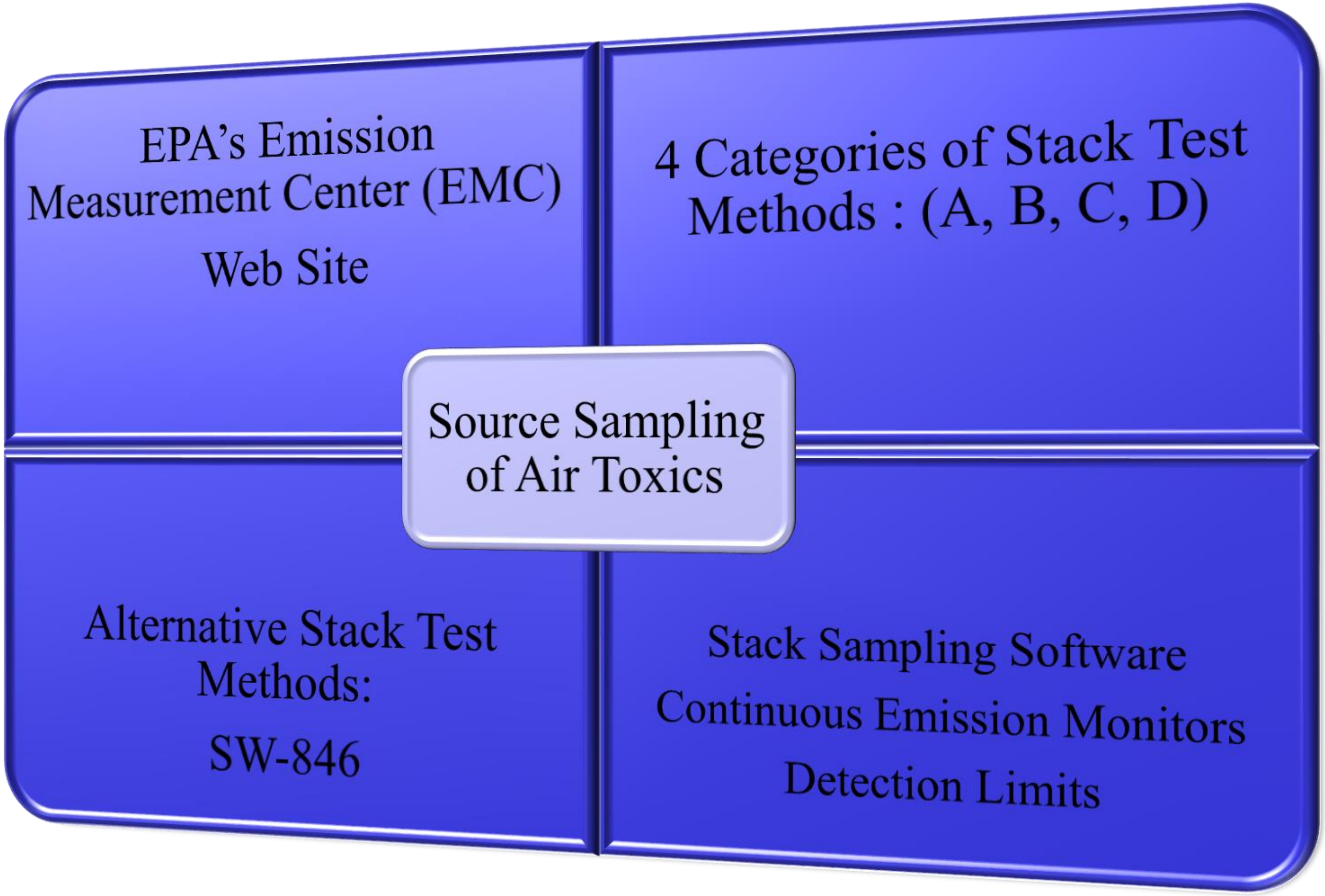
Chapter Eleven

Source Sampling of Air Toxics



Source Sampling of Air Toxics

EPA's Emission Measurement Center (EMC)

Web Site

4 Categories of Stack Test Methods : (A, B, C, D)

Alternative Stack Test Methods:

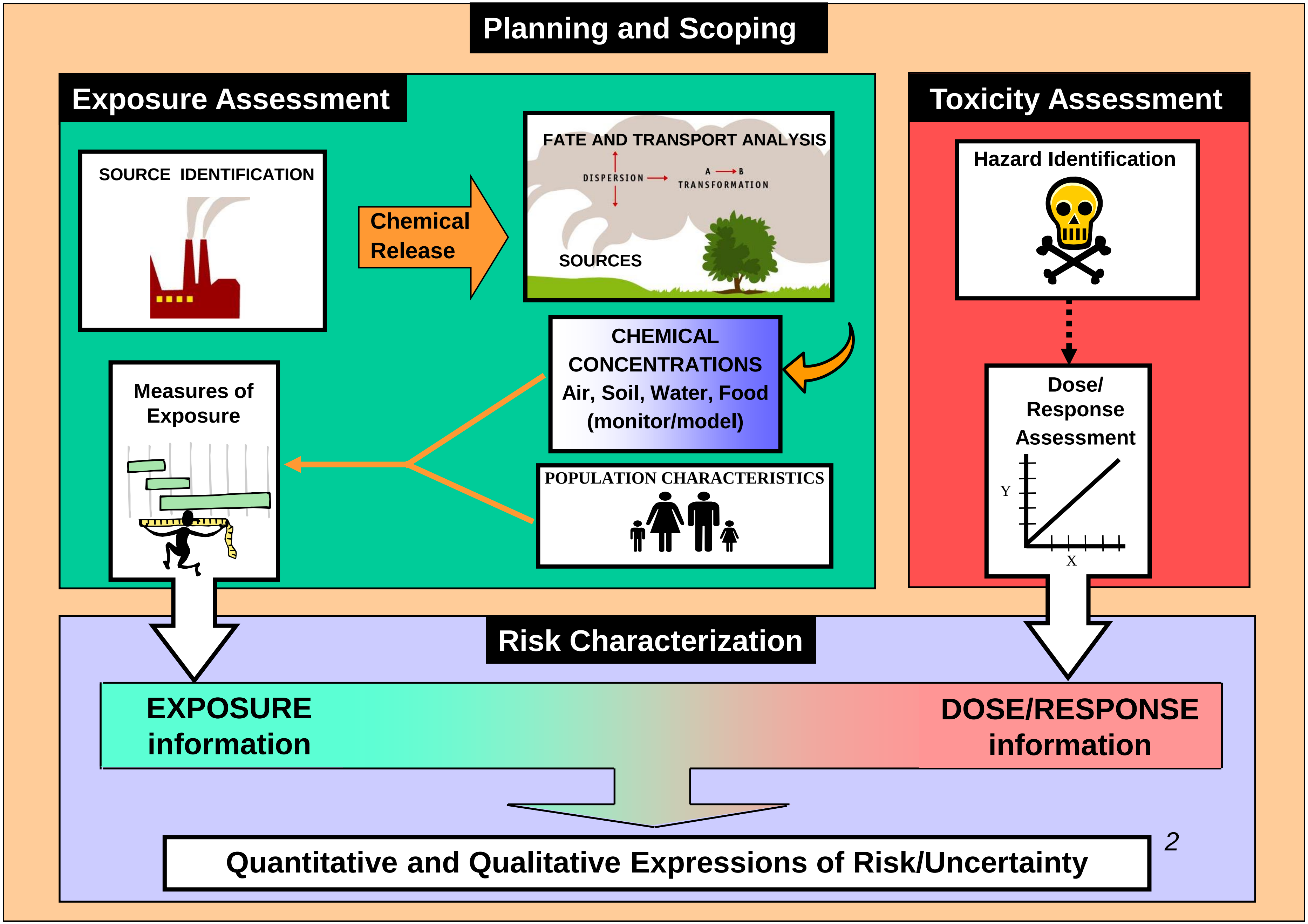
SW-846

Stack Sampling Software

Continuous Emission Monitors

Detection Limits

The Detailed Air Toxics Risk Assessment Process



Planning and Scoping

Exposure Assessment

SOURCE IDENTIFICATION

Chemical Release

FATE AND TRANSPORT ANALYSIS

CHEMICAL CONCENTRATIONS
Air, Soil, Water, Food
(monitor/model)

POPULATION CHARACTERISTICS

Measures of Exposure

Toxicity Assessment

Hazard Identification

Dose/ Response Assessment

Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty

The Detailed Air Toxics Risk Assessment Process

Planning and Scoping

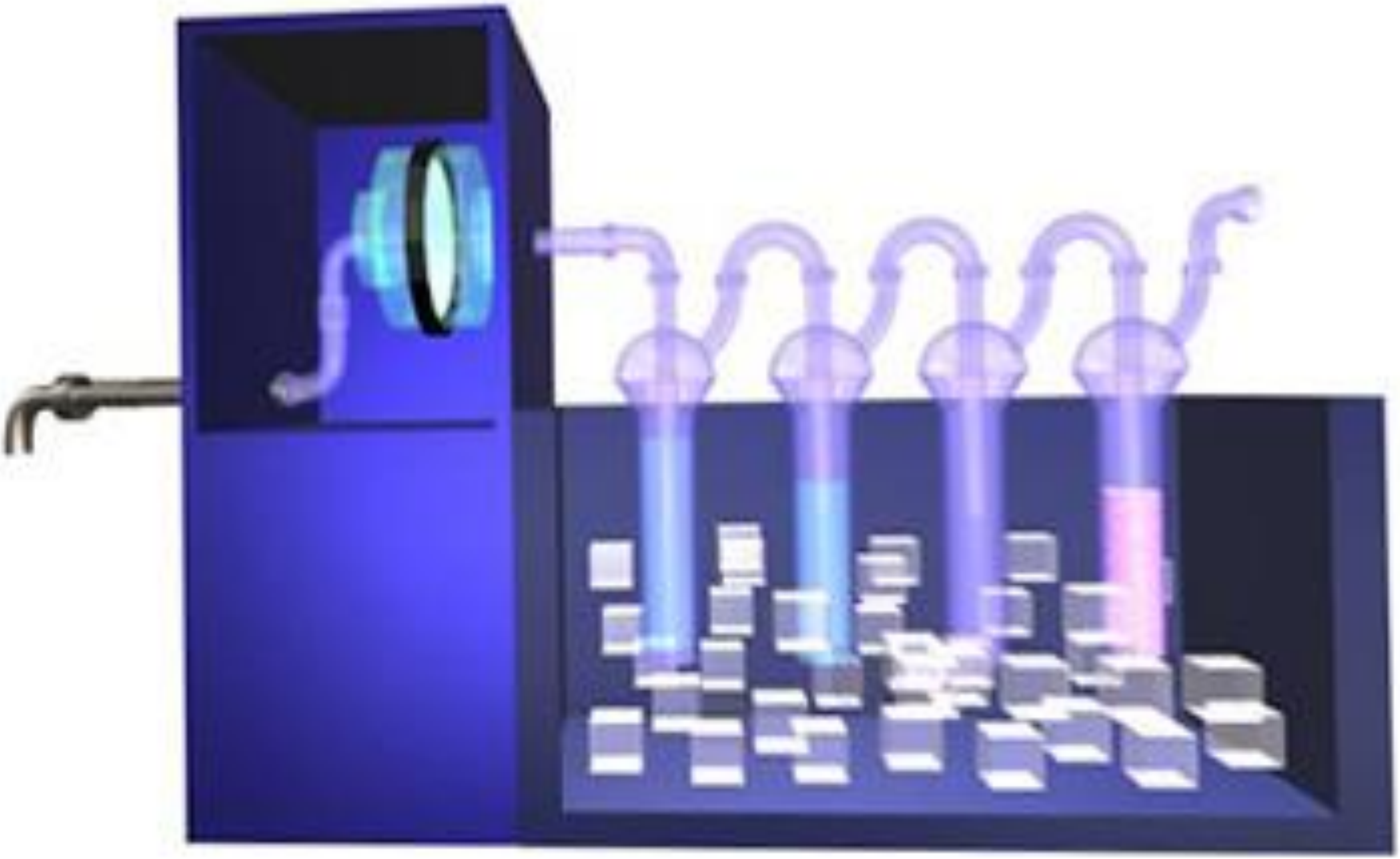
Exposure Assessment

SOURCE MEASUREMENT

Toxicity Assessment

Risk Characterization

EPA's Test Methods Numbering System



EPA's Test Methods Numbering System

- **Between 1 and 100**: New Source Performance Standards (NSPSs).
  - These methods are found in 40 CFR Part 60, Appendix A.
- The **100 series**: National Emission Standards for Hazardous Air Pollutants (NESHAPs).
  - These methods are found in 40 CFR Part 61, Appendix B.
- The **200 series**: State Implementation Plans (SIPs).
  - These methods are found in 40 CFR Part 51, Appendix M.
- The **300 series**: Maximum Acievable Control Technology (MACT) standards.
  - These methods are found in 40 CFR Part 63, Appendix A

Objectives of Stack Testing for HAP’s or Any Pollutant

- The objectives of performing a stack test is to determine the pollutant mass rate (pmr) or emission rate (E) of pollutant going up the stack to:
  - determine whether compliance limits are being met,
  - Assist in establishing emission standards &
  - For screening tests that will provide a preliminary indication of levels of pollution.

What is the Driving Force

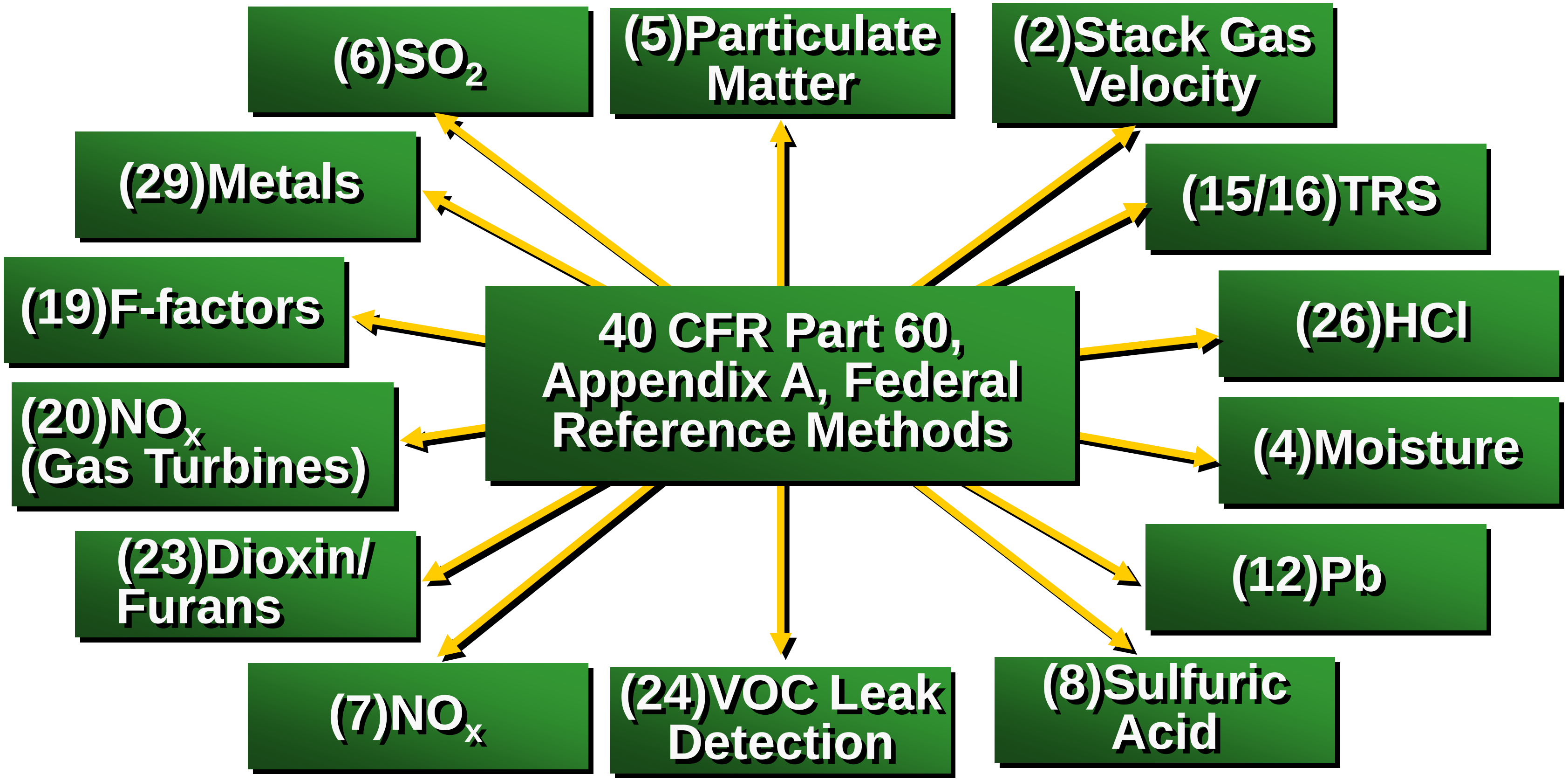
- New Source Performance Standards (NSPS-1970)
- National Emission Standards for Hazardous Air Pollutants
  - NESHAPS pre 1990 CAAA
  - NESHAPS post 1990 CAAA

Where Do We Find the Test Methods?

- Federal Test Methods- Methods are those (Federal Reference Methods and others) specified in the applicable standards as the test methods used to demonstrate compliance with emission limits or to quantify emissions in meeting regulatory initiatives.
- EPA's Emission Measurement Center Website:
- www.epa.gov/ttn/emc/tmethods.html

40 CFR Part 60 New Source Performance Standards Methods (00 Series, Appendix A)

New Source Performance Standard (NSPS) Reference Methods-00 Series



40 CFR Part 60, Appendix A, Federal Reference Methods

(6)SO_2

(5)Particulate Matter

(2)Stack Gas Velocity

(29)Metals

(15/16)TRS

(19)F-factors

(26)HCl

(20)NO_x (Gas Turbines)

(4)Moisture

(23)Dioxin/ Furans

(12)Pb

(7)NO_x

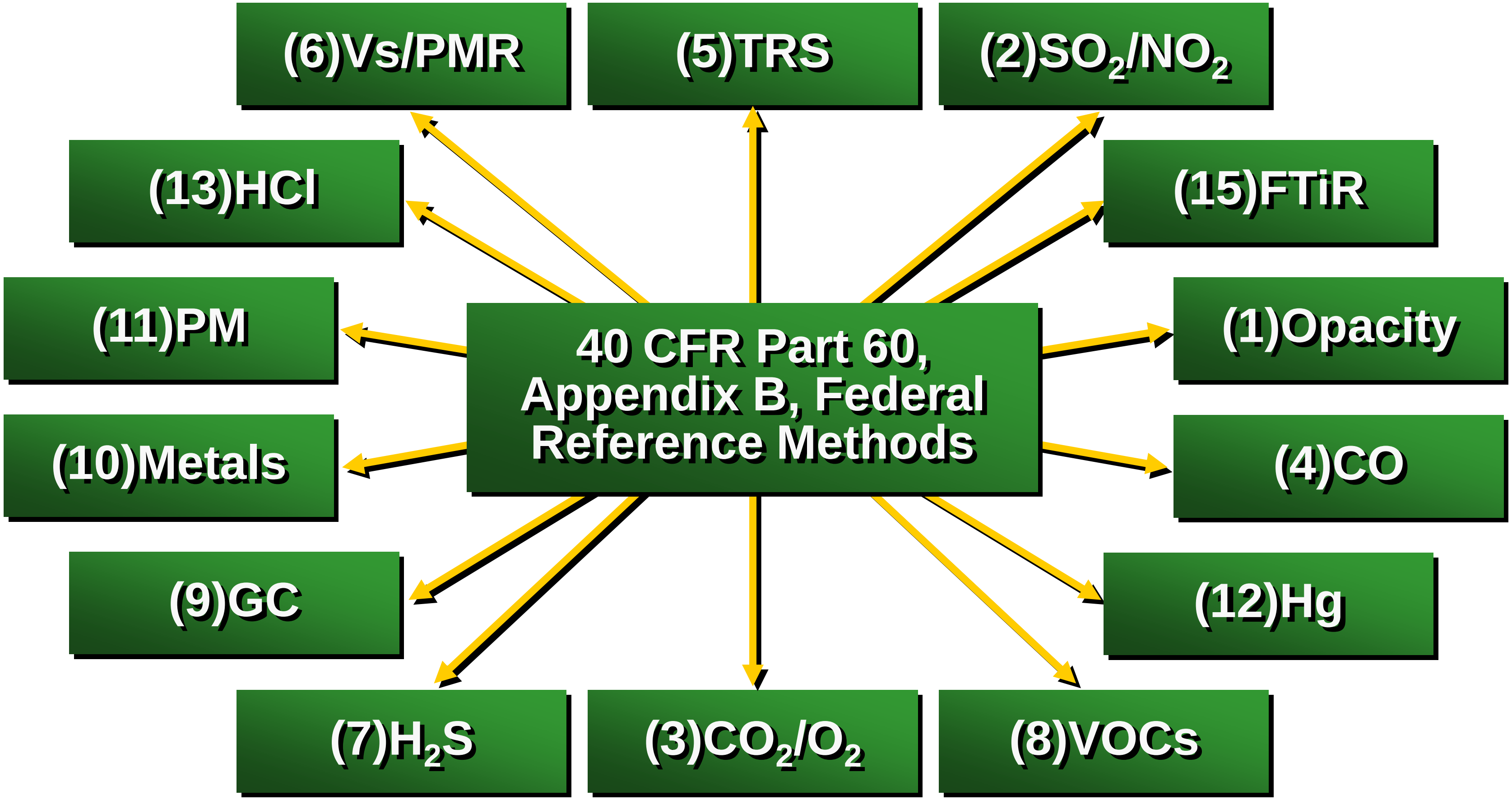
(24)VOC Leak Detection

(8)Sulfuric Acid

- 40 CFR Part 60
  Performance Specification Test (PST) Methods (00 Series)

- 40 CFR Part 61
  State Implementation Plan (SIP) Methods (200 Series, Appendix M)

Performance Specification Test (PSTs)-00 Series



40 CFR Part 60, Appendix B, Federal Reference Methods

(6)Vs/PMR

(5)TRS

(2)SO_2/NO_2

(13)HCl

(15)FTiR

(11)PM

(1)Opacity

(10)Metals

(4)CO

(9)GC

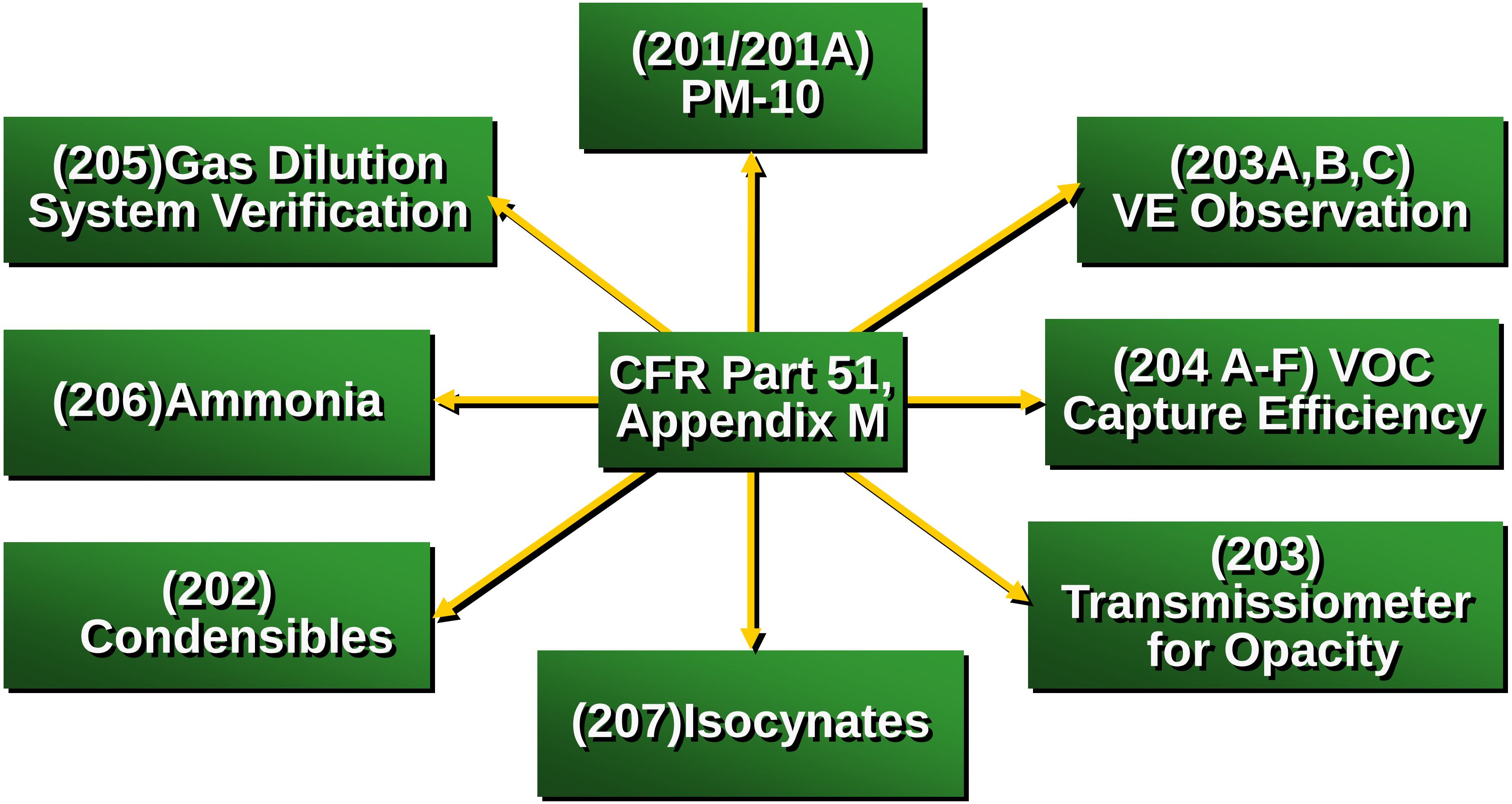
(12)Hg

(7)H_2S

(3)CO_2/O_2

(8)VOCs

State Implementation Plan (SIP)- 200 Series



CFR Part 51, Appendix M

(201/201A) PM-10

(203A,B,C) VE Observation

(204 A-F) VOC Capture Efficiency

(203) Transmissiometer for Opacity

(207)Isocynates

(202) Condensibles

(206)Ammonia

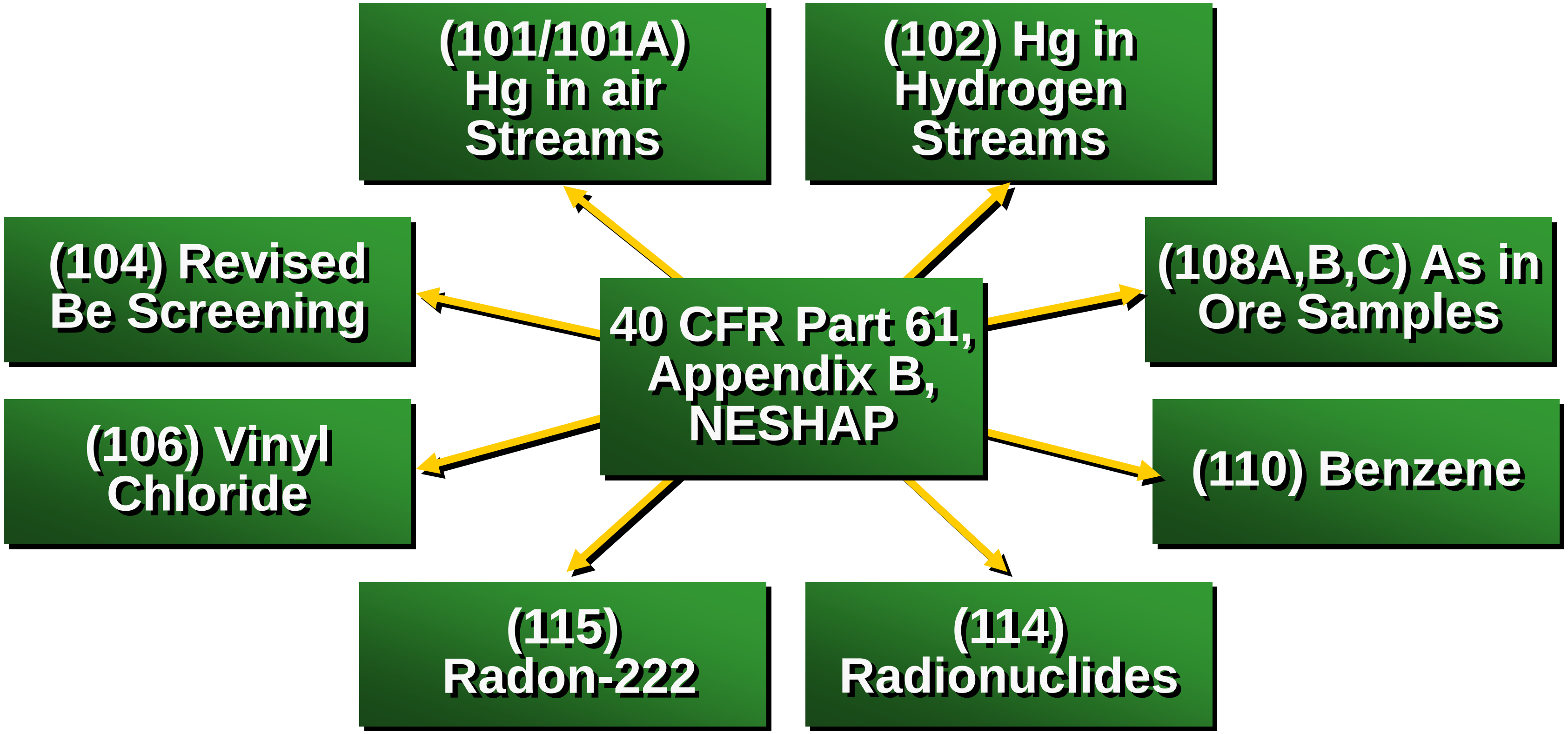
(205)Gas Dilution System Verification

National Emission Standards for Hazardous Air Pollutants (NESHAPs)

- NESHAPS pre 1990 CAA Amendments
  - 40 CFR Part 61
  - 100 Series
  - Appendix B

- NESHAPS post 1990 CAA Amendments
  - 40 CFR Part 63 (MACTs)
  - 300 Series
  - Appendix A

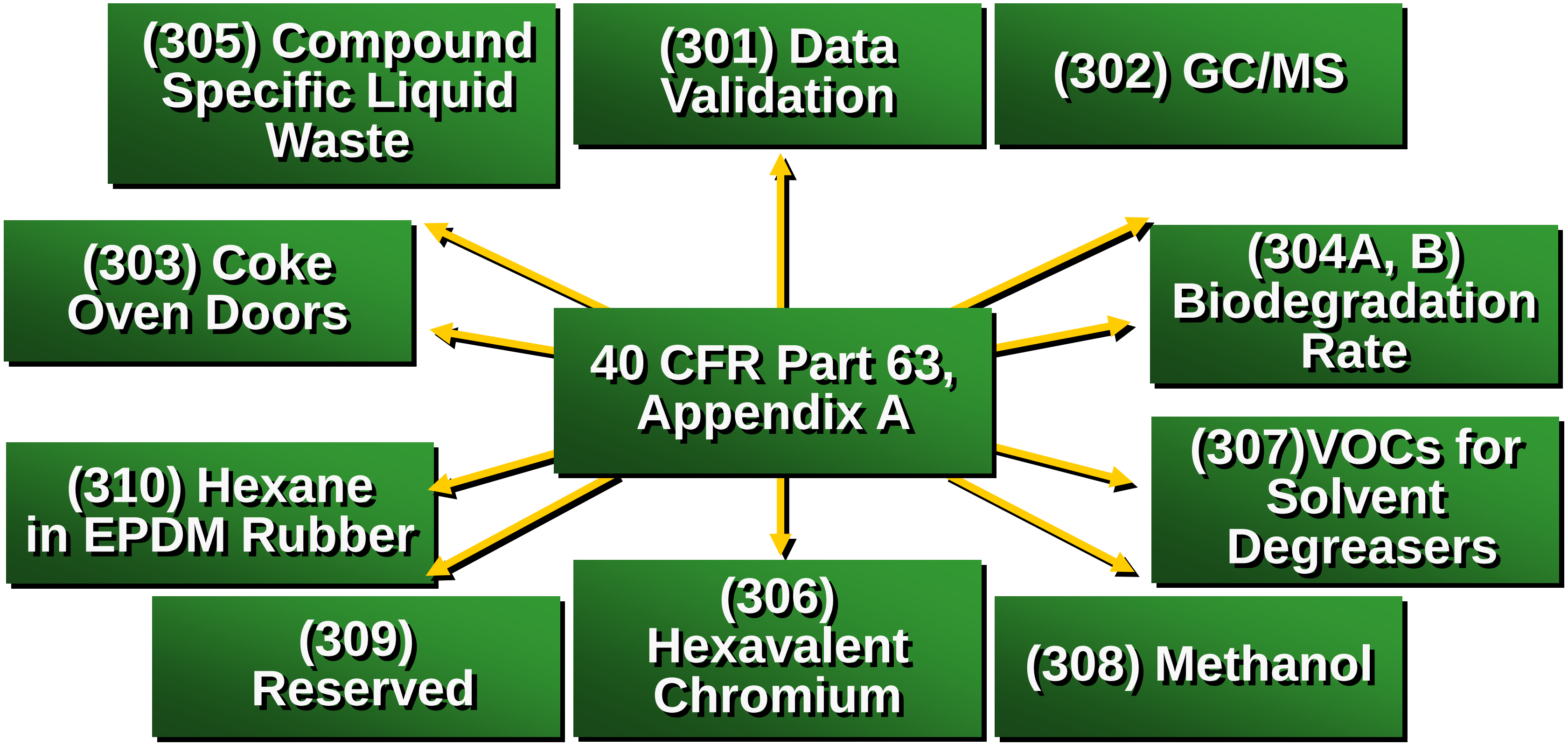
National Emission Standards For Hazardous Air Pollutants (NESHAPs)- 100 Series



40 CFR Part 61, Appendix B, NESHAP

- (101/101A) Hg in air Streams
- (102) Hg in Hydrogen Streams
- (104) Revised Be Screening
- (108A,B,C) As in Ore Samples
- (106) Vinyl Chloride
- (110) Benzene
- (115) Radon-222
- (114) Radionuclides

Maximum Achievable Control Technology (MACT)-300 Series



40 CFR Part 63, Appendix A

(305) Compound Specific Liquid Waste

(301) Data Validation

(302) GC/MS

(303) Coke Oven Doors

(304A, B) Biodegradation Rate

(310) Hexane in EPDM Rubber

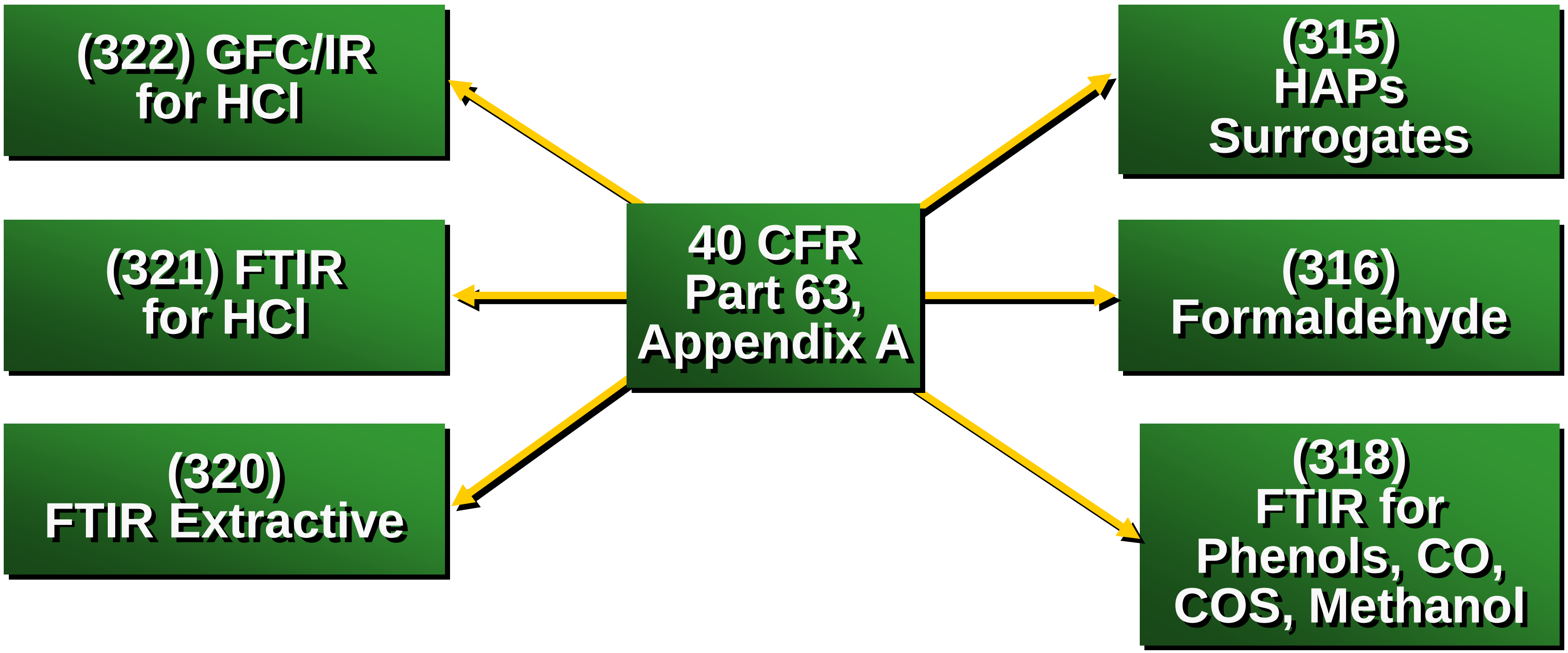
(307)VOCs for Solvent Degreasers

(309) Reserved

(306) Hexavalent Chromium

(308) Methanol

Maximum Achievable Control Technology (MACT)-300 Series



40 CFR Part 63, Appendix A

(322) GFC/IR for HCl

(321) FTIR for HCl

(320) FTIR Extractive

(315) HAPs Surrogates

(316) Formaldehyde

(318) FTIR for Phenols, CO, COS, Methanol

EPA's Categories of Stack Test Methods

- **Category A**: Methods proposed or promulgated in Federal Register
  - Compliance Methods for 40 CFR Parts 60, 61, & 63
  - Use the # Series: 00 – 100 – 200 - 300
- **Category B**: Source category approved alternative methods
  - Are approved alternatives to the methods required by 40 CFR Parts 60, 61 and 63
  - Methods may be used by sources for determining compliance with the requirements of these Parts without further EPA approval.

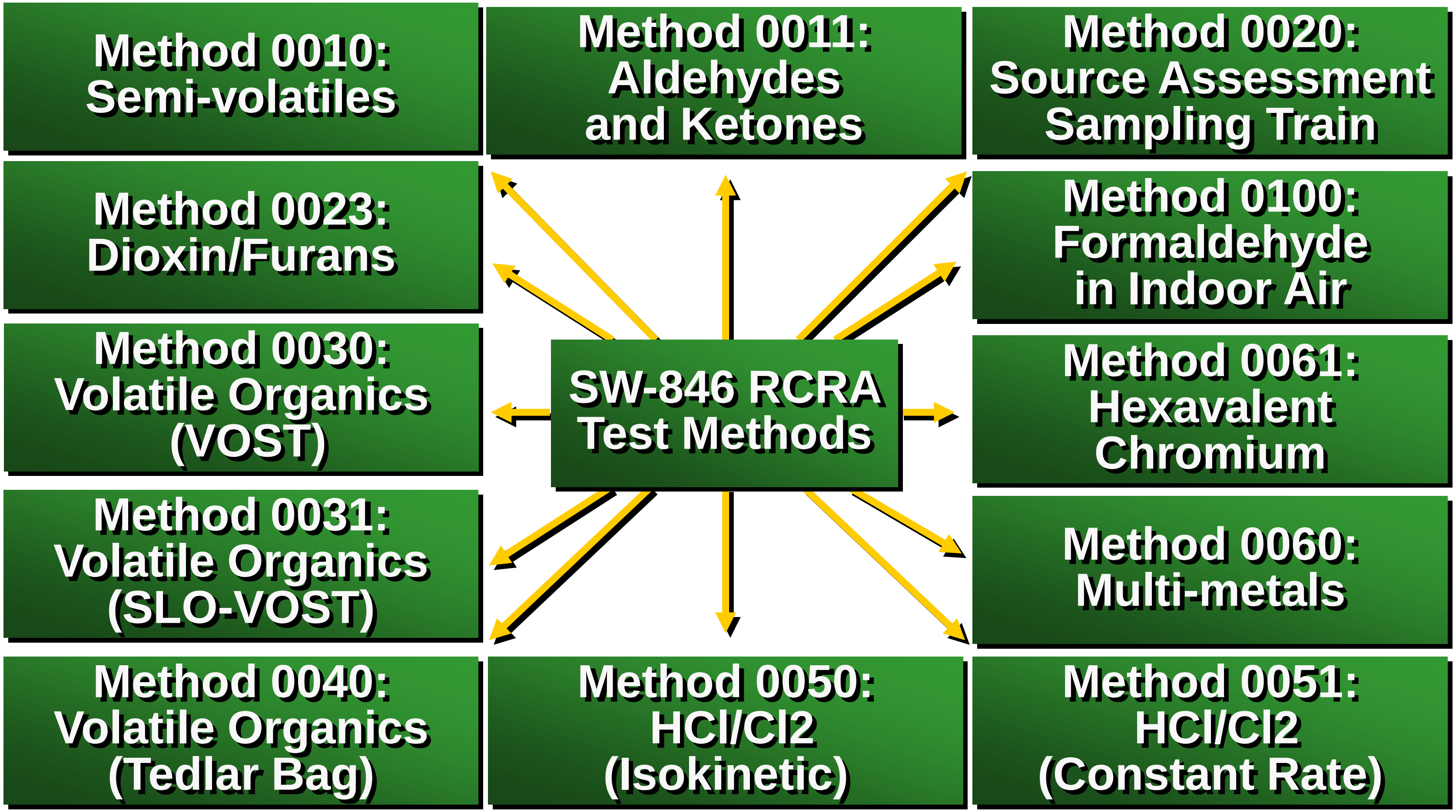
EPA's Categories of Stack Test Methods

- **Category C**: Other test methods which have not yet been subject to Federal rulemaking process.
  - Considered as alternative methods to meet Federal requirements under 40 CFR Parts 60, 61, and 63. However, they must be approved as alternatives before a source may use them for this purpose.
- **Category D**: Historic Methods - methods that were categorized as conditional test methods before EMC's method categories were revised.
  - Category is closed & no new methods will be added.
  - Must be approved as alternatives before a source may use them to meet 40 CFR Part 60, 61, and 63.

Resource Conservation And Recovery Act (RCRA)

- Many of the stack test methods for criteria pollutants were combined with analytical methods for hazardous materials to establish sampling methods for HAPs.
- SW-846 is the compendium of analytical and test methods used in determining regulatory compliance under RCRA.
- Can be found at EPA’s EMC web page

SW-846 Stack Test Methods



SW-846 RCRA Test Methods

Method 0010: Semi-volatiles

Method 0011: Aldehydes and Ketones

Method 0020: Source Assessment Sampling Train

Method 0023: Dioxin/Furans

Method 0100: Formaldehyde in Indoor Air

Method 0030: Volatile Organics (VOST)

Method 0061: Hexavalent Chromium

Method 0031: Volatile Organics (SLO-VOST)

Method 0060: Multi-metals

Method 0040: Volatile Organics (Tedlar Bag)

Method 0050: HCl/Cl2 (Isokinetic)

Method 0051: HCl/Cl2 (Constant Rate)

Stack Testing of VOCs

- The majority of CAA Section 112 HAPs are volatile organic compounds (VOC)
- Testing for volatile organic compounds is often confusing for a variety of reasons:
  - There is no straightforward way to measure the VOC emissions since there is no way to separate VOCs by vapor pressure.
  - All of the reference methods for organic compounds have inherent limitations that restrict their applicability, and
  - No one method can satisfy characterization of organic emissions from an industrial source.

Definitions

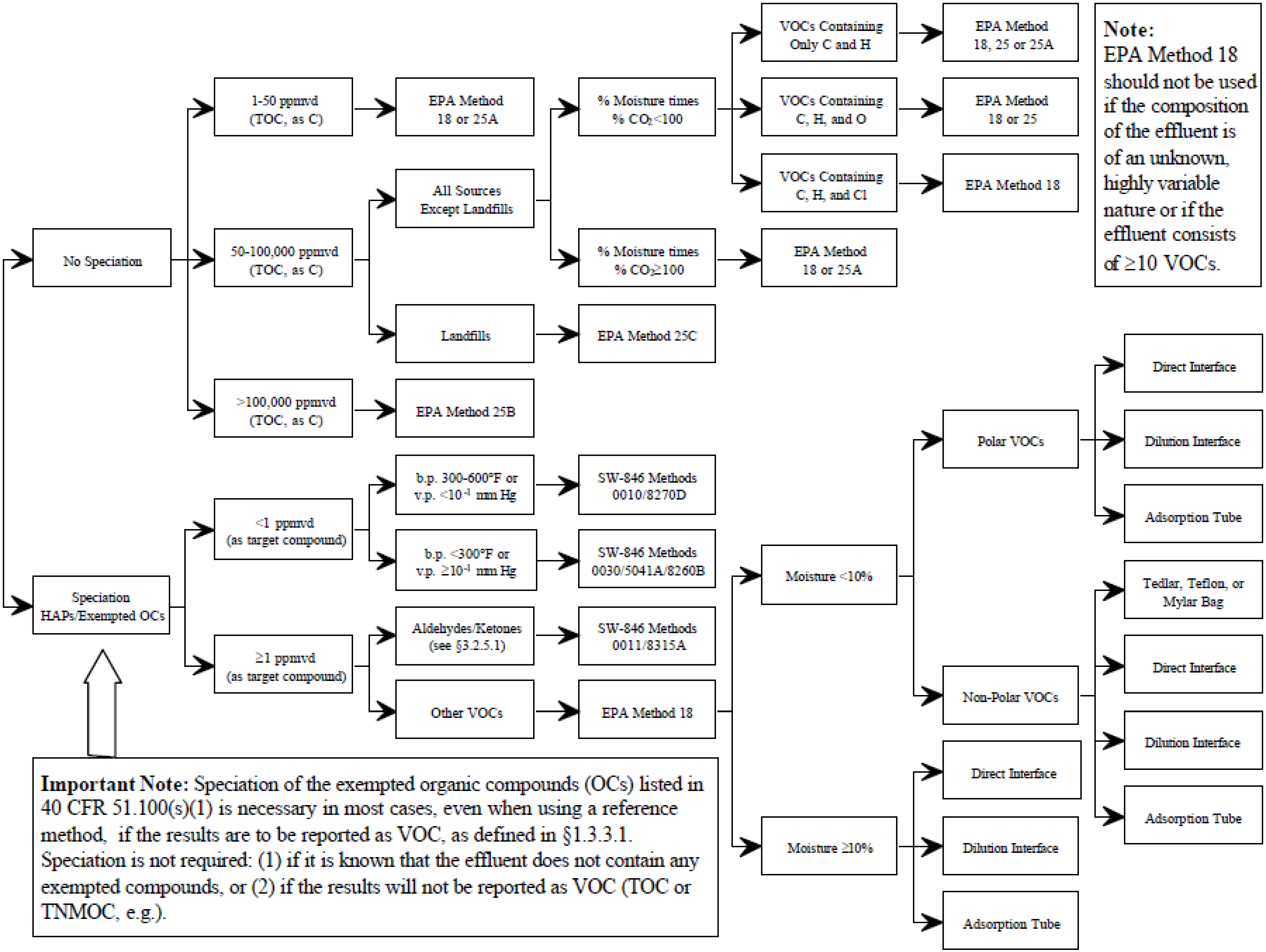
- Volatile Organic Compounds (VOCs): An organic compound that participates in atmospheric photochemical reactions; (excluding exempted compounds listed in 40 CFR §51.100(s)(1)).
  - VOCs usually have high vapor pressures (greater than 0.1 mm Hg).
- Semi-volatile Organic Compounds (SVOC): This definition can vary depending on the test method. Usually SVOCs are organic compounds with vapor pressure between 0.1 and 10^{-7} mm Hg.

Definitions

- Total Organic Compounds (TOCs): The sum of all volatile organic compounds and all exempted compounds.
- Total Hydrocarbons (THCs): The subset of total organic compounds containing only carbon and hydrogen.
- Total Non-Methane Organic Compounds (TNMOCs): The sum of all volatile organic compounds and all exempted compounds listed in 40 CFR§51.100(s)(1), except methane.

Selection of VOC Test Methods

- Pennsylvania Department of Environmental Protection, "*Source Testing Manual*" (Revision 3.3), provides a general scheme for the selection of a VOC test method.
- The selection scheme does not address all of the possibilities.
- Scheme follows 2 different paths:
  - Speciated VOCs
  - Non-speciated VOCs



Note: EPA Method 18 should not be used if the composition of the effluent is of an unknown, highly variable nature or if the effluent consists of ≥10 VOCs.

Important Note: Speciation of the exempted organic compounds (OCs) listed in 40 CFR 51.100(s)(1) is necessary in most cases, even when using a reference method, if the results are to be reported as VOC, as defined in §1.3.3.1. Speciation is not required: (1) if it is known that the effluent does not contain any exempted compounds, or (2) if the results will not be reported as VOC (TOC or TNMOC, e.g.).

No Speciation VOC Methods

- Method 18 (VOC by gas chromatograph (GC)): Based on separating components of a gas mixture in a GC column and measuring separated components with suitable detector (i.e., FID).
  - Applicable to VOC concentrations greater than 1ppm in the sampled gas.
- Method 25 (non-methane organic compounds) applies to the measurement of VOCs as total gaseous non-methane organics, condensable and non-condensable, as carbon in source emissions. (All compounds are converted to methane before measuring with a FID.)

No Speciation VOC Methods

- <u>Method 25A</u> (organic concentration using a FID): This method is applicable to total gaseous organic concentration of vapors consisting primarily of <u>alkanes, alkenes, and/or aromatic hydrocarbons</u>.
  - Results are expressed in terms of volume concentration of <u>propane</u> (or other appropriate organic calibration gas) or in terms of <u>carbon</u>.
- <u>Method 25B</u> (organic concentration using an infrared analyzer)
- <u>Method 25C</u> (non-methane organic compounds from landfills).

Federal Reference Method 18

General GC Methodology

Method 18

Gas Chromatography (GC)

- Generic GC method
- Determines the concentration of discrete organic compounds in the sample
- Applies to the analysis of approximately 90% of total gaseous organics emitted from an industrial source

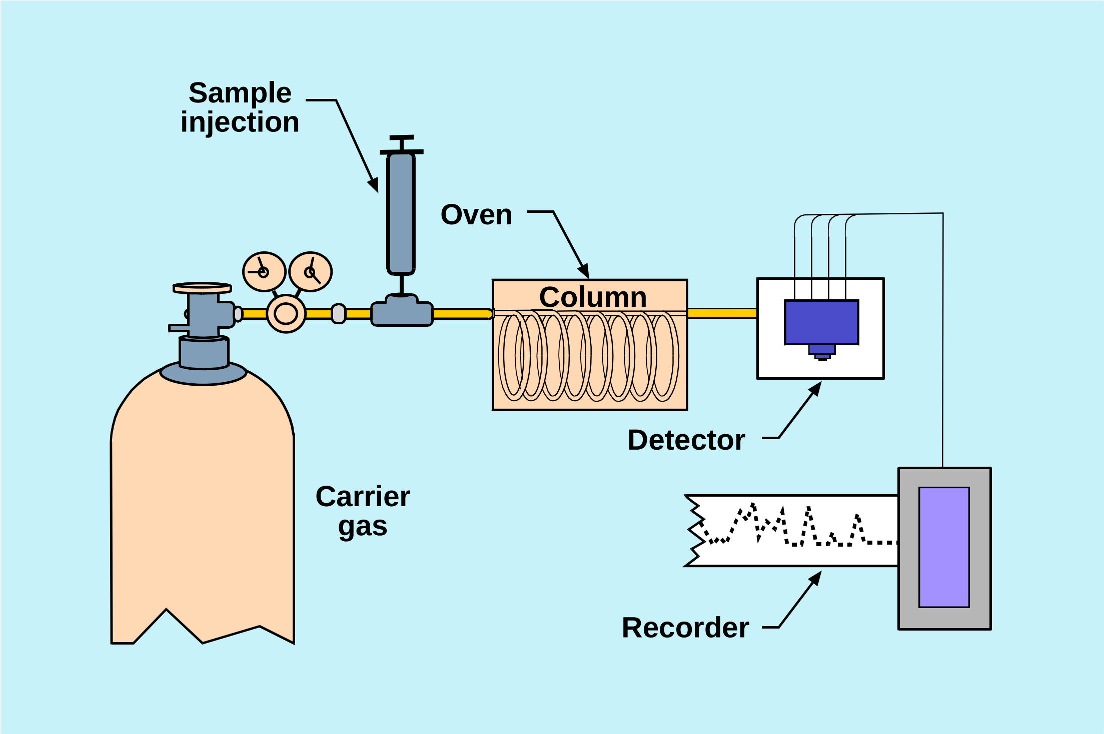
Applicability & Principle

- Applicability: FRM 18 will not determine compounds that are
  - Polymeric (high molecular weight)
  - Analytes that can polymerize before analysis
  - Analytes that have very low vapor pressure at stack or instrument conditions
- Principle: Based on separating components of a gas mixture in a gas chromatographic column and measuring separated components with suitable detector

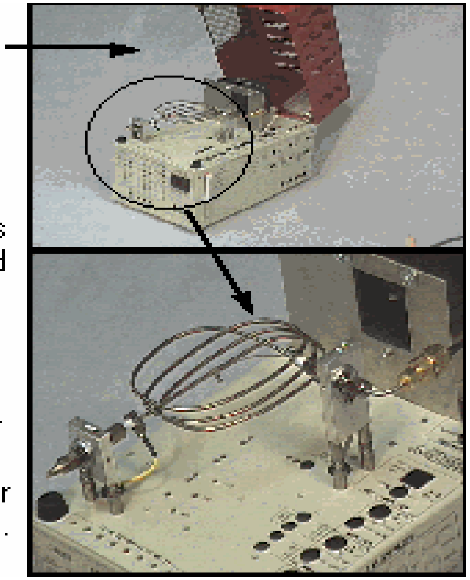
FRM 18 Sampling Methods

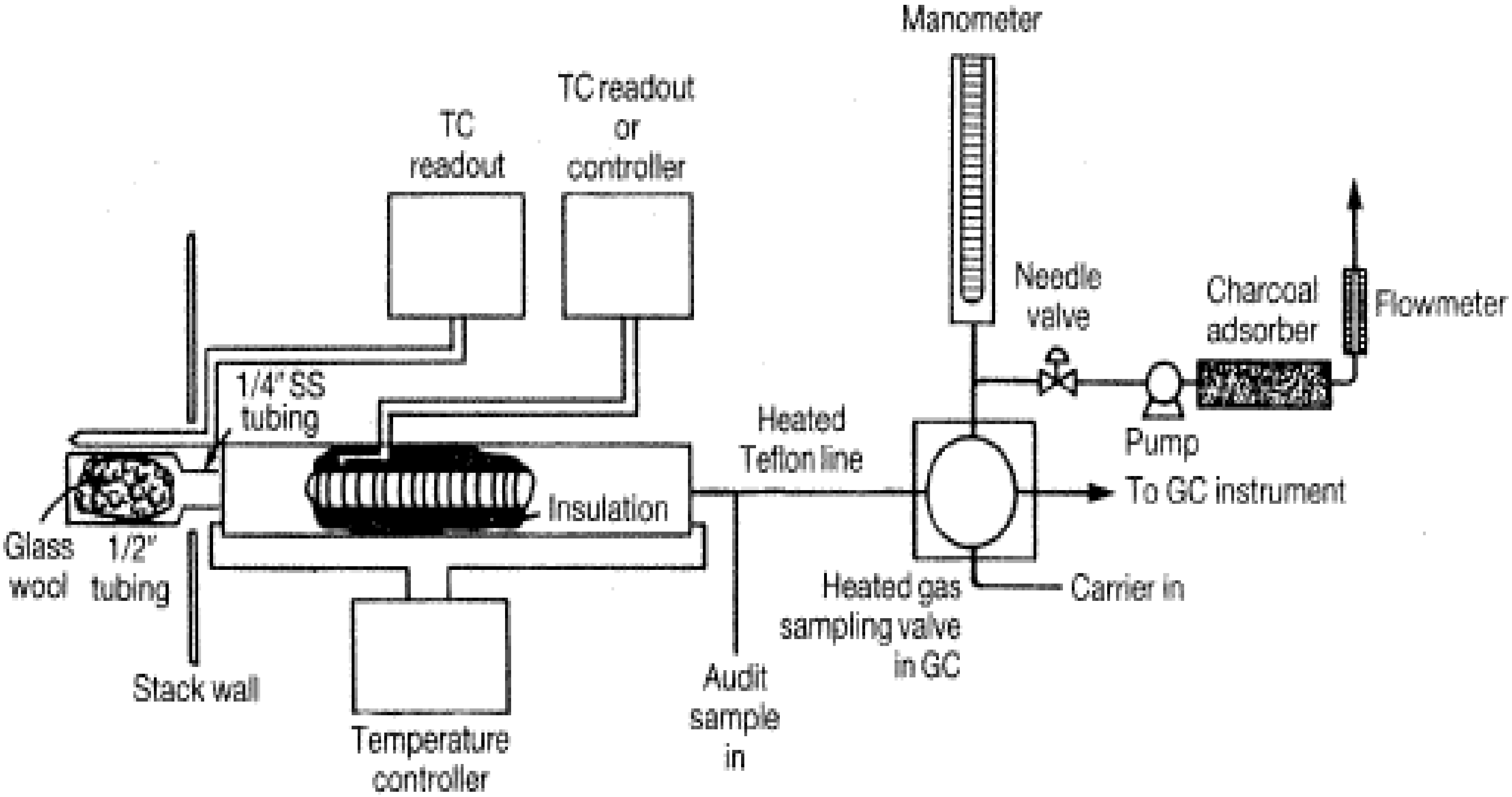
- Direct Interface
- Integrated bag
- Glass sampling flask
- Adsorbent tubes
  - Charcoal
  - Silica Gel
  - Florisil®
  - CarboTrap® 300
  - Tenax® TA

Method 18

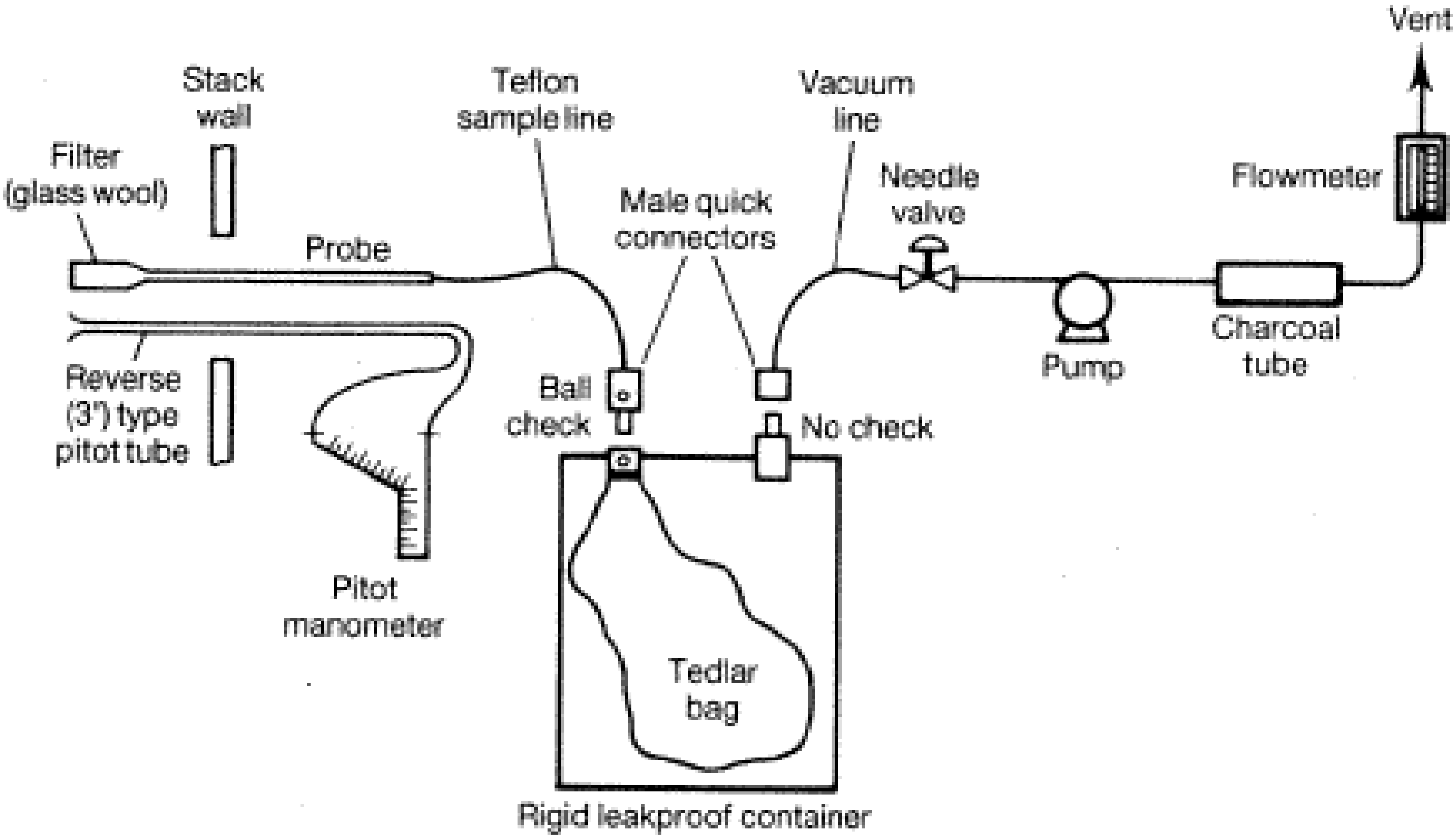


"Virtual Oven" shown mounted on 110 chassis. Column is connected to heated injector and detector blocks for higher temperature samples.





Method 18 Direct Interface Sampling



Method 18 Integrated Bag Sampling System

Speciation VOC Methods

- All of the following methods are from SW-846:
  - Method 0010 for semi-volatile organics
  - Method 0011 is used for aldehydes and ketones.
  - Method 0030 is used for volatile organic compounds (compounds with boiling points less than 100^{O}C but normally above 30^{O}C).

General Classification of HAPs

Classification	Vapor Pressure mm Hg	Boiling Point °C
Volatiles (VV/V)	$> 10^{-1}$	< 100° C
Semi-volatiles (SV)	10^{-1} to 10^{-7}	100 - 300° C
Particles (NV)	$< 10^{-7}$	> 300° C

Number of HAPs in each Volatility Class

Volatility Class	No. of HAPs in Class
VVOC	15
VVINC	6
VOC	82
VINC	3
SVOC	64
SVINC	2
NVOC	5
NVINC	12

Definition of Semi-Volatiles

- Semi-volatile compounds are those with boiling points greater than 100°C
- Three major groups
  - – Polycyclic aromatic hydrocarbons (PAHs)
  - – Dioxin and furans (D/Fs)
  - – Biphenyls (PCBs)

Semi-Volatile Compound Boiling Points(°C)

- Bis(chloromethyl)ether - 104°C
- Chlorobenzene - 132°C
- Benzyl Chloride - 176°C
- Hexachlorobutadiene - 215°C
- 2,4,6-Trichlorophenol - 245°C
- 3,3’-Dichlorobenzidine - 402°C

SW-846, Method 0010 Sampling and Analysis for Semi-volatile Organic Compounds

Title III
Method 0010 Analytes

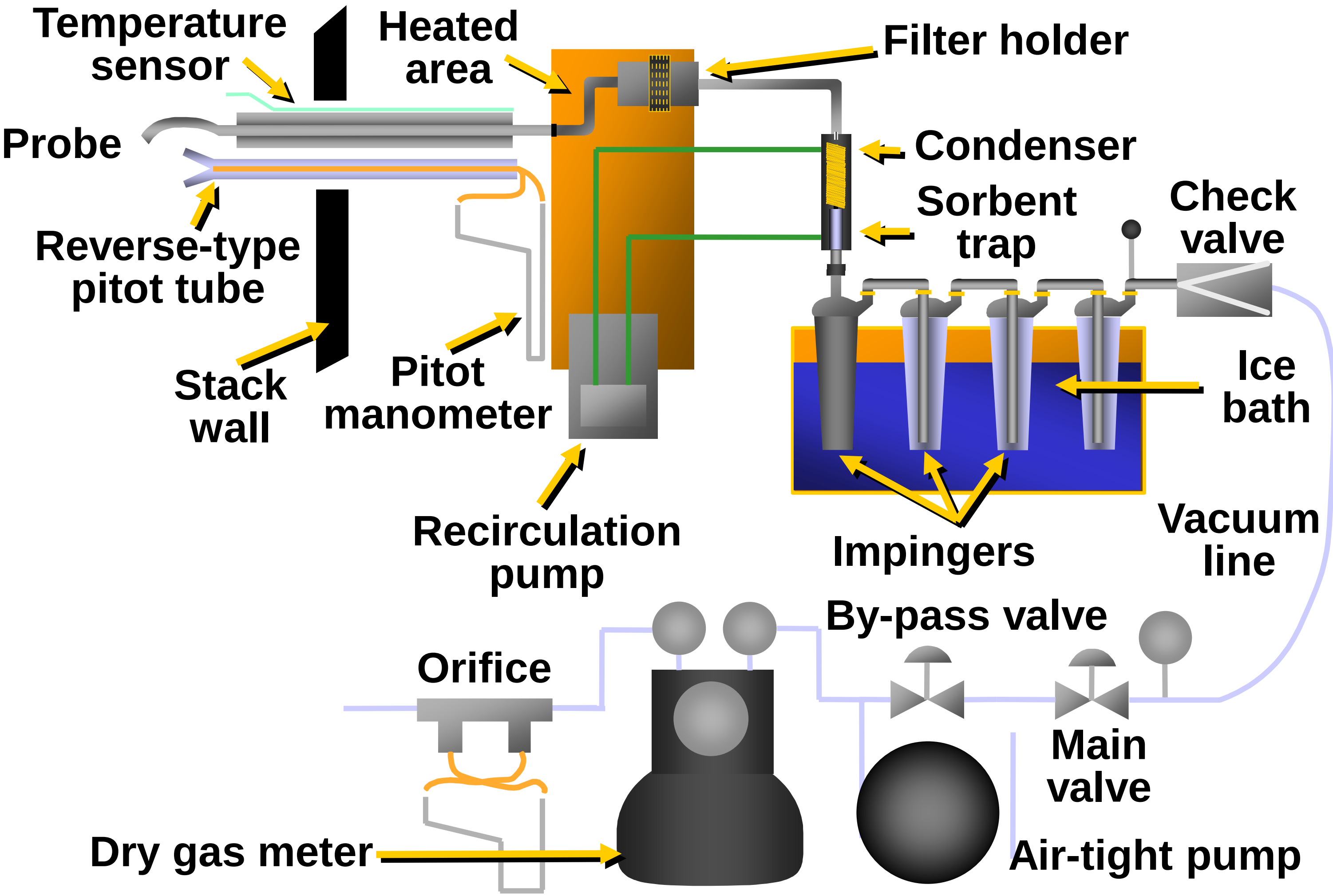
- Acetaldehyde
- Acetonitrile
- Biphenyl
- 1,3 - Butadiene
- Carbonyl Sulfide
- Chlorobenzene
- Cresols
- Cumene
- 1,4 - Dichlorobenzene
- Ethylbenzene
- Ethylene Glycol
- Ethylene Oxide
- Methanol
- Methyl Ethyl Ketone
- Methyl Isobutyl Ketone
- Naphthalene
- Phenol
- Propionaldehyde
- Styrene
- Toulene
- Xylenes (o -, m-, p -)

Method 0010 Sampling Train

- Sample is collected in a sampling train that is similar to FRM 5 for particulates.

1. A high efficiency glass filter is used to collect organic-laden particulates
2. A packed bed of porous polymeric resin (XAD-2^{TM}) serves to adsorb semi-volatile organic species, and
3. A series of water filled impingers may collect some semi-volatile organics that pass through the filter and sorbent.

Method 0010 Sampling Train



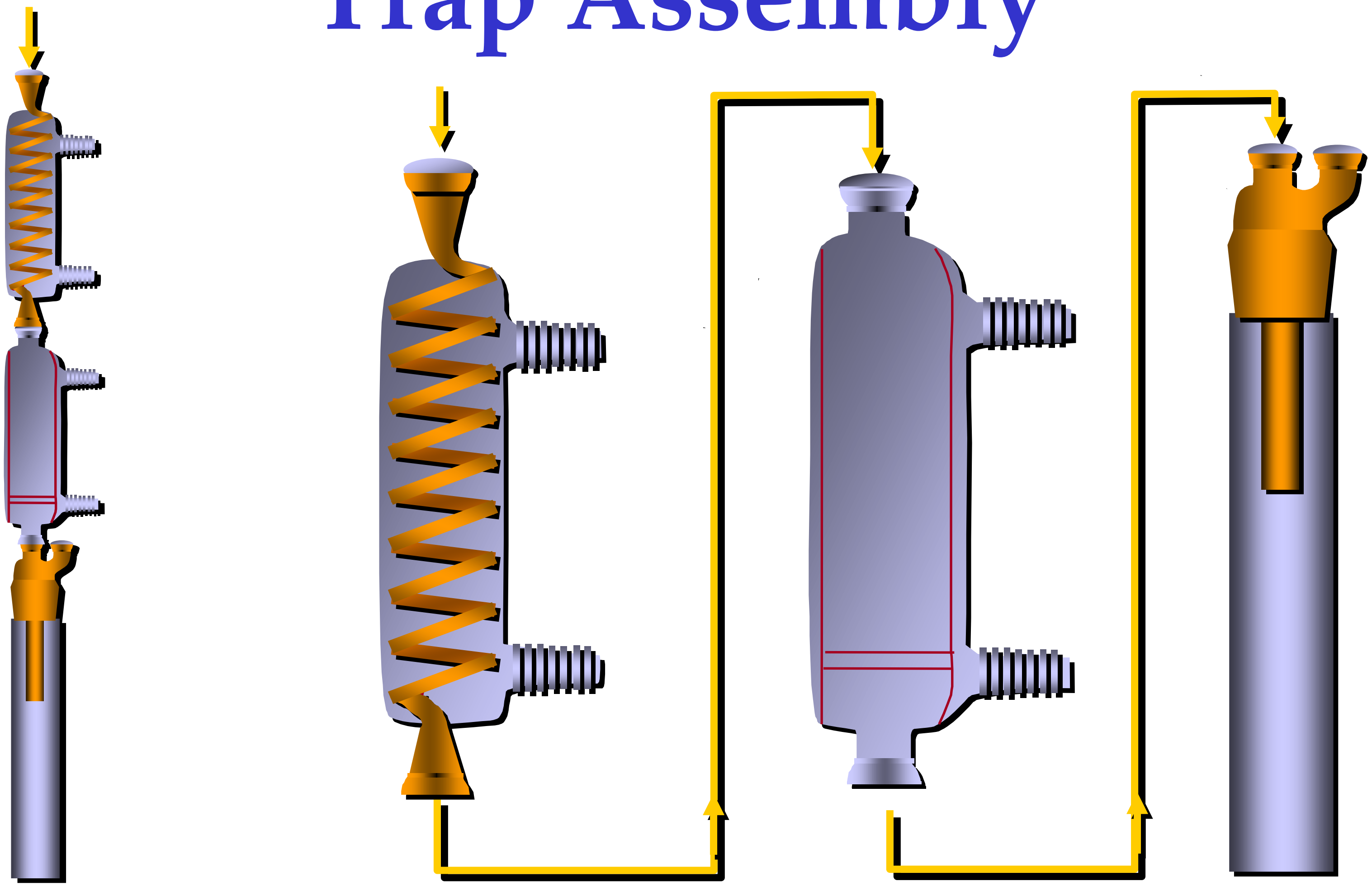
Method 0010 Configuration

- Same configuration used for PCBs and dioxin/furans
- Collect all in one train for better detection limits
  - 10 µg for PAHs
  - 1 µg for D/F’s

XAD-2 Resin Trap

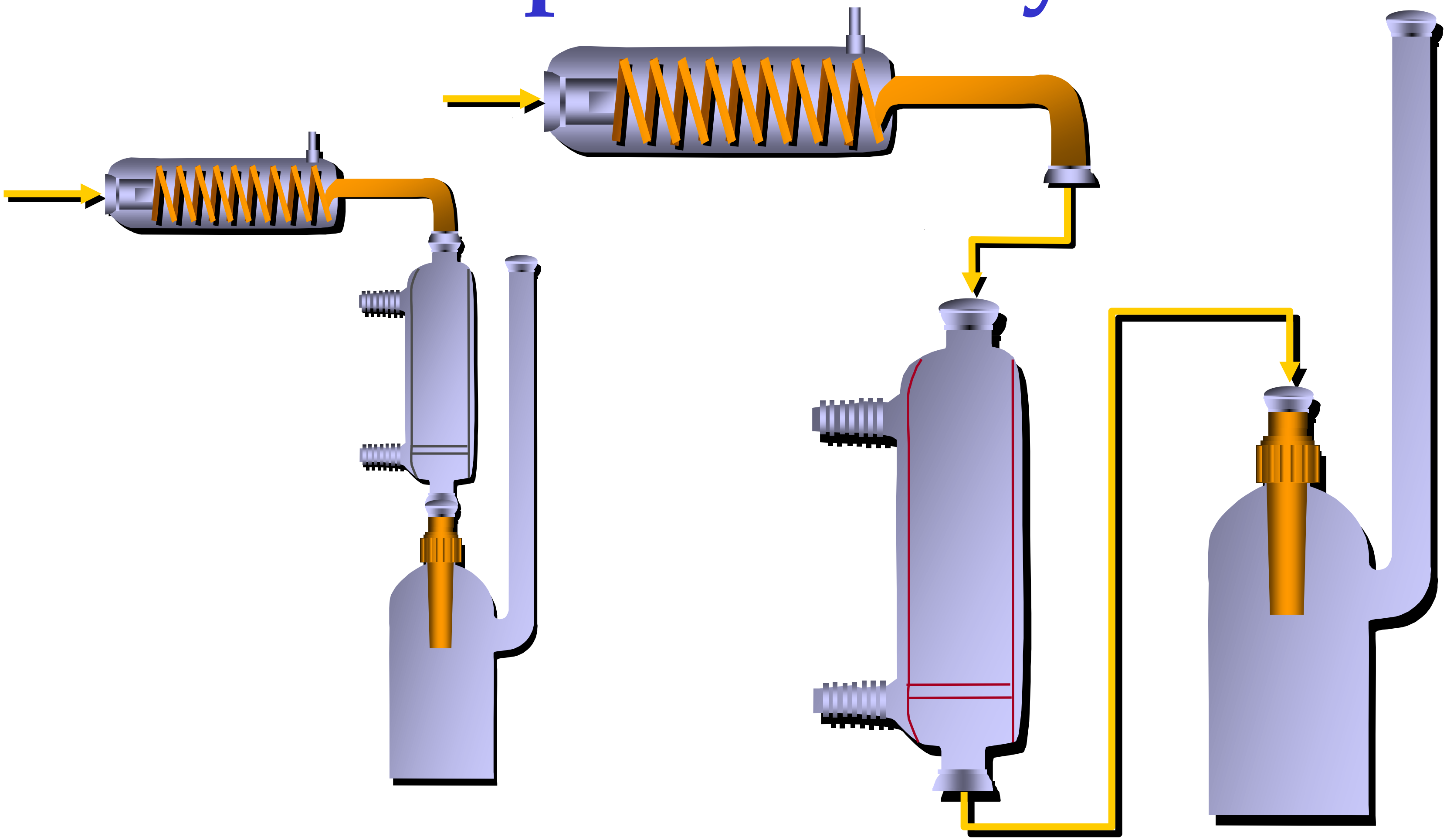
- XAD-2 is a cross-linked styrene-divinylbenzene
  - Organic Polymeric Adsorbent
- pAmberlite XAD-2 physical characteristics
  - Mesh Size: 20-60
  - Bulk Density: 1.08 g/mL
  - Surface Area: 300 m^2/g
    - large surface area
  - Temp. Max: 190°C
    - Therefore, it can’t be thermal debsorbed due to breakdown of XAD-2

Vertical Condenser/XAD-2 Trap Assembly

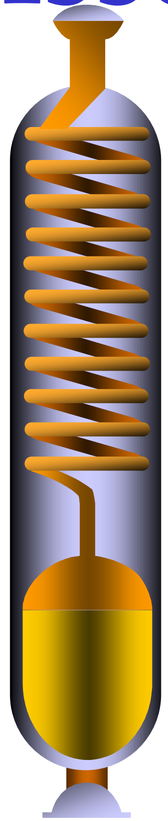


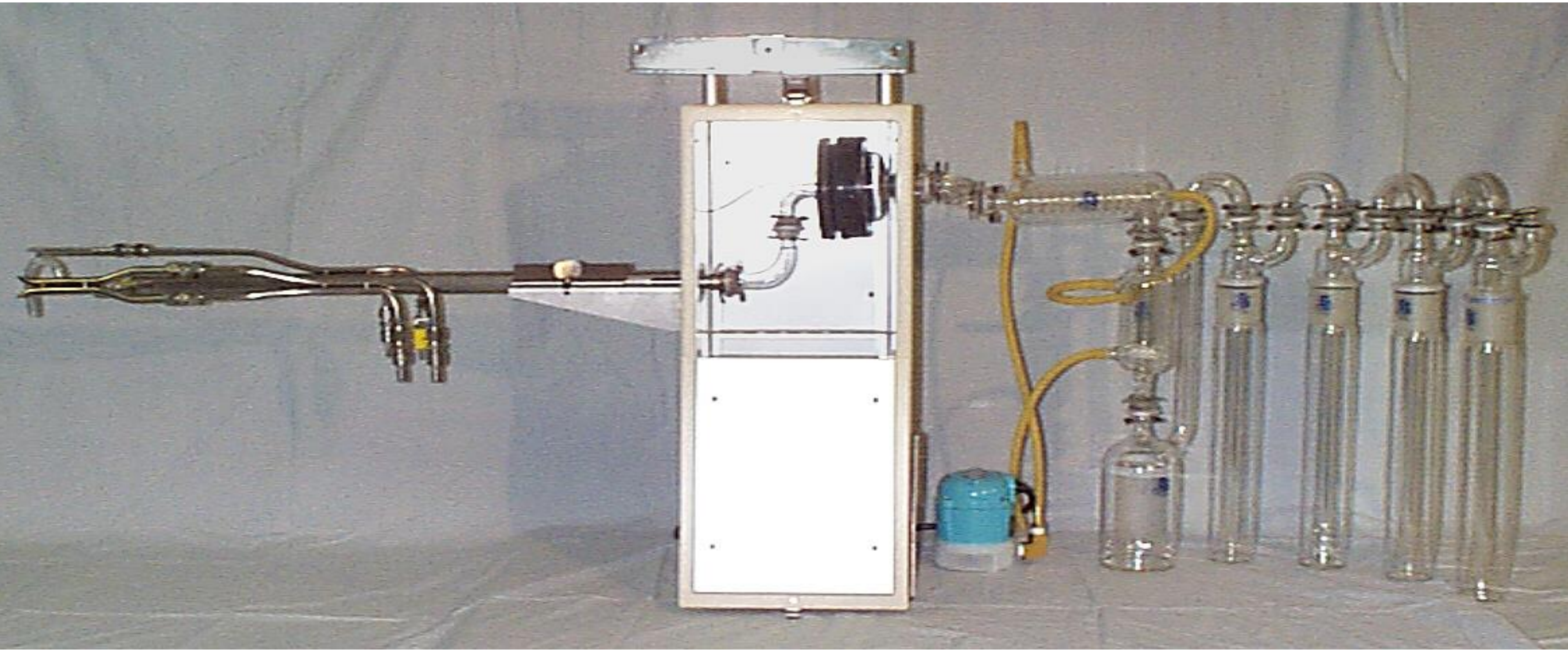

APEX
INSTRUMENTS
PROBE
FILTER
AUX

Horizontal Condenser/ XAD-2 Trap Assembly



Vertical Single Unit Condenser/ XAD-2 Trap Assembly





Definition of Volatile Organic Compounds (VOCs)

- Volatile organic compounds (VOCs) are those compounds with boiling points < 100°C, but normally above 30°C
- VOCs with boiling points < 30°C may break through adsorbent

Volatile Organic Compounds Boiling Points

Acrylonitrile(same problem)	77.0°C
Benzene	80.0°C
Carbon Tetrachloride	77.0°C
Chloroform	60.5°C

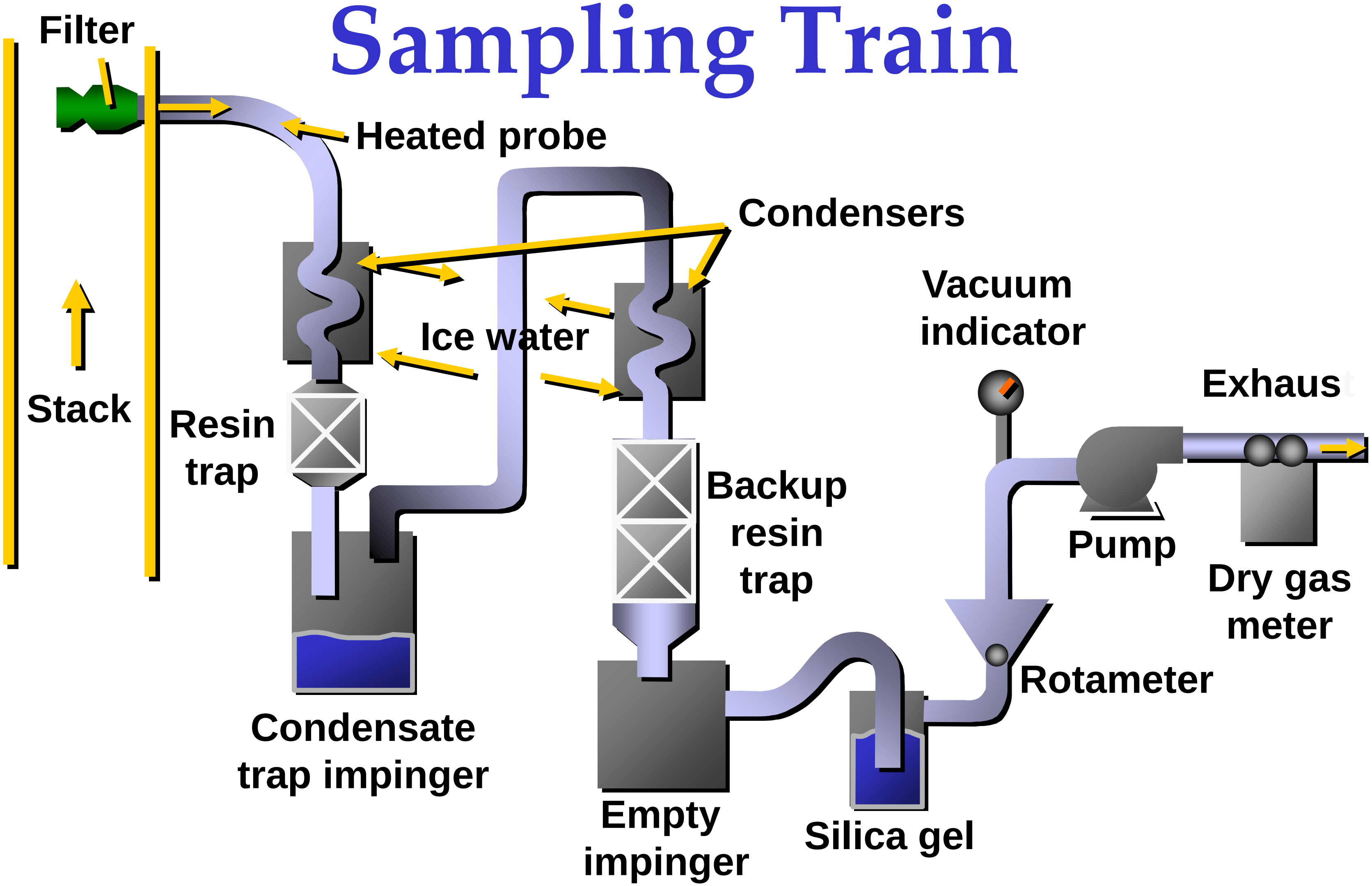
Method 0030: Applicability

- This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semi-volatile Principal Organic Hazardous Compounds (POHCs) from incinerator systems

Title III
Method 0030 Analytes

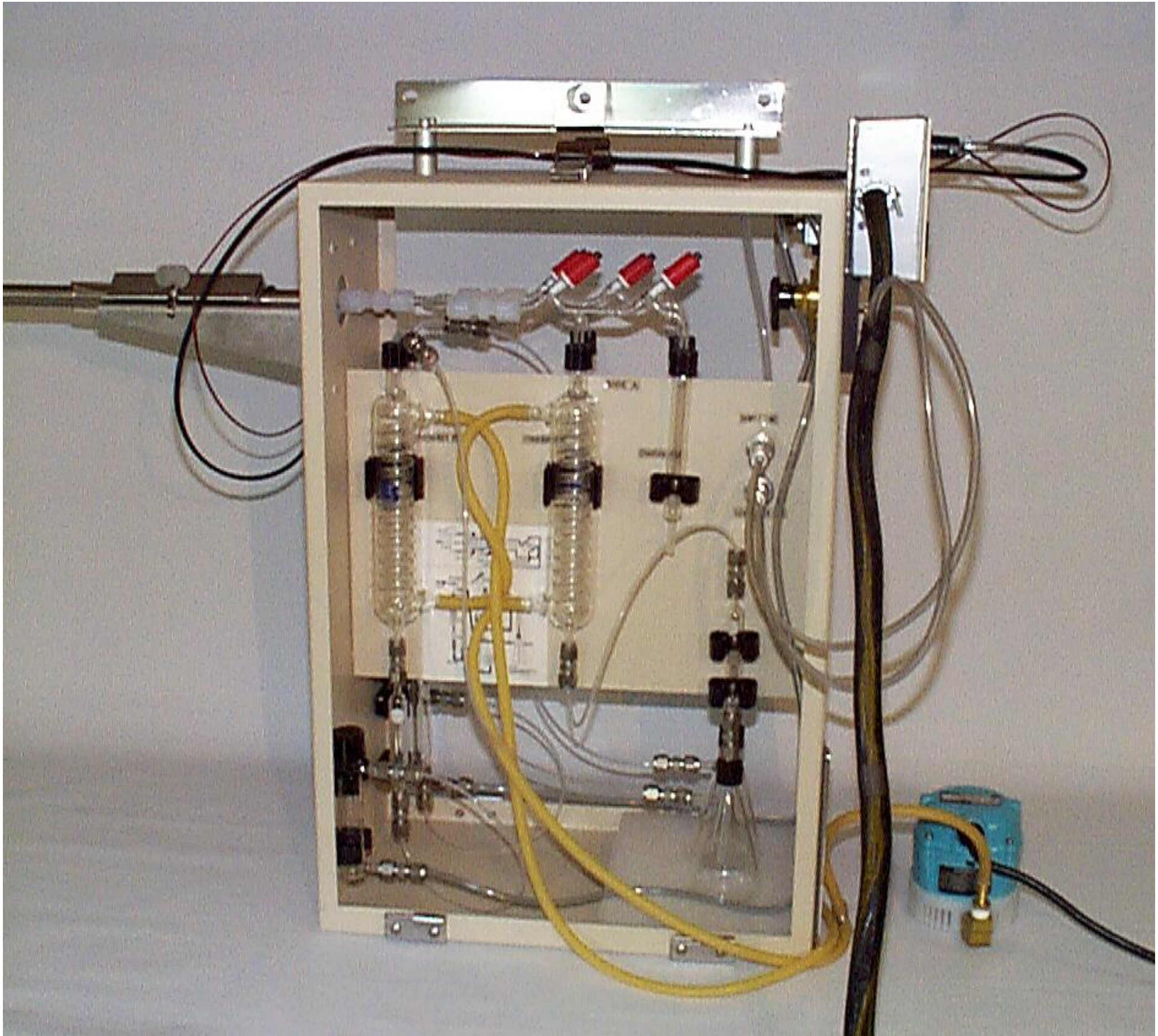
Acrylonitrile
Benzene
Carbon Disulfide
Carbon Tetrachloride
Chloroform
Chloroprene
Ethyl Chloride
Ethylene Dichloride
Methyl Chloride
Methyl Chloroform
Methylene Chloride
Propylene Dichloride
Propylene Oxide
Tetrachloroethylene
Trichloroethylene
Vinyl Acetate
Vinyl Chloride

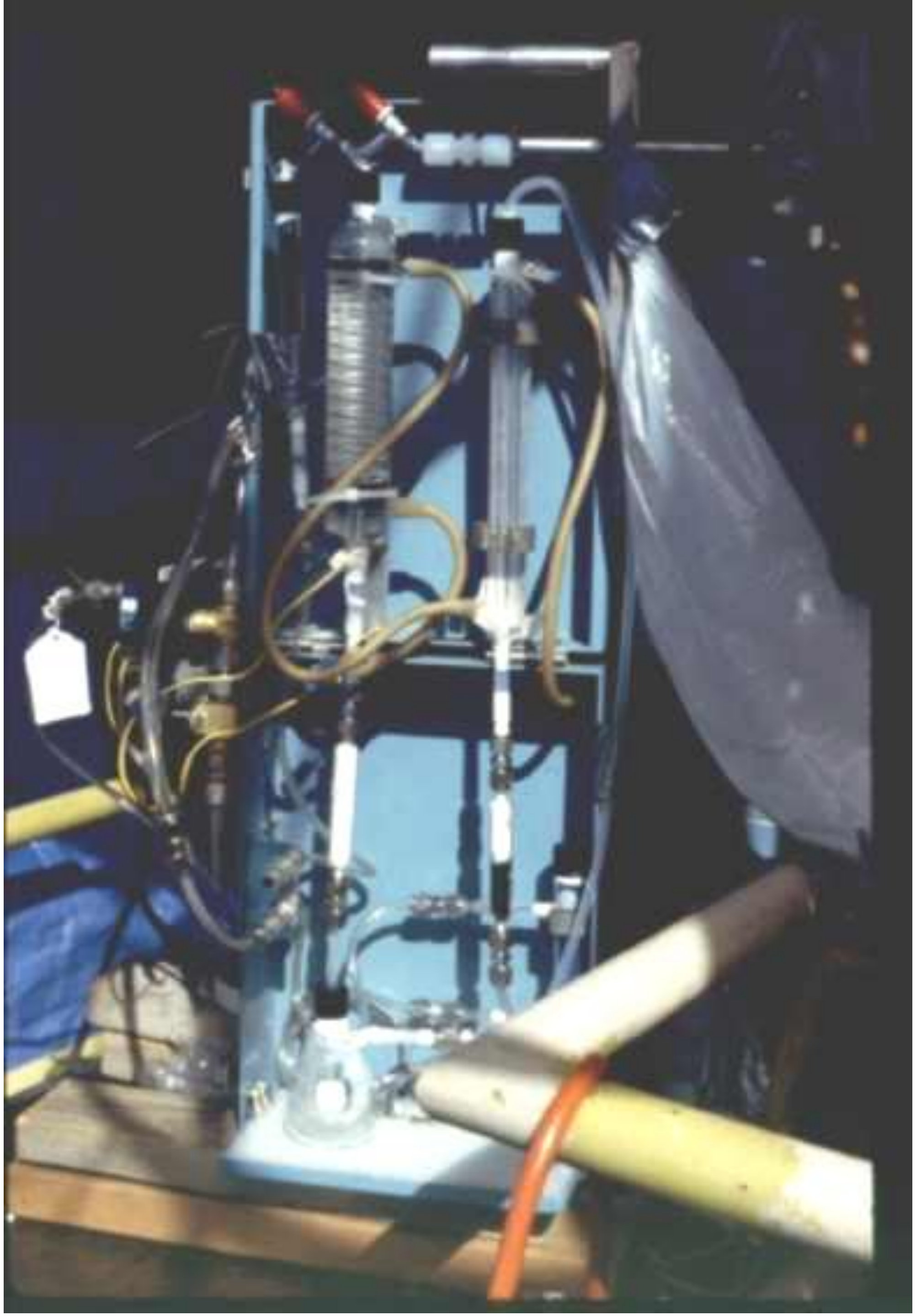
Method 0030 Sampling Train



Tenax® Resin Trap

- Tenax® is 2,6-diphenyl-p-phenylene oxide polymer
- Simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), poly-nuclear aromatic hydrocarbons (PAHs), and semi-volatile organic compounds (SVOCs) can also be performed along with PCDDs and PCDFs



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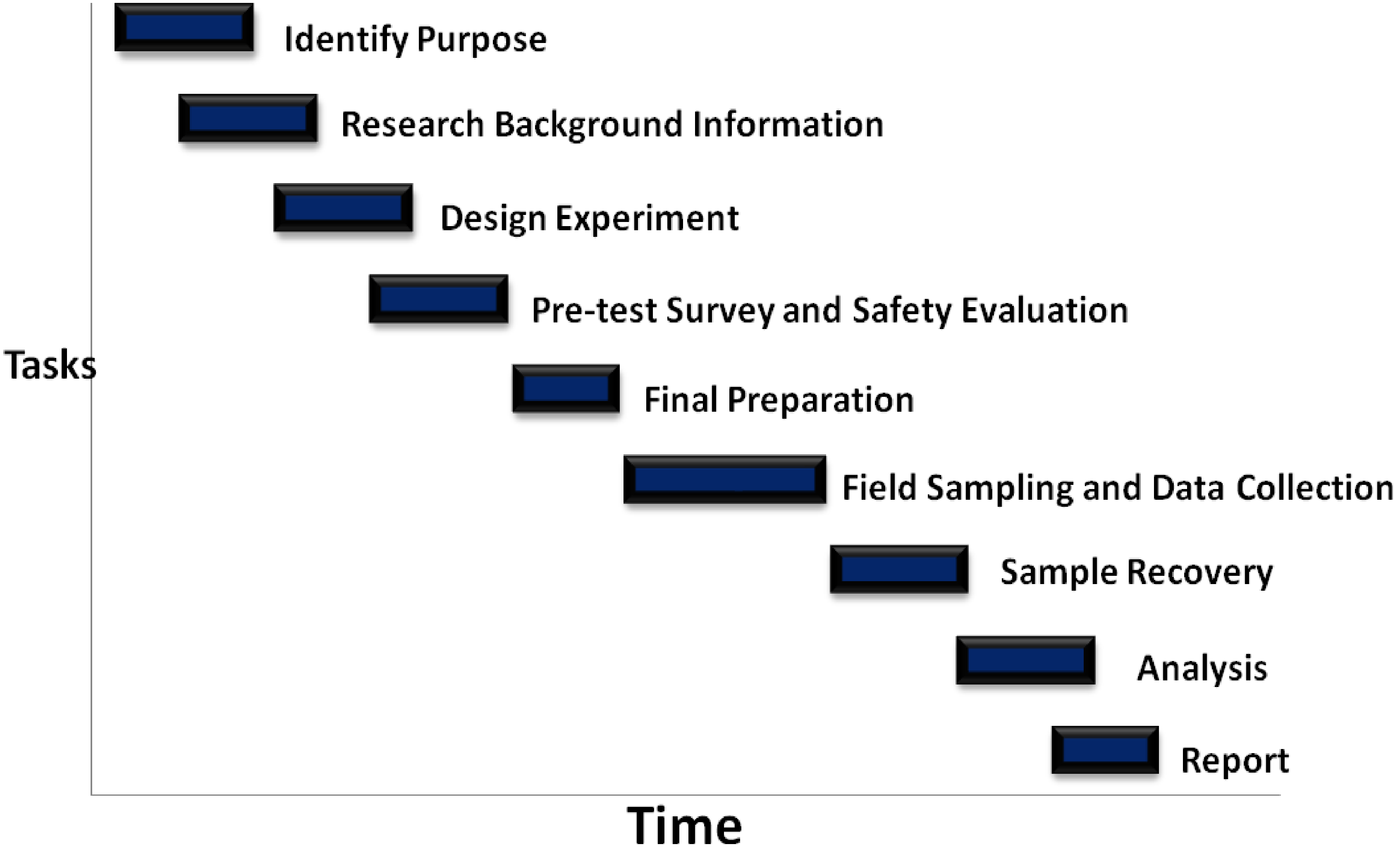
Tasks in Planning & Conducting a Source Test



Detection Limits

- The “limit of detection” is the smallest amount of a substance that an analytical method can reliably distinguish from zero.
  - It is the minimum concentration or amount of a target analyte that produces a signal the tester can distinguish, at a specified confidence level, from the signal produced by a blank.
- The “limit of quantification” is the minimum concentration or amount of an analyte that a method can measure with a specified degree of precision.

EPA’s EMC Web Site: Software

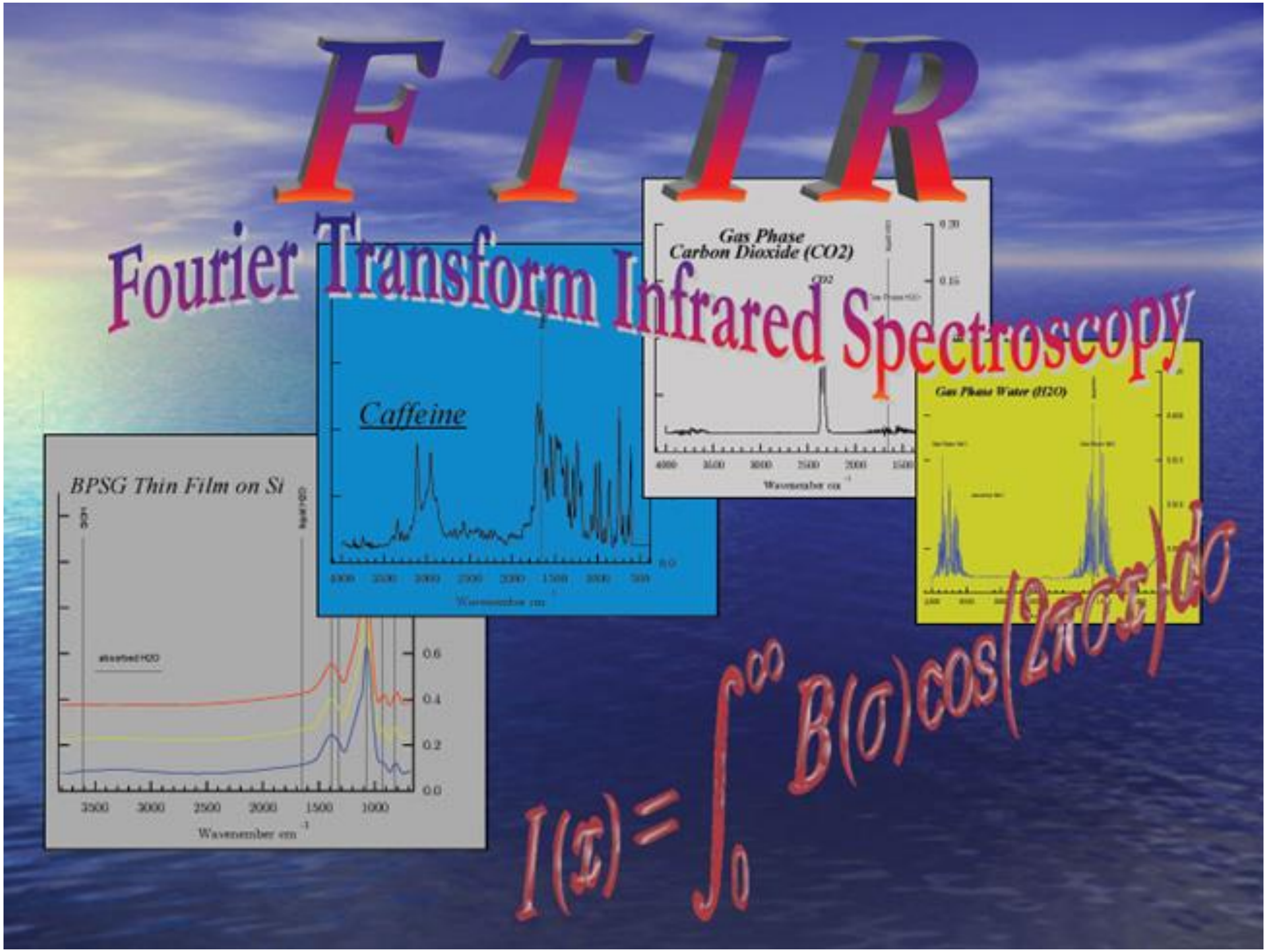
- Test Method Storage and Retrieval software, PC Nomograph program, Manual Emission Testing Cost Model PC program, and CEM cost estimation & methods spreadsheet programs.
- In 2007, EMC added: the Electronic Reporting Tool (ERT).
  - ERT replaces the time-intensive manual preparation emissions test plans and reports prepared by contractors, and the time-intensive manual quality assurance evaluations and documentation performed by State agencies.

Continuous Emission Monitors: 2 Types

- Extractive CEMs draw a sample from a stack, condition the sample gas (i.e., remove particulate matter and moisture), and analyze for the specific compounds of interest.
- In-situ CEMs provide a measure a measure of target compounds in the stack without sample extraction or conditioning.
  - The components of in-situ CEMs commonly include a light or radiation source, a detector, and a data reduction device mounted on the stack.

Continuous Emission Monitors

- VOC concentrations are detected using analyzer methods such as flame ionization detection (FID), photo-ionization detection (PID), or non-dispersive infrared (NDIR) absorption.
- These VOC analyzers do not specifically identify VOCs nor do they respond equally to all VOCs. They only provide a measure of the relative VOC concentration of the mixture of compounds.



FTIR

Fourier Transform Infrared Spectroscopy

$$I(x)=\int_0^\infty B(\sigma)\cos(2\pi\sigma x)\,d\sigma$$

FTIR Background

- Wavelength of light absorbed is characteristic of the chemical bond
- FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint"
- The infrared spectrum of a mixture contains the superimposed spectra of each mixture component
- An FTIR CEM provides the capability to continuously measure multiple components in a sample using a single analyzer

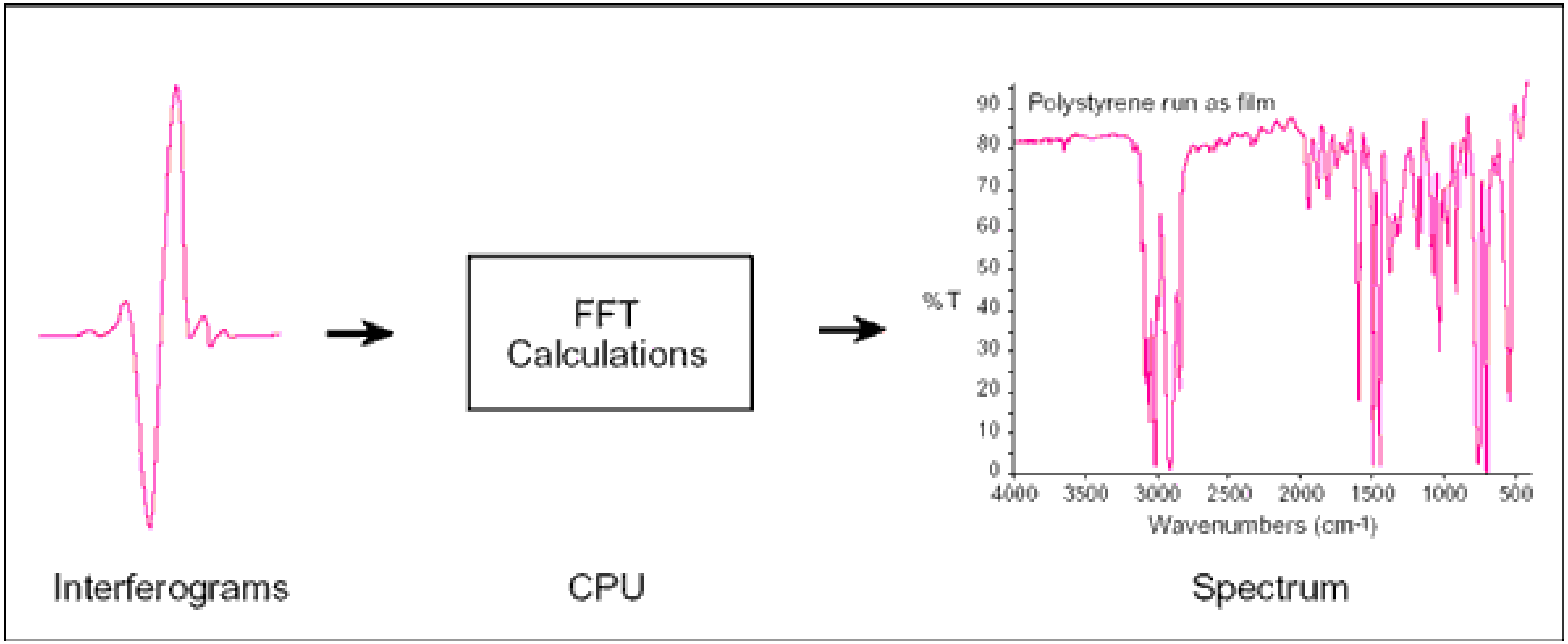
FTIR System

- Instrument to measure spectra in the mid-infrared spectral region (500 to 4000 cm-1)
  - Infrared source
  - Interferometer
  - Sample gas cell
  - Infrared detector
  - Computer

FTIR Interferences

- Compound Interferences In The Infrared
  - Water
  - Carbon Monoxide
  - Carbon Dioxide
  - Particulate Matter

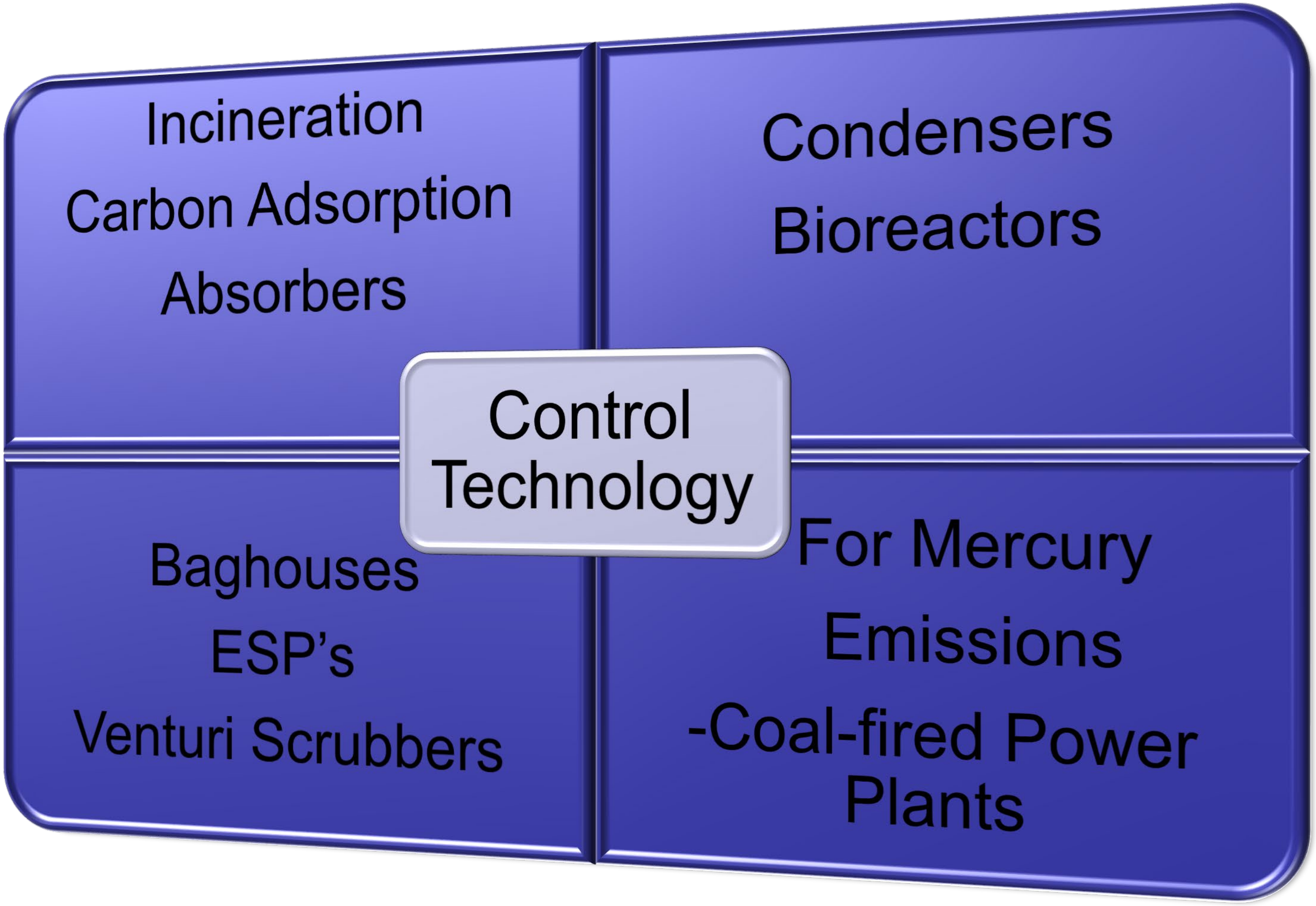
FTIR



An illustration of how an interferogram is Fourier transformed to generate a single beam infrared spectrum.

Chapter Twelve

Air Toxics Controls for Stationary Sources



Incineration
Carbon Adsorption
Absorbers

Condensers
Bioreactors

Control Technology

Baghouses
ESP's
Venturi Scrubbers

For Mercury Emissions
-Coal-fired Power Plants

By: Bill Franek

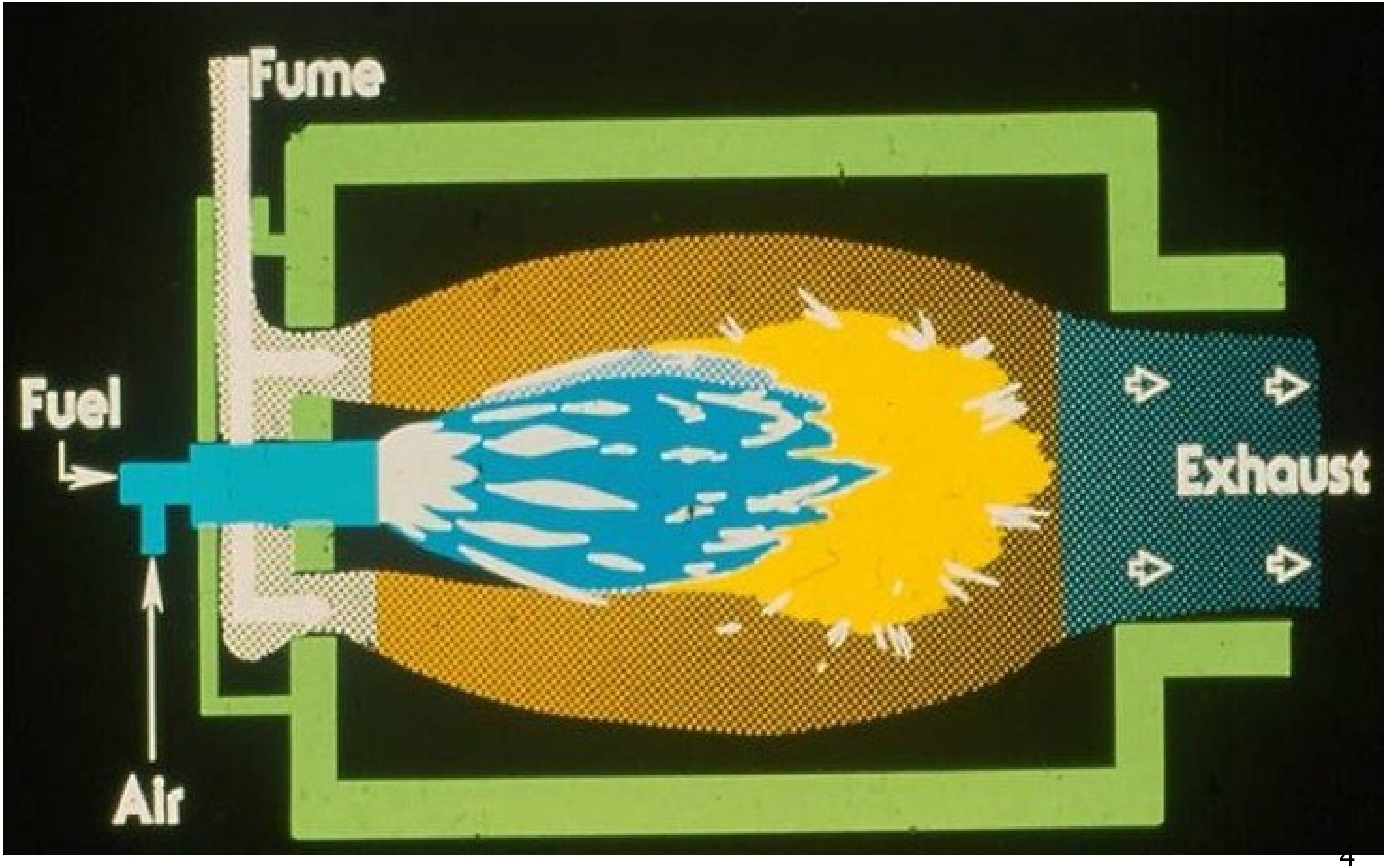
Types of Control Technologies for Gaseous Hazardous Air Pollutants

- Thermal Incineration (Oxidation)
- Catalytic Incineration
- Flares
- Boilers/Process Heaters
- Adsorption
- Absorption
- Condensers

Thermal Incineration (Oxidation)

- VOC-laden air stream is heated to temperatures several hundred degrees Fahrenheit above the auto-ignition temperatures of the HAP/VOC compounds that need to be oxidized.
- Due to these very high temperatures, thermal oxidizers are refractory-lined combustion chambers (also called fume incinerators)

Thermal Incineration (Oxidation)



Thermal Incineration (Oxidation)

- The HAP/VOC-laden gas stream is held at this temperature for residence times ranging from a fraction of a second to more than two seconds.
- Temperatures of the exhaust gas from the refractory-lined combustion chambers are often 1,000 to 2,000°F.
- Thermal oxidizers usually provide VOC destruction efficiencies that exceed 95% and often exceed 99%.

Thermal Incineration (Oxidation)

- One limitations of thermal oxidizers is the large amount of fuel required to heat the gas stream to the temperature necessary for high-efficiency HAP/VOC destruction.
- Heat exchangers are used to recover some of this heat. A recuperative heat exchanger. has a heat recovery efficiency ranging from 30 to 60% depending on the size of the unit.

Thermal Incineration (Oxidation)

- Some types of thermal oxidizers use large regenerative beds for heat exchange. These beds have heat recovery efficiencies up to 95%.
- Regenerative thermal oxidizers (RTOs) require less fuel to maintain the combustion chamber at the necessary temperature.

Thermal Incineration (Oxidation)

- Thermal oxidizers can be used for almost any HAP/VOC compound in a gas streams.
- It can handle VOC concentrations in a range of less than 10 ppm up to the very high concentrations approaching 10,000 ppm.

LEL and Thermal Incinerators

- Thermal oxidizers are rarely used on gas streams having VOC concentrations exceeding approximately 25% of the lower explosive limit (LEL).
- This limit is imposed due to the possibility that a short-term concentration spike would exceed the LEL, and the gas stream would explode.
- The 25% LEL limit depends on the actual gas constituents and usually is in the 10,000 to 25,000 ppm range (1% to 2.5%).

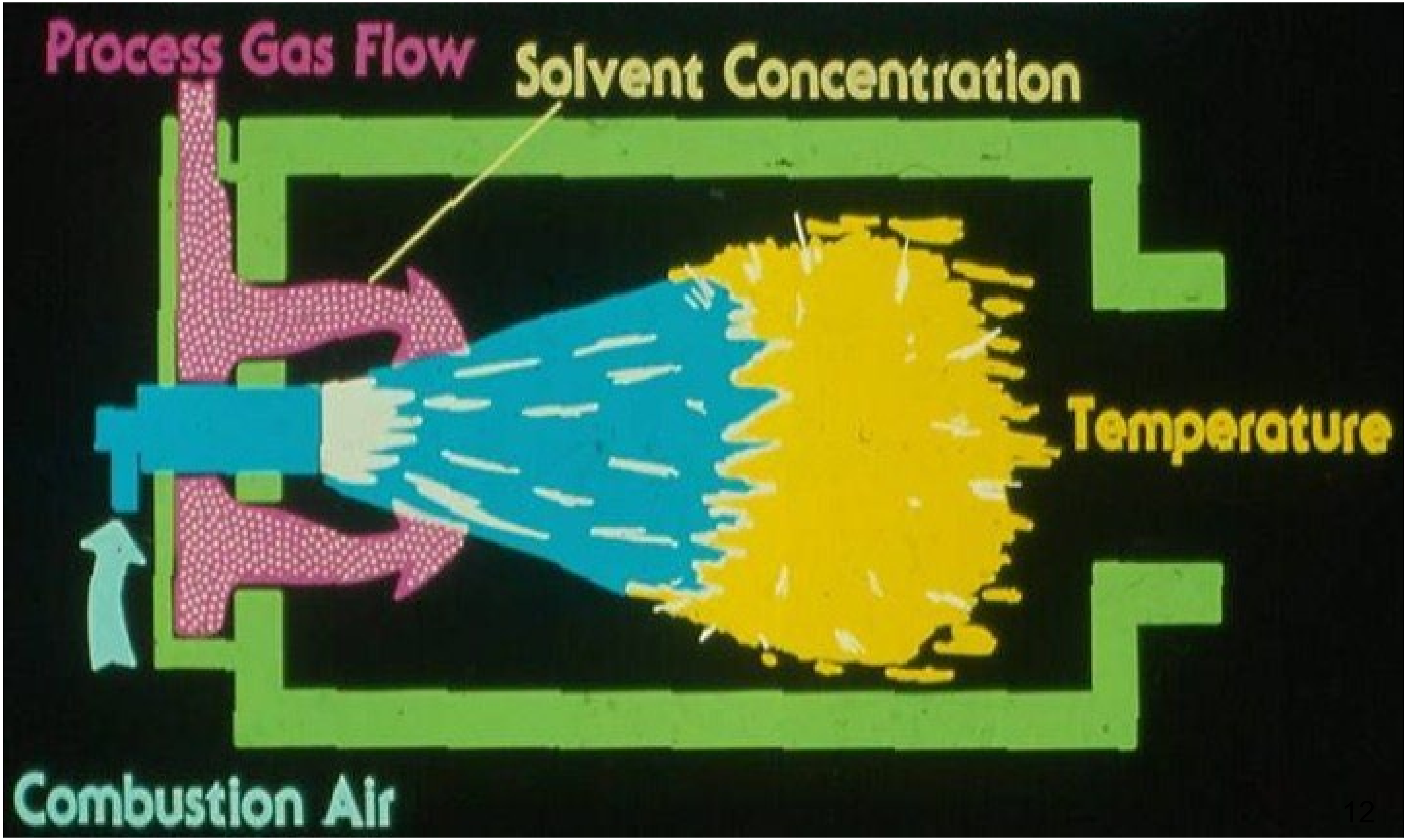
Limits of Flammability of Combustible Organic Compounds in Air at Atmospheric Pressure, Room Temperature

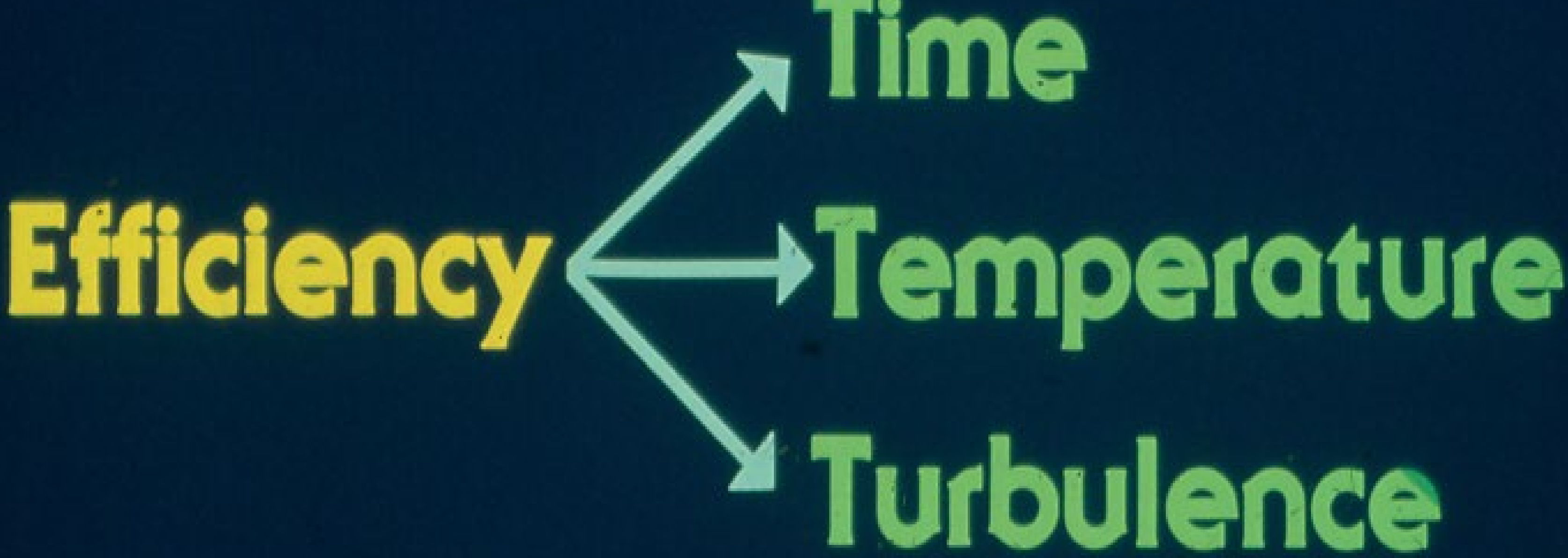
Compound	Molecular Weight	LEL (volume %)	UEL (volume %)
Methane	16.04	5.00	15.00
Ethane	30.07	3.00	12.50
Propane	44.09	2.12	9.35
Butane	58.12	1.86	8.41
Pentane	72.15	1.40	7.80
Hexane	86.17	1.18	7.40
Octane	114.23	0.95	
Nonane	128.25	0.83	
Decane	142.28	0.77	
Ethylene	28.05	2.75	28.60
Propylene	42.08	2.00	11.10
Acetylene	26.04	2.50	80.00
Cyclohexane	84.16	1.26	7.75
Benzene	78.11	1.40	7.10
Toluene	92.13	1.27	6.75

Additional LEL Information

- Additional flammability characteristics of combustible organic compounds can be found on Table 4.2.1 in “Control Technologies for Hazardous Air Pollutants” by USEPA at the following web site:
- http://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryID=124752
- The manual is a revision of the first (1986) edition of the Evaluation of *Control Technologies for Hazardous Air Pollutants*, which incorporated information from numerous sources into a single, self-contained reference source.

Thermal Incineration Design Parameters

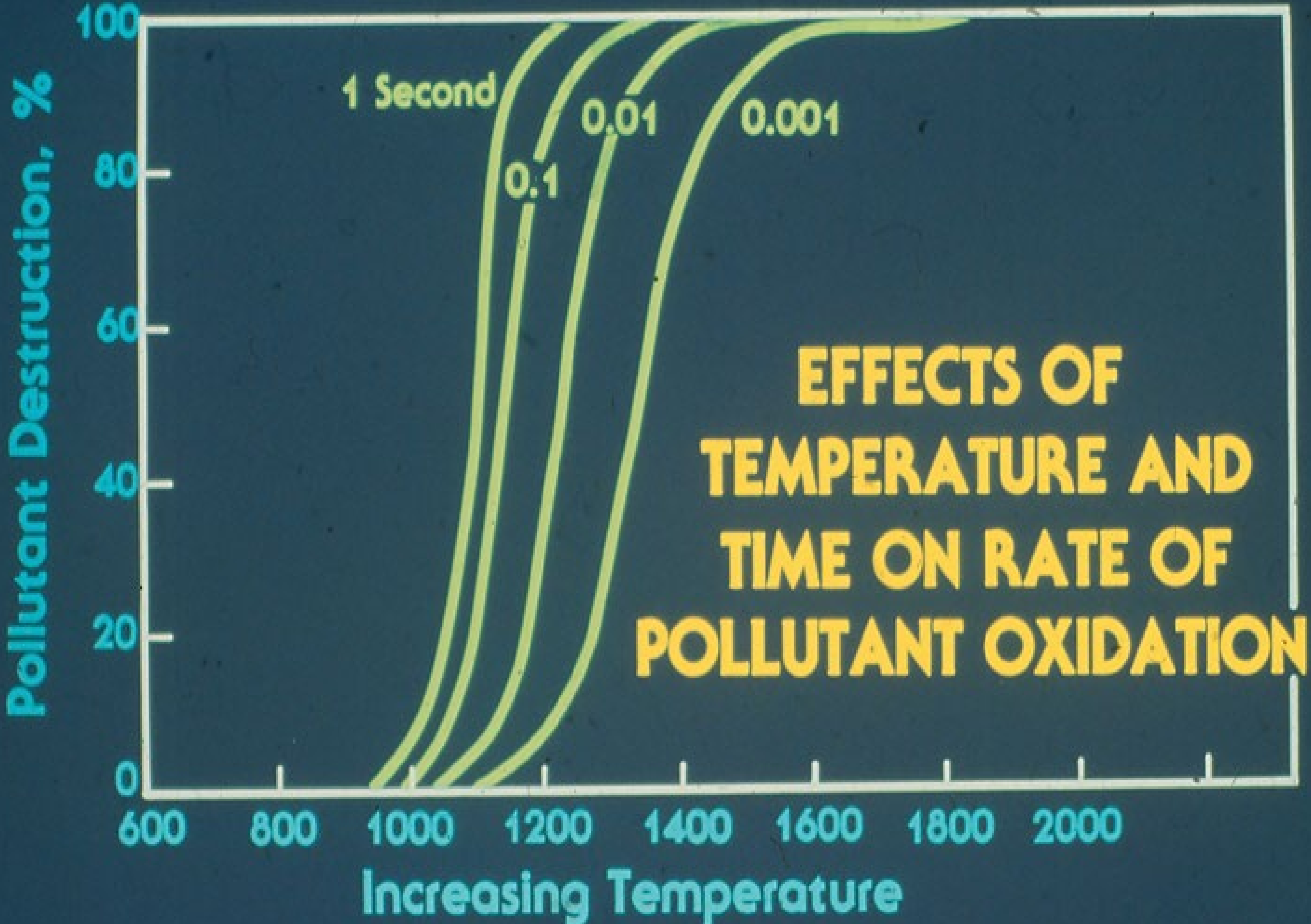




Efficiency

- Time
- Temperature
- Turbulence

EFFECTS OF TEMPERATURE AND TIME ON RATE OF POLLUTANT OXIDATION



General Incineration Design Ranges

Temperature	1300° - 1500°F
Retention Time	0.3 – 0.5 seconds

Destruction Efficiencies

- VOC/HAP destruction efficiency depends on design criteria (i.e. chamber temperature, residence time, inlet VOC concentration, compound type, and degree of mixing).
- Typical thermal incinerator design efficiencies range from 98 to 99.99%, depending on system requirements and characteristics of the contaminated stream.
- The typical design conditions to meet 98% or greater control or a 20 ppm by volume compound exit concentration are 1600 º F combustion temperature and 0.75 second residence time.

Efficient Operating Conditions for Incinerations

- Sufficient Residence Time
- No Dependency
- Low fuel/Oxygen Rate
- Unaltered Flame and Radiation Pattern
- Non-fouling or Acid Fumes

Thermal Design Factors

Efficiency Increases with:

- Operating temperature
- Retention time
- Higher inlet VOC concentration
- Increasing flame/VOC contact
- Good gas mixing
- Increasing CO removal (at temperatures > 1300 °F)

Theoretical Combustion Temperatures Requirements for 99.99% Destruction Efficiencies of HAP/VOC Compounds

Compound	Combustion Temperature (° F)	Residence Time (Seconds)
Acrylonitrile	1,344	1
Allyl chloride	1,276	1
Benzene	1,350	1
Chlorobenzene	1,407	1
1,2- dichloroethane	1,368	1
Methyl chloride	1,596	1
Toluene	1,341	1
Vinyl chloride	1,369	1

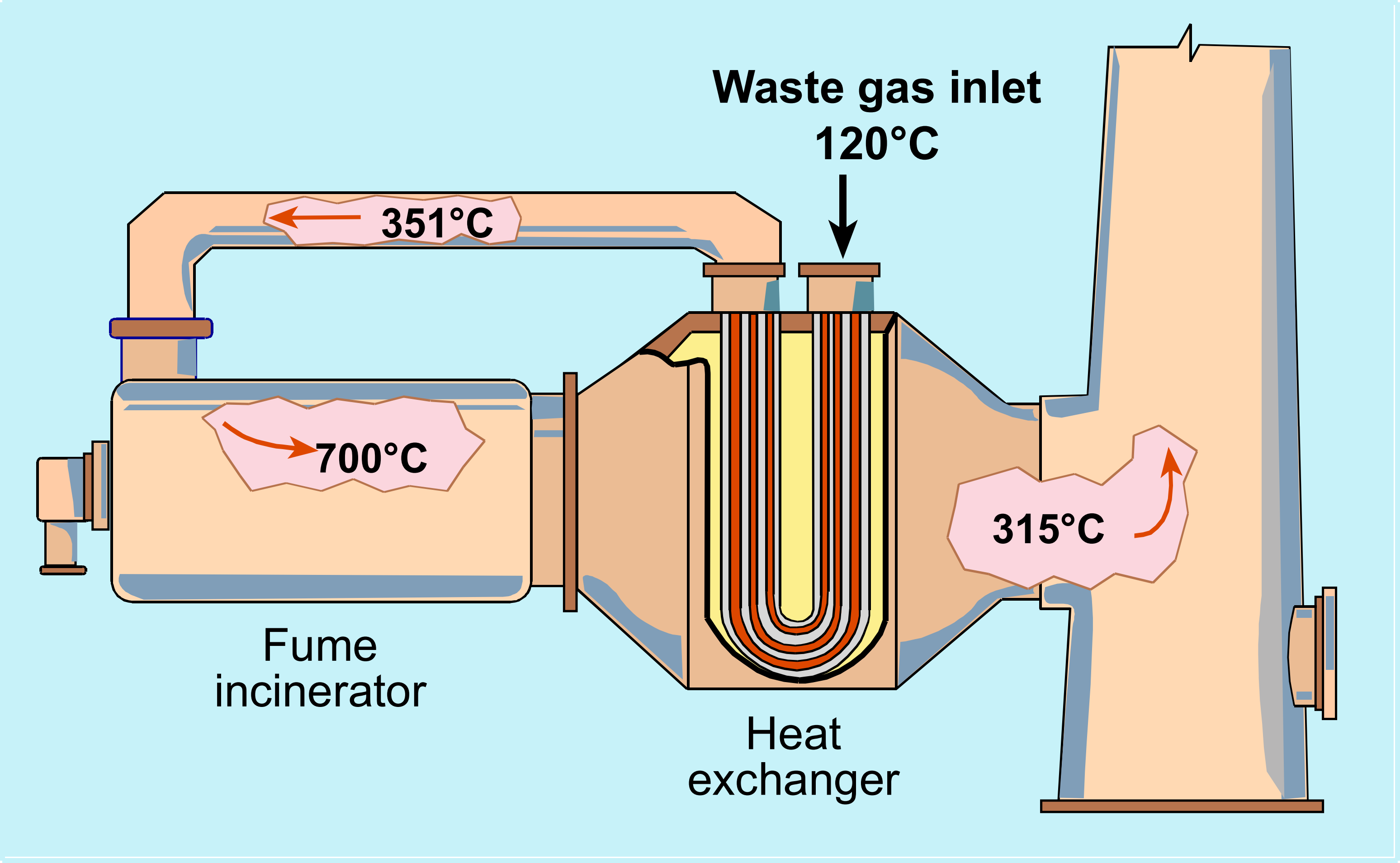
Specific Thermal Incinerator Design Variables

	Non-Halogenated Stream		Halogenated Stream	
Required Destruction Efficiency (DE) (%)	Combustion Temperature T (ºF)	Residence Time t_r (sec)	Combustion Temperature T (ºF)	Residence Time t_r (sec)
98	1600	0.75	2000	1.0
99	1800	0.75	2200	1.0

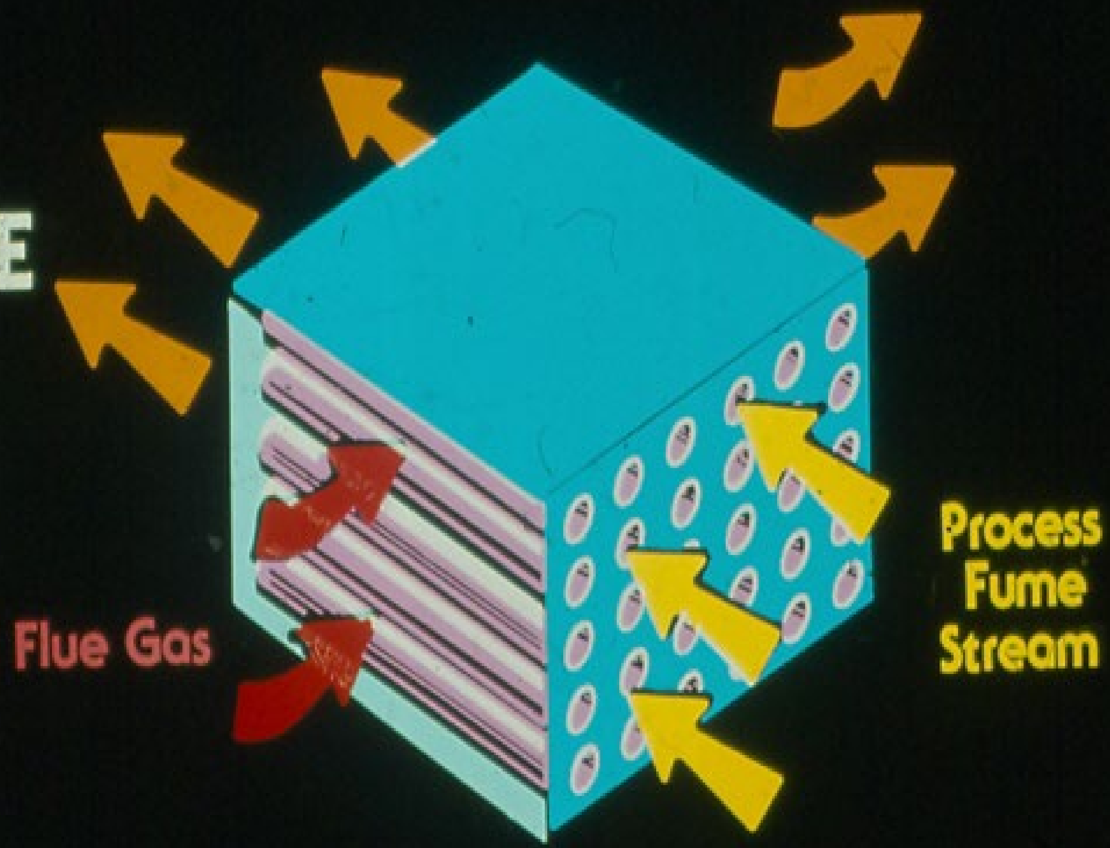
Generation of Problematic Compounds

- Thermal oxidizers handling HAP/VOC materials that contain chlorine, fluorine, or bromine atoms generate HCl, Cl_2, HF, and HBr as additional reaction products during oxidation.
- A gaseous absorber (scrubber) can be used as part of the air pollution control system to collect these contaminants prior to gas stream release to the atmosphere.

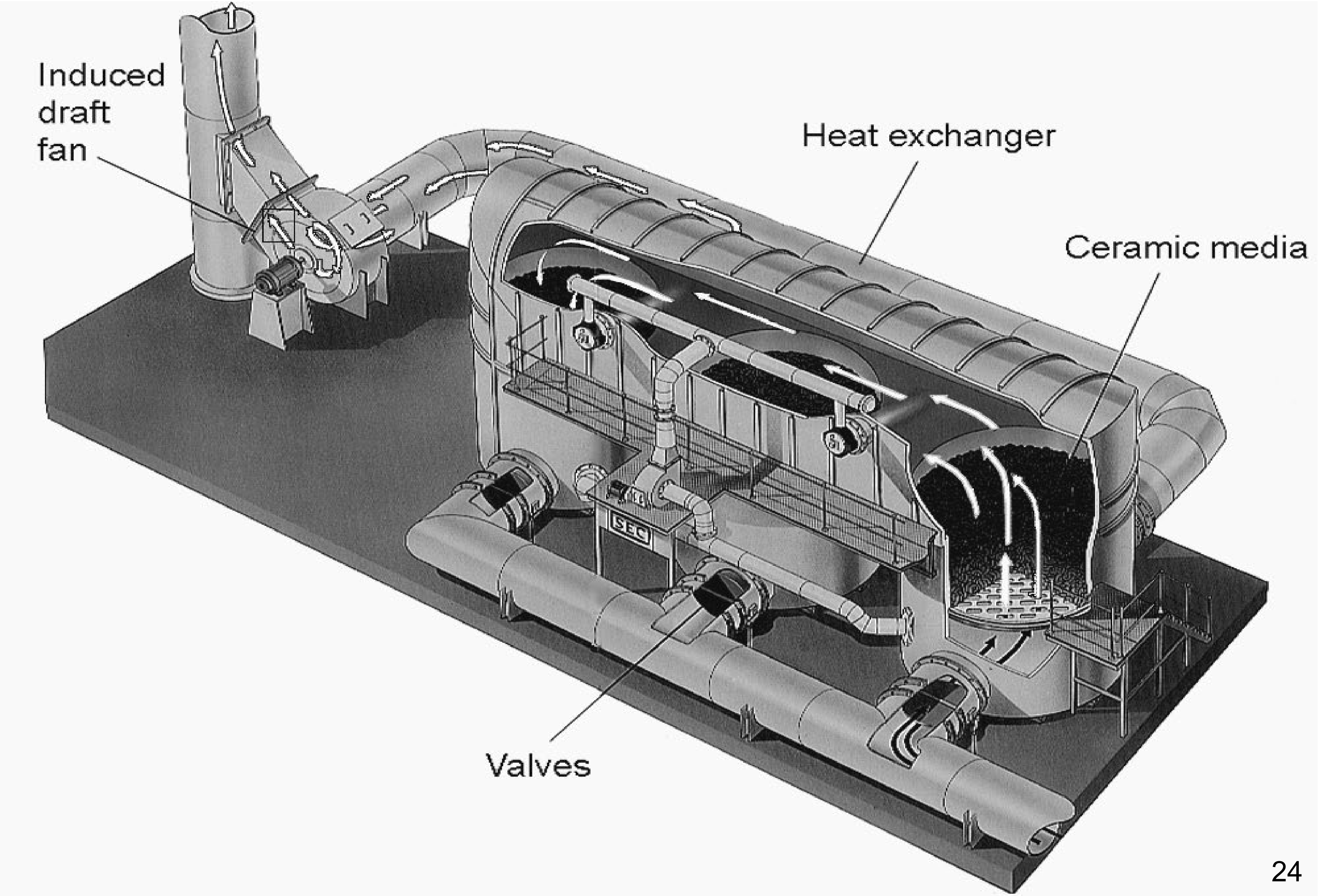
Recuperative Thermal Oxidizer



RECUPERATIVE HEAT RECOVERY DEVICE

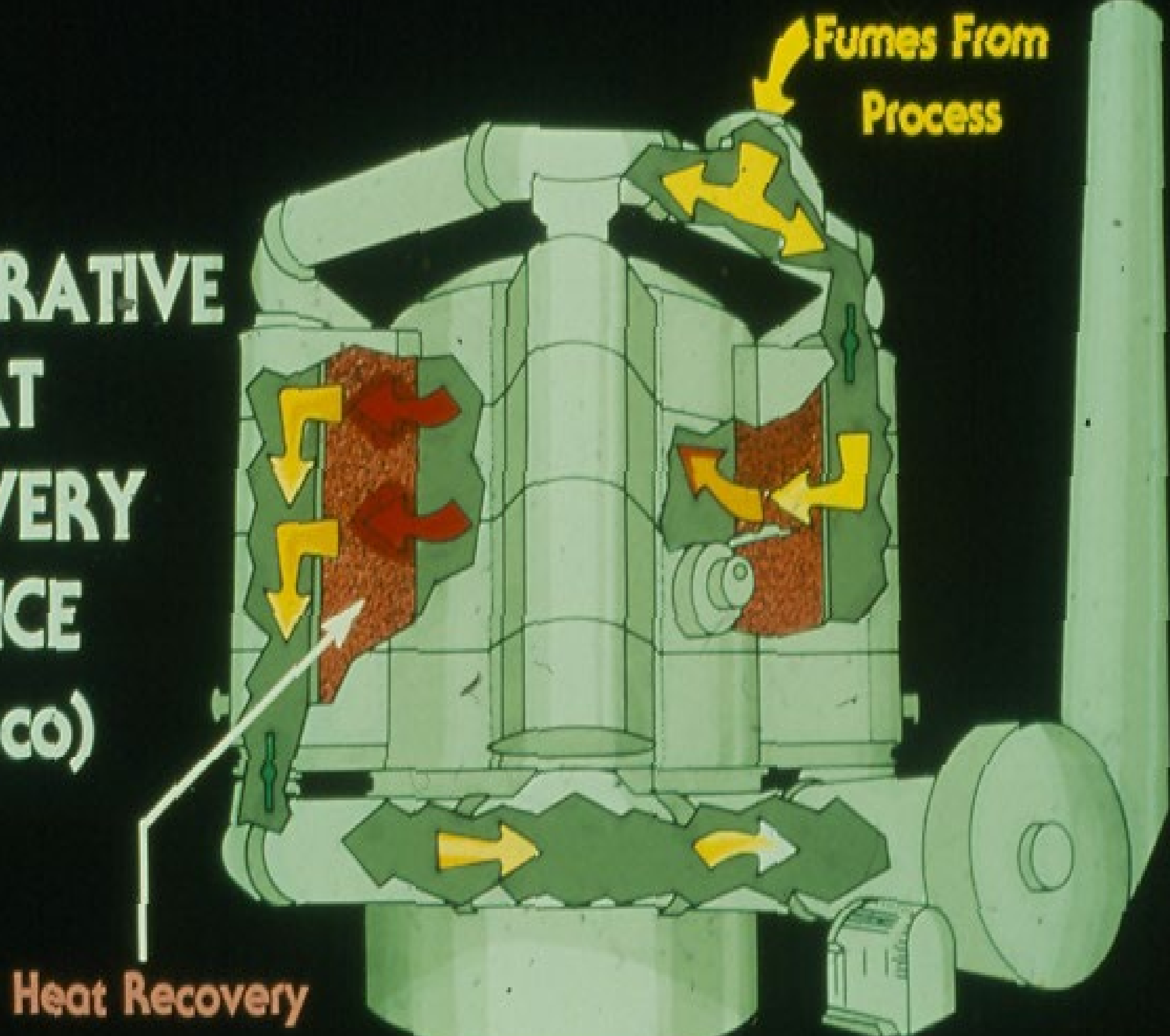


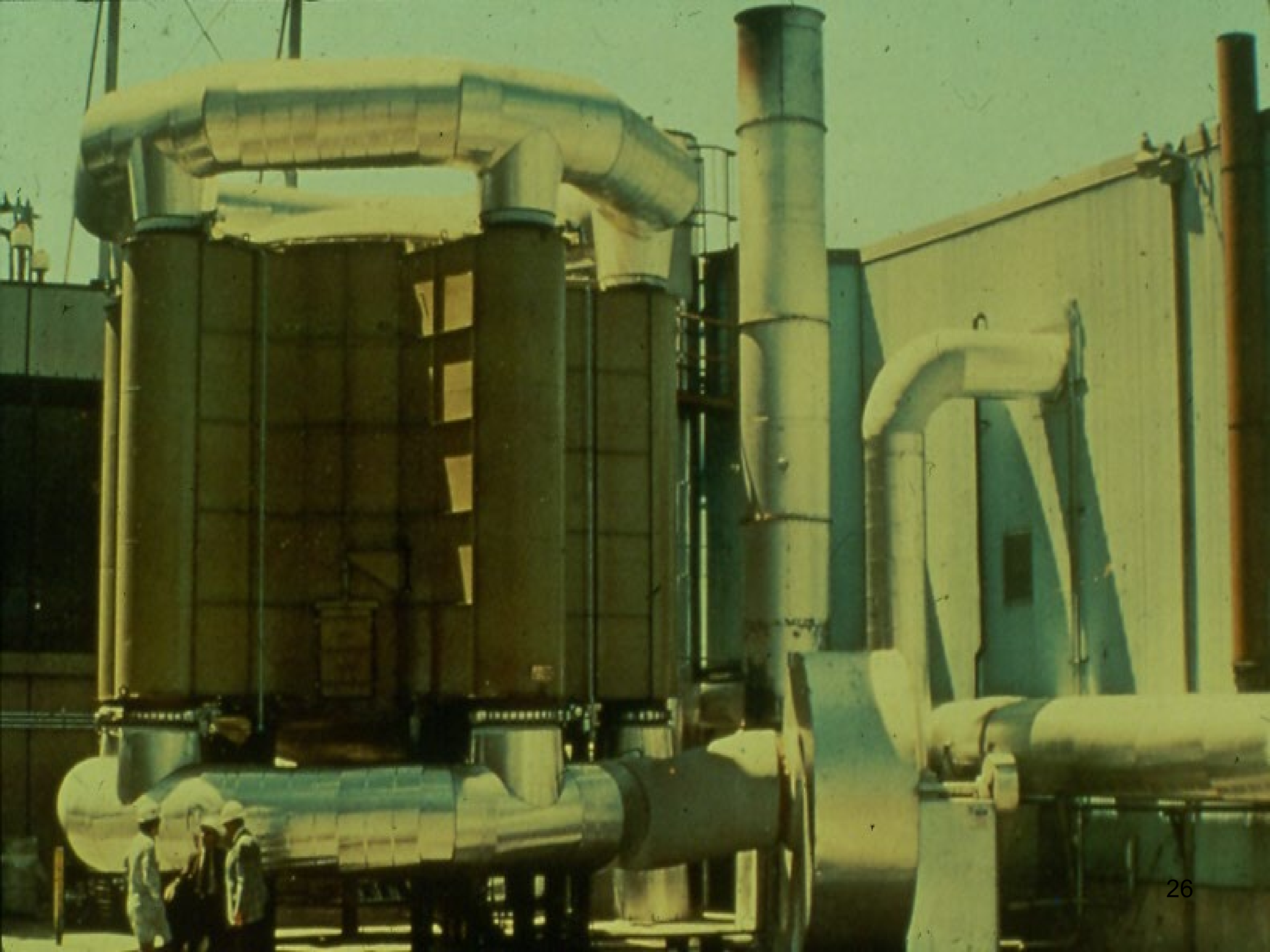
Regenerative Thermal Oxidizer



Smith Engineering Ontario, California in Control of Gaseous Emissions 415 APTI January 2000

REGENERATIVE HEAT RECOVERY DEVICE (Reeco)

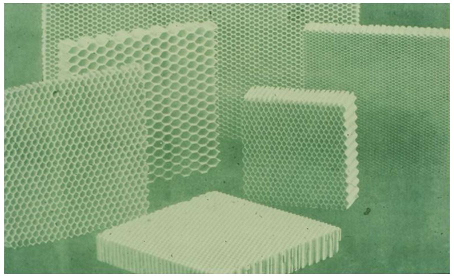




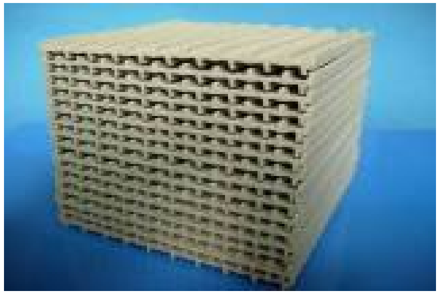
Types of Ceramic Heat Recovery Media

- Random packing

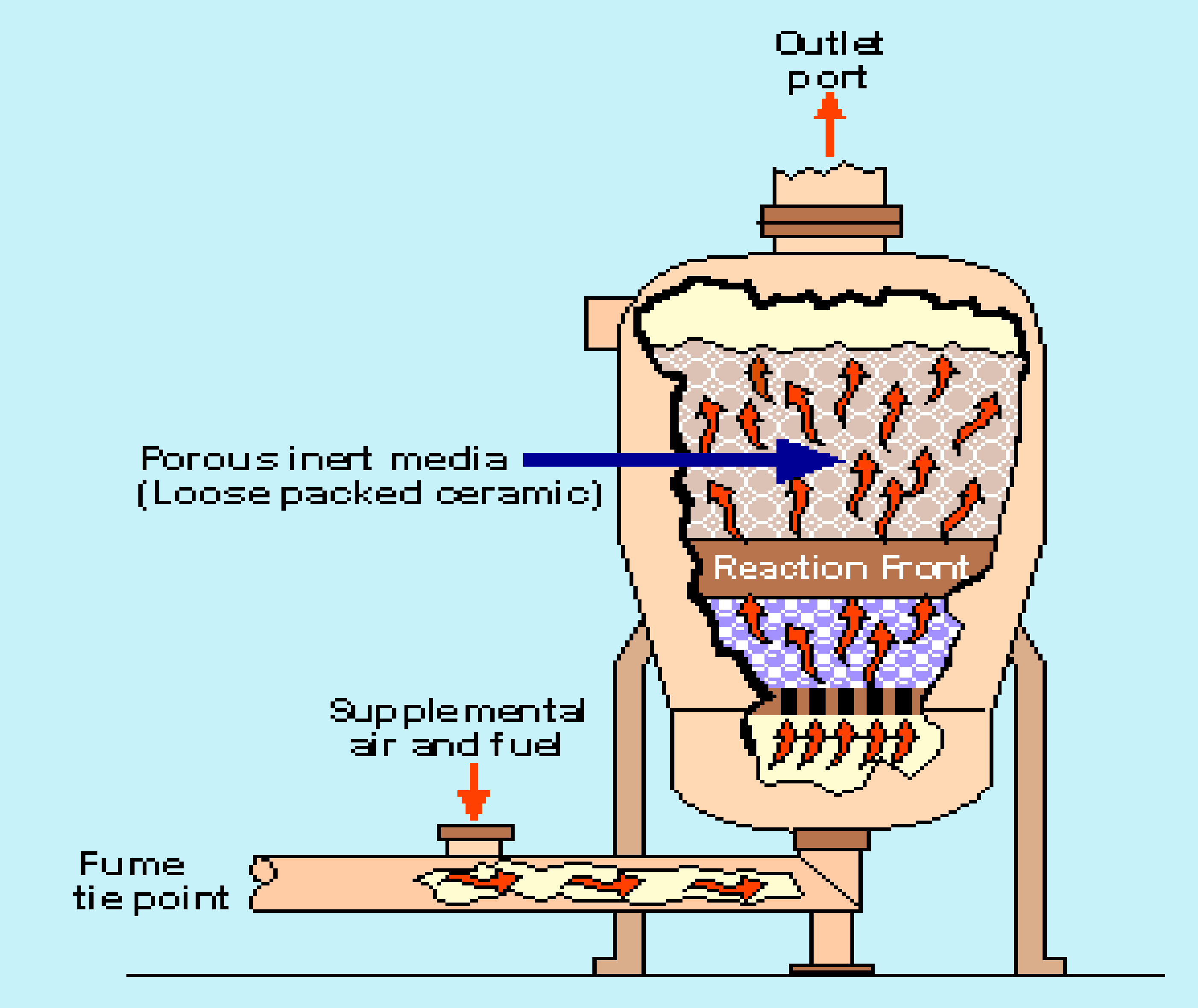
- Extruded Honeycomb Monolith



- Structured Multi-Layered Media



Flameless Thermal Oxidizer



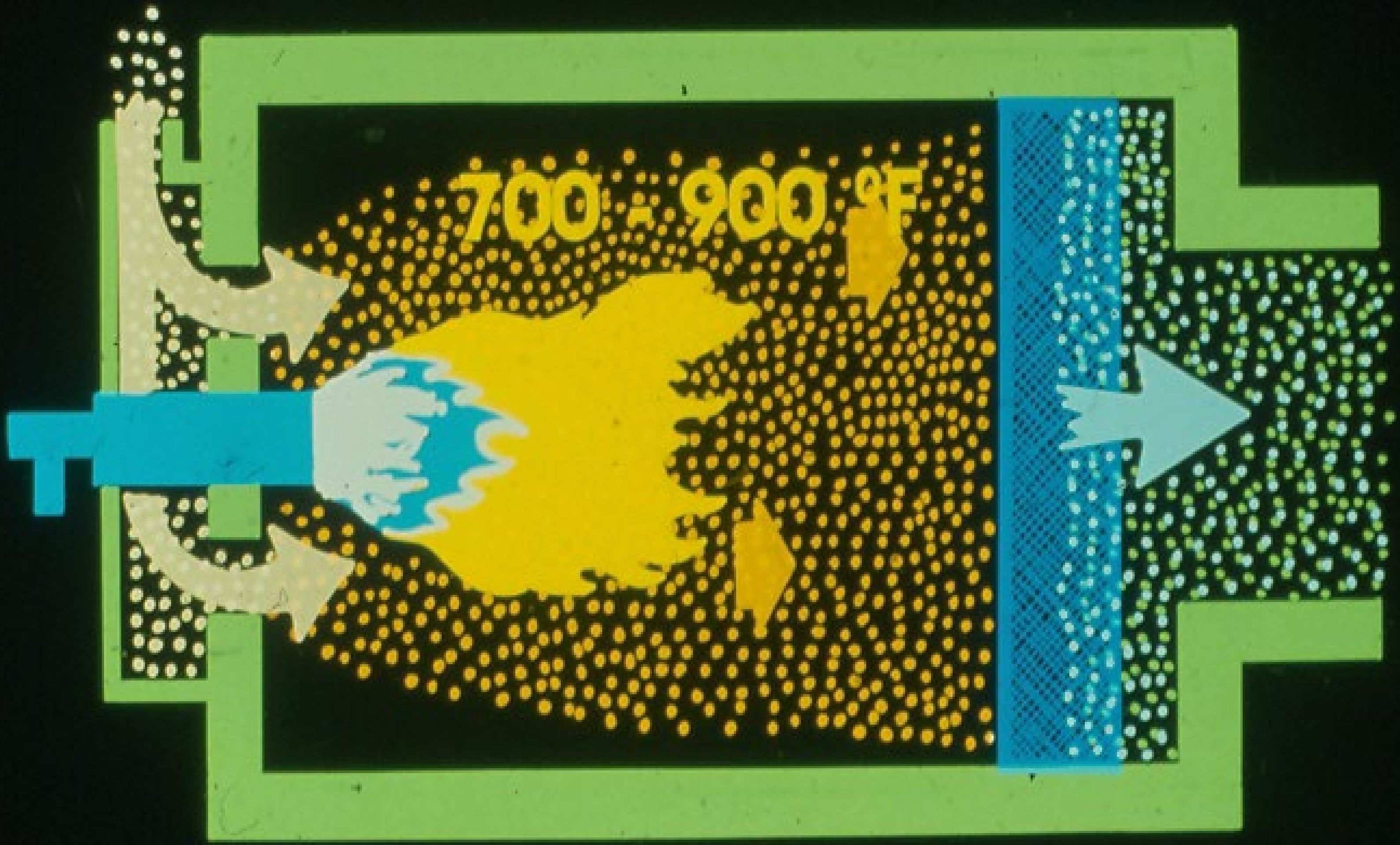
Flameless Thermal Oxidizer

- Combustion in FTO systems occurs within a chemically inert, porous ceramic bed heated to oxidation temperatures.
- The mixing zone for the FTTO is where the fuel is pre-mixed with off-gas at the inlet of the reactor before it passes through a pre-heated ceramic matrix, which heats the organic vapors.
- Once the vapors reach oxidation temperature, they auto-ignite in the system’s reaction zone.

Flameless Thermal Oxidizer

- The FTO is a destructive technology that has been used for process and waste stream off-gas treatment of VOC’s and in the treatment of VOC and chlorinated volatile organic compounds (CVOCs) off gases generated during site remediation.
- The FTO process converts the VOCs and CVOCs to CO_2, H_2O and HCl.
- The FTO provides destruction and removal efficiencies (DREs) in excess of 99.99 for VOCs and CVOCs.

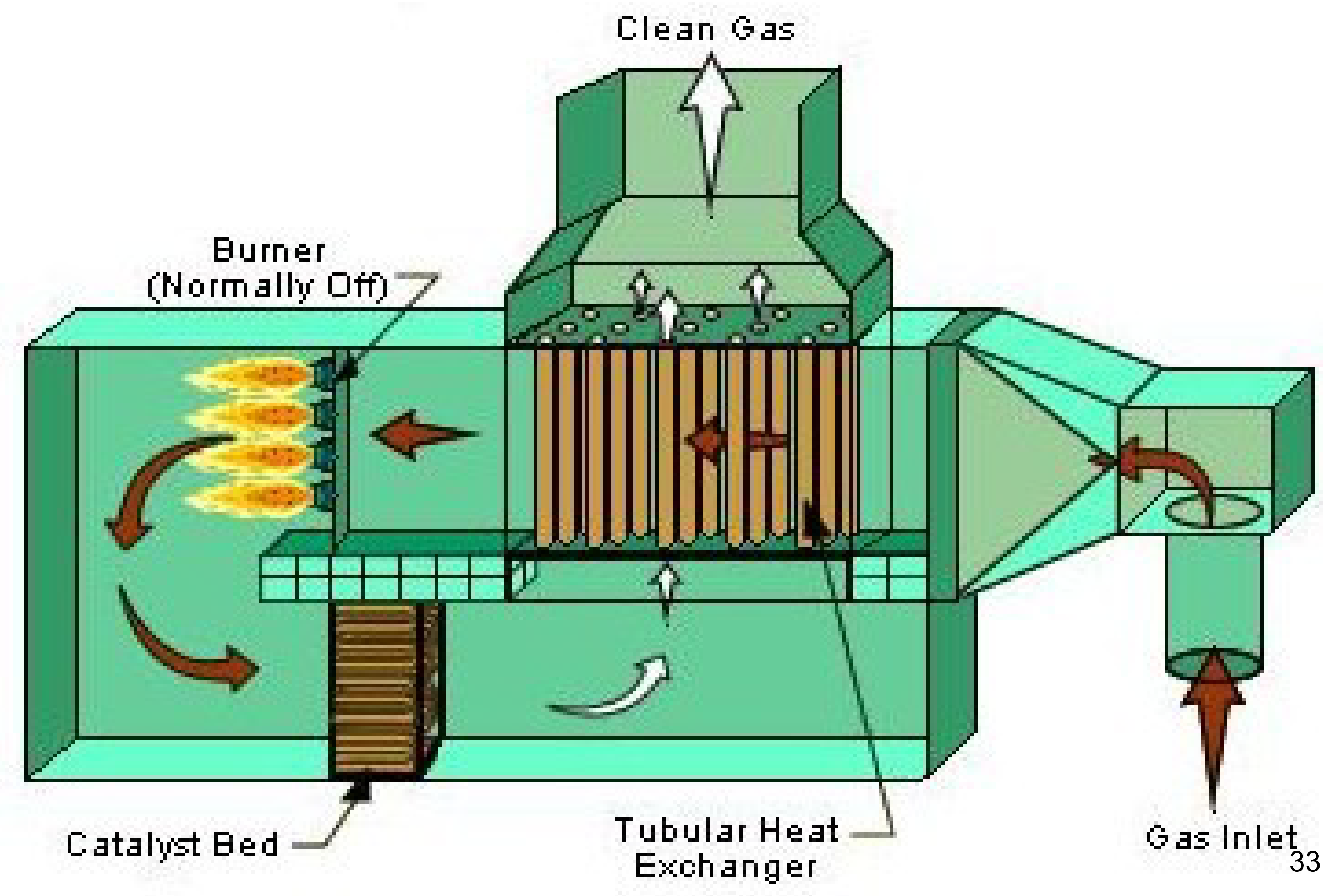
CATALYTIC INCINERATION



Catalytic Oxidation

- Catalytic oxidizers operate at substantially lower temperatures than thermal oxidizers. The catalytic oxidation reactions can be performed at temperatures in the range of 500 to 1000°F.
- Common types of catalysts include noble metals (i.e. platinum and palladium) and ceramic materials. HAP/VOC destruction by catalytic oxidizers usually exceeds 95% and could exceeds 99%.

Catalytic Oxidizer



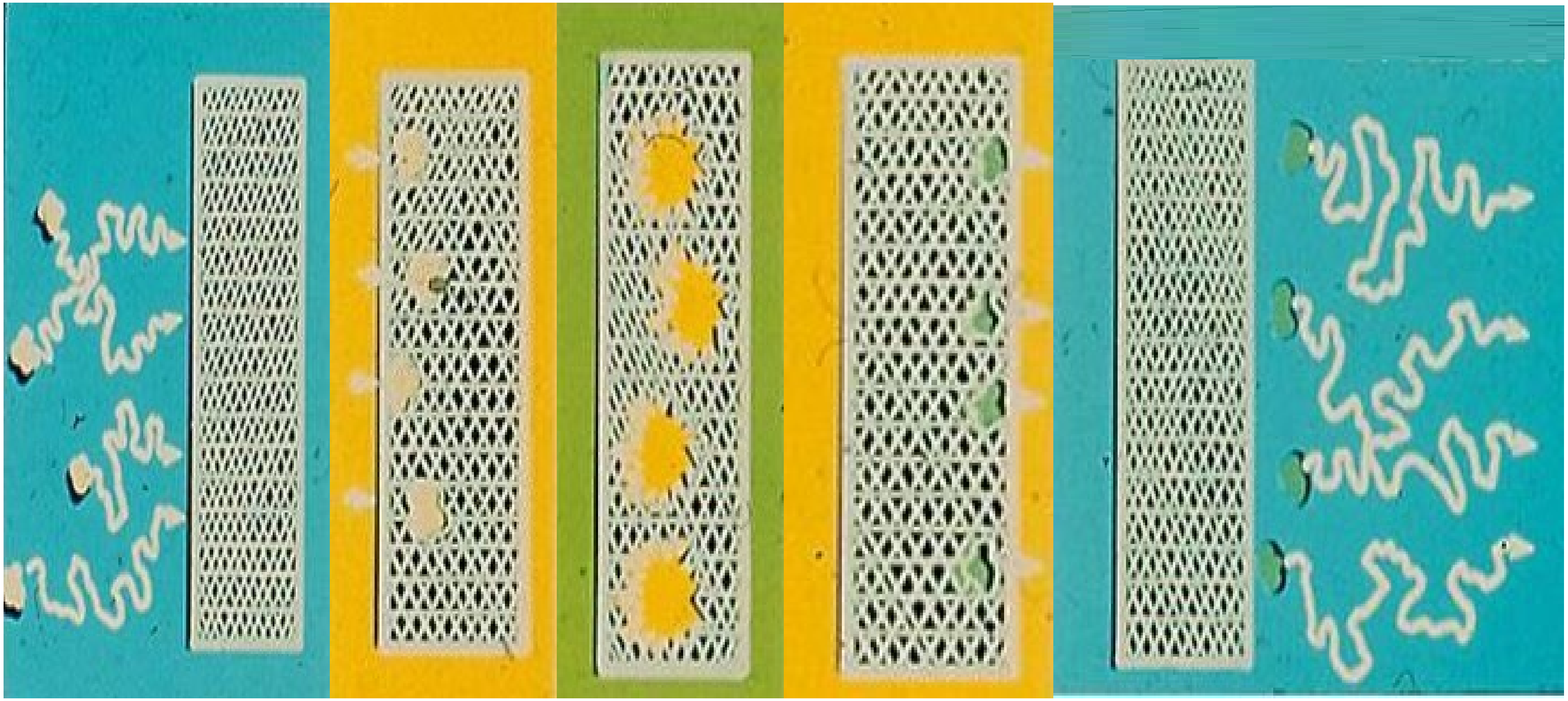
Catalytic Oxidation

- The relatively low gas temperatures in the combustion chamber, can eliminate the need for a refractory lining.
- The overall weight is minimized for and provides an option for mounting the units on roofs close to the point of VOC generation.
- This can also reduce the overall cost of the system by limiting the distance the VOC-laden stream must be transported in ductwork.

Catalytic Incineration Principles of Operation

- Diffusion
- Adsorption
- Reaction
- Desorption
- Diffusion and Mixing

Catalytic Incineration Principles of Operation



Diffusion **Adsorption** **Reaction** **Desorption** **Diffusion and Mixing**

Common Types of Catalysts

Noble Metals

- Platinum
- Palladium
- Rhodium

Metal Oxides

- Chromium oxide
- Magnesium oxide
- Cobalt oxide
- Alumina

Platinum Catalytic Suppressants

- **Sulfur**
- **Halogens**

Suppressant Action is reversible

Platinum Catalyst Poisons

Fast Acting	Slow Acting	High Temperature
P	Zn	(2500°F)
Bi	Pb	Fe
As	Sn	Cu
Sb		
Hg		

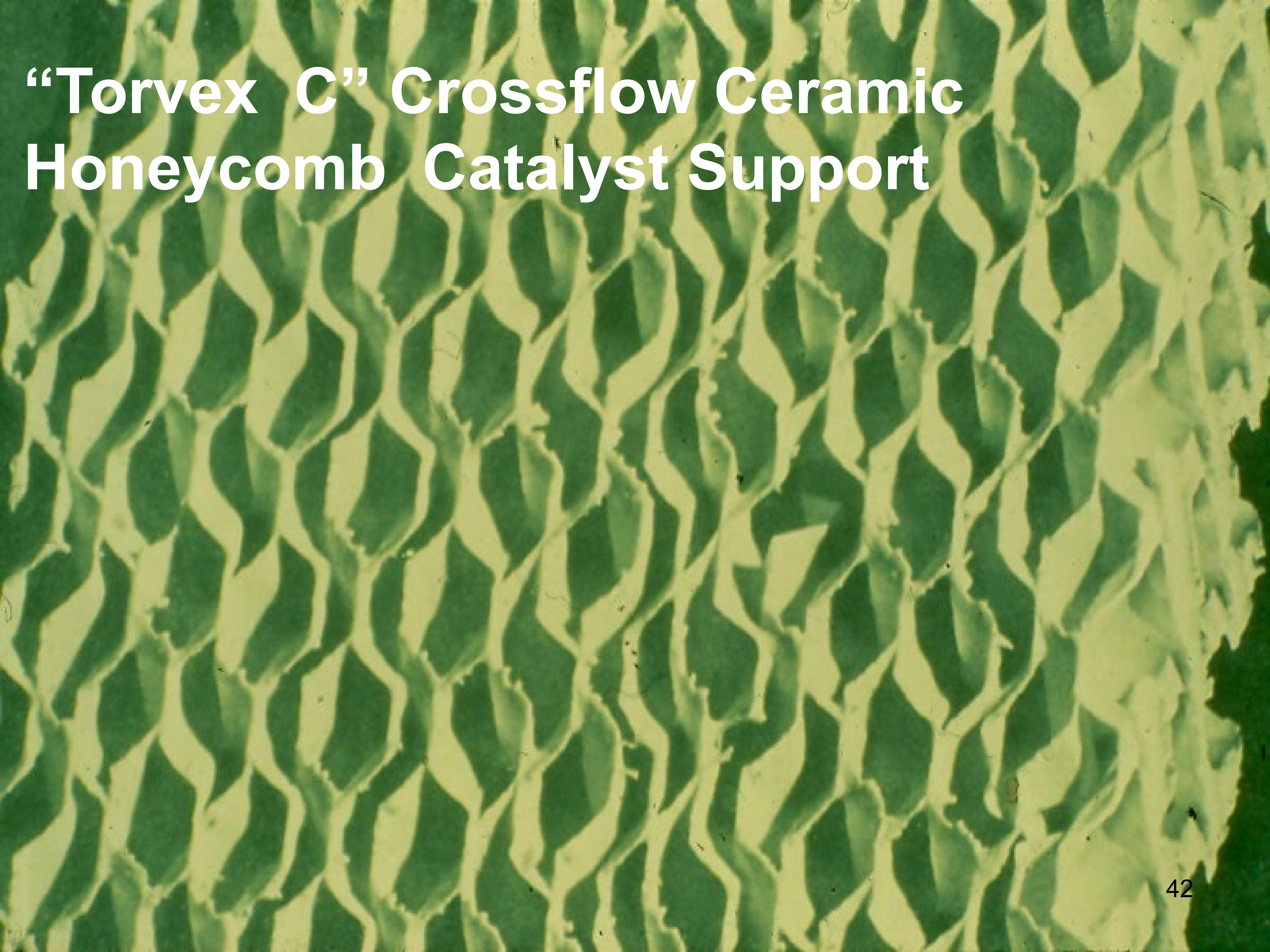
Fixed-Bed Catalytic Incinerators

Fixed-bed catalytic incinerators may use a monolith catalyst or a packed-bed catalyst.

- The most widespread method of contacting the VOC containing stream with the catalyst is the catalyst monolith. The catalyst is impregnated on a porous solid block containing parallel, non-intersecting channels aligned in the direction of the gas flow.
- Monoliths offer the advantages of minimal attrition due to thermal expansion/ contraction during startup/shutdown and low overall pressure drop.

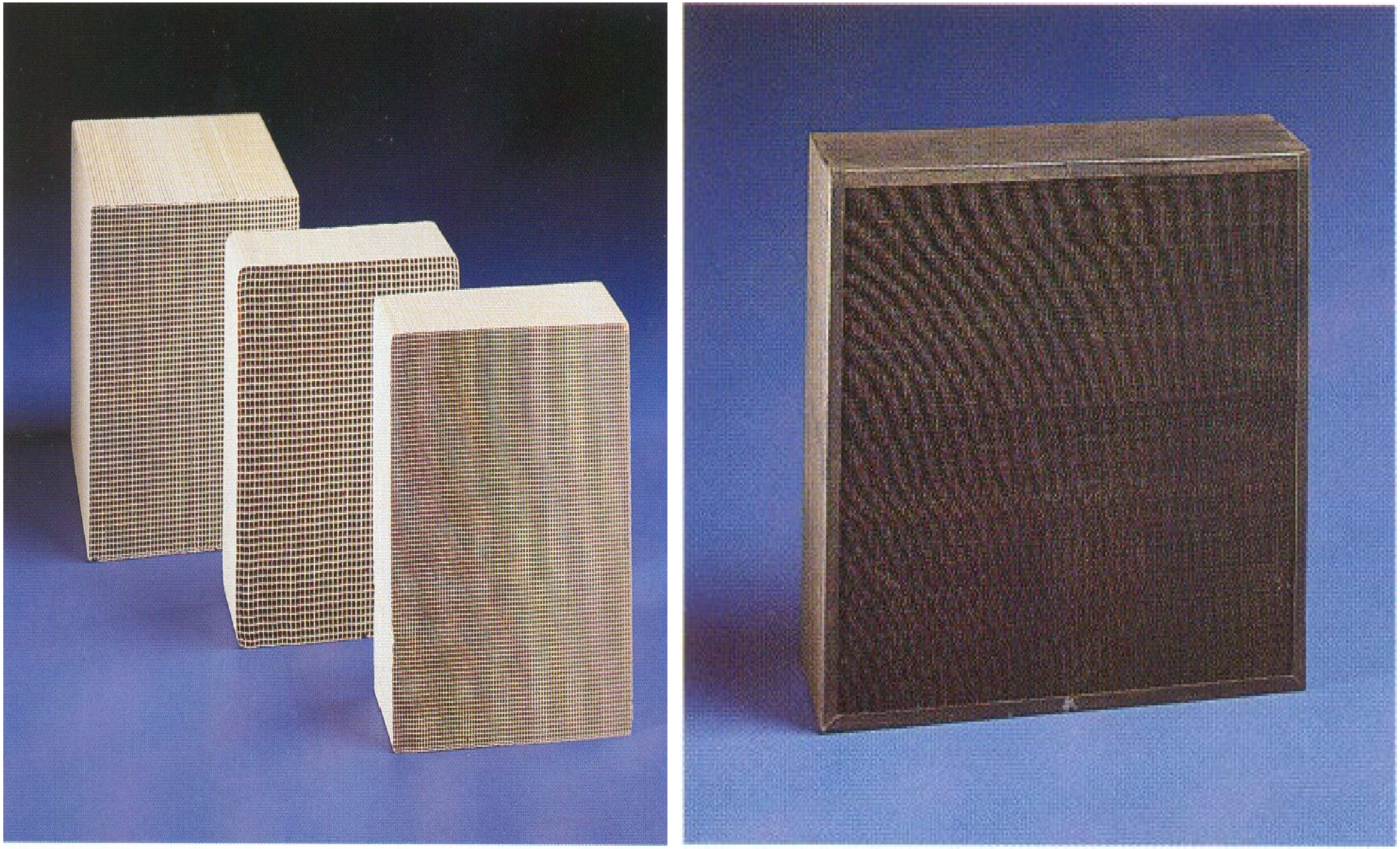
Packed-Bed Catalytic Incinerators

- In packed-bed catalytic incinerators, the catalyst particles are supported, either in a tube or in shallow trays through in which the gases pass through. However, it has higher pressure drop, compared to a monolith.
- In a tray type arrangement the catalyst is pelletized and is used within several industries (e.g., heat-set web-offset printing).
- Use of pelletized catalyst is advantageous where large amounts of such contaminants as phosphorous or silicon compounds are present.



“Torvex C” Crossflow Ceramic Honeycomb Catalyst Support

Ceramic and Metallic Monolith Catalysts (Prototech Company)



http://www.sud-chemie.com/scmcms/web/page_en_6283.htm

“Torvex B” Honeycomb Alumina Catalyst Support

“Therma Comb” Honeycomb Catalyst Support

Thermal Oxidizer Operation

- Inlet VOC concentration maintained at <25% LEL
- Combustion chamber kept at 200 °F to 300°F above the autoignition temperature
- Combustion chambers sized for residence times of 0.5 to 2.0 seconds

Catalytic Incinerator System Design Variables

			Space Velocity- SV (hr^{-1}) SV = Flow rate/Bed Volume	
Required Destruction Efficiency (%)	**Temperature at the Catalyst Bed Inlet °F**	**Temperature at the Catalyst Bed Outlet °F**	**Base Metal**	**Precious Metal**
95	600	1000 - 1200	10,000 – 15,000	30,000 – 40,000
98 - 99	600	1000 - 1200	Based on Specific Process Conditions	Based on Specific Process Conditions

HAP/VOC Destruction Efficiency for Catalytic Incinerators

- In a US EPA pilot scale study (“Parametric Evaluation of VOC/HAP” Destruction Via Catalytic Incineration) testing verified that destruction efficiencies in the 98 to 99 percent range are achievable for the following compounds:
- Alcohols, acetates, ketones, cellosolve compounds/dioxane, aldehydes, aromatics and ethylene/ethylene oxide.
- Destruction efficiencies of at least 97% are achievable for acrylonitrile and cresol.

HAP/VOC Destruction Efficiency for Catalytic Incinerators

- Catalytic incinerators can achieve efficiencies on the order of 98 to 99% for HAP/VOCs in selected industries.
- The destruction efficiency for a given compound may vary depending on whether the compound is the only VOC in the gas stream or part of a mixture.

Advantages of Catalytic Incineration

- Lower operating Temperatures
- Lower supplemental fuel use
- Lower construction materials cost

Disadvantages of Catalytic Incineration

- Particulate fouling
- Thermal aging
- Catalytic poisoning
- Suppressants

Oxidizer Manufacturers' web sites

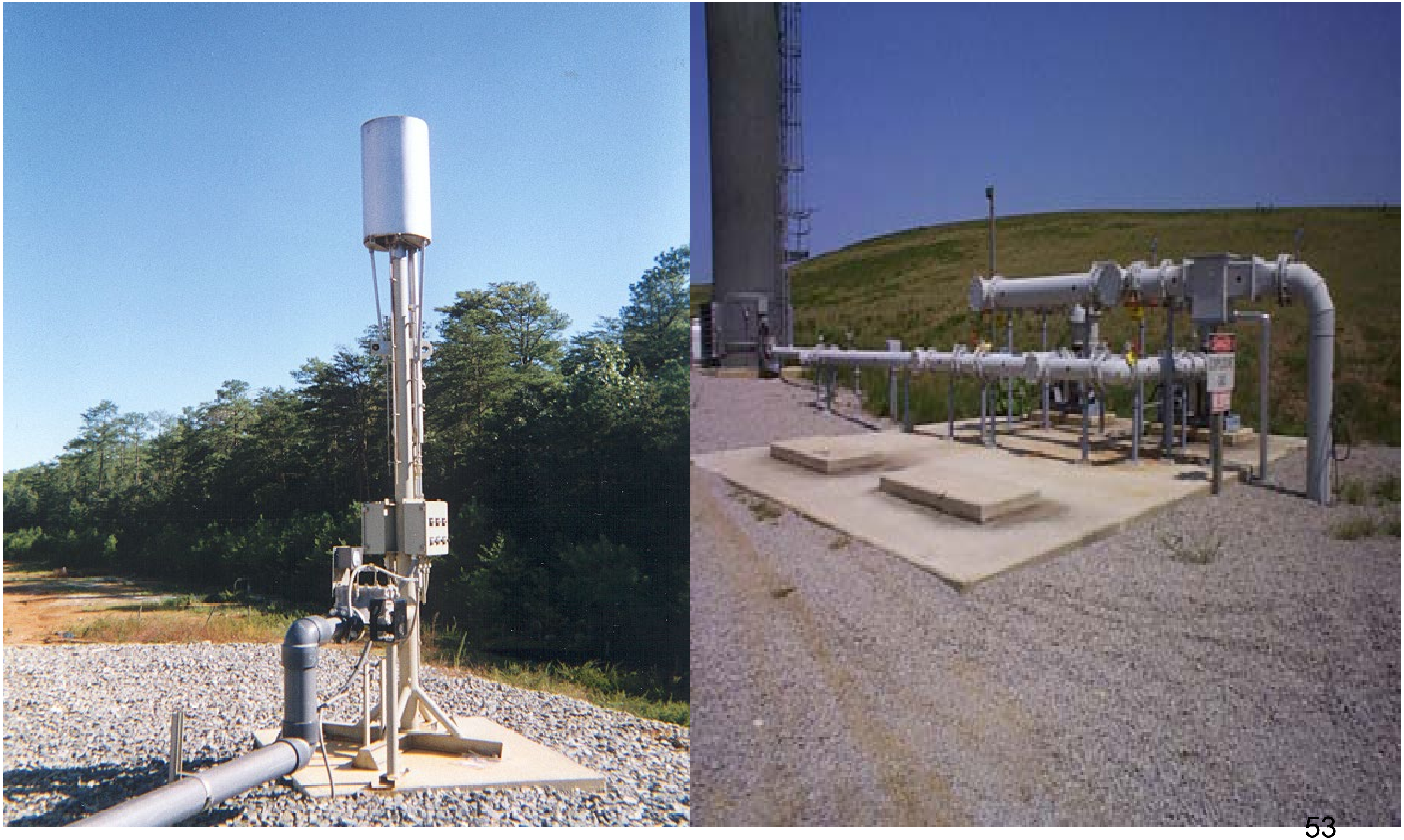
http://www.anguil.com/prregthe.php

http://www.smithenvironmental.com/splash.asp

http://www.megtec.com/index.php

http://www.met-prosystems.com/

FLARES

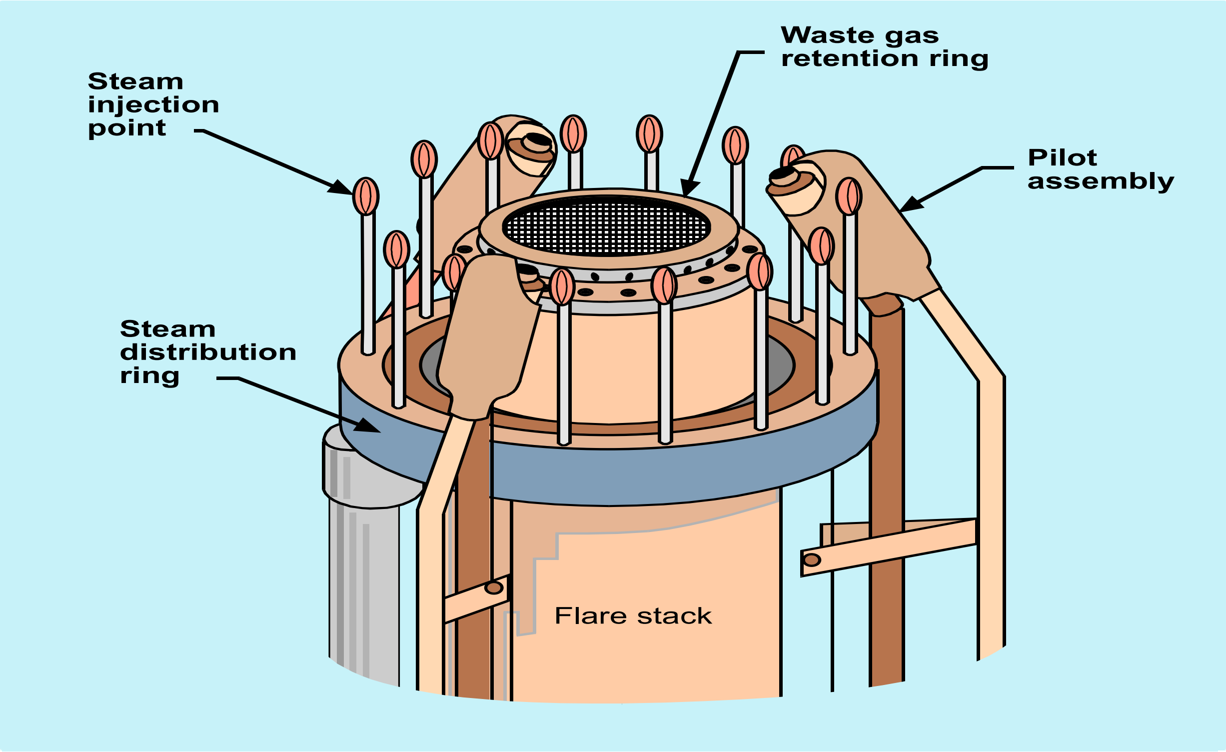


Type of Flares

- **Steam-Assisted Flares**
- **Air-Assisted Flares**
- **Non-Assisted Flares**
- **Pressure-Assisted Flares**
- **Enclosed Ground Flares**

Flare Performance Requirements

- **The EPA requirements for steam-assisted, air-assisted, and non-assisted open flares are specified in 40 CFR Section 60.18.**



Flare Design Criteria

The design and operating requirements for steam-assisted, elevated flares state are:

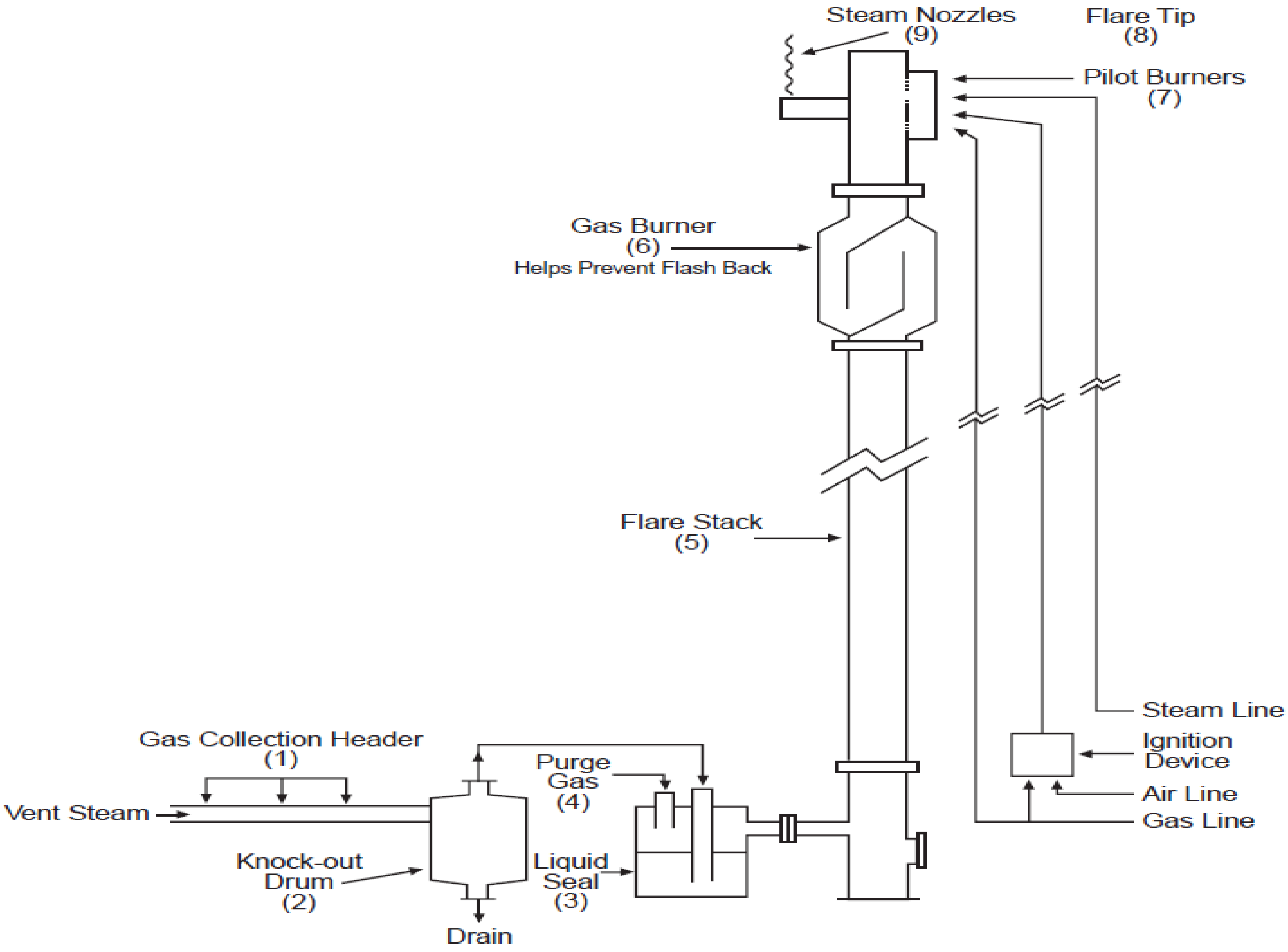
- An exit velocity at the flare tip of less than 60 ft/sec for 300 Btu/scf gas streams less than 400 ft/sec for >1,000 Btu/scf gas streams.
- For gas streams between 300-1,000 Btu/scf the maximum permitted velocity V_{max}, in ft/sec is determined by the following equation:

$$\log_{10}(V_{max}) = \frac{B_V + 1{,}214}{852}$$

Steam-Assisted Flares

- Steam-assisted flares are single burner tips, elevated above ground level for safety reasons.
- They burn the vented gas in essentially a diffusion flame.
- To ensure an adequate air supply and good mixing, this type of flare system injects steam into the combustion zone to promote turbulence for mixing and to induce air into the flame.

Typical Steam Assisted Flare System



Air-Assisted Flares

- These flares use forced air to provide the combustion air and the mixing required for smokeless operation.
- They are built with a spider-shaped burner (with many small gas orifices) located inside but near the top of a steel cylinder two feet or more in diameter.
- Combustion air is provided by a fan in the bottom of the cylinder. The amount of combustion air can be varied by varying the fan speed.

Non-Assisted Flares

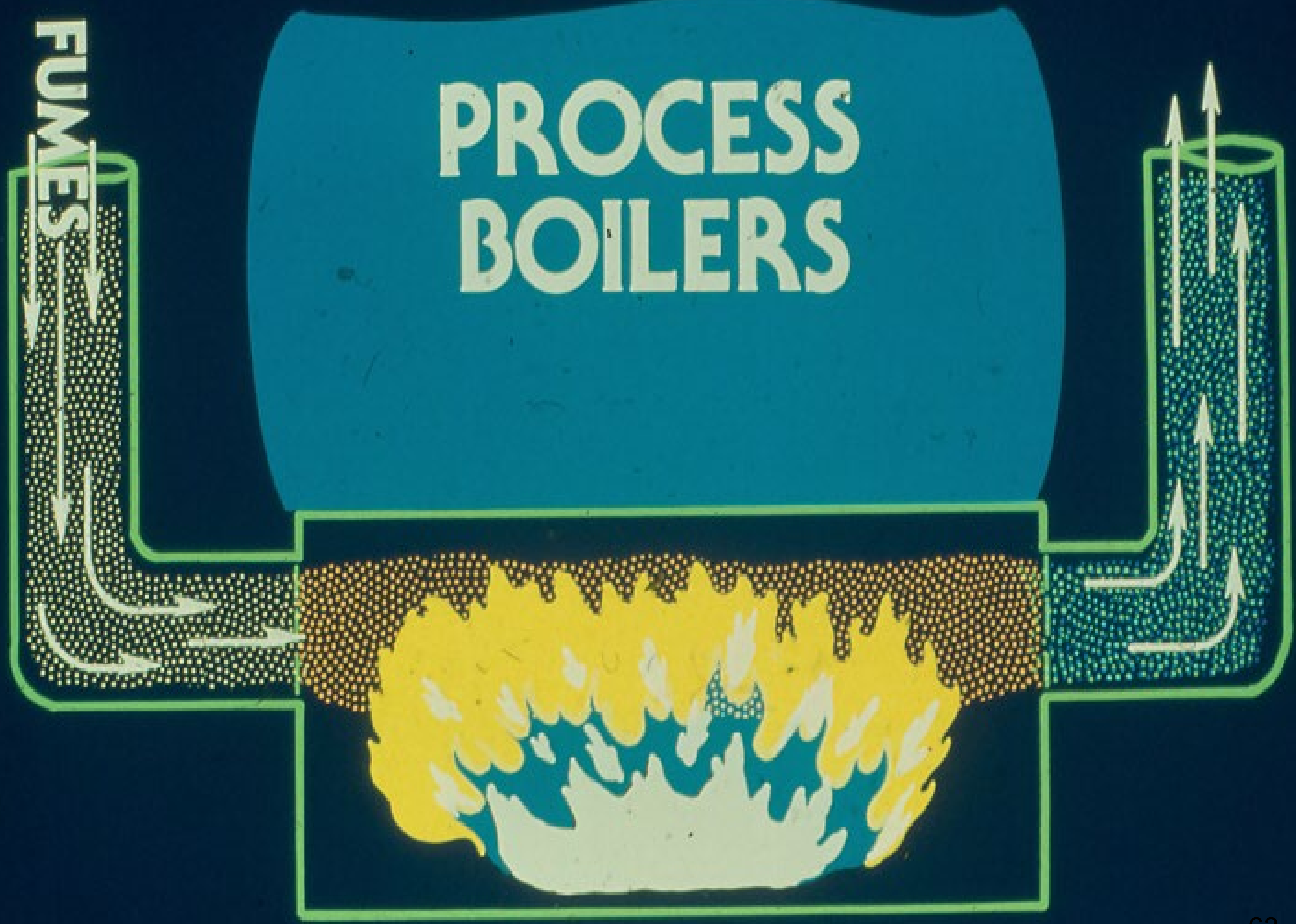
- The non-assisted flare is just a flare tip without any auxiliary provision for enhancing the mixing of air into its flame.
- Its use is limited essentially to gas streams that have a low heat content and a low carbon/hydrogen ratio that burn readily without producing smoke.
- These streams require less air for complete combustion, have lower combustion temperatures that minimize cracking reactions.

Pressure-Assisted Flares

- Pressure-assisted flares use the vent stream pressure to promote mixing at the burner tip.
- These flares can be applied to streams previously requiring steam or air assist for smokeless operation.
- Pressure-assisted flares generally (but not necessarily) have the burner arrangement at ground level, They have multiple burner heads that are staged to operate based on the quantity of gas being released.

Enclosed Ground Flares

- An enclosed flare's burner heads are inside a shell that is internally insulated shell which reduces noise, luminosity, and heat radiation and provides wind protection.
- The height must be adequate for creating enough draft for sufficient and for dispersion of the thermal plume.
- Enclosed flares are used to combust continuous and constant flow vent streams.
- Enclosed flares are typically found at landfills.

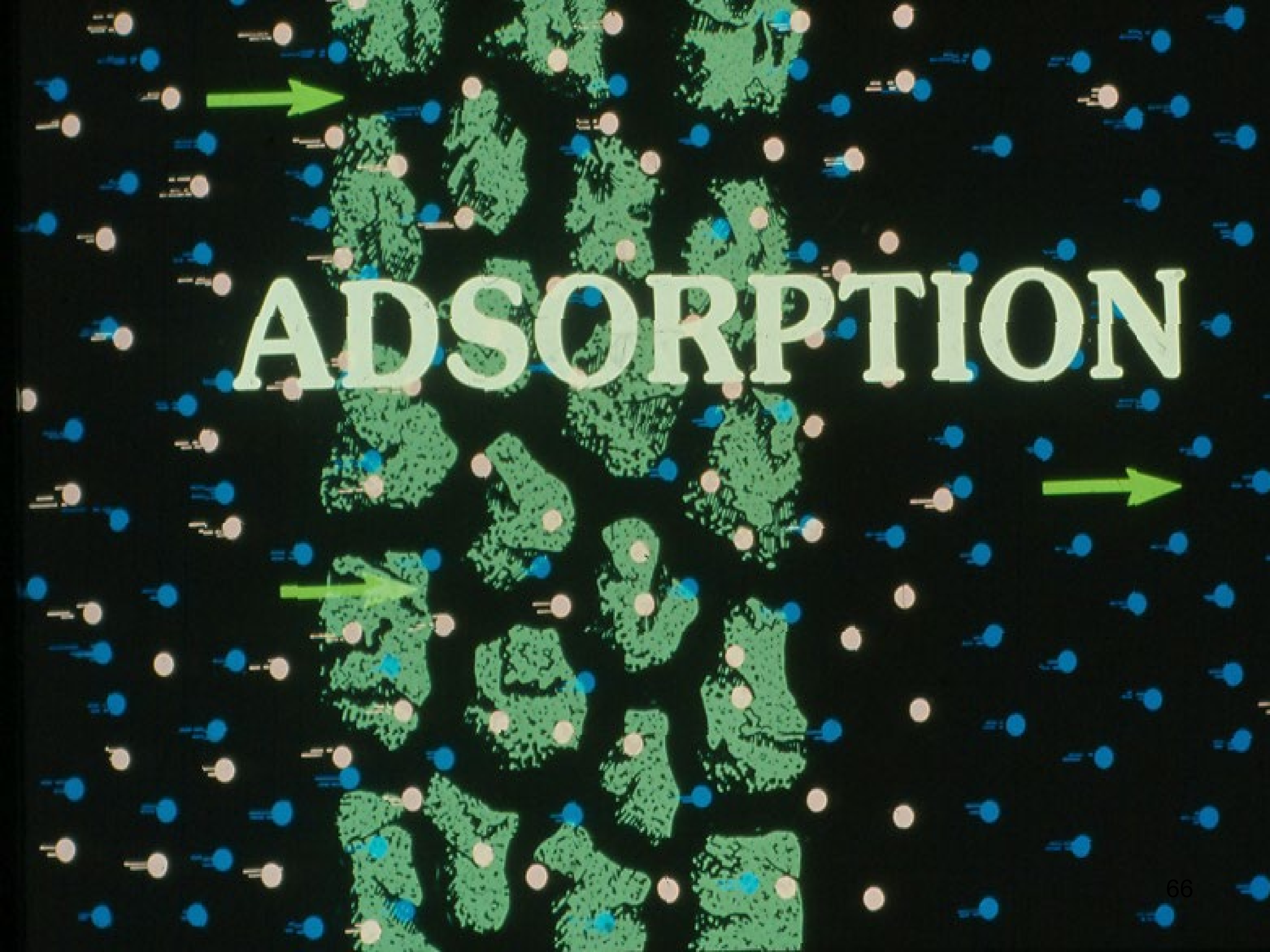

PROCESS
BOILERS
FUMES

Process Equipment for Emission Control

- Fired-process equipment or furnaces include boilers, heaters and incinerators. Indirect- fired furnaces (boilers and process heaters) are those in which heating media are separated from the process streams.
- The parameters that affect the destruction efficiency for boilers and process heaters are the same traditional thermal oxidizing devices. They are temperature, residence time, inlet concentration, compound type and flow regime.

Process Control Effectiveness

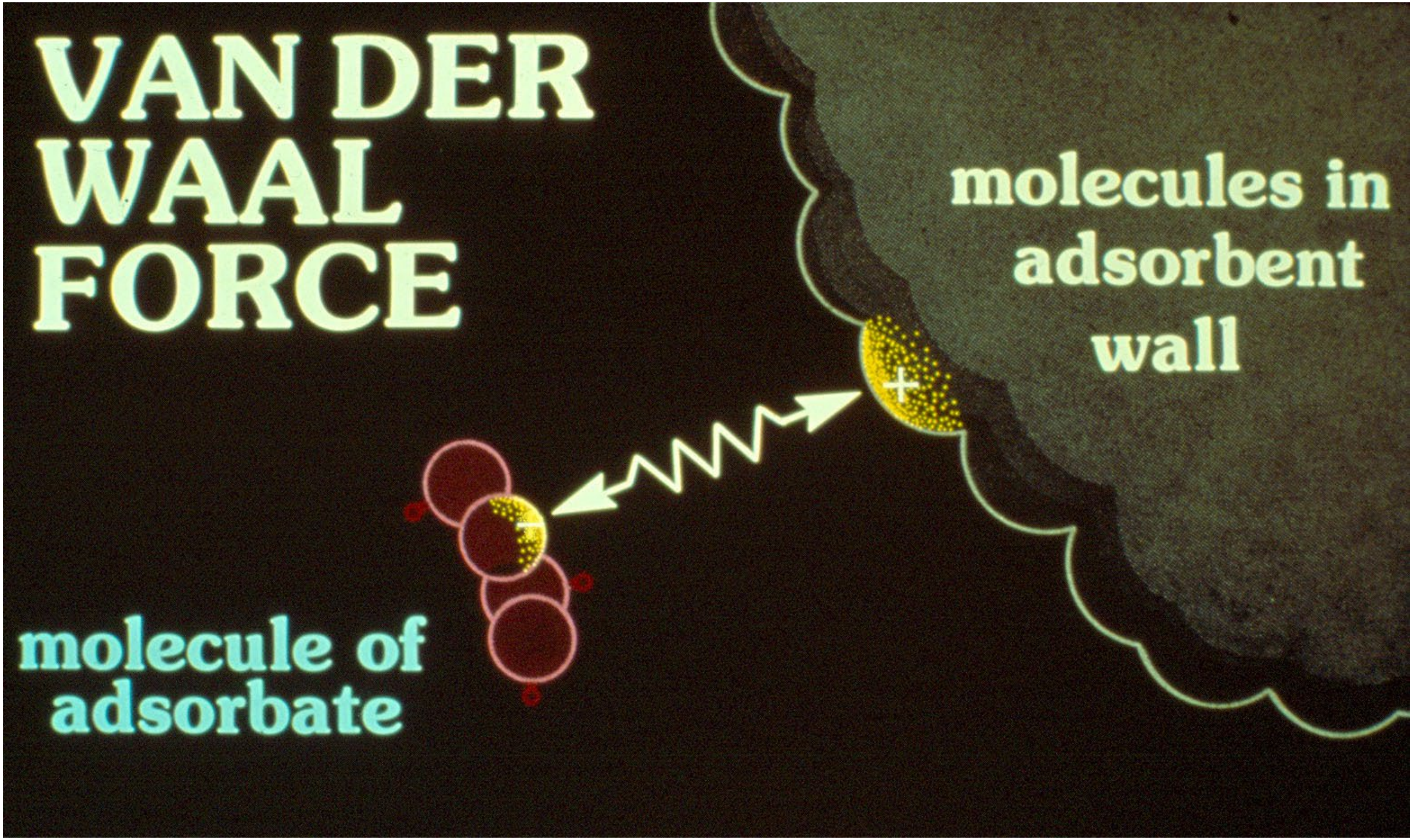
- A series of EPA-sponsored studies of organic vapor destruction efficiencies for industrial boilers and process heaters were conducted in 1998.
- The results of these tests showed 98 to 99 percent overall destruction efficiencies for C_1 to C_6 hydrocarbons.
- The Boiler/Heater must operate continuously and concurrently with the pollution generating source.

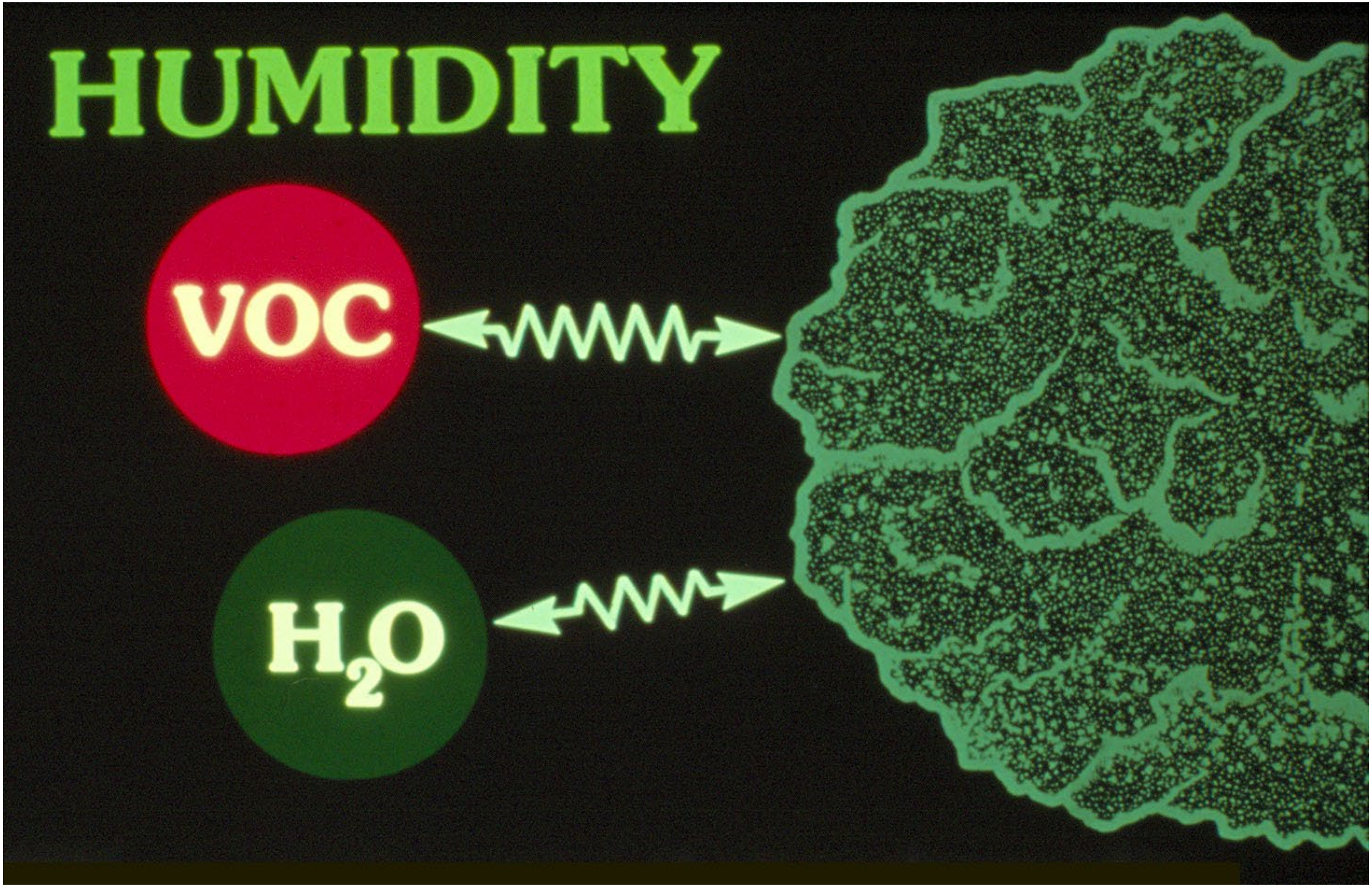


ADSORPTION

WHAT ARE ADSORBERS?

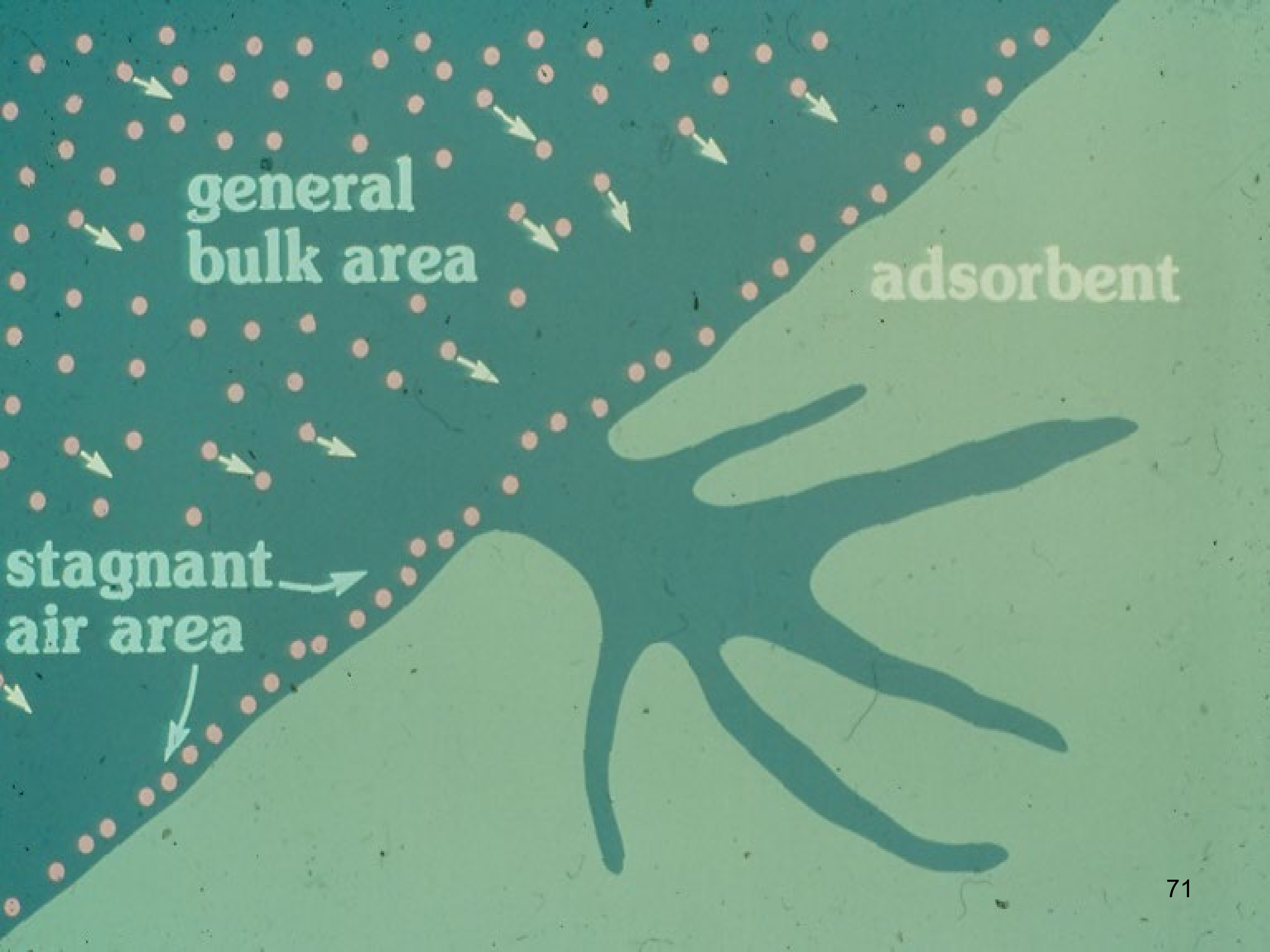
- Adsorption is where the pollutant is adsorbed on the surface (mostly on the internal surface) of a granule, bead, or crystal of adsorbent material.
- The adsorbed material is held physically (not chemically) and can be released (desorbed) rather easily by either heat or vacuum.


VAN DER WAAL FORCE
molecules in adsorbent wall
+
−
molecule of adsorbate



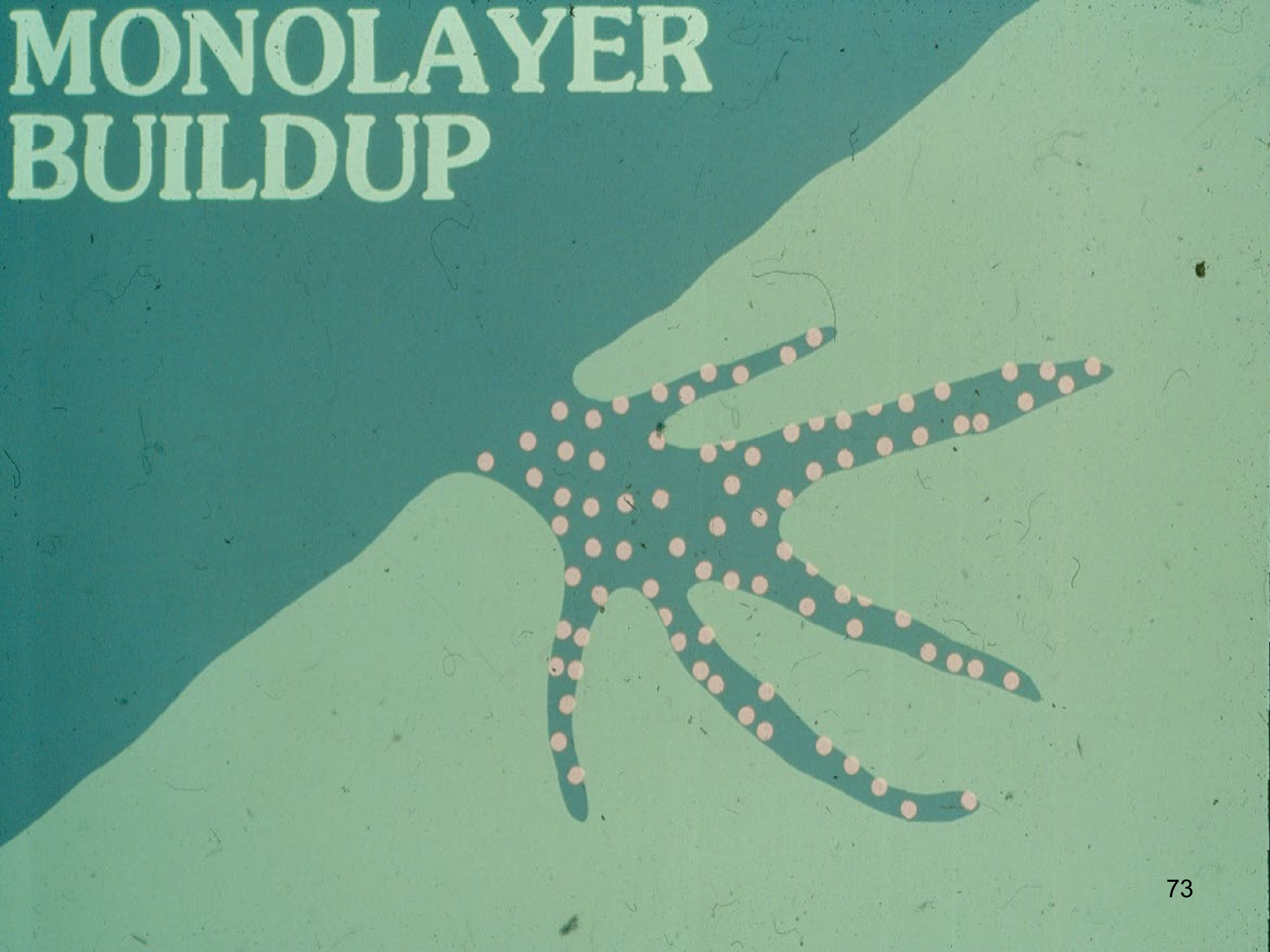
HUMIDITY

ADSORPTION PHENOMENA

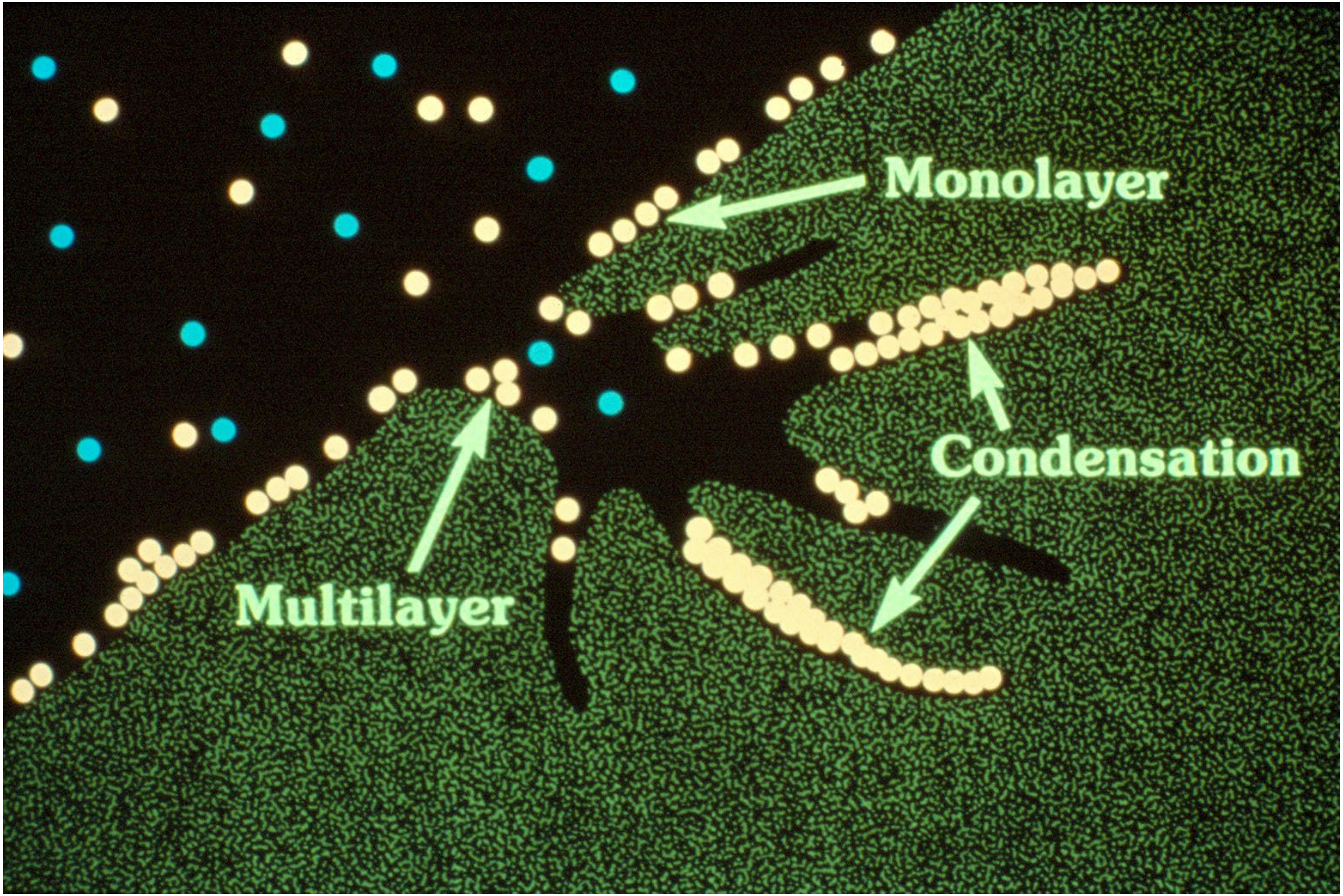

general bulk area
adsorbent
stagnant air area

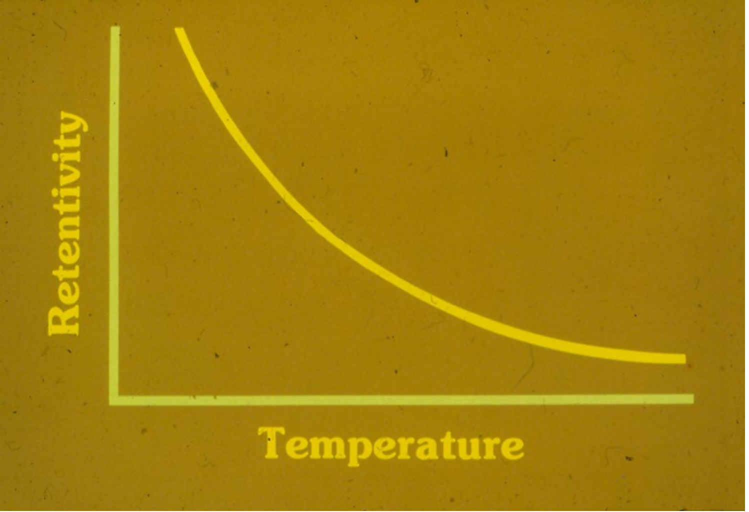
DIFFUSION INTO PORES

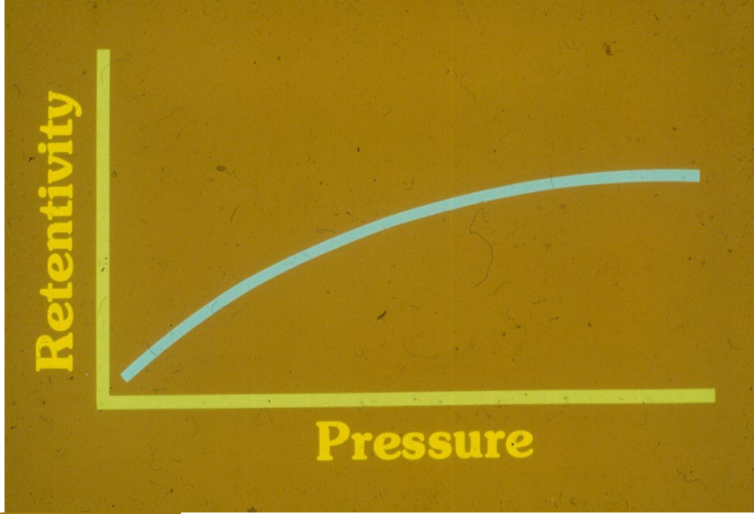
MONOLAYER BUILDUP

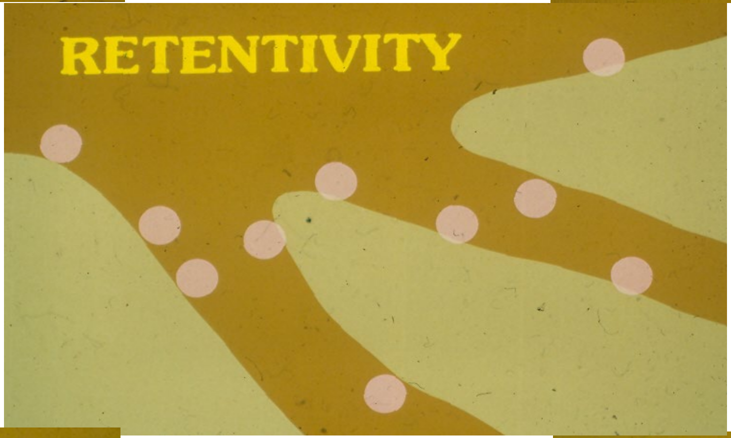


HEAT OF ADSORPTION


Monolayer
Condensation
Multilayer



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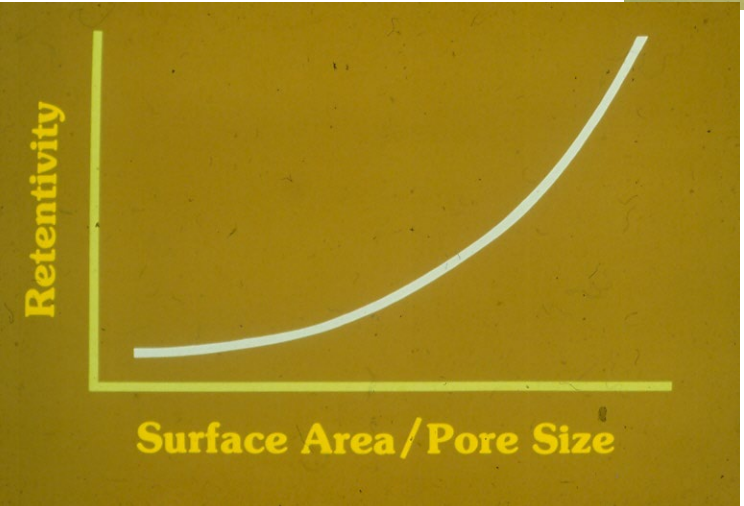
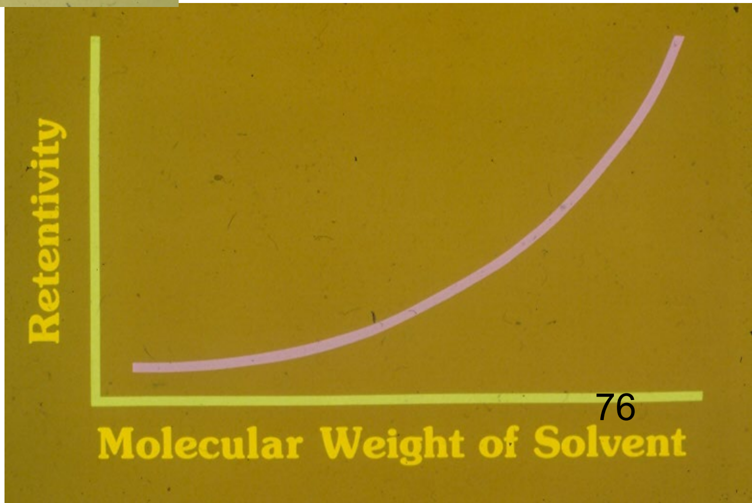
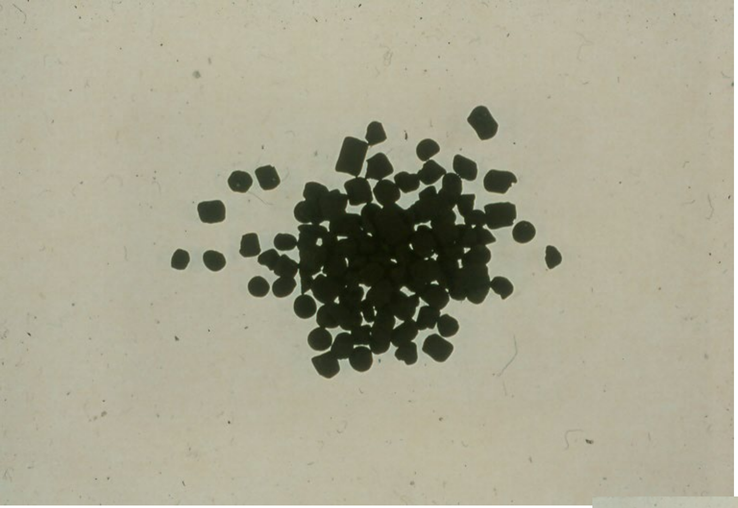


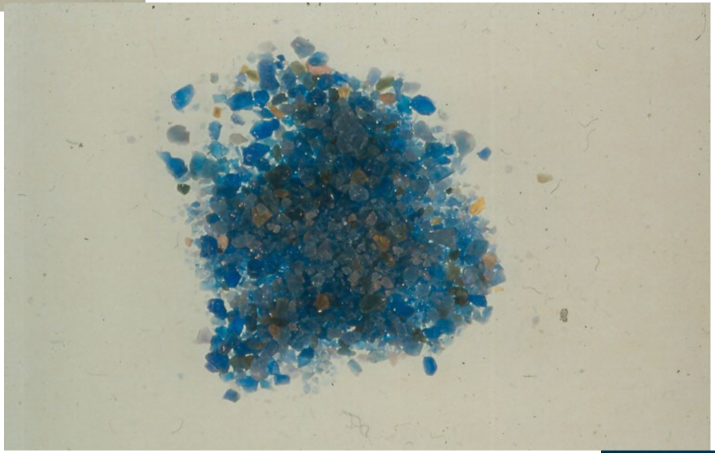


Types of Adsorbents

Polar	Nonpolar
Silica gel	Activated Carbon
Activated oxides	Polymeric adsorbents
Molecular sieves	Zeolites (siliceous)



Activated Carbon



Silica gel

Molecular sieves

Types of Adsorption Processes

- Chemical adsorption
- Physical adsorption

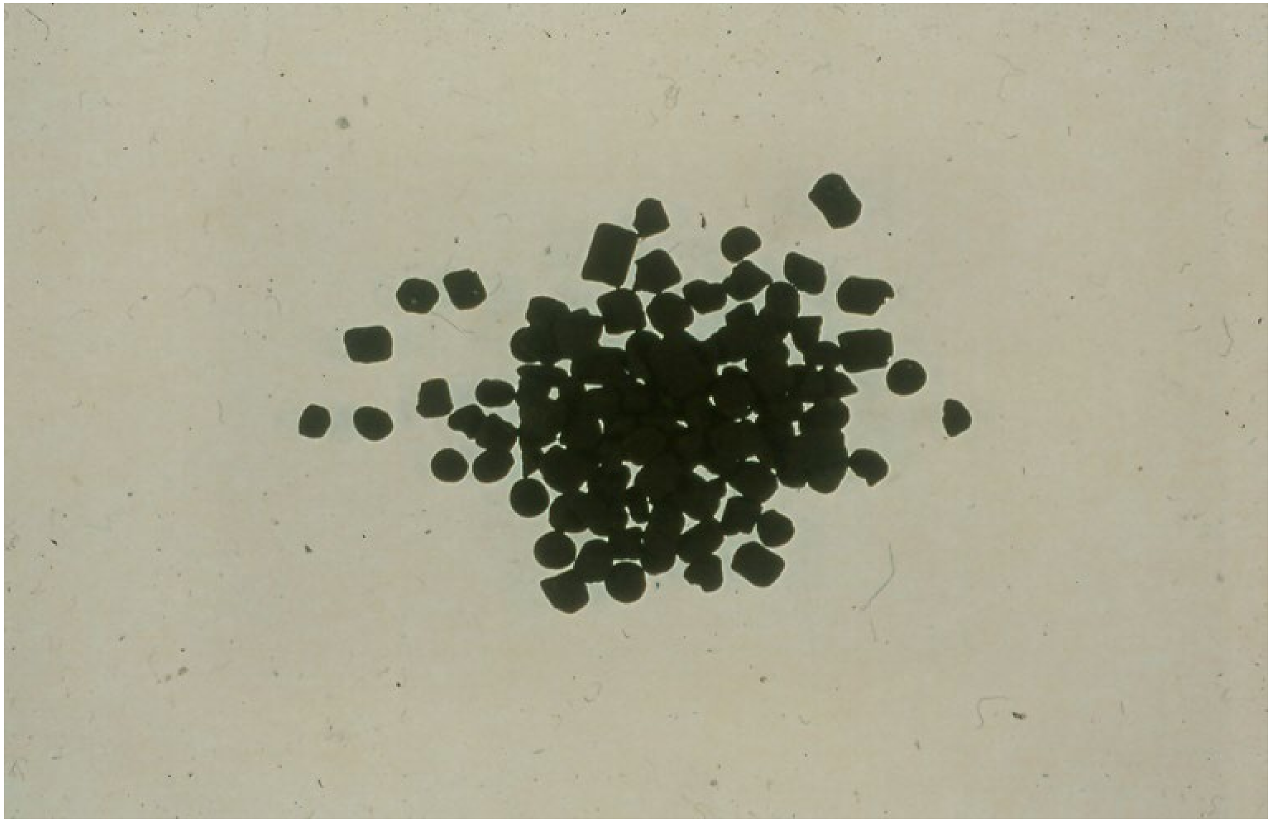
Adsorption Characteristics

Chemisorption	Physical Absorption
Releases high heat 80 – 120 calories/mole	Releases low energy 40 calories/mole
Forms a chemical compound	Dipolar interaction
Desorption is difficult	Easy desorption
Impossible adsorbate recovery	Easy adsorbate recovery

Adsorption Systems

- **Non-regenerative**
- **Regenerative**

Carbon Adsorption



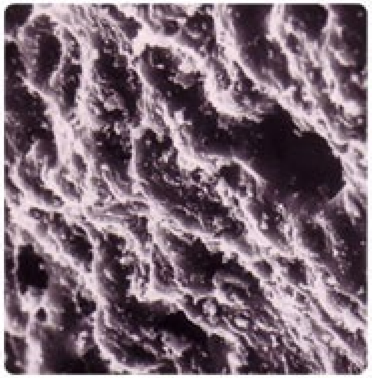
Activated Carbon

- One of the adsorbents is called “absorbent carbon.” This persisting misnomer came from the time before adsorption became understood in the 1920's. A better term is “activated carbon.”
- Carbon is activated by the pyrolysis of carbon/organic feed stocks which remove all the volatile material as a gas or vapor, and leave only the carbon. This carbon may then also be partially oxidized to enlarge its pores.

Activated Carbon

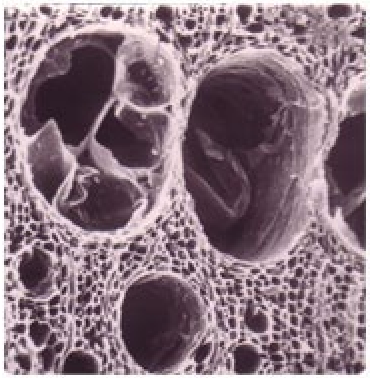
- Classes of feed stock materials
- Produced from coal, wood, nut shells and petroleum-based products
- Activation process
  - Heat material to ~1,100°F without oxygen
  - Use stream, air or CO_2 to increase pore structure

Stereo Scan Electron Micrograph Photos of Activated Carbons from Cameron Carbon web site



Coal

Coconut



Wood

http://www.cameroncarbon.com/activated_carbons.html

Zeolite Adsorbers

- Another adsorbent is the alumino-silicate crystal structure known as “zeolite,” which has uniformly sized pores (also called windows) throughout its crystal structure.
- The crystal structure for the 118 established types of zeolite is determined by the ratio of silicon to aluminum in the crystal when the crystal is formed.

Zeolite Adsorbers

- All naturally occurring zeolite is hydrophilic (having an affinity for polar molecules, such as water) and contains aluminum.
- Dealuminizing natural zeolite makes it hydrophobic (having affinity for non-polar substances, such as many VOC).
- Zeolite is dealuminized by chemical replacement of the aluminum with silicon without changing the crystal structure.

Adsorber Control Description

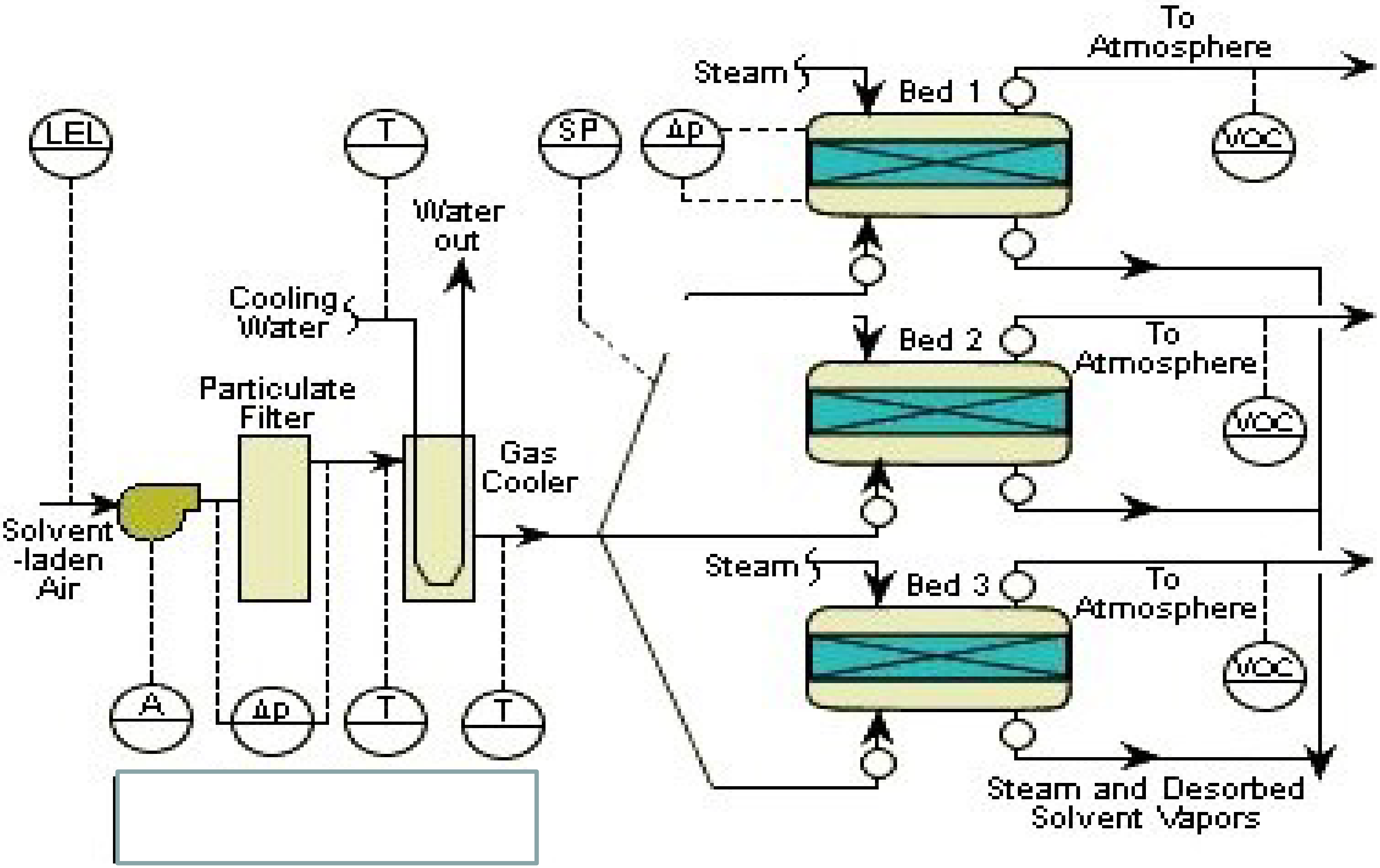
- Adsorption technology can control the HAP/VOCs in concentrations from 20 ppm to one-fourth of the Lower Explosive Limit (LEL).
- In the lower end of this range the small concentrations may be difficult or uneconomical to control by another technology.
- Incinerators, membrane separators, and condensers may be economically feasible when used in place of adsorbers at the upper end of the range.

Adsorber Control Description

Adsorption systems beds are generally used in the following different situations:

- When the VOC-laden gas stream only contains one to three organic solvent compounds, and it is economical to recover and reuse these compounds
- When the VOC-laden gas stream contains a large number of organic compounds at low concentration, and it is necessary to pre-concentrate these organics prior to thermal or catalytic oxidation.

Multi-Bed Adsorber System for Solvent Recovery



Adsorber Operation

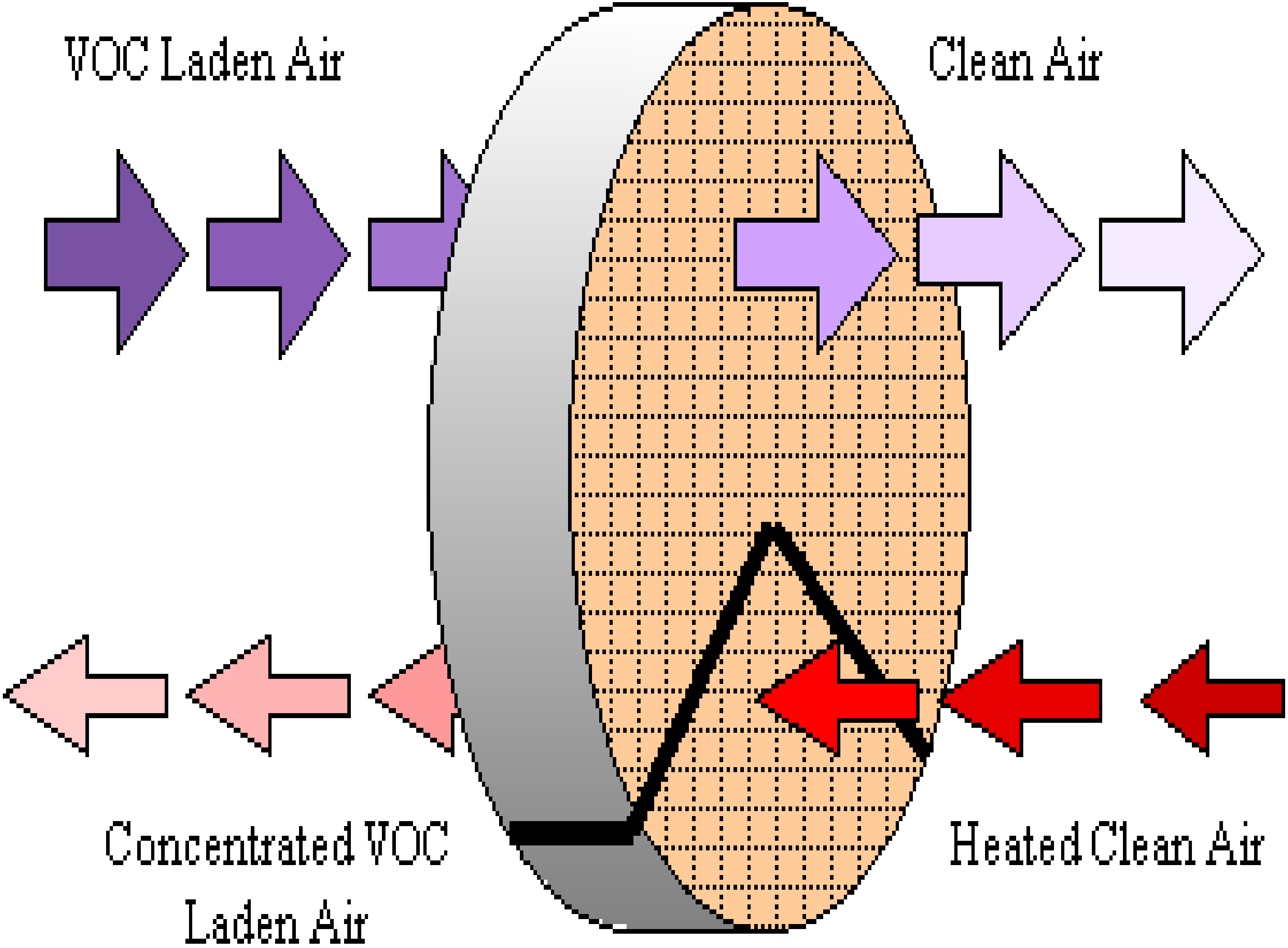
- The VOC-laden gas is often cooled prior to entry into the adsorption system because the effectiveness of adsorption improves at cold temperatures.
- When the adsorbent is approaching saturation with organic vapor, a bed is isolated from the gas stream and desorbed.
- Low-pressure steam or hot nitrogen gas is often used to remove the weakly adsorbed organics.

Adsorber Operation

- The concentrated stream from the desorption cycle is treated to recover the organic compounds.
- After desorption, the adsorption bed is returned to service, and another bed in the system is isolated and desorbed.

Pre-concentrator Adsorber systems

- In pre-concentrator systems, the VOC-laden stream passes through a rotary wheel containing zeolite or carbon-based adsorbents.
- Approximately 75-90% of the wheel is in adsorption service while the remaining portion of the adsorbent passes through an area where the organics are desorbed into a very small, moderately hot gas stream.
- The concentrated organic vapors are then transported to a thermal or catalytic oxidizer for destruction and reduces the fuel usage.



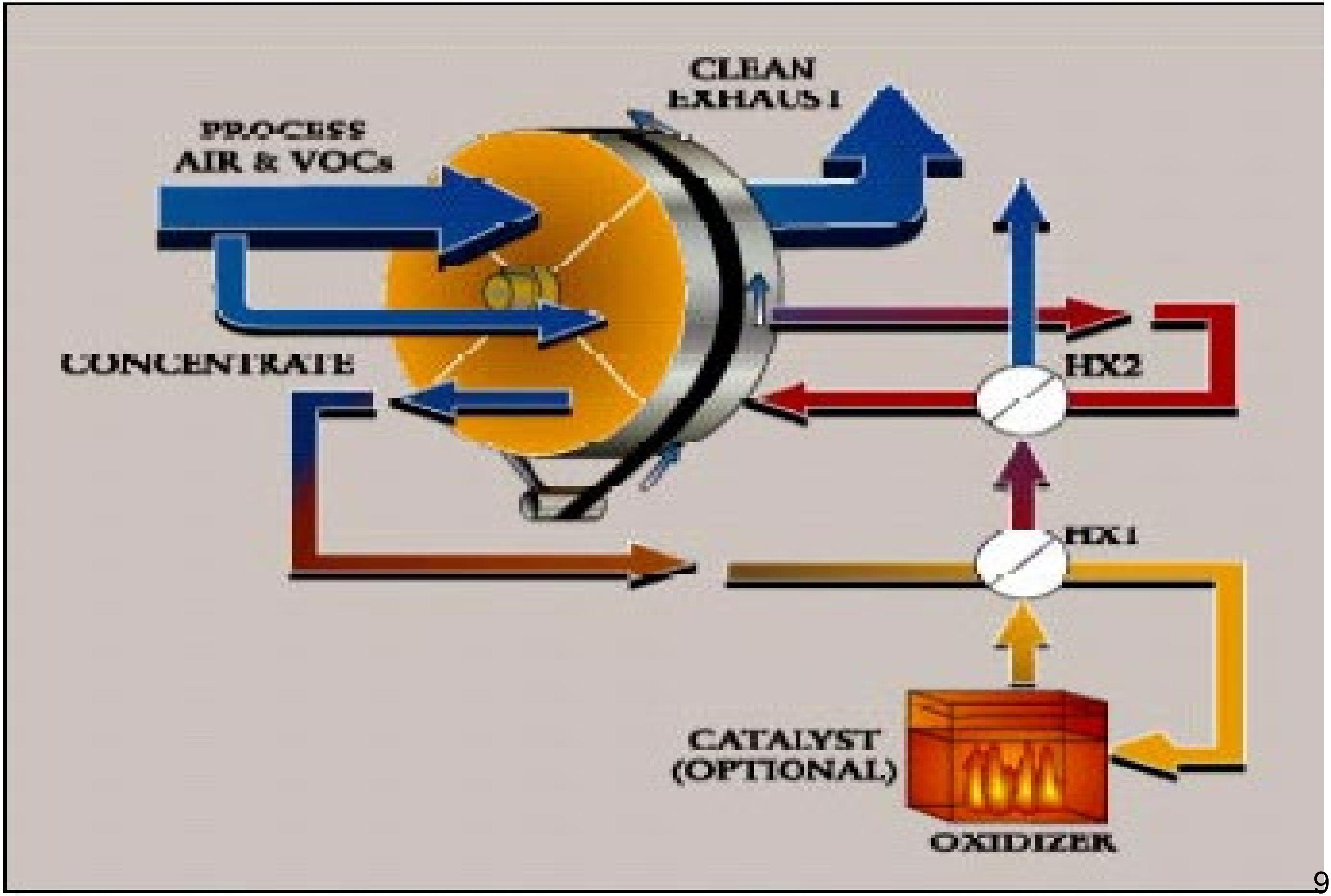
VOC Laden Air

Clean Air

Concentrated VOC Laden Air

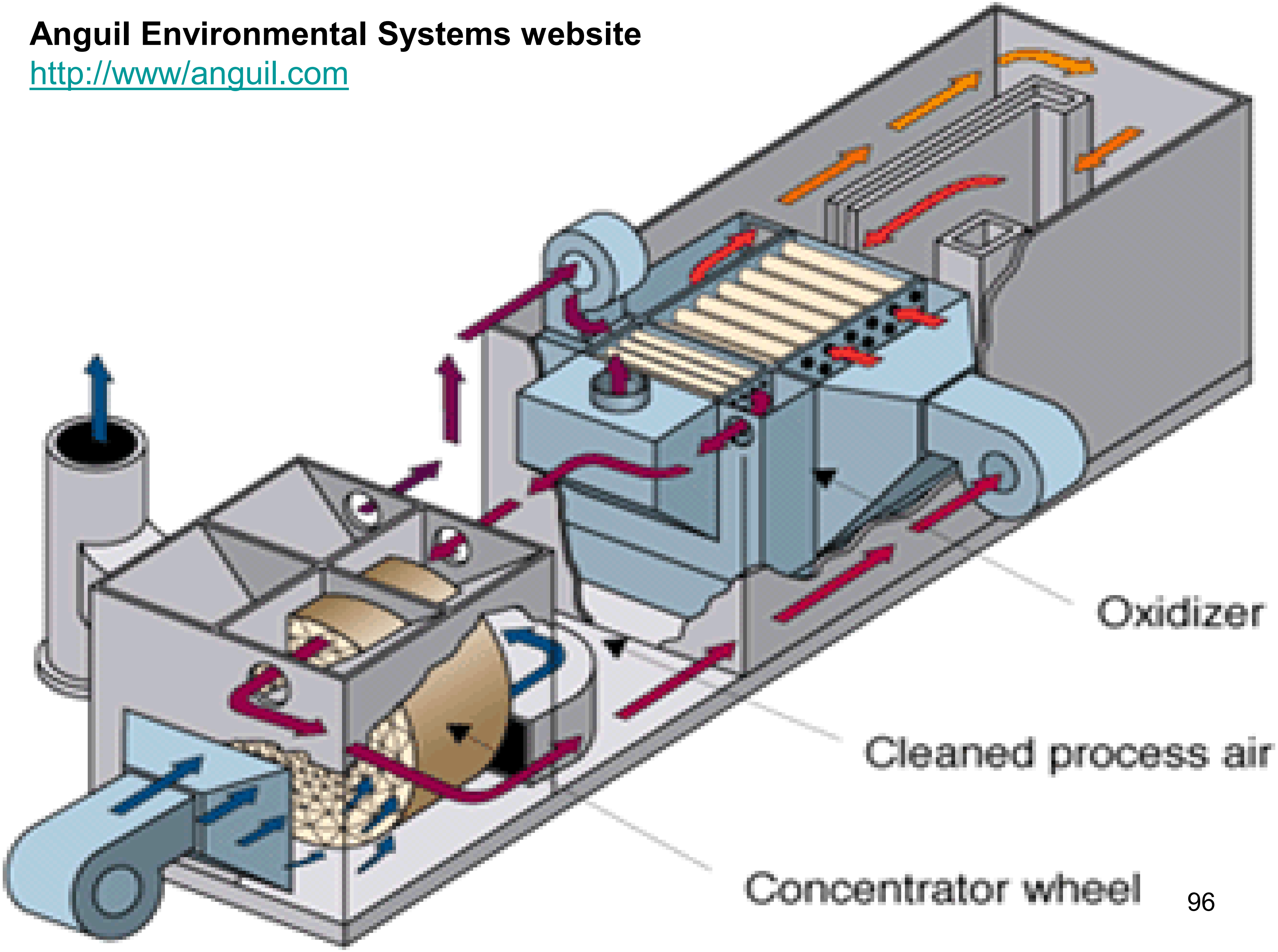
Heated Clean Air

Munters ZEOL: Innovative Solutions for VOC Abatement Brochure



http://www.munters.us/upload/Case%20studies/Munters%20Zeol%20Brochure-Zeolite%20Rotor%20Concentrators.pdf

Anguil Environmental Systems website
http://www/anguil.com

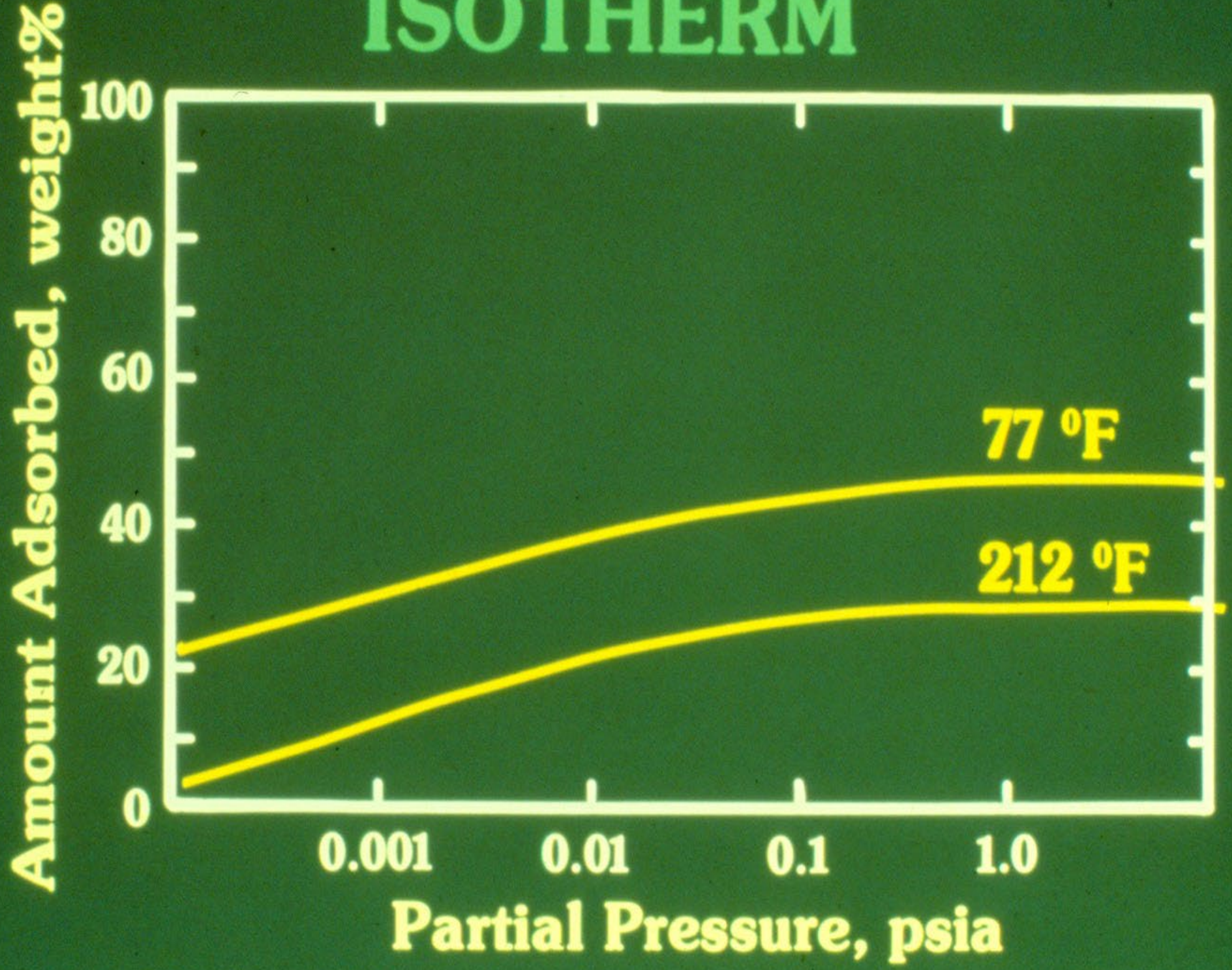


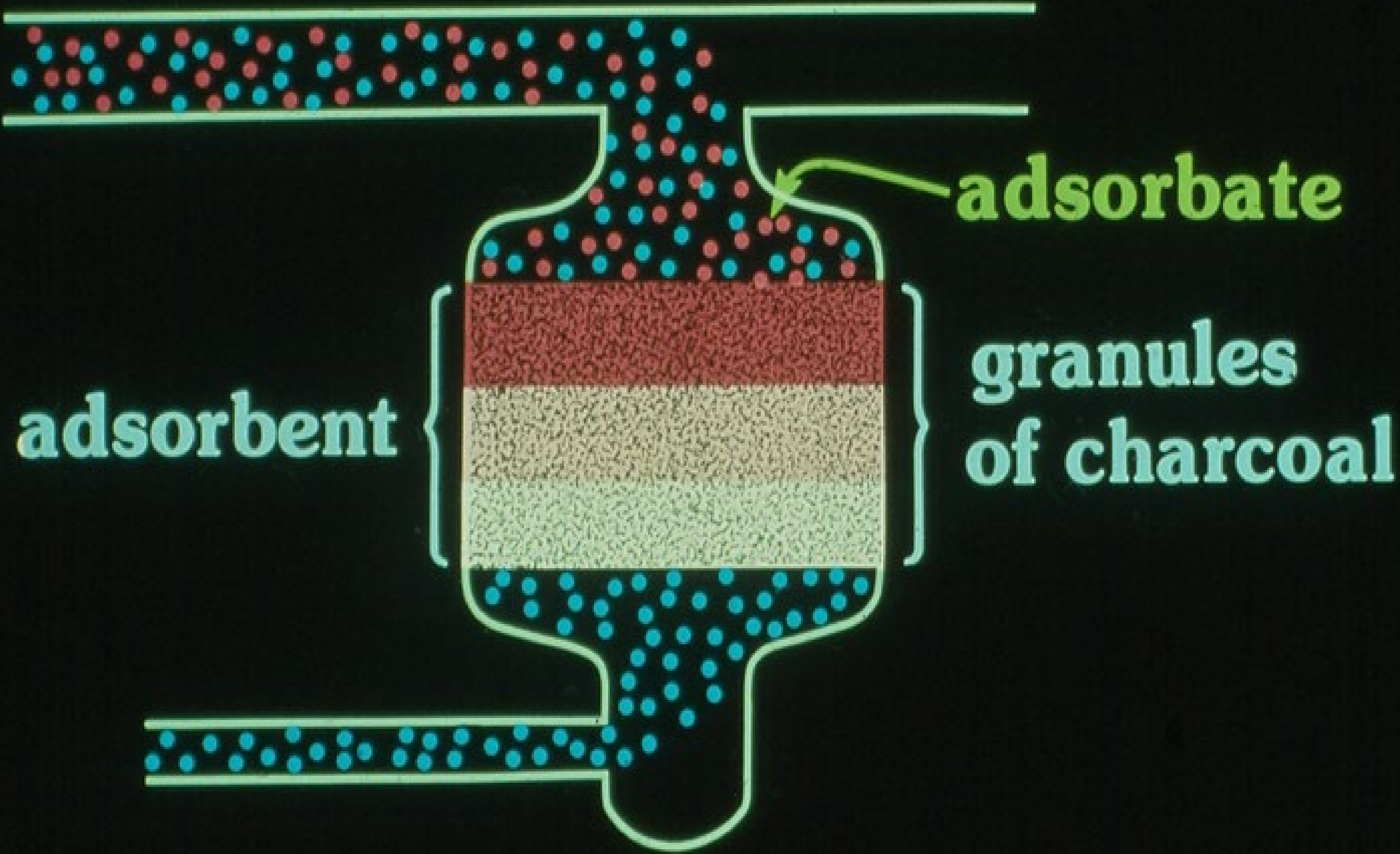
Adsorption Capacity

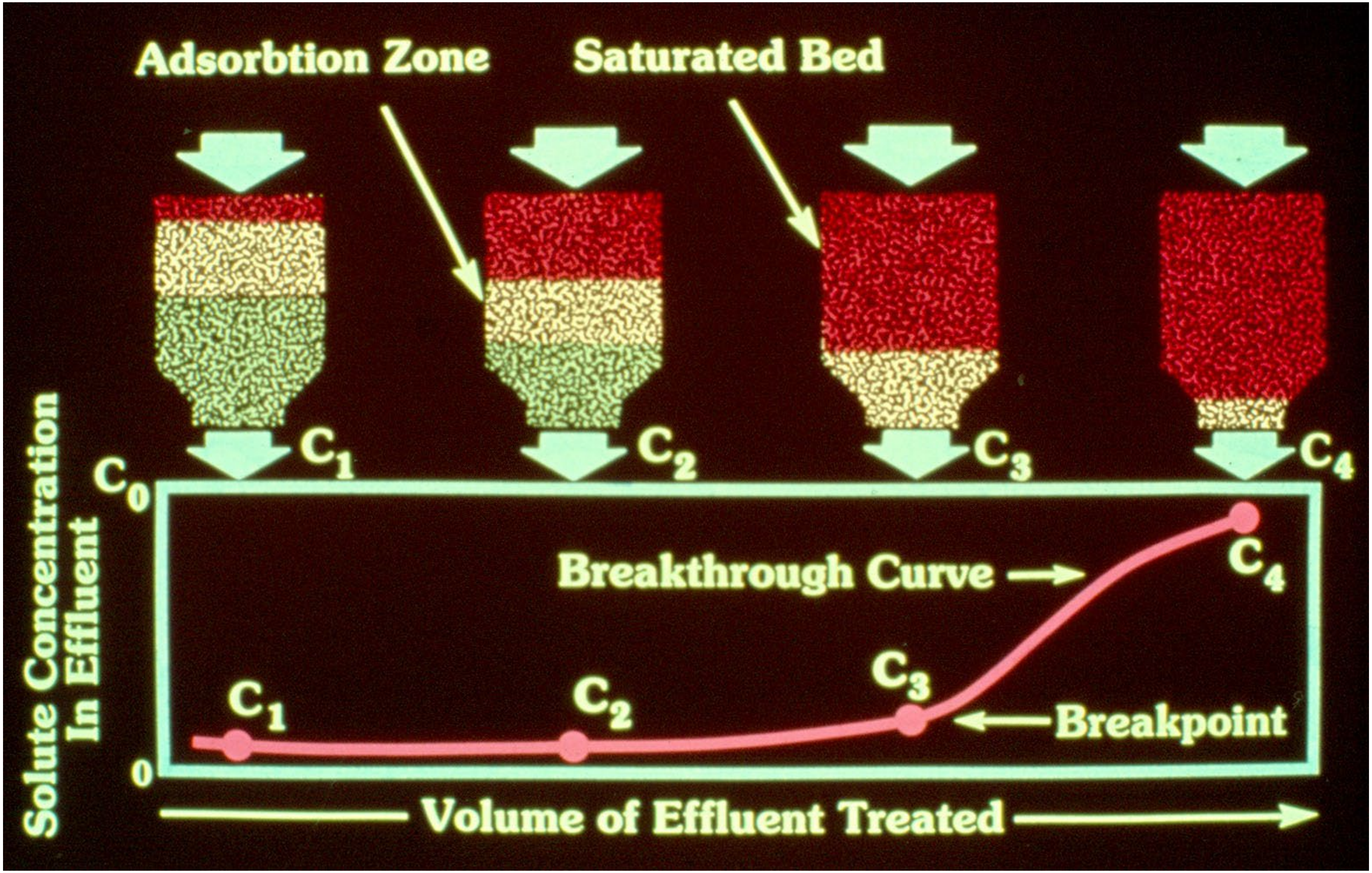
Retention

- Lbs of VOC adsorbed per 100 lbs of carbon
- Weight percent

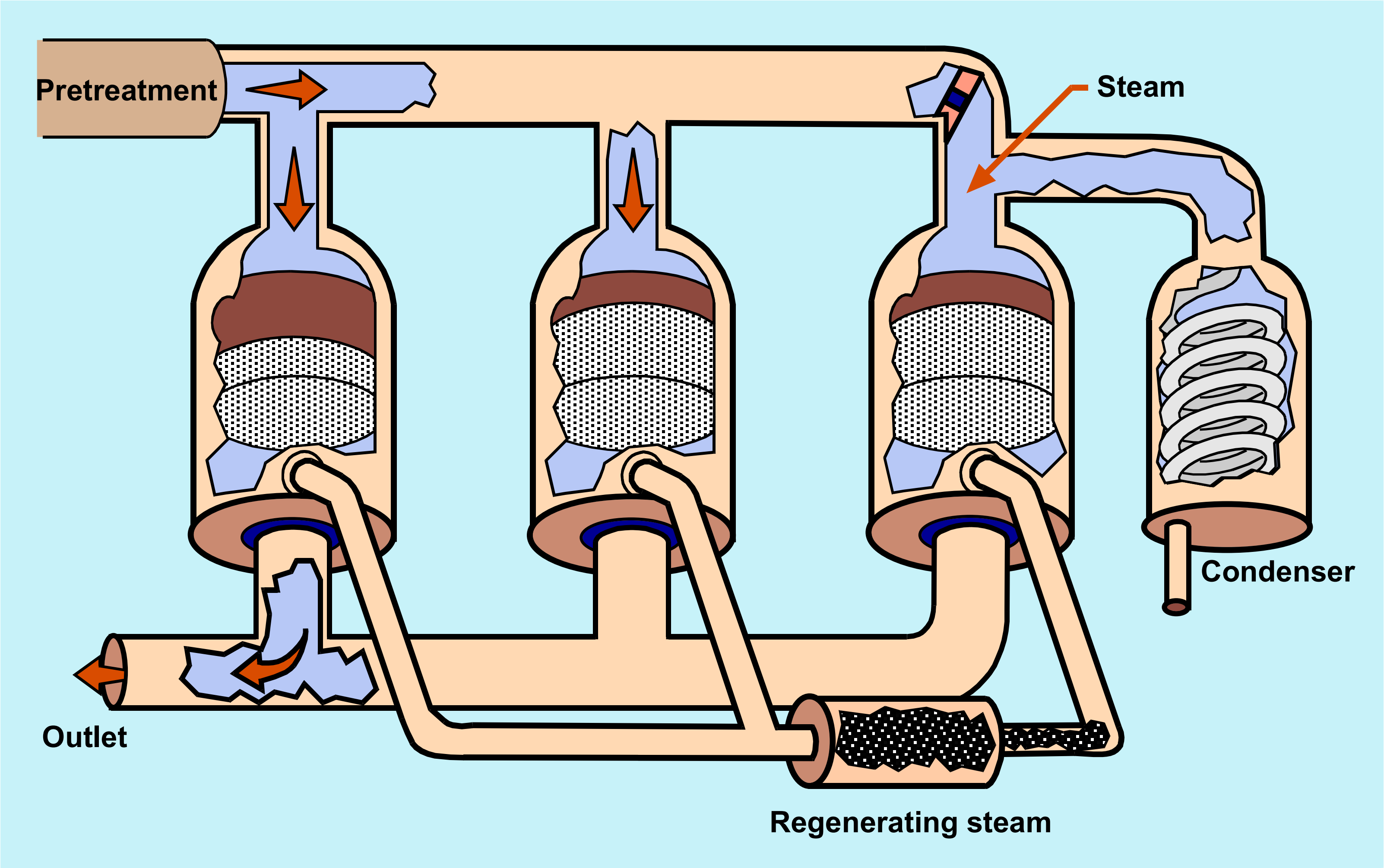
TYPICAL ADSORPTION ISOTHERM




adsorbate
adsorbent
granules
of charcoal


Adsorbtion Zone
Saturated Bed
C_1
C_2
C_3
C_4
C_0
Solute Concentration In Effluent
0
Breakthrough Curve →
C_4
C_3
C_1
C_2
← Breakpoint
Volume of Effluent Treated

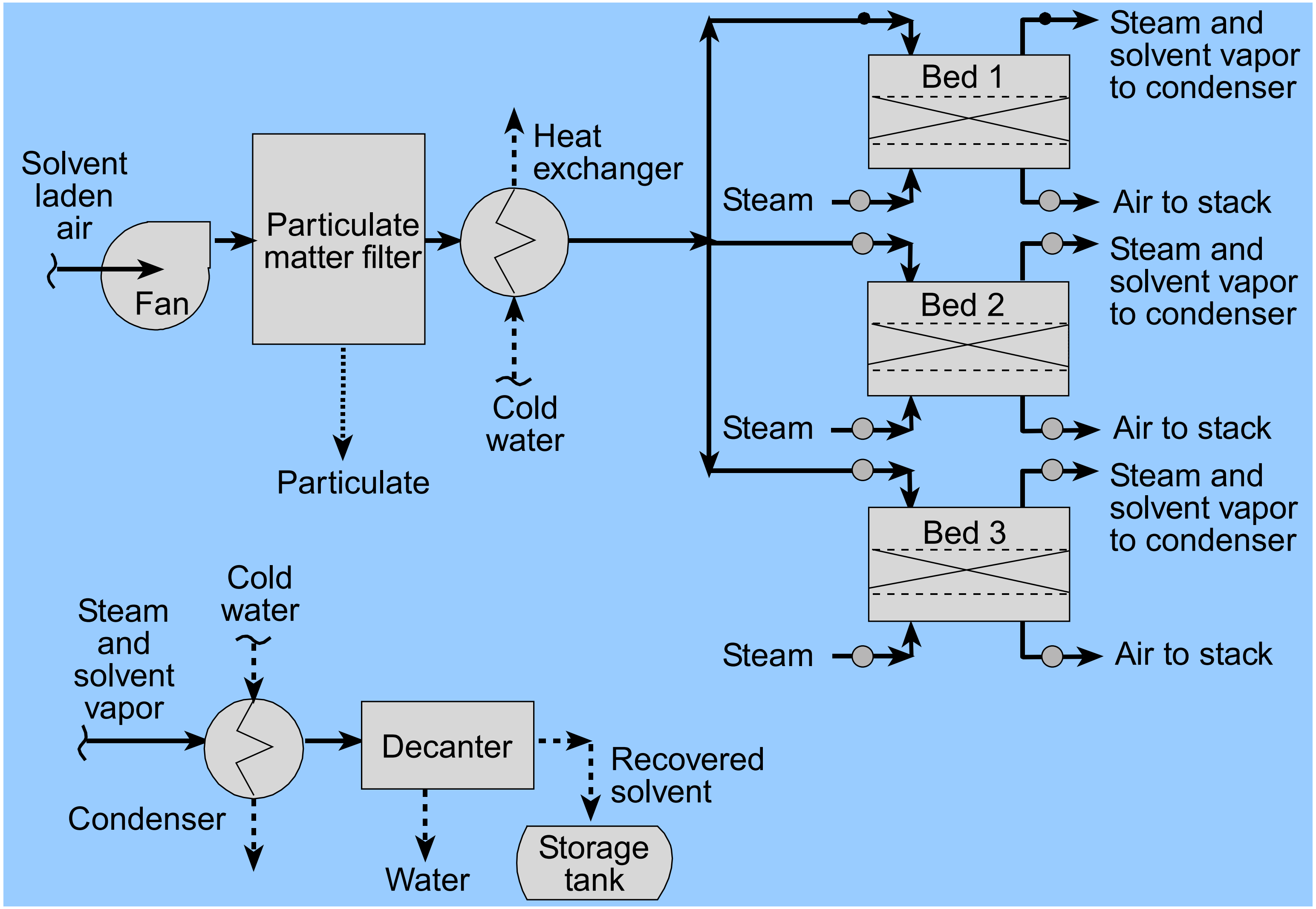
On-Site Regeneration Fixed-Bed System



Regeneration Methods

- Thermal swing
  - Steam
  - Hot gas
- Pressure swing

Steam Regeneration



Carbon Adsorption Control Operation

- Carbon adsorption control systems function as a constant outlet concentration devices.
- The outlet concentration from a carbon adsorber control is a function of the heel buildup within the bed that remains after regeneration.
- Even though inlet concentrations can vary significantly, the outlet concentration will remain relatively constant until breakthrough is approached.

Carbon Adsorption Control Operation

- The removal efficiency of a properly sized and operated carbon adsorber is largely dependant on the inlet concentration and the regeneration of the bed.
- The more rigorous the generation, the lower the outlet concentration.

Carbon Adsorption Control Operation

- Carbon adsorption systems must be designed based on 1) specific compound or compounds being recovered, 2) mass loading of pollutant, 3) gas stream flowrate and 4) gas stream temperature.
- When specific adsorbed compounds (i.e. cyclohexanone) react on the carbons surface to form higher molecular weight products, the subsequent build up can result in a steady decrease in adsorptive capacity.

Carbon Adsorption Control Operation

- As a carbon bed ages, it’s total adsorptive capacity gradually decreases due to fouling.
- The working capacity can be maintained in some cases by increasing steam flow during desorption which would also increase operating costs.
- Maintaining design values and high removal efficiency can be accomplished by frequent carbon changes, but will also increase operating.

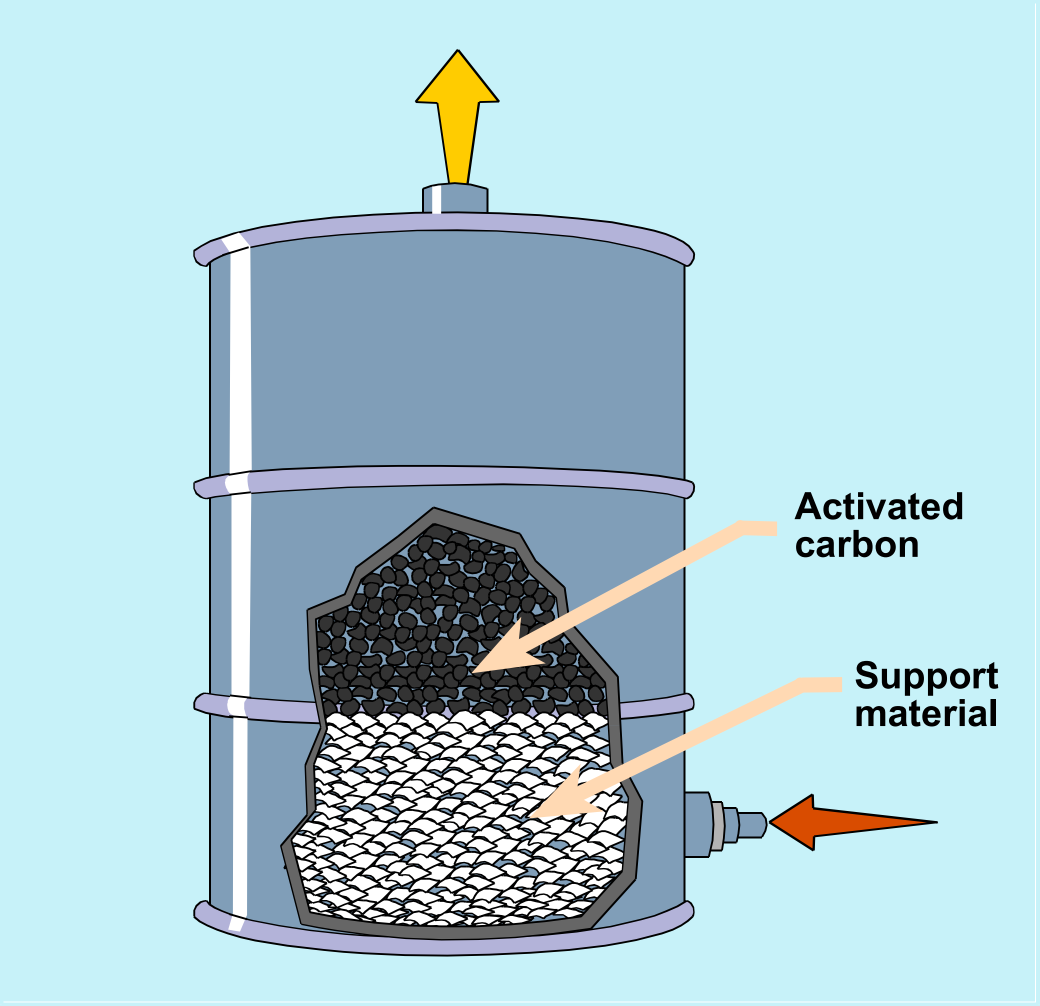
Carbon Adsorber HAP Control Parameters

Outlet HAP Concentration (ppmv)	Adsorption Cycle Time (hr)	Regeneration Cycle (hr)	Steam Requirement for Regeneration (lb steam/lb carbon)
70	2	2	0.3
10 - 12	2	2	1.0

HAP/VOC Adsorption Control Efficiency & Bed Life

Facility	Solvent Blend	Reported Bed Life	Removal Efficiency(%)
A	44% Cyclohexanone 14% MEK 23% Tetrahydrofuram 19% Toluene		99.4
B	50% Toluene 50% Isopropyl Acetate	> 6 Years	98.0
C	95% Toluene 5% Hexane	10 Years	99.5
D	MEK	5 Years	99.5

Non-Regenerable Canister Adsorber



Uses of Non-regenerable Adsorbers

- Control of odors
- Control of trace contaminants

Non-Regenerative Carbon Adsorption Drums controlling mercaptan odors from re-refined crankcase oil product


ACOFOR-8
EMPTY
VP-55
CAUTION

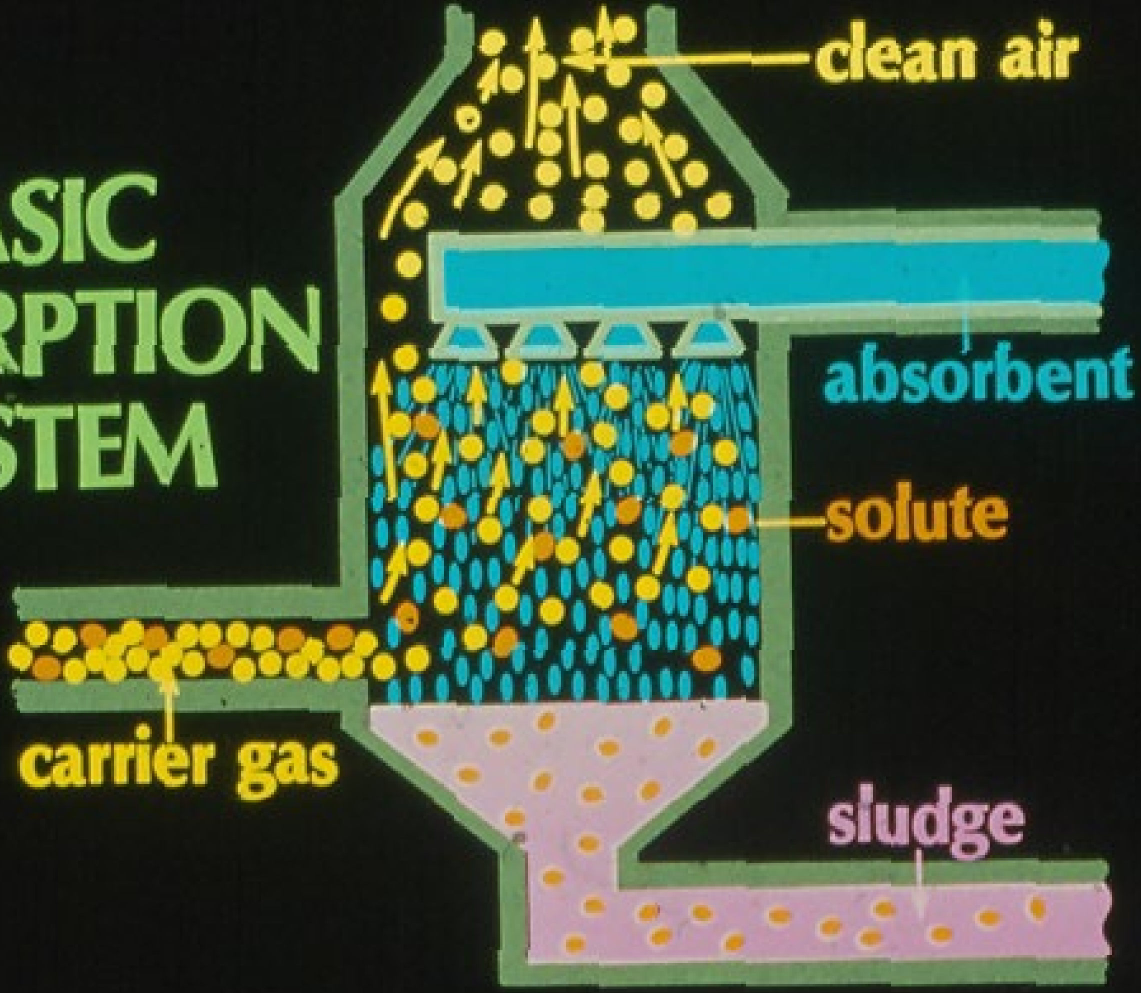
Additional Information

- Additional information on adsorption systems can be found in

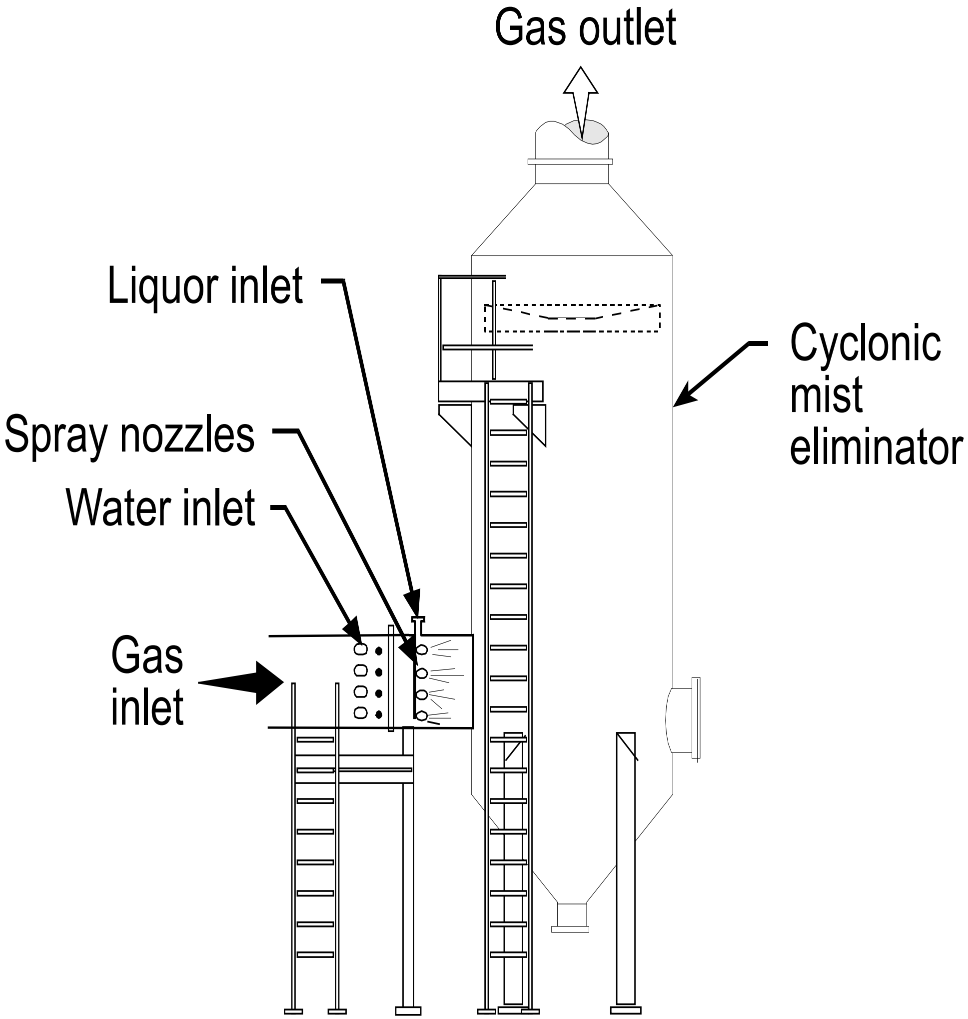
  CATC TECHNICAL BULLETIN
- CHOOSING AN ADSORPTION SYSTEM FOR VOC: CARBON, ZEOLITE, OR POLYMERS?
- EPA-456/F-99-004 May 1999
- http://www.epa.gov/ttn/catc/dir1/fadsorb.pdf

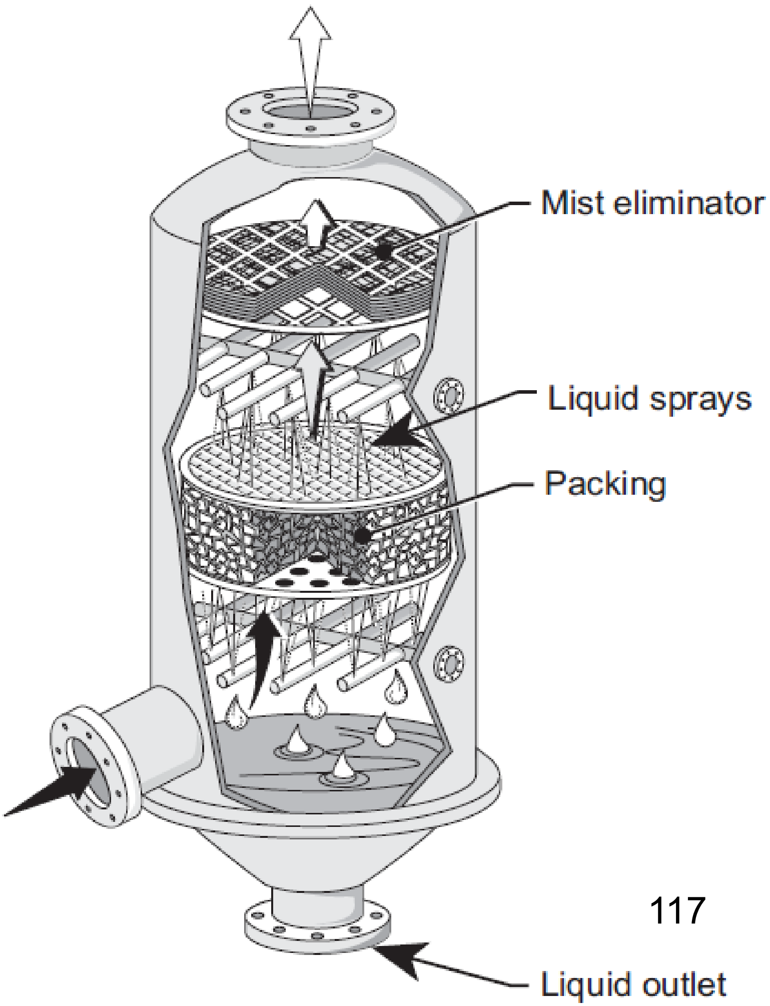
Absorption

BASIC ABSORPTION SYSTEM



Types and Components of Absorbers (Scrubbers)





Absorber Operation

- Absorbers are used for a wide variety of organic and acid gas compounds. Absorber systems can be divided into two fundamentally different groups:

  (1) those limited by solubility equilibrium limits

  (2) those using reactions in solution to minimize equilibrium limits

- In both systems, there must be sufficient scrubbing liquid to provide good gas-liquid contact. In absorbers subject to solubility equilibrium limits, there must also be sufficient liquid to effectively capture the gaseous contaminant.

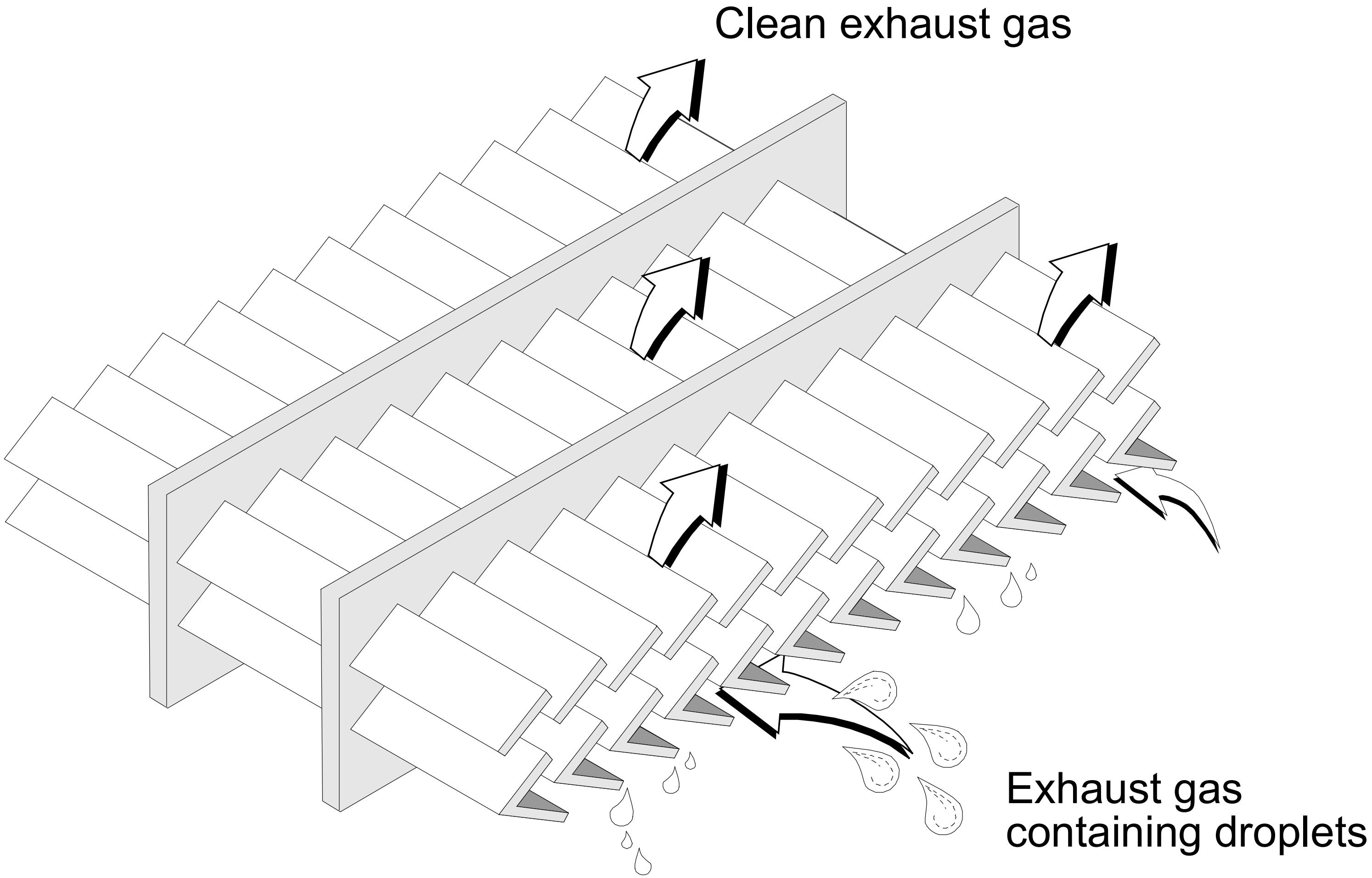
Absorption Principles

- Daltons Law $Y = p_A/P_{total}$
- Henry's Law $Y = \mathit{H}\, x_A$
- where $$H = \frac{\text{mole fraction in gas}}{\text{mole fraction in liquid}}$$

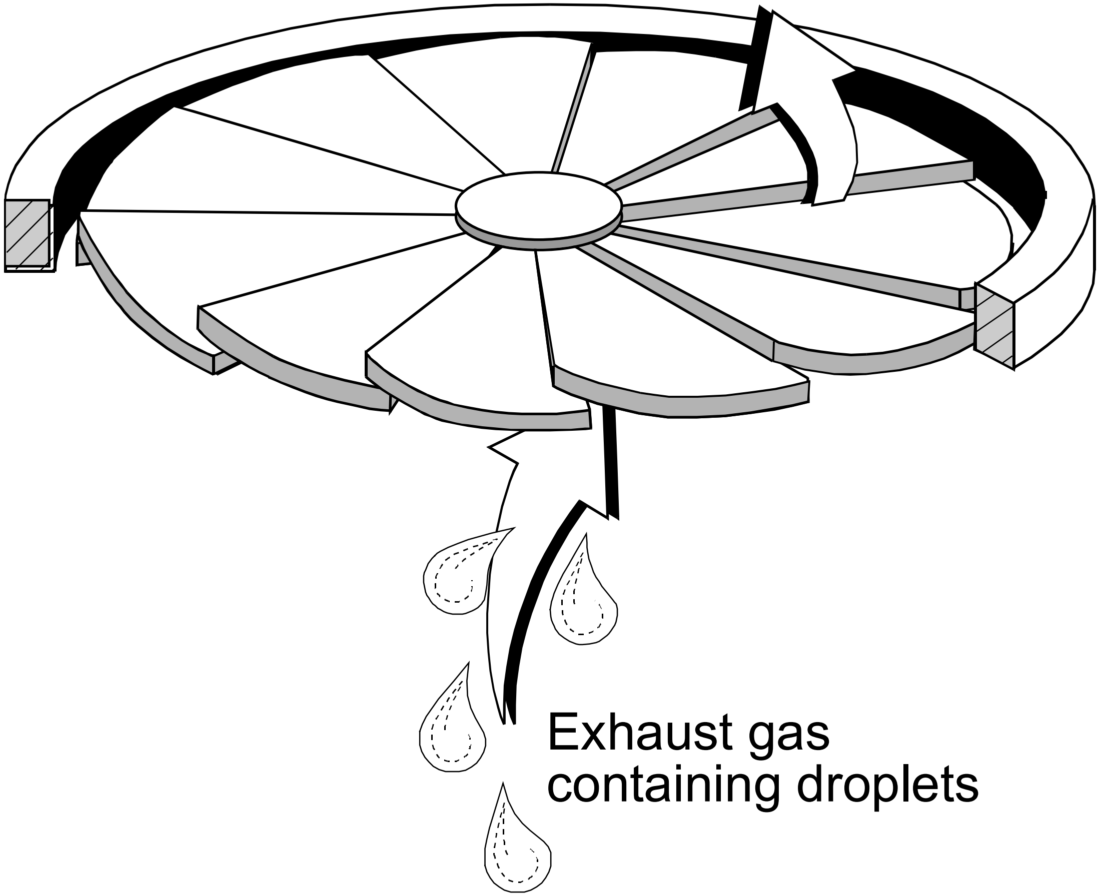
Venturi Scrubbers are used to remove very fine dust, mist and can also remove gases.

Packed Towers are primarily used for gas absorption.

Chevron Mist Eliminators on Absorbers



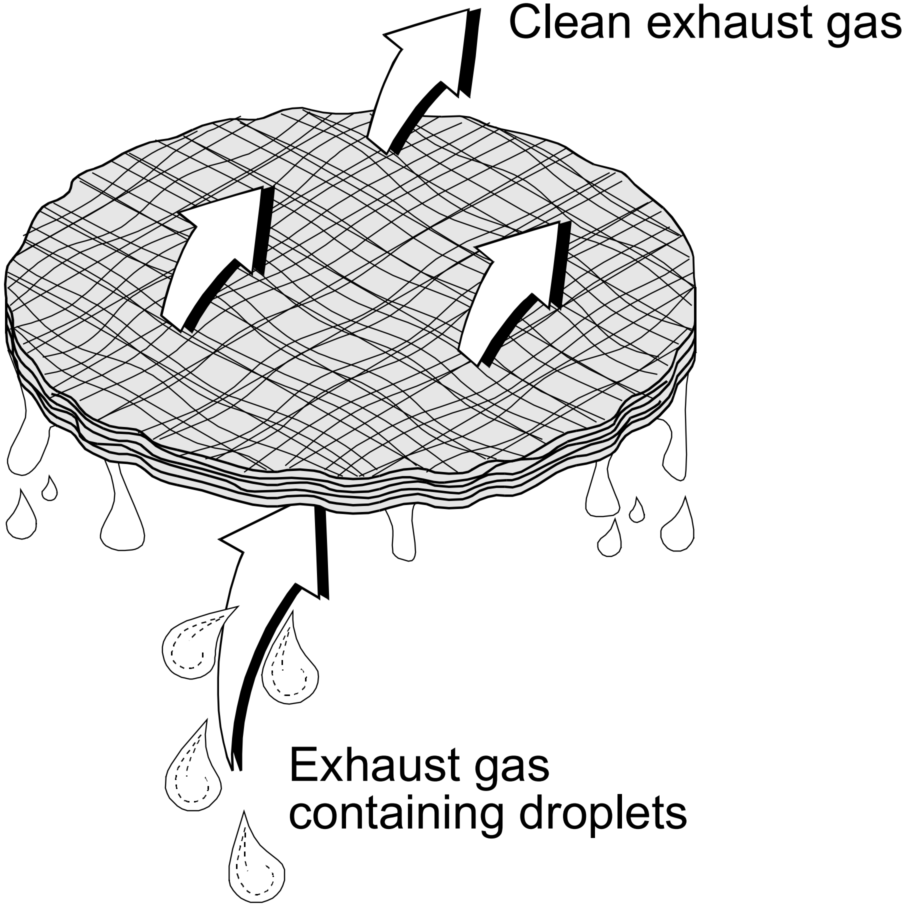
Radial vane mist eliminator on Absorbers



Clean exhaust gas

Exhaust gas containing droplets

Mesh Pad Mist Eliminators for Absorbers



Control Methods for Various Inorganic HAP Vapors

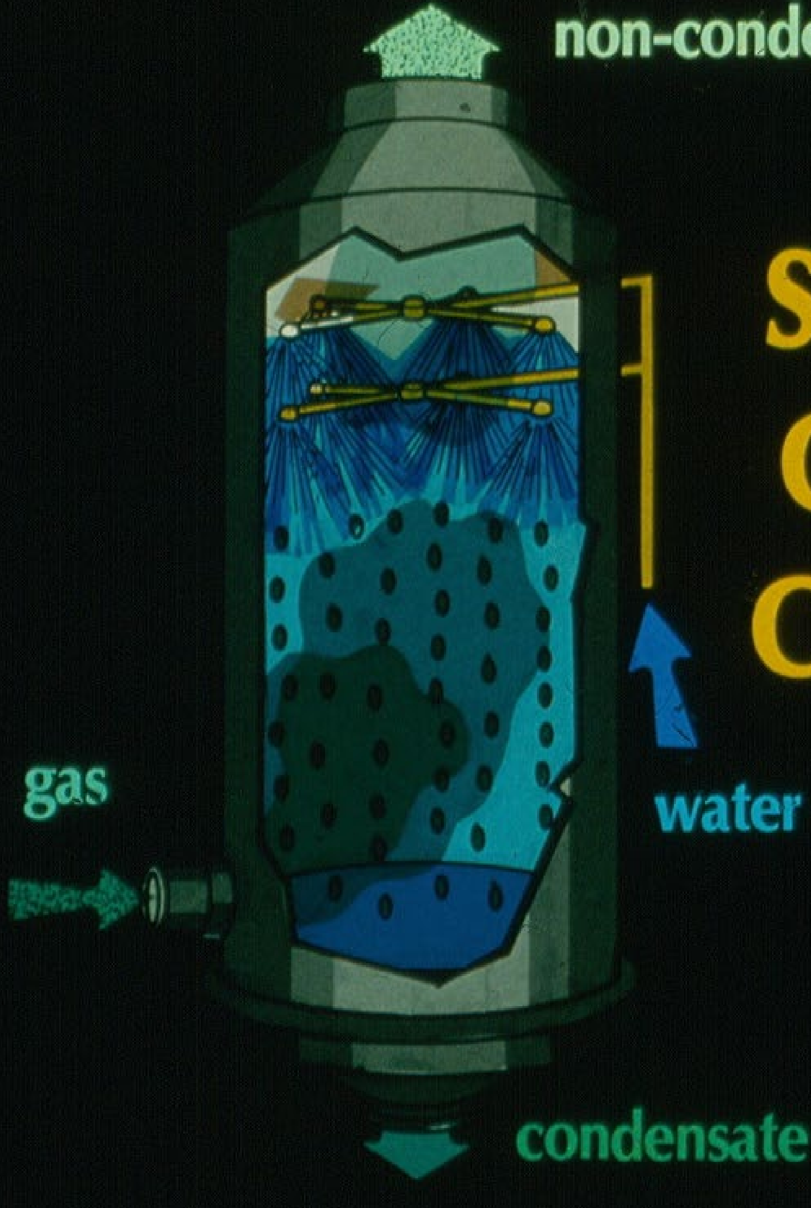
	Absorption		Adsorption	
Inorganic Vapor	**Reported Removal Efficiency(%)**	**Solvent**	**Reported Removal Efficiency(%)**	**Adsorbant**
Mercury (Hg)	95	Brine/ hypochlorite	90	Sulfur impregnated activated carbon
Hydrogen Chloride (HCl)	98	Water		
Hydrogen Sulfide (H2S)	98	Sodium carbonate/Water	100	Ammonia impregnated activated carbon
Calcium Fluoride (CaF2)	95	Water		
Silicon Tetrafluoride (SiF4)	95	Water		
Hydrogen Fluoride (HF)	85 – 95	Water	99	Calcined alumina
Hydrogen Bromide (HBr)	99.95	Water		
Titanium tetrachloride	99	Water		
Chlorine (Cl2)	90	Alkali Solution		
Hydrogen Cyanide (HCN)				Ammonia impregnated activated carbon

Condensers

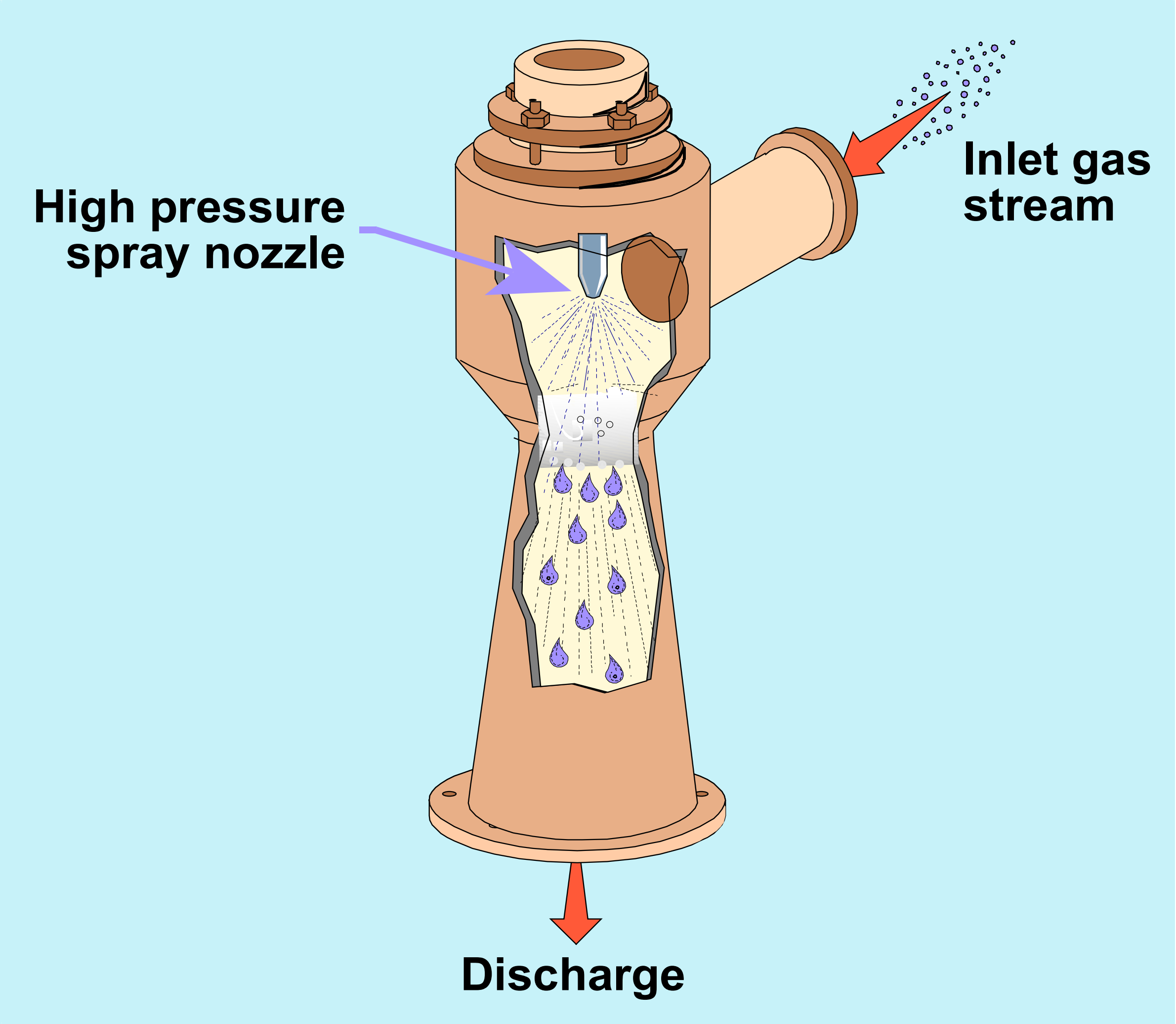
Types of Condensers

- Contact
- Surface
- Refrigeration

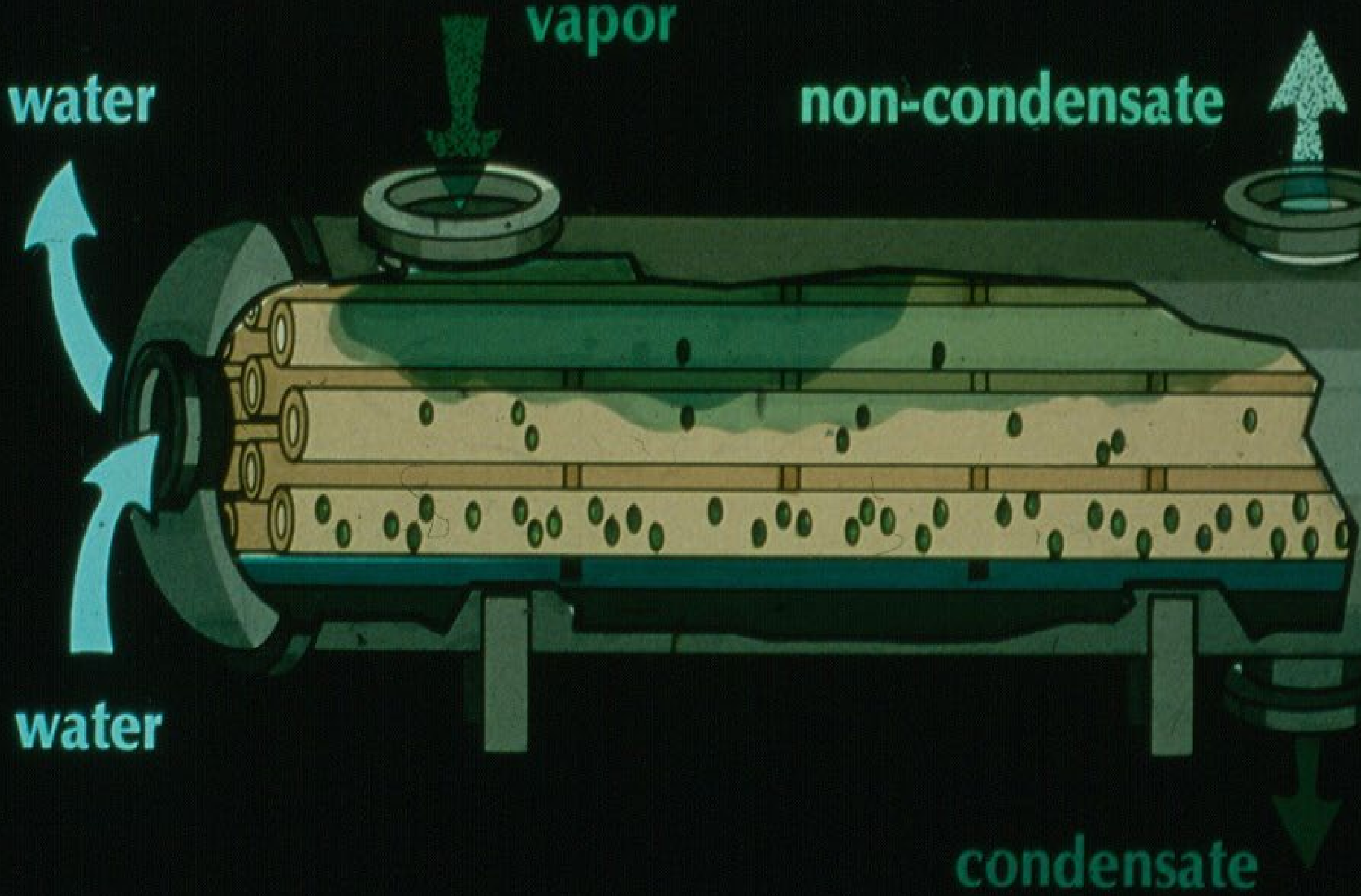
SPRAY TYPE CONTACT CONDENSER



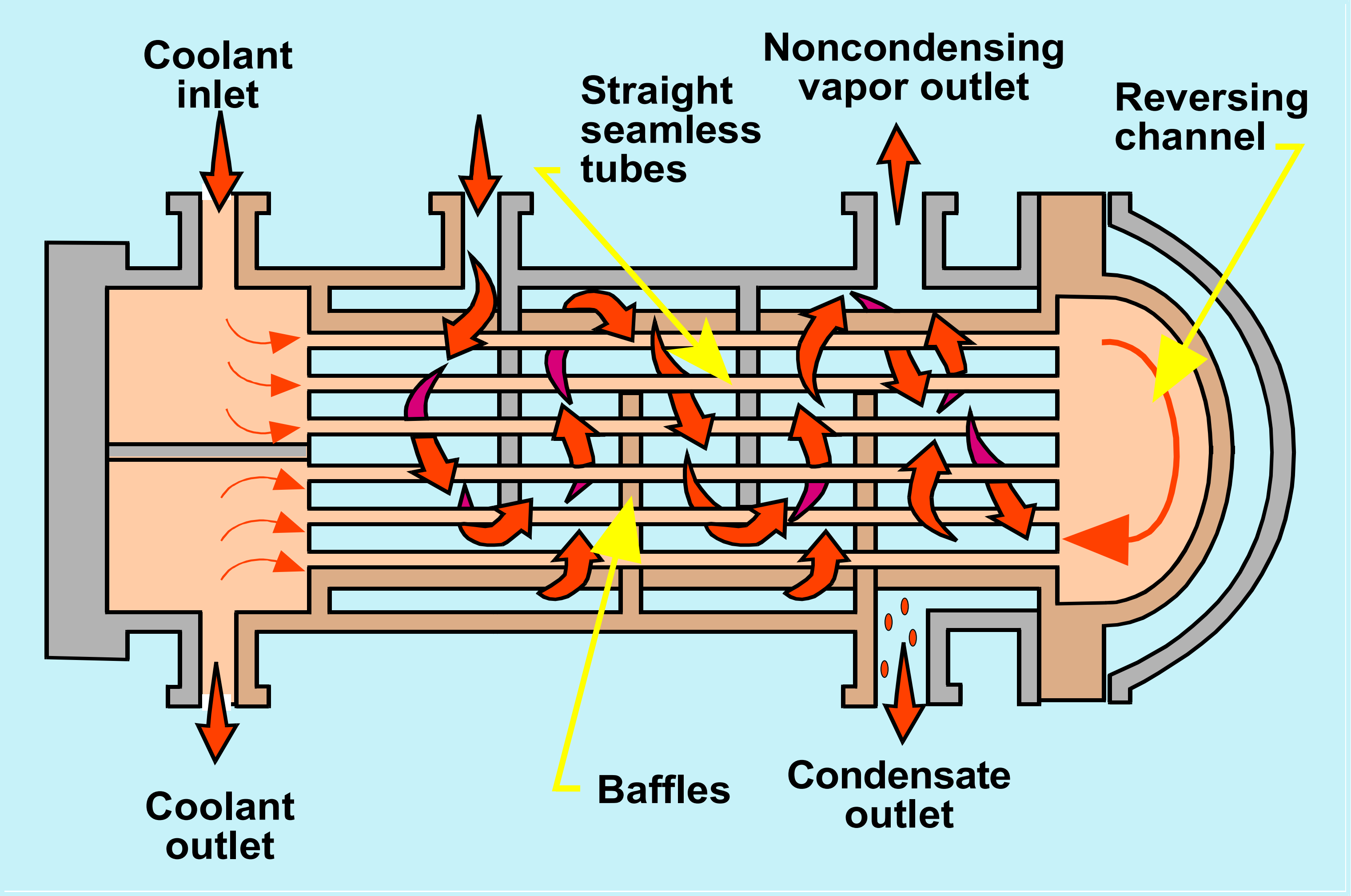
Ejector Condenser



SHELL-AND-TUBE CONDENSER



Shell and Tube Condenser



Surface and Contact Condenser Comparison

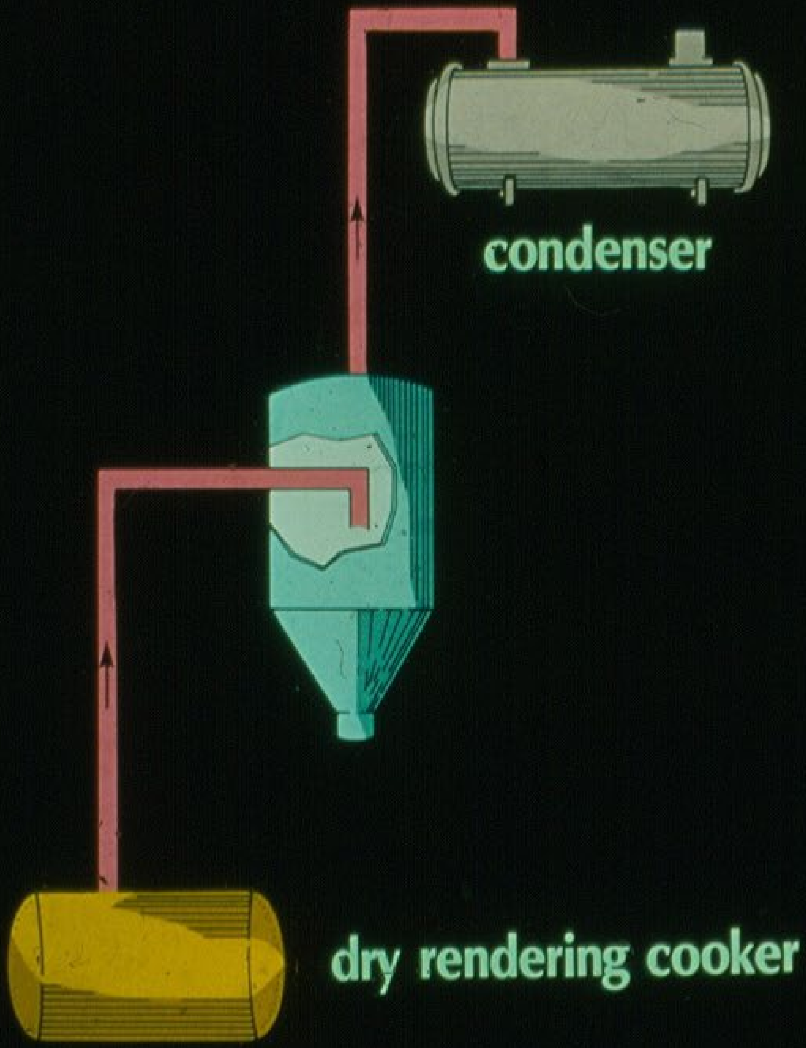
Surface Condensers

- less coolant required
- less condensate produced
- Product easily recovered
- No separation problem

Contact Condensers

- simpler
- less expensive
- less maintenance required
- separation problems
- (coolant and pollutant)

RENDERING PLANTS

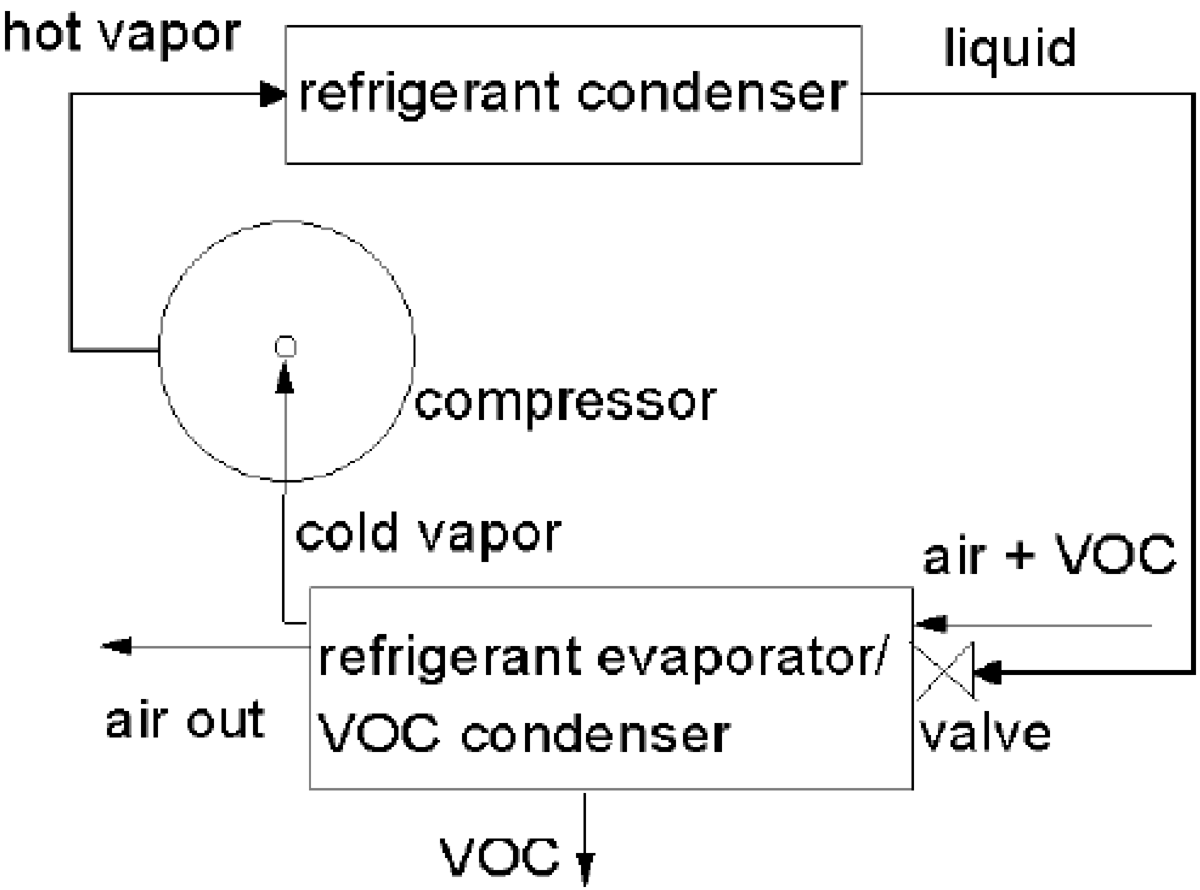


- Odor Control
  - cookers
  - dryers
  - grease processing
  - raw materials

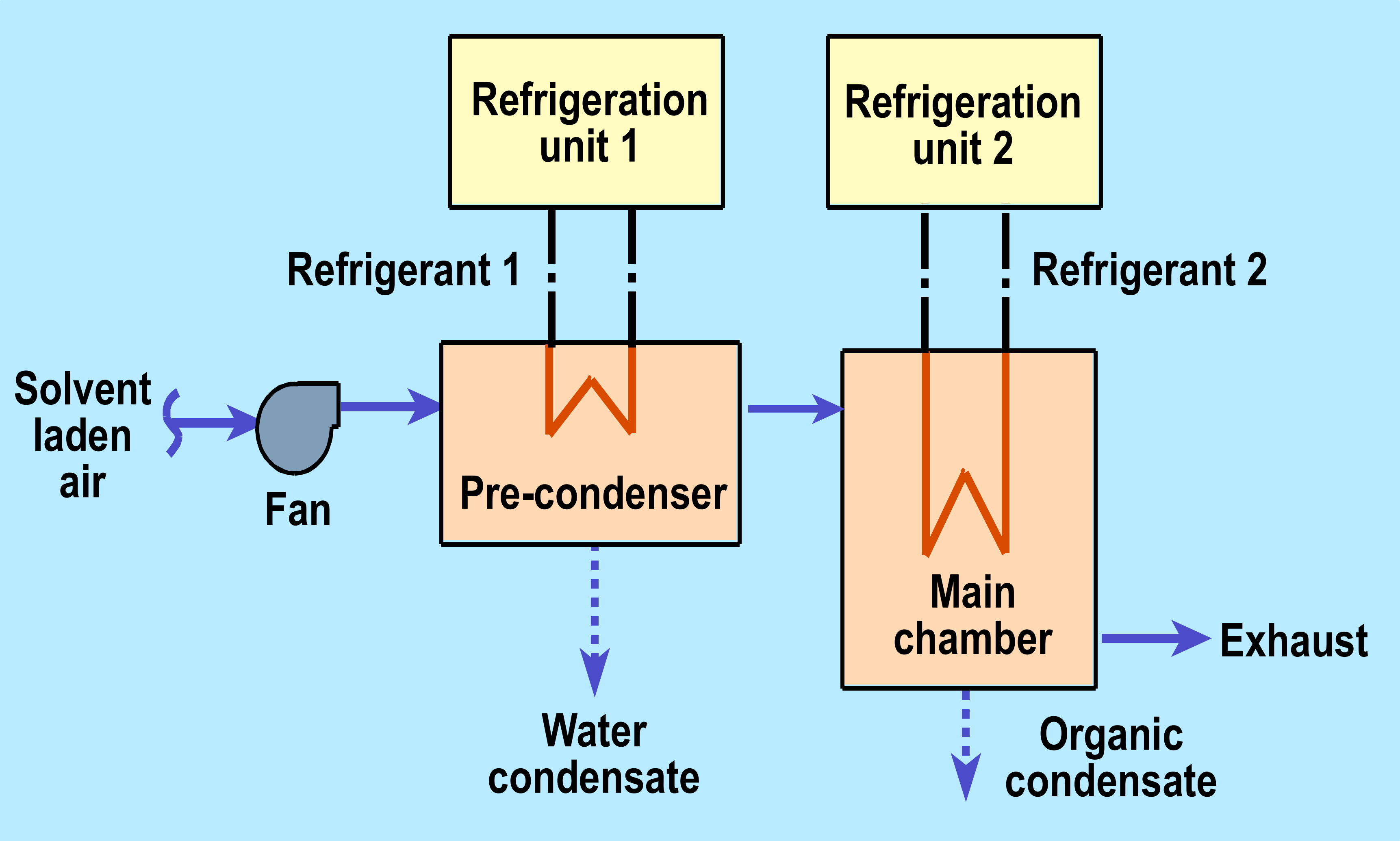
Refrigeration Condenser

- Refrigeration units are basically “heat pumps,” absorbing heat on the “cold side” of the system and releasing heat on the “hot side” of the system.
- All refrigeration systems have a hot side and a cold side. Some have a compressor.
- The difference between refrigeration systems is whether the refrigerant is actually liquified within the apparatus and how low a temperature the “cold side” can reach.

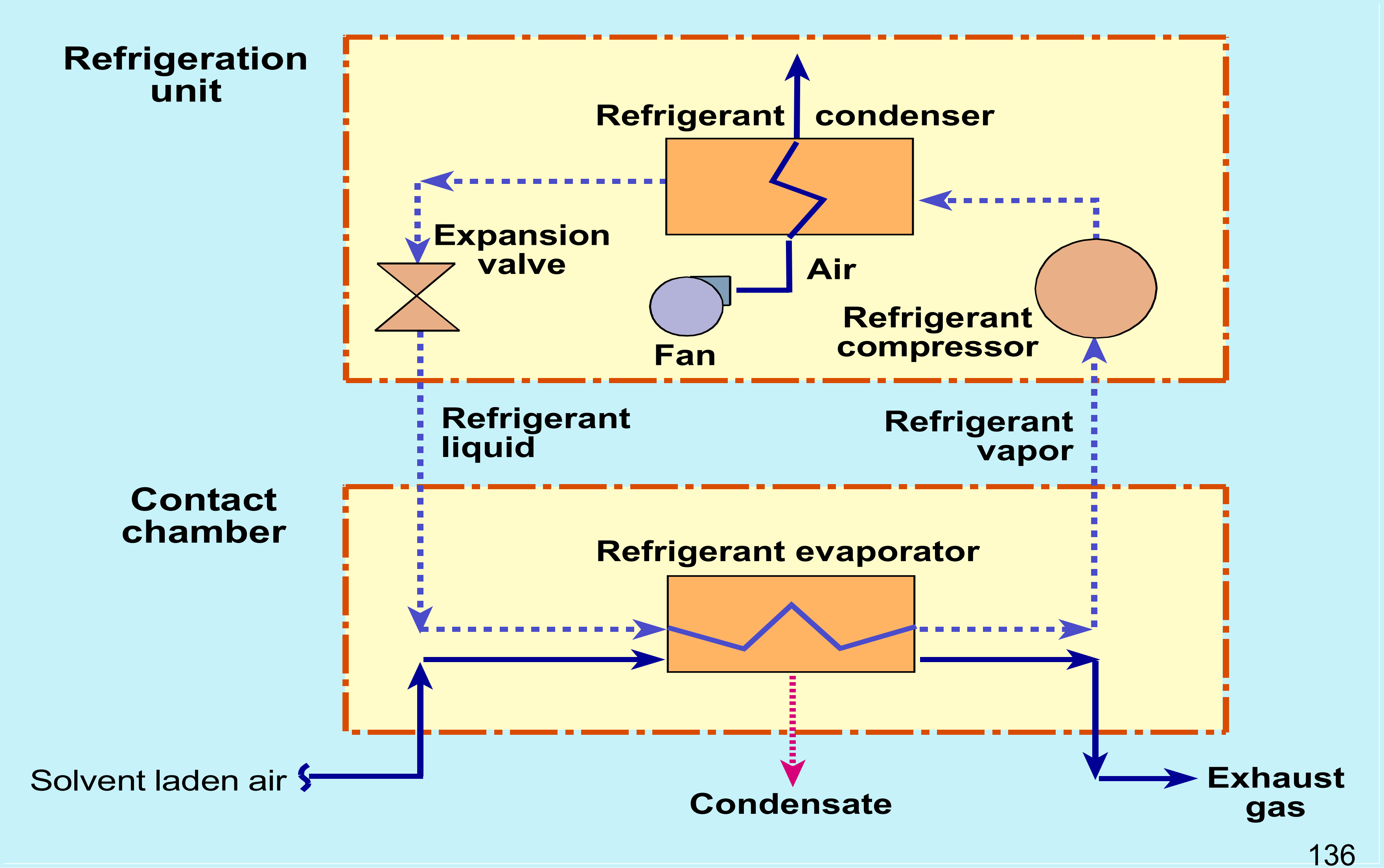
Mechanical Compression Refrigeration System



Refrigeration System

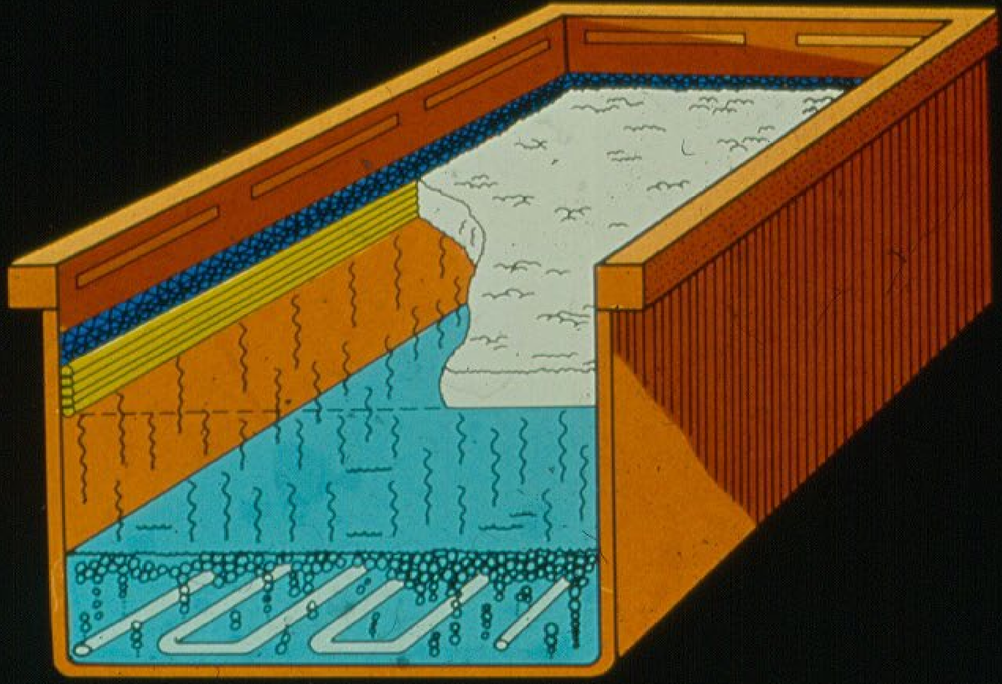


Refrigeration Cycle



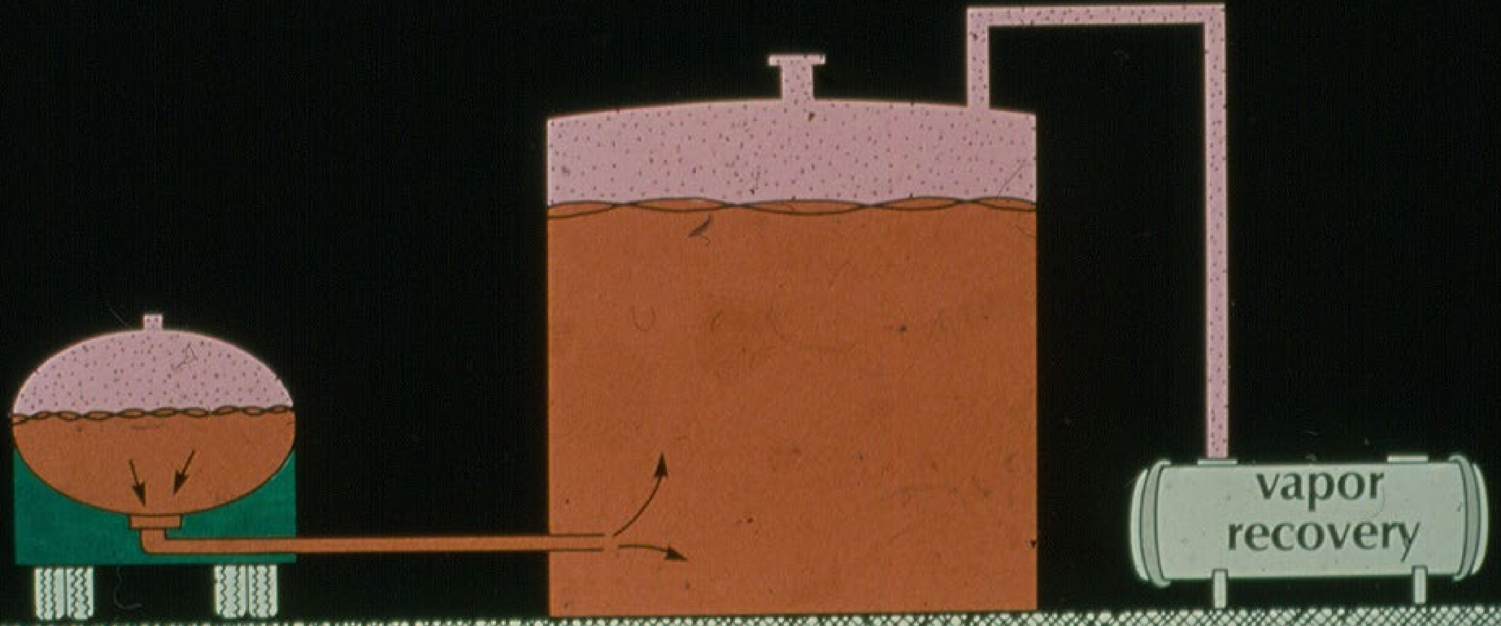
DEGREASING OPERATIONS

- Solvent Vapor Containment and Recovery
- Use condensation coils



PETRO-CHEMICAL INDUSTRY

- Vacuum Distillation of Petroleum
- Vapor Recovery in Bulk Terminals



Bioreactors and Biofiltration

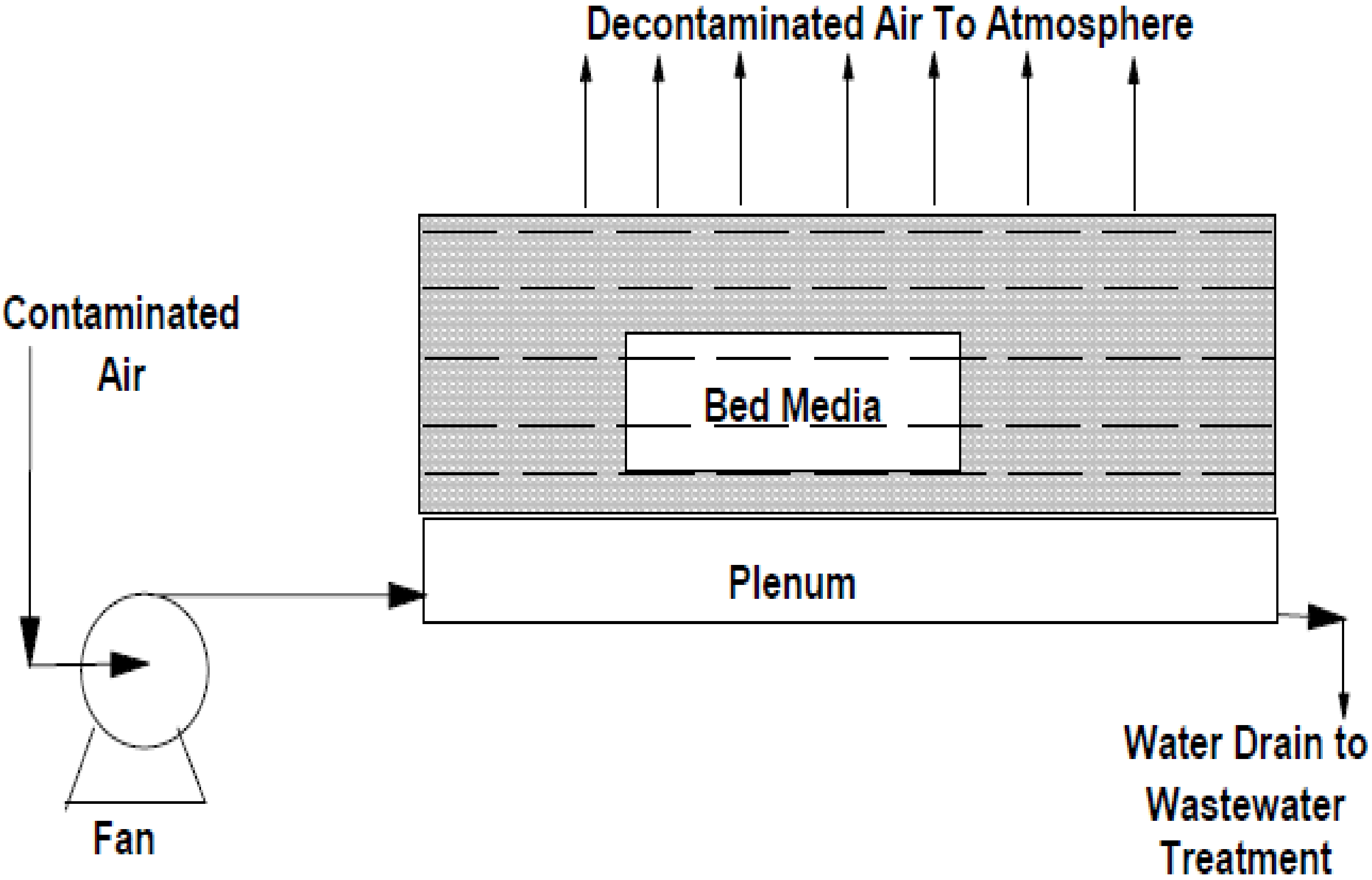
Biofiltration or Bioreactors

- In air pollution, biofiltration or bioreaction is the use of microbes to consume pollutants from a contaminated air stream.
- Most substances, with the help of microbes, will decompose (decay) given the proper environment and is especially true for organic compounds.
- Certain microbes can also consume inorganic compounds such as hydrogen sulfide and nitrogen oxides.

How Biofiltration or Bioreactors Work

- Bioreactors use microbes to remove pollutants from emissions by consuming the pollutants.
- About sixty years ago, Europeans began using bioreactors to treat contaminated air (odors), particularly emissions from sewage treatment plants and rendering plants.
- The initial process used a device called a "biofilter“ is a filter (usually a rectangular box) that contains an enclosed plenum on the bottom, a support rack above the plenum, and several feet of media (bed) on top of the support rack.

Basic Biofilter



Biofilter Basics

- Various materials are used for bed media such as peat, composted yard waste, bark, coarse soil, gravel or plastic shapes .
- Oyster shells (for neutralizing acid build-up) and fertilizer (for macronutrients) can be mixed with bed media.
- The support rack is perforated to allow air from the plenum to move into the bed media to contact microbes that live in the bed. The perforations also permit excess, condensed moisture to drain out of the bed to the plenum.
- A fan is used to collect contaminated air from a building or process.

Biofilter Basics

- If the air is too hot, too cold, too dry, or too dirty (with suspended solids), it may be necessary to pre-treat the contaminated air stream to obtain optimum conditions before introducing it into a bioreactor.
- Contaminated air is ducted to a plenum and emissions flow through the bed media, the pollutants are absorbed by moisture on the bed media and come into contact with microbes.
- Microbes reduce pollutant concentrations by consuming and metabolizing pollutants. During the digestion process, enzymes in the microbes convert compounds into energy, CO2 and water.
- Material that is indigestible is left over and becomes residue.

Bioreactors and Biofiltration

- Three primary mechanisms that are responsible for this transfer and the subsequent biodegradation in organic media biofilters are:
- 1. Gas stream → adsorption on organic media → desorption/ dissolution in aqueous phase → biodegradation.
- 2. Gas stream → direct adsorption in biofilm → biodegradation.
- 3. Gas stream → dissolution in aqueous phase → biodegradation.

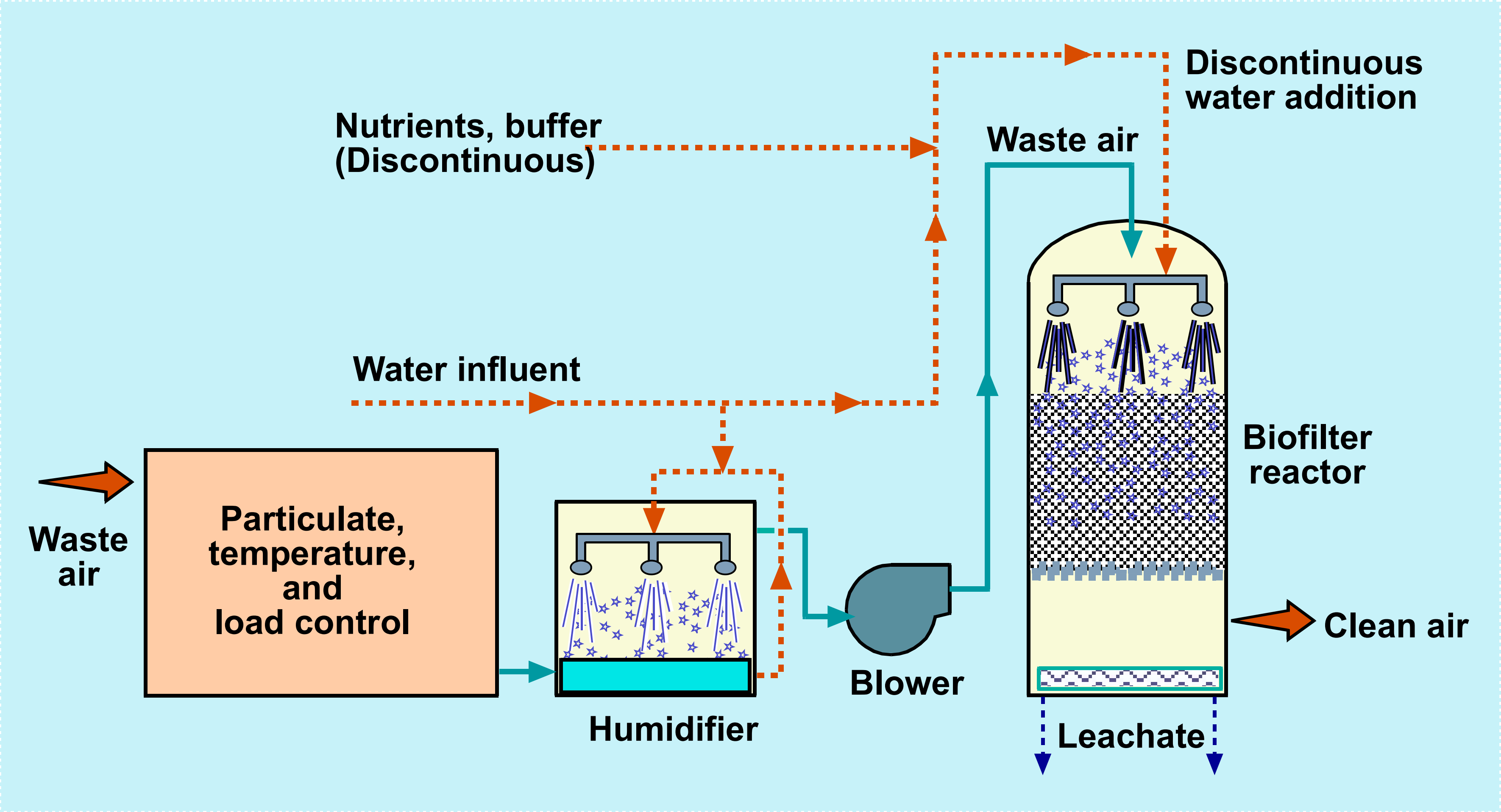
Microbial Population Requirements

- Sufficient moisture
- Sufficient nutrients
- Temperature of 60°F to 85°F
- pH of 6 to 8

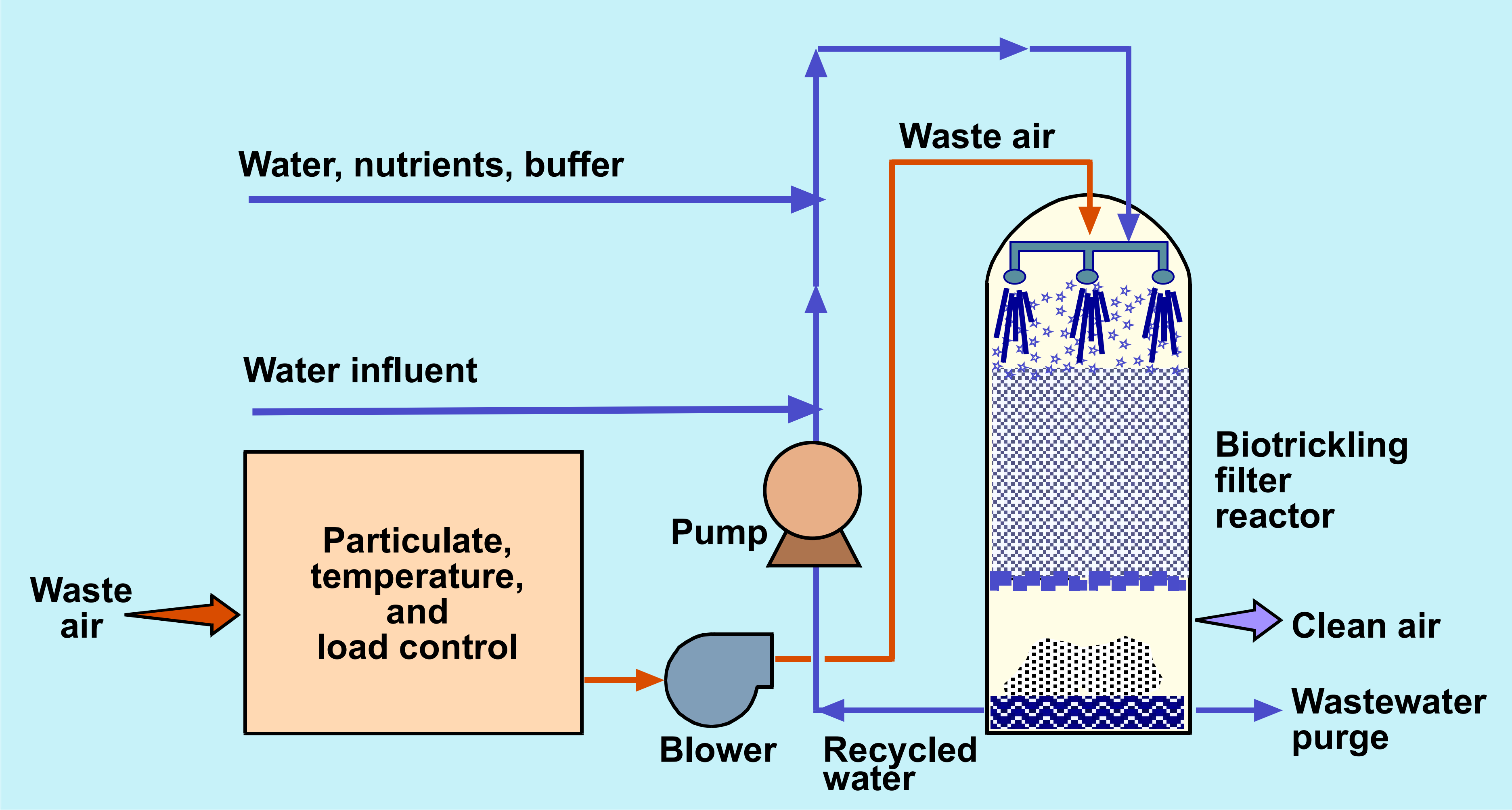
Bioreaction

- Biofilters
- Biotrickling filters
- Bioscrubbers

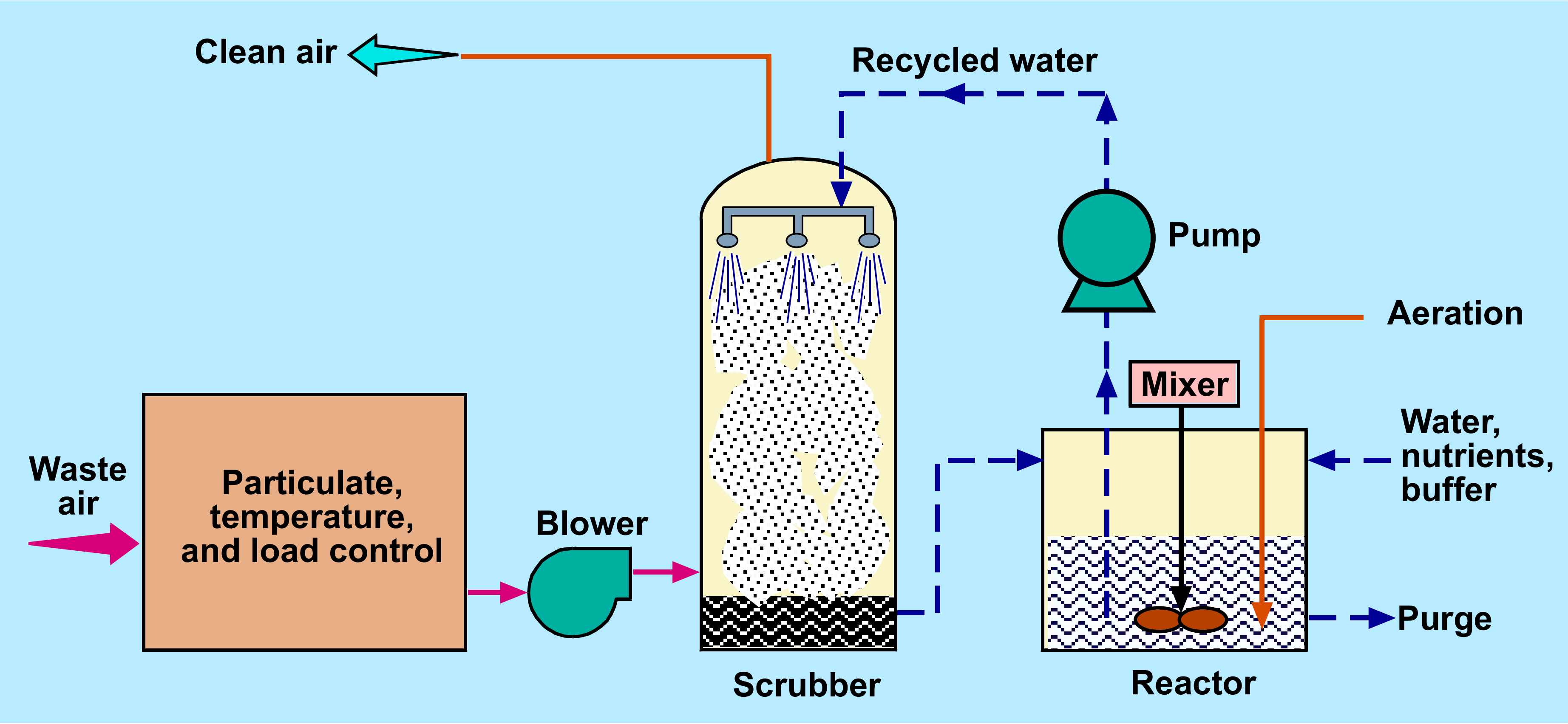
Biofilter System



Biotrickling Filter System



Bioscrubber System



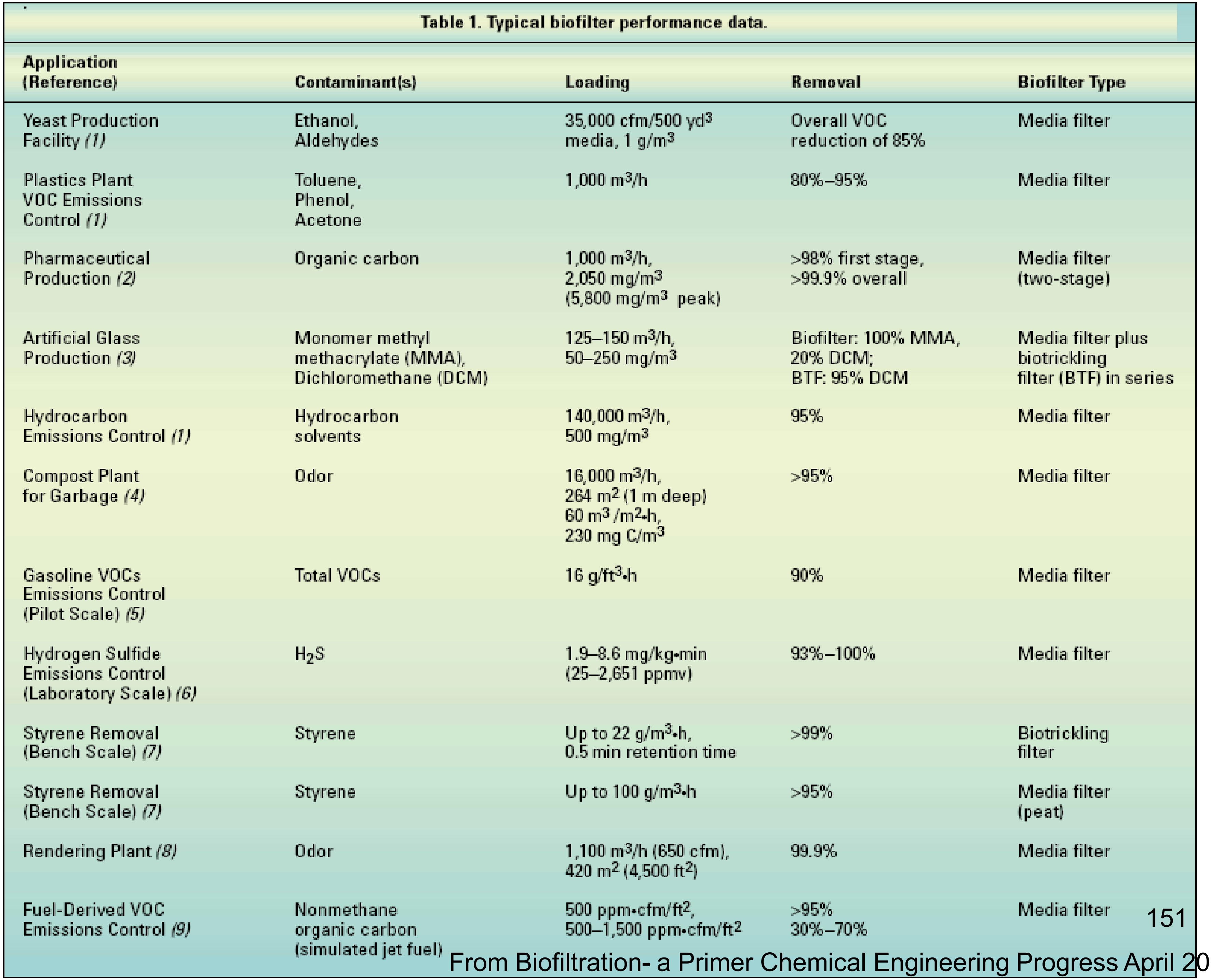


Table 1. Typical biofilter performance data.

Application (Reference)	Contaminant(s)	Loading	Removal	Biofilter Type
Yeast Production Facility *(1)*	Ethanol, Aldehydes	35,000 cfm/500 yd^3 media, 1 g/m^3	Overall VOC reduction of 85%	Media filter
Plastics Plant VOC Emissions Control *(1)*	Toluene, Phenol, Acetone	1,000 m^3/h	80%–95%	Media filter
Pharmaceutical Production *(2)*	Organic carbon	1,000 m^3/h, 2,050 mg/m^3 (5,800 mg/m^3 peak)	>98% first stage, >99.9% overall	Media filter (two-stage)
Artificial Glass Production *(3)*	Monomer methyl methacrylate (MMA), Dichloromethane (DCM)	125–150 m^3/h, 50–250 mg/m^3	Biofilter: 100% MMA, 20% DCM; BTF: 95% DCM	Media filter plus biotrickling filter (BTF) in series
Hydrocarbon Emissions Control *(1)*	Hydrocarbon solvents	140,000 m^3/h, 500 mg/m^3	95%	Media filter
Compost Plant for Garbage *(4)*	Odor	16,000 m^3/h, 264 m^2 (1 m deep) 60 m^3/m^2•h, 230 mg C/m^3	>95%	Media filter
Gasoline VOCs Emissions Control (Pilot Scale) *(5)*	Total VOCs	16 g/ft^3•h	90%	Media filter
Hydrogen Sulfide Emissions Control (Laboratory Scale) *(6)*	H_2S	1.9–8.6 mg/kg•min (25–2,651 ppmv)	93%–100%	Media filter
Styrene Removal (Bench Scale) *(7)*	Styrene	Up to 22 g/m^3•h, 0.5 min retention time	>99%	Biotrickling filter
Styrene Removal (Bench Scale) *(7)*	Styrene	Up to 100 g/m^3•h	>95%	Media filter (peat)
Rendering Plant *(8)*	Odor	1,100 m^3/h (650 cfm), 420 m^2 (4,500 ft^2)	99.9%	Media filter
Fuel-Derived VOC Emissions Control *(9)*	Nonmethane organic carbon (simulated jet fuel)	500 ppm•cfm/ft^2, 500–1,500 ppm•cfm/ft^2	>95% 30%–70%	Media filter

From Biofiltration- a Primer Chemical Engineering Progress April 2001

US EPA Bioreactor Publication

“USING BIOREACTORS TO CONTROL AIR POLLUTION” EPA-456/R-03-003

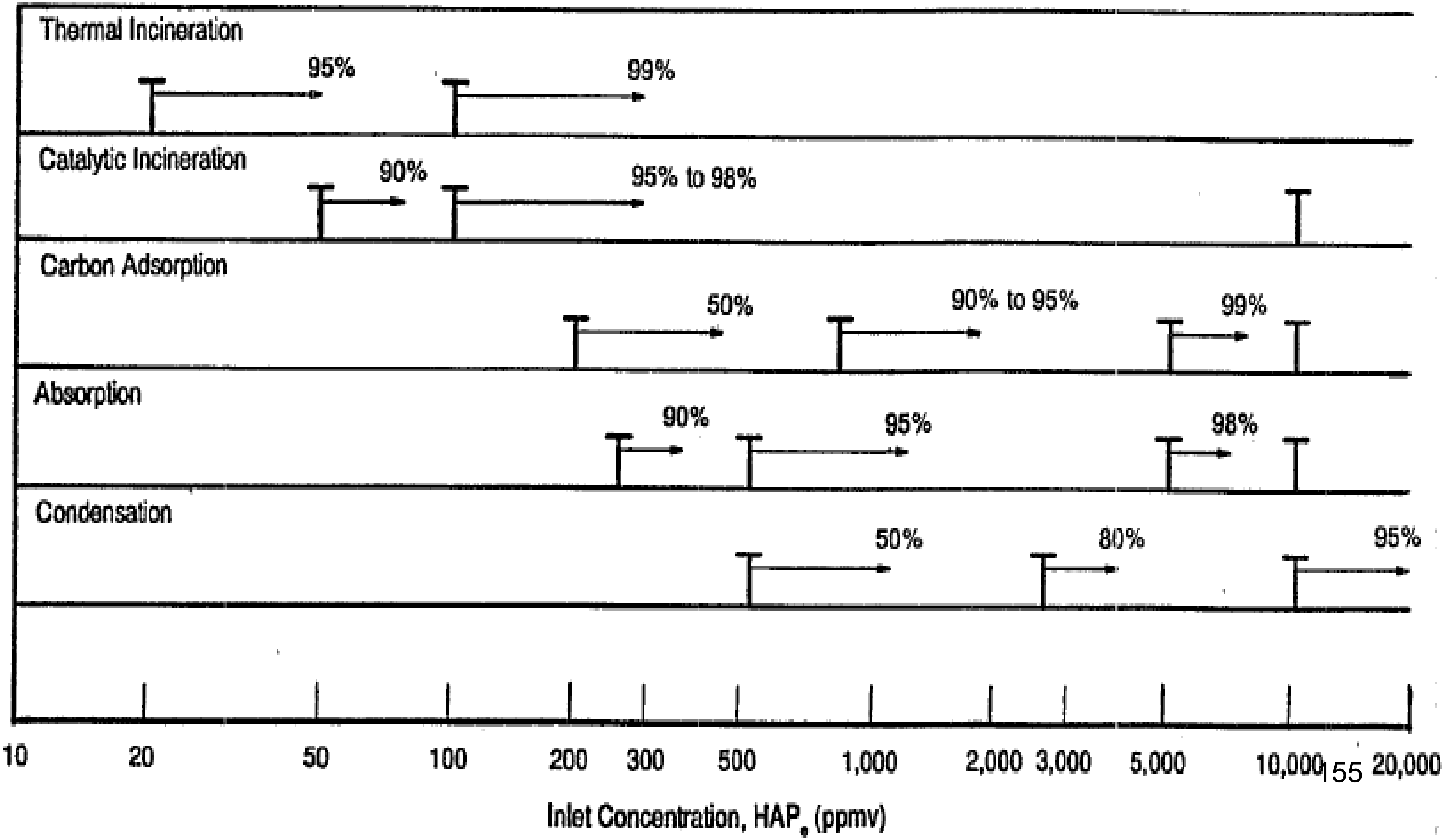
http://www.epa.gov/ttn/catc/dir1/fbiorect.pdf

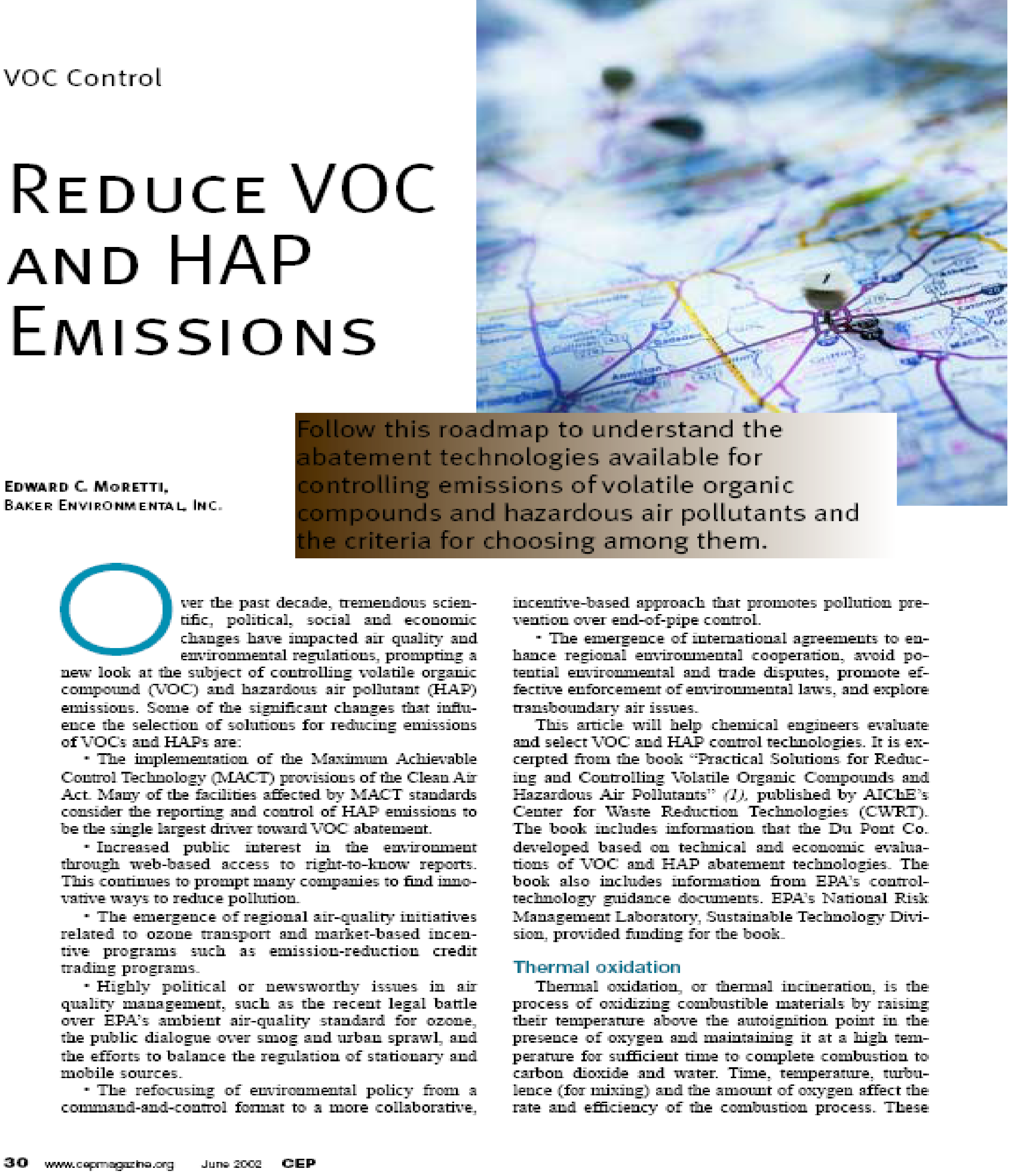
Review of Control Technologies for Gaseous Hazardous Air Pollutants

Emission Stream & HAP Characteristics for Selecting Control Techniques

	Emission Stream Characteristics					HAP Characteristics			
Control Device	HAP/Organic Contents (ppmv)	Heat Content Btu/scf	Moisture Content %	Flow Rate (scfm)	Temp (°F)	Molecular Weight (lb/lb-mole)	Solubility	Vapor Pressure (mm Hg)	Adsorptive Properties)
Thermal Incinerator	➢20; (< 25% of LEL)			< 50,000					
Catalytic Incinerator	50 – 10,000; (<25% of LEL)			< 50,000					
Flare		>300		< 2,000,000					
Boiler/ Process Heater		>150		Steady					Must be able to adsorb and desorb from adsorbent
Carbon Adsorber	700 – 10,000 (<25% of LEL)		<50%	300-200,000	< 130	45-130			
Absorber	250 – 10,000			1,000-100,000			Must be soluble in water or other solvents		
condenser	>5,000 – 10,000			<2000				>10 at room temperature	

Approximate Percent HAP Reduction Ranges for Applicable Control Devices





VOC Control

REDUCE VOC AND HAP EMISSIONS

Follow this roadmap to understand the abatement technologies available for controlling emissions of volatile organic compounds and hazardous air pollutants and the criteria for choosing among them.

EDWARD C. MORETTI,
BAKER ENVIRONMENTAL, INC.

Over the past decade, tremendous scientific, political, social and economic changes have impacted air quality and environmental regulations, prompting a new look at the subject of controlling volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions. Some of the significant changes that influence the selection of solutions for reducing emissions of VOCs and HAPs are:

- The implementation of the Maximum Achievable Control Technology (MACT) provisions of the Clean Air Act. Many of the facilities affected by MACT standards consider the reporting and control of HAP emissions to be the single largest driver toward VOC abatement.
- Increased public interest in the environment through web-based access to right-to-know reports. This continues to prompt many companies to find innovative ways to reduce pollution.
- The emergence of regional air-quality initiatives related to ozone transport and market-based incentive programs such as emission-reduction credit trading programs.
- Highly political or newsworthy issues in air quality management, such as the recent legal battle over EPA's ambient air-quality standard for ozone, the public dialogue over smog and urban sprawl, and the efforts to balance the regulation of stationary and mobile sources.
- The refocusing of environmental policy from a command-and-control format to a more collaborative, incentive-based approach that promotes pollution prevention over end-of-pipe control.
- The emergence of international agreements to enhance regional environmental cooperation, avoid potential environmental and trade disputes, promote effective enforcement of environmental laws, and explore transboundary air issues.

This article will help chemical engineers evaluate and select VOC and HAP control technologies. It is excerpted from the book "Practical Solutions for Reducing and Controlling Volatile Organic Compounds and Hazardous Air Pollutants" *(1)*, published by AIChE's Center for Waste Reduction Technologies (CWRT). The book includes information that the Du Pont Co. developed based on technical and economic evaluations of VOC and HAP abatement technologies. The book also includes information from EPA's control-technology guidance documents. EPA's National Risk Management Laboratory, Sustainable Technology Division, provided funding for the book.

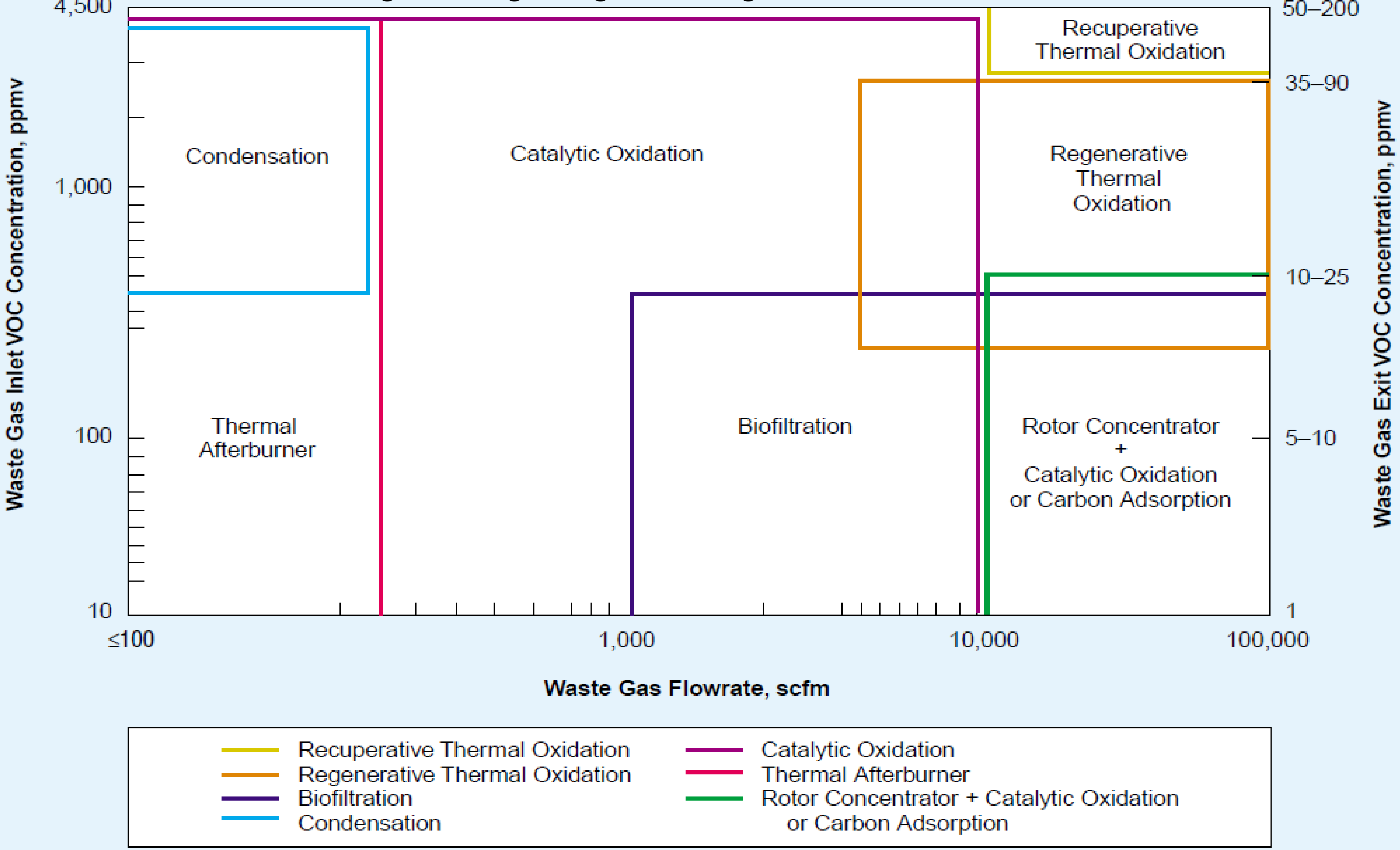
Thermal oxidation

Thermal oxidation, or thermal incineration, is the process of oxidizing combustible materials by raising their temperature above the autoignition point in the presence of oxygen and maintaining it at a high temperature for sufficient time to complete combustion to carbon dioxide and water. Time, temperature, turbulence (for mixing) and the amount of oxygen affect the rate and efficiency of the combustion process. These

Chemical Engineering Progress Magazine June 2002

http://people.clarkson.edu/~wilcox/Design/emisredn.pdf

Chemical Engineering Progress Magazine June 2002



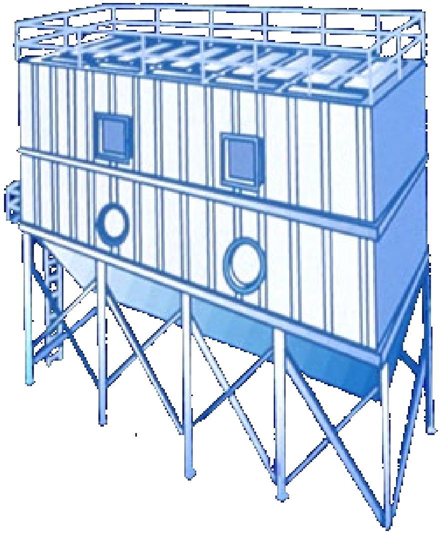
Basis: 4,500 ppmv = 25% of Lower Explosive Limit
Contains no halogenated organics
Contains no catalyst poisons
Contains no particulates

Note: Consider carbon adsorption for recovery when
- Recovered solvent value > $0.15/lb
- Concentration > 500 ppmv
- Gas flowrate > 1,000 scfm > 500 ppmv

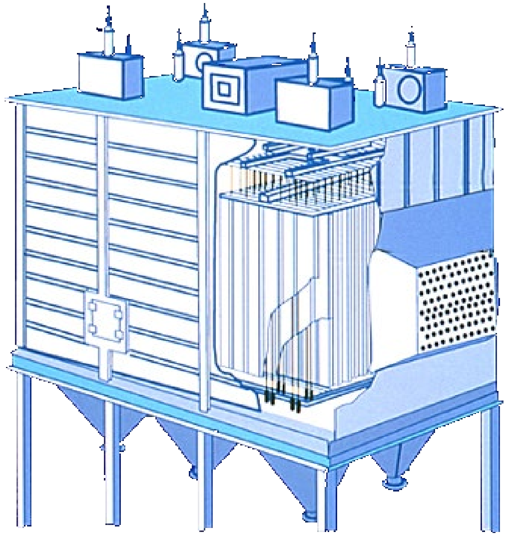
http://people.clarkson.edu/~wilcox/Design/emisredn.pdf

Control Technologies for Particle Hazardous Air Pollutants Emissions

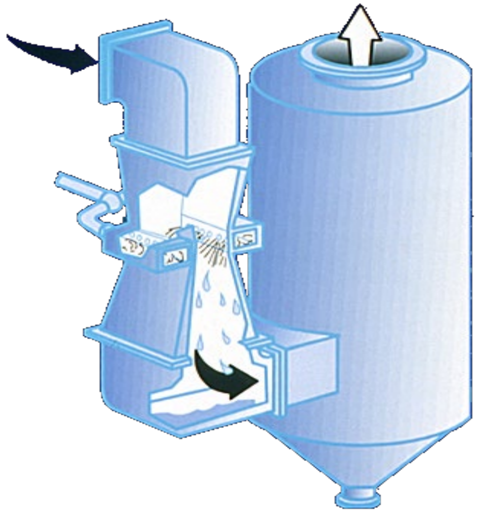
Efficient Types of Control Technologies for Particle Hazardous Air Pollutants



Fabric Filters



Electrostatic Precipitators



Venturi Wet Collectors

Control Devices for HAP's Particle Emissions

- The of control devices applicable to particulate laden emission streams from point sources are: fabric filters (baghouses), electrostatic precipitators (ESP's), and venturi scrubbers.
- The control efficiencies and applicability of these devices are dependant on the physical and/or chemical/electrical properties of the airborne particulate matter under consideration.

Selection of Control Devices for HAP's Particle Emissions

- Selection of the these control devices is determined following studies of the specific stream characteristics (i.e., particle size, temperature, corrosiveness, resistivity, and moisture content) and the parameters (i.e., required collection efficiency) that affect the applicability of each control device.

Fabric Filters (Baghouses)

- Fabric filters collect particles (submicron to several hundred microns in diameter) at efficiencies generally in excess of 99 or 99.9 percent.
- The layer of dust, or dust cake, collected on the fabric is primarily responsible for such high efficiency.
- Gas temperatures up to about 500^{O}F, with surges to about 550^{O}F can be accommodated with high temperature bags.

Electrostatic Precipitators (ESP's)

- In an ESP particles are given an electrical charge by forcing them to pass through a corona glow region around charging electrodes in which gaseous ions are flowing.
- The electrical field quickly draws the charged particles to the walls (collecting plates) from charging electrodes which are maintained at high voltage in the center of the flow lanes between plates.
- An ESP can achieve a 99.9% overall mass collection efficiency and over 97-98% of all 0-5 micron particles.

Venturi Scrubbers

- A venturi scrubber has a “converging-diverging” flow channel.
- The narrowest area is referred to as the “throat ” where the decrease in area causes high gas velocities and turbulence to increase.
- Scrubbing liquid is injected into the scrubber slightly upstream of the throat or directly into the throat section.
- High collection efficiencies, ranging from 70% to 99% for smaller diameter particles.

Web Sites For Additional Control Device Information

- http://www.epa.gov/ttn/catc/products.html
- http://cfpub.epa.gov/oarweb/mkb/control.cfm

Control Technologies for Mercury Emissions

- Mercury’s high vapor pressure at typical APCD operating temperatures causes collection by PM control devices is highly variable.
- Factors that enhance mercury control are low temperature, high levels of carbon in the fly ash and the presence of hydrogen chloride (HCl).
- Conversely, sulfur dioxide (SO_2) in flue gas can convert oxidized mercury to elemental mercury, making it more difficult to collect.

Common Controls to Reduce Mercury Emissions

Some of the most common add-on controls to reduce mercury emissions include:

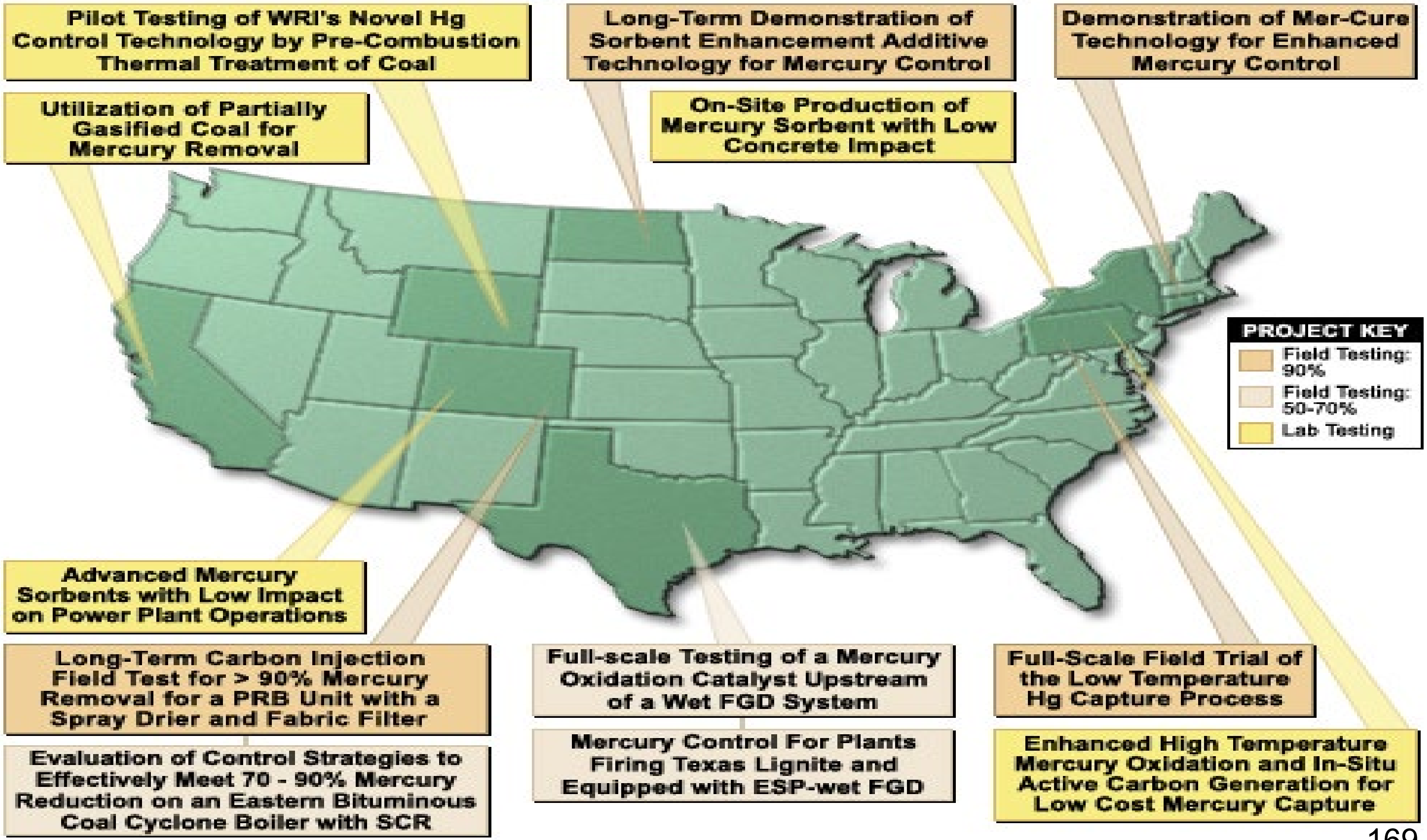
- Carbon filter beds
- Wet scrubbing
- Selenium filters
- Activated carbon injection

Controlling Power Plant Mercury Emissions

Currently, there are two main approaches being considered for controlling power plant mercury emissions:

- Reducing mercury emissions using technologies primarily designed to remove SO_2, NO_X, and particulate emissions (often called co-benefit reductions), and
- Reducing mercury emissions using technologies specifically designed to reduce mercury in coal prior to burning.

DOE/NETL's Phase II Mercury Emission Control Program



Pilot Testing of WRI's Novel Hg Control Technology by Pre-Combustion Thermal Treatment of Coal

Long-Term Demonstration of Sorbent Enhancement Additive Technology for Mercury Control

Demonstration of Mer-Cure Technology for Enhanced Mercury Control

Utilization of Partially Gasified Coal for Mercury Removal

On-Site Production of Mercury Sorbent with Low Concrete Impact

PROJECT KEY

- 🟧 Field Testing: 90%
- ⬜ Field Testing: 50-70%
- 🟨 Lab Testing

Advanced Mercury Sorbents with Low Impact on Power Plant Operations

Long-Term Carbon Injection Field Test for > 90% Mercury Removal for a PRB Unit with a Spray Drier and Fabric Filter

Evaluation of Control Strategies to Effectively Meet 70 - 90% Mercury Reduction on an Eastern Bituminous Coal Cyclone Boiler with SCR

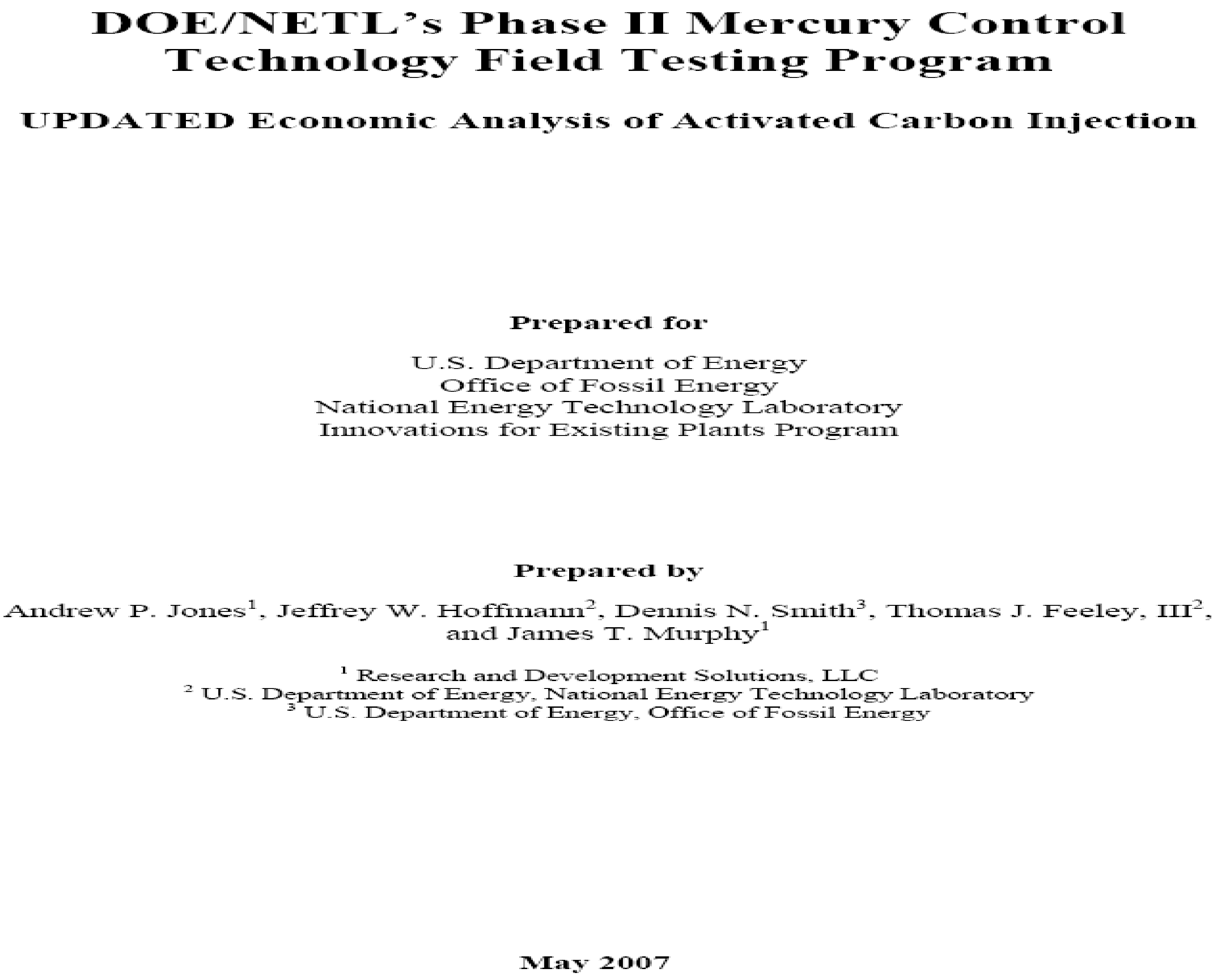
Full-scale Testing of a Mercury Oxidation Catalyst Upstream of a Wet FGD System

Mercury Control For Plants Firing Texas Lignite and Equipped with ESP-wet FGD

Full-Scale Field Trial of the Low Temperature Hg Capture Process

Enhanced High Temperature Mercury Oxidation and In-Situ Active Carbon Generation for Low Cost Mercury Capture

DOE/NETL's Phase II Mercury Control Program



DOE/NETL's Phase II Mercury Control Technology Field Testing Program

UPDATED Economic Analysis of Activated Carbon Injection

Prepared for

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
Innovations for Existing Plants Program

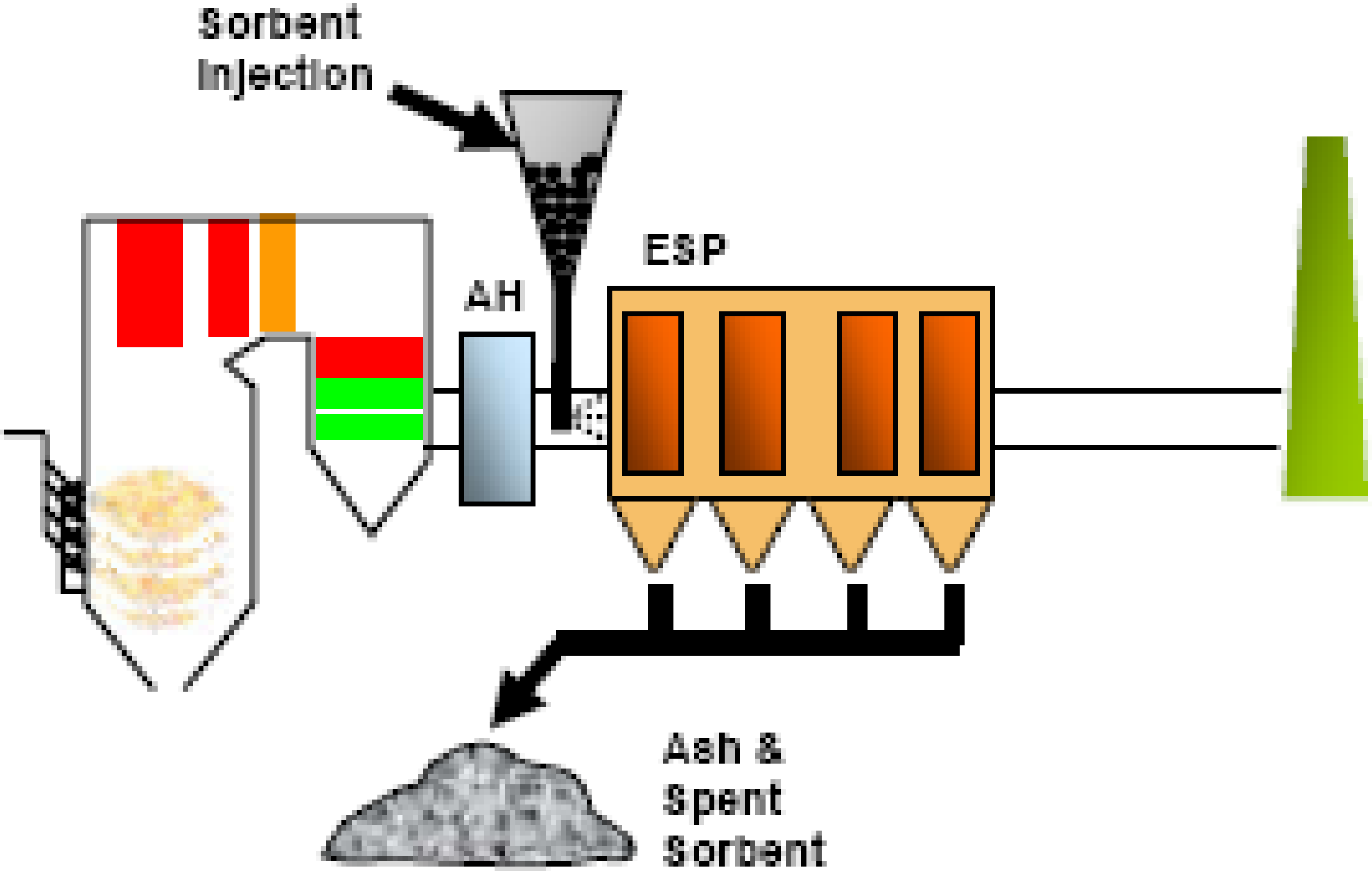
Prepared by

Andrew P. Jones[1], Jeffrey W. Hoffmann[2], Dennis N. Smith[3], Thomas J. Feeley, III[2], and James T. Murphy[1]

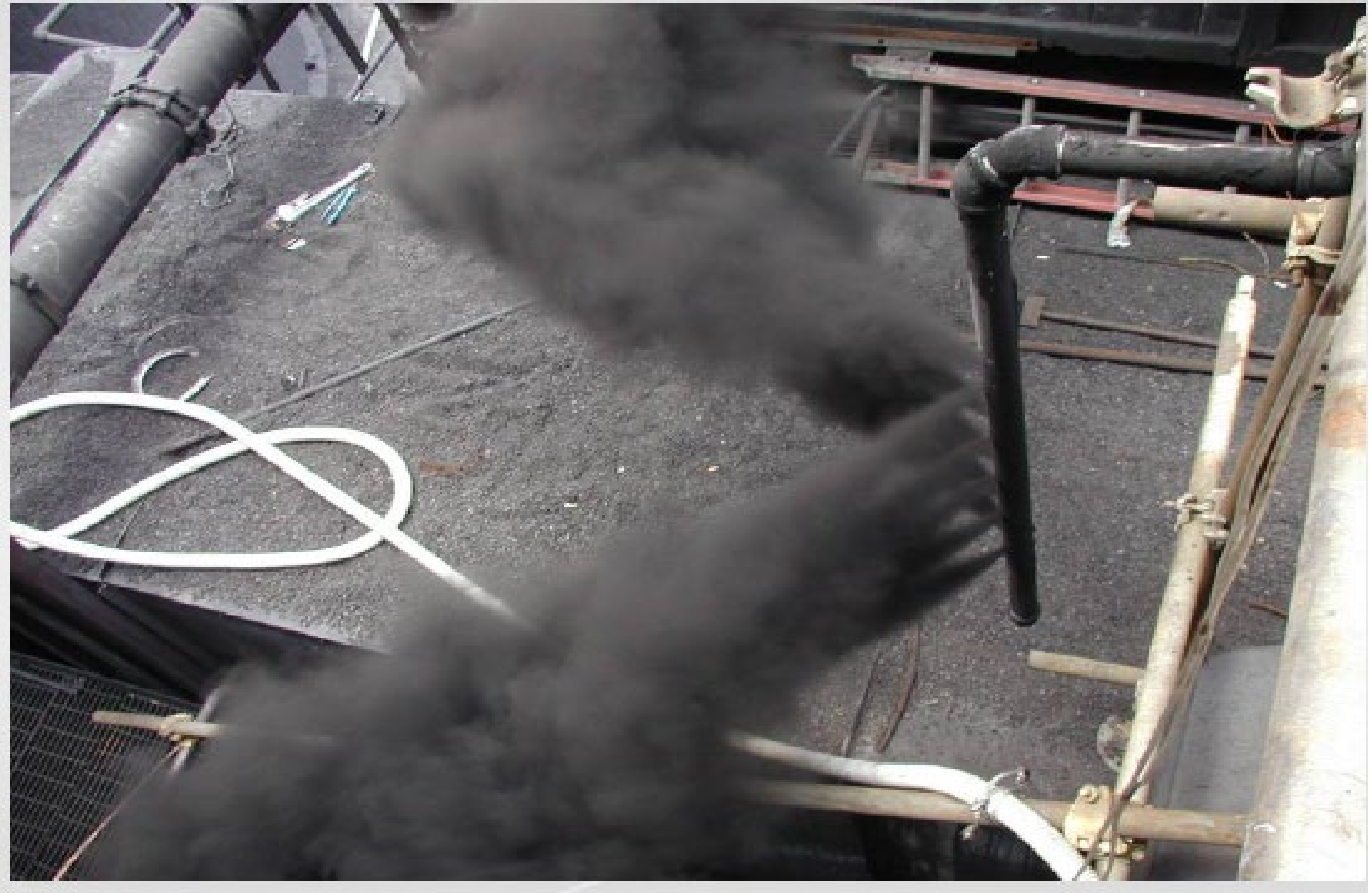
[1] Research and Development Solutions, LLC
[2] U.S. Department of Energy, National Energy Technology Laboratory
[3] U.S. Department of Energy, Office of Fossil Energy

May 2007

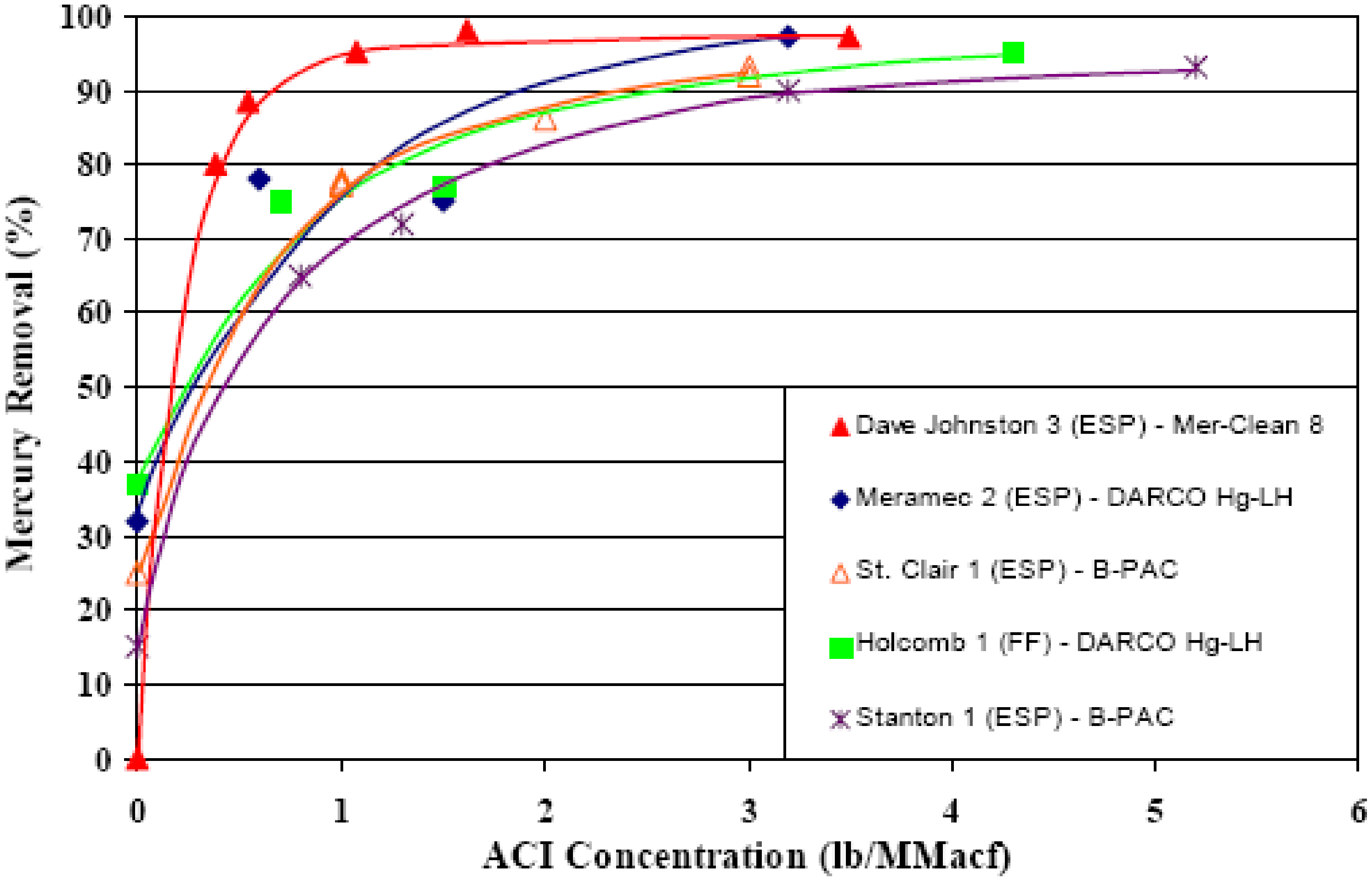
Activated Carbon Injection Technology Schematic



Powdered Activated Carbon Injection



ACI Performance Data for Phase II Units Firing PRB Coal



NETL’s Web Site

http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/index.html

2006 Mercury Control Technology Conference December 11-13, 2006 Table of Contents

http://www.netl.doe.gov/publications/proceedings/06/mercury/index.html#oxidation