation plans (SIPs) are air pollution control strategies used by the States to attain and maintain the NAAQS.
6. Which of the following is ***not*** a possible objective of ambient air quality monitoring?
   a. determine attainment of NAAQS
   b. evaluate progress in achieving/maintaining NAAQS
   c. develop or revise SIPs
   d. review air quality impacts of new sources of air pollution
   e. determine emission rates of pollutants from stacks

7. Which of the following is a(are) possible objective(s) of ambient air quality monitoring?
   a. establish baseline air quality levels for preventing the significant deterioration of air quality
   b. provide data for the development/validation of air pollution dispersion models
   c. provide data for the development/validation of in-situ stack emission monitors
   d. both a and b, above
   e. all of the above

8. In the typical sampling train depicted below, a, b, c, and d are the ___(?)___ respectively.
   a. flow measuring device, sample collection device, air mover, and contaminant detector
   b. sample collection device, contaminant detector, air mover, and flow measuring device
   c. air mover, sample collection device, sample manifold, and contaminant detector
   d. sample collection device, sample manifold, air mover, and flow measuring device



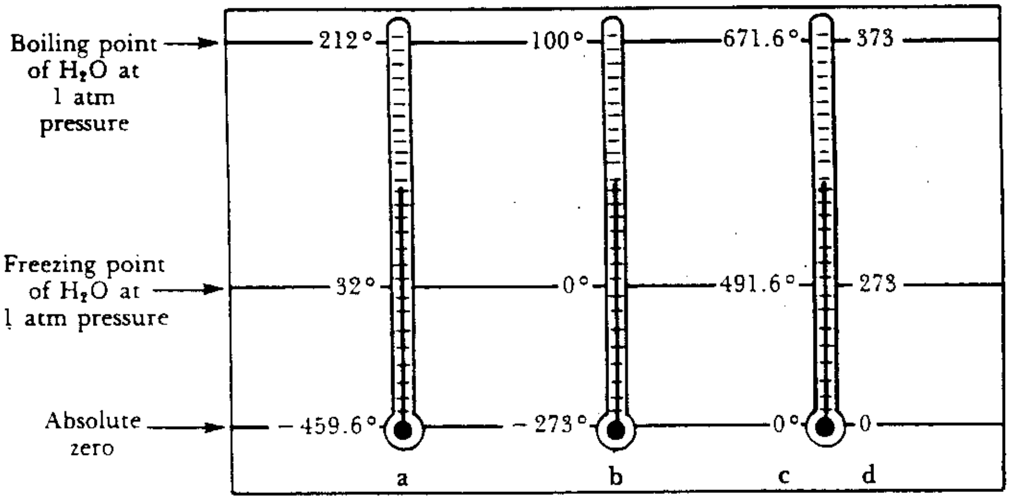
9. In air sampling trains, air movers and flow measuring devices should be placed ___(?)___ sample collection devices to avoid contamination of the sample air stream.
   a. downstream of
   b. upstream of
   c. at the same location as

10. In an air sampling train, inert materials should be used ____(?)____ of the sample collection device to avoid contamination/loss of the pollutant being sampled.
    a. downstream
    b. upstream
    c. upstream and downstream

11. True or False? Use of long sampling lines should be avoided because they enhance the possible sampling line wall loss of sample pollutant.

12. True or False? Components of air sampling trains must be protected from damage caused by sampled air and products of the measurement system.

13. In the figure below, a, b, c, and d are the ____(?)____ temperature scales respectively.
    a. Fahrenheit, Celsius, Rankine, and kelvin
    b. Celsius, Fahrenheit, kelvin, and Rankine
    c. kelvin, Fahrenheit, Celsius, and Rankine
    d. Rankine, Fahrenheit, kelvin, and Celsius



14. 68 degrees Fahrenheit equals ____(?)____ degrees Celsius.
    a. 38
    b. 6
    c. 20
    d. 25

15. 10 degrees Celsius equals ____(?)____ degrees Fahrenheit.
    a. 50
    b. −14
    c. 32
    d. 65

16. 25 degrees Celsius equals ___(?)___ kelvin.
    a. 248
    b. 273
    c. 298
    d. 312

17. 25 degrees Fahrenheit equals ___(?)___ degrees Rankine.
    a. 460
    b. 435
    c. 550
    d. 485

18. The temperature at which a gas, if it did not condense, would theoretically have a volume of zero is called ___(?)___.
    a. critical temperature
    b. dew point temperature
    c. absolute zero

19. Absolute zero is equal to ___(?)___ degrees Celsius and ___(?)___ degrees Fahrenheit.
    a. 273, 460
    b. −273, −460
    c. −460, −273
    d. 460, 273

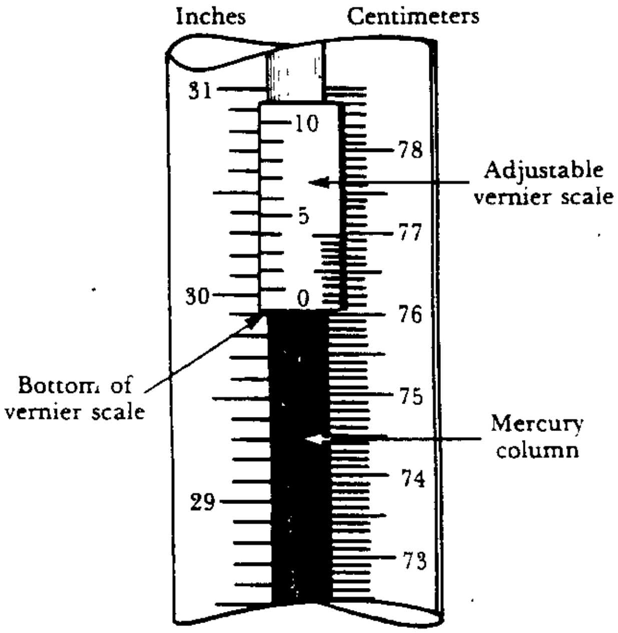
20. Pressure is expressed as ___(?)___ per unit ___(?)___.
    a. force, area
    b. force, volume
    c. area, force
    d. volume, force

21. Pressure is equal in ___(?)___ directions at a point within a volume of fluid and acts ___(?)___ to a surface.
    a. some, perpendicular
    b. all, horizontal
    c. all, perpendicular
    d. some, horizontal

22. The height of the mercury column in a Fortin barometer is measured from the ___(?)___ of the ivory index point to the ___(?)___ of the mercury column.
    a. middle, top
    b. tip, top
    c. tip, middle
    d. middle, middle

23. Before measuring barometric pressure using a Fortin barometer, the mercury level in the barometer's cistern is adjusted until the ivory index point ___(?)___ the surface of the mercury.
    a. is completely under
    b. is halfway below
    c. just pricks

24. The barometer scale depicted below indicates a barometric pressure of ___(?)___ cm of mercury.
    a. 29.94
    b. 76.50
    c. 76.00
    d. 76.05



25. Aneroid barometers are usually ___(?)___ as(than) Torricelli-type barometers.
    a. not as accurate
    b. as accurate
    c. more accurate

26. For a barometric pressure of 760 mm of mercury, systems having internal pressures of 770 mm and 750 mm of mercury would have gage pressures of ___(?)___ and ___(?)___ mm of mercury respectively.
    a. 770, 750
    b. 10, − 10
    c. − 10, 10

27. True or False? The total pressure of a gas mixture is the sum of its partial pressures.

28. At constant temperature, the volume of a gas ___(?)___ as the pressure exerted on it ___(?)___.
   a. decreases, increases
   b. decreases, decreases
   c. increases, increases

29. At constant pressure, the volume of a gas ___(?)___ as the temperature of the gas ___(?)___.
   a. decreases, increases
   b. increases, decreases
   c. increases, increases

30. EPA's standard temperature and pressure (STP) conditions for ambient air monitoring are ___(?)___ degrees Celsius and ___(?)___ mm of mercury.
   a. 20, 760
   b. 25, 760
   c. 25, 700
   d. 20, 700

31. Molar volume at EPA's STP conditions is ___(?)___ liters.
   a. 22.41
   b. 24.46
   c. 20.08
   d. 26.35

32. The density of sulfur dioxide (molecular weight: 64 g/g•mol) at EPA's STP conditions is ___(?)___ g/ℓ.
   a. 2.6
   b. 1.0
   c. 16.3
   d. 46.2

33. Which of the following equations is used to correct air volumes sampled to EPA's STP conditions?
   a. $V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$
   b. $V_2 = (V_1)\left(\frac{P_2}{P_1}\right)\left(\frac{T_2}{T_1}\right)$
   c. $V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_1}{T_2}\right)$
   d. $V_2 = (V_1)\left(\frac{P_1}{T_1}\right)\left(\frac{P_2}{T_2}\right)$

   Where:
   V_2 = corrected volume of air at P_2 and T_2, ℓ
   V_1 = initial volume of air at P_1 and T_1, ℓ
   T_1 = initial temperature of air, K
   T_2 = 298 K
   P_1 = initial pressure of air, mm Hg
   P_2 = 760 mm Hg

34. The viscosity of a gas ___(?)___ as the temperature of the gas ___(?)___.
   a. increases, increases
   b. increases, decreases
   c. decreases, increases

35. The ___(?)___ the Reynold's number, the ___(?)___ is the effect of viscous forces.
   a. smaller, smaller
   b. larger, smaller
   c. larger, larger

36. Which of the following should be considered when reporting measured pollutant concentrations?
   a. Ideally, units reported should be the same as units measured.
   b. Should avoid multiplying measured values by larger numbers for extrapolation purposes.
   c. When air volumes are sampled, sampling temperature and pressure should be reported.
   d. all of the above

For each of questions 37 through 42, select the preferred reporting unit for each of the following parameters.

37. particulate pollutant concentration
38. gaseous pollutant concentration
39. temperature
40. time
41. pressure
42. air sampling rate

a. $\mu g/m^3$ at EPA's STP
b. ppm/ppb
c. degrees Fahrenheit
d. degrees Celsius
e. inches of mercury
f. mm of mercury
g. 12:00 am to 12:00 pm
h. 0000 to 2400
i. m^3/min
j. ft^3/min

43. 0.489 ppm of SO_2 (molecular weight: 64 g/g•mol) at EPA's STP is equal to ___(?)___ $\mu g/m^3$ of SO_2.
   a. 1,400
   b. 1.28
   c. 187
   d. 1,280

44. 640 $\mu g/m^3$ of SO_2 (molecular weight: 64 g/g•mol) at EPA's STP is equal to ___(?)___ ppm of SO_2.
   a. 0.245
   b. 245
   c. 1.67
   d. 16.7

For each of questions 45 through 57, match the term with its definition.

45. pressure
46. absolute pressure
47. pressure-head
48. partial pressure
49. density
50. viscosity
51. laminar flow
52. turbulent flow
53. specific gravity
54. Reynold's number
55. standard barometric pressure
56. molar volume
57. efficiency

a. resistance to flow
b. mass per volume
c. unit compressive stress in a fluid
d. the sum of barometric pressure and gauge pressure
e. pressure exerted by one component of a gas mixture
f. the height of a column of fluid required to produce a given pressure at its base
g. $\frac{\text{inertial force of a fluid}}{\text{viscous force of a fluid}}$
h. parallel movement of fluid layers
i. $\frac{\text{attained performance}}{\text{absolute performance}}$
j. haphazard movement of fluid
k. $\frac{\text{density of a substance}}{\text{density of a reference substance}}$
l. the average atmospheric pressure at sea level, 45° north latitude, and 35 degrees Fahrenheit; equivalent to a pressure of 1033.23 grams-force per cm^2 exerted at the base of a column of mercury having a height of 760 mm
m. the volume of one mole of a gas at a specified temperature and pressure

58. A barograph is the combination of a(n) ____(?)____ and a(n) ____(?)____.
    a. aneroid barometer, Fortin barometer
    b. aneroid barometer, automatic recording device
    c. Fortin barometer, automatic recording device

59. Ideal gases are gases whose molecules ____(?)____ one another and which occupy ____(?)____.
    a. do not attract, no space
    b. do not attract, space
    c. attract, no space
    d. attract, space

60. A mole of a substance is the substance's ____(?)____ expressed in mass units.
    a. density
    b. atomic number
    c. molecular weight
    d. viscosity

Section A-1

Review Exercise Answers

		Page(s) of *Atmospheric Sampling: Student Manual*
1.	e	1-1
2.	a	1-1
3.	a	1-1
4.	b	1-1
5.	True	1-1
6.	e	1-1, 1-2
7.	d	1-1, 1-2
8.	b	1-3
9.	a	1-4
10.	b	1-4
11.	True	1-4
12.	True	1-4
13.	a	2-2
14.	c	2-1
15.	a	2-1
16.	c	2-1
17.	d	2-1
18.	c	2-1
19.	b	2-1
20.	a	2-3
21.	c	2-3
22.	b	2-5
23.	c	2-5
24.	d	2-6
25.	a	2-6
26.	b	2-9
27.	True	2-11
28.	a	2-12
29.	c	2-12
30.	b	2-15
31.	b	2-14
32.	a	2-14
33.	a	2-15
34.	a	2-17
35.	b	2-18
36.	d	2-22
37.	a	2-23
38.	b	2-23

		Page(s) of *Atmospheric Sampling: Student Manual*
39.	d	2-23
40.	h	2-23
41.	f	2-24
42.	i	2-24
43.	d	2-24, 2-25
44.	a	2-24, 2-25
45.	c	2-3
46.	d	2-9
47.	f	2-11
48.	e	2-11
49.	b	2-14
50.	a	2-15
51.	h	2-20
52.	j	2-20
53.	k	2-33
54.	g	2-17
55.	l	2-3
56.	m	2-14
57.	i	2-28
58.	b	2-7
59.	a	2-12
60.	c	2-13

Required Readings

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ICES Ltd.
180 Providence Road, Suite 1A
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Table of Contents

Appendix 2: Code of Federal Regulations – Title 40

Chapter 1

An Introduction to Atmospheric Sampling

Objectives of Air Monitoring

National Ambient Air Quality Standards (NAAQS) for sulfur dioxide, total suspended particulate matter (TSP), carbon monoxide, ozone, nitrogen dioxide, and lead are in effect under the authority of the Clean Air Act (as amended August, 1977). There are two types of ambient air quality standards—primary standards and secondary standards. As stated in Section 109 of the Clean Air Act, primary standards are those, "the attainment and maintenance of which are requisite to protect the public health." The section further defines a secondary ambient air quality standard as, "a level of air quality attainment and maintenance of which is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutants in the ambient air."

These primary and secondary ambient air quality standards must be achieved throughout the United States and its possessions. In order to meet the standards, states are required to develop and implement air pollution control strategies through the mechanism of State Implementation Plans (SIPs). The implementation plans may contain control strategies such as industrial and urban zoning, the development or expansion of mass transit systems and vehicle inspection and maintenance programs, and the establishment of stationary source emissions standards for specific industrial categories. Ambient air monitoring plays a vital role in the development and evaluation of these control strategies. During the development phase, air quality data is used to determine if an area is attaining or not attaining the air quality standards. This determination is critical for the proper designing of control strategies for the area in question because attainment areas usually require less stringent control measures than nonattainment areas. Furthermore, air quality data may be used to generate or validate computer models of air pollution dispersion which are then used in the development of control strategies. After the implementation plans containing their various control strategies have been put into force, further ambient air quality monitoring is required in both attainment and nonattaiment areas. For areas that have achieved attainment, further monitoring is necessary to assure that attainment is maintained. Additional monitoring is required in nonattainment areas for evaluating progress toward reaching attainment.

In addition to the requirement that the primary and secondary National Ambient Air Quality Standards be achieved and maintained throughout the country, the Clean Air Act also stipulates that no significant deterioration of existing air quality will be allowed in any portion of any state. In order to comply with this provision, it is necessary to determine the impact on the existing air quality of an area by a planned new emissions source. The estimated emissions contributed by the new source must be compared to the existing air quality to ascertain whether the new source would significantly deteriorate the present air quality. Ambient air quality monitoring data is used to establish the preexisting air quality of the area in question.

It should be recognized that the overall goal of an air quality monitoring network is the protection of human health and welfare. The aforementioned monitoring objectives should assure the attainment of this goal under ordinary circumstances. However, rarely occurring meteorological conditions such as temperature inversions, which cause poor air pollutant dispersion, may result in the formation of pollutant levels that could cause significant harm to public health. These significant harm levels are listed in Table 1-1. Air pollution emergency episode plans are utilized to prevent pollutant levels from reaching concentrations which would cause significant harm to the health of persons. The plans specify incremental reductions of source emissions based on up-to-date ambient air monitoring data.

Table 1-1. Significant harm levels established by the Environmental Protection Agency.

Pollutant	Concentration	Averaging time
SO_2	2620 $\mu g/m^3$ 1.0 ppm	24 hr.
Particulate matter (TSP)	1000 $\mu g/m^3$	24 hr.
(SO_2) (particulate matter)	490×10^3 $(\mu g/m^3)^2$	24 hr.
CO	57.5 mg/m^3 50 ppm	8 hr.
	86.3 mg/m^3 75 ppm	4 hr.
	144 mg/m^3 125 ppm	1 hr.
Ozone	1200 $\mu g/m^3$ 0.6 ppm	1 hr.
NO_2	3750 $\mu g/m^3$ 2.0 ppm	1 hr.
	938 $\mu g/m^3$ 0.5 ppm	24 hr.

Sampling Train Design

Most atmospheric sampling techniques make use of a sampling train similar to the block diagram in Figure 1-1. Air containing the pollutant of interest enters the sampling train and passes through a sample collection device. This device either physically or chemically removes the pollutant from the air stream, holds the polluted air for later analysis, or allows the pollutant to be analyzed simultaneously with the collection. Ideally, only the pollutant of interest is collected. This is seldom the case, however; hence, interferences must be considered when measurements are made.

Many sampling techniques use collection devices that remove the pollutant from the air for later analysis. Wet chemical methods, such as the pararosaniline method for sulfur dioxide (SO_2), remove the pollutant from the air and hold the pollutant by means of a chemical reaction for later analysis. In the pararosaniline method, the sample collection device is a bubbler containing an absorbing reagent. The High Volume method for total suspended particulate matter (TSP) uses a filter as the sample collection device. In either case, the pollutant is held by the collector for analysis by a contaminant detector. [The contaminant detector in the pararosaniline method is a spectrophotometer; for TSP High Volume sampling, it is a gravimetric balance.]

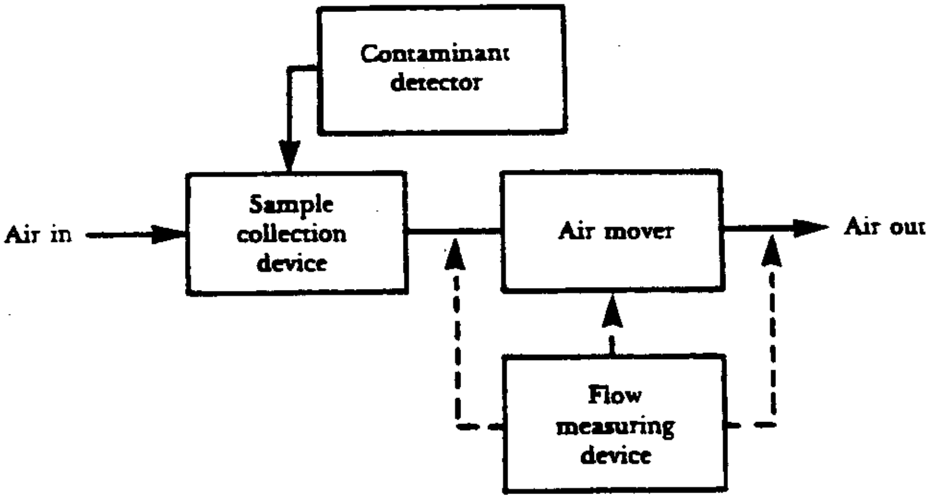


Figure 1-1. Typical sampling train.

Instrumental methods such as chemiluminescence for nitrogen dioxide (NO_2) and ozone (O_3) combine the sample collector and the contaminant detector into one device.

Some methods of air sampling are used that collect a volume of polluted air for later analysis. These methods usually make use of grab or integrated sampling using containers made of stainless steel, glass, or pliable plastic, or by using simple hypodermic syringes. Many factors are important in considering what material should be used when grab sampling; many uses have been found for plastic bags. In this type of sampling, the plastic bag, syringe, stainless steel or glass container is the sample collection device. Contaminant detection is usually accomplished by instrumental analysis.

Mechanisms used to move air through the sample collection device and measure the quantity of air are integral parts of sampling trains. Air movers are usually motor-driven pumps. When motor-driven pumps are not practical, ejectors, displacement methods, and evacuated flasks can be used. Some typical flow measuring (or controlling) devices for sampling are rotameters, mass flow meters, and critical and subcritical orifices. It is often necessary to determine how long an air mover has pulled a certain flow rate to determine the volume sampled (*volume = flow rate × time*); therefore, the sampling time is recorded. Placement of the flow measuring device is dependent on what device is used. Air movers and flow measuring devices are usually placed after sample collection devices to avoid contamination of the air stream.

Materials used in a sampling train (at least to as far as the collector) must be sufficiently inert to the pollutant of interest so as not to interfere with collection. If the air mover and flow measuring device must be placed before the collection step, then parts of those devices contacting the air stream must be inert. Glass, Teflon®, and stainless steel are generally considered to be nonreactive. Hence, these materials have been used extensively in sampling train construction. However, the materials listed as being generally nonreactive can become reactive if used to sample the wrong environment. For instance, glass could not be used if a sampling train were being built to monitor hydrofluoric acid. Even if a material is considered nonreactive, significant wall loss can occur if sampling lines are too long.

Interference with the measurement of an air pollutant is not the only consideration important to the selection of sampling train materials. Care must be taken to protect sampling train components from damage caused by the sampled air or products of the measurement system. If a rubber diaphragm pump is to be used in conjunction with an analyzer that measures nitrogen oxides by the reaction of nitric oxide (NO) with ozone (O_3), then a charcoal filter must be used before the pump to remove excess ozone. If ozone is allowed to contact the rubber diaphragm of the pump, the rubber will deteriorate. Other sampling train components that usually need protection are rotameters and small orifice meters. In this case, a filter and moisture trap are placed in front of the orifice or rotameter to prevent them from becoming clogged.

References

Schuette, F. J. 1967. Plastic bags for collection of gas samples. *Atmospheric Environment* 1:515-519.

U.S. Environmental Protection Agency (EPA). June 1977. *Air Monitoring Strategy for State Implementation Plans*. EPA 450/2-77-010.

U.S. Environmental Protection Agency (EPA). 40 CFR Pt. 50 (July 1, 1979).

U.S. Environmental Protection Agency (EPA). 40 CFR Pt. 51 (July 1, 1979).

Chapter 2

Basic Gas Properties and Mathematical Manipulations

Temperature

The Fahrenheit and Celsius Scales

The range of units on the Fahrenheit scale between the freezing and boiling point of water at one atmosphere (atm) pressure is 180 (212°F − 32°F = 180°F); on the Celsius scale, the range is 100 (100°C − 0°C = 100°C). Therefore, each Celsius degree is equal to 9/5 or 1.8 Fahrenheit degrees. To be able to convert from one system to the other, the following equations can be used:

(Eq. 2-1) $$°F = 1.8°C + 32$$

(Eq. 2-2) $$°C = \frac{(°F - 32)}{1.8}$$

Where:
°F = degrees Fahrenheit
°C = degrees Celsius.

Absolute Temperature

Experiments in which a gas volume is determined as a function of temperature (at a constant pressure) yield results similar to the data presented in Figure 2-1(a). The solid portion of each line represents the gaseous state. If each line is extrapolated (dashed portion of line) to a volume of zero, they all intersect at a common temperature (−273.15°C or −459.67°F). This is the temperature at which a gas, if it did not condense, would theoretically have a volume of zero. This temperature (−273.15°C or −459.67°F) is called ***absolute zero***. Another temperature scale, developed by and named after English physicist Lord Kelvin, begins at absolute zero and has temperature intervals equal to Celsius units. This absolute temperature scale is in units of ***degrees Kelvin*** (K). A similar scale was developed to parallel the Fahrenheit scale and is called the ***Rankine scale*** (°R). The following formulas can be used to convert temperatures to their respective absolute scales.

(Eq. 2-3) $$K = °C + 273.16$$

(Eq. 2-4) $$°R = °F + 459.67$$

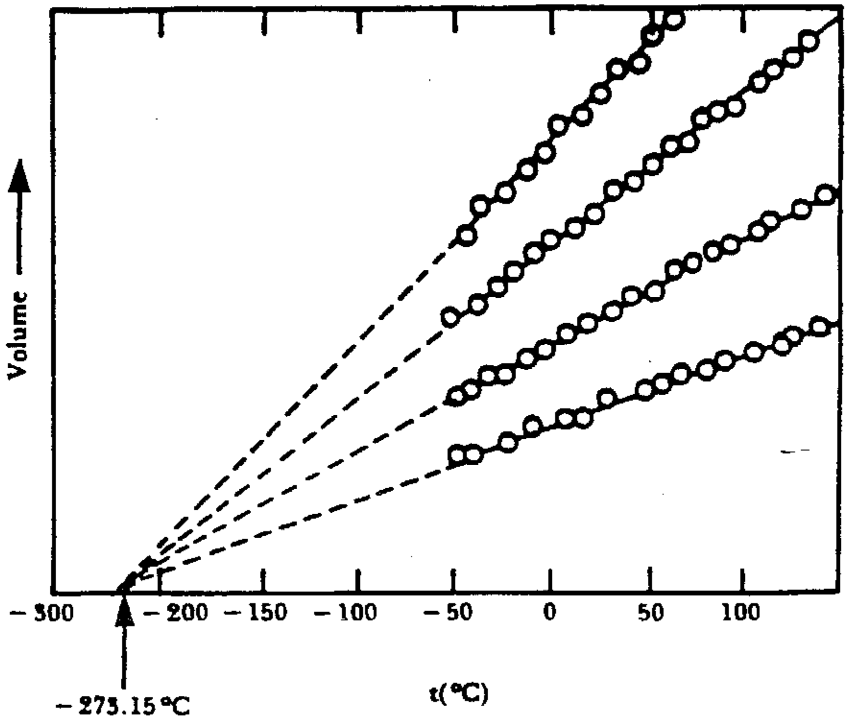


Figure 2-1(a). Temperature relationships.

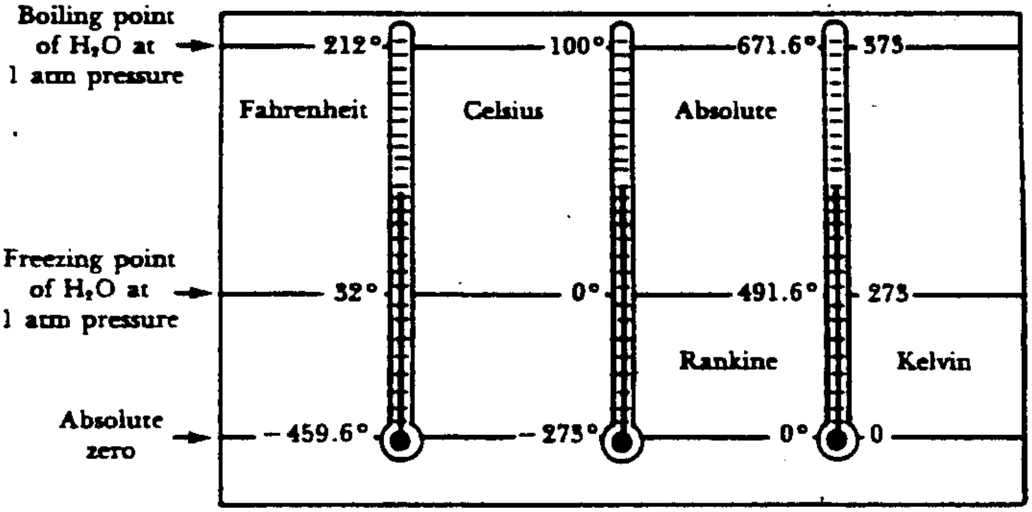


Figure 2-1(b). Relationships of the absolute temperature systems.

Relationships of the absolute temperature systems are shown graphically in Figure 2-1(b). The symbol "T" will be used throughout this manual to denote absolute temperatures, and the "t" will be used to indicate Fahrenheit or Celsius degrees. The absolute temperatures are always in volume calculations involving temperature and pressure.

Pressure

Definition of Pressure

A body may be subject to three kinds of stress: shear, compression, and tension. Fluids are unable to withstand tensile stress; hence, they are subject to shear and compression only. *Unit compressive stress in a fluid is termed pressure* and is expressed as *force per unit area.*

Pressure

Metric	English
gm_f/cm^2	$lb_f/in.^2$ (psi)

Pressure is equal in all directions at a point within a volume of fluid and acts perpendicular to a surface.

Barometric Pressure

Barometric pressure and atmospheric pressure are synonymous. These pressures are measured with a barometer and are usually expressed as inches or millimeters of mercury. *Standard barometric pressure is the average atmospheric pressure at sea level, 45° north latitude at 35°F and is equivalent to a pressure of 14.696 pounds-force per square inch exerted at the base of a column of mercury 29.921 inches high (in the English System). In the metric system, standard barometric pressure is equivalent to a pressure of 1033.23 grams-force per square centimeter exerted at the base of a column of mercury 760 mm high.* Weather and altitude are responsible for barometric pressure variations.

Torricelli Barometer

The Torricelli, or mercurial, barometer was first used by one of Galileo's students, Torricelli, in 1643. A mercurial barometer is made by sealing a tube, about 32 inches long, at one end. The tube is filled with mercury. It is then inverted and placed into a container that is partially filled with mercury. The mercury in the tube will fall until the weight of the mercury in the tube is equal to the force of the air pressure on the mercury in the container. As shown in Figure 2-2, the manometer and the mercurial barometer work on the same principle—atmospheric pressure being measured with reference to a vacuum.

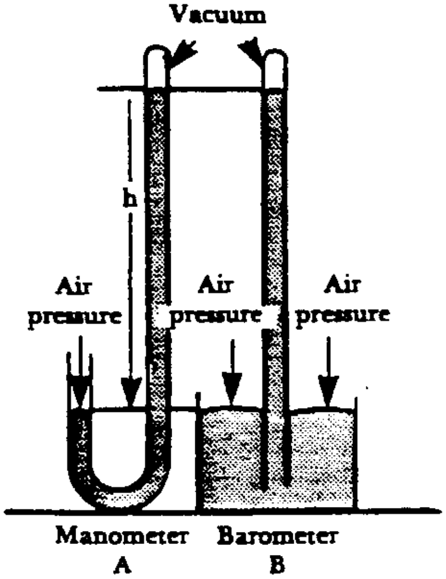


Figure 2-2. The manometer and mercurial barometer.

Fortin Barometer

Since the mercurial barometer is the most accurate measurement (calibration uncertainty of 0.001 to 0.03% of reading) of atmospheric pressure, it is still in wide use today. The most common modified version of the mercurial barometer is the Fortin type shown in Figure 2-3.

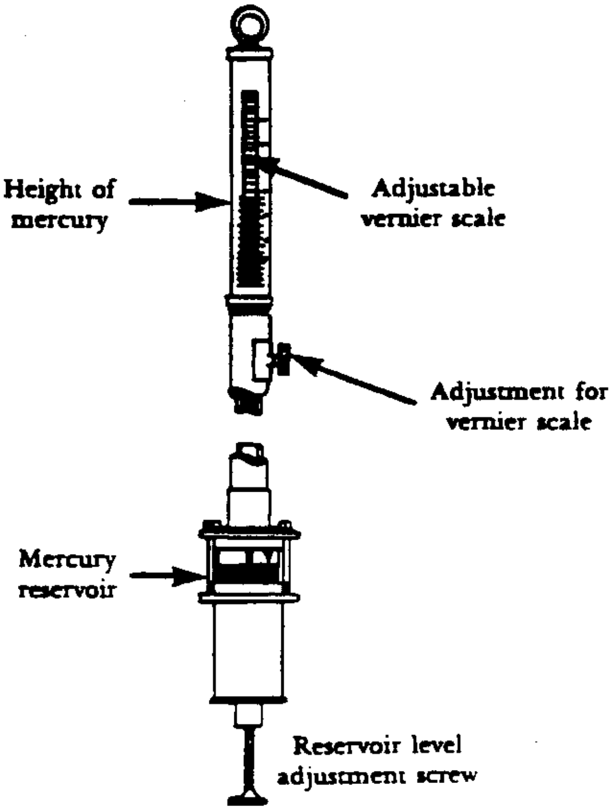


Figure 2-3. Fortin barometer.

The height of the mercury column in a Fortin barometer is measured from the tip of the ivory index point (see the enlargement in Figure 2-4) to the top of the mercury column. The mercury level in the glass cylinder (ambient-vented cistern) is adjusted until the ivory index point just pricks the surface of the mercury. This is done by turning the datum-adjusting screw. Then the vernier scale is adjusted until the bottom of it is even with the top of the mercury meniscus. After the vernier scale is adjusted, the height of the mercury column is read.

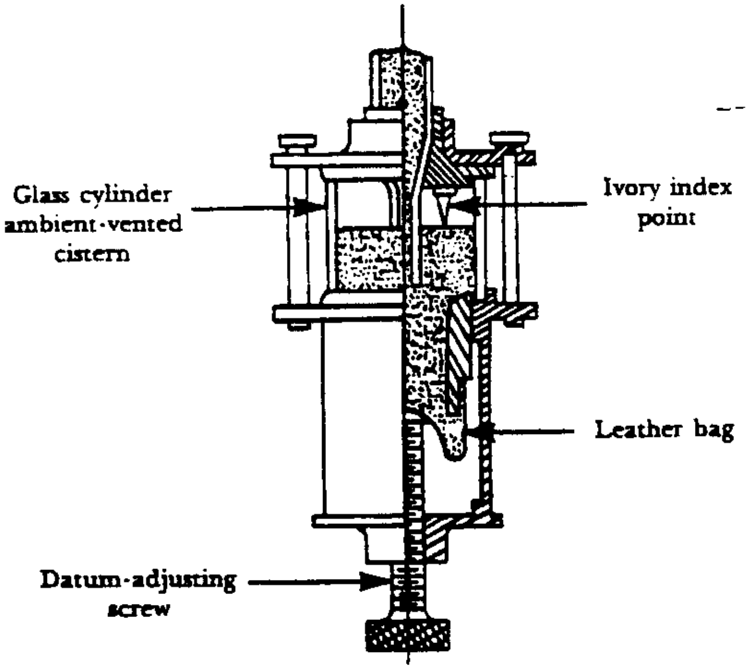


Figure 2-4. Blow-up of Fortin barometer.

A typical vernier scale is shown in Figure 2-5. The barometric pressure indicated in the figure is determined in the following way:

> The bottom of the vernier scale indicates not only the integer component of the barometric pressure, but also the tenths components—in this case, 29.9. The hundredths component is indicated by the match between the outer scale and the vernier—in this case, 0.04. The readings are totaled to determine the barometric pressure: 29.9 + 0.04 = 29.94 in. Hg. The equivalent metric reading is 76.05 cm.

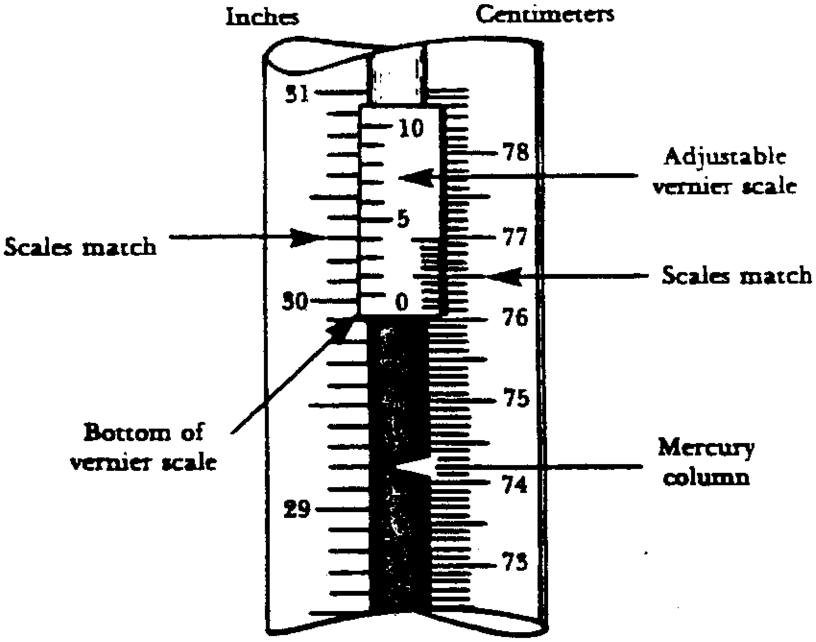


Figure 2-5. Blow-up of vernier scale.

Aneroid Barometer

The aneroid barometer is usually not as accurate as a Torricelli barometer. However, aneroid barometers are more widely used because they are smaller, more portable, less expensive, and easier to adapt to recording instrumentation than are Torricelli barometers.

The aneroid barometer usually consists of a metal chamber, bellows, or sylphon (accordian-like) cell that is partially evacuated. A spring is used to keep the metal chamber from collapsing (see Figure 2-6). The width of the chamber is determined by the balance between the spring and the force exerted by the atmosphere. The width of the chamber is indicated by a pointer and scale that can be calibrated to read directly in units of pressure (i.e., millimeters or inches of mercury, etc.). The pointer movement can be amplified by using levers. Read-out systems can vary from visual scales to recording devices. The combination of an aneroid barometer and an automatic recording device is called a barograph.

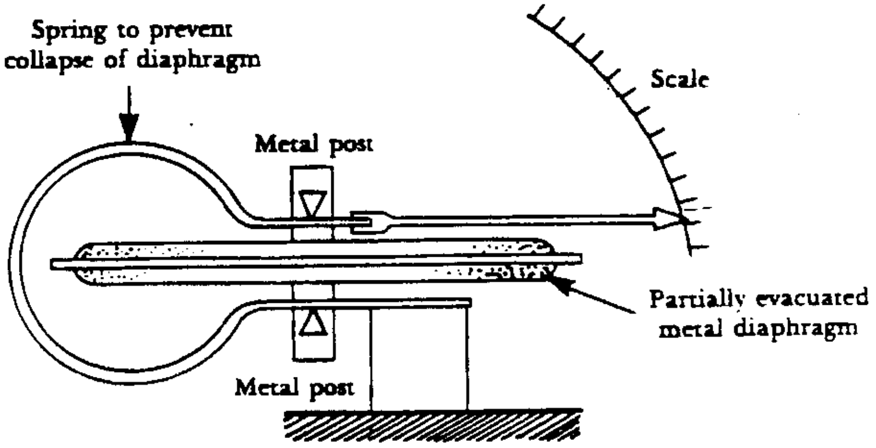


Figure 2-6. Aneroid barometer.

Pressure Transducers

A transducer is a device that is activated by power from one system and supplies power in some other form to a second system. Conventional pressure transducers use an elastic element that converts the energy from a pressure differential into a displacement of a mechanical device. An example of a mechanical pressure transducer is shown in Figure 2-7. Other pressure transducers convert the mechanical displacement into an electrical signal. An example of an electrical transducer is shown in Figure 2-8. Electrical pressure transducers have become very popular because the signal is easy to measure, control, amplify, transmit, and record.

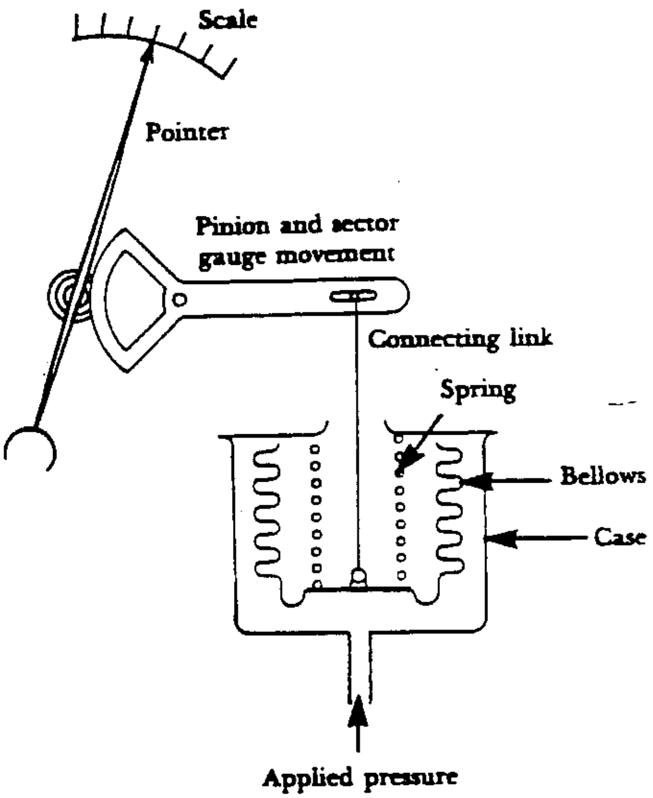


Figure 2-7. Mechanical pressure transducer.

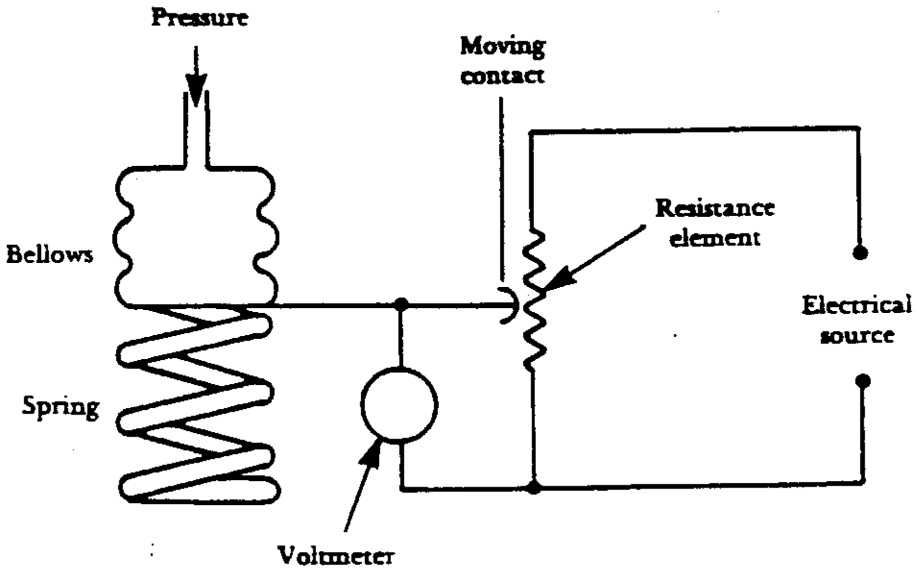


Figure 2-8. Electrical pressure transducer.

Gauge Pressure

Gauges indicate the pressure of the system of which they are a part relative to ambient barometric pressure. If the pressure of the system is greater than the pressure prevailing in the atmosphere, the gauge pressure is expressed as a positive value; if smaller, the gauge pressure is expressed as a negative. The term "vacuum" designates a negative gauge pressure.

The abbreviation "*g*" is used to specify a gauge pressure. For example, *psig* means pounds-force per square inch gauge pressure.

Absolute Pressure

Because gauge pressure (which may be either positive or negative) is the pressure relative to the prevailing atmospheric pressure, the gauge pressure, added algebraically to the prevailing atmospheric pressure (which is always positive), provides a value that is called "absolute pressure." The mathematical expression is:

(Eq. 2-3)
$$P = P_b + p_g$$

Where:
P = *absolute pressure*
P_b = *atmospheric pressure*
p_g = *gauge pressure.*

Note: P, P_b, and p_g must be in the same units of pressure before they can be added (i.e., all must be in inches of mercury, mm of mercury, etc.).

The abbreviation "*a*" is sometimes used to indicate that the pressure is absolute. For example, *psia* means pounds per square inch absolute pressure.

Equation 2-3 allows conversion of one pressure system to the other. The relationship of the two pressure systems is shown graphically in Figure 2-9 using two typical gauge readings, 1 and 2. Gauge reading 1 is above the prevailing atmospheric pressure and, hence, is expressed as a positive value. Gauge reading 2 is below the prevailing atmospheric pressure and, therefore, is expressed as a negative value. Gauge reading 3 has both sides open to the atmosphere; hence, the gauge pressure is zero.

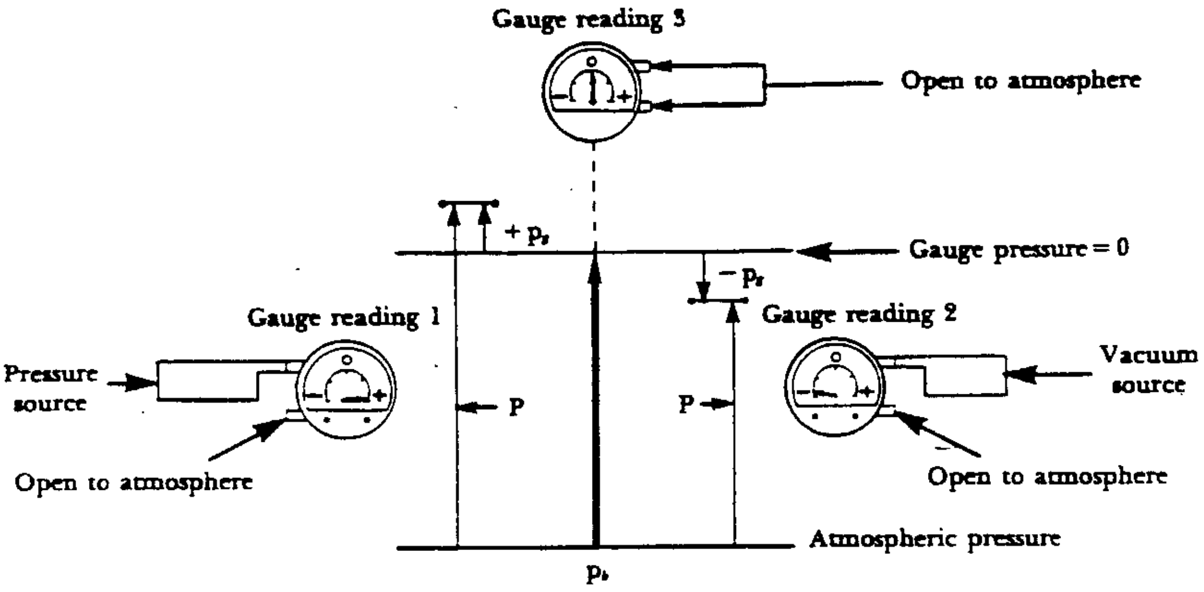


Figure 2-9. Absolute-atmospheric-gauge pressure relationship.

Example Problems

Problem 1:

The primary *pressure* gauge of a regulator attached to a compressed nitrogen cylinder indicates a reading of 2000 *psig*. An aneroid barometer mounted on the wall indicates that the atmospheric pressure is 14.2 *psi*. What is the absolute pressure inside the tank?

Solution:

$$P = P_b + p_g = 14.2 + 2000$$
$$P = 2014.2 \ psia.$$

Problem 2:

A water manometer is used to measure the pressure inside an evacuated flask. The water manometer indicates that the evacuated flask has a vacuum of 26 inches of water. A nearby Fortin barometer indicates that atmospheric pressure is 752.6 mm Hg. What is the absolute pressure inside the flask?

Solution:

Before p_g and P_b can be added to give P, both must be in the same unit of pressure. It is most common for p_g to be converted to the same units as P_b since P_b is in much larger units.

Since 1 inch of Hg = 13 inches H_2O (Hg is 13 times denser than water),

$$\left(26 \text{ inches } H_2O\right)\left(\frac{1 \text{ inch Hg}}{13 \text{ inches } H_2O}\right)\left(\frac{25.4 \text{ mm}}{1 \text{ inch}}\right) = 50.8 \text{ mm Hg}.$$

Now p_g and P_b can be added. p_g is negative because the evacuated flask is at a *vacuum, or below atmospheric pressure.*

$$P = P_b + p_g = 752.6 \text{ mm Hg} + (-50.8 \text{ mm Hg})$$
$$P = 701.8 \text{ mm Hg}$$

The Concept of Pressure-head

Pressure-head is the height of a column of fluid required to produce a given pressure at its base.

The relationship between pressure and pressure-head is:

(Eq. 2-4) $$p = \varrho_f h\left(\frac{g}{g_c}\right)$$

Where:

p = *pressure, force/area*

ϱ_f = *density of fluid, mass/volume*

g = *local acceleration due to gravity, length/time²*

g_c = *dimensional constant*

h = *pressure-head in terms of* ϱ_f, *length.*

Pressure-head may be expressed in terms of any fluid that is convenient—e.g., Hg or H_2O.

Dalton's Law of Partial Pressure

When gases or vapors (having no chemical interaction) are present as a mixture in a given space, the pressure exerted by a component of the gas-mixture at a given temperature is the same as would be exerted if the gas-mixture filled the whole space alone. *The pressure exerted by one component of a gas-mixture is called its partial pressure. The total pressure of the gas-mixture is the sum of the partial pressures.*

Expressed mathematically:

$$P_{total} = \Sigma p_i$$

Where:

P_{total} = *total pressure exerted by the system*

p_i = *pressure of each component of the system*

$\Sigma p_i = p_1 + p_2 + \ldots + p_n$

(Σ: means "sum of").

The Ideal Gas Laws

Ideal gases are gases whose molecules do not attract one another and which occupy no part of the whole volume. Although there are no gases which have these properties, real gases, which deviate very slightly from ideal gas behavior under ordinary temperature and pressure conditions, may be considered to be ideal gases.

Boyle's Law

Boyle's Law states: when the ***temperature*** (*T*) is held constant, the ***volume*** (*V*) of a given mass of an ideal gas of a given composition varies inversely as the absolute pressure, i.e.:

$$V \alpha \frac{1}{P} \text{ (at constant } T)$$

Where: α = *proportional to.*

One can see that, as the pressure on a gas system increases, the volume of the gas system will decrease and vice versa.

Charles' Law

Charles' Law states: when the ***pressure*** (*P*) is held constant, the ***volume*** (*V*) of a given mass of an ideal gas of a given composition varies directly as the ***absolute temperature*** (*T*), i.e.,:

$$V \alpha T \text{ (at constant } P).$$

In other words, as the temperature of a gas system increases, the volume will also increase and vice versa.

The Law for Ideal Gases

Both Boyle's and Charles' Law are satisfied in the following equation:

(Eq. 2-5)
$$PV = nRT$$

Where:
P = *absolute pressure*
V = *volume of a gas*
T = *absolute temperature*
R = *universal gas-constant*
n = *number of moles of a gas.*

A *mole* of a substance is the substance's molecular weight, expressed in mass units, where the substance's molecular weight is the sum of the atomic weights of the atoms which compose the substance.

We know that

$$n = \frac{m}{M}$$

Where: m = *mass of a gas*
M = *molecular weight of a gas*

therefore:

$$PV = nRT = \frac{m}{M}RT.$$

The units of R depend upon the units of measurement used in the equation. Some useful values are:

(1) $R = 0.082\ (\ell)\ (atm)\ (\mathrm{K})^{-1}(\text{g-}mole)^{-1}$
(2) $R = 62.4\ (\ell)(\text{mm Hg})\ (\mathrm{K})^{-1}(\text{g-}mole)^{-1}$

Where the units are: $V(\ell)$
$m(\mathrm{g})$
$M(\mathrm{g}/\text{g-}mole)$
$T(\mathrm{K})$
$P[atm$ for (1) or
mm Hg for (2)].

Different values of R can be obtained by utilizing the appropriate conversion factors.

Molar Volume ($\bar{V}$)

One mole of any gas at 273 K and 760 mm Hg will occupy 22.414 liters. This constant is obtained from the ideal gas law. From Equation 2-5:

If: $P = 760$ mm Hg
$n = 1$ *mole*
$R = 62.4\ (\ell)\ (\text{mm Hg})\ (\text{g-}mole)^{-1}(\mathrm{K})^{-1}$
$T = 273$ K
$V = \bar{V}$ *(molar volume)*

then: $P \times V = n \times R \times T$

$$(760 \text{ mm Hg})\ (V) = (1 \text{ g-}mole)\left(62.4\,\frac{\ell\text{•mm Hg}}{\text{g-}mole \text{ K}}\right)(273 \text{ K})$$

$$V = \frac{(1)(62.4)(273)}{760}\,\ell$$

$$V = 22.414\ell = \bar{V}.$$

Therefore, one *mole* of an ideal gas at 273 K and 760 mm Hg occupies 22.414ℓ. In other words, the molar volume ($\bar{V}$) of an ideal gas at 273 K and 760 mm Hg is *22.414 ℓ/mole.*

At *EPA standard conditions (760 mm Hg, 298 K)*, one *mole* of any gas will occupy 24.46ℓ. The volume per *mole* constant for any gas at a given pressure and temperature is called the *molar volume* and is symbolized by $\bar{V}$.

Gas Density

Gas density can be determined by rearranging Equation 2-5 and letting density $\varrho = m/V$.

(Eq. 2-6)

$$PV = nRT = \frac{m}{M}RT$$

$$\frac{m}{V} = \varrho = \frac{PM}{RT}$$

Where:

ϱ = *density*
P = *absolute pressure*
M = *molecular weight*
T = *absolute temperature*
R = *universal gas constant*

Another method of determining density is by utilizing the fact that there are 24.46 liters per g-*mole* at 298 K and 760 mm Hg.

In the relationship, $\varrho = m/V$: if V is in terms of molar volume, $\bar{V}$ (ℓ/g-*mole* of a gas at STP), then m must be in terms of molecular weight, M (g/g-*mole*). So $\varrho = M/V$ at a given temperature and pressure.

$$\varrho = \frac{M\dfrac{298}{T}\dfrac{P}{760}}{24.46}$$, *corrected to standard temperature and pressure conditions (STP)*

Where:

ϱ = *gas density* (g/ℓ)
M = *molecular weight* (g/g-*mole*)
24.46 = *molar volume* (ℓ/g-*mole*) *at standard conditions*
298 = *temperature* (K) *at standard conditions*
T = *temperature* (K) *at actual conditions*
760 = *pressure* (mm Hg) *at standard conditions*
P = *pressure* (mm Hg) *at actual conditions.*

Standard Conditions for Atmospheric Sampling

To be able to compare gas sampling data collected by various agencies and other organizations, all gas volumes must be corrected to a set of predetermined ("standard") conditions. For atmospheric or ambient sampling, these conditions are:

25 °C or 298 K, and 760 mm Hg.

The equation used to correct volumes sampled to standard conditions is:

(Eq. 2-7)
$$V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$$

$$V_2 = (V_1)\left(\frac{P_1}{760 \text{ mm Hg}}\right)\left(\frac{298 \text{ K}}{T_1}\right)$$

$$V_2 = (V_1)(0.39)\left(\frac{P_1}{T_1}\right)$$

Where:

V_2 = *volume of gas at 2nd conditions or at* P_2 *and* T_2, ℓ
V_1 = *volume of gas at 1st conditions of* P_1 *and* T_1, ℓ
T_1 = *initial temperature of gas,* K
T_2 = *final temperature of gas, in this case* = 298 K
P_1 = *initial pressure of gas,* mm Hg
P_2 = *final pressure of gas, in this case* = 760 mm Hg

$$0.39 = \frac{298}{760}.$$

The term "standard conditions for temperature and pressure" is abbreviated STP.

Origin and Definition of Viscosity

Viscosity is the result of two phenomena: (a) intermolecular cohesive forces and (b) momentum transfer between flowing strata caused by molecular agitation perpendicular to the direction of motion. Between adjacent strata of a flowing fluid a shearing stress results that is directly proportional to the velocity gradient. (Figure 2-10). *Viscosity is often defined as resistance to flow.*

The relationship of these forces is shown in Equation 2-8.

(Eq. 2-8)
$$g_c \mathrm{T} = \mu \frac{dv}{dy}$$

Where:

g_c = *dimensional constant*
T = *unit shearing stress between adjacent layers of fluid*
$\frac{dv}{dy}$ = *velocity gradient*
μ = *proportionality constant (viscosity).*

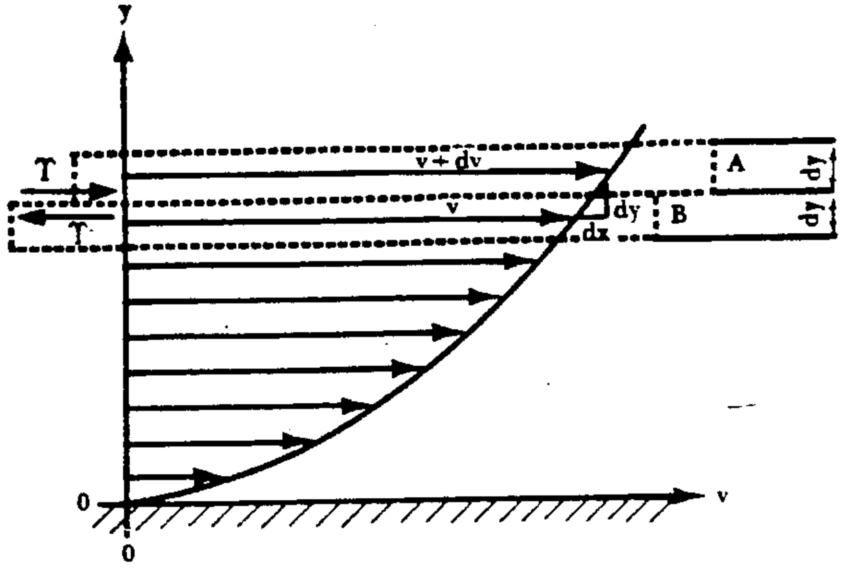


Figure 2-10. Velocity gradient.

The proportionality constant, μ, is called the coefficient of viscosity, or merely, *viscosity*. It should be noted that the pressure does not appear in Equation 2-8, indicating that the shear (T) and the viscosity (μ) are independent of pressure. (Viscosity actually increases very slightly with pressure, but this variation is negligible in most engineering problems.)

Kinematic Viscosity

Kinematic viscosity is defined according to the following relationship:

(Eq. 2-9)

$$\nu = \frac{\mu}{\varrho}$$

Where: ν = *kinematic viscosity*
μ = *viscosity of the gas*
ϱ = *density of the gas (note the absence of dimensions of force).*

Liquid Viscosity Versus Gas Viscosity

Liquid Viscosity

In a liquid, transfer of momentum between strata having different velocities is small, compared to the cohesive forces between the molecules. Hence, shear stress (T) is predominantly the result of intermolecular cohesion. Because forces of cohesion decrease with an increase in temperature, the shear stress decreases with an increase in temperature. Equation 2-8 shows that shear stress is directly proportional to the viscosity. Therefore, liquid viscosity decreases when the temperature increases.

Gas Viscosity

In a gas, the molecules are too far apart for intermolecular cohesion to be effective. Thus, shear stress is predominantly the result of an exchange of momentum between flowing strata caused by molecular activity. Because molecular activity increases with temperature increases, the shear stress increases with a rise in the temperature. Therefore, gas viscosity is increased when the temperature increases.

Determination of Viscosity of Gases

The viscosity of a gas may be found accurately from the following formula:

(Eq. 2-10)
$$\frac{\mu}{\mu^{\circ}} = \left(\frac{T}{273.1}\right)^{n}$$

Where:
μ = *viscosity at temperature* T (K)
μ° = *viscosity at* 0 °C *and prevailing pressure*
T = *absolute prevailing temperature* (K)
n = *an empirical exponent* ($n = 0.768$ *for air*).

The viscosity of air and other gases at various temperatures and at a pressure of 1 atmosphere can be determined from the nomograph in Figures 2-11 and 2-12, or from Equation 2-10. The unit of the viscosity coefficient is the poise:
1 poise = gm/cm sec. A centipoise (cp) is equal to 10^{-2} poise.

Reynold's Number

Definition

Typical inertial force per unit volume of fluid:

$$\frac{\varrho v^{2}}{g_c L}$$

Typical viscous force per unit volume of fluid:

$$\frac{\mu v}{g_c L^{2}}$$

The first expression divided by the second provides the dimensionless ratio known as Reynold's Number:

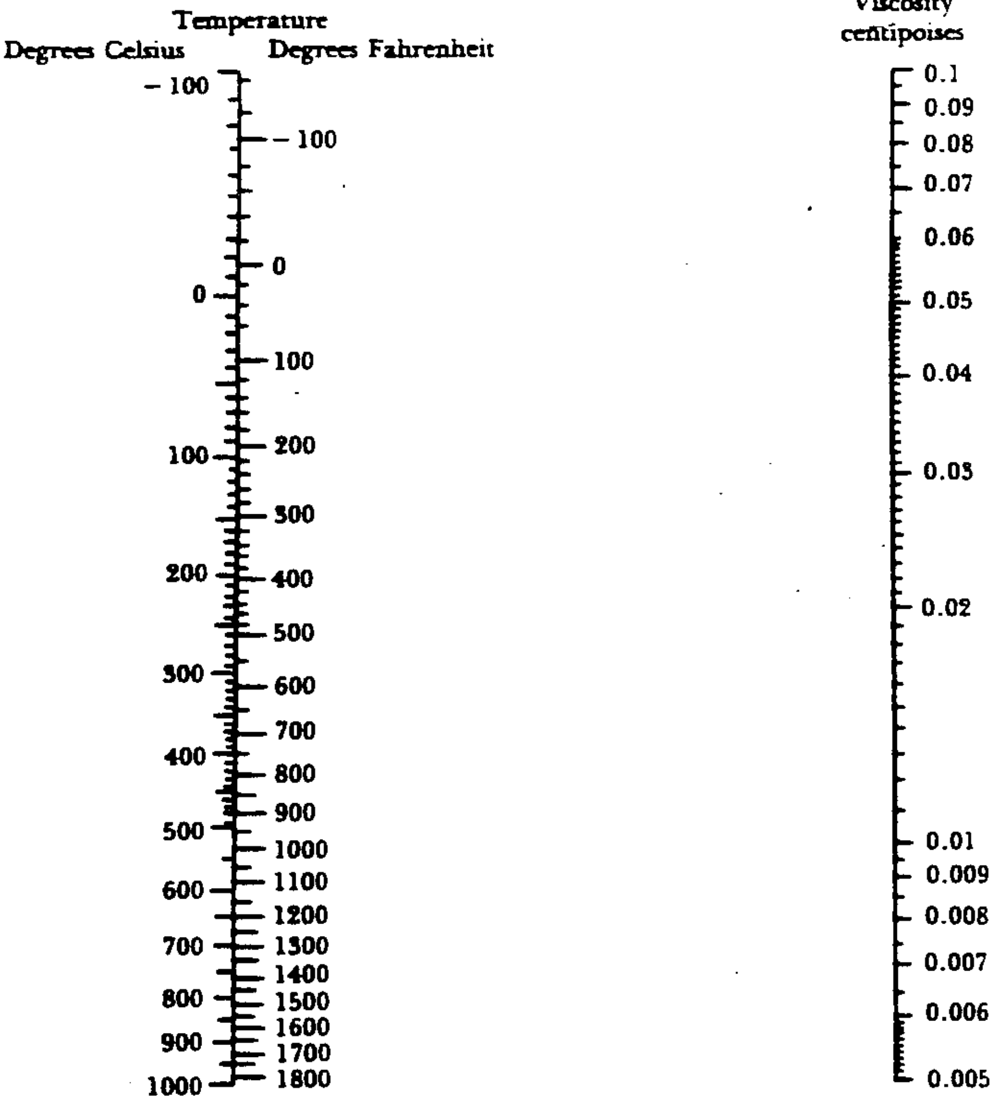
(Eq. 2-11)
$$N_{Re} = \frac{L v \varrho}{\mu} = \frac{\text{inertial force}}{\text{viscous force}}$$

Where:
ϱ = *density of the fluid (mass/volume)*
v = *velocity of the fluid*
g_c = *dimensional constant*
L = *a linear dimension*
μ = *viscosity of the fluid*
N_{Re} = *Reynold's Number.*

The larger the Reynold's Number, the smaller is the effect of viscous forces; the smaller the Reynold's Number, the greater the effect of the viscous forces.

The linear dimension, L, for flow through tubes and ducts is a length characteristic of the flow system. It is equal to four times the mean hydraulic radius, which is the cross-sectional area divided by the wetted perimeter. Thus for a circular pipe, L = diameter of the pipe; for a particle settling in a fluid medium, L = diameter of the particle; for a rectangular duct, L = twice the length times the width divided by the sum; and for an annulus such as a rotameter system, L = outer diameter minus the inner diameter.

Viscosity of air at 1 atmosphere*



(1)centipoise	$(10)^{-2} \frac{gm}{cm-sec}$ $(10)^{-2}$ poise	$209(10)^{-7}$ $\frac{lb_f-sec}{ft^2}$	$2.09(10)^{-5}$ $\frac{slug}{ft-sec}$	$6.72(10)^{-4}$ $\frac{lb_m}{ft-sec}$

*Perry, J. H. *Chemical Engineer's Handbook*. McGraw-Hill Book Co., New York (1950).

Figure 2-11. Viscosity nomograph for air.

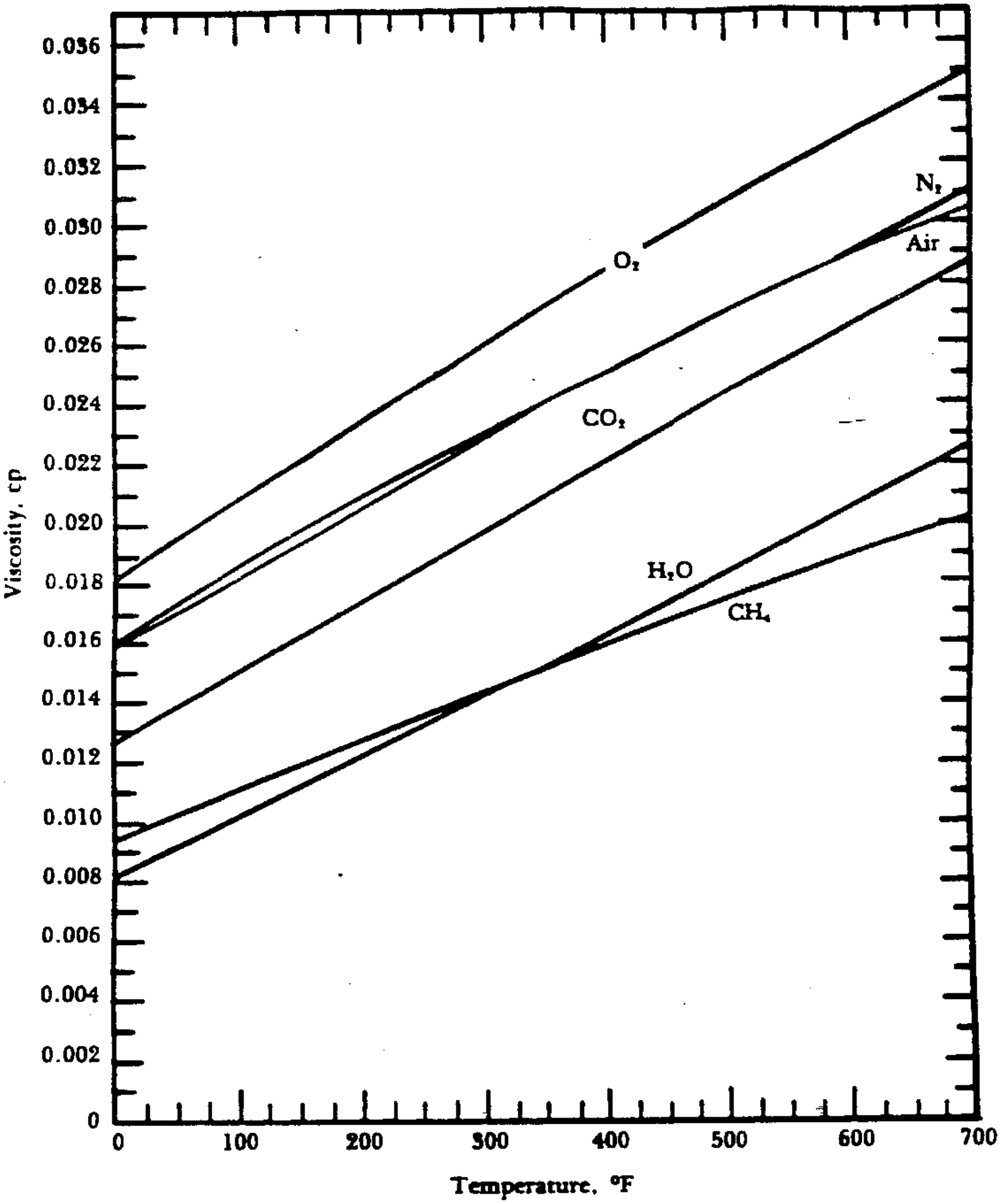


Figure 2-12. Viscosity nomograph of various gases at 1 atmosphere.

Laminar and Turbulent Flow

Laminar Flow

In laminar flow, the fluid is constrained to motion in layers (or laminae) by the action of viscosity. The layers of fluid move in parallel paths that remain distinct from one another; any agitation is of a molecular nature only. Laminar flow occurs when Reynold's Number is less than 0.1 for particles settling in a fluid medium.

Turbulent Flow

In turbulent flow, the fluid is not restricted to parallel paths but moves forward in a haphazard manner. Fully turbulent flow occurs when Reynold's Number is greater than 1000 for settling particles having diameters greater than 40 μm in air with a 60% RH at 20°C.

Summary of Useful Equations

Temperature

$$
\begin{aligned}
{}^\circ\mathrm{C} &= ({}^\circ\mathrm{F} - 32)/1.8 \\
{}^\circ\mathrm{F} &= 1.8\,{}^\circ\mathrm{C} + 32 \\
\mathrm{K} &= {}^\circ\mathrm{C} + 273
\end{aligned}
$$

Where:

°F = *degrees Fahrenheit*
°C = *degrees Celsius*
K = *degrees Kelvin.*

Pressure

$$P = P_b + p_g$$

$$P = \varrho_f \left(\frac{g}{g_c} \right) h$$

$$\varrho_{f(1)} h_{f(1)} = \varrho_{f(2)} h_{f(2)}$$

$$
\begin{aligned}
1\ \textit{std atm} &= 29.92\ \text{in. Hg} \\
&= 760\ \text{mm Hg}
\end{aligned}
$$

Where:

P = *absolute pressure*
ϱ = *density*
h = *pressure-head or height*
g = *gravitational acceleration*
g_c = *dimensional constant*

Subscripts

g = *gauge*
f = *fluid*
b = *barometric or atmospheric*

Ideal Gas Law

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

$$R = \frac{0.08205\ (\text{liters})(atm)}{(\text{g-}mole)(\text{K})}$$

$$= \frac{62.4\ (\text{liters})(\text{mm Hg})}{(\text{g-}mole)(\text{K})}$$

1 g-*mole* ≡ 22.414 liters at 273 K and 760 mm Hg (molar volume)

Where:

P = *absolute pressure*
V = *volume*
m = *mass*
M = *molecular weight*
R = *gas constant*
T = *absolute temperature*
n = *number of g-moles of a gas.*

Gas Density

$$\varrho = \frac{PM}{RT}$$

Where:

ϱ = *density*
P = *absolute pressure*
R = *gas constant*
T = *absolute temperature*
M = *molecular weight.*

Viscosity, μ

$$1\ cp \equiv 6.72 \times 10^{-4} \frac{\text{lb}_m}{\text{ft} \cdot \text{sec}}$$

$$1\ poise = 1 \frac{\text{g}}{\text{cm} \cdot \text{sec}}$$

$$1\ cp = 10^{-2}\ \text{poise}$$

Reynold's Number

$$N_{Re} = \frac{Lv\varrho}{\mu} = \frac{\textit{inertial force}}{\textit{viscous force}}$$

Where:

ϱ = *density of the fluid (mass/volume)*
v = *velocity of the fluid*
g_c = *dimensional constant*
L = *a linear dimension*
μ = *viscosity of the fluid*
N_{Re} = *Reynold's Number.*

Units of Measurement

Recommended Units

At the present time, air pollution personnel are confronted with a multitude of confusing and conflicting units of expression. A search through the literature has shown a wide variation in the methods of reporting data. Many of the units of expression are carry-overs from other fields, such as water pollution studies and industrial hygiene surveys. While these methods of expression are correct, their application to air pollution studies is often misleading. This section of the manual covers the units presently being used and those recommended for the more commonly measured air pollution parameters.

The recommended units were selected so that the reported values would be small whole numbers in the metric system. If possible, the reported units should be the same as those that are actually measured. For example, weight should be reported in grams or milligrams, and volume in cubic meters. The measured value should never be multiplied by large numbers to extrapolate to extremely large areas or volumes. If this is done, the resulting values are misleading. For example: To report particulate fallout on a weight per square mile basis, the area actually sampled, which is about 1 square foot, would have to be extrapolated to a square mile by multiplying the measured results by almost 28,000,000. Reporting the results on the basis of a square mile is misleading, because we are saying that the 1 square foot that we sampled is representative of a square mile surrounding this sampling site. This we know, in most cases, is not true.

When reporting results, the type of sampling instrument should be described, and when volumes of air are sampled, the temperature and pressure at the time of the sampling should be reported.

Table 2-1. Measurement units.

Parameter	Units in use	Unit recommended	Typical range
Particle fallout	Tons per square mile per month Tons per square mile per year Pounds per acre per month Pounds per acre per year Pounds per thousand square feet per month Ounces per square foot per month Grams per square foot per month Grams per square meter per month Kilograms per square kilometer per month Grams per month per 4-inch or 6-inch jar Milligrams per square inch per month Milligrams per square centimeter per time interval	$mg/cm^2/mo$ (or yr)	0.5 to 135 $mg/cm^2/mo$
Outdoor airborne particulate matter	Milligrams per cubic meter Parts per million by weight Grams per cubic foot Grams per cubic meter Micrograms per cubic meter Micrograms per cubic foot Pounds per thousand cubic feet	$\mu g/m^3$ (std)	10 to 5000 $\mu g/m^3$
Gaseous materials	Milligrams per cubic meter Micrograms per cubic meter Micrograms per liter Parts per million by volume Parts per hundred million Parts per billion by volume Parts per trillion by volume Ounces per cubic foot Pounds per cubic foot Grams per cubic foot Pounds per thousand cubic feet	ppm or ppb by volume	Parts per trillion to parts per million
Standard conditions for reporting gas volumes	760 millimeters Hg pressure and 20°C 760 millimeters Hg pressure and 0°C 760 millimeters Hg pressure and 65°F 760 millimeters Hg pressure and 25°C 700 millimeters Hg pressure and 0°C 700 millimeters Hg pressure and 20°C 30 inches of mercury pressure and 65°F	760 mm Hg and 25°C	--
Particle counting	Number per cubic meter of gas Number per liter of gas Number per cubic centimeter of gas Number per cubic foot of gas	Number of particles/m^3 of gas	10 million and above particles/m^3
Particle count in sedimentation devices (horizontal and vertical)	--	Number of particles/cm^2/mo (or yr)	--
Temperature	Degrees Celsius Degrees Fahrenheit	°C	--
Time	12:00 a.m. to 12:00 p.m., 0000 to 2400	0000 to 2400 (military time)	--

Table 2-1. Measurement units, continued.

Parameter	Units in use	Unit recommended	Typical range
Pressure	Atmospheric pressure Atmospheres Millimeters of mercury Inches of mercury Sampling pressure Millimeters of mercury Inches of mercury Millimeters of water Inches of water	mm Hg	— —
Sampling rates	Cubic meters per second Cubic meters per minute Cubic feet per second Cubic feet per minute Liters per second Liters per minute Cubic centimeters per second Cubic centimeters per minute	m^3/min, liters per minute	ℓ/min to 3 m^3/min
Visibility	Miles and fractions of a mile Kilometers and fractions of a kilometer	km	— —

Conversion Problems

Sample Particulate Matter Problem

Convert 89.0 tons per square mile to the recommended units (milligrams per square centimeter).

Solution:

$$89.0\,\frac{\text{tons}}{\text{mi}^2} \times \frac{2000\text{ lb}}{\text{ton}} \times \frac{453.6 \times 10^3\text{ mg}}{\text{lb}} \times \frac{\text{mi}^2}{(5280)^2\text{ft}^2} \times \frac{\text{ft}^2}{(12)^2\text{in}^2} \times \frac{\text{in}^2}{(2.54)^2\text{cm}^2} = \frac{3.2\text{ mg}}{\text{cm}^2}$$

Sample Gas Problem

Discussion:
The expression parts per million is without dimensions, i.e., no units of weight or volume are specifically designed. Using the format of other units, the expression may be written:

$$\frac{\text{parts}}{\text{million parts}}.$$

"Parts" are not defined. If cubic centimeters replace parts, we obtain:

$$\frac{\text{cubic centimeters}}{\text{million cubic centimeters}}.$$

Similarly, we might write pounds per million pounds, tons per million tons, or liters per million liters. In each expression, identical units of weight or volume appear in both the numerator and denominator and may be cancelled out, leaving a dimensionless term.

An analog of parts per million is the more familiar term "percent." Percent can be written:

$$\frac{\text{parts}}{\text{hundred parts}}.$$

To convert from parts per million by volume, ppm$_v$ ($\mu\ell/\ell$), it is necessary to know the molar volume at the given temperature and pressure and the molecular weight of the pollutant.

At 25 °C and 760 mm Hg, one mole of any gas occupies 24.46 liters.

Convert the following:

2.5 ppm by volume of SO_2 was reported as the atmospheric concentration.

a. What is this concentration in micrograms (μg) per cubic meter (m^3) at 25 °C and 760 mm Hg?

b. What is the concentration in $\mu g/m^3$ at 37 °C and 752 mm Hg?

Solution:

Let parts per million equal $\mu\ell/\ell$, then 2.5 ppm = 2.5$\mu\ell/\ell$. The molar volume at 25° and 760 mm Hg is 24.46ℓ, and the molecular weight of SO_2 is 64.1 g/mole.

$$\text{(a)}\ \frac{2.5\ \mu\ell}{\ell} \times \frac{1\ \mu mole^*}{24.46\ \mu\ell} \times \frac{64.1\ \mu g}{\mu mole} \times \frac{1000\ \ell}{m^3} = 6.5 \times 10^3\ \frac{\mu g}{m^3}\ \text{at STP}$$

$$\text{(b)}\ (24.46\ \mu\ell)\left(\frac{310\ K}{298\ K}\right)\ \frac{760\ mm\ Hg}{752\ mm\ Hg} = 25.73\ \mu\ell$$

$$\frac{2.5\ \mu\ell}{\ell} \times \frac{1\ \mu mole}{25.73\ \mu\ell} \times \frac{64.1\ \mu g}{\mu mole} \times \frac{1000\ \ell}{m^3} = 6.2 \times 10^3\ \frac{\mu g}{m^3}\ \text{at 37 °C, 752 mm Hg}$$

This sample problem also points out the need for reporting temperature and pressure when the results are presented on a weight-to-volume basis.

---

*Since, at STP, 1 mole of a gas occupies 24.46 liters, 1 μmole = 24.46 $\mu\ell$.

Problems

1. Convert the following:
   a. 68°F – °C (answer 20°C)
   b. 28°C – K (answer 301 K)
   c. 29.03 in. Hg – mm Hg (answer 737.3 mm Hg)
2. An ideal gas occupies a volume of 2000 mℓ at 700 mm Hg and 20°C. What is the volume of the gas at STP? (answer 1874 mℓ)
3. If a concentration of carbon monoxide (CO) is noted as 10 ppm, what is this concentration in terms of $\mu g/m^3$ at STP? (CO = 28 g/mole) (answer 11,440 $\mu g/m^3$, 11.4 mg/m^3)
4. Ambient air was sampled at a rate of 2.25 liters per minute for a period of 3.25 hours at 19°C, 748 mm Hg. What volume of air was sampled at STP? (answer 441 ℓ)
5. Convert 1000 $\mu g/m^3$ SO_2 at STP to ppm. (SO_2 = 64 g/mole) (answer 0.38 ppm)

Tables to use in this task appear in Appendix A3 of this manual.

Definitions

Air at EPA Standard Conditions	Air at 25°C and 760 mm Hg (29.92 in. Hg).
Air Pollution	The presence of unwanted material in the air. The term "unwanted material" here refers to material concentrations present for a sufficient time and under circumstances to interfere significantly with comfort, health, or welfare of persons, or with the full use and enjoyment of property.
Arrester	A term for an air cleaning device.
Aspirator	Any apparatus, such as a squeeze bulb, fan, pump, or venturi, that produces a movement of a fluid by suction.
Atmosphere, The	The whole mass of air surrounding the earth and being composed largely of oxygen and nitrogen.
Atmosphere, An	A specific gaseous mass, occurring either naturally or artificially, containing any number of constitutents and in any proportion.
Breathing Zone	That location in the atmosphere at which persons breathe.
Chimney Effect	A phenomenon consisting of a vertical movement of a localized mass of air or other gases due to temperature differences.
Collection Efficiency	The percentage of a specified substance retained by a gas cleaning or sampling device.
Collector	A device for removing and retaining contaminants from air or other gases. Usually this term is applied to cleaning devices in exhaust systems.
Cloud	A visible dispersion occupying a discrete portion of space, with apparent boundaries.
Condensate	Liquid or solid matter formed by condensation from the vapor phase. In sampling, the term is applied to the components of an atmosphere that have been isolated by simple cooling.
Condensation	The process of converting a material in the gaseous phase to a liquid or solid state by decreasing temperature, by increasing pressure, or both. Usually in air sampling only cooling is used.
Condensoid	The particles of a dispersion formed by condensation.
Contaminant	Unwanted material.
Count Median Size	A measurement of particle size for samples of particulate matter, consisting of that diameter of particle such that one half of the number of particles is larger and half is smaller.

Density	The mass per unit volume of substance.
Diffusion, Molecular	A process of spontaneous intermixing of different substances, attributable to molecular motion and tending to produce uniformity of concentration.
Dispersion	The most general term for a system consisting of particulate matter suspended in air or other gases.
Dispersoid	The particles of a dispersion.
Diurnal	The term means recurring daily. Applied to (variations in concentration of) air contaminants, diurnal indicates variations following a distinctive pattern and recurring from day to day.
Dust	A loose term applied to solid particles predominantly larger than colloidal and capable of temporary suspension in air or other gases. Dusts do not tend to flocculate except under electrostatic forces; they do not diffuse but settle under the influence of gravity. Derivation from larger masses through the application of physical force is usually implied.
Dust Fall	See Particle Fall.
Dust Loading	An engineering term for "dust concentration," usually applied to the contents of collection ducts and the emission from stacks.
Droplet	A small liquid particle of such size and density as to fall under still conditions, but which may remain suspended under turbulent conditions.
Efficiency	The ratio of attained performance to absolute performance, commonly expressed in percent.
Efficiency, Fractional	The mean collection efficiency for specific size fractions of a contaminant. Commonly this term has been applied to the performance of air cleaning equipment toward particulate matter in various size ranges.
Ejector	A device that uses a fluid under pressure, such as steam, air, or water, to move another fluid by developing suction. Suction is developed by discharging the fluid under pressure through a venturi.
Emissions	The total of substances discharged into the air from a stack vent, or other discrete source.
Emission Mixture	The total mixture in the outside atmosphere of emission from all sources.
Flocculation	Synonymous with agglomeration.
Flowmeter	An instrument for measuring the rate of flow of a fluid moving through a pipe or duct system. The instrument is calibrated to give volume or mass rate of flow.

Fly Ash	The finely divided particles of ash entrained in flue gases arising from the combustion of fuel. The particles of ash may contain incompletely burned fuel. The term has been applied predominantly to the gas-born ash from boilers with spreader stoker, underfeed stoker, and pulverized fuel (coal) firing.
Fog	A loose term applied to visible aerosols in which the dispersed phase is liquid. Formation by condensation is usually implied; in meteorology, a dispersion of water or ice.
Freezing Out	See Sampling, Condensation.
Fume	Properly, the solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometimes coalesce. Popularly, the term is used in reference to any of all types of contaminant, and in many laws or regulations, with the added qualification that the contaminant have some unwanted action.
Gas	One of the three states of aggregation of matter, having neither independent shape nor volume and tending to expand indefinitely.
Grab Sample	See Sampling, Instantaneous.
Impaction	A forcible contact of particles of matter, a term often used synonymously with impingement.
Impactor	A sampling device that employs the principle of impaction (impingement). The "cascade impactor" refers to a specific instrument employing several impactions in series to collect successively smaller sizes of particles.
Impingement	The act of bringing matter forcibly in contact. As used in air sampling, impingement refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface.
Impingement, Dry	The process of impingement carried out so that particulate matter carried in the gas stream is retained upon the surface against which the stream is directed. The collecting surface may be treated with a film of adhesive.
Impingement, Wet	The process of impingement carried out within a body of liquid, the latter serving to retain the particulate matter.
Impinger	Broadly, a sampling instrument employing impingement for the collection of particulate matter. Commonly, this term is applied to specific instruments, the "midget" and "standard" impinger.

Impinger, Midget	A specific instrument employing wet impingement, using a liquid volume of 10 ml and a gas flow of 0.1 cu. ft. per min. (Note: See J. R. Littlefield, E. L. Feicht, and H. H. Schrenk, "Midget Impinger for Dust Sampling," U.S. Bureau of Mines. Report of Investigations 3360 (1937).)
Impinger, Standard	A specific instrument employing wet impingement, using a liquid volume of 75 ml and a gas flow of 1 cu. ft. per min. (Note: See L. Greenburg and G. W. Smith, "A New Instrument for Sampling Aerial Dust," U.S. Bureau of Mines, Report of Investigations 2392 (1922). See also T. Hatch, H. Warren, and P. Drinker, Journal Industrial Hygiene, No. 14, p. 301 (1932).)
Isokinetic	A term describing a condition of sampling in which the flow of gas into the sampling device (at the opening or face of the inlet) has the same flow rate and direction as the gas stream being sampled.
Mass Concentration	Concentration expressed in terms of mass of substance per unit volume of gas or liquid.
Mass Median Size	A measurement of particle size for samples of particulate matter, consisting of that diameter such that the mass of all larger particles is equal to the mass of all smaller particles.
Mist	A loose term applied to dispersions of liquid particles, the dispersion being of low concentration and the particles of large size. In meteorology, a light dispersion of water droplets of sufficient size to be falling.
Month	For reporting analyses of outdoor air on a monthly rate, results are calculated to a base of 30 days.
Odor	That property of a substance affecting the sense of smell; any smell; scent; perfume.
Odor Concentration	The number of unit volumes that a unit volume of sample will occupy when diluted to the odor threshold.
Odor Unit	Unit volume of air at the odor threshold.
Odorant	Odorous substance.
Orifice Meter	A flowmeter, employing as the measure of flow rate the difference between the pressures measured on the upstream and downstream sides of the orifice (that is, the pressure differential across the orifice) in the conveying pipe or duct.
Particle	A small discrete mass of solid or liquid matter.

Particle Concentration	Concentration expressed in terms of number of particles per unit volume of air or other gas. (Note: On expressing particle concentration, the method of determining the concentration should be stated.)
Particle Fall	A measurement of air contamination consisting of the mass rate at which solid particles deposit from the atmosphere. A term used in the same sense as the older terms Dust Fall and Soot Fall but without any implication as to nature and source of the particles.
Particle Size	An expression for the size of liquid or solid particles expressed as the average or equivalent-diameter.
Particle Size Distribution	The relative percentage by weight or number of each of the different size fractions of particulate matter.
Precipitation, Electrostatic	A process consisting of the separation of particulate matter from air or other gases under the influence of an electrostatic field.
Precipitation, Meteorological	The precipitation of water from the atmosphere in the form of hail, mist, rain, sleet, and snow. Deposits of dew, fog, and frost are excluded.
Precipitation, Thermal	A process consisting of the separation of particulate matter from air and other gases under the influence of a relatively large temperature gradient extending over a short distance. In the "Thermal Precipitator" (a sampling instrument), the air or gas is drawn through a narrow chamber across which extends a heated wire, particulate matter being deposited upon the adjacent collecting surface.
Precipitation, Ultrasonic	A process consisting of the separation of particulate matter from air and other gases following agglomeration induced by an ultrasonic field.
Precipitator, Electrostatic	Apparatus employing electrostatic precipitation for the separation of particles from a gas stream. The apparatus may be designed either for sampling or for cleaning large volumes of gas.
Precision	The degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the mean result obtained by repetitive testing of a homogenous sample under specified conditions. The precision of a method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations.
Pressure Static	The pressure of a fluid at rest, or in motion, exerted perpendicularly to the direction of flow.

Pressure, Velocity	That pressure caused by and related to the velocity of the flow of fluid; a measure of the kinetic energy of the fluid.
Pressure, Total	The pressure representing the sum of static pressure and velocity pressure at the point of measurement.
Pressure, Gauge	The difference in pressure existing within a system and that of the atmosphere. Zero gauge pressure is equal to atmospheric pressure.
Probe	A tube used for sampling or for measuring pressures at a distance from the actual collection or measuring apparatus. It is commonly used for reaching inside stacks and ducts.
Rotameter	A device, based on the principle of Stoke's Law, for measuring rate of fluid flow. It consists of a tapered vertical tube having a circular cross-section, and containing a float that is free to move in a vertical path to a height dependent upon the rate of fluid flow upward through the tube.
Sample, Integrated	A sample obtained over a period of time with (1) the collected atmosphere being retained in a single vessel, or (2) with a separated component accumulating into a single whole. Examples are dust sampling in which all the dust separated from the air is accumulated in one mass of fluid; the absorption of acid gas in an alkaline solution; and collection of air in a plastic bag or gasometer. Such a sample does not reflect variations in concentration during the period of sampling.
Sample, Continuous	Withdrawal of a portion of the atmosphere over a period of time with continuous analysis or with separation of the desired material continuously and in a "linear" form. Examples are continuous withdrawal of the atmosphere accompanied by absorption of a component in a flowing stream of absorbent or by filtration on a moving strip or paper. Such a sample may be obtained with a considerable concentration of the contaminant, but it still indicates fluctuations in concentration that occur during the period of sampling.
Sampling	A process consisting of the withdrawal or isolation of a fractional part of a whole. In air or gas analysis, the separation of a portion of an ambient atmosphere with or without the simultaneous isolation of selected components.
Sampling, Condensation	A process consisting of the collection of one or several components of a gaseous mixture by simple cooling of the gas stream in a device that retains the condensate.

Sampling, Continuous	Sampling without interruptions throughout an operation or for a predetermined time.
Sampling, Instantaneous	Obtaining a sample of an atmosphere in a very short period of time such that this sampling time is insignificant in comparison with the duration of the operation or the period being studied.
Sampling, Intermittent	Sampling successively for limited periods of time throughout an operation or for a predetermined period of time. The duration of sampling periods and of the intervals between are not necessarily regular and are not specified.
Series Collection	An operation involving the use of two or more collectors joined in a series.
Settling Velocity	The terminal rate of fall of a particle through a fluid as induced by gravity or other external force; the rate at which frictional drag balances the accelerating force (or the external force).
Smog	A term derived from smoke and fog, applied to extensive atmospheric contamination by aerosols which arise partly through natural processes and partly from the activities of human subjects. Now sometimes used loosely for any contamination of air.
Smoke	Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material, and present in sufficient quantity to be observable independently of the presence of other solids.
Soot	Agglomerations of particles of carbon impregnated with "tar," formed in the incomplete combustion of carbonaceous material.
Sorbent	A liquid or solid medium in or upon which materials are retained by absorption or adsorption.
Sorption	A process consisting of either absorption or adsorption or both.
Specific Gravity	The ratio of the density of the substance in question to the density of a reference substance at specified conditions of temperature and pressure.
Temperature, Absolute	(a) Temperature measured on the thermodynamic scale, designated as degrees Kelvin (K). (b) Temperature measured from absolute zero (−273.15°C or −459.67°F). The numerical values are the same for both the Kelvin scale and the ideal gas scale.

Vapor	The gaseous phase of matter which normally exists in a liquid or solid state.
Volume Concentration	Concentration expressed in terms of gaseous volume of substance per unit volume of air or other gas, usually expressed in percent or parts per million.
Week	For reporting analyses of outdoor air on a weekly rate, results are calculated to a base of 7 consecutive 24-hour days.
Year	For reporting analyses of outdoor air on a yearly rate, twelve 30-day months are to be used.

References

Benedict, Robert P. 1969. *Fundamentals of temperature, pressure, and flow measurements.* New York: John Wiley and Sons, Inc.

Lemon, M. B., and Ference, M. 1946. *Analytical experimental physics.* Chicago: The University of Chicago Press.

Perry, J. H. *Chemical engineer's handbook.* New York: McGraw-Hill Book Co., Inc.

Nebergall, William H.; Schmidt, Frederic C.; and Holtzclaw, Henry, F., Jr. 1968. *General chemistry.* Lexington, MA: Reytheon Education Company.

Terraglio, F. P.; Sheehy, J. P.; and Manganelli, R. M. 1958. Recommended units of expression for air pollution. *J. Air Poll. Cont. Assoc.* 8:220-222.

Uennard, J. K. 1947. *Elementary fluid mechanics.* New York: John Wiley and Sons, Inc.

Weast, R. C., and Astle, M. J. 1979. *Handbook of chemistry and physics.* 60th ed. Boca Raton, FL: Chemical Rubber Publishing Co.

Section A-2

Air Movers and Air Measuring Instruments

Reading Assignment

Pages 3-1 through 3-52 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Air Movers
- Air Measuring Instruments

Learning Goals and Objectives

Learning Goal

The purpose of this section is to familiarize you with air movers and air measuring instruments.

Learning Objectives

At the end of this section, you should be able to

1. recall at least six considerations in selecting an air mover for atmospheric sampling.
2. recall at least three evaluation criteria for determining the ease of maintenance of an air mover.
3. identify piston, diaphragm, and centrifugal pumps from their diagrams.
4. recall the effects of sample flow rate and pressure drop on the performance of air sampling pumps.
5. describe the thirteen air measuring devices discussed in this section and classify them according to air measuring device category and standard meter class.
6. name at least four air movers that are used in atmospheric sampling.
7. recognize equations used to correct measured flow rates and air volumes to EPA's Standard Temperature and Pressure (STP) conditions.
8. recall that gas density has an effect on flow rate measurements made by rotameters.

9. recall the effects of gas temperature, pressure, and thermal properties on flow rate measurements made by mass flow meters.
10. name at least two advantages of a dry test meter over a wet test meter.
11. identify at least four sources of pressure drop in a typical sampling train.
12. identify at least four flowmeters used for $PM_{2.5}$ sampler calibration.

Reading Guidance

1. Refer often to the equations, example calculations, and figures of the assigned reading material as you progress through the assignment.
2. When you have finished the reading assignment, complete the review exercise for Section A-2. It begins on the following page.
3. After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
4. For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment indicated on the answers page.
5. After you have reviewed your incorrect answers (if any), proceed to Section A-3 of this guidebook.

Review Exercise

Now that you've completed the assignment for Section A-2, please answer the following questions. These will help you determine whether or not you are mastering the material.

1. Which of the following is NOT a consideration in selecting an air mover for atmospheric sampling?

   a. sampling flow rate
   b. physical/chemical nature of the air to be sampled
   c. cost of the air mover
   d. noise of the air mover

2. Which of the following should be considered in evaluating the ease of maintenance of an air mover?

   a. accessibility of repair parts
   b. type of calibration equipment necessary
   c. cost of repair parts
   d. both a and c

3. In general, _____ preventive maintenance activities _____ air mover malfunctions.

   a. increasing / increases
   b. decreasing / decreases
   c. increasing / decreases

4. Piston and diaphragm pumps are _____ pumps.

   a. centrifugal
   b. radial flow
   c. axial flow
   d. positive displacement

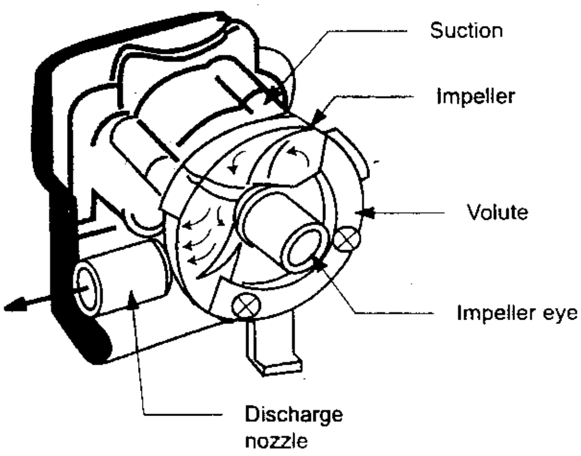
For each of questions 5 through 7, match the pump with its appropriate diagram.

5. piston pump ___

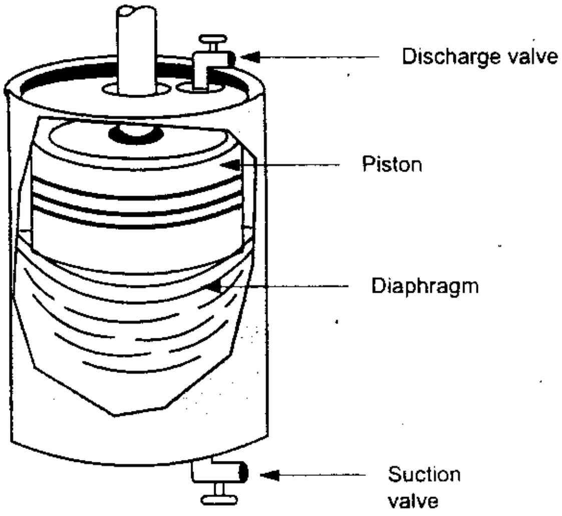
6. diaphragm pump ___

7. centrifugal pump ___

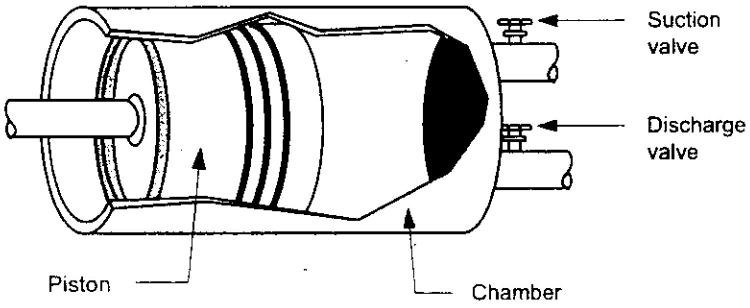
a.



b.



c.



8. The total suction pressure required for a pump to operate (its head) is _____ the total pressure drop between the intake of the sample collection device and the pump's intake.

   a. equal to
   b. greater than
   c. less than

9. Which of the following are air movers used in atmospheric sampling?

   a. evacuated flask, liquid displacer, ejector, precipitator
   b. liquid displacer, precipitator, centrifugal pump, ejector
   c. centrifugal pump, ejector, evacuated flask, plastic bag
   d. centrifugal pump, ejector, plastic bag, precipitator

10. Generally, air mover flow rate _____ as the sampling train's resistance to flow _____.

    a. increases, increases
    b. decreases, increases
    c. decreases, decreases

11. True or False? The collection efficiency of an air sampling device may be affected by fluctuations in sampling flow rate.

    a. True
    b. False

12. Which of the following is a source of pressure drop in a typical sampling train?

    a. pump
    b. noise reduction linings
    c. flow exhaust
    d. friction in connecting lines

13. Which of the following equations is appropriate for calculating the volume of air sampled?

a. $V = \frac{Q}{t}$

b. $V = \frac{t}{Q}$

c. $V = \left(\frac{Q}{t}\right)Q$

d. $V = (Q)(t)$

Where:
V = *volume of air sampled*
Q = *sampled flow rate*
t = *sampling time*

14. _____ meters measure the total _____ of gas passed through them over some specified time period.

a. Volume, volume
b. Rate, rate
c. Velocity, velocity

15. _____ meters measure the time _____ of flow through them.

a. Volume, volume
b. Rate, rate
c. Velocity, velocity

16. True or False? Measurement of sampling flow rate and sampling time affects the determination of the volume of air sampled.

a. True
b. False

17. Which of the following is(are) <u>NOT</u> (a) type(s) of standard meters used to calibrate air measuring devices?

a. primary standard meters
b. secondary standard meters
c. tertiary standard meters
d. all of the above

18. _____ standard meters are those whose volumes can be determined by measurement of internal physical dimensions alone. Accuracies better than ± 0.30% can be achieved.

a. Primary
b. Secondary
c. Tertiary

19. Which of the following flowmeters are used for $PM_{2.5}$ sampling?

a. bubble flowmeter, piston flowmeter, mass flowmeter, laminar flow element
b. bubble flowmeter, piston flowmeter, laminar flow element, spirometer
c. bubble flowmeter, piston flowmeter, spirometer, pitot tube
d. bubble flowmeter, spirometer, pitot tube, laminar flow element

For each of questions 20 through 23, match the air measuring device with its appropriate diagram.

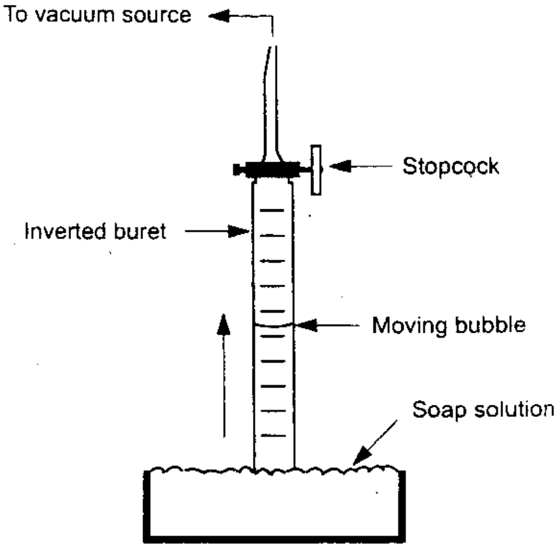
20. Spirometer ___

21. Displacement bottle technique ___

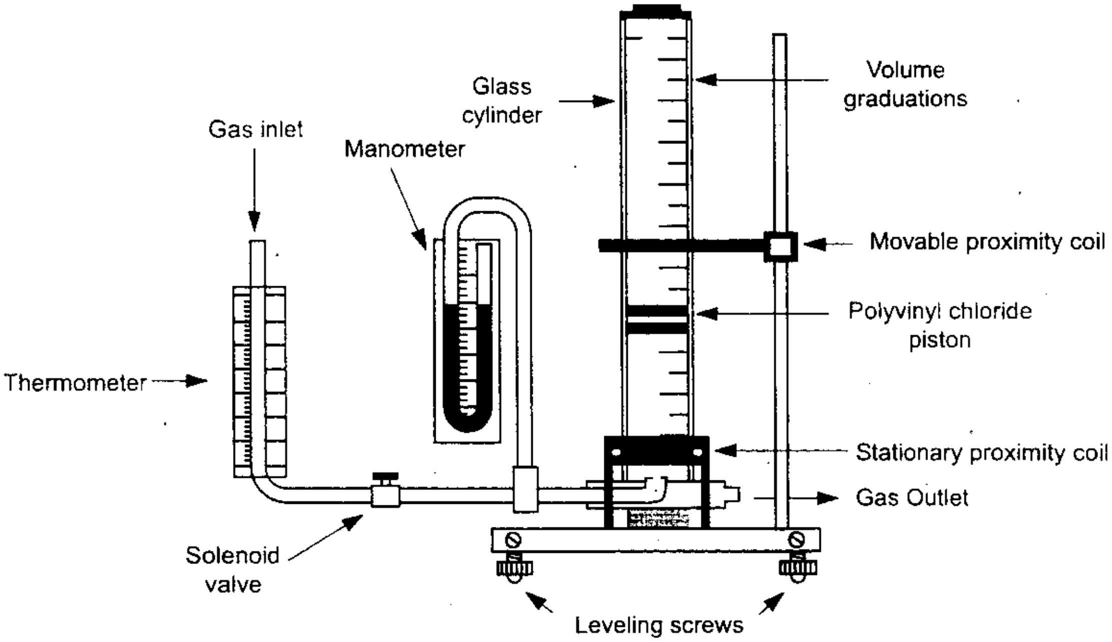
22. Moving bubble meter ___

23. Mercury-sealed piston ___

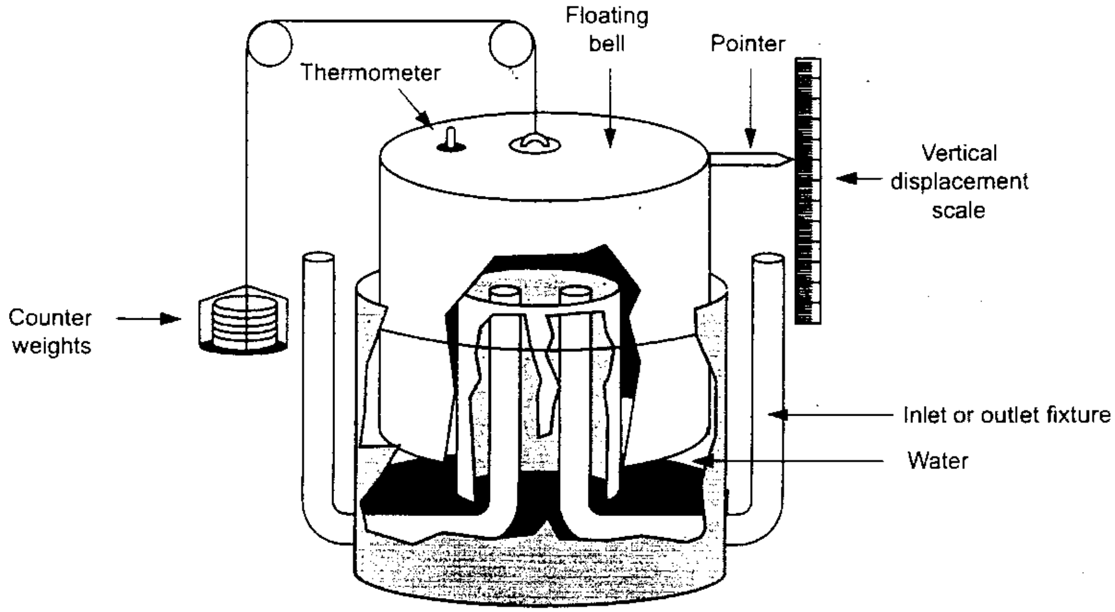
a.



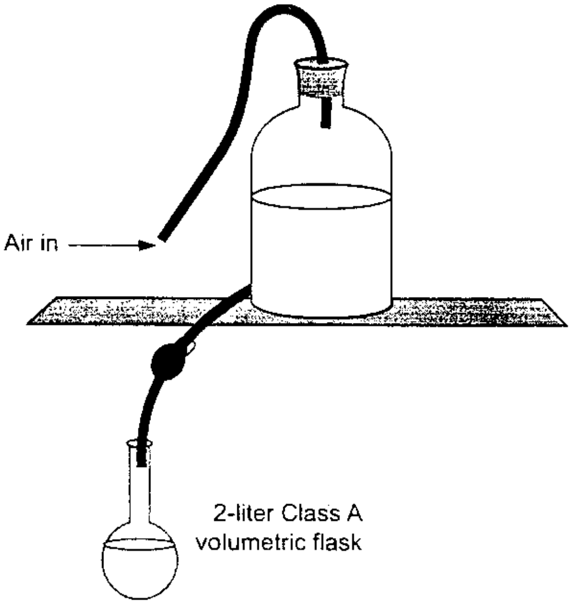
b.



c.


Floating bell
Pointer
Thermometer
Vertical displacement scale
Counter weights
Inlet or outlet fixture
Water

d.


Air in
2-liter Class A volumetric flask

For each of questions 24 through 36, match the air measuring device with its appropriate description.

Air Measuring Devices

24. Mass flow meter ___

25. Spirometer ___

26. Displacement bottle technique ___

27. Moving bubble meter ___

28. Mercury-sealed piston ___

29. Wet test meter ___

30. Roots meter ___

31. Dry test meter ___

32. Orifice meter ___

33. Venturi meter ___

34. Rotameter ___

35. Standard pitot tube ___

36. S-type pitot tube ___

Descriptions (for use with questions 24-36)

a. This device works on the principle that as a gas passes over a heated surface, heat is transferred from the surface to the gas. The amount of current required to keep the surface at a constant temperature is a measure of the velocity of the gas.

b. This device consists of two identical tubes mounted back to back. The sampling ends of the tubes are oval with the openings parallel to each other. In use, one oval opening should point directly upstream, the other directly downstream.

c. This device consists of a vertically graduated glass tube, slightly tapered in bore, with the diameter decreasing from top to bottom, containing a float of the appropriate material and shape. The fluid to be measured passes upward through the conical tube, which is inserted in the flow circuit.

d. This device consists of a short cylindrical inlet, an entrance cone, a short cylindrical throat, and finally a diffuser cone. Two pressure taps, one in the cylindrical inlet and one in the throat, serve to measure the pressure drop.

e. This device can consist of a thin plate having one circular hole coaxial with the pipe into which it is inserted. Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop, which can be correlated to the time rate of flow.

f. This device consists of two concentric tubes. The center tube measures the impact pressure while the static pressure is measured by the holes located on the side of the outer tube.

g. The interior of this device contains two or more movable partitions, or diaphragms, attached to the case by a flexible material so that each partition may have a reciprocating motion. The gas flow alternately inflates and deflates each bellows chamber, simultaneously actuating a set of slide valves that shunt the incoming flow at the end of each stroke. The inflation of the successive chambers also actuates, through a crank, a set of dials that registers the volume of gas passed through the device.

h. This device consists of a series of inverted buckets or traps mounted radially around a shaft and partially immersed in water. The location of the entry and exit gas ports is such that the entering gas fills a bucket, displacing the water and causing the shaft to rotate due to the lifting action of the bucket full of air. The entrapped air is released at the upper portion of the rotation and the bucket again fills with water. In turning, the drum rotates index pointers that register the volume of gas passed through the meter.

i. This device consists of a cylinder of known volume, closed at one end, with the open end submerged in a circular tank of fluid. The cylinder can be opened or closed to the atmosphere by a valve. As the cylinder is lowered into the water, the water displaces the air and causes it to be discharged from the cylinder; the rate of discharge can be regulated.

j. This device consists basically of two oppositely rotating impellers of two-lobe or "figure 8" contour, operating within a rigid casing. The casing is arranged with inlet and outlet gas connections on opposite sides.

k. This device consists of a precision-bored, borosilicate glass cylinder with a close-fitting polyvinyl chloride piston. The piston and cylinder wall are sealed with a ring of mercury that stays in place because of its high viscosity and the closeness of the fit between the cylinder and piston.

l. This device consists of a bottle filled with a liquid and a tube through which air can enter the bottle. As the liquid in the bottle is drained or siphoned out, air is drawn in, to take the place of the volume of liquid lost. The volume of gas sampled is equal to the volume of liquid displaced. The volume of displaced liquid can be measured with a Class A volumetric flask.

m. This device consists of a cylindrical glass tube with graduated markings. Either a vacuum at the top or slight positive pressure at the bottom of the tube moves a soap bubble up the tube. By timing this movement and noting the volume traversed by the bubble over the measured time span, volumetric flow rate can be calculated.

For each of questions 37 through 41, match the air measuring device with its appropriate standard meter classification.

Air Measuring Devices

37. Orifice meter ___

38. Venturi meter ___

39. Rotameter ___

40. Standard pitot tube ___

41. S-type pitot tube ___

Standard Meter Classifications

a. primary

b. secondary

42. Which of the following equations is used to correct air volumes measured by soap bubble meters and wet test meters to dry conditions?

a. $$V_c = V_{meas}\left(\frac{P_b + P_w}{P_b}\right)$$

b. $$V_c = V_{meas}\left(\frac{P_b}{P_b + P_w}\right)$$

c. $$V_c = V_{meas}\left(\frac{P_b - P_w}{P_b}\right)$$

d. $$V_c = V_{meas}\left(\frac{P_b}{P_b - P_w}\right)$$

Where:

V_c = *corrected volume*
V_{meas} = *measured volume*
P_b = *atmospheric pressure*
P_w = *vapor pressure of water at the room's temperature during measurement*

43. Which of the following is an(are) advantage(s) of a dry test meter over a wet test meter?

a. Measured air volumes do not have to be corrected to dry conditions when using a dry test meter.
b. Dry test meters are lighter and easier to use.
c. both a and b, above
d. none of the above

44. Which of the following equations is used to correct air volumes measured by volume meters to EPA's STP conditions?

a. $$V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$$

b. $$V_2 = (V_1)\left(\frac{P_2}{P_1}\right)\left(\frac{T_2}{T_1}\right)$$

c. $$V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_1}{T_2}\right)$$

d. $$V_2 = (V_1)\left(\frac{P_1}{T_1}\right)\left(\frac{P_2}{T_2}\right)$$

Where:

V_2 = *corrected volume of air at EPA's STP conditions*
V_1 = *measured volume of air at* P_1 *and* T_1
T_1 = *measured temperature of gas, K*
T_2 = *298 K*
P_1 = *measured pressure of gas, mm Hg*
P_2 = *760 mm Hg*

45. True or False? Variable pressure meters are those in which a stream of fluid creates a significant pressure difference that can be measured and correlated with the time rate of flow.

a. True
b. False

46. The pressure drop across a variable area meter _____ as the flow rate through the variable area meter changes.

a. increases
b. decreases
c. remains constant

47. True or False? A critical orifice is an orifice meter having a pressure drop such that any further decrease in its downstream pressure or increase in its upstream pressure will not change the gas flow rate through it.

a. True
b. False

48. True or False? Plastic bags can usually be used to collect fairly large sample volumes.

- a. True
- b. False

49. True or False? Under typical sampling conditions, gas temperature and pressure affect flow rate measurements made by mass flow meters.

- a. True
- b. False

50. Using the following information, calculate the total volume of air sampled:

Sampling time = 24 hours
Sampled flow rate = 16.7 L/min
Temperature = 25°C
Pressure = 715 mm Hg

- a. 24048 L
- b. 0.193 L
- c. 86.22 L
- d. 8.292 L

Section A-2

Review Exercise Answers

		Page(s) of *Atmospheric Sampling: Student Manual*
1.	c	3-2, 3-3, 3-4
2.	d	3-3
3.	c	3-3
4.	d	3-4
5.	c	3-6, 3-7
6.	b	3-9
7.	a	3-1 through 3-17
8.	a	3-3
9.	c	3-2, 3-15, 3-16
10.	b	3-16
11.	a	3-17
12.	d	3-18
13.	d	3-18
14.	a	3-17
15.	b	3-18
16.	a	3-18, 3-19
17.	c	3-18, 3-19
18.	a	3-18, 3-19
19.	a	3-49, 3-50
20.	c	3-19
21.	d	3-21
22.	a	3-22
23.	b	3-25
24.	a	3-45
25.	i	3-19
26.	l	3-21
27.	m	3-22
28.	k	3-25
29.	h	3-27
30.	j	3-31
31.	g	3-33
32.	e	3-36
33.	d	3-37
34.	c	3-38
35.	f	3-42
36.	b	3-44
37.	b	3-36
38.	b	3-37
39.	b	3-38
40.	a	3-42
41.	b	3-44
42.	c	3-24
43.	c	3-27, 3-33
44.	a	3-20
45.	a	3-36
46.	c	3-36
47.	a	3-36
48.	b	3-14
49.	b	3-45
50.	a	3-20

Required Readings

Chapter 3

Air Measuring Instruments

Introduction to Air Movers

The primary purpose of an air mover in the sampling process is to create a flow of air that will allow the contaminant in the air to be analyzed directly or to be captured by a collection device for subsequent analysis. Collection devices include filters, impingers, and impactors. Air movers range in capacity from a few cubic centimeters per minute (cm^3/min) of air up to tens of cubic meters per minute (m^3/min). In operational complexity, air movers range from a squeeze bulb to a multistage pump.

Relationship of Air Movers to Other Sampling System Components

Air movers are vital components of sampling trains used for the sampling and analysis of air for its pollutant content (see Figure 3-1). Several of the considerations governing the selection of an air mover for a particular application will be mentioned in this discussion.

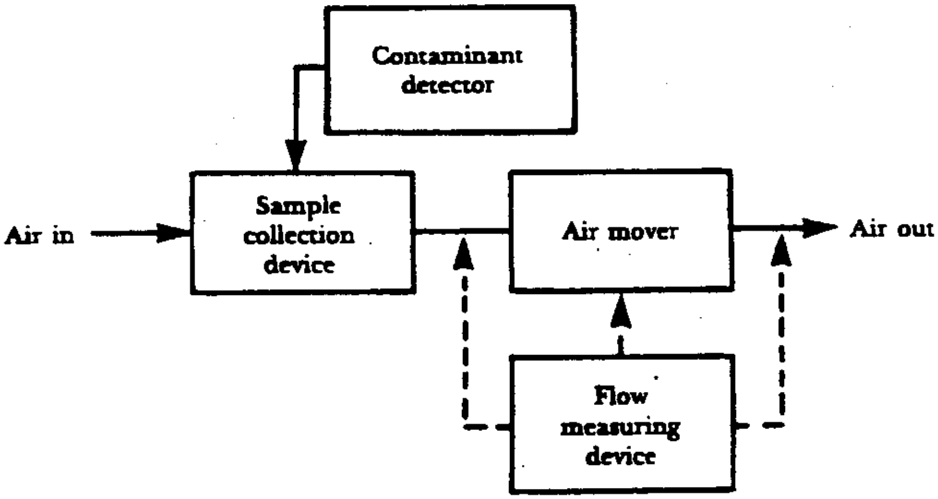


Figure 3-1. A sampling train.

Air Mover Classification

There are many parameters by which air movers can be evaluated and classified. Classification of air movers can be made according to their function, capacity, "driving" force, and principle of operation, among other parameters. The classification scheme often depends to a great extent on the classifier. The actual types of air movers to be discussed in this text are *pumps, ejectors, liquid displacers*, and *air displacers*.

Air Mover Selection Criteria

Since there is no one "typical" air sampling train, equipment selection is an important aspect of any airborne sampling scheme, meaning that air mover selection must be made along with the selection of other sampling train components. Here are some of the many factors to be considered before selection is discussed. The itemizing of the considerations is not necessarily in order of their importance.

Pollutant Concentration and Sampling Time

The required flow rate of the air mover is often determined by the sensitivity of the analysis method, which in turn sets the minimum quantity of the contaminant required for analysis. For example, if the analysis procedure required 10 μg of material to obtain the desired precision, and if the air contains 1 $\mu g/m^3$ of that material, a sample size of 10 m^3 would be required, assuming 100% collection efficiency. The required flow rate of the air mover can be calculated by determining the available sampling time and the sample volume required. For example, if the above-mentioned 10 m^3 of air had to be moved (sampled) in a period of 10 hours, an air mover of 1 m^3/hr capacity could be used. In many instances it is more feasible to sample for longer periods of time, and sometimes at higher rates, than those required. As long as the sample size is greater than the minimum detectable and less than the concentration that theoretically saturates the collection medium, this may be of no consequence.

Sampling Rate Required

In some instances it may be necessary to sample at some required flow rate to ensure efficient sample collection. An example is the collection of a sample by using a chemical reaction. The reaction kinetics may depend on the length of time the contaminant is in the presence of the reacting substance, and the length of contact time is dependent on the sampling rate. Other examples include the collection of particulate matter by use of impinger or impactors. For example, collection of a sample at a low flow rate should increase the time that the air is in contact with the reagent and may also decrease the size of the bubbles, thus increasing the surface area of air in contact with the reagent. The particle size collected will be dependent on the approach velocities, and these in turn are dependent on the sampling rates.

Physical and Chemical Nature of Air to be Sampled

The operation of the air mover selected must be compatible with the physical and chemical characteristics of the air and contaminant to be sampled. Air of a corrosive or abrasive nature can create problems with the air mover unless the internal parts are nonreactive with the sample air.

In instances where sampling is to be done in an environment of a potentially explosive nature, approved explosion-proof air movers or explosion-sealed air movers should be selected. A completely sealed electric motor for a pump, in conjunction with non-sparking metal parts, is an example of an explosion-sealed air mover.

Portability of Air Mover

Air sampling is often performed at temporary sampling sites. When sampling trains must be moved from location to location, it is important that each component be as portable and lightweight as possible. At permanent sampling locations, air mover portability is not such an important consideration.

The power source for the air mover may be the limiting factor in its portability, especially when the power source must be AC line voltage.

Air Mover Noise

Since air sampling may be required in areas having noise restrictions, the noise produced by an air mover must be considered. Also, the suppression of air mover noise has aesthetic values. Noise levels may be considered in relation to the length of the sampling period; that is, for short periods high noise levels *may* be acceptable. Many commercially available air movers have special sound-adsorbing liners, vibration-reducing cushioning material, or mufflers as noise-reducing components of the mover itself.

Air Mover Maintenance

It is an established fact that manmade equipment, whether air sampler components or computers, will not be maintenance-free. Maintenance considerations are of special importance for equipment to be used in the field, because valuable time can be lost in transit between the repair shop and the sampling location. There are three particular points to consider about air mover maintenance: (a) air mover parts that might need repairing should be easily accessible; (b) the complete repair should not be very time consuming; and (c) air mover parts should not be overly expensive. In general, increasing preventive maintenance activities decreases air mover malfunctions.

Resistance

Flow resistance considerations may dictate the selection of an air mover of a particular type (see Figure 3-2). The sample collection device will offer some resistance to the flow of air through it; therefore, the air mover must be able to overcome this resistance so that efficient sample collection can be accomplished.

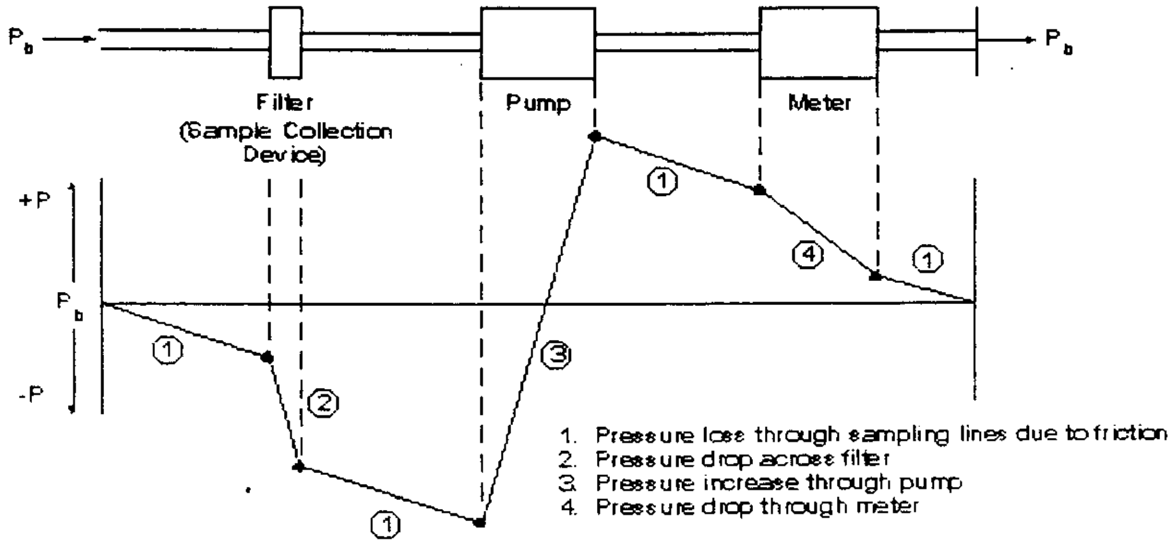


Figure 3-2. Pressure profile for basic sampling apparatus.

Constant Flow Rate

It is often desirable to collect a sample at a constant flow rate. Variation in sample conditions or other external influences can make this difficult. For example, the resistance of a filter can be expected to increase with sample "buildup," thereby decreasing the flow rate through the sample apparatus. Poor voltage regulation can result in variable motor speeds, leading to variable sampling rates. However, some commercially available air movers feature constant flow rates despite varying sampling conditions; others require flow regulation devices in order to have constant flow rates. Some flow regulation mechanisms will be discussed later in the chapter. Another factor of importance in some applications is the ability to vary the flow rate of the air mover and then to maintain constancy at the selected rate. This topic will also be discussed in more detail later.

Pumps

Pumps have been defined as devices that raise or transfer fluids. Since air is a fluid, a pump that moves air either raises it to another level or transfers it to another location. In air sample collection, the air is transferred from one location through, or into, a sample collection device.

Classification of Pumps

Categorization of pumps is a difficult task because of the many variables. This section will discuss pumps in terms of two broad classes based on flow variation with pressure. These two major classes will be subdivided into categories according to specific principles of operation: (a) *positive displacement pumps* and (b) *centrifugal pumps.*

Positive Displacement Pumps

Positive displacement pumps are often characterized by a linear relationship between the suction pressure and pump capacity (see Figure 3-3). This indicates that $\Delta Q/\Delta p$ (ΔQ is the change in flow rate; Δp is the pressure drop across the pump) is a constant value. Figures 3-3 and 3-5 are representative of characteristic curves of pumps to be discussed later.

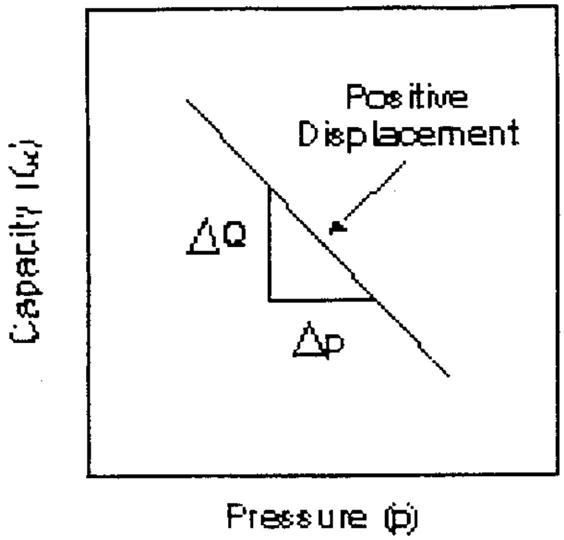
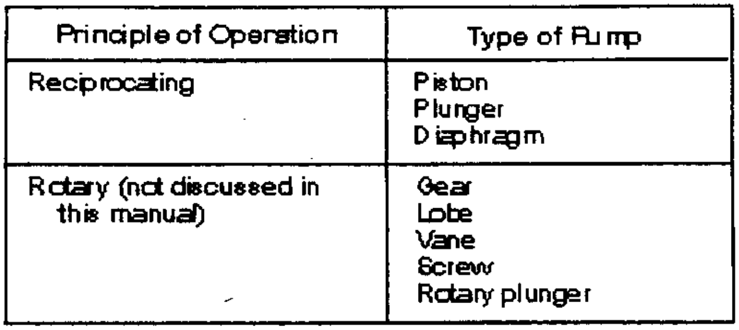


Figure 3-3. Positive displacement pump.

The name *positive displacement* arises from the fact that the inner parts of these pumps are movable and tight-fitting, and the air is displaced through them by the movement (displacement) of these tight parts. Figure 3-4 indicates a further subdivision of positive displacement pumps, this division being made according to the principle of operation. Reciprocating pumps are characterized by fixed casings containing movable pistons that work only forward-and-backward or up-and-down and by the pressure of suction and discharge valves.



Principle of Operation	Type of Pump
Reciprocating	Piston Plunger Diaphragm
Rotary (not discussed in this manual)	Gear Lobe Vane Screw Rotary plunger

Figure 3-4. Classification of positive displacement pumps.

The operation of some of the specific types of reciprocating pumps will be discussed later in this section.

Centrifugal Pumps

Centrifugal pumps are representative of pumps other than positive displacement pumps. Centrifugal pumps do not have a straight line relationship between suction pressure and capacity; thus, ΔQ/Δp is not constant (see Figure 3-5).

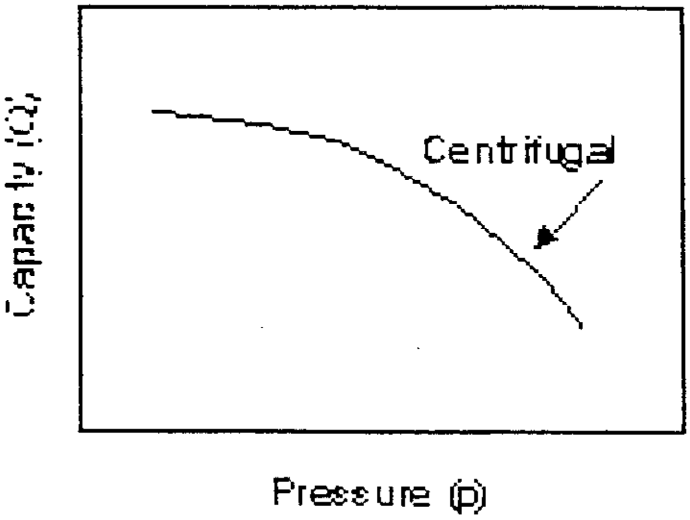


Figure 3-5. Centrifugal pump.

A centrifugal pump moves fluids by a centrifugal force created by a wheel, called an impeller, revolving in a tight casing. Some additional examples of pumps other than positive displacement pumps are: (a) turbine pumps, (b) propeller pumps, and (c) screw drag pumps. Each of these exhibit the same general pressure-capacity relationship as the centrifugal pump.

Positive Displacement Pump Operation

Some of the positive displacement pumps previously classified will now be discussed.

Piston Pump (Reciprocating)

The principle of operation of a piston pump is that air is drawn into a chamber or grinder on the suction stroke of a piston, then pushed out on the discharge stroke, as illustrated in Figure 3-6. On the suction stroke, the suction valve is open, allowing air to flow in; on the discharge stroke, the suction valve closes and the discharge valve opens, allowing air to flow out. An internal combustion engine is an example of a piston pump. Piston pumps vary in complexity of operation from manually operated ones to models with many working parts.

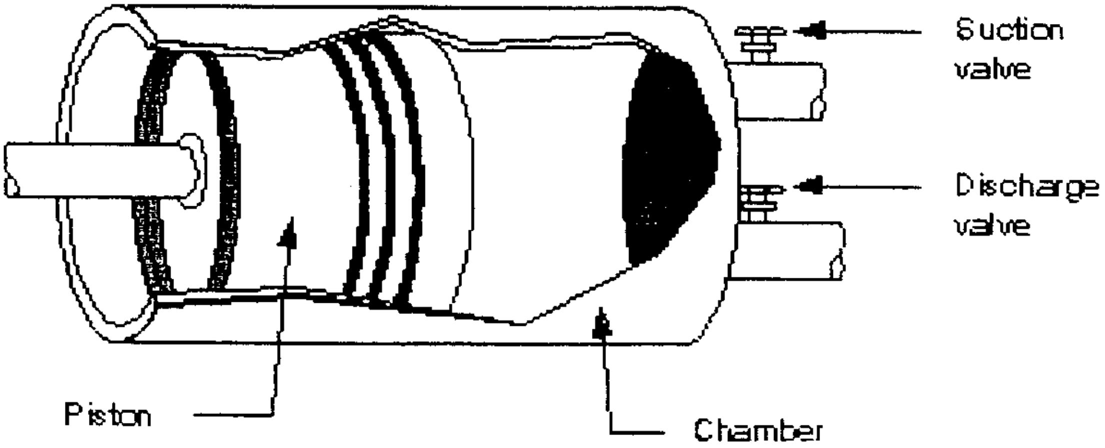


Figure 3-6. Piston pump.

Diaphragm Pumps (Reciprocating)

In principle, the operation of a diaphragm pump is very similar to a piston pump. The piston (plunger) in a diaphragm pump does not move in a tightly fitted chamber as in the piston pump, but is attached to the center of a circular diaphragm, the outer edge of which is bolted to a flange on the pump casing. The diaphragm may be made of metal or some soft material such as Teflon® or neoprene. The most important characteristics of the diaphragm material are its flexibility and resistance to reaction with the air being moved. The up-and-down motion of the plunger is permitted by diaphragm flexibility without the rubbing of one part on another (see Figure 3-7). On upward movement of the plunger, air flows into the pump through a suction valve. Downward movement of the plunger closes the suction valve and the air is forced through a discharge valve, perhaps located in the plunger itself. An automobile fuel pump is an example of a diaphragm pump.

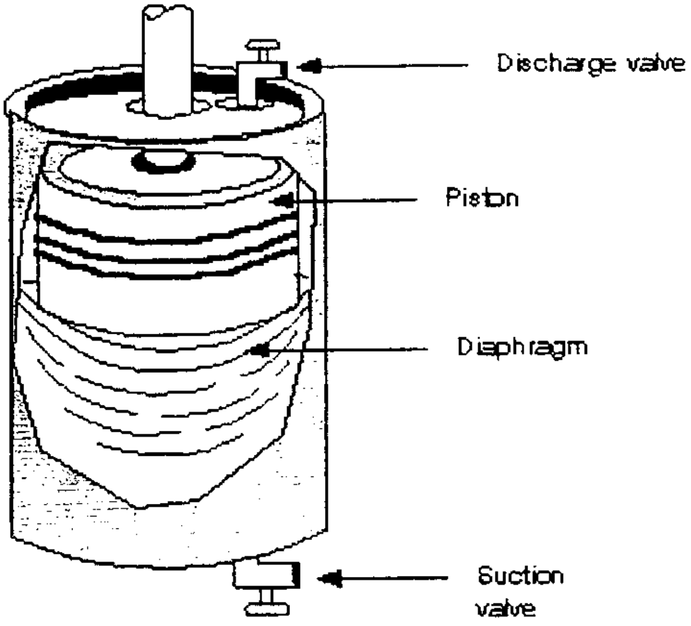


Figure 3-7. Diaphragm pump.

Centrifugal Pump Operation

Centrifugal pumps (or fans) employ centrifugal force to move air. The simplest form of this type of pump consists of an impeller routing in a volute ("snail's shell") casing (see Figure 3-8). The rotation of the impeller creates a decreasing pressure at the impeller "eye," causing air to be drawn into the pump. Air drawn into the center of the impeller is "picked up" by the vanes and accelerated to a high velocity by rotation of the impeller. It is then discharged by centrifugal force into the casing and out the discharge nozzle.

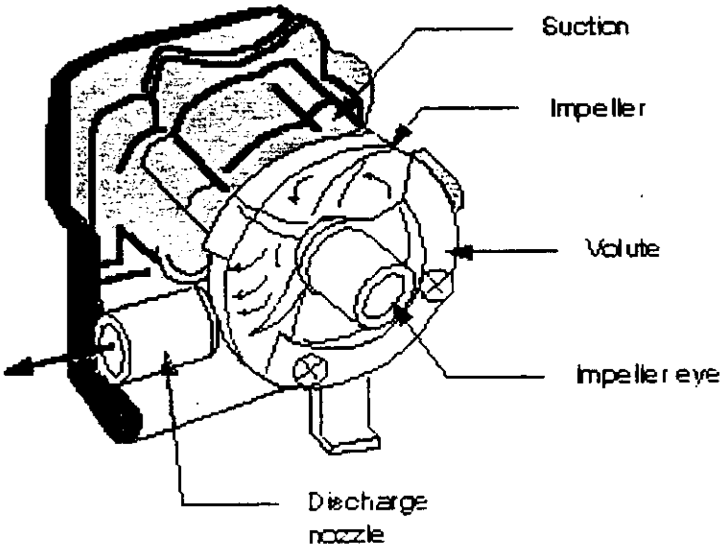


Figure 3-8. Centrifugal pump operation.

Centrifugal pumps encountered in air sampling can be divided primarily into three categories: (a) radial flow, (b) axial flow, and (c) mixed flow. Centrifugal pumps may also be classified into single-stage or multistage. Single-stage indicates a pump in which the total head is developed by one impeller; multistage indicates a pump having two or more impellers acting in series in one casing.

"Driving Forces" for Pumps

All pumps have at least one common characteristic - they have movable parts. The movement of the parts is the basis for the transfer of the particular fluid of interest. For the parts to move there must be a "driving force." Driving forces for pumps can be categorized as: (a) manual and (b) motors.

Some air movers in the general category of pumps can be operated manually. A hand-operated hypodermic syringe (piston pump) and a tire pump using a foot petal are examples. The hand-operated, portable MSA Midget Impinger Sampler has seen much use. It is operated by a hand-cranked, 4-cylinder pump that draws air through a small glass nozzle at a relatively high velocity. A relatively constant flow rate can be obtained by use of this sampler. Two obvious disadvantages of manually-operated pumps are that only small sample volumes can be collected, and that sampling time is limited because of personnel requirements.

Electric motors operated by commercial power, motor-generation sets, or batteries are all used for driving air sampling pumps. When batteries are to be used as the driving force, several factors should be considered, among which are the motor power requirements and the required length of sampling. The length of the sample time is important in relation to the life of the battery.

In instances where constant flow is required, it is important that the driving force for the pump be constant and not be affected by environmental factors. If the driving force is variable, measures may have to be taken to try to regulate it. For example, a voltage regulator may be required in conjunction with an electric motor that is driving an air pump where variable voltage power sources arc encountered.

Characteristic Curves

Pumps perform differently under different conditions; therefore, "characteristic curves," showing the relationships between the various conditions affecting their performance, are usually supplied by the manufacturer. The characteristic curves of most interest in air sampling are those indicating the pressure-flow relationship (see Figures 3-9 and 3-10).

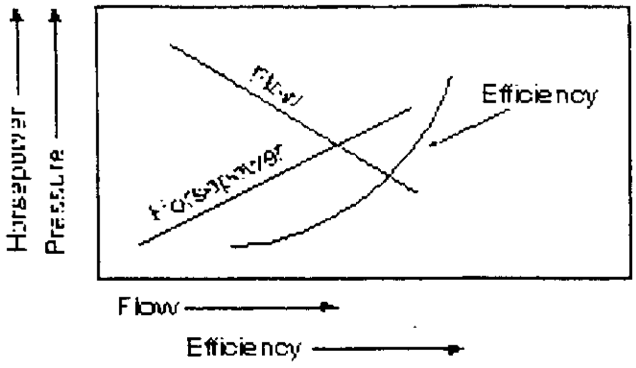


Figure 3-9. Characteristic curve for a positive displacement pump.

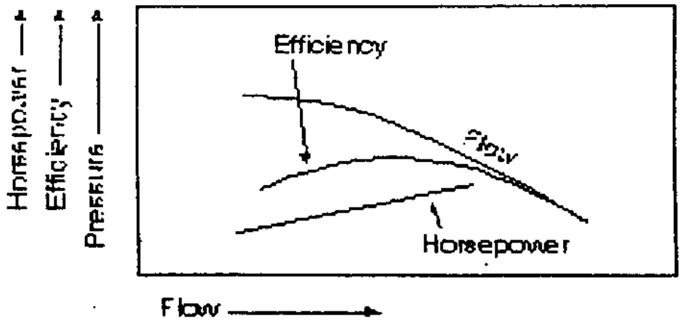


Figure 3-10. Characteristic curve for a centrifugal pump.

The quantity of flow is usually expressed in terms of a flow rate - e.g., cubic feet per minute (cfm), liters per minute (lpm), and cubic feet per hour (cfh). The pressure represents the amount of suction that must be available to overcome the resistance of the air to movement through the sampling train. Pressure can be expressed in pounds per square inch gauge (psig) or in inches of an equivalent height of a fluid. The suction pressure at which a pump is required to operate is often referred to as its head. The total head is equal to the total pressure drop between intake of the sample collection device and the pump intake. Other parameters such as efficiency, horsepower, and speed are indicated in the characteristic curves for certain pumps. Empirical equations relating various parameters are also available. It should be noted from Figures 3-9 and 3-10 that different types of pumps possess different characteristics. As flow increases for a rotary pump, the efficiency increases; for a centrifugal pump, the efficiency increases and then decreases as flow increases.

Selecting a Pump

It is evident that often a choice must be made between pumps. The selection may be limited to certain categories of air movers due to the sampling rate required. On the other hand, if flow rate is not critical, a wide variety of air movers may be applicable, necessitating a more involved evaluation and choice. A comparison of some of the advantages and disadvantages of certain types of pumps is contained in Figure 3-11. A comparison of this type, although it is not necessarily complete in all considerations, should be of value in responsible pump selection.

Pump type	Advantages	Disadvantages
Piston pump (reciprocating)	1. Can operate at high suction pressure 2. Can be metered	1. Small capacity 2. Seal required between piston & piston chamber 3. Working parts such as check valves and piston rings may cause difficulties 4. Pulsating flow 5. Moderate maintenance
Diaphragm pump (reciprocating)	1. Wide range of capacities 2. No seal required 3. Good in continuous operation	1. Limited materials of construction 2. Operation at limited suction pressures 3. Pulsating flow 4. Periodic diaphragm replacement 5. Moderate maintenance
Centrifugal pump	1. Large range of capacities 2. No close clearance 3. Can obtain high suction heads by multistages 4. Light maintenance	1. No small capacities 2. Turbulence 3. Operational noise

Figure 3-11. Pump comparison.

There are many features of commercially available pumps that may or may not warrant consideration. Some features may have direct applicability for certain uses; others may provide flexibility, making the pumps more generally usable. In this discussion, only gauges and continuous operation capability will be considered.

Pump Gauges

Many pumps have inlet vacuum gauges and/or outlet pressure gauges. These gauges, upon proper calibration, can be used to determine the approximate flow rate through the pump. The flow rate determination can be made by use of the pump's characteristic curve for the pressure-flow relationship (see Figure 3-12). or by direct reading if the gauge is calibrated in terms of cfm on its dial.

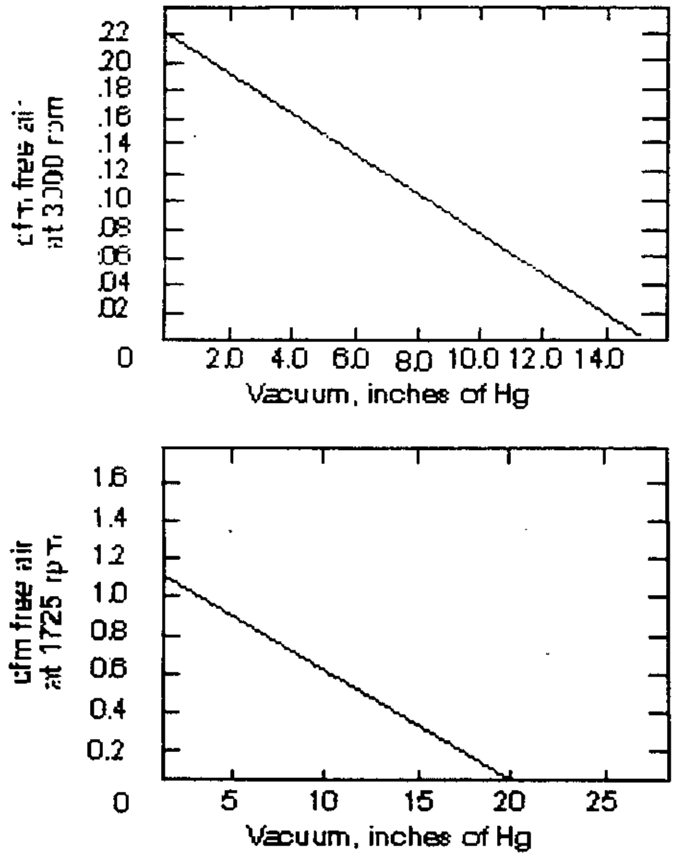


Figure 3-12. Pressure-flow relationship for metal bellows pumps for vacuum.

Continuous Operation Capability

Pumps are often required to operate continuously for long periods of time (hours to days) at high vacuum. Some pumps such as rotary or diaphragm pumps used in ambient air monitors are capable of continuous operations at high vacuum, while others would tend to "burn" themselves out. The importance of this capability would be dependent on the sampling time required.

Ejectors

Another classification of air movers is known as ejectors. Ejectors are also referred to as aspirators.

Principle of Operation

As depicted in Figure 3-13, ejectors operate according to the jet principle. At the nozzle, the pressure head of the driving force is converted into a high velocity stream. The passage of the high velocity stream through the suction chamber creates a decreased pressure (vacuum), thus drawing air into the chamber itself. The incoming air is mixed with the high velocity driving force mixture and can be ejected against moderate pressure through the diffuser.

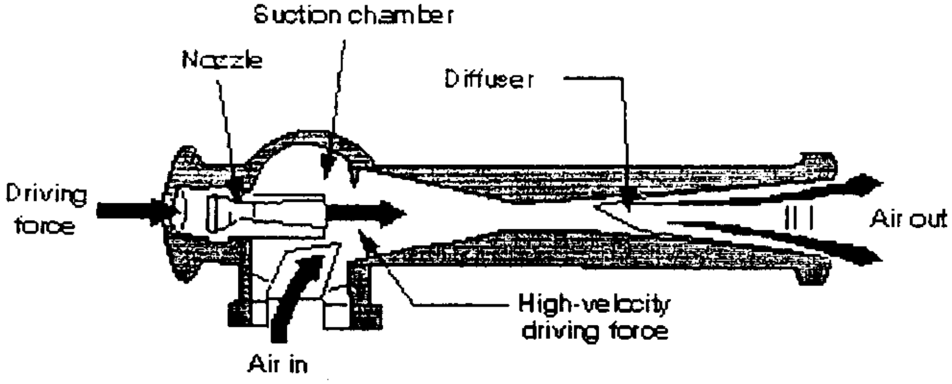


Figure 3-13. Ejector operation.

Driving Forces

The pressurized fluid that is converted into a high velocity jet stream in an ejector may be of several types. Some examples of fluids used are water, steam, compressed air or CO_2, and other gases such as freon.

Sampling Use of Ejectors

Using ejectors as samplers, air moved is adequate for lower sampling rates. The sampling rates vary from a few liters per minute up to several cubic feet per minute. The flow rate through an ejector can be regulated to some extent by adjusting the nozzle opening. A limitation to the use of ejectors is that the pressurized driving force may have a time limit on its available effectiveness (i.e., if pressurized gas cylinder is used, it may last only for a limited amount of time).

Liquid Displacers

Air movers that operate according to the principle of liquid displacement incorporate two sampling train components into one entity. In this case, the liquid displacement unit serves as the sample collection device and the air mover together, or it may provide the air moving capability for a second device which may act as the sample collection device.

Principle of Operation

Gravity flow of liquid from a container creates a vacuum within the container, thus drawing air into the container to fill the displaced volume (see Figure 3-14).

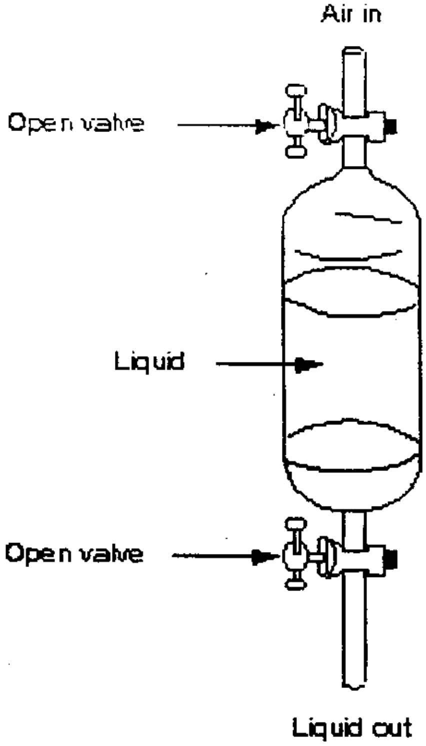


Figure 3-14. Liquid displacement.

Sampling by Use of Liquid Displacement

Liquid displacement is usually used only for grab sampling. The sample volume capacity is limited to the size of the liquid container. Some examples of liquids used are water, mercury (Hg), and organic solvents.

Air Displacers

Air displacement operates by the simple displacement of air or creation of a vacuum in a closed container.

Evacuated Flask

Principle of Operation

A flask is evacuated by a vacuum pump to a very low pressure that must be determined. The flask is sealed and transported to the sampling location. When a valve is opened on the flask, the surrounding air moves into the flask because of the pressure differential. On closing the valve, the sample is confined for subsequent analysis.

Sampling by Use of Evacuated Flasks

Evacuated flasks are usually used only for grab sampling; consequently, only relatively small sample volumes can be collected. Careful consideration should also be given to the possibility of flask "implosion" when glass containers are used, and appropriate protective means should be undertaken.

Plastic Bag

Air moving by use of a plastic bag is another example of an air displacer.

Principle of Operation

A plastic bag is either mounted within a rigid, airtight outer container and filled by creating a slight vacuum in the space around the bag, or, if there is no rigid outside container, air is pumped directly into the plastic bag.

Sampling by Use of Plastic Bags

Plastic bags are usually used only for grab sampling; consequently, only relatively small sample volumes can be collected.

Flow Rate Control

Control by Diversion

The principle of flow diversion is simply that the air moved by the air mover is not all passed through the sample collection device. As depicted in Figure 3-15, a "bleed" valve control in the sampling train allows the variation of the actual flow through the sample collection device. The position of the flow measuring device is such that it measures only the flow passing through the sample collection device.

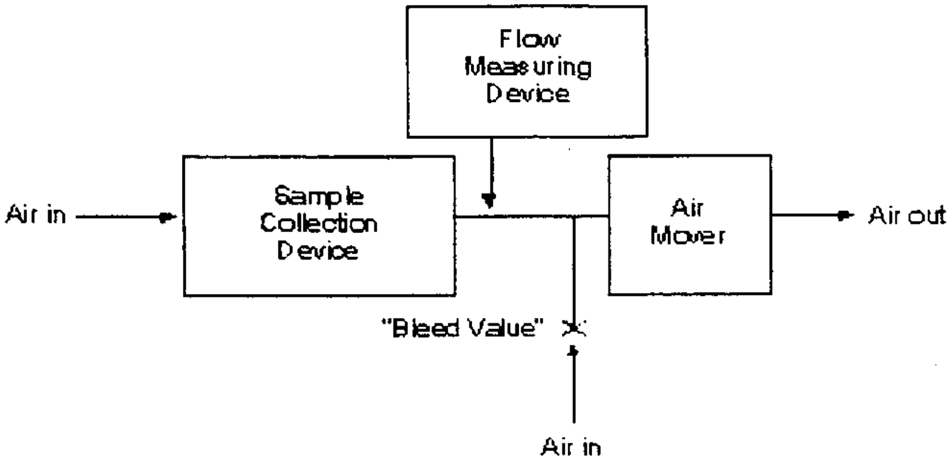


Figure 3-15. Flow rate control by diversion.

Resistance Control

In most air-moving devices, the flow rate decreases as the resistance it must overcome increases. Examples of this are depicted in Figures 3-9 and 3-10, which show sample characteristic curves for several pumps. The flow rate of the air mover can, therefore, be regulated by controlling the resistance it must overcome. A common method of control is to partially close a valve in the intake line, thus creating a greater resistance. Reproducible flow control can be accomplished by using needle valves with resettable marking.

Driving Force Control

It may be possible to control the air mover driving force, thereby controlling the rate of air flow. Adjustment of the nozzle opening on an ejector can be considered as a driving force control because it affects the velocity of the pressurized gas stream. The velocity of the gas stream, in turn, affects the suction pressure.

Another example of driving force control is electric motor speed regulation. This can be accomplished on some pump motors by use of a variable transformer, which controls the amount of power sent to the motor. These variable transformers are known by several names, such as variacs and powerstats.

Flow Rate for Sampling

After a particular flow rate has been selected for sampling, and after it has been set for the sampling train, it is usually necessary to maintain the flow at exactly that rate.

Need for Control

A variation of the desired flow rate can be caused by a variation in the air mover driving force or a variation in the resistance to air flow. The resistance to air flow is equivalent to the head the pump must overcome,(suction head). Some sampling conditions affecting flow variation have been mentioned above. Flow variation during sampling may affect more than the determination of the volume of air sampled; it may also affect the performance of the sample collection device. For example, the absorption rate of a bubbler may be altered by a variation of the flow rate through it.

Control Mechanisms

Many flow rate control mechanisms operate by keeping at a constant value the effective resistance that the pump must overcome. In other words, as depicted in Figure 3-16, the pressure drop (Δp) from the environment being sampled to the pump intake is held constant.

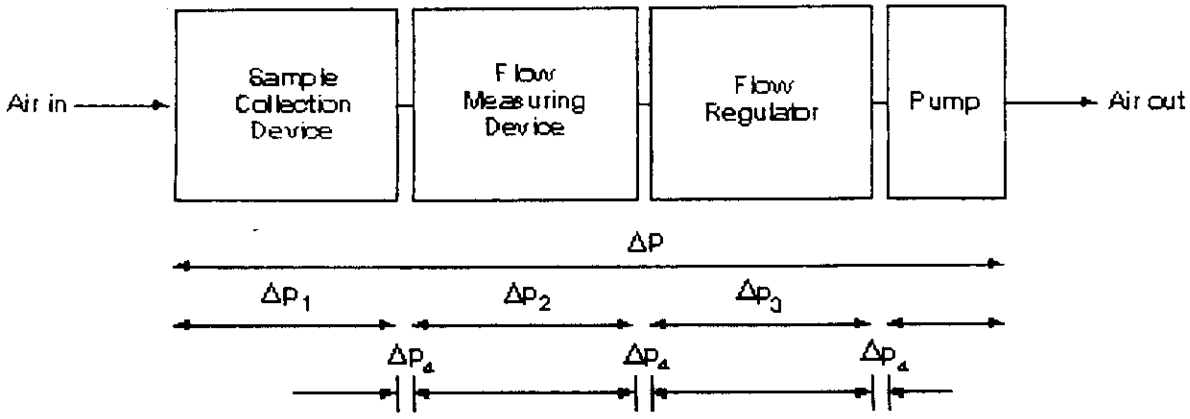


Figure 3-16. Flow rate control mechanism.

Sources of pressure drop in a system of this type include:

- the pressure drop across the sample collection device (Δp_1),
- the pressure drop across the flow measuring device (Δp_2),
- the pressure drop across the flow regulator (Δp_3), and
- the pressure drop due to friction in connecting lines (Δp_4).

Friction losses and flow measuring losses are usually considered as being constant.

The resulting relationship can be shown in Equations 3-1, 3-2, 3-3, 3-4.

(Eq. 3-1) $\Delta p = \Delta p_1 + \Delta p_2 + \Delta p_3 + \Sigma \Delta p_4$

(Eq. 3-2) $\Delta p_2 + \Sigma \Delta p_4 = \text{constant}$

(Eq. 3-3) $\Delta p - \Delta p_2 - \Sigma \Delta p_4 = \Delta p \text{ adjusted}$

(Eq. 3-4) $\Delta p \text{ adjusted} = \Delta p_1 + \Delta p_3$

Initially in the sample collection, the sample collection device resistance (Δp_1) is low; therefore, the regulator would have to offer a higher resistance (Δp_3). As sampling proceeds, the sample collector resistance (Δp_1) increases, thus automatically lowering the flow regulator resistance (Δp_2) and keeping Δp_{adj} at a constant value. The regulator resistance control may be actuated by several mechanisms, usually a pressure drop directly related to time rate.

Another type of control mechanism accomplishes control by varying the pump motor speed. As the pressure drop across the sample collection device increases, a switching arrangement increases the pump motor speed - thus drawing a constant air flow.

Summary

The air mover in a sampling train is certainly an important component. There are many factors for consideration involved in the selection of an air mover. Air movers can be classified according to their principle of operation: pumps, ejectors, liquid displacement, and evacuated flasks being some of the categories. There also may be further subdivisions of the general categories of air movers. In many instances, the ability to change the flow rate of the air mover and then to keep it constant at that rate is important.

Air Measuring Instruments

Introduction

The accuracy and precision of a given method for the determination of the concentration of an air pollutant are based on two factors:

- the accuracy and precision of the sampling method, and
- the accuracy and precision of the analytical method.

Examine the following term:

(Eq. 3-5)

$$\frac{\mu g}{M^3}\left(\frac{\textit{Mass of Pollutant}}{\textit{Volume of air sampled}}\right).$$

You can see that the "μg" (*mass of pollutant*) term is a result of the analytical process, while the "M^3" (*volume of air sampled*) term is a result of the sampling process. Not only is the mass of pollutant important in the final calculation of $\mu g/M^3$, but the volume of air sampled is also important. We will concentrate in this section on the measurement of the volume of air sampled.

The accuracy and precision of the sampling method depend on these factors:

- the environmental conditions during sampling,
- the collection efficiency of the sampling method,
- the accuracy and precision of the flow rate measurement, and
- any interferences.

The determination of the volume of air sampled, V, generally involves a measurement of flow rate, Q, and sampling time, t.

(Eq. 3-6)

$$V = Q \times t$$

The flow rate during atmospheric sampling can be measured by a variety of air measuring devices. These devices and their calibrations will be discussed in this chapter.

Types of Air Measuring Devices

Air measuring devices can be broadly classified into three categories:

- volume meters,
- rate meters, and
- velocity meters.

Volume meters measure the total volume, V, of gas passed through the meter over some specified time period. If the time period, t, is measured with a timing device, flow rate can be calculated by:

(Eq. 3-7)

$$Q = \frac{V}{t}$$

Rate meters measure the time rate of flow through them. Flow rate is measured through some property of the gas.

Velocity meters measure the linear velocity, $\bar{u}$, of a gas in a duct. Volumetric flow rate can then be calculated by measuring the cross-sectional area, A, of the duct through which the gas is flowing, by:

(Eq. 3-8)

$$Q = A \times \bar{u}$$

Calibration

Air that is to be sampled often is moved at a known rate over a known time period. The determinative process used to establish this known flow rate and known time period is a form of calibration. Remember that $V = Q \times t$, or that volume sampled, V, is the product of flow rate, Q and time t. The calibration process applied to both the flow rate and time allows the accurate determination of volume.

The frequency with which calibration occurs depends on a number of conditions. Some of these are:

- instrument use—What are the conditions under which the instrument is used?
- instrument users—How many different people use the instrument? What are the qualifications of the people?
- instrument characteristics—How often does the instrument require calibration under controlled laboratory conditions? How sensitive is the instrument?

The basic equipment required for calibrating air flow measuring instruments includes a standard meter, an air mover, and often a source of constant power.

Standard meters are of two types:

- primary standards,
- secondary standards.

Primary standard meters are those whose volumes can be determined by measurement of internal physical dimensions alone. The measured internal dimensions are regular, and accuracies better than ± 0.30% can be achieved. *Secondary standards* are those calibrated against primary or intermediate standards under known conditions of gas type, temperature, and pressure. Accuracies less than 5% are achievable.

Volume Meters

Volume meters measure the volume of gas passing through the meter. When coupled with a timing device (like a calibrated stopwatch), flow rate (volume/time) can be calculated. There are seven volume meters commonly used in air sampling and analysis.

The Spirometer (or "Bell Prover")—Primary Standard

The spirometer consists of a cylinder of known volume, closed at one end, with the open end submerged in a circular tank of fluid (Figure 3-17). The cylinder can be opened or closed to the atmosphere by a valve. As the cylinder is lowered into the water, the water displaces the air and causes it to be discharged from the cylinder. the rate of discharge can be regulated.

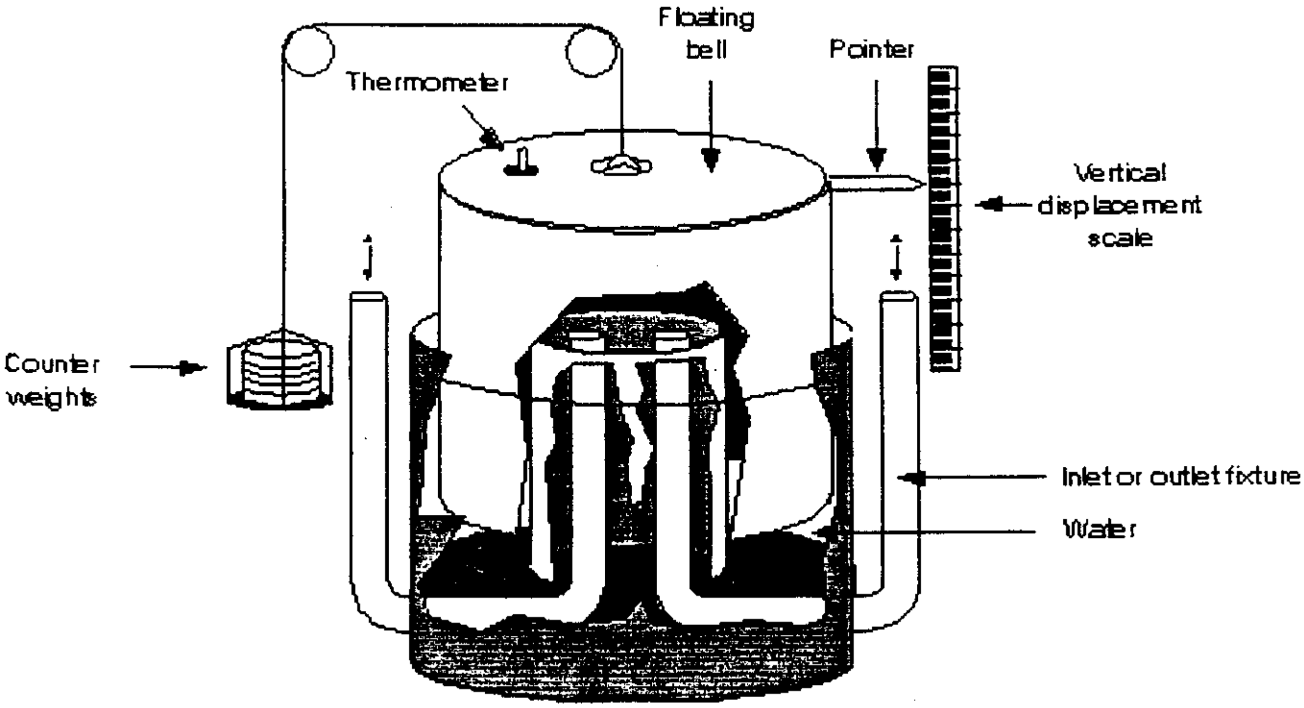


Figure 3-17. Spirometer.

The volume of the cylinder is determined from its dimensions. A counterweight and cycloid counterpoise allow pressure differentials across the spirometer as low as 0.02 inches of water (Figure 3-18).

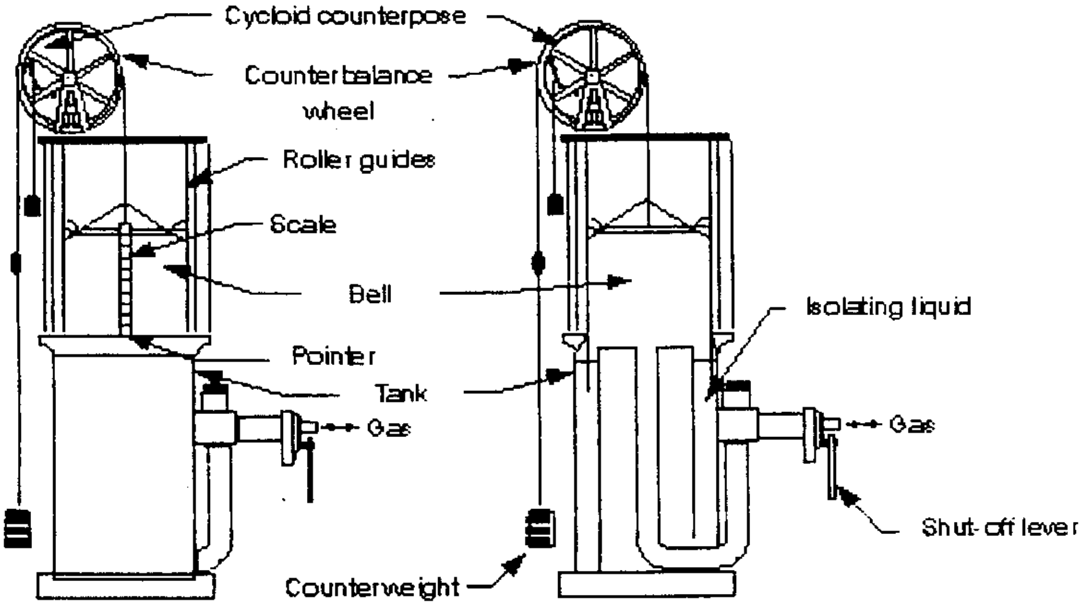


Figure 3-18. Orthographic and cross-sectional views of a 5-ft^3 spirometer.

The volume of air passed through a spirometer is given by the following formula:

(Eq. 3-9)

$$V = \frac{\pi d^2 h}{4}$$

Where: *V = volume of air passed through spirometer*
π = a constant = 3.14
d = diameter of bell
h = vertical displacement of bell

The fluid in the spirometer should be at the same temperature as the room. This is to ensure that the fluid and the air will be in thermal equilibrium and thereby minimize spirometer fluid evaporating into the air. This thermal equilibrium also simplifies volume corrections since temperature is constant during the calibration procedure. This is true for water, but some spirometers use oil. The real importance of thermal equilibrium is that the air displaced from the bell must be at the same temperature as the room for volume calculations. The pressure inside the bell is also brought into equilibrium with room conditions.

Once the volume of air is determined using room conditions a conversion to standard conditions must be made to determine the true volume of air that has passed through the spirometer. This conversion to standard conditions is made using the following formula (see Equation 2-7):

(Eq. 3-10)

$$V_2 = V_1\left(\frac{P_1}{760\text{ mm Hg}}\right)\left(\frac{298\text{ K}}{T_1}\right)$$

Where:

V_2 = *volume of gas at 2^{nd} conditions or at P_2 and T_2*, *l*
V_1 = *a volume of gas at 1^{st} conditions of P_1 and T_1*, *l*
T_1 = *initial temperature of gas*, K
T_2 = *final temperature of gas, in this case* = 298 K
P_1 = *initial pressure of gas*, mm Hg
P_2 = *final pressure of gas, in this case* = 760 mm Hg

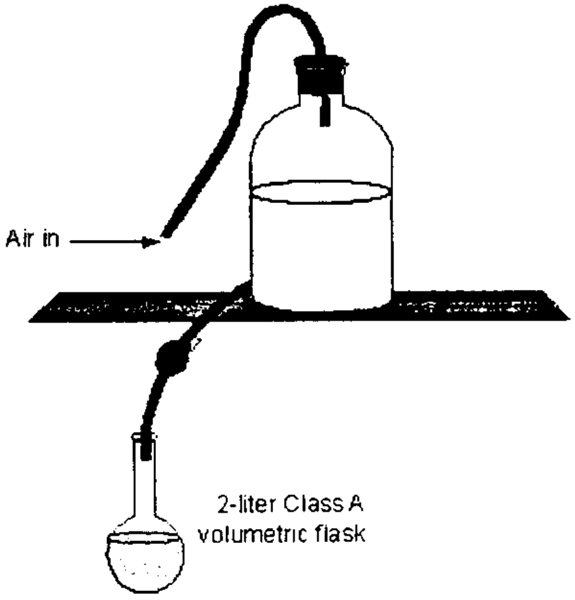
The spirometer is calibrated by the manufacturer against a National Bureau of Standards (NBS) "cubic-foot" bottle. If an owner suspects that his spirometer is in error, he can check the calibration with an NBS-certified "cubic-foot" bottle or by a "strapping" procedure.

The "strapping" procedure involves the measurement of the dimensions of the bell with a steel tape and subsequent calculation of the volume. Experienced personnel routinely obtain accuracies of ± 0.2% when calibrating a spirometer by the "strapping" procedure. Nelson (1972) gives a very detailed procedure for performing the "strapping" procedure. Manufacturers of spirometers include example calculations in the literature accompanying their instruments.

Flow rates can be measured by timing the volume of air passing to or from the spirometer and determining the rate of flow. The spirometer is simple, inexpensive, dependable and is used almost solely as a primary standard for calibration of other types of flow- and volume-measuring devices. Because the spirometer can be produced in large sizes, it has typically been used to calibrate Roots meters, which are positive displacement meters.

Displacement Bottle Technique-Primary Standard

The displacement bottle consists of a bottle filled with water (or some other liquid) and a tube through which air can enter the bottle (Figure 3-19). As the liquid in the bottle is drained or siphoned out, air is drawn in to take the place of the volume of liquid lost. The volume of gas



sampled is equal to the volume of liquid displaced.

Figure 3-19. Displacement bottle technique.

The fluid in the displacement bottle should be in thermal equilibrium with the room temperature. This equilibrium will ensure no liquid evaporation from the bottle water to the air, and simplify volume corrections for T and P. The volume of displaced liquid can be measured with a graduated cylinder or Class A volumetric flask, depending on how accurately the volume needs to be measured. Accuracy can range from 1 to 5%, depending on what measuring device is used.

Again, once the volume of air has been determined at room conditions, it should be converted to the volume at standard conditions. This conversion uses the relationship previously stated in Equation 3-10.

Frictionless Pistons-Primary Standards

The soap-bubble meter and the mercury-sealed piston are two frictionless pistons that will be discussed in this section. Accurate and convenient measurement of flows between 1 and 1000 mL/min can be made with a soap-bubble meter. Mercury-sealed pistons are available that can accurately measure flows from 100 cm^3/min to 24,000 cm^3/min.

Moving-bubble Meter

A bubble meter consists simply of a cylindrical glass tube with graduated markings, usually in milliliters. Inverted burets are often used as soap-bubble meters (Figure 3-20); however, burets cannot be used with anything other than a vacuum source. Simple bubble meters (Figure 3-21) can be purchased, although the basic design can be made conveniently by a competent glass blower.

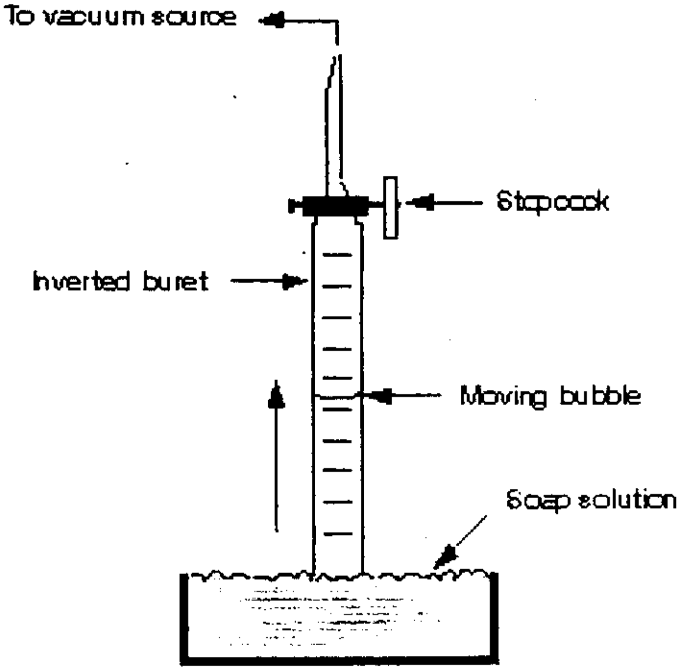


Figure 3-20. Moving-bubble meter.

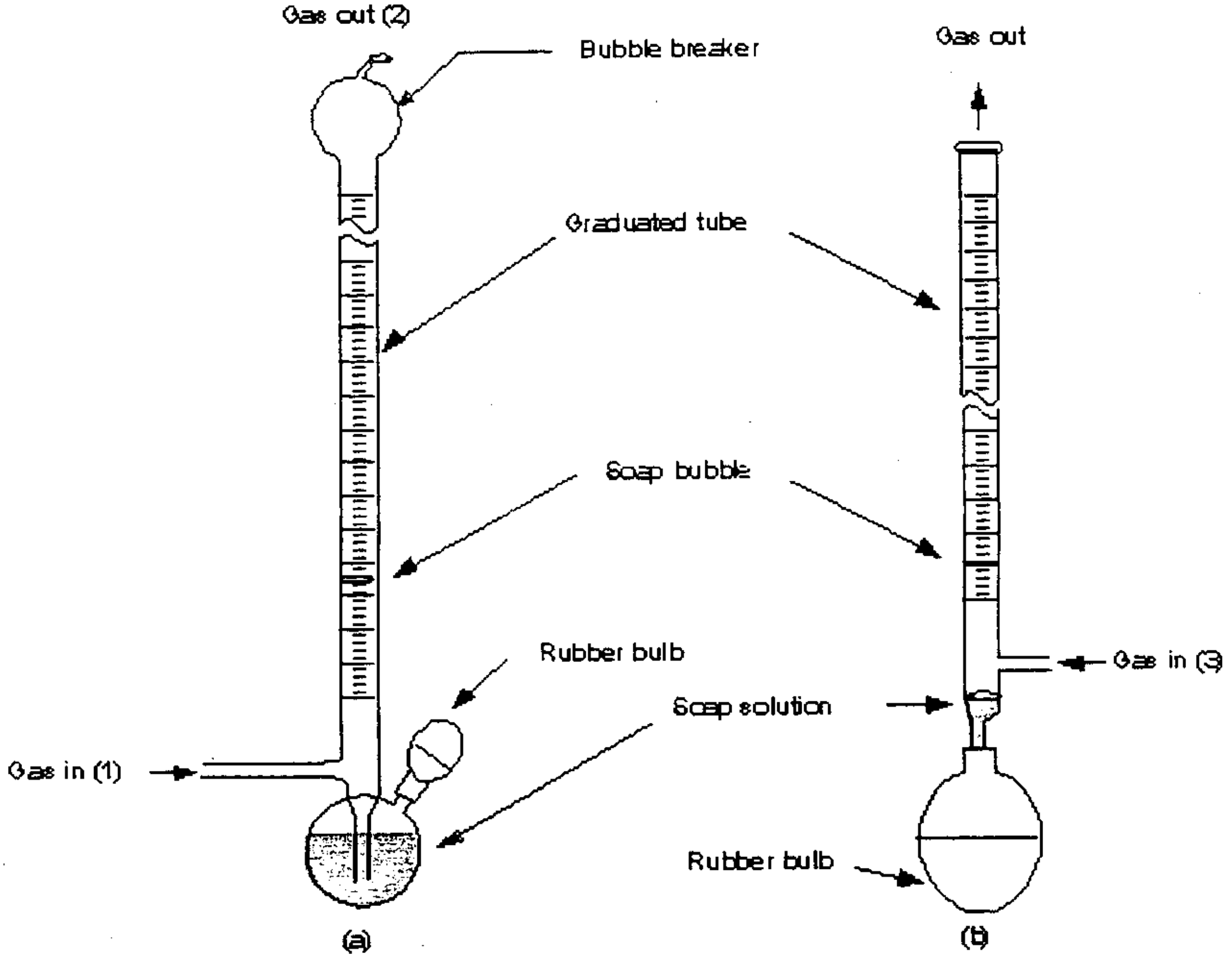


Figure 3-21. Moving bubble meters. (a) one with bubble breaker and capability of handling vacuum at (2) or pressure at (1); (b) one capable of handling only pressure at (3).

The moving-bubble meter is one of the simplest of primary standards. The inside walls of the tube are wetted with a soap solution. A bubble is formed by touching the tip of the buret to the soap solution, as in Figure 3-20, or by squeezing the rubber bulb until the soap solution is raised above the gas inlet (Figure 3-21).

Either a vacuum at the top or slight positive pressure at the bottom of the tube moves the bubble (a frictionless piston) up the tube. By timing this movement and noting the volume traversed by the bubble over the measured time span, volumetric flow rate can be calculated.

The volume measured by a moving bubble meter must be corrected for two conditions. First, if the room temperature and pressure are different from standard atmospheric conditions, the volume must be corrected by the relationship previously stated (Equation 3-10):

(Eq. 3-11)

$$V_2 = V_1\left(\frac{P_1}{760\text{ mm Hg}}\right)\left(\frac{298\text{K}}{T_1}\right).$$

Where:

V_2 = *volume of gas at 2nd conditions or at* P_2 *and* T_2, *l*
V_1 = *a volume of gas at 1st conditions of* P_1 *and* T_1, *l*
T_1 = *initial temperature of gas,* K
T_2 = *final temperature of gas, in this case* = 298 K
P_1 = *initial pressure of gas,* mm Hg
P_2 = *final pressure of gas, in this case* = 760 mm Hg

Second, the measured volume can be slightly larger than the volume because water from the bubble evaporates into the gas behind the bubble. If the gas behind the bubble has a relative humidity greater than 50%, the error is small. If the gas is dry, the error can be large and must be corrected by the following formula:

(Eq. 3-12)

$$V_c = V_{meas}\left(\frac{P_b - P_w}{P_b}\right)$$

Where:

V_c = *corrected volume*
V_{meas} = *measured volume*
P_b = *atmospheric pressure,* mm Hg
P_w = *vapor pressure of water at the room temperature,* mm Hg.

Note that P_b and P_w must have the same units.

Table 3-1. Vapor pressure table.

TEMPERATURE (C°)	VAPOR PRESSURE (TORR)
15° C	12.8
16° C	13.6
17° C	14.5
18° C	15.5
19° C	16.5
20° C	17.6
21° C	18.7
22° C	19.8
23° C	21.1
24° C	22.4
25° C	23.8
26° C	25.2
27° C	26.8
28° C	28.4
29° C	30.1
30° C	31.9

Moving-bubble meters can be calibrated by measuring the dimensions of the tube; however, poor control on glass dimensions in manufacturing make this inaccurate. The bubble meter is usually calibrated by filling the tube with a liquid (water or mercury for example), then draining the liquid from the top graduation to the bottom graduation. The volume or weight of the collected liquid can be measured. With proper corrections for temperature, this calibration is accurate. The moving-bubble meter should only be used to measure volumes between graduations that have been calibrated.

The bubble meter is used almost exclusively in laboratory situations for calibration of other air-measuring instruments. In average laboratory conditions, the moving-bubble meter is accurate to about ± 1%, depending on how accurately it is calibrated. Accuracy decreases for flows below 1 mL/min and above 1 L/min mainly because of gas permeation through the bubble. A detailed description of the calibration and use of bubble meters has been published by Levy (1964). Increased accuracies have been reported for bubble meters fitted with automatic sensing devices that start and stop a timer.

Mercury-sealed Piston

If a bubble meter is unsuitable, an electronically actuated mercury-sealed piston may meet the need. Although the mercury-sealed piston is expensive, its accuracy (± 0.2% for time intervals greater than 30 seconds) and simple operation make it an extremely useful tool.

The mercury-sealed piston consists of a precision-bored, borosilicate glass cylinder with a close-fitting polyvinyl chloride piston (Figure 3-22). The piston and cylinder wall are sealed with a ring of mercury that stays in place because of its high viscosity and the closeness of the fit between the cylinder and piston. Gas entering the solenoid valve is vented until the measurement cycle is actuated. When the measurement cycle is started, the solenoid valve closes the vent, allowing gas to enter the cylinder.

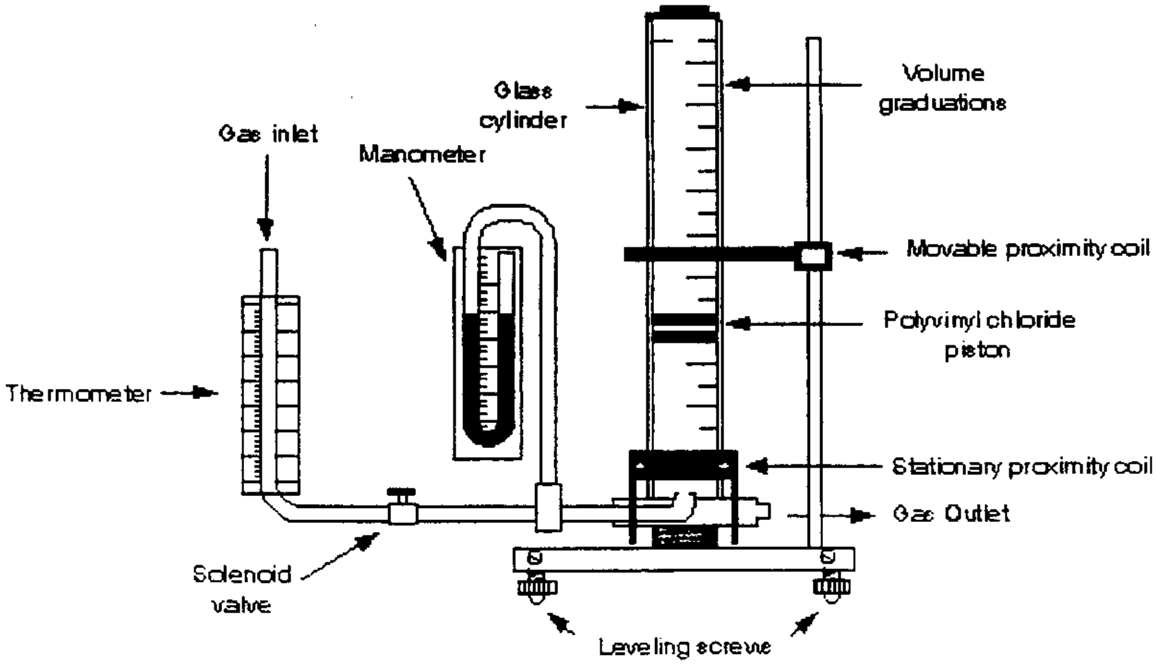


Figure 3-22. Mercury-sealed piston volume meter.

A timer is started and stopped as the mercury seal passes the lower and upper proximity coils (metal detectors). The volume displaced can be set by adjusting the upper proximity coil. The volume is corrected to standard conditions using the pressure drop across the piston (usually < 3 inches of water). The measured time and the corrected volume can be used to calculate volumetric flow. The system shown in Figure 3-23 has a reported accuracy of ± 0.2%.

Calibration of the mercury-sealed piston volume meter is usually performed by the manufacturer. The borosilicate glass cylinder is bored to a precise diameter. The inside diameter is air-gauged at least every inch to check for consistency. Before the instrument is sent out it is compared to a standard-mercury-sealed piston volume meter that is traceable to NBS. If a multi-cylinder unit is purchased, then the cylinders must be aligned. One cylinder is chosen to be correct and all others are aligned with the set screw located on top of the piston (Figure 3-24), which changes the displaced volume slightly.

The mercury seal can be broken by erratic movement of the instrument. For this reason the mercury-sealed piston instrument is used as a primary standard in laboratory settings. Mercury-sealed piston volume meters are available for accurate flow measurement over a wide range (100 cm^3/min to 24,000 cm^3/min).

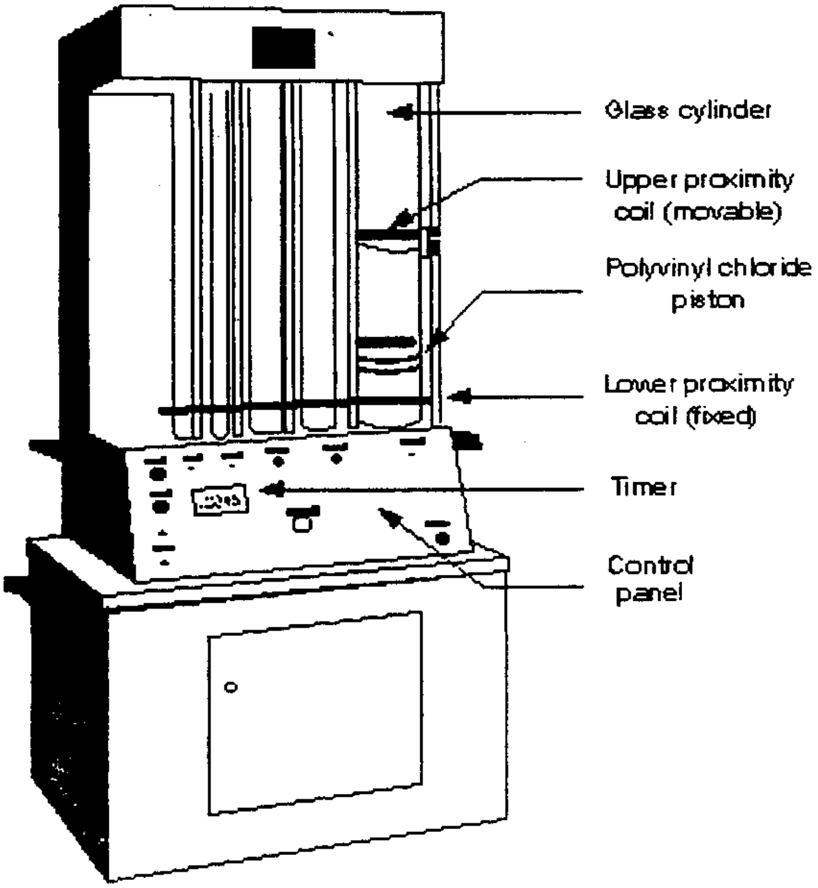


Figure 3-23. Calibrator console, front view (Brooks model 1051). (Courtesy Brooks Instrument Division, Emerson Electric Co.)

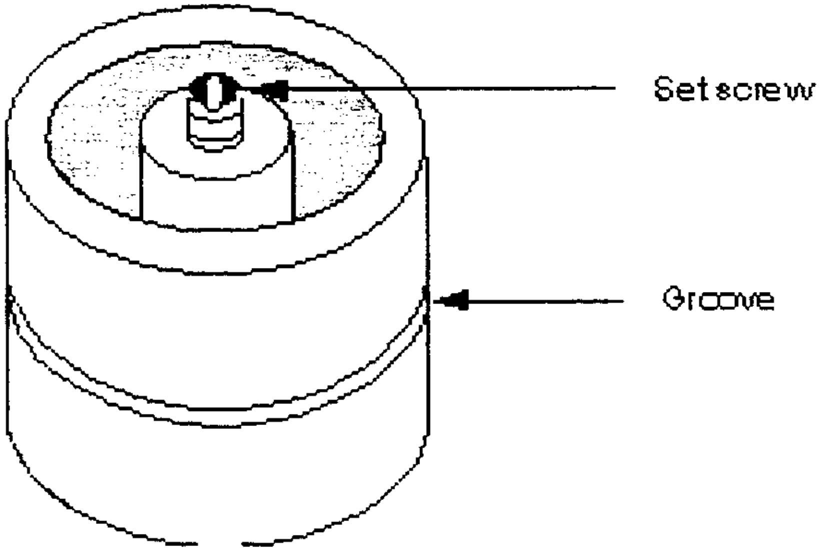


Figure 3-24. PVC piston for mercury-sealed piston volume meter.

Wet Test Meter (WTM) - Secondary Standard

The wet test meter consists of a series of inverted buckets or traps mounted radially around a shaft and partially immersed in water (Figure 3-25a). The location of the entry and exit gas ports is such that the entering gas fills a bucket, displacing the water and causing the shaft to rotate due to the lifting action of the bucket full of air. The entrapped air is released at the upper portion of the rotation and the bucket again fills with water. In turning, the drum rotates index pointers that register the volume of gas passed through the meter (Figure 3-25b).

After the meter is leveled, the proper water level is achieved by using the filling funnel, fill cock, and drain cock (Figure 3-25c) to bring the meniscus of the water in touch with the tip of the calibration index point. The calibration gas should be passed through the meter for one hour to saturate the water with the gas. The water in the meter should be at the same temperature as the surrounding atmosphere. If any water is added, sufficient time must be allowed for complete equilibration.

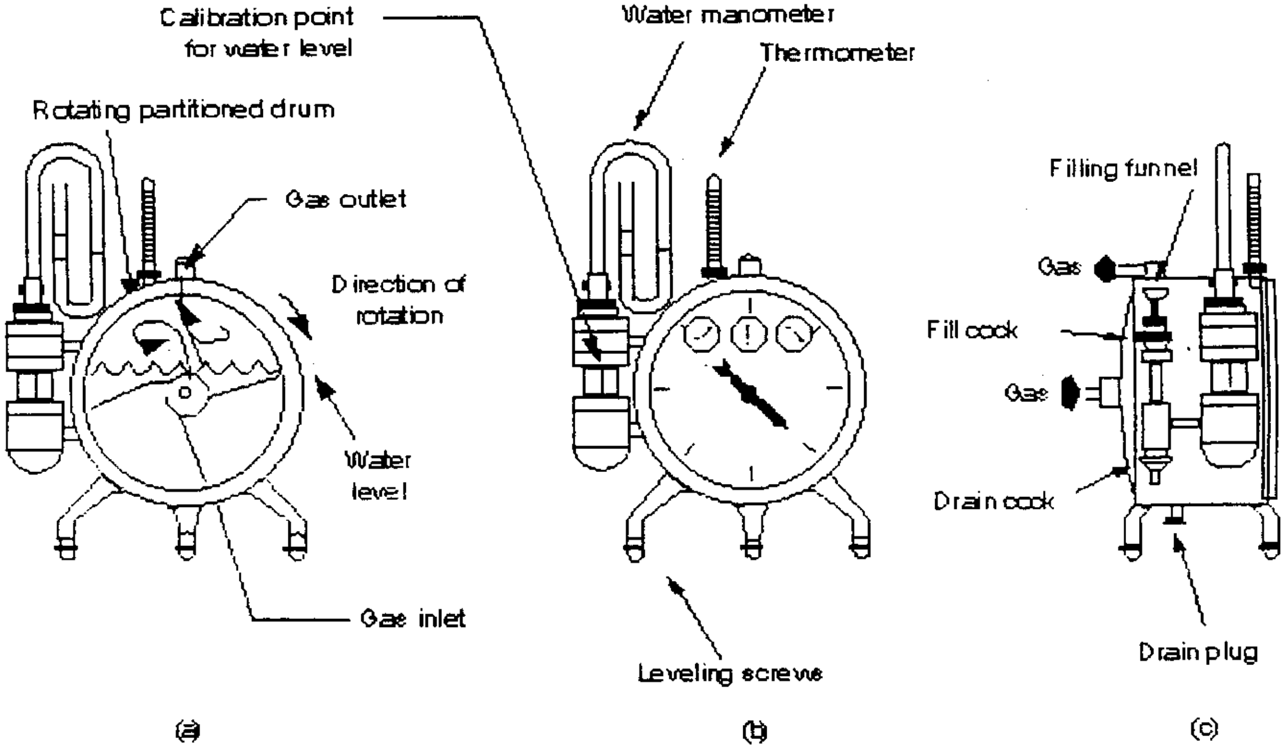


Figure 3-25. Wet test meter.

Once the water level is set and the meter is equilibrated, the wet test meter is ready for calibration (or use if it is already calibrated). An accurate calibration of a wet test meter can be done with a spirometer (Figure 3-26).

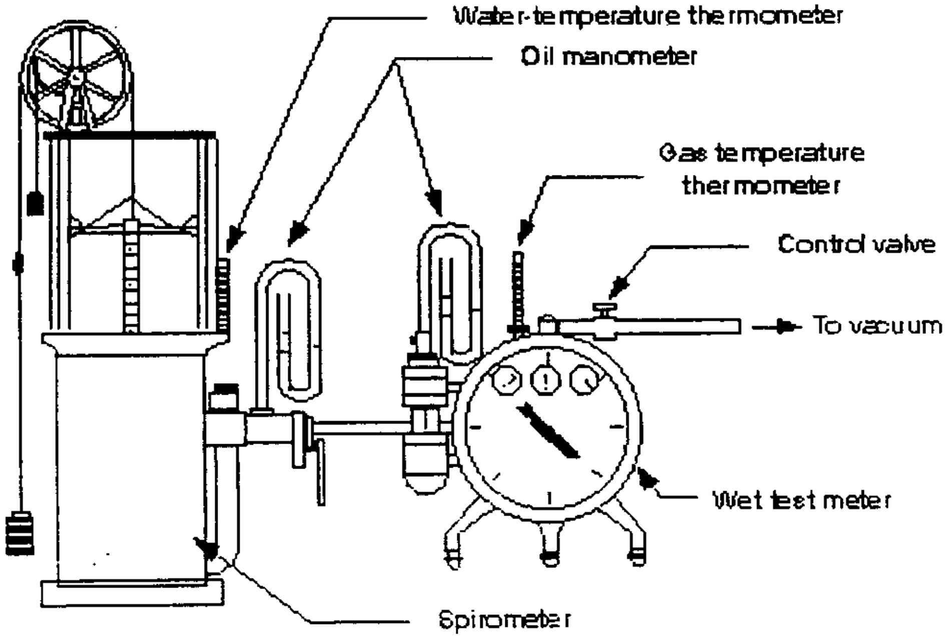


Figure 3-26. Setup for calibrating a wet test meter against a spirometer.

The wet test meter can also be calibrated against a mercury-sealed piston, as shown in Figure 3-27.

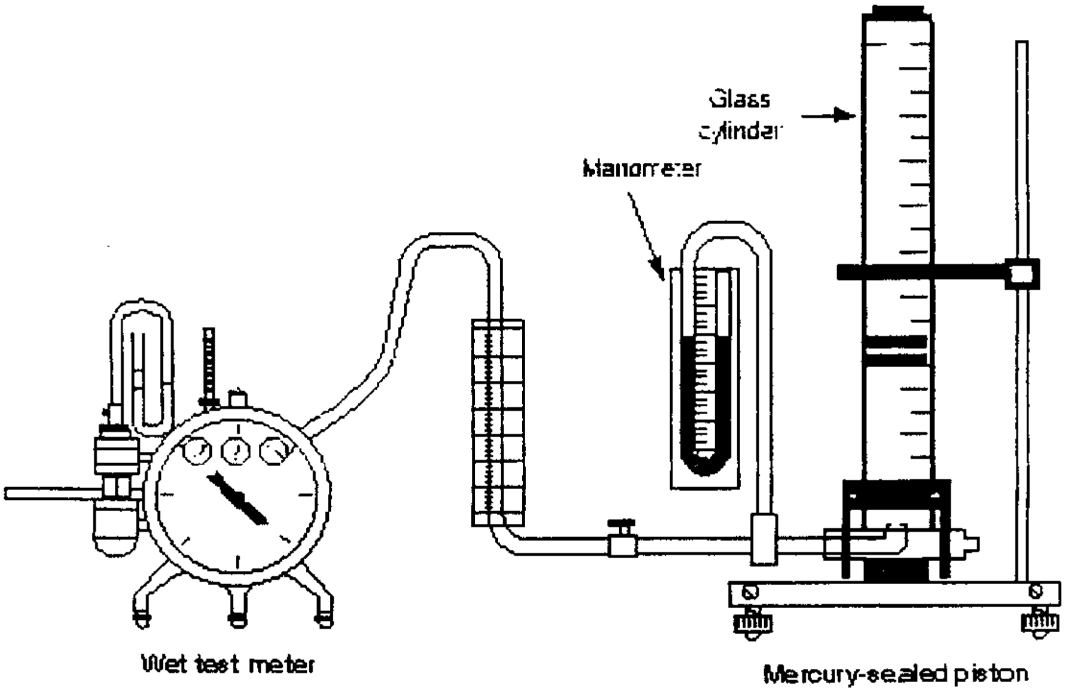


Figure 3-27. Calibration of a wet test meter against a mercury-sealed piston.

Enough gas is drawn through either system (Figure 3-26 or 3-27) to turn the wet test meter at least three revolutions and to significantly move the spirometer drum or piston. The measurement is made several times. Atmospheric pressure and temperature, and the temperature and pressure differential for both the wet test meter and calibrating device, are needed to correct the volume to standard conditions (taking pressure differentials into consideration). Since both the calibration device and the wet test meter are measuring a dry gas stream, a significant error is introduced if the measured volume is not corrected to dry conditions. This correction is the same as for the soap-bubble meter correction:

(Eq. 3-13)

$$V_c = V_{meas}\left(\frac{P_b - P_w}{P_b}\right)$$

Where:

V_c = *corrected volume*

V_{meas} = *measured volume*

P_b = *atmospheric pressure*, mm Hg

P_w = *vapor pressure of water at the room temperature*, mm Hg.

A simple calibration check can be performed using a displacement bottle, as shown in Figure 3-28. After all the water is thermally equilibrated, the wet test meter is properly set up, the drain tube of the displacement bottle is filled, and the pinch clamp is opened, allowing two liters of water to drain into a 2-liter Class A volumetric flask. The corresponding wet test meter readings are taken. This is repeated several times (usually four).

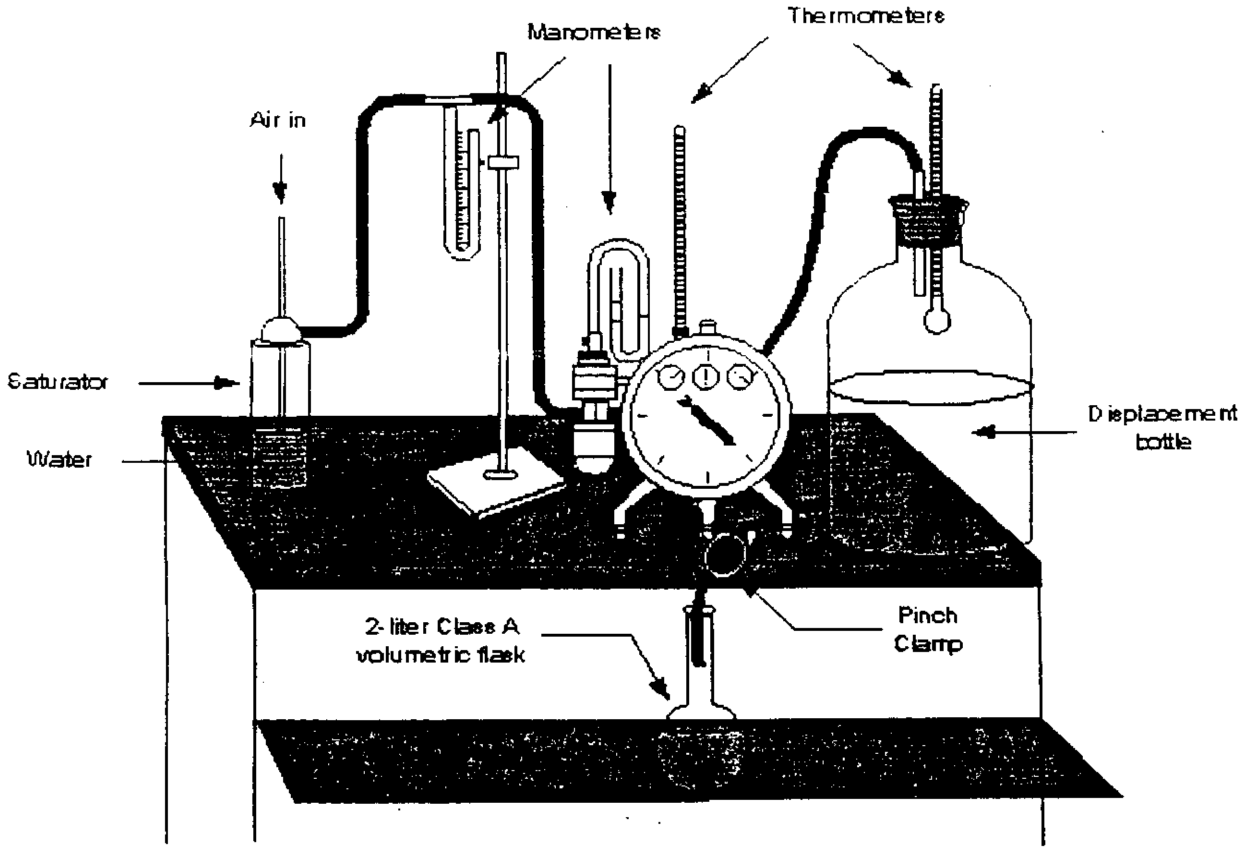


Figure 3-28. Calibration of wet test meter with displacement bottle.

The calibration data can be used to:

Option 1: Draw a multipoint calibration curve for flow for Figures 3-26 and 3-27 setups.

Option 2: Adjust the calibration index point so that the meter volume is correct.

Option 3: Calculate a correction factor for the wet test meter.

Wet test meters should check within ± 0.5 % if option 2 is used.

All volumes measured by a wet test meter should be corrected to standard conditions by Equation 3-10.

Wet test meters are used as transfer standards because of their high accuracy (less than ± 1%). Because of their bulk, weight, and equilibration requirements, they are seldom used outside a laboratory setting. Wet test meters are useful for laboratories that need an accurate standard yet do not have the funds or space for a spirometer or mercury-sealed piston. Wet test meters can be used to measure flow rates up to 3 rev/min, at which point the meter begins to act as a limiting orifice and obstructs the flow. Typical ranges of wet test meters are 1, 3, and 10 L/rev.

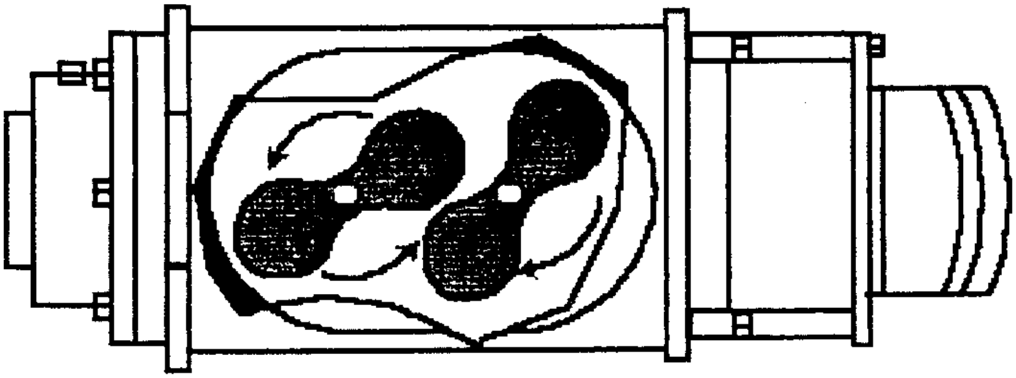
Roots Meter—Secondary Standard

The Roots meter is a positive displacement, rotary-type meter for measuring volume flow. It is suitable for handling most types of clean, common gases. It is not suitable for handling liquids, and its operation can be impeded by excessive particulate matter carried in the gas stream.

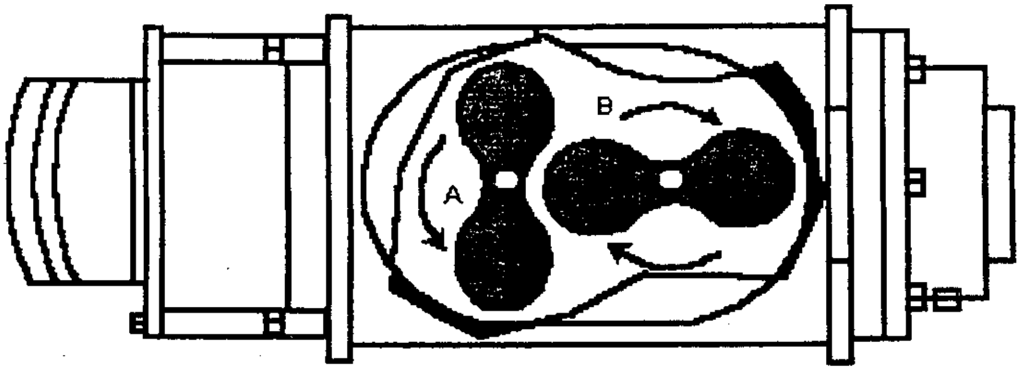
Roots meters consist basically of two oppositely rotating impellers of two-lobe or "figure 8" contour, operating within a rigid casing (Figure 3-29). The casing is arranged with inlet and outlet gas connections on opposite sides. Impeller contours are mathematically developed and accurately produced, and are of such form that a continuous seal without contact can be maintained between the impellers at all positions during rotation. To accomplish this, the correct relative impeller positions are established and maintained by precision-grade timing gears. Similar seals exist between the tips of the impeller lobes and the two semicircular parts of the meter casing. As a result of this design, the gas inlet side of the meter is always effectively isolated from the gas at the outlet side of the impellers. Consequently, the impellers can be caused to rotate by a very small pressure drop across the meter.

The rotation of the impellers is in the direction indicated in Figure 3-29, and as each impeller reaches a vertical portion (twice in each revolution), it traps a known specific volume of gas between itself and the adjacent semicircular portion of the meter casing at A and B (Figure 3-29, Position 2). Thus, in one complete revolution, the meter will measure and pass four similar gas volumes, and this total volume is the displacement of the meter per revolution.

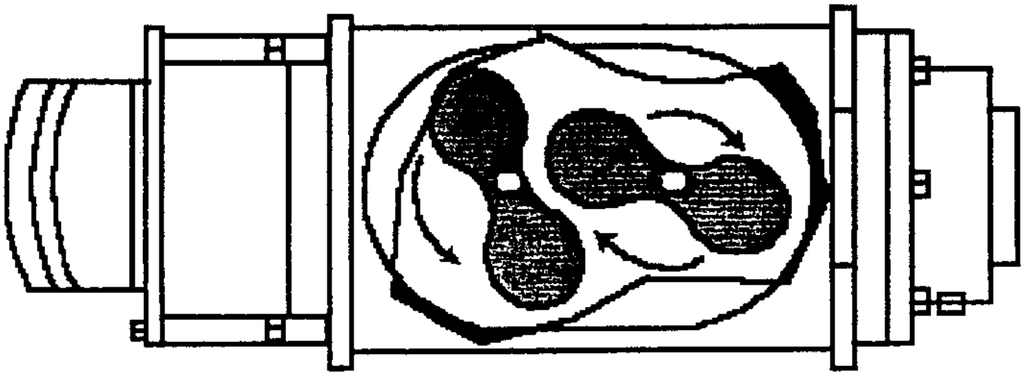
The displacement of volume of the Roots meter is precisely determined by the manufacturer, both by calculation and by testing it using a known volume of air or other gas. Roots meters are usually calibrated against large spirometers prior to shipment. Users do not usually have a way to calibrate Roots meters and must depend on the supplied calibration data. Volumetric accuracy of the Roots meter is permanent and nonadjustable (except for linkage adjustment), because its measuring characteristics are established by the dimensions and machined contours of nonwearing fixed and rotating parts.



Position 1



Position 2



Position 3

Figure 3-29. Principle of gas flow through the Roots meter.

The revolutions of the impellers are indexed with the meter reading calibrated in a volume unit (i.e., ft^3 or m^3). Units are sold that have temperature compensation devices, but corrections to standard temperature and pressure conditions are easily made with the previously mentioned formula given in Equation 3-10 (pressure drop across the Roots meters should be taken into consideration).

(Eq. 3-14)

$$V_2 = V_1\left(\frac{P_1}{760\ \text{mm Hg}}\right)\left(\frac{298\text{K}}{T_2}\right)$$

Where:

V_2 = *volume of gas at 2nd conditions or at* P_2 *and* T_2, *l*
V_1 = *a volume of gas at 1st conditions of* P_1 *and* T_1, *l*
T_1 = *initial temperature of gas*, K
T_2 = *final temperature of gas, in this case* = 298 K
P_1 = *initial pressure of gas*, mm Hg
P_2 = *final pressure of gas, in this case* = 760 mm Hg

The symbol P_1, in this instance, is the atmospheric room pressure (P_b, in mm Hg) minus the pressure drop across the Roots meter Δp, in mm Hg.

(Eq. 3-15)

$$P_1 = P_b - \Delta p$$

The metering unit is magnetically coupled to the impellers. The entire counting unit is enclosed in a plastic cover. The cover also holds an oil that lubricates the metering device. The proper oil level is set by the inscribed oil level lines on the ends of the plastic covers. The user of a Roots meter must be careful not to severely tilt the meter when oil is in the plastic cover, as this can force oil into the impeller casing. If the oil gets into the impeller casing, flushing with kerosene can remove the oil.

Although Roots meters are widely used in industrial applications, they have been used almost exclusively as the standard for high-volume sampler flow rate in atmospheric sampling applications.

Dry Test Meter—Secondary Standard

Dry *test* meters are an improvement over the more common dry *gas* meters (Figure 3-30). Dry *gas* meters (a secondary standard) are most commonly used in residential and industrial settings to measure gas flow (e.g., natural gas). The dry *test* meter (a secondary standard) works on the same principle as the dry *gas* meter (a secondary standard), but a different indexing method (read-out) makes it more accurate (usually ± 1 to 2% when new). The dry test meter shown in Figure 3-31 shows the new read-out mechanism.

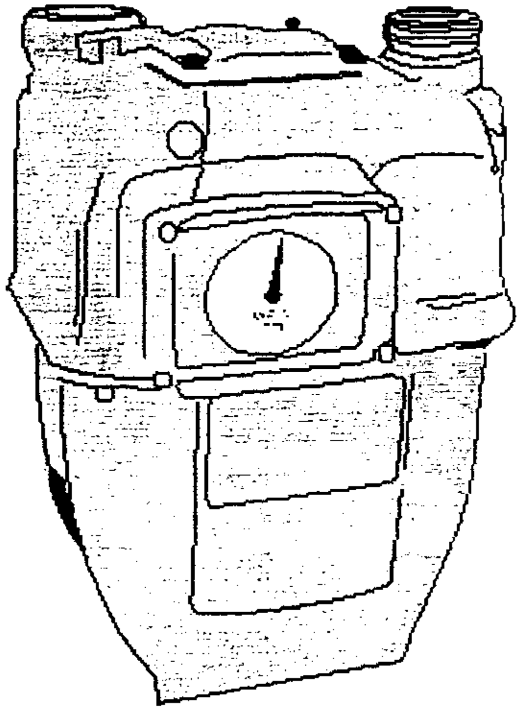


Figure 3-30. Dry gas meter.

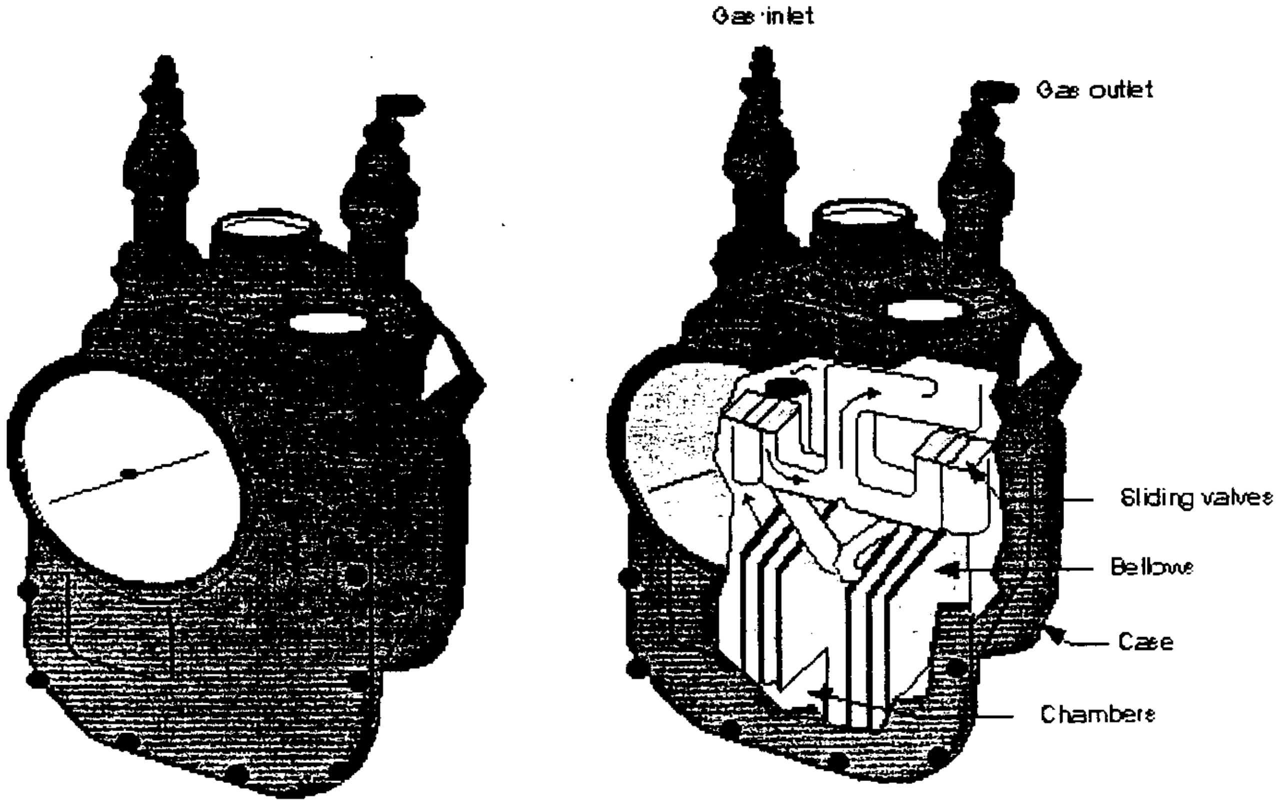


Figure 3-31. Dry test meter.

The interior of the dry test meter contains two or more movable partitions, or diaphragms, attached to the case by a flexible material so that each partition may have a reciprocating motion (Figure 3-32). The gas flow alternately inflates and deflates each bellows chamber, simultaneously actuating a set of slide valves that shunt the incoming flow at the end of each stroke. The inflation of the successive chambers also actuates, through a crank, a set of dials that register the volume of gas passed through the meter.

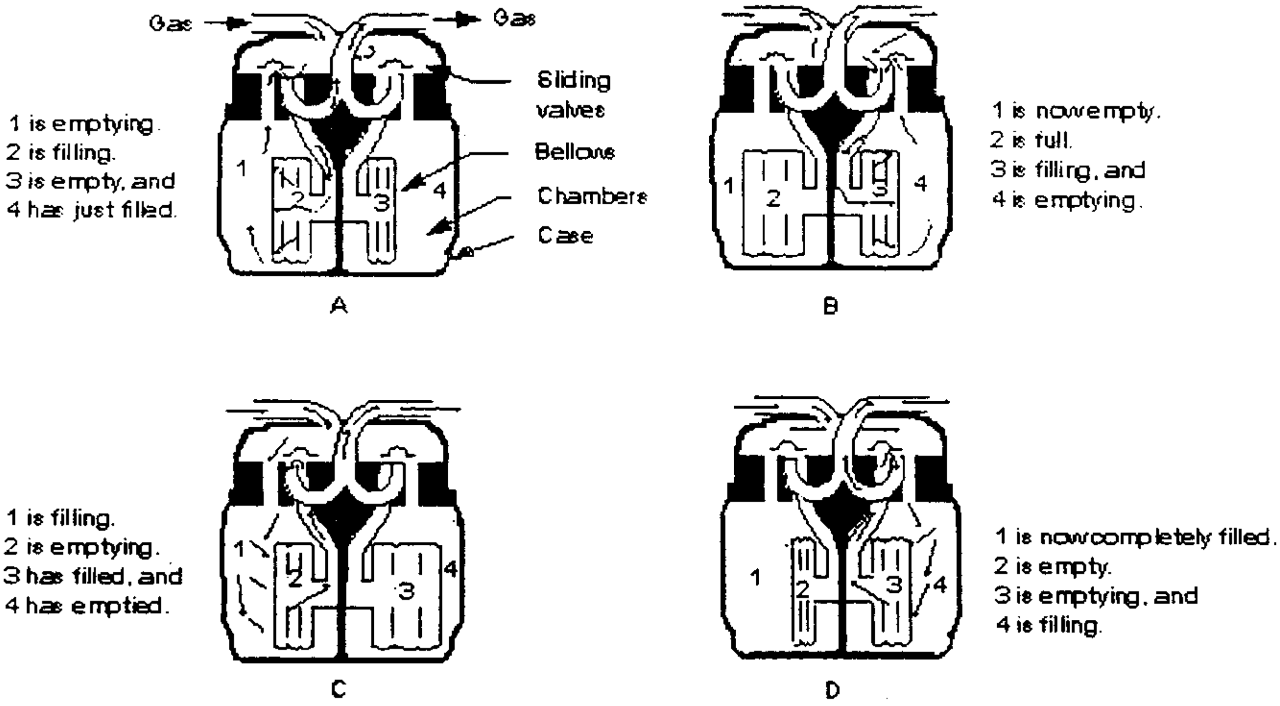


Figure 3-32. Working mechanism of dry test meter.

The dry test meter is calibrated against a spirometer, mercury-sealed piston, or displacement bottle similar to the wet test meter. One big advantage of the dry test meter over the wet test meter is that no correction for water vapor is needed. If the dry test meter is off calibration by more than 2%, it can be corrected by adjustment of the meter linkage. If linkage adjustment cannot correct the problem, then the dry test meter must be returned to the manufacturer for repairs.

Dry test meters are used in the field as well as in laboratory calibrations. Since the dry test meter does not contain water, it is lighter and easier to use than the wet test meter. Also, the dry test meter is more rugged than the wet test meter. Accuracy of the dry test meter does, however, worsen with age.

Rate Meters

Rate meters measure, indirectly, the time rate of the fluid flow through them. Their response depends on some property of the fluid related to the time rate of the flow.

Variable-Pressure Meters—Head Meters

Head meters are those in which the stream of fluid creates a significant pressure difference that can be measured and correlated with the time rate of flow. The pressure difference is produced by a constriction in the stream of flow causing local increase in velocity.

Orifice Meter— Noncritical— Secondary Standard

An orifice meter can consist of a thin plate having one circular hole coaxial with the pipe into which it is inserted (Figure 3-33). Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop, which can be correlated to the time rate of flow. Watch jewels, small bore tubing, and specially manufactured plates or tubes with small holes have been used as orifice meters. The pressure drop across the orifice can be measured with a manometer, magnehelic, or pressure gauge.

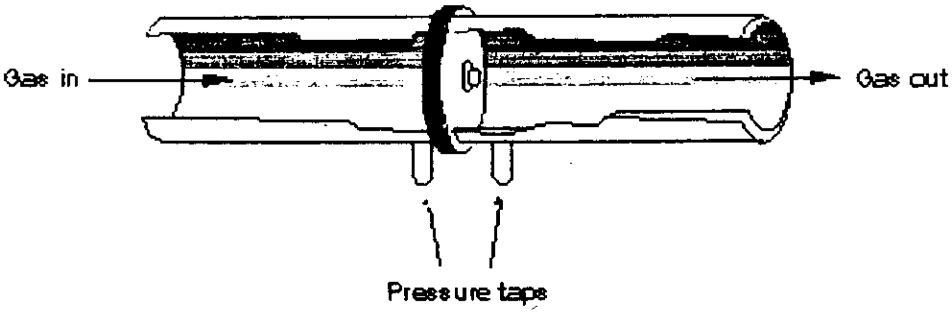


Figure 3-33. Orifice meter.

Flow rates for an orifice meter can be calculated using Poiseuille's Law; however, this is not done for practical use. Instead, the orifice meter is usually calibrated with either a wet or dry test meter, or a soap-bubble meter. A typical calibration curve is shown in Figure 3-34.

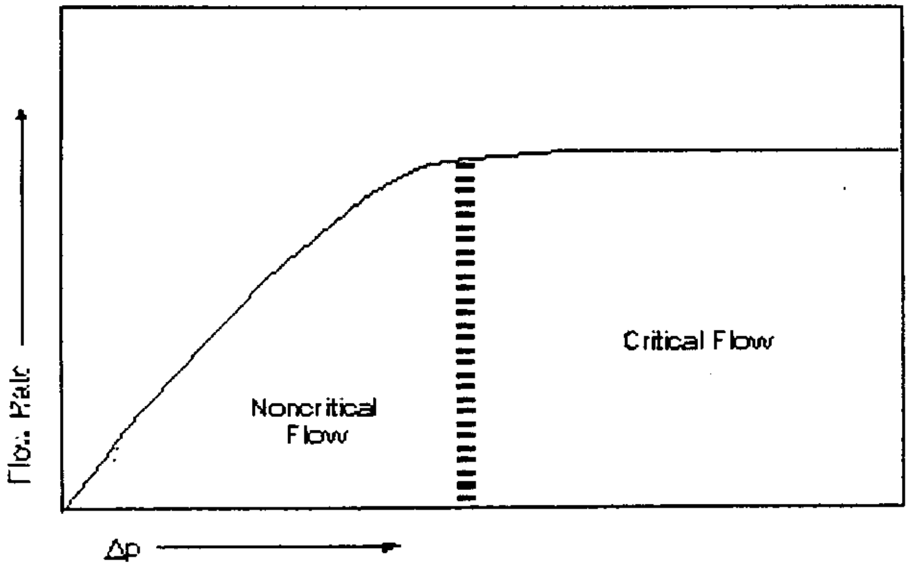


Figure 3-34. Typical orifice meter calibration curve.

Calibration curves for orifice meters are nonlinear in the upper and lower flow rate regions and are usually linear in the middle flow rate region.

Orifice meters can be made by laboratories with a minimum of equipment. They are used in many sampling trains to control the flow. Care must be exercised to avoid plugging the orifice with particles. A filter placed upstream of the orifice can eliminate this problem. Orifice meters have long been used to measure and control flows from a few mL/min to 50 L/min.

Orifice Meter—Critical—Secondary Standard

If the pressure drop across the orifice (Figure 3-33) is increased until the downstream pressure is equal to approximately 0.53 times the upstream pressure (for air and some other gases), the velocity of the gas in the constriction will become acoustic, or sonic. Orifices used in this manner are called critical orifices. The constant 0.53 is purely a theoretical value and may vary. Any further decrease in the downstream or increase in the upstream pressure will not affect the rate of flow. As long as the 0.53 pressure relationship exists, the flow rate remains constant for a given upstream pressure and temperature, regardless of the value of the pressure drop (Figure 3-34). The probable error of an orifice meter is in the neighborhood of 2%.

Only one calibration point is needed for a critical orifice. The critical flow is usually measured with a moving-bubble meter, or a wet or dry test meter. Corrections for temperature and pressure differences in calibration and use are made with the following formula:

(Eq. 3-16)

$$Q_2 = Q_1\left(\frac{P_1 \times T_2}{P_2 \times T_1}\right)^{1/2}$$

Where:

Q = *flow*

P = *pressure*

T = *temperature in K*

1 = *initial conditions*

2 = *final conditions*

The same formula can be used to correct orifice meter flows to standard conditions by substituting P_2 = 760 mm Hg and T_2 = 298 K. Note the square root function of *T* and *P*. *Any time that rate meters are corrected for T and P, this square root function is needed.*

Critical orifices are used in the same types of situations as noncritical orifices. Care must also be taken not to plug the orifice.

Venturi Meter- Secondary Standard

The venturi meter consists of a short cylindrical inlet, an entrance cone, a short cylindrical throat, and finally a diffuser cone (Figure 3-35). Two pressure taps, one in the cylindrical inlet and one in the throat, serve to measure the pressure drop. There is no abrupt change of cross section as with an orifice; thus the flow is guided both upstream and downstream, eliminating turbulence and reducing energy losses. Venturi meters are, of course, more difficult to fabricate. The probable error of a venturi is 1%.

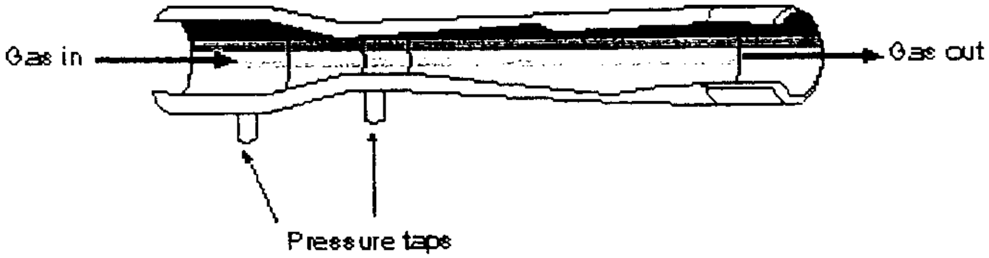


Figure 3-35. Venturi meter.

The venturi meter is calibrated in the same manner as the orifice meter. The calibration curve generated plots pressure drop across the venturi versus flow rates determined by the standard meter.

Variable-Area Meters

The variable area meter differs from the fixed orifice; the pressure drop across it remains constant while the cross-sectional area of the constriction (annulus) changes with the rate of flow. A rotameter is an example of a variable area meter.

The Rotameter—Secondary Standard

The rotameter consists of a vertically graduated glass tube, slightly tapered in bore with the diameter decreasing from top to bottom, containing a float of the appropriate material and shape (Figure 3-36). The fluid to be measured passes upward through the conical tube, which is inserted in the flow circuit.

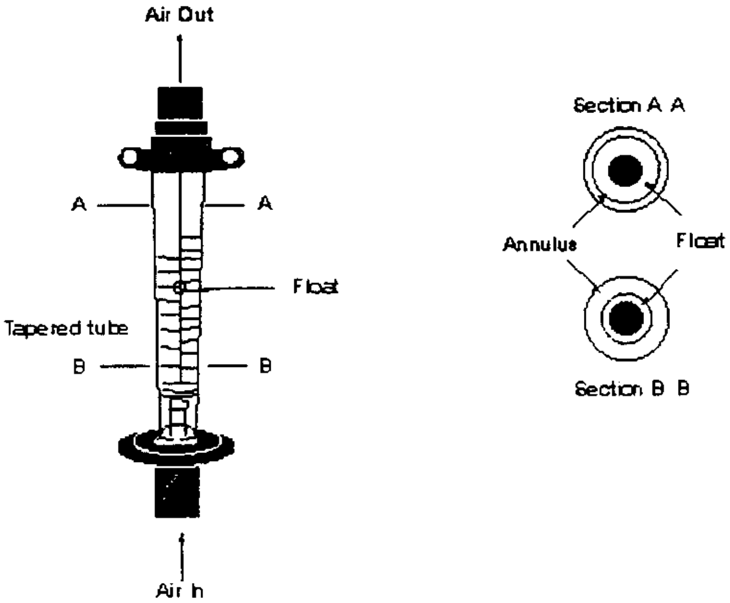


Figure 3-36. Rotameter.

A specially shaped float, with a diameter slightly greater than the minimum bore of the conical tube, is carried upward by the passage of the fluid until it reaches a position in the tube where its weight is balanced by the upward forces due to the fluid flowing past it. A variable ring or annulus is created between the outer diameter of the float and the inner wall of the tube. As the float moves upward in the tube, the area of the annulus increases. The float will continue to move upward until a pressure drop across the float, which is unique for each rotameter, is reached. This pressure drop across the float is constant regardless of the flow rate. A measure of the flow is noted by the float position on a vertical scale compared with a calibration chart.

The flow rate through a rotameter can be calculated from the tube diameters, float dimensions, float composition, and gas characteristics; this is not commonly done for calibration purposes. A detailed development of the flow equations for rotameters is contained in the appendix of this manual. Manufacturers generally provide accurate calibration curves for rotameters; it is advisable, however, to calibrate a rotameter under its operating conditions.

Most rotameters are used and calibrated at room temperature with the downstream side at atmospheric pressure. Corrections for pressure and temperature variations can be made using the previously mentioned formula:

(Eq. 3-17)

$$Q_2 = Q_1 \left(\frac{P_1 \times T_2}{P_2 \times T_1} \right)^{1/2}$$

Where:
Q = *flow*
P = *pressure*
T = *temperature in K*
1 = *initial conditions*
2 = *final conditions*

If a gas is measured with a different density from the calibration gas, the flow rate can be corrected using the following formula:

(Eq. 3-18)

$$Q_1 = Q_2 \left(\frac{q_2}{q_1} \right)^{1/2}$$

Where:
Q_1 = *flow rate with gas 1*
Q_2 = *flow rate with gas 2*
q_2 = *density of gas 2*
q_1 = *density of gas 1*

Because corrections of this type are cumbersome and add inaccuracies, rotameters are usually calibrated under normal operating conditions against a primary standard.

Rotameters are the most widely used laboratory and field method for measuring gas or liquid flow. Their ease of use makes them excellent for spot flow checks. Many atmospheric sampling instruments use rotameters to indicate the sample flow rate. With proper calibration, the rotameter's probable error is 2 to 5%.

Velocity Meters

Velocity meters measure the linear velocity or some property that is proportional to the velocity of a gas. Several instruments exist for measuring the velocity of a gas; we will discuss only the pitot tube and the mass flow meter. Volumetric flow information can be obtained from velocity data, if the cross-sectional area of the duct is known, using the following formula:

(Eq. 3-19)

$$Q = A\bar{v}$$

Where:

Q = *volumetric flow rate*, m^3/min

$\bar{v}$ = *average velocity*, m/min

A = *cross sectional area*, m^2

Pitot Tube-Primary Velocity Standard

The pitot tube is a simple pressure-sensing device used to measure the velocity of fluid flowing in an open channel. The complexity of the underlying fluid-flow principles involved in a pitot tube gas-velocity measurement is not apparent in the simple operation of this device. The pitot tube should, however, be considered and treated as a sophisticated instrument.

The pitot tube actually measures the velocity pressure (Δp) of a gas stream. Gas streamlines approaching a round object placed in a duct flow around the object except at point "P_+," where the gas stagnates and the stagnation pressure (P_+) is found (Figure 3-37 and Figure 3-38a).

The static pressure in a gas stream is defined as the pressure that would be indicated by a pressure gauge if it were moving along with the stream so as to be at rest, or relatively "static," with respect to the fluid. The static pressure can be measured as shown in Figure 3-38b.

The difference between the stagnation pressure (P_+) and the static pressure (P_z) is the velocity pressure differential (Δp). This is shown in Figure 3-38c.

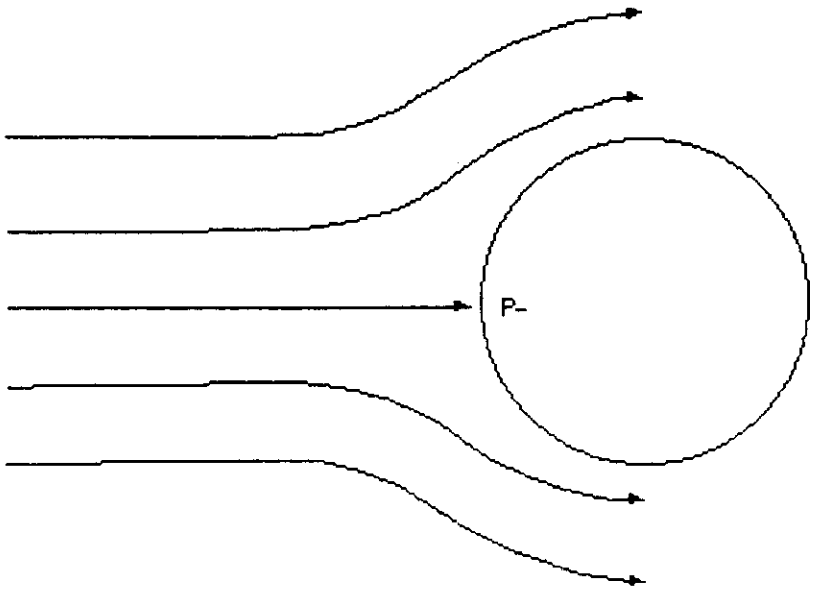


Figure 3-37. Gas stagnation against an object.

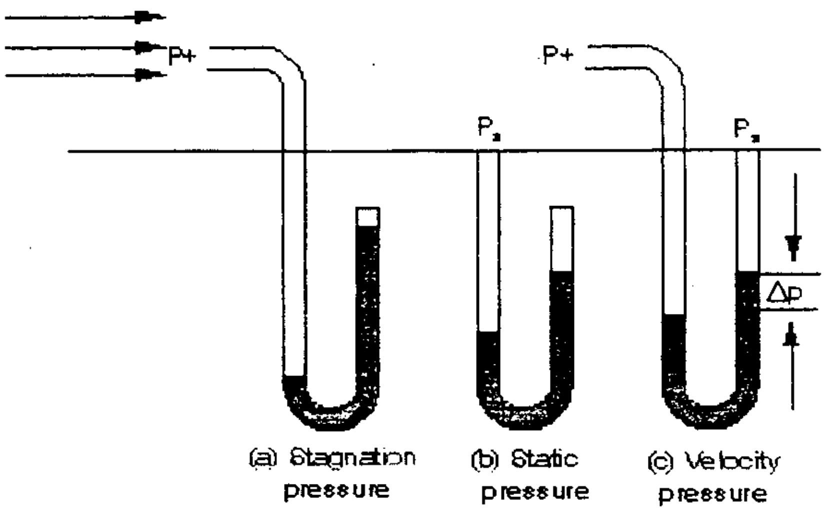


Figure 3-38. Pitot tube pressure components.

Bernoulli's Theorem relates pitot tube velocity pressure (Δp) to gas velocity in the following equation:

(Eq. 3-20)

$$v = K_p C_p \left(\frac{T \Delta p}{PM} \right)^{1/2}$$

Where:

v = *velocity of the gas stream,* ft/sec
T = *absolute temperature,* R (°F+460)
P = *absolute pressure,* in. Hg
M = *molecular weight of the gas,* lb/lb-mole
Δp = *velocity pressure,* in. H_2O

$$K_p = 85.49\ ft/sec \sqrt{\frac{(lb/lb \bullet mole)(in.\ Hg)}{(in.\ H_2O)(^\circ R)}}$$

C_p = *pitot tube coefficient, dimensionless.*

Pitot tubes are used extensively in ventilation work to measure air flow in ducts. Literature sources describe pitot tubes in detail. The standard and S-type pitot tubes are the most commonly used.

Standard Pitot Tube—Secondary Velocity Standard

The standard pitot tube (Figure 3-39) consists of two concentric tubes. The center tube measures the stagnation or impact pressure, and the static pressure is measured by the holes located on the side of the outer tube. The pitot tube must be placed in the flowing air stream so that it is parallel with the streamlines. The velocity pressure differential (Δp) can be measured with a U-tube manometer, inclined manometer, or any suitable pressure-sensing device. Only velocities greater than 2500 ft/min can be measured with a U-tube manometer, but flows as low as 600 ft/min can be measured with a carefully adjusted inclined manometer. Standard pitot tube velocity pressures are typically 0.14 inches of water at 1500 ft/min and 0.56 inches of water at 3000 ft/min.

The standard pitot tube was first calibrated against an orifice meter using Bernoulli's Theorem. Repeated calibrations proved that different standard pitot tubes have the same characteristic flow calibration. If the static pressure holes are six outer tube diameters from the hemispherical tip and eight outer tube diameters from the bend (Figure 3-39), then the C_p value in the previously mentioned formula is 1.

(Eq. 3-21)

$$v = K_p C_p \left(\frac{T \Delta p}{PM} \right)^{1/2}$$

Where:

v = *velocity of the gas stream,* ft/sec
T = *absolute temperature,* R (°F+460)
P = *absolute pressure,* in. Hg
M = *molecular weight of the gas,* lb/lb-mole
Δp = *velocity pressure,* in. H_2O

$$K_p = 85.49\ ft/sec \sqrt{\frac{(lb/lb \bullet mole)(in.\ Hg)}{(in.\ H_2O)(^\circ R)}}$$

C_p = *pitot tube coefficient, dimensionless.*

Standard pitot tubes can be used to measure linear velocity in almost any situation except in particle-laden gas streams. The particulate matter will foul the carefully machined tip and orifices. The velocity of gas streams with high particulate matter concentrations can be measured better with an S-type pitot tube.

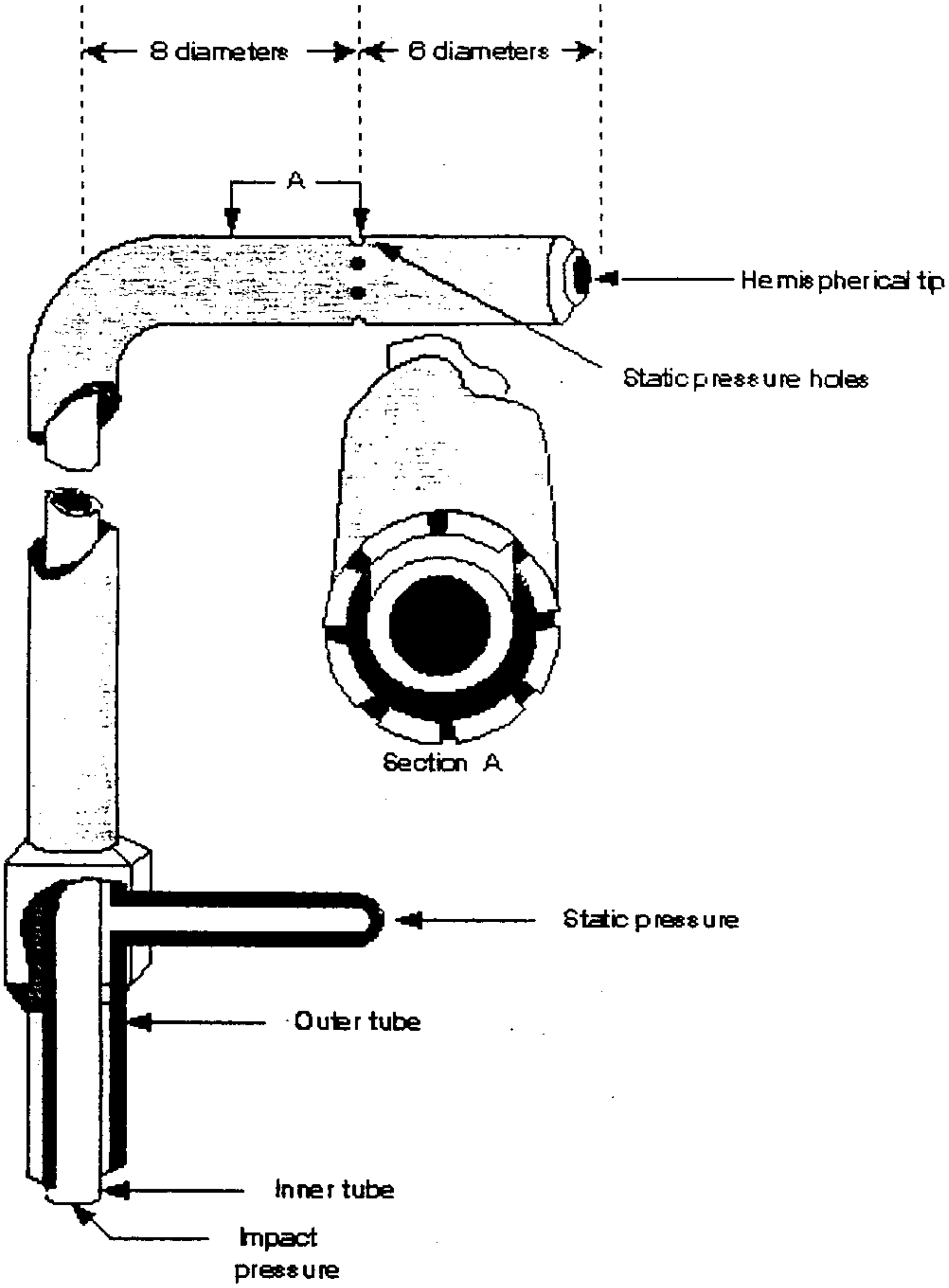


Figure 3-39. Standard pitot tube.

S-type Pitot Tube-Secondary Velocity Standard

The S-type pitot tube consists of two identical tubes mounted back to back (Figure 3-40). The sampling ends of the tubes are oval with the openings parallel to each other. In use, one oval opening should point directly upstream, the other directly downstream. The tubes should be made of stainless steel or quartz if they are used in high temperature gas streams. The alignments shown in Figure 3-40 should be checked before use or calibration, as this may cause variations in the calibration coefficient (C*p*).

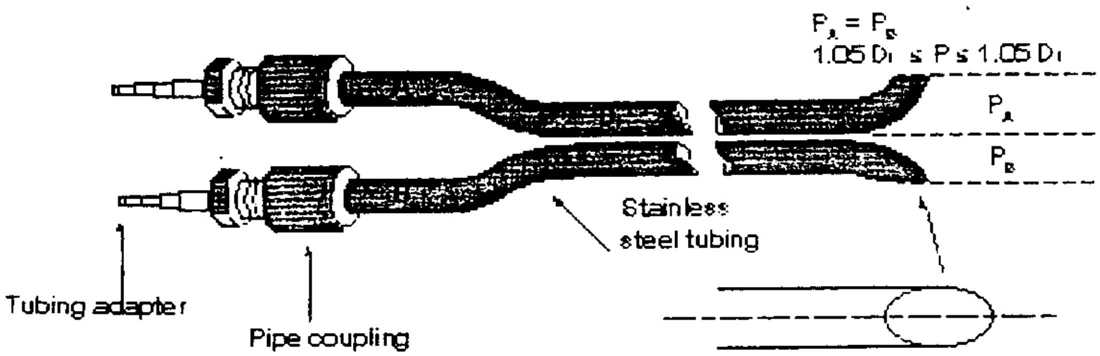


Figure 3-40. S-type pitot tube.

Calibration of the S-type pitot tube is performed by comparing it to a standard pitot tube. Both the standard and S-type pitot tubes are placed alternately into a constant air flow. Pressure readings are taken for the standard pitot tube and for leg A of the S-type tube, facing the direction of flow, and leg B, facing the direction of the flow (Figure 3-40). The pitot tube coefficient (C_p) is calculated using the following formula:

(Eq. 3-22)

$$C_{p(S)} = C_{p(STD)}\left(\frac{\Delta p_{STD}}{\Delta p_S}\right)^{1/2}$$

Where:

$C_{p(s)}$ = *S-Type Pitot tube coefficient*

$C_{(STD)}$ = *Standard pitot tube coefficient*

Δp_{STD} = *velocity pressure of Standard pitot tube*, in H_2O

Δp_S = *velocity pressure of S-Type pitot tube*, in H_2O

The average C_p is calculated from several readings and should have a value of approximately 0.84. The C_p for leg A and leg B should differ by less than 0.01. The C_p value can then be used to calculate velocity by the previously mentioned formula.

(Eq. 3-23)

$$v = K_p C_p \left(\frac{T\Delta p}{PM}\right)^{1/2}$$

Where:

v = *velocity of the gas stream,* ft/sec

T = *absolute temperature,* R (°F+460)

P = *absolute pressure,* in. Hg

M = *molecular weight of the gas.* lb/lb-mole

Δp = *velocity pressure,* in. H_2O

$$K_p = 85.49\ ft/sec\sqrt{\frac{(lb/lb \bullet mole)(in.\ Hg)}{(in.\ H_2O)(^{\circ}R)}}$$

C_p = *pitot tube coefficient, dimensionless.*

The S-type pitot tube maintains calibration in abusive environments. The large sensing orifices minimize the chance of plugging with particulates. The S-type pitot tube also gives a high manometer reading for a given gas velocity pressure, which can be helpful at low gas velocities. These feature make the S-type pitot tube the most frequently used instrument to measure stack gas velocity.

Mass Flow Meter—Secondary Velocity Standard

Mass flow meters work on the principle that when a gas passes over a heated surface, heat is transferred from this surface to the gas. The amount of current required to keep the surface at a constant temperature is a measure of the velocity of the gas. Since the amount of heat transferred depends on the mass and velocity of the gas, these meters measure mass flow rate.

Atmospheric sampling applications of the mass flow meter are usually limited to the measurement of volumetric flow. Since these devices measure mass flow directly, they should be calibrated against a primary or secondary volumetric standard. The standard meter flow is corrected to standard conditions and compared to the mass flow rate measured. No corrections for temperature and pressure need to be made to the mass flow meter readings. Calibration must be done with the same gas as will be measured in use, because different gases have different thermal properties.

Mass flow meters are most often used for flow measurement or as calibration transfer devices in the field and laboratory. Their insensitivity to temperature and pressure makes them a useful tool for standard conditions measurement.

Summary

The calibration and use of flow measuring devices are basic to the measurement of air pollutants. Most atmospheric measurements require the accurate knowledge of either the total volume of air or the flow rate. Many devices exist to aid in the measurement of volume and flow rate. Three types are most commonly used in atmospheric sampling—volume, rate, and velocity meters. Standard devices exist at the primary and secondary levels.

Sample Problems

Problem 1. Volume Conversion to Standard Conditions

A volume of 20 m^3 was drawn from a spirometer at 20°C and 700 mm Hg. What was the standard volume drawn?

$$V_2 = V_1\left(\frac{P_1T_2}{P_2T_1}\right)$$

Where:

V_2 = *volume at condition* 2

V_1 = *volume at condition* 1 = 20 m^3

P_1 = *pressure at condition* 1 = 700 mm Hg

P_2 = *pressure at condition* 2 = 760 mm Hg

T_1 = *temperature at condition* 1 = 20°C + 273 = 293 K

T_2 = *temperature at condition* 2 = 25°C + 273 = 298K

$$V_2 = (20\text{m}^3)\left(\frac{700\text{ mm Hg}}{760\text{ mm Hg}}\right)\left(\frac{298\text{ K}}{293\text{ K}}\right)$$

$$V_2 = 18.7\text{ m}^3$$

Problem 2. Orifice Conversion When Used at Other Calibration Conditions

An orifice was calibrated at 21°C and 760 mm Hg. It is to be used to calibrate a sampler at conditions of 25°C and 700 mm Hg. The flow at field conditions is 0.85 m^3/min (30 CFM): (a) What is the flow rate at calibration conditions? (b) What is the flow rate at standard conditions?

$$Q_2 = Q_1\left(\frac{T_2P_1}{P_2T_1}\right)^{1/2}$$

Where:

	Part a	*Part b*
Q_2 = *Flow* 2	_ *(cal. condt.)*	_ *(STD condt.)*
Q_1 = *Flow* 1	0.85 m^3/min	Q_2 in Part a
P_2 = *Press.* 2	760 mm Hg	760 mm Hg
P_1 = *Press.* 1	700 mm Hg	760 mm Hg
T_2 = *Temp.* 2	21° + 273° = 294 K	298 K
T_1 = *Temp.* 1	25° + 273° = 298 K	294 K

(a) *The flow rate at calibration conditions:*

$$Q_2 = (0.85\ \text{m}^3/\text{min})\left(\frac{700\ \text{mm Hg} \times 294\ \text{K}}{760\ \text{mm Hg} \times 298\ \text{K}}\right)^{1/2}$$
$$Q_2 = 0.81\ \text{m}^3/\text{min}$$

(b) *The flow at standard conditions (using orifice data at calibration conditions and the flow derived in part a):*

$$Q_2 = Q_1\left(\frac{P_1 \times 298\text{K}}{760\ \text{mm Hg} \times \text{T}_1}\right)^{1/2}$$

$$Q_2 = 0.81\left(\frac{760\ \text{mm Hg} \times 298\ \text{K}}{760\ \text{mm Hg} \times 294\ \text{K}}\right)^{1/2}$$

$$Q = 0.82\ \text{m}^3/\text{min}.$$

Problem 3. Conversion for Different Gas Used with a Rotameter

A rotameter was calibrated with air at 0°C and 760 mm Hg. The rotameter is now to be used to add helium as a carrier gas at 0°C and 760 mm Hg. If the flow reading at point X on the rotameter corresponded to 28.3 liters/min (1 ft^3/min) when air is used, to what flow will point X correspond when helium is used? (Density of helium = 0.1785 g/L; density of air = 1.2929 g/L.

$$Q_2 = Q_1\left(\frac{q_1}{q_2}\right)^{1/2}$$

Where:

Q_2 = *flow with gas* 2
Q_1 = *flow with gas* 1 = 28.3 L/min
q_1 = *density of gas* 1 = 1.2929 g/L *(air)*
q_2 = *density of gas* 2 = 0.1785 g/L *(helium)*

$$Q_2 = 28.3\left(\frac{1.2929\ \text{g/L}}{0.1785\ \text{g/L}}\right)^{1/2}$$
$$= 28.3\ (7.2431)^{1/2}$$

$Q_2 = 76.2$ L/min.

Problem 4. Pump Capacity

Can a pump with the following capacity curve (Figure 3-41) be used to drive critical orifices that have flow rates of (a) 50 cc/min and (b) 250 cc/min at criticality? (Hint: atmospheric pressure = 30 in. Hg.)

For an orifice to be critical,
$P_{downstream} \leq 0.53$ or $\leq 0.53\ (30)$ or ≤ 16 in. Hg.
$P_{downstream} = P_b + p_z$, therefore
$P_z = 30 - 16 = 14$ in. Hg gauge vacuum.

At a gauge vacuum of 14 in. Hg, the pump can pull approximately 130 to 140 cc/min. Therefore, this pump could operate orifice (a) at 50 cc/min but not (b) at 250 cc/min.

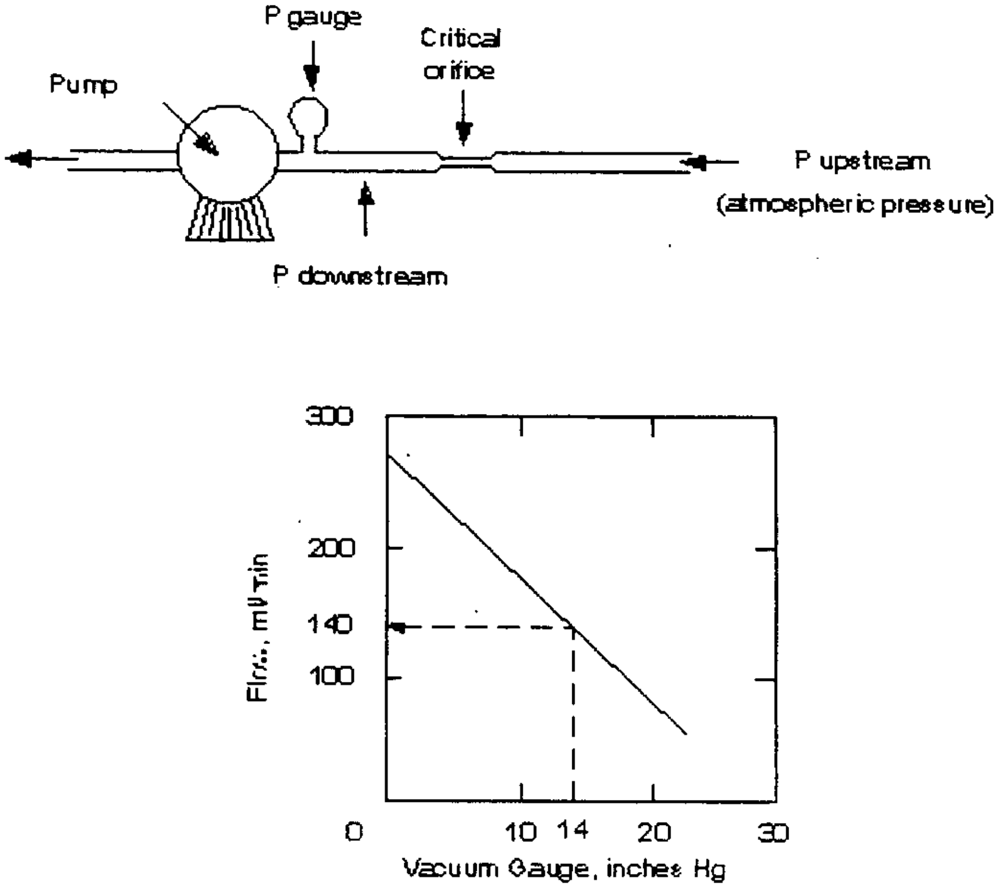


Figure 3-41. Problem 4: Pump capacity.

Additional $PM_{2.5}$ Flowmeters and Devices

Flow rate standards used for calibrating or verifying a $PM_{2.5}$ sampler's flow rate measurement device must have an accuracy of ± 2%. This flow rate standard must be a separate, stand-alone device designed to connect to the flow rate measurement adapter. The flow rate standard must have its own certification and must be traceable to a NIST primary standard for volume or flow rate.

The following section includes the advantages and disadvantages of some of the various types of flow rate standards that might be considered for $PM_{2.5}$ sampler calibration.

Bubble Flowmeters

Although manually operated and timed bubble flowmeters are available, a semiautomatic instrument is easier to use and is likely to provide more uniform flow rate measurements. Because the liquid used to form the bubbles is usually water-based, a water vapor correction may be required to compensate for a volume increase due to evaporation of the water in the instrument. Furthermore, the instrument cannot be used below 0°C because the soap solution will freeze.

Piston Flowmeters

Automatic dry-piston flowmeters are relatively easy to use and are not subject to the water vapor correction of the liquid freezing limitation of the bubble flowmeters. However, they may still be subject to a lower operational temperature limit due to LCD readouts. Alternatively, hard-copy printouts could be used to log results.

Mass Flowmeters

Although mass flowmeters may be considered as calibration standards, they have a number of shortcomings in this application. They have a high pressure drop, which could change the sampler flow rate or otherwise affect the operation of the sampler. Mass flowmeters also require conversion of the measured mass flow rate to the actual volumetric flow rate for comparison to the $PM_{2.5}$ sampler displayed value. The flow rate measured by the sampler may also have to be corrected to account for significant pressure drop introduced by the mass flowmeter itself. Finally, mass flowmeters are subject to zero or span drift, particularly over the wide range of temperatures encountered at field sites, so their accuracy should be reverified frequently over a wide temperature range.

Orifice Devices

Orifice devices are simple and reliable, but they require corrections for temperature and pressure and may have a significant pressure drop. They also require a very accurate and sensitive differential pressure measurement device, such as a manometer of an aneroid differential pressure gauge, whose accuracy must be reverified frequently. Electronic micromanometers are convenient to use with an orifice device. Readings from electronic micromanometers should be crosschecked against a water manometer prior to a round of sampler verifications or calibrations.

Laminar Flow Elements

Laminar flow elements generally have a lower pressure drop than orifice devices but otherwise have the same requirements and disadvantages.

Wet Test Meters

Wet test meters are generally not practical for field use but may be used for laboratory calibrations.

Dry Gas Meters

Dry gas meters may be considered for field calibration. Some meters may have a substantial pressure drop. They should be checked for leaks and mechanical problems and be recertified at least annually. Dry gas meters may take a much longer period of time to use since instantaneous and semi-instantaneous values are not available..

References

American Society of Mechanical Engineers. 1937. ASME *research publication: fluid meters, their theory and application.* 4th ed. New York: The American Society of Mechanical Engineers.

Babbitt, Harold E., and Doland, James J. *Water supply engineering.* 5th ed. New York: McGraw Hill Book Company, Inc.

Brenchley, D. L. 1972. Use of watch jewels as critical flow orifices. *J. Air Poll. Cont. Assoc.* 22:967.

Corn, M., and Bell, W. A. 1963. A technique for construction of predictable low-capacity critical orifices. *Am. Ind. Hyg. Assoc.* 24:502.

Daughtery, A. G., and Ingersoll, A. C. 1954. *Fluid mechanics.* New York: McGraw-Hill Book Company, Inc.

Frisone, G. J. 1965. A simple and precise soap-bubble flow meter. *Chemist-Analyst* 54:46.

Furtado, V. C., and Harris, William B. 1972. *Air movers. Air sampling instruments.* 4th ed. American Conference of Governmental Industrial Hygienists.

Harrison, Walter K.; Nader, John S.; and Fugman, Frank S. 1960. Constant flow regulators for the high-volume air sampler. *Am. Ind. Hyg. Assoc. J.* 21:115.

Hering, Susanne V. "Impactors, Cyclones, and Other Inertial and Gravitational Collectors" in *Air Sampling Instruments for evaluation of atmospheric contaminants,* 8th ed. Cohen and Hering, ed. ACGIH: Cincinnati, OH. 1995.

Hydraulic Institute. 1955. *Standards of the hydraulic institute.* 10th ed. New York: The Hydraulic Institute.

Industrial ventilation. 1968. 10th ed. Ann Arbor, MI: Edwards Brothers.

Institute of Industrial Health. 1956. *Encyclopedia of instrumentation for industrial hygiene.* Ann Arbor, MI: University of Michigan.

Kristal, Frank A., and Annett, F. A. 1953. *Pumps.* New York: McGraw-Hill Book Company, Inc.

Lapple, C. E., et al. 1956. *Fluid and particle mechanics.* 1st ed. Newark, DE: University of Delaware.

Levy, A. 1964. The accuracy of the bubble meter method for gas flow measurements. *J. Sci. Instr.* 41:449.

Lippman, Morton. "Airflow Calibration" in *Air Sampling Instruments for evaluation of atmospheric contaminants.* 8th ed. Cohen and Hering, ed. ACGIH: Cincinnati, OH. 1995.

Liptak, B. G. 1969. *Instrument engineers handbook.* Vol. 1. Philadelphia: Chilton Book Company.

Lodge, J. P., et al. 1966. The use of hypodermic needles as critical orifices in air sampling. *J. Air Poll. Cont. Assoc.* 16:197.

Mitchell, Charles B. 1956. *Which pump and why? Fluid flow in practice.* New York: Reinhold Publishing Corporation.

Nelson, G. O. 1972. *Controlled test atmospheres.* 1st ed. Ann Arbor, MI: Ann Arbor Science.

Ower, E., and Pankhurst, R. C. 1966. *The measurement of air flow.* 4th ed. Elmsford, NY: Permagon Publishing Company.

Posner, J. C., and Woodfin, W. J. "Sampling with Gas Bags – Loss of Analyte with Time." *Appl. Ind. Hyg.* 1:163 (1986).

Randolf Company. 1971. *Catalog no. 38.*

Robson, Charles D., and Foster, Kirk E. 1962. Evaluation of air particulate sampling equipment. *Am. Ind. Hyg. Assoc.* J. 23:404.

Rubow, Kenneth L. "Air Movers and Samplers" in *Air Sampling Instruments for evaluation of atmospheric contaminants,* 8th ed. Cohen and Hering, ed. ACGIH: Cincinnati, OH. 1995.

Salvato, Joseph A. 1958. *Environmental sanitation.* New York: John Wiley and Sons, Inc.

Schmidt, A.C., and Wiltshire, L.L. June, 1955. A constant flow suction unit- for aerosol sampling work. *Am. Ind. Hyg. Assoc. Qtrly.*

Stern, Arthur C. 1962. *Air pollution.* Vol. I. New York: Academic Press.

---. 1976. *Air pollution.* Vol. III. New York: Academic Press.

Swift, David L., and Lippman, Morton. "Electrostatic and Thermal Precipitators" in *Air Sampling Instruments for evaluation of atmospheric contaminants,* 8th ed. Cohen and Hering, ed. ACGIH: Cincinnati, OH. 1995.

Taylor, R.D. 1972. Report UCRL-51239, TID-4500, UC-41. Levermore, CA: Lawrence Radiation Lab, University of California.

Section A-3

Particulate Matter Sampling

Reading Assignment

Pages 4-1 through 4-102 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Inertial Sampling Devices
- Filtration Sampling
- Filter Media
- Gravitational Sampling
- Electrostatic and Thermal Precipitators
- High-Volume Sampling for TSP
- Reference Method for PM_{10}
- Reference Method for $PM_{2.5}$
- Continuous Sampling

Learning Goal and Objectives

Learning Goal

The purpose of this section is to familiarize you with the sampling of particulate matter.

Learning Objectives

At the end of this section, you should be able to

1. describe four principal particulate matter collection methods: gravity, filtration, inertia, and precipitation.
2. identify common sources of error in the collection of particulate matter by impactors.
3. describe the mechanism for size-fractioning particles using inertia.
4. define collection efficiency.
5. recognize factors that affect the inertia of particles and the collection efficiency of an impactor.
6. recognize properties of collecting devices that affect the collection efficiency of impactors.

7. describe the rationale for size-fractioning ambient particulate matter.
8. recall some of the advantages and disadvantages of cellulose, glass-fiber, and membrane filters.
9. describe the components of a FRM particulate sampler.
10. describe the procedure used to calibrate a particulate matter flow measuring device.
11. recognize the differences between bias, accuracy, and precision.
12. calculate the particulate matter concentration of a $PM_{2.5}$ sample, given filter weights, flow rate, and sampling time.
13. calculate the particulate matter concentration of a PM_{10} sample, given filter weights, flow rate, and sampling time.
14. calculate the particulate matter concentration of a TSP sample, given filter weights, flow rate, and sampling time.
15. identify and describe solutions for potential errors associated with particulate matter measurement.
16. identify and describe solutions for potential errors associated with the lead reference method.
17. calculate the total air volume sampled, given flow rate and sampling time.

Reading Guidance

- Refer often to the equations and figures of the assigned reading material as you progress through the assignment.
- When you have finished the reading assignment, complete the review exercise for Section A-3. It begins on the following page.
- After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
- For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment indicated on the answers page.
- After you have reviewed your incorrect answers (if any), take Quiz 1. Follow the directions listed in the Course Introduction section of this guidebook.
- After completing Quiz 1, proceed to Section A-4 of this guidebook.

Review Exercise

Now that you've completed the assignment for Section A-3, please answer the following questions. These will help you determine whether or not you are mastering the material.

1. True or False? The PM_{10} fraction ranges from 0 to 10 µg, and the $PM_{2.5}$ size fraction ranges from 0 to 2.5 µg in aerodynamic diameter.

    a. True
    b. False

2. Particles having diameters of approximately _____ or less are generally thought to be inhaled in the lower respiratory system.

    a. 100 µm
    b. 50 µm
    c. 75 µm
    d. 15 µm

3. Inertial collectors work on the principle that particles in a gas stream are _____ dense than the fluid (air) in which they are suspended.

    a. more
    b. less
    c. neither more nor less
    d. none of the above

4. True or False? Impaction devices collect and retain particles of an air stream on a surface.

    a. True
    b. False

5. The Andersen impactor is an example of

   a. a two stage impactor.
   b. a multi-stage impactor.
   c. neither of the above
   d. both of the above

6. How do impingement devices differ from impactors?

   a. The jet is immersed in a collecting fluid.
   b. The striking surface is immersed in a collecting fluid.
   c. both of the above
   d. none of the above

7. True or False? Centrifugal separation is a variant form of the inertial collection process which works by spinning the sampling chamber rapidly in a circular motion.

   a. True
   b. False

8. Particle collection efficiency can be generally defined as

   a. the percentage of the particles in an incident aerosol stream that is drawn through the sampler.
   b. the percentage of particles present in any sampled aerosol stream.
   c. the fraction of the particles in an incident aerosol stream that is retained on the collection surface of the sampling device.
   d. the amount of particulate matter that can be collected by a given sampler in a given amount of time.

9. Which of the following inertial collecting device properties has the greatest effect on collection efficiency?

   a. jet shape
   b. jet to collection surface distance
   c. filter type
   d. collection surface size

10. True or False? Large conglomerates (greater than 100 µg) and agglomerates are readily shattered upon impaction.

    a. True
    b. False

11. True or False? Basic inertial sampling is the most widely used approach for the collection of atmospheric particulates.

    a. True
    b. False

12. True or False? Air filtration works primarily as a sieving process.

    a. True
    b. False

13. Which of the following is a parameter of filter collection efficiency?

    a. percent diffusion
    b. percent penetration
    c. percent impaction
    d. percent filtration

14. Which of the following is <u>NOT</u> a type of particulate matter filter paper?

    a. glass fiber
    b. membrane
    c. cellulose fiber
    d. graphite fiber

15. True or False? Cellulose fiber filters are very effective at high operating temperatures.

    a. True
    b. False

16. Glass fiber filters are typified by _____ and are _____.

    a. high collection efficiency / hygroscopic
    b. the ability to withstand high temperatures / hygroscopic
    c. low collection efficiency / nonhygroscopic
    d. high collection efficiency / nonhygroscopic

17. Gravitational sampling refers to the _____ which reaches the ground over a stated period of time.

    a. amount of precipitation
    b. percentage of particulate matter
    c. particulate haze
    d. none of the above

18. Which of the following is an advantage of electrostatic precipitators?

    a. The sampling rate is unaffected by air volume.
    b. The sampling rate is unaffected by mass loading.
    c. The sampling rate is unaffected by temperature.
    d. all of the above

19. Thermal precipitators have

    a. a low sampling velocity which prevents particle shattering.
    b. a high collection efficiency.
    c. both a and b, above
    d. none of the above

20. True or False? The TSP reference method is the official sampling method for obtaining samples to determine compliance with the national ambient air quality standard for Total Suspended Particulates.

    a. True
    b. False

21. True or False? Glass fiber filters are the dominant choice for high volume sampling.

    a. True
    b. False

22. Which of the following is NOT a proper high volume filter handling precaution?

   a. Filters should be equilibrated for 24 hours prior to weighing.
   b. Filters should be visually inspected for holes, tears, or other damage.
   c. Filters should be permanently identified by stamping a serial number on two diagonally opposite corners.
   d. Filters should be carefully folded prior to sampling to protect the filter surface from contamination.

23. Procedures for the calibration of orifice-type flow rate transfer standards, as well as the calibration of sampler flow rate measuring devices, have been specified in

   a. Appendix C of 40 CFR 50.
   b. Appendix B of 40 CFR 50.
   c. Appendix B of 40 CFR 53.
   d. Appendix C of 40 CFR 53.

24. True or False? Filters from high volume samplers are useful only for mass concentration determination.

   a. True
   b. False

25. Which of the following factors can influence the accuracy and precision of high volume sampling methods?

   a. humidity of the air
   b. sampler operating characteristics
   c. filter characteristics
   d. all of the above

26. _____ is the degree of agreement between and observed value and an accepted reference value.

   a. Precision
   b. Accuracy
   c. Bias
   d. Quality assurance

27. True or False? Potential sources for error in measuring PM_{10} concentration levels using the PM_{10} reference method include volatile particles, filter handling, and air volume determination.

   a. True
   b. False

28. Which type of filter is considered ideal for PM_{10} sampling?

   a. glass fiber
   b. membrane
   c. cellulose
   d. No filter is ideal in all respects.

29. The accuracy of a $PM_{2.5}$ sampler's flow rate should be within _____ of the sampler's design flow rate.

   a. ± 2 %
   b. ± 3 %
   c. ± 4 %
   d. ± 5 %

30. A Class II equivalent method for $PM_{2.5}$ monitoring is a

   a. method very similar to reference methods, with only minor deviations.
   b. method unable to qualify as other equivalent due to profound differences from reference method requirements.
   c. filter-collection-based method that differs substantially from reference method requirements.
   d. method usable for either $PM_{2.5}$ or PM_{10} sampling.

31. True or False? The ambient air flow rate through a $PM_{2.5}$ reference sampler's sampling inlet and filter assembly has little relationship to measurement precision.

   a. True
   b. False

32. How many continuous fine particle analyzers are required in each metropolitan area with a population greater than 1 million?

a. one
b. three
c. two, both at the same core site
d. none of the above

33. As the jet size of an impactor _____, the impaction velocity _____.

a. increases / increases
b. decreases / decreases
c. decreases / increases
d. The two factors are unrelated.

34. True or False? The collection efficiency of an impaction device is affected by the flow rate of sample air through the device.

a. True
b. False

35. True or False? The TSP reference method is currently in use.

a. True
b. False

36. The air flow rate of an ambient air $PM_{2.5}$ sampler was reported as 16.2 L/min at atmospheric conditions of 755 mm Hg and 26° C. What is this flow rate in m^3/hour?

a. 9.782 m^3
b. 9.720 m^3
c. 0.972 m^3
d. 0.978 m^3

37. A $PM_{2.5}$ sampler with an average flow rate of 17.1 L/min for a 23.5 hour sampling period would have a total sample volume in m^3 of _____.

a. 24.55 m^3
b. 23.11 m^3
c. 24.11 m^3
d. 22.11 m^3

38. A $PM_{2.5}$ filter weighed 145.350 mg before sampling and 145.875 mg after sampling. What is the total $PM_{2.5}$ mass in μg?

  a. 0.535 μg
  b. 0.515 μg
  c. 505 μg
  d. 525 μg

39. A $PM_{2.5}$ filter weighed 150.100 mg before sampling and 150.750 mg after sampling. The flow rate at atmospheric conditions of 745 mm Hg and 23° C was 16.5 L/min. The sampling period was 24 hours. What is the $PM_{2.5}$ concentration in $\mu g/m^3$ at actual sampling conditions?

  a. 26.4 $\mu g/m^3$
  b. 27.4 $\mu g/m^3$
  c. 25.6 $\mu g/m^3$
  d. 27.6 $\mu g/m^3$

40. A $PM_{2.5}$ filter weighed 150.100 mg before sampling and 150.750 mg after sampling. The flow rate at atmospheric conditions of 745 mm Hg and 20° C was 16.5 L/min. The sampling period was 24 hours. What is the $PM_{2.5}$ concentration in $\mu g/m^3$ at standard conditions of 760 mm Hg and 25° C?

  a. 27.4 $\mu g/m^3$
  b. 26.6 $\mu g/m^3$
  c. 26.1 $\mu g/m^3$
  d. 25.6 $\mu g/m^3$

41. A $PM_{2.5}$ filter weighed 145.250 mg before sampling and 145.555 mg after sampling. The flow rate at atmospheric conditions of 745 mm Hg and 23° C was 16.68 L/min. The sampling period was 23.75 hours. What is the $PM_{2.5}$ concentration in $\mu g/m^3$ at standard atmospheric conditions of 760 mm Hg and 25° C?

  a. 12.6 $\mu g/m^3$
  b. 13.3 $\mu g/m^3$
  c. 13.0 $\mu g/m^3$
  d. 12.7 $\mu g/m^3$

42. The initial standard flow rate of a high volume total suspended particulate (TSP) matter sampler was 40 ft^3/min and the final flow rate was 38.2 ft^3/min. The sampling period was 23 hours and the atmospheric pressure was 750 mm Hg and 24° C. The weight of the filter before sampling was 4.6550 g and the weight after sampling was 4.7705 g. What is the TSP concentration in μg/m^3 at standard conditions of 760 mm Hg and 25° C? Note that 1 m^3/min is equal to 35.3144 ft^3/min.

a. 74.9 μg/m^3
b. 76.9 μg/m^3
c. 74.4 μg/m^3
d. 76.1 μg/m^3

43. The initial standard flow rate of a high volume total suspended particulate (TSP) matter sampler was 40 ft^3/min and the final flow rate was 39 ft^3/min. The sampling period was 22.5 hours and the atmospheric pressure was 725 mm Hg and 20° C. The weight of the filter before sampling was 4.7550 g and the weight after sampling was 4.8100 g. What is the TSP concentration in μg/m^3 at standard conditions of 760 mm Hg and 25° C? Note that 1 m^3/min is equal to 35.3144 ft^3/min.

a. 35.3 μg/m^3
b. 34.2 μg/m^3
c. 36.4 μg/m^3
d. 37.5 μg/m^3

44. The initial standard flow rate of a high volume total suspended particulate (TSP) matter sampler was 39 ft^3/min and the final flow rate was 39 ft^3/min. The sampling period was 24 hours and the atmospheric pressure was 760 mm Hg and 23° C. The weight of the filter before sampling was 4.6100 and the weight after sampling was 4.7200g. What is the TSP concentration in μg/m^3 at standard conditions of 760 mm Hg and 25° C? Note that 1 m^3/min is equal to 35.3144 ft^3/min.

a. 70.9 μg/m^3
b. 70.0 μg/m^3
c. 69.0 μg/m^3
d. 68.1 μg/m^3

45. A PM_{10} filter weighed 155.60 mg before sampling and 156.28 mg after sampling. What is the total PM_{10} mass in µg?

a. 0.680 µg
b. 0.670 µg
c. 680 µg
d. 670 µg

46. A dichotomous sampler was used for measuring PM_{10} concentrations in the atmosphere. Two filter weights were obtained: one for fine particulate and one for coarse particulates. In measuring PM_{10} concentrations with a dichotomous sampler, the two filter weights are combined to determine the PM_{10} concentrations. In this sampling situation the final gross weight for the fines was 101.220 mg with a tare weight of 100.300 mg. The final gross weight of the coarse particles was 104.123 mg with a tare weight of 103.245 mg. The average total flow rate for the 24-hour sampling period was 16.80 L/min. The average atmospheric pressure was 745 mm Hg and the average temperature was 23.5° C. The PM_{10} concentration for this sample reported as $\mu g/m^3$ at actual atmospheric conditions is:

a. 70.5 $\mu g/m^3$
b. 74.3 $\mu g/m^3$
c. 77.0 $\mu g/m^3$
d. 75.0 $\mu g/m^3$

47. The combined filter weights from a PM_{10} dichotomous sampler were determined to be 1,575 µg. The sampling period was 23.5 hours and the average total flow was 16.60 L/min. The average atmospheric pressure and temperature was 750 mm Hg and 23° C. What is the calculated concentration in $\mu g/m^3$ at standard conditions of 760 mm Hg and 25° C?

a. 66.7 $\mu g/m^3$
b. 68.5 $\mu g/m^3$
c. 65.8 $\mu g/m^3$
d. 67.7 $\mu g/m^3$

48. The gross weight of the fine particulate filter from a PM_{10} dichotomous sampler was 0.990550 g with a tare weight of 0.990100 g. The gross weight and tare weight of the coarse particulate filter was the same as that of the fine particulate matter. The total volume sampled at actual atmospheric conditions of 755 mm Hg and 24° C was 24,330 L. The calculated PM_{10} concentration in $\mu g/m^3$ at actual atmospheric conditions is _____.

a. 36.5 $\mu g/m^3$
b. 37.0 $\mu g/m^3$
c. 37.8 $\mu g/m^3$
d. 36.0 $\mu g/m^3$

49. The gross weight of the fine particulate filter from a PM_{10} dichotomous sampler was 0.990550 g with a tare weight of 0.990100 g. The gross weight and tare weight of the coarse particulate filter was the same as that of the fine particulate matter. The total volume sampled at actual atmospheric conditions of 755 mm Hg and 24° C was 24,330 L. The calculated PM_{10} concentration in $\mu g/m^3$ at standard atmospheric conditions of 760 mm Hg and 25° C is _____.

a. 36.3 $\mu g/m^3$
b. 35.3 $\mu g/m^3$
c. 37.9 $\mu g/m^3$
d. 37.1 $\mu g/m^3$

50. The air flow rate of an ambient air $PM_{2.5}$ sampler was reported as 16.67 L/min at standard conditions of 760mm Hg and 25 °C. Correcting this flow to atmospheric conditions of 750 mm Hg and 24 °C would result in the following flow rate in m^3/min _____.

a. 0.0158 m^3/min
b. 0.0168 m^3/min
c. 16.84 m^3/min
d. 17.00 m^3/min

Section A-3

Review Exercise Answers

		Page(s) of *Atmospheric Sampling: Student Manual*
1.	a	4-2
2.	d	4-1
3.	a	4-3
4.	a	4-4
5.	b	4-5
6.	c	4-12
7.	b	4-12
8.	c	4-17
9.	b	4-18, 4-19
10.	b	4-19
11.	b	4-27
12.	b	4-28
13.	b	4-28
14.	d	4-33 through 4-37
15.	b	4-34
16.	d	4-34, 4-35
17.	a	4-47
18.	b	4-48. 4-49
19.	c	4-50
20.	b	4-51
21.	a	4-54
22.	d	4-55 through 4-57
23.	b	4-58
24.	b	4-71
25.	d	4-71 through 4-75
26.	b	4-81
27.	a	4-82
28.	d	4-83
29.	a	4-87
30.	c	4-92
31.	b	4-93
32.	a	4-96
33.	c	4-18
34.	a	4-19
35.	a	4-51
36.	c	4-94, 4-95
37.	c	4-94, 4-95
38.	d	4-94, 4-95
39.	b	4-94, 4-95
40.	a	4-94, 4-95
41.	c	4-94, 4-95
42.	d	4-68 through 4-70
43.	d	4-68 through 4-70
44.	c	4-68 through 4-70
45.	c	4-84 through 4-86
46.	b	4-84 through 4-86
47.	d	4-84 through 4-86
48.	b	4-84 through 4-86
49.	d	4-84 through 4-86
50.	b	4-94, 4-95

Required Readings

Chapter 4
Particulate Matter Sampling

Introduction

This Chapter provides a definition for the subclasses of particulate matter (PM), addresses the rationale for size fractionation of particulates, and discusses particulate matter sampling techniques in ambient air. PM is the generic term for a broad class of chemically and physically diverse substances that exist as discrete particles (liquid droplets or solids) over a wide variation in the size of the particles. The sizes range from molecular clusters of ~0.005 micrometers (µm) in diameter to coarse particles of ~100 µm. Particle size or diameter refers to aerodynamic diameter, which is defined as the diameter of a spherical particle with equal settling velocity and a material density of 1 g/cm^3 normalizing particles of different shapes and densities. The size of the particles is important because of the adverse health effects associated with particles in certain size ranges. Larger particles (~15 µm or larger) that are inhaled are removed in the nose and throat, while smaller particles (~ 10 µm and less) are inhaled into the lower respiratory system. Figure 4-1 shows the respiratory collection of particles.

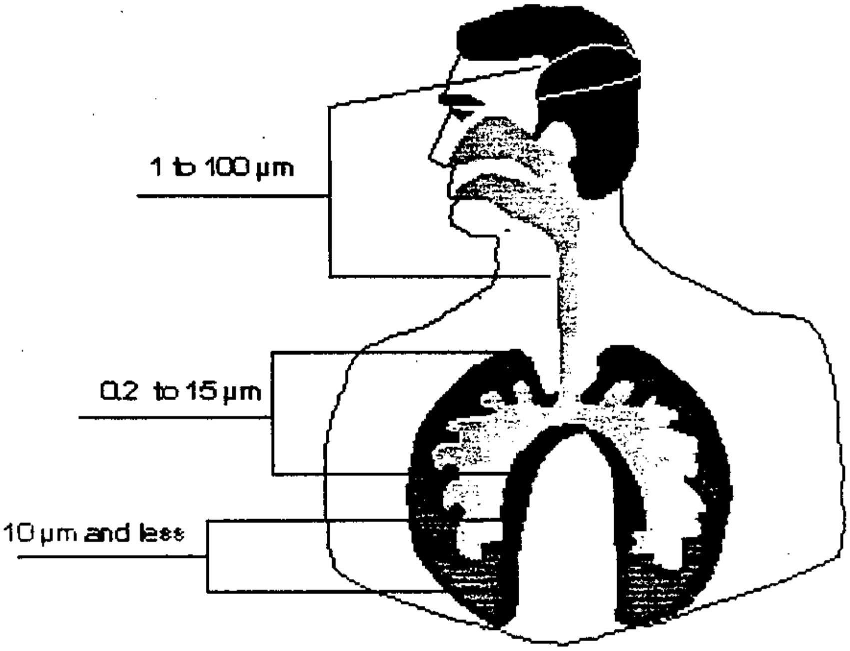


Figure 4-1. Respiratory collection of particles.

In addition to being characterized by their size, particles can also be described by their origin or formation mechanism, chemical composition, and physical properties, as well as in terms of what is measured by a particular sampling technique. Figure 4-2 presents particle size distributions of several sources of particulate emissions. The original national ambient air quality standards (NAAQS) for particulate matter were first established in 1971, and were measured based on the use of total suspended particulate (TSP) samplers known as high-volume samplers. The high-volume sampler, which is based on a filtration technique, typically captures particles from 0 to 45 µm and usually up to a nominal size of 25 to 45 µm. In 1979, EPA added PM_{10} to TSP as the indicator for particles, where PM_{10} refers to particles with a mean aerodynamic diameter less than or equal to 10 µm. On July 18, 1997, EPA promulgated new PM standards which included NAAQS for particulate matter with an aerodynamic diameter less than or equal to 2.5 µm, referred to as $PM_{2.5}$. Figure 4-3 shows the idealized size distribution of particles in ambient air (Chow, 1997). The $PM_{2.5}$, PM_{10}, and TSP size fractions are seen in Figure 4-3 by the portion of the micrometer size they occupy. The mass collected is proportional to the area under the size distribution within each size range. The TSP size fraction ranges from 0 to about 45 µm, the PM_{10} fraction ranges from 0 to 10 µm, and the $PM_{2.5}$ size fraction ranges from 0 to 2.5 µm in aerodynamic diameter. No sampling device operates as a sharp step function, passing 100% of all particles below a certain size and excluding 100% of the particles larger than that size. When sampling, each of these size ranges contains a certain amount of particles above the upper size designation of each range.

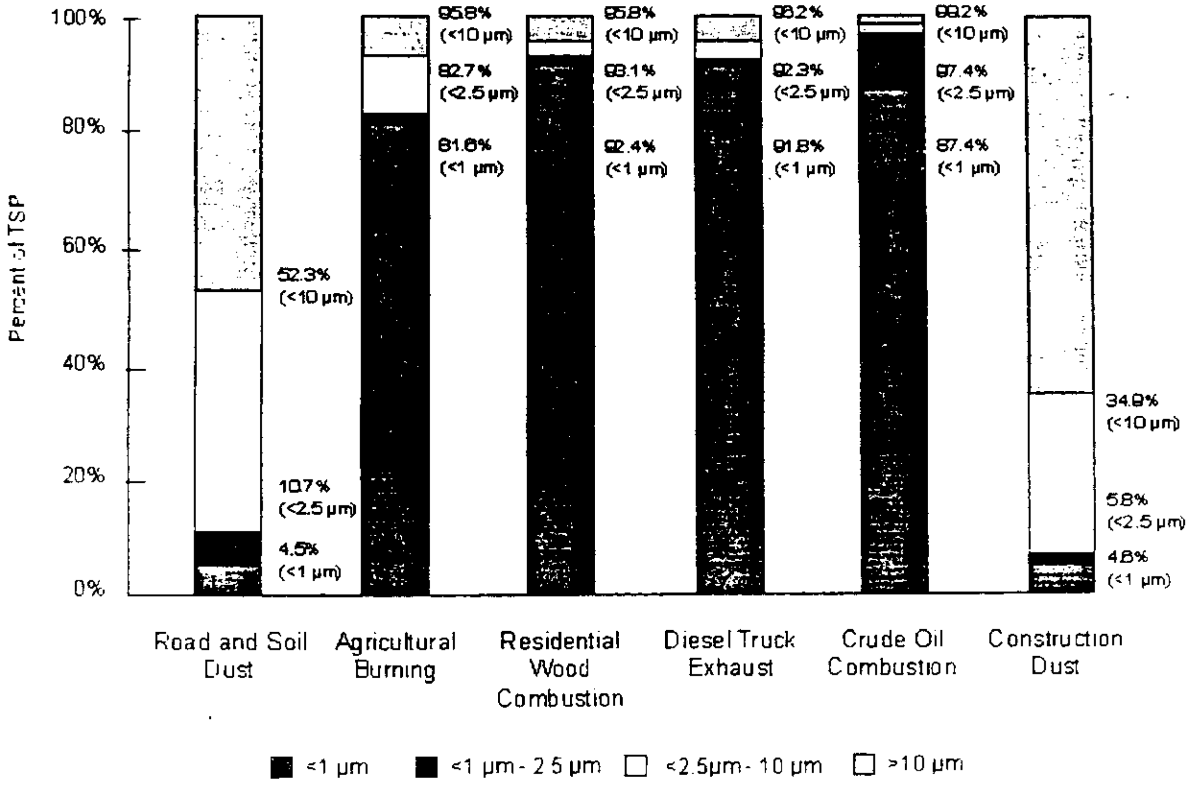


Figure 4-2. Particle size distributions of sources of particulate emissions.

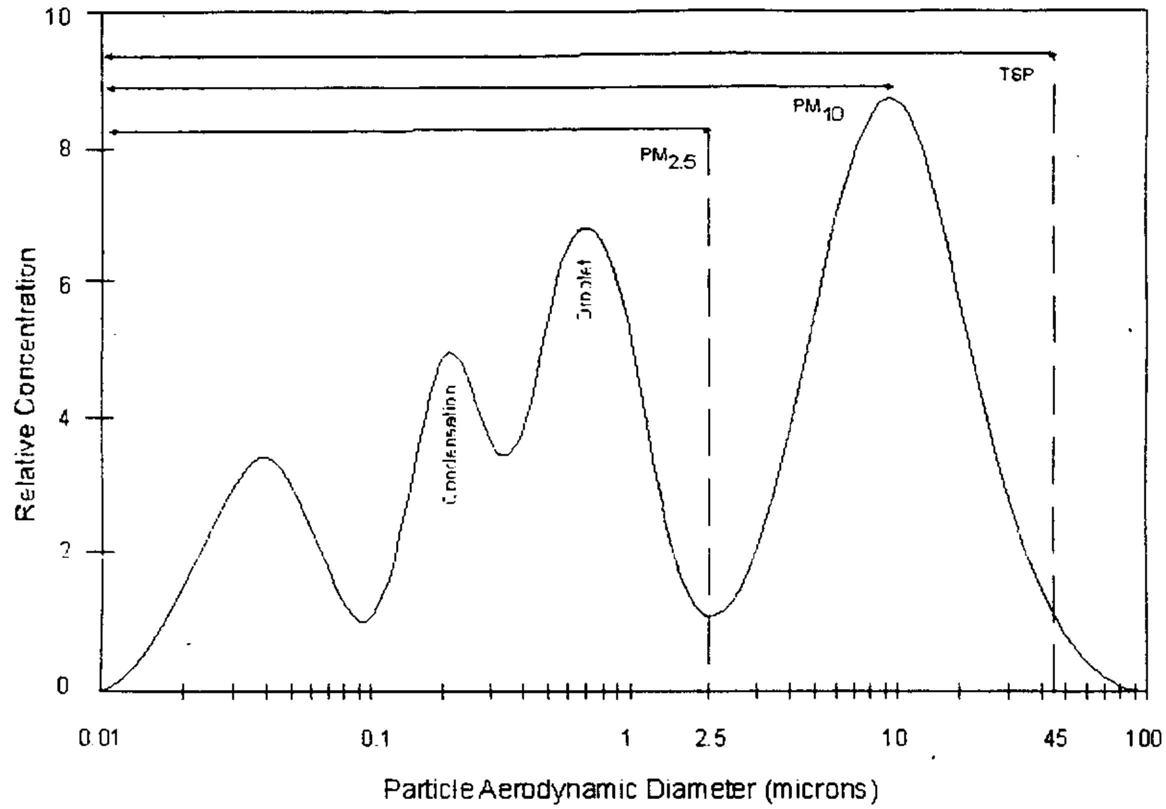


Figure 4-3. Idealized size distribution of particle in ambient air.

In this Chapter, the discussion of particulate matter sampling will include inertial collection techniques, along with filtration, gravitational, and precipitation techniques. Discussion of samplers within each category will be restricted to those commonly used in ambient air sampling.

Principles of Inertial Collection

A number of factors and general principles associated with liquid and solid aerosol particles are considered helpful in selecting and using an ambient air sampling device for effective collection of particles suspended in the atmosphere. In addition to the size and nature of the particles, other important aspects to consider include the theory of inertial impaction, particle settling, the effects of thermal and electrical forces, and the theory of filtration. A discussion of these general aspects begins with the topic of inertial collection.

Introduction

Inertial collectors are designed to give a size-representative sample of particles in the atmosphere using the principle that particles in a gas stream are more dense than the fluid (air) in which they are suspended. A particle moving in an air stream with approximately the same velocity as the air stream has more momentum (*mass × velocity*) than the volume of air that it displaces because of its higher mass. The momentum, or inertia, possessed by a particle in a moving air stream will cause the particle to be deflected less than the air in the vicinity of the particle when the air stream undergoes a sudden change in direction. Such a deflection will occur when an obstacle is placed directly in the path of an aerosol stream. If the resulting deflection of the particle from the air trajectory around the obstacle is great enough, the particle will strike the obstacle. High incident velocities will increase the momentum of particles in the air stream, thereby enhancing their removal. High velocities can be attained by passing the air stream through an orifice (jet) prior to the stream striking the obstacle as shown in Figure 4-4.

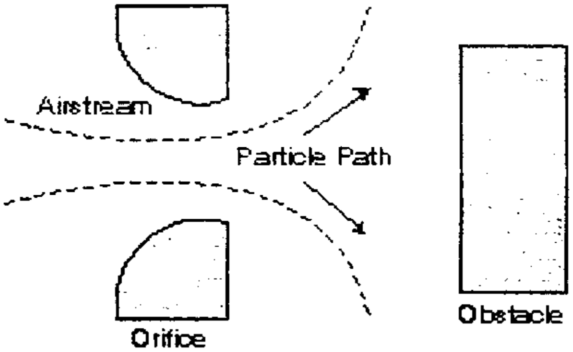


Figure 4-4. Particle collection by impaction.

Under the proper conditions, most of the particles within a certain size range that can be made to strike the obstacle will become attached to and remain on the collection surface.

A practical discussion of inertial sampling devices follows, including examples of numerous particulate matter collectors used in ambient air sampling.

Inertial Sampling Devices

The inertial collection process is subdivided into two main types, impaction and impingement. The distinction is made by the manner in which the sample material is retained in the sampling device.

Impaction Devices

Impaction devices collect and retain particles from an aerosol stream on a collecting surface. The collecting surface is removed from the instrument and the sample analysis is, in many cases, performed directly on the collecting surface. Particle adhesion is caused primarily by electrostatic attraction and by molecular surface phenomena known as Van der Waals forces. Some loss of large particles occurs with high aerosol velocities. It is believed that in the case of small particles (several micrometers or less), nearly all of those striking the collecting surface are retained on the surface. The collection surface in many impaction devices is coated with a thin film of oil or light grease to aid in particle retention. In some devices, retention is aided by passing the incoming particles through a zone of moisture-saturated air; moist particles adhere more readily to a collection surface.

Coating of the plates and water saturation of the particles affect the calibration of an impactor and must be accounted for if the impactor is to be used for determining particle size distributions.

Two Stage Impactor

Figure 4-5 shows a schematic of a two stage impactor. The air stream containing the various size particles flows through the first large jet nozzle and impinges on a collection plate oriented perpendicular to the axis of the nozzle. At the first nozzle exit, the air stream is deflected sharply by the collection plate. Larger particles continue forward and are collected on the first plate, while the smaller particles follow the air stream into the second nozzle, which has a smaller jet and a higher velocity, allowing the smaller particles to be collected on the second collection plate.

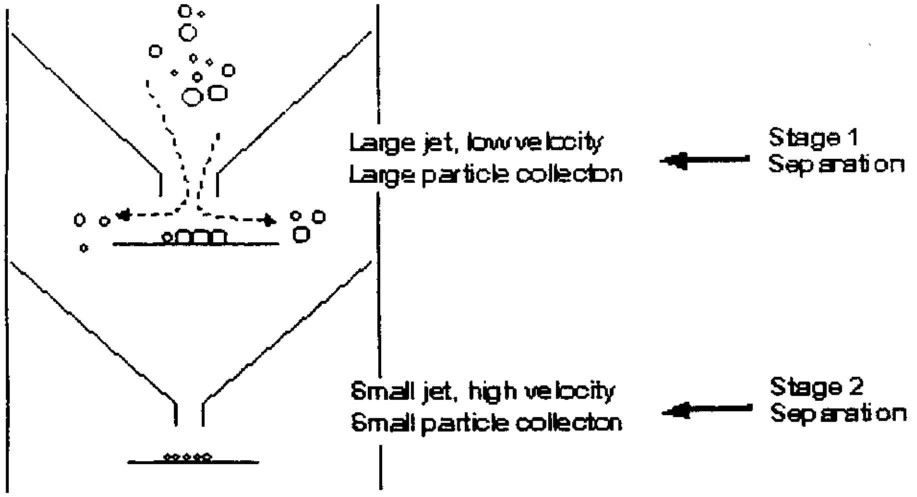


Figure 4-5. Two stage impactor.

Andersen Samplers

An example of a multi-stage impactor is the Andersen standard sampler. This sampler usually contains six to eight stages with numerous, successively smaller, evenly distributed holes (orifices) in each stage. A constant flow rate is maintained through the Andersen sampler which causes the aerosol stream velocity to increase at each stage, resulting in a deposition of particles in size fractions. Each stage of the sampler consists of a perforated disc located above a collection medium (Figure 4-6). The sample air passes through the openings in the disc and must then make an abrupt change of direction over the collection medium. The particles possessing too great a momentum to continue in the air stream are impacted on the collection surface. The collection surface can be coated with a light oil, silicone grease, filter media, aluminum foil, or wax to help increase the collection efficiency. The thickness of the coating is not important, as long as it is at least the thickness of the particle that is to be collected. However, a heavy coating is not recommended since this will likely clog the orifices. Such coatings may also interfere with subsequent chemical analysis and the size ranges of particles collected.

The greatest limitation of the Andersen sampler is the relatively low flow rate, 0.028 cubic meters per minute (1 cubic foot per minute, cfm), that must be maintained. This flow rate limits the amount of sample that can be collected. Figure 4-7 shows the collection efficiency of the Andersen sampler at this flow rate over the particle size range of 0.3 μm to 11 μm.

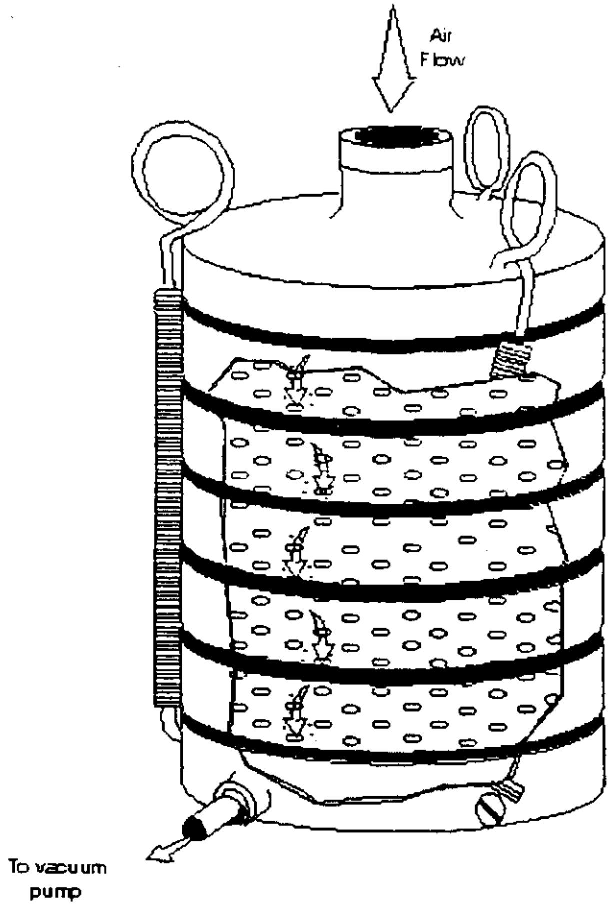


Figure 4-6. Andersen sampler.

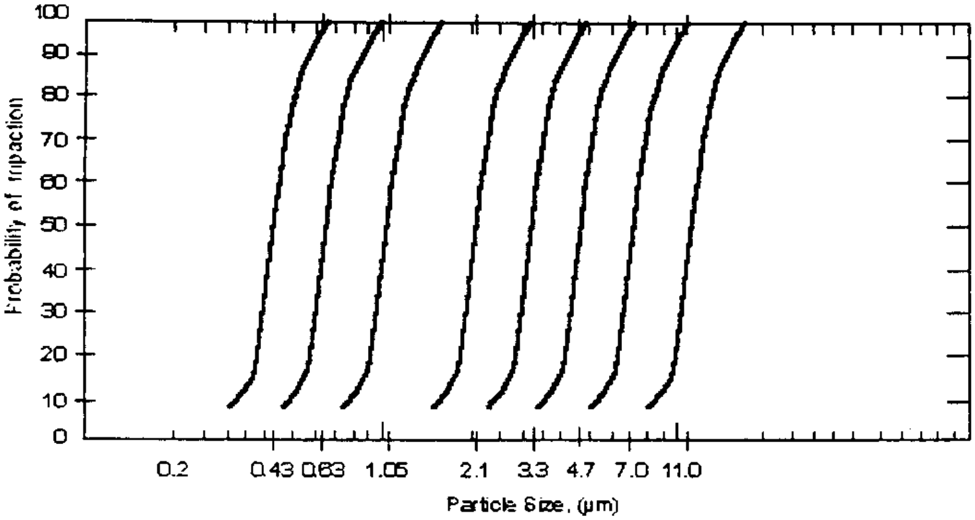


Figure 4-7. Collection efficiency of Andersen sampler.

High-Volume Andersen Cascade Impactor

A modification of the Andersen sampler has led to the high-volume (hi-vol) Andersen impactor, which can be used at flow rates as high as 0.57 m^3/min (20 cfm). This sampler consists of five stages with the typical Andersen perforated discs. Below the discs are gaskets and collection surfaces (Figures 4-8 and 4-9). The collection surfaces, usually glass fiber filters or aluminum foil, are supported by the plates themselves; i.e., the collection surface for plate 1 is supported by plate 2 and so on. To allow unrestricted aerosol flow, the collection surface has holes that line up with the orifices of the plate supporting it. The five stages are held together by a central bolt and are aligned by four evenly spaced rods. The impactor is mounted on a hi-vol sampler. An 8- by 10-inch filter mounted on the hi-vol sampler is the back-up filter for the impactor. Figure 4-10 shows the collection efficiency of the hi-vol Andersen impactor operated at 20 ft^3/min over the particle size range of 0.75 µm to 8 µm.

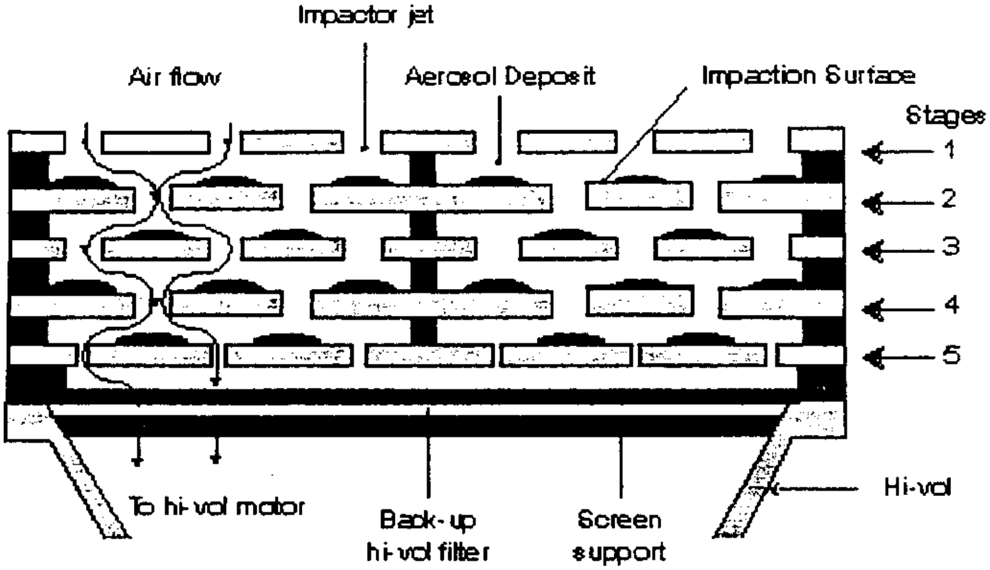


Figure 4-8. Cross-sectional view of a hi-vol Andersen impactor.

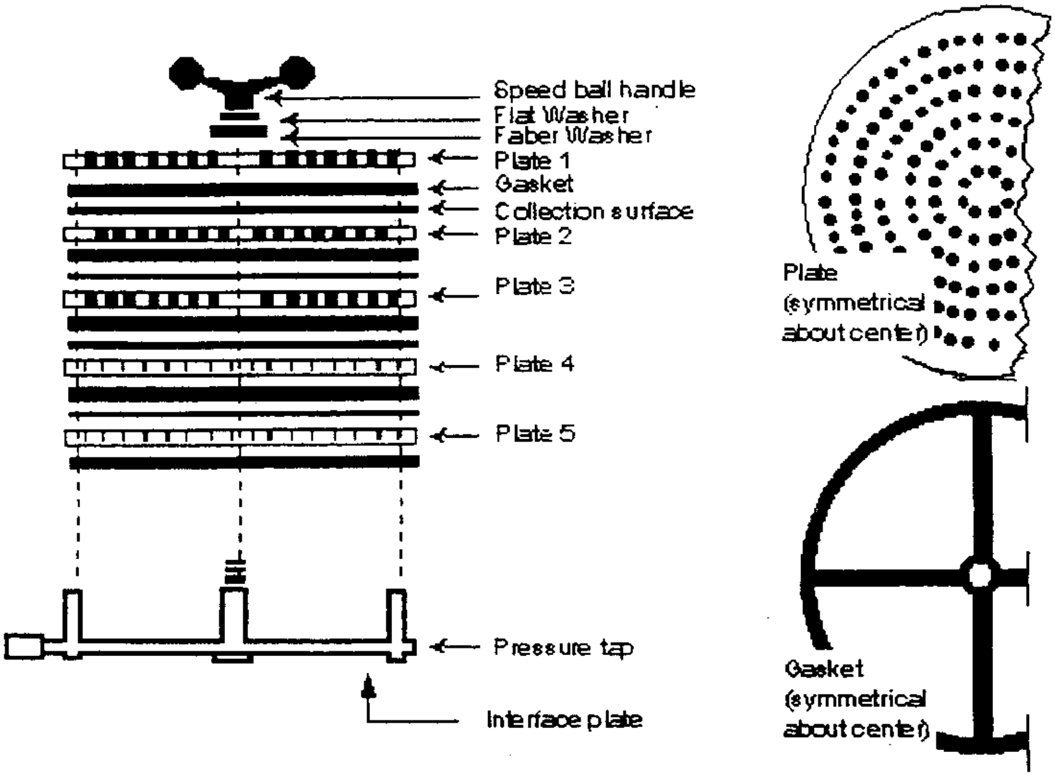


Figure 4-9. Expanded view of a hi-vol Andersen impactor.

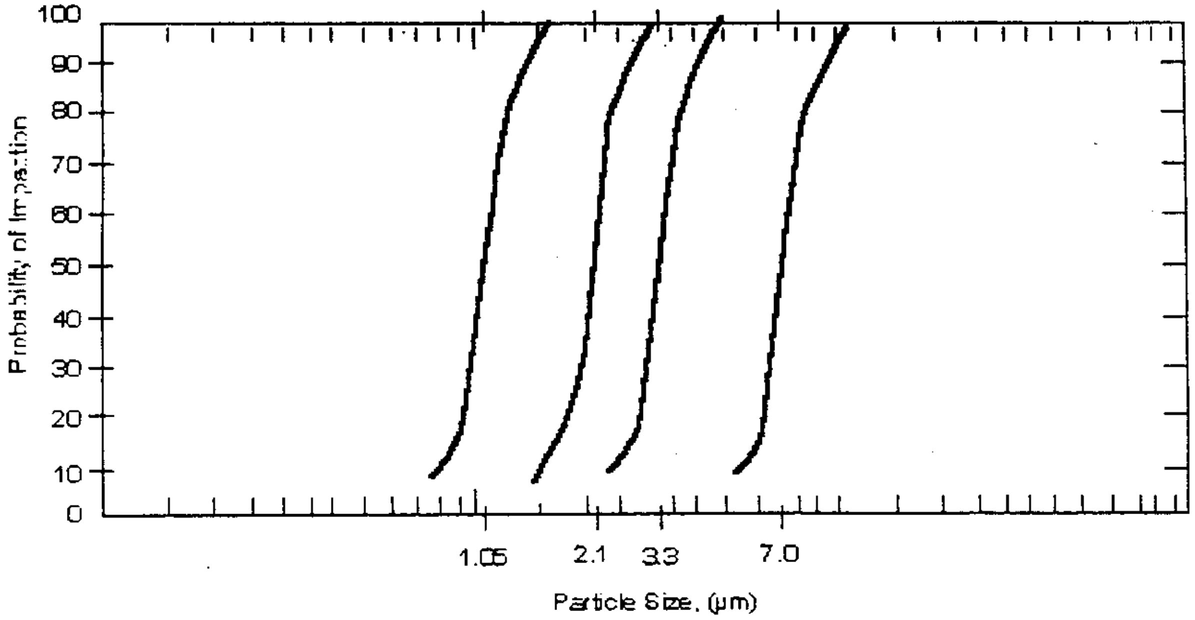


Figure 4-1Q. Collection efficiency of hi-vol Andersen impactor (20 ft^3/min).

Multiple-slit High-volume Cascade Impactor

Another high-volume cascade impactor utilizes a typical high-volume sampler with an adapter comprised of six stages with successively smaller slit openings. Behind each slit is a filter for retaining particles. The sixth stage of this impaction device uses a typical hi-vol filter for collection of small particles.

The air sample is drawn through the slits and collection filters (Figure 4-11). The slits become increasingly narrower, thus causing the velocity to increase at each stage so particles of decreasing size are impacted on each successive filter. The distance from the slits to the collection filter becomes smaller with each stage to increase the collection efficiency. This impactor incorporates the advantage of hi-vol sampling (high flow rate [1.13 m^3/min. 40 cfm] and, therefore, large sample size) and the advantage of impactor sampling (particle sizing).

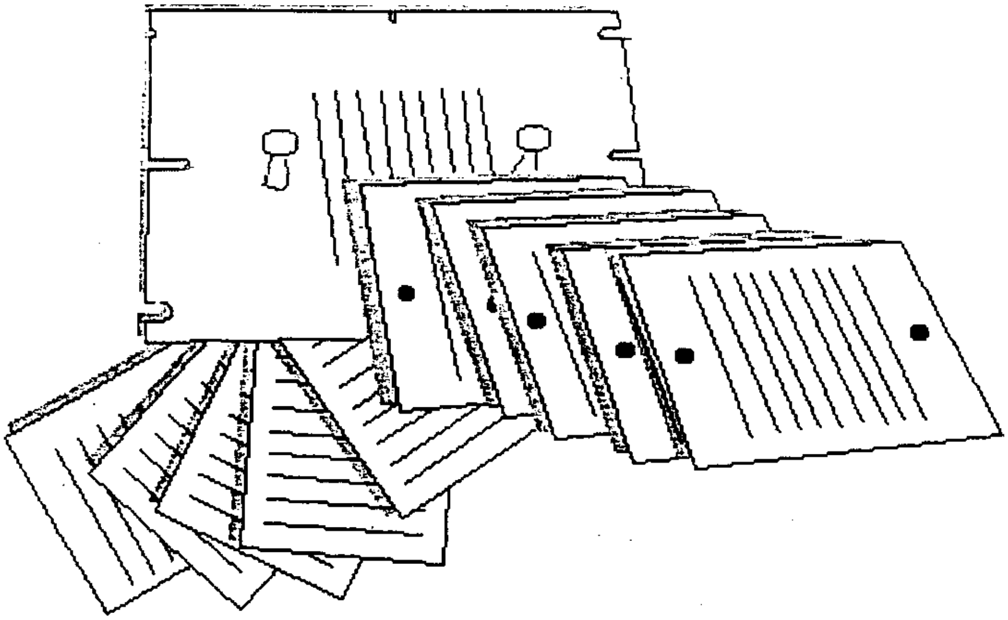


Figure 4-11. Multiple-slit high-volume cascade impactor.

Cascade impactors that provide somewhat real-time particulate matter concentrations have been developed by using oscillating quartz crystals as impaction surfaces. Particles impacting on the crystals cause their oscillation frequencies to change. The amount of change in frequency of a crystal is proportional to the mass of the particles collected on the crystal. Therefore, this relationship can be used to measure particle concentration. However, the proportional relationship is only valid over a certain frequency range and depends on the physical characteristics (e.g., dry versus sticky) of the particles collected. One such impactor is depicted in Figure 4-12. It provides concentration measurements for particles in ten size ranges (from 0.5 to 35 µm) by using ten impactor stages, each having an oscillating quartz crystal that is connected to the sampler's electronic display.

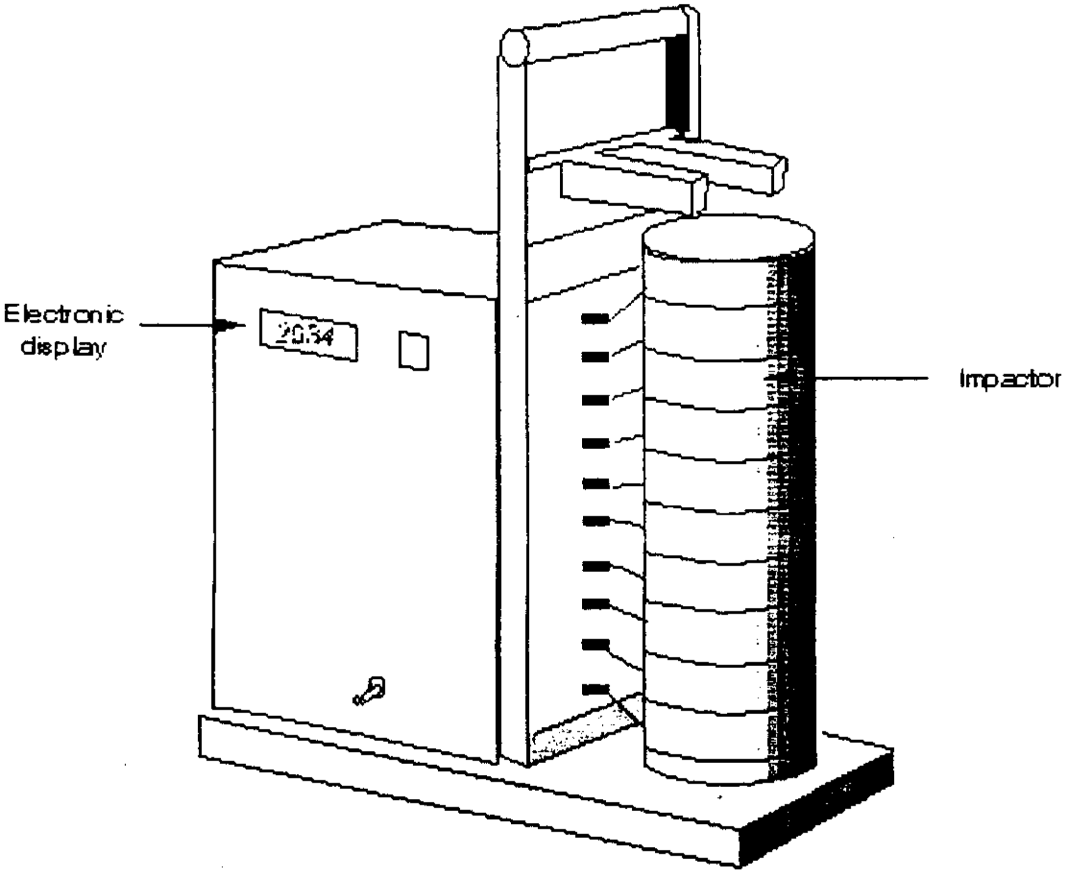


Figure 4-12. Quartz crystal cascade impactor.

$PM_{2.5}$ Inertial Particle Size Separator

EPA's Federal Reference or Class I equivalent method (FRM or FEM) sampler for $PM_{2.5}$ provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 2.5 µm in ambient air over a 24-hour sampling period. The sampler pulls ambient air at a constant volumetric flow rate into a specially shaped inlet and through an inertial particle size separator (WINS impactor, or Well Impactor Ninety-Six) where the suspended particulate matter in the $PM_{2.5}$ size range is separated for collection on a polytetraflouroethylene (PTFE) filter. Figure 4-13 shows the inlet of the sampler, which only allows for the collection of particles less than 10 µm. Figure 4-14 illustrates the WINS particle impactor and filter holder assembly. The well of the assembly contains a 37 mm diameter glass fiber filter that is immersed in 1 mL of low volatility, low viscosity diffusion oil. The oiled glass fiber filter helps remove particles between 10 and 2.5 µm in diameter by preventing the bouncing of the incoming particles off the loaded impactor.

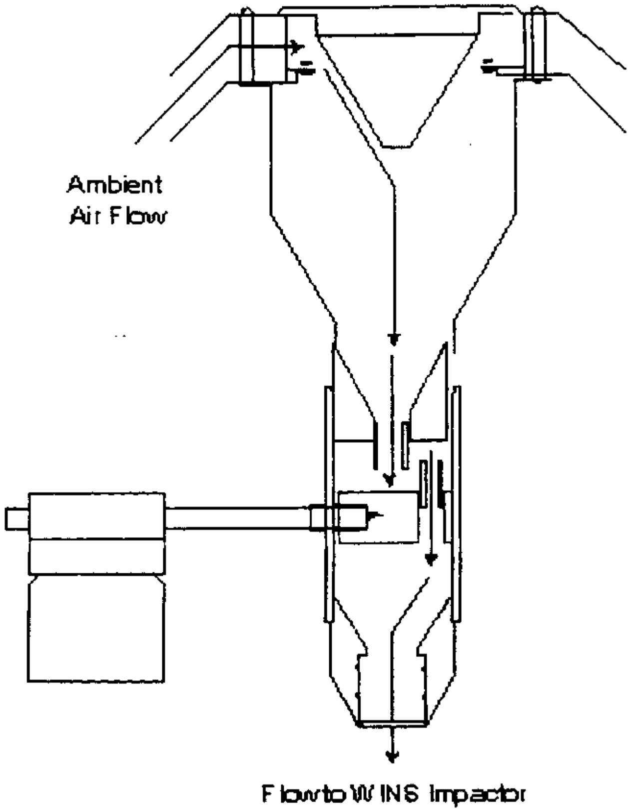


Figure 4-13. Inlet of $PM_{2.5}$ inertial particle size separator.

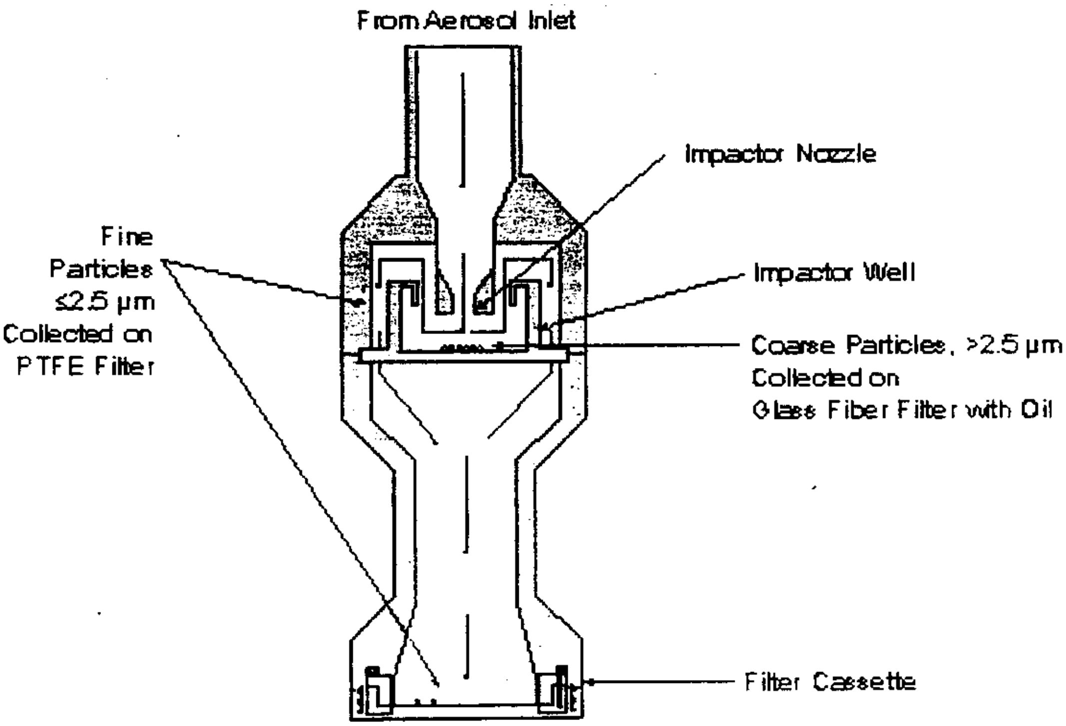


Figure 4-14. WINS particle impactor and filter holder assembly.

Impingement Devices

Impingement devices differ from impactors because the jet and striking surface are immersed in a collecting fluid such as water. The particles that are removed from the aerosol stream are wetted by and retained in the fluid. Most impingers in use are variations of the instrument developed by Greenburg and Smith (Balzer 1972). The Greenburg-Smith type of impinger consists of a glass cylinder with a small concentric glass tube insert. A glass jet and impingement plate are attached to one end of the tube, which is immersed in the collecting fluid. These impingers collect a sample at flow rates of about 0.1 to 1 ft^3/min.

Impingers are most commonly used in collecting dusts, mists, and fumes in the evaluation of occupational health hazards. In addition to collecting soluble gases and particulate matter, the Greenburg-Smith impinger efficiently collects insoluble particles that are greater than 2 µm in diameter.

Centrifugal Separation Devices

Centrifugal separation is a variation of the inertial collection process in which particles are removed from an air stream by the centrifugal force created by moving an aerosol rapidly through a circular path.

There are several types of sampling devices employing the principle of centrifugal separation.

Cyclone Samplers

Cyclone samplers are small versions of the large cyclones used in air cleaning. The cyclone shown in Figure 4-15 contains no moving parts and is designed so that air drawn through it moves in either a circular or a helical path of decreasing radius, thereby increasing its collection efficiency for small particles. As the gas stream surges through the cyclone, particles are separated at the inside surface of the cyclone's wall by the centrifugal force created. In most cyclone samplers, the particles adhere to the wall or drop into a collection space below the cyclone 's chamber.

Most cyclones are not efficient collectors of particles having diameters less than 2 or 3 µm, depending on particle density. However, small cyclones can be designed to collect particles below 1 µm in diameter. The collection efficiency of a cyclone sampler is strongly dependent on flow rate.

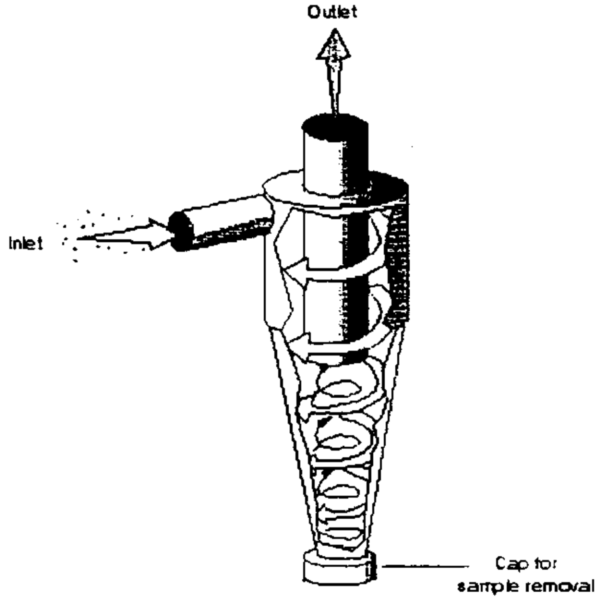


Figure 4-15. Cyclone sampler.

Virtual Impactors- Dichotomous Sampler

In the virtual impaction method, instead of the larger particles impacting onto a solid collection surface, they impact into a slowly pumped void and are later collected on a filter downstream. Thus, these larger particles impact through a non-existent, or virtual, surface. As depicted in Figure 4-16, the smaller (fine) particles follow the streamlines of the faster flow (F_f); the larger (coarse) particles are impacted into the slower flow (F_c). A small fraction of the fine particles is impacted and collected with the coarse particles. This can be mathematically corrected when determining fine and coarse particulate concentrations.

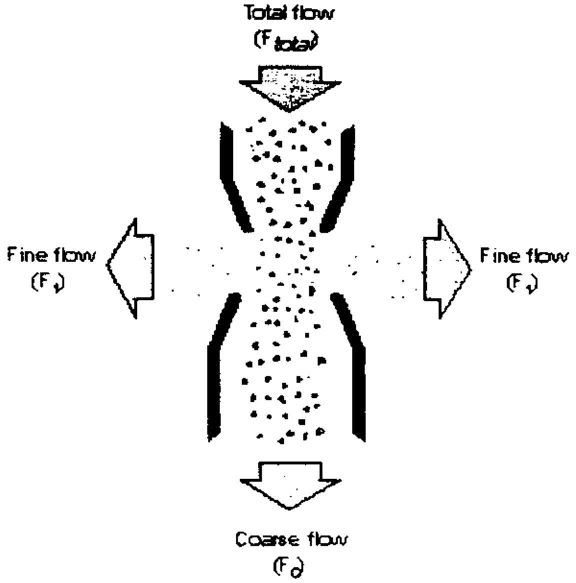


Figure 4-16. Schematic of virtual impactor.

The most recent use for virtual impaction has been in the EPA's efforts to develop a sampler that will separate and collect particulate matter both above and below a 2.5 µm aerodynamic diameter. These efforts have led to the development of the dichotomous sampler. As its name implies, the dichotomous sampler separates particles into two size ranges: fine particles (less than 2.5 µm aerodynamic diameter) and coarse particles (>2.5 to 10 µm aerodynamic diameter) as shown in Figures 4-17 and 4-18.

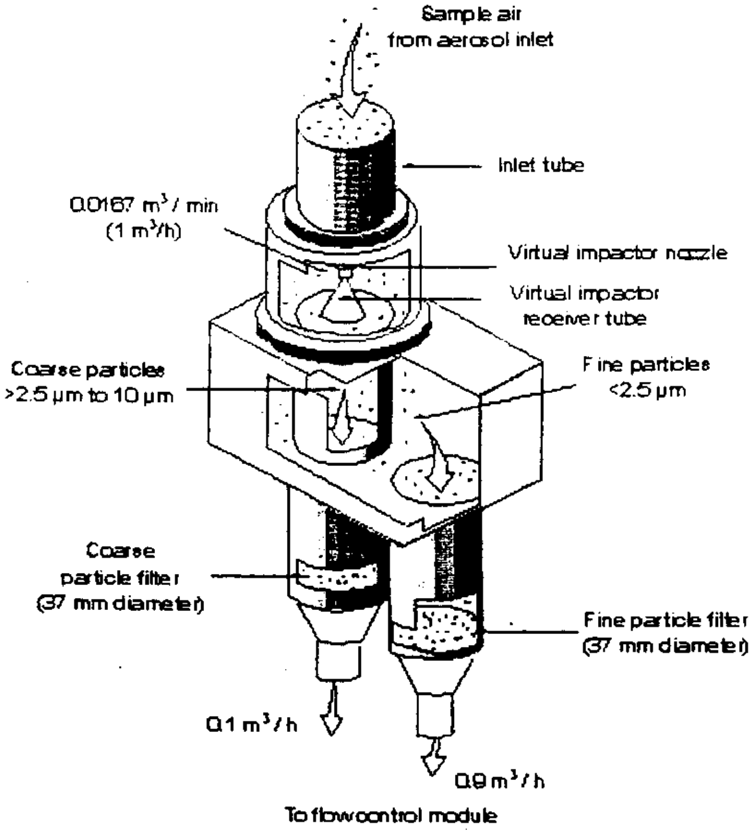


Figure 4-17. Diagram of the sampling module of a dichotomous sampler.

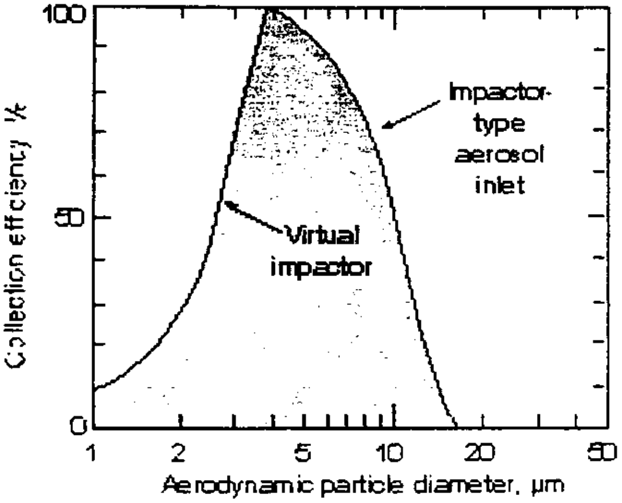


Figure 4-18. Collection efficiencies for a dichotomous sampler.

Virtual impactors have several advantages over conventional impactors:

- Problems associated with conditional impaction, such as particle bounce and reentrainment, nonuniform particle deposition, and cumbersome sample handling, are essentially eliminated.
- Uniform particle deposition onto the filters is ideally suited for photo-excited x-ray fluorescence (a nondestructive chemical analysis technique) and beta-gauge mass measurement.
- No grease or oil is needed to improve collection efficiency.
- Filters can be chosen to eliminate or minimize interferences.

Teflon® membrane filters are normally used to collect both coarse and fine particles because of the following advantages:

- Their collection efficiency for particles above 0.01 μm is greater than 99%.
- They have an extremely stable mass for high gravimetric accuracy.
- They have a negligible tendency to absorb or react with gases (therefore, low artifact formation of nitrate and sulfate).
- They contain minimal impurities to interfere with analyses for chemical and elemental species.
- They have low mass per unit area (desirable for gravimetric, x-ray fluorescence, and beta-gauge measurements).

However, these Teflon® membrane filters will not support themselves; therefore, they are bonded to a thin annular polyester ring.

Two aerosol inlets are available for providing 10 μm cut points (50% collection efficiencies) for dichotomous samplers. One type functions as a single-stage impactor (Figure 4-19). After entering the inlet and passing through a bug screen, particles in the sample air are accelerated as they pass through a nozzle to an impactor target module. Because of their momentum, particles having diameters greater than the inlet's 10 μm cut point impact onto the surface (target) of the impactor module. Smaller particles rise through the impactor module and pass to the virtual impactor of the dichotomous sampler. The other aerosol inlet uses a cyclone to remove particles having diameters greater than its 10 μm cut point from the sample air before the air enters the virtual impactor. Because of their symmetrical designs, both inlets are wind-direction insensitive. Also, wind speeds from 2 to 24 km/hr have a negligible effect on the cut point of both inlets.

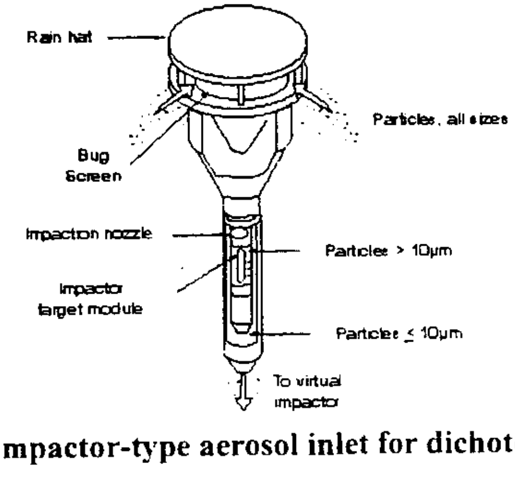


Figure 4-19. Impactor-type aerosol inlet for dichotomous sampler.

Figures 4-20 and 4-21 depict a current manual dichotomous sampler. Samplers that automatically change fine and coarse particle filters at preset time intervals are also commercially available.

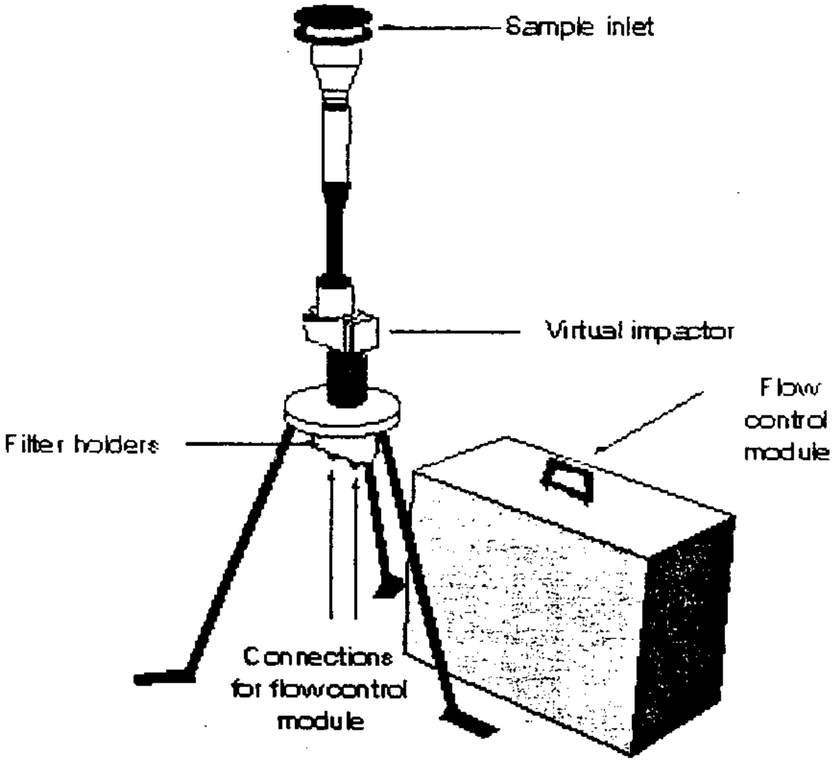


Figure 4-20. Dichotomous sampler.

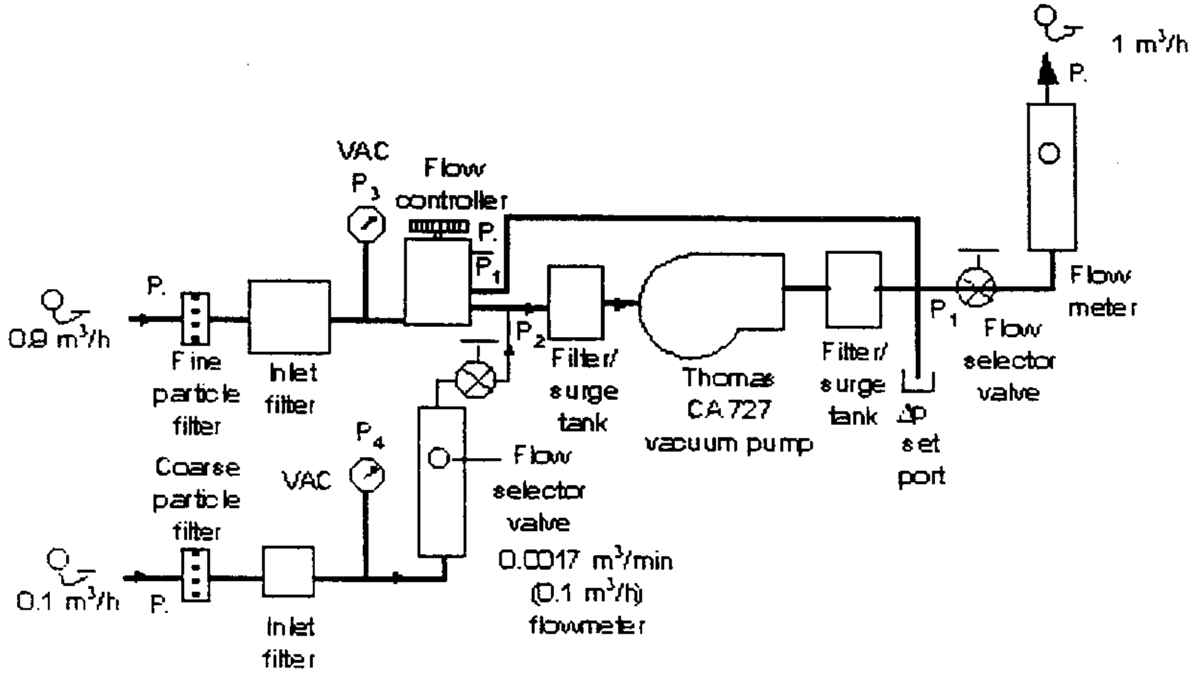


Figure 4-21. Flow schematic of control module.

Collection Efficiency of Inertial Sampling Devices

Though the principle is the same for all types of inertial sampling devices, the parameters are somewhat different for the basic single-stage or cascade impactor than for the air centrifuge or cyclone. The discussion in this section is confined to the jet type of impactor, and this discussion may not be applicable without modification to other types. In this section, discussions of particle size refer to the equivalent aerodynamic particle size, or diameter (Stoke's diameter), unless otherwise stated. The equivalent diameter is the diameter that a unit density particle of spherical shape would have if it behaved the same as the particle being studied.

Definition of Collection Efficiency

Particle collection efficiency for inertial sampling devices has been defined in several ways by various people. The collection efficiency of an impaction device is a function of several parameters, making the theoretical and empirical expressions that have been derived somewhat difficult to use for specific applications.

The collection efficiency of an impaction device can be defined as the ratio of the number of particles striking an obstacle to the number that would strike if the stream lines were not deflected.

For the purposes of this discussion, *the collection efficiency will simply be defined as the fraction of the particles in an incident aerosol stream that is retained on the collection surface of the sampling device.* The efficiency of impaction can be plotted as a function I, the inertial impaction parameter, to give an efficiency curve for an impaction device. Studies on the calibration of cascade impactors are available.

Impactor Performance Characteristics

Instead of plotting efficiency of impaction against I, it can be plotted against particle size for a given device, since I is a function of particle size and several other parameters. The efficiency of impaction when plotted against particle size follows a sigmoid (or S-shaped) curve, such that there is a minimum size below which no particles are collected and a maximum size above which all particles are collected. For a well-designed impactor, the range between these two sizes is sufficiently narrow that a functional size separation is made. The most effective way to describe the ability of an impactor stage to separate particle sizes is to show the efficiency of collection as a function of size.

Properties of Aerosols Affecting Inertial Collection Efficiency

For a given collection device, several properties of the *aerosol* affect the efficiency of collection.

Particle Size

For any device there is a minimum particle size below which no particles are collected and a maximum particle size above which all particles are collected or removed from the sampling stream. Above 50 µm, some particle loss occurs by impaction on the walls of the sampling device. Particles and droplets greater than about 200 µm are seldom found on the sample collection area because they are shattered or lost on the walls of the device. Particles below about 0.5 µm in diameter are difficult to collect with impaction devices because their momentum is not appreciably different from that of the air, so they are not readily deflected. Most impacting devices have a high collection efficiency for particles with diameters greater than 0.5 µm. Collection efficiencies of nearly 100% are claimed for several impaction devices for particles in the size range from 0.5 to 10 µm.

Particle Density

Impaction devices are efficient collectors of high density particles; they have been used to selectively sample work atmosphere of plutonium dusts. Sub-micrometer particles of high density can be efficiently collected, since they are equivalent to unit density particles of much greater size.

Aerosol fluid Properties

The physical properties of the gas in which the particles are dispersed will affect the collection efficiency of an inertial collector. For example, any factor which affects the gas's viscosity, such as temperature, will in turn affect the collection efficiency.

Properties of the Collecting Device Influencing Collection Efficiency

Impactors and impingers are designed for sampling a variety of aerosols. The efficiency of collection for a certain aerosol can be optimized by design considerations.

Jet Size

The impaction jet size will influence the collection efficiency by affecting the velocity with which the incident air stream strikes the collection surface. As jet size decreases, the impaction velocity increases, as shown by the relationship

(Eq. 4-1) $$v = Q/A.$$

Where:
v = *air velocity*
Q = *volumetric flow rate*
A = *cross-sectional area of the air stream*

In a multistage impaction device, jet velocities range from several meters per second in the first stage to greater than 50 meters per second in the last stage. The corresponding jet cross-sectional areas range from about 70 mm^2 in the first stage to less than 5 mm^2 in the last stage in a typical multistage impaction device.

Many multistage impaction devices are operated at a flow rate of approximately 18 L/min. This approximates the human respiration rate. The flow rate affects the collection efficiency of a device as well as the characteristics of the sampler.

Jet Shape

Studies of impaction efficiency showed only small differences in collection efficiency between round and rectangular jets.

Jet to Collection Surface Distance

The distance between the jet opening and the collection surface controls the degree of deflection of the aerosol stream. By decreasing the distance between the jet and the collection surface, the angle of deflection of the aerosol stream is increased. A large deflection angle is required to remove the smaller particles from an aerosol stream. In the common cascade impactor with a single jet at each stage, the distance from the jet to the collection surface is decreased at each successive stage.

Collection Surface

Detailed studies of collection efficiency as a function of the shape of the collecting surface have been performed for spherical, cylindrical, and flat surfaces with round and rectangular shapes. For most applications, flat collection surfaces are used because particle retention is greatest on these surfaces and microscope slides are often required in collections for particle size analysis.

Limitations and Sources of Error in Inertial Collection

Inherent Errors in Sample Collection

In many cases it is impossible to characterize a system without altering the system by the act of measurement itself. In other words, do the particles collected by an impactor sample fairly represent the particulate matter as it is suspended in ambient air? There are several inherent sources of error in the impaction process.

Particle Shattering

Large particles (greater than 200 μm) and agglomerates are readily shattered upon impaction, and, at the high velocities attained in some impaction devices, particles with diameters as small as two or three micrometers can be shattered. In studies where the number of particles per unit volume of air is of interest, shattering of particles upon collection results in erroneously high results. In size distribution studies, there will appear to be fewer large particles and more small particles than actually exist in the aerosol. Figure 4-22 is a picture taken by an electron microscope of a shattered fly ash particle.

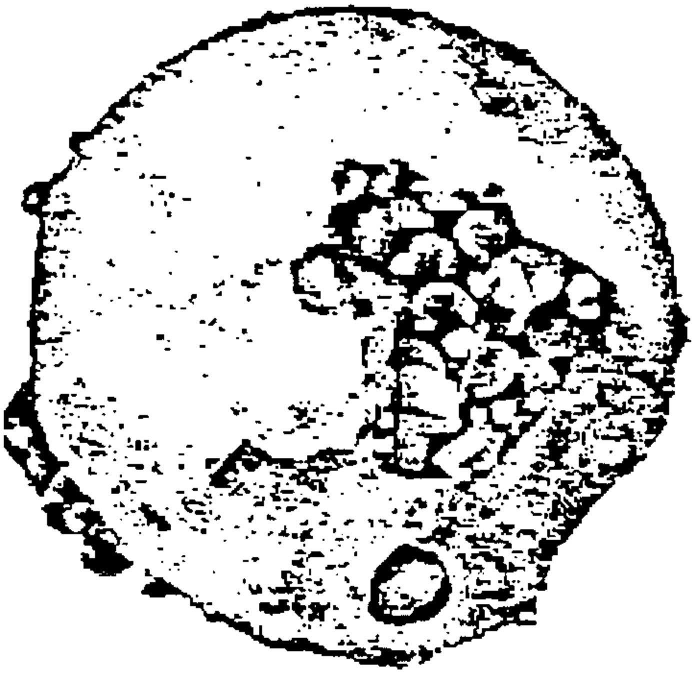


Figure 4-22. Particle shattering.

Particle Bounce, Reentrainment of Particles, and Wall Loss

At high impaction velocities, a small fraction of the particles collected may be reentrained in the air stream. This occurs most often with fragments of large particles that have shattered upon striking the collection surface. Some of the pieces of the shattered particles may be lost from the sample by impacting on the walls of the instrument. A few of the large particles may impact directly on the walls of the instrument.

Limited Sample Quantity

The small quantity of sample collected also restricts the choice of analytical methods to those with high sensitivity. Care must be taken to preserve all sample material intact, since with only a few micrograms of sample, the loss of any particulate matter becomes significant.

Some types of inertial samplers, such as cyclones, are not so limited in this respect. Some of these can collect gram quantities of particulate matter.

Sample Loss in Collection

If too much particulate matter collects on the sample collection surface, subsequent particles that impact may be lost by reentrainment when they strike particles already collected instead of the collection surface.

A phenomenon called "ghost depositing" can occur when particles bounce off the collection area and are redeposited by eddy currents a few millimeters on either side of the sample.

When aerosols containing mists or droplets are being sampled, care must be taken to avoid collection of too much material. If too many droplets are collected, they will merge on the collection surface. The individual drops will be lost for size analysis and some material may be lost by run-off.

Poor Particle Resolution for Size Analysis

Particles that collect close to and on top of each other will introduce error in concentration and size studies through the inability to distinguish between individual particles and clumps of particles when examined optically. However, if a representative portion of the collected material is properly remounted, these problems can be minimized.

Errors Associated with the Calibration of Collection Devices

When impactors are used to collect aerosol samples for particle size or mass distribution studies, the instrument must be calibrated. The particle collection efficiency as a function of the desired parameter (e.g., size or mass) must be determined. One method of calibration is to determine empirically the collection efficiency in the laboratory. In this procedure, a known quantity of a monodisperse aerosol (a gas stream with only one size particle suspended in it) is passed through the impactor. The amount of material collected on each stage is weighed. By varying the size of the monodisperse aerosol, the cut points for each stage can be determined. Detailed studies of theoretical collection efficiencies for several types of impaction devices have been performed. The efficiency curves that have been derived for several types of impactors show varying agreement with experimental curves. These curves are usually given in terms of an inertial collection parameter or equivalent particle size such as the one in Figure 4-7. If a particular curve is to be used in a sampling application, the user should be satisfied that the curve is valid for that particular application. Most commercially available inertial samplers are provided with a curve of collection efficiency. In most cases, the methods used to obtain these curves will not be known to the user. Without specific knowledge of the manner in which the curves were obtained, care should be exercised in the application.

Errors in Sample Analysis

Investigations of aerosols in which the sample is collected with an inertial collection device may utilize any of several kinds of sample analysis. The analyses that are performed on samples collected by impactors may also be used in conjunction with other sampling methods and are discussed elsewhere. Mention of the error associated with the analytical procedure to be used is made because it would be considered in the overall error assessment of the sampling procedure. The information desired in an investigation may require the use of an inertial collection device, which in turn may limit the choice of analytical procedure. The reverse could also occur; i.e., the information desired, such as particle distribution, may dictate the use of an impaction device to collect the sample. One should be aware of the limitations and error associated with each analytical procedure that is considered.

Size Selective Inlets for Aerosol Sampling

As discussed earlier in this Chapter, numerous inlets are available for particulate matter sampling. The particular choice is generally made based upon a number of concerns such as monitoring objective, particle size, and expected particulate matter concentrations. An excellent summary of available inlets is addressed in the draft EPA Guideline on Speciated Particulate Monitoring (Chow 1997). Table 4-1 taken from this guideline shows the variety of size selective inlets available, the inlet manufacturer, operating principle, the cutpoint, and flow rate, with selected comments.

Table 4-1. Size-selective inlets for aerosol sampling.

Inlet Identifier (Manufacturer)	References	Operating Principle	d50 (μm); Slope (no unit)	Flow Rate (L/min)	PM_{10} Reference of Equivalence Reference No.a	Comments
High-Volume						
Sa[a] or GMC[c] Model 320 (Graseby Andersen, Atlanta, GA)	McFarland et al. (1980)	Impactor	15; 1.5	1,133	None	Single-stage, not greased shim.
SA or GMW Model 321A	McFarland and Oritz (1984; Hayes et al. (1988)	Impactor	10.2; 1.45	1,133	RFPS-1287-065	Two-stage with greased shim.
SA or GMW Model 321B	Hayes et al. (1988); McFarland and Ortiz (1987)	Impactor	9.7; 1.40	1,133	RFPS-1287-064	Two-stage with greased shim.
SA or GMW Model 1200	Purdue (1988); Wedding et al. (1988); Mathai et al. (1988); Hoffman et al. (1988); Hayes et al. (1988)	Impactor	9.7; 1.40	1,133	RFPS-1287-063	Single-stage with greased shim (body hinged).
GMW Wedding PM_{10} (General Metal Works, Village of Cleves, OH)	Woods et al. (1986)	Cyclonic Flow	8.8;	1,133	None	No inlet cleaning port.
Wedding $IP_{10}PM_{10}$ (Wedding & Associates, Fort Collins, CO)	Wedding and Weignand (1985); Woods et al. (1986)	Cyclonic Flow	9.6; 1.37	1,133	RFPS-1087-062	Inlet cleaning port on top of inlet.

Medium-Volume SA 254 Medium-Volume PM_{10} Inlet	Olin and Bohn (1983)	Impactor	10; 1.6^{d}	113	RFPS-0389-071	Several small screws must be removed to clean.
Wedding Medium Flow PM_{10} Inlet	Wedding et al. (1983)	Cyclonic Flow	9.5; 1.12	113	None	Has a cleaning port. Can use a bottle brush to clean.
Bendix 240 Cyclone (Sensidyne, Inc., Clearwater, FL)	Chan and Lippman (1977); Mueller et al. (1983)	Cyclonic Flow	2.5; 1.7	113	None	Plastic cup acts as a hopper to collect large particles
Low-Volume SA 246B	McFarland and Ortiz (1984); Van Osdell and Chen (1990)	Virtual Impactor	10.2; 1.41	16.7	RFPS-0789-073 EQPM-0990-076	Top unscrews to allow access to impaction surface.
Sierra-Anderson 224 and 245	McFarland et al. (1978); Olin (1978)	Virtual Impactor	2.5;	16.7	None	Virtual impactor can be re-assembled backwards when taken apart for cleaning.
AirMetrics Inc. (Springfield, OR)	Chow and Watson (1996)	Direct Impactor	10; 2.5;	5; 5	None	Nylon impactor needs to be cleaned and regreased after every 72 hours of sampling.
WINS (Well Impactor- Ninety Six)	U.S. EPA (1997b)	Direct Impactor	2.5; 1.18^{d}	16.7	None	Inlet used in $PM_{2.5}$ FRM.

USEPA/HEAD Impactor	Koutrakis et al. (1990)	Direct Impactor	2.1; 1.08[d]	10	None	Oiled glass impactor needs to be replaced after every 24 hours of sampling.
Wedding TP_{10}	Wedding et al. (1982)	Cyclonic Flow	9.9; 1.32[d]	16.7	EQPM-0391-081	Plastic cap acts as a hopper to collect large particles.
Bendix Unico 18	Chan and Lippmann (1977)	Cyclonic Flow	2.5; 1.83[d]	18	None	
AIHL Cyclone (Air & Industrial Hygiene Laboratory, Berkeley, CA)	John and Reishel (1980)	Cyclonic Flow	2.2; 1.87[e] 2.5; 1.38[e] 3.5; 1.40[e]	26.6 21.7 15.4	None	Screw-on cap acts as a hopper to collect large particles.
Stacked Filter Unit (Corning CoStar [formerly Nuclepore Corp.], Cambridge, MA)	Flocchini et al. (1981); John et al. (1983); Cahill et al. (1990)	Selective Filtration	2 to 3;	10	None	Uses large pore (8μm) etched in polycarbonate filters.
BGI-4 (BGI Inc., Waltham, MA)	Blackman and Lippmann (1974); Hering (1995)	Cyclonic Flow	4;	2.3	None	Generally used in personal sampling applications.
MSA (Mine Safety Appliances Co., Pittsburgh, PA)	Blackman and Lippmann (1974); Hering (1995)	Cyclonic Flow	3.5;	2	None	Generally used in personal sampling applications.

Sensidyne Model BDX 99R (Sensidyne Inc., Clearwater, FL)	Blackman and Lippman (1974); Hering (1995)	Cyclonic Flow	3.5;	1.7	None	Also known as Dorr-Oliver design. Generally used in personal sampling applications
SKC Cat. No. 225-01-02 (SKC Inc., Eighty Four, PA)	Blackman and Lippman (1974); Hering (1995)	Cyclonic Flow	5;	1.9	None	Generally used in personal sampling applications
MST Low Flow Rate Sharp Cut Impactor (Harvard Impactor) (Air Diagnostic and Engineering, Harrison, ME)	Marple et al. (1987)	Direct Impactor	2.5; 1.02[d] 10; 1.11[d]	4, 10, 20 4,10	None None	Oiled aluminum impactor plate needs to be replaced after every 24 hours of sampling. Designed for use in indoor air pollution health studies.

[a] See Table 4-5 for Federal Register citation and notice date.
[b] Sierra-Andersen, Atlanta, GA.
[c] General Metal Works, Atlanta, GA.

[d] Slope = $\sqrt{d_{16}/d_{84}}$, as defined in text.

[e] Slope is estimated based on $\sqrt{d_{10}/d_{90}}$.

[f] Inlet for Modules A, B, and C of IMPROVE samplers.

Filtration Sampling

Introduction

Filtration sampling, or a combination of filtration/impaction sampling, is the most widely used approach for the collection of atmospheric particulates. The filters are relatively low in cost, easily stored, and may be used for subsequent analysis. Filters capture particles from an air stream by a number of different mechanisms. These mechanisms include direct interception, inertial deposition, diffusional deposition, electrical attraction, and gravitational attraction. The predominant mechanism depends on the flow rate, the composition and nature of the particles, and the type of filter media.

Topics to be discussed in this section include the basic advantages and disadvantages of air sampling with filters, filtration theory, and some of the criteria necessary for the selection of a filter medium to be used in a specific sampling program. Although the term "filter media" can be extended to cover a large number of media, such as glass fiber, quartz, Teflon®, filter thimbles, and granular beds, this discussion will be confined to the more common media used for particulate matter sampling.

General Considerations

Advantages

Filter sampling for particulate matter has several advantages over other methods. A primary one is the feasibility of handling large volume rates of flow. Some dust sampling instruments, such as midget impingers and thermal precipitators, do not have this capability for large flow rates. Also, after collection, the filtered sample is usually readily available for direct observation.

The number of sizes of filters available has proved to be another advantage. By changing the size of the filter paper, the volume of air samples can be varied while maintaining the same linear flow rate through the filter. The selection of sizes also allows filter borders to be designed for use in a variety of situations. This is a definite advantage when the sampling space confines limit accessibility. The variability among filters extends beyond the matter of size alone. Appropriate filters can be obtained that are capable of sampling a wide range of environmental conditions of temperature, humidity, and dust loadings. Further, filters can be found that are adaptable to analysis schemes ranging from microscopic examination to elaborate chemical separation schemes.

Disadvantages

The use of filter media for sampling is not without its difficulties. One disadvantage is related to the variation in physical and chemical properties among a quantity of examples of any given filter. In the case of an impaction instrument, once its operating characteristics have been determined, these should remain relatively fixed. On the other hand, in sampling with filters, the media is changed between each sample collection. Although filters that minimize the variability between individual filters of a specific type can be obtained, it is more common to find some differences in performance, particularly between different lots of filters.

Another case in which filters are at a disadvantage is in conjunction with selective particle sizing. A cascade impactor can be designed so that particles of different size ranges can be collected on different stages of the impactor. Such a size separation cannot be done with filter media, although some gradations are possible.

The Theory of Filtration

The most common misconception about air filtration is that it is primarily a sieving mechanism. If this were the case, only particles larger than the pore size would be trapped and the theory of collection would be relatively simple. Actually, except for the kitchen strainer, very few media could be classified as pure mechanical strainers. In air filtration, a number of mechanisms contribute to the collection of particulate matter. The degree to which each one contributes is a function of a number of parameters, discussed below. For a more complete discussion of filtration theory, see R. D. Cadle's book, *The Measurement of Airborne Particulates* (Wiley-Interscience, 1975).

Diffusion

Diffusion is defined as the irregular movement of particles suspended in a fluid, where the fluid is ambient air. The collection of particles on a filter by diffusion depends on a particle concentration gradient between the filter and the air passing between the fibers. The highly concentrated particles in the air stream diffuse to the filter fiber where the concentration is near zero. The diffusion theory further postulates that when the particle comes in contact with the filter, it remains there. The contribution made by diffusion depends on the transit time of particles through the filter, with a longer time resulting in greater diffusion contribution. The amount of diffusion will then depend on linear rate of flow, filter thickness, size of particle, interfiber distance, and particle concentration in the air.

Direct Interception

Direct interception can be considered as that part of the filter collection mechanism that is analogous to mechanical straining. The interception mechanism takes place when a particle following its air movement streamline comes within a distance from the filter material which is equal to, or less than, the particle radius, so that it comes in contact with the filter medium. As with simple straining, this type of collection predominates where the particles are greater in diameter than the interfiber distance, or pore size. The effectiveness of direct interception increases with increasing particle size.

Inertial Collection

As a particle is carried by an air stream, it possesses a certain amount of inertia, depending on its mass and velocity. When a sufficient inertial force has been established, the particle will, as the air stream turns, leave its streamline and continue on its previous path. If the inertia of a particle causes it to strike a filter fiber during the passage of the air stream around the fiber, the particle will be collected. The mechanism of inertial collection plays a major part where high linear velocities of airflow are present.

Increasing the particle size and decreasing the fiber diameter (or pore diameter) improves the effect of inertial collection.

Electrical Force

If the aerosol particle has an electrical charge, and the filter fiber has a charge of opposite sign, the particle will be attracted to the filter media. Many investigators feel that such a mechanism has a part to play in the filter sampling of air. Experiments have indicated that both atmospheric particles and filter media possess electrical charges, and that collection does occur by this means. The magnitude of the effect is not well known, but it probably does contribute to the process of collecting particles smaller than the pore size.

Combined Factors

During actual filtration, all four of the above-mentioned collection mechanisms are working together so that it is often difficult to separate one from another. Furthermore, other mechanisms occur that complicate the situation. All four of the methods of collection that have been discussed postulate that once a particle touches the filter material, it stays there. This is not entirely so — there is some reentrainment of particles resulting from the airflow through the filter, picking up and carrying material that has been previously deposited some distance before the particles are once more entrapped by the filter fibers. Increasing the filter face velocity (the velocity across the face or surface of the filter) will increase the chances of reentrainment.

Collection Efficiency of Filters

In any procedure where an attempt is made to relate a sample activity to an activity concentration in the environment, the volume of the original sample must be known. In the sampling of air particulate matter by filtration, not all particles in the air are collected. That is to say, the collection mechanisms that have been discussed are not 100% efficient. It is, therefore, not sufficient just to know what volume of air was passed through the filter; the fraction of the airborne particles collected must also be known. Collection efficiency may be stated in terms of several parameters. The most common is to determine the *percent penetration* (percent passing through the filter) of a certain particle size as a function of the linear velocity (volume rate of flow divided by the filter area) through the filter. Another way of presenting the efficiency would be to have *percent collection* of a certain particle size as a function of linear velocity through the filter. Although efficiencies of this type are useful, it is most difficult to use them to determine the fraction of the atmospheric particles collected unless the particle size distribution existing in the atmosphere is known.

There is one other type of filter collection efficiency reported in the literature. This is a *mass collection efficiency* based entirely on the percentage of the mass of the airborne particles that is collected. This can be grossly misleading because the small particles predominate in number, and yet, constitute a minor fraction of the total particulate matter mass. The only time a mass collection efficiency would represent a total particle collection efficiency would be if all the particles were of the same size.

Theory of Collection Efficiency

Before continuing the discussion of collection efficiency, it is necessary to discuss the theory of collection efficiency for the various collection mechanis ms previously mentioned, and also, the effect of various parameters on collection. Figure 4-23 shows a qualitative picture of the theoretical percent penetration versus linear velocity that might be expected for a given filter and an aerosol with a specific size particle. By referring to this graph, and the associated notes, the interrelation of the various mechanisms can be examined.

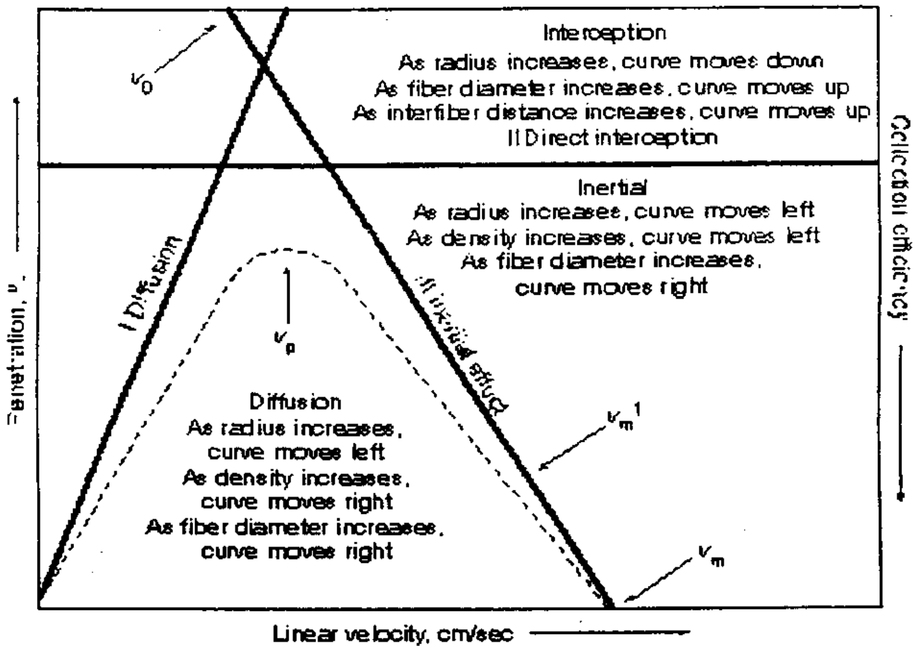


Figure 4-23. Filtration mechanisms.

Diffusion Efficiency

The diffusion line I of Figure 4-23 shows how the diffusion mechanism is affected by linear velocity. As the velocity increases, the diffusion mechanism decreases. As previously mentioned, this is due to the shorter transit time through the filter at the higher flow rates. The diffusion function always passes through the origin, but the slope varies with the particle radius, the filter fiber diameter, and the distance between filter fibers.

As the particle radius increases, the slope becomes greater, thus resulting in a reduced diffusion effect for a given linear velocity. This is because larger particles are not as readily affected by diffusion mechanisms as are smaller particles.

The effects of fiber diameter and interfiber distance are quite similar. As either of these two parameters increases, the influence of the diffusional mechanism increases and the slope of the line decreases. A greater fiber diameter increases the diffusion effect because, for a given linear velocity, the particle spends a longer time passing by a filter fiber. The effect of interfiber distance is similar, as it too affects the transit time of the particle by a filter fiber. The greater the open space in the filter is, the larger the interfiber distance. Therefore, for a given overall linear velocity, the velocity in the open space of the filter is less for larger interfiber distance, and transit time is longer.

Direct Interception Efficiency

As previously mentioned, direct interception is analogous to simple mechanical straining. Direct interception is shown in line II of Figure 4-23. It shows that there would not be any effect by changing linear velocity on this collection mechanism.

The effects of the particle radius and interfiber distance on the interception mechanism are quite simple. As the particle radius increases, the percent penetration decreases, as would be expected for straining. As interfiber distance increases, the percent penetration increases for a mechanical straining.

The relation between particle penetration and fiber diameter for interception is somewhat more involved. As the fiber diameter increases in size, the air flowlines are affected at an increasing distance upstream from the fiber. This may cause some of the flowlines to diverge from a path that would have brought the particle within contact distance of the fiber. Therefore, as the fiber diameter increases, the collection efficiency due to interception decreases.

Inertial Effect Efficiency

The inertial collection of particles depends on the particles leaving their air flowlines and contacting a filter fiber due to their inertial forces. For a particle of a given size, this effect would start to show at some velocity, v_o, and would reach a maximum at some greater velocity, v_m. The fact that the effect increases with velocity is due to the dependence of inertial forces on both mass and velocity. Although Figure 4-23, line III, shows a zero percent penetration for this mechanism at v_m, the penetration might be significant, depending on the interfiber distance. If a larger interfiber distance existed, the maximum effect might occur at some point v^{I}_{m}, in which case a definite amount of penetration would occur.

The effect of increasing particle radius in inertial collection is improved collection for a given linear velocity. This is related to the fact that the larger the particle, the greater the probability of it coming within a distance from the filter fiber where it will make contact. Figure 4-24 lists the collection efficiency of some filter media as a function of particle size. (All of the $PM_{2.5}$ filters are included in Table 4-2 at the end of this section.)

The effect of increasing particle density also improves inertial collection. Like the effect of velocity, this is due to the increase of inertial forces, thus causing greater deviation from the air flowlines.

As the filter fiber diameter increases, the effect of inertial collection decreases. With the air flowlines being affected at a greater distance upstream from the fiber, the change in their trajectory is much more gradual and, therefore, the tendency of inertial forces to cause a particle to leave a flowline is less.

Membrane and Teflon® filters										
Filter	% Efficiency for removal of particles of equivalent spherical diameters, μ									
	Size, mm	No. of trials	0.32	0.4	0.5	0.64	0.8	1.0	1.3	1.6
0.8 μ Nucleopore	47	1	82	96	99	99	100	100	100	100
5.0 μ Nucleopore	90	1	83	95	98	97	98	100	100	100
3.0 μ MF millipore (SS)	90	3	99.93	99.98	100	100	100	100	100	100
5.0 μ MF millipore (SM)	47	1	100	100	100	100	100	100	100	100
5.0 μ MF millipore (SM)	90	1	100	100	100	100	100	100	100	100
5.0 μ Teflon® millipore (LS)	90	1	99	99.6	100	100	100	100	100	100
8.0 μ MF millipore (SC)	47	1	96	99	99	99	96	99	100	—
10 μ Teflon® millipore (LC)	90	1	96	99	99	99	100	100	100	100
1.2 μ Silver membrane	47	2	99.9	100	100	100	100	100	100	100
S&S 0.45 (B6A) cellulose acetate	47	1	100	100	100	100	100	100	100	100
Gelman GA-1 cellulose acetate	47	1	99	100	100	100	100	100	100	100
Glass fiber filters										
Gelman A	47	2	99.8	99.8	99.6	99.7	99.1	99	99	97
Gelman A	25	1	100	100	100	100	100	100	100	100
Gelman A acid washed	25	1	99.9	100	100	100	100	100	100	100
Reeves angel # 900 AF	47	1	99.9	100	99.9	100	100	100	100	100
MSA 1106 BH	47	1	100	100	100	100	100	100	100	100
S&S #25 acid washed	47	3	26	53	65	64	69	71	79	88
TFA[b]	47	2	38	67	80	81	83	85	84	87
Whatman 41	47	1	63	83	90	84	89	81	94	100
S&S green ribbon #559	47	1	69	84	88	87	93	98	97	100

[a] Face velocity, cm/sec for 25-, 47-, and 90-mm filters is 0.82, 0.31, and 0.11, respectively.

[b] After sampling 500 ft^3 of room air, the filtration efficiency of TFA increased to 90% for 0.3 μ particles with other values in the range of 80 to 90% for sizes up to 1.6 μ. This efficiency was not significantly altered by discharging the filter over a radioactive source.

Figure 4-24. Initial efficiency of filtration of particle ≥ 0.3 μ diameter via Royco particle counter[a].

Overall Efficiency

In filter sampling, all of the collection mechanisms are taking place simultaneously and their effects are algebraically additive. The overall relation between percent penetration and linear velocity might well look like the dotted line in Figure 4-23.

From this overall efficiency curve, there appears to be some velocity, v_p, where a maximum penetration occurs. It should be pointed out, however, that if the direct interception effect is dominant enough, the overall efficiency curve may well have a flat plateau, rather than a single velocity of maximum penetration.

The mechanism of electrical forces has not been covered in this discussion of the theory of collection efficiency. The degree to which it will change the overall efficiency is dependent on many factors. The theoretical aspect of this effect is beyond the scope of this discussion, but the fact that it may well play an important part in overall efficiency in certain instances is not to be ignored.

Experimental Collection Efficiencies

Several investigators have studied the actual collection efficiencies of filter media, and their results are reported in the literature (ACGIH 1985, Caroff 1973, Liu 1978, Ramskill 1951). A degree of caution must be exercised in utilizing this experimental data. A number of different types of particulate matter have been used, including dioctyl phthalate (DOP) smoke, atmospheric dust, duraluminum dust, radon daughter products, polystyrene aerosols, and lead fumes. The experimental results of the various investigators often appear to be in great disagreement for many of the filter media, and these differences should be evaluated in selecting an efficiency value to use.

One additional complicating factor should be mentioned in relation to filter efficiency. During the time that the sampler is running, the increasing amount of particles that accumulate on the filter will cause the collection efficiency to improve as sampling continues. At the same time, however, the resistance of the filter to airflow also increases, thus perhaps interfering with the sampling procedure and decreasing the flow rate.

Characteristics of Filter Media

A great number of individual types of filter papers are available. For particulate matter sampling, in general, they fall into four main categories: cellulose fiber, glass fiber, mixed fiber, and membrane filters. These various categories will be discussed in terms of their general characteristics, sampling considerations, and analysis considerations. (See Table 4-2 at the end of the section.)

Cellulose Fiber Filters

The filter papers in this category are typically called chemical filters. They were designed for use in "wet" chemistry where liquid-solid separations were desired. Although not designed with air sampling in mind, a number of these filters have seen extensive application in this area (see Figure 4-25).

Filter	Void size microns	Fiber diameter microns	Thickness microns	Weight per unit area mg/cm^2	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance 100 ft/min in. H_20
Whatman	2+	—	130	8.7	0.06	150	1.67 kg/cm	40.5
1								
4	4+	—	180	9.2	0.06	150		11.5
32	1-	—	150	10.0	0.025	150		38 (1 fm)
40	2	—	150	9.5	0.01	150		54
41	4+	—	180	9.1	0.01	150	1.41 kg/cm	8.1
42	>1	—	180	10.0	0.01	150		46 (28 1 fm)
44	>1	—	150	8.0	0.01	150		40 (28 1 fm)
50	1	—	100	10.0	0.025	150		49 (28 1 fm)
541	4+	—	130	8.2	0.008	150	2.24 kg/cm	—
S&S 604	—	—	200	—	0.03	80		8.5
MSA Type S	—	—	100.0		1.3	120		6.5
Cellulose	—	—	1000		1.3	120		
Corrugated	—	—						
Cellulose	—	—	1000		1.3	120		
MSA BM-2133			1830	32.7	0.12		0.58 kg/cm	9.1
IPC 1478	—	Av. 17	560-760	14.6	0.04	120	0.18 kg/cm	0.31
Gelman W-41	24							

Figure 4-25. Cellulose fiber filters.

Sampling Considerations

Cellulose fiber filters are made of purified cellulose pulp, which can easily ignite, thus rendering them ineffective at high operating temperatures. The low ash content of these filters makes them highly suitable to analysis where heat or chemical ashing is a required preparation. These filters generally have a high affinity for moisture. This limitation means that the relative humidity must be controlled while weighing the filters to ensure there is no error introduced by absorbed moisture. Recent studies show that cellulose filters irreversibly absorb water; thus, a control blank is required when humidity is a problem. Cellulose filters also enhance the artifact formation of sulfate and nitrate.

Specific Filters

Whatman 41 filter paper is the most widely used of the cellulose fiber filters. Whatman 41 has become the preferred substitute for glass fiber filters for high-volume sampling, because of its good collection efficiency and acceptability for further chemical analyses. It has also received wide use in all metals analysis, including neutron activation analysis, because of the low blanks or background levels of metals on the clean filters (see Figure 4-25). This filter has also found applications as the tape used with paper tape samplers for the determination of soiling index.

The Mine Safety Appliances (MSA) type "S" filter is well adapted to high-volume sampling because of the low pressure drop associated with this technique. This filter is difficult to handle because of its bulkiness, and its variable ash content and organic binder make it unsuitable for some chemical analyses.

TFA filters have also been used for high-volume sampling when extensive chemical analysis is required. Whatman 41 is preferred over this filter because of the higher collection efficiency (see Figure 4-25).

Glass Fiber Filters

These filter papers are made from finely spun glass fiber by combining the fiber with an organic binder and compressing this material in a paper machine. These filters have seen increasing use in air sampling.

Sampling Considerations

Glass fiber filters have the ability to withstand high temperatures (up to 540°C), thus making them most attractive for stack sampling. They are further typified by high collection efficiency. In some cases, the organic binder may interfere with subsequent analysis, so the filter is flash-fired to remove the binder material. This causes some loss in tensile strength and usually requires that a backing material be used during sampling. The glass filters are nonhygroscopic, thus allowing them to be used in areas where humidity is high. Being glass also makes them the filter choice for most corrosive atmospheres. All of the filters in this category are quite fragile and must be handled with care.

Glass fiber filters, because of the high silicate content, are extremely difficult to ash by chemicals or heat. Therefore, extraction procedures are performed on these filters to remove the sample for subsequent chemical analysis. Overall, flash-fired glass fiber filters, because they are nonhygroscopic, can be used in corrosive atmospheres and are free of organic binders that are widely used for ambient air sampling.

The pH of the filter will affect the collection of the sample. It has been recommended that neutral pH ($6.5 < pH < 7.5$) filters be used because there is less absorption of acid gases onto the filter. Significantly different results can be obtained when sampling side-by-side with filters of different pH values.

Specific Filters

The MSA 1106 BH is one of the flash-fired glass fiber filters and, therefore, is free of organic binder. The Gelman Spectro Grade Type A Glass Fiber Filter is a neutral pH glass fiber filter rated as ultra-pure for metals analysis to minimize interference with trace metal background values. (Each box of 8- by 10-inch filters contains assay information on trace metals for the enclosed filters.) Spectro grade filters do not absorb detectable amounts of SO_2 from the atmosphere, thereby minimizing its effect. A summary of the physical characteristics of glass fiber filters is given in Figure 4-26.

Filter	Void size microns	Fiber diameter microns	Thickness microns	Weight per unit area mg/cm^2	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance 100 ft/min in. H_20	Benzene extract/ 100 in.2 mg
MSA									
1106B*			180-270	6.1	- 95	540	3.5 lb/in.	19.8	17.3
1106BH*			180-460	5.8	- 100	540	1.5 lb/in.	19.8	0.6
									0.6
Gelman									
A*			380	9.3	99.4	480		18.9	
E*			380	10.0	98.1	480		18.9	
G			810	11.6		480		3.0	
M			580	10.8		480		6.1	
H			510	12.7		480		21.7	
Whatman									
AGF/A*	>1		340	5.3	100	540	1.29 lb/in.		0.8
AGF/B*	>1		840	15.0	100	540	3.14 lb/in.		3.2
AGF/D	>1		460	5.5	100	540	0.56 lb/in.	2.3@2 1fm	
AGF/E	>1		890	15.0	100	540	1.07 lb/in.		
AGF/F	>1		380	6.3	100	540	0.73 lb/in.		
H&V									
H-93		0.6	460-560	9.3	96-99	540	2.5 lb/in.		
H-94		0.5-3	380	8.2	96-99	480	2.5 lb/in.		
S&S									
24*									
26*			200	6.05					0.3
27*			125-180		98	400			
29*			127	5.4	98	400			0.6

* without organic binder

* with organic binder

Figure 4-26. Glass fiber filter characteristics.

Mixed Fiber Filters

These filters possess the characteristics of the individual fibers composing them. The chemical analysis of mixed fiber filters also depends on the individual fiber constituents. General characteristics of a number of the members of this category are given in Figure 4-27.

Filter designation	Composition	Void size microns	Fiber diameter microns	Thickness microns	Weight per unit area mg/cm^2	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance at 100 ft/min (~50 cm/sec) in. H_20
H&V H-70, 9 mil	Cellulose asbestos		0.1-35	230	8.2	20-25	150	2.5 lb/in.	17
H-70, 18 mil	Cellulose asbestos		0.1-35	460	15.4	20-25	150	4.0 lb/in.	26
H-64	Cellulose asbestos		0.1-35	830-1090	22.7	15-20	150	2.0 lb/in.	15
H-90	Cellulose glass		9-35	685	13.4	70	150	3.2 lb/in.	0.4
H-91	Cellulose glass		1.5-35	710	13.5	80	150	3.5 lb/in.	0.89
N-15	Synthetic fiber & glass		0.5-15	1270	24.9	15	150	1.0 lb/in.	9.9
S-G	Synthetic fiber glass & cotton		0.5-15	685	14.5	4-6	150	gauze backed	2.0
MSA glass & cellulose	Glass & cellulose			1000			120		
Whatman ACG/A	Glass & cellulose	>1		330	5.5		150	270 gm/cm	0.9 (20 1 fm)
ACG/B	Glass & cellulose	>1		990	19.5		150	330 gm/cm	2.6 (20 1 fm)
H&V CWS-6	Cellulose asbestos			762		11%			17
H&V AEC-1	Cellulose asbestos			762		13%			13.3
VM-100 Gelman	Vinyl metracel	10.0							
VM-1	Vinyl metracel	5.0							

Figure 4-27. Mixed fiber filter characteristics.

Membrane Filters

This filter media consists of dry gels of cellulose esters, usually produced as cellulose acetate, or cellulose nitrate, polyvinyl chloride, acrylonitrile, and Teflon®. The filters are cast on a smooth, flat substrate and exposed to a controlled atmosphere. This process can control both the internal membrane structure and pore size. Some filters are formed with pores while others are formed as sheets with pores formed later.

Sampling Considerations

Membrane filters are typically very brittle and require careful handling. In air sampling, they should be backed by some support structure to avoid breakage. The filters are not well suited to sampling at elevated temperatures, as they have an operating temperature range comparable to cellulose fiber filters (see Figure 4-28).

The particle size collected by membrane filters has been found to be much smaller than the pore size; this is thought to be due to electrostatic forces.

Membrane filters have appreciable pressure drops, and this may limit the volume of air that can be sampled. Another factor limiting the volume of air that can be sampled is the build-up of a second layer of dust on the filter surface. This layer has a tendency to slough off, causing loss of part of the sample.

Analysis Consideration

One advantage of membrane filters is that they are primarily surface collectors: consequently, the problem of self-absorption of radiation becomes negligible.

The membrane filters lend themselves very readily to particle size analysis by microscopy. By using an immersion oil with an index of refraction (N_D) equal to that of the filter, the filter can be made transparent to light, thus allowing light-transmitted microscopic analysis. However, care must be taken to ensure that the N_D of the particle is not the same as the N_D of the immersion oil.

Membrane filters can also be readily ashed and leave very little residue. This can be a definite advantage in some analysis schemes. Most membrane filters are also readily soluble in many organic solvents, thus allowing removal of particulate matter with little problem.

Filter	Pore size microns	Index refraction	Thickness microns	Weight per unit area mg/cm^3	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance 100 ft/min in. H_2O
Millipore SM	5.0	1.495	170	3.6	0.0001	125	100 psi	19
SS	3.0	1.495	170	3.8	0.0001	125	150 psi	38
WS	3.0		150	4.9	"	"		-100
RA	1.2	1.512	150	4.2	"	"	300 psi	62
AA	0.80	1.510	150	4.7	"	"	350 psi	91 (39)*
DA	0.67	1.510	150	4.8	"	"	400 psi	120
HA	0.45	1.510	150	4.9	"	"	450 psi	210
WH	0.45		150	5.7	0.0001	"		-270
							0.41 kg/cm^2	11
Gelman	5.0		200	3.6		"	0.72 kg/cm^2	33
AM-1								
AM-3	2.0		200	6.6		"		73
AM-4	0.65		200			"		
AM-5	0.65		200			"		
AM-6	0.40		200	5.8		"		
S&S	7.5		180-250	6.3-8.7	0.01	Continuous 100		
AF-600								
AF-400	4.0		180-250	6.3-8.7	0.01	Peak 200		
AF-250	2.0		160-210	5.6-7.3	0.008	"		
AF-150	0.85		160-210	5.6-7.3	0.008	"		
AF-100	0.70		Av-150	Av 5.3	0.007	"		
AF-50	0.60		Av-135	Av 4.7	0.006	"		
AF-30	0.40		Av-120	Av 4.2	0.005	"		
Gelman	5.0	1.49				Dry 176		
GM-1								
GM-3	1.2	1.49				176		
GM-4	0.80	1.49				176		
GM-6	0.45	1.49				176		
GM-8	0.20	1.49				176		
GM-9	0.10	1.49				176		
GM-10	0.05	1.49				176		

*Alternate value reported

Figure 4-28. Membrane filter media.

Sample Problems

Problem 1: Filter Selection

A filter is to be chosen for subsequent analysis by a chemical ashing technique. The maximum vacuum flow resistance the pump can overcome is about 10 in. of water when the face velocity is about 100 ft/min. When dealing with atmospheric sampling, the temperature is not a limiting factor since most filters will operate at temperatures over 100°C (212°F). Which filter, based on the available information, would be the best choice?

Solution

From Figures 4-26 and 4-27 it can be seen that glass fiber and mixed fiber filters have relatively high ash contents, making them impractical for chemical ashing. From Figures 4-25 and 4-28 it can be seen that cellulose fiber filters and membrane filters exceed the requirements of the pumps. From Figure 4-25 it can be seen that Whatman 41, S&S 604, MSA BM-2133 and the IPC 1478 all have ash contents less than 1% and flow resistances less than 10 in. H_2O. These would all be acceptable and availability would determine which would be used.

Problem 2: Filter Selection

The pump capacity from Problem 1 has now been doubled so that 20 in. H_2O@100 ft/min can now be sampled. An efficiency of 100% for all particles down to 0.3 µm is desired. Which filter should be used?

Solution

From Figure 4-24, the 5.0 µm MF Millipore (SM) 47 mm and 90 mm, S&S B6A cellulose acetate, Gelman A 25 mm and MSA 1106 BH all show apparent particle efficiencies of 100% for all sizes. From Figure 4-26 both the Gelman and MSA filters show an ash content over 95%, and therefore are not acceptable. The S&S B6A does not appear on Figures 4-25 through 4-28, but since the cellulose acetate is a mixed fiber filter, we can assume the ash content is also too high. From Figure 4-28, the 5.0 µ Millipore SM has a low ash content (0.0001%), an acceptable flow resistance (19 in. H_2O), and is the most acceptable filter.

Problem 3: Filter Extraction

A filter is needed for subsequent analysis by acid extraction. The sampling atmosphere is very humid. The flow resistance must be kept below 10 in. H_2O. Which filter should be used?

Solution

Cellulose filters are very hygroscopic, so they should not be used in this situation. Membrane filters have extremely high flow resistances, so they, too, should not be used in this situation. Glass fiber filters are non-hygroscopic and are the filters of choice in water-vapor laden atmospheres. By referring to Figure 4-26, Gelman G or M filters could be used since they both qualify for the low flow resistance requirements.

Summary

No single type of filter is the right one for all air sampling problems. In evaluating a filter one must consider many factors: general filter characteristics, collection efficiency, background filter impurities, sampling conditions, ease of analysis, self-absorption, flow resistance, and the purpose for which the sample is being taken.

Commonly Used Filter Media for Particulate Sampling and Analysis

The 1997 draft EPA Guideline on Speciated Particulate Monitoring (Chow 1997) includes a discussion on the commonly used filter media for particulate sampling and analysis, including $PM_{2.5}$ and PM_{10}. A summary table taken from this reference, presenting filter type, filter size, physical characteristics, chemical characteristics, compatible analysis methods, and cost per filter, is included here as Table 4-2.

Table 4-2. Commonly used filter media for particulate sampling and analysis.

Filter Type, (Major Manufacturer, and Catalog No. or Trade Name)	Filter Size	Physical Characteristics	Chemical Characteristics	Compatible Analysis Methods[a]	Cost per Filter	No. of Filters per Box
Ringed Teflon®-membrane (Gelman Scientific; Ann Arbor, MI; Teflon® R2PJ047, R2PJ037	25 mm 37 mm 47 mm	Thin membrane stretched between polymethlypentane ring. White surface, nearly transparent. Minimal diffusion of transmitted light. High particle collection efficiencies. Cannot be accurately sectioned. 1.2, 2.0, 3.0, 5.0 and 10μm pore sizes (determined from liquid filtration). Melts at ~60°C. High flow resistance.	Usually low blank levels, but several contaminated batches have been found. Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Low hygroscopicity. Low blank weight.	Gravimetry, OA, XFR, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	$3.78 $4.04 $4.38	50 50 50
Ringed Teflon®-membrane (Pallflex, Putnam, CT)	25 mm 37 mm 47 mm	Thin film of Teflon® attached to polyolefin ring without adhesive.	Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Low hygroscopicity. Low blank weight.	Gravimetry, OA, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	$2.36 $2.50	25 25

Backed Teflon® membrane, (Gelman Scientific, Ann Arbor, MI; "Zeflour": 2µm, P5PJ037 or P5PJ047; 1µm, P5PL037 or P5PL047	37 mm 47 mm 20.3 × 25.4cm	Thin membrane mounted on thick polypropylene backing. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Melts at ~60°C. High flow resistance. 1 µm and 2 µm pore sizes.	Usually low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Higher background levels for XRF and PIXE than Teflon® owing to greater filter thickness. Low hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	$1.98 $2.30 $29.40	50 50 25
Backed Teflon® membrane, (Pallflex, Putnam, CT)	25 mm 37 mm 47 mm	TFE porous membrane on TFE support. Smooth surface. 0.30 µm @ 99% efficiency.	Neutral pH. Usually low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Higher background levels for XRF and PIXE than Teflon®, due to greater filter thickness. Low hygroscopicity. High blank weight. Retains average tare weight of 7.6 grams.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	$2.14 $2.57	50 50
Nylon membrane, (Gelman Scientific, Ann Arbor, MI: "Nylasorb", #66509)	47 mm 90 mm	Thin membrane of pure nylon. White opaque surface, diffuses transmitted light. 1µm pore size. Melts at ~60°C. High flow resistance.	High HNO_3 collection efficiency. Passively adsorbs low levels of NO, NO_2, PAN, and SO_2. Low hygroscopicity. Low blank weight.	IC, AC	$1.70 $5.00	100 50

Silver membrane (Millipore Corp., Marlborough, MA)	25 mm[b] 37 mm[c]	Thin membrane of sintering, uniform metallic silver particles. Grayish-white surface diffuses transmitted light. Melts at ~350°C. High flow resistance.	Resistant to chemical attack by all fluids. Passively adsorbs organic vapors. Low hygroscopicity. High blank weight.	Gravimetry, XRD	$2.71 $3.88	50 25
Cellulose esters membrane (Millipore Corp., Marlborough, MA; "Nitrocellulose"	37 mm 47 mm[d]	Thin membrane of cellulose nitrate mixed esters, and cellulose acetate. White opaque surface diffused transmitted light. 0.025, 0.05, 0.1, 0.22, 0.30, 0.45, 0.65, 0.80, 1.2, 3.0, 5.0, and 8.0 µm pore sizes. Melts at ~70°C. High flow resistance.	High hygroscopicity. Negligible ash content. Dissolves in many organic solvents. Low hygroscopicity. Low blank weight.	Gravimetry, OM, TEM, SEM, XRD Biomedical applications	$0.70 $0.67	100 100
Polyvinyl Chloride membrane (Millipore Corp., Marlborough, MA).	25 mm 37 mm 47 mm	Hospital-grade polyvinyl chloride membrane. White opaque surface, diffuses transmitted light. 0.2, 0.6, 0.8, 2.0, and 5.0 µm pore sizes. Melts at ~50°C. High flow resistance.	Dissolves in some organic solvents. High hygroscopicity. Low blank weight.	XRD	$0.76 $1.03 $1.19	100 100 100

Polycarbonate membrane, (Corning CoStar, [formerly Nuclepore Corp.], Cambridge, MA; #111129) (Poretics, Minnetonka, MN)	25mm 37mm 47mm[b]	Smooth, thin, polycarbonate surface with straight through capillary holes. Used for particle size classification. Light gray surface, nearly transparent. Minimal diffusion of transmitted light. Low particle collection efficiencies, <70% for some larger pore sizes. Retains static charge. 0.1, 0.3, 0.4, 0.6, 1.0, 2.0, 3.0, 5.0, 8.0, 10.0, and 12.0 µm uniform pore sizes. Melts at ~60°C. Moderate flow resistance.	Low blank levels (made of carbon-based material, so inappropriate for carbon analysis). Low hygroscopicity. Low blank weight.	Gravimetry, OA, OM, SEM, XRF, PIXE	\$0.32 \$0.44 \$0.51	100 100 100
Pure quartz-fiber (Pallflex Corp., Putnam, CT; 2500 QAT-UP)	25 mm 37 mm 47 mm 20.3 × 25.4 cm	Mat of pure quartz fibers. White opaque surface; diffuses transmitted light. High particle collection efficiencies. Soft and friable edges flake in most filter holders. Melts at >900°C. Moderate flow resistance.	Pre-washed during manufacture-low blank levels for ion. Contains large and variable quantities of Al and Si. Some batches contain other metals. Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. Low hygroscopicity.	ICP/AES, ICP/MS, IC, AC, T, TOR, TMO, TOT, OA	\$1.10 \$0.62 \$0.50 \$6.70	100 25 25 25

Mixed quartz-fiber (Whatman Corp., Hillsboro, OR; QM/A #1861865	37 mm 47 mm 20.3 × 25.4 cm	Quartz (SiO_2) fibers with ~5% borosilicate content. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Some batches can melt at ~500°c. Effects on thermal carbon analysis are unknown. Becomes brittle when heated. Low flow resistance.	High blank weight. Contains large and variable quantities of Na, Al, and Si in all batches. Variable levels of other metals are found in many batches. Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. Low hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, AA, ICP/AES, ICP/MS for some metals, IC, AC, T, TOR, TMO, TOT	$0.67 $0.74 $6.40	100 100 25
Cellulose-fiber 41 (Whatman Corp., Hillsboro, OR; #1441047)	25 mm 47 mm	Thick mat of cellulose fibers, often called a "paper" filter. White opaque surface, diffuses transmitted light. Low particle collection efficiencies, <70% for some variations of this filter. High mechanical strength. Burns at elevated temperatures (~150°C, exact temperature depends on nature of particle deposit). Variable flow resistance.	High purity, low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Adsorbs gases, especially water vapor. Most appropriate for adsorbing gases such as HNO_3, SO_2, NH_3, and NO_2 when impregnated with reactive chemicals. High hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	$0.10 $1.05	100 100

Cellulose-fiber 31ET (Whatman Corp., Hillsboro, OR; #3031F915	47 mm 46×47 cm		High purity, low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Adsorbs gases, especially water vapor. Most appropriate for adsorbing gases such as HNO_3, SO_2, NH_3, and NO_2 when impregnated with reactive chemicals. High hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	\$0.17^c \$7.28	100 25
Teflon®-coated glass-fiber (Pallflex, Putnam, CT; TX40H120)	37 mm 47 mm	Thick mat of borosilicate glass fiber with a layer of Teflon® on the surface. Glass fiber supporting Teflon® is shiny. High particle collection efficiencies. Glass melts at ~500°C. Teflon® melts at ~60°C. Low flow resistance.	Low blank levels for ions (glass backing and carbon content make it less suitable for elemental and carbon analyses). Inert to adsorption of HNO_3, NO_2, and SO_2. Low hygroscopicity. High blank weight.	Gravimetry, IC, AC	\$0.60 \$0.63	100 100
Glass fiber (Gelman Scientific, Ann Arbor, MI; Type A/E)	25 mm 47 mm 20.3 × 25.4 cm (available in 13 mm to 293 mm sizes)	Borosilicate glass fiber. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Melts at ~500°C. Low flow resistance.	High blank levels. Adsorbs HNO_3, NO_2, SO_2, and organic vapors. Low hygroscopicity. High blank weight.	Gravimetry, OA, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC	\$0.14 \$2.40 \$12.90	500 100 100

[a] AAS = Atomic Absorption Spectrophotometry
AC = Automated Colorimetry
IC = Ion Chromatography
ICP/AES = Inductively-Coupled Plasma with Atomic Emission Spectrophotometry
ICP/MS = Inductively-Coupled Plasma with Mass Spectrophotometry
INAA = Instrumental Neutron Activation Analysis
OA = Optical Absorption or Light Transmission (b_{abs})
OM = Optical Microscopy
PIXE = Proton-Induced X-Ray Emissions
SEM = Scanning Electron Microscopy
T = Thermal Carbon Analysis
TEM = Transmission Electron Microscopy
TMO = Thermal Manganese Oxidation Carbon Analysis
TOR = Thermal/Optical Reflectance Carbon Analysis
TOT = Therman Optical Transmission Carbon Analysis
XRD = X-Ray Diffraction
XRF = X-Ray Fluorescence

[b] Available in 0.45 µm pore size.

[c] Available in 0.80 µm pore size.

[d] Filter disc is available in-size between 13 mm to 293 mm depending on the pore size.

[e] Available by special order.

Gravitational Sampling

Gravitational sampling, as briefly discussed here, refers to the amount of precipitation (solid or liquid) which reaches the ground over a stated period of time. The sampling time periods reported for total solids are 24 hours or more, and as much as a 30 day time period. This discussion addresses the use of dustfall buckets or jars for solids and nonrecording and recording gauges typically used for rainfall.

Dustfall Bucket or Jar

The dustfall bucket had been one of the earliest sampling devices for particulate matter in the atmosphere. The bucket or jar was made of resistant material and often placed in a stand to prevent the container from spilling. A wire rim was used to prevent the container from collecting bird droppings. Results were calculated by filtering the liquid, with subsequent weighing of the remaining solids.

Precipitation Collectors

As reported in EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV-Meteorological Measurements, EPA/600/R-94/0-38d, revised 1995, the national weather bureau station's precipitation collectors are of two basic types: nonrecording and recording devices. The nonrecording precipitation collector or gauge is constructed of a cylinder, closed at one end and open at the other. The depth of the liquid in the collector is typically measured with a measuring ruler calibrated in subdivision of centimeters or inches. To improve precipitation resolution as in the case of the standard 8-inch gauge, the collector is constructed to satisfy national weather station (NWS) specifications which require a ratio of 10:1 between the area of the outside collector cylinder and the inside measuring tube. A funnel attached to the gauge directs the precipitation into the collecting tube and minimizes evaporation losses. A specialized nonrecording gauge is available for collecting programs involving the chemical and/or radioactive analysis of precipitation. The collector includes a sensor that detects the start and end of precipitation and automatically releases a lid to open and close the precipitation gauge.

Recording gauges consist of two basic designs based on their operating principles: the weighing-type gauge and the tipping bucket-type gauge. The weighing gauge is known as the Universal gauge because it allows usage for liquid and frozen precipitation. This gauge incorporates a chart drum that is made to rotate either by an 8-day spring-wound clock or a battery-powered clock. A quartz crystal mechanism with gear shafts allows for a wide range of rotation periods from 12 hours to 30 days. In the tipping bucket gauge, the balance of the buckets and the leveling of the bucket frame are critical. Power is typically 6V.d.c and the signal is provided by a switch closure each time the bucket tips (0.01 inches of rainfall per bucket). The accuracy of the gauge is given as 1% for rainfall rates of 1 in./hr or less, 4% for rates of 3 in./hr, and 6% for rates up to 6 in./hr.

Electrostatic and Thermal Precipitators

This section addresses the use of electrostatic and thermal precipitators for the collection of particulate matter. Only a brief discussion is included since these techniques are more commonly used in air cleaning applications or special air monitoring research projects than for routine use in ambient air sampling. The following discussion was extracted from Chapter 15 of the 8th Edition of Air Sampling Instruments for Evaluation of Atmospheric Contaminants, Swift and Lippman (1995).

Electrostatic Precipitators

Introduction

Separation of particles from an air stream using electrostatic precipitators is based on the use of electrostatic forces. Since the electrostatic force is placed directly on the particles instead of on the entire gas volume, relatively less energy is needed to collect the particles or to move the gas stream through the collector, compared to other collection mechanisms. For example, in the case of inertial collectors most of the energy is used to drive the gas through the collector, and high collection efficiency is reflected in very high pressure drops.

Two advantages of electrostatic precipitator samplers compared to filter samplers are: (1) the sampling rate is not affected by mass loading, and (2) the collected sample is in a readily recoverable form. In one type of precipitator sample the particles are collected on a large surface, where the surface may be covered by a paper or a liquid film depending on the follow-up analysis. On a second type of electrostatic sampler, the electron microscope grid sampler, the sampler collects small samples for particle size distribution analyses. This type of sampler collects representative samples quickly without sample losses and alterations that occur when transferring membrane filter samples to electron microscope grids.

Principles of Electrostatic Precipitation

Two operations are involved in collecting particles by electrostatic precipitation. They are electric charging of the particles and accelerating the charged particles toward an oppositely charged electrode. A number of mechanisms for charging particles have been used, including friction with solid material, flame ionization, radioactive charging, and high-voltage corona discharge. The most widely used mechanism is the corona discharge because of its efficiency, speed, and controllability. Figure 4-29 shows an axial view of high-voltage corona discharge. The electric field close to the high voltage wire speeds up free electrons that ionize the gas molecules which end up with the corona glow. The affinity of the charged particles toward the collecting electrode depends on the number of charges acquired, the viscous drag of the air, and the electric field strength.

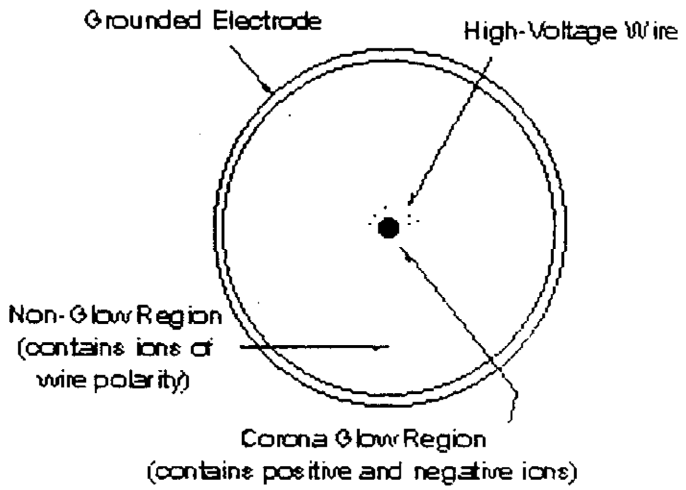


Figure 4-29. Axial view of high voltage corona discharge.

Collection Efficiency

Variables affecting the collection efficiency of electrostatic samplers include such items as current, flow rate, voltage, particle size, particle shape, particle concentration, humidity, pressure, and temperature. High charging currents, high voltage gradients, and low flow rates improve the collection efficiency, while very high humidity reduces the collection efficiency because of electrical breakdown that occurs in a humid atmosphere. Maintaining as high a voltage as possible during the entire sampling period, without inducing excessive sparking, will result in the maximum collection efficiency.

Specific Applications

Electrostatic precipitator samplers have been developed for a number of applications including mass concentration analysis, sampling for radioactive particles, and sampling for particle size analysis. In the past, a field instrument employing a negative corona central electrode was used for the collection of atmospheric samples that allowed for gravimetric mass analysis and subsequent particle speciation. Also, high-volume samplers with sampling rates as high as 10,000 L/min have been designed for gravimetric and other particle analysis. Using this sampler, particles were collected on a rotating plate coated with a thin film of liquid. Swift and Lippman (1995) report that instruments employing electrostatic sampling have been used for the sampling of radioactive particles. Also, because particles travel at various distances in an electrostatic sampler before reaching a grounded collector, variations in particle size occur along the length of a simple coaxial precipitator. This aspect allows for particle size analysis using the electrostatic precipitator. However, the particle travel distance is also influenced by other variables such as the linear air velocity in the tube, radial position at which the particle enters the tube, particle dielectric properties, ion density, and voltage gradient. A discussion of several particle sizing electrostatic precipitator samplers is also included in the Swift and Lippman 1995 reference.

Thermal Precipitators

Introduction

Thermal precipitators collect particles from an air stream by passing the air sample through a narrow channel having a significant temperature gradient perpendicular to the direction of flow. The particles move towards the decreased temperature surface and deposit on it, allowing for subsequent analysis of the collected particles. Figure 4-30 illustrates a schematic view of a thermal precipitator.

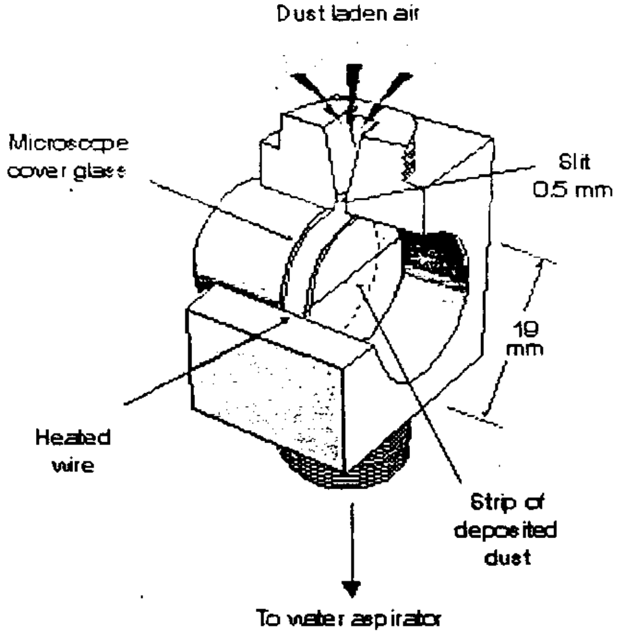


Figure 4-30. Sampling head of thermal precipitator.

Collection Efficiency and Deposition Pattern

Generally all particles 5 to 0.005 µm and less in diameter are collected in a thermal precipitator sampler, provided that the thermal gradient is about 10^4 K/cm. For particles larger than 5 µm, gravitational and inertial effects may interfere with the collection efficiency. Also, at windspeeds greater than 6 m/sec, the sample collection efficiency will be reduced. It is interesting to note that because the deposition pattern of particles on the collection surface in a direction parallel to air flow is Gaussian, the particle concentration can be determined by extrapolation of the spatial distribution curve.

Advantages and Disadvantages of Thermal Precipitators

The major advantage of the thermal precipitator is the extremely high collection efficiency, particularly in comparison to liquid impingers and cascade impactors. Also, the low sampling velocity prevents the shattering or breakup of the collected particles during the sampling cycle, and particles may be collected on a wide variety of surfaces allowing for numerous types of special analysis including optical microscopy, electron microscopy, photometry, and radioactivity. Disadvantages of the sampler are that the low sampling rate renders the sampler unsuitable for some analysis, volatile aerosols cannot be collected, and the standard thermal precipitator has poor size selection characteristics. This latter disadvantage is especially important if too large a sample size is taken.

High-volume Air Sampling for TSP (Federal FRM for Lead Sampling)

Introduction

When air pollution agencies attempt to determine the nature and magnitude of air pollution in their communities, and the effectiveness of their control programs, they collect samples of suspended, and sometimes settleable particulate matter.

Several different sampling techniques and devices --- filtration, electrostatic and thermal precipitation, and impaction --- may be employed to collect suspended particulate pollutants from ambient air. Of the various techniques, filtration has been found to be the most suitable for routine air sampling. The so-called high-volume (hi-vol) sampler for total suspended particulate matter (TSP) was the most widely used sampler since it was the Federal FRM (FRM) for measuring compliance with the particulate matter standard. Approximately 20,000 hi-vols were operating at Federal, State, and local air pollution control agencies, industries, and research organizations for either routine or intermittent use in the 1970's. As reduction in TSP levels decreased, the number of TSP samplers in operation was greatly diminished. With the promulgation of the PM_{10} standard in 1987, the number of TSP samplers operated by State and local agencies was down to approximately 2800 and the number of PM_{10} samplers was 636. By 1997 the number of TSP samplers operated by State and local control agencies was reduced to approximately 450. Although there is no TSP standard, the TSP FRM remains as the official sampling method for obtaining samples to determine compliance with the national ambient air quality standard for lead.

Development of the High-volume Sampler

In 1948, Silverman (Silverman and Viles 1948) developed an aerosol collector that consisted of a household vacuum sweeper motor encased in an airtight sheet metal housing adapted to hold a 4-inch diameter filter. Provision was made for measuring the air flow through the system. Because this sampler operated at a much higher flow rate than other available samplers, it was identified as a high-volume sampler and the designation persists. Replacement of the thin sheet metal motor housing with one of cast aluminum by the Staplex Company in the early 1950s improved the Silverman sampler. Adoption of a stainless steel filter holder to accommodate an 8- by 10-inch filter permitted 24-hour operation of the sampler and collection of a much larger sample of particulate matter than was previously possible (Figure 4-31).

Although the Staplex sampler performed satisfactorily, it was decided after several years of experience that a more rugged sampler was needed to meet the requirements of a large-scale sampling network operation. Accordingly, in 1957, a new high-volume sampler, developed in collaboration with General Metal Works, was introduced. The new sampler used a different motor that was completely enclosed in a cast aluminum housing, eliminating the sheet metal and rubber components used in the Staplex sampler, thus simplifying brush and motor replacement. This sampler and others similar to it were widely accepted.

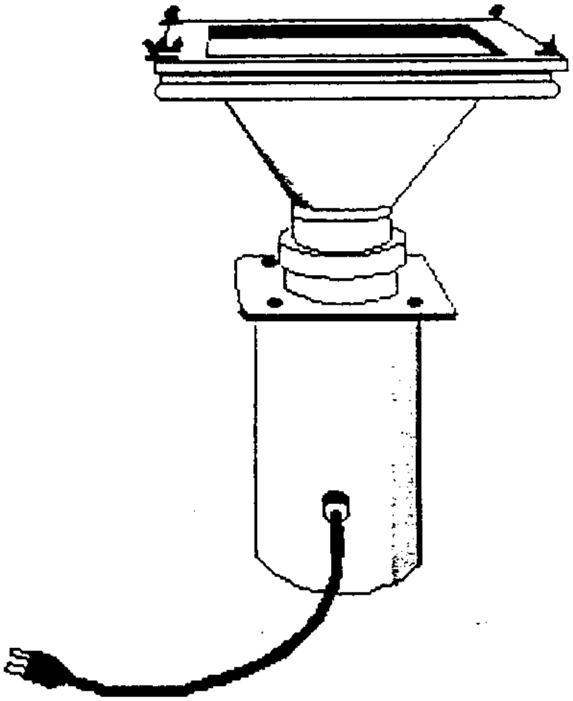


Figure 4-31. Hi-vol sampler components (motor, filter, housing).

Equipment

Sampler-Shelter Combination

The sampler and its shelter should be considered as a single, functioning unit (Figure 4-32). The shelter must provide protection for the sampler, and at the same time allow unrestricted access of ambient air from all directions without direct impingement of particles on the filter. A high-volume sampler with a 7- by 9-inch exposed filter area operated in a standard shelter at a sampling flow rate of 1.1 to 1.7 cubic meters per minute (39 to 60 cubic feet per minute) collects particles of up to 25 to 50 μm in aerodynamic diameter, depending on wind speed and direction, and uniformly distributes the sample over the filter surface. The standard peak roof of the shelter, which acts as a plenum above the filter, is placed to provide a total opening area of slightly more than the 63-square-inch exposed filter area, thereby permitting free flow of air into the plenum space (Figure 4-33).

The size of the opening to the filter and the volume of air filtered per unit time will affect the particle size range collected. Distribution of particles on the filter may also be affected. Therefore, any high-volume sampler purchased after February 3, 1983, and used for Federally mandated air monitoring must have uniform sample air inlets that are sized to provide an effective particle capture air velocity of between 20 and 35 cm/sec at their recommended sampling flow rates. The particle capture air velocity is determined by dividing the sample air flow rate by the inlet area measured in a horizontal plane at the lower edge of the sampler's roof. Ideally, the inlet area and sampling flow rate of these samplers should be selected to obtain a capture air velocity of 25 ± 2 cm/sec.

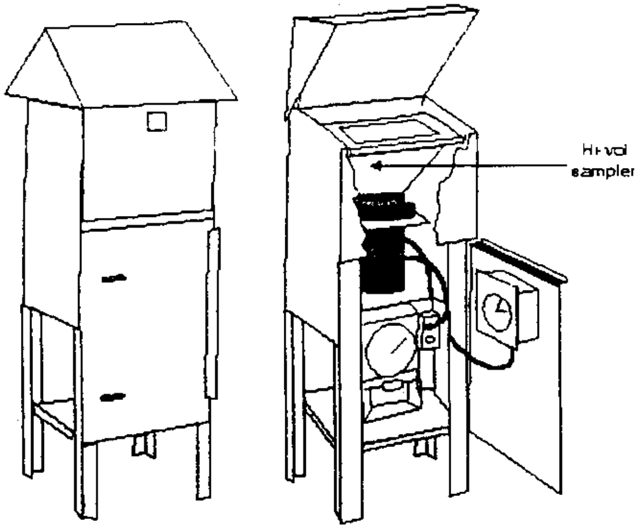


Figure 4-32. Hi-vol sampler in shelter.

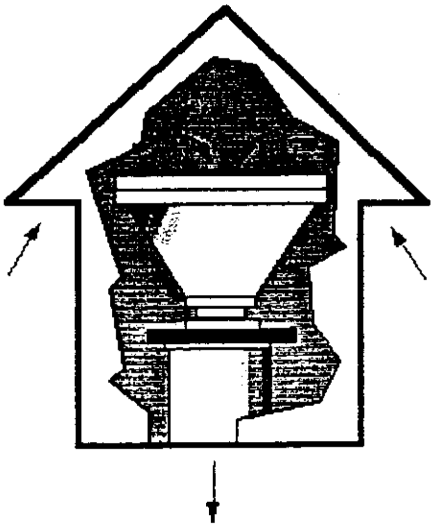


Figure 4-33. Air flow of hi-vol sampler in shelter.

Filter Media for High-volume Sampler

Choice of filter media is influenced by the objectives of the sampling program and the characteristics of the sampler to be employed. An excellent discussion of filter media and filtration sampling is presented in Air Sampling Instruments (American Conference of Governmental Industrial Hygienists 1985).

Glass fiber filters have been extensively used for total suspended particulate matter sampling. Such filters have a collection efficiency of at least 99% for particles having aerodynamic diameters of 0.3 μm and larger, low resistance to air flow, and low affinity for moisture, all of which are distinct advantages during sampling. However, in order to eliminate possible weight errors due to small amounts of moisture, both unexposed and exposed filters should be equilibrated between 15°C and 30°C with less than ± 3°C variation at a relative humidity below 50% with less than ± 5% variation for 24 hours before weighing.

Samples collected on glass fiber filters are suitable for analysis of a variety of organic pollutants and a large number of inorganic contaminants including trace metals and several nonmetallic substances. Also, glass fiber filters are excellent for monitoring gross radioactivity. However, satisfactory analyses for materials already present in substantial amounts in the filter are not possible. A random, but statistically significant, sample of new filters should be analyzed to determine whether the filter blank concentration is high enough to interfere with a particular analysis. It is wise to obtain this information before purchasing large numbers of filters to avoid potential problems caused by high filter blanks.

While glass fiber filter material has been dominant in the measurement of total suspended particulate matter, numerous applications have been found for cellulose filters. Cellulose filters have relatively low metal contents, making them a good choice for metals analysis by neutron activation, atomic absorption, emission spectroscopy, etc. Conventional high-volume samplers usually have to be modified to use cellulose filters because the filters clog rapidly, causing flow to sometimes decrease by as much as a factor of two during a one-day sampling interval. Other disadvantages of cellulose are its absorption of water and enhanced artifact formation of nitrates and sulfates. These disadvantages can usually be overcome by using a control blank filter. Spectro-quality grade glass fiber filters have sufficiently low background metal contents to make them acceptable for metal analysis, if cellulose cannot be used.

Filters used for Federally mandated TSP sampling must meet the specifications listed in Table 4-3. Filters supplied by the U.S. EPA can be assumed to meet these specifications.

Table 4.3. U.S. EPA specifications for TSP filters.

Parameter	Specification
Size	20.3 ± 0.2 x 25.4 ± 0.2cm (nominal 8 x 10 in.)
Nominal exposed area	406.5 cm^2 (63 $in.^2$)
Material	Glass fiber filter or other relatively inert, nonhygroscopic material
Collection efficiency	99% minimum as measured by the DOP test (ASTM-2986) for particles of 0.3-µm aerodynamic diameter
Recommended pressure drop range	42 to 54 mm Hg (5.6 to 7.2 kPa) at a flow rate of 1.5 std m^3/min through the nominal exposed area
pH	6 to 10
Integrity	2.4 mg maximum weight loss
Pinholes	None
Tear strength	500 g minimum for 20-mm wide strip cut from filter in weakest dimension (ASTM Test D828-60)
Brittleness	No cracks or material separations after single lengthwise crease

Precautions in Filter Handling

After the desired filters have been chosen, each should be permanently identified by stamping a serial number on two diagonally opposite corners (one number on each side of the filter). Care should be taken not to tear the filter when affixing the identification number. Filters should then be inspected visually for holes, tears, particles, or other imperfections that may cause uneven loading, loss of particulate matter, or other failure during the sampling period. A backlighting device, such as a light table, should be used during the inspection.

Before the filters are weighed, they should be equilibrated for at least 24 hours in a conditioning environment (15°C to 30°C not to vary more than ± 3°C, relative humidity less than 50% not to vary more than ± 5%) free of acidic or basic gases that might react with the filter material. The analytical balance used for the weighing should be calibrated with three to five standard weights over a range including the expected weights of unexposed and exposed filters. The filters should be taken directly from the conditioning chamber to the balance to minimize the risk of contaminating the filter. They should then be weighed to the nearest milligram, and the weight and number of each filter should be recorded. Filters must not be folded or creased before use as this may establish erroneous flow patterns during sampling.

To install a clean filter in the sampler, the wing nuts are loosened and the faceplate is removed (Figure 4-34). The filter, with its rough side up, should be centered so that the gasket forms an airtight seal on the outer edge of the filter when the faceplate is in position. The faceplate is then replaced and the wing nuts are tightened. The gasket should not be tightened to the point that filter damage might occur. Hi-vol filter cartridges similar to the one pictured in Figure 4-35 make installation of filters easier. Installation and removal of a filter can be performed inside a building, thus eliminating handling problems due to lack of space and windy conditions.

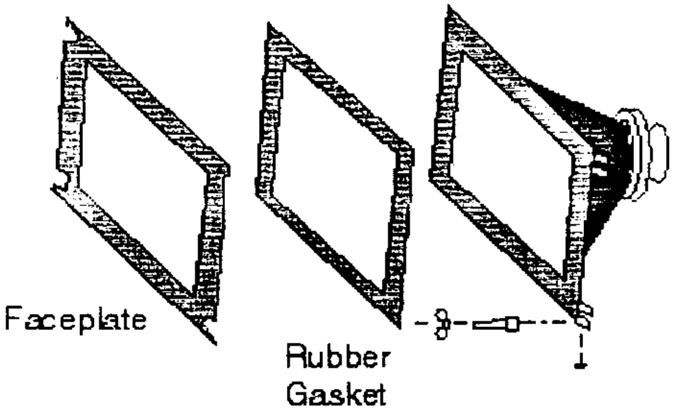


Figure 4-34. Hi-vol sampler filter adapter assembly.

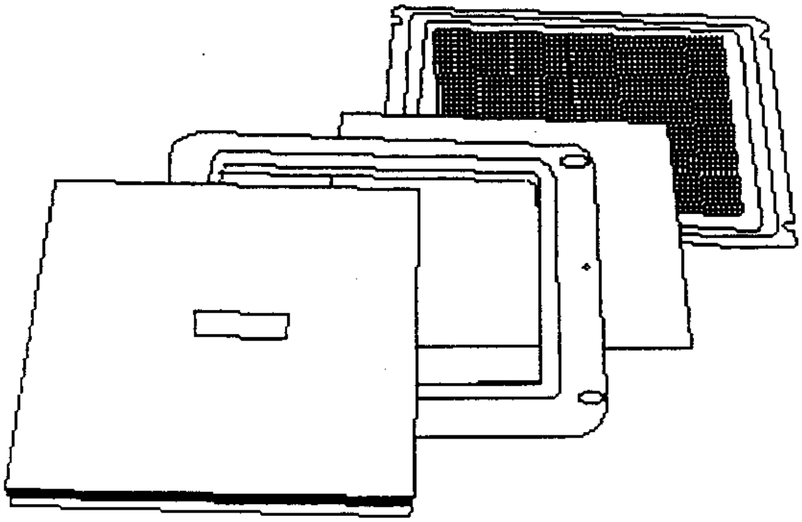


Figure 4-35. Hi-vol filter cartridge.

When the filter is removed, it should be checked for holes or other physical damage and foreign material (such as insects). Caution should be observed to minimize filter damage when removing the faceplate and the gasket. If the filter's border appears fuzzy or nonexistent, there may be an air leak around the gasket (Figure 4-36). The sample should be voided and the gasket checked. After the visual check, the filter should be folded in half lengthwise so that sample touches sample. This minimizes sample loss during transport to the lab. The filter is then placed in a glassine envelope or a manila folder and taken to the lab for weighing and analysis. The filter should be placed in the conditioning environment for at least 24 hours before weighing to ensure that the same humidity and temperature conditions are present during the final weighing as were present during the initial weighing.

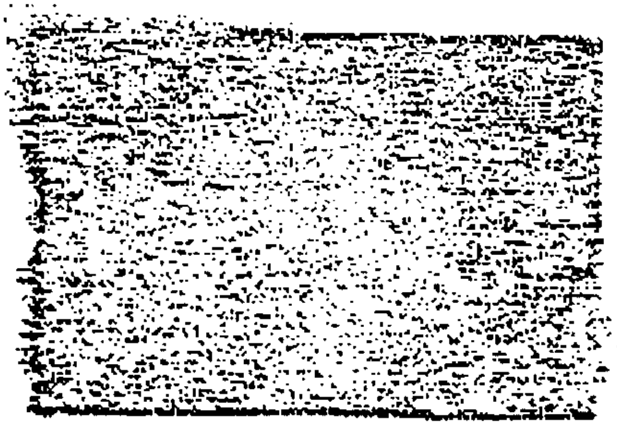


Figure 4-36. Fuzzy or nonexistent filter border.

Documentation of all these steps is for legal purposes and to ensure data reliability. The operator who starts the sampler is responsible for recording the following information:

- Filter serial number
- Sampling site identification number and/or address
- Sampler identification number
- Starting time
- Initial sampling flow rate
- Sampling date (including day, month and year)
- Summary of conditions that may affect results (e.g., meteorology, construction activities, etc.)
- Operator's initials or signature
- Ambient temperature and barometric pressure, if necessary (see calibration section of this chapter)

The operator who removes the sample is responsible for recording the following information:

- Stop time and elapsed time (if available)
- Final sampling flow rate
- Operator's initials or signature

- Ambient temperature and barometric pressure, if necessary (see calibration section of this chapter)
- Comments concerning voided samples
- Summary of existing conditions that may affect results

Calibration

Most high-volume samplers use an orifice/pressure indicator. an electronic mass flowmeter, or a rotameter (visifloat) for measuring sampling flow rate (Figure 4-37). All flow rate measuring devices must be calibrated against known flow rates. This is accomplished by calibrating the devices with a flow rate transfer standard that has been calibrated with a positive-displacement standard volume meter having a calibration that is traceable to the National Institute of Standards and Technology.

The U.S. EPA has specified procedures in Appendix B of 40 CFR 50 for the calibration of orifice-type flow rate transfer standards as well as the calibration of sampler flow rate measuring devices. These procedures are described below.

A flow rate transfer standard is calibrated by attaching it by means of a filter adapter to the inlet of a positive-displacement standard volume meter, such as a Roots meter (Figure 4-38). Air is then drawn through the transfer standard and the standard volume meter at a minimum of five different, but constant, evenly distributed flow rates with at least three of the flow rates within a range of 1.1 to 1.7 m^3/min (39 to 60 ft^3/min) by a high-volume air pump, such as a high-volume sampler motor, attached to the outlet of the standard volume meter. The flow rates are determined by timing the flow of a known volume (at least 3 m^3) of air through the transfer standard as indicated by the standard volume meter.

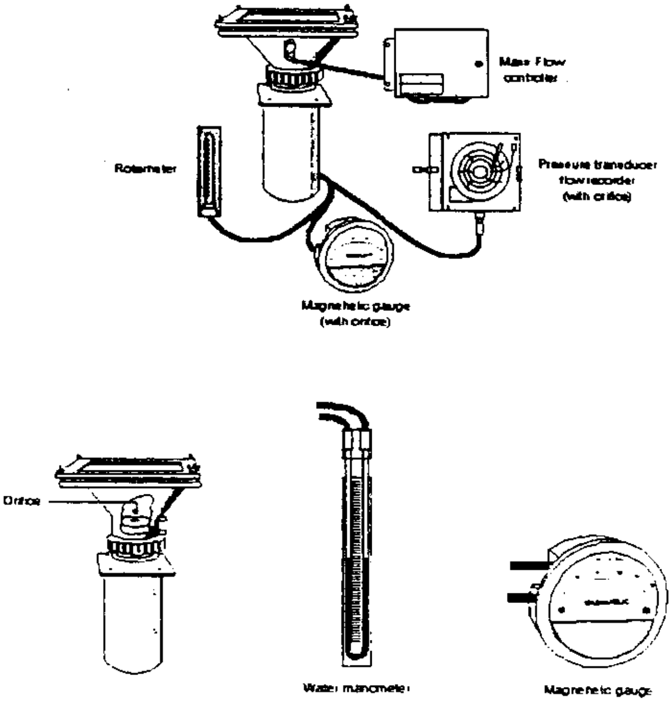


Figure 4-37. Typical flow rate indicating devices.

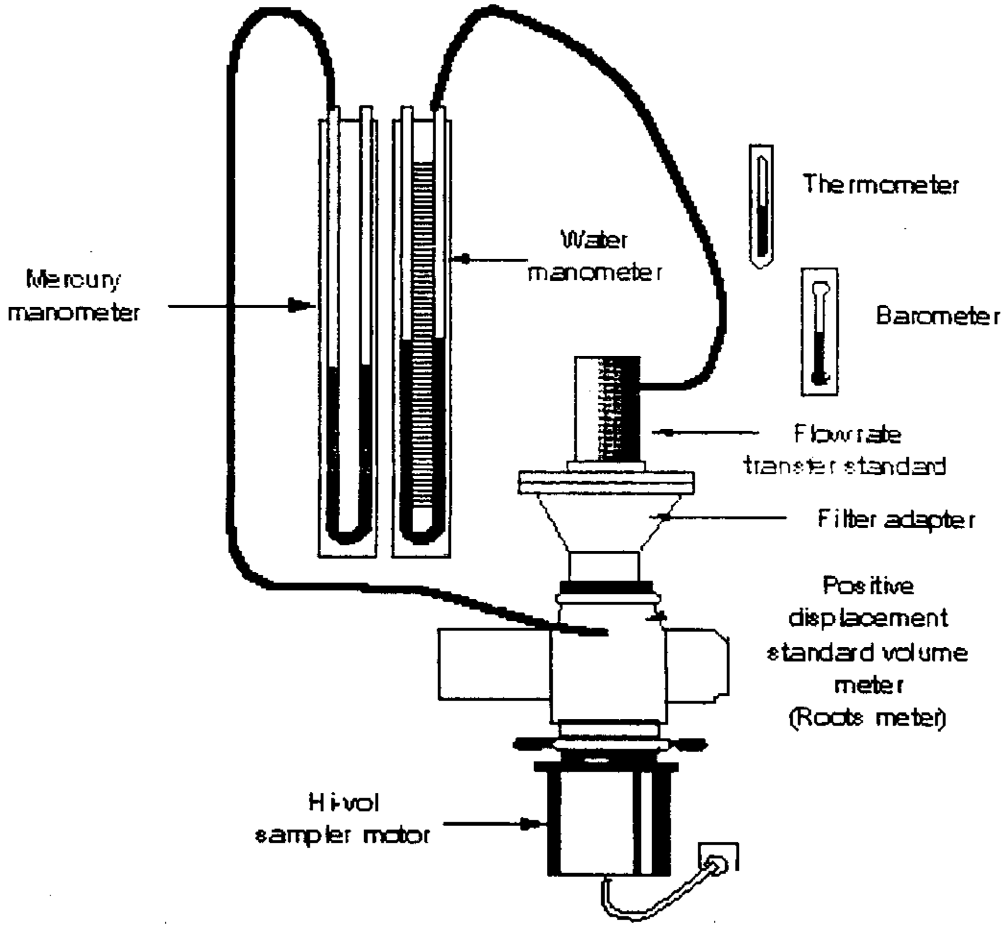


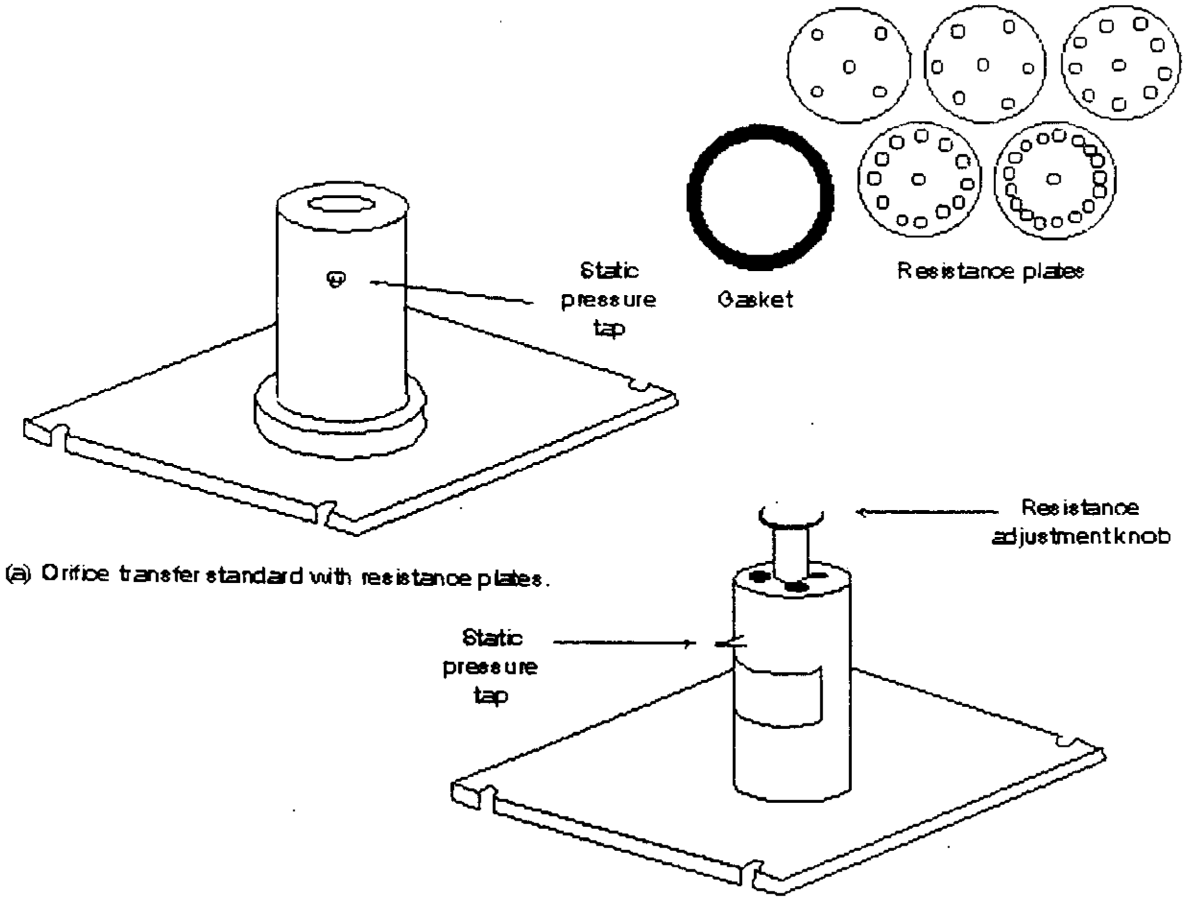
Figure 4-38. Flow rate transfer standard calibration setup.

Air passing through the orifice-type transfer standard causes a pressure drop that varies directly with flow rate (i.e., pressure drop increases as flow rate increases). The pressure drop (ΔH) associated with each flow rate of air through the transfer standard is measured by means of a water manometer that is attached to the static pressure tap of the transfer standard.

A pressure drop is also caused in the standard volume meter by air passing through it. However, this pressure drop varies inversely with flow rate (i.e., pressure drop decreases as flow rate increases). The pressure drop (ΔP) associated with each flow rate of air through the standard volume meter is measured by means of a mercury manometer that is attached to a static pressure tap located just below the inlet of the standard volume meter.

Before any flow rates are measured, the calibration setup is checked for air leaks by temporarily clamping both manometer lines, blocking the inlet of the transfer standard by using a rubber stopper, cellophane tape, or other suitable means, and activating the high-volume air pump. Any change in the reading of the standard volume meter indicates an air leak, which must be eliminated before proceeding with the calibration.

After all leaks have been eliminated, the high-volume air pump is deactivated, the manometers are unclamped and "zeroed," and the inlet of the transfer standard is unblocked. Different, but constant, flow rates are then generated by operating the high-volume air pump at a constant voltage and installing resistance plates (metal plates having differing numbers of holes) in the transfer standard (Figure 4-39a), adjusting a variable resistance plate of the transfer standard (Figure 4-39b), or by varying the voltage to the high-volume air pump. If resistance plates are used, the leak check described above must be repeated each time a resistance plate is installed.



(a) Orifice transfer standard with resistance plates.

(b) Variable resistance orifice transfer standard.

Figure 4-39. Typical orifice-type flow rate transfer standards.

The air volume measured by the standard volume meter is corrected to standard volumes (std m^3) by using the following equation:

(Eq. 4-2)
$$V_{std} = V_m \frac{P_1 - \Delta P}{P_{std}} \frac{T_{std}}{T_1}$$

Where:
V_{std} = *standard volume,* std m^3
V_m = *actual volume measured by the standard volume meter*
P_1 = *barometric pressure during calibration,* mm Hg or kPa
ΔP = *pressure drop at inlet to volume meter,* mm Hg or kPa
P_{std} = 760 mm Hg or 101 kPa
T_{std} = 298 K
T_1 = *ambient temperature during calibration,* K.

Standard flow rates are then calculated to the nearest 0.01 std m^3/min by using Equation 4-3.

(Eq. 4-3)
$$Q_{std} = \frac{V_{std}}{t}$$

Where:
Q_{std} = *standard volumetric flow rate,* std m^3/min
t = *elapsed time,* minutes

After the standard flow rates have been determined, $\sqrt{\Delta H (P_1 / P_{std})(298/T_1)}$ is calculated for each flow rate and plotted against its associated standard flow rate (Q_{std}). The transfer standard calibration curve is then determined either by drawing a line of best fit between the individual plotted points (Figure 4-40), or calculating the slope and *y*-intercept of the curve by linear least squares regression analysis.

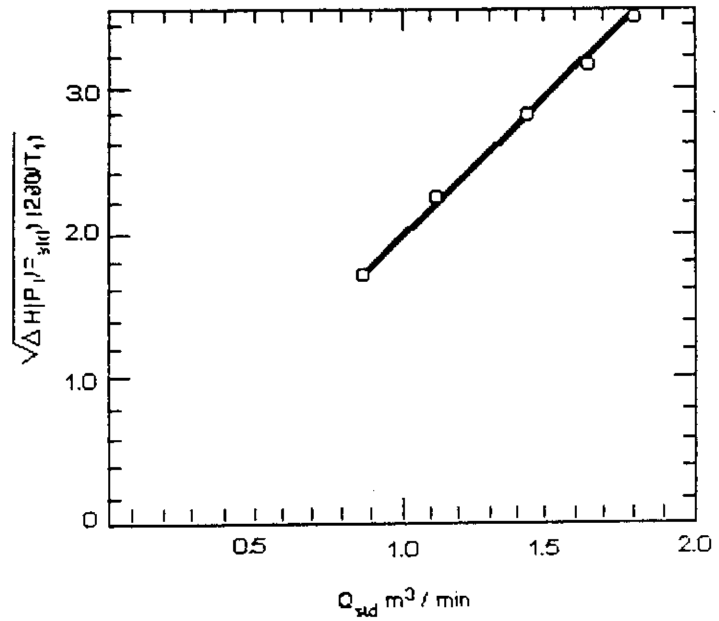


Figure 4-40. Typical calibration curve for a flow rate transfer standard.

Damage such as nicks or dents could affect the calibration curves of flow rate transfer standards. Therefore, the transfer standards should be recalibrated if they show signs of damage. If no damage is visible, transfer standards should be recalibrated at least once per year.

A sampler flow rate measuring device is calibrated by attaching a calibrated flow rate transfer standard to the inlet of the device's associated high-volume sampler (Figure 4-41). It must be ensured that there are no air leaks between the transfer standard and the high-volume sampler, and the sampler must be allowed to reach thermal equilibrium. Then, air is drawn through the transfer standard and the high-volume sampler at several different, but constant, flow rates, distributed over a flow rate range that includes 1.1 to 1.7 std m^3/min by the motor of the high-volume sampler. The flow rates should not be generated by varying the voltage to the sampler's motor if an orifice-type flow rate measuring device located downstream of the motor is being calibrated.

Pressure drop (ΔH) within the transfer standard measured by a water manometer that is attached to the static pressure tap of the transfer standard, and the flow rate indication (I) of the sampler's flow rate measuring device, are recorded for each flow rate of air. Where P_2 is the barometric pressure (mm Hg or kPa) and T_2 is the ambient temperature (K) during the calibration, $\sqrt{\Delta H(P_2/P_{std})(298/T_2)}$ is calculated for each flow rate. The calculated values are then used to determine the flow rates at standard conditions (Q_{std}) either by referring to a graph of the transfer standard's calibration curve, such as Figure 4-40, or by calculating Q_{std} using the slope and y-intercept of the transfer standard's calibration curve.

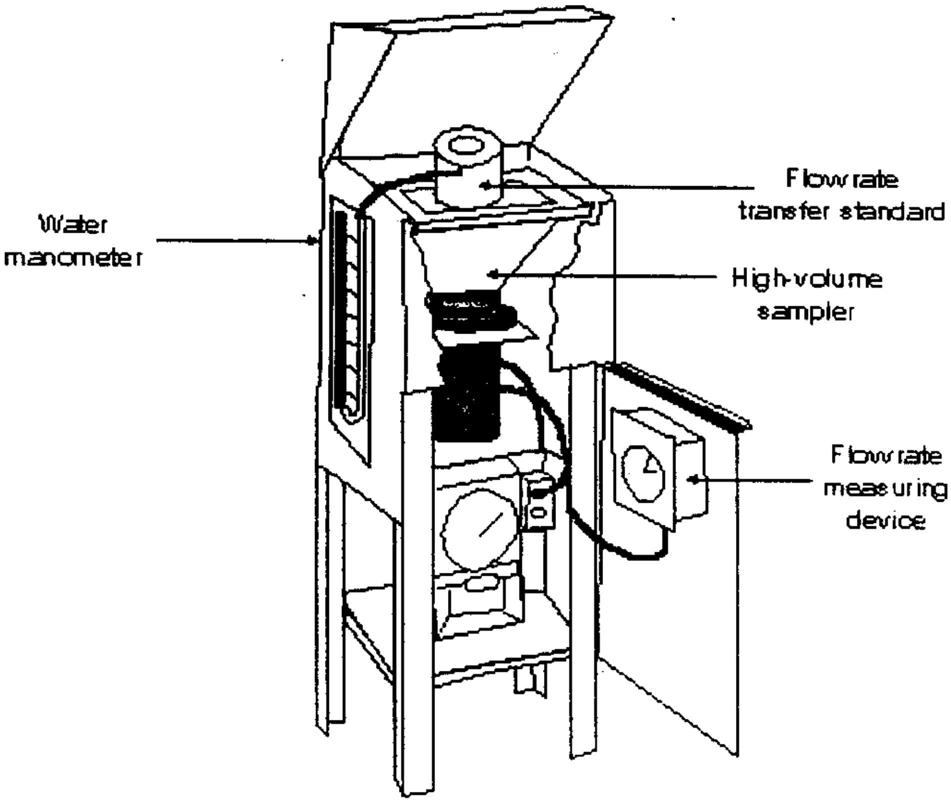


Figure 4-41. Flow rate measuring device calibration setup.

Flow rates indicated (*I*) by a sampler's flow rate measuring device are then expressed, with regard to the type of flow rate measuring device used and the method of correcting sample air volumes for ambient temperature and barometric pressure, by using the formulas of Table 4-4. The formulas for geographic average barometric pressure (P_a) and seasonal average temperature (T_a) may be used to approximate actual pressure and temperature conditions during sampling for a seasonal period if the actual barometric pressure and temperature at the sampling site do not vary by more than ± 60 mm Hg from P_a or ± 15°C from T_a, respectively. Furthermore, P_a may be estimated from an altitude-pressure table or by making an approximate elevation correction of - 26 mm Hg (-3.46 kPa) for each 305 m (1000 ft) that the sampler is above sea level (760 mm Hg or 101 kPa), and T_a may be estimated from weather station or other records.

Table 4-4. Formulas for expressing indicated flow rates of sampler flow rate measuring device calibration.

Type of sampler flow rate measuring device	Expression	
	For actual pressure and temperature corrections	For incorporation of geographic average barometric pressure (P_a) and seasonal average temperature (T_a)
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having a square root scale*	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

After the flow rates indicated by the sampler's flow rate measuring device have been properly expressed, the resulting values are plotted against their associated standard flow rates (Q_{std}). The calibration curve for the sampler flow rate measuring device is then determined either by drawing a line of best fit that is readable to 0.02 std m^3/min between the individual plotted points (Figure 4-42) or by calculating the slope, y-intercept, and correlation coefficient of the curve by linear least squares regression analysis.

The calibration of flow rate measuring devices of high-volume samplers having flow controllers depends on the operating histories of the samplers. Flow-controlled samplers having operating histories demonstrating that their flow rates are stable and reliable may be calibrated solely at their controlled flow rates by using a clean (unexposed) filter (i.e., calibrated at only one flow rate near the lower limit of the controlled flow rate range). In these cases, the sampler flow rate measuring devices may remain uncalibrated at flow rates outside their controlled flow rate ranges, but they should be used to indicate any relative change between initial and final sampling flow rates, and they should be frequently recalibrated at their controlled flow rates to minimize potential loss of samples because of controller malfunctions. Flow rate measuring devices of flow-controlled samplers not having operating histories as described above are calibrated at several flow rates, as described previously for non-flow-controlled samplers, except that their flow controllers are disabled before calibration.

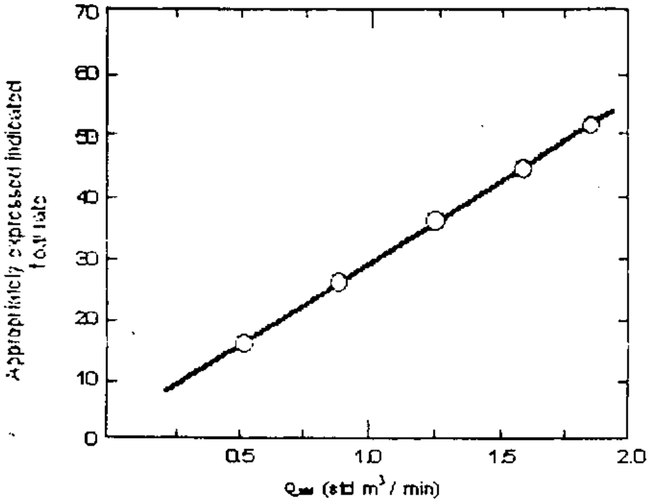


Figure 4-42. Typical calibration curve for a sampler flow rate measuring device.

Whichever calibration procedure is used for flow-controlled samplers, the abilities of their flow controllers should be verified after their calibrations. If a sampler is calibrated at several flow rates, its flow controller should be re-enabled after the calibration and a clean filter should be installed to verify its controlled sampling flow rate. After the sampling flow rate has been verified, two or more filters should be stacked and added to the sampler to determine if the flow controller maintains the controlled sampling flow rate. For a sampler that is calibrated only at its controlled sampling flow rate, one or two additional filters should be stacked and installed after the calibration to verify that the flow controller maintains the controlled sampling flow rate.

Flow rate transfer standards (e.g., Figure 4-43) and sampler flow rate measuring devices that are not described in the calibration procedures of Appendix B of 40 CFR 50, but meet specifications described in Appendix B and have U.S. EPA-calibration procedures, may be used for Federally mandated air monitoring.

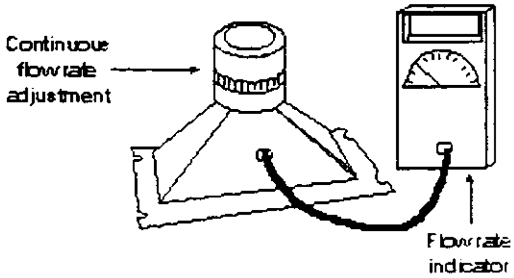


Figure 4-43. Electronic flowmeter transfer standard with externally adjustable resistance.

U.S. EPA High-volume Sampling Procedure for TSP (Appendix B of 40 CFR 50)

The following procedure is specified in Appendix B of 40 CFR 50 for the sampling of suspended particulate matter.

In 1987, EPA abolished the NAAQS for total suspended particulate matter and established a particulate matter standard for PM_{10}. Determining compliance with the new PM_{10} standard requires use of a reference or equivalent method for PM_{10}. As a result, the high-volume sampler FRM was no longer used to determine compliance with EPA's particulate matter standard. However, the high-volume sampler FRM remains as the reference sampling method for determining compliance with the lead NAAQS.

1. Number each filter, if not already numbered, near its edge with a unique identification number.
2. Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.
3. Equilibrate each filter for at least 24 hours.
4. Following equilibration, weigh each filter to the nearest milligram and record this tare weight (W_1) with the filter identification number.
5. Do not bend or fold the filter before collection of the sample.
6. Open the shelter and install a numbered, preweighed filter in the sampler, following the supplier manufacturer's instructions. During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter. Filter cartridges that can be loaded in the laboratory may be used to minimize this problem.
7. Close the shelter and run the sampler for at least five minutes to establish run-temperature conditions.
8. Record the flow indicator reading and, if needed, the barometric pressure (P_3) and the ambient temperature (T_3).
9. Stop the sampler.
10. Determine the sampler flow rate. If it is outside the acceptable range (1.1 to 1.7 m^3 min [39 to 60 ft^3/min]), use a different filter, or adjust the sampler flow rate. Warning: Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.
11. Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).
12. Set the timer to start and stop the sampler so that the sampler runs 24 hours, from midnight to midnight (local time).
13. As soon as practical following the sampling period, run the sampler for at least five minutes to again establish run-temperature conditions.
14. Record the flow indicator reading and, if needed, the barometric pressure (P_3) and the ambient temperature (T_3).

    Note: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration. For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For a sampler having flow recorders but not constant flow controllers, the average temperature and pressure at the site *during the sampling period* should be estimated from weather bureau or other available data.

15. Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter.
16. Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).
17. Record the ending time or elapsed time on the filter information record, either from the stop set point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1440 ± 60 min for a valid sample.
18. Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement. If the sample is known to be defective, void it at this time.
19. Equilibrate the exposed filter for at least 24 hours.
20. Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number.
21. Determine the average sampling standard flow rate (Q_{std}) during the sampling period. If the sampler has a continuous flow rate recorder, determine the average indicated flow rate (I) for the sampling period from the recorder trace. Express I with regard to the type of flow rate measuring device used and the method of correcting sample air volumes for ambient temperature and barometric pressure by using the formulas of Table 4-5. Use the resulting value to determine Q_{std}, either by referring to a graph of the calibration curve for the sampler flow rate measuring device or by calculating Q_{std} using the following equation:

(Eq. 4-4)

$$Q_{std} = \frac{\textit{Expressed value of } I - b}{m}$$

Where:

Q_{std} = *standard volumetric flow rate*, std m^3/min

I = *indicated flow rate*

b = *y-intercept of calibration curve for sampler flow rate measurement device*

m = *slope of calibration curve for sampler flow rate measurement device*

If the sampler does not have a continuous flow rate recorder, express the initial and final indicated flow rates (I) with regard to the type of flow rate measuring device used and the method for correcting sample air volumes for ambient temperature and barometric pressure using the formulas of Table 4-5. Use the resulting values to determine the initial and final sampling standard flow rates (Q_{std}) either by referring to a graph of the calibration curve for the sampler's flow rate measuring device or by calculating initial and final Q_{std} using Equation 4-4.

Table 4-5. Formulas for expressing indicated sampling flow rates.

Type of sampler flow rate measuring device	Expression	
	For actual pressure (P_2) and temperature (T_2) corrections	For use when geographic average barometric pressure and seasonal average temperature have been incorporated into the sampler calibration
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I}$
Rotameter, or orifice and pressure recorder having a square root scale*	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	I

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

After the initial and final sampling standard flow rates have been determined, calculate the average sampling standard flow rate (Q_{std}) using the following equation:

(Eq. 4-5)

$$Q_{std} = \frac{Q_I + Q_F}{2}$$

Where:

Q_{std} = *standard volumetric flow rate,* std m^3/min
Q_I = *initial sampling standard flow rate,* std m^3/min
Q_F = *final sampling standard flow rate,* std m^3/min.

22. Calculate the total air volume sampled using the following equation:

(Eq. 4-6)

$$V = Q_{std} \times t$$

Where:

V = *total air volume sampled,* std m^3
Q_{std} = *average sampling standard flow rate,* std m^3/min
t = *sampling time,* min.

23. Calculate and report the particulate matter concentration using the following equation:

(Eq. 4-7)

$$TSP = \frac{(W_f - W_i)10^6}{V}$$

Where:

TSP = *mass concentration of total suspended particulate matter*, µg/std m^3
W_i = *initial weight of clean filter*, g
W_f = *final weight of exposed filter*, g
V = *air volume sampled*, std m^3
10^6 = *conversion of* g *to* µg.

24. If desired, the actual particulate matter concentration can be calculated as follows:

(Eq. 4-8)

$$(TSP)_{act} = TSP(P_{act} / P_{std})(T_{std} / T_{act})$$

Where:

$(TSP)_{act}$ = *actual concentration at field conditions*, µg/m^3
TSP = *concentration at standard conditions*, µg/std m^3
P_{act} = *average barometric pressure at the field during sampling period*, mm Hg
P_{std} = 760 mm Hg (or 101 kPa)
T_{act} = *average ambient temperature at the field during the sampling period*, K
T_{std} = 298 K.

Sample Problems

Problem 1: High Volume Sampling

Determine the total suspended particulate matter (TSP) concentration at actual sampling conditions from the following sampling and analysis data.

Mass of filter before sampling – 3.182 g
Mass of filter after sampling – 3.455 g
Ambient temperature – 20° C or 293 K
Ambient pressure – 740 mm Hg
Starting flow rate – 1.70 m^3/min.
Ending flow rate – 1.41 m^3/min
Sampling period – 24 hours.

Solution

Q_{act} = Average sampling flow rate at field sampling conditions =

$$\frac{\text{Initial actual flow rate + Final actual flow rate}}{2}$$

$$Q_{act} = \frac{1.70\ m^3/min + 1.41\ m^3/min}{2} = 1.555\ m^3/min$$

$V_{act} = (Q_{act})$(sampling period)

$V_{act} = 1.555\ m^3/min\ (24hr)(60\ min/hr) = 2239.2\ m^3$

Mass of TSP collected = 3.455 g − 3.182 g = 0.273 g (10^6 μg/g) = 273.000 μg

TSP_{act} concentration = Mass of TSP/V_{act}

$TSP_{act} = 273{,}000\ \mu g/2239.2\ m^3$

TSP_{act} concentration = 122 μg/m^3

Problem 2: High Volume Sampling

What is the TSP concentration at standard conditions?

Solution

$TSP_{std} = TSP_{act}\ (P_{std}/P_{act})\ (T_{act}/T_{std})$

$TSP_{std} = 122\ \mu g/m^3\ (760\ mm/740\ mm)\ (293\ K/298\ K)$

$TSP_{std} = 123\ \mu g/m^3$

Problem 3: High Volume Sampling

The initial standard flow rate of a high-volume total suspended particulate (TSP) matter sampler was 38 ft^3/min and the final flow rate was 36 ft^3/min. The sampling period was 23 hours and the atmospheric pressure was 740 mm Hg and 20 °C. The weight of the filter before sampling was 4.5550 g and the weight after sampling was 4.6850 g. What is the TSP concentration in μg/m^3 at standard conditions of 760 mm Hg and 25 °C? Note that 1 m^3/min is equal to 35.3144 ft^3/min.

Solution

Sampling period = 23 hrs × 60 min/hr = 1,380 min

Q_{act} = average flow rate at field sampling conditions

$$Q_{act} = \frac{38\frac{ft^3}{min} + 36\frac{ft^3}{min}}{2} = \frac{37\,ft^3}{min}$$

$$Q_{act} = 37\frac{ft^3}{min} \times \frac{1\,m^3}{35.3144\,ft^3} = 1.05\,m^3/min$$

Mass = Final weight - initial (tare) weight

$$\text{Mass }(\mu g) = (4.6850\,g - 4.5550\,g) \times 10^6\,\frac{\mu g}{g} = 130{,}000\,\mu g$$

$V_{act} = (Q_{act})(\text{sampling period})$

$$V_{act} = 1.05\frac{m^3}{min} \times 1{,}380\,min = 1{,}449\,m^3$$

$V_{std} = V_{act}\,(P_{act}/P_{std})(T_{std}/T_{act})$

$$V_{std} = 1{,}449\,m^3\left(\frac{740\,mm}{760\,mm}\right)\left(\frac{298\,K}{293\,K}\right) = 1{,}435\,m^3$$

TSP_{std} concentration = $\mu g/V_{std}$

$$TSP_{std}\text{ concentration} = \frac{130{,}000\,\mu g}{1{,}435\,m^3} = 90.59\,\mu g/m^3 \text{ or } 90.6\,\mu g/m^3$$

Analysis of High-volume Filters

Filters from hi-vol samplers can be analyzed much more thoroughly than by just simple mass concentration determination. After a filter has been weighed, it can be cut into sections for subsequent analysis. Destructive extraction techniques that might be used in preparing the filter for analysis are organic solvent extraction, acid extraction, and aqueous extraction. To determine the amount of organic aerosol present in the ambient air, organics on a portion of a filter can be extracted with an organic solvent, such as chloroform, in conjunction with a Soxhlet extractor. The resulting organic fraction can then be analyzed by appropriate techniques, such as infrared or ultraviolet spectrometry. Metals can be extracted from the particulate matter of a portion of a high-volume filter by placing the filter portion in an acid solution. Any filter matter that disintegrates in the acid can be removed by centrifugation. After extraction, the resulting soluble metal solution can be analyzed by a number of methods, including atomic absorption spectrophotometry, atomic emission spectroscopy, polarography, and inductively coupled plasma emission spectroscopy. Water-soluble species (such as sulfates and nitrates) of the particulate matter of a high-volume filter can be extracted using deionized, distilled water. The resulting solution can then be analyzed using methods such as ultraviolet or visible spectrometry.

Sometimes it is necessary that the filter remain intact after analysis. Nondestructive analytical techniques, such as neutron activation x-ray fluorescence, and electron or optical microscopy, can be used in these cases.

The above-mentioned analyses are not required for all filters. Therefore, it must be carefully decided what analyses should be performed on individual filters.

Sampling Accuracy and Precision

The limits of accuracy and precision of any sampling method must be understood for proper interpretation of data obtained using that method. Factors influencing the accuracy and precision of high-volume sampling include sampler operating characteristics, accuracy of calibration, filter characteristics, location of sampler, nature and concentration of particulate matter and gases in the air being sampled, and the humidity of the air.

Accuracy

As defined in Section 3 of Appendix A of 40 CFR Part 58, accuracy is the degree of agreement between an observed value and an accepted reference value. It includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. The accuracy of the particulate measurements can be affected by several known inherent sources of error in the sampling of particulate matter. These include airflow variation, air volume measurement, loss of volatiles, artifacts, humidity, filter handling and nonsampled particulate matter.

Airflow variation. The weight of material collected on the filter represents the integrated sum of the product of the instantaneous flow rate times the instantaneous particle concentration. Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period. The error resulting from a nonconstant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration. Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period.

The most popular method of constant flow rate regulation uses a constant temperature thermal anemometer sensor to measure mass flow in the throat of the high-volume sampler's filter adapter (sampling head). Electronic feedback circuitry adjusts the sampler's motor speed to maintain a constant mass flow. Since mass flow is controlled, the volumetric flow rate can be maintained at standard conditions. Thus, flow variations caused by temperature, pressure, line voltage, and particulate matter loading are all compensated for by this system. The system can be retro-fitted to any high-volume sampler (Figure 4-44).

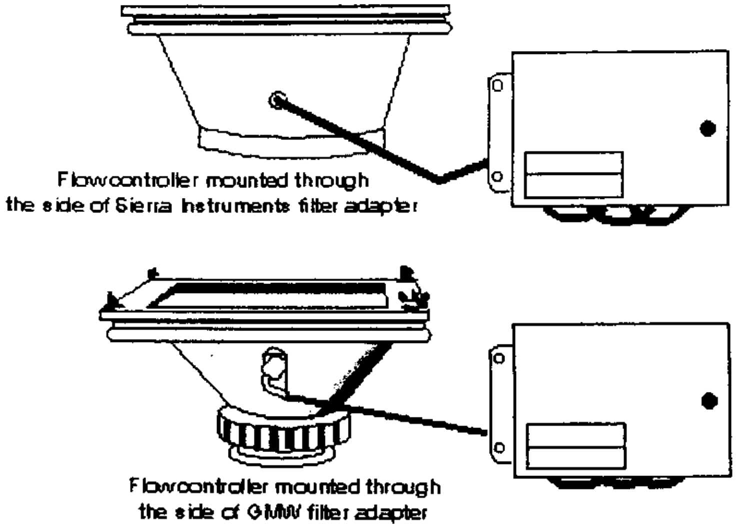


Figure 4-44. Constant flow controllers.

Air volume measurement. If the flow rate changes substantially or nonuniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the presampling and postsampling flow rates. Greater air volume measurement accuracy may be achieved by equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period or by using a calibrated, continuous flow rate recording device to record the actual flow rate during the sampling period and integrating the flow rate over the period.

A high-volume sampler can be modified to provide a continuous recording of flow rate by installing a fixed orifice in the sampler's motor housing and using a pressure transducer to monitor air flow through the sampler and a chart recorder to record the air flow. Such modified high-volume samplers are commercially available (Figure 4-45).

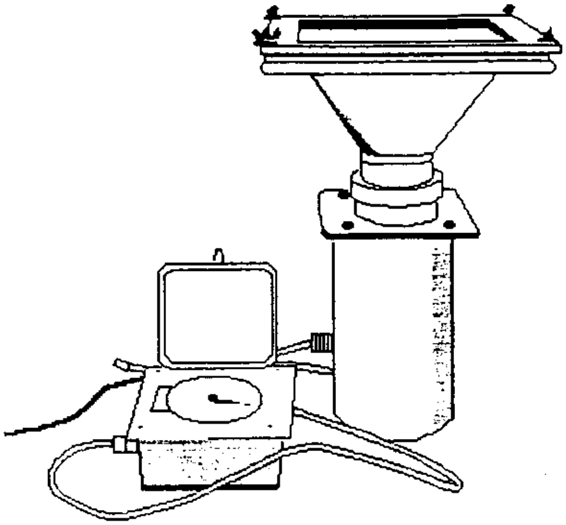


Figure 4-45. Hi-vol sampler modified for continuous recording of flow rate.

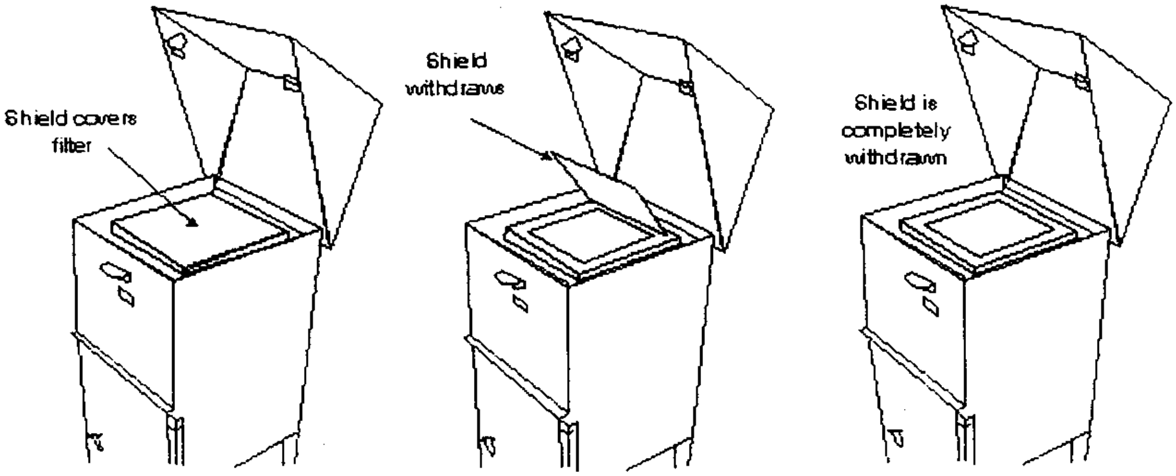
Loss of volatiles. Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the postsampling weighing. Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as practical.

Artifact particulate matter. Artifact particulate matter can be formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher than true TSP determination. This effect usually occurs early in the sampling period and is a function of the filter pH and the presence of acid gases. It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant when relatively small particulate matter weights are encountered.

Humidity. Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can absorb moisture. The moisture conditioning procedure minimizes, but may not completely eliminate, error due to moisture.

Filter handling. Careful handling of the filter between the presampling and postsampling weighings is necessary to avoid error due to loss of fibers or particles from the filter. A filter cartridge used to protect the filter can minimize handling errors.

Nonsampled particulate matter. Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. Errors from this source can be minimized by using an automatic mechanical device that keeps the filter covered during nonsampling periods (Figure 4-46), or by timely installation and retrieval of filters to minimize the nonsampling periods prior to and following sampler operation.



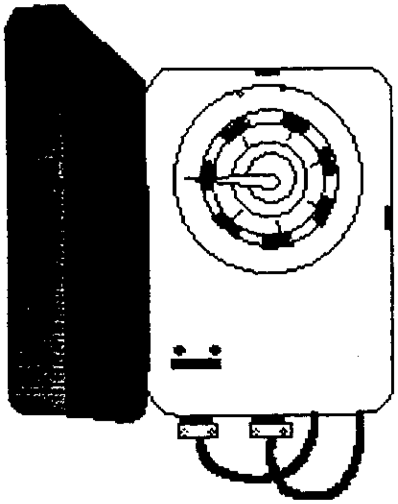
Shield covers hi-vol filter when not sampling, thus eliminating nonsampled particulate matter.

Just before sampling, shield automatically withdraws.

Shield does not obstruct air flow during sampling.

Figure 4-46. Modification for minimizing sampling error caused by nonsampled particulate matter.

Timing errors. Samplers are normally controlled by clock timers (Figure 4-47a) set to start and stop the sampler at midnight. Errors in the nominal 1440-min sampling period may result from a power interruption during the sampling period or from a discrepancy between the start or stop time recorded on the filter information record and the actual start or stop time of the sampler. Such discrepancies may be caused by poor resolution of the timer set points, timer error due to power interruption, missetting of the timer, or timer malfunction. In general, digital electronic timers have much better set point resolution than mechanical timers, but require a battery back-up system to maintain continuity of operation after a power interruption. A continuous flow recorder or elapsed time meter (Figure 4-47b) provides an indication of the sampler run-time, as well as indication of any power interruption during the sampling period.



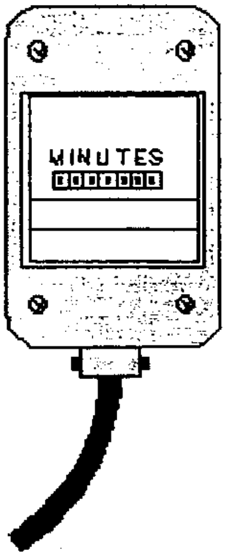


Figure 4-47a. Seven-day mechanical clock timer. Figure 4-47b. Elapsed time meter.

Recirculation of sampler exhaust. Under stagnant wind conditions, sampler exhaust air can be resampled. Resampling does not appear to affect the TSP measurement substantially, but may result in increased carbon and copper in the collected sample caused by reentrainment of particles from the sampler's motor. This problem can be reduced by ducting the exhaust air well away (at least 40 cm), preferably downwind, from the sampler's air inlet.

Wind speed and direction sensitivity. The rectangular, gabled roof of the high-volume sampler causes the size of the particles collected by the sampler to vary with wind speed and direction.

Independent performance audits should be conducted to estimate the accuracies of the flow rate calibrations of high-volume samplers. A Reference Flow device (ReF device), developed by the National Institute of Science and Technology (NIST) under contract to the U.S. EPA, can be used for the performance audits (Figure 4-48). The ReF device is a modified orifice with five resistance plates that can be mounted directly to the filter adapters of high-volume samplers. The resistance plates are used to produce known flow rates of air through the samplers. However, if high-volume samplers equipped with constant flow controllers are being audited, a clean filter should be used in place of the resistance plates, because resistance plates may cause abnormal flow patterns around the controller flow sensors, thus affecting the performance of the flow controllers.

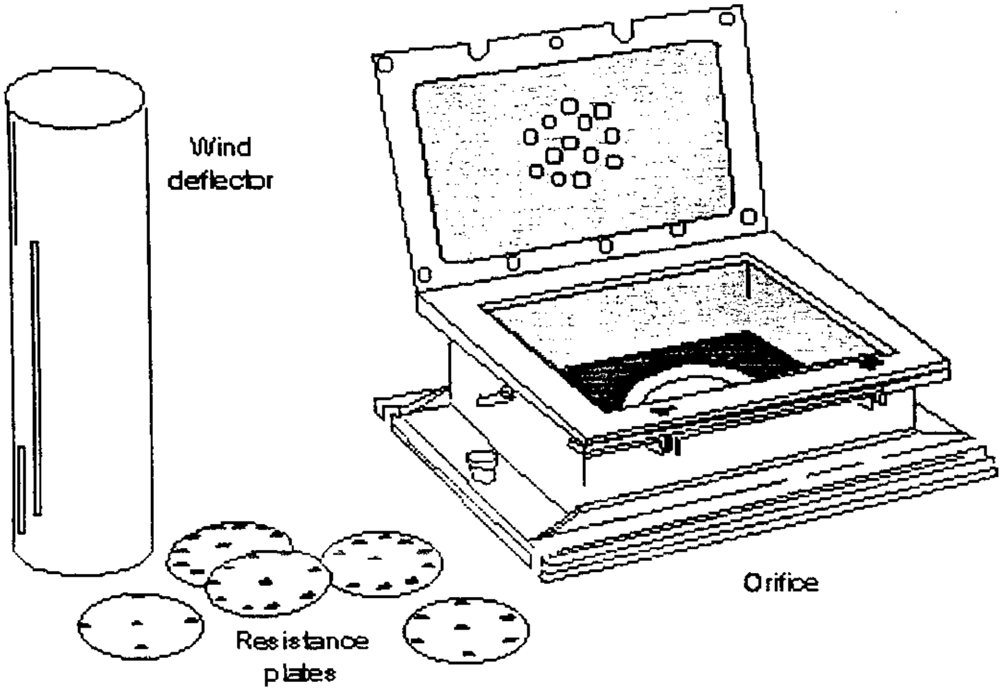


Figure 4-48. U.S. EPA Reference Flow device (ReF device).

Precision

Precision can be defined as the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of standard deviation. Collaborative testing has shown that the high-volume sampling method for total suspended particulate matter is capable of achieving a relative standard deviation (coefficient of variation) for single analyst precision (repeatability) of 3.0% and a relative standard deviation for interlaboratory precision (reproducibility) of 3.7%. However, collaborative tests are often performed under ideal conditions. Therefore, collocated samplers should be used to estimate precision under field conditions for high-volume samplers of air monitoring networks.

Maintenance

The high-volume sampler requires less maintenance than most air monitoring instruments, but a certain level of preventive maintenance is needed to ensure dependable operation. The sampler motor maintenance consists of periodic motor brush replacement (if the sampler does not use a brushless motor), usually after 400 to 500 hours of operation at normal line voltage of 115 volts. The life of these brushes can be extended from 400 to 500 hours to approximately 600 to 750 hours by using a "step-down" transformer (Figure 4-49). Worn brushes, if not replaced, will result in damage to the motor. The flow rate measuring device should be cleaned whenever foreign material is detected in the device or the device behaves erratically. The faceplate gasket, which seals the filter to the filter adapter, will deteriorate in time and will need periodic replacement.

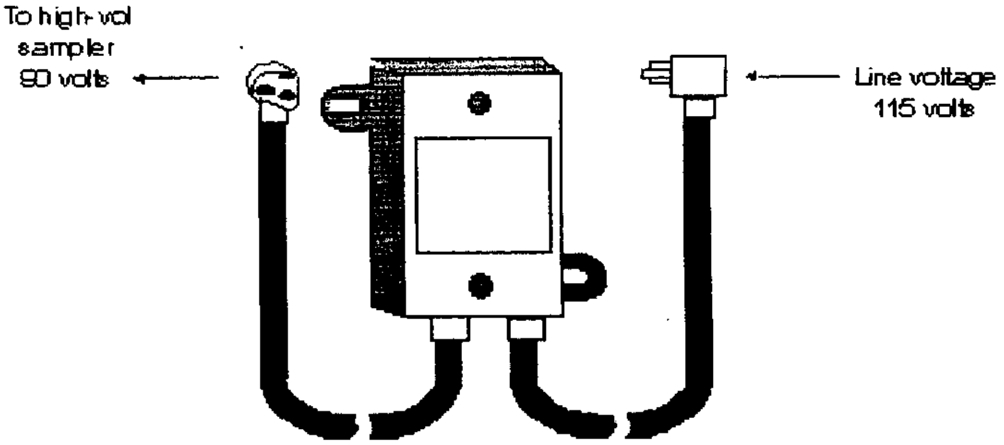


Figure 4-49. "Step-down" transformer.

Deterioration is indicated by indistinct margin patterns around the edge of the filter after sampling (Figure 4-36). New filters can be secured with rubber contact cement or double-side adhesive tape. There are also two motor gaskets that should be replaced when worn.

Any leaks in the housing should be repaired, especially openings in the roof or in the filter adapter housing. The inside and outside of the shelter must be kept clean and free of accumulated debris, as this material might be drawn onto the filter. Time indicators and 24-hour timers must also be kept operational along with any power cords and electrical connections. Plastic tubing used in the indication of flow rate must also be kept clean.

Samplers must be recalibrated after any major maintenance. This includes replacement of the motor or motor brushes any time the flow rate measuring device is replaced or repaired (including cleaning), or any time tubing is replaced or cleaned. If motor brushes are replaced, the motor must be operated against a flow resistance that is equal to a clean filter for several hours in order to properly seat the brushes against the motor's armature before the sampler can be recalibrated. Table 4-6 summarizes major maintenance activities.

Table 4-6. High volume sampler maintenance activities.

Equipment	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Sampler motor	400 h of motor brush operation; no malfunction	Visually check upon receipt and after each 400 h of operation	Replace motor brushes; other maintenance as indicated
Faceplate gasket	No leaks at the filter seal	Visually check after each sampling period	Replace the gasket
Flow rate measuring device	No foreign materials; stable operation	Visually check for each sample	Clean; replace if damaged
Motor gaskets	Leak-free fit	Visually check after each 400 h of operation	Replace gaskets
Filter adapter (sampling head)	No leaks	Visually check after each 200 h of operation	Replace filter adapter

FRM for the Determination of Particulate Matter as PM_{10} in the Atmosphere

Applicability

The method for PM_{10} described here is provided in Appendix M of 40 CFR Part 50. This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 µm (PM_{10}) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter specified in Sec. 50.7 of this chapter. The measurement process is nondestructive, and the PM_{10} sample can be subjected to subsequent physical or chemical analyses. Quality assurance procedures and guidance are provided in 40 CFR Part 58, Appendices A and B and in Volume II of the QA Handbook.

Principle

An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM_{10} size range (Figures 4-50 and 4-51). Each size fraction in the PM_{10} size range is then collected on a separate filter over the specified sampling period. The particle size discrimination characteristics (sampling effectiveness and 50% cutpoint) of the sampler inlet are prescribed as performance specifications in 40 CFR Part 53. Two types of samplers that meet EPA FRM designation for PM_{10} requirements are the high-volume (1000 L/min) PM_{10} sampler and the dichotomous sampler (16.7 L/min).
Each filter (or both filters, in the case of the dichotomous sampler) is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM_{10}. The total volume of air sampled, measured at the actual ambient temperature and pressure, is determined from the measured flow rate and the sampling

time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of collected particles in the PM_{10} size range divided by the volume of air sampled, and is expressed in micrograms per cubic meter.

A method based on this principle will be considered a FRM only if (a) the associated sampler meets the requirements specified in this appendix and the requirements in Part 53 of this chapter, and (b) the method has been designated as a FRM in accordance with Part 53 of this chapter.

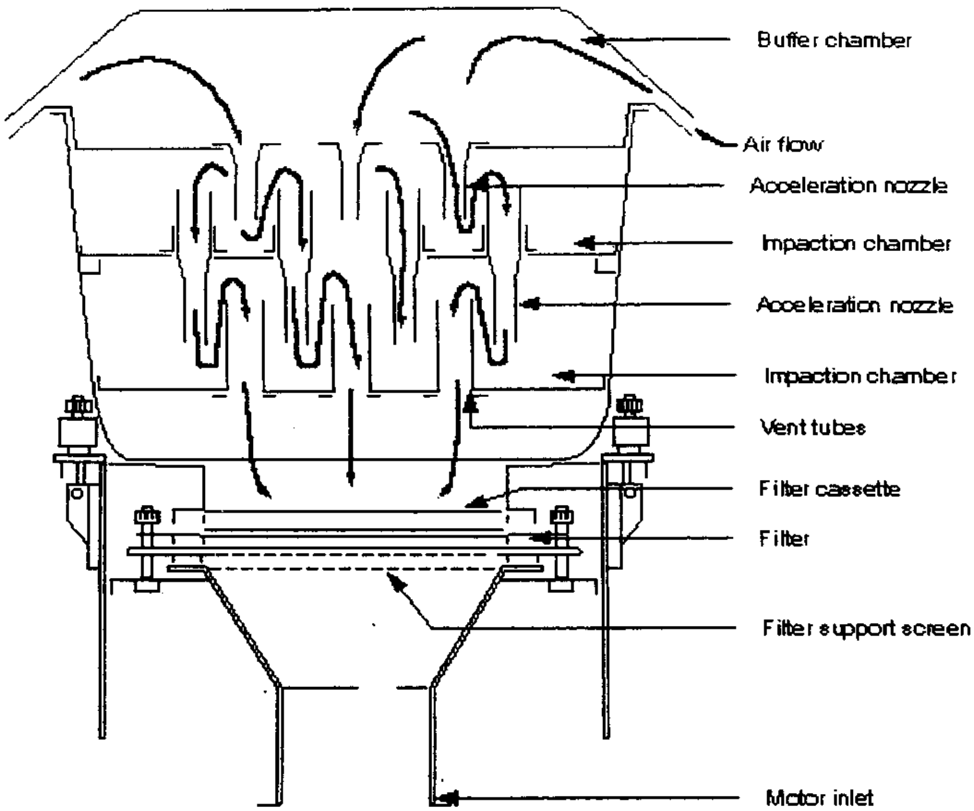


Figure 4-50. Schematic diagram of an impaction inlet.

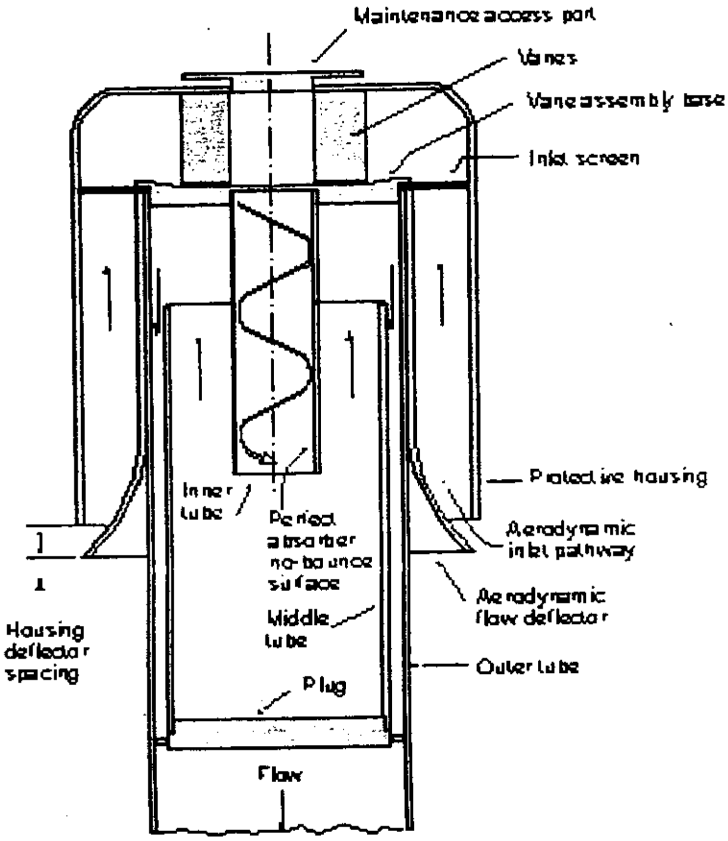


Figure 4-51. Schematic diagram of a cyclonic inlet.

Range

The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading, beyond which the sampler no longer maintains the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour PM_{10} mass concentrations of at least 300 µg/std m^3 while maintaining the operating flow rate within the specified limits.

Precision

State and Local Air Monitoring Stations (SLAMS) measurement system precision. Appendix A of 40 CFR Part 58 addresses the QA/QC requirements applicable to SLAMS and includes the provision that all ambient monitoring methods or analyzers used in SLAMS shall be tested periodically to quantitatively assess the quality of the SLAMS data. The terminology used to define the quality or uncertainty of the SLAMS measurements include precision, accuracy, and bias. In Appendix A, Section 3.01, precision is defined as the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of the standard deviation. The SLAMS precision goal for PM_{10} is ± 15% (QA Handbook, Volume II, Section 2.011).

Estimates of the precision of SLAMS automated methods for PM_{10} are made based on checks of the operational flow rate of each analyzer using a flow rate transfer standard. These checks must be conducted at least once every 2 weeks. For networks using manual methods for PM_{10}, precision is determined using collocated samplers at selected sites. One of the samplers is designated as the primary sampler whose data will be used to report air quality for the site, and the other sampler is designated as the duplicate sampler. Estimates of the precision are calculated according to the procedures specified in Section 5 of Appendix A of Part 58.

Initial operational precision of a FRM sampler. In addition to the Part 58 precision requirements associated with SLAMS PM_{10} measurements, there are specifications in Appendix J of 40 CFR Part 50 which address the initial operational precision of a candidate FRM sampler. These specifications state that the precision of PM_{10} samplers must be 5 $\mu g/m^3$ for PM_{10} concentrations below 80 $\mu g/m^3$ and 7% for PM_{10} concentrations above 80 $\mu g/m^3$. The detailed and lengthy tests to determine whether or not a candidate sampler complies with the precision specifications are included in 40 CFR Part 53. Part 53 contains the provisions for EPA designation of reference and equivalent methods for candidate PM_{10} monitors and all other candidate criteria pollutant monitors.

Accuracy

SLAMS measurement system accuracy. Appendix A of Part 58 defines accuracy as the degree of agreement between an observed value and an acceptable reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. The accuracy goal for SLAMS PM_{10} measurements is ± 20% (QA Handbook, Volume II, Section 3.01). The accuracy of automated PM_{10} analyzers is determined by conducting quarterly audits of at least 25% of the SLAMS analyzers so that each analyzer is audited at least once per year. The audit is performed by measuring the analyzer's normal operating flow rate, using a certified flow rate transfer standard. The percent difference between the sampler's indicated flow rate and the transfer standard flow rate is used to calculate accuracy according to the procedures specified in section 5.4.1 of Appendix A of Part 58.

Initial operational accuracy of a FRM sampler. It is difficult to define the absolute accuracy of PM_{10} samplers because of the variation in the size of atmospheric particles and the variation in concentration with particle size. Therefore, 40 CFR Part 53 includes the specification for the sampling effectiveness of PM_{10} samplers that are candidates for reference or equivalent method designation. This specification requires that the expected mass concentration calculated for a candidate PM_{10} sampler, when sampling a specified particle size distribution. be within ± 10% of that calculated for an ideal sampler whose sampling effectiveness is explicitly specified. In addition, the particle size for 50% sampling effectiveness is required to be 10 ± 0.5 μm. Other accuracy specifications for reference or equivalent method designation are also prescribed in Part 53. These specifications are related to flow measurement and calibration, filter media, analytical weighing procedures, and artifacts.

Potential Sources of Error

There are a number of possible sources of error in measuring PM_{10} concentration levels in ambient air. These include volatile particles, artifacts, humidity, filter handling, flow rate variation, and air volume determination. The FRM also addresses the configuration of the sampler, filter calibration, operational procedure, and concentration calculation.

Volatile particles. Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the postsampling weighing. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses.

Artifacts. Positive errors in PM_{10} concentration measurements may result from retention of gaseous species on filters. Such errors include the retention of sulfur dioxide and nitric acid. Retention of sulfur dioxide on filters, followed by oxidation to sulfate, is referred to as artifact sulfate formation, a phenomenon which increases with increasing filter alkalinity. Little or no artifact sulfate formation should occur using filters that meet the alkalinity specification in section 7.2.4 of Appendix M of 40 CFR Part 50. Artifact nitrate formation, resulting primarily from retention of nitric acid, occurs to varying degrees on many filter types, including glass fiber, cellulose ester, and many quartz fiber filters. Loss of true atmospheric particulate nitrate during or following sampling may also occur due to dissociation or chemical reaction. This phenomenon has been observed on Teflon® filters and inferred for quartz fiber filters. The magnitude of nitrate artifact errors in PM_{10} mass concentration measurements will vary with location and ambient temperature; however, for most sampling locations, these errors are expected to be small.

Humidity. The effects of ambient humidity on the sample are unavoidable. The filter equilibration procedure in section 9.0 of Appendix M of 40 CFR Part 50 is designed to minimize the effects of moisture on the filter medium.

Filter handling. Careful handling of filters between presampling and postsampling weighings is necessary to avoid errors due to damaged filters or loss of collected particles from the filters. Use of a filter cartridge or cassette may reduce the magnitude of these errors.

Flow rate variation. Variations in the sampler's operating flow rate may alter the particle size discrimination characteristics of the sampler inlet. The magnitude of this error will depend on the sensitivity of the inlet to variations in flow rate and on the particle distribution in the atmosphere during the sampling period. The use of a flow control device is required to minimize this error.

Air volume determination. Errors in the air volume determination may result from errors in the flow rate and/or sampling time measurements. The flow control device serves to minimize errors in the flow rate determination, and an elapsed time meter is required to minimize the error in the sampling time measurement.

Apparatus

PM$_{10}$ Sampler

The sampler is designed to

a. draw the air sample into the sampler inlet and through the particle collection filter at a uniform face velocity.

b. hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter.

c. allow the filter to be installed and removed conveniently.

d. protect the filter and sampler from precipitation and prevent insects and other debris from being sampled.

e. minimize air leaks that would cause error in the measurement of the air volume passing through the filter.

f. discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air.

g. minimize the collection of dust from the supporting surface.

Filters

Filter Medium

No commercially available filter medium is ideal in all respects for all PM$_{10}$ samplers. The user's goals in sampling determine the relative importance of various filter characteristics (e.g., cost, ease of handling, physical and chemical characteristics, etc.) and, consequently, determine the choice among acceptable filters. Furthermore, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler's flow control device. However, samplers equipped with automatic filter-changing mechanisms may allow use of these types of filters. Filter specifications are provided in the FRM and address collection efficiency, integrity, and alkalinity. The filter medium collection efficiency must be greater than 99% as measured by the dioctyl phthalate (DOP) test American Society of Testing Materials (ASTM) 2986. This test requires the use of 0.3 µm particles at the sampler's operating face velocity. The integrity of the filter medium is a measure of the filter's mass stability. It is measured as the PM$_{10}$ concentration corresponding to the average difference between the initial and the final weights of a random sample of test filters that are weighed and handled under actual or simulated sampling conditions, but have no air sample passed through them. The integrity specification is ± 5 $\mu g/m^3$, assuming the sampler is operating for 24-hours at its normal sampler flow rate. The alkalinity requirement of the filter medium is less than 25 microequivalents/gram of filter as measured by the alkalinity procedure specified in Appendix A of the QA Handbook, Volume II, Part II.

The filter conditioning environment must control the temperature to ± 3°C and the relative humidity to ± 5%. Other topics covered in the FRM include the analytical balance calibration procedure, sampler operational procedure, and sample maintenance.

Calculations

Calculate the total volume of air sampled as

(Eq. 4-9) $$V_{act} = Q_a t$$

Where:

V_{act} = *total air sampled at ambient temperature and pressure*, m^3

Q_a = *average sample flow rate at ambient temperature and pressure*, m^3/min

t = *sampling time*, min.

Calculate the PM_{10} concentration as:

(Eq. 4-10) $$PM_{10} = \frac{(W_f - W_i) \times 10^6}{V_{std}}$$

Where:

PM_{10} = *mass concentration of* PM_{10}, $\mu g/m^3$

W_f, W_i = *final and initial weights of filter collecting* PM_{10} *particles*, in g

10^6 = *conversion of* g *to* µg. *(Use* 10^3 *to convert mg to* µg.)

V_{std} = *volume at EPA standard temperature and pressure*

Note: If more than one size fraction in the PM_{10} size range is collected by the sampler, the sum of the net weight gain by each collection filter $[\Sigma(W_f - W_i)]$ is used to calculate the PM_{10} mass concentration.

Sample Problems

Problem 1: PM_{10} Sampling

A dichotomous sampler was used for measuring PM_{10} concentrations in the atmosphere. Two filter weights were obtained: one for fine particulates and one for coarse particulates. In measuring PM_{10} concentrations with a dichotomous sampler, the two filter weights are combined to determine the PM_{10} concentrations. In this sampling situation, the final gross weight of the fine particles was 101.080 mg with a tare weight of 100.100 mg. The final gross weight of the coarse particles was 104.100 mg with a tare weight of 103.175. The average flow rate for the 23-hour sampling period was 16.80 L/min. The average atmospheric pressure was 745 mm Hg, and the average temperature was 23.5 °C. What is the PM_{10} concentration for this sample required as $\mu g/m^3$ at actual atmospheric concentration?

Solution

Sampling period = 23 hrs × 60 min/hr = 1,380 min

$V_{act} = Q_a t$

$V_{act} = 16.8\ L/min \times 1,380\ min = 23,184\ L \times m^3/1000L = 23.18\ m^3$

$$PM_{10} = \frac{(W_f - W_i) \times 10^6}{V_{act}}$$

$$PM_{10} = \frac{(101.080\text{mg} - 100.100\text{ mg}) + (104.100\text{ mg} - 103.175\text{ mg}) \times 10^3}{V_{act}}$$

Mass = Final weight -initial (tare) weight

Mass of fine particles = 101.080 mg -100.100 mg = 0.98 mg × 10^3 µg/mg

Mass of fine particles = 980 µg

Mass of coarse particles = 104.100 mg - 103.175 mg = 0.925 mg × 10^3 µg/mg = 925 µg

Total mass of particles = 980 µg + 925 µg = 1,905 µg

PM_{10} Concentration$_{act}$ = µg/V_{act} = 1,905 µg/ 23.18 m^3 = 82.18 µg/m^3 or 82.2 µg/m^3

Problem 2: PM_{10} Sampling

The gross weight of the fine particulate filter from a PM_{10} dichotomous sampler was 0.990660 g with a tare weight of 0.990100 g. The gross weight and tare weight of the coarse particulate filter were the same as the fines. The total volume sampled at actual atmospheric conditions of 750 mm Hg and 23 °C was 24,330 L. What is the calculated PM_{10} concentration in μg/m3 at actual atmospheric conditions?

Solution

$V_{act} = 24.330 \text{ L} \times \text{m}^3/1000 \text{ L} = 24.33 \text{ m}^3$

$$PM_{10} = \frac{(W_f - W_i) \times 10^6}{V_{std}}$$

$$PM_{10} = \frac{2\,(0.990660\text{g} - 0.990100\text{g}) \times 10^6}{(24.330\text{ L})(\text{m}^3 / 1000\text{ L})} = \frac{1120\text{ mg}}{24.33\text{ m}^3} = 46.03\ \mu\text{g/m}^3$$

Mass = Final weight - initial (tare) weight

Mass fine particles = 0.990660 g - 0.990100 g = 0.000560 g

Mass fine particles = 0.000560×10^6 μg/g = 560 μg

Mass of coarse particles is the same, or 560 μg

Total mass of fine and coarse = 1.120 μg

PM_{10} Concentration$_{act}$ = Total mass/V_{act}

PM_{10} Concentration$_{act}$ = 1,120 μg/24.33 m^3 = 46.03 μg/m^3 or 46.0 μg/m^3

FRM For the Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere

Applicability

This method provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 µm ($PM_{2.5}$) in ambient air over a 24-hour period. The measurements provide data to determine whether the primary and secondary national ambient air quality standards for fine particulate matter specified in § 50.6 of Part 50 are met. The measurement process is considered to be nondestructive, and the $PM_{2.5}$ sample obtained can be subjected to subsequent physical or chemical analyses. Quality assessment procedures are provided in Part 58. Appendix A of 40 CFR.

Principle

An electrically powered air sampler draws a 24-hour ambient air sample at a constant volumetric flow rate into a specially shaped inlet (Figure 4-13) and through an inertial particle size separator (impactor). The suspended particulate matter in the $PM_{2.5}$ size range is separated from the larger particles (Figure 4-14) and then collected on a polytetrafluoroethylene (PTFE) filter. Each filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net gain in weight of $PM_{2.5}$. The total volume of air sampled at actual temperature and pressure conditions is calculated from the measured flow rate and sampling time. The mass concentration of $PM_{2.5}$ collected, in micrograms per cubic meter ($\mu g/m^3$), is calculated by dividing the net gain in weight by the total volume of air sampled.

$PM_{2.5}$ Measurement Range

Lower concentration limit. The lower detection limit of the mass concentration measurement range is estimated to be approximately 2 $\mu g/m^3$, based on noted mass changes in field blanks in conjunction with the 24 m^3 nominal total air sample volume specified for the 24 hour sample.

Upper concentration limit. The upper limit of the mass concentration range is determined by the filter mass loading, beyond which the sampler can no longer maintain the operating flow rate within specified limits (10% of 16.67 L) due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, the individual filter used, the capacity of the sampler flow rate control system, and perhaps other factors. Nevertheless, all samplers are estimated to be capable of measuring 24-hour $PM_{2.5}$ mass concentrations of at least 200 $\mu g/m^3$ while maintaining the operating flow rate within the specified limits.

Sample period. The required sample period for $PM_{2.5}$ concentration measurements by this method is 1380 to 1500 minutes (23 to 25 hours).

Precision

SLAMS measurement system precision. As stated in Appendix A, Section 3.01, precision is defined as the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of the standard deviation. A data quality objective of 10% coefficient of variation (CV) or better has been established for the SLAMS operational precision of $PM_{2.5}$ monitoring data (Section 5.0, Appendix L, 40 CFR Part 50).

Precision measurements using collocated procedures for automated and manual methods of $PM_{2.5}$. Section 3.5 of Appendix A describes the requirements for measuring the precision of automated and manual methods for $PM_{2.5}$ using collocated samplers. The requirements include: (1) SLAMS operators must report the number or percent of collocated samplers per reporting organization, (2) an EPA FRM must be collocated with a monitor having the same EPA FRM designation, (3) for monitors designated as an EPA FEM, 50% of the designated monitors shall be collocated with a monitor having the same designation and 50% shall be collocated with an FRM monitor, and (4) during the initial deployment of the SLAMS network, collocated sites should be in areas likely to be in violation of the NAAQS.

For each pair of collocated samplers at the selected sites, one of the samplers is designated as the primary sampler for the site, and the other sampler is designated as the duplicate sampler. The duplicate sampler must be operated concurrently with the primary sampler and on a one-in-six day sampling schedule. Estimates of the precision are calculated using the procedures specified in Section 5.5.2 of Appendix A of Part 58.

Initial operational precision of a FRM sampler. In addition to the requirements associated with SLAMS $PM_{2.5}$ precision measurements, there are tests in Section 53.58 of 40 CFR Part 53 which are intended to determine the operational precision of candidate $PM_{2.5}$ samplers during a minimum of 10 days of field operation using three collocated test samplers. In this Section, precision is defined as the standard deviation or relative standard deviation of a set of $PM_{2.5}$ measurements obtained concurrently with three or more collocated samplers in actual ambient air field operation. Calculations to determine whether or not the candidate method passes the precision test are specified in Section 53.58.

Accuracy and Bias

SLAMS measurement system accuracy and bias. Appendix A of Part 58 defines accuracy as the degree of agreement between an observed value and an acceptable reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations. An accuracy goal for the $PM_{2.5}$ sampler's flow rate has been specified in Section 2.12 of the QA Handbook, Vol. II, Part II. The goal for accuracy of the sampler flow rate is to be within ± 2% of the value indicated by the audit device (during multipoint verification/calibration), or ± 4% (during one-point verification checks and audits), and to be within ± 2% of the sampler's design flow rate of 16.67 L/min (40 CFR Part 50 Appendix L, Section 9.2.6).

Automated methods accuracy. Estimates of the accuracy of the flow rate SLAMS automated methods for $PM_{2.5}$ are made based on checks of the operational flow rate of each analyzer using a certified flow rate transfer standard. These checks must be conducted at least once every 2 weeks and a randomization with respect to time of day, day of week, and routine service and adjustments is encouraged. An alternative procedure that does not use an external flow rate transfer standard is permissible to obtain the flow rate data from the analyzer's internal flow meter. This alternative procedure is allowed if several conditions are met, one of which requires the flow meter to be audited with an external flow rate transfer standard at least every six months. The other conditions can be found in Section 3.5.1.1.2 of Appendix A of Part 58. For either procedure, the difference between the flow rate transfer standard and the indicated flow rate of the sampler is used to assess the accuracy of the flow rate using the calculation procedures contained in Section 5.5 of Appendix A.

Manual methods accuracy. For networks using manual sampling methods for $PM_{2.5}$, the accuracy of the sampler's flow rate is determined by auditing the flow rate of each SLAMS sampler each calendar quarter. A certified flow rate transfer standard is used for the audit. The audit flow rate and the indicated flow rate of the sampler are reported and the difference between the two is used to calculate the flow rate accuracy.

Initial operational accuracy of a FRM sampler. It is difficult to define the absolute accuracy of $PM_{2.5}$ samplers because of the variation in the size of atmospheric particles and the variation in concentration with particle size. Therefore, 40 CFR Part 53 includes the specification for the sampling effectiveness of $PM_{2.5}$ samplers that are candidates for reference or equivalent method designation. This specification requires that the expected mass concentration calculated for a candidate $PM_{2.5}$ sampler, when sampling a specified particle size distribution, be within ± 10% of that calculated for an ideal sampler whose sampling effectiveness is explicitly specified. In addition, the particle size for 50% sampling effectiveness is required to be 10 ± -0.5 μm. Other specifications for reference or equivalent method designation related to accuracy apply to flow measurement and calibration, filter media, analytical weighing procedures, and artifacts.

Measurement system bias. Bias is defined as the systematic or persistent distortion of a measurement process that causes errors in one direction. The measurement system bias goal is to be within ± 10% of the measurement obtained by an independent sampler audit. The sampler bias is assessed from the results of an independent FRM performance evaluation to be administered through the EPA Regional Offices. More details on these requirements are contained in the QA Handbook, Vol. II, Part II, Section 2.12, Subsection 13.3.

Filter for $PM_{2.5}$ Sample Collection

The filters specified in the FRM for $PM_{2.5}$ are 46.2 mm diameter filters of polytetrafluoroethylene (PTFE Teflon®), with an integral support ring made of polymethylpentene (PMP) or equivalent inert material. In addition to the type of filter material and support ring, the method includes other filter specifications such as pore size, filter thickness, maximum pressure drop, and filter weight stability. A list of the filter specifications follows.

- *Size.* Circular, 46.2 mm diameter ± 0.25 mm.
- *Medium.* Polytetrafluoroethylene (PTFE Teflon®), with integral support ring.

- *Support ring.* Polymethylpentene (PMP) or equivalent inert material. 0.38 ± 0.04 mm thick, outer diameter 46.2 mm ± 0.25 mm. and width of 3.68 mm (± 0.00, -0.51 mm).
- *Pore size.* 2 µm as measured by ASTM F 316-94.
- *Filter thickness.* 30 to 50 µm.
- *Maximum pressure drop (clean filter).* 30 cm H_20 column @ 16.67 L/min clean air flow.
- *Maximum moisture pickup.* Not more than 10 µg weight increase after 24-hour exposure to air of 40% relative humidity, relative to weight after 24-hour exposure to air of 35% relative humidity.
- *Collection efficiency.* Greater than 99.7%, as measured by the DOP test (ASTM D 2986-91) with 0.3 µm particles at the sampler's operating face velocity.
- *Filter weight stability.* Filter weight loss shall be less than 20 µg, as measured in each of the following two tests. The following conditions apply to both of these tests: Filter weight loss shall be the average difference between the initial and the final filter weights of a random sample of test filters selected from each lot prior to sale. The number of filters tested shall not be less than 0.1% of the filters of each manufacturing lot, or 10 filters, whichever is greater. The filters shall be weighed under laboratory conditions and shall have had no air sample passed through them, i.e., filter blanks. Each test procedure must include initial conditioning and weighing.

  Test for loose, surface particulate contamination. After the initial weighing, install each test filter, in turn, in a filter cassette and drop the cassette from a height of 25 cm to a flat hard surface, such as a particle-free wood bench. Repeat two times, for a total of three drop tests for each test filter. Remove the test filter from the cassette and weigh the filter. The average change in weight must be less than 20 µg.

  Test for temperature stability. After weighing each filter, place the test filters in a drying oven set at 40°C ± 2°C for not less than 48 hours. Remove, condition, and reweigh each test filter. The average change in weight must be less than 20 µg.
- *Alkalinity.* Less than 25 microequivalents/gram of filter, as measured by the guidance given in Reference 2 in Section 13.0 of this appendix.
- *Supplemental requirements.* Although not required for determination of $PM_{2.5}$ mass concentration under this FRM, additional specifications for the filter must be developed by users who intend to subject $PM_{2.5}$ filter samples to subsequent chemical analysis. These supplemental specifications include background chemical contamination of the filter and any other filter parameters that may be required by the method of chemical analysis. All such supplemental filter specifications must be compatible with and secondary to the primary filter specifications.

$PM_{2.5}$ Sampler Configuration

The sampler consists of a sample air inlet, downtube, particle size separator (impactor), filter holder assembly, air pump, flow rate control system, and a flow rate measurement device (Figure 4-52). Other required components include an ambient and filter temperature monitoring system, barometric pressure measurement system, timer, outdoor environmental enclosure, and suitable mechanical, electrical, or electronic control capabilities to meet or exceed the design and functional requirements specified in the FRM.

The sampler is specified by a combination of design and performance requirements. The components explicitly specified by design are the sample inlet, downtube, particle size separator, filter cassette, and the internal configuration of the filter holder assembly. All other aspects of the sampler are specified in terms of operational function and performance. The design of these other aspects, however, is optional, subject to acceptable operational performance. The test procedures to demonstrate compliance with the design and performance requirements are contained in Subpart E of 40 CFR Part 53.

Designated Methods for $PM_{2.5}$

As of January 4, 1999, seven methods have been designated as EPA FRMs for measuring mass concentrations of particulate matter as $PM_{2.5}$ in the ambient air. A list of these methods follows:

RFPS-0498-116, "BGI Incorporated Model PQ200$PM_{2.5}$ Ambient Fine Particle Sampler."
RFPS-0498-116, "BGI Incorporated Model PQ200A$PM_{2.5}$ Ambient Fine Particle Sampler." The Model PQ200A is a portable audit sampler and includes a set of three carrying cases.
RFPS-0498-117, "Rupprecht & Patashnick Company, Incorporated Partisol®-FRM Model 2000 $PM_{2.5}$ Air Sampler."
RFPS-0498-118, "Rupprecht & Patashnick Company, Incorporated Partisol® FRM Model 2025 $PM_{2.5}$ Sequential Air Sampler."
RFPS-0598-119, "Graseby Andersen Model RAAS2.5-100 $PM_{2.5}$ Ambient Air Sampler."
RFPS-0598-120, "Graseby Andersen Model RAAS2.5-300 $PM_{2.5}$ Ambient Air Sampler."
RFPS-1098-123, "Thermo Environmental Instruments Incorporated Model 605 Computer Assisted Particle Sampler (CAPS)."

Updated lists of EPA designated reference and equivalent methods can be obtained at EPA's Ambient Monitoring Technology Information (AMTIC) Web page:
http://www.epa.gov/ttn/amtic

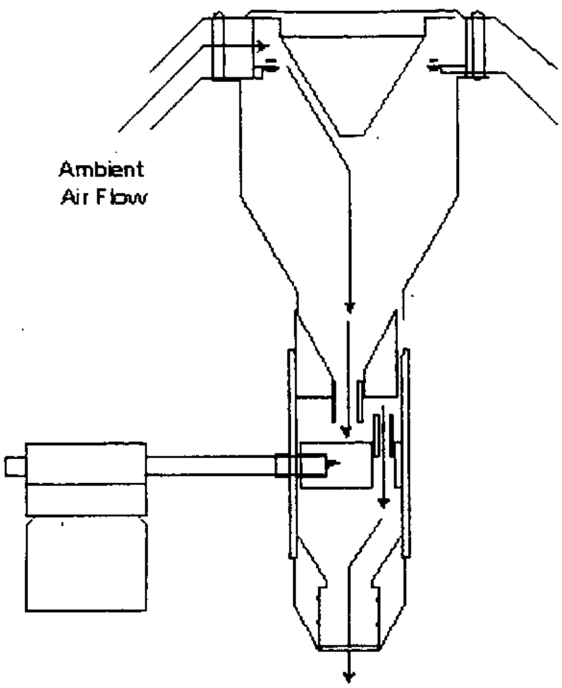


Figure 4-52. Schematic of $PM_{2.5}$ ambient air sampler.

Equivalent Methods for $PM_{2.5}$

Equivalent methods for $PM_{2.5}$ have a much wider latitude in their design, configuration, and operating principle than FRMs. These methods are not required to be based on filter collection of $PM_{2.5}$; therefore, continuous or semicontinuous analyzers and new types of $PM_{2.5}$ measurement technologies are not precluded as possible equivalent methods. Equivalent methods are not necessarily required to meet all the requirements specified for FRMs, but they must demonstrate both comparability to FRM measurements and similar $PM_{2.5}$ measurement precision.

The requirements that some (but not all) candidate methods must meet, to be designated as equivalent methods by EPA, are specified in 40 CFR Part 53. Three classes of equivalent methods have been established in the 40 CFR Part 53 regulations, based on the degree to which a candidate method deviates from the FRM requirements. All three classes of equivalent methods are acceptable for SLAMS or SLAMS-related $PM_{2.5}$ monitoring. But not all types of equivalent methods may be equally suited to specific $PM_{2.5}$ monitoring requirements or applications.

Class I equivalent methods are based on samplers that have minor deviations from the specifications for FRM samplers. However, they must meet the 40 CFR Part 53 tests and other requirements that are applicable to FRM samplers. Also, they must be tested to make sure that the modifications of the candidate Class I equivalent method sampler do not significantly compromise sampler performance. Finally, they must be tested for possible loss of $PM_{2.5}$ in any new or modified components in the sampler inlet upstream of the sampler filter.

Class II equivalent method samplers are filter-collection based methods that will generally have one or more substantial deviations from the design or performance specification of the FRM. These deviations would cause the sampler to be disqualified as a FRM sampler. For example, they might have a different inlet, particle size separator, volumetric flow rate, filter, or filter face velocity than a FRM sampler. Consequently, more extensive performance testing is required for designation of Class II equivalent methods. The tests and their specific applicability to various types of candidate Class II equivalent method samplers are contained in Subpart F of 40 CFR Part 53.

Class III equivalent methods cover any $PM_{2.5}$ equivalent method samplers that cannot qualify as reference or Class I or II equivalent methods because of more profound differences from the FRM requirements. This class encompasses $PM_{2.5}$ methods such as continuous or semicontinuous $PM_{2.5}$ analyzers and potential new $PM_{2.5}$ measurement technologies. The requirements for designation as Class III methods are the most extensive, and, because of the wide variety of $PM_{2.5}$ measurement principles that could be employed for candidate Class III equivalent methods, the designation requirements are not explicitly provided in 40 CFR Part 53. For similar reasons, much of the information and guidance in this document may not be applicable to operation of Class III equivalent methods.

Limitations of $PM_{2.5}$ Reference and Class I Equivalent Methods

There are several conditions or effects that limit the degree to which a $PM_{2.5}$ reference or Class I equivalent method can precisely determine the mass concentration of particulate matter in the atmosphere. One limitation is maintaining the specified ambient air flow rate through the sampling inlet and filter assembly. The flow rate determines the size of the particles that will be collected. The effects of this limitation are minimized by following sampler construction requirements and by employing procedures and checks to ensure the proper flow rate is maintained within close tolerances. Refer to Section 6.0, "Calibration Procedures," and to Section 8.0, "Field Operation," of EPA's QA Handbook Vol. II, Part II, Section 2.12, for guidance.

Another important limitation involves changes in the weight of a collected sample due to mishandling, chemical reactions, and volatilization. Handling procedures, choice of filter media, humidity and temperature control of the filter and sample during collection and subsequent processing, and promptness in weighing the sample following collection all help control filter artifacts. The chemical makeup of the $PM_{2.5}$ particulate matter will vary with sampling location and source. Thus, the magnitude of $PM_{2.5}$ weight changes due to chemical and physical processes will also vary with site location.

Weight loss due to mechanical removal of particles from the filter is minimized by carefully removing the filter, in its cassette, from the sampler, storing the filter/cassette in a protective container during transit to the weighing laboratory, and carefully removing the filter from the cassette, conditioning the filter, and neutralizing the static charge on the filter before weighing. Refer to Section 7.0, "Filter Preparation and Analysis." The choice of an essentially neutral Teflon® media filter as the collecting surface minimizes the weight gain that occurs when sulfate-containing particles form by chemical reactions of sulfur dioxide gas at the surface of alkaline media such as glass fiber filters. If nitric acid vapor is present at a sampling location, it can deposit on a Teflon® filter and cause small weight gains in proportion to the amount of nitric acid present in the atmosphere.

This weight gain may not be controllable. Weight losses can occur due to the thermal or chemical decomposition or evaporation of compounds like ammonium nitrate (NH_4NO_3), which releases ammonia and nitric acid as gases. Semivolatile organic compounds (SVOCs) may be part of the sample makeup; if so, they may evaporate and cause sample weight losses. Such weight losses are minimized or standardized by maintaining the sampler temperature near ambient conditions during the sampling process, keeping the sample cool during transport to the laboratory, and promptly conditioning and weighing the sample following its receipt in the laboratory. Weight gain or loss due to absorption or desorption of water vapor on the filter or on the particulate matter is minimized by specifying low moisture pickup for manufactured filters and by conditioning the filters within specified humidity and temperature ranges, both before use and after receipt from the field. Refer to Section 7.0, "Filter Preparation and Analysis," for further guidance.

Errors in the gravimetric analysis of samples can also result from the buildup of electrostatic charge on filters during their manufacture or during sampling. This static buildup will interfere with the microbalance weighing, but it can be reduced or eliminated by the use of Poloniom-210 (^{210}Po) antistatic strips before the weighing process begins.

Calculations

The $PM_{2.5}$ concentration is calculated as:

$$PM_{2.5} = (W_f - W_i)/V_{act}$$

where:

$PM_{2.5}$ = *mass concentration of $PM_{2.5}$, $\mu g/m^3$*

W_f, W_i = *final and initial weights, respectively of the filter used to collect the $PM_{2.5}$ particle sample in μg*

V_{act} = *total air volume sample at actual ambient air conditions as provided by the sampler, m^3.*

Sample Problems

Problem 1: $PM_{2.5}$ Sampling

A $PM_{2.5}$ filter weighed 150.200 mg before sampling and 150.900 mg after sampling. The flow rate at atmospheric conditions of 740 mm Hg and 20 °C was 16.5 L/min. The sampling period was 24 hours. What is the $PM_{2.5}$ concentration in $\mu g/m^3$ at standard conditions of 760 mm Hg and 25 °C?

Solution

Mass = Final weight - initial (tare) weight

Mass (μg) = 150.900 mg − 150.200 mg = 0.700 mg × 10^3 $\mu g/mg$ = 700 μg

Sampling period ≐ 24 hrs × 60 min/hr = 1,440 min

V_{act} = flowrate$_{act}$ × time

V_{act} = 16.5 L/min × 1,440 min = 23,760 L × m^3/1,000L = 23.76 m^3

PM$_{2.5}$ concentration$_{act}$ = 700 µg/ 23.76 m^3 = 29.46 µg/m^3 or 29.5 µg/m^3

$V_{std} = V_{act}\,(P_{act}/P_{std})(T_{std}/T_{act})$

V_{std} = 23.76 m^3 × (740 mm Hg/760 mm Hg) (298 K/293 K) = 23.53 m^3

PM$_{2.5}$ concentration$_{std}$ = µg/V_{std}

PM$_{2.5}$ concentration$_{std}$ = 700 µg/23.53 m^3 = 29.75 µg/m^3 or 29.8 µg/m^3

-Or-

PM$_{2.5}$ concentration$_{std}$ = PM$_{2.5}$ concentration$_{act}$ $(P_{std}/P_{act})(T_{act}/T_{std})$

PM$_{2.5}$ concentration$_{std}$ = 29.5 µg/m^3 × (760 mm Hg/ 740 mm Hg) × (293 K/298 K) = 29.79 µg/m^3 or 29.8 µg/m^3

Problem 2: PM$_{2.5}$ Sampling

A PM$_{2.5}$ filter weighed 143.300 mg before sampling and 143.700 mg after sampling. The flow rate at atmospheric conditions of 745 mm Hg and 23 °C was 16.7 L/min. The sampling period was 24 hours. What is the PM$_{2.5}$ concentration in µg/m^3 at actual atmospheric conditions?

Solution

Mass = Final weight - initial (tare) weight

Mass = 143.700 mg – 143.300 mg = 0.400 mg × 1,000 µg/mg = 400 µg

Sampling period = 24.0 hrs × 60 min/hr = 1,440 min

V_{act} = flowrate$_{act}$ × time

V_{act} = 16.7 L/min × 1,440 min = 24,048 L × m^3/1,000L = 24.05 m^3

PM$_{2.5}$ concentration$_{act}$ = µg/V_{act}

PM$_{2.5}$ concentration$_{act}$ = 400 µg/24.05 m^3 = 16.63 µg/m^3 or 16.6 µg/m^3

Continuous Monitoring for Particulate Matter

Continuous fine particulate monitoring is required at Core State and local air monitoring stations (SLAMS). Core SLAMS means community-oriented monitoring sites representative of community-wide exposures that are the basic component sites of the $PM_{2.5}$ SLAMS regulatory network. The Core requirement is specified in Section 2.8.1.3.8 of Appendix D of 40 CFR Part 58 and was part of the July 18, 1997 final rule making on the revised requirements for ambient air quality surveillance for particulate matter (Federal Register, Vol. 62, no. 138). Under this regulation, at least one continuous fine particulate analyzer is required at a core monitoring $PM_{2.5}$ site in each metropolitan area with a population greater than 1 million. The purpose of these analyzers is to provide improved temporal resolution to better understand the sources and causes of elevated $PM_{2.5}$ concentrations in the atmosphere, facilitate public reporting of $PM_{2.5}$ air quality, reduce site visits and network operation costs, and implement periodic control strategies.

In addition to the use of continuous analyzers at these SLAMS, correlated acceptable continuous (CAC) analyzers may be used by control agencies as an alternative to the everyday sampling schedule for certain core SLAMS. Under this alternative, which is specified in Section 58.13 (f), a core SLAMS monitor may operate on a 1 in 3-day schedule and produce data that may be used to compare to the NAAQS, provided that it is collocated with a CAC that is correlated with the reference or equivalent method. More information is found in a draft report titled, *Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring Networks* (March 3, 1998). This draft report was a survey of alternatives for continuous measurement of suspended particles, their chemical components, and their gaseous precursors.

The report summarizes that continuous monitors can adequately measure several of the major chemical components. Organic and elemental carbon, sulfate, and nitrate each have proven continuous methods, but need to be evaluated, accepted, and packaged. Instruments are lacking for ammonium, crustal elements, and liquid water with the possible exception of the single particle mass spectrometers. Continuous measurement methods for particle size, based on inertial, optical, electrical, and condensation properties, are also adequate to characterize the ultrafine as well as the accumulation modes of suspended particles.

EPA did not specify the requirements for Class III automated equivalent methods for $PM_{2.5}$ because of the wide range of non-filter based measurement technologies that could be applied and the likelihood that these requirements will need to be specifically adopted for each type of technology. Specific requirements will be developed as needed.

References

American Conference of Governmental Industrial Hygienists. 1985. 8th edition. *Air Sampling Instruments.* Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

Appel, B. R., and Wesolowski, J. J. Selection of filter media for particulate sampling with a Lundgren impactor. State of California Air and Industrial Hygiene Laboratory Report 125.

Appendix L to 40 CFR Part 50 – FRM for the Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere, Final Rule. 40 CFR Part 50, Federal Register, Friday, July 18, 1997, pp. 57-95.

Appendix M to 40 CFR Part 50 – FRM for the Determination of Particulate Matter as PM_{10} in the Atmosphere, Final Rule. 40 CFR Part 50, Federal Register, Friday, July 18, 1997, pp. 96-98.

Arthur D. Little, Inc. 1973. *Development of a High Purity Filter for High Temperature Particulate Sampling and Analysis.* EPA 650/2-73-032.

Balzer, J. L. 1972. Inertial collectors. *Air sampling instruments for evaluation of atmospheric contaminants.* American Conference of Governmental Industrial Hygienists.

Bruckman, L., and Rubino. 1976. High-volume sampling: errors incurred during passive sample exposure periods. *J. Air Pollut. Control Assoc.* 26:881.

Burton, R. M.; Howard, J. N.; Penley, R. L.; Ramsay, P. A.: and Clark, T. A. 1972. Field evaluation of the high-volume particle fractionating cascade impactor - a technique for respirable sampling. Paper #72-30, presented at the 65th Annual Meeting of the Air Pollution Control Association, 18-22 June 1972.

Cadle, R. D. 1975. *The Measurement of Airborne Particulates.* Wiley-Interscience.

Caroff, M.; Choudhary, K. R.; and Gentry, J. W. 1973. Effect of pore and particle size distribution on efficiencies of membrane filters. *J. Aerosol Science 4:93.*

Chahal, H. S., and Romano, D. J. 1976. High-volume sampling: effect of wind-borne particulate matter deposited during idle periods. *J. Air Pollut. Control Assoc.* 26:885.

Chambers, L. 1954. Filter media for air sampling. *Industrial Hygiene Quarterly* 15:290.

Chow, J.C. 1995. Critical Review: Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particulates. *JAWMA*

Chow, J.C., and Watson, J.G. November 6, 1997. *Guideline on Speciated Particulate Monitoring,* Special Report prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

Cohen, A. L. 1973. Dependence of hi-vol measurements on airflow race. *Environ. Sci. Tech.* 7:60-61.

Dams, R; Heindrychx, K. 1973. A high-volume sampling system for use with cellulose fibers. *Atmos. Environ.* 7:319.

Dams, R.; Rahn, K. A.; and Winchester, J. W. 1972. Evaluation of filter materials and impaction surfaces for nondestructive neutron activation analysis of aerosols. *Environ. Sci. Tech.* 6:441.

Demuynck, M. 1975. Determination of irreversible absorption of water by cellulose filters. *Atmos. Environ.* 9:523.

Dzubay, T. G.; Hines, L. E.; and Stevens, R. K. 1976. Particle bounce errors in cascade impactors. *Atmos. Environ.* 10:229.

Dzubay, T. G., and Stevens, R. K. 1978. *Dichotomous Sampler - A Practical Approach to Aerosol Fractionation and Collection.* EPA 600/2-78-112.

Dzubay, T. G.; Stevens, R. K.; and Peterson, C. M. 1977. Application of the dichotomous sampler to the characterization of ambient aerosols. In *X-ray fluorescence analysis of environmental samples,* ed. T. G. Dzubay, p. 99. Ann Arbor, MI: Ann Arbor Science.

Federal Register. 6 December 1982. FRM for the determination of suspended particulates in the atmosphere (high-volume method). 40 CFR Appendix B.

Federal Register. Vol. 62, No. 138. 18 July 1997. Revised Requirements for $PM_{2.5}$ and Ambient Air Quality Surveillance for Particulate Matters; Final Rule. 40 CFR Part 53 and 58.

Federal Register. Vol. 62, No. 138, National Ambient Air Quality Standard for Particulate Matter; Final Rule 40 CFR Part 50.

Fitzgerald, J., and Detwiler, C. Collection efficiency of air-cleaning and air-sampling filter media. AEC Report KAPL-1088.

Fuchs, N. A. 1964. *The Mechanics of Aerosols.* New York: McMillan Co.

Gelman, C., and Marshall, J. C. 1975. High purity fibrous air sampling media. *Am. Ind. Hyg. Assoc. J.* 36:512.

Gelman Instrument Company. 1964. *Dust topics.* Vol. 1, No. 1.

Gillespie, J. 1955. The role of electric forces in the filtration of aerosols by fiber filters. *Journal of Colloid Science* 10:299.

Gordon, R. J. 1976. Distribution of airborne polycyclic aromatic hydrocarbons throughout Los Angeles. *Environ. Sci. Tech.* 10:370.

Green, H. L., and Lane, W. R. 1957. *Particulate Clouds: Dusts, Smokes, and Mists.* D. Van Nostrand Inc.

Gussman, R. A.; Sacco, A. M.; and Ladd, R. E. 1972. Design and calibration of a high-volume cascade impactor. Paper #72-27, presented at the 65th Annual Meeting of the Air Pollution Control Association, 18-22 June 1972.

Harrison, W. K; Nader, J. S.; and Fugan, F. S. 1960. Constant flow regulators for the high-volume air sampler. *Am. Ind. Hyg. Assoc. J.* 22:115.

Hering, S.V. 1995. Impactors, Cyclones, and Other Inertial and Gravitational Collectors. *Sampling Instruments of Atmospheric Contaminants*, 8th ed., B. Cohen, S.V. Hering, ed., American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

Hertz, M. B. 1972. Size-segregating mass-sampling comparisons of single two-stage, and multistage sampling. Presented at the 13th Conference on Methods in Air Pollution and Industrial Hygiene Studies, 30-31 October 1972.

Hidy, G. M. et al. 1974. Summary of the California aerosol characterization experiment. Paper #74-119, presented at the 67th Annual Meeting of the Air Pollution Control Association 9-13 June 1974.

Hounam, R. F. 1962. The filtering efficiency of selected papers. *Ann. Occup. Hyg.* 4:301.

Hu, J. N. 1971. An improved impactor for aerosol studies - modified Andersen sampler. *Environ. Sci. Tech.* 5:251-253.

Ketseridis, G.; Hahn, J.; Jaeniche, R.; and Junge, C. 1976. The organic constituents of atmospheric particulate matter. *Atmos. Environ.* 10:603.

Kirsh, A. A.; Stechkina, I. B.; and Fuchs, N. A. 1975. Efficiency of aerosol filters made of ultrafine polydisperse fibres. *J. Aerosol Science* 6:119.

Kretzschmar, J. G. 1975. Comparison between three different methods for the estimation of the total suspended matter in urban air. *Atmos. Environ.* 9:931.

Lattore, P., and Silverman, L. 1955. Collection efficiencies of filter papers for sampling lead fume. *AMA Arch. of Indust. Health* 11:243.

Lee, K.W., and Ramamurthi, M. 1993. Filter Collection. *Aerosol Measurement: Principles, Techniques and Applications,* K. Willeke, P.A. Baron, Eds. Van Nostrand, Reinhold, New York City, pp. 179-205.

Lee, M. L., et al. 1976. Gas chromatography/mass spectrometric and nuclear magnetic resonance determination of polynuclear aromatic hydrocarbons in airborne particulates. *Anal. Chem.* 48:1566.

Lee, R. E., and Goranson, S. 1972. National air surveillance cascade impactor network, I. Size distribution measurements of suspended particulate matter in air. *Environ. Sci. Tech.* 6:1019.

Lindeken, C., et al. 1964. Surface collection efficiency of large-pore membrane filters. *Health Physics* 10:495.

Lippman, M. 1959. Review of cascade impactors for particle size analysis and a new calibration for the Casella cascade impactor. *Am. Ind. Hyg. Assoc. J.* 20:406.

--- 1970. Respirable dust sampling. *Am. Ind. Hyg. Assoc. J.* March-April 1970.

--- 1972. Filter media and filter holders for air sampling. *Air sampling instruments for evaluation of atmospheric contaminants.* Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

--- 1995. Filters and Filter Holders. *Air Sampling Instruments for Evaluation of Atmospheric Contaminants,* 8th ed., B. Cohen, S.V. Hering, ed. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

Lippman, M., and Harris, W. B. 1962. Size selective samplers for estimating "respirable" dust concentrations. *Health Physics* 8:155.

Liu, Benjamin Y. H., and Kuhlmey, G. A. 1978. Efficiency of air sampling filter media. Presented at the Symposium and Workshop on X-ray Fluorescence Analysis of Environmental Samples. 26-28 January 1978, at Chapel Hill, NC. Particle Technology Laboratory Publication No. 293. Minneapolis, MN: University of Minnesota.

Lockhart, L. B., Jr., and Patterson, R. L., Jr. 1963. Intercalibration of the major North American networks employed in monitoring airborne fusion products. NRL Report 6025. Washington, DC: U S. Naval Research Laboratory.

Lockhart, L. B., Jr.; Patterson R. L., Jr.; and Anderson, W. L. 1964. Characteristics of air filter media used for monitoring radioactivity NRL Report 6054. Washington, DC: U.S. Naval Research Laboratory.

Loo, Billy W.; Jaklevic, J. M.; and Goulding, F. S. 1976. Dichotomous virtual impactors for large scale monitoring of airborne particulate matter. In *Fine particles*, ed. B. Y. H. Liu, pp. 311-350. New York: Academic Press.

Lundgren, D. A. 1967. An aerosol sampler for determination of particle concentration as a function of size and time. *J. Air Poll. Control Assoc.* 17:225.

Magill, P. L.; Holden, F. R.; and Ackely, C., eds. 1956. *Air Pollution Handbook.* McGraw-Hill.

McKee, H. C., et al. 1972. Collaborative testing of methods to measure air pollutants, I. The high-volume method for suspended particulate matter. *J. Air Pollut. Control Assoc.* 22:342.

Mueller, P. K.; Twiss, S.; and Sanders, G. 1972. Selection of filter media: an annotated outline. Presented at the 13th Conference on Methods in Air Pollution and Industrial Hygiene Studies, 30-31 October 1972.

Neustadter, H. E., et al. 1975. The use of Whatman-41 filters for high-volume air sampling. *Atmos. Environ.* 9:101.

Olin, J. G., and Kurz, J. L. 1975. High-volume air sampling. *Pollut. Eng.* p. 30 January 1975.

Paciga, J. J., and Jervis, R. E. 1976. Multielement size characterization of urban aerosols. *Environ. Sci. Tech.* 10:1124.

Parker, R. D., et al. 1977. A two stage respirable aerosol sampler using nuclepore filters in series. *Atmos. Environ.* 11:617.

Pate, J. B., and Tabor, E. C. 1962. Analytical aspects of the use of glass fiber filters for the collection and analysis of atmospheric particulate matter. *Am. Ind. Hyg. Assoc. J.* 23:144-145.

Peterson, C. M. 1972. Aerosol sampling and the importance of particle size. *Air sampling instruments for evaluation of atmospheric contaminants.* American Conference of Governmental Industrial Hygienists.

Picknett, R. G. 1972. A new method of determining aerosol size distributions from sampler data. *Journal of Aerosol Science* 3:189.

Pupp, Christian; Lao, R. C.; Murray J. J.; and Pottie, R. F. 1974. Equilibrium vapor concentrations of some polycyclic aromatic hydrocarbons, AS_4O^6, and $Se0_2$ and the collection efficiencies of these air pollutants. *Atmos. Environ.* 8:915.

Ramskill, E., and Anderson, W. 1951. The inertial mechanism in the mechanical filtration of aerosols. *Journal of Colloid Science* 6:416.

Ranz, W. E., and Wong, J. B. 1952. Impaction of dust and smoke particles on surface and body collectors. *Journal of Industrial and Engineering Chemistry* 44:1371.

Revised Requirements for Designation of Reference and Equivalent Methods for $PM_{2.5}$ and Ambient Air Quality Surveillance for Particulate Matter, Final Rule. 40 CFR Parts 53 and 58, Federal Register, Friday, July 18, 1997, pp. 1-86.

Robson, C. D., and Foster, K. E. 1962. Evaluation of air particulate sampling equipment. *Am. Ind. Hyg. Assoc. J.* 24:404.

Sawicki, E., et al. 1960. Benzo(a)pyrene content of the air of American communities. *Am. Ind. Hyg. Assoc. J.* 21:443.

Setter, L. R.; Zimmer, C. E.; Licking, D. S.; and Tabor, E. C. 1961. Airborne particulate beta radioactivity measurements of the national air sampling network, 1953-1959. *Am. Ind. Hyg. Assoc. J.* 22:19200.

Silverman, L., and Viles, F. G. 1948. A high-volume air sampling and filter weighing method for certain aerosols. *J. Indust. Hyg. and Toxicol.* 30:124.

Smith, F., and Nelson, A. C. June 1973. *Guidelines for development of a quality assurance program-FRM for the determination of suspended particulates in the atmosphere (high-volume method).* Prepared for Research Triangle Institute under Contract 68-02-0598.

Smith, J., and Surprenant, N. Properties of various filtering media for atmospheric dust sampling. *Proceedings of the American Society of Testing Materials* 53:1122.

Spirtas, R. Personal communication.

Stem, S., et al. 1960. The aerosol efficiency and pressure drop of a fibrous filter at reduced pressures. *Journal of Colloid Science* 15:546.

Stevens, R. K., and Dzubay, J. G. 1978. *Dichotomous Samper - A Practical Approach to Aerosol Fractionation and Collection.* EPA 600/2-78-112.

Stevenson, H. J. R. *Sampling and Analysis of Respirable Sulfates.* Division of Air Pollution, U.S. Public Health Service.

Sugimas, A. 1975. Sensitive emission spectrometric method for the analysis of airborne particulate matter. *Anal. Chem.* 47:1840.

Swartz, D. B.; Denton, M. B.; and Moyen, J. L. 1973. On calibrating of cascade impactors. *Am. Ind. Hyg. Assoc. J.* 34:429.

Swift, D.L., and Lippman, M. 1995. Electrostatic and Thermal Precipitation. Sampling Instruments of Atmospheric Contaminants. 8th edition. B. Cohen, S.V. Hering, eds., American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

Tabor, E. C. 1965. Pesticides in urban atmospheres. *J. Air Pollut. Control Assoc.* 15:415.

Tabor, E. C.; Hauser, T. R.; Lodge, J. P.; and Burtschell, R. H. 1958. Characteristics of the organic particulate matter in the atmosphere of certain American cities. *AMA Arch. Indust. Health* 17:58.

Watson, J.G., et al. March 6, 1998 draft. *Guidance for Using Continuous Monitors in* $PM_{2.5}$ *Monitoring Networks*, prepared for U.S. Environmental Protection Agency. Research Triangle Park, NC 27711.

U.S. Public Health Service. *Air Pollution on Measurements of the National Air Sampling Network- Analysis of Suspended Particulates, 1957-1961.* Public Health Service Publication No. 978. Washington, DC.

Section A-4

Introduction to Pertinent Statistical Techniques for Air Monitoring

Reading Assignment

Pages 10-1 through 10-24 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Data Plots
- Measures of Central Tendency
- Measures of Dispersion
- Distribution Curves
- The Data Quality Objectives Process

Learning Goal and Objectives

Learning Goal

The purpose of this section is to familiarize you with statistical techniques pertaining to air monitoring.

Learning Objectives

At the end of this section, you should be able to

1. identify and define the two statistical variables associated with atmospheric sampling data.
2. identify a data frequency table, frequency polygon, histogram, and cumulative frequency distribution curve relating to a given set of air quality data.
3. describe a data distribution.
4. use probability graph paper.
5. define and use linear regression.
6. calculate the arithmetic mean, median, geometric mean, and range.
7. identify normal and log normal distribution curves.
8. identify equations used to calculate standard deviation and the standard geometric deviation and recognize their usefulness.
9. identify the steps of the Data Quality Objectives Process.

10. identify the outputs of the Data Quality Objectives Process.

Reading Guidance

1. Refer often to the equations, example calculations, and figures of the assigned reading material as you progress through the assignment.
2. When you have finished the reading assignment, complete the review exercise for Section A-4. It begins on the following page.
3. After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
4. For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment-indicated on the answers page.
5. After you have reviewed your incorrect answers (if any), proceed to Section B-1 of this guidebook.

Review Exercise

Now that you've completed the assignment for Section A-4, please answer the following questions. These will help you determine whether or not you are mastering the material.

1. Which of the following is a(are) general variable(s)?

   a. continuous variable
   b. discrete variable
   c. both a and b, above

2. True or False? A continuous variable is one that can assume any value within some interval of values.

   a. True
   b. False

3. True or False? Discrete variables are those whose possible values are integers.

   a. True
   b. False

4. As a rule of thumb, a data frequency table should consist of _____ data class intervals.

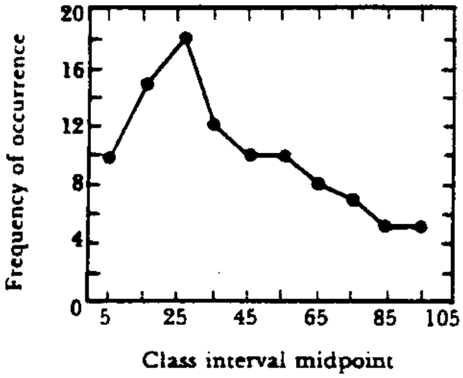
   a. 1 to3
   b. 3 to 5
   c. 8 to 15
   d. 20 to 30

5. Which one of the following frequency polygons represents the data given in the frequency table below?

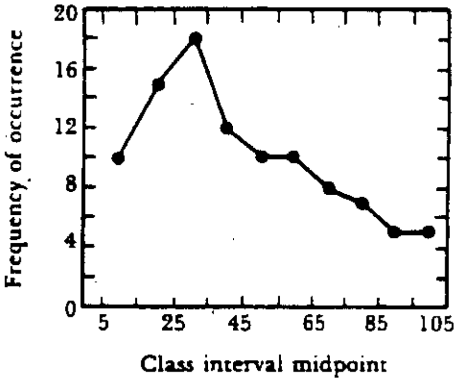
Frequency table

Class interval	Frequency of occurrence
0-10	10
10-20	15
20-30	18
30-40	12
40-50	10
50-60	10
60-70	8
70-80	7
80-90	5
90-100	5

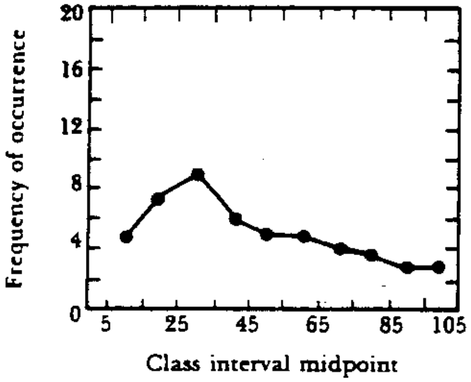
a.



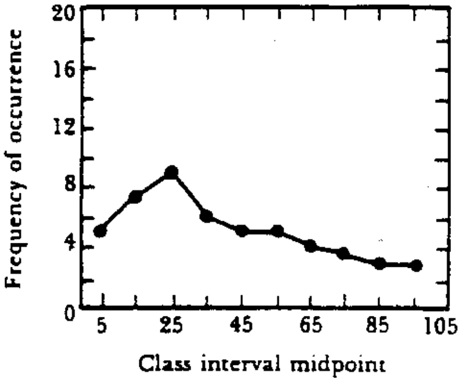
b.



c.



d.

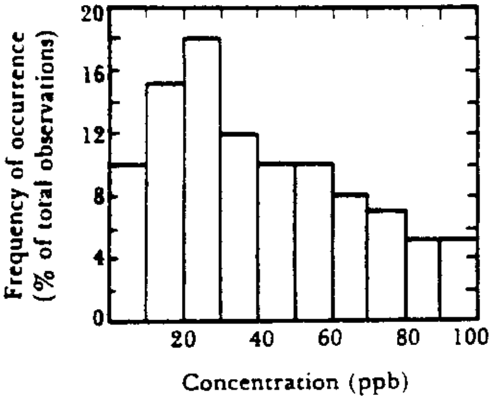


6. Which one of the following histograms represents the data given in the frequency table below?

Frequency table

Concentration class interval (ppb)	Frequency of occurrence
0-10	10
10-20	15
20-30	18
30-40	12
40-50	10
50-60	10
60-70	8
70-80	7
80-90	5
90-100	5

a.



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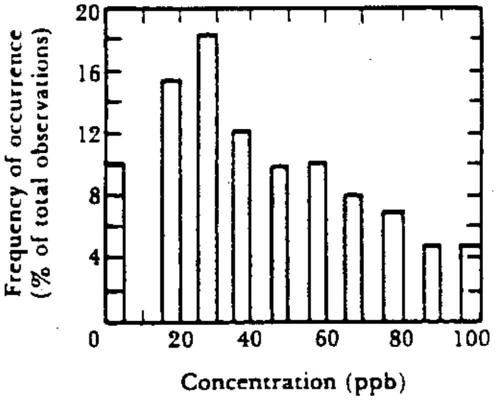
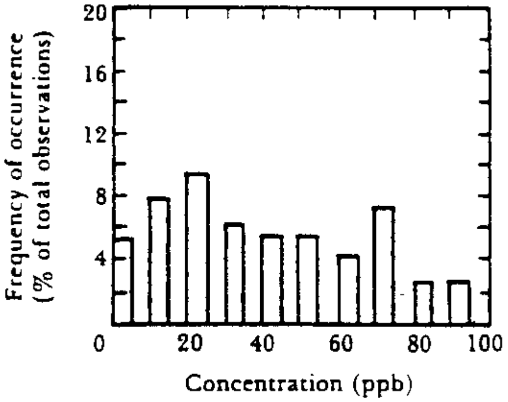
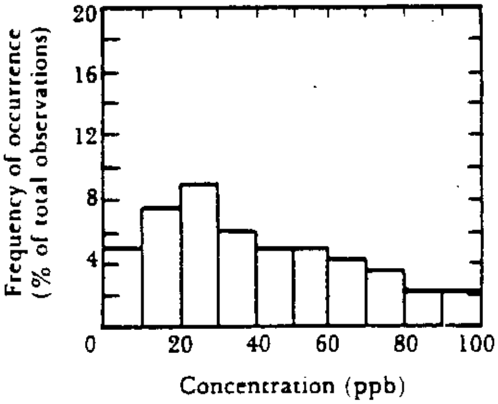


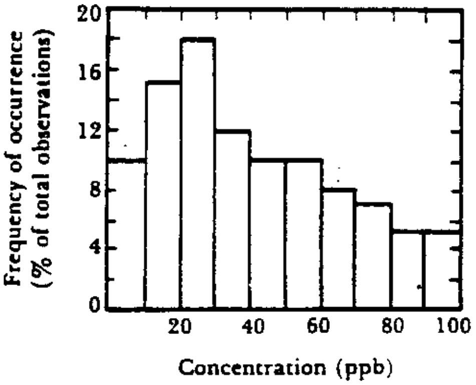
c.



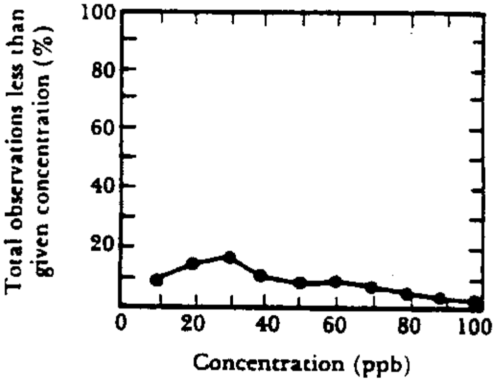
d.



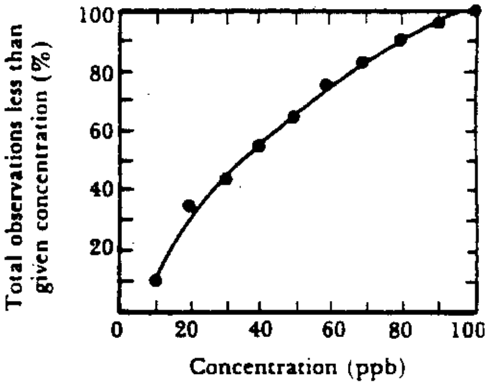
7. Which one of the following cumulative frequency distribution curves represents the data given in the histogram below?



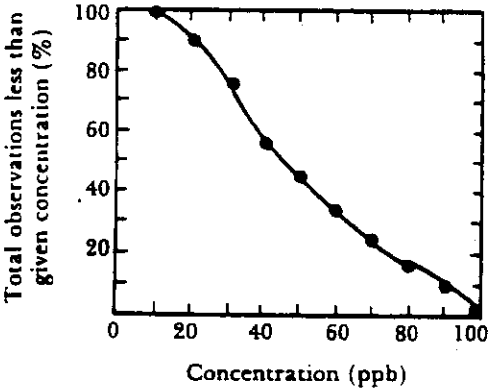
a.



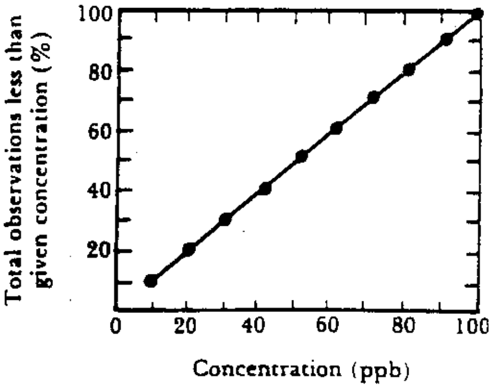
b.



c.



d.

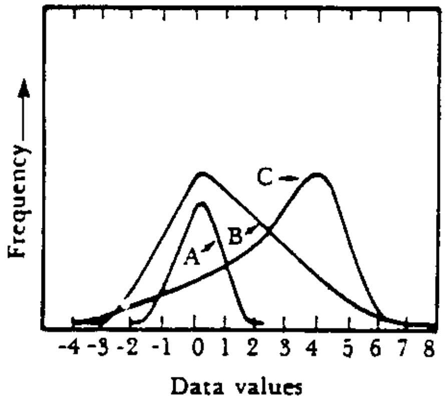


8. Which of the following is a(are) basic characteristic(s) of data distributions?

   a. central location
   b. dispersion
   c. skewness
   d. all of the above

9. In the figure below, curve _____ is skewed to the right, curve _____ is skewed to the left, and curve _____ is not skewed.

   a. A, B, C
   b. L, C, A
   c. C, B. A
   d. A, C. B



10. True or False? When the arithmetic and logarithmic scales of a data cumulative frequency distribution curve are plotted on probability graph paper, the scale which causes the frequency distribution curve to be more nearly a straight line better approximates a normal data distribution.

   a. True
   b. False

11. The _____ percentile of a data set's cumulative frequency distribution curve plotted on probability graph paper is an estimate of the mean of the data set.

a. 25th
b. 50th
c. 75th
d. 100th

12. The distance between the _____ percentile and the _____ percentile of a data set's cumulative frequency distribution curve plotted on probability graph paper is an estimate of the standard deviation of the data set.

a. 75th, 50th
b. 50th, 25th
c. 50th, 16th
d. 35th, 14th

13. True or False? Linear regression is the mathematical process of minimizing the vertical distance between all the points of a data set and a straight line represented by the data set.

a. True
b. False

14. Which one of the following equations gives the best straight line using the data set below?

x	y
4	10
10	20
16	30

a. $y = 1.13x - 2.0$
b. $y = 0.87x + 2.8$
c. $y = 1.72x + 1.67$
d. $y = 1.67x + 3.3$

For each of questions 15 through 17, match the parameter with its value for the following data set: 2, 4, 8, and 12.

Parameter	Value
15. Mean ___	a. 10
	b. 6.5
	c. 6
16. Median ___	
17. Range ___	

18. Extreme values of a data set have _____ influence on the data set's mean than(as) on the data set's median.

    a. greater
    b. lesser
    c. the same

19. The geometric mean of a data set consisting of five data values is calculated by taking the _____ root of the _____ of the five data values.

    a. square, product
    b. square, sum
    c. 5th, sum
    d. 5th, product

20. The geometric mean of a log normally distributed data set gives _____ measure of the data set's central location as(than does) the data set's arithmetic mean.

    a. the same
    b. a more accurate
    c. a less accurate

21. True or False? The standard deviation is the most commonly used measure of dispersion for a normally distributed data set.

a. True
b. False

22. Which one of the following equations is the most accurate and easiest to use for calculating standard deviation?

a. $$\sqrt{\frac{\Sigma\left(X_i - \overline{X})^2\right)}{n-1}}$$

b. $$\sqrt{\frac{\Sigma X_i^{\,2} - \frac{(\Sigma X_i)^2}{n}}{n-1}}$$

c. $$\text{antilog}\left[\frac{\Sigma\left(\log X - \overline{\log X}\right)^2}{n-1}\right]^{1/2}$$

d. $$\text{antilog}\left[\frac{\Sigma(\log X)^2 - \frac{(\Sigma \log X)^2}{n}}{n-1}\right]^{1/2}$$

Where:

X_i = *a data value*
$\overline{X}$ = *the mean of the data sample*
n = *the number of observations*

23. True or False? The standard geometric deviation is an appropriate measure of the dispersion of a log normally distributed data set.

a. True
b. False

24. Which one of the following equations is the most accurate and easiest to use for calculating standard geometric deviation?

a. $$\sqrt{\frac{\Sigma(X_i - \overline{X})^2)}{n-1}}$$

b. $$\sqrt{\frac{n\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n(n-1)}}$$

c. $$\text{antilog}\left[\frac{\Sigma(\log X - \overline{\log X})^2}{n-1}\right]^{1/2}$$

d. $$\text{antilog}\left[\frac{\Sigma(\log X)^2 - \frac{(\Sigma \log X)^2}{n}}{n-1}\right]^{1/2}$$

Where:

X_i = *a data value*
$\overline{X}$ = *the mean of the data sample*
n = *the number of observations*

25. Which of the following is a(are) characteristic(s) of a normal (Gaussian) distribution curve?

a. It has symmetry.
b. Its mean and median are both found in the center of the curve.
c. It has an infinite range.
d. all of the above

For each of questions 26 through 28, match the normal (Gaussian) distribution curve parameter with its corresponding percent area under the normal curve.

Parameter

26. ± 1 standard deviation from the mean __

27. ± 2 standard deviations from the mean __

28. ± 3 standard deviations from the mean __

Percent Area

a. 50.4%
b. 68.2%
c. 95.4%
d. 99.7%

For each of questions 29 and 30, match the data distribution curve with its appropriate figure.

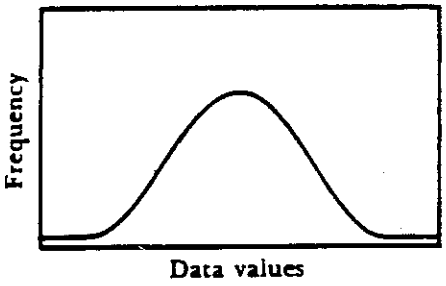
Curve

29. normal (Gaussian) ___

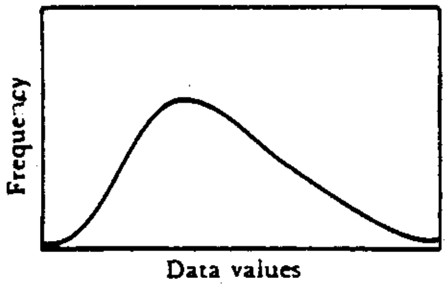
30. log normal distribution curve ___

Figure

a.



b.



31. True or False? A data value of a data set that is more than ± 3 standard deviations away from the mean of the data set is probably an erroneous value.

   a. True
   b. False

32. What is the first step of the Data Quality Objectives Process?

   a. Develop a decision rule.
   b. Optimize the design.
   c. State the problem.
   d. Identify the decision.

33. The Data Quality Objectives Process is designed to help establish criteria for _____ and for developing data collection designs.

   a. data quality
   b. study objectives
   c. tolerable limits on decision errors
   d. data appropriateness

34. True or False? The final product of the Data Quality Objectives Process is a data collection design that meets the quantitative and qualitative needs of the study.

   a. True
   b. False

Section A-4

Review Exercise Answers

		Page(s) of *Atmospheric Sampling: Student Manual*
1.	c	10-3
2.	a	10-3
3.	a	10-3
4.	c	10-3
5.	a	10-5
6.	a	10-5, 10-6
7.	b	10-7, 10-8
8.	d	10-8
9.	b	10-8
10.	a	10-10, 10-11
11.	b	10-10, 10-11
12.	c	10-10, 10-11
13.	a	10-11
14.	d	10-12
15.	b	10-13
16.	c	10-14
17.	a	10-16
18.	a	10-16
19.	d	10-15
20.	b	10-15
21.	a	10-17
22.	b	10-17
23.	a	10-19
24.	d	10-19
25.	d	10-20, 10-21
26.	b	10-20, 10-21
27.	c	10-20, 10-21
28.	d	10-20, 10-21
29.	a	10-20, 10-21
30.	b	10-22, 10-23
31.	a	10-22
32.	c	10-2
33.	a	10-1
34.	a	10-2

Required Readings

Chapter 10

Statistical Techniques Employed in Atmospheric Sampling

Introduction

Proper use of statistics and statistical techniques is necessary for assessing the quality of ambient air sampling data. For a comprehensive discussion of the subject of data quality assessment (DQA), review EPA's technical assistance document. *Guidance for Data Quality Assessment, Practical Methods of Data Analysis*, EPA QA/G-9, EPA/600/R-96/084, January 1998. This reference document provides practical demonstrations on how to use the data quality assessment (DQA) technique in evaluating environmental data sets and shows how to apply some graphic and statistical tools for performing DQA.

This chapter is intended as an introduction to statistics and statistical concepts and their use in analyzing ambient air sampling data. Topics addressed include: (a) Data Quality Objectives; (b) Data Plotting; (c) Measures of Central Tendency; (d) Measures of Dispersion; and (e) Distribution Curves. Although these topics are not simple, they can be understood and used by non-statisticians. If a detailed statistical analysis of data is required, it is recommended that an experienced statistician be consulted.

The Data Quality Objectives (DQO) Process

While the Data Quality Objectives (DQO) Process is not a statistical technique, per se, it is important because it helps to establish criteria for data quality and the development of data collection designs. DQOs provide the appropriate context for understanding the purpose of the ambient air sampling and analysis data collection effort. Also, they establish the qualitative and quantitative criteria for assessing the quality of the collected data set, based on the predefined intended use of data. G4 guidance for the Data Quality Objectives Process is available at http://es.epa.gov/ncerqa/qa/index.html.

DQOs are qualitative and quantitative statements derived from the outputs of the first six steps of the DQO Process that encompasses the following:

- Clarify the study objective.
- Define the most appropriate type of data to collect.
- Determine the most appropriate conditions from which to collect the data.
- Specify tolerable limits on decision errors which will be used as the basis for establishing the quantity and quality of data needed to support the decision.

The DQOs are then used to develop a scientific and resource-effective data collection design.

The Seven Steps of the DQO Process

*Step 1: **State the Problem*** – Concisely describe the problem to be studied. Review prior studies and existing information to gain a sufficient understanding to define the problem.

*Step 2: **Identify the Decision*** – Identify what questions the study will attempt to answer.

*Step 3: **Identify the Inputs to the Decision*** – Identify the information that needs to be obtained and the measurements that need to be taken to resolve the decision statement.

*Step 4: **Define the Study Boundaries*** – Specify the time periods and spatial area to which decisions will apply. Determine when and where data should be collected.

*Step 5: **Develop a Decision Rule*** – Define the statistical parameters of interest, specify the action level, and integrate the previous DQO outputs into a single statement that describes the logical basis for choosing among alternative actions.

*Step 6: **Specify Tolerable Limits on Decision Factors*** – Define the decision maker's tolerable decision error rates based on a consideration of the consequences of making and incorrect decision.

*Step 7: **Optimize the Design*** – Evaluate information from the previous steps and generate alternative data collection designs. Choose the most resource-effective design that meets all DQOs.

Outputs of the DQO Process

The DQO Process leads to the development of a quantitative and qualitative framework for a study. Each step of the Process derives valuable criteria that will be used to establish the final data collection design. The first five steps of the DQO Process identify mostly qualitative criteria, such as what problem has initiated the study and what decision it attempts to resolve. These steps also define the type of data that will be collected, where and when the data will be collected, and a decision rule that specifies how the decision will be made.

The sixth step defines quantitative criteria expressed as limits on decision errors that the decision maker can tolerate.

The final step is used to develop a data collection design based on the criteria developed in the first six steps. The final product of the DQO Process is a data collection design that meets the quantitative and qualitative needs of the study.

Data Collection Design

A data collection design specifies the final configuration of the environmental monitoring or measurement effort required to satisfy the DQOs. It designates:

- the types and quantities of samples or monitoring information to be collected;
- where, when, and under what conditions they should be collected;
- what variables are to be measured; and
- QA/QC procedures to ensure that sampling design and measurement errors are controlled sufficiently to meet the tolerable decision error rates specified in the DQOs.

Data Plotting

Data is usually uninterpretable in the form in which it is collected. In this section, we shall consider the graphical techniques of summarizing such data so that the meaningful information can be extracted from it. There are two kinds of variables to which we assign data: continuous variables and discrete variables. A continuous variable is one that can assume any value in some interval of values. Examples of continuous variables are weight, volume, length, time, and temperature. Most air pollution data are taken from continuous variables. Discrete variables, on the other hand, are those variables whose possible values are integers. Therefore, they involve counting rather than measuring. Examples of discrete variables are the number of sample stations, number of people in a room, and number of times a control standard is violated. Since any measuring device is of limited accuracy, measurements in real life are actually discrete in nature rather than continuous, but this should not keep us from regarding such variables as continuous. When a weight is recorded as 165 pounds, it is assumed that the actual weight is somewhere between 164.5 and 165.5 pounds.

Graphical Analysis

Frequency Tables

Let us consider the set of data in Table 10-1, which represents SO_2 levels for a given hour for 25 days. The first step in summarizing the data is to form a frequency table. A frequency table is a table prepared by dividing a data set into selected units or class intervals, then counting and inserting the number of points (frequency of occurrences) within the units or class intervals. Table 10-2 is a frequency table prepared from the SO_2 data set given in Table 10-1.

In constructing the frequency table, we have divided the 25 points in the data set into 11 class intervals with each interval being 15 units in length. The choice of dividing the data into 11 intervals was purely arbitrary. However, in dealing with data it is best to choose the length of the class interval such that 8 to 15 intervals will include all of the data under consideration. Deriving the frequency of occurrence column involves nothing more than counting the number of values in each interval. The relative frequency column is obtained by dividing the number of points or frequency of occurrences within a unit by the total number of events within the data set, which in this example is 25.

From observation of the frequency table, we can now see the data taking form. The values appear to be clustered between 25 and 85 ppb. In fact, nearly 80% are in this interval.

Table 10-1. SO_2 levels.

Days	SO_2 concentration (ppb)*
1	53
2	72
3	59
4	45
5	44
6	85
7	77
8	56
9	157
10	83
11	120
12	81
13	35
14	63
15	48
16	180
17	94
18	110
19	51
20	47
21	55
22	43
23	28
24	38
25	26

*ppb = parts per billion collected SO_2 levels.

Table 10-2. Frequency table.

Class Interval (ppb)	Frequency of occurrence (total 25)	Relative frequency
25 - 40	4	4/25 = 0.16
40 - 55	7	7/25 = 0.28
55 - 70	4	4/25 = 0.16
70 - 85	4	4/25 = 0.16
85 - 100	2	2/25 = 0.08
100 - 115	1	1/25 = 0.04
115 - 130	1	1/25 = 0.04
130 - 145	0	0.00
145 - 160	1	1/25 = 0.04
160 - 175	0	0.00
175 - 190	1	0.04

The Frequency Polygon

The next step is to graph the information in the frequency table. One way of doing this would be to plot the frequency for the midpoint of each class interval. The solid line connecting the points of Figure 10-1 forms a frequency polygon.

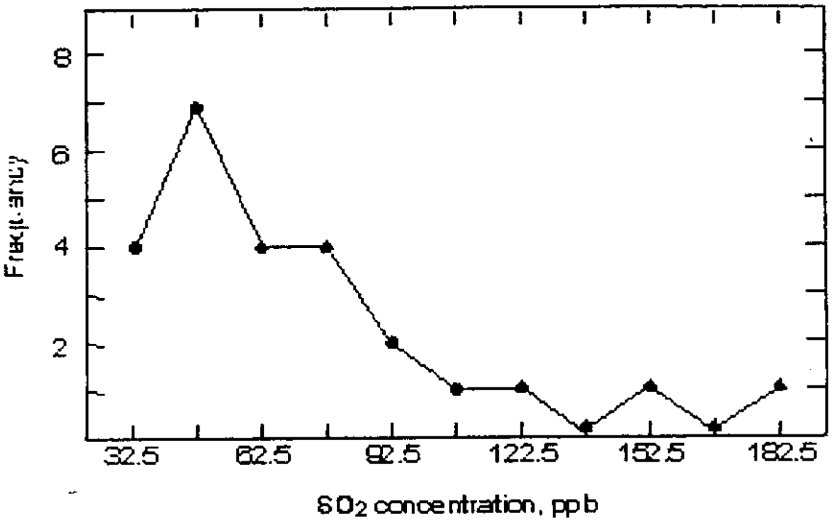


Figure 10-1. Pollution concentration (midpoint of class interval) frequency polygon.

The Histogram

Another method of graphing the information would be by constructing a histogram as shown in Figure 10-2. The histogram is a two-dimensional graph in which the length of the class interval is taken into consideration. The histogram can be a very useful tool in statistics, especially if we convert the given frequency scale to a relative scale so that the sum of all the ordinates equals one. This is shown in Figure 10-3. Thus, each ordinate value is derived by dividing the original value by the number of observations in the sample, in this case 25. The advantage in constructing a histogram like this one is that we can read probabilities from it, if we can assume a scale on the abscissa such that a given value will fall in any one interval is the area under the curve in that interval. For example, the probability that a value will fall between 55 and 70 is equal to its associated interval's portion of the total area of intervals, which is 0.16.

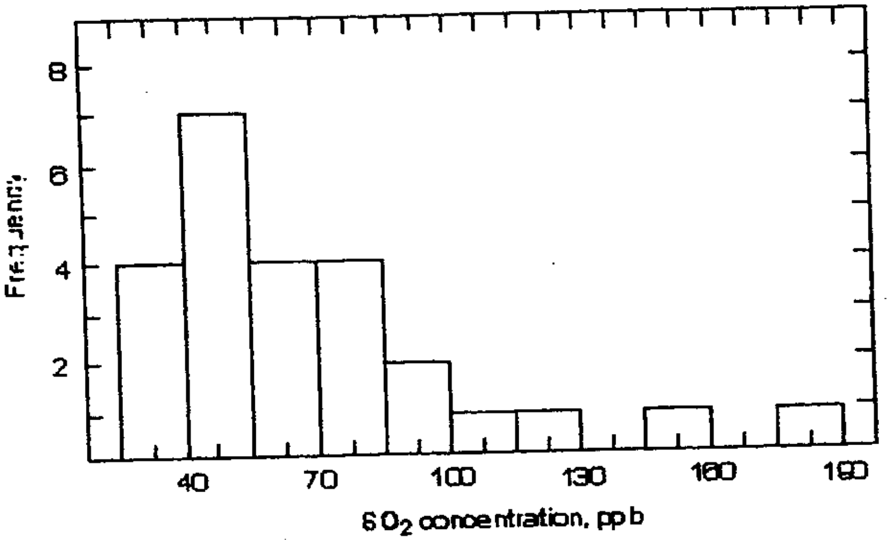


Figure 10-2. Pollutant concentration histogram of frequency distribution curve.

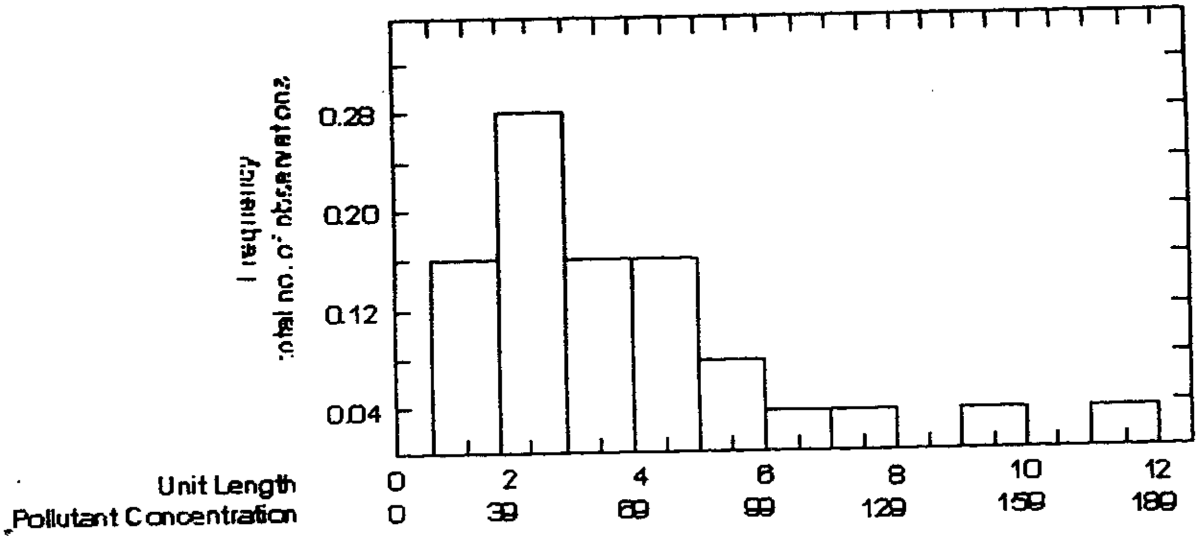


Figure 10-3. Histogram of percent frequency distribution curve.

The Cumulative Frequency Distribution

Using the frequency table and histogram discussed above, we can construct a cumulative frequency table and curve as shown in Table 10-3 and Figure 10-4.

Table 10-3. Cumulative frequency table.

SO_2 level		Cumulative frequency	Relative cumulative frequency
Under	40	4	0.16
"	55	11	0.44
"	70	15	0.60
"	85	19	0.76
"	100	21	0.84
"	115	22	0.88
"	130	23	0.92
"	145	23	0.92
"	160	24	0.96
"	175	24	0.96
"	190	25	1.00

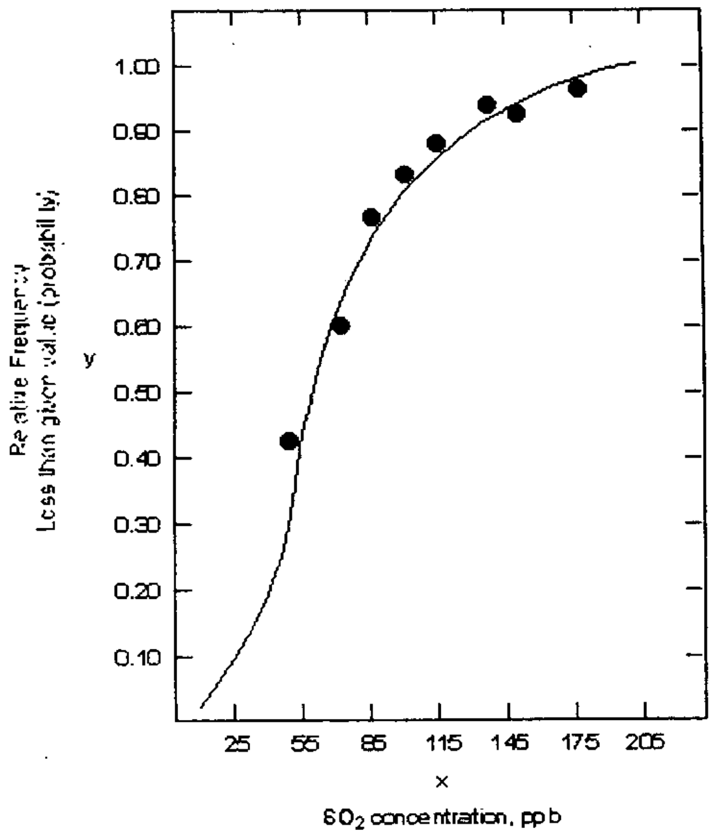


Figure 10-4. Cumulative frequency distribution curve.

The cumulative frequency table gives the number of observations less than a given value. Probabilities can be read from the cumulative frequency curve or cumulative frequency table. For example, to find the probability that a value will be less than 85, we read up to the curve at the point $x = 85$ and across to the value 0.76 on the *y-axis*. An alternative way to use the table is to go to the row where the SO_2 level shows under 85, then go across to the relative cumulative frequency value of 0.76.

Distribution of Data

When we draw a histogram for a set of data, we are representing the distribution of the data. Different sets of data will vary in relation to one another and, consequently, their histograms will look different. In this chapter, we identify three characteristics that will distinguish the distributions of different sets of data. These are central location, dispersion, and skewness. These are characterized in Figure 10-5. Curves A and B have the same central location, but B is more dispersed. However, both A and B are symmetrical and are, therefore, said not to be skewed. Curve C is skewed to the right and has a different central location than A and B. Mathematical measures of central location and dispersion will be discussed later.

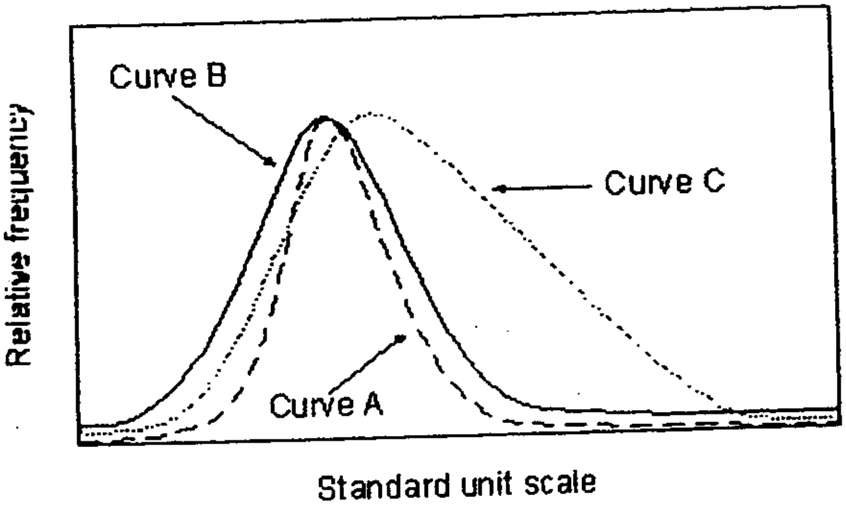


Figure 10-5. Relative frequency distribution showing: Curve A and B both centrally located; Curve B being more disperse than Curve A and the skewness of Curve C.

Transformation of Data

In most statistical work, data that closely approximate a particular symmetrical curve, called the normal curve, are required. Both curves A and B in Figure 10-5 are examples of normal curves. In dealing with skewed curves, such as C in the same figure, it is desirable to transform the data in some way so that a symmetrical curve resembling the normal curve results. Referring to the frequency table (Table 10-2) and histogram (Figure 10-2) of the data used earlier, it can be seen that for this set of data the distribution is skewed (in the opposite direction as Curve C above), hence the data are not normally distributed.

The Logarithmic Transformation

One of the most successful ways of deriving a symmetrical distribution from a skewed distribution is by expressing the original data in terms of logarithms. The logarithms of the original data are given in Table 10-4.

Arbitrarily dividing the logarithmic data into nine class intervals, each of 0.1 unit in length, we can prepare the logarithmic frequency table in Table 10-5. As can be seen in Figure 10-6, a frequency plot of the log transformed data more closely approximates a symmetrical curve than the arithmetic plot of the original data.

Table 10-4. Logarithmic transformation.

Day	Pollutant conc. X	$\text{Log}_{10}X$
1	53	1.724
2	72	1.857
3	59	1.771
4	45	1.653
5	44	1.644
6	85	1.929
7	77	1.887
8	56	1.748
9	157	2.196
10	83	1.919
11	120	2.079
12	81	1.909
13	35	1.544
14	63	1.799
15	48	1.681
16	180	2.255
17	94	1.973
18	110	2.041
19	51	1.708
20	47	1.672
21	55	1.740
22	43	1.634
23	28	1.447
24	38	1.580
25	26	1.415

Table 10-5. Logarithmic frequency table.

Class interval	Frequency of occurrence	Cumulative frequency	Relative cumulative frequency
1.4 – 1.5	2	2	0.08
1.5 - 1.6	2	4	0.16
1.6 - 1.7	5	9	0.36
1.7 - 1.8	6	15	0.60
1.8 - 1.9	2	17	0.68
1.9 - 2.0	4	21	0.84
2.0 - 2.1	2	23	0.92
2.1 - 2.2	1	24	0.96
2.2 - 2.3	1	25	1.00

Probability Graph Paper

Probability graph paper is used in the analysis of cumulative frequency curves; for example, the graph paper can be used as a rough test of whether the arithmetic or the logarithmic scale best approximates a normal distribution. The scale, arithmetic or logarithmic, on which the cumulative frequency distribution of the data is more nearly a straight line is the one providing the better approximation to a normal distribution. Plotting the cumulative distribution curve of the data above on the two scales shows that the logarithmic scale yields the better fit (Figure 10-6).

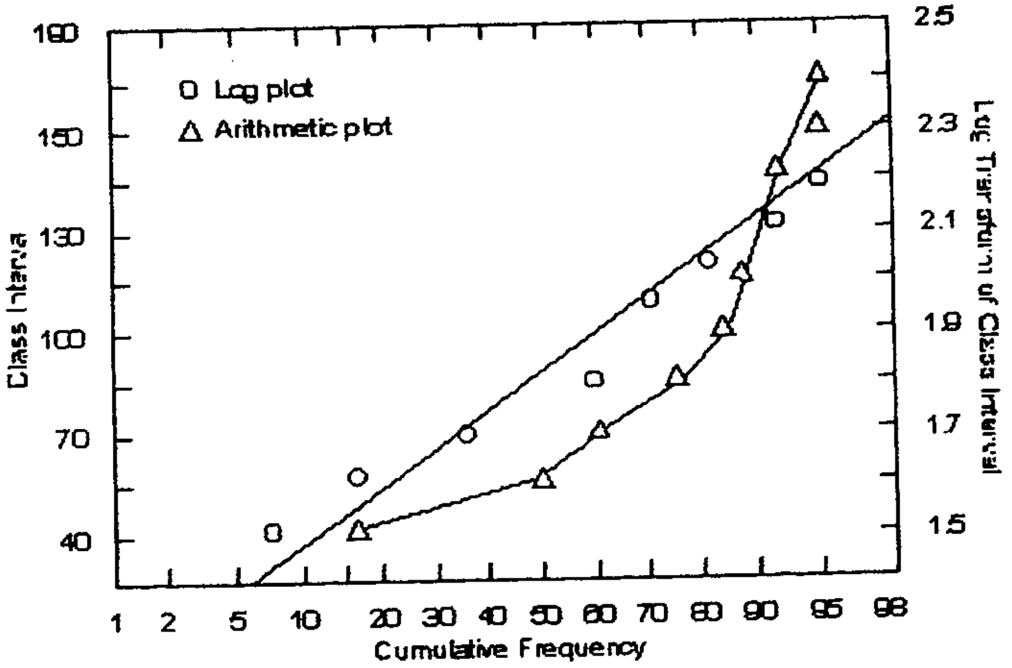


Figure 10-6. Normalized data plot vs. non-transformed data.

These probability plots can be used, if the data are normally distributed. to estimate the mean and standard deviation of the data. The estimate of the mean, as will be shown later, is the 50th percentile point, and the estimation of the standard deviation is the distance from the 50th percentile to the 16th percentile. A percentile is a measure of the relative position of one of several observations in relation to all of the observations, and provides a measure of relative standing that is useful for summarizing data.

Least Square Linear Regression

If the linear relationship between two variables is significant, a least square linear regression line, or line of "best fit," may be drawn to represent the data. This relationship can then be used to determine the value of an unknown variable. For example, if the ambient air concentration is unknown, but linearly related to the response of an ambient air monitor, we can estimate the ambient air concentration based on an observed response from the air monitor. Algebraically, a straight line has the following form:

(Eq. 10-1) $$y = mx + b$$

Where:
y = *dependent variable plotted on the ordinate*
x = *explanatory variable plotted on the abscissa*
b = *the point at which the line intercepts the y-axis at* $x = 0$
m = *slope, which shows how much a change of 1 unit of* x *affects* y.

Linear regression minimizes the vertical distance between all data points and the straight line (Figure 10-7).

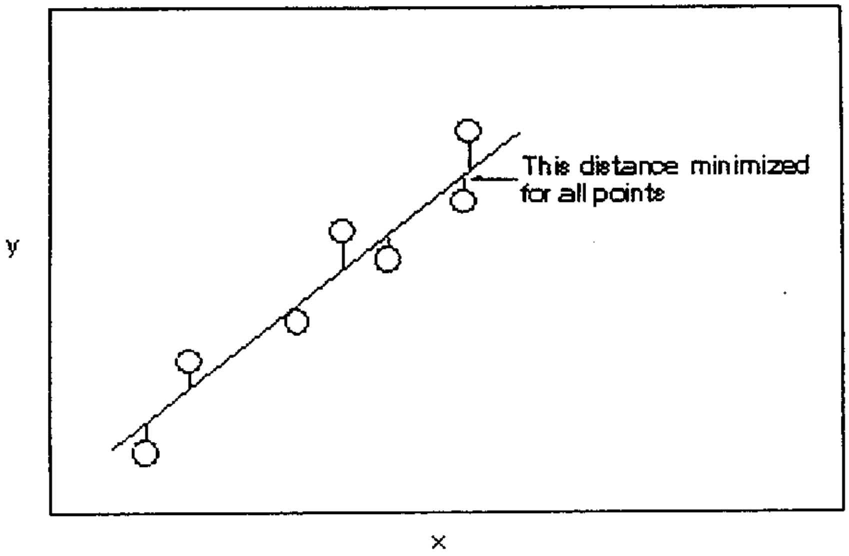


Figure 10-7. Linear regression curve.

The constants m and b for the "least square" line can be determined using the following equations:

(Eq. 10-2)
$$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}}$$

(Eq. 10-3)
$$b = \bar{y} - m\bar{x}$$

Where: n = *number of observations*
$\bar{y} = \sum y / n; \bar{x} = \sum x / n$

Example Problem

Calibration of an ambient air analyzer is required before it can be used to provide reliable ambient air concentration measurements. A typical calibration consists of the introduction of known and certified standard concentrations, typically in parts per million (ppm) over the linear operational range of the instrument, and the recording of the corresponding response of the instrument in units such as volts. Based on the recorded responses and the known concentrations, a least square line relationship between the variables can be calculated and subsequently used to determine ambient concentrations based on the response of the analyzer.The following data were collected during a calibration of a chemiluminescent NO_x analyzer.

x = Concentration NO_x (ppm)	0.05	0.10	0.20	0.30	0.45
y = Instrument response (volts)	1.20	2.15	3.90	6.20	9.80

Values for m and b for the least square or "best fit" line can be calculated from $\sum x$, $\sum y$, $\sum x^2$, $\sum xy$, n, $\bar{y}$, and $\bar{x}$.

Solution:

$\sum x = 0.05 + 0.10 + 0.20 + 0.30 + 0.45 = 1.1$
$\sum y = 1.20 + 2.15 + 3.90 + 6.20 + 9.80 = 23.25$
$\sum x^2 = (0.05)^2 + (0.10)^2 + (0.20)^2 + (0.30)^2 + (0.45)^2 = 0.345$
$\sum xy = (0.05)(1.20) + (0.10)(2.15) + (0.20)(3.90) + (0.30)(6.20) + (0.45)(9.80) = 7.33$
$n = 5$

$$\bar{x} = \frac{\sum x}{n} = \frac{1.1}{5} = 0.22$$

$$\bar{y} = \frac{\sum y}{n} = \frac{23.25}{5} \cong 4.65$$

$$m = \frac{7.33 - \frac{(1.1)(23.25)}{5}}{0.345 - \frac{(1.1)^2}{5}} = \frac{2.22}{0.103} = 21.6$$

$$b = 4.65 - (21.6)(0.22) = -0.102$$

The equation for this calibration curve would be y = 21.6x – 0.102, where y (the instrument response in volts) is equal to the ambient concentration in ppm times the slope of the line which is 21.6, plus the y-intercept of x which is a – 0.102.

To calculate ambient concentrations in ppm, we solve the equation for "x":

$$\text{x(ppm)} = \frac{\text{y} - \text{b}}{\text{m}}$$

$$\text{x(ppm)} = \frac{\text{y} + 0.102}{21.6}$$

Measures of Central Tendency

Arithmetic Average, or Mean

A basic way of summarizing data is by the computation of a central value. The most commonly used central value statistic is the arithmetic average, or the mean. This statistic is particularly useful when applied to a set of data having a fairly symmetrical distribution. The mean is an efficient statistic in that it summarizes all the data in the set, and because each piece of data is taken into account in its computation. The formula for computing the mean is:

(Eq. 10-4)
$$\bar{X} = \frac{X_1 + X_2 + X_3 \ldots + X_n}{n} = \frac{\sum X_i}{n}$$

Where:

$\bar{X}$ = *arithmetic mean*

X_i = i^{th} *measurement*

n = *total number of observations*

The arithmetic mean is not a perfect measure of the true central value of a given data set. Arithmetic means overemphasize the importance of one or two extreme data points. Many measurements of a normally distributed data set will have an arithmetic mean that closely approximates the true central value.

Example Problem

Calculate the mean of 3.0, 2.5, 2.2, 3.4, 3.2.

Solution:

$$\bar{X} = \frac{X_1 + X_2 + X_3 + X_4 \ldots + X_n}{n} = \frac{\sum X_i}{n}$$

$$\bar{X} = \frac{3.0 + 2.5 + 2.2 + 3.4 + 3.2}{5}$$

$$\bar{X} = \frac{14.3}{5} = 2.86$$

Median

When a distribution of data is asymmetrical, such as that of Figure 10-8, it is sometimes desirable to compute a different measure of central value. This second measure, known as the median, is simply the middle value of a distribution, or the quantity above which half the data lie and below which the other half of the data lie. If *n* data are listed in their *order of magnitude*, the median is the [(n+1)/2] value. If the number of data is even, then the numerical data of the median is the value midway between the two data nearest the middle. The median, being a positional value, is less influenced by extreme values in a distribution than the mean.

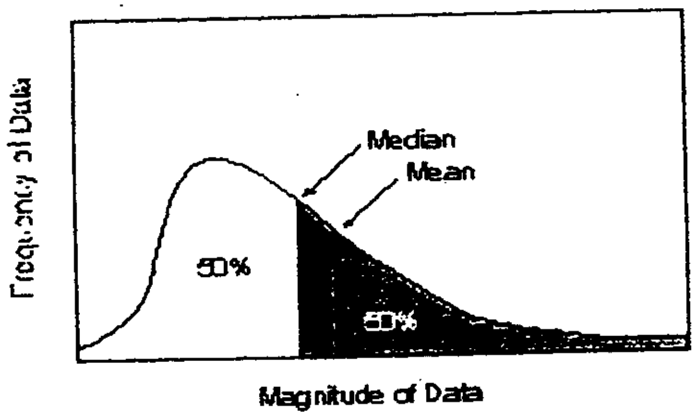


Figure 10-8. Example of an asymmetrical distribution of data (median vs. mean).

Example Problem

Find the median of 22, 10, 15, 8, 13, 18.

Solution: The data must first be arranged in order of magnitude, such as:

8, 10, 13, 15, 18, 22

Since n = 6, the median is the 7/2 = 3.5 value, thus the median is 14, or the value halfway between 13 and 15, since this data set has an even number of measurements.

Geometric Mean

Another measure of central tendency used in more specialized applications is the geometric mean ($\bar{X}_z$). The geometric mean is defined by using the following equation:

(Eq. 10-5)

$$\bar{X}_z = \sqrt[n]{(X_1)(X_2)\ldots(X_n)}$$

If scientific calculators are not available, a formula that more readily lends itself to a four-function calculator is:

$$Log_{10}\bar{X}_z = \frac{1}{n}\Sigma\, Log_{10}X_i$$

The formula is derived as follows.

$$Log\bar{X}_z = Log\left[\sqrt[n]{(X_1)(X_2)...(X_n)}\right] = Log[(X_1)(X_2)...(X_n)]^{1/n}$$

where log is to the base 10

$$but \quad LogX^{1/n} = \frac{1}{n}LogX$$

$$and \quad Log(X \times Y) = LogX + LogY$$

$$\therefore Log\bar{X}_2 = \frac{1}{n}Log[(X_1)(X_2)...(X_n)]^{1/n}$$

$$= \frac{1}{n}(Log\ X_1 + Log\ X_2 ... + Log\ X_n)$$

$$= \frac{1}{n}\sum_i Log\ X_i$$

The geometric mean is most often used for data whose causes behave exponentially rather than linearly, such as in the growth of bacteria, measurements that are ratios, or lognormal distributions.

In a distribution shaped like that of Figure 10-8, the geometric mean, like the median, will yield a value closer to the main cluster of values than will the mean. The arithmetic mean is always higher than the geometric mean.

Example Problem: Geometric Mean

Calculate the geometric mean of 3.0, 2.5, 2.2, 3.4, 3.2.

Solution:

$$\bar{X}_z = \sqrt[5]{(3.0)(2.5)(2.2)(3.4)(3.2)} = 2.8$$

or

$$Log_{10}\bar{X}_z = \frac{1}{5}(0.477 + 0.398 + 0.342 + 0.531 + 0.505)$$

$$Log_{10}\bar{X}_z = 0.4506$$

$$\bar{X}z = 10^{0.4506} = 2.8$$

Measures of Dispersion

Measures of central tendency are more meaningful if accompanied by information on measures of dispersion or how the data spread out from the center. Examples of measures of dispersion in a data set include the range, sample standard deviation, coefficient of variation, and the standard geometric deviation.

The Range

The easiest measure of dispersion of a set of data is the difference between the maximum and the minimum values in the set, termed the *range*. The range does not make full use of the information contained in the data, since only two of the data points are taken into account. Thus the range is a useful measure of variability for data sets of 10 or less.

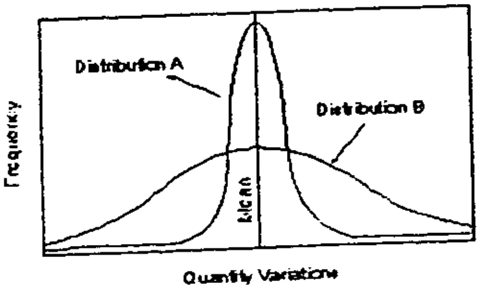


Figure 10-9. Dispersion characteristic curves.

Standard Deviation

The most commonly used measure of dispersion, or variability, of sets of data is the standard deviation. Its defining formula is given by the expression:

(Eq. 10-6)

$$s = +\sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n-1}}$$

Where:
s = *the standard deviation (always positive)*
X_i = i^{th} *measurement*
$\bar{X}$ = *the mean of the data sample*
n = *the number of observations*

The expression (X_i - $\bar{X}$) shows how the deviation of each measurement from the overall mean is incorporated into the standard deviation.

An algebraically equivalent formula that makes computation much easier is:

$$s = +\sqrt{\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n-1}}$$

where the variables are defined as above.

Example Problem: Standard Deviation

X_i	X_i^2
3.00	9
2.5	6.25
2.2	4.84
3.4	11.56
3.2	10.24
------	--------
14.31 ΣX_i	41.89 ΣX_i^2

$$s = +\sqrt{\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n-1}}$$

$$s = +\sqrt{\frac{41.89 - \frac{(14.30)^2}{5}}{5-1}}$$

$$s = +\sqrt{\frac{41.89 - \frac{204.49}{5}}{5-1}}$$

$$s = +\sqrt{\frac{41.89 - 40.90}{4}}$$

$$s = +\sqrt{\frac{0.990}{4}}$$

$$s = +\sqrt{.248}$$

$$s = 0.498$$

Coefficient of Variation

The coefficient of variation (CV) is a unitless measure that allows the comparison of dispersion across several sets of data. It is the standard deviation divided by the sample mean. The CV is often used in environmental applications because variability (expressed as standard deviation) is often proportional to the mean.

(Eq. 10-7) $$CV = s/\overline{X}$$

Where:

s = *standard deviation*

$\overline{X}$ = *sample mean*

Example Problem: Coefficient of Variation

$$CV = s/\overline{X}$$

$$CV = 0.498/2.86$$

$CV = 0.174$

Standard Geometric Deviation

Dispersion of skewed data such as lognormal distributions is measured by the standard geometric deviation. The standard geometric deviation is very similar to the standard deviation. The dispersion in the log of the measurements is measured by the geometric standard deviation instead of the dispersion of the measurements. The log calculation normalizes the data to better approximate a normal distribution. The formula for calculating the standard geometric deviation is:

(Eq. 10-8)

$$s_z = antilog\left[\frac{\Sigma\left(logX_i^2 - \overline{logX_i}\right)^2}{n - 1}\right]^{1/2}$$

Where:

log is to the base 10
S_z = *standard geometric deviation*
X_i = *i^{th} measurement*
$\bar{X}$ = *the mean of the sample*

The following formula is mathematically identical, yet it is much easier to use in calculation:

$$s_z = antilog\left[\frac{\Sigma(logX_i)^2 - \frac{(\Sigma logX_i)^2}{n}}{n-1}\right]^{1/2}$$

Example Problem: Standard Geometric Deviation

X_i	log X_i	(log X_l)^2
3.0	0.4771	.2276
2.5	0.3979	.1584
2.2	0.3424	.1173
3.4	0.5315	.2825
3.2	0.5051	.2552

Σ log $X_l = 2.2541$
Σ (log $X_l)^2 = .0409$
(Σ log $X_l)^2 = 5.0810$

$$s_z = antilog\left[\frac{\Sigma(logX_i)^2 - \frac{(\Sigma\, logX_i)^2}{n}}{n-1}\right]^{\frac{1}{2}}$$

$$s_z = antilog\left[\frac{1.0409 - \frac{5.0810}{5}}{5-1}\right]^{\frac{1}{2}}$$

$$s_z = antilog\left[\frac{1.0409 - 1.0162}{4}\right]^{\frac{1}{2}}$$

$$s_z = antilog\left[\frac{0.0247}{4}\right]^{\frac{1}{2}}$$

$$s_z = antilog[0.0062]^{\frac{1}{2}}$$

$$s_z = antilog[0.0786]$$

$$s_z = 1.1984 \text{ or } 1.20$$

Distribution Curves

Distribution curves are graphical displays of the individual data points in a data set and are important because they can identify patterns and trends in data that might go unnoticed if the data were not plotted.

Many types of distribution curves exist: binomial, t, chi, F, normal, and lognormal are just a few of the existing distributions. However, in air pollution measurements, the normal and lognormal are the most commonly occurring ones. Thus, only these two will be discussed.

The Normal Distribution

One reason the normal (Gaussian) distribution is so important is that a number of natural phenomena are normally distributed or closely approximate it. In fact, many experiments when repeated a large number of times will approach the normal distribution curve. In its pure form, the normal curve is a continuous symmetrical, smooth curve shaped like the one shown in Figure

10-10. Naturally, a finite distribution of discrete data can only approximate this curve. The normal curve has the following definite relations to the descriptive measures of a distribution.

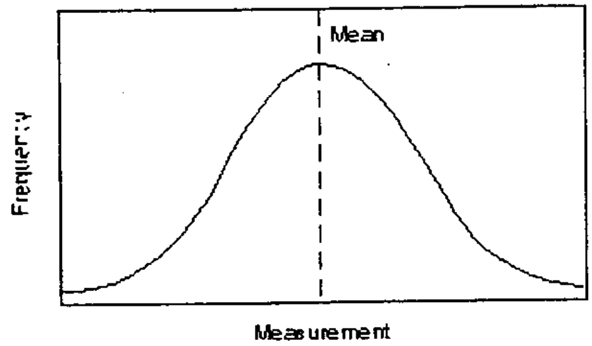


Figure 10-10. Normal distribution curve.

The Mean and Median

The normal distribution curve is symmetrical; therefore, the mean and the median are equal and are found at the center of the curve. Recall that, in general, the mean and median of an asymmetrical distribution do not coincide.

The Range

The normal curve ranges along the *x-axis* from minus infinity to plus infinity. Therefore, the range of a normal distribution is infinite.

The Standard Deviation

The standard deviation, *s*, becomes a most meaningful measure when related to the normal curve. A total of 68.2% of the area lying under a normal curve is included by the part ranging from 1 standard deviation below to 1 standard deviation above the mean. A total of 95.4% lies ± 2 standard deviations from the mean and 99.7% lies within 3 standard deviations (Figure 10-11). By using tables found in statistics texts and handbooks, one can determine the area lying under any part of the normal curve.

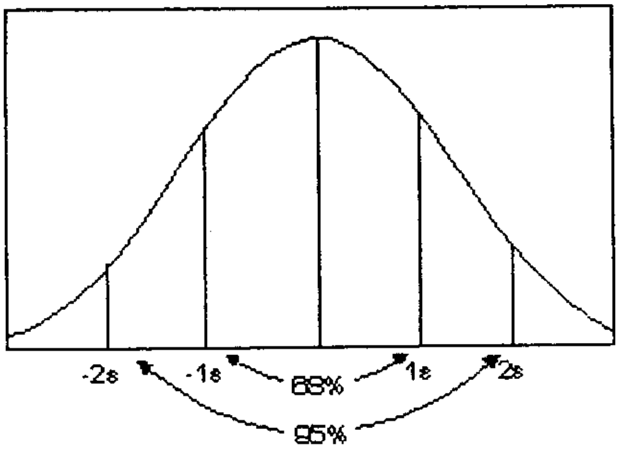


Figure 10-11. Characteristics of the normal distribution.

These areas under the normal distribution curve can be given probability interpretations. For example, if an experiment yields a nearly normal distribution with a mean equal to 30 and a standard deviation of 10, we can expect about 68% of a large number of experimental results to range from 20 to 40, so that the probability of any particular experimental result's having a value between 20 and 40 is about 0.68.

In applying the properties of the normal curve to the testing of data readings, one can determine whether a change in the conditions being measured is shown or whether only chance fluctuations in the readings are represented. For a well-established set of criterion data, a frequently used set of control limits is ± 3 standard deviations. That is, a special investigation of data readings trying these limits can be used to determine whether the conditions under which the original data were taken have changed. Since the limits of 3 standard deviations on either side of the mean include 99.7% of the area under the normal curve, it is very unlikely that a reading outside these limits is due to the conditions producing the criterion set of data. The purpose of this technique is to separate the purely chance fluctuations from the other causes of variation. For example, if a long series of observations of an environmental measurement yield a mean of 50 and a standard deviation of 10, then control limits will be set up as 50 ± 30 — in other words, ± 3 standard deviations, or from 20 to 80. So, a value of 81 would suggest that the underlying conditions have changed, and that a large number of similar observations at this time would yield a distribution of results with a mean different (larger) than 50.

This process of determining whether a value represents a significant change is closely related to the use of control charts. In setting up control limits, it is often necessary to divide the available data into subgroups and calculate the mean and standard deviations of each of these groups, making careful note of the conditions prevailing under each subgroup. In collecting data to establish control limits, as much information as possible should be gathered about the causes and conditions in effect during the period of obtaining a criterion set of data. Generally, the conditions during this period should be "normal," or as much in control as possible.

In the situation where one takes readings of some environmental quantity, the appearance of data beyond the control limits might suggest the starting of a new data grouping to further ascertain whether the underlying environmental variable has changed.

It should be kept in mind that the limits of ± 3 standard deviations are traditional rather than absolute. They have been found through experience to be very useful in many control situations, but each experimenter must decide what limits would be most suitable for a given purpose by determining what levels of probability would be needed to quantify acceptance and rejection bounds.

Lognormal Distributions

Lognormal distributions can best be demonstrated by means of an example:

If hourly sulfur dioxide concentrations are plotted against frequency of occurrence as in the Data Plotting Section, a skewed distribution would exist similar to the one in Figure 10-12. Such a curve indicates that many concentrations are close to zero and that few are very high. Unlike temperature, sulfur dioxide concentrations are blocked on the left because values less than zero do not exist. Because numerous aids exist for normal distributions, it is desirable to normalize this type of distribution. By plotting the log of hourly SO_2 concentrations against the frequency of occurrence, a "bell-shaped" curve similar to Figure 10-10 is obtained. By making this ample normalizing feature, all existing normal distribution tables can be used to make probability interpretations.

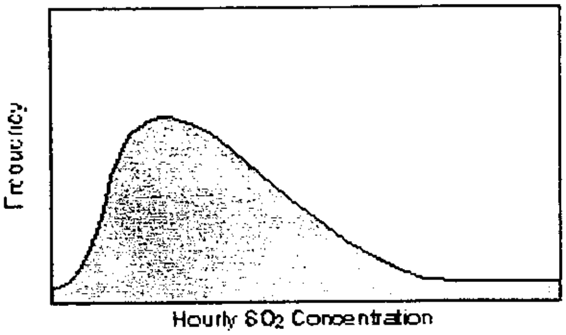


Figure 10-12. Frequency vs. concentration of SO_2.

References

Bennett, C. A., and Franklin, N. L. 1954. *Statistical analysis in chemistry and the chemical industry*. New York: Wiley and Sons, Inc.

Cadle, R. D. 1975. *The measurement of airborne particulates*. New York: Wiley-Interscience.

Dixon, W. J., and Massey, F. J., Jr. 1957. *Introduction to statistical analysis*. New York: McGraw-Hill Book Company.

Hayslett, H. T. 1968. Statistics made simple — a comprehensive course for self-study and review. New York: Doubleday & Company, Inc.

Neville, A. M., and Kennedy, J. B. 1964. *Basic statistical methods for engineers and scientists*. Scranton, PA: International Textbook Company.

Spiegel, Murray R. 1961. *Statistics*, Shaum's Outline series. New York: McGraw-Hill Book Company.

U.S. Environmental Protection Agency. 1973. *Quality Control Practices in Processing Air Pollution Samples*. APTD 1132.

U.S. Environmental Protection Agency. September 1994. *Guidance for the Data Quality Objectives Process*. EPA QA/G-4.

U.S. Environmental Protection Agency, OAQPS. June 1996. *Quality Management Plan*.

U.S. Environmental Protection Agency. January 1998. *Guidance for Data Quality Assessment, Practical Methods for Data Analysis*. EPA QA/G-9, EPA/600/R-96/084.

Section B-1

Manual Sampling of Gaseous Pollutants

Reading Assignment

Pages 5-1 through 5-39 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Absorption of gaseous pollutants
- Adsorption of gaseous pollutants
- Grab sampling
- Freezeout sampling

Learning Goal and Objectives

Learning Goal

The purpose of this lesson is to familiarize you with manual sampling techniques for the sampling of gaseous pollutants.

Learning Objectives

At the end of this section, you should be able to:

1. identify at least nine terms associated with the sampling of gaseous pollutants using absorption or adsorption devices.
2. recognize at least seven desirable qualities for a solvent to be used in a physical absoprtion process.
3. name at least two conditions that are necessary for the adequate collection of a gaseous pollutant using a physical absorption process.
4. recognize at least three criteria for selecting an absorbent to be used in a chemical absorption process.
5. identify and describe the effects of at least five sampling conditions on the collection efficiencies of liquid absorbers.
6. recognize the most accurate method for determining the collection efficiency of a liquid absorber.
7. name one advantage and two disadvantages of fritted-glass absorbers.
8. identify and describe the effects of at least four sampling conditions on the adsorption of gaseous pollutants.
9. define adsorption isotherm and associate general adsorption isotherms with chemical and physical adsorption processes.

10. recognize at least seven desirable qualities for an adsorbent to be used in gaseous pollutant sampling.
11. identify characteristics of polar and nonpolar adsorbents.
12. recognize at least four typical problems associated with adsorption air sampling.
13. identify four grab sampling devices and five potential grab sampling problems associated with atmospheric sampling.
14. recognize the freezeout sampling method for ambient air pollutants.

Reading Guidance

- Refer often to the figures of the assigned reading material as you progress through the assignment.
- When you have finished the reading assignment, complete the review exercise for Section B-2. It begins on the following page.
- After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
- For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment indicated on the answers page.
- After you have reviewed your incorrect answers (if any) proceed to Section B-3 of this guidebook.

Review Exercise

Now that you've completed the assignment for Section B-2, please answer the following questions. These will help you determine whether or not you are mastering the material.

For each of questions 1 through 9, match the stated term with its appropriate definition.

1. absorption
2. absorbate
3. absorbent
4. physical absorption
5. adsorption
6. adsorbate
7. adsorbent
8. chemical adsorption
9. physical adsorption

a. the usually reversible process of dissolving a pollutant in a liquid
b. the process by which gases are attracted, concentrated, and retained at a boundary surface
c. adsorption caused by van der Waals' interactions, dipole-dipole interactions, and electrostatic interactions
d. the process of combining gas molecules with an adsorbent to form a surface compound
e. the process of transferring one or more gaseous components into a liquid or solid medium
f. an absorbing medium
g. an absorbed substance
h. an adsorbing medium
i. an adsorbed substance

10. Which of the following is a(are) general absorption mechanism(s)?
    a. physical absorption
    b. chemical absorption
    c. both a and b, above
    d. none of the above
11. Which of the following is a(are) desirable quality(ies) for a solvent to be used in a physical absorption process?
    a. relatively nonvolatile
    b. nonpolar
    c. noncorrosive
    d. both a and b, above
    e. both a and c, above

12. Which of the following conditions is(are) necessary for the adequate collection of a gaseous pollutant using a physical absorption process?
    a. high pollutant solubility in the absorbing medium
    b. small pollutant to absorbing medium ratio
    c. both a and b, above
    d. none of the above

13. Which of the following should be considered when choosing an absorbent for a chemical absorption pollutant sampling process?
    a. pollutant solubility in absorbent
    b. reactive properties of the pollutant and the absorbent
    c. both a and b, above
    d. method of pollutant analysis
    e. all of the above

14. Which of the following affect(s) the collection efficiency of a liquid absorber?
    a. sample air flow rate
    b. bubble size
    c. height of the liquid (absorbent) column
    d. both a and b, above
    e. all of the above

15. The collection efficiency of a liquid absorber ___(?)___ as the flow rate of sample air passing through it increases.
    a. remains the same
    b. increases
    c. decreases

16. The collection efficiency of a liquid absorber ___(?)___ as the sample air bubble size decreases.
    a. remains the same
    b. increases
    c. decreases

17. The collection efficiency of a liquid absorber ___(?)___ as the length of its absorbent column increases.
    a. remains the same
    b. increases
    c. decreases

18. True or False? The sensitivity of the method used to analyze the pollutant collected in a liquid absorber may limit the height of the absorber's liquid column.

19. True or False? The absorbing solution of a liquid absorber should contain an excess of reactant in order to ensure that all the pollutant that is being sampled is collected and that the reaction rate between the pollutant and the reactant is at a maximum.

20. The collection efficiency of a liquid absorber ___(?)___ as the sampled pollutant's solubility in its absorbent increases.
   a. remains the same
   b. increases
   c. decreases

21. The collection efficiency of a liquid absorber ___(?)___ as the sampled pollutant's partial pressure (concentration) increases.
   a. remains the same
   b. increases
   c. decreases

22. The collection efficiency of a liquid absorber usually ___(?)___ as sampling temperature increases.
   a. remains the same
   b. increases
   c. decreases

23. True or False? The most accurate method of determining the collection efficiency of a liquid absorber is testing it under simulated sampling conditions.

24. Which of the following is a(are) general liquid absorber(s)?
   a. fritted-glass absorbers
   b. impingers
   c. both a and b, above
   d. none of the above

25. True or False? Impingers have somewhat higher collection efficiencies than fritted-glass absorbers.

26. Which of the following is a(are) disadvantage(s) of fritted-glass absorbers?
   a. possibility of surface reactions at the frit
   b. fritted-glass absorbers having frit pore sizes of approximately 50 μm or less gradually become clogged with use
   c. both a and b, above
   d. none of the above

27. Which of the following is a(are) general adsorption mechanism(s)?
   a. physical adsorption
   b. chemical adsorption
   c. both a and b, above

28. True or False? Critical temperature may be defined as that temperature above which it is impossible to liquify a gas regardless of the external pressure applied to the gas.

29. The ability of a gas to be adsorbed ___(?)___ as gas boiling point increases.
   a. remains the same
   b. increases
   c. decreases

30. The ability of a gas to be adsorbed ___(?)___ as gas critical temperature increases.
    a. remains the same
    b. increases
    c. decreases

31. True or False? Chemical adsorption is enhanced by higher sampling temperatures.

32. True or False? Physical adsorption is usually limited to monolayer molecular adsorption.

33. True or False? Chemical adsorption usually involves multilayer molecular adsorption.

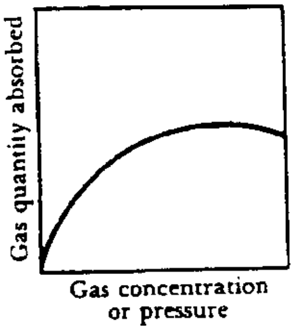
34. Which of the following is an(are) optimum condition(s) for the physical adsorption of a gas?
    a. low adsorbate concentration
    b. large adsorbing surface
    c. no molecules other than adsorbate molecules competing for adsorption sites
    d. high temperature
    e. both b and c, above
    f. all of the above

35. The ability of a gas to be adsorbed ___(?)___ as its concentration increases.
    a. remains the same
    b. increases
    c. decreases

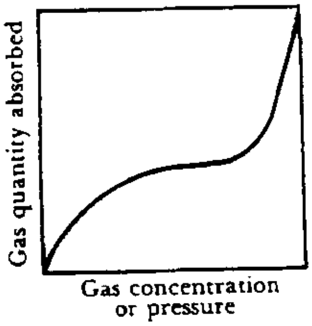
36. True or False? An adsorption isotherm describes the relationship between the quantity of a gas adsorbed at a constant temperature and the gas's concentration or pressure.

37. Which of the general adsorption isotherms depicted below is(are) associated with chemical adsorption?

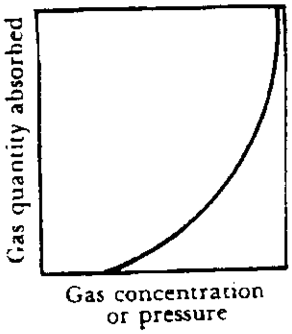
a.



b.



c.



d. all of the above

38. Which of the general adsorption isotherms depicted in question 37 is(are) associated with physical adsorption?

a. isotherm a
b. isotherm b
c. isotherm c
d. isotherms a and b
e. isotherms a, b, and c

39. For a gas to be adequately collected by physical adsorption, it must have a molecular weight that is ____(?)____ the molecular weight of the normal components of air.
    a. the same as
    b. larger than
    c. smaller than

40. True or False? For a gas to be adequately collected by physical adsorption, its particles must be small enough to allow Brownian motion or gas velocities to effectively cause contact of the gas with the adsorbent.

41. An adsorbate's adsorption rate ____(?)____ as the number of other substances competing for adsorption sites of the adsorbent increases.
    a. remains the same
    b. increases
    c. decreases

42. Which of the following is ***not*** a desirable quality for an adsorbent?
    a. granular
    b. high resistance to air flow
    c. inert except for a specific adsorbate
    d. resistant to breakage, deterioration, and corrosion
    e. easily activated
    f. provides an easy release of adsorbate
    g. high adsorptive capacity

43. An adsorbent's collection efficiency ____(?)____ as its surface area increases.
    a. remains the same
    b. increases
    c. decreases

44. True or False? Adsorbent activation involves distilling out various impurities from the adsorbent, thus forming a larger free surface area for adsorption.

45. True or False? Adsorbent pore size is an important consideration when selecting an adsorbent to collect a particular adsorbate.

46. True or False? The chemical nature of the surface of an adsorbent does not affect the adsorbent's collection efficiency.

47. Which of the following is a(are) general adsorbent property(ies)?
    a. polar (exhibiting strong polarity)
    b. nonpolar (exhibiting little or no polarity)
    c. both a and b, above

For each of questions 48 through 50, match the adsorbent with its appropriate characteristic(s).

48. polar
49. nonpolar
50. molecular sieve

a. prefers molecules that have little or no polarity
b. strongly prefers polar molecules
c. strongly prefers polar molecules, has very high porosity, is specific for adsorbate size and shape, has high adsorptive capacity.

51. True or False? Nonpolar adsorbents are more selective in adsorbing substances than are polar adsorbents.

52. Which of the following is a(are) characteristic(s) of activated carbon?
    a. polar
    b. absorbs almost all volatile substances
    c. has a high adsorptive capacity
    d. both b and c, above
    e. all of the above

53. Which of the following is a(are) typical adsorption air monitoring problem(s)?
    a. irreversible adsorption of the adsorbate
    b. variable desorption efficiency of the adsorbate during analysis
    c. both a and b, above
    d. in-situ reactions on the adsorbent during sampling
    e. all of the above

54. True or False? Grab sampling consists of removing a small representative portion of a large sample within an interval of a few seconds to a few minutes.

For each of questions 55 through 58, match the grab sampling device with its appropriate diagram.

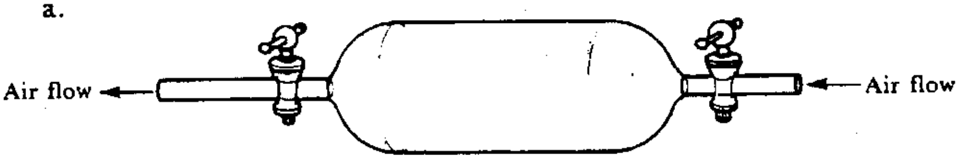
55. evacuated flask

56. liquid-displacement collector

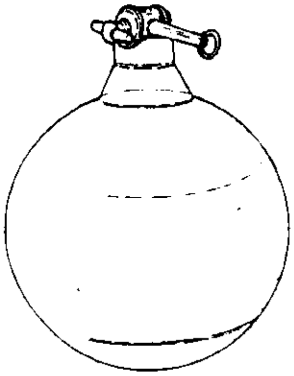
57. gas-displacement collector

58. bag inflation sampler

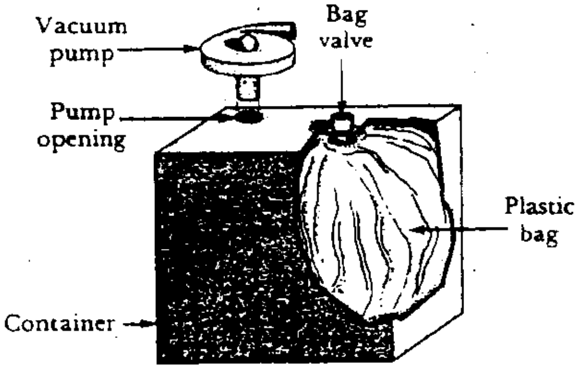
a.



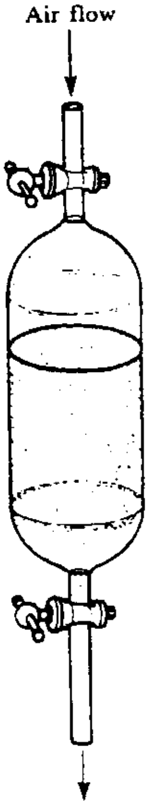
b.



c.



d.



59. Which of the following is a(are) potential sampling problem(s) when using bag grab sampling techniques?
    a. sample contamination and memory effects caused by the bag wall.
    b. sample deterioration over time
    c. both a and b, above
    d. in-situ reactions
    e. all of the above

60. True or False? Usually the most sensitive analytical techniques must be used to detect the small pollutant concentrations found in grab samples.

61. True or False? The freezeout sampling method consists of drawing sample air through collection chambers having progressively lower temperatures. Each component of the sample air condenses to a liquid and is collected in the chamber having a temperature which is approximately equal to or less than its boiling point.

62. Which of the following increase(s) the collection efficiency of a freezeout sampling train?
    a. increasing collection chamber cold surface area
    b. decreasing the flow rate of sample air through the sampling train
    c. both a and b, above
    d. none of the above

63. True or False? Increasing the cold surface area of a freezeout sampling train allows a shorter sample detention time to be used.

64. The sample detention time of a freezeout sampling train ___(?)___ as the flow rate of sample air through the sampling train increases.
    a. remains the same
    b. increases
    c. decreases

Section B-1

Review Exercise Answers

		Page(s) of *Atmospheric Sampling: Student Manual*
1.	e	5-1
2.	g	5-8, 5-9
3.	f	5-1, 5-9
4.	a	5-1
5.	b	5-9
6.	i	5-9
7.	h	5-9
8.	d	5-10
9.	c	5-10
10.	c	5-1
11.	e	5-1
12.	c	5-2
13.	e	5-2
14.	e	5-3
15.	c	5-3, 5-23
16.	b	5-3, 5-23
17.	b	5-3, 5-23
18.	True	5-3, 5-4
19.	True	5-4
20.	b	5-4
21.	b	5-4
22.	c	5-4
23.	True	5-5
24.	c	5-5
25.	False	5-8
26.	c	5-3, 5-7
27.	c	5-9
28.	True	5-10
29.	b	5-10
30.	b	5-10
31.	True	5-11
32.	False	5-11
33.	False	5-11
34.	e	5-11
35.	b	5-11
36.	True	5-12
37.	a	5-12
38.	e	5-12

		Page(s) of *Atmospheric Sampling: Student Manual*
39.	b	5-13
40.	True	5-14
41.	c	5-14
42.	b	5-14
43.	b	5-14
44.	True	5-15
45.	True	5-15
46.	False	5-15
47.	c	5-15, 5-16
48.	b	5-16
49.	a	5-15
50.	c	5-17
51.	False	5-16
52.	d	5-16
53.	e	5-17
54.	True	5-26
55.	b	5-28
56.	d	5-30
57.	a	5-29
58.	c	5-31
59.	e	5-31
60.	True	5-31
61.	True	5-32
62.	c	5-35
63.	True	5-35
64.	c	5-35

Required Readings

Chapter 5

Gaseous Sampling

Principles of Absorption

Introduction

Absorption of pollutants in various media plays an important role in air pollution monitoring. It is particularly important in the wet-chemical methods of analysis. Before the advent of continuous monitoring instrumentation, techniques employing absorption were the most inexpensive and up-to-date methods available.

Absorption is the process "of transferring one or more gaseous components into a liquid or solid medium in which they dissolve." Absorption of gaseous pollutants in solution is frequently utilized in atmospheric sampling because of the numerous methods available to analyze the resulting solution. These methods include photometric, conductimetric, and titrimetric techniques. Details of sampling and analysis of specific gaseous pollutants by absorption are given elsewhere. This discussion concentrates on a description of the gas-liquid absorption process and factors affecting collection efficiency. Devices frequently utilized in gas-liquid absorption and several current applications are also discussed.

Types of Absorption

In gas-liquid absorption the collecting liquid (i.e., the absorbent) may change either chemically or physically, or both, during the absorption process. In gas-liquid absorption sampling, two types of absorption have been recognized: (a) physical absorption and (b) chemical absorption.

A typical chemical absorption process would involve drawing a volume of air through a solution that reacts with the gaseous contaminant to form a nongaseous compound; for example, an acid mist is drawn through a volume of sodium hydroxide. The acid reacts with the base to form a stable salt. Titration of the unreacted base with standard acid indicates the quantity of pollutant reacted.

Physical Absorption

Physical absorption involves the physical dissolving of the pollutant in a liquid. The process is usually reversible in that the pollutant exhibits a relatively appreciable vapor pressure. The solubility of the pollutant in a given absorbent is dependent on the partial pressure of the pollutant in the atmosphere and the temperature and purity of the absorbent. An ideal solvent would be relatively nonvolatile, inexpensive, noncorrosive, stable, nonviscous, nonflammable, and nontoxic. In many cases distilled water fulfills many of these characteristics and is used as the solvent for collecting some gases. The suitability of distilled water for several selected gases is presented in Table 5-1.

Table 5-1. Solubility of selected gases in distilled water at 20°C.

Gas	Volume absorbed per volume of water*
Nitrogen	0.015
Oxygen	0.031
Nitric oxide	0.047
Carbon dioxide	0.878
Hydrogen sulfide	2.582
Sulfur dioxide	39.374

*Gas volumes reduced to 0°C and 760 mm Hg.

The physical absorption process involves collecting the pollutant by solution in the absorbent. The solution is then analyzed for pollutant concentration by a convenient analytical method. In general, low efficiency will be obtained for physical absorption unless the pollutant is very soluble and the ratio of dissolved gas to liquid volume is small. For this reason, physical absorption is rarely the only absorption process involved in collecting gaseous pollutants.

Chemical Absorption

In contrast to physical absorption, chemical absorption is a process that involves a liquid absorbent that reacts with the pollutant to yield a nonvolatile product. The solvent selected is one that reacts with the pollutant in an irreversible fashion—for example, the reactions of ammonia and carbon dioxide gases with acidic and basic solvents, respectively. These reactions produce carbonic acid (H_2CO_3) and ammonium hydroxide (NH_4OH). The solubilities of these acids and bases are much greater than gaseous CO_2 or NH_3. Primary factors affecting the choice of an absorbent in chemical absorption are the solubility of the pollutant, reactive properties of pollutant and absorbent, and the subsequent analytical method to be used. Care should be taken to avoid an absorbent that will interfere with subsequent chemical analysis.

A typical process involving chemical absorption is the reaction of SO_2 and aqueous H_2O_2 to produce sulfuric acid. The concentration of SO_2 is determined by titrating the H_2SO_4 formed with Ba $(ClO_4)_2$. This procedure is currently the reference method for determining SO_2 emissions from stationary sources.

Collection Efficiency

Each absorption sampling device must be assembled from units found to be most suitable for the specific pollutant involved. It is not necessary to have 100% collection efficiency; however, the efficiency under sampling conditions should be known and reproducible. In some circumstances a sampling system having a relatively low collection efficiency (e.g., 60 to 70%) could be used provided that the desired sensitivity, reproducibility, and accuracy are obtainable.

There is much information available in the literature concerning optimum flow rates for specific pollutants and collection efficiencies with respect to the pollutant and absorbent for many sampling devices. However, much more information is needed on the variation of collection efficiency with the rate of sampling concentrations of a variety of compounds, and the nature of the collecting medium. For available information on gas-liquid absorption theory and the mathematical treatment of the variables affecting collection efficiency, the reader is referred to the literature (Reference section of this chapter). In the present discussion only a qualitative description of the factors affecting collection efficiency has been attempted.

Factors Affecting Collection Efficiency

The variables affecting the collection efficiency of methods that use absorbers for the collection of gaseous contaminants may be conveniently considered as: (a) those associated with the absorber, such as an acceptable flow rate, bubble size, and height of the liquid column; (b) the chemical characteristics of the sampling situation, such as the chemical nature and concentration of the pollutant in the air and the absorbing medium, the chemical nature and concentration of the absorbing solution, and the reaction rate; and (c) the physical characteristics of the sampling situation, such as temperature, pressure, and pollutant solubility.

Absorber Characteristics

The gas flow rate through the absorber is one of the major factors determining the collection efficiency of an absorber. Absorption collection efficiency varies inversely with the flow rate. An increase in the flow rate through the solution will decrease the probability of adequate gas-liquid contact. In addition, high flow rates increase the possibility of liquid entrainment in the effluent gas. If varying flow rates are used in sampling, a collection efficiency versus flow rate curve should be determined for each absorber and absorber type. All other variables (e.g., temperature, pollutant and absorbent types, etc.) should be held at the desired values.

The collection efficiency of the absorption process for a gas or vapor by chemical absorption or physical absorption depends on the probability of successful collisions of reagent or solvent molecules with gas molecules. For a given concentration of reagent, this probability of collision will depend on the surface area of the gas bubbles, on the length of the column of liquid through which the bubbles must pass, and on the rate at which they rise through the liquid. As the volume of individual bubbles decreases, the surface area presented to the liquid increases. Hence, smaller bubbles have a greater possibility of gas transfer into the absorbent phase. For this reason many absorption devices use fritted discs as opposed to injection-type dispersion tubes to achieve a smaller bubble size. However, due to possible surface reactions that can take place at the frit, fritted bubblers may not be appropriate for certain types of sampling (e.g., for ozone). The length of the column of liquid in the absorber is another prime factor affecting the collection efficiency. The longer the gas bubble is in contact with the liquid, the more pollutant is transferred. However, in many cases this variable cannot be used to its maximum advantage; for example, when the sampled pollutant has a low concentration in the atmosphere, it must be collected in a small absorbent volume so that it is in the sensitivity range of the subsequent analytical method to be used. Bubble rise time is a function of bubble size and absorbent height. A compromise is usually reached by having the smallest feasible bubble size combined with the highest absorbent column possible for the particular analysis.

Chemical Characteristics

The best situation, with respect to collection efficiency, is to choose an absorbent with a very large capacity for absorbing the pollutant without building up appreciable vapor pressure. This can be accomplished by choosing a chemical reagent that reacts with the pollutant in an irreversible fashion—for example, the irreversible reaction that occurs when carbon dioxide is absorbed in a sodium hydroxide solution to form the carbonate ($CO_3^=$) ion.

The concentration of the absorbing medium to be used is a function of the expected concentration of the contaminant encountered, and the rate of the particular chemical reaction being used. An excess of the reactant in the absorbing solution is preferable to ensure that all the pollutant is collected and that the reaction rate is at a maximum. Ideally the reaction should be instantaneous since the period of contact between the pollutant and the absorbent is a short one.

Since the rate of reaction is proportional to concentrations of the reacting substances, other variables being equal, the rate of the process falls off as the reaction proceeds. This phenomenon must be compensated for by increasing the concentration of the absorbing liquid, thereby forcing the reaction to approach completion rapidly.

Physical Characteristics

The primary physical characteristics affecting collection efficiency are pressure, temperature, and pollutant solubility in the absorbing medium. In many sampling situations, these variables are fixed by ambient conditions.

The solubility of the pollutant in the absorbing medium is related to its partial pressure (by Henry's law), and the partial pressure of the pollutant in turn is related to its concentration. The net effect considering ideal gas behavior is that an increase in pollutant concentration in the air will result in an increase in pollutant solubility in the liquid. Increased pollutant solubility, other variables being equal, results in a higher collection efficiency.

An increase in temperature enhances chemical reactions but decreases pollutant solubility in the absorbent. In most cases the net effect is a decrease in collection efficiency with increasing temperature.

Determination of Collection Efficiency

The method of determining collection efficiency will depend on how the results are to be used. If the most accurate values are needed, the best available method for determining collection efficiency should be used. On the other hand, if only approximate values are needed, a less stringent method for determining collection efficiency may be satisfactory. In all cases collection efficiency should be defined with respect to the method of determination.

The most accurate method of determining the collection efficiency of a particular absorber is by a trial on a synthetic atmosphere, duplicating in every respect the actual sampling conditions. Calibration techniques consist of both dynamic dilution and static dilution systems. In dynamic dilution, a continuous supply of a known pollutant concentration is available that can be sampled, while the static system consists of a container holding a known volume of pollutant of a known concentration. In both of these calibration procedures the investigator must be assured that the atmosphere being sampled actually contains the pollutant concentration it is believed to contain.

Another method that may be used for collection efficiency calibration is the comparison of the technique of interest to a previously calibrated method. In this technique the conditions of the calibrated method are imposed on the method of interest. All variables in both methods should be identical, especially with respect to interferences.

Absorption Devices

A variety of devices have been used for sampling pollutants from the atmosphere. One of the simplest and most common devices used is an ordinary gas-washing bottle containing the absorbent plus a gas-dispersion tube for introduction of the pollutant into the solution. A typical device of this type is illustrated in Figure 5-1.

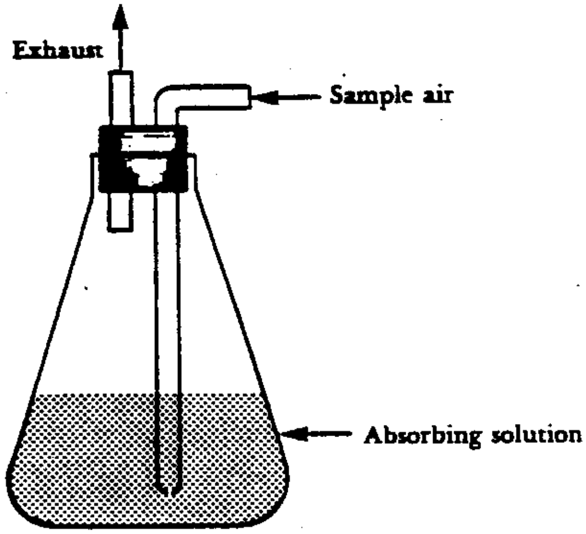


Figure 5-1. Absorption device adapted from an Erlenmeyer flask.

Gas flows from the unrestricted opening into the absorbent solution. A variety of absorbers of this type are available. They are usually glass and may be conical or cylindrical in shape. Typical flow rates through the various devices range from 1 to 5 liters per minute.

The majority of other absorption devices used in atmospheric sampling fall into two categories: (a) fritted-glass absorbers and (b) impingers.

Fritted-glass Absorbers

A great variety of shapes and sizes of these absorbers are being used. A few are illustrated in Figure 5-2.

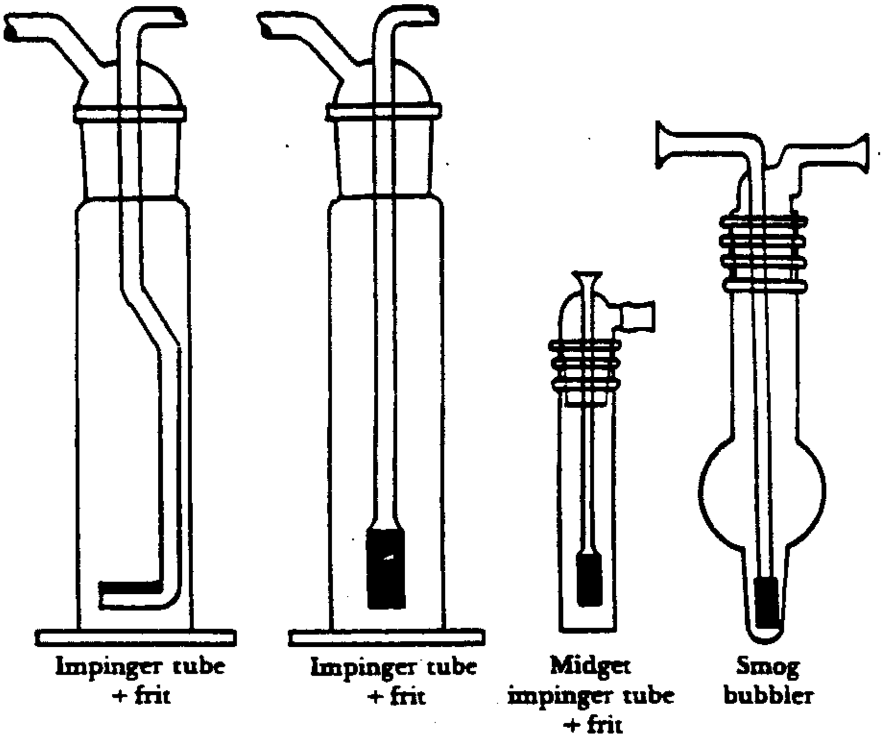


Figure 5-2. Typical fritted-glass absorbers.

These units usually provide the most efficient collection of gaseous pollutants. In addition to the commercially available units, homemade devices may be created using normal gas-dispersion tubes. The fritted part of the dispersion tube is readily available in the form of a disc or cylinder of various pore size. The coarse and extra-coarse frits provide good pollutant dispersion with a minimum head loss.

The collection efficiency of any one device will depend on the factors previously mentioned. However, under optimal conditions of flow rate, absorbing medium and pollutant type, many of the fritted-glass absorbers have a collection efficiency in excess of 90%. Several of their more important characteristics are presented in Table 5-2.

Table 5-2. Absorption sampling devices.

Principle of operation	Devices	Capacity (ml)	Sampling rate ℓ/min	Efficiency* %	Comment
Simple gas-washing bottles. Gas flows from unrestricted opening into solution. Glass, conical or cylindrical shape	Standard	125–500	1–5	90–100	Bubblers are large. Reduction of sampling rate increases efficiency. Several units in series raises efficiency
	Drechsel	125–500	1–5	90–100	Similar to above
	Fleming	100	1–5	90–100	Difficult to clean
Modified gas-washing bottles	Fritted bubbler	100–500	1–5	95–100	Fritted tubes available for simple gas washing, items above. Smaller bubblers provide increased gas-liquid contact
	Glass bead bubbler	100–500	1–5	90–100	Provides for longer gas-liquid contact smaller bubbles
Large bubbler traverses path extended by spiral glass insert	Fisher Milligan bottle	275	1–5	90–100	
	Greiner-Friedrichs	100–200	1–5	90–100	Similar to Fisher Milligan
Impingers—designed principally for collection of aerosols. Used for collection of aerosols	Greenburg-Smith	500	1–5	90–100	Cylindrical shape
Used for collection of gases. Restricted opening. Fritted tubes available which allow use as bubbler	Midget	100	0.1–0.5	90–100	
Smog bubbler	Fritted bubbler	10–20	1–4	95–100	

*Under optimum conditions of flow rate, absorbing medium, etc., for a particular pollutant.

Absorbers that use frits with a pore size of approximately 50 micrometers or less gradually become clogged with use. They may be cleaned by surging the appropriate cleaning solution back and forth through the frit and then rinsing with distilled water in the same fashion. Various substances may be removed from the frits by cleaning with the appropriate solvent (e.g., hot hydrochloric acid for dirt, hot concentrated sulfuric acid containing sodium nitrite for organic matter, etc.).

Impingers

Impingers are often used in sampling for gaseous and vaporous pollutants from the atmosphere. Two types of impingers are shown in Figure 5-3.

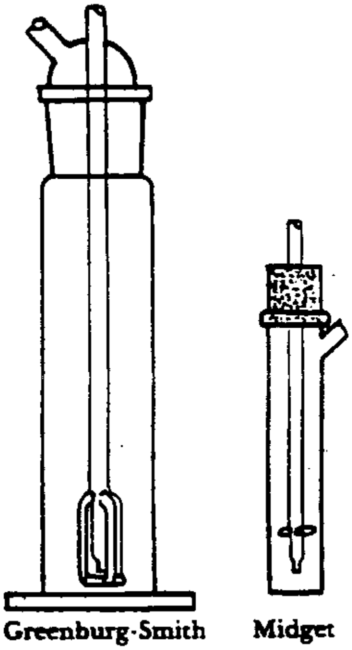


Figure 5-3. Two types of impingers.

A limited amount of investigation has indicated that the impinger is somewhat less efficient than the fritted absorber for collecting gaseous pollutants. When several types of absorbers were operated under optimal conditions, the midget impingers were found to be less efficient than the fritted-glass absorber. In addition, the threshold concentration for collection with the midget impinger was found to be somewhat higher than that for several types of fritted-glass absorbers.

Summary

Gas-liquid absorption is the process by which a gaseous pollutant is dissolved in a liquid medium. If a chemical reaction occurs between the pollutant (absorbate) and absorbent, the process is termed chemical absorption, whereas physical solution of the pollutant in the absorbent is termed physical absorption.

The collection efficiency of any particular absorption process is a function of the characteristics of the absorption device, and the chemical and physical properties of the absorbate-absorbent pair. A collection efficiency should be determined for each sampling analysis situation by a method that gives the accuracy desired.

Principles of Adsorption

Basic Principles

Adsorption is the phenomenon by which gases, liquids, and solutes within liquids are attracted, concentrated, and retained at a boundary surface. The boundary surface may be the interface between a gas and liquid, liquid and liquid, gas and solid, liquid and solid, or solid and solid. Of the various boundary surfaces, the adsorption mechanism between liquid and solid, and gas and solid have received the most attention—the former with respect to removal of substances from solution with a solid adsorbent (e.g., purification), and the latter with respect to removing gaseous pollutants on solid adsorbents of high surface area.

A solid adsorbent has a crystal lattice structure. The atoms at the surface of the lattice are arranged in a regular sequence, which depends on the particular solid's crystalline structure. The valence or other attractive forces at the surface of a solid are unsatisfied, or unsaturated, because they are not united with other atoms. As a result of this unbalanced condition, the solid surfaces will tend to satisfy their residual forces by attracting and retaining gases or other substances with which they come in contact. This surface concentration of substance is the adsorption process. The attracted substance is known as the adsorbate, while the surface substance is called the adsorbent.

In air pollution work, adsorption techniques are commonly used for collecting a specific gas or combination of gases. A typical process consists of passing a gas stream through a container filled with an adsorbent such as activated charcoal, alumina, or silica gel. The gas is bound to the adsorbent by molecular forces and, if condensation does not occur, the gas remains physically and chemically unchanged. Following collection, the gas may be removed from the absorbent for analysis or ultimate deposition by applying heat, passing inert carrier gases through the system, or treating chemically.

Adsorption can be distinguished from absorption. In absorption the material is not only retained on the surface, but it passes through the surface and is distributed throughout the absorbing medium. The term absorption in many cases implies a chemical reaction between the absorbing medium (absorbent) and the collected substance (absorbate). For example, water is absorbed by a sponge and by anhydrous calcium chloride. However, various gases are adsorbed on the surface of activated carbon. Often when the true process is not known, the term sorption is used.

Types of Adsorption

Investigation of the adsorption of gases on various solid surfaces has revealed that the operating forces are not the same in all cases. Two types of adsorption have been recognized: (a) physical, or Van der Waals', adsorption (physiosorption) and (b) chemical adsorption (chemisorption).

Physical Adsorption

In physical adsorption, the attractive forces consist of Van der Waals' interactions, dipole-dipole interactions, and/or electrostatic interactions. These forces are similar to those causing the condensation of a gas to a liquid. The process is further characterized by low heats of adsorption, on the order of 2 to 15 kilocalories per mole of adsorbate, and by the fact that adsorption equilibrium is reversible and rapidly established.

Physical adsorption is a commonly occurring process. For example, this is the type of adsorption that occurs when various gases are adsorbed on charcoal. If the temperature is low enough, any gas will be physically adsorbed to a limited extent. The quantity of various gases adsorbed under the same conditions is roughly a function of the ease of condensation of the gases. The higher the boiling point or critical temperature* of the gas, the greater is the amount adsorbed. This concept will be discussed in more detail subsequently.

Chemical Adsorption

In contrast to physical adsorption, chemical adsorption is characterized by high heats of adsorption, on the order of 20 to 100 kilocalories per mole of adsorbate, which leads to a much stronger binding of the gas molecules to the surface. Heats of adsorption are on the same order of magnitude as chemical reactions, and it is evident that the process involves a combination of gas molecules with the adsorbent to form a surface compound. This type of adsorption resembles chemical bonding and is called chemical adsorption, activated adsorption, or chemisorption. For example, in the adsorption of oxygen on tungsten it has been observed that tungsten trioxide distills from the tungsten surface at about 1200 K. However, even at temperatures above 1200 K, oxygen remains on the surface, apparently as tungsten oxide. Additional examples of chemical adsorption are the adsorption of carbon dioxide on tungsten, oxygen on silver, gold on platinum, and carbon and hydrogen on nickel.

A comparison of physical and chemical adsorption can be made by considering the adsorption of oxygen on charcoal. If oxygen is allowed to reach equilibrium with the charcoal at 0°C, most of the oxygen may later be removed from the charcoal by evacuating the system at 0°C with a vacuum pump. However, a small portion of the oxygen cannot be removed from the charcoal no matter how much the pressure is decreased. If the temperature is now increased, oxygen plus carbon monoxide and carbon dioxide are released from the charcoal. Thus, most of the oxygen is physically adsorbed and can be easily removed, but a small quantity undergoes a chemical reaction with the adsorbent and is not readily removed. In some cases, chemical adsorption may be preceded by physical adsorption, the chemical adsorption occurring after the adsorbent has received the necessary activation energy.

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*Critical temperature may be defined as that temperature above which it is impossible to liquify a gas no matter how high an external pressure is applied.

In general, with respect to the adsorbent-adsorbate pairs, chemical adsorption is more specific in nature than physical adsorption. It is usually a much slower process, requiring the displacement or selection of the molecules where the reaction is to occur. The chemisorption process is enhanced at higher temperatures where existing energy barriers between the adsorbent and adsorbate are overcome. At low temperatures, chemical adsorption in some systems may be too slow to reach a measurable amount. In many cases the adsorption occurring is a combination of both types. At low temperatures physical adsorption may predominate, whereas at higher temperatures chemisorption may be more prominent. This situation is true for the adsorption of hydrogen on nickel. However, because of the non-specificity of Van der Waals' forces, physical adsorption may be occurring but be hidden by chemisorption. Finally, chemical adsorption is usually limited to the formation of a single layer of molecules on the adsorbent's surface (monolayer adsorption), whereas in physical adsorption the adsorbed layer may be several molecules thick (multilayer adsorption).

In most of the adsorption equipment in air pollution control work, physical adsorption plays the most prominent part.

Variables Affecting Gas Adsorption

The quantity of a particular gas that can be adsorbed by a given amount of adsorbent will depend on the following factors: (a) concentration of the gas in the immediate vicinity of the adsorbent; (b) the total surface area of the adsorbent; (c) the temperature of the system; (d) the presence of other molecules competing for a site on the adsorbent; and (e) the characteristics of the adsorbate such as weight, electrical polarity, and chemical reactivity. Ideal physical adsorption of a gas would be favored by a high concentration of material to be adsorbed, a large adsorbing surface, freedom from competing molecules, low temperature, and by aggregation of the adsorbate into a form that conforms with the pore size of the attracting adsorbent.

Several of the above listed variables will now be discussed in greater detail.

Adsorption Isotherms

Adsorption processes where physical adsorption rather than chemisorption represents the final state can be explained in terms of equilibrium measurements. For a given amount of adsorbent with a given surface area, the amount of gas adsorbed is dependent on the pressure (or concentration) of the gas surrounding the adsorbent. The higher the pressure or concentration of the gas at a given temperature, the greater the amount of gas adsorbed. When an adsorbent and gas are mixed, the amount adsorbed will gradually increase while the concentration of the adsorbate in the system decreases until the rate of adsorption becomes equal to the rate of desorption. Thus, an equilibrium between the two reactions is established. If additional gas is added to the system, the amount adsorbed will increase until equilibrium is again established. Likewise, if the gas concentration is decreased, the adsorbent will lose gas to its surroundings until equilibrium is again reached.

The description of the relationship between the quantity of gas adsorbed at various concentrations or pressures at constant temperature is called an adsorption isotherm. An adsorption isotherm consists of a plot of the data obtained from measuring the amount of gas adsorbed (e.g., grams adsorbed per gram of adsorbent) at various gas concentrations or pressures (e.g., moles per liter or atmospheres), as the case may require, at equilibrium under a condition of constant temperature. Adsorption isotherms are useful in that they provide a means of evaluating: (a) the quantity of gas adsorbed at various gas concentrations; (b) adsorptive capacities at various gas concentrations; (c) the adsorptive capacity as a function of concentration and type of gas; and (d) the surface area of a given amount of adsorbent.

Types of Adsorption Isotherms

The graphic plots of adsorption isotherms yield a wide variety of shapes. Six general types of isotherms have been observed in the adsorption of gases on solids; these are illustrated in Figure 5-4. In physical adsorption all six isotherms are encountered, while in chemisorption only Type 1 occurs.

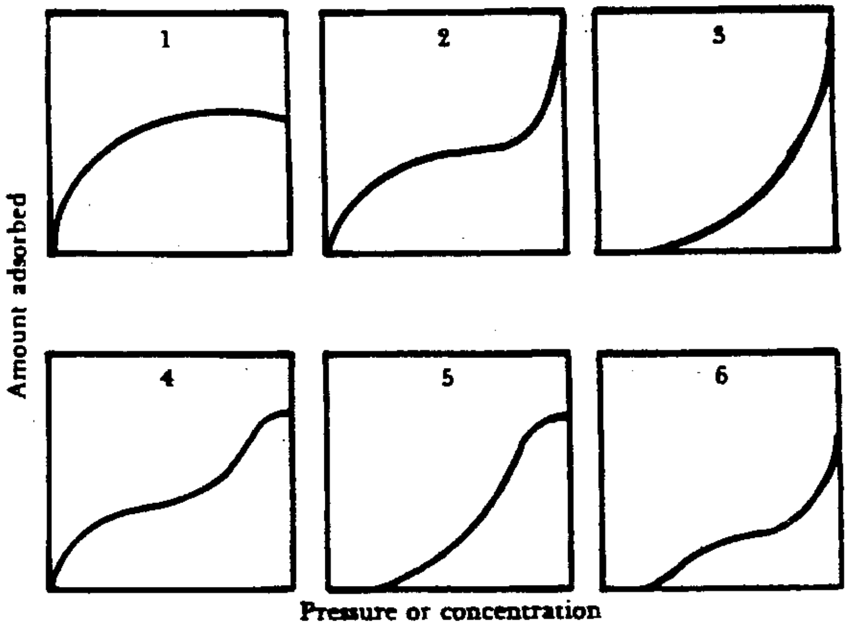

Figure 5-4. Gas adsorption isotherms.

Type 1 – This type represents the adsorption of a single layer of gas molecules on the adsorbent. There is no interaction between the adsorbed molecules.

Type 2 – This isotherm begins like Type 1 but is modified at high pressure by multilayer adsorption. There is definite interaction between the layers of adsorbed gas molecules.

Type 3 – This type of isotherm is rare. It occurs only when initial adsorption favors a very few strong sites. The interaction between adsorbed molecules is so strong that vacant sites next to occupied sites are stronger than any other vacant sites. In this type of adsorption the number of effective sites increases with coverage of the adsorbent.

Types 4 and 5—These two are similar to Types 2 and 3 respectively, except that they continue to exhibit adsorption at high adsorbent coverage.

Type 6—This type resembles Type 3 with monolayer adsorption first and then continued deposition of a multilayer film.

Adsorbate Characteristics

The major adsorbate-characteristics affecting the amount of gas adsorbed are the ease of liquefaction of the gas, adsorbate size, concentration of the gas, and presence of other gases.

Gas Liquefaction

The specificity by which certain gases are adsorbed on solid adsorbents is illustrated in Table 5-3, where the volumes of different gases adsorbed by one gram of charcoal at 15°C are tabulated.

Table 5-3. Adsorption of gases on one gram of charcoal at 15°C*.

Gas	Volume adsorbed (cc)	Critical temperature (K)
H_2	4.7	33
N_2	8.0	126
CO	9.3	134
CH_4	16.2	190
CO_2	48.0	304
HCl	72.0	324
H_2S	99.0	373
NH_3	181.0	406
Cl_2	235.0	417
SO_2	380.0	430

*Volumes of gases have been reduced to standard conditions (0°C and 1 atmosphere pressure).

Table 5-3 indicates that the extent of adsorption parallels the increase in critical temperature. This correlation suggests that gases which liquify easily (high critical temperatures) are more readily adsorbed. However, it does not imply that the adsorbates exist as liquids on the adsorbent's surface. A similar relationship is obtained with boiling points.

Adsorbate Size

The size of the gas molecule to be removed by adsorption is characterized by a lower and upper range. The lower size limit is imposed on physical adsorption by the requirement that the pollutant must be higher in molecular weight than the normal components of air. In general, gases with molecular weights greater than 45 are readily removed by physical adsorption. This size includes most odorous and toxic gases of air pollution interest. Gases of interest of lower molecular weight, such as formaldehyde and ammonia, may be removed by chemical adsorption methods using appropriately impregnated adsorbents.

For the upper limit, the individual particles must be sufficiently small so that Brownian motion, or kinetic velocities, will ensure effective contact by collision between them and the granular adsorbent. Although moderate efficiencies may be obtained for very fine mists, the upper limit is generally in the range of molecular size.

Gas Concentration

As seen from the examination of adsorption isotherms, the quantity of gas adsorbed is a function of the gas concentration or pressure. An increase in concentration or pressure in the vicinity of the adsorbent results in an increase of the total amount of gas adsorbed.

Presence of Other Gases

Since the presence of additional gas molecules in a particular adsorbent-adsorbate system causes competition for the limited number of adsorption sites present, the observed effect is a reduction in the amount of adsorbate removed.

Adsorbent Characteristics

Most of the common adsorbents in use are more or less granular in form and are supported in a column through which the gas to be sampled is drawn. Common adsorbents have the capacity to adsorb 8 to 40% of their weight. An ideal adsorbent should be granular and of such size and form that it offers little or no resistance against flow. It should have a high adsorptive capacity; be inert and specific; be resistant to breakage, deterioration, and corrosion; be easily activated; and provide an easy release of adsorbate. Unfortunately, no one adsorbent possesses all these characteristics, so it becomes a matter of choosing the best adsorbent for a particular job.

Surface Area

All solids are capable of adsorbing gases to some extent. However, since adsorption is a surface phenomenon, it is not very pronounced unless the adsorbent possesses a large surface area for a given mass. For this reason, materials like silica gel and charcoals obtained from wood, bone, coconut shells, and lignite are very effective adsorbing agents. Since large surface areas are desirable for extensive adsorption, this factor is of primary importance in determining the amount of absorbate that can be held by a unit of adsorbent. Solid adsorbents may vary in surface area from less than 1 to over 2000 square meters per gram. Typical approximate surface areas of several adsorbents are presented in Table 5-4. The latter two substances owe their high surface area to their porosity. They are thus capable of taking up large volumes of various gases.

Table 5-4. Typical surface areas of adsorbents.

Adsorbent	Area (m^2/g)
Clay	5 – 15
Asbestos	10 – 20
Chalk	20 – 30
Carbon black	50 – 100
Silica or alumina gel	200 – 800
Activated carbon	500 – 2000

The extent of adsorption can be further increased by activating the adsorbents by various methods. For example, wood charcoal is activated by heating to between 350 and 1000°C in a vacuum, in air, in steam, and/or in the presence of other gases to a point where the adsorption of carbon tetrachloride at 24°C can be increased from 0.011 gram per gram of charcoal to 1.48 gram. The activation process involves distilling out various impurities from the adsorbent, thus leading to the formation of a larger free surface area for adsorption. Occasionally, large surface areas are produced by the original cellular structure of the plant, as in the case of coconut shell charcoal. However, the activation process will increase the porosity of the material and may, under some circumstances, cause it to be less stable as an adsorbent. For example, if the temperature is raised, the porous structure of the adsorbent may aggregate into larger units that tend to become smooth and inactive. In many cases the past history of the adsorbent, with respect to preparation and method of activation, is just as important as the chemical characteristics in determining the adsorption capacity.

Often the adsorbent will exhibit an inherent preference for the adsorption of certain gases. This preference is primarily due to such factors as the method of preparation and activation, and the chemical nature of the adsorbent's surface. Preparation and activation methods not only may increase total adsorptive capacity, but they may also affect the adsorption process with respect to adsorbate size.

Pore Size

The pore size in the more porous adsorbents may vary in diameter from a few to several hundred angstrom units. This may become a critical factor in selecting an adsorbent to remove a particular adsorbate. For example, iodine may be adsorbed on an adsorbent with a pore size of 10 Å in diameter, while methylene blue is excluded by pores having a diameter less than about 15 Å.

Chemical Nature

The chemical nature of the adsorbent's surface is an additional factor of considerable importance. It is of particular interest in chemical adsorption, where a rapid rate and a large degree of chemical reaction is desirable. In physical adsorption the nature of the surface is one of the primary factors influencing the strength of the adsorbent-absorbate attraction. For example, a pure graphite surface physically adsorbs hydrophobic (i.e., water-hating) compounds to a large extent, while oxygenated surfaces are generally required to adsorb hydrophilic (i.e., water-loving) compounds appreciably at room temperature.

Typical Adsorbents

The various adsorbents used in physical adsorption may be classified according to their degree of polarity. For example, activated carbon, which is commonly known as a non-polar adsorbent, is largely composed of neutral atoms of a single species exhibiting little polarity. The non-polar adsorbents are most effective for gross decontamination of moist air streams containing materials of little polarity (e.g., organic molecules).

The majority of the commercially important adsorbents other than carbon derivatives are simple or complex oxides. Their surfaces consist of heterogeneous distributions of charge on a molecular scale. They are strongly polar in nature. These adsorbents show a greater selectivity than do the carbon derivatives and exhibit a much stronger preference for polar than for non-polar molecules. In separation of various gases, the polar solvents are more useful than carbon derivatives. However, they are much less useful for overall decontamination of moist air streams, since the strongly polar water molecules are preferentially adsorbed.

Carbon

Various forms of carbon serve as efficient adsorbents. It has been shown that the material from which the carbon is prepared has a demonstrable effect upon the ability of the carbon to adsorb various gases. Carbon prepared from logwood, for instance, has approximately twice the capacity for adsorption as carbon from rosewood. Similarly, coconut shell is about twice as efficient as logwood. Strangely enough the carbon prepared from harder, denser materials such as peach and other fruit pits, and coconut shells have the highest adsorptive capacities. Primary carbon is not nearly as efficient as activated carbon. The adsorbents "activated charcoal," "active carbon," "adsorbent carbon," and "adsorbent charcoal" may be activated in a slightly different manner, but the terms are generally considered synonymous.

Activated carbon has a high adsorptive capacity, a high degree of hardness, high reliability, and other premium qualities. Almost all volatile materials, whether they are chemicals or mixtures of odor-causing substances, are retained within the microscopic porous structure to some extent. The only gaseous materials that it will not adsorb very well are low molecular weight gases such as oxygen, nitrogen, and carbon monoxide. Activated carbon finds its major application in solvent recovery and odor removal. It is also employed to a limited extent in the removal and monitoring of hydrogen sulfide, sulfur dioxide, and other toxic gases. Activated carbon is perhaps the most widely used adsorbent in air pollution control. The following substances are some of those that have been shown to be appreciably adsorbed upon activated carbon:

- acetic acid
- benzene
- ethyl alcohol
- carbon tetrachloride
- methyl alcohol
- chloroform
- acetone
- acetaldehyde
- mercury vapor
- iodine
- carbon disulfide
- diethyl ether
- ammonia
- hydrochloric acid
- nitrous oxide
- carbon dioxide
- noble gases
- PVC

Molecular Sieve

Molecular sieve adsorbents* are synthetic sodium or calcium alumino-silicate zeolites of very high porosity. They are another representative of the siliceous adsorbents.

The structural formula of a typical molecular sieve is

$$Me_{x/n}(AlO_2)_y \cdot mH_2O$$

where Me represents exchange cations of charge n. The zeolite is precipitated as a white powder, bonded with clay, and formed into roughly spherical beads of four to twelve mesh size. The adsorbent is activated with heat to drive off water of hydration. The resulting product is a crystalline solid of very porous structure. Again, the adsorptive characteristics are dependent on the method of preparation.

Molecular sieves can be made very specific with respect to pore size. This characteristic gives them the outstanding property of being specific on the basis of adsorbate size and shape. Molecular sieves show a strong preference for the more polar molecules. For example, these adsorbents will not adsorb organic molecules that match their pore size from a moist stream of air, the accompanying water molecules being adsorbed in preference. Molecular sieves are truly selective adsorbents because they can separate mixtures on the basis of differences in molecular size, degree of polarity, and extent of carbon bond saturation. In addition to their selective properties, molecular sieves possess a high adsorptive capacity over wide ranges of concentration and temperature. They also are capable of removing impurities to extremely low concentrations. These adsorbents have been tested successfully on carbon dioxide, hydrogen sulfide, acetylene, ammonia, and sulfur dioxide. They show promise for adsorption of compounds of low molecular weight.

Adsorption Losses in Air Sampling

Each adsorption medium used in atmospheric sampling has different limitations and problems. The problems most frequently encountered are:

- irreversible adsorption,
- variable desorption efficiency, and
- interference by water vapor.

Activated carbon is used extensively because of its high affinity for organic substances. Irreversible adsorption and variable desorption efficiencies are two principal problem areas associated with carbon sampling devices. Carbon can also serve as a potent catalyst creating the possibility of *in-situ* reactions during sampling.

Other alternative adsorption media that have recently been used extensively in air sampling are thermally stable, polystyrene divinyl benzene co-polymers. These media were used at ambient temperatures to collect volatile organic compounds. The volatile organic compounds were recovered by thermal desorption followed by gas chromatographic analysis. These polymers are non-polar and have little affinity for water. Water desorption represents a severe problem in the analysis procedure. Adsorption sampling devices are being used primarily for the collection of volatile organic compounds. ,

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*Often referred to as molecular sieve absorbents.

Current Applications of Adsorption in Atmospheric Sampling

Carbon, porous polymers such as Porapack Q, Porapack P, Tenax GC, XAD-resins, and polyurethane foam have been used extensively in collecting pesticides, polychlorinated biphenyls, and other organic compounds in ambient air. These media can be used in sampling devices, which can be modifications of the hi-volume sampler (see Figure 5-5). Here polyurethane foam is used to collect organics, namely PCBs.

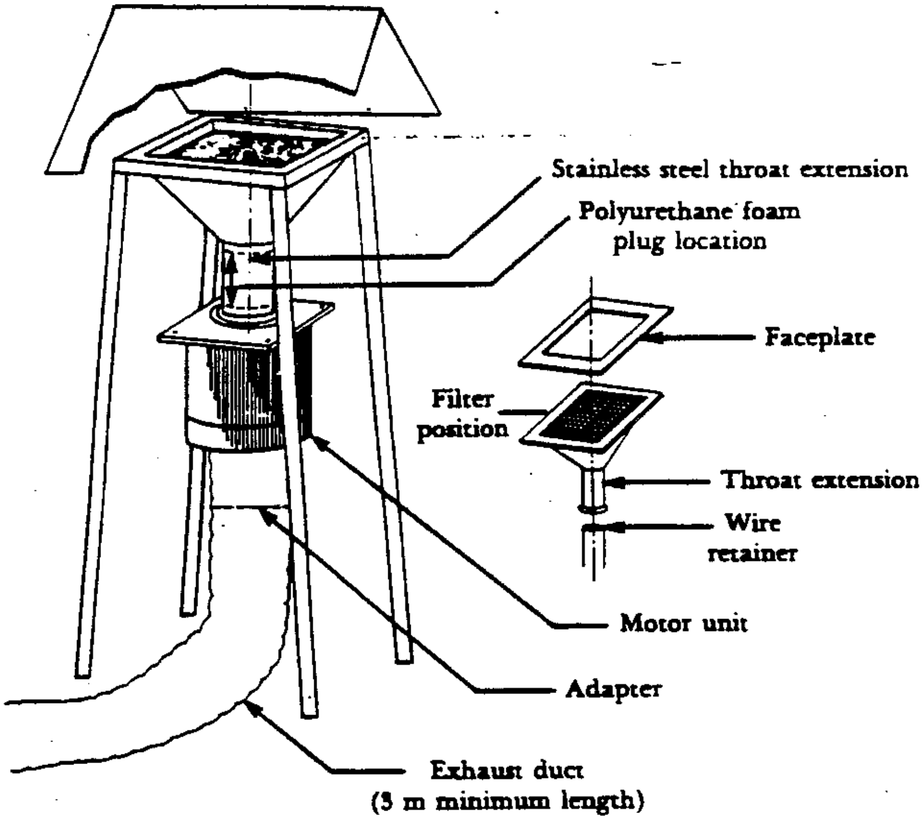


Figure 5-5. Assembled sampler and shelter with exploded view of the filter holder.

Figure 5-6 illustrates an adsorbent sampling cartridge and Figure 5-7 shows a cartridge placed in a thermal desorption system. Figure 5-8 shows dynamic enrichment, which is repeated absorption from many different cartridges onto a single cartridge to attain enough of the specie of interest for measurement.

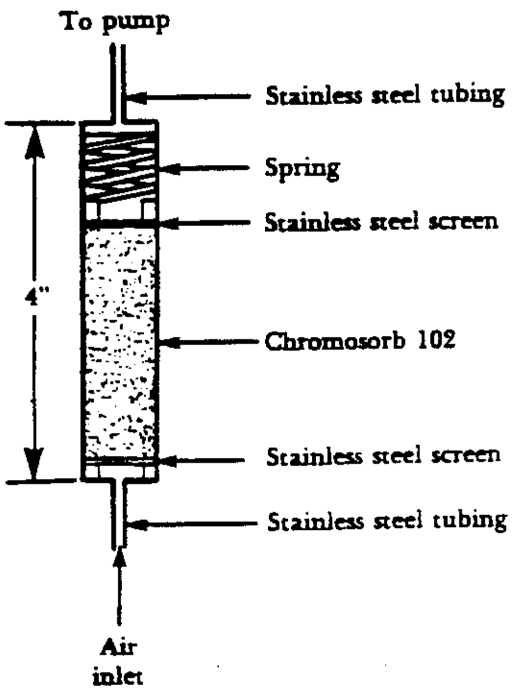


Figure 5-6. High-speed organic vapor collector.

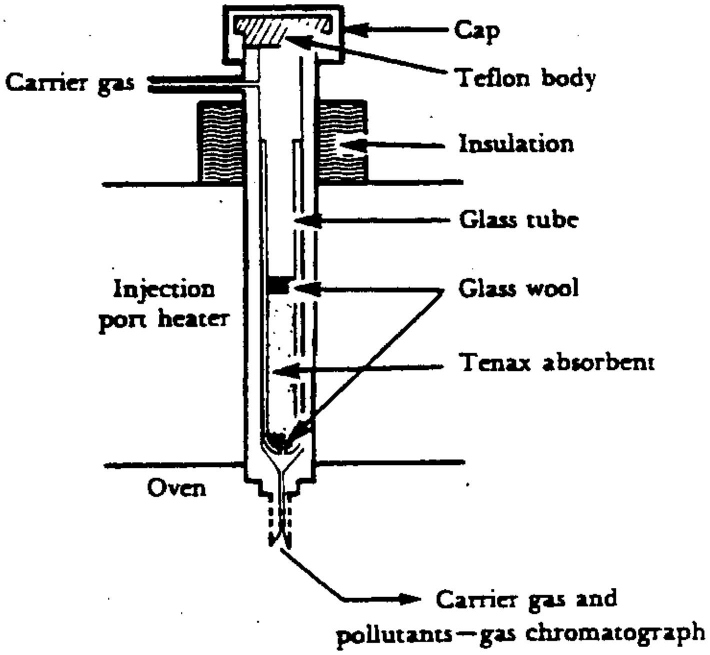


Figure 5-7. Desorption of pollutants from a Tenax-GC cartridge.

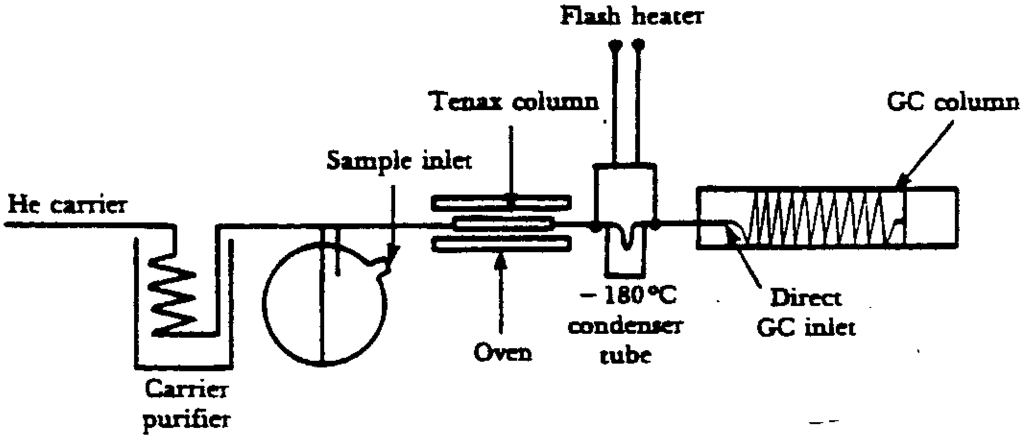


Figure 5-8. Dynamic enrichment on adsorption column (experimental setup).

Summary

The adsorption process is characterized by either physical or chemical forces. In some cases both types may be involved. Where physical forces predominate, the process is termed physical adsorption, whereas chemical adsorption describes chemical action.

Adsorption phenomena may be quantitated by considering such adsorbate-adsorbent characteristics as gas composition, concentration, and temperature, as well as adsorbent type, surface area, and pore size.

Selection and Performance of Wet Collector Media

Introduction

In the design of sampling trains, the most important component of the entire system is the collector. The process of pollutant removal is generally accomplished by absorption, adsorption, etc. The collector may take the form of a bubbler, impinger, etc. The process to be discussed is that of using a wet collector for the collection of gases, vapors, and particulate matter. Some of the more important factors to consider are:

- gas flow rate,
- bubble size,
- height of liquid column,
- reaction rate, and
- solubility of pollutant.

General Considerations

Solubility of Pollutant

The solubility of a pollutant in a solvent must be considered in determining the type of absorber to choose. It will also determine the conditions under which the sample will be taken. The absorption coefficient is one method employed to express the results of solubility measurements with gases. The absorption coefficient α is given by:

(Eq. 5-7)
$$\alpha = \frac{V_o}{(V)(p)}$$

Where:
V_o = *the volume of gas dissolved (ml)*
V = *the volume of solvent (ml)*
p = *the partial pressure of the gas (atm).*

Some typical absorption coefficients are given in Table 5-5.

Table 5-5. Absorption coefficient of gases at 20°C.

Solvent	H_2	He	N_2	O_2	CO	CO_2	NO	H_2S	NH_3
Water	.017	.009	.015	.028	.025	.88	.047	2.68	710
Carbon disulfide	.031	—	.049	—	.076	.83	—	—	—
Chloroform	—	—	.120	.205	.177	3.45	—	—	—
Ethyl alcohol	.080	.028	.130	.143	.177	3.0	—	—	—
Acetone	.065	.030	.129	.207	.198	6.5	—	—	—
Ethyl ether	.12	—	.24	.415	.38	5.0	—	—	—
Benzene	.066	.018	.104	.163	.153	—	—	—	—

(Glasstone, S. *Textbook of Physical Chemistry*, p. 695. D. Van Nostrand, New York, 1946.)

Influence of temperature—When gases dissolve in a liquid, there is generally a liberation of heat; it follows, therefore, that an increase of temperature will result in a decrease of solubility. It is for this reason that gases may be readily expelled from solution by boiling. By thermodynamic methods, it is possible to show that an increase in temperature will decrease the solubility of a gas. This effect can be seen in Table 5-6.

Table 5-6. Influence of temperature on solubilities of gases in water.

Gas/temp	Helium	Nitrogen	Oxygen	Carbon dioxide
0°C	.0094	.0235	.0489	1.713
30°C	.0081	.0134	.0261	.665

(Glasstone, S. *Textbook of Physical Chemistry*, p. 696.)

Influence of pressure—The most important factor influencing the solubility of a gas is pressure; increasing the pressure of the gas will tend to increase its solubility. The pressure is expressed by Henry's law, which states that the mass of a gas dissolved by a given volume of solvent, at constant temperature, is proportional to the pressure of the gas with which it is in equilibrium.

(Eq. 5-9) $$m = kp$$

Where:
m = *mass of gas dissolved by unit volume of solvent (g)*
p = *equilibrium pressure (atm)*
k = *constant.*

Some examples of pressure versus solubility effects are given in Table 5-7.

Table 5-7. Influence of pressure on solubility of CO_2 in various solvents at −59°C.

Solvent/pressure	Methyl alcohol	Acetone	Methyl acetate
100 mm	42.5	67.2	75.8
200 mm	42.7	68.0	77.1
400 mm	43.1	69.2	77.6
700 mm	43.3	72.8	79.0

(Glasstone, S. *Textbook of Physical Chemistry*, p. 697.)

Rate of Reaction

All chemical reactions take place at a definite rate, depending on process conditions. The most important factors are concentration of reactants, temperature, and presence of a catalyst or inhibitor. Some reactions are so rapid that they appear to be instantaneous, whereas others are so slow at ordinary temperatures that no detectable change would be observed in the course of years. Between these two extremes are many processes taking place with measurable velocities at temperatures easily accessible in the laboratory.

Since the rate of a reaction is proportional to the concentration of the reacting substances, it is evident that the rate of the process must fall off as the reaction proceeds. This phenomenon can, however, be used to advantage by increasing the concentration of the absorbing liquid, thereby forcing the reaction to approach completion rapidly.

Collection Efficiency

There are three major factors inherent in the design of a bubbler that can affect the efficiency of the absorber:

- flow rate,
- bubble size, and
- height of liquid column.

Bubble Size

The surface area at the gas-liquid interface is inversely related to the average volume of the gas bubble. As the volume of individual bubbles decreases, the surface area at the gas-liquid interface increases.

The efficiency of absorption of a gas or vapor by chemical reaction or physical absorption depends on the probability of successful collisions with molecules of reagent or solvent at the gas-liquid interface. For a given concentration of reagent this will depend on the surface area of the gas bubbles, on the length of the column of liquid through which the bubbles must pass, and the rate at which they rise through the liquid.

Collection efficiency varies inversely with flow rate and bubble size, and varies directly with the height of the liquid column.

Flow Rate

The gas flow rate through an absorber is one of the factors determining the efficiency of an absorber. Figure 5-9 shows clearly that as flow rate increases, for the absorbers studied, the efficiency decreases. This efficiency versus flow rate curve should be determined for each absorber and used in any analysis.

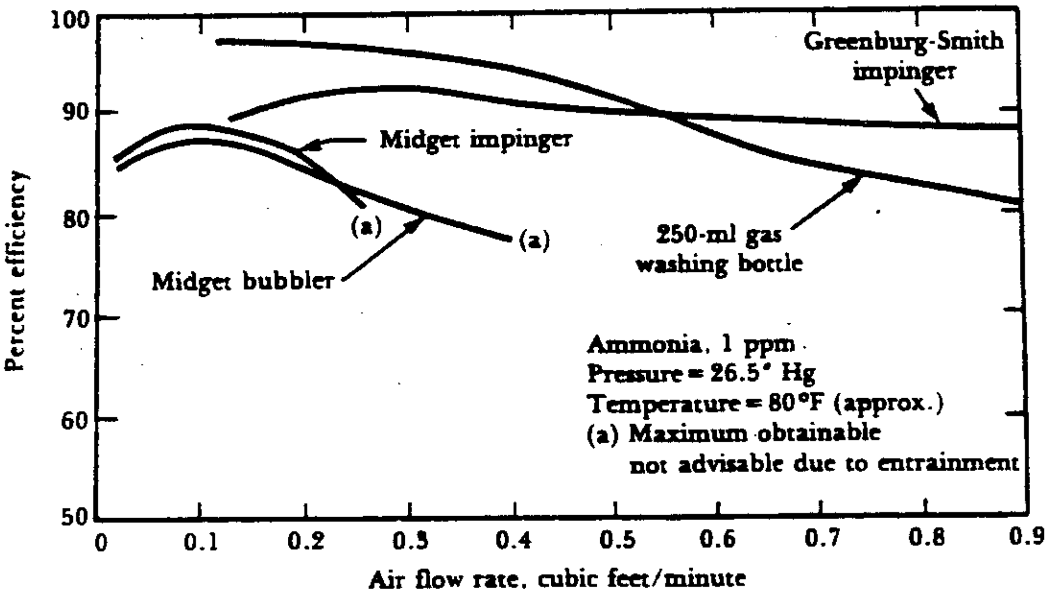


Figure 5-9. Performance curves—commercially available absorbers.

Height of Liquid Column

The length of the column of liquid in an absorber is important in determining efficiency. The velocity of rise of bubbles is approximately constant at 24 cm/sec for bubble diameters greater than 0.2 cm. Since the bubbles rise at approximately 24 cm/sec, they will be in contact with a liquid column 24 cm long for 1 second, 48 cm long for 2 seconds, etc. *The longer the gas bubble is in contact with the liquid, the more pollutant is transferred* from the gas phase to the liquid phase until gas-liquid equilibrium is approached.

Retention of Gases and Vapors by Solution

The equation defining Raoult's law is:

(Eq. 5-10) $$p = Np_o$$

Where:

p = *partial pressure of gas to be dissolved (atm)*
N = *mole fraction of gas*
p_o = *vapor pressure of gas (atm).*

From this relationship one can calculate the solubility of a gas below its critical temperature, on the assumption that the solution behaves in an ideal manner. For example, the critical temperature of ethane is 34 °C. At 25 °C the pure liquid has a vapor pressure of 42 atm. According to Raoult's law, therefore, the solubility of ethane at 25 °C and a pressure of 1 atm in any solvent in mole fraction can be determined by the following:

$$N = \frac{p}{p_o} = \frac{1}{42} = 0.024$$

since p is 1 atm, and p_o is 42 atm. The actual solubility in n-hexane at 25 °C and 1 atm pressure is 0.017 mole fraction. This variation is due to n-hexane being a non-ideal solvent.

To extend the method for calculating gaseous solubilities to temperatures above the critical temperature, it is necessary to estimate the hypothetical vapor pressure of the liquid by a suitable extrapolation. This is best done by using the integrated form of the Clapeyron-Clausius equation, which is,

(Eq. 5-11) $$\log \frac{p_2}{p_1} = \frac{L_e}{4.576}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

Where: L_e = *latent heat of vaporization.*

If the vapor pressure at any two temperatures is known, the value at any other temperature may be evaluated on the assumption that the molar heat of vaporation remains constant. The critical temperature of methane is 95.5 °C, and the hypothetical vapor pressure of the liquid at 20 °C is 310 atm, giving an ideal solubility at this temperature and a pressure of 1 atm of $1/310 = 0.0032$ mole fraction; this is very close to the solubilities actually found in n-hexane and m-xylene. Since the solubility in mole fractions of a gas at 1 atm pressure is equal to $1/p$, where p is the vapor pressure of the liquified gas, it is evident that, for ideal solutions, the lower the vapor pressure at the given temperature, the greater will be the solubility of the gas. Gases that are liquified only with difficulty, that is to say, those having very low boiling points, may be regarded as having high vapor pressures; such gases will, therefore, have low solubilities. *It follows that, in general, easily liquifiable gases will be the most soluble; this is in agreement with observation in most cases.*

Although the solubility of a gas, in mole fractions, should theoretically be independent of the nature of the solvent, this is not true in practice because of departure from ideal behavior. Some data for solutions of gases showing deviations are listed in Table 5-8. The solubilities in water are exceptionally low; since water is both polar and associated, and also has a very high internal pressure, solutions of gases of the type mentioned would hardly be expected to behave ideally. Even chlorine and carbon dioxide, which interact with water and are generally regarded as relatively soluble gases, have solubilities considerably below the calculated values, because of their low polarity and internal pressure. A quite different type of behavior is shown by ammonia, which is a highly polar substance with a high internal pressure. In hydrocarbon solvents, therefore, solubility is considerably below the ideal value, whereas in alcohol and water the observed solubility is somewhat greater than that calculated. If allowance could be made for interaction between ammonia and the solvent, good agreement would be found. A corollary to the foregoing conclusions is that for a number of *gases of similar polarity and internal pressure (e.g., hydrogen, nitrogen, carbon monoxide, oxygen) that do not react with the solvent, the ratio of the solubilities in various solvents should be approximately independent of the nature of the gas*. This generalization is roughly true in practice, and only gases such as carbon dioxide and ammonia, which are not in the same category, are exceptions.

Table 5-8. Ideal and observed solubilities at 20°C.

Gas	Ideal	Nitrobenzene	Ethyl alcohol	Aniline	Water
Nitrogen	10	2.6	3.3	1.1	0.13
Carbon dioxide	11	3.9	4.5	1.9	0.19
Oxygen	16	—	—	—	0.17
Argon	21	—	6.5	—	0.17

Retention of Gases and Vapor by Chemical Reaction

The usual objective in the selection of an absorbent for scrubbing a gas is to find a liquid, possibly a solution, with a very large capacity for absorbing the solute without building up an appreciable equilibrium back pressure. This can be accomplished readily by choosing a chemical with which the solute reacts irreversibly, as when an aqueous solution of sodium hydroxide is used to absorb carbon dioxide. There are indeed very few absorptions of a gas in a liquid that are not accompanied by a chemical reaction to some degree. Thus, when ammonia dissolves in water, ionization occurs that may be looked upon as a chemical change. A similar phenomenon, though potentially weaker, occurs when carbon dioxide dissolves in water. A much stronger and more definite chemical change takes place when ammonia is dissolved in an acid, or carbon dioxide in a base.

There is no sharp line dividing pure physical absorption from absorption controlled by the rate of a chemical reaction. Most cases fall in the intermediate range, the rate of absorption being limited both by resistance to diffusion and by the finite rate of reaction. Simultaneous occurrence of a chemical reaction renders the mechanism of absorption more complicated. The theory of purely physical absorption rests on the assumption of the two-film concept. This theory may be carried over to the case where a simultaneous reaction occurs; however, modification in film resistance will become apparent. Thus, when carbon dioxide is dissolved in water, the rate-controlling factor is not the migration of the dissolved carbon dioxide from the liquid surface into the liquid interior, simply because the rate of solution of the gas in water is small from the very start. On the other hand, if — absorption of carbon dioxide in a solution of sodium hydroxide is considered, the rate of absorption is very rapid, and the rate of migration of the carbonate into the main body of the liquid becomes rate controlling.

These phenomena are complex and, although considerable advances have been made, the situation is still very obscure. *Whenever there is a pronounced chemical reaction occurring simultaneously with absorption, there are essentially two effects that must be considered*; these pertain to:

- *modification of capacity (rate) data, and*
- *modification of the driving force.*

Capacity coefficients will generally, but not always, increase when a chemical reaction occurs simultaneously with absorption. At present there is no data available to permit a correlation that will allow for estimation of capacity data.

As far as driving force is concerned, an increase is usually observed as a consequence of a chemical reaction. In many cases the dissolved gas, once having reacted with a constituent in the liquid, offers virtually no resistance to further absorption. This is the case when carbon dioxide or sulfur dioxide is dissolved in basic solutions.

Retention of Particulate Matter

The design of the absorber plays a most important part in the retention of particulate matter by a liquid. A liquid absorber is highly efficient for retaining particles only when the velocity of the air at the jet approaches that of sound and the particles impinge with high velocity on a surface in the liquid. The sudden change in kinetic energy results in the virtually complete trapping of all particles having a diameter greater than 1 micrometer.

Principles of Grab Sampling

Introduction

The term "grab sample" suggests two concepts: (a) a sample taken at a particular time and place within an interval of a few seconds to a minute or two, and (b) a small representative portion removed from the gross sample with no alteration.

Grab samples are usually collected in one of the following ways:

- using an evacuated container,
- purging (displacement of air),
- displacement of a liquid,
- inflation of a plastic bag
- using a syringe, and
- using an adsorbent cartridge.

Evacuated Containers

Evacuated containers used for grab sampling are of several types. One common type is a strong glass tube of 250 to 300 ml capacity, although tubes with volumes as large as 1 to 2 liters are sometimes used (Figure 5-10).

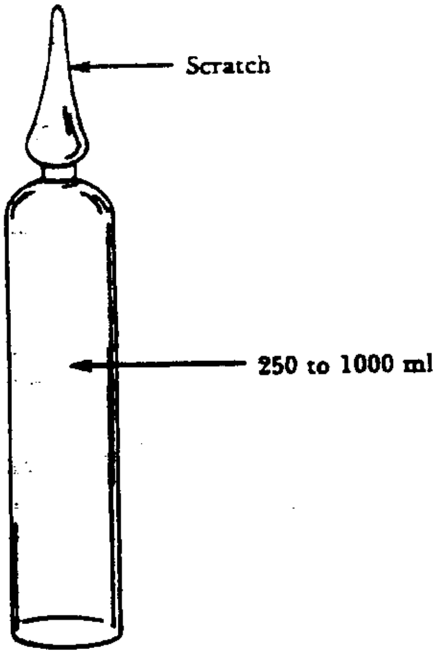


Figure 5-10. Vacuum tube.

To use this type of container, the tube is evacuated until almost all the air has been removed. In the last stages of evacuation, the neck is sealed. Then at the sampling site, the neck is scratched and broken. Sampling is instantaneous, and will continue until the internal pressure is equivalent to the external pressure. The broken end is then sealed with wax and sent to the lab for analysis.

There are several advantages in the use of this collector: it is simple to use and no pump or manometer need be taken to the sampling site. However, the tube must be redrawn, re-evacuated, and resealed if it is to be used again. There is also the danger of breakage.

An evacuated flask fitted with a stopcock or vacuum cap can also be used in this type of sampling (Figure 5-11). The flask is evacuated and then sealed by giving the cap a half turn. When sampling is to occur, the cap is turned to the "open" position and the air will be drawn into the flask. The cap is closed after sampling and the flask is returned to the laboratory.

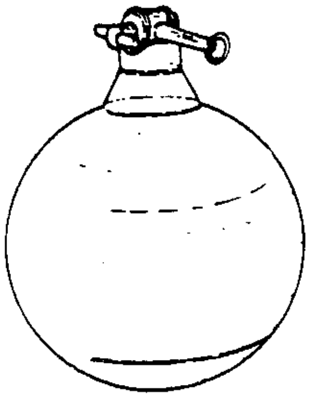


Figure 5-11. Vacuum flask.

During the transport of the evacuated container to the sampling site there is a possibility of slow leakage through poorly fitted stopcocks. This would, of course, completely invalidate the results. The pollutants to be analyzed may also degrade or react with other compounds in the evacuated flask. This apparatus has the advantage of being easy to reuse. Such collectors should be placed in a protective container or wrapped with adhesive tape to reduce hazards of implosion.

If for some reason the containers are not completely evacuated, it may be necessary to subtract a residual volume from the volume of the flask to determine the volume of air sampled. Let V_f be the volume of the vessel; after evacuation let the temperature and residual pressure in the flask be T_1 and P_1. The flask is transported to the sampling site and opened; the flask temperature and pressure now become T_2 and P_2. The volume of air sampled, V_s, is given by:

(Eq. 5-12)
$$V_s = V_f - V_x$$

where V_x is the volume occupied by the residual gas. Assuming gas ideality for the residual gas:

(Eq. 5-13)
$$\frac{P_2 V_x}{T_2} = \frac{P_1 V_f}{T_1}\cdot$$

Hence:
$$V_s = V_f \left(1 - \frac{P_1 T_2}{P_2 T_1}\right).$$

If the ratio P_1/P_2 is small (almost complete evacuation), then the correction can be neglected and

$$V_s = V_f .$$

The presence of the pollutant in the residual gas would further complicate the matter.

Air Displacement or Purging

Cylindrical tubes with stopcocks at each end are used as collectors (Figure 5-12). The stopcocks are opened and the tube is thoroughly purged. After sampling, the tube should be held in place until the stopcocks have been closed and the aspirating device has been removed.

Figure 5-12. Gas-displacement collector.

Metal containers of the same general design have been employed, but they have been found to react with many samples. Their real advantage lies in the fact that they are virtually unbreakable.

The sample air is drawn through the container using any of a variety of pumps. Enough air must be drawn through to completely flush out old, unrepresentative air that may be present.

The necessary volume of air required will vary, but in all cases it will be at least several times greater than the volume of the container. Theoretically all of the old air can never be eliminated by pumping. Since this pumping process may take a relatively long time, it is not strictly an instantaneous sample. If the concentration of pollutant in the air changes radically during purging, the results will not necessarily be close to the average over the time interval involved.

Liquid Displacement

Another technique used in gas sampling is liquid displacement. In this method a liquid is allowed to drain from the bottom of a container, while an opening at the top allows the gas to enter and fill the space left by the liquid. Any suitable liquid that will not dissolve the sample nor react with it can be used. The choice of liquid will depend upon the material being sampled; some commonly used liquids are water, brine, mercury, or water saturated with the gas to be sampled.

Containers used are of two basic types: (a) a glass tube with two stopcocks as used in air displacement (Figure 5-13) and (b) an aspirator bottle (Figure 5-14).

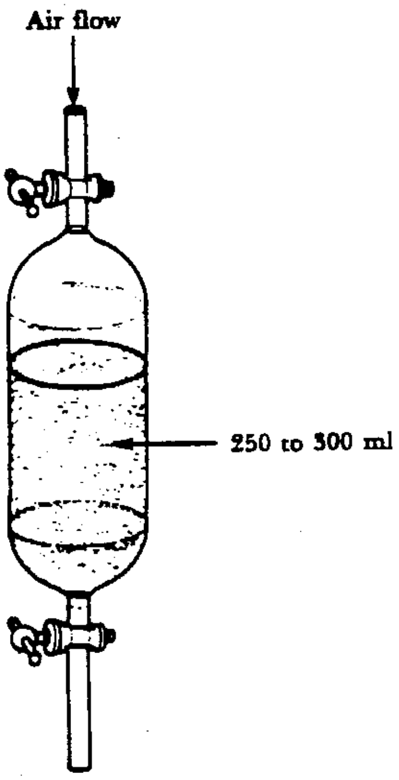


Figure 5-13. Liquid-displacement collector.

Figure 5-14. Aspirator bottle.

In both cases, the liquid is allowed to drain through the lower opening (the rate can be controlled by adjusting the stopcock), and the gas is drawn in through the upper stopcock or tube. This method requires a minimum of equipment and no special training. The container may be calibrated to indicate the volume of gas sampled.

Inflation

A fourth gas sampling method is the collection of a sample by inflation of a plastic bag. Plastics of various types have been used. The choice of material will depend on the gas to be sampled and the storage period.

Some hazards to look out for in "bag sampling" are wall effects, memory effects (where previous constituents linger), sample deterioration over time, sample deterioration due to sunlight in some cases, and the possibility of reactions among the various gases in the bag.

The deflated plastic bag is placed in a closed, air-tight box, with only a tube extending outside the box. An opening in the box itself is connected to a vacuum source, and the air is pumped out of the box. As the air is removed from the outer container, the bag will inflate, drawing in the sample. The air may be metered as it is pumped out of the box, thus indicating the volume of gas sample drawn into the bag (Figure 5-15).

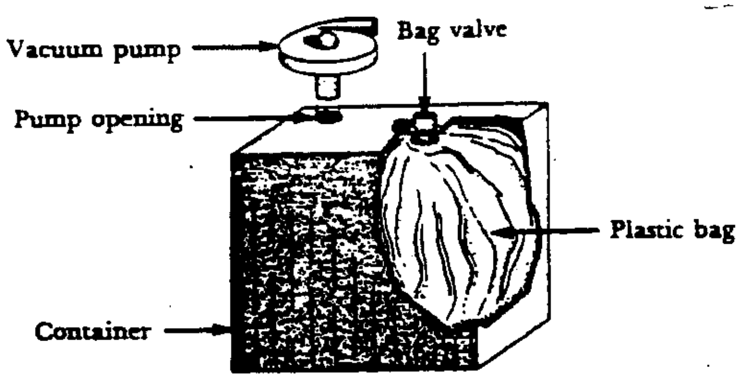


Figure 5-15. Inflation sampler.

Syringes

Syringes may be used in the collection of small gas samples. This technique has been widely applied in the field of odor measurement.

Grab Sampling Techniques

Grab sampling techniques are preferable to continuous sampling in certain situations. Some constituents have absorption rates too slow for efficient collection by absorption. Field conditions (lack of electricity and lab facilities) often necessitate this type of sampling.

Grab sampling is useful when concentrations vary considerably over a period of time, and it is necessary to obtain a sample at a specific time. Most grab sampling techniques utilize a minimum of equipment and require little or no special training or experience on the part of the operator.

Grab sampling has a serious limitation—the sample obtained is generally not large enough to detect very small quantities of materials except by the most sensitive techniques.

Principles of Freezeout Sampling

Introduction

Air pollutants existing as gases can be trapped or removed by the freezeout, or condensation, method. Trapping in this discussion refers to the mechanism of sample collection, and removed implies an air-cleaning mechanism to rid unwanted gas contaminants from the gas stream. The method has a very high efficiency at relatively low flow rates. Certain problems are encountered when using the freezeout method, thus necessitating an appraisal of the method for particular applications.

Concept

The method consists essentially of drawing air through collection chambers with progressively lower temperatures. If the temperatures of the chambers are approximately equal to or less than the boiling point (the temperature at which a liquid is converted to a gas) of the gaseous components of the air passing through it, these components will exhibit a phase change from the gaseous phase to the liquid phase. The condensate (liquid phase) is collected in the chamber where the phase change occurs. The gaseous contaminants to be collected will determine the temperatures required in the collection chambers. The temperatures of the chambers can be controlled by using different immersion bath liquids. Contaminants with boiling points as low as −195 °C can be collected by this method.

Equipment

The type of freezeout equipment required depends to a large extent on the application. The required amount of equipment of a given type depends on whether the sampling apparatus is a single or multistage unit.

The size of the collection chamber varies according to the immersion bath for which it was designed. The collection chambers themselves are placed in Dewar flasks containing the cooling solutions (Figure 5-16).

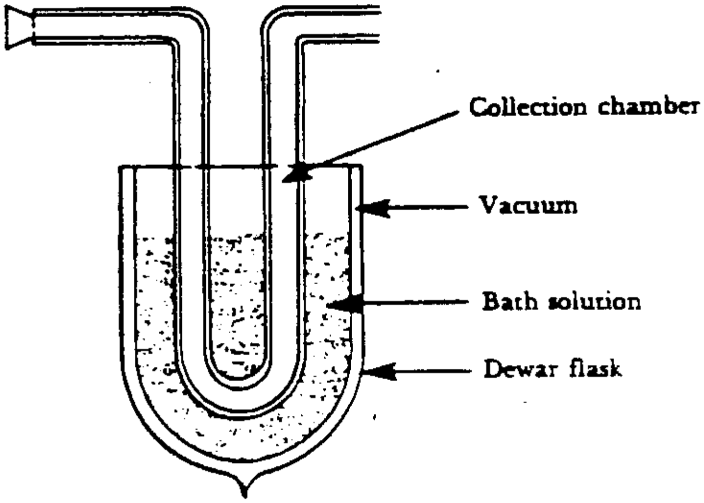


Figure 5-16. Freezeout unit.

Table 5-9 indicates various bath solutions and some sizes of the Dewar flasks that have been used for each. The volume of the bath solutions and, thus, the size of the collecting chamber itself are partially due to factors such as:

- temperature gradients across the collecting chambers as related to the criticality of the boiling point of the contaminant being collected,
- the surface area as related to the evaporation rate of the bath solution, and
- the condensation of water vapor in the primary collection chambers, thus necessitating a larger volume.

Table 5-9. Bath solutions.

Bath solution	Temperature	Volume of solution
Ice + salt	−16°C	≅2 liter
Dry ice & acetone or methyl-cellosolve	−80°C	750 ml
Liquid oxygen	−183°C	100 ml
Liquid nitrogen	−195°C	100 ml

The level of the solutions in the baths should be kept at 2" to 4" within the top of the collection chambers in an attempt to maintain a constant temperature throughout the chamber.

Among the collection chambers utilized, U-shaped and spiral-shaped tubes are prominent. Large radius bends should be designed into the tubes to facilitate smooth airflow and to prevent ice accumulation at the bends. Freezeout devices can be classified into two categories, single-stage and multistage units.

Single-stage Units

A single-stage unit (Figure 5-16) consists of one collection chamber (glass or metal) immersed in a bath solution. As has already been mentioned, the temperature of the bath and, consequently, the liquid of the bath will depend on the particular gas to be sampled.

Multistage Units

Multistage units consist of a series of collection chambers. These chambers can be arranged in either horizontal or vertical trains (Figures 5-17 and 5-18). In these trains the temperatures of the baths are progressively lower. This allows for condensation of different gases in different chambers.

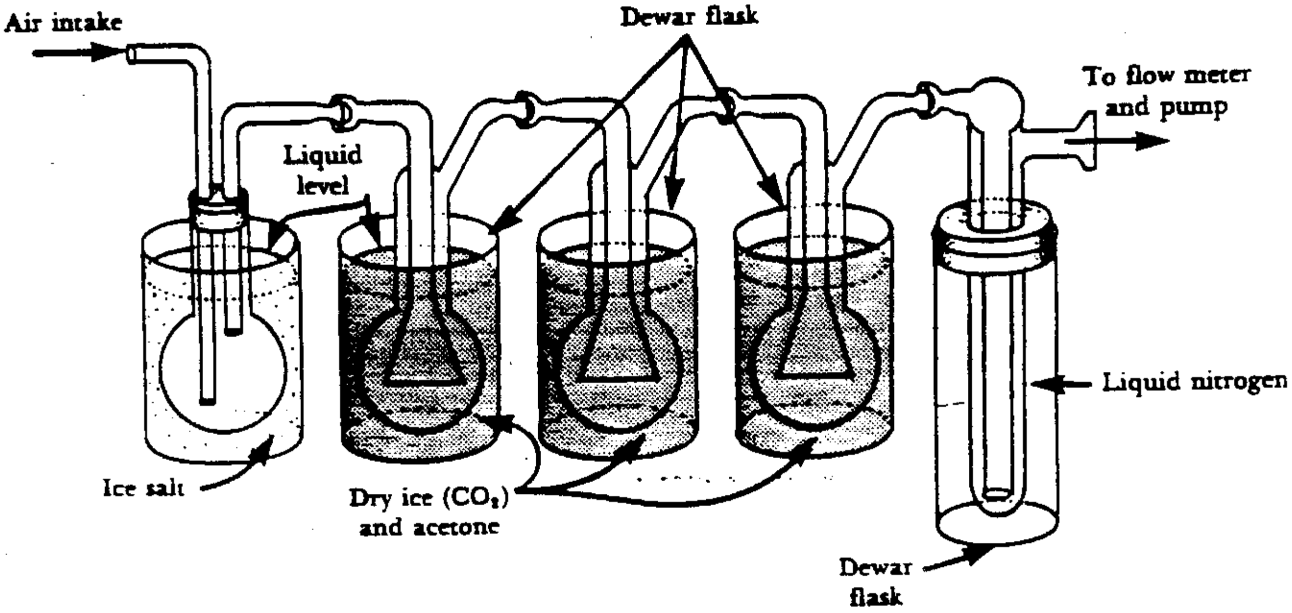


Figure 5-17. Freezeout equipment for atmospheric samples (horizontal sampling train).

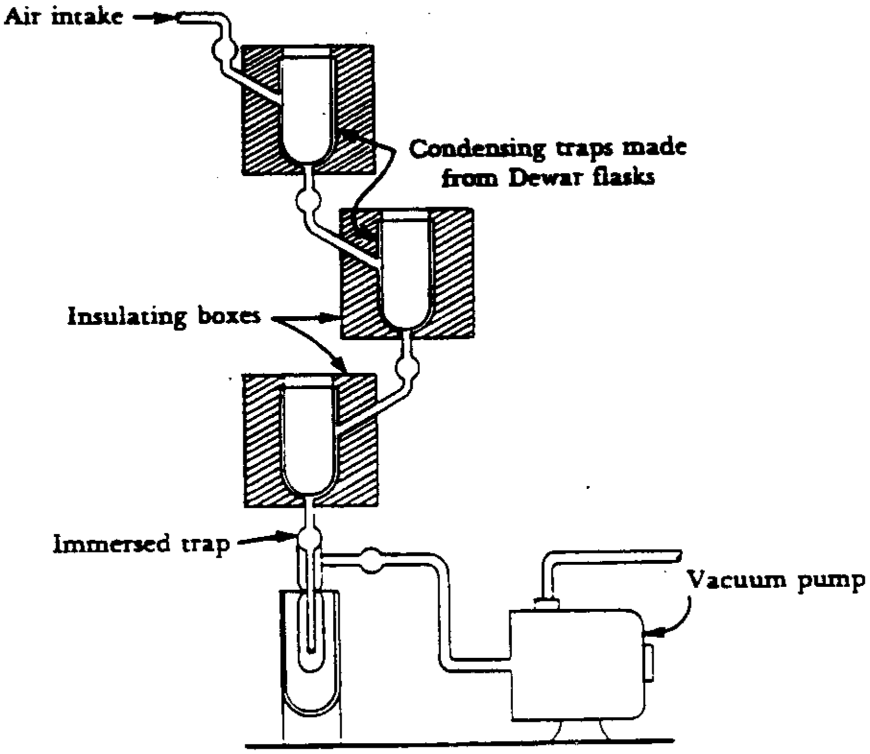


Figure 5-18. Freezeout equipment for atmospheric samples (vertical sampling train).

Efficiency

The collection efficiencies of the previously described systems are not very good. To efficiently condense gases it is necessary for the gas to come in contact with the cold surface of the collection chamber. Therefore, the efficiency of collection by freezeout can be improved by: (a) filling the collection chamber with some type of material that will increase the cold surface area and (b) reducing the flow rate.

Packing Materials

To increase the cold surface area within the collection chamber, various materials such as glass beads, metal packing, and activated carbon have been used (Figure 5-19). In one application, for collecting benzene and formaldehyde, the glass beads and metal packing increased the efficiency from 50% to 65% and 80%, respectively. The lower collection efficiency of the unpacked train was due partly to the formation of a fine mist that was not retained by the walls of the traps.

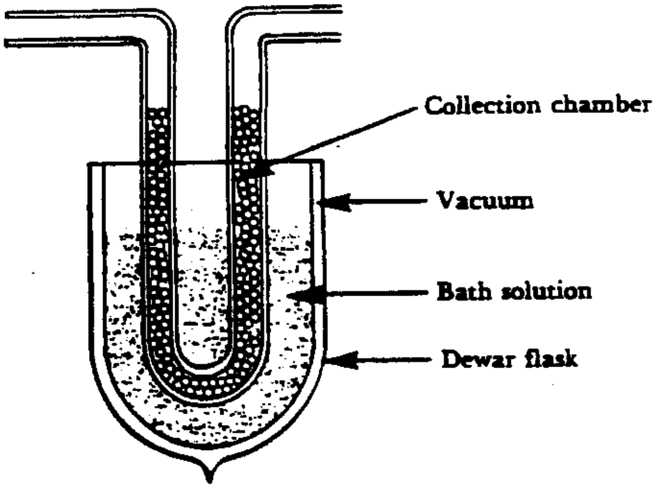


Figure 5-19. Freezeout unit showing packing material.

In another application using activated carbon, a collection efficiency of 100% was reported for xenon and krypton. The activated carbon gave a much larger surface area for the gas to pass over. The use of activated carbon will give the added advantage of adsorbing gases from the air stream.

Flow Rate

The flow rate through the train should be such that a sufficient "detention time" (time allowed for the gas to come into equilibrium with its surrounding temperature) is available to allow the desired collection efficiency. For an unpacked train the detention time must be relatively large due to the small, cold surface area. By packing the train with a surface-area-increasing material, the cold surface area will increase and the detention time can become smaller. With a smaller required detention time, the rate of flow through the train can be greater. Flow rates on the order of 0.1 to 0.2 cfm have been reported for unpacked trains, while 1 to 2 cfm have been reported for trains packed with activated carbon.

Another factor affecting flow rate is the formation of ice crystals in the bends of the collection chambers. This will be discussed in another section.

Errors

One possible source of error is that gases soluble in water will be removed to some extent prior to their removal in a collection chamber. Other errors may be introduced when electrostatic precipitators, drying towers, etc., are placed ahead of the freezeout train. Electrostatic precipitators will aid in the removal of particulate matter, but they may also alter the gas chemically. Adsorption of vapors by a desiccant placed before the collection chamber has also been reported. This adsorption might introduce errors in the final results.

Sensitivity

The sensitivity of the freezeout method depends primarily on the gas collected, volume of air sampled, and how the collected gas is analyzed. Hydrocarbon samples were analyzed on a mass spectrometer to detect pollutant concentrations of 10^{-4} ppm from a 1-liter sample. With larger sample volumes, concentrations on the order of 10^{-6} ppm have been reported.

Applications

The freezeout method has proved useful in sampling gases. The freezeout device can be used as a collecting train itself, or it can be used in conjunction with other sample collection devices. Also, freezeout traps are used in the lab to concentrate trace amounts of pollutants (such as halogenated hydrocarbons) desorbed from adsorption cartridges in order to increase their detectibilities. This probably is its chief use today.

Freezeout Train

Trains composed of several collection chambers have the ability of collecting several gases at the same time. This may aid in the gross analysis of the sample because the sample will be broken into fractional parts according to the various boiling points of the gases.

Probably the main disadvantage of a freezeout train is the plugging of the collection chambers by ice crystals. Drying towers placed on the inlet side of the train will help alleviate this problem as well as filter some particulate matter. Flow rates of 1 to 2 cfm have been reported when using a drying tower.

Liquid oxygen creates another problem when it is used as a bath solution or when collected in a collection chamber. When used as a bath solution, extreme care must be employed because of the ability of liquid oxygen to support combustion. Therefore, a restricted personnel area around the sampler must be maintained. Oxygen (B.P. = -183 °C) will condense when liquid nitrogen (B.P. = -196 °C) is used as a bath solution. This is undesirable since it will dilute the collected contaminants. If the solution is allowed to warm up after sampling, a portion of the contaminants may be carried off by the escaping oxygen.

Multicollection Train

The freezeout train may be part of a larger train where particulate matter filters, electrostatic precipitators, activated charcoal cartridges, etc., make up the rest of the train. The major advantage of such a train would be the removal of particles and gases that were not of interest. Probably the main disadvantage of the larger train is the possibility of altering the chemical composition of the gas of interest.

Summary

Freezeout trains have proved to be an efficient collection device. Collection efficiencies of 100% for flow rates up to 2 cfm have been reported for certain contaminants. Problems such as water vapor condensation with subsequent plugging of collecting chambers can be alleviated by using a desiccant on the inlet side of the train. Collection efficiency improvements such as increasing the cold surface area can be accomplished by using a packing material. The use of freezeout devices for "field" operations has its limitations because of its bulkiness and the problem of keeping the bath solutions at a constant level.

References

Altshuller, A. P.; Wartburg, A. F.; Cohen, I. R.; and Sleva, S. F. 1962. Storage of gases and vapors in plastic bags. *Int. J. Air Wat. Poll.* 6:75-81.

American Conference of Governmental Industrial Hygienists. *Air sampling for evaluation of atmospheric contaminants.* 5th ed., chpt. B-6. Cincinnati, OH.

———. *Air sampling instruments,* chpts. A-1 and B-6. Cincinnati, OH.

Becker, H. G. 1924. Mechanism of absorption of moderately soluble gases in water. *Industrial and Engineering Chemistry* 16:1220.

Brey, W. S., Jr. 1958. *Principles of physical chemistry,* chpt. 7, pp. 244-253. New York: Appleton-Century-Crafts, Inc.

Browning, W. E. 1960. Removal of volatile fission products from gases. *Nuclear Reactor Chemistry.* 1st Conference, TID-7610, October 1960, at Gatlinburg, TN.

Cadle, R. D.; Rolston, Myra; and Magill, P. L. 1951. Cold-surface collection of volatile atmospheric contaminants. *Anal. Chem.* 23:475-477.

Calvert, Seymour, and Workman, Walter. 1960. Estimation of efficiency for bubble-type gas absorbers. *Talanta* 4:89-100.

———. 1961. The efficiency of small gas absorbers. *J. Ind. Hygiene* 22:318-324.

Codudal, M. 1955. Determination of radon in uranium mines by sampling on activated charcoal. *J. Phys. Radium* 16:479.

Connor, William D., and Nader, J. S. 1964. Air sampling with plastic bags. *Amer. Indust. Hyg. Assoc. J.* 25:291-297.

Daniels, F., and Alberty, R. A. 1955. *Physical chemistry,* chpt. 7, pp. 522-526. New York: John Wiley and Sons, Inc.

Dankwerts, P. V. 1955. Gas absorption accompanied by chemical reaction. *A. I. Ch. E. J.* 1:456.

Devorken, H.; Chass, R. L.; Fudurich, A. P.; and Kanter, C. V. 1963. *Source testing manual.* Los Angeles: Air Pollution Control District.

Dravnieks, A., et al. 1971. High-speed collection of organic vapors from the atmosphere. *Env. Sci. and Tech.* 5:1220.

Droege, H. F., and Ping, A. Y. 1964. Relative efficiencies of various collection devices used for source testing. Presented at the 6th Conference on Methods in Air Pollution Studies, 6-7 January 1964, at Berkeley, CA.

Elkins, H. B.; Hobby, A. K.; and Fuller, J. E. 1937. The determination of atmospheric contaminants I. Organic halogen compounds. *J. Indust. Hyg. and Toxicol.* 19:474-485.

Flygare, J. K. Jr.; Wehmann, George; Harbertson, A. R.; and Sill, C. W. 1959. *A method for the collection and identification of radioactive xenon and krypton.* 6th AEC Air Cleaning Conference, TID-7593, pp. 18-25.

Gage, J. C. 1960. The efficiency of absorbers in industrial hygiene air analysis. *Analyst* 85:196-203.

Graham, D. 1959. *Adsorption equilibrium, adsorption, dialysis, and ion exchange.* Chemical Engineering Progress Symposium Series 24, pp. 17-23. New York: American Institute of Chemical Engineers.

Gresmer, G. J.; Jones, R. A.; and Lautensach, H. 1959. *Molecular sieves, adsorption, dialysis, and ion exchange.* Chemical Engineering Progress Symposium Series, pp. 45-50. New York: American Institute of Chemical Engineers.

Halsom, R. T.; Hershey, R. L.; and Keen, R. H. 1924. Effect of velocity and temperature on roles of absorption. *Industrial and Engineering Chemistry* 16:1224.

Hochheiser, Seymour. 1964. *Methods of measuring and monitoring atmospheric sulfur dioxide, environmental health series*—Air Pollution, No. 999-AP-6.

Holland, F. A. 1964. Brush-up your absorption theory. *British Chemical Engineering* 9:294.

Jacobs, M. B. 1949. *The analytical chemistry of industrial poisons, hazards and solvents.* New York: Interscience Publishers, Inc.

Johns, Fred B., Chief, Projects, Southwestern Radiological Health Laboratory. Personal communication.

Leva, M. 1951. *Tower packings and packed tower designs.* Akron: United States Stoneware Co.

Lewis, R. G.; Brown, A. R.; and Jackson, M. D. 1977. Evaluation of polyurethane foam for sampling of pesticides, polychlorinated biphenyls and polychlorinated naphthalenes in ambient air. *Anal. Chem.* 40:2232.

Magill, P. L.; Holden, F. R.; and Ackley, C. 1956. *Air pollution handbook,* chpt. 13, p. 83. New York: McGraw-Hill Book Company, Inc.

Maron, S. H., and Prutton, D. F. 1958. *Principles of physical chemistry,* chpt. 7, pp. 214-225. New York: The MacMillan Co.

McConnon, D. 1963. *Radioiodine sampling with activated charcoal cartridges.* AEC Research and Development Report, HW-77126.

Perry, R. H., and Pigford, R. L. 1953. Kinetics of gas-liquid reactions. *Industrial and Engineering Chemistry* 45:1247-1253.

Roberts, Louise R., and McKee, Herbert C. 1959. Evaluation of absorption sampling devices. *J. Air Pollut. Control Assoc.* 9:41-53.

Saltzman, B. E. 1961. Preparation and analysis of calibrated low concentrations of sixteen toxic gases. *Anal. Chem.* 33:1100-1112.

Sell, C. W., and Flygare, J. K., Jr. 1960. Iodine monitoring at the national reactor testing station. *Health Physics* 2:261-268.

Shepherd, M.; Rock, S. M.; Howard, R.; and Stormes, S. 1951. Isolation identification and estimation of gaseous pollutants of air. *Anal. Chem.* 23:1413-1440.

Sherwood, T. K., and Pigford, R. L. 1952. *Absorption and extraction.* New York: McGraw-Hill Book Company, Inc.

Shleien, B. 1963. The simultaneous determination of atmospheric radon by filter paper and charcoal adsorptive techniques. *J. Amer. Industrial Hygiene* 24:180-187.

Silverman, Leslie. 1947. *Industrial air sampling and analysis.* Philadelphia: Industrial Hygiene Foundation.

Stern, Arthur C. 1962. *Air pollution.* Vol. I, pp. 392-424. New York: Academic Press.

———. 1962. *Air pollution.* Vol. I, chpt. 11. New York: Academic Press.

———. 1965. *Air pollution.* Vol. II, chpt. 33. New York: Academic Press.

Stratton, Charles L., et al. 1978. *A Method for the Analysis of Polychlorinated Biphenyls (PCBs) in Air.* EPA 600/4-78-048.

Versino, B.; de Groot, M.; and Caeiss, F. 1974. Air pollution—sampling by adsorption columns. *Chromatographia* 7:302.

Williams, F. N., et al. 1969. Determination of trace contaminants in air by concentrating on porous polymer bead. *Anal. Chem.* 40:2232.

Zlatkis, A., et al. 1973. Concentration and analysis of trace volatile organics in gases and biological fluids with a new solid adsorbent. *Chromatographia* 6:67.

Section B-2

Preparation of Calibration Gases

Reading Assignment

Pages 6-1 through 6-31 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Static systems for the preparation of calibration gases
- Dynamic systems for the preparation of calibration gases
- Preparation of zero air

Learning Goal and Objectives

Learning Goal

The purpose of this section is to familiarize you with the preparation of calibration gases.

Learning Objectives

At the end of this section, you should be able to:

1. recognize two general systems for the preparation of calibration gases.
2. identify three static systems for the preparation of calibration gases.
3. recognize optimum conditions for the preparation of calibration gases using compressed gas cylinders, bags, and permeation tubes.
4. calculate concentrations of calibration gases prepared using bags, permeation tubes, single dilution systems, and double dilution systems.
5. identify NO_2 and SO_2 permeation tubes.
6. recognize a method of preparing ozone calibration gas.
7. define zero air for air sampling purposes.
8. identify and recognize characteristics of three adsorbents which are commonly used in the preparation of zero air.
9. name three methods of removing water vapor from a gas stream and identify advantages and disadvantages of three adsorbents commonly used.

Reading Guidance

- Preparation of calibration gases using compressed gas cylinders, permeation tubes, and other dynamic calibration devices is discussed in this reading assignment. EPA will verify your compressed gas standards, permeation tube rates, and calibration device outputs at no cost to you. If you would like to use this service, contact: U.S. EPA, Quality Assurance Division, Standards Laboratory, EMSL, MD 77, Research Triangle Park, North Carolina 27711 (telephone: Commercial: (919) 541-2366, FTS: 629-2366).
- Refer often to the equations and figures of the assigned reading material as you progress through the assignment.
- When you have finished the reading assignment, complete the review exercise for Section B-3. It begins on the following page.
- After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
- For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment indicated on the answers page.
- After you have reviewed your incorrect answers (if any), take Quiz 2. Follow the directions listed in the Course Introduction section of this guidebook.
- After completing Quiz 2, proceed to Section B-4 of this guidebook.

Review Exercise

Now that you've completed the assignment for Section B-3, please answer the following questions. These will help you determine whether or not you are mastering the material.

1. Which of the following is a(are) general system(s) for the preparation of calibration gases?
   a. static system
   b. dynamic system
   c. both a and b, above
   d. none of the above
2. Which of the following is a(are) general static system(s)?
   a. pressurized system (compressed gas cylinder)
   b. permeation system
   c. bag system
   d. both a and c, above
   e. all of the above
3. Which of the following is an(are) important consideration(s) in preparing calibration gases using compressed gas cylinders?
   a. Due to compressional heating, the cylinder should be allowed to equilibrate to room temperature before reading the gas pressure to be used in calculating the concentration of the calibration gas.
   b. Gases should be thoroughly mixed after their introduction to the gas cylinder to avoid gas layering.
   c. both a and b, above
   d. none of the above
4. ____(?)____ μℓ of 100% carbon monoxide must be introduced into a 10ℓ bag to prepare 10ℓ of 50 ppm (μℓ/ℓ) calibration gas.
   a. 5
   b. 0.2
   c. 50
   d. 500
5. Which of the following is an(are) important consideration(s) in preparing calibration gases using bags?
   a. Pollutant gas should be introduced into the stream of the diluent gas as the bag is filling.
   b. Calibration gas will deteriorate over time in a bag.
   c. both a and b, above
   d. none of the above

6. True or False? A permeation tube consists of a tube which is partially filled with a liquified gas. The gas above the liquid is able to permeate through the walls of the tube.

7. The permeation rate of a permeation tube ___(?)___ as the temperature of the permeation tube increases.
   a. remains the same
   b. increases
   c. decreases

8. The pollutant concentration generated by a permeation system ___(?)___ as the diluent gas flow rate of the system increases.
   a. remains the same
   b. increases
   c. decreases

9. If an SO_2 (molecular weight: 64 g/g•mol) permeation tube has a permeation rate of 1.000 μg/min at a temperature of 25 °C and a pressure of 760 mm of mercury. What is the SO_2 concentration (ppm) at EPA's STP conditions generated by a permeation system using the permeation tube and having a total dilution flow rate of 1.000 ℓ/min?
   a. 0.382
   b. 2.62
   c. 0.350
   d. 2.86

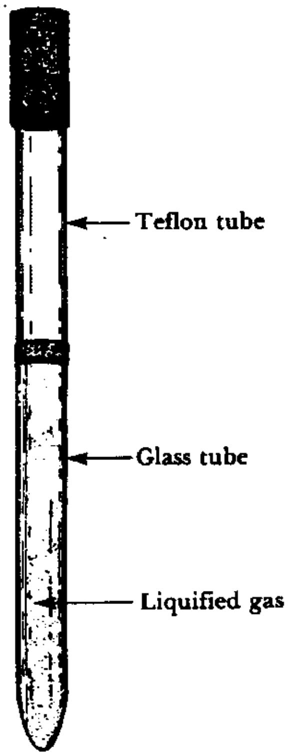
10. Which of the following is an(are) important consideration(s) in using a permeation tube system?
    a. Absorbed moisture on a permeation tube can form acids that may cause tube blistering, thus changing the tube's permeation rate.
    b. Diluent gas which passes over the permeation tube must be kept at a constant temperature and zero humidity in order to maintain a constant permeation rate.
    c. Permeation tubes should be equilibrated at their operating temperatures and zero humidity for two to three days before they are used to generate calibration gas.
    d. both a and b, above
    e. all of the above

For each of questions 11 and 12, match the permeation tube with its appropriate diagram.

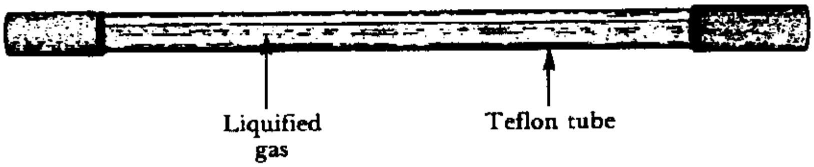
11. NO_2 permeation tube

12. SO_2 permeation tube

a.



b.



13. What is the SO_2 concentration (ppm) generated by a single dilution system if the system's undiluted SO_2 concentration is 100 ppm, the flow rate of undiluted SO_2 is 1 ℓ/min, and the flow rate of diluent gas is 9 ℓ/min?
    a. 90
    b. 11
    c. 10
    d. 100

14. What is the SO_2 concentration (ppm) generated by a double dilution system if the initial dilution system's undiluted SO_2 concentration is 100 ppm, the flow rate of undiluted SO_2 is 1 ℓ/min, and the flow rate of diluent gas is 9 ℓ/min; and the final dilution system's flow rate of diluent gas is 10 ℓ/min?
   a. 0.5
   b. 5.0
   c. 10
   d. 4.5

15. Which of the following is a(are) method(s) of preparing ozone calibration gas?
   a. mixing ozone with nitrogen in compressed gas cylinders
   b. irradiating oxygen with an ultraviolet light
   c. both a and b, above
   d. none of the above

16. True or False? Some calibration gases can be prepared by injecting liquid pollutant into a moving diluent gas stream.

17. True or False? Zero air can be defined as air that is free of contaminants and interferences for a particular analytical technique.

18. True or False? Regardless of its use, zero air always has the same composition.

19. True or False? Activated charcoal can remove ozone, SO_2, NO_2, and many organic vapors from a gas stream.

20. True or False? Neither soda lime nor Ascarite can remove CO_2 from a gas stream.

21. True or False? Ascarite can remove acid gases from a gas stream.

22. Which of the following is a(are) general method(s) of removing water vapor from a gas stream?
   a. adsorption
   b. impaction
   c. condensation
   d. both a and c, above
   e. all of the above

23. Which of the following is a(are) general method(s) of removing gaseous contaminants from a gas stream?
   a. impaction
   b. adsorption
   c. absorption
   d. both b and c, above
   e. both a and b, above

24. Which of the following is a(are) common absorbent(s) for removing water vapor from a gas stream?
    a. silica gel
    b. calcium sulfate
    c. anhydrous magnesium perchlorate
    d. all of the above

For each of questions 25 through 27, match the adsorbent with its advantage(s).

25. silica gel
26. calcium sulfate
27. anhydrous magnesium perchlorate

a. very high efficiency for removing water vapor
b. easy to handle, can be indefinitely regenerated
c. easy to regenerate, has a constant water vapor removal efficiency over a wide range of temperatures

For each of questions 28 through 30, match the adsorbent with its disadvantage(s).

28. silica gel
29. calcium sulfate
30. anhydrous magnesium perchlorate

a. not the most efficient adsorbent for removing water vapor
b. not the most efficient absorbent for removing water vapor, cannot be indefinitely regenerated
c. may explode in the presence of organic vapors, melts when removing water vapor

Section B-2

Review Exercise Answers

		Page(s) of *Atmospheric Sampling: Student Manual*
1.	c	6-1, 6-7
2.	d	6-1, 6-3, 6-4
3.	c	6-2, 6-3
4.	d	6-4
5.	c	6-5, 6-6
6.	True	6-7
7.	b	6-10
8.	c	6-7
9.	a	6-7
10.	e	6-8, 6-9
11.	a	6-12
12.	b	6-12
13.	c	6-14
14.	b	6-15
15.	b	6-16
16.	True	6-17
17.	True	6-18
18.	False	6-18
19.	True	6-20
20.	False	6-21
21.	True	6-24
22.	d	6-25
23.	d	6-19
24.	d	6-25
25.	b	6-26
26.	c	6-27
27.	a	6-26, 6-27
28.	a	6-26, 6-27
29.	b	6-26, 6-27
30.	c	6-27

Required Readings

Chapter 6

Generation of Standard Test Atmospheres

Introduction

Calibration of atmospheric sampling equipment is very important for air monitoring, and it must be done to ensure that the data generated by air monitors represent the actual concentration of pollutants in air. Many factors may affect the calibration of sampling or monitoring devices, preventing them from providing a true measure of the atmospheric contaminant concentrations. The generation of standard test atmospheres is essential to the calibration procedures for continuous air monitoring instrumentation.

There is a need for reliable, accurate methods to generate pollutant gases of known concentration. For example, an air monitor may be designed to operate at a certain efficiency, but due to factors such as reagent deterioration, electrical or electronic component variability, and flow rate changes, data generated by an air monitor may differ from the true concentration of a pollutant in air. To evaluate the performance of sampling equipment, known contaminant concentrations must be introduced; by knowing the input concentration, the output of the monitor can be determined for accuracy and a function generated showing the relationship between the input concentration and output instrument response. The purpose of this section is to discuss the methods of preparing gases of known concentration.

The most important factor in the preparation of these standard atmospheres is devising a method of preparing gases of known concentration. Moreover, in the preparation of the standard atmospheres, devising a method of creating accurate calibration gases at the extremely small concentrations typically found in the atmosphere is often difficult. Many methods are now available for creating gases in high concentrations, but atmospheric testing often requires concentrations in the sub-part-per-million range.

Static Systems

Pressurized Systems

Although pressurized tanks of known contaminant concentrations are usually purchased, they may be prepared by the following procedures. Cylinders containing a pollutant gas are prepared by adding a known volume of pollutant gas and then pressurizing the cylinder with a diluent gas. The gas is then of known concentration and can be used for calibration purposes. The range of concentrations that can be achieved by this method is typically less than 100 ppm to more than 5000 ppm, depending on the stability of the gaseous pollutant. The concentration of the mixture can be calculated as follows:

(Eq. 6-1)
$$c_{ppm} = \frac{10^6 \times V_c}{V_d + V_c} = \frac{10^6 p_c}{p_t}$$

or

(Eq. 6-2)
$$c_{\%} = \frac{10^2 \times V_c}{V_d + V_c} = \frac{10^2 p_c}{p_t}$$

Where:

c_{ppm} = *concentration of gas mixture, ppm by volume*
$c_{\%}$ = *concentration of gas mixture, percent*
V_c = *volume of contaminant gas*
V_d = *volume of diluent gases*
p_c = *partial pressure of contaminant gas*
p_t = *total pressure of the gas mixture*

Using the rigid container procedure, it is necessary to construct a gas-handling manifold that interconnects the vacuum source, the calibrated volume, the source of contaminant gas, and the gas cylinder. Subsequently, the entire system is evacuated; the known calibration volume is flushed and filled at atmospheric pressure with the contaminant gas and isolated, and connecting lines are again evacuated. The contaminant gas is then swept by diluent carrier gas into the cylinder, and the cylinder is pressurized with diluent gas to the desired pressure. Because of compressional heating, the cylinder should be allowed to equilibrate at room temperature before reading the pressure to be used in the concentration calculations. The concentration of the mixture is calculated as follows:

(Eq. 6-3)
$$c_{ppm} = \frac{10^6 \times V_c \times P_b}{V_{cyl} \times P_t}$$

Where:

c_{ppm} = *concentration of mixture, ppm by volume*
V_c = *volume of pure contaminant gas*
V_{cyl} = *volume of cylinder*
P_b = *barometric pressure at time of filling*
P_t = *final total pressure of cylinder*

One factor that must be watched closely when preparing gas mixtures by this method is the thoroughness of the mixing. When introducing the gases into the cylinder one at a time, a layering effect may occur and result in incomplete mixing. This effect can be counteracted by allowing for adequate mixing time before use.

It should be noted that at room temperature and pressure most gas mixtures conform closely to the ideal gas law. However, at the higher pressures that are present in the cylinders, gaseous mixtures can deviate from this law and create errors of up to 20%. This can be corrected by using a quantity called the compressibility factor (K). The units for the pressure and volume are not important as long as P_c and P_t are in the same units and V_c and V_d are in the same units, since both parts-per-million and percent are unitless quantities.

In commercial practice, compressed gas cylinders of calibration gases are often prepared using high load mass balances; in this procedure, a precise tare weight for an evacuated cylinder is obtained, and the cylinder is weighed again following the addition of the desired trace constituent and after the addition of the diluent gas (prepurified nitrogen in most cases) under pressure. The mass fraction of the contaminant gas is converted to a volumetric concentration by application of the usual formula involving molecular weight and molar volume.

When prepared by the user, a pressure dilution technique of some sort is generally necessary. Here the volume of the contaminant gas introduced, V_c, the volume of the cylinder, V_{cyl}, the evacuation pressure, P_{vac}, and the final total pressure in the cylinder, P_t, must be known.

Using this procedure the cylinder is evacuated using a vacuum pump capable of producing a very low pressure. Depending on the exact capacity of the pump, the previous contents and size of the cylinder, and the final pressure to be used, the evacuation pressure may be ignored in the calculations. For example, if the cylinder was evacuated to a few torrs and the final pressure was 30 atmospheres, the calculation error in ignoring the evacuation pressure (i.e., assuming it is zero) would only be about 1 part in 10,000. Following the evacuation of the cylinder, the contaminant gas is introduced using a syringe technique, as described in the bag procedure, or using a small rigid container of precisely known volume.

As a matter of good practice, cylinders should be continued in the same service and not interchanged; for example, a cylinder formerly used for SO_2 span gas should not be converted to NO_2 service. Further, cylinder materials consistent with the gases to be contained therein should be used.

For certain purposes of Federally mandated monitoring, the EPA requires that the concentrations of calibration gases contained in compressed gas cylinders be determined by measuring pollutant concentrations generated by the gases using ambient air quality analyzers that have been calibrated using NBS standard reference materials (SRMs) or certified reference materials (CRMs). An EPA-recommended procedure for these determinations, entitled "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Air Pollution Analyzers (Protocol No. 2)," is contained in EPA 600/4-77-027a *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II.*

Rigid Chambers

Rigid chambers such as the one illustrated in Figure 6-1 are another method of preparing an analytical gas standard.

The gaseous contaminant is introduced into the vessel, mixed with the diluent gas, and sampled. The volume of the chamber may vary with the type of application, but the principle remains the same. Preparation of standard gas mixtures by this procedure has been largely replaced by more accurate permeation devices and pressurized cylinders containing a specified pollutant concentration.

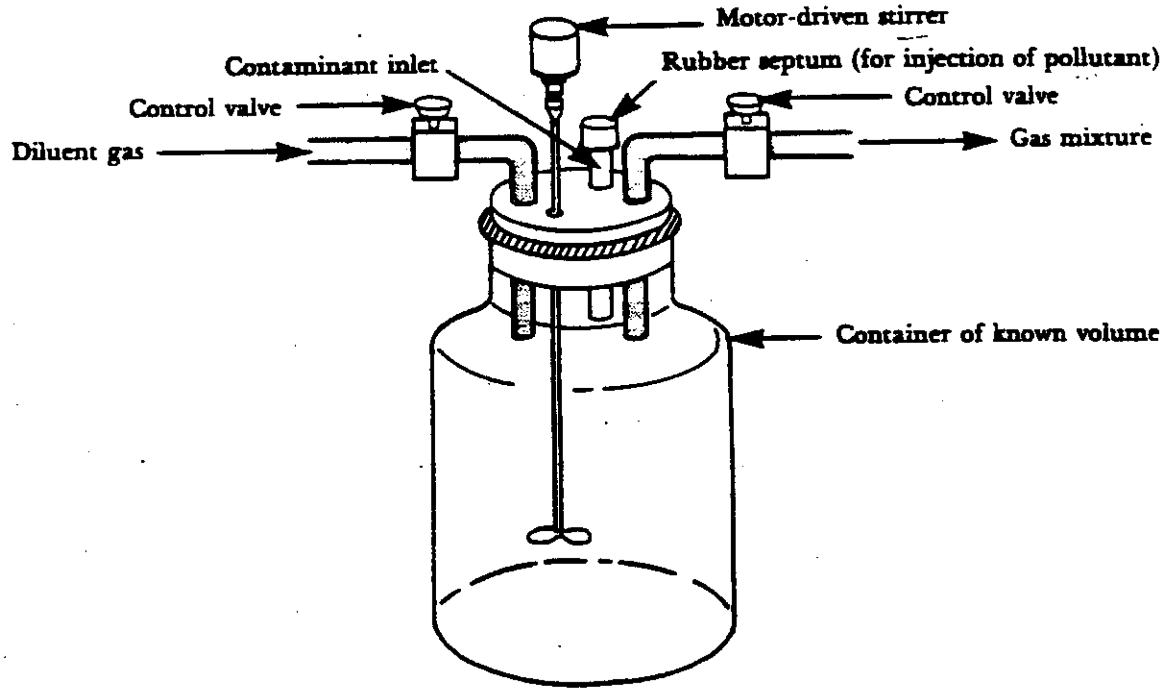


Figure 6-1. Rigid chamber used for producing standard gas mixture.

Nonrigid Chambers—Bag Samples

In this procedure, a bag, usually of a flexible, nonreactive plastic material, is filled with a known volume of diluent gas, and a known volume of contaminant gas is added to the system. The diluent gas should be cleaned of all interfering constituents and be nonreactive to the desired contaminant. After allowing for complete mixing in the bag, a sample can be drawn off for calibration purposes. The concentration of contaminant in the bag mixture can be calculated by (if the initial contaminant concentration is 100%):

(Eq. 6-4)

$$c = \frac{V_c}{V_d + V_c}$$

Where:

c = *concentration of diluted contaminant, ppm by volume*
V_c = *volume of contaminant gas, μℓ*
V_d = *volume of diluent gas, ℓ.*

One of the first and most important steps in this preparation is the selection of the bag. The bag must be of a flexible material and be chemically inert to the gases it will contain. Chemical inertness is very important; if the contaminant gas reacts with the bag, the amount of contaminant will decrease and the actual concentration of the bag mixture will be unknown. Teflon®, Mylar® and copolymer Tedlar® bags have been widely used because they are inert to most materials. Before any bag is to be used, it should be tested with the contaminant gas to be sure that no reaction will take place between the bag and the gas. After the bag has been selected, it should be checked for leaks, particularly the seams of the bag and the area around the valve, before the sample is introduced. The bag should be flushed and evacuated at least three times to ensure that all unwanted contaminants have been removed. The actual filling of the bag must be done under controlled conditions to guarantee measurement of the volume. Clean air is pumped into the bag through an accurately calibrated flowmeter. The flow rate of the diluent gas must be kept as constant as possible throughout the filling procedure to obtain an accurate measure of volume. After the flow rate is set, a stopwatch is used to get an accurate filling time. The product of the flow rate and the filling time is the total volume of diluent gas added to the system.

The contaminant sample should be introduced into the stream of diluent gas as the bag is filling. This should be done after the bag has filled to about one-quarter of the desired volume. By introducing the sample at this time, mixing can take place as the bag fills to its final volume. The sample is introduced into the diluent gas stream with the use of a syringe. A rubber septum and tee assembly is located in the filling line for insertion of the syringe. Care must be used when handling the syringe to ensure that the desired quantity of contaminant is introduced.

The syringe should have a graduated barrel so that the amount of contaminant entered can be read directly. The plunger of the syringe must be gas-tight so no sample will escape while being injected into the diluent gas stream. A Teflon® cap can be fitted over the plunger to eliminate gas escaping during introduction. The sample gas is extracted with the syringe from a source of known concentration. When drawing the sample, the syringe should be filled and evacuated at least six times with the sample gas to eliminate any air that may have been present in the needle. The plunger of the syringe should be drawn well past the desired volume when entering the sample. Just before introducing the sample into the diluent gas stream, the syringe should be adjusted to the desired volume to eliminate any error from air that may have diffused into the needle. Care should be taken in handling the syringe; it should never be held by the barrel or the needle. Heat from the hand of an analyst will cause the gas in the syringe to expand and part of the sample will be lost from the needle. When introducing the sample, the tip of the needle should be in the middle of the diluent gas stream to prevent the sample from being lost on the walls of the filling lines. After depressing the plunger, remove the needle from the gas stream immediately to ensure that none of the sample will diffuse out of the needle and into the gas stream, giving a higher resulting concentration. Mixing time can be decreased by kneading the bag for several minutes.

The concentration of the calibrated gas will change during storage. The decay rate will depend upon the substance being stored, the relative humidity, and the bag material. Substances such as nitrogen dioxide and ozone will decay faster than carbon monoxide and hydrocarbons. Figure 6-2 illustrates the rate of decay with time of a known concentration of SO_2 stored in a bag. The decay rate can be decreased if the bag is preconditioned. The preconditioning requires that the bag be flushed several times with the sample gas. The bag should be left overnight at least once with a sample gas in it as a preconditioning step.

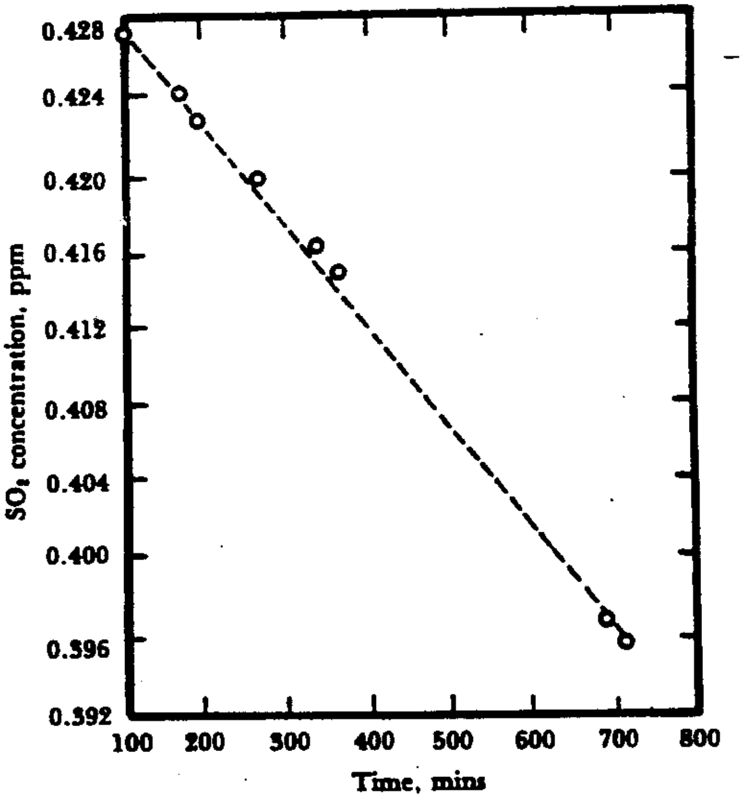


Figure 6-2. Rate of decay of SO_2 concentration in a bag.

It should be noted that the bag-filling method is only an approximate method of preparing a known gas-mixture concentration. A reference method should be used to determine the actual concentration of the bag mixture.

Polasek and Bullin (1978) found that sample stability depends clearly on the compound and type of bag material used. Table 6-1 gives the results of carbon monoxide deterioration with time in bags of various materials.

Table 6-1. Carbon monoxide sample deterioration with time in bags of various materials.

Bag material	pvc	Tedlar	Snout*	Aluminized polyester
No. of bags tested	10	10	5	3
Concn of calibration gas used to fill bags, ppm	9.0	9.0	8.2	8.2
0 h after filling, av ppm	8.9	8.5	8.2	8.0
Av deviation, ppm	− 0.12	− 0.5	0	−0.17
Av sqd deviation, ppm²	0.056	0.352	0.012	0.030
24 h after filling, av ppm	8.5	7.5	8.0	7.9
Av deviation, ppm	− 0.50	− 1.5	−0.16	−0.30
Av sqd deviation, ppm²	0.306	4.2	0.048	0.097
48 h after filling, av ppm	8.4	6.8	8.3	8.2
Av deviation, ppm	− 0.63	− 2.2	0.10	−0.03
Av sqd deviation, ppm²	0.497	7.7	0.010	0.010
100 h after filling, av ppm	7.9	5.2	8.0	7.7
Av deviation, ppm	− 1.2	− 3.8	−0.18	−0.50
Av sqd deviation, ppm²	1.5	17.8	0.066	0.25

*Consists of layers of polyester, polyvinyl chloride, aluminum, polyamide, and polyethylene.

Dynamic Systems

Permeation Systems

The use of permeation techniques for preparation of standard mixtures is very useful for some contaminants. The method is based on the theory that a gas confined above its liquefied form at a constant temperature will permeate through some materials at a constant rate. By putting a liquefied gas into a Teflon® tube, for example, permeation of the vapor through the tube will take place because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentration can be generated.

The actual concentration of a sample gas at the EPA's STP (25 °C, 760 mm Hg) can be calculated by Equation 6-5.

(Eq. 6-5)
$$c = \frac{(PR)\left(\frac{24.46}{M}\right)}{Q}$$

Where:
c = *concentration, µℓ/ℓ or ppm by volume*
PR = *permeation rate, µg/min*
Q = *total flow rate, corrected to STP, std ℓ/min*
M = *molecular weight of the permeating gas, µg/µ-mole*
24.46 = *molar volume (V) of any gas at 25 °C and 760 mm Hg, µℓ/µ-mole*

Permeation tubes allow for the generation of gases with concentrations in the sub-part-per-million range.

Permeation tubes are made from a variety of different materials. The material must allow the diffusion of the contaminant gas through the walls and also be inert to the diffusing gas. If some reaction took place between the tube material and the gas, the permeation rate would be affected and might no longer be constant. Teflon®, Mylar®, and Saran Wrap® are materials often used because of their chemical inertness and good permeation properties. Before any material is used for the permeation tube, it should be tested to ensure that no changes will occur in the material when it comes in contact with liquefied gas. To test the material, a piece should be placed in some of the liquefied gas it will contain. The material should be removed after a few days and checked to see if any changes in the material have occurred (i.e., brittleness, holes, stickiness, etc.). If there are no apparent changes, the material is probably suitable for use.

The first step in the construction of the tube is to compress the desired sample gas to a liquid state. The liquefied gas is then put into a tube and the tube ends are sealed. One method of sealing the tube ends is to force glass beads or stainless steel balls into the tube ends. To seal properly, these beads should be approximately one and one-half times the inside diameter of the tube. Once the tube has been prepared, it should be stored for at least 36 hours in order to equilibrate. Since the permeation rate is extremely dependent on temperature and relative humidity, the permeation tube should be stored at a constant temperature with dry air or nitrogen passing over it. After equilibration, the permeation rate of the tube can be determined either gravimetrically or by use of a calibrated analyzer.

For the gravimetric determination, the tube should be weighed on an analytical balance and replaced in the storage area. Time required to weigh the tube should be minimized and kept constant to compensate for the effects of moisture absorption. High humidity will cause the permeation tube to absorb moisture, thereby increasing the tube weight. This will yield an erroneously low value for the permeation rate. Absorbed moisture on the tube can form acids that may cause tube blistering, thus changing the permeation rate. The tube should be stored and weighed several times to yield enough data to demonstrate that the permeation rate is constant. The results of these weighings should be plotted on a graph as weight versus time. From the slope of the resulting best "fit" line, the permeation rate can be calculated in micrograms per minute as shown in Figure 6-3.

For certain purposes of Federally mandated monitoring, the EPA requires that permeation rates of permeation tubes used in routine monitoring be determined by measuring pollutant concentrations generated by the tubes using ambient air quality analyzers that have been calibrated using NBS standard reference materials (SRMs) or certified reference materials (CRMs). An EPA-recommended procedure for this type of permeation rate determination, entitled "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Air Pollution Analyzers (Protocol No. 2)," is contained in EPA 600/4-77-027a *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II.*

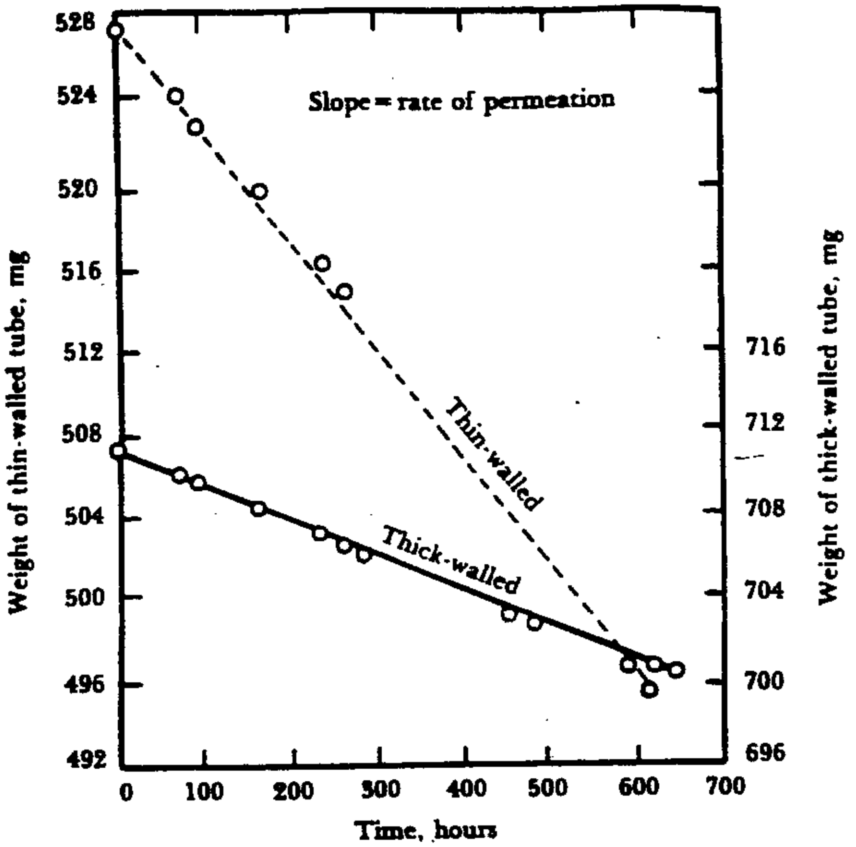


Figure 6-3. Calibration of two permeation tubes.

Once the tube has been calibrated, it can be used to generate test gases of known concentration. The permeation tube is placed in a stream of diluent gas. The gas passes over the tube and the permeated gas is mixed into the gas stream. The desired concentration can be varied by varying the flow rate of the diluent gas or by varying the permeation tube length. The diluent gas must be kept at a constant temperature during the time the calibration gas is being generated to be sure the permeation rate is constant. The temperature dependence of the permeation rate is illustrated for four gases in Figure 6-4. To accomplish this, the diluent gas is drawn through a constant temperature chamber before passing over the tube as in Figure 6-5. Permeation tubes are commercially available from many sources offering a variety of precalibrated tubes with different permeation rates. The National Bureau of Standards offers some reference sources. Table 6-2 lists permeation rates of a number of compounds through a Teflon® film. A number of configurations other than the original tube design are also commercially available. Some of these are designed to provide a longer useful life. Table 6-3 lists some materials used to construct a permeation tube.

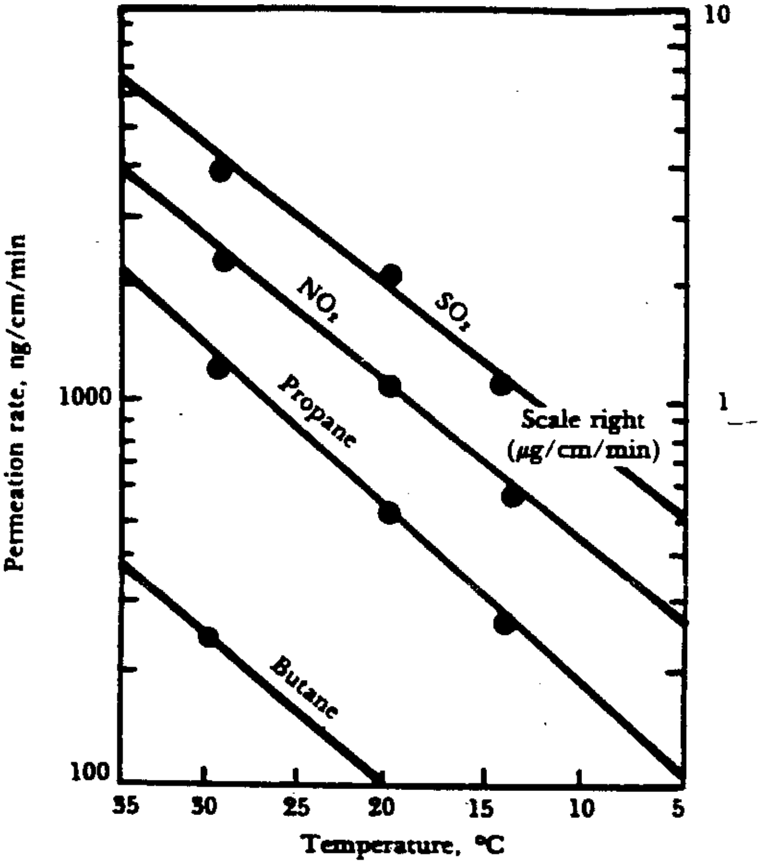


Figure 6-4. Permeation rate vs. temperature for four gases.

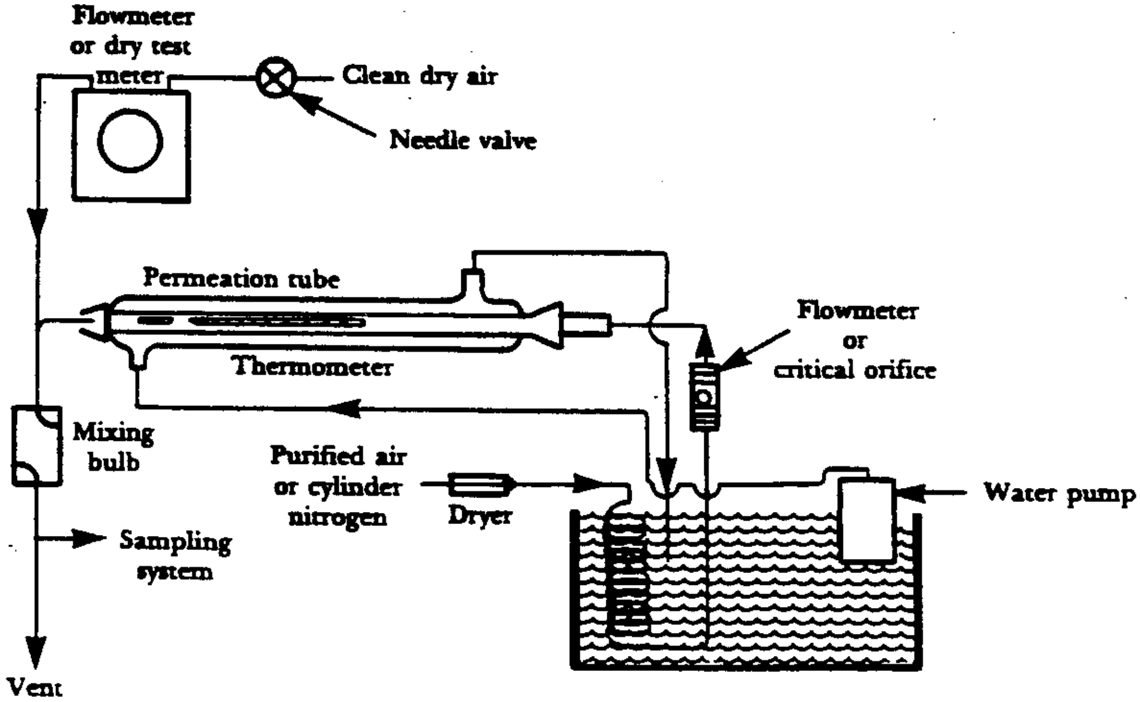


Figure 6-5. Components and flow of a typical permeation system.

Table 6-2. Permeation rates of some typical compounds through FEP Teflon®.

Compound	Thickness (in.)	Temperature (°C)	Permeation rate (ng/cm/min)
SO_2	0.012	20 ± 0.5	215
	0.030	20 ± 0.5	138
	0.012	20.1	205
	0.012	29.1	396
NO_2	0.012	13.8	605
	0.012	21.1	1110
	0.012	29.1	2290
Propane	0.012	21.1	53
	0.012	29.1	119
Butane	0.012	15.5	6.4
	0.012	29.1	22.3
CHF_2Cl	0.012	20	2.8
$CF_3CHClBr$	0.016	93	1.3
$CH_2=CHCH_3$	0.030	31	0.29
n-C_6H_{12}	0.016	93	0.065
$C_6H_5CH_3$	0.030	20	0.00006

Table 6-3. Some materials used to construct a permeation tube.

Material	Trade name	Thickness (in.)
Fluorinated ethylene propylene resin	FEP Teflon	0.030
Fluorinated ethylene propylene resin	FEP Teflon	0.012
Fluorinated ethylene propylene resin	FEP Teflon	0.001
Polyethylene	—	0.027 to 0.526
Polyethylene	Alathon	0.025
Polyethylene	—	0.001 to 0.037
Polyvinyl acetate	—	0.135 to 1.332
Polyvinylidene chloride	Saran Wrap	0.025
Polyamide	Nylon 6	0.113
Polyester	Mylar	0.031
Polyethylene terephthalate	Mylar	0.00031 to 0.006
Polythene	Diothene	0.0635 to 0.0254 mm

The performance of a permeation device depends on the polymer films used to construct these tubes and the pollutant for which a standard concentration is needed. The important factors to be considered in the use of a permeation device are temperature, humidity, gas stability, equilibration time, etc. These parameters have been studied for nitrogen dioxide, sulfur dioxide, and recently for numerous halogenated hydrocarbons and for permeation tubes constructed with FEP (fluorinated ethylene propylene copolymer) Teflon®. In the case of nitrogen dioxide, the permeation device demonstrating the greatest stability and utility in terms of equilibration time and lifetime is illustrated in Figure 6-6.

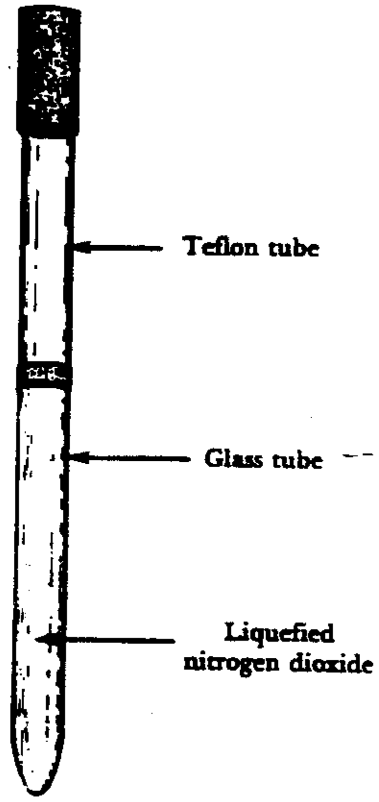


Figure 6-6. Nitrogen dioxide permeation device.

Experimental results indicated that a small permeating area of Teflon® was required for NO_2 due to the rapid permeation rate of NO_2 through the Teflon® wall. Tubes constructed as in Figure 6-6 have a usable lifetime of up to two years. In contrast, the permeation rate of sulfur dioxide through the same Teflon® wall is considerably slower. Permeation tubes containing this pollutant are constructed as shown in Figure 6-7.

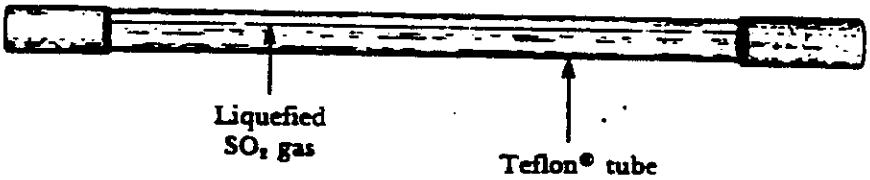


Figure 6-7. SO_2 permeation tube (NBS—standard reference material).

To determine the rate of permeation in this type of device, the tube may simply be removed from the permeation system and weighed to the nearest 0.1 mg on an analytical balance. Generally weighings can be made daily, weekly, or monthly, depending on the gas and type of permeation device. As indicated previously, the permeation rate can be determined by measuring the slope of the least-squares error line used to fit the weight vs. time data. A more rapid calibration, however, can be obtained by using the apparatus shown in Figure 6-8.

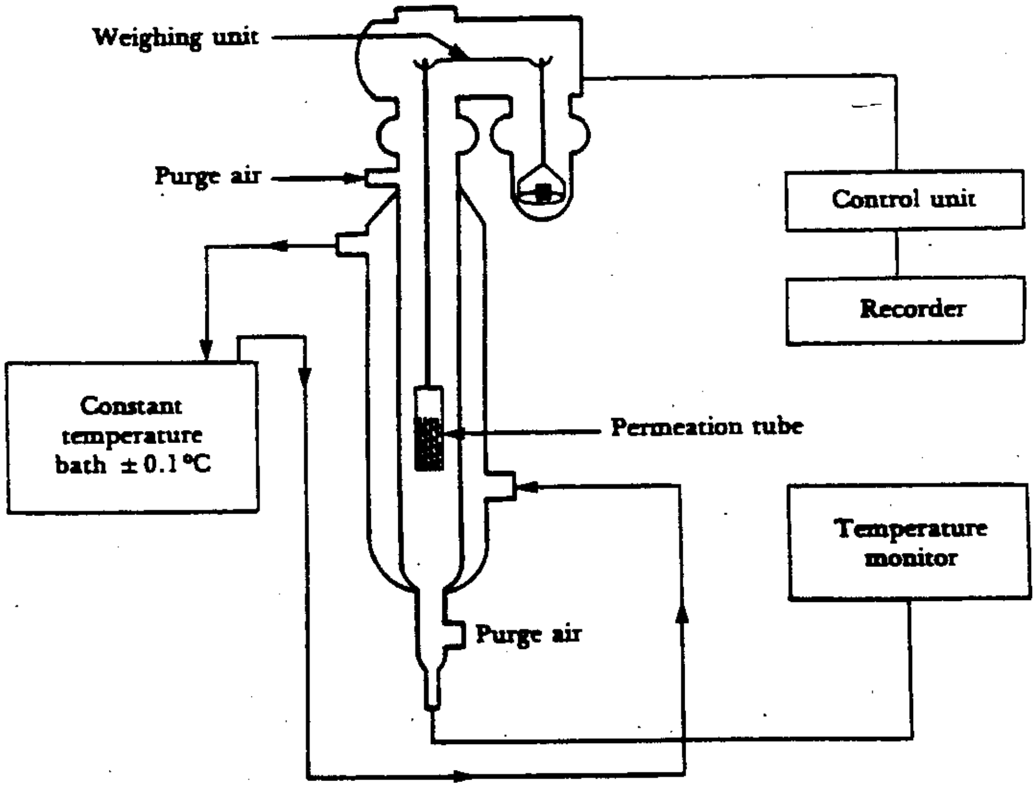


Figure 6-8. Gravimetric calibration apparatus.

In addition to rapid calibration, this apparatus has the advantage of continuous direct read-out of weight change (Figure 6-9), and the permeation tube is maintained in the constant temperature bath at all times. The potential problem of spurious weight increase due to the hygroscopic nature of some pollutants (e.g., SO_2, NO_2) is eliminated with this device, for the tube need never have to leave the constant temperature bath.

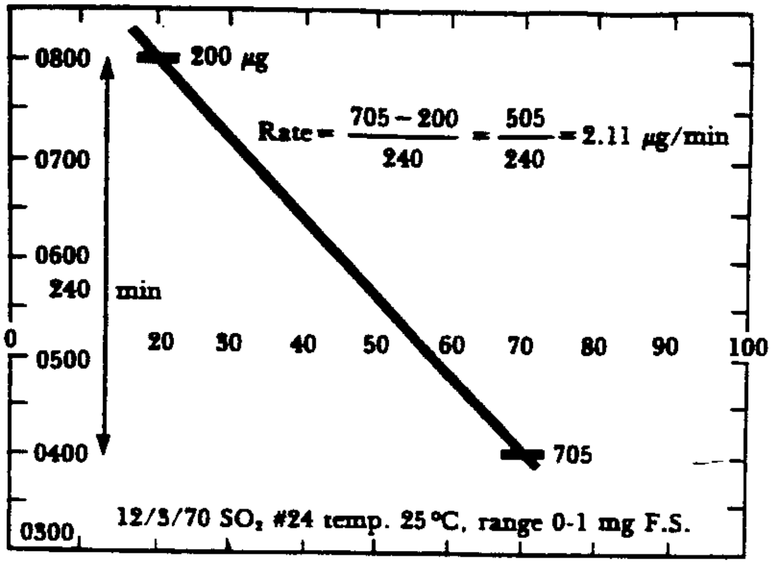


Figure 6-9. Typical stripchart read-out from an *in situ* gravimetric apparatus.

Dilution Systems

Single Dilution

A simple system for diluting gas entails mixing the gas with the diluent in a mixing chamber after measuring their flow rates. A single dilution system using rotameters to measure flow is illustrated in Figure 6-10. The concentration of the test mixture can be calculated with the following formula:

(Eq. 6-6)

$$c_u Q_u = c_d (Q_u + Q_d)$$

$$\frac{c_u Q_u}{(Q_u + Q_d)} = c_d$$

Where:

c_u = concentration of undiluted contaminant gas
c_d = concentration of diluted test mixture
Q_u = flow of undiluted contaminant gas
Q_d = flow of diluent gas.

Flow measuring devices other than rotameters are frequently used to increase the accuracy and precision of the test mixture concentration.

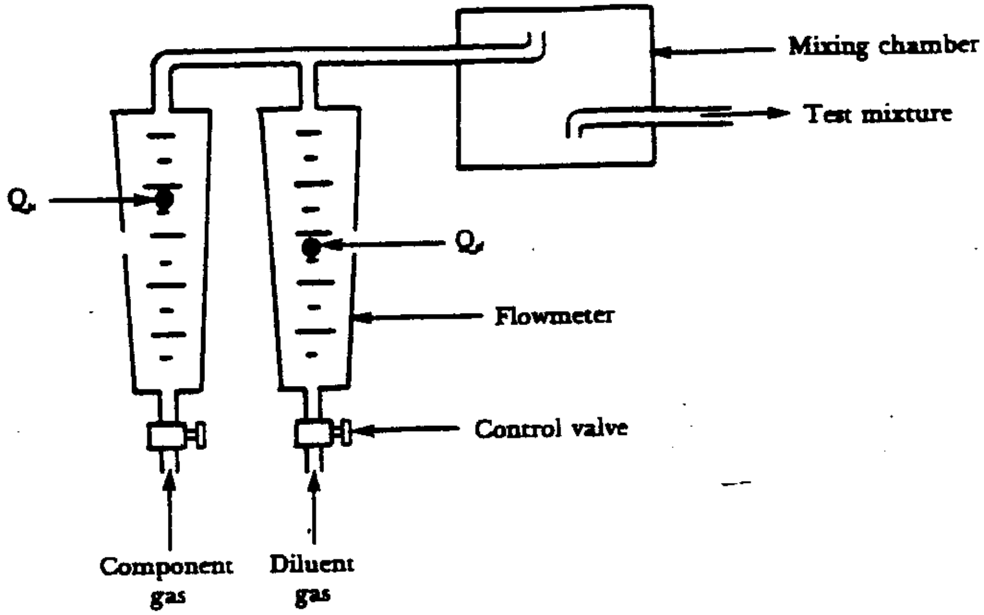


Figure 6-10. Single dilution system.

Multiple Dilution

Low-level concentrations of pollutants may be obtained by a multiple dilution system. A system such as that shown in Figure 6-11 for a double dilution avoids high dilution ratios and the use of low flow rotameters. Other methods for measuring and controlling flow (i.e., orifices, mass flowmeters, etc.) in a multiple dilution system provide a variety of means for constructing multiple dilution systems. The test mixture concentration can be calculated with the following equation:

(Eq. 6-7)

$$c_{tm} = \frac{\left(\frac{c_u Q_c}{Q_c + Q_{d1}}\right)}{Q_m + Q_{d2}} \; Q_m$$

Where (see Figure 6-11):

Q_c = *flow of undiluted contaminant gas*
Q_{d1} = *flow of first diluent gas*
Q_m = *flow of first diluent mixture*
Q_{d2} = *flow of second diluent gas*
c_u = *concentration of undiluted contaminant gas*
c_{tm} = *concentration of final test mixture.*

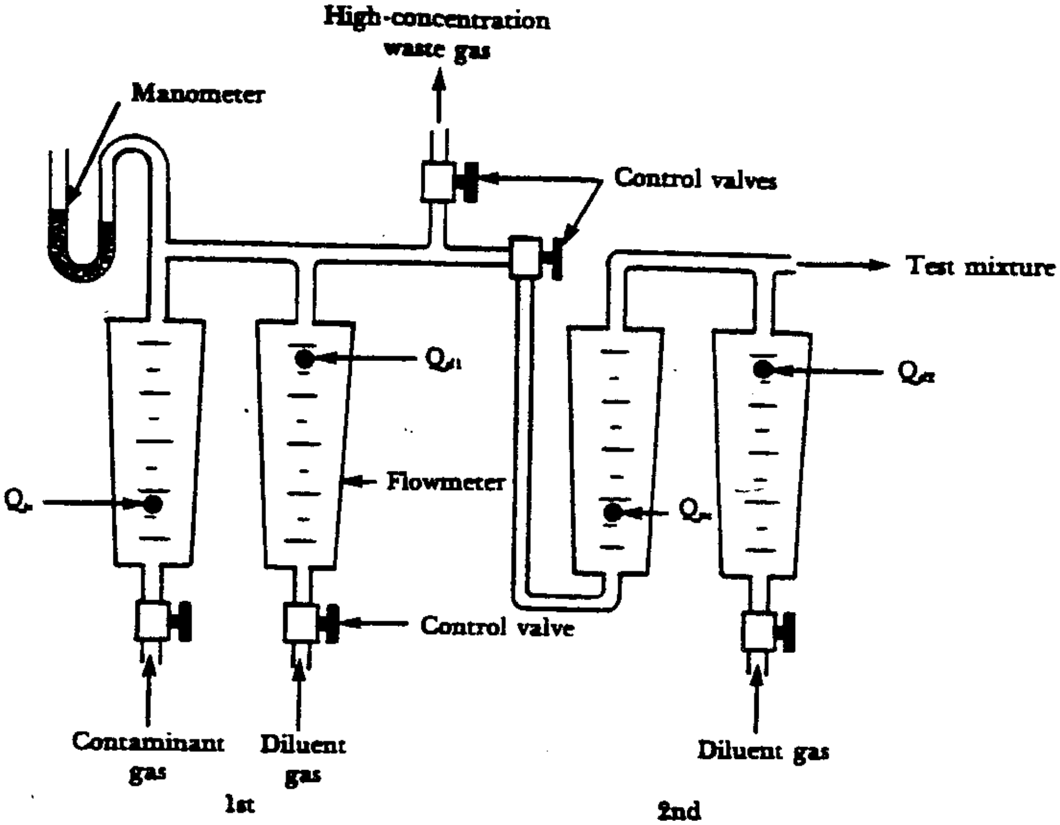


Figure 6-11. Sketch of a system for making double dilutions.

Ozone Generation

Ozone is unlike most of the gaseous pollutants in that there are no gaseous calibration standards available. This is due to ozone's instability, which makes it impossible to produce gas cylinders of standardized ozone concentrations or ozone permeation tubes. The only means available for the calibration of ozone monitors is to produce stable, known amounts of ozone at the site of calibration.

Ozone is most commonly produced by irradiating oxygen with an ultraviolet light source in an ozone generator. An ozone generator may utilize a tubular quartz chamber into which ozone-free air is admitted at a controlled, constant rate. This incoming air (from a zero air source) is subjected to ultraviolet radiation from a mercury vapor lamp.

The mercury vapor lamp is housed within an aluminum shield which can be adjusted to expose a selected portion of the lamp, thereby controlling the amount of ultraviolet radiation to which the air stream is exposed. In this way, varying amounts of ozone can be produced by simply moving the shield to a number of positions across the mercury lamp. Using a pressure regulator to assure a stable flow through the generator plus a constant line source transformer to assure constant voltage to the UV lamp, the ozone generator can be expected to give stable ozone concentrations which vary by no more than ± 10 parts per billion.

Varying concentrations of ozone can also be obtained by dilution of a stable ozone source (from an ozone generator) with varying amounts of zero air (ozone-free air). One or more of the dilution techniques previously mentioned can be employed.

Evaporative Systems

Gases may be introduced into a test atmosphere by injection of the gas in the liquid phase into the moving diluent gas stream. Figures 6-12 through 6-14 exemplify several types of systems for introducing a liquefied gas into a system that will produce an atmosphere of known concentrations.

Careful consideration should be given to the specific pollutant and the type of injection used. For example, syringe injection of nitrogen dioxide into a bag through a rubber septum is unadvisable since nitrogen dioxide will react with the rubber, giving rise to spurious concentrations.

The approximate concentration of the test mixture can be calculated with the following formula.

$$c = \frac{Q_\ell \varrho_\ell \bar{V} 10^6}{(M) Q_d} \quad \text{(Eq. 6-8)}$$

Where:
c = *concentration of test mixture, in ppm*
Q_ℓ = *flow of liquid contaminant, in mℓ/min*
ϱ_ℓ = *density of liquid, in g/mℓ*
$\bar{V}$ = *molar volume of ideal gas at operating temperature and pressure, in ℓ/mole*
M = *molecular weight of contaminant, in g/gm-mole*
Q_d = *flow of diluent gas, in ℓ/min*
10^6 = *conversion to ppm*

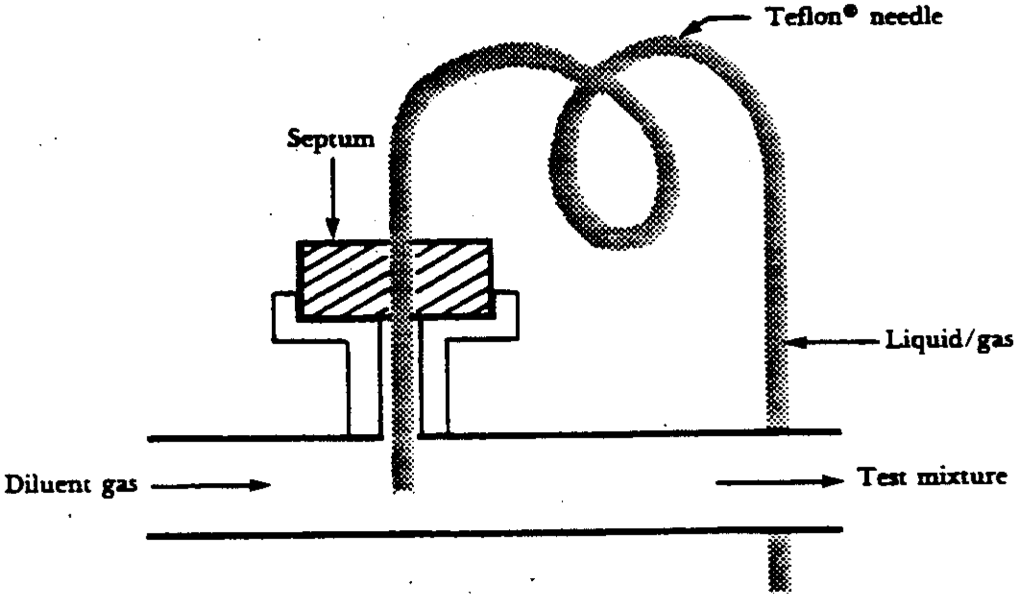


Figure 6-12. Method for injecting liquids and gases into a test atmosphere.

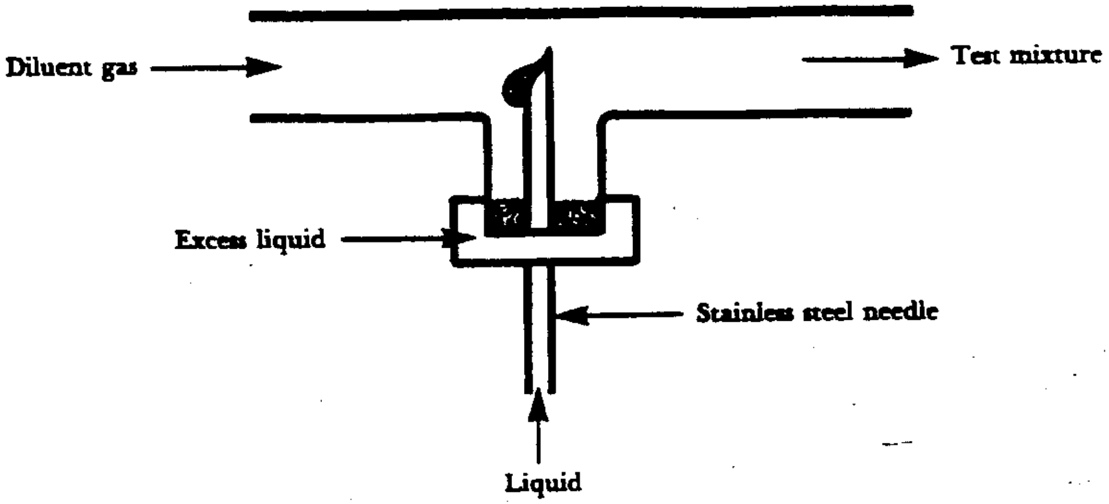


Figure 6-13. Methods for injecting liquids into a test atmosphere.

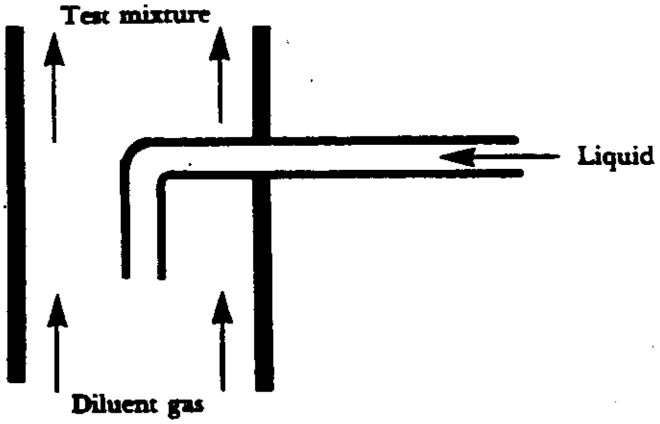


Figure 6-14. Methods for injecting liquids into a test atmosphere.

Preparation of Zero Air

Introduction

Zero air can be defined as air that is free of contaminants and interferences for a particular analysis technique. It is important to note that a zero air for one analysis may not be a zero air for another analysis. For example, an analysis technique may require a zero air that has only sulfur dioxide and water vapor removed while another analysis technique may call for only hydrocarbons to be removed.

Zero gases are used extensively in atmospheric sampling, both in laboratory and field applications. Many continuous monitors require a constant supply of zero air for parallel path reference cells. Cylinder air can be used, but by applying the proper adsorption or absorption column on the inlet gas stream, zero gas can be continuously produced from atmospheric air. This can cut costs and eliminate the necessity of replenishing zero air cylinders. The contaminants and their typical concentrations found in clean, dry ambient air are summarized in Table 6-4.

Table 6-4. Typical composition of clean, dry air near sea level.

Component	Formula	Content	
		% by Volume	ppm
Nitrogen	N_2	78.09	780,900
Oxygen	O_2	20.94	209,400
Argon	Ar	0.93	9,300
Carbon dioxide	CO_2	0.033	330
Neon	Ne	18×10^{-4}	18
Helium	He	5.2×10^{-4}	5.2
Methane	CH_4	1.5×10^{-4}	1.5
Krypton	Kr	1.0×10^{-4}	1.0
Hydrogen	H_2	0.5×10^{-4}	0.5
Nitrous oxide	N_2O	0.5×10^{-4}	0.5
Xenon	Xe	0.08×10^{-4}	0.08
Ozone*	O_3	0.03×10^{-4}	0.03
Ammonia	NH_3	0.01×10^{-4}	0.01
Iodine	I_2	0.01×10^{-4}	0.01
Nitrogen dioxide	NO_2	0.001×10^{-4}	0.001
Sulfur dioxide	SO_2	0.0002×10^{-4}	0.0002
Carbon monoxide	CO	0 to trace	—

*Ozone content in winter is 0.02 ppm and in summer is 0.03 ppm.

There are many techniques for producing zero air. The purpose of this section is to discuss the most widely used methods for removing contaminants from a gas stream to produce a zero air. It should be noted that water vapor is a contaminant that must be removed from many gas streams. This is especially true when introducing a gas stream into a permeation tube system where the gas must be free from water vapor. This ensures proper permeation through the walls of the permeation tube. For this reason, a separate discussion of drying a gas stream is provided in this section.

Gaseous Contaminant Removal

There are many ways of removing a gaseous contaminant from a gas stream, including the use of catalytic devices, adsorption, and absorption. Figure 6-15 lists the more commonly used materials.

Material	Purpose	Preparation
1. Activated charcoal (6 × 16 mesh)	Removes many gases such as ozone, SO_2, NO_2, higher molecular weight organic vapors. Does not completely remove CO, CO_2.	Commercially activated coconut hull charcoal 6 × 16 mesh.[a] Place in 2 inch I.D. × 18 inch long section of plastic pipe. Use glass wool plugs to retain charcoal in place. Plastic pipe caps on each end of cylinder are drilled and threaded to accept standard ½ inch O.D. tube fittings. Containers of other materials and similar configuration and volume may be used.
2. NO oxidizer (a) Chromium trioxide (CrO_3)	Converts NO to NO_2 for subsequent removal with TEA or soda lime.[4]	Soak firebrick or alumina 15-40 mesh in a solution containing 16 g CrO_3 in 100 ml of water. Drain, dry in an oven at 105-115°C for 30 to 60 minutes and cool. Spread a thin layer of the dry pellets in a dish and place in a desiccator containing a saturated salt solution which maintains the relative humidity (RH) between 50 to 70%. The reddish color changes to a golden orange when equilibrated. Place in a ½ inch I.D. × 15 inch glass tube. Use glass wool plugs to hold pellets in place. (Caution: protect eyes and skin when handling this material. Do not breathe oxidizer dust.) Before using, pass air containing 30 to 70% RH through the oxidizer for about 1 hour at 0.5 ℓ/min to condition. Discard when more than ¾ of the oxidizer bed depth turns brown.
(b) Humidifier	Furnishes water vapor for proper operation of oxidizer.	Pass dilute NO air stream over water at a fixed temperature such that the humidity of the air stream is maintained within 50 ± 20% RH.
3. Triethanolamine (TEA)	Removes NO_2.	Soak firebrick 10-20 mesh in a 20% aqueous solution of TEA. Drain, spread on a dish and dry for 30 to 60 min at 95°C. Pellets should be free-flowing. Place in a ½ inch O.D. (7/16 inch I.D.) × 15 inch long polyethylene or stainless steel tube with standard ½ inch O.D. tube fittings on each end. Use glass wool plugs to hold the pellets in place.

4. Desiccant	Removes water.	Commercial 6 × 16 mesh silica gel with color indicator.[b] Place in 3 inch I.D. × 24 inch long clear plastic cylinder capped at both ends. Caps are drilled and threaded to accommodate standard ½ inch O.D. tube fittings. Use glass wool to hold granules in place. When the change in color exceeds ¾ of the desiccant bed depth, regenerate by exposing the silica gel to 120°C atmosphere overnight.
5. Carbon monoxide Oxidizer (Hopcalite)	Catalytically oxidizes CO to CO_2 for subsequent removal with Ascarite or soda lime.	Commercial mixture of copper and manganese oxides.[c] Place granules in a ½ inch O.D. (7/16 inch I.D.) × 15 inch long section of copper pipe with standard ½ inch O.D. tube fittings on each end. Use glass wool to hold granules in place.
6. CO_2 absorber	Removes CO_2, H_2O.	a. Soda lime[d]: commercial preparation of calcium and sodium hydroxides; 4 to 8 mesh. b. Ascarite[e]: a commercial preparation of sodium hydroxide in an asbestos matrix, 8-30 mesh. Place soda lime or Ascarite in a 2 inch I.D. × 15 inch long section of plastic pipe. Plastic caps at both ends are drilled and threaded to accept standard ½ inch O.D. tube fittings.

[a] Activated coconut hull charcoal, Type PCB 6 × 16 mesh, Pittsburgh Activated Charcoal, Merk & Co., Inc. Pittsburgh, PA 15230.

[b] Silica gel, indicating, 6 × 16 mesh, Grace Davison Chemical, Baltimore, MD 21226.

[c] Carbon monoxide purifier, (Hopcalite) Model RAF-BCHDI, Robbins, Aviation, Inc., Vernon, CA 90058.

[d] Soda lime, 4 to 8 mesh, J. T. Baker Chemical Co., Phillipsburg, NJ 08865.

[e] Ascarite, 8-30 mesh, ibid.

Figure 6-15. Materials used in producing zero air up to 30 ℓ/min.

Catalytic Devices

Catalytic devices have been used to selectively remove a gas from the sample stream. This leaves a reference or zero gas that is minus only the pollutant to be measured. Using this method, the change in output when the catalyst bed is bypassed will be due only to the pollutant measured. An example of a specialized catalytic conversion is the UV absorption ozone monitor. Ozone is selectively removed from the sample using a manganese dioxide catalyst that reduces ozone to oxygen. This ozone-free sample, which still contains all other gases, is the reference, or zero, air for the UV ozone monitor and is used as the baseline. The gas stream then bypasses the catalyst, and the ozone-carrying gas enters the monitor where the change in output can be attributed specifically to the ozone.

Adsorption

Adsorption is a widely used method for removing contaminants from a gas stream to form a reference, or zero, air. Solid adsorbents have the ability to absorb quantities of gases because they have extremely high surface areas per unit weight; e.g., activated carbon has a surface area ranging from 300 to 1400 m^2/gm. A more detailed discussion of the porous quality of adsorbents may be found in the literature (Hersh 1961; Mantell 1951; Pittsburgh Activated Carbon Co.). Table 6-5 lists the properties of some common adsorbents.

Table 6-5. Typical properties of adsorbents.

Adsorbent	Form	External surface area, ft^2/lb	Pore volume ft^3/lb	Reactivation temp., °F	Max. gas flow, CFH/lb	Sp. heat, C_p Btu/(lb°R)	Typical adsorbates
Activated carbon	Pellets	10.5—21.5	0.010—0.013	200—1000	/	0.25	CH_4 through n-C_8H_{18}, CO_2, H_2S
	Beads (G)	15.0—24.0		200—1000	/	0.25	
Silica gel	Beads (G)	5.0—16.0	0.007	250—450	75	0.22	CH_4 through C_4H_{10}, C_2H_4 through C_6H_6, H_2O, H_2S, SO_2
	Beads (S)	6.0		300—450	75	0.25	
Activated alumina	Beads (G)	7.0—18.5	0.006	350—600	50	0.22	H_2O, H_2S
	Beads (S)	4.0— 8.0		350—1000	50	0.25	Oil vapors
Molecular sieves	Pellets	9.0—14.5	/	300—600	/	0.23	See Tables 6-7 6-8, and 6-9
	Beads (G)	32.0	/	300—600	/	0.23	
	Beads (S)	7.5—12.5	/	300—600	/	0.23	

G = Granules
S = Spheroids

Activated carbon and molecular sieves are the most widely used solid adsorbents for the removal of contaminants. Activated carbon has been used extensively for the adsorption of many contaminant gases in a sample stream not only in atmospheric sampling and in laboratory use but also as an industrial adsorbent in continuous flowing adsorption towers. The term "activated" carbon derives from a method of enhancing the adsorption properties of regular carbon. The carbon is "activated" by heating at 900 °C in a reducing atmosphere to increase the porous nature of the carbon, thereby increasing the adsorbency of the carbon. Activated carbon can be made from many substances including soft coal, fruit pits, nut shells, and coconut shells. Coconut shell carbon is the desired form of activated carbon because of its porous nature. Table 6-6 lists the adsorptive capacity of activated carbon for several gases.

Table 6-6. Adsorption of gases by carbon (1 gm of adsorbent, temperature 15°C).

Gas	Volume adsorbed, cm^3
SO_2	380
CH_3Cl	277
NH_3	181
H_2S	99
HCl	72
C_2H_2	49
CO_2	48
CH_4	16
CO	9
O_2	8
N_2	8
H_2	5

Molecular sieves are also widely used as adsorbents because of their porous nature. The molecular sieves are usually made from synthetic zeolite crystals or metal aluminosilicates. The diameter of the pores or passageways of the molecular sieve regulates the size of the molecules that may pass through the sieve. Because of this, molecular sieves have been used extensively in the fractionation of organic gases (hydrocarbons) as packing material in gas chromatographic columns. Various properties of molecular sieves are summarized in Tables 6-7, 6-8, and 6-9.

Table 6-7. Molecular sieve adsorption characteristics.

Adsorbed on 4A and 5A molecular sieve	Adsorbed on 5A but not 4A molecular sieve	Not adsorbed on 5A or 4A molecular sieve
Water CO_2 CO* H_2S SO_2 NH_3 NO_2* O_2* CH_4* Methanol Ethane Ethylene Acetylene Propylene n-Propanol Ethylene oxide	Propane and higher n-paraffins to C_{14} Butene and higher n-olefins n-butanol and higher n-alcohols Cyclopropane Freon 12	Isobutane and all iso-paraffins Isopropanol and all iso-, sec- and tert-alcohols Benzene and all aromatics Cyclohexane and all cyclics with at least 4 numbered rings Carbon tetrachloride Sulfur hexafluoride Hexachlorobutadiene Freon 114 and 11 Boron trifluoride Molecules larger than 5 Å

*Adsorbed below −20°F.

Table 6-8. Molecular sieves—Linde type.

Type	Nominal pore diameter, μm	Molecules adsorbed*	Remarks
3A	0.003	< 3 Å effective diameter (e.g., H_2O, NH_3)	Used for drying and dehydration
4A	0.004	< 4 Å diameter (e.g., H_2S, ethanol, CO_2, SO_2, C_2H_4, and C_3H_6)	Scavenge water from solvents and sat. hydrocarbons (HC)
5A	0.005	< 5 Å diameter (e.g., n-C_4H_9-OH n-C_4H_{10}, C_3H_8 to $C_{22}H_{46}$)	Separates n-paraffins from branched and cyclic HC
10X	0.008	< 8 Å diameter (e.g., iso-paraffin and olefins, C_6H_6)	Separates aromatic HC
13X	0.010	< 10 Å diameter	Drying, H_2S and mercaptan removal (gas sweetening)

*Each type adsorbs listed molecules plus those of preceding types.

Table 6-9. Effective sorption capacities of molecular sieves.

Zeolite	Amount sorbed @ 25°C (g/100g of molecular sieve)		
	H_2O	n-C_6H_{14}	Cyclohexane
4A	24.5	—	—
5A	24.5	12.0	—
B	20.0	—	—
X	31.5	16.8	18.5
Y	28.0	16.5	19.0
Erionite	11.3	4.4	6.7
Offretite	16.6	8.6	5.3
Mordentite	13.3	6.1	7.3

Acid gases in the atmosphere can prove to be interferences for analytical and continuous monitoring techniques. An adsorbent often used for these gases is Ascarite. This strongly basic adsorbent, 91% NaOH, will remove acid gases from the sample stream. Ascarite has also been used extensively for selectively removing carbon dioxide from a gas stream.

Absorption

Absorption is also a means of removing unwanted gases from the sample stream. One absorptive method could be much like the sampling of gases through impingers: the contaminant could be scrubbed from the system using a liquid solution. Solid absorbents are also used. Levaggi et al. (1972) discuss a method of absorbing nitrogen dioxide from a gas stream by using triethanolamine on firebrick. This will selectively absorb nitrogen dioxide while allowing the passage of nitric oxide.

Water Vapor Removal

As mentioned previously, water vapor removal is very important in the preparation of calibration gases using permeation tubes. Water vapor removal is also important when using some catalysts or adsorbents. For example, water vapor must be removed before passing a gas stream over a bed of Hopcalite, because water vapor causes Hopcalite to lose its oxidizing properties. There are many other situations where water vapor must be removed. The three most widely used laboratory and air sampling methods of removing water vapor (drying) from a gas stream are adsorption, absorption, and condensation.

Adsorption

Adsorption of water vapor on solid desiccants is the most common method of drying a gas stream. This is because solid desiccants are readily available, easy to handle and store, can be regenerated, and can be prepared with an indicator material in them that changes color when the desiccant is spent.

The choice of a drying agent should not be based solely on its drying ability. Other factors, such as stability, temperature dependency, ability to perform in high humidity situations, emission of gases through reaction with the moisture, etc., should be taken into account.

The three most widely used drying adsorbents are silica gel, calcium sulfate, and anhydrous magnesium perchlorate. Efficiency and capacities of these and other solid desiccants are listed in Tables 6-10 and 6-11.

Table 6-10. Comparative efficiency of various drying agents.

Material	Volume of air per hr per ml desiccant, ml	Total vol. of air per ml of desiccant, liters	Residual water vapor per liter of air, mg
$CuSO_4$ (anhy.)	36 to 50	0.45 to 0.7	2.8 (2.7-2.9)
$CaCl_2$ (gran.)	66 to 165	6.1 to 24.2	1.5 (1.4-1.6)
$CaCl_2$ (tech. anhy.)	115 to 150	4.0 to 5.8	1.25 (1.23-1.27)
$ZnCl_2$ (sticks)	120 to 335	0.8 to 2.1	0.98 (0.94-1.02)
$Ba(ClO_4)_2$ (anhy.)	26 to 36	2.3 to 3.7	0.82 (0.76-0.88)
NaOH (sticks)	75 to 170	2.3 to 8.9	0.80 (0.78-0.83)
$CaCl_2$ (anhy.)	75 to 240	1.2 to 7.8	0.36 (0.33-0.38)
$Mg(ClO_4)_2 \cdot 3H_2O$	65 to 160	4.0 to 7.2	0.031 (0.028-0.033)
Silica gel	65 to 135	6.5 to 7.7	0.03 (0.02-0.04)
KOH (sticks)	55 to 65	3.2 to 7.2	0.014 (0.010-0.017)
Al_2O_3	65 to 135	6.5 to 7.7	0.005 (0.004-0.009)
$CaSO_4$ (anhy.)	75 to 150	1.2 to 18.5	0.005 (0.004-0.006)
CaO	60 to 90	7.6 to 10.1	0.003 (0.003-0.004)
$Mg(ClO_4)_2$ (anhy.)	95 to 130	6.4 to 13.2	0.002 (0.002-0.003)
BaO	64 to 66	10.6 to 25.0	0.00065 (0.006-0.0008)

Table 6-11. Comparative efficiencies and capacities of various solid desiccants in drying a stream of nitrogen.[a]

Desiccant	Initial composition	Regeneration requirements		Average efficiency[b] (mg/liter)	Relative capacity[c] (liters)
		Drying time (hr)	Temperature (°C)		
Sodium hydroxide[g]	$NaOH \cdot 0.03\ H_2O$	—	—	0.513	178
Anhydrous barium perchlorate	$Ba\ (ClO_4)_2$	16	127	0.599	28
Calcium oxide	CaO	6	500, 900	0.656	51
Magnesium oxide	MgO	6	800	0.753	22
Potassium hydroxide[g]	$KOH \cdot 0.52\ H_2O$	—	—	0.939	18.4
Mekohbite[g]	68.7% NaOH	—	—	1.378	68
Anhydrous magnesium perchlorate[d]	$Mg(ClO_4)_2 \cdot 0.12\ H_2O$	48[e]	245[e]	0.0002	1168
Anhydrone[d, f]	$Mg(ClO_4)_2 \cdot 1.48\ H_2O$	—	240	0.0015	1157
Barium oxide	96.2% BaO	—	1000	0.0028	244
Activated alumina	Al_2O_3	6 to 8	175, 400	0.0029	263
Phosphorus pentoxide[g]	P_2O_5	—	—	0.0035	566
Molecular sieve 5A[f]	Calcium aluminum silicate	—	—	0.0039	215
Indicating anhydrous magnesium perchlorate[d]	88% $Mg\ (ClO_4)_2$ and 0.86% $KMnO_4$	48[e]	240[e]	0.0044	435
Anhydrous lithium perchlorate[g]	$LiClO_4$	12[e], 12	70[e], 110	0.013	267
Anhydrous calcium chloride[j]	$CaCl_2 \cdot 0.18\ H_2O$	16[e]	127[e]	0.067	33
Drierite[f]	$CaSO_4 \cdot 0.02\ H_2O$	1 to 2	200 to 225	0.067	232
Silica gel	—	12	118 to 127	0.070	317
Ascarite[f]	91.0% NaOH	—	—	0.093	44
Calcium chloride[g]	$CaCl_2 \cdot 0.28\ H_2O$	—	200[e]	0.099	57
Anhydrous calcium chloride[g]	$CaCl_2$	16[e]	245[e]	0.137	31
Anhydrocel[f]	$CaSO_4 \cdot 0.21\ H_2O$	1 to 2	200 to 225	0.207	683

[a] Nitrogen at an average flow rate of 225 ml/min was passed through a drying train consisting of three Swartz drying tubes (14 mm i.d. by 150 mm deep) maintained at 25 °C.

[b] The average amount of water remaining in the nitrogen after it was dried to equilibrium.

[c] The average maximum volume of nitrogen dried at the specified efficiency for a given volume of desiccant.

[d] Hygroscopic.

[e] Dried in a vacuum.

[f] Trade name.

[g] Deliquescent.

Silica gel is easy to handle, and it can readily and indefinitely be regenerated at temperatures near 120 °C. Attempting to regenerate silica gel above 260 °C will cause loss of the water vapor extractive properties. More often, a series of adsorbents are used for drying a gas stream. A popular series method for water vapor removal is silica gel followed by molecular sieve. The silica gel, which can be regenerated easily, removes a major portion of the water vapor, then the molecular sieve, which is a more efficient drying agent, removes most of the remaining water vapor.

Calcium sulfate also has excellent regenerative capabilities (1 to 2 hours at 200 °C); however, unlike silica gel, it will gradually lose its drying properties because of the destruction and reformation of the dehydration elements. Calcium sulfate is also able to operate at a constant efficiency over a wide range of temperatures. Drierite® and Anhydrocel® are trade names for commercially available calcium sulfate mixtures, and, as with silica gel, these adsorbents are available in indicating and non-indicating forms. Anhydrous magnesium perchlorate has the best drying efficiency of the compounds named, but it has a certain drawback: explosive compounds may be formed if the regeneration step occurs in the presence of organic vapors. For this reason, hydrocarbons must be removed from the gas stream before regeneration. Anhydrous magnesium perchlorate is also deliquescent; i.e., it will melt when removing moisture from the air.

Absorption

Absorption is another method of drying a gas stream. Absorption, usually with liquid desiccants, is not as efficient as with solid desiccants, but it has a higher drying capacity because the liquid can be constantly recirculating. This process with liquid desiccants takes place in much the same way as in a scrubbing tower: the gas comes into contact with the liquid and the water vapor is absorbed. Strong acids and bases are good liquid desiccants, but they will emit corrosive vapors.

Condensation

Drying gases by condensation (cooling) is an excellent method for some purposes; all that is required is that the gas be cooled below its dew point, thereby removing the water vapor from the gas stream. The process is quite simple; the sample gas enters a vessel and is cooled. When the gas has been cooled below the dew point, the water vapor condenses on the inner walls of the vessel and is removed from the gas stream; e.g., a solution of dry ice and acetone at a temperature of −78.5 °C will remove all but 0.01 mg/liter, and a cooling bath of liquid nitrogen at a temperature of −196 °C will remove all but 1×10^{-23} mg of water vapor/liter of air. Table 6-12 lists various cold bath solutions and their temperatures.

Table 6-12. Summary of cold bath solutions.

Coolant	Temperature, °C
Ice and water[a]	0
Ice and NaCl	-21
Carbon tetrachloride slush[a,b]	-22.9
Chlorobenzene slush[a,b]	-45.2
Chloroform slush[a,b]	-63.5
Dry ice and acetone[a]	-78.5
Dry ice and cellosolve[a]	-78.5
Dry ice and isopropanol[a]	-78.5
Ethyl acetate slush[a,b]	-83.6
Toluene slush[b]	-95
Carbon disulfide slush[a,b]	-111.6
Methyl cyclohexane slush[a,b]	-126.3
n-Pentane slush[b]	-130
Liquid air	-147
Isopentane slush[b]	-160.5
Liquid oxygen	-183
Liquid nitrogen	-196

[a] Adequate for secondary temperature standard.

[b] The slushes may be prepared by placing solvent in a Dewar vessel and adding small increments of liquid nitrogen with rapid stirring until the consistency of a thick milkshake is obtained.

Mechanical refrigeration devices especially designed for water removal are commercially available.

Summary

Molecular sieves and activated carbon are used extensively for removal of gaseous contaminants. These solid adsorbents have a porous quality that gives them an extremely high surface area per unit weight, thus increasing their adsorptive capacities.

There are adsorbents and absorbents that will selectively remove one gas from an air stream and leave the others. These include Hopcalite® for selectively removing CO from an air stream, manganese dioxide for removing ozone from an air stream, Ascarite for removing CO_2 from an air stream, and triethanolamine on firebrick for selectively removing NO_2 from an air or NO_x stream.

For the removal of water vapor, there are basically three methods used: condensation, absorption and adsorption. Condensation is the most efficient means of drying a gas stream, but may be awkward to use. Absorption, using liquid desiccants, has the greatest capacity for drying a gas stream because the liquid can be recirculated continuously. This method, too, may be awkward for field work. Adsorption of water vapor using solid adsorbents is used extensively because of the ease of handling and storage and the advantage of the regenerative properties.

Sample Problems

Problem 1

A sample gas stream containing sulfur dioxide is to be scrubbed with an adsorbent while the sample collection is performed. The SO_2 concentration is known to be approximately 10 ppm (10 $\mu\ell/\ell$). The adsorbent to be used is activated carbon. The sampling rate is 200 ℓ/min to be maintained for 24 hours. How much activated carbon would be needed to remove all of the SO_2 for the entire length of the sampling period?

Solution

The total amount of sampled air can be calculated 200 ℓ/min × 60 min/hour × 24 hours = 288,000 liters.

The total amount of SO_2 that must be scrubbed from the sample is calculated: 288,000 ℓ of air × 10 $\mu\ell$ of SO_2/ℓ of air = 2,880,000 $\mu\ell$ of SO_2 to be removed. For the purposes of this example 1 mℓ = 1 cm^3 (this will actually add very little error). $2.88 \times 10^6\ \mu\ell\ SO_2 \times 10^{-3}\ m\ell/\mu\ell \times 1\ cm^3/m\ell = 2880\ cm^3$ of SO_2 to be removed.

From Table 6-6, activated carbon will adsorb 380 cm^3 of SO_2 per gram of adsorbent (assuming adsorption takes place at 15 °C).

The total carbon that is necessary can be calculated:

$$\frac{2880\ cm^3\ SO_2}{380\ cm^3\ SO_2/1\ g\ carbon} = 7.6\ g\ carbon.$$

7.6 grams of carbon would be needed to effectively remove the SO_2 from the gas sample. This is an approximate amount.

Problem 2

A sample stream contains approximately 2% (by weight) water vapor, which must be removed. Molecular sieve Type 4A has been chosen as the drying agent. Sampling is to be performed at 2.5 ℓ/min for 8 hours. How much 4A molecular sieve is needed to dry the air for the length of the sample period? (Assume adsorption takes place at 25 °C.)

Solution

The total amount of air sampled:
2.5 ℓ/min × 60 min/hour × 8 hours = 1200 liters.
The density of air at 25 °C and 1 atm is 1.1844 mg/mℓ.
The weight of the air sampled:
= 1200 liters × 1000 mℓ/ℓ × 1.1844 mg/mℓ = 1,421,300 mg of air sampled.
The weight of water vapor to be removed:
1,421,300 mg × 0.001 g/mg × 0.02 = 28.43 g.
From Table 6-9, 4A molecular sieves will remove 24.5 g of H_2O per 100 g of sieve. The amount of sieve necessary to fully dry the air stream (this is an approximate value):

$$\frac{28.43\ g\ H_2O}{24.5\ g\ H_2O/100\ g\ sieve} = 116\ g\ \text{of molecular sieve Type 4A.}$$

Summary

Standard test atmospheres are very important as calibration sources for atmospheric monitors. The bag-filling method is best suited for "batch" calibration purposes where only a small amount of calibrated gas is needed at one time. For example, a series of known CO concentrations can be made very quickly with this technique. The cylinder method, permeation tube method, and ozone generators are best used where a constant flow of calibration gas is needed. Some continuous atmospheric monitors and all manual sampling trains require this type of calibration technique because of the finite time required to obtain an adequate sample.

References

American Public Health Association. 1972. *Methods of air sampling and analysis*. Intersociety Committee, American Public Health Association, New York.

Bowman, L. D., and Horak, R. F. 1972. *A continuous ultraviolet absorption ozone photometer*, pp. 102-108. Dasibi Corporation, ISA AID 72430.

Bryan, R. J., and Cherniak, I. 1964. *A comparison study of various types of ozone and oxidant detectors which are used for atmospheric air sampling*. Presented at the 57th Annual Meeting of the Air Pollution Control Association, June 1964, at Houston, TX.

Hersh, C. K. 1961. *Molecular sieves*. New York: Reinhold Publishing Co.

Hesketh, H. E. 1972. *Understanding and controlling air pollution*. Ann Arbor, MI: Ann Arbor Science Publishers.

Hughs, E. E., et al. 1977. Performance of a nitrogen dioxide permeation device. *Anal. Chem*. 49:1823.

Jorgenson, R., ed. 1970. *Fan engineering*. Buffalo, NY: Buffalo Forge Company.

Landolt, G. R. 1971. Method for rapid determination of adsorption properties of molecular sieves. *Anal. Chem*. 43:613-615.

Levaggi, D. A.; Siu, W.; Feldstein, M.; and Kothny, L. 1972. Quantitative separation of nitric oxide from nitrogen dioxide at atmospheric concentration ranges. *Environ. Sci. Tech*. 6:250.

Mantell, C. L. 1951. *Adsorption*. New York: McGraw-Hill Book Company.

Mueller, P. K., et al. 1973. *A Guide for the Evaluation of Atmospheric Analyzers*. Calif. Dept. of Health, Air and Industrial Hygiene Laboratory, for EPA under Contract 68-02-0214.

Nelson, G. O. 1972. *Controlled test atmospheres*. Ann Arbor, MI: Ann Arbor Science Publishers, Inc.

Pittsburgh Activated Carbon Co. Basic concepts of adsorption on activated carbon. Pittsburgh, PA.

Polasek, J. C., and Bullin, J. A. 1978. Evaluation of bag sequential bag sampling technique for ambient air analysis. *Environ. Sci. Tech*. 12:709.

Purdue, L. J., and Thompson, R. J. 1972. A rapid, sensitive method for calibration of permeation devices. *Anal. Chem*. 44:6.

Saltzman, B. E.; Burg, W. R.; and Ramaswamy, G. 1971. Performance of permeation tubes as standard gases. *Environ. Sci. Tech.* 5:1121.

Scaringelli, F. P.; O'Keeffe, A. E.; Rosenberg, E.; and Bell, J. P. 1970. Preparation of known concentrations of gases and vapors with permeation devices calibrated gravimetrically. *Anal. Chem.* 42:871.

Scaringelli, F. P.; Rosenberg, E.; and Rehme, K. A. 1970. Comparison of permeation devices and nitrite ion as standards for the colorimetric determination of nitrogen dioxide. *Environ. Sci. Tech.* 4:924.

Sheeny, J. P.; Achinger, W. C.; and Simon, R. A. 1968. *Handbook of air pollution*. Public Health Service Publication, No. 999-AP-44.

Smith, G. F. *Dehydration using anhydrous magnesium perchlorate*. Columbus, OH: G. Frederick Smith Chemical Co.

Stern, A. C. 1968. *Air pollution*. Vol. II. New York: Academic Press.

Treybal, R. E. 1968. *Mass-transfer operations*. New York: McGraw-Hill Book Company.

Mine Safety Appliance Corp. (MSA). Bulletin No. 0102-2.

Section B-3

Introduction to the Reference Methods and Reference Measurement Principles for the Criteria Pollutants, Continuous Air Quality Monitors, and Design of Air Quality Monitoring Networks

Reading Assignment

Pages 7-1 through 9-11 of EPA 450/2-80-004 *APTI Course 435 Atmospheric Sampling: Student Manual.*

Reading Assignment Topics

- Reference Methods and Reference Measurement Principles for the Criteria Pollutants
- Continuous Air Quality Monitors
- Design of Air Quality Monitoring Networks

Learning Goal and Objectives

Learning Goal

The purpose of this section is to familiarize you with the reference methods and reference measurement principles for the criteria pollutants, continuous air quality monitors, and the design of air quality monitoring networks.

Learning Objectives

At the end of this section, you should be able to

1. locate the National Ambient Air Quality Standards (NAAQS), descriptions of the reference methods and reference measurement principles, and designation requirements for reference and equivalent methods in the *Code of Federal Regulations*.
2. identify the four general types of reference and equivalent methods.
3. describe requirements for the designation of automated reference methods and manual and automated equivalent methods.
4. identify the reference method or reference measurement principle for each criteria pollutant.
5. identify advantages of using continuous instrumental methods for monitoring ambient air quality.
6. identify advantages and disadvantages of coulometric, amperometric, second derivative spectroscopic, flame photometric, fluorescence, chemiluminescence, ultraviolet photometric, and nondispersive infrared air quality monitors.
7. identify two major subsystems of an air quality monitoring network.
8. identify major considerations in designing an air quality monitoring network.
9. associate typical spatial scales of representativeness with their corresponding linear dimensions.
10. identify and define network design considerations unique to particulate monitoring.

Reading Guidance

1. Three correspondence courses concerning the siting of ambient air quality monitors, *APTI Course 432: Site Selection for the Monitoring of SO_2 in Ambient Air, APTI Course 433: Network Design and Site Selection for Monitoring $PM_{2.5}$ and PM_{10} in Ambient Air, and APTI Course 437: Site Selection for the Monitoring of CO and Photochemical Pollutants in Ambient Air* have been prepared for EPA. If you would like information concerning these courses, contact EPA's Air Pollution Training Institute at the address or phone number given in the Course Introduction section of this guidebook.
2. Refer often to the equations and figures of the assigned reading material as you progress through the assignment.
3. When you have finished the reading assignment, complete the review exercise for Section B-3. It begins on the following page. After you have answered the review exercise questions, check your answers. The correct answers are listed on the page immediately following the review exercise.
4. For any review exercise questions that you answered incorrectly, review the page(s) of the reading assignment indicated on the answers page.
5. After you have reviewed your incorrect answers (if any) take the final examination for the course. Follow the directions listed in the Course Introduction section of this guidebook.
6. Your course grade results will be mailed to you.

Review Exercise

Now that you've completed the assignment for Section B-3, please answer the following questions. These will help you determine whether or not you are mastering the material.

For each of questions 1 through 3, match the item with its location in the *Code of Federal Regulations.*

Item	Location
1. National Ambient Air Quality Standards (NAAQS) ___	a. Title 40 Part 53
	b. Title 40 Part 50
	c. Appendices of Title 40 Part 50
2. descriptions of the reference methods and reference measurement principles for monitoring pollutants having NAAQS ___	
3. designation requirements for reference and equivalent methods ___	

4. Which of the following is a(are) general type(s) of reference methods?

   a. manual method
   b. automated method
   c. both a and b, above
   d. none of the above

5. Which of the following is(are) necessary for the designation of an automated equivalent method?

   a. Performance specifications for automated methods must be met.
   b. A measurement principle different from the reference measurement principle must be used.
   c. both a and b, above
   d. none of the above

For each of questions 6 through 12, match the pollutant with the description of its reference method or reference measurement principle.

Pollutant

6. sulfur dioxide ___
7. nitrogen dioxide ___
8. carbon monoxide ___
9. lead ___
10. $PM_{2.5}$ ___
11. PM_{10} ___
12. ozone ___

Description

a. pararosaniline method
b. chemiluminescence with ozone
c. chemiluminescence with ethylene
d. low-volume sampling method
e. high-volume sampler, atomic absorption spectrophotometric analysis
f. nondispersive infrared spectrometry
g. high-volume sampling method

13. Which of the following is a(are) potential problem(s) when using the lead reference method?

    a. nonuniform distributions of lead on high-volume sampler filters when sampling near heavily traveled roadways
    b. chemical and light scattering interferences during lead analysis
    c. both a and b, above
    d. none of the above

14. Which of the following is an(are) advantage(s) of using continuous instrumental methods for monitoring ambient air quality?

    a. real-time data output
    b. in-situ measurements
    c. ability to transmit data directly into computer systems
    d. all of the above

For each of questions 15 through 22, match the instrumental method with its description.

Method

15. nondispersive infrared ___
16. coulometric ___
17. flame photometric ___
18. fluorescence ___
19. amperometric ___
20. second derivative spectroscopic ___
21. chemiluminescence ___
22. ultraviolet photometric ___

Description

a. uses an electrical charge generated by oxidation-reduction reactions occurring in an electrolytic cell to measure gaseous pollutant concentration

b. uses the light emitted due to the excitation of a gaseous pollutant with ultraviolet-visible light

c. relates the slope and curvature characteristics of energy absorption bands to gaseous pollutant concentration

d. uses the energy emitted by a pollutant in a hydrogen-rich flame to measure the pollutant's concentration

e. uses the energy emitted due to electronic transitions to measure pollutant concentration

f. uses the light emitted due to the reaction of a gaseous pollutant with a reagent gas to measure the pollutant's concentration

g. uses the absorption of energy due to electronic transitions to measure pollutant concentration

h. uses the absorption of infrared energy to measure pollutant concentration

For each of questions 23 through 26. match the instrumental method with its advantage(s).

Method		Advantages
23. flame photometric ___	a.	highly specific for pollutant monitored, no support gases are needed for its operation
24. coulometric/amperometric ___	b.	no support gases are needed for its operation
25. second derivative spectroscopic ___	c.	no support gases are needed for its operation, relatively insensitive to temperature and sample air flow variations
26. fluorescence ___	d.	highly specific for sulfur compounds, no chemical solutions are needed for its operation, low maintenance requirements, high sensitivity for sulfur compounds, fast response

For each of questions 27 through 30, match the instrumental method with its disadvantage(s).

Method		Disadvantages
27. fluorescence ___	a.	must use a scrubber to remove sample air components that react with halogens
28. second derivative spectroscopic ___	b.	complexity of measurement principle
29. flame photometric ___	c.	if monitoring for a specific sulfur compound, must use a scrubber to remove other sulfur compounds from the sample air; potential carbon dioxide interference; must use hydrogen
30. coulometric/amperometric ___	d.	must use a scrubber to remove hydrocarbons from the sample air

31. In the $PM_{2.5}$ reference method, an electrically powered air sampler draws air at a constant _____ flow rate into a specially shaped inlet and through a(n) _____ particle size separator (impactor) where the suspended particulate matter in the $PM_{2.5}$ range is separated for collection on a _____ filter over the specified sampling period.

    a. volumetric / inertial / cellulose
    b. volumetric / cyclonic / glass fiber
    c. volumetric / inertial / PTFE
    d. volumetric / cyclonic / PTFE

32. True or False? Sampling flow rate is <u>NOT</u> a potential source of error with the PM_{10} reference method.

    a. True
    b. False

33. Which of the following is a(are) major subsystem(s) of a data system?

a. data recording and transmission system
b. data processing system
c. both a and b, above
d. none of the above

34. True or False? Before designing an air quality monitoring network, the uses of the data that will be generated by the network should be established.

a. True
b. False

For each of questions 35 through 39, match the spatial scale of representativeness with its corresponding dimension.

Scale

35. microscale ___

36. middle scale ___

37. neighborhood scale ___

38. urban scale ___

39. regional scale ___

Dimension

a. 100 meters to 0.5 kilometer
b. greater than 50 kilometers
c. less than 100 meters
d. 4 to 50 kilometers
e. 0.5 to 4 kilometers

40. Which of the following should be considered when determining what pollutants to monitor?

a. pollutants having air quality standards
b. pollutants suspected of being hazardous to public health/welfare
c. both a and b, above
d. none of the above

41. True or False? Most of the EPA ambient air monitoring regulations are found in Title 40 Part 58 of the *Code of Federal Regulations.*

a. True
b. False

42. True or False? When designing a data transmission system, the speed with which the data will be used should be determined.

a. True
b. False

43. Which of the following is a(are) component(s) of a data processing system?

a. data format
b. data validation
c. data analysis
d. all of the above

44. True or False? A data format is a systematic listing of the data recorded.

a. True
b. False

45. True or False? Data validation should be performed by an independent operator not intimately familiar with the network in question.

a. True
b. False

46. Which of the following is <u>NOT</u> a basic type of monitoring station?

a. SLAMS
b. WAMS
c. NAMS
d. IMPROVE

47. MPA boundaries may consist of aggregates of

a. counties.
b. census blocks.
c. established air quality management districts.
d. all of the above

48. True or False? A community monitoring zone is designed to represent the total $PM_{2.5}$ measurement for that population area.

a. True
b. False

49. $PM_{2.5}$ monitors are intended to represent

a. maximum concentrations.
b. minimum concentrations.
c. "hot spots."
d. all of the above

50. Which of the following should be considered as a siting consideration when placing $PM_{2.5}$ monitors?

a. exposure to large buildings or nearby trees
b. distance from nearby emitters
c. proximity to other measurements
d. all of the above

Section B-3

Review Exercise Answers

	Page(s) of *Atmospheric Sampling: Student Manual*
1. b	7-1
2. c	7-1
3. a	7-1
4. c	7-1
5. c	7-1
6. a	7-2
7. b	7-2
8. f	7-2
9. e	7-2
10. d	7-2
11. g	7-2
12. c	7-2
13. c	7-2
14. d	8-1
15. h	8-14 through 8-20
16. a	8-21 through 8-24
17. d	8-2 through 8-4
18. b	8-4 through 8-6
19. g	8-21 through 8-24
20. c	8-12 through 8-14
21. f	8-7 through 8-9
22. e	8-10 through 8-11
23. d	8-2 through 8-4
24. b	8-21 through 8-24
25. a	8-12 through 8-14
26. c	8-4 through 8-6
27. d	8-4 through 8-6
28. b	8-12 through 8-14
29. c	8-2 through 8-4
30. a	8-21 through 8-24
31. c	7-3
32. b	7-4
33. c	9-7, 9-8
34. a	9-1, 9-2
35. c	9-3
36. a	9-3
37. e	9-3
38. d	9-3
39. b	9-3
40. c	9-3
41. a	7-1
42. a	9-7
43. d	9-7
44. a	9-7
45. b	9-8
46. b	9-4, 9-5
47. d	9-9
48. b	9-9, 9-10
49. a	9-9
50. d	9-10

* ERRATA *

Requirements for Successful Completion of Course CC:434

In order to receive 5.0 Continuing Education Units (CEU's) and a certificate of course completion you must:

- * complete and submit a final exam to the APTI
- * achieve a final course grade of at least 70%.

The quizzes associated with the course are for review purposes. The answers are enclosed for the student to use to correct his or her own quizzes. This way the student can assses his/her understanding of the material before taking the final exam. Do not send in the answer sheets to the quizzes to be graded. The final exam counts for 100% of the course grade.

If you have questions please contact:

Registrar
Air Pollution Training Institute
US EPA MD-17
Research Triangle Park, NC 27711

Required Readings

Chapter 7

Standard Methods for Criteria Pollutants

Introduction

To protect the public health from harmful air pollution, the 1970 Amendments to the Clean Air Act (CAA) authorized the US Environmental Protection Agency (EPA) to specify national ambient air quality standards (NAAQS). The NAAQS regulate ambient concentrations of criteria pollutants as outlined in "National Primary and Secondary Ambient Air Quality Standards," Part 50 of Chapter 40 of the *Code of Federal Regulations* (40 CFR 50). States may choose to adopt either the NAAQS or more stringent standards.

To demonstrate compliance with the NAAQS, a network of national air monitoring stations (NAMS), State and local air monitoring stations (SLAMS), and prevention of significant deterioration (PSD) monitoring stations are operated nationwide. These stations test the ambient air and report the results to EPA. To ensure nationwide uniformity of these results, EPA established reference test methods for use in this network of stations. These methods are detailed in the appendices to 40 CFR 50.

Reference Method and Equivalent Method

A reference method uses a measurement principle specified in one of the appendices to 40 CFR 50. An equivalent method is a method which uses a different measurement principle, but which achieves a high degree of correlation to the reference method.

The responsibility for reviewing applications, designating reference and equivalent methods, and approving modifications resides with the Reference and Equivalent Methods (R&E) Program. Currently, this Program is part of the EPA's Office of Research and Development of the National Exposure Research Laboratory (NERL).

Reference and equivalent methods designated by the R&E Program may be either manual or automated. If a manual method is to be considered for equivalent designation, it must demonstrate a consistent relationship to the reference method when both methods are used to measure pollutant concentrations in a real atmosphere.

The distinction between automated reference and equivalent methods is based on the *measurement principle* that an instrument employs. For example, the reference measurement principle for automated methods for the detection of the oxides of nitrogen is based on the chemiluminescent reaction of nitric oxide with ozone. Any instrument, therefore, which meets the performance specification for automated methods and uses a chemiluminescent reaction of nitric oxide with ozone for detection is a reference method. Instruments using other measurement principles would be designated equivalent methods, provided they meet the performance specifications. The exception is $PM_{2.5}$ methods, where certain parts of the sampling device must be identical to the Federal specifications in form and function, as well as performance.

This section is designed to provide a brief overview of the reference methods as they are described in the *Code of Federal Regulations,* and discuss potential problem areas and some quality assurance considerations from a practical standpoint. With the exception of sulfur dioxide (see below), equivalent methods are not discussed in detail in this section.

Criteria Pollutants and Measurement Methods

The United States has established National Ambient Air Quality Standards (NAAQS) for six pollutants. These standards have been promulgated by the US Environmental Protection Agency (EPA) to protect public health and welfare.

There are two types of NAAQS: primary and secondary. Primary standards are designed to protect public health, while secondary standards protect public welfare, including effects of air pollution on vegetation, materials, and visibility. These pollutants and standards are listed in Table 7-1.

Table 7-1. National ambient air quality standards.

Pollutant	**Type of standard**	**Averaging time**	**Frequency Parameter**	**Concentration**		**Reference method/principle**
				μg/m³	**ppm**	
Carbon monoxide (CO)	Primary and secondary	1 hr 8 hr	Maximum[a] Maximum[a]	40,000 10,000	35 9	Nondispersive infrared photometry
Nitrogen dioxide (NO_2)	Primary and secondary	1 yr	Arithmetic mean	100	0.053	Gas-phase chemiluminescence
Ozone (O_2)	Primary and secondary	8 hr	Daily maximum[c]	—	0.08	Gas-phase chemiluminescence with ethylene
Particulate matter – $PM_{2.5}$	Primary	24 hr	Maximum[a]	65	—	Low-volume sampling method
	Secondary	1 yr	Three year annual average	15	—	
– PM_{10}	Primary	24 hr	Maximum	150	—	High-volume sampling method
	Secondary	1 yr	Three year annual average	50	—	
Sulfur dioxide (SO_2)	Primary	24 hr 1 yr	Maximum[a] Annual geometric mean	365 80	0.14 0.03	Pararosaniline Method
	Secondary	3 hr	Maximum[a]	1,300	0.5	
Lead	Primary and Secondary	Qtr	Arithmetic mean	1.5	—	High-volume sampling with atomic absorption analysis

[a] Not to be exceeded more than once per year.

[b] As a guide to be used in assessing implementation plans for achieving the annual maximum 24-hour standard.

[c] The expected number of days exceeding the standard should not exceed one per year averaged over the previous three-year period.

The national monitoring networks used to determine compliance with these NAAQS must use methods approved through the R&E Program. Following is a brief discussion regarding each of these pollutants and its associated reference method.

Particulate Matter

$PM_{2.5}$

The reference method for $PM_{2.5}$ provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 µm in ambient air. The method requires sampling over a 24-hour period for purposes of determining whether the primary and secondary NAAQS are met.

An electrically powered air sampler draws ambient air at a constant volumetric flow rate into a specially shaped inlet and through an inertial particle size separator (impactor) where the suspended particulate matter in the $PM_{2.5}$ range is separated for collection on a polytetrafluoroethylene (PTFE) filter over the specified sampling period.

Each filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net gain due to collected $PM_{2.5}$. The total volume of air sampled is determined by the sampler from the measured flow rate (at actual ambient temperature and pressure) and the sampling time. The mass concentration of $PM_{2.5}$ in the ambient air is computed as the total mass of collected particles in the $PM_{2.5}$ size range divided by the actual volume of air sampled, and is expressed in micrograms per cubic meter of air ($\mu g/m^3$).

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, and timing errors. These problems are discussed more fully in Chapter 4, Particulate Matter Sampling.

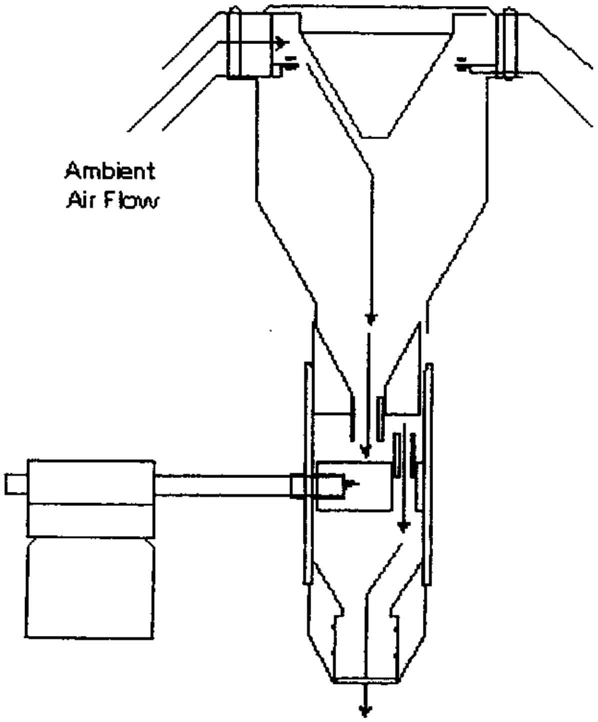


Figure 7-1. Schematic image of $PM_{2.5}$ sampler.

PM_{10}

The reference method for PM_{10} provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 10 micrometers in ambient air. The method requires sampling over a 24-hour period for purposes of determining whether the primary and secondary NAAQS are met.

An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM_{10} size range. Each size fraction in the PM_{10} size range is then collected on a separate filter over the specified sampling period.

Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM_{10}. The total volume of air sampled, corrected to EPA reference conditions (25°C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of collected particles in the PM_{10} size range divided by the total volume of air sampled, and is expressed in micrograms per standard cubic meter ($\mu g/std\ m^3$).

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, and timing errors. These problems are discussed more fully in Chapter 4, Particulate Matter Sampling.

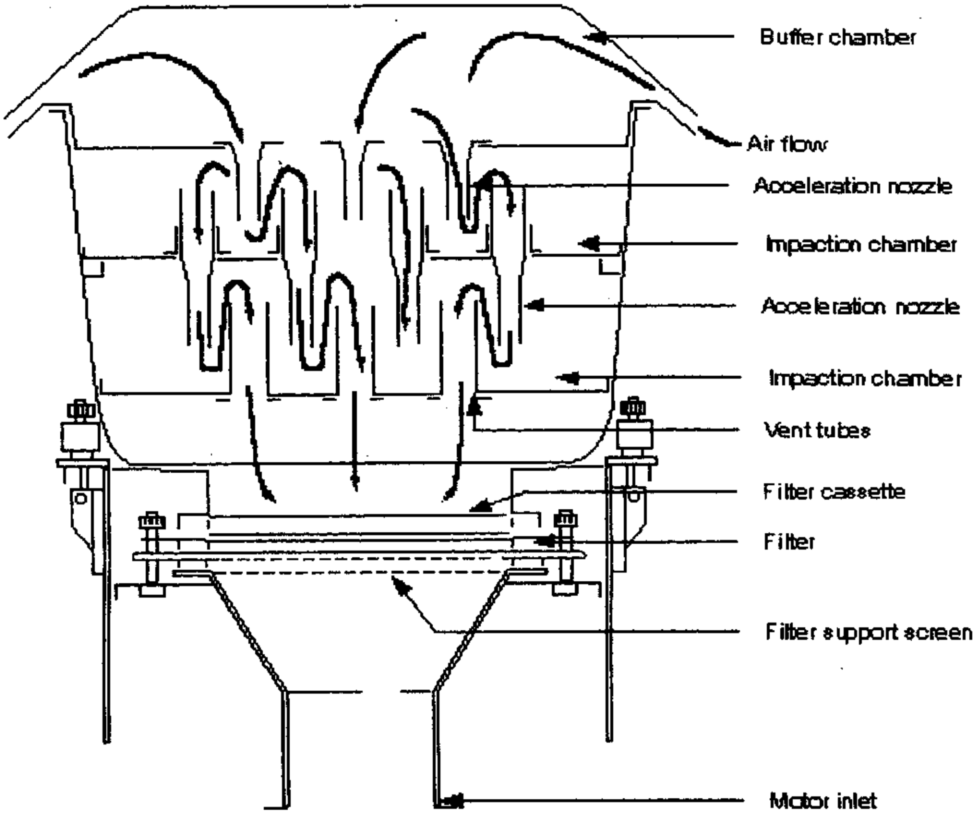


Figure 7-2. Schematic of PM_{10} sampler.

Ozone

The reference measurement principle for the measurement of ozone is the gas-phase chemiluminescence resulting from the reaction of ozone with ethylene. Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with ethylene to emit light, which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

The unstable nature of ozone requires that ozone be generated *in situ* in order to calibrate ozone monitors. Ultraviolet (UV) photometry has been designated as the calibration procedure. A schematic of a typical UV photometric calibration system is shown in Figure 7-3.

Most ozone monitoring locations now use the equivalent method, which is an ultraviolet method.

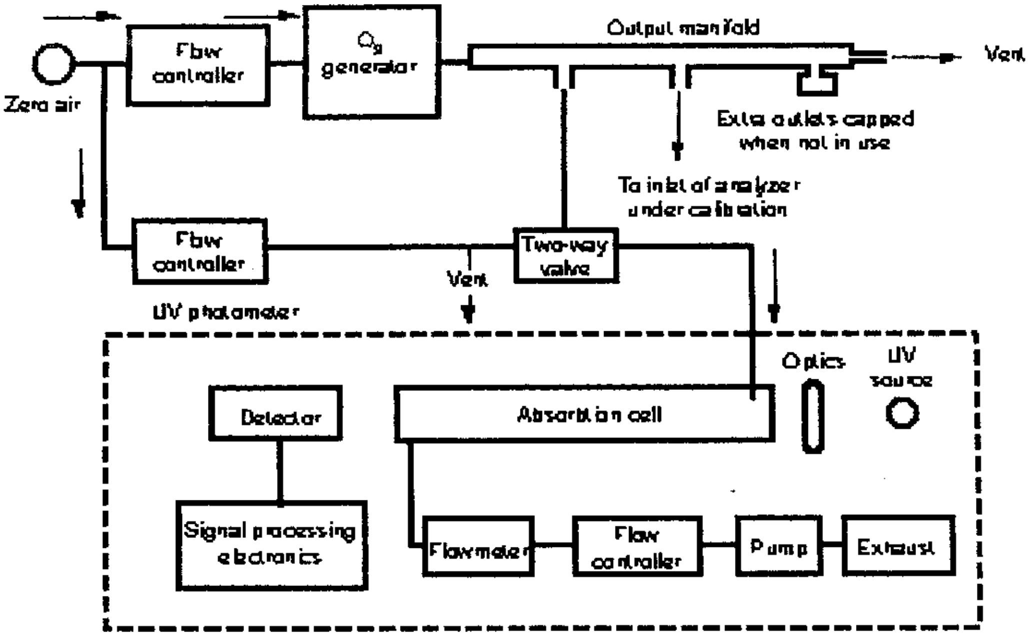


Figure 7-3. Schematic diagram of a typical photometric calibration system.

Carbon Monoxide

The reference measurement principle used to measure ambient levels of carbon monoxide is nondispersive infrared (NDIR) photometry. A complete discussion of the operations of NDIR photometers is contained in Chapter 8. In brief, a signal is produced as a result of the infrared absorption of carbon monoxide which can be related to the absolute CO concentration by calibrating the photometer as specified in Appendix C of 40 CFR 50.

The problem areas associated with this method are the broad band absorption of carbon dioxide and water vapor. These two compounds' absorption results in an interference. The techniques of "negative filtering" or gas filter correlation (discussed in detail in Chapter 8) alleviate these problems.

Nitrogen Dioxide

The reference measurement principle for the determination of nitrogen dioxide is the gas-phase chemiluminescence reaction of nitric oxide with ozone (Eq. 7-1). A more complete discussion of chemiluminescence will be given in Chapter 8.

(Eq. 7-1) $NO + O_3 \rightarrow NO_2 + O_2 + h\nu$ *(light)*

Nitrogen dioxide is measured indirectly by measuring total oxides of nitrogen ($NO_x = NO_2 + NO$) and electronically subtracting the nitric oxide concentration, yielding a nitrogen dioxide determination. A measure of the total oxides of nitrogen is obtained by passing the sample across a catalytic converter, which reduces nitrogen dioxide to nitric oxide (Eq. 7-2).

(Eq. 7-2) $NO_2 + \text{catalytic converter} \rightarrow NO + O$

The calibration of the NO and NO_x channels of the instrument is accomplished by diluting a pressurized tank of NO. The calibration of the NO_2 channel is accomplished with a permeation device or the gas-phase titration of an NO standard gas with ozone. The gas-phase titration involves the following reaction (Eq. 7-3).

(Eq. 7-3) $NO + O_3 \rightarrow NO_2 + O_2$

This produces a known amount of nitrogen dioxide which allows one to calibrate the NO_2 channel of the monitor. The other calibration procedure specified in Appendix F, 40 CFR 50, uses a dynamic dilution system in combination with a permeation device to produce a known amount of NO_2. The use of permeation devices and dynamic calibration procedures is discussed in Chapter 6 of this manual.

The problem areas associated with this method are interferences such as peroxyacetyl nitrate and other nitrogen-containing compounds. In periods of high photochemical activity, corrections for these interferences may be necessary. A smog chamber study (Joshi and Bufalini 1978) indicated that the presence of high levels of halocarbons gave a positive interference in a reference method NO_2 analyzer.

The chemical composition of the atmosphere plays an important role in determining the validity of the nitrogen dioxide measurements obtained using a reference method analyzer. For most ambient air measurements, however, interferences such as the ones mentioned previously are minimal. The frequency of calibration and other maintenance (e.g., replacement of charcoal ozone filter, check of converter efficiency, etc.) are important quality assurance considerations.

Sulfur Dioxide

The reference method for the measurement of Sulfur dioxide in ambient air is a manual wet-chemical method—the pararosaniline method. Sulfur dioxide is bubbled through a solution of potassium tetrachloromercurate (TCM) which forms a monochlorosulfonatomercurate complex. This complex forms an intensely colored solution upon addition of pararosaniline dye and formaldehyde. The concentration of sulfur dioxide can be determined spectrophotometrically by measuring the absorbance of the colored solution.

The potential problems associated with interferences are minimized by the procedures listed in Table 7-2.

Table 7-2. Parasaniline interferences.

Interference	Corrective procedure
Ozone	Time delay
Heavy metals	Addition of EDTA and phosphoric acid
Oxides of nitrogen	Addition of sulfamic acid

Other precautions to be considered relate to the sampling train (Figure 7-4) and to sampling conditions. The inner diameter of the tip of the impinger stem should be checked to make sure that a No. 79 jeweler's drill bit will pass through, but a No. 78 jeweler's drill bit will not. The temperature instability of the monochlorosulfonatomercurate complex during sampling also poses potential problems. This is minimized by using a temperature control device to maintain a temperature of 15° ± 10°C during sampling. Collected samples must be kept at a temperature of 5° ± 5°C. Since this method involves a laboratory analysis of the sample after collection in the field, care should be taken in handling the sample once it has been collected to avoid contamination.

[NOTE: Most current monitoring sites do not use this reference method for sulfur dioxide sampling. The majority of sulfur dioxide monitoring sites utilize a continuous equivalent method.]

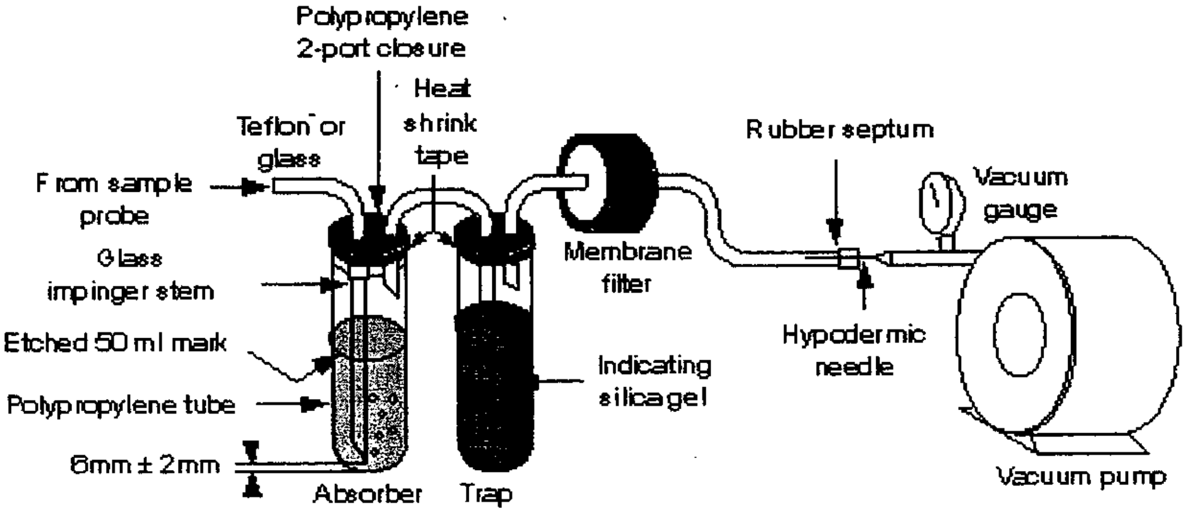


Figure 7-4. SO_2 sampling train for 24-hour sampling.

Lead

The reference method for lead consists of measuring the lead content of particulate matter collected by the total suspended particulate reference method's high-volume sampling procedure as described below. After sample collection, lead is acid-extracted from the particulate matter of a ¾ in. x 8 in. strip of the high-volume filter. Finally, the lead content of the resulting solution is determined by atomic absorption spectrometry.

In the high-volume method, air is drawn through a filter composed of glass fibers or other relatively inert, nonhygroscopic material, and the amount of particulate matter collected is determined gravimetrically. A flow rate measurement device for the sampler is calibrated against actual air flow with a flow rate transfer standard, which is first calibrated against a positive displacement standard volume meter.

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, timing errors, recirculation of sampler exhaust, and the wind direction sensitivity of the sampler.

Potential problems exist in the analysis portion of the method as well. In addition to the sampling problems associated with the high-volume method, lead is nonuniformly distributed across the filter when sampling near heavily traveled roadways. The problem can be alleviated by analyzing a larger portion of the filter. Chemical and light-scattering interferences may be encountered during the atomic absorption spectrophotometric analysis. Chemical interferences can be overcome using the method of standard additions. Light-scattering interferences can be corrected using a dual-channel atomic absorption spectrophotometer equipped with a continuum light source, by using a nonabsorbing wavelength that is near the lead analytical wavelength, or by using a chelating agent to chemically isolate potential interferences during the analysis so that they do not interfere. Furthermore, for accurate particulate lead analyses, it is necessary that the variation of lead content from filter to filter within a given batch of blank filters be small.

References

The Clean Air Act.

U.S. Environmental Protection Agency. 40 CFR Pt. 50, Appendix A (July 1, 1997).

U.S. Environmental Protection Agency. 40 CFR Pt. 53.

U.S. Environmental Protection Agency. 42 Fed. Reg. 1271-1289 (December 14, 1977).

U.S. Environmental Protection Agency. 43 Fed. Reg., no. 194, pp. 46258-46261 (October 5, 1978).

U.S. Environmental Protection Agency. 40 CFR Pt. 58.

U.S. Environmental Protection Agency. *Quality Assurance Handbook for Air Pollution Measurement Systems.* (EPA 454/R-98-004).

Ambient Monitoring Technology Information Center. http://www.epa.gov/ttn/amtic

Chapter 8

Continuous Air Monitoring Instrumentation

Introduction

Instrumental (automated, continuous) methods are assuming an increasingly prominent role in monitoring gaseous pollutants in air. The advantages of instrumental methods, together with advances in the associated technology, have made many manual, older wet-chemical methods largely obsolete. Real-time data output, greater sensitivity in meeting the requirements of specific applications, *in-situ* measurement, and the ability to transmit data directly into computer systems represent major advantages of instrumental methods over manual methods.

The methods that are used for the measurement of oxides of nitrogen exemplify the advantages of an instrumental method. The wet-chemical methods involve analyzing a grab sample (phenoldisulfonic acid method) for source samples and a 24-hour sample (TGS-ANSA or Sodium Arsenite method) for ambient samples. These methods, while reliable and relatively inexpensive, require considerable sample handling and lack real-time data output. The development of a continuous instrumental method that measures the chemiluminescence produced by the reaction of nitric oxide with ozone has provided a reliable real-time method for the measurement of oxides of nitrogen. This method has been applied to both source and ambient *in-situ* monitoring.

Optical techniques that measure chemiluminescence and other spectroscopic properties of molecules provide the basis for many continuous air monitoring instruments. These instruments utilize characteristics of a gaseous pollutant that are relatively specific for the pollutant. The absorption of ultraviolet light by ozone and absorption of infrared light by carbon monoxide are examples of the spectroscopic properties measured in instrumental methods. The ability of a particular pollutant to oxidize halogens is also used in continuous monitors. This section deals with the advantages, disadvantages, principles of operation, and current applications of several of the many instruments using physical and chemical properties of air pollutants.

Flame Photometric Instruments

Principles of Operation

Instruments using flame photometric detection measure the emission intensity at a selected wavelength while the pollutant is introduced into a hydrogen-rich flame. Figure 8-1 illustrates the principal components of a flame photometric detector (FPD).

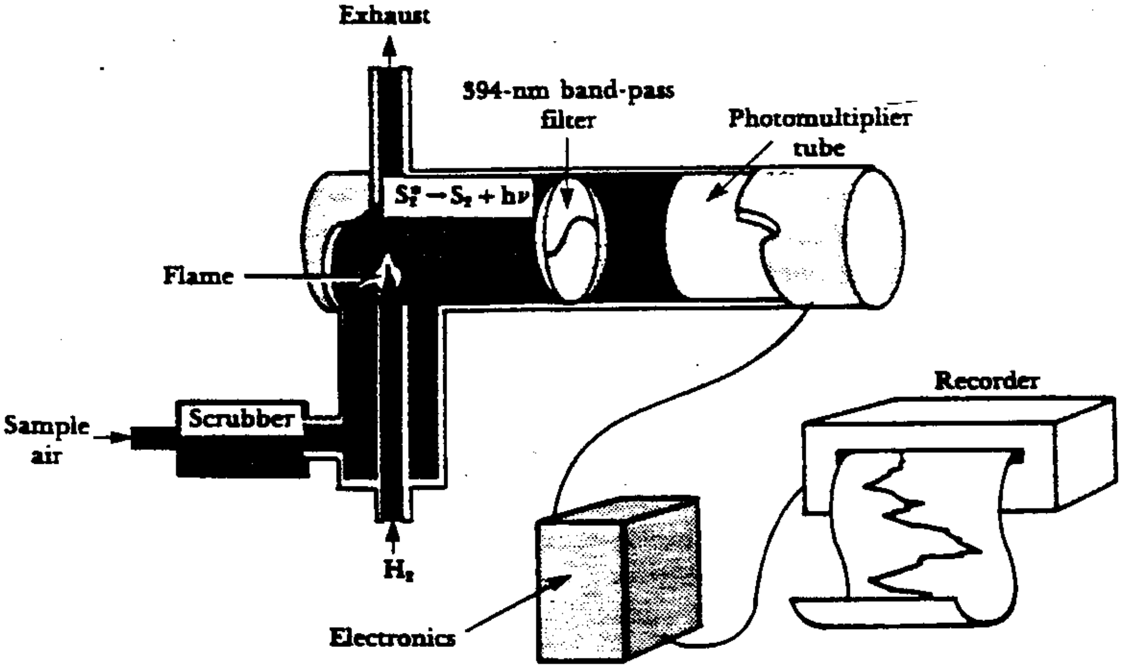


Figure 8-1. Flame photometric detector.

The sample gas containing sulfur pollutants is introduced into the hydrogen-rich flame, producing an S_2 species that reacts with the available hydrogen and hydroxyl radicals to produce a high-energy species S_2^*. The principal reactions involved in the formation of the high-energy S_2^* from the sulfur-containing pollutant are discussed in an excellent review by Farwell et al. (1976). They are briefly summarized in Equations 8-1 through 8-8.

(Eq. 8-1) $\text{Sulfur compound} \xrightarrow{heat} S \text{ atoms or indirectly by}$

(Eq. 8-2) $\text{Sulfur compound} \xrightarrow{heat} H_2S$

(Eq. 8-3) $H_2S + \cdot H \rightarrow HS + H_2$

(Eq. 8-4) $HS + \cdot H \rightarrow S + H_2$

Excited S_2^* molecules are formed in the cool outer cone of the flame by the following set of reactions:

(Eq. 8-5) $$\cdot H + \cdot H + S_2 - H_2 + S_2^*$$

where the recombination of atomic hydrogen furnishes the excitation energy for $S_2 - S_2^*$ or by the reaction

(Eq. 8-6) $$\cdot H + \cdot OH + S_2 - S_2^* + H_2O$$

where the formation of H_2O supplies the excitation energy for $S_2 - S_2^*$.

The mechanism for the production of a strong luminescent emission with the concurrent conversion of the high-energy S_2^* to the lower-energy-state S_2 may be summarized:

(Eq. 8-7) $$S_2 + \cdot H + \cdot H - S_2^* + H_2$$

$$S_2^* - S_2 + h\nu$$

or $$S + S + M - S_2^* + M \text{ (where } M \text{ is a third body)}$$

(Eq. 8-8) $$S_2^* - S_2 + h\nu.$$

The observed luminescent emission ($h\nu$) is related to the concentration of the sulfur pollutant by Equation 8-9.

(Eq. 8-9) $$I_{S_2} = I_o[S]^n$$

Where I_{S_2} = *observed intensity of the molecular emission due to the* S_2 *species*
$[S]$ = *concentration of sulfur atoms*
I_o = *constant under given experimental conditions*
n = *constant (usually assumed to be 2) under given experimental conditions*

The concentration of sulfur pollutant is not linearly proportional to the observed intensity. Most instruments, however, use linearizing electronic circuitry to yield a linear voltage output. Moreover, instruments using FPD must be calibrated with various concentrations of the particular pollutant gas since this measurement is not absolute.

Recent Applications

The flame photometric detector is most frequently used in the detection of ambient sulfur dioxide. This instrument uses a scrubber to remove potential interferences (usually sulfur compounds other than SO_2) and the signal is converted to a linear ppm SO_2 output. The flame photometric detector, in combination with gas chromatography, has been used to detect mixtures of sulfur-containing pollutants

(SO_2, H_2S, CH_3SH, and others). Stevens et al. (1970), for example, described a gas chromatographic system using flame photometric detection to separate and quantitate various sulfur pollutants.

Potential Interferences

Instrumentation designed to monitor for a specific sulfur compound, such as SO_2, must contain scrubbers that remove all other sulfur-containing compounds. This is because the flame photometric detector does not discriminate between different sulfur-containing compounds. Moreover, as noted by Farwell (1976), the presence of other organic compounds in the sample gas (as well as variable carbon dioxide) may result in a change in the response of the FPD. This change in response may be attributed to "the inactivation of the excited S_2^* species by their combination or collision with organic compounds and/or the organic degradation products." Ambient relative humidity may represent another potential interference.

Advantages

The principal advantages of FPD analyzers are low maintenance, high sensitivity, fast response, and selectivity for sulfur compounds. No solutions are needed, and the only reagents for the flame are hydrogen and air.

Fluorescence Instruments

Fluorescence emission can be differentiated from other kinds of luminescence by the excitation energy employed. Chemiluminescence, for example, uses a chemical reaction, x-ray fluorescence uses x-rays, and fluorescence uses ultraviolet-visible light. Fluorescence can be distinguished from phosphorescence mechanistically and empirically by observing the lifetime of the excited states ($\sim 10^{-8}$ second for fluorescence; several seconds for phosphorescence). The energy level diagram in Figure 8-2 illustrates the mechanism involved in fluorescence emission.

In fluorescence, the molecule is in a high vibrational state after an electronic transition occurs (e.g., $S_0 \rightarrow S_2$). Upon loss of some energy by vibrational relaxation, the molecule reverts to the lower energy state and emits light in the process (e.g., $S_1 \rightarrow S_0$). This radiation is termed fluorescence.

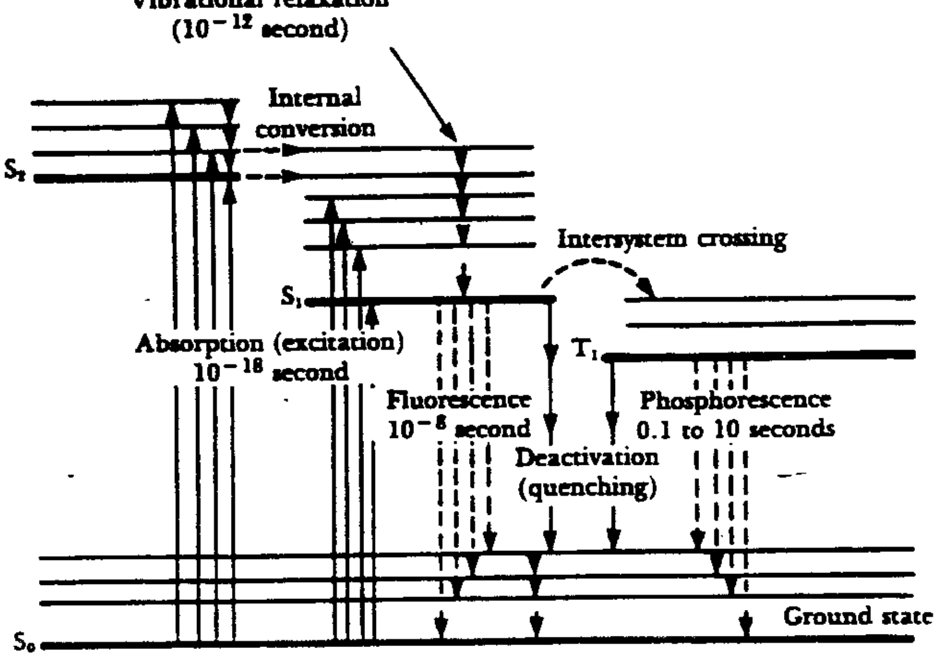


Figure 8-2. Energy levels in fluorescence emission.

Recent Applications

The principal application of fluorescence spectroscopy is for the measurement of ambient and source sulfur dioxide. Okabe et al. (1973) first applied this mode of detection to the measurement of sulfur dioxide. Since that time, commercial monitors have been developed, and these instruments have been designated by the Environmental Protection Agency as equivalent methods for monitoring ambient SO_2. One method, termed *pulsed fluorescence*, uses a short-pulsed, high-intensity ultraviolet light source in the 210-nm region to excite the SO_2 molecules. The subsequent fluorescence emission is detected by a photomultiplier tube and processed electronically to yield direct ppm SO_2 (Figure 8-3). These instruments must be calibrated with different concentrations of standard SO_2 since, like other luminescence methods, the method is not absolute.

Advantages

These instruments use no consumable gases, as does the FPD, and the inherent stability enables them to operate for long unattended periods. The instruments produce linear measurements over a wide range (0.5 to 5000 ppm) and are insensitive to temperature and flow variations.

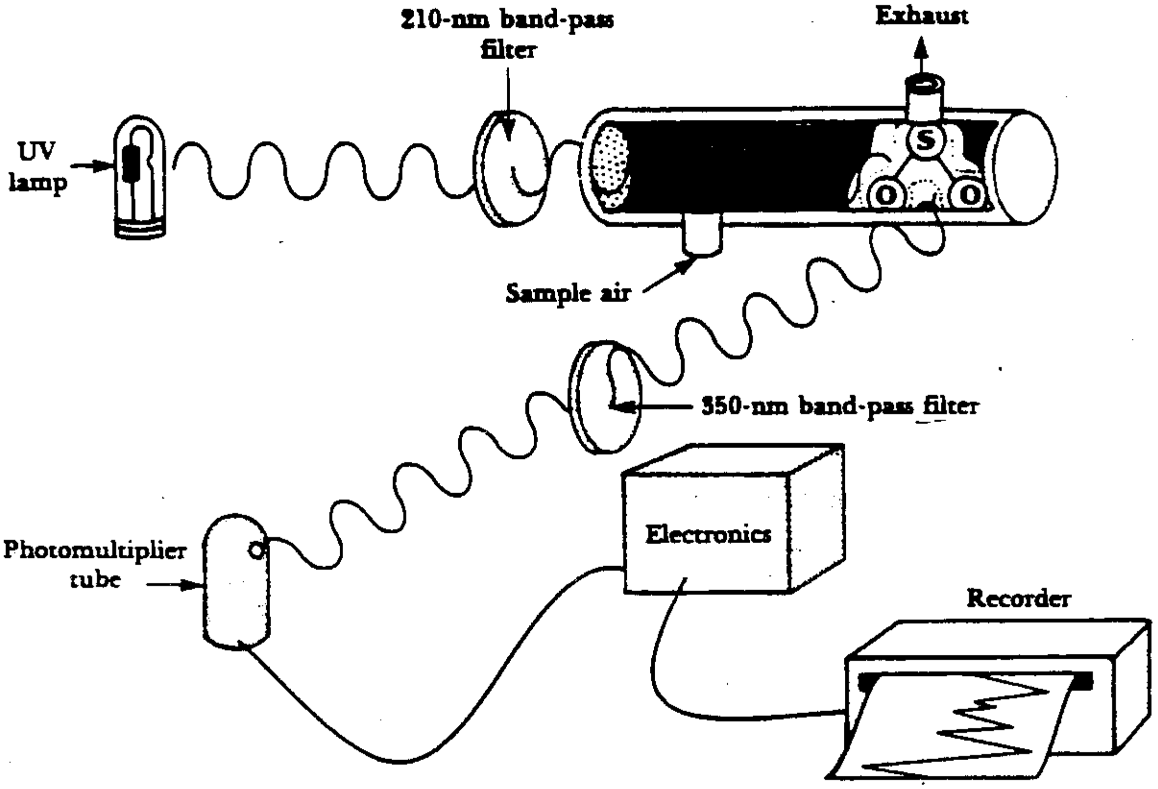


Figure 8-3. Fluorescence SO_2 monitor.

Potential Interferences and Disadvantages

The interferences in *UV fluorescence* instruments are related primarily to the quenching effects of O_2, N_2, CO_2, and water vapor. For ambient monitoring, the levels of O_2, N_2, and, for the most part, CO_2 and water vapor are constant; thus, the quenching effect is fairly constant. In flue gases, however, the levels of CO_2, water vapor, and O_2 vary considerably. Consequently, the SO_2 values may be spurious. Jahnke et al. (1976) have obtained approximate values for the quenching coefficients of these gases providing corrections for different concentrations of CO_2, N_2, and O_2. Hydrocarbons may also interfere, but all *equivalent* analyzers now come equipped with a hydrocarbon scrubber ("cutter") to eliminate this potential problem.

Chemiluminescence Instruments

Principles of Operation

Chemiluminescence instruments used in air pollution monitoring measure the emission of light produced by the reaction of a gaseous pollutant with a reagent gas. The process involved in homogeneous gas-phase chemiluminescence is summarized in Equations 8-10 and 8-11.

(Eq. 8-10) $$A + B - C^{*} + D$$

(Eq. 8-11) $$C^{*} - C + h\nu$$

The reaction of pollutant *A* with excess reagent gas *B* produces a chemi-excited species C^{*}, which reverts to a lower energy state by emission of light ($h\nu$). The light produced passes through an optical filter to isolate a given spectral region and strikes a photomultiplier tube (PMT). The PMT signal is amplified and is directly proportional to the concentration of pollutant.

Instruments using chemiluminescence as described above are compound or pollutant specific and should be distinguished from the flame detector (flame photometric detector) described previously, which is element specific. The chemiluminescence instruments discussed here use a reagent gas rather than a hydrogen-rich flame to produce a chemi-excited species.

Figure 8-4 illustrates the basic components and gas flow of a compound-specific chemiluminescence detector. Sample gas containing the pollutant enters the reaction chamber and reacts with the reagent gas.

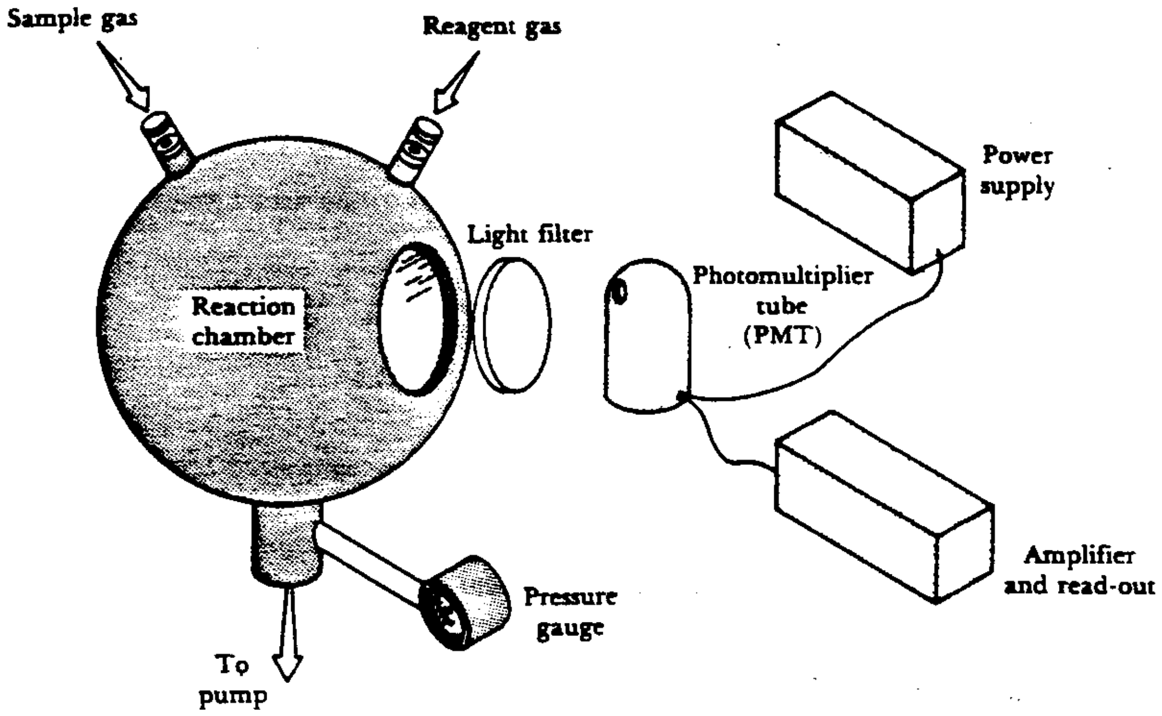


Figure 8-4. Compound specific chemiluminescence detector.

The intensity of the light produced is related to the concentration of pollutant and reagent gas (Equation 8-12).

(Eq. 8-12) $$I = k[A][B]$$

Where:
I = *intensity of light emitted*
k = *rate coefficient (a constant)*
$[A]$ = *concentration of pollutant*
$[B]$ = *concentration of reagent gas*

Since the reagent gas is usually present in large excess, its concentration is assumed to be constant. Equation 8-13 can be used to relate the intensity to the concentration of pollutant.

(Eq. 8-13) $$I = c[A]$$

Where:
I = *intensity of light emitted*
c = *constant under given experimental conditions*
$[A]$ = *concentration of pollutant*

Recent Applications

Chemiluminescence techniques are routinely used for the measurement of ozone and oxides of nitrogen. The chemiluminescence resulting from an ethylene/ozone reaction was first reported by Nederbragt et al. (1965) and forms the basis for present ozone monitors using homogeneous gas-phase chemiluminescence. This reaction produces an excited aldehyde linkage that emits light. After extensive field testing and evaluation of prototype instruments, ozone/ethylene chemiluminescence was designated as the reference principle for ozone detection by the Environmental Protection Agency.

The reaction of ozone (O_3) with nitric oxide (NO) produces an emission spectrum that is shown in Figure 8-5.

This spectrum results from the chemiluminescence of ozone and nitric oxide shown in Equations 8-14 and 8-15.

(Eq. 8-14) $$NO + O_3 - NO_2^* + O_2$$

(Eq. 8-15) $$NO_2^* - NO_2 + h\nu$$

Nitric oxide is measured directly. Nitrogen dioxide measurements can be made by catalytic conversion of nitrogen dioxide to nitric oxide with carbon-based or metal converters, resulting in a total oxide of nitrogen concentration $[NO_x] = [NO] + [NO_2]$. The difference between total oxides of nitrogen $[NO_2] + [NO]$ and nitric oxide is a measure of nitrogen dioxide concentration.

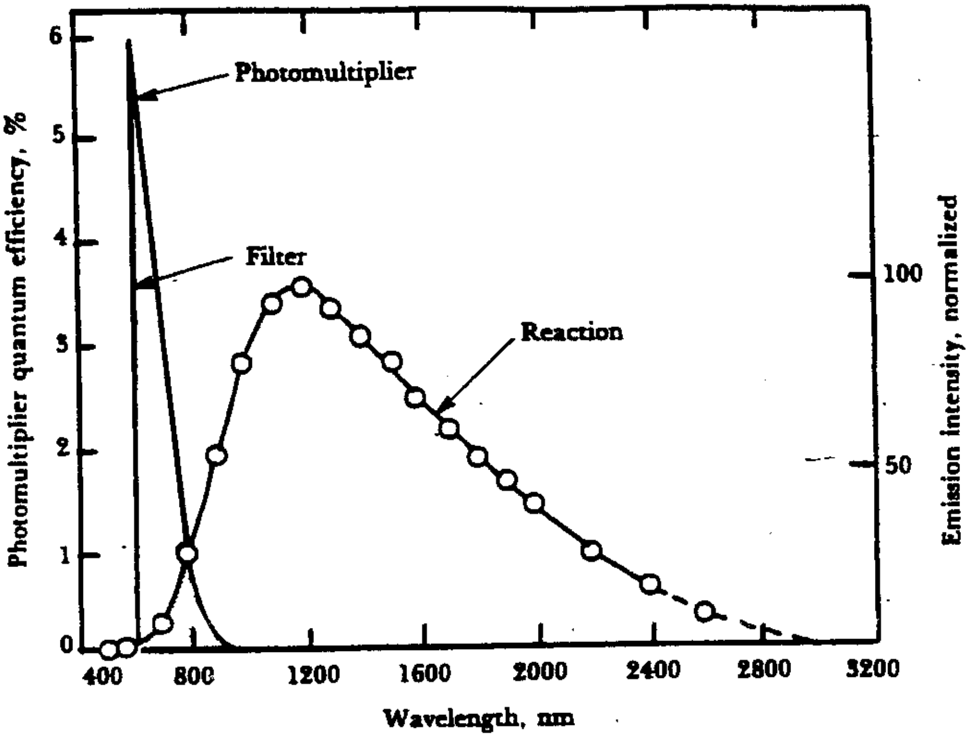


Figure 8-5. Emission spectrum of ozone/nitric oxide.

Potential Interferences

For a positive interference, a species must react with the reagent to yield chemiluminescence in the spectral region of the pollutant emission. In nitric oxide detectors a filter that absorbs emissions below 600 nm is placed between the reaction chamber and photomultiplier tube. This eliminates emissions from the reaction of ozone with olefins that could produce a positive interference. Ambient instruments also respond to other nitrogen pollutants such as peroxyacetyl nitrate, ammonia, and other organic nitrates. These nitrogen compounds are converted to NO in the converter. Quenching effects are a source of negative interference. In ambient air, molecular nitrogen and oxygen are the predominate quenching agents; but, since these agents do not vary significantly in concentration, the quenching effect is generally constant.

Advantages

The advantage of gas-phase chemiluminescence is that emissions are relatively specific for the pollutant being monitored. Gas-phase reactions in instruments using continuous flow are insensitive to changes in surface properties in the reaction chamber. Furthermore, a linear response in the range of 4 ppb to 100 ppm can be obtained.

Ultraviolet Photometric Instruments

Principle of Operation

The visible and ultraviolet absorption of molecules is associated with electronic energy level transitions. For example, $\pi-\pi^*$ or $\sigma-\sigma^*$ transitions could result in ultraviolet absorption. Instruments making use of the ultraviolet absorption of pollutants measure the absorption at a specific wavelength that can be related to the concentration of the pollutant by Beer's law (Equation 8-16).

Recent Applications

The ultraviolet absorption of ozone is shown in Figure 8-6. This characteristic of ozone is used by the Environmental Protection Agency to calibrate ozone monitors using chemiluminescent detection. Figure 8-7 shows the gas flow and components of an instrument using UV photometry for the detection of ozone.

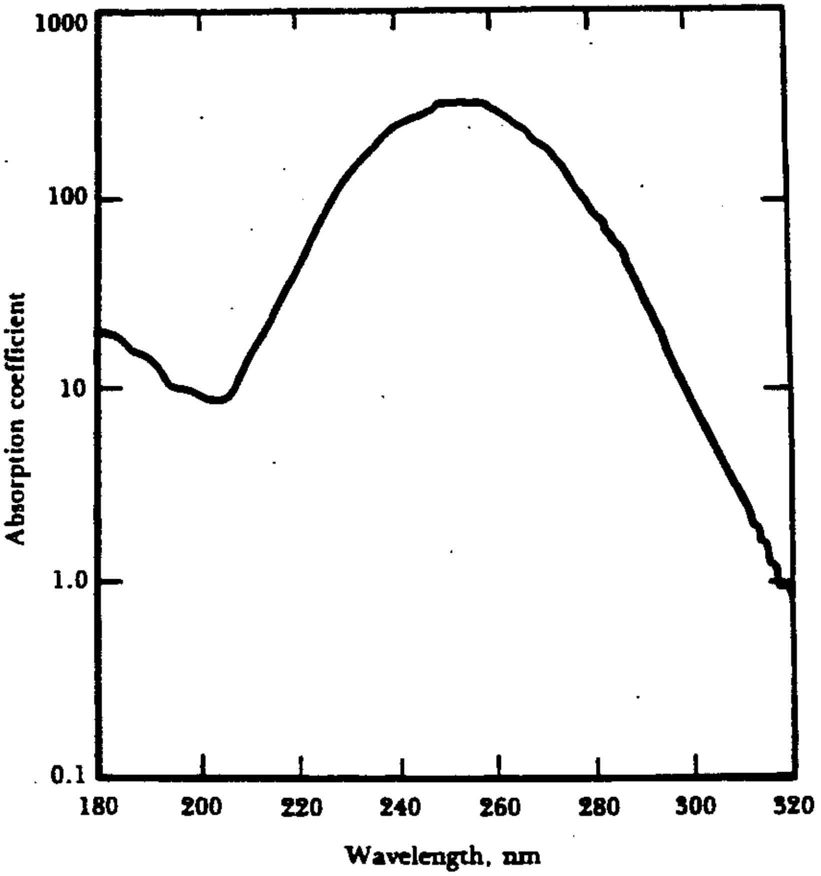


Figure 8-6. Ultraviolet absorption of ozone.

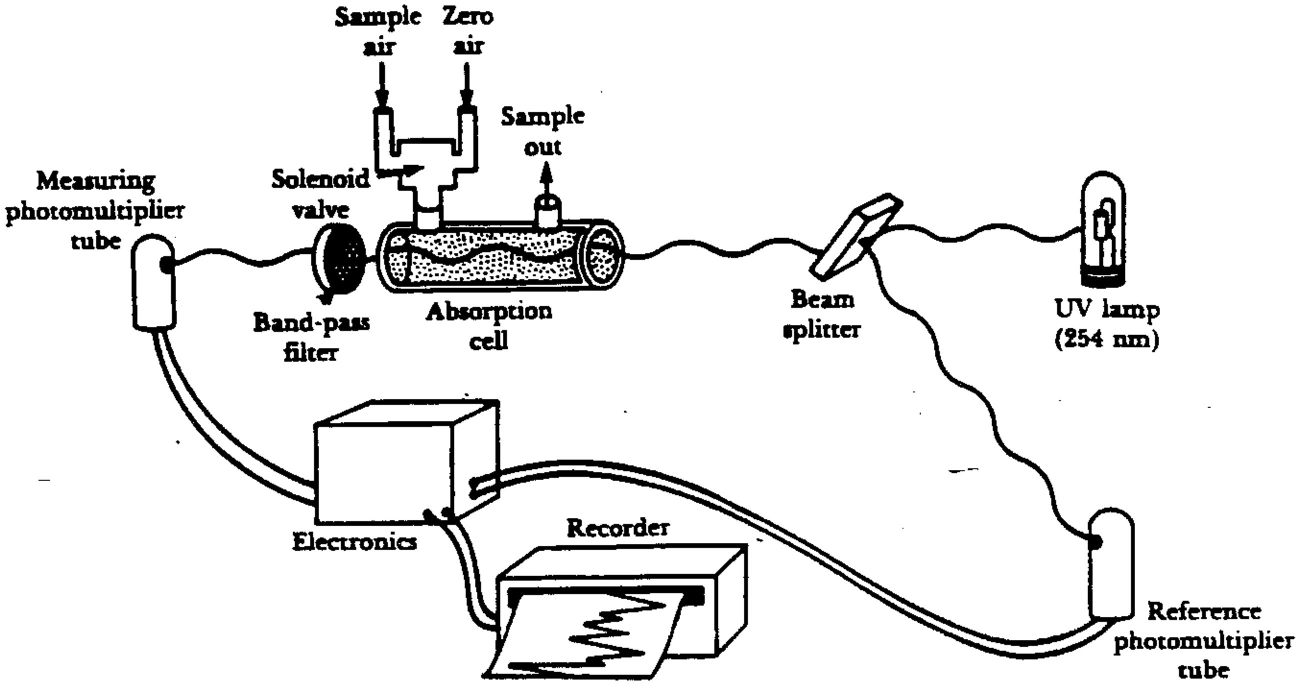


Figure 8-7. Flow and components of ozone detector using UV photometry.

Advantages

The UV photometric method for calibrating ozone monitors eliminated a wet-chemical method—***the NBKI procedure,*** which had demonstrated "some inherent short-comings" (43 Fed. Reg., no. 121). In source applications, instruments measure the difference in absorption of radiation (in the UV-visible region) by the stack gas at two different wavelengths. This provides continuous measurement of gaseous pollutants (NO_x, SO_2, etc.) in stacks. These instruments have several advantages over wet-chemical techniques, which require considerable sample handling and lack continuous data output.

Second Derivative Spectroscopic Instruments

Principles of Operation

In direct absorption spectroscopy, pollutant gases absorb energy at a specific wavelength of light (λ), and the absorption is related to concentration by Beer's law:

(Eq. 8-16)

$$I(\lambda)=I_0(\lambda)e^{-\alpha(\lambda)c\ell}$$

Where:

$I_0(\lambda)$ = *incident intensity at* λ
$I(\lambda)$ = *observed intensity at* λ
c = *concentration of absorbing gas*
ℓ = *path length of light through the gas*
$\alpha(\lambda)$ = *absorption coefficient of the gas at* λ
e = *natural log function.*

Second derivative instruments, on the other hand, relate the slope and curvature characteristics of absorption bands to the concentration of gaseous pollutants. These instruments, rather than produce a second derivative spectrum, produce a signal from which a voltage output proportional to the second derivative can be extracted. This can be accomplished by using phase lock amplifier circuits. The second derivative voltage output produced by the instrument is directly related to concentration by Equation 8-17.

(Eq. 8-17)

$$\underset{\substack{\textbf{signal from}\\ \textbf{derivative}\\ \textbf{spectrometer}}}{S=\frac{\left(\frac{d^2I}{d\lambda^2}\right)_{\lambda_0}}{I}} = \underset{\substack{\textbf{constant,}\\ \textbf{independent}\\ \textbf{of intensity}}}{\frac{I}{I_0}\left(\frac{d^2I_0}{d\lambda^2}\right)_{\lambda_0}} - \underset{\substack{\textbf{term linear}\\ \textbf{with gas}\\ \textbf{concentration}\\ \textbf{with fixed}\\ \textbf{pathlength}}}{c\ell\left(\frac{d^2\alpha}{d\lambda^2}\right)_{\lambda_0}}$$

Where: λ_0 = *the wavelength of the absorption peak maximum*

The method for producing a second derivative signal consists of using a wobbler to modulate with time essentially monochromatic light with the amplitude of light approximately equal to the band width being detected. This light is passed through the sample gas and strikes a photomultiplier tube. The $(d^2I/d\lambda^2)/I$ second derivative portion of the signal is extracted by the electronics—"signal analysis"—and can be related to the concentration of the pollutant. Figure 8-8 illustrates the arrangement of the optics employed to produce a second derivative signal. Since second derivative instruments, like direct absorption spectrometers, do not provide absolute measurements, they must be calibrated with various concentrations of the pollutant being measured.

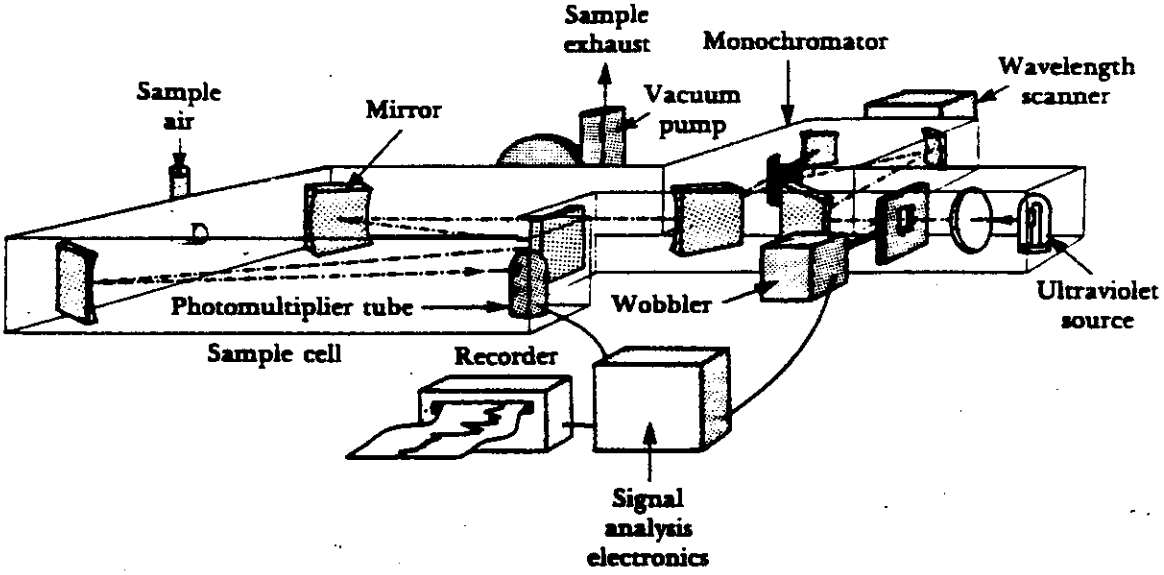


Figure 8-8. Typical second derivative spectrometer.

Recent Applications

Second derivative spectrometers are used to measure both source and ambient pollutants. They have been used to measure nitrogen dioxide, sulfur dioxide, and ammonia concentrations in air. Another interesting application has been the determination of trace nitrogen dioxide concentrations in high-purity argon.

Advantages

Second derivative spectrometers have the advantage of being highly specific for trace analysis of complex mixtures of atmospheric pollutants. Broad band absorption by interfering gases and light scattering by particulate matter are minimized by these instruments. Also, these instruments have been adapted to *in-situ* stack sampling and unattended ambient monitoring. Furthermore, no support gases or reactive solutions are required.

Disadvantages

As a practical consideration, the high cost of these instruments in comparison to other instrumental and wet-chemical techniques is the major disadvantage. The mathematical basis for the instrument is complex, and the lack of trained pers[illegible] install and maintain these instruments are further disadvantages.

NDIR Instruments

Principle of Operation

Nondispersive infrared (NDIR) analyzers have been developed to monitor SO_2, NO_x, CO, CO_2, hydrocarbons, and other gases that absorb infrared radiation, a form of thermal energy. They are termed nondispersive analyzers because they do not use a prism or grating to disperse the infrared radiation. A narrow band-pass filter that absorbs infrared radiation at all wavelengths except the ones of interest is used. Figure 8-9 illustrates the essential components and gas flow of a typical Luft-type NDIR carbon monoxide analyzer.

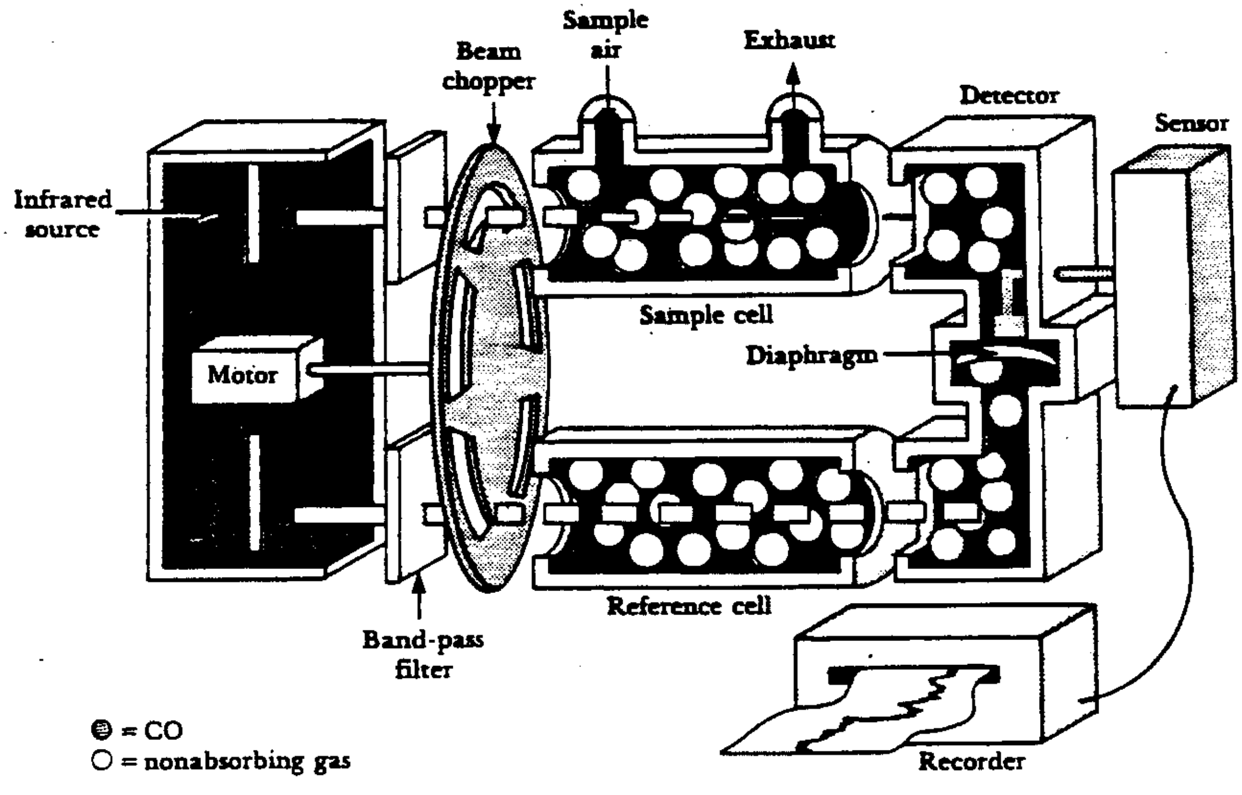


Figure 8-9. Typical Luft-type carbon monoxide NDIR analyzer.

Infrared radiation is emitted at the same intensity by two infrared radiation sources. The radiation from one source passes through a sample cell containing ambient air. Radiation from the other source passes through a reference cell containing a nonabsorbing gas, such as nitrogen. After passing through either the sample cell or the reference cell, the infrared radiation enters a detector cell containing carbon monoxide which is divided into two sections by a thin metal diaphragm. Any distention of the diaphragm produces a capacitance change that is converted to a voltage output. The voltage output is used to activate a device, such as a strip chart recorder, that displays carbon monoxide concentrations in parts per million.

If the sample air doesn't contain carbon monoxide, the same amount of infrared radiation enters the sample section of the detector as enters the reference section. Therefore, the same amount of radiation is absorbed by the carbon monoxide in the sample section of the detector as is absorbed in the reference section. Furthermore, pressure resulting from the absorption of radiation is equal in both sections of the detector. The diaphragm which separates the detector section doesn't move because equal pressure is being exerted on both sides of it. Hence, no voltage is created to activate the analyzer's strip chart recorder, so a zero carbon monoxide concentration reading is displayed.

If the sample air contains carbon monoxide, less infrared radiation enters the sample section of the detector than enters the reference section, because some of the radiation is absorbed by the carbon monoxide in the sample cell. Therefore, less pressure is produced in the detector's sample section than in the reference section. This causes less pressure to be exerted against the diaphragm by the sample section than by the reference section, thus creating a distention of the diaphragm. The distention, which is directly proportional to the concentration of carbon monoxide in the sample cell, creates a voltage output which is used to indicate the carbon monoxide concentration in parts per million on a strip chart recorder. The beam chopper simply creates an alternating current (AC) signal that can be easily amplified.

This technique, while seemingly specific for CO, suffers from interferences due to the broad band absorption of carbon dioxide, water vapor, and hydrocarbons (HC). Figure 8-10 shows the absorption of carbon monoxide and the broad band interferences.

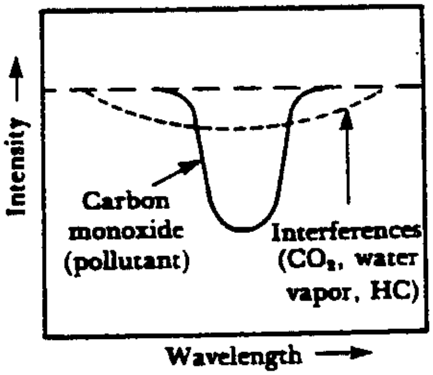


Figure 8-10. Overlap of carbon monoxide and broad band absorption curves.

If broad band interferences were present, the NDIR depicted in Figure 8-9 would yield a higher CO concentration than was actually present.

Luft-type NDIR analyzers have been designed to minimize these broad band interferences. In one instrument, two detector cells are placed in series as shown in Figure 8-11.

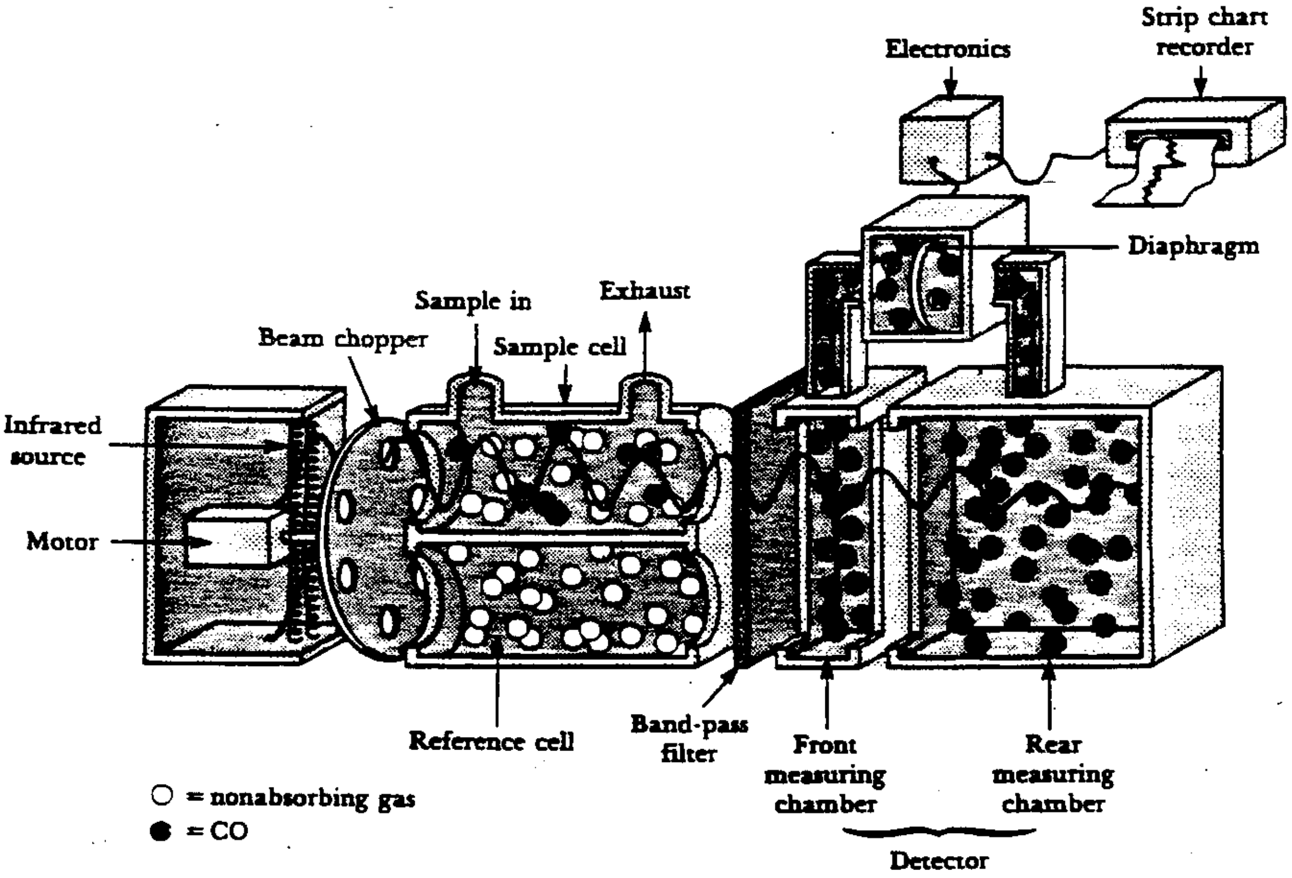
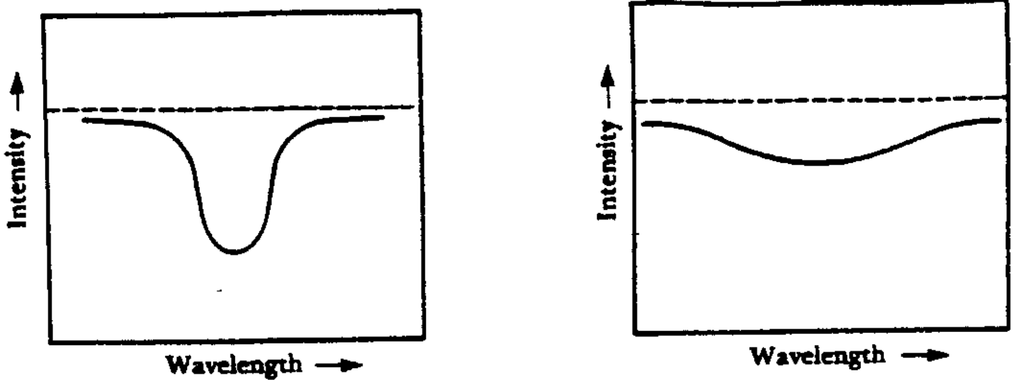


Figure 8-11. "Negative filter" analyzer.

As infrared radiation enters the sample cell, the sample air absorbs energy in the CO spectral region. The carbon monoxide in the front detector cell absorbs the reduced energy from the sample cell, principally from the center wavelengths of the CO band (Figure 8-12a). The rear measuring chamber absorbs the remaining energy (Figure 8-12b). The longer cell path of the rear measuring chamber allows for more absorption in the rear chamber. The resulting distention in the diaphragm, then, is a ratio of the CO absorption in the front and rear measuring chambers. If the interferences are basically linear across the CO absorption band, this ratio will accurately reflect the CO concentration; that is, the absorbances in the front and rear chambers will increase by the same amount due to interferences, but the ratio will be constant regardless of the amount of positive interference. This technique differs significantly from the NDIR discussed previously and is termed *negative filtering*.



a. Front measuring chamber absorbs energy from center wavelengths.

b. Rear measuring chamber absorbs remaining energy.

Figure 8-12. Infrared absorption in the detector of a "negative filter" NDIR analyzer.

In another type of analyzer (Figure 8-13), sample air continuously flows through a reference cell as well as through a sample cell. However, before flowing through the reference cell, the sample air passes through a catalytic converter that transforms any CO present in the sample air to CO_2. Therefore, any interfering species present in the sample cell are also present in the reference cell in the same concentrations, except possibly for CO_2, since any CO present in the sample air is converted to CO_2 before entering the reference cell. However, because of the large ratio of CO_2 to CO in ambient air, any difference between the amounts of CO_2 present in the reference cell and the sample cell is negligible. Sample air in the reference cell allows the absorption of infrared radiation by interfering species in the sample cell to be offset by interfering species in the reference cell.

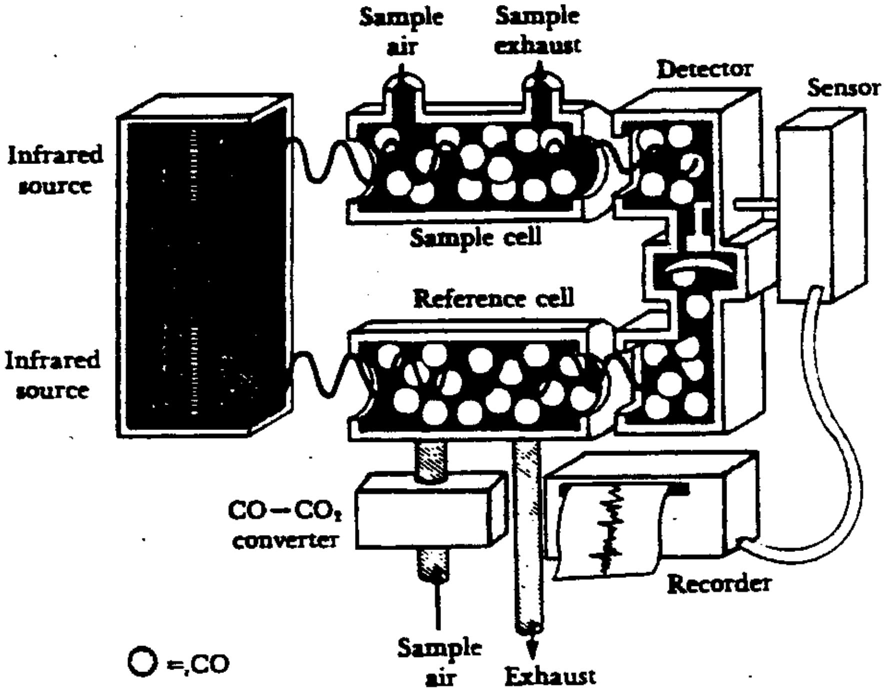


Figure 8-13. Flowing reference cell NDIR carbon monoxide analyzer.

Recently, NDIR CO analyzers based on gas filter correlation have been developed. In an NDIR gas filter correlation CO analyzer, chopped radiation from an infrared source alternately passes through a cell filled with CO (the reference beam) and a cell filled with nitrogen that is aligned with a neutral density filter (the measure beam) before entering the analyzer's sample chamber. After leaving the sample chamber and passing through a band-pass filter, the alternating radiation beams are measured by an electronic detector to obtain the carbon monoxide concentration of the sample air.

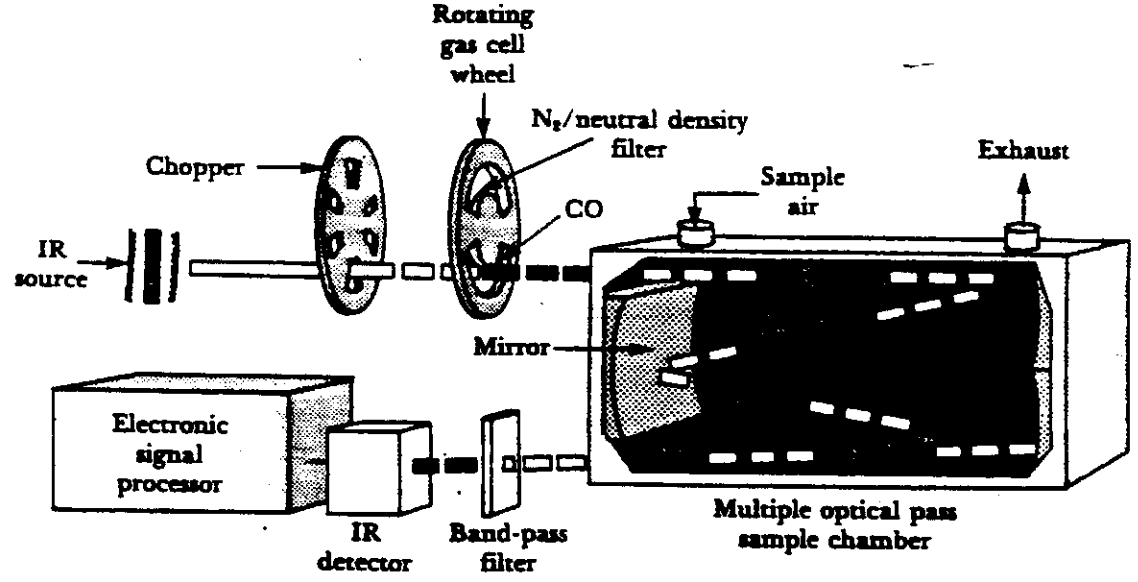


Figure 8-14. Gas filter correlation NDIR CO analyzer.

The CO cell absorbs any radiation that can be absorbed by CO present in the sample air contained in the sample chamber. No absorption takes place in the nitrogen cell. However, after leaving the nitrogen cell, infrared radiation passes through a neutral density filter that reduces its energy to equal the remaining energy of the infrared beam that passed through the CO cell.

The detector determines the CO concentration of the sample air by measuring the difference in energy of the two infrared beams. Any energy difference creates an electronic signal that is proportional to CO concentration. If no CO is present in the sample air, no absorption of the infrared beam that passed through the nitrogen cell takes place. Therefore, the energies of both beams measured by the detector will be equal, and no electronic signal related to CO concentration will be generated (Figure 8-15a). However, if CO is present in the sample air, some of the infrared radiation that passed through the nitrogen cell will be absorbed. Therefore, its energy will be less than the energy of the infrared radiation that passed through the CO cell, and an electronic signal will be generated by the detector (Figure 8-15b).

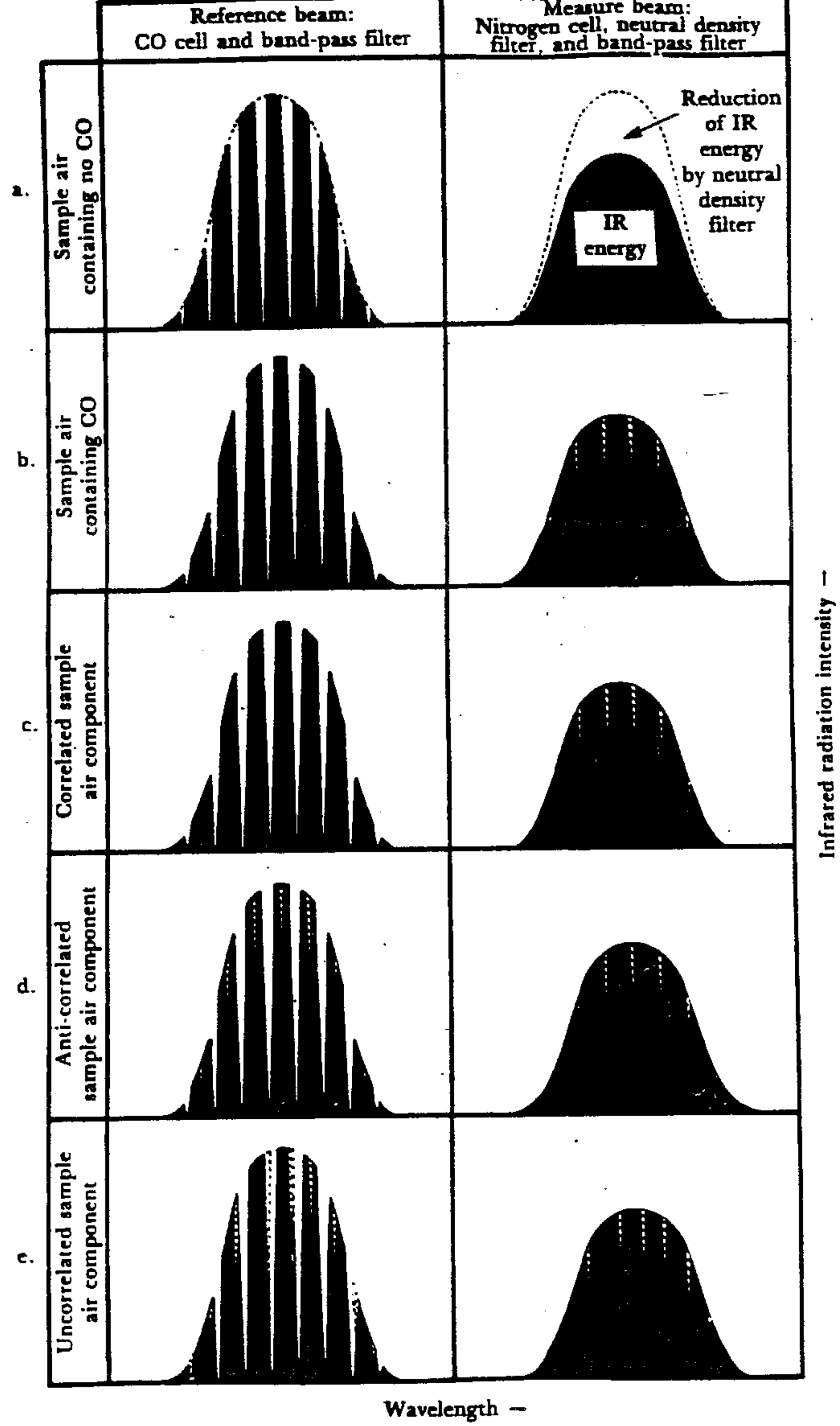


Figure 8-15. Infrared energy spectra received by the detector.

For a component of the sample air having a spectral pattern that perfectly correlates (overlaps) the spectral pattern of CO, the analyzer would erroneously indicate a positive CO concentration (Figure 8-15c). Conversely, the analyzer would erroneously indicate a negative CO concentration for a sample air component having a spectral pattern that perfectly anti-correlates (does not overlap) the spectral pattern of CO (Figure 8-15d). This is caused by more infrared energy being lost from the reference beam than from the measure beam, because absorption of the reference beam takes place at higher radiation intensities than does absorption of the measure beam.

Fortunately, spectra of sample air components are usually uncorrelated (neither perfectly correlated nor perfectly anti-correlated). Components of the sample air having totally uncorrelated absorption spectra (having equal amounts of correlated and anti-correlated absorbances) absorb the same amounts of infrared radiation in both the measure and reference beams, thus producing no erroneous indication of CO concentration (Figure 8-15e). However, usually the spectra of sample air components are not totally uncorrelated, so a small CO interference could occur (Thermo Electron Corporation).

Recent Applications and Advantages

NDIR analyzers in ambient monitoring are used principally for the measurement of carbon monoxide. The NDIR photometric technique has been designated as the reference measurement principle for the continuous measurement of carbon monoxide in air by the Environmental Protection Agency. It is a relatively inexpensive, reliable method that does not require highly trained personnel for its operation.

Potential Interferences and Disadvantages

Since NDIR photometry is most frequently used in the measurement of carbon monoxide, the two most prominent interferences are carbon dioxide and water vapor. These interferences must be removed from sample air measured by Luft-type analyzers, or Luft-type analyzers must be modified (e.g., flowing reference cell, "negative filtering") to minimize their effects. Gas filter correlation analyzers greatly reduce the effects of potential interferences. Furthermore, hydrocarbon concentrations usually encountered in ambient air are too small to cause significant interference.

Coulometric and Amperometric Instruments

Principles of Operation

Coulometric analytical techniques use the electrical charge generated by oxidation-reduction reactions occurring in an electrolytic cell to measure gaseous pollutant concentrations. The air sample containing the pollutant flows through the cell and oxidizes (or reduces) part of the solution at one electrode. A balancing reaction occurs at the other electrode, causing a small current to flow across the cell. The concentration can be determined by Faraday's law, which states that one gram-equivalent of a material is oxidized or reduced by one Faraday of electricity. By measuring the current across the cell, the concentration of the sample may be determined, since the quantity of electricity (Q, coulombs) is given as the integral of current (i, amperes) over the time interval (t, seconds):

(Eq. 8-17)
$$\int_0^t (i)dt = Q = \frac{zmF}{M}$$

Where:

m = mass in grams of the species consumed or produced during electrolysis
M = gram molecular weight of pollutant being analyzed
z = number of Faradays (equivalents) of electricity required per gram mole (i.e., the number of electrons appearing in the equation for the net reaction of interest)
F = proportionality constant: 96,494 coulombs/mole.

This coulometric technique measures the amount (i.e., coulombs) of electricity directly produced as the result of a reaction of a pollutant at the electrode.

In present instrumentation, however, pollutant concentration is determined indirectly by measuring the current required to maintain a constant halogen concentration. These halogens are typically bromine (Br_2) or iodine (I_2). The sample gas passes through an electrolytic cell and reduces the halogen to halide (for example, Br_2 + pollutant — Br^-), thereby reducing the halogen concentration. The current required to maintain the electrochemical balance is directly proportional to the pollutant concentration. Since electric current and not charge is measured, these analyzers are properly termed ***amperometric*** analyzers.

Recent Applications

Amperometric techniques have been most widely applied to analyzing ambient sulfur dioxide. A constant iodine concentration can be generated by application of a constant current to the electrodes in the detector cell. Upon entering the cell, sulfur dioxide undergoes hydrolysis, and the hydrolysis product reduces the steady state concentration of iodine in the electrolytic cell.

(Eq. 8-18)
$$SO_2 + I_2 + 2H_2O - SO_4^{=} + 2I^- + 4H^+$$

Since the iodine concentration has been reduced, the cell loses the capacity to carry the full applied anodic current to the cathode. As a result, current flows through the reference electrode until the electrochemical balance in the cell has been restored. Figure 8-16 illustrates the flow of current and the reactions occurring at each electrode.

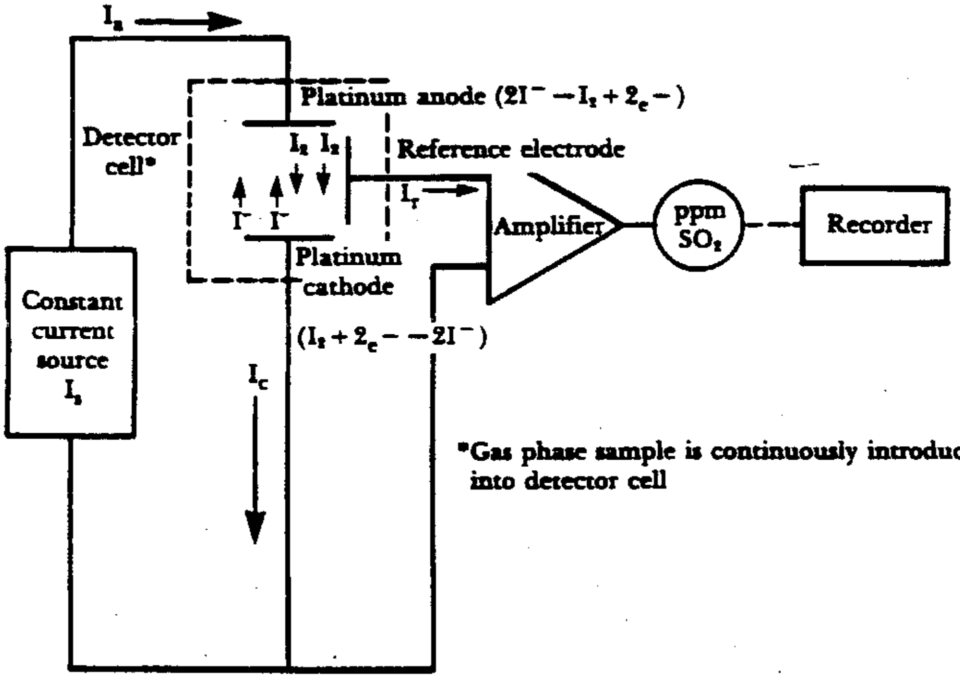


Figure 8-16. Amperometric titration of iodine.

Instrumentation also employing this type of amperometric titration measures the reduction of bromine rather than iodine. Typically, the bromine concentration is maintained at a constant level by a set of sensor-reference electrodes and by the electronic circuits. As sulfur dioxide is introduced into the detector cells, the bromine (Br_2) concentration is reduced by the reaction given in Equation 8-19.

(Eq. 8-19) $$SO_2 + Br_2 + 2H_2O - 2H_2SO_4 + 2Br^- + 2H^+$$

This reaction disturbs the Br_2/Br^- ratio, and this change is measured by sensor-reference electrodes. The current required to regenerate the bromine (Br_2) through the generator-auxiliary electrodes is proportional to the sulfur dioxide concentration. Figure 8-17 illustrates the four electrodes and the circuit employed in this type of instrument.

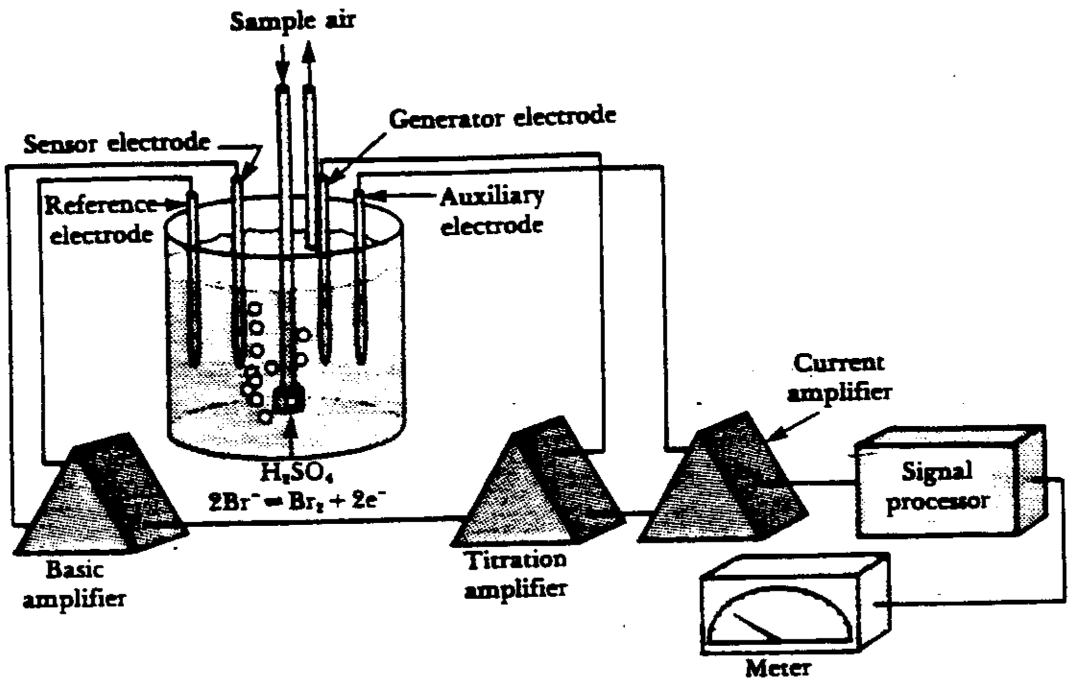


Figure 8-17. Amperometric titration of bromine.

Lindqvist (1978) described a sulfur dioxide monitor based on the anodic oxidation of sulfur dioxide in a galvanic cell. In this type of instrument, sulfur dioxide is oxidized directly by the electrode, and the resulting current can be related to the sulfur dioxide in ambient air. The design of this detector is unique in that current generated by interferences is eliminated by a differential measuring technique.

The cell contains two anodes. One anode is the reference electrode; the other, the measuring electrode. By measuring the potential difference (ΔV) across the cell section when the air flow is equal in both anode sections, the current generated by interferences will be eliminated, and the current will be due solely to the presence of sulfur dioxide. The oxidation of sulfur dioxide at the measuring anode in Equation 8-20 can be related to concentration by Faraday's law.

(Eq. 8-20) $$SO_2 + 2H_2O \rightarrow SO_4^{=} + 4H^+ + 2e^-$$

Advantages

As Lindqvist has noted, one of the principal advantages of coulometric/amperometric analyzers for ambient SO_2 monitoring is that these instruments require no compressed gases as do instruments using gas chromatography and flame photometric methods. Therefore, they can be used in aircraft and at other sites where the use of compressed hydrogen might pose a potential explosion hazard.

The major advantage is that coulometric/amperometric analyzers require minimal maintenance. The halide contained in the cell is regenerated, and volatilization of the halogen is not a problem. The electrolyte solution lost by evaporation can be replaced by condensation from air, or a thermistor (a device for temperature measurement) can be used to automatically maintain the reservoir at a certain level.

Potential Interferences and Disadvantages

The potential interferences in the sulfur dioxide (SO_2) coulometric/amperometric instruments described are compounds that are able to oxidize halogens, reduce halogens, or combine with halogens. Sulfur compounds such as hydrogen sulfide, mercaptans, organic sulfides, and organic disulfides are the most notable interferences. Nitric oxide (NO), ozone (O_3), nitrogen dioxide (NO_2), chlorine (Cl_2), and ethane (CH_3CH_3), among others, are also interferences, but of much less significance than sulfur compounds. Chemical filters used to remove these interferences are usually incorporated into coulometric/amperometric sulfur dioxide analyzers.

References

Beckman Instruments, Inc. 1972. *Model 906A sulfur dioxide analyzer*. Beckman Instruments, Inc., Fullerton, CA.

Bowman, L. D., and Horak, R. F. 1972. A continuous ultraviolet absorption ozone photometer. Presented at the 18th Annual Symposium of the Analysis Instrument Division of the Instrument Society of America, 3-5 May 1972.

Farwell, S. O., and Rasmussen, R. A. 1976. Limitations of the FPD and ECD in atmospheric analysis: a review. *J. Chromatog. Sci.* 14:224.

Finlayson, B. J.; Pitts, J. N.; and Atkinson, R. 1974. Low-pressure gas-phase ozone-olefin reactions. Chemiluminescence, kinetics, and mechanisms. *J. Amer. Chem. Soc.* 96:5356.

Fontijn, A. Chemiluminescence techniques in air pollution monitoring. *Modern Fluorescence Spectroscopy*. Vol. 1, ed. Milton Birnbaum, pp. 159-192.

Fontijn, A.; Sabadell, A. J.; and Ronco, R. J. 1976. Homogenous chemiluminescence measurement of nitric oxide with ozone. *Anal. Chem.* 42:575-579.

Hager, R. N. 1973. Second derivative spectroscopy as applied to the measurement of trace nitrogen dioxide. Presented at the Eastern Analytical Symposium and Society for Applied Spectroscopy National Meeting, at New York, NY.

Hager, R. N. 1973. Derivative spectroscopy with emphasis on trace gas analysis. *Anal. Chem.* 45:1131A.

Hollowell, Craig D.; Gee, Glenn Y.; and McLaughlin, Ralph D. 1973. Current instrumentation for continuous monitoring for SO_2. *Anal. Chem.* 45:63A.

Jahnke, J. A., and Aldina, G. J. 1978. *Continuous Source Monitoring Systems Handbook*. Prepared for ERIC under EPA contract #68-03-2561.

Jahnke, J. A.; Cheney, J. L.; and Homolya, J. B. 1976. Quenching effects in SO_2 fluorescence monitoring instruments. *Environ. Sci. Technol.* 10:1246.

Karasek, F. W. 1976. Fluorescence spectrometry. *Research/Development* (January 28, 1976).

Lindqvist, Finn. 1978. Galvanic detection of sulfur dioxide in ambient air at trace levels by anodic oxidation. *J. Air Pollut. Control Assoc.* 28:138.

Nederbragt, G. W.; van der Horst, A.; and van Duyn, J. 1965. Ozone determination near an accelerator. *Nature* 206:87.

Okabe, H.; Splitstone, P. L.; and Ball, J. J. 1973. Ambient and source SO_2 detector based on a fluorescence method. *J. Air Pollut. Control Assoc.* 28:514.

Philips Electronics Industries, Inc. 1975. *Philips PW9700 SO_2 analyzer*. Philips Electronics Industries, Inc., Mahwah, NJ.

Shults, W. D. 1966. Coulometric methods. *Standard methods of chemical analysis*. Vol. 3, ed. F. J. Welcher, pp. 459-492. Princeton, NJ: D. Van Nostrand Co.

Staudner, R. 1976. Derivative spectroscopy. *Proc. Analyt. Div. Chem. Soc.* 212.

Stevens, R. K., and O'Keefe, A. E. 1970. Modern aspects of air pollution monitoring. *Anal. Chem.* 42:143A.

Thermo Electron Corporation. *Gas filter correlation spectrometer for ambient CO monitoring*, pp. 3-7. Thermo Electron Corporation, Hopkinton, MA.

U.S. Environmental Protection Agency, 36 Fed. Reg., no. 228, 22384-97 (November 25, 1971).

U.S. Environmental Protection Agency. 43 Fed. Reg., no. 121, 26962-86.

Winer, A. M.; Peters, J. W.; Smith, P. J.; and Pitts, J. N. 1972. Response of commercial chemiluminescence NO-NO_2 analyzers to other nitrogen-containing compounds. *Environ. Sci. Technol.* 6:348.

Chapter 9

Design of Surveillance Networks

Elements of Surveillance Networks

All ambient air surveillance networks are composed of several major elements that can be divided into two subsystems: a sensor subsystem and a data subsystem. The latter subsystem can be further divided into a data recording and transmission system, and a data processing system. This chapter will describe the elements of each subsystem, along with the basic considerations necessary for overall design. It should be remembered throughout this process that designing an ambient air surveillance network is a complex process requiring some experience. There are no easy procedures to follow that will eliminate all potential problems. This chapter will introduce you to a basic approach and will provide you with sufficient information to design basic air monitoring networks.

Defining Network Uses and Objectives

Before beginning considerations for system components for your surveillance network, the ultimate uses of the data must first be identified. The design of an effective network must establish these uses and employ them throughout the design process. For example, several of the major uses for sulfur dioxide (SO_2) data are:

1. Judging attainment of SO_2 NAAQS;
2. Evaluating progress in achieving/maintaining the NAAQS or State/local standards;
3. Developing or revising State Implementation Plans (SIPs) to attain/maintain NAAQS; evaluating control strategies;
4. Reviewing new sources;
5. Establishing baseline air quality levels for preventing significant deterioration (PSD) and for air quality maintenance planning (AQMP);
6. Developing or revising national SO_2 control policies, e.g., new source performance standards (NSPS), tall stacks, supplementary control systems (SCS);
7. Providing data for model development and validation;
8. Providing data to implement the provisions of the Energy Supply and Environmental Coordination Act (ESECA) of 1974;
9. Supporting enforcement actions;
10. Documenting episodes and initiating episode controls;
11. Documenting population exposure and health research;
12. Providing information to:
    a. public air pollution indices; and
    b. city/regional planners, air quality policy/decision makers - for activities related to programs such as air quality maintenance planning (AQMP), prevention of significant deterioration (PSD), and the preparation of environmental impact statements.

These uses are broad and program-oriented and, therefore, serve to delineate the direction of the whole program. The second step in the design process is to generate a list of specific objectives from the above design criteria. To continue the example of SO_2, some of the specific objectives and the associated data uses are as follows (*data use* numbers refer to above list of SO_2 data uses).

1. Determination of peak concentrations in urban areas
    - major data uses: 1, 2, and 3.
    - other data uses: 8, 9, and 12.
2. Determination of the impact of individual point sources in multisource urban settings
    - major data uses: 3, 4, 6, 8, and 9.
    - other data uses: 12.
3. Determination of the impact of isolated point sources
    - major data uses: 3, 4, 6, 8, and 9.
    - other data uses: 5 and 12.
4. Assessment of interregional SO_2 transport
    - major data uses: 2, 3, 5, and 12.
5. Determination of base concentrations in areas of projected growth
    - major data uses: 5 and 12.
6. Initiation of emergency episode abatement actions
    - major data uses: 10 and 12.
7. Determination of population exposure
    - major data uses: 11 and 12.
8. Assessment of background concentrations in rural areas
    - major data uses: 5 and 12.
    - other data uses: 2 and 3.

Having identified specific objectives, there are some additional general considerations that must be discussed before beginning the actual design of the two subsystems. It should be remembered, however, that these objectives should be the basis for the total design of the surveillance network. They should be prioritized on the basis of several points, including legal requirements, topography, population data, source characteristics, administrative and political concerns, and, of course, cost. Some of these topics will be covered in the section following on specific siting procedures. By organizing these objectives by priorities, it should be possible to minimize expense while still meeting the identified needs.

Sensor Subsystem

Having established the "why" of our monitoring network, we can now begin to choose a sensor system. The first step in choosing an appropriate sensor is to identify what is to be monitored. If we are monitoring for more than one pollutant, it may be necessary to have more than one type of shelter probe and monitoring location. For example, measurements made in a street canyon may be valid for determining maximum CO concentrations, but probably are not valid for regional SO_2 measurements. This problem centers around the spatial scale of representativeness of a site. A spatial scale of representativeness is the volume of air surrounding an air monitoring site that can be described by measurements made at the site.

It is important to be aware of the distinction between the spatial scale *desired* to be represented by a measurement, and the spatial scale *actually* represented by that measurement The spatial scales and the corresponding dimensions characterizing each are:

- **Microscale.** Ambient air volumes with dimensions ranging from meters up to about 100 meters are associated with this scale.
- **Middle Scale.** This scale represents dimensions of the order from about 100 meters to 0.5 kilometers and characterizes areas up to several city blocks in size.
- **Neighborhood Scale.** Neighborhood scale measurements would characterize conditions over areas with dimensions in the 0.5 to 4.0 kilometer range.
- **Urban Scale.** Urban scale measurements would be made to represent conditions over areas with dimensions on the order of 4 to 50 kilometers.
- **Regional Scale.** Conditions over areas with dimensions of as much as hundreds of kilometers would be represented by regional-scale measurements. These measurements would be applicable mainly to large homogeneous areas, particularly sparsely populated areas.
- **National and Global Scales.** These measurement scales represent concentrations characterizing the nation and the globe as a whole.

These dimensions are approximate, but provide useful divisions for defining the final site. Within each scale, there may be more than one site required to define the area: for pollutants that have large, individual sources; for areas with steep concentration gradients (concentrations changing rapidly over relatively short distances); and for reactive pollutants. The concentration gradients would be determined from previous sampling or dispersion modeling.

The choice of "what" will be monitored should be based on the needs, uses, and objectives that we defined. At this stage, we should prioritize these needs based on the individual considerations of each case. Each case will represent a unique situation. Some common considerations include:

- Pollutants with legal standards;
- Available resources, material, and personnel;
- Political factors;
- Problem pollutants - expected hazards.

The importance given each of these factors will vary with each case.

Monitoring Methods

Once we have decided what we're going to monitor, we can move to the next step in designing the sensor subsystem- how are we going to monitor? If a criteria pollutant is being monitored, one of the EPA Federal reference methods should be considered. These are included in the appendix of this manual. Also available from EPA* is the "List of Designated Reference and Equivalent Methods" which provides a current listing of all EPA-approved methods for measuring ambient concentrations of criteria air pollutants. There are cases where you will be required to use a reference or equivalent method, such as when monitoring for State

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* http://www.epa.gov/ttn/amtic/criteria.html

Implementation Plans (SIPs) or most monitoring required under the Prevention of Significant Deterioration (PSD) regulations (40 CFR 51.24). If use of the EPA Federal reference or equivalent methods is not required, it is important to ascertain if the method of sampling is specified by a law or statute. If the data is to be used in legal proceedings, this fact may be of considerable importance. Other sources of analytical methods exist, including the National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods and *Methods of Air Sampling and Analysis*, published by the American Public Health association.

If using an automated or instrumental method, maintenance and calibration are important. It can be difficult to estimate time and money costs for these items, but there are sources of information available. For maintenance, the manufacturer should be able to provide some estimates. It has been noted that these estimates can be somewhat optimistic. Another source may be others who are or who have used the instrument. Experience can be an accurate, if time-consuming, instructor. There may even exist previous in-house maintenance records that will provide valuable information.

For calibration requirements, again the manufacturer should provide some estimates. However, there may be legal requirements such as those specified in the appendices to 40 CFR 58 detailing minimum requirements for PSD or SIP monitoring. Calibration guidance is also contained in the *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volumes I and II. The time requirements for calibration and the frequency of audits may vary as in-house records establishing performance are developed. For example, with a new instrument, calibration may be weekly for the first 3 months, then biweekly with weekly audits, and, finally, monthly with biweekly audits as performance parameters are documented for that particular instrument. Of course, detailed records of maintenance and calibration must be maintained.

Monitoring Stations

There are five basic types of monitoring stations which comprise existing surveillance networks. Preexisting sites from some or all of these station types may be used when developing a new surveillance network.

1. SLAMS — State and Local Air Monitoring Stations
    a. Required for SIP networks
    b. Data used for local air pollution control purposes
    c. Operated by State or local air pollution control agencies with the approval of the appropriate EPA regional office
2. NAMS — National Air Monitoring Stations
    a. Subset of SLAMS
    b. Primarily the data used for national policy decisions
    c. Operated by State or local air pollution control agencies with the approval of EPA's Office of Air Quality Planning and Standards
3. PAMS — Photochemical Assessment Monitoring Stations
    a. Track trends in ozone precursor emissions
    b. Primarily used for regional-scale ozone assessment

   c. Operated by State or local air pollution control agencies with the approval of EPA's Office of Air Quality Planning and Standards

4. IMPROVE — Interagency Monitoring of Protected Visual Environments
   a. Provide long-term measurements of $PM_{2.5}$ and other visibility-related observables in National Parks and Wildernesses
   b. May qualify as background or transport sites for $PM_{2.5}$ networks
   c. Operated by State or local air pollution control agencies with the approval of EPA's Office of Air Quality Planning and Standards

5. SPMS — Special Purpose Monitoring Stations
   a. Not required for SIP networks
   b. Operated by State or local air pollution control agencies
   c. No EPA approval necessary unless data are used for SIP purposes
   d. Example: PSD — Prevention of Significant Deterioration Stations

Siting

Having established "why," "how," and "what," the next step in designing the sensor system is "where." This topic involves properly siting the sensor to collect representative data. Since 1975, the EPA has issued several documents detailing a procedure for selecting the proper site for a pollutant for different purposes. By following the procedure outlined in these documents, it is possible to logically select a proper site for a particular purpose and to clearly document the procedure followed. This allows for a subsequent audit or review of the site selection process to react to changing conditions without having to duplicate earlier work. The documents available are:

"Selecting Sites for Carbon Monoxide Monitoring."
September 1975. EPA 450/3-75-077.

"Optimum Site Exposure Criteria for SO_2 Monitoring."
April 1977. EPA 450/3-77-013.

"Site Selection for the Monitoring of Photochemical Air Pollutants."
April 1978. EPA 450/3-78-013.

"Enhanced Ozone Monitoring Network Design and Siting Criteria Guideline Document."
November 1991. EPA 450/4-91-033.

"Guideline on Ozone Monitoring Site Selection."
April, 1998. EPA 454/R-98-002.

"Guidance for Siting Ambient Air Monitors Around Stationary Lead Sources."
August 1997. EPA 454/R-92-009R.

"Selecting Sites for Monitoring Total Suspended Particulates."
June 1977. EPA 450/3-77-018.

"Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10}."
December 1997. Finalized Version. U.S. EPA. Research Triangle Park, NC.

Generally speaking, sites should be designed to meet at least one of six basic monitoring objectives:

1. Determine highest concentrations expected to occur in the area covered by the network.
2. Determine representative concentrations in areas of high population density.
3. Determine the impact on ambient pollution levels of significant sources or source categories.
4. Determine general background concentration levels.
5. Determine the extent of Regional pollutant transport among populated areas, and in support of secondary standards.
6. Determine the welfare-related impacts in more rural and remote areas (such as visibility impairment and effects on vegetation).

However, it should also be noted that each siting case may be unique and the "proper site" is not necessarily an absolute, fixed item. Given the same background information and a similar siting objective, two "experts" may arrive at different site locations. Often there is a lack of needed information, and even under the best of conditions, siting sensors involves the abstract correlation of large amounts of chemical, meteorological, geographical, and political information. There are no "instant experts" or short cuts to actual experience. However, by following a set of logical procedures, it is possible to arrive at a site location that will adequately meet the program objectives and allow for concise documentation of the selection process.

Section 40 CFR 58.20 requires an annual review of each surveillance network. These changes to the EPA monitoring regulations were promulgated August 12, 1994. In addition to organizing and revising almost all of the EPA ambient monitoring regulations into one section of the *Code of Federal Regulations*, there is also siting and network design guidance contained in Appendix D of these regulations. The guidance in Appendix D is consistent, both in approach and content, with that contained in the individual siting documents. The documents contain more detail and greater depth than is possible in the regulations.

The location of the sensor is only part of the answer to the "where" of monitoring. Besides locating the sensor, it is also important to obtain a correct probe location. In this instance, "probe" refers to the actual mechanical portion of the sensor where sampling occurs. The location of the probe depends on the chemistry of the specie sampled and, of course, the monitoring objectives. Guidance on probe location is contained in the siting documents and also in Appendix E of 40 CFR 58. By adopting a uniform probe location for each pollutant, comparison of the data from different projects and times is simplified. As mentioned earlier for sensor location, the probe location may vary for each pollutant and each objective. The final choice would represent an optimal compromise between needs and resources.

As part of our network design system, we have specified the "why," "how," "what," and "where" of our sensor package and network. There are two remaining systems of the data subsystem to define: the recording and transmission system, and the data processing system. Both of these systems are concerned with the collection and processing of the data or signals produced by the sensor system, and there is some overlapping. It is important to spend time on properly planning each of these, as a great deal of resources have been expended needlessly in these areas. We will discuss each separately.

Data Subsystem

Data Recording

The first part of this subsystem concerns data recording. We may have an electrical signal from one or more instruments from one or more locations, or a set of analytical results from manual methods. In either case, the data must be recorded. If we have an electrical output from an analyzer, several choices are available. We can manually read a meter and record data, use a strip chart recorder, record on punch cards or paper tape, or record on machine-readable magnetic tape or discs. When designing data systems, the major problem is usually optimizing man and machine interactions. In some cases you may have excess manpower and little automation, while the opposite may be true in other cases. Therefore, the first step in this process is to identify the needs. Is data required or produced continuously, are all outputs from analyzers matched, is there a mix of manual and automated sensor systems, and, finally, is the data for immediate or future use? If the data is to be used for a daily Pollutant Standards Index or to operate a Supplemental Control System, there may be a need for automated recording and processing. However, if the data is to be used for annual trend reports, monthly strip charts may be the best choice.

With the needs identified, available resources should be assessed. This assessment allows a realistic data system to be designed. Again, the goal here should be to meet the program requirements while minimizing costs. Too often, overly elaborate systems have been designed with no consideration of needs. Needs must be prioritized, separating necessary items from desirable, but less essential, components. The total mix of components in a system must also be accounted for in the design. If grounding and interface problems exist, it may be advantageous to solve these separately and use one data logger for each station rather than separate strip charts or other separate recorders. Unfortunately, no hard and fast rules exist to assist in making these decisions. Advice should be sought from competent systems engineers or other personnel familiar with the equipment involved.

Data Transmission

As with the data recording subsystem, it is important not to overdesign the data transmission system and thus waste resources. In reviewing the data needs, speed of utilization must be determined. If it arrives quickly, but is not going to be processed for a month, a simpler system may be more cost-effective. The best rule to follow is to make it as simple and inexpensive as is feasible. The choice between on-site pickup of data versus telemetered data will be based on data needs, resources available, and the existing network. Signal conditioning must be designed by a competent electrician to avoid later problems.

Data processing comprises the final part of the Data Subsystem. The data processing system involves the selection of a format, validation, analysis storage, and retrieval. A format is simply a systematic listing of the data recorded. All ambient air quality data for SO_2, CO, O_3, NO_2, Pb,

PM_{10}, and $PM_{2.5}$ must be coded into the format used by the AIRS Air Quality Subsystem, or AQS. This subsystem contains all the air quality data that used to be in the SAROAD system and includes air toxic data as well as trace metals data from the National Filter Analysis Network.

Data Validation

After the data are recorded using the chosen format, validation can begin. The validation should be performed by an air pollution professional with intimate knowledge of the sensors, recording system, transmission system, as well as any peculiarities of the air pollution problem in the area. This validation should be performed at the lowest level possible to permit the maximum possible recovery of valid data. For example, if there is a two-week period in a month's data that has values three times the "normal" values, several possibilities exist. The data may have been analyzed by a substitute while the usual person was on vacation and a factor of three may have been dropped from the denominator of an equation; the instrument may have malfunctioned; meteorological conditions (poor dispersion, stable atmosphere, low mixing depth) may have resulted in increased concentrations. Obviously, in the first case the data can be corrected by including the factor and recomputing; in the second case the data probably will have to be invalidated unless an accurate correction factor can be determined; and in the third case, the data are correct. Only an air pollution professional would recognize the difference, and the closer that person is to the network, the less expensive this process will be. Computer validation is possible to identify outliers, or abnormal values, but manual checking is needed to perform final validation.

Data Analysis

After the data have been validated, the final analysis can be performed. Depending on the nature of the data and the final data use, a variety of statistical procedures can be used. These techniques and their use with aerometric data are complex and a professional statistician should be consulted. The type of analysis may be dictated by the standard (requiring arithmetic or geometric means), or the data (long-term trends represented by log-normal distributions). Advice from a statistician can help prevent erroneous conclusions.

Storage of the data and/or the samples should prevent physical deterioration, provide a logical system, and should be secure to provide a legal chain-of-custody. If using thermally sensitive chart paper, storage in a warehouse subject to elevated daytime temperatures would prove problematic and soon the records would be uniformly gray. A logical system provides continuity and, along with a secure storage area and sign-off sheets, helps establish a legal chain-of-custody for records.

The storage system should not, however, prevent easy access to the data by the proper personnel. Retrieval procedures should not be overly complex, yet must provide a systematic procedure ensuring data security. In automated systems, provisions can be made to restrict access with confidential identification codes or restricted data discs.

After designing the sensor and data subsystems, one final item requiring allocation of resources exists. This is to incorporate a comprehensive quality control program to assure the data produced are correct. Guidance on these programs is contained in the Quality Assurance Handbooks mentioned earlier and in Appendices A and B of 40 CFR 58. Without adequate quality control of each subsystem, the question of ultimate data validity may be impossible to answer.

$PM_{2.5}$ Network Design Considerations

The material presented so far in this chapter provides a general overview of network design and site selection for any criteria pollutant. There are, however, certain special considerations in the case of particulate monitoring which must be addressed separately. [NOTE: This is a very brief overview of some of the unique elements of $PM_{2.5}$ network design and siting. These are covered at length in SI:433, *Network Design and Site Selection for Monitoring $PM_{2.5}$ and PM_{10} in Ambient Air*, as well as in an instructional video available from EPA's Air Pollution Training Institute -- U.S. Environmental Protection Agency, Education and Outreach Group (MD-17), Research Triangle Park, NC 27711. PHONE: 919-541-3724. FAX: 919-541-3513.]

In July of 1997, the Federal Register presented the new NAAQS for particulate matter, introducing required monitoring of $PM_{2.5}$, or particles 2.5 microns or smaller in diameter. These NAAQS focus on particulates in this range because studies have shown them to be the most threatening to human health and well-being, due to their tendency to be absorbed or penetrate deeply into human lung tissue. Based on the epidemiological data used to set the standards, $PM_{2.5}$ monitoring networks are designed somewhat differently and engender some new concepts, among them **community-oriented monitoring** and **spatial averaging**. $PM_{2.5}$ networks are intended to monitor the exposure levels of people where they live, work, and play.

The basic planning unit for $PM_{2.5}$ monitoring is the Monitoring Planning Area, or MPA. An MPA is a contiguous geographic area with established, well-defined boundaries. These boundaries may include aggregates of:

- Counties
- Zip code regions
- Census blocks
- Established air quality management districts

Community-Oriented Monitoring

Community-oriented monitoring sites are intended to measure ambient $PM_{2.5}$ concentrations representative of areas at least 0.5 km in diameter. These measurements should approximate both the short- and long-term exposures of people within an area of neighborhood to urban-scale zone of representation. Data from these sites are eligible for comparison to the annual and 24-hour $PM_{2.5}$ NAAQS, as long as they are outside the zone of influence of a specific emitter. Data collected from sites that are representative of relatively unique population-oriented micro-scale and middle-scale impact sites (that is, within the zone of influence of a specific emitter) are ONLY eligible for comparison to the 24-hour NAAQS.

In addition, $PM_{2.5}$ monitoring introduces the concept of the **core site**, which is sited to represent community-wide air quality, and is a subset of the SLAMS network.

Community Monitoring Zones

The community monitoring zone, or CMZ, is applicable only to $PM_{2.5}$. It is intended to represent the spatial uniformity of $PM_{2.5}$ concentrations, and should have dimensions of 4 to 50 km with boundaries defined by existing political demarcations with population attributes. Each CMZ would ideally equal the collective zone of representation of one or more community-oriented monitors within that zone. Ideally, an MPA should be completely covered by one or more contiguous CMZs when spatial averaging (see below) is used.

More than one monitor may be needed to evaluate the spatial uniformity of $PM_{2.5}$ concentrations and to accurately calculate the spatial average for comparison with the annual NAAQS.

Spatial Averaging

The annual $PM_{2.5}$ standard allows annual average concentrations among eligible monitors within a CMZ to be averaged. This provides an indicator of average $PM_{2.5}$ air quality which may be more reflective of the exposure levels of the people who live, work, and play in that area. Annual average concentrations from $PM_{2.5}$ monitors are not intended to represent hot spots.

In order to be eligible for inclusion in a CMZ's spatial average, a site must first represent a neighborhood or larger spatial measurement scale. Then, the annual averages for that site must be within ± 20% of the CMZ-wide average on an annual basis, be influenced by similar sources, and be reasonably correlated ($r > 0.6$) on a daily basis.

In addition, there are several other factors which should be considered when placing $PM_{2.5}$ monitors within a CMZ for spatial averaging, including the following:

- Year-to-year variability of each site
- Effect of changing emissions over time
- Relative distribution of concentrations among the sites
- Spatial patterns within the CMZ
- Similarities and differences in speciated $PM_{2.5}$, and
- Relationships between population density and air quality patterns.

Other Siting Considerations

In addition to the new elements of network design required by the new particulate matter standards, there are also external monitor placement requirements to consider. These external siting criteria refer to the environs surrounding a measurement location.

- Exposure – Large nearby buildings and trees extending above the height of the monitor may present barriers or deposition surfaces for PM. Certain trees may also be sources of PM in the form of detritus, pollen, or insect parts. Locate monitors at a safe distance away from these obstacles.
- Distance from Nearby Emitters – The monitor should be outside the zone of influence of sources located within the designated zone of representation for the monitor site. In this instance, for example, the monitor on the factory "fence post" would not be a good siting choice.
- Proximity to Other Measurements – Other air quality and meteorological measurements can aid in the interpretation of high PM levels, and, with all other considerations being equal, $PM_{2.5}$ sites should give preference to existing sites that make other measurements.

References

Ball, R. J., and G. E. Anderson. April 1977. *Optimum Site Exposure Criteria for SO_2 Monitoring* EPA 40/3-77-013, U.S. EPA, Research Triangle Park, NC.

Ludwig, F. L., and J. H. S. Kealoha. September 1975. *Selecting Sites for Carbon Monoxide Monitoring*. EPA 450/3-77-018. U.S. EPA, Research Triangle Park, NC.

Environmental Protection Agency. November 1991. *Enhanced Ozone Monitoring Network Design and Siting Criteria Guideline Document*. EPA 450/4-91-033. U.S. EPA, Research Triangle Park, NC.

Environmental Protection Agency. December 19, 1997. *Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10}*. Finalized Version. U.S. EPA, Research Triangle Park, NC.

Environmental Protection Agency. March 31, 1998. *SI:433. Network Design and Site Selection for Monitoring $PM_{2.5}$ and PM_{10} in Ambient Air.*

Environmental Protection Agency. April 1998. *Guideline on Ozone Monitoring Site Selection.* EPA 454/R-98-002.

Environmental Protection Agency. August 1997. *Guidance for Siting Ambient Air Monitors Around Stationary Lead Sources*. EPA 454/R-92-009R.