APTI Course 482

Sources and Control of Volatile Organic Air Pollutants

Volatile Organic Compound (VOC)

"…any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions."

---40CFR51.100

Course Objective

- Provide information on sources of VOCs and techniques for controlling their emission
- Focus is on reduction of VOCs for attaining or maintaining ozone NAAQS

Course Topics

Topic	Chapter
Properties and Fundamentals	2
Source Measurement Techniques	3
National Sources and the Regulatory Approach	4
Surface Coating	5
Graphic Arts	6
Calculating the VOC Content of Paints and Inks	7

Course Topics

Topic	Chapter
Petroleum Refining	8
Petroleum Product Storage and Distribution	9
Degreasing	10
Dry Cleaning	11
Liquid Asphalt	12
Introduction to Control Technology	13

Chapter 2

Properties and Fundamentals

Importance of Organic Compounds

- Volatile compounds contribute to the formation of ozone and photochemical oxidants
- Compounds can have toxic effects on plants and animals

Topics Covered

- Review of organic chemistry
- Formation of ozone and photochemical smog
- Properties of organic vapors

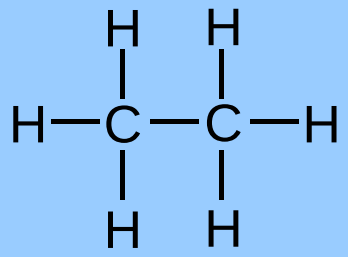
Review of Organic Chemistry

- Chemistry of the compounds of carbon
- Number of organic compounds exceeds 8 million
- Number of inorganic compounds is about 300,000

Characteristics of the Carbon Atom

- Atomic number = 6
- Atomic weight = 12
- Total electrons = 6
- Valence electrons = 4
- Forms covalent bonds
  - Single
  - Double
  - Triple

Molecular, Structural and Semi-Structural Formulas

Molecular Formula	*Structural Formula*	*Semi-structural Formula*
C_2H_6		$CH_3—CH_3$

Hydrocarbons

Compounds formed only from carbon and hydrogen

- Alkanes
- Alkenes
- Alkynes
- Cyclic compounds

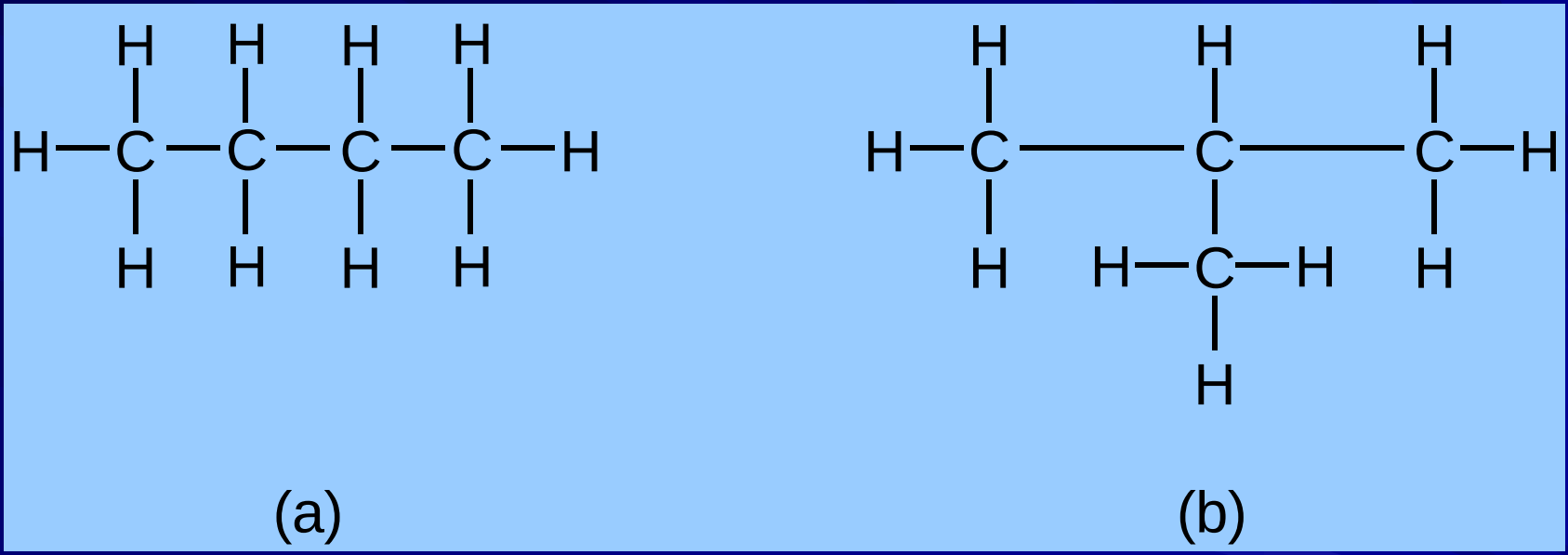
Alkanes

Carbon atoms linked only by single bonds

General formula: C_nH_{2n+2}

Methane (CH_4)
Ethane (C_2H_6)
Propane (C_3H_8)
Butane (C_4H_{10})
Pentane (C_5H_{12})

Isomers of Butane



n-butane

i-butane

Isomers

Compounds with the same molecular formulas, but with different structures

- All alkanes with four or more carbon atoms exist as isomers
- Alkanes with five or more carbon atoms exist as more than two isomers

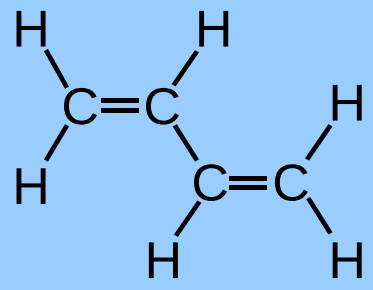
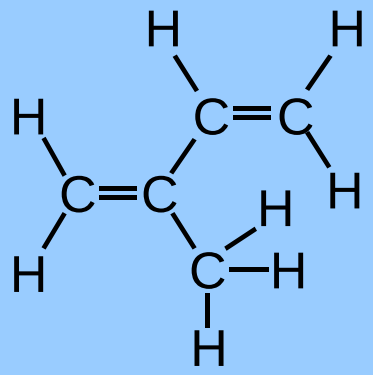
Alkenes

Hydrocarbons that contain one double bond

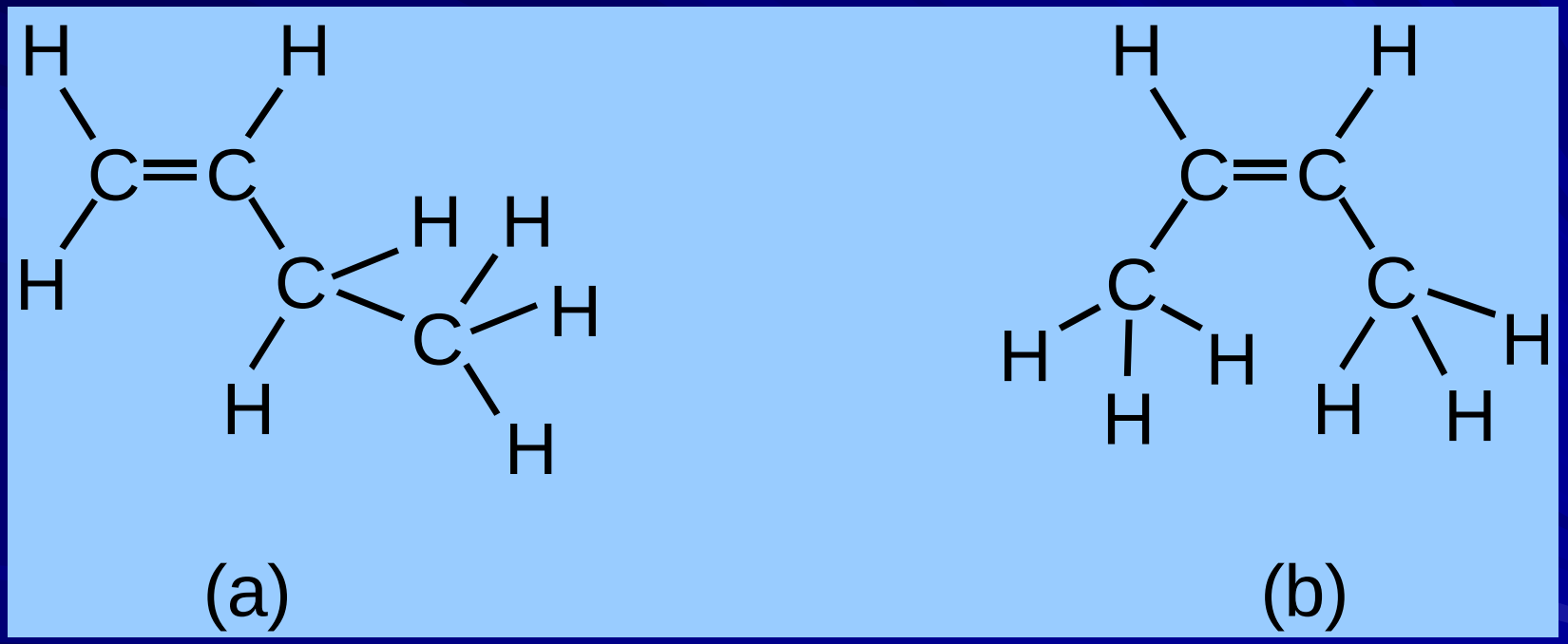
General formula: C_nH_{2n}

Ethylene (C_2H_4)
Propylene (C_3H_6)
Butylene (C_4H_8)
Pentylene (C_5H_{10})

Diolefin Compounds

Molecular Formula	*Name*	*Structural Formula*	*Semi-structural Formula*
C_4H_6	butadiene		$CH_2{=}CH{-}CH{=}CH_2$
C_5H_8	2-methyl butadiene		$CH_2{=}C(CH_3){-}CH{=}CH_2$

Butylene Isomers



Alkynes

Hydrocarbons that contain one triple bond

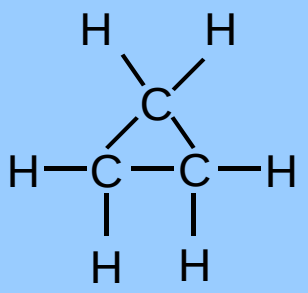
General formula: C_nH_{2n-2}

Ethyne (C_2H_2)
Propyne (C_3H_4)
Butyne (C_4H_6)
Pentyne (C_5H_8)

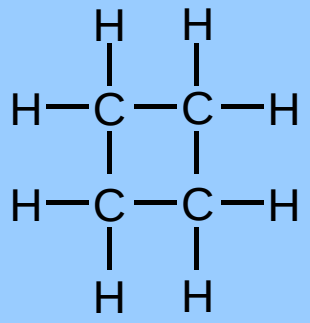
Cyclic Compounds

- Cycloparaffins
- Aromatic hydrocarbons

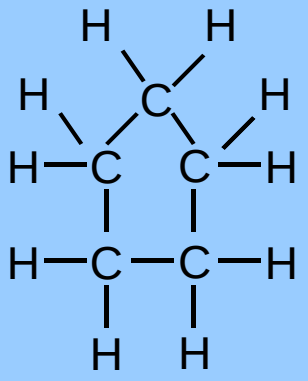
Examples of Cycloparaffin Compounds



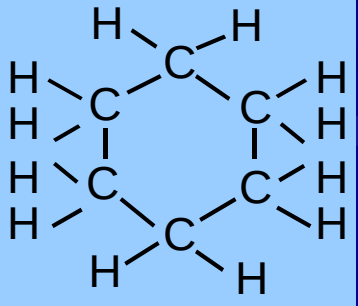
Cyclopropane



Cyclobutane

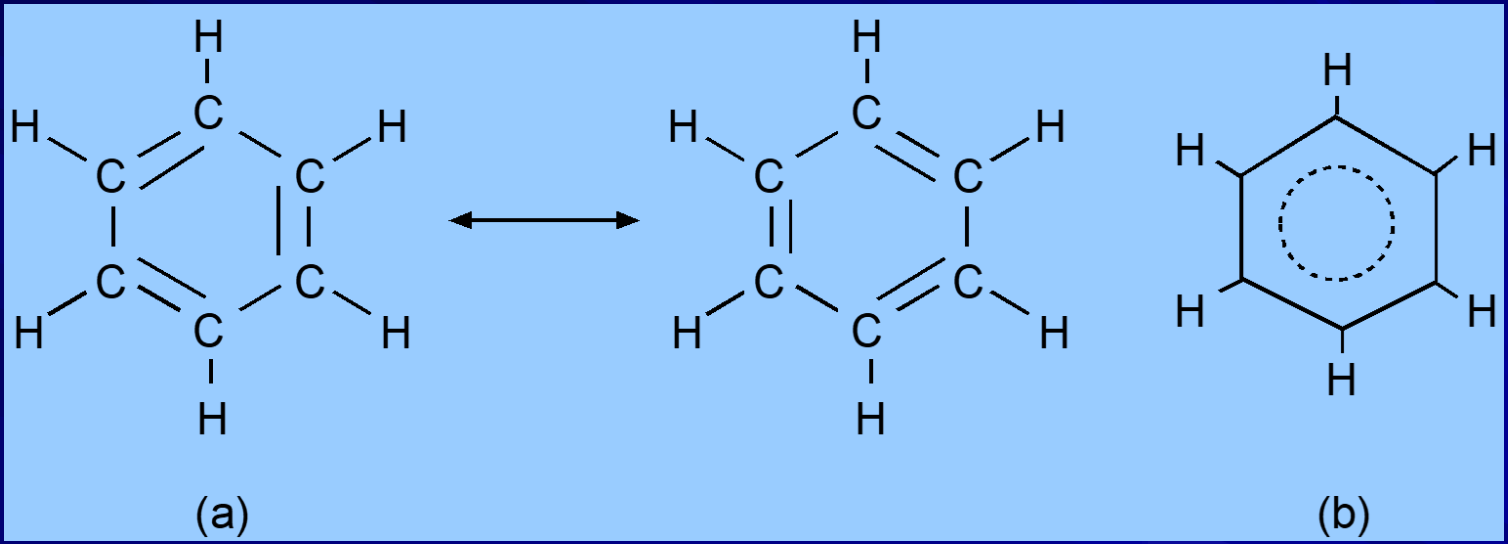


Cyclopentane

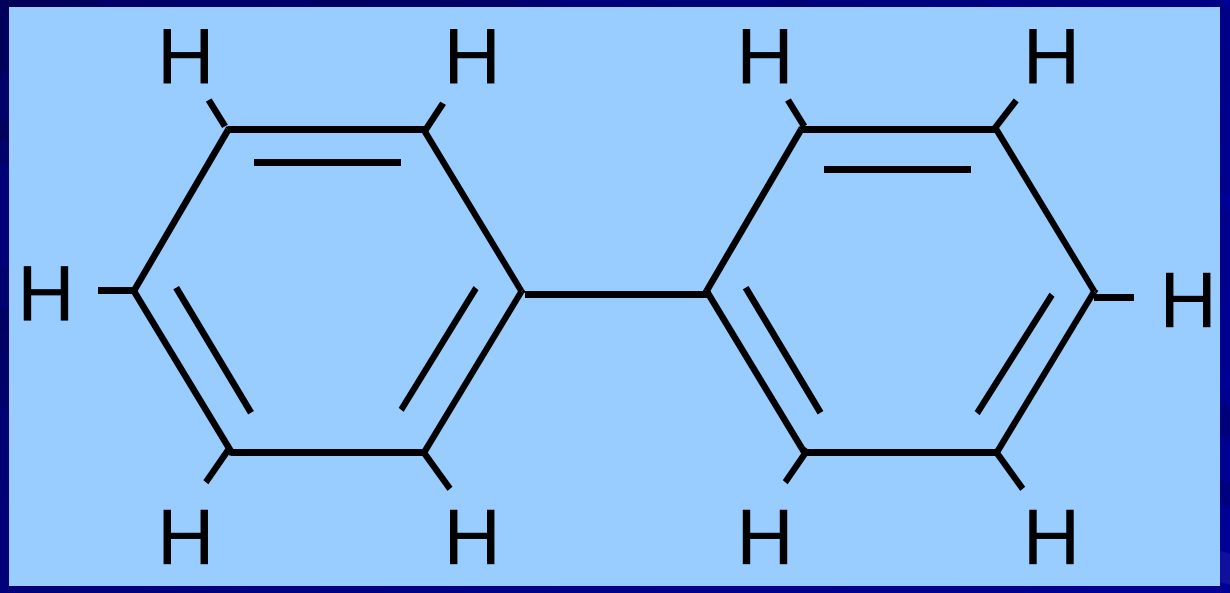


Cyclohexane

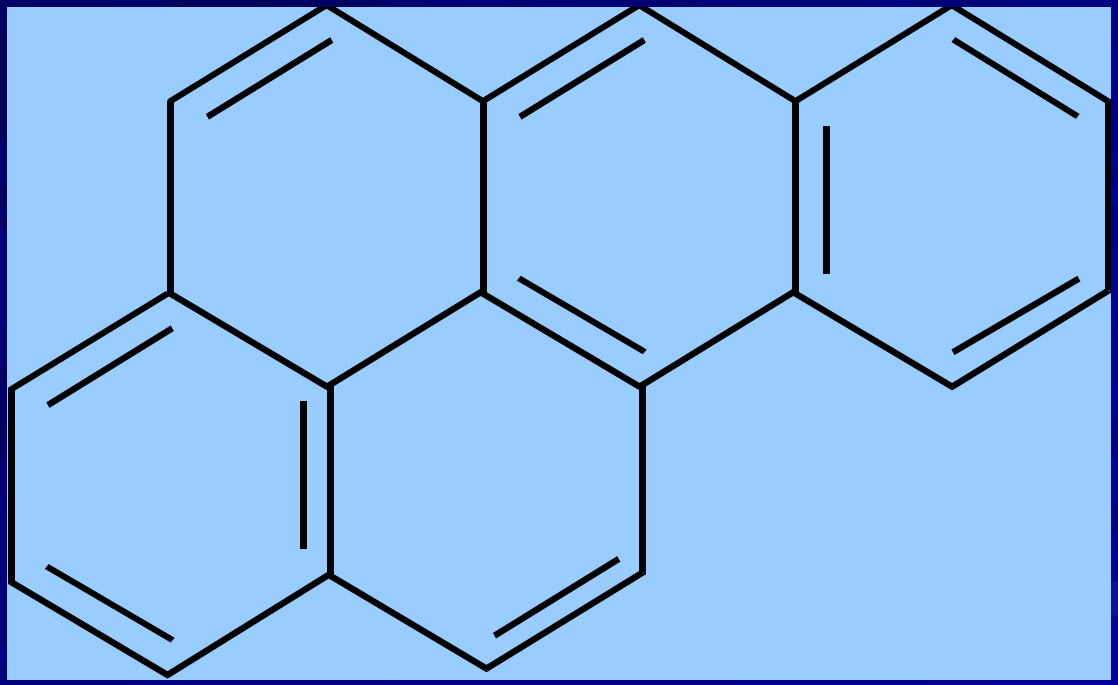
Benzene Structure



Biphenyl



Benzo (α) pyrene



Nomenclature

1 carbon	meth-	CH_4	methane
2 carbons	eth-	C_2H_6	ethane
3 carbons	prop-	C_3H_8	propane
4 carbons	but-	C_4H_{10}	butane
5 carbons	pent-	C_5H_{12}	pentane
6 carbons	hex-	C_6H_{14}	hexane
7 carbons	hep-	C_7H_{16}	heptane
8 carbons	oct-	C_8H_{18}	octane

Functional Groups

Alcohols	-OH
Amines	$-NH_2$
Mercaptans	-SH
Chlorides	-Cl

Location of Substitution

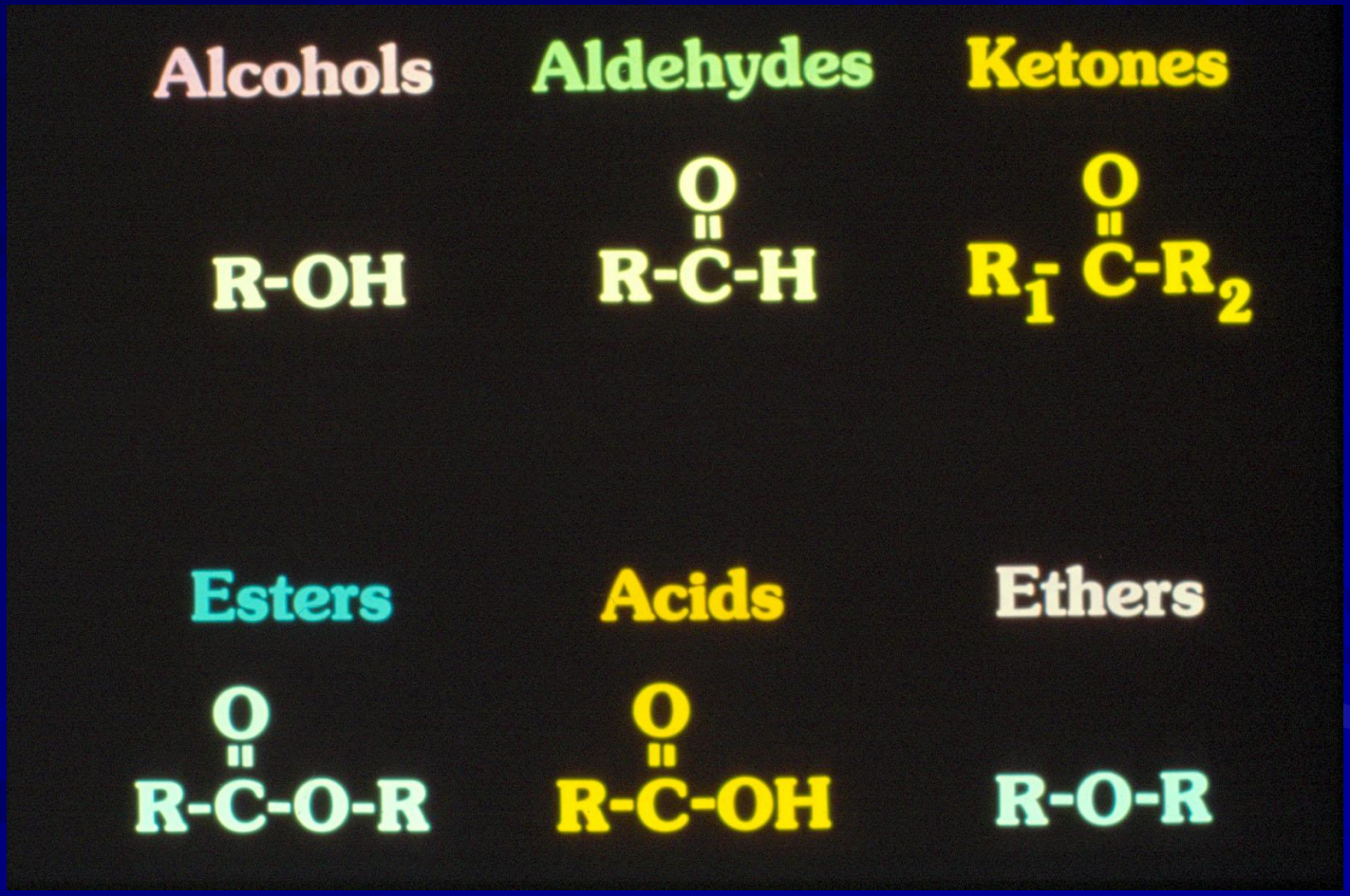
1,1,1-trichloroethane

2-propylamine

1,1,2,2-tetrachloroethylene

Perchloroethylene

Functional Groups Containing Oxygen



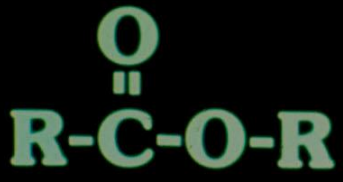
Alcohols

R-OH

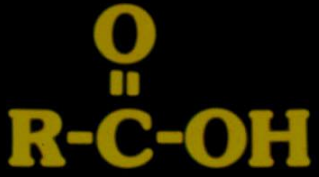
Aldehydes

Ketones

Esters



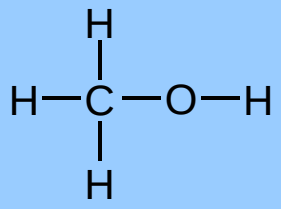
Acids



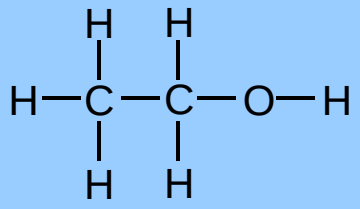
Ethers

R-O-R

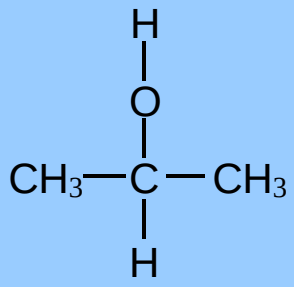
Common Alcohols



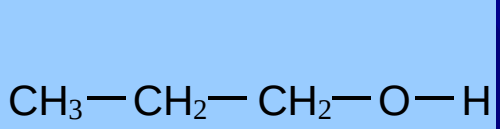
Methyl alcohol



Ethyl alcohol

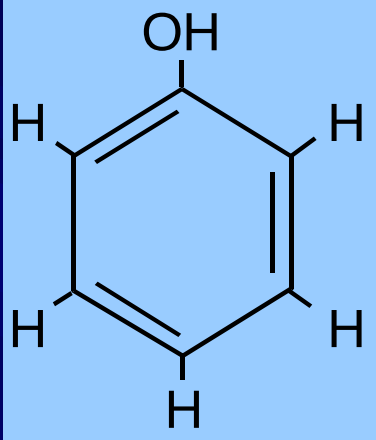


Isopropyl alcohol (Isopropanol)

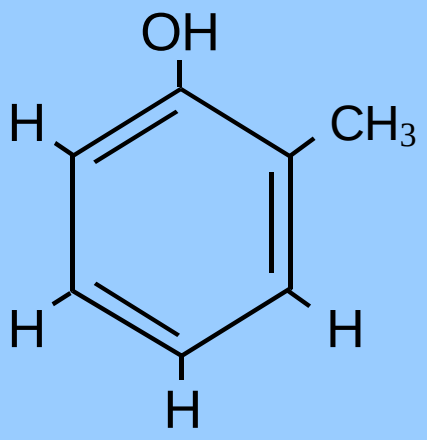


n-propyl alcohol

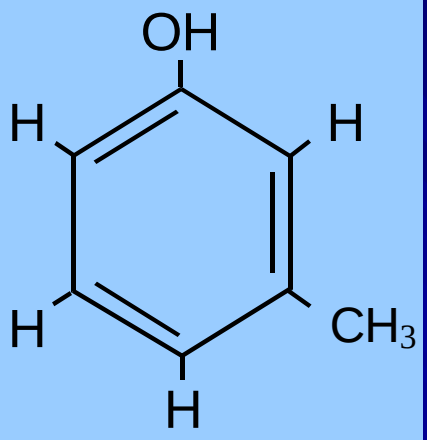
Phenols



Phenol

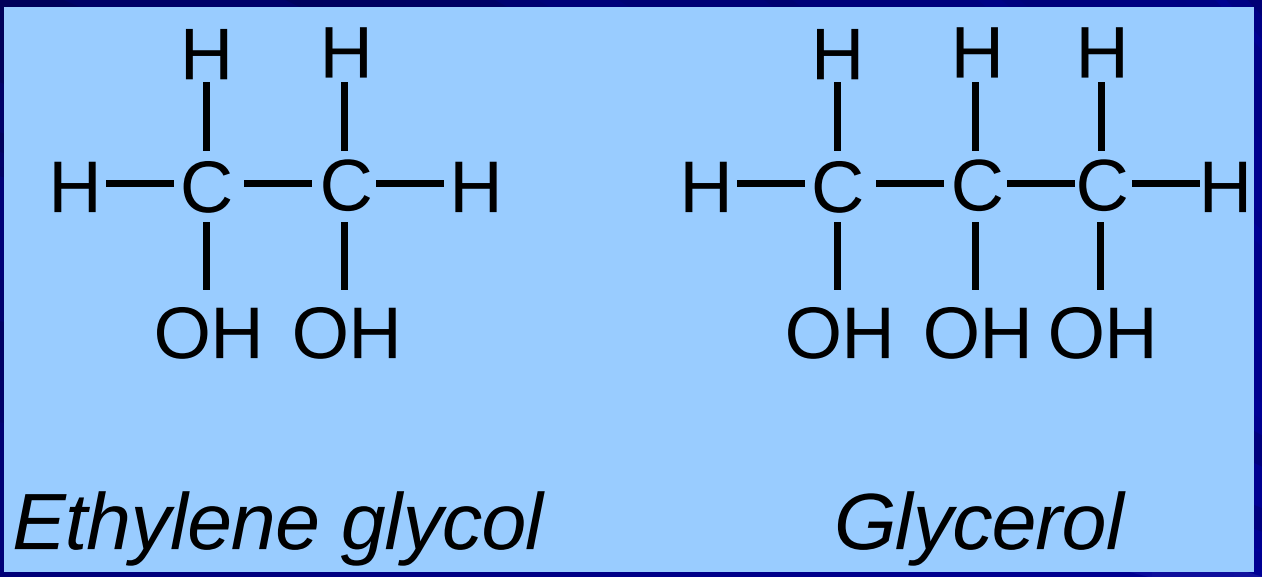


Ortho-cresol
(o-cresol)



Meta-cresol
(m-cresol)

Polyhydric Alcohols



Ethylene glycol *Glycerol*

Alcohols

Aldehydes

Ketones

Esters

Acids

Ethers

Ether Compounds

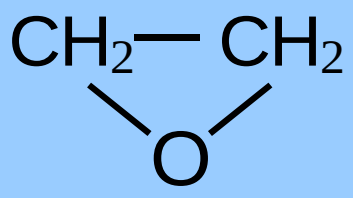
- Diethyl ether

  $CH_3CH_2\text{-}O\text{-}CH_2CH_3$

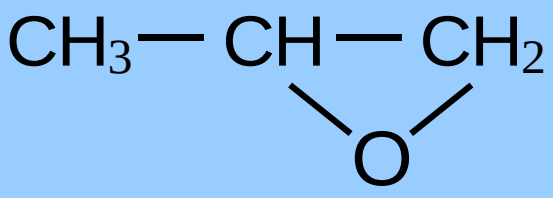
- Methyl ethyl ether

  $CH_3\text{-}O\text{-}CH_2CH_3$

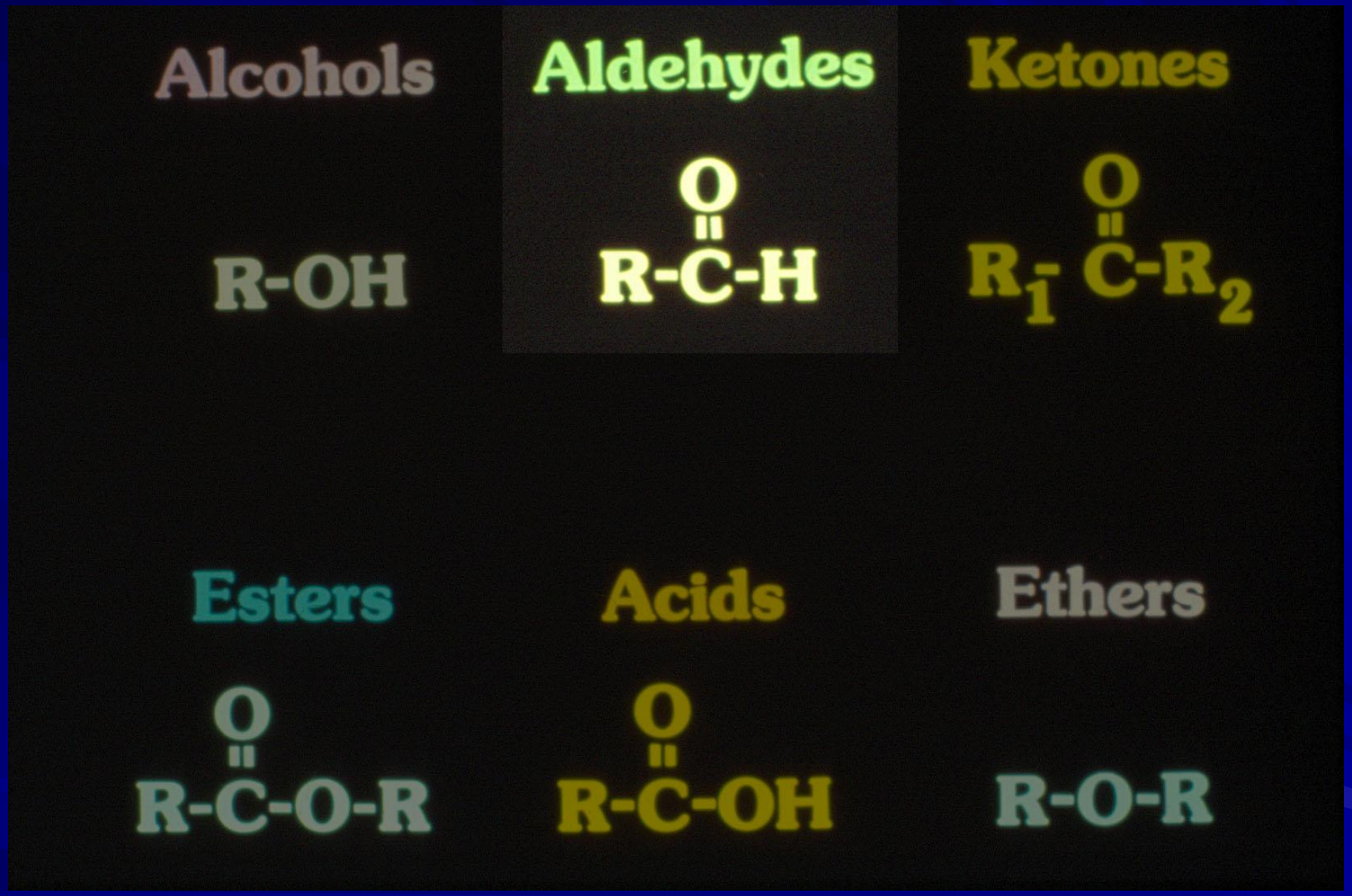
Cyclic Ethers



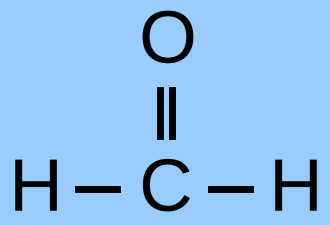
Ethylene oxide



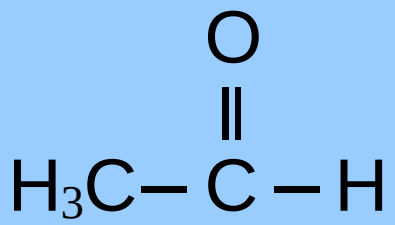
Propylene oxide


Alcohols
R-OH
Aldehydes
O
R-C-H
Ketones
O
R1 C-R2
Esters
O
R-C-O-R
Acids
O
R-C-OH
Ethers
R-O-R

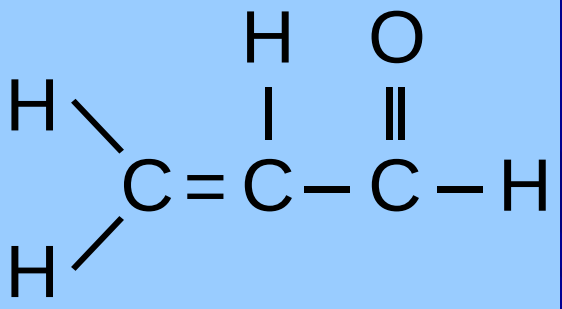
Aldehydes



Formaldehyde



Acetaldehyde



Acrolein

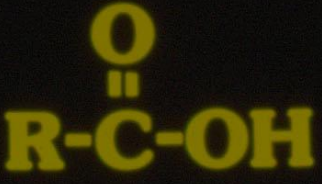
Alcohols

Aldehydes

Ketones

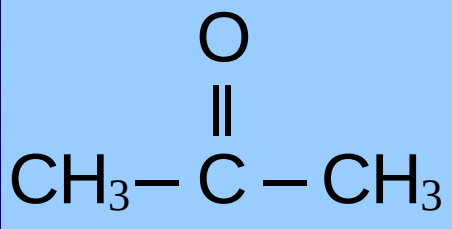
Esters

Acids

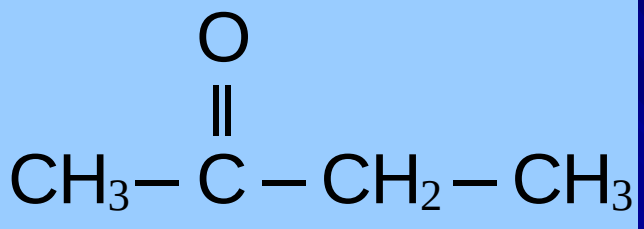


Ethers

Ketones



Acetone



Methyl ethyl ketone (MEK)

Alcohols

Aldehydes

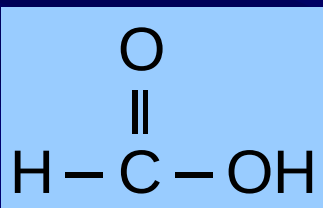
Ketones

Esters

Acids

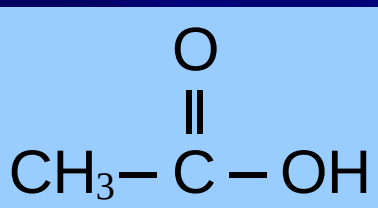
Ethers

Acids



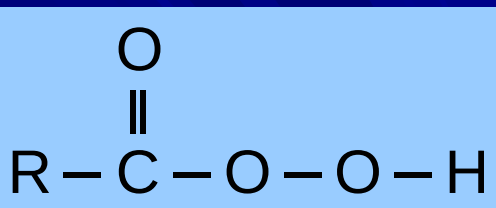
Formic acid

(a)



Acetic acid

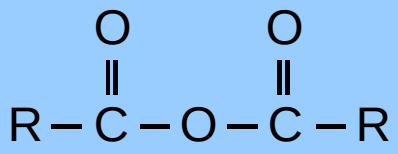
(b)



Peroxyacids

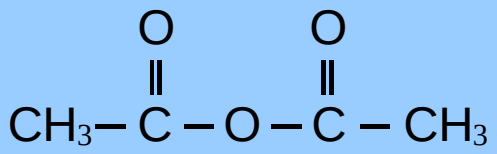
(c)

Acid Anhydrides



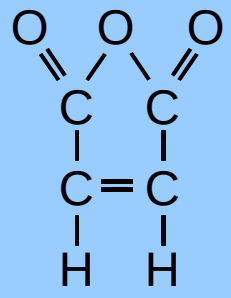
Representation of an acid anhydride

(a)



Acetic anhydride

(b)



Maleic anhydride

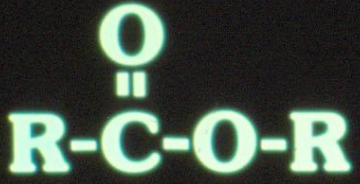
(c)

Alcohols

Aldehydes

Ketones

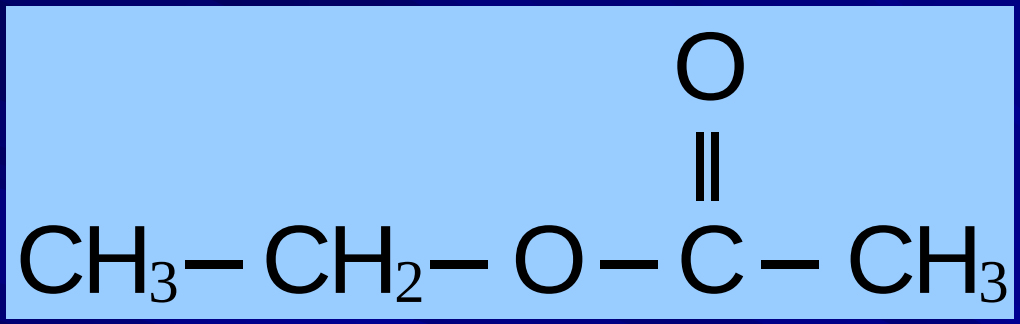
Esters



Acids

Ethers

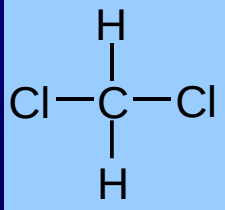
Ethyl Acetate



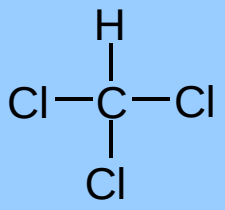
Organic Compounds Containing Halides

Organic Chlorides

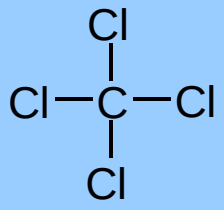
Chlorides of methane and ethane



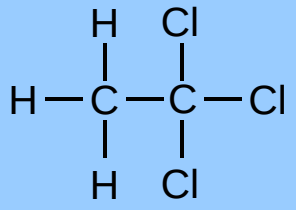
Methylene chloride



Chloroform



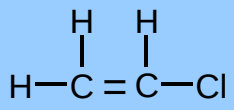
Carbon tetrachloride



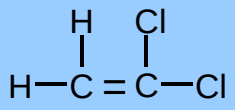
Methyl chloroform (1,1,1 - trichloroethane)

Organic Chlorides
(continued)

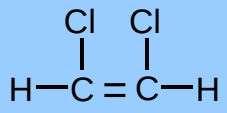
Chlorides of ethylene



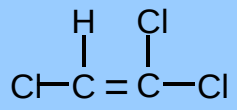
Vinyl chloride (chloroethene)



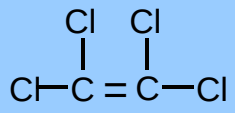
Vinylidene chloride



Ethylene dichloride



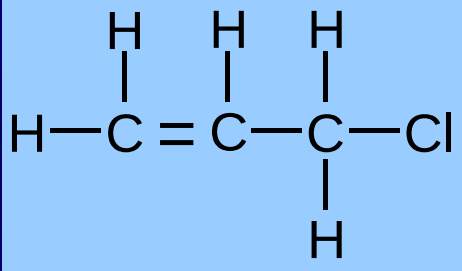
Trichloroethylene



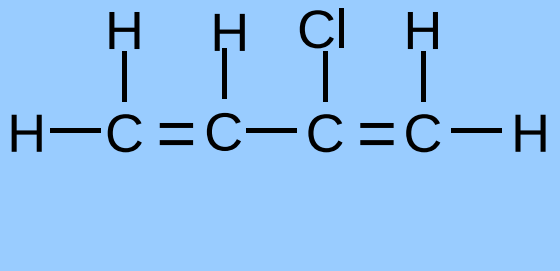
Perchloroethylene

Organic Chlorides
(continued)

Other double-bonded chlorides



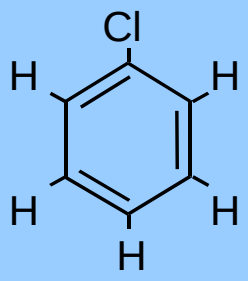
Allyl chloride



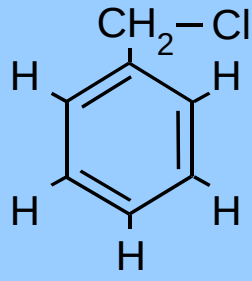
Chloroprene

Organic Chlorides
(continued)

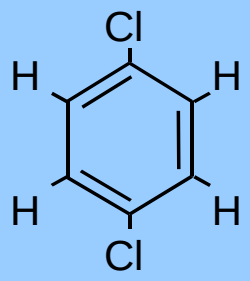
Chlorides of benzene



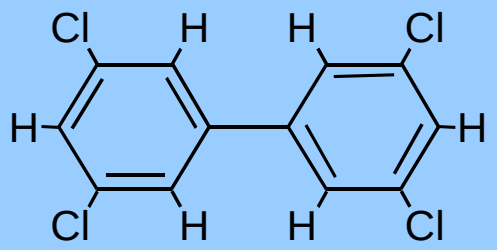
Chlorobenzene



Benzylchloride

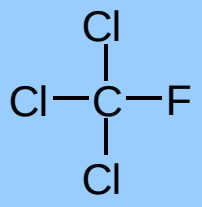


p-dichlorobenzene

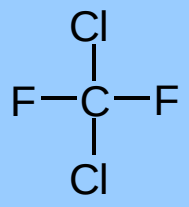


Example of a polychlorinated biphenyl (PCB)

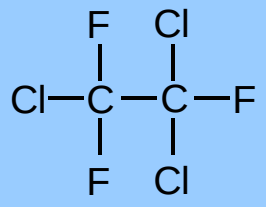
Chlorofluorocarbons



Trichlorofluormethane
(Freon 11)

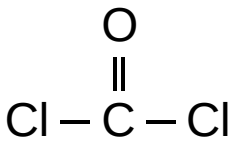


Dichlorodifluoromethane
(Freon 12)



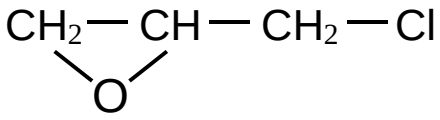
Trichlorotrifluoroethane
(Freon 13)

Compounds Containing Both Oxygen and Chlorine



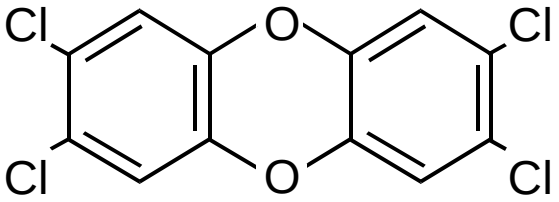
Phosgene

(a)



Epichlorohydrin

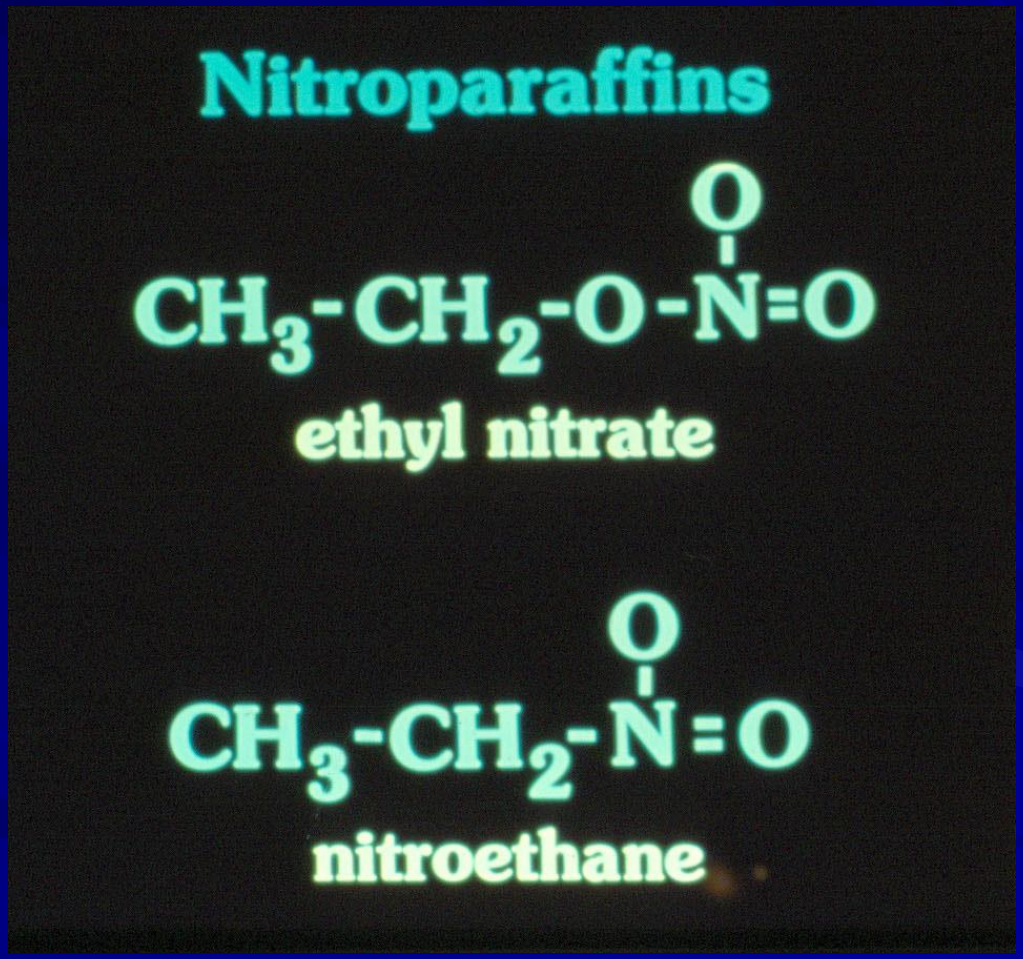
(b)



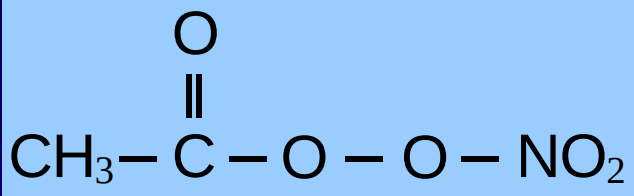
Dioxin (TCDD)
2,3,7,8, tetrachlorodibenzo-p-dioxin

(c)

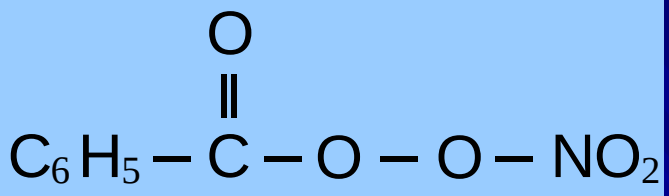
Organic Compounds Containing Nitrogen



PAN and PBN Compounds

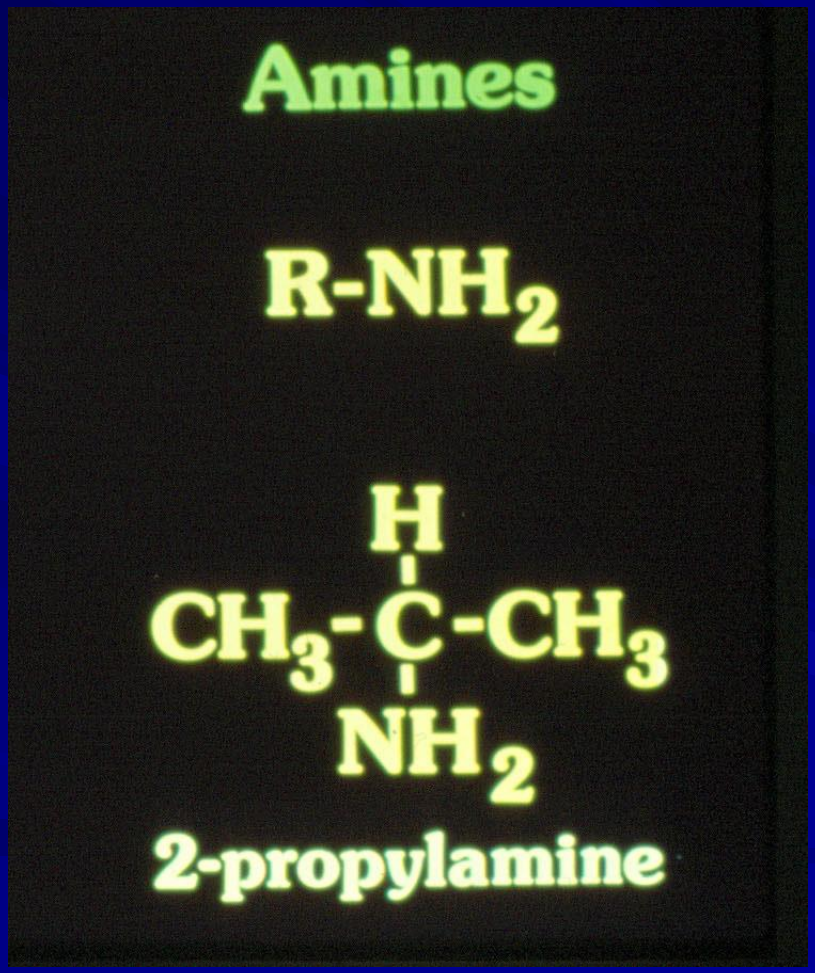


Peroxyacetyl nitrate



Peroxybenzoyl nitrate

Organic Compounds Containing Nitrogen



Amine Compounds

- Primary amine: RNH_2

  CH_3NH_2

- Secondary amine: R_2NH

  $CH_3NHC_2H_5$

- Tertiary amine: R_3N

  $(C_2H_5)_3N$

Organic Compounds Containing Sulfur

- Methyl mercaptan

CH_3SH

- Dimethyl sulfide

CH_3SCH_3

Formation of Ozone and Photochemical Smog

Photochemical Reactions

$$A \xrightarrow{h\nu} A^*$$

$$A^* \rightarrow B + C + \ldots$$

Wavelengths of interest are 280 nm to 730 nm

Variables Affecting Intensity

- Latitude
- Time of day
- Time of year
- Presence of clouds or aerosols

Summer maximum = 2×10^{16} photons $cm^{-2}sec^{-1}$
for 4-6 hours

Winter values = $0.7\text{-}1.5 \times 10^{16}$ photons $cm^{-2}sec^{-1}$
for 2-4 hours

Energy Absorbing Molecules

- NO_2
- O_3
- H_2O_2
- HNO_2
- Aldehydes
- Ketones

Basic Photochemical Cycle

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

Role of VOCs

$$O_3 \xrightarrow{h\nu} O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH\cdot$$

Understanding OH· reactions is key

Reactions of Formaldehyde

Photolysis:

$$HCHO \xrightarrow{h\nu} H\cdot + HCO\cdot$$

Reaction with OH:

$$HCHO + OH\cdot \rightarrow HCO\cdot + H_2O$$

Reactions of Formaldehyde (cont'd)

$$H\cdot + O_2 \xrightarrow{M} HO_2\cdot$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$$

Reactions of Formaldehyde (cont'd)

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$

$$OH\cdot + NO_2 \rightarrow HNO_3$$

Reactions of Acetaldehyde

Photolysis:

$$CH_3CHO \xrightarrow{h\nu} CH_3\cdot + HCO\cdot$$

Reaction with OH:

$$CH_3CHO + OH\cdot \rightarrow CH_3CO\cdot + H_2O$$

Reactions of Acetaldehyde (cont'd)

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$$

$$CH_3O_2\cdot + NO \rightarrow NO_2 + CH_3O\cdot$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$$

Reactions of Acetaldehyde (cont'd)

$$CH_3CO\cdot + O_2 \rightarrow CH_3COO_2\cdot$$

$$CH_3COO_2\cdot + NO \rightarrow NO_2 + CH_3COO\cdot$$

$$CH_3COO\cdot + O_2 \rightarrow CH_3O_2\cdot + CO_2$$

$$CH_3COO_2\cdot + NO_2 \rightarrow CH_3COO_2NO_2$$

Summary

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 \xrightarrow{h\nu} O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH\cdot$$

Photolysis of Aldehydes

$$RCHO \xrightarrow{h\nu} R\cdot + HCO\cdot$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

Reaction of OH with Aldehydes

$$RCHO + OH\cdot \rightarrow RCO\cdot + H_2O$$

$$RCO\cdot + O_2 \rightarrow RCOO_2\cdot$$

$$RCOO_2\cdot + NO \rightarrow NO_2 + RCOO\cdot$$

$$RCOO\cdot \rightarrow R\cdot + CO_2$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

Reaction of OH with Hydrocarbons

$$RH + OH\cdot \rightarrow R\cdot + H_2O$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$$

$$RO_2\cdot + NO \rightarrow RONO_2$$

$$RO\cdot + O_2 \rightarrow HO_2\cdot + RCHO$$

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$

Properties of Organic Vapors

- Gas and vapor definitions
- Molecular weight and the mole
- Equation of state
- Vapor pressure
- Partial pressure and partial volume
- Concentration expressions
- Explosive limits

Gas and Vapor Definitions

- A gaseous material below its critical temperature is a vapor. Compressing a vapor at constant temperature will cause it to condense.
- A gaseous material above its critical temperature is a gas. Compressing a gas at constant temperature will not cause it to condense.

Molecular Weight

Molecular weight is the sum of the atomic weights of all atoms in a molecule

$$MW_{mixture} = \sum_{i=1}^{n} \chi_i MW_i$$

χ_i = mole fraction of component I

MW_i = molecular weight of component i

The Mole

A mole is a mass of material that contains a certain number of molecules. It is numerically equal to the molecular weight.

The gram-mole is the mass of material that contains Avogadro's number of molecules.

Equation of State

The ideal gas law:

$$PV = nRT$$

P = absolute pressure

V = gas volume

n = number of moles

R = constant

T = absolute temperature

Values for R

10.73 psia-ft^3/lb-mole-°R

0.73 atm-ft^3/lb-mole-°R

82.06 atm-cm^3/g-mole-K

8.31 x 10^3 kPa-m^3/kg-mole-K

Volume Correction

$$\frac{PV}{T} = nR = \text{CONSTANT} \; (\text{if } n = \text{CONSTANT})$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

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

Molar Volume

$$\frac{V}{n} = \frac{RT}{P}$$

At 68°F and 1 atm:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(0.73 \frac{atm - ft^3}{lb - mole \cdot °R}\right)(528°R)}{1 atm} = 385.4 \frac{ft^3}{lb - mole}$$

Gas Density

$$PV = \left(\frac{m}{MW}\right)RT$$

$$\rho = \frac{m}{V} = \frac{P \cdot MW}{RT}$$

Vapor Pressure

Antoine equation:

$$\ln(p^*) = A - \frac{B}{T + C}$$

p* = vapor pressure

T = temperature

A,B,C = constants

Partial Pressure

Dalton stated that the total pressure of a gas mixture is the sum of the individual pressures of each component

$$\frac{p_i}{P_T} = \frac{n_i}{n_T}$$

Partial Volume

Amagat stated that the total volume of a gas mixture is the sum of the individual volumes of each component

$$\frac{\nu_i}{V_T} = \frac{n_i}{n_T}$$

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} = \frac{\nu_i}{V_T}$$

Concentration Expressions

- Partial pressure
- Parts per million by volume (ppmv)

$$ppmv_i = \left(\frac{v_i}{V_T} \right) x10^6$$

- Mass per unit volume

Conversion Equation

$$1\,\text{ppmv} = \frac{1\,\text{ft}^3\,\text{VOC}}{10^6\,\text{ft}^3}\left(\frac{1}{V_{molar}}\frac{\text{lb}-\text{mole VOC}}{\text{ft}^3\,\text{VOC}}\right)\left(MW_{VOC}\frac{\text{lb VOC}}{\text{lb}-\text{mole VOC}}\right)$$

$$1\,\text{ppmv} = \frac{MW_{VOC}}{V_{molar}\,x10^6}\frac{\text{lb VOC}}{\text{ft}^3}$$

Explosive Limits

- LEL is the concentration of VOC below which combustion will not be self-sustaining
- UEL is the concentration of VOC that produces a non-burning mixture because of the lack of oxygen

Explosive Limits of Selected VOCs

	Explosive Limit (Volume %)	
Substance	Lower	Upper
Methane	5.00	15.00
n-Hexane	1.18	7.40
Ethylene	2.75	28.60
Toluene	1.27	6.75
Xylene	1.00	6.00
Methanol	6.72	36.50
Ethanol	3.28	18.95
Gasoline	1.40	7.60

Chapter 3

Source Measurement Techniques

Measurement Methods

- Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography
- Method 25, Determination of Total Gaseous Non-Methane Organic Emissions as Carbon
- Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

Method 18

- Sample is extracted from a single point at a rate proportional to gas velocity
- Organic components in the sample are separated by gas chromatography
- Separated compounds are analyzed with a suitable detector

Method 18 Applicability

- Suitable for measurement of about 90% of organics emitted by industrial processes
- Detection limit is about 1 ppmv
- Does not include techniques to identify and measure trace concentrations
- Will not determine compounds that are polymeric, can polymerize before analysis, or that have very low vapor pressure

Pre-Survey Sampling Techniques

- Evacuated or purged glass sampling flasks
- Flexible bags
- Adsorption tubes

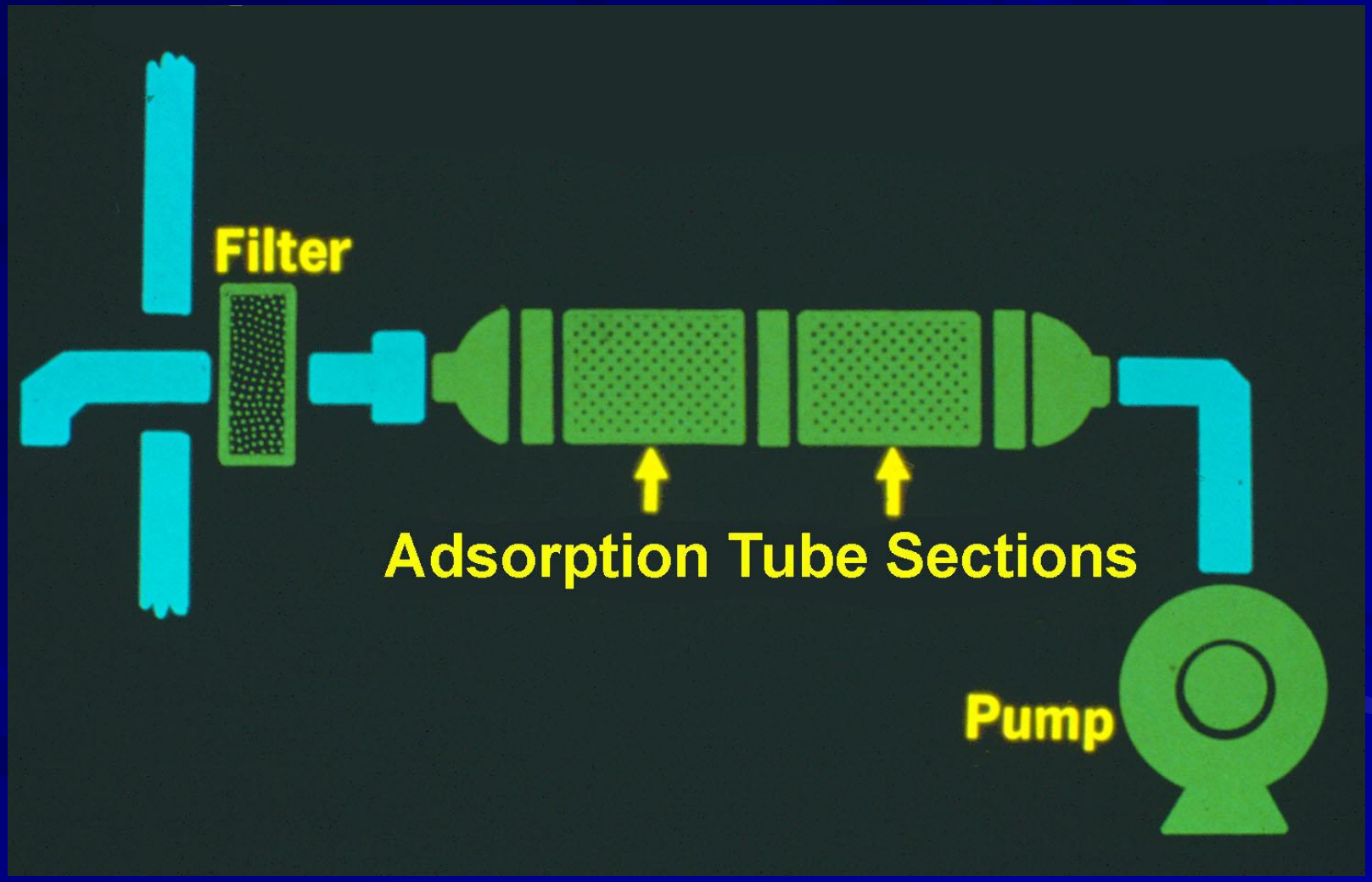
Final Sampling Techniques

- Direct interface
- Dilution interface
- Adsorption tubes
- Flexible bags

Direct or Dilution Interface Sampling

- Strengths
  - No loss or alteration of compounds
  - Method of choice when temperature is below 100°C and VOC concentrations are suitable
- Weaknesses
  - GC must be located at sampling site
  - Cannot sample proportionally or obtain time integrated sample

Adsorption Tube Sampling



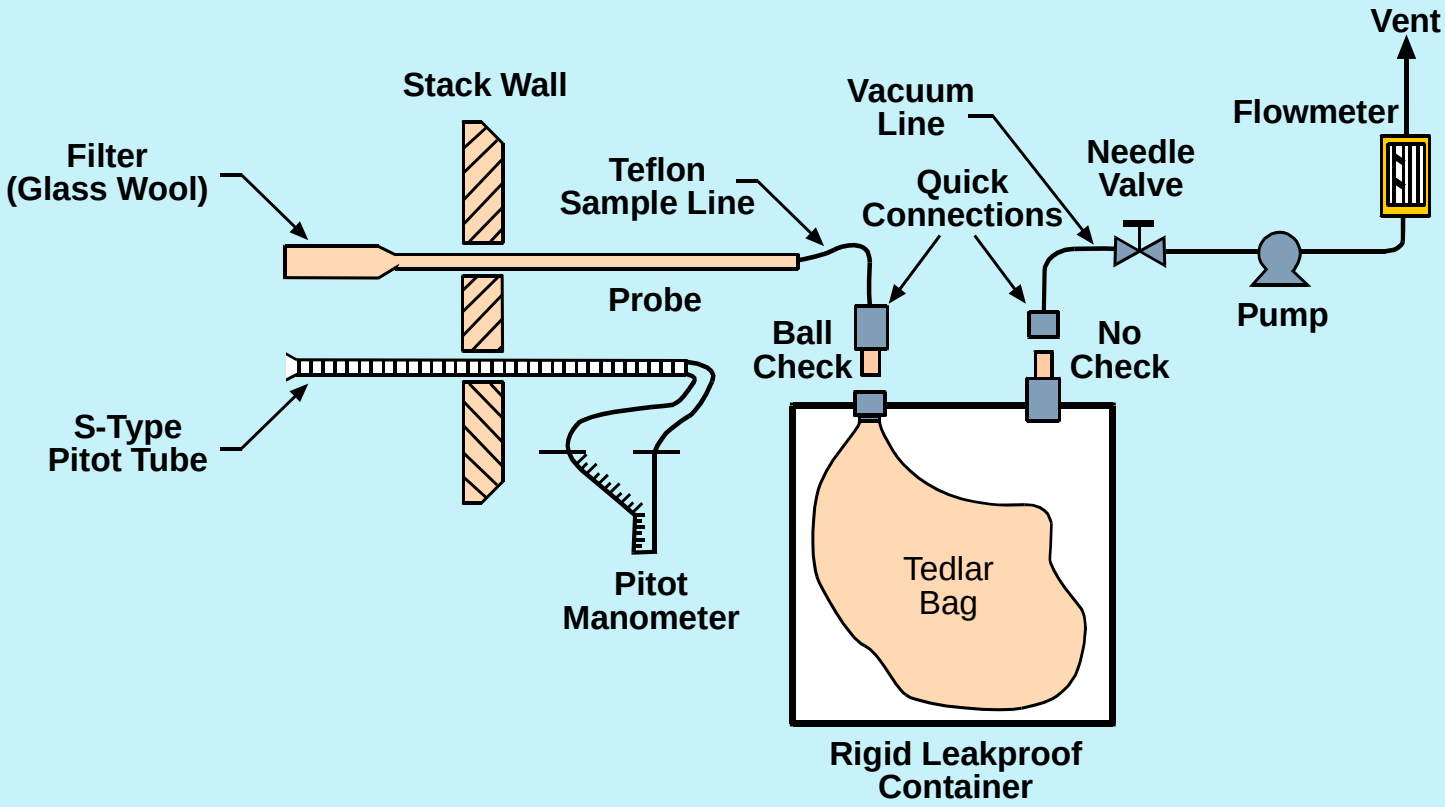
Adsorbent Media

- Activated carbon
- Silica gel
- Tenax
- XAD resin

Adsorption Tube Sampling

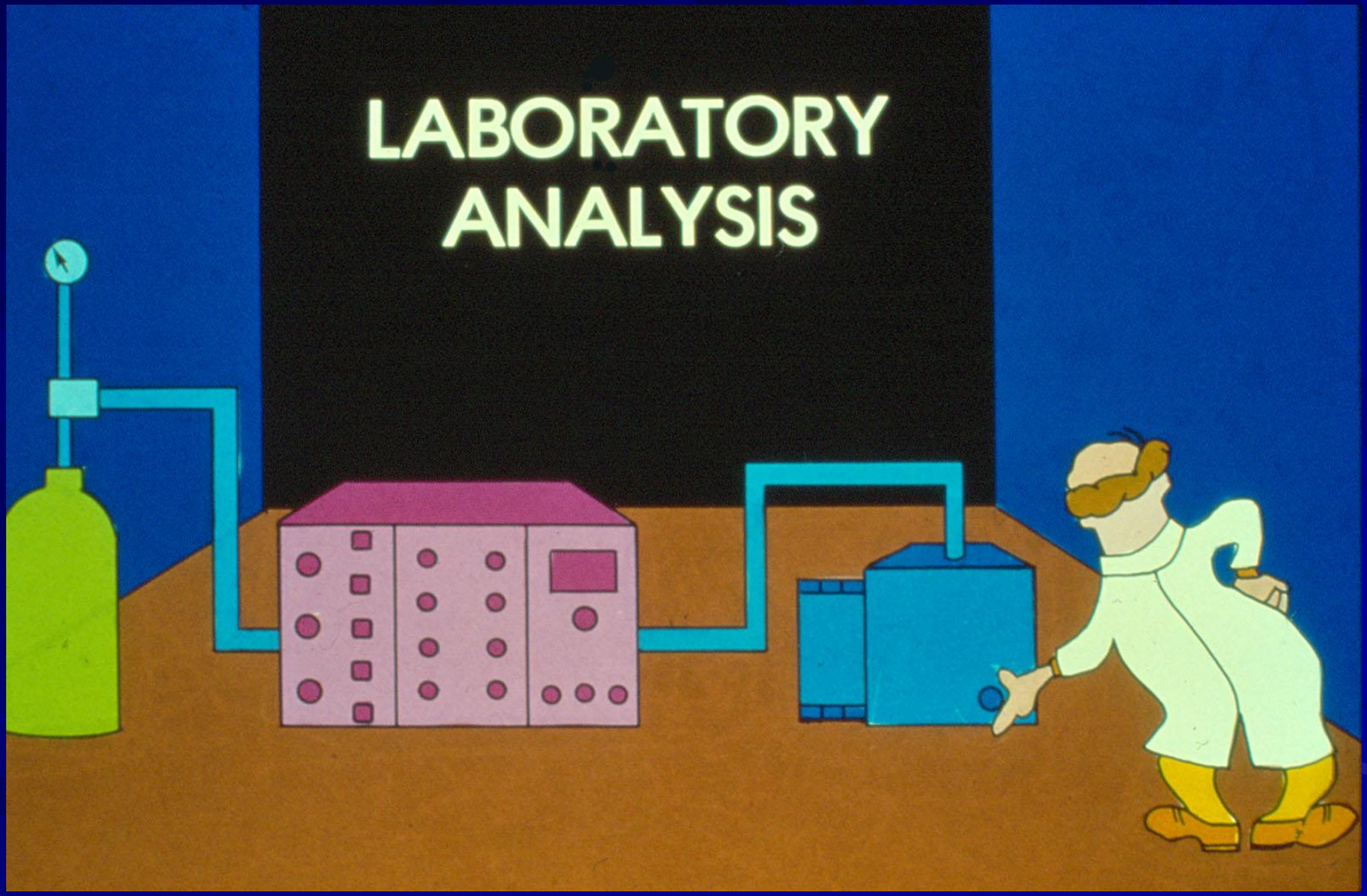
- Strengths
  - Samples are compact and easy to handle
  - Samples returned to lab for analysis
  - Can be stored up to a week at 0°C
- Weaknesses
  - Breakthrough capacity must be known
  - Effect of moisture must be known
  - Quantitative recovery of compounds must be known
  - Samples must be collected at a constant rate

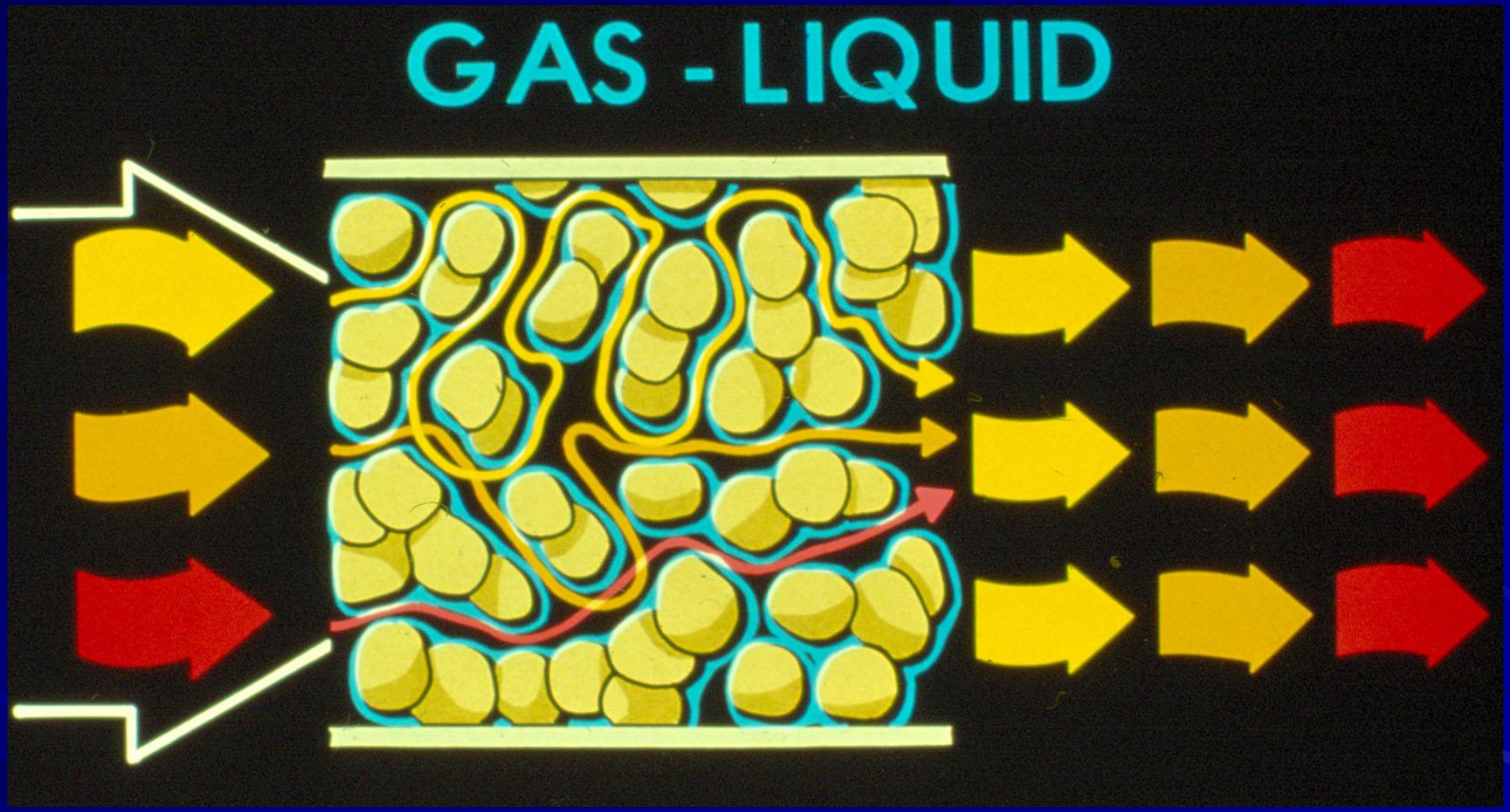
Flexible Bag Sampling



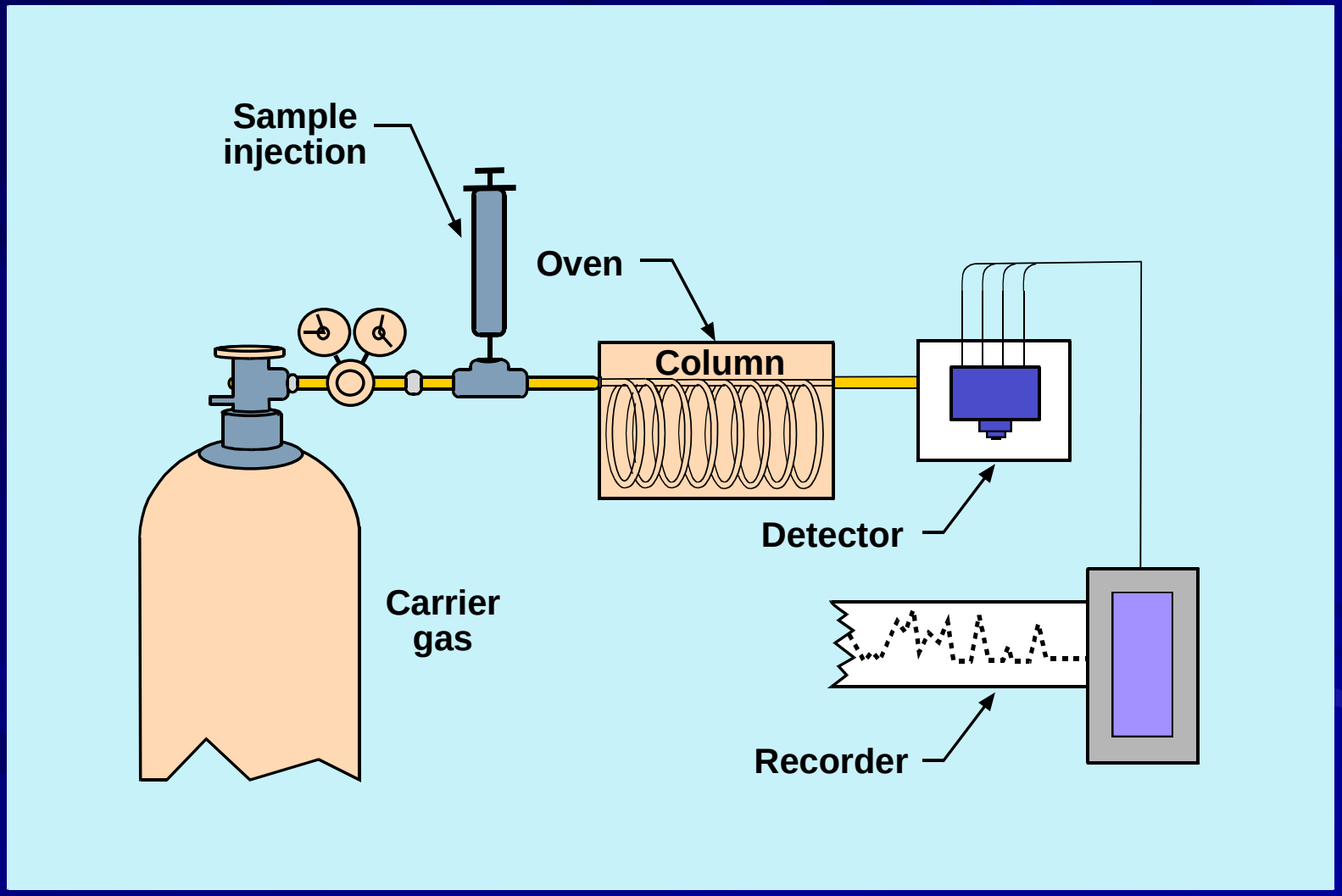
Flexible Bag Sampling

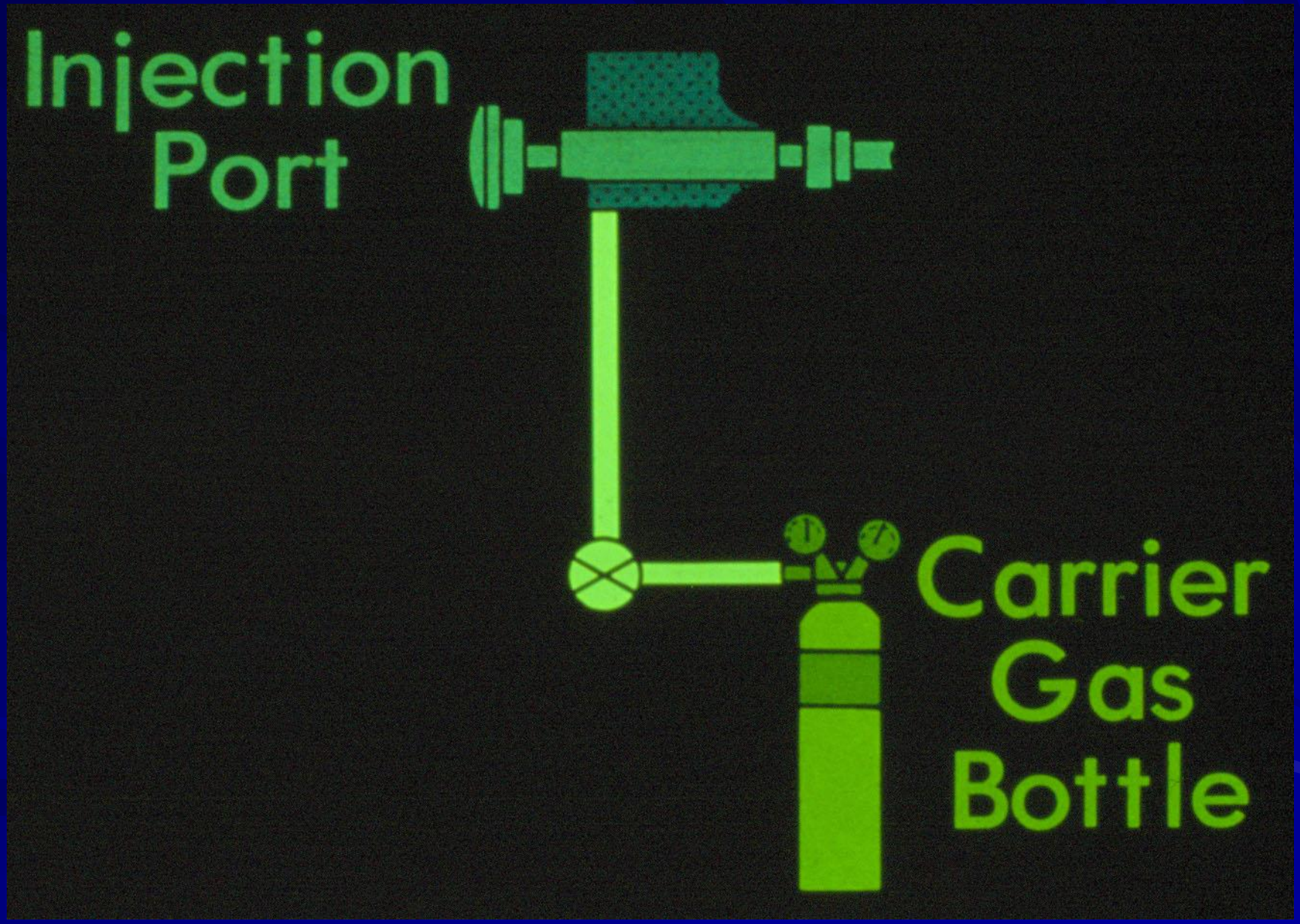
- Strengths
  - Samples approximate form in stack
  - Samples are returned to lab for analysis
  - Samples may be collected proportionally
- Weaknesses
  - Bags are awkward and bulky and prone to leaks
  - Compounds may adsorb onto bag surface
  - Compounds may react with bag surface or with each other
  - Storage time is generally less than 24 hours

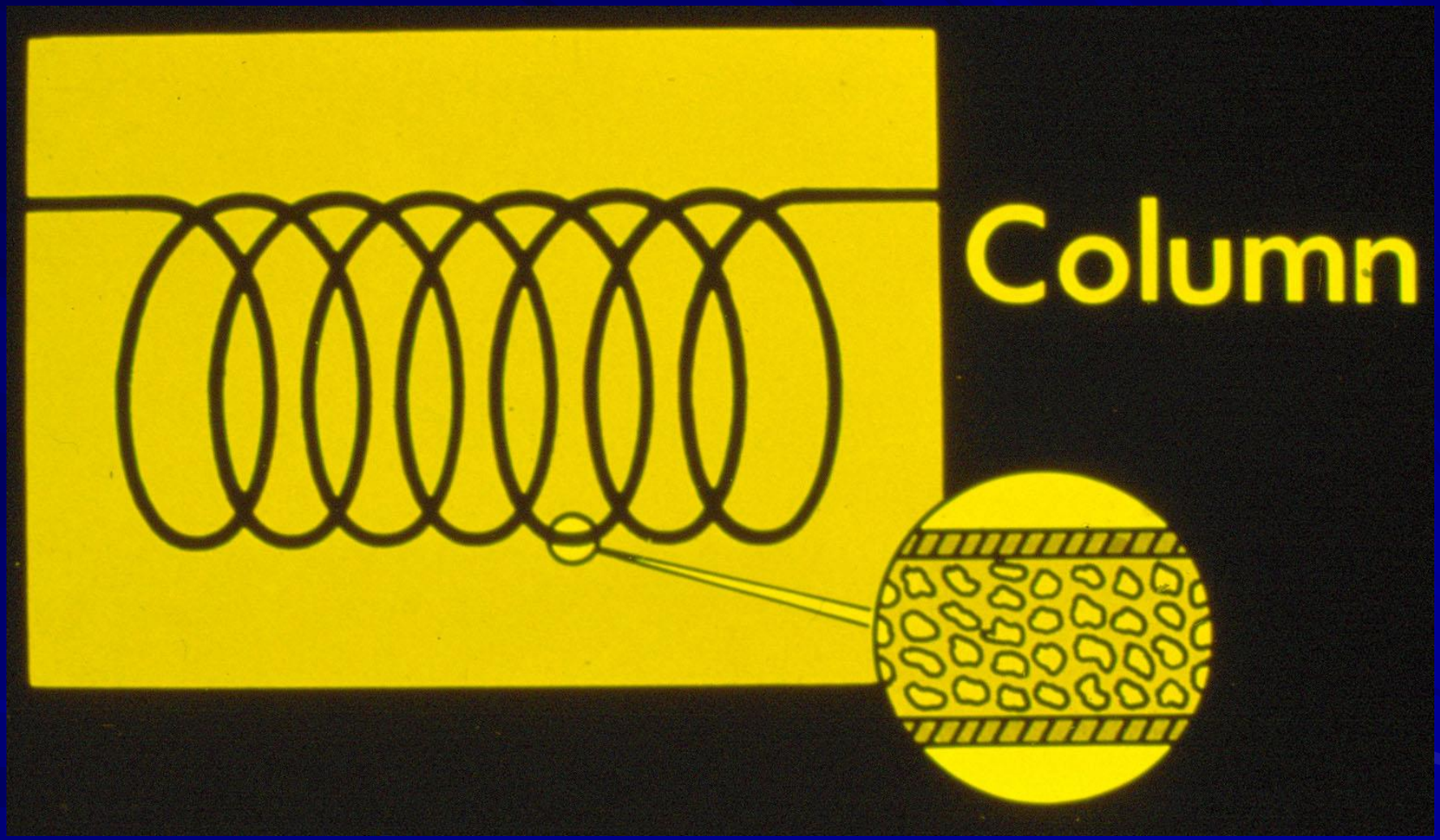

LABORATORY
ANALYSIS

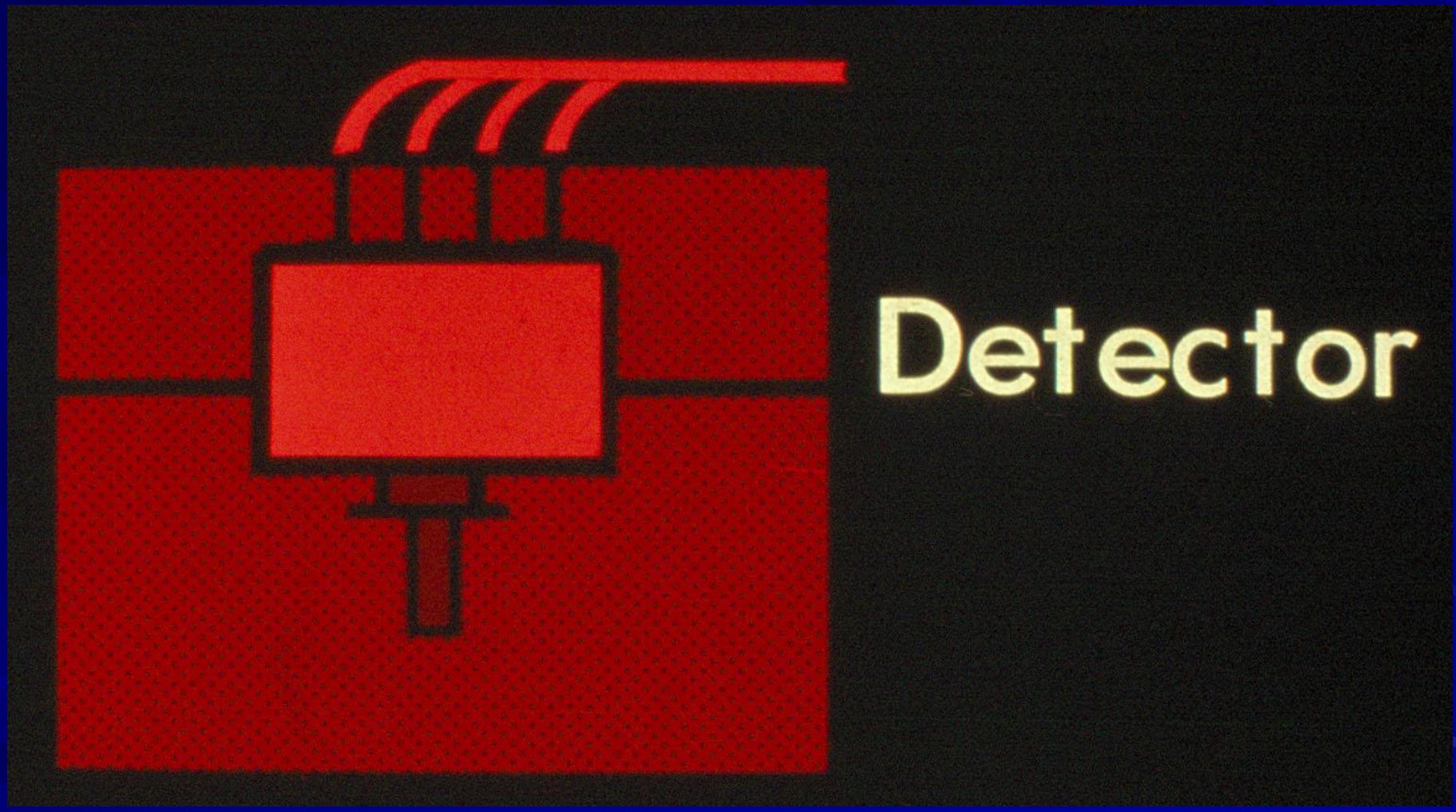

GAS - LIQUID

Gas Chromatographic System

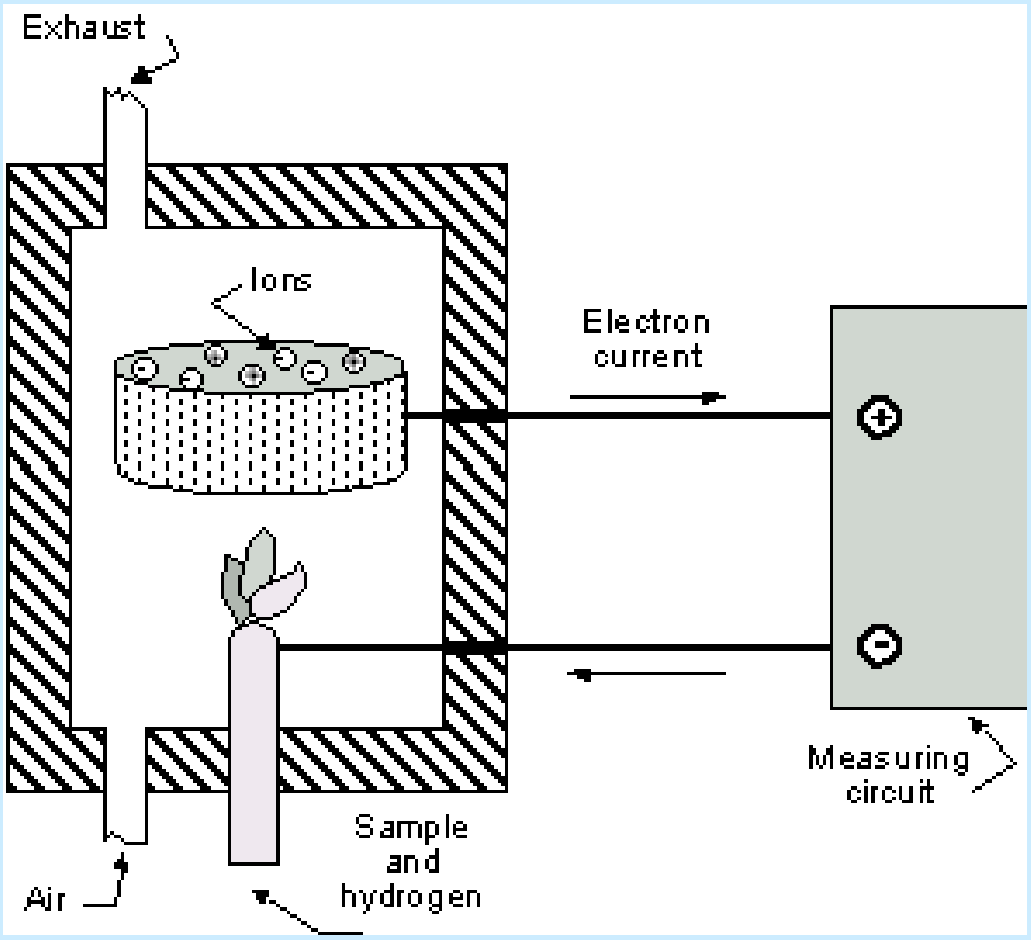



Injection Port
Carrier Gas Bottle

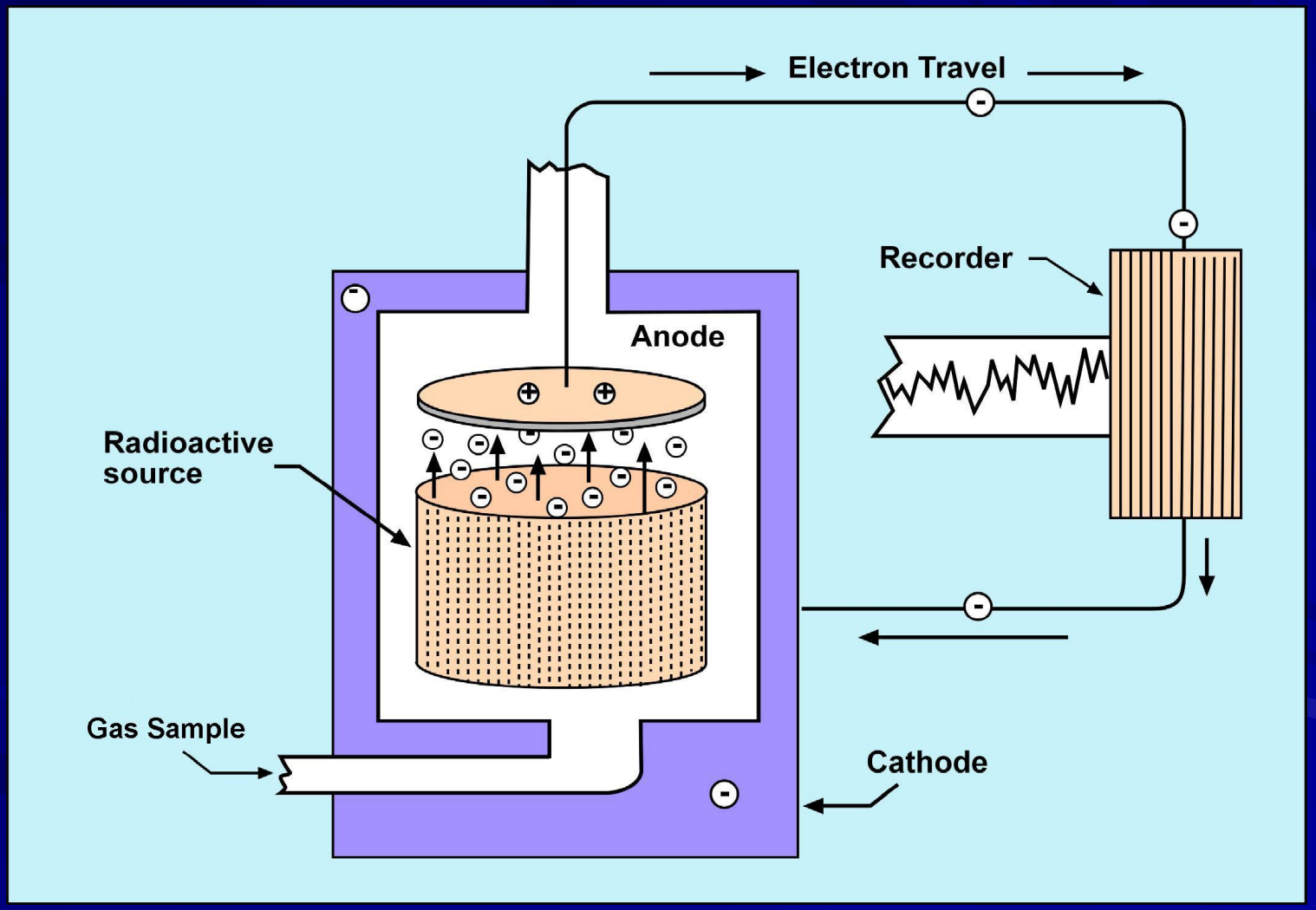

Column

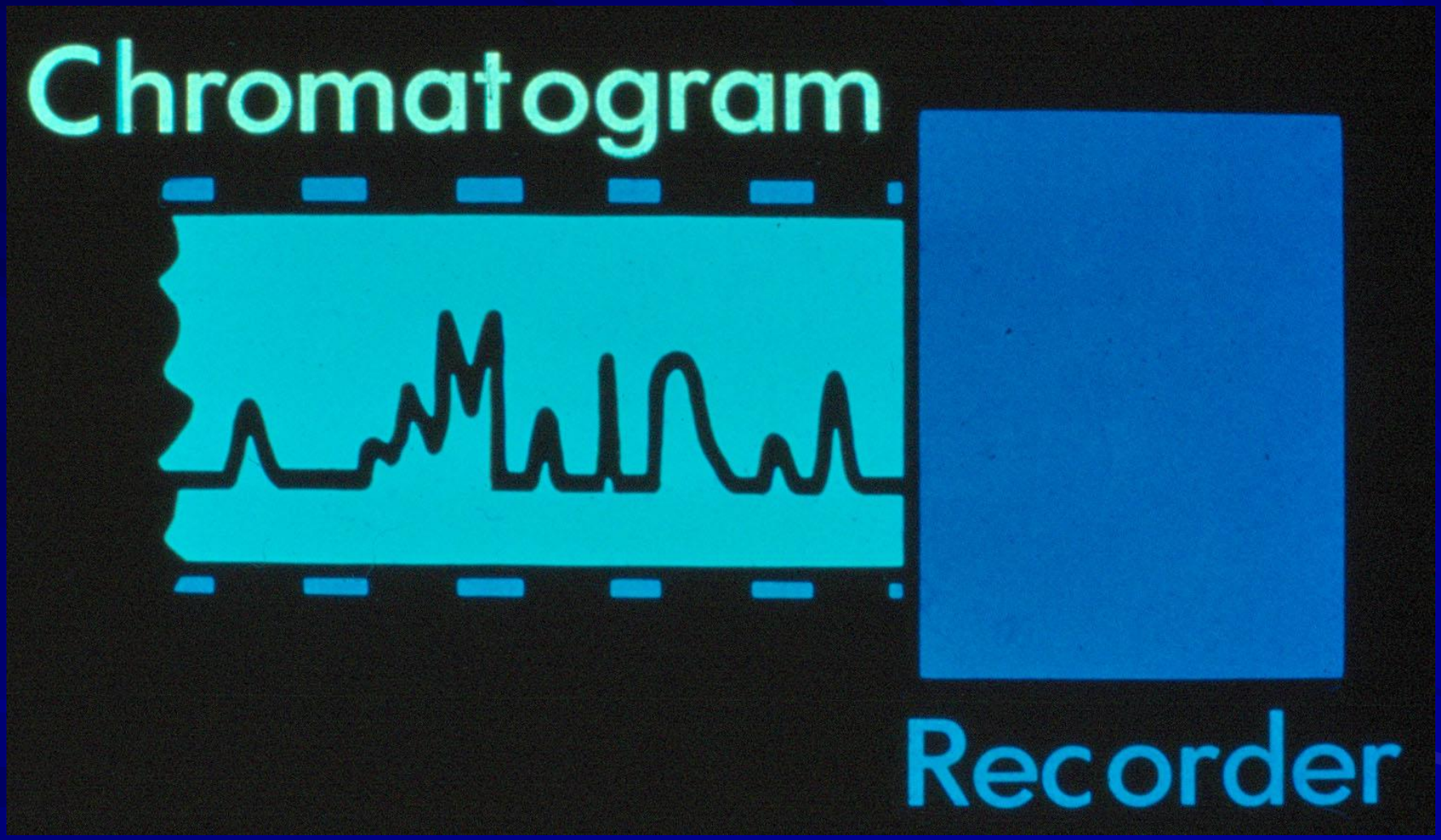

Detector

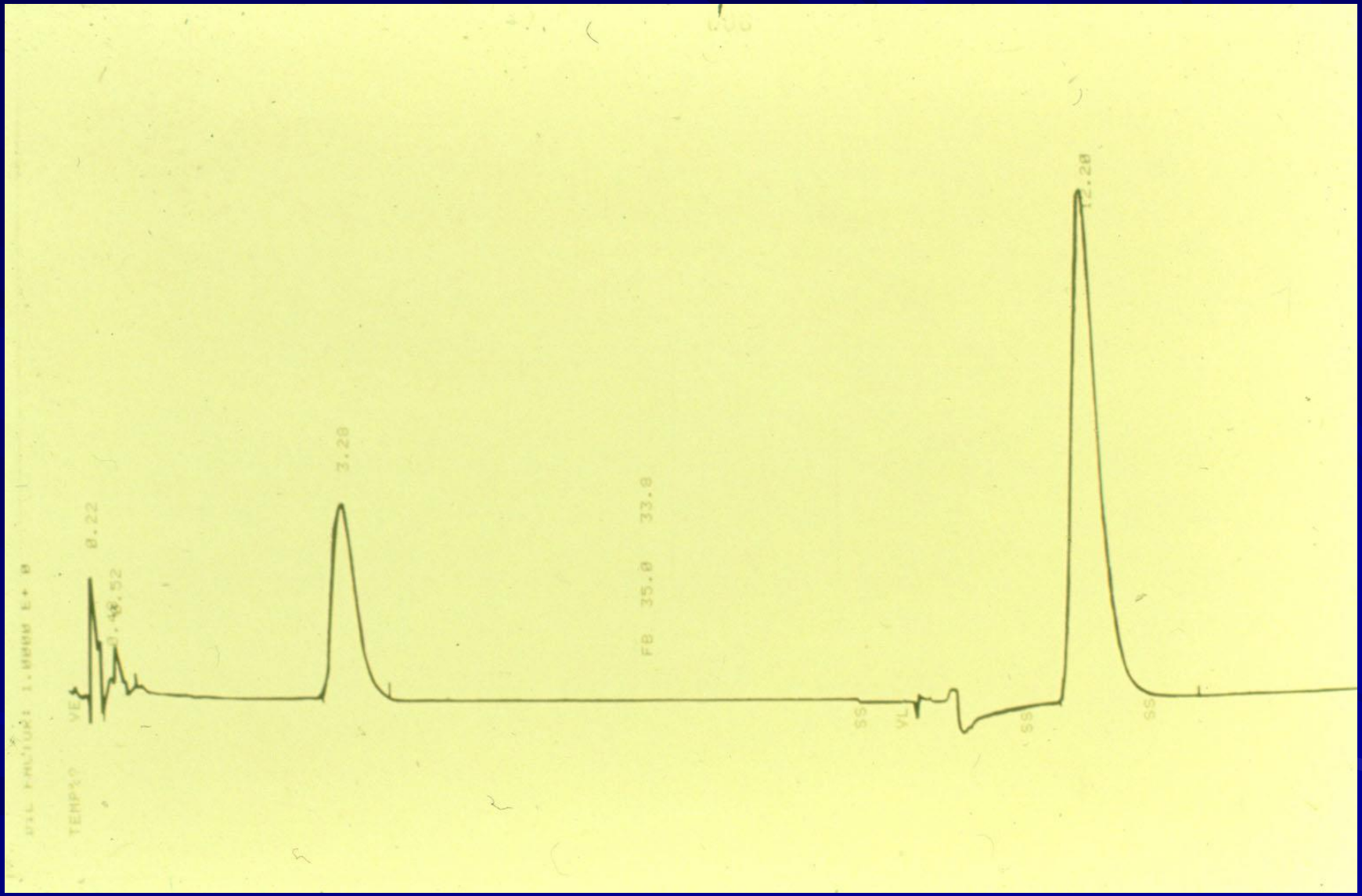
Flame Ionization Detector



Electron Capture Detector




Chromatogram
Recorder


TEMPO
0.22
3.28
FB 35.0 33.8
12.28

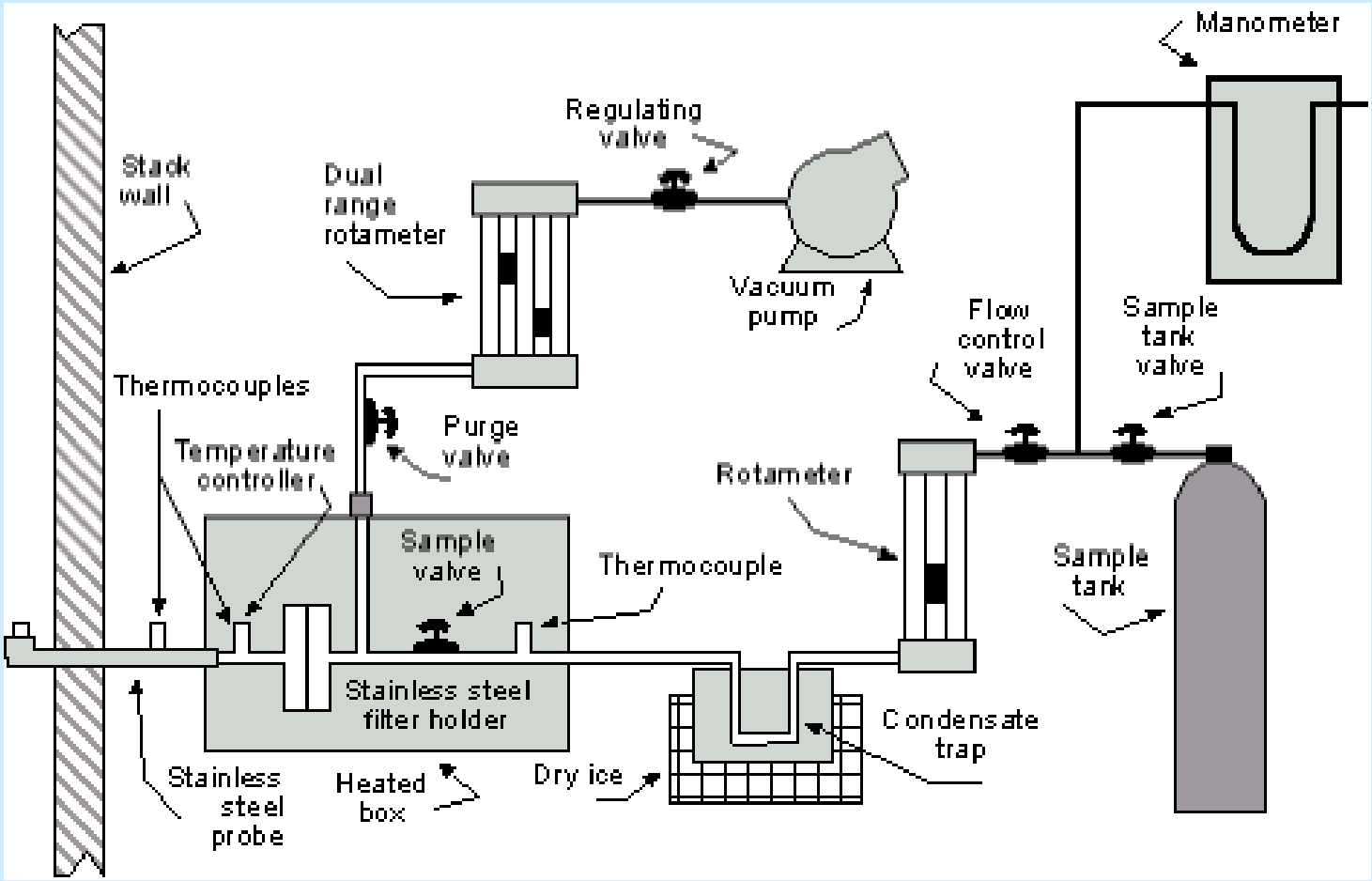
Method 25

- Sample is extracted from a single point at a rate proportional to gas velocity
- Sample is separated into condensable and non-condensable fractions
- Analysis yields total gaseous non-methane organic emissions as carbon

Method 25 Applicability

- Organic compounds which are a gas or have significant vapor pressure at or below 250°F
- Sources with concentrations of 50 ppmv to 5% by volume
- High concentrations of CO_2 and water vapor can cause interference at low concentrations

Method 25 Sampling Train



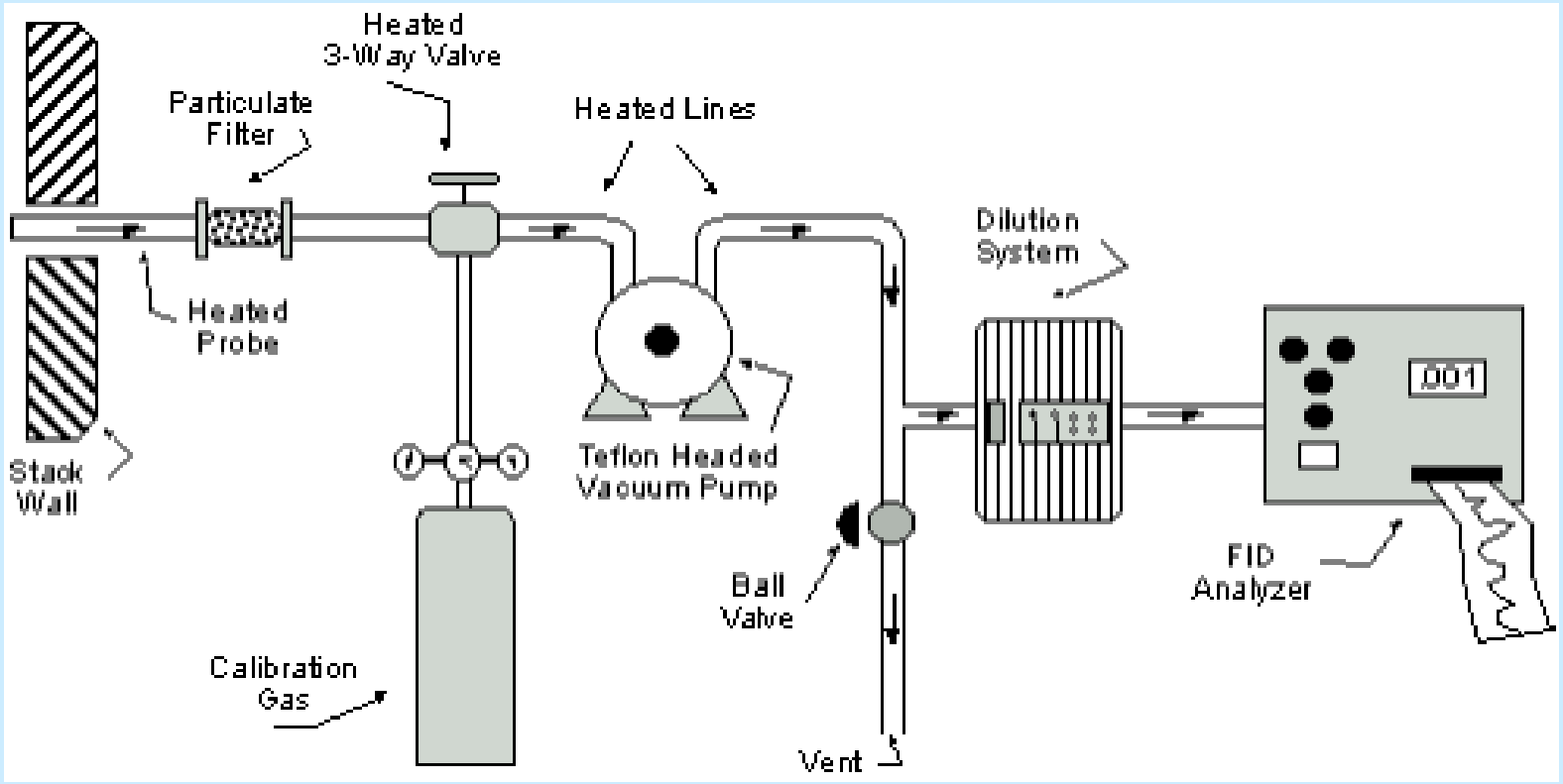
Method 25 Analysis

- Condensate trap is purged with zero air and purged gas is collected in the sample tank
- Condensed VOCs are volatilized, oxidized to CO_2, and collected in a second tank
- VOCs in the sample tank are separated with GC, oxidized to CO_2, reduced to methane and measured by FID
- CO_2 peak in second tank is measured and counted as VOCs
- Total VOCs is the sum of both analyses

Method 25A

- Measures total organic concentration on a continuous, real-time basis using an FID
- Method is best applied to the measurement of vapors consisting primarily of alkanes, alkenes or aromatic hydrocarbons
- Gives reduced response to compounds that are highly substituted or chlorinated

Method 25A Sampling Train



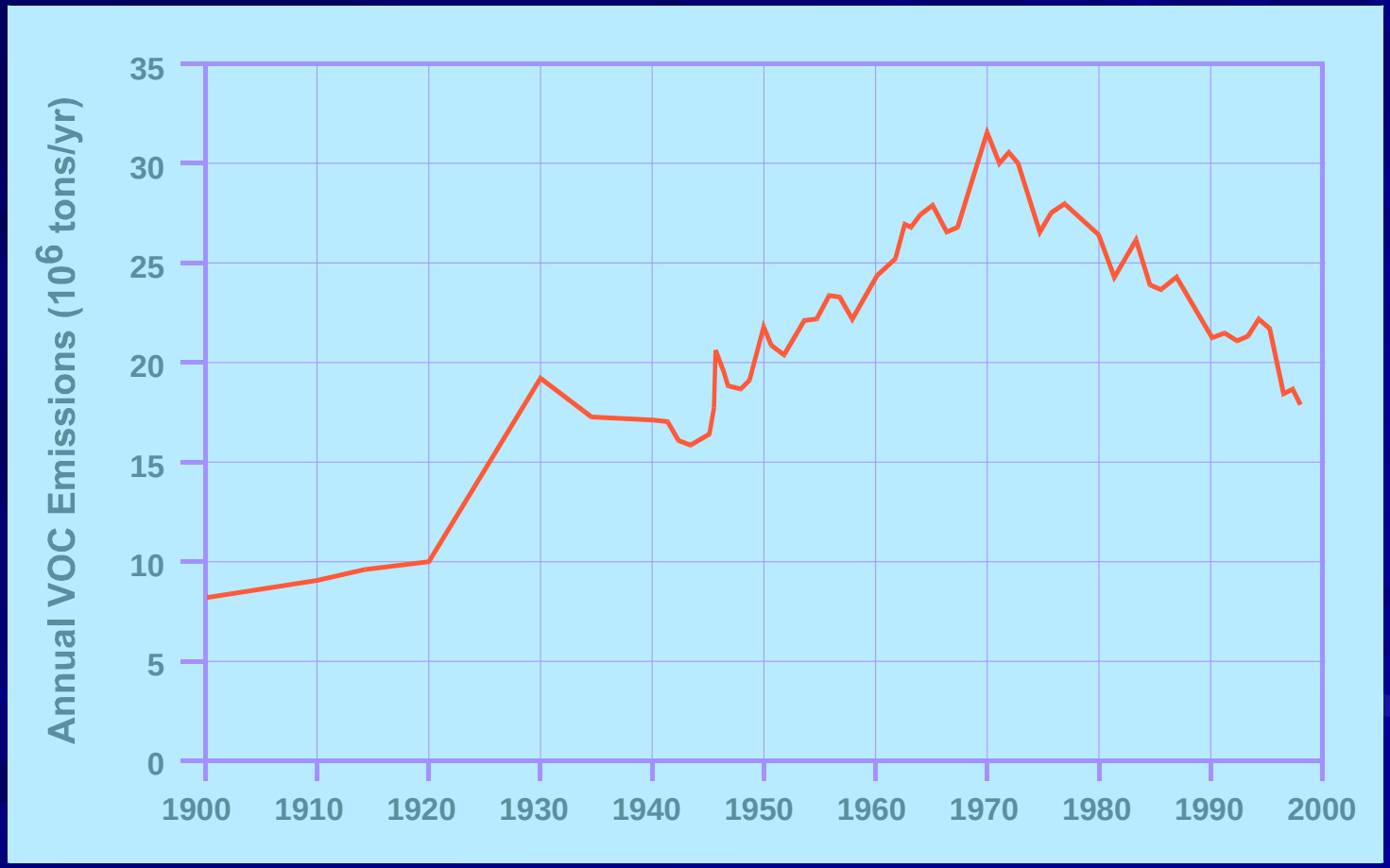
Chapter 4

National Sources and the Regulatory Approach

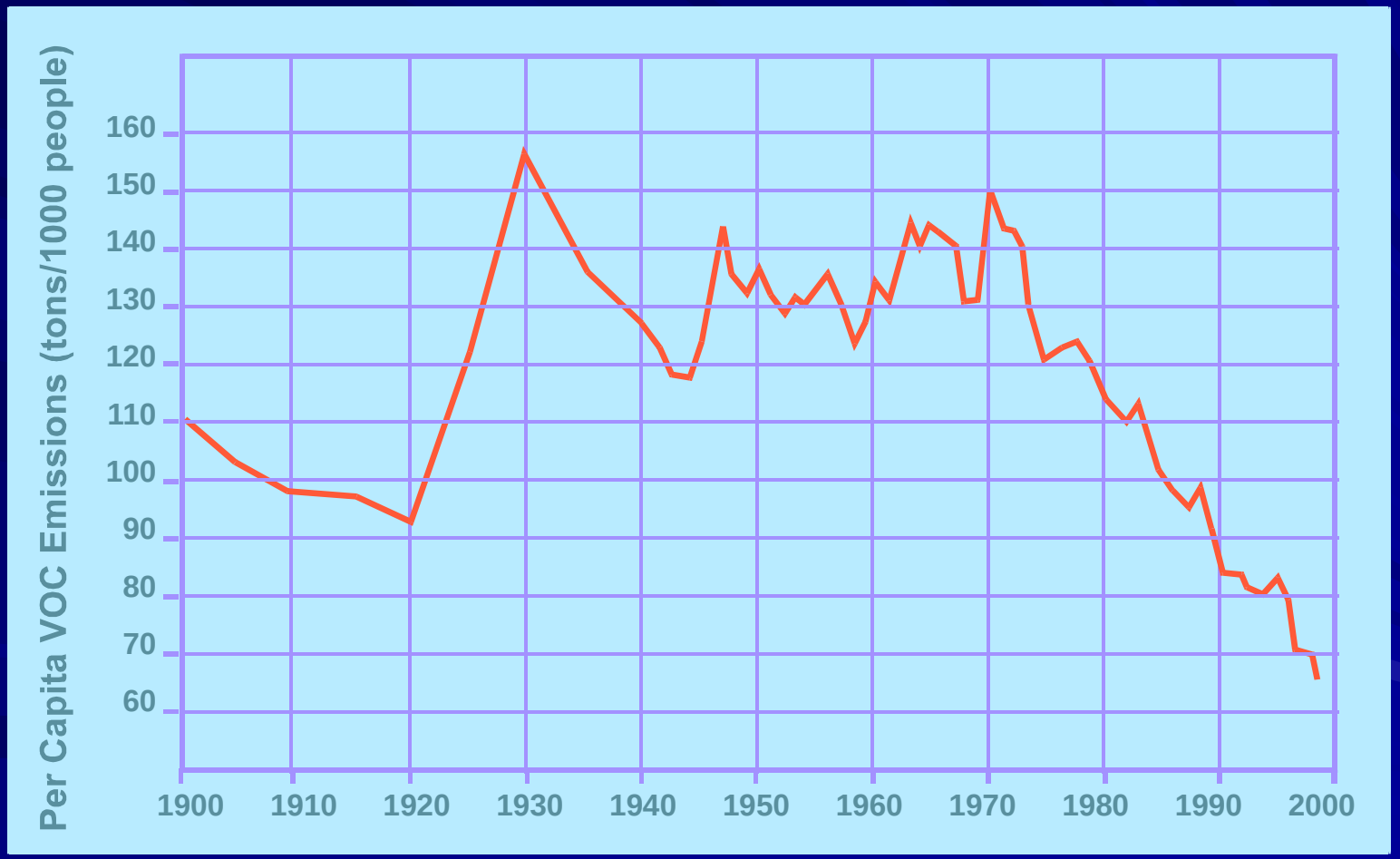
National Sources and the Regulatory Approach

- Emission trends
- Emission inventory
- Regulatory approach
  - Nonattainment area classifications
  - Regulation of existing sources
  - Regulation of new and modified sources
  - Regulation of hazardous air pollutants

Trend in National VOC Emissions



Trend in National Per Capital VOC Emissions



State Ranking of VOC Emissions (1998)

Rank	State	Emissions (10^3 tons/year)	% of Total
1	Texas	1,388	7.75
2	California	1,215	6.78
3	Florida	891	4.97
4	Michigan	765	4.27
5	New York	753	4.20
6	Illinois	748	4.17
7	Ohio	706	3.94
8	North Carolina	605	3.38
9	Georgia	576	3.21
10	Pennsylvania	575	3.21

State Ranking of VOC Emissions (1998)
(continued)

Rank	State	Emissions (10^3 tons/year)	% of Total
11	Tennessee	528	2.95
12	Indiana	518	2.89
13	Virginia	471	2.63
14	Alaska	457	2.55
15	Louisiana	425	2.37
16	Alabama	419	2.34
17	New Jersey	408	2.28
18	Wisconsin	400	2.23
19	Minnesota	381	2.13
20	Missouri	360	2.01

State Ranking of VOC Emissions (1998)
(continued)

Rank	State	Emissions (10^3 tons/year)	% of Total
21	Washington	347	1.94
22	South Carolina	334	1.86
23	Kentucky	330	1.84
24	Mississippi	304	1.70
25	Oklahoma	295	1.65
26	Arizona	281	1.57
27	Colorado	274	1.53
28	Oregon	272	1.52
29	Massachusetts	264	1.47
30	Kansas	257	1.43

State Ranking of VOC Emissions (1998)
(continued)

Rank	State	Emissions (10^3 tons/year)	% of Total
31	Iowa	239	1.33
32	Arkansas	223	1.24
33	Maryland	183	1.02
34	Utah	161	0.90
35	Connecticut	156	0.87
36	Nebraska	154	0.86
37	West Virginia	141	0.79
38	New Mexico	140	0.78
39	Idaho	115	0.64
40	Maine	109	0.61
41	North Dakota	106	0.59

State Ranking of VOC Emissions (1998)
(continued)

Rank	State	Emissions (10^3 tons/year)	% of Total
42	Montana	105	0.59
43	Nevada	98	0.55
44	South Dakota	78	0.44
45	New Hampshire	74	0.41
46	Wyoming	68	0.38
47	Hawaii	54	0.30
48	Delaware	51	0.28
49	Rhode Island	49	0.27
50	Vermont	44	0.25
51	DC	22	0.12
Total		17,917	100.00

National Anthropogenic VOC Emissions

Source Category	Emissions (10^3 tons/year)				%
	1970	1980	1990	1998	1998
On-road vehicles	12,972	8,979	6,313	5,326	29.7
Non-road vehicles and engines	1,878	2,312	2,545	2,461	13.7
Stationary fuel combustion	721	1,050	1,005	893	5.0
Industrial processes	10,653	11,101	7,114	6,006	33.5
Non-industrial solvent use	1,674	1,002	1,900	2,012	11.2
Waste disposal and recycling	1,984	758	986	433	2.4
Natural sources			14	14	0.1
Miscellaneous	1,100	1,134	1,059	772	4.3
Total	30,982	26,336	20,936	17,917	100.0

Emissions from On-Road Vehicles

	1970	1980	1990	1998	%
On-road vehicles	12,972	8,979	6,313	5,326	29.7
Light-duty gas vehicles & motorcycles	9,193	5,907	3,947	2,832	15.8
Light-duty gas trucks	2,770	2,059	1,622	2,015	11.2
Heavy-duty gas vehicles	743	611	432	257	1.4
Diesel vehicles	266	402	312	222	1.2

Emissions from Non-Road Vehicles and Engines

	1970	1980	1990	1998	%
Non-road vehicles and engines	1,878	2,312	2,545	2,461	13.7
Aircraft	97	146	180	177	1.0
Railroads	22	33	52	50	0.3
Marine vessels	7	19	32	35	0.2
Recreational marine vessels	736	830	787	783	4.4
Recreational equipment	138	152	129	136	0.8
Lawn and garden equipment	514	587	710	655	3.7
Farm equipment	49	155	146	132	0.7
Commercial equipment	122	135	184	172	1.0
Construction equipment	121	174	225	229	1.3
Industrial equipment	63	61	73	64	0.4
Other non-road equipment	9	20	27	28	0.2

Emissions from Non-Industrial Solvent Use

	1970	1980	1990	1998	%
Non-industrial solvent use	1,674	1,002	1,900	2,012	11.2
Cutback asphalt	1,045	323	199	144	0.8
Pesticide application	241	241	258	405	2.3
Adhesives			361	313	1.7
Consumer solvents			1,082	1,099	6.1
Other	388	438		51	0.3

Emissions from Stationary Fuel Combustion

	1970	1980	1990	1998	%
Stationary fuel combustion	721	1,050	1,005	893	5.0
Electric utility	30	45	47	54	0.3
Industrial	150	157	182	161	0.9
Commercial	11	11	12	16	0.1
Residential	530	837	756	654	3.7
Other			8	8	0.0

National Industrial VOC Emissions

Source Category	Emissions (10^3 tons/year)				%
	1970	1980	1990	1998	1998
Chemical manufacturing	1,341	1,595	634	396	6.6
Metals processing	394	273	122	75	1.2
Petroleum industries	1,195	1,440	612	497	8.3
Solvent utilization	5,499	5,581	3,850	3,265	54.4
Storage and transport	1,954	1,975	1,495	1,323	22.0
Other industrial processes	270	237	401	450	7.5
Total	10,653	11,101	7,114	6,006	100.0

Emissions from Solvent Utilization

	1970	1980	1990	1998	%
Solvent utilization	5,499	5,581	3,850	3,265	54.4
Degreasing	707	513	744	457	7.6
Graphic arts	319	373	274	311	5.2
Dry cleaning	263	320	215	169	2.8
Surface coating	3,570	3,685	2,523	2,224	37.0
Other	640	690	94	104	1.7

Emissions from Storage and Transport

	1970	1980	1990	1998	%
Storage and transport	1,954	1,975	1,495	1,323	22.0
Petroleum product storage	899	823	516	395	6.6
Petroleum product transport	92	61	151	122	2.0
Service stations	937	1,045	786	773	12.9
Organic chemical storage/transport	26	46	40	31	0.5
Other			2	2	0.0

Emissions from Petroleum Industries

	1970	1980	1990	1998	%
Petroleum industries	1,195	1,440	612	497	8.3
Oil and gas production	411	379	301	268	4.5
Petroleum refining	773	1,045	308	224	3.7
Asphalt manufacturing	11	16	3	5	0.1

Emissions from Chemical Manufacturing

	1970	1980	1990	1998	%
Chemical manufacturing	1,341	1,595	634	396	6.6
Organic chemicals	629	884	192	137	2.3
Inorganic chemicals	65	93	2	3	0.0
Polymers and resins	271	384	242	125	2.1
Pharmaceuticals	40	77	20	8	0.1
Other	336	157	178	123	2.0

Biogenic Emissions (1997)

Biogenic	28.194 x 10^6 tons	59.90%
Anthropogenic	18.876 x 10^6 tons	40.10%
Total	47.070 x 10^6 tons	100.00%

Regulatory Approach

Ozone NAAQS

- 1-hour standard: 0.12 ppmv
- 8-hour standard: 0.08 ppmv

Ozone Nonattainment Classifications

Classification	Concentration (ppm)	Attainment Date
Marginal	0.121-0.138	November 15, 1993
Moderate	0.138-0.160	November 15, 1996
Serious	0.160-0.180	November 15, 1999
Severe	0.180-0.190 0.190-0.280	November 15, 2005 November 15, 2007
Extreme	0.280 and above	November 15, 2010

Marginal Area SIP Requirements

- Existing vehicle I&M programs must comply with USEPA guidelines.
- RACT must be required for existing sources of VOCs.
- New or modified major sources must obtain permits and undergo review.
- The VOC emission offset ratio for new or modified major sources must be $\geq$1.1 to 1.
- VOC emissions must be inventoried every three years.
- Stationary sources of VOCs or NOx must submit annual emission statements.

Moderate Area SIP Requirements

- A basic vehicle I&M program must be implemented.
- RACT required for all existing sources of VOC for which a CTG has been issued and for all existing major sources.
- The VOC offset ratio for new or modified major sources must be $\geq$1.15 to 1.
- VOCs must be reduced at least 15% each year.
- Automatic contingency measures must be developed.

Serious Area SIP Requirements

- Improved ambient and source monitoring.
- Major source defined as potential to emit ≥50 tons per year.
- VOC offset ratio must be at least 1.2 to 1.
- If source offsets ≥1.3:1, BACT, rather than LAER, will be required.
- Changes that increase emissions from major source triggers permit requirements.
- Facilities selling >10,000 gallons per month must install Stage II controls.
- Enhanced program to reduce emissions from in-use vehicles in urban areas with 1980 population ≥200,000.
- VOCs must be reduced at least 3% each year.
- Transportation control measures must be implemented.

Severe Area SIP Requirements

- Major source defined as potential to emit ≥25 tons of VOCs per year.
- VOC offset ratio must be ≥1.3 to 1. If all existing major sources use BACT, the required offset is 1.2 to 1.
- Transportation control measures must be implemented to offset growth in vehicle miles traveled.
- Companies employing ≥100 persons must reduce employee work-related trips and increase ridership.

Extreme Area SIP Requirements

- Major source defined as potential to emit ≥10 tons of VOCs per year.
- VOC offset ratio must be ≥1.5 to 1. If all existing major sources use BACT, the required offset is 1.2 to 1.
- Any VOC increase from a major source will trigger NSR.
- Electric utilities and industrial and commercial boilers with actual emissions >25 tons/year must burn clean fuel 90% of time or use advanced control technology for control of NO_x emissions.
- Traffic control measures during heavy traffic hours to reduce use of high-polluting vehicles.
- Hoped-for development of new or improved control technologies may be used, if not needed in first 10 years.

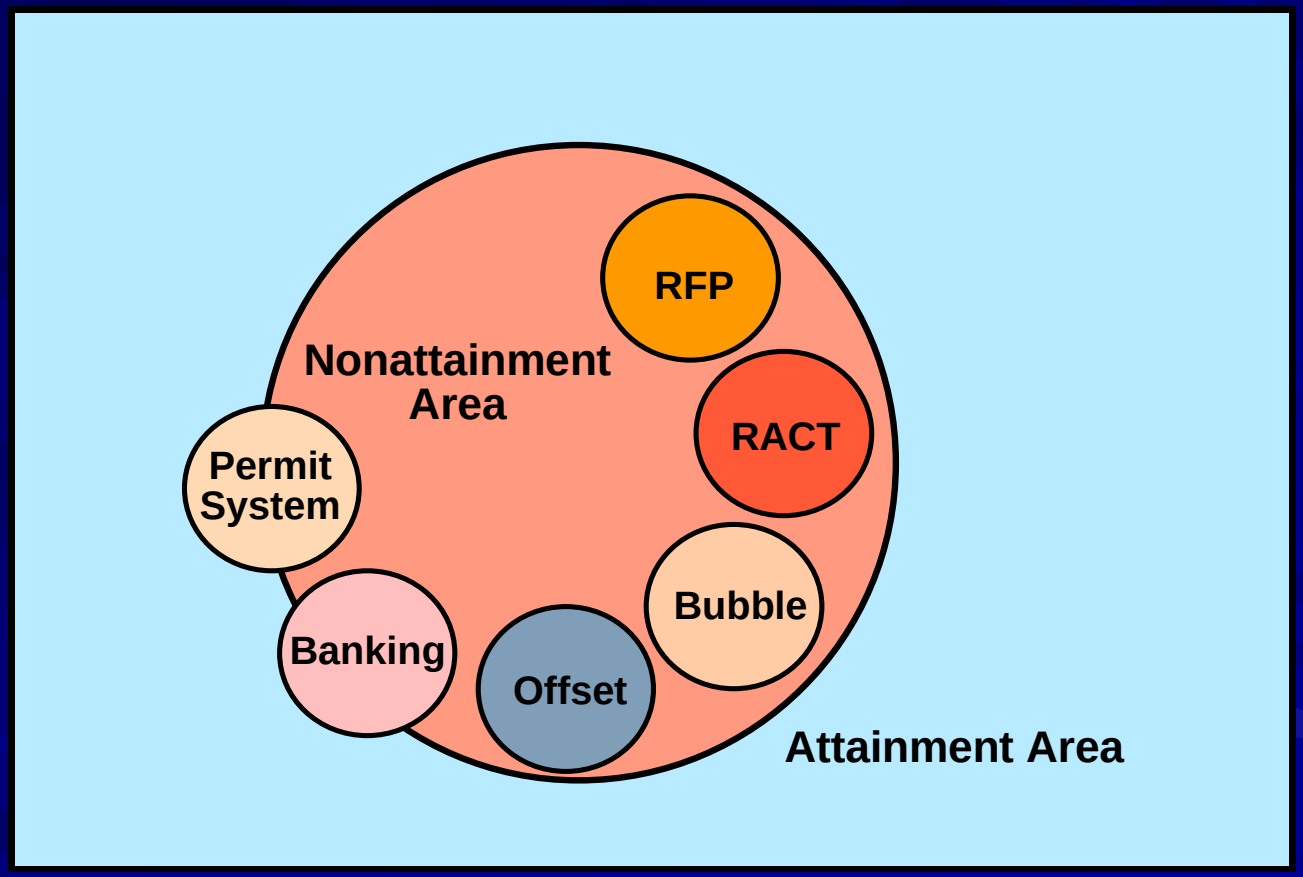
Ozone Transport Regions

- Enhanced I&M program in MSAs with a population ≥100,000.
- RACT required for all existing sources of VOC for which a CTG has been issued and for all existing major sources.
- Major sources of VOCs must undergo NSR. Major source defined as potential to emit ≥50 tons of VOCs per year.
- Major stationary sources of NO_x may be required to comply with RACT and NSR.
- Stage II vapor recovery must be implemented.

Northeast Ozone Transport Region

- Connecticut
- Delaware
- Maine
- Maryland
- Massachusetts
- New Hampshire
- New Jersey
- New York
- Pennsylvania
- Rhode Island
- Vermont
- DC CMSA

Regulation of Existing Sources



Control Technique Guideline Documents

- Definition of the affected facilities
- Number of affected facilities in the country
- National VOC emissions from the facilities
- VOC emission range per facility
- Source size emitting at least 100 tons/year
- Recommended RACT emission limit
- VOC reduction per facility after RACT is applied
- Capital and annual costs and cost per ton of VOC removed

Group I Control Technique Guideline Documents

Source Category	Reference No.
Surface coating operations	EPA 450/2-76-028
Surface coating of cans, coils, paper, fabrics, automobiles, and light-duty trucks	EPA 450/2-77-008
Surface coating of metal furniture	EPA 450/2-77-032
Surface coating of insulation of magnet wire	EPA 450/2-77-033
Surface coating of large appliances	EPA 450/2-77-034
Storage of petroleum liquids in fixed roof tanks	EPA 450/2-77-036
Bulk gasoline tanks	EPA 450/2-77-035
Solvent metal cleaning	EPA 450/2-77-022
Use of cutback asphalt	EPA 450/2-77-037
Refinery vacuum producing systems, wastewater separation, and process unit turnarounds	EPA 450/2-77-025
Hydrocarbons from tank truck gasoline loading terminals	EPA 450/2-77-026
Design criteria for Stage I vapor control systems--gasoline service stations	USEPA, OAQPS, November 1975

Group II Control Technique Guideline Documents

Source Category	Reference No.
Control techniques for volatile organic emissions from stationary sources	EPA 450/2-78-022
Leaks from petroleum refinery equipment	EPA 450/2-78-036
Surface coating of miscellaneous metal parts and products	EPA 450/2-78-015
Manufacture of vegetable oils	EPA 450/2-78-035
Surface coating of flat wood paneling	EPA 450/2-78-032
Manufacture of synthesized pharmaceutical products	EPA 450/2-78-029
Manufacture of pneumatic rubber tires	EPA 450/2-78-030
Graphic arts--rotogravure and flexography	EPA 450/2-78-033
Petroleum liquid storage in external floating roof tanks	EPA 450/2-78-047
Perchloroethylene dry cleaning systems	EPA 450/2-78-050
Leaks from gasoline tank trucks and vapor collection systems	EPA 450/2-78-051

Group III Control Technique Guideline Documents

Source Category	Reference No.
Manufacture of high-density polyethylene, polypropylene, and polystyrene resins	EPA 450/3-83-008
Synthetic organic chemical, polymer, and resin manufacturing equipment	EPA 450/3-83-006
Large petroleum dry cleaners	EPA 450/3-82-009
Air oxidation processes in synthetic organic chemical manufacturing industry	EPA 450/3-84-015
Leaks from natural gas/gasoline processing plants	EPA 450/3-83-007

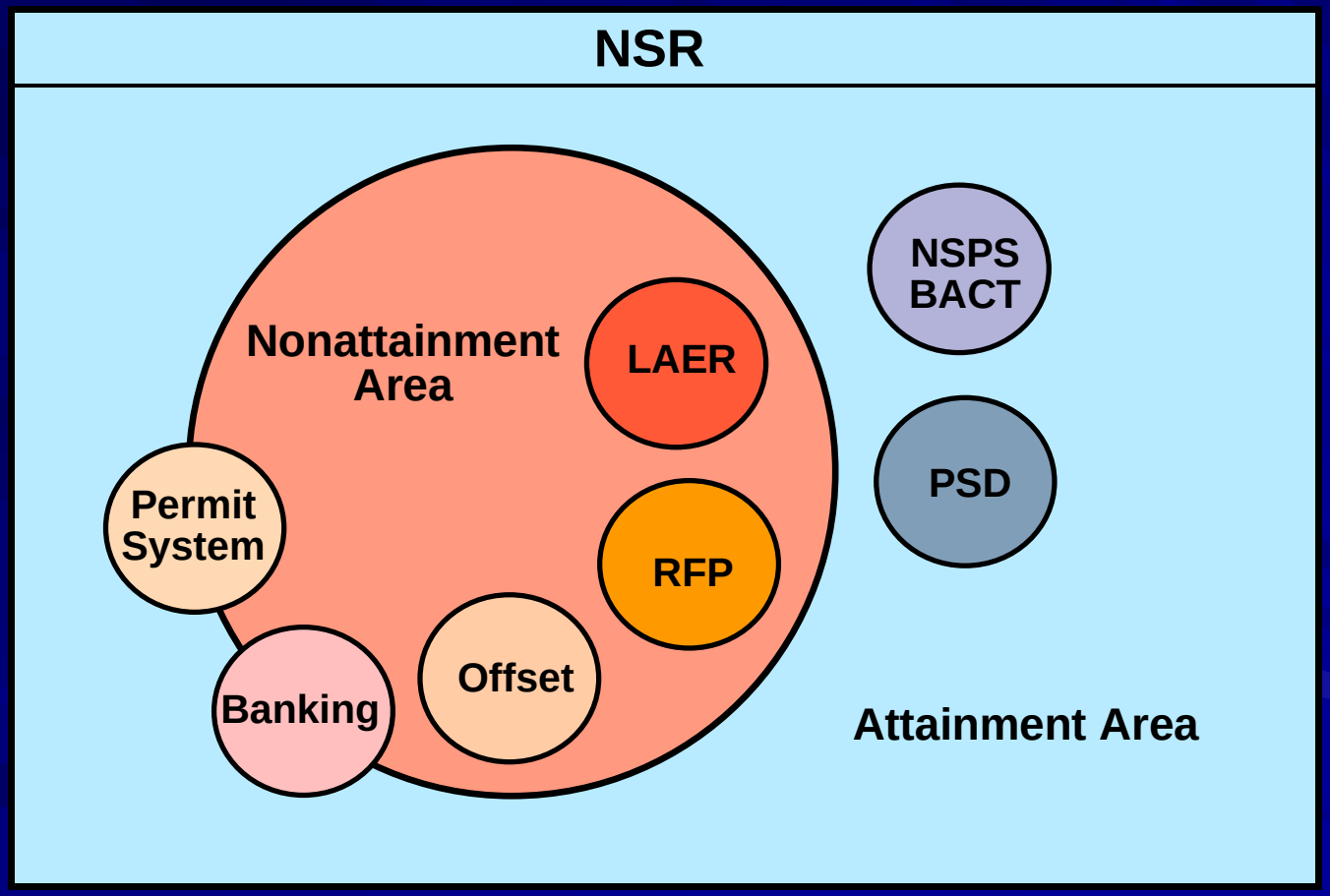
Post-1990 Control Technique Guideline Documents

Source Category	Reference No.
Control techniques for VOC emissions from stationary sources	EPA 453/R-92-018
Reactor processes and distillation operations in SOCMI	EPA 450/4-91-031
Offset lithographic printing	EPA 453/D-95-001
Wood furniture manufacturing operations	EPA 453/R-96-007
Shipbuilding and ship repair operations (surface coating)	61FR44050 August 27, 1996
Coating operations at aerospace manufacturing and rework operations	EPA 453/R-97-004
Beyond VOC RACT CTG requirements	EPA 453/R-95-010
Batch processes	EPA 453/R-93-017
Industrial wastewater	EPA 450/D-93-056
Volatile organic liquid storage tanks	EPA 453/D-93-057

Alternative Control Technology Documents

Source Category	Reference No.
Halogenated solvent cleaners	EPA 450/3-89-030
Application of traffic markings	EPA 450/3-88-007
Ethylene oxide sterilization/fumigation operations	EPA 450/3-89-007
Automobile refinishing	EPA 453/R-94-031
Organic waste process vents	EPA 450/3-91-007
Polystyrene foam manufacturing	EPA 450/3-90-020
Bakery oven emissions	EPA 453/R-92-017
Carbon reactivation processes	EPA 453/R-92-019
Surface coating operations at shipbuilding and ship repair facilities	EPA 453/R-94-032
Batch processes	EPA 453/R-94-020
Industrial cleaning solvents	EPA 453/R-94-015
Air emissions from industrial wastewater	CTG with revised option tables: 4/94
Offset lithographic printing	EPA 453/R-94-054
Application of agricultural pesticides	EPA 453/R-92-011
Surface coating of automotive/transportation and business machine plastic parts	EPA 453/R-94-017
Volatile organic liquids storage in floating and fixed roof tanks	EPA 453/R-94-001

Regulation of New and Modified Sources



New Source Performance Standards for VOC Sources (40CFR60)

Subpart	Source Category
K	Storage vessels for petroleum liquids (constructed after June 11, 1973)
Ka	Storage vessels for petroleum liquids (constructed after May 18, 1978)
Kb	Volatile organic liquid storage vessels (constructed after July 23, 1984)
EE	Surface coating of metal furniture
MM	Automobile and light-duty truck surface coating operations
QQ	Graphic arts industry: Publication rotogravure printing
RR	Pressure sensitive tape and label surface coating operations
SS	Industrial surface coating: Large appliances
TT	Metal coil surface coating
VV	Equipment leaks of VOC in the SOCMI
WW	Beverage can surface coating industry
XX	Bulk gasoline terminals
BBB	Rubber tire manufacturing industry
DDD	VOC emissions from the polymer manufacturing industry
FFF	Flexible vinyl and urethane coating and printing
GGG	Equipment leaks of VOC in petroleum refineries
HHH	Synthetic fiber production facilities
III	VOC emissions from the SOCMI air oxidation unit processes
JJJ	Petroleum dry cleaners
KKK	Equipment leaks of VOC from onshore natural gas processing plants

New Source Performance Standards for VOC Sources (40CFR60)
(continued)

Subpart	Source Category
NNN	VOC emissions from SOCMI distillation operations
QQQ	VOC emissions from petroleum refinery wastewater systems
RRR	VOC emissions from SOCMI reactor processes
SSS	Magnetic tape coating facilities
TTT	Industrial surface coating: Plastic parts for business machines
VVV	Polymeric coating of supporting substrates facilities
WWW	Municipal Solid Waste Landfills

MACT Standards for VHAP Sources (40CFR63)

Subpart	Source Category
F	Organic hazardous air pollutants from the SOCMI
G	Organic hazardous air pollutants from the SOCMI for process vents, storage vessels, transfer operations and wastewater
H	Organic hazardous air pollutants for equipment leaks
I	Organic hazardous air pollutants for certain processes subject to the negotiated regulation for equipment leaks
M	Perchloroethylene dry cleaning facilities
O	Ethylene oxide emissions from sterilization facilities
R	Gasoline distribution facilities
T	Halogenated solvent cleaning
U	Group I polymers and resins
W	Epoxy resins production and non-nylon polyamides production
Y	Marine tank vessel loading operations
CC	Petroleum refineries
DD	Off-site waste and recovery operations
EE	Magnetic tape manufacturing operations

MACT Standards for VHAP Sources (40CFR63)

(continued)

Subpart	Source Category
GG	Aerospace manufacturing and re-work facilities
HH	Oil and natural gas production
II	Shipbuilding and ship repair (surface coating)
JJ	Wood furniture manufacturing operations
KK	Printing and publishing industry
GGG	Pharmaceuticals production
HHH	Natural gas transmission and storage
III	Flexible polyurethane foam production
JJJ	Group IV polymers and resins
MMM	Pesticide active ingredient production
OOO	Group III polymers and resins
PPP	Polyether polyols production
CCCC	Manufacturing nutritional yeast
GGGG	Solvent extraction for vegetable oil production
VVVV	Boat manufacturing

Chapter 5

Surface Coating

Surface Coating

The application of a wet or dry coating material to the surface of another material, either for decoration or for protection against damage or corrosion.

Process Description

- Surface preparation
- Coating application
- Drying or curing of coating

Surface Preparation

- Cleaning
- Acid etching
- Phosphate treatment
- Chromate conversion coating
- Drying

Types of Coatings

- Conventional
- High solids
- Waterborne
- Powder
- Radiation cured

Conventional Coatings

- Use only organic solvents
- Coatings dry quickly
- Produce durable, high-quality surface
- Limited monomers and pre-polymers

Conventional Coatings Used in Coil Coating

Coating	Volatile Content, Wt %
Acrylics	40% to 45%
Adhesives	70% to 80%
Alkyds	50% to 70%
Epoxies	45% to 70%
Fluorocarbons	55% to 60%
Phenolics	50% to 75%
Polyesters	45% to 50%
Silicones	35% to 50%
Vinyls	60% to 75%
Zincromet®	35% to 40%

Typical Solvent Content of Conventional Coatings Used in Various Industries

Industry	Coating	Volatile Content, vol %
Metal furniture	Not specified	65%
Automobile and light-duty truck	Enamel	67% to 76%
Automobile and light-duty truck	Lacquer	82% to 88%
Automobile refinishing	Enamel	72% to 76%
Automobile refinishing	Lacquer	87% to 91%
Large appliance	Not specified	70%
Traffic marking	Alkyd	50%

High-Solids Coatings

- Typically greater than 60% solids by volume
- Less drum handling
- Reduced freight costs
- Reduced solvent removal energy
- Increased viscosity

Emission Reductions for High-Solids Coatings

Coating	Emission Reduction %
60% solids by volume	61% to 62%
65% solids by volume	69%
70% solids by volume	75%
80% solids by volume	85%

Waterborne Coatings

- Contain 2-15% by volume organic solvent
- Types of waterborne coatings:
  - Water-soluble dispersions
  - Water-soluble polymers
  - Emulsions

Waterborne Coatings

- Wide range of formulations
- Can be used with high solids
- Easier clean up
- Increased drying energy
- Need better surface preparation
- Corrosion potential

Emission Reductions for Waterborne Coatings

Coating	Application Method	Emission Reduction, %
82/18 waterborne	Electrostatic spraying	80% to 82%
82/18 waterborne	Dip and flow coating	82%
82/18 waterborne	Electrodeposition	95%
67/33 waterborne	Electrostatic spraying	67%
67/33 waterborne	Dip and flow coating	67%

Powder Coatings

- Contain no solvent carrier
- Thermoplastic coatings melt when heated
- Thermosetting coatings polymerize
- Small quantities of VOC may be emitted during polymerization

Powder Coatings

- Better chemical and abrasion resistance
- Decreased curing energy
- Excess powder easily recovered
- Higher coating cost
- Limited number of formulations
- Higher capital equipment costs
- Higher temperatures required for curing
- Color mixing may occur during changes

Emission Reductions for Powder Coatings

Coating	Type	Emission Reduction, %
Epoxy	Thermosetting	97% to 99%
Acrylics	Thermosetting	99%
Urethane polyester	Thermosetting	96% to 98%
Polyester	Thermoplastic	99%
Acrylics	Thermoplastic	99%

Radiation-Cured Coatings

- Contain no solvent carrier
- Cures by polymerization with UV or electron beam radiation
- High line speeds
- Decreased operating cost
- Reduced floor space
- Higher coating cost
- Limited number of formulations
- Higher capital equipment costs
- Operational hazards

Coating Application

- Spray coating
- Dip coating
- Flow coating
- Roller coating
- Electrodeposition coating

Coating Application Methods for Various Industries

Method	Coil Coating	Metal Furniture	Auto & Light Truck	Large Appliances
Air-atomized spray			X	X
Airless spray				X
Electrostatic spray		X	X	X
HVLP			X	
Electrostatic bell & disk				X
Dip		X		X
Flow		X		X
Roller	X			
Electrodeposition	X		X	X

Coating Application Methods for Various Industries (cont'd)

Method	Can	Auto Refinish	Traffic Marking	Wood Bldg Products	Fabric
Air-atomized spray	X	X	X	X	X
Airless spray		X		X	X
Electrostatic spray		X		X	X
HVLP		X		X	X
Electrostatic bell & disk				X	X
Dip				X	X
Flow				X	
Roller	X			X	X
Electrodeposition					

Transfer Efficiency

$$\text{Transfer efficiency} = \frac{\text{Solids applied to surface}}{\text{Total solids used}} \text{ x } 100$$

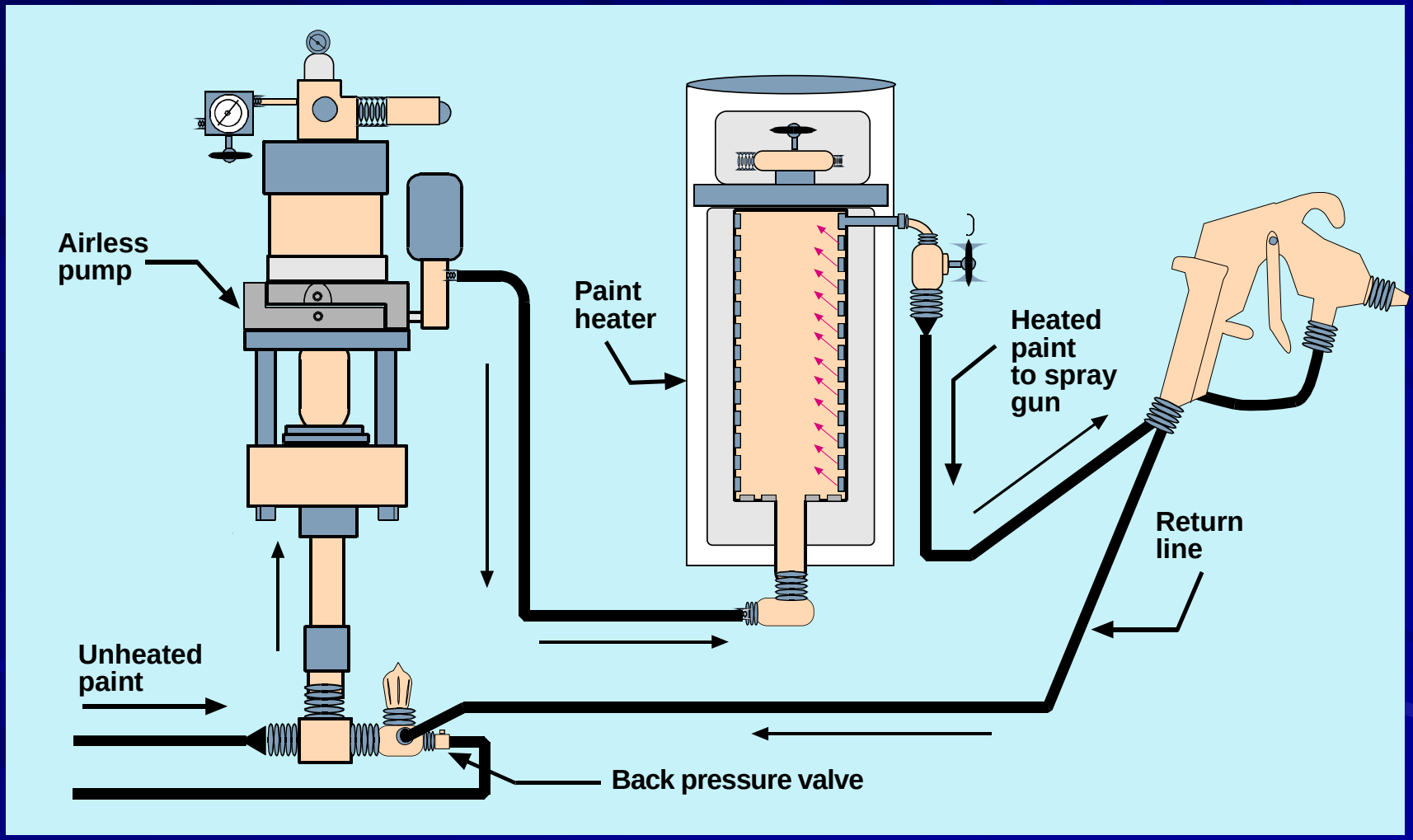
Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure spray

Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure spray

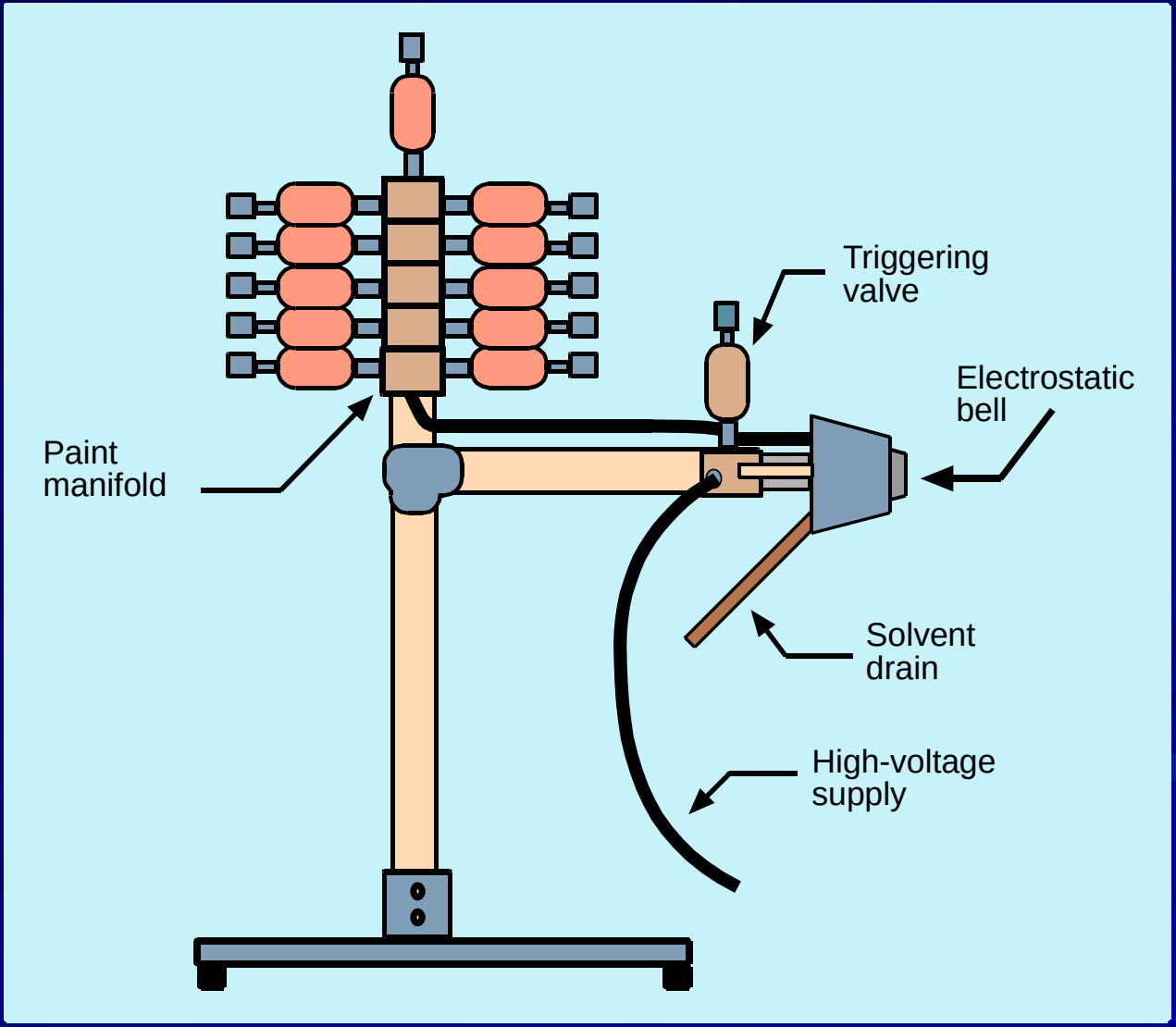
Airless Spray Gun

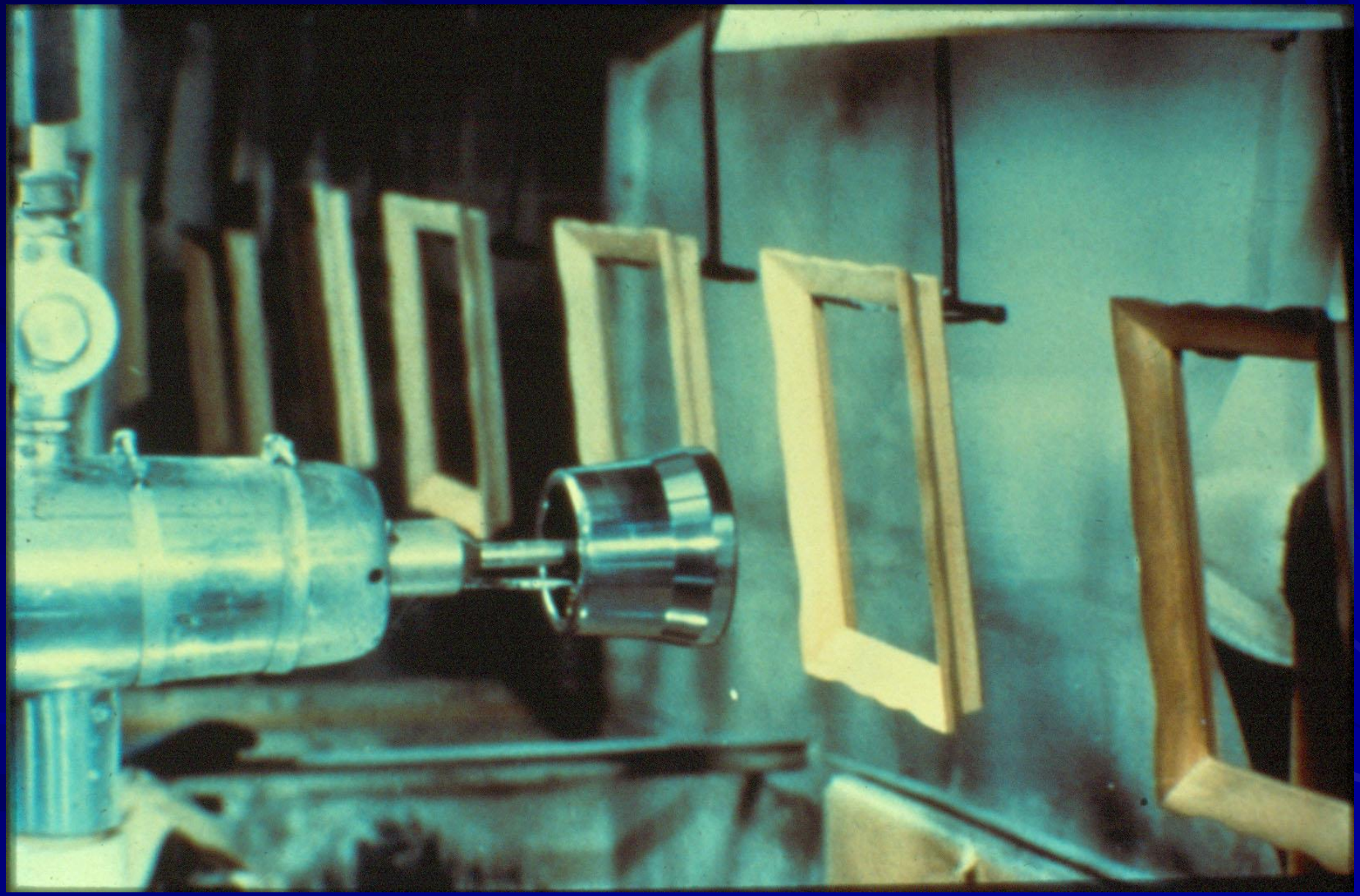


Spray Coating

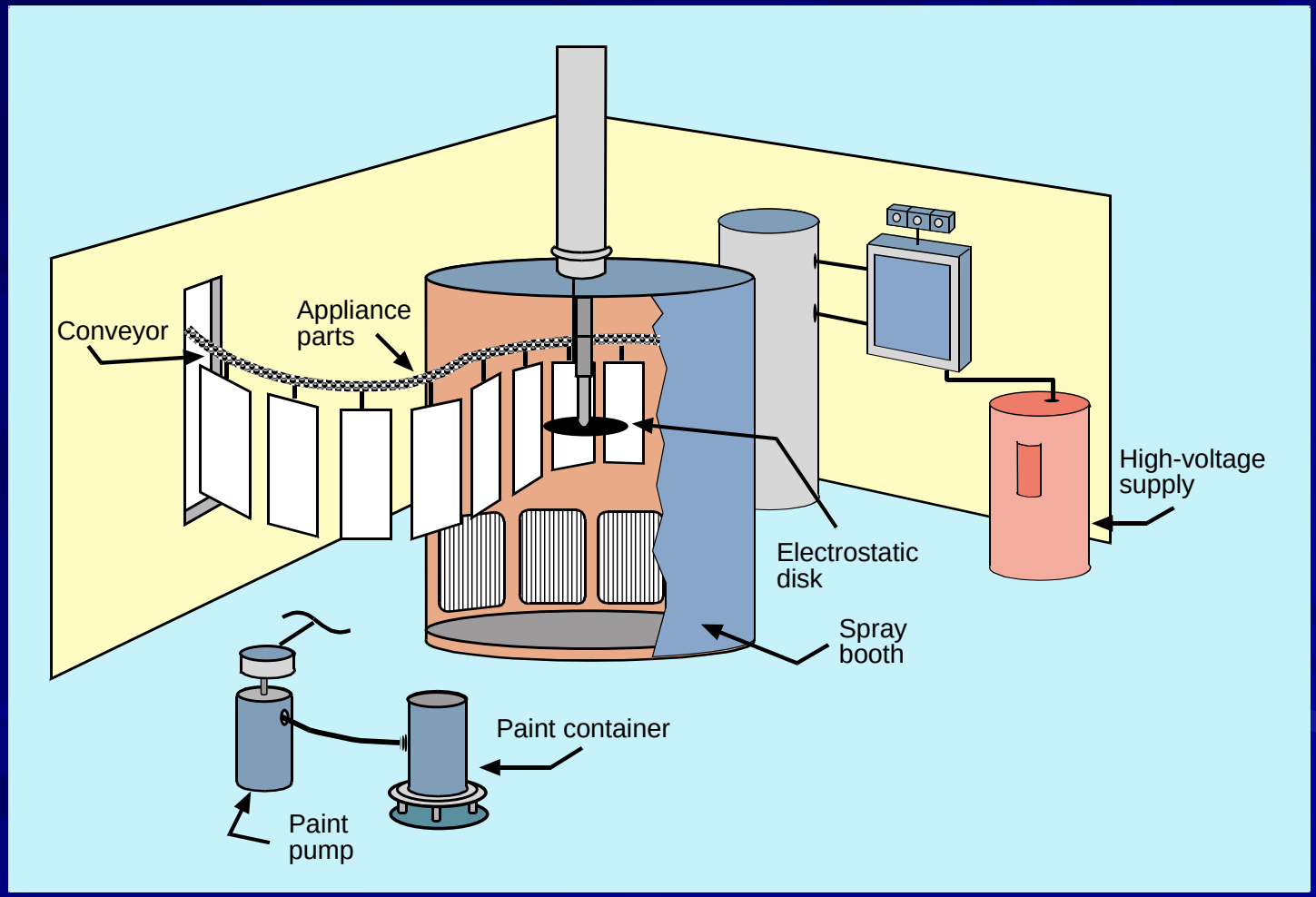
- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure spray

Electrostatic Bell





Reciprocating Disk



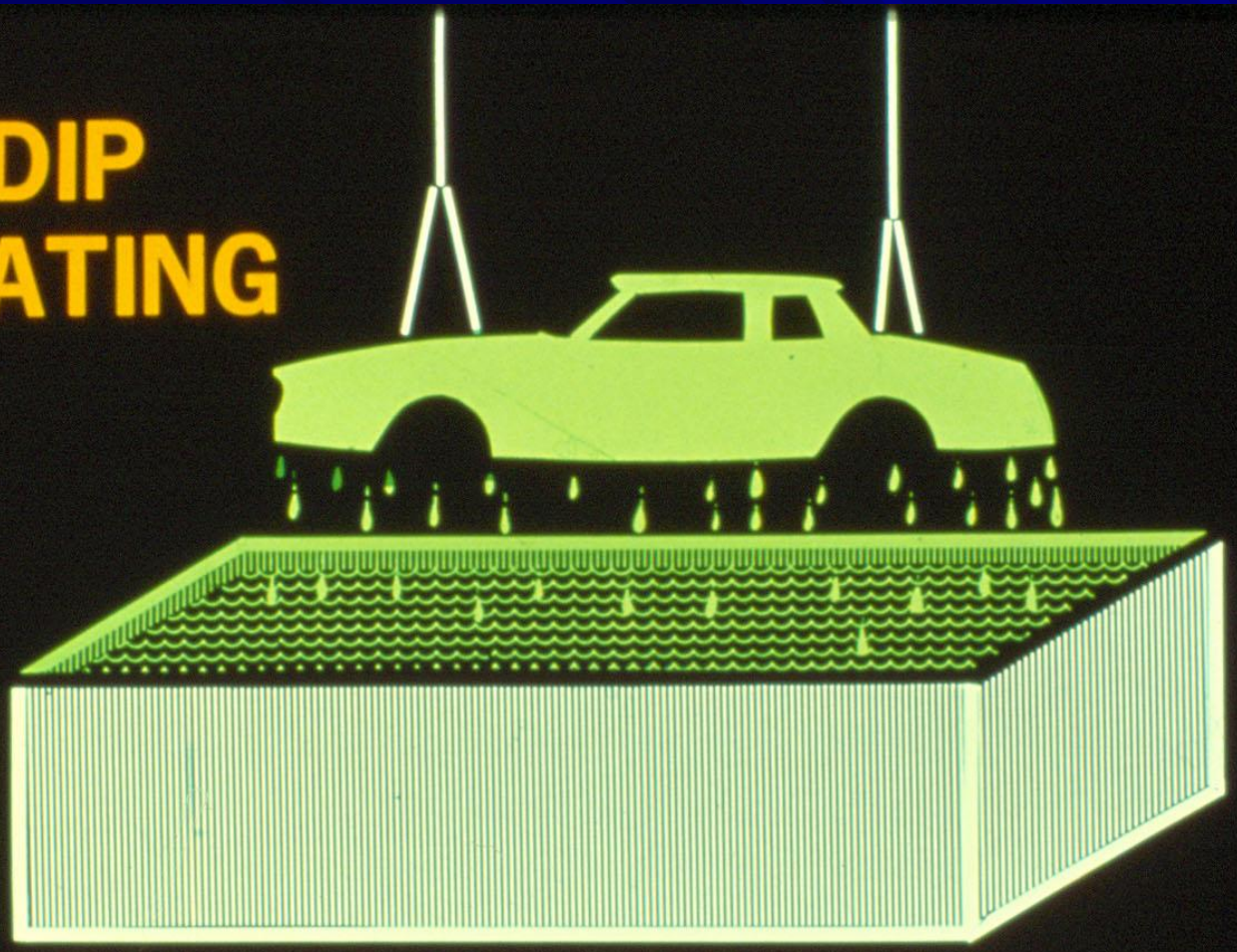
Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure spray

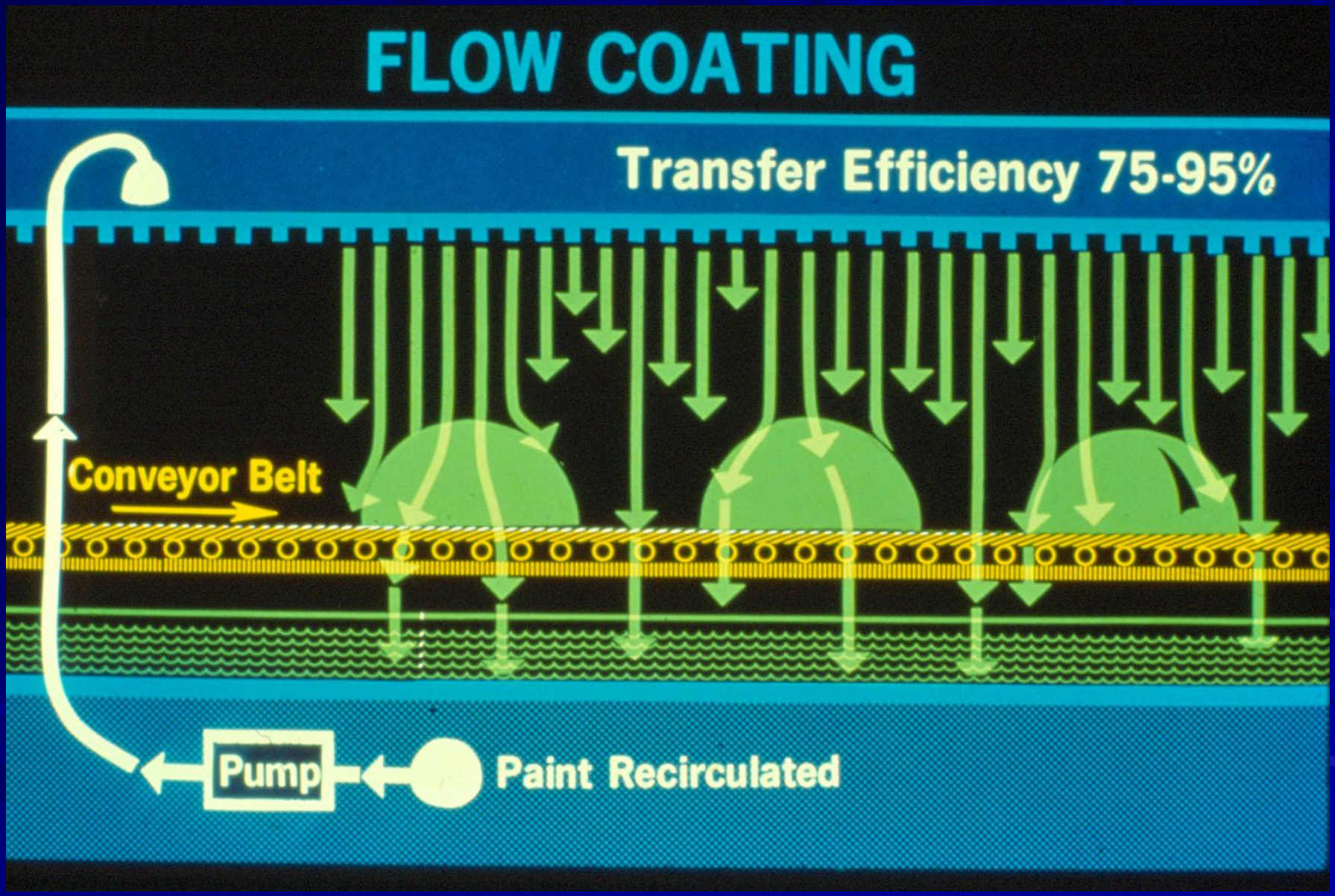
Transfer Efficiencies for Spray Application

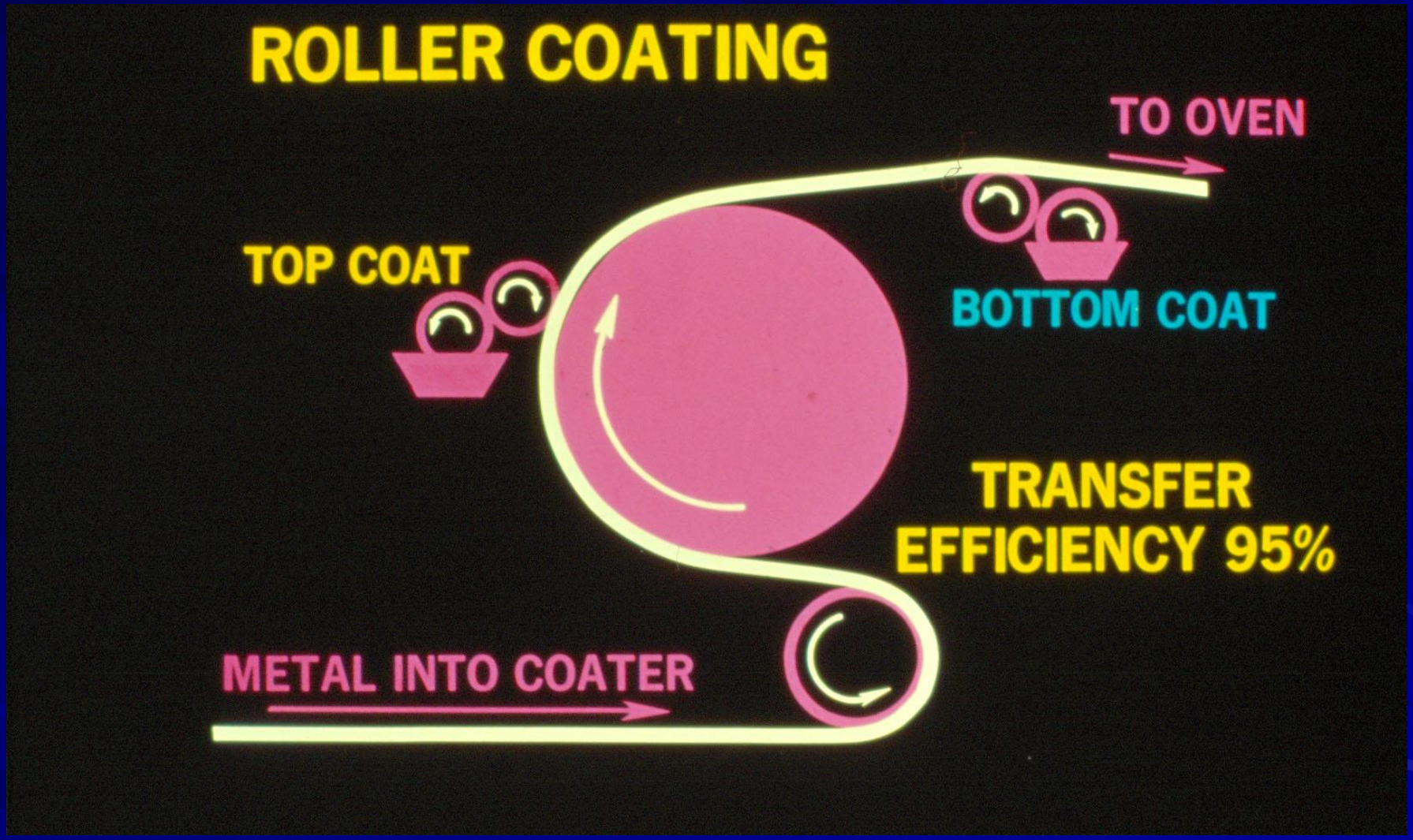
Spraying Method	Flat Surface	Table-Leg Surface	Bird-Cage Surface
Air-atomized	50	15	10
Airless	75-80	10	10
Electrostatic air-atomized	75	65	65
Electrostatic airless	80	70	70
Electrostatic disk	95	90-95	90-95

DIP COATING



Transfer Efficiency 75% - 95%


FLOW COATING
Transfer Efficiency 75-95%
Conveyor Belt
Pump
Paint Recirculated


ROLLER COATING
TO OVEN
TOP COAT
BOTTOM COAT
TRANSFER
EFFICIENCY 95%
METAL INTO COATER

Electrodeposition Coating

Curing

- Pre-drying
- Staged temperature ovens
- Explosion potential
- Cooling

Emission Control Techniques

- Reduced-VOC coating
- Higher transfer efficiency application
- Add-on control equipment

Percent of Total Emissions by Coating Step for Different Coating Methods

Coating Method	Application	Pre-Dry	Oven
Spray coating	30-50	10-30	20-40
Dip coating	5-10	10-30	50-70
Flow coating	30-50	20-40	10-30
Roller coating	0-5	10-20	60-80

Emission Regulation

Surface Coating of Large Appliances, Control Technique Guideline Document, EPA-450/2-77-034

Recommended standard:

An emission limit of 2.8 lbs of VOC per gallon of coating less water

Standards of Performance for Industrial Surface Coating: Large Appliances, 40CFR60, Subpart SS

Applicability Date: December 24, 1980
Applicability Size: All

Standard:

An emission limit of 7.51 lbs of VOC per gallon of solids applied

Surface Coating of Metal Coils, Control Technique Guideline Document, EPA-450/2-77-008

Recommended standard:

An emission limit of 2.6 lbs of VOC per gallon of coating less water.

Standards of Performance for Metal Coil Surface Coating, 40CFR60, Subpart TT

Applicability Date: January 5, 1981
Applicability Size: All

Standard:

- An emission limit of 2.34 lbs of VOC per gallon of solids applied (no control device); or
- An emission limit of 1.17 lbs of VOC per gallon of solids applied (control device); or
- An emission limit of 10% of the VOCs applied for each calendar month (control device); or
- An emission limit between 1.17 and 2.34 lbs of VOC per gallon of solids applied

Process Inspection

- Review coating composition and consumption records
- Observe coating preparation
- Observe coating application
- Observe pre-drying area
- Observe curing area

Review Coating Composition and Consumption Records

- Composition data evaluated to determine compliance with permit and regulations
  - Solvent content
  - Solids content
  - Water content
  - Solvent density
  - Coating density
- Consumption data evaluated to determine compliance with permit

Observe Coating Preparation

- Determine if area is ventilated
- Note if drums are kept closed
- Determine if solvents have changed
- Observe spill cleanup
- Get sample of “as applied” coating

Observe Coating Application

- Determine if area is ventilated
- Note changes in application method
- Determine changes in application rate
- Determine if control system is adjusted
- Observe spill cleanup

Observe Pre-Drying Area

- Determine if area is ventilated
- Determine if control system is adjusted

Observe Curing Area

- Check physical integrity of oven
- Check oven temperatures
- Determine changes in line speed
- Determine if control system is adjusted