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# **Inspection Workshop for Volatile Organic Air Pollutants**

## **Selected Readings**

**Prepared for:**

**USEPA, Region VIII  
999 18th Street, Suite 1300  
Denver, Colorado 80202**

**February 1991**

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TABLE 1. RESPONSE FACTORS FOR TECO MODEL 580  
PHOTOIONIZATION TYPE ORGANIC VAPOR ANALYZERS  
10.0 ev Lamp

Compound	Ionization Potential (ev)	Response Factor
Acetone	9.58	1.7
Acetophenone	N.D.	4.2
Acrolein	N.D.	25.0
Ammonia	10.15	24.5
Aniline	7.70	0.6
Benzene	9.25	0.7
1,3 Butadiene	9.07	1.0
Carbon disulfide	10.0	2.3
Chlorobenzene	9.07	0.5
Cyclohexane	9.98	2.1
1,2-Dichloroethane	N.D.	50.0
Diethylamine	N.D.	2.0
Dimethyl sulfide	8.69	1.3
Ethyl benzene	8.75	1.7
Ethylene oxide	10.57	33.8
Ethyl ether	9.53	1.5
Hexane	10.18	11.3
Hydrogen sulfide	10.45	7.3
Isopropanol	10.16	19.8
Methyl ethyl ketone	9.53	1.6
Methyl isocyanate	10.57	12.5
Methyl mercaptan	9.4	1.3
Methyl methacrylate	N.D.	4.2
Nitric oxide	9.25	44.9
Ortho chloro toluene	8.83	0.5
Ortho xylene	8.56	0.8
Pyridine	9.32	0.6
Styrene	N.D.	3.3
Sec butyl bromide	9.98	1.7
Tetrachloroethene	9.32	1.6
Tetrachloroethylene	N.D.	1.9
Tetrahydrofuran	9.54	3.7
Toluene	8.82	0.5
Trichloroethylene	N.D.	1.3

Table 2. RESPONSE FACTORS FOR THE HUN SYSTEMS, INC.  
MODEL ISPI-101 PHOTOIONIZATION ANALYZER

Compound	Actual Concentration	Instrument Concentration	Response Factor
Acetal	1000	925	1.1
	5000	7200	0.69
	10000	13200	0.76
Carbon Disulfide	1000	1990	0.50
	10000	12900	0.78
Carbon tetrachloride	500	784	0.64
	1000	1070	0.94
	10000	6070	1.6
Chloroform	1000	756	1.3
	5000	2550	2.0
	10000	5250	1.9
Diketene	1000	148	6.8
	5000	318	16.0
	10000	460	22.0
Perchloromethyl mercaptan	5000	103	48.0
Toluene	1000	1180	0.85
Tetrachloroethane, 1,1,2,2-	1000	736	1.4
	5000	1170	4.3
	10000	1880	5.3
Trichloroethane, 1,1,	1000	1020	0.98
	5000	6170	0.81
	10000	9430	1.1
Trichlorotrifluoroethane 1,1,2-	5000	155	32.0
	10000	430	23.0

Table 3. RESPONSE FACTORS FOR FOXBORO OVA-108 AND  
BACHARACH TLV SNIFFER AT 10,000 ppmv RESPONSE

Compound	Response Factor OVA-108	Response Factor TLV Sniffer
Acetic acid	1.64	15.60
Acetic ahydride	1.39	5.88
Acetone	0.80	1.22
Acetonitrile	0.95	1.18
Acetyl chloride	2.04	2.72
Acetylene	0.39	B
Acrylic acid	4.59	B
Acrylonitrile	0.97	3.49 I
Allene	0.64	15.00
Allyl alcohol	0.96	X
Amylene	0.44	1.03
Anisole	0.92	3.91
Benzene	0.29	1.07
Bromobenzene	0.40	1.19
Butadiene, 1,3-	0.57	10.90
Butane, N	1.44 I	4.11
Butanol, sec-	0.76	1.25
Butanol, tert	0.53	2.17
Butene, 1-	0.56	5.84
Butyl acetate	0.66	1.38
Butyl acrylate, N-	0.70	2.57 I
Butyl ether, N	2.60	3.58 I
Butyl ether, sec	0.35	1.15
Butylamine, N	0.69	2.02
Butylamine, sec	0.70	1.56
Butylamine, tert-	0.63	1.95
Butyrandehyde, N-	1.29	2.30
Butyronitrile	0.52	1.47 I
Carbon disulfide	B	3.92
Chloroacetaldehyde	9.10	5.07
Chlorobenzene	0.38	0.88
Chloroethane	5.38 I	3.90 P
Chloroform	9.28	B
Chloropropene, 1-	0.67	0.87
Chloropropene, 3-	0.80	1.24
Chlorotoluene, M-	0.48	0.91
Chlorotoluene, O-	0.48	1.06
Chlorotoluene, P-	0.56	1.17 I

Table 3. RESPONSE FACTORS FOR FOXBORO OVA-108 AND  
BACHARACH TLV SNIFFER AT 10,000 ppmv RESPONSE

Compound	Response Factor OVA-108	Response Factor TLV Sniffer	
Crotonaldehyde	1.25		B
Cumene	1.87		B
Cyclohexane	0.47	0.70	
Cyclohexanone	1.50	7.04	
Cyclohexene	0.49	2.17	
Cyclohexylamine	0.57	1.38	
Diacetyl	1.54	3.28	
Dichloro-1-propene, 2, 3-	0.75	1.75	
Dichloroethane, 1, 1-	0.78	1.86	
Dichloroethane, 1, 2-	0.95	2.15	
Dichloroethylene, cis 1, 2-	1.27	1.63	
Dichloroethylene, trans 1, 2-	1.11	1.66	
Dichloromethane	2.81	3.85	
Dichloropropane, 1, 2-	1.03	1.54	
Diisobutylene	0.35	1.41	
Dimethoxy ethane, 1, 2-	1.22	1.52	
Dimethylformamide, N, N-	4.19	5.29	
Dimethylhydrazine 1, 1-	1.03	2.70	
Dioxane	1.48	1.31	
Epichlorohydrin	1.69	2.03	
Ethane	0.65	0.69	I
Ethanol	1.78		X
Ethoxy ethanol, 2-	1.55	1.82	
Ethyl acetate	0.86	1.43	
Ethyl acrylate	0.77		X
Ethyl chloroacetate	1.99	1.59	
Ethyl ether	0.97	1.14	
Ethylbenzene	0.73	4.74	D
Ethylene	0.71	1.56	
Ethylene oxide	2.46	2.40	
Ethylenediamine	1.73	3.26	
Formic acid	14.20		B
Glycidol	6.88	5.55	
Heptane	0.41	0.73	I
Hexane, N-	0.41	0.69	
Hexene, 1-	0.49	4.69	D
Hydroxyacetone	6.90	15.20	
Isobutane	0.41	0.55	

Table 3. RESPONSE FACTORS FOR FOXBORO OVA-108 AND  
BACHARACH TLV SNIFFER AT 10,000 ppmv RESPONSE

Compound	Response Factor OVA-108	Response Factor TLV Sniffer
Isobutylene	3.13	B
Isoprene	0.59	X
Isopropanol	0.91	1.39
Isopropyl acetate	0.71	1.31
Isopropyl chloride	0.68	0.98
Isovaleraldehyde	0.64	2.19 D
Mesityl oxide	1.09	3.14
Methacrolein	1.20	3.49 D
Methanol	4.39 P	2.01
Methoxy-ethanol, 2-	2.25	3.13
Methyl acetate	1.74	1.85
Methyl acetylene	0.61	6.79
Methyl chloride	1.44	1.84
Methyl ethyl ketone	0.64	1.12
Methyl formate	3.11	1.94
Methyl methacrylate	0.99	2.42
Methyl-2-pentanol, 4-	1.66	2.00
Methyl-2-pentone, 4-	0.56	1.63
Methyl-3-butyne-2-ol, 2	0.59	X
Methylcyclohexane	0.48	0.84
Methylcyclohexene	0.44	2.79
Methylstyrene, a-	13.90	B
Nitroethane	1.40	3.45
Nitromethane	3.52	7.60
Nitropropane	1.05	2.02
Nonane-n	1.54	11.10
Octane	1.03	2.11
Pentane	0.52	0.83
Picoline, 2-	0.43	1.18
Propane	0.55 I	0.60 P
Propionaldehyde	1.14	1.71
Propionic acid	1.30	5.08 D
Propyl alcohol	0.93	1.74
Propylbenzene, n-	0.51	B
Propylene	0.77	1.74 I
Propylene oxide	0.83	1.15
Pyridine	0.47	1.16
Styrene	4.22	B

Table 3. RESPONSE FACTORS FOR FOXBORO OVA-108 AND  
BACHARACH TLV SNIFFER AT 10,000 ppmv RESPONSE

Compound	Response Factor OVA-108	Response Factor TLV Sniffer
Tetrachloroethane, 1,1,1,2	4.83 D	6.91
Tetrachloroethane, 1,1,2,2	7.89	25.40
Tetrachloroethylene	2.97	B
Toluene	0.39	2.68 D
Trichloroethane, 1,1,1-	0.80	2.40
Trichloroethane, 1,1,2-	1.25	3.69
Trichloroethylene	0.95	3.93
Trichloropropane, 1,2,3-	0.96	1.99
Triethylamine	0.51	1.48
Vinyl chloride	0.84	1.06
Vinylidene chloride	1.12	2.41
Xylene, p-	2.12	7.87
Xylene, m-	0.40	5.87 D
Xylene, o-	0.43	1.40

I Inverse Estimation Method  
D Possible Outliers in Data  
N Narrow Range of Data  
X No Data Available  
B 10,000 ppvm Response Unachievable  
P Suspect Points Eliminated

## **FUGITIVE VOC REGULATIONS**

### **SIGNIFICANCE OF LEAKS**

Fugitive emissions from thousands of individual components in refineries and chemical plants are collectively significant.

### **TYPES OF REGULATIONS**

Several sets of regulations have been Promulgated.

- o NSPS Regulations
  - Subpart VV - Synthetic Chemical Plants
  - Subpart GGG - Refineries
  - Subpart KKK - On-Shore Natural Gas
  - Subpart DDD - Polymer Plants
- o NESHAPS Regulations
  - Subpart V - Fugitive Leaks
  - Subpart F - Vinyl Chloride
  - Subpart J - Benzene

### **TYPES OF REQUIREMENTS**

Each NSPS and NESHAPS regulations has several types of requirements.

- o Work Practice Standards
- o Equipment Design
- o Performance Limits

### **LEAK DETECTION AND REPAIR PROGRAMS**

These are the main type of work practice standards and they involve frequent monitoring of components with portable VOC analyzers and other visual checks.

The portable VOC analyzers simply determine if there is or is not a leak as defined in the regulations.

Due to compound-by-compound differences in instrument response factors, the instrument reading is not a direct indication of concentration.

## **COMPARISON OF NSPS AND NESHAPS REGULATIONS**

### **SIMILARITIES**

- o Leak Definition
- o Screening Method
- o Repair/Retest Procedures
- o Recordkeeping and Reporting
- o Components Subject to Regulations

### **DIFFERENCES**

- o Types of Exemptions
- o Definition of Light and Heavy Liquids
- o Component Labeling Requirements

## **TYPES OF STANDARDS**

### **WORK PRACTICE**

- o Leak Detection and Repair Programs

### **EQUIPMENT STANDARDS**

- o Equipment Specifications
- o Design Specifications

### **PERFORMANCE STANDARDS**

- o No Detectable Emission Limits

## **VALVE SCREENING FREQUENCIES**

### **GENERAL**

- o Monitor Monthly
- o Skip to Quarterly Monitoring for EACH VALVE Not Leaking for 2 Successive Months

### **ALTERNATIVE 1**

- o Notify Administrator
- o Conduct Performance Test
- o Screen All Valves Annually in a 1 Week Period
- o >2% Valves Leaking is a Violation

### **ALTERNATIVE 2**

- o Notify Administrator
- o Conduct Monthly Tests
- o Option 1 - After 2 Successive Quarters with < 2% Leaking Skip to Semi-Annual Monitoring
- o Option 2 - After 5 Successive Quarters with < 2% Leaking Skip to Annual Monitoring
- o Revert to Monthly Monitoring When >2% of Valves Leaking



## INVENTORIES

### CLOSED VENT SYSTEM AND CONTROL DEVICE DATA

#### COMPONENT DATA

- o List of Identification Numbers
- o List of Components Subject to the No Detectable Limit
- o Dates of Compliance Tests
- o Instrument Readings
- o List of Equipment in Vacuum Service
- o List of Difficult-to-Monitor Valves
- o List of Unsafe-to-Monitor Valves

#### FACILITY DATA

- o Design Capacity
- o Equipment Not in VOC Service

## RECORDKEEPING

### TAG LEAKS

#### MAINTAIN LOGS FOR 2 YEARS

- o Component's Identification Number
- o Operator's Identification Number
- o Instrument's Identification Number
  
- o Dates Leak Detected
- o Dates Repair Attempted
- o Date of Successful Repair
- o Expected Date of Repair is >15 Days
- o Dates of Outages While Component Remained Unrepaired
  
- o Repair Method Used
- o Reason Repair Delayed
- o >10,000 ppm Instrument Reading After Unsuccessful Repair

## OTHER RECORDS

### CLOSED VENT SYSTEMS AND CONTROL DEVICES

- o Schematics
- o Specifications
- o Piping and Instrumentation Drawings
- o Monitoring Plan
- o Non-operational Periods
- o Start-up/Shut-down Dates

### VALVES, UNSAFE-TO-MONITOR

- o Identification Numbers
- o Reasons Why Classified as Unsafe
- o Monitoring Plan

### VALVES, DIFFICULT-TO-MONITOR

- o Identification Numbers
- o Reasons Why Classified as Difficult-to-Monitor
- o Monitoring Plan

### EXEMPTIONS

- o Design Capacities
- o Feed Material Analyses
- o Not-in-VOC Service Support Data

## NSPS INITIAL REPORTS

### PROCESS UNIT "A"

- o Number of Valves in Gas/Vapor or Light Liquid Service
- o Number of Pumps in Light Liquid Service
- o Number of Compressors

### PROCESS UNITS "B" . . . "N"

- o Number of Valves in Gas/Vapor or Light Liquid Service
- o Number of Pumps in Light Liquid Service
- o Number of Compressors

## BENZENE/VINYL CHLORIDE INITIAL REPORTS

### STATEMENT OF INTENT

#### PROCESS UNIT "A"

- o Equipment Identification
- o Equipment Type
- o Percent VHAP
- o State of VHAP
- o Method of Compliance

#### PROCESS UNIT "B"... "N"

- o Equipment Identification
- o Equipment Type
- o Percent VHAP
- o State of VHAP
- o Method of Compliance

### SUBMISSION DATES

## BENZENE/VINYL CHLORIDE REPORTING

### INITIAL

#### SEMI-ANNUAL, Process Unit "A" . . . "N" (List for Each)

- o Number of Valves Leaking
- o Number of Valves Leaking That Were Not Repaired
- o Number of Pumps Leaking
- o Number of Pumps Leaking That Were Not Repaired
- o Number of Compressors Leaking
- o Number of Compressors Leaking That Were Not Repaired
- o Shut-down Infeasibility Support Information
- o Dates of Shut-downs
- o Inventory Revision/Update

## **INSPECTION PROCEDURES and TIME REQUIREMENTS**

### **PRE-INSPECTION REVIEW (0.5 to 2.0 Hours)**

- o Initial Reports
- o Semi-Annual Reports
- o Notifications
  
- o Previous Inspection Reports
- o Plant Safety Equipment Guidelines
  
- o Portable VOC Instrument Prechecks and Calibration (Level 3 Inspections Only)

### **TRAVEL TO INSPECTION SITE (1 to 4 Hours)**

### **PRE-INSPECTION MEETING (0.5 Hours)**

- o Inspection Scope
- o Inspection Agenda
- o Data and Information Considered Confidential by Source
- o Semi-Annual Reports Received from Source
- o Notifications Received from Source

### **REVIEW OF RECORDS (1-2 Hours)**

- o Monitoring Frequencies
- o Extent of Time Repair
- o Reasons for Delay of Repair
- o Portable Instrument Calibrations, Calibration Precision Tests, and Response Time Tests

### **OBSERVE COMPONENT SCREENING PROCEDURES (2-3 Hours)**

- o Observe Instrument Check-out/Start-up and Calibration
- o Observe Screening of 20 to 50 Components
- o Observe Several Difficult-to-Monitor Valve Locations
- o Observe Several Unsafe-to-Monitor Valve Locations
- o Confirm Proper Tagging
- o Conduct Independent Screening Tests  
(Level 3 Inspection Only)

### **CHECK COMPLIANCE WITH EQUIPMENT STANDARDS (0.5 to 1 Hour)**

- o Closed Sampling Lines
- o Alarms
- o Control Device Operating Conditions

### **POST-INSPECTION MEETING (0.5 Hours)**

### **TRAVEL BACK TO AGENCY OFFICE (1 to 4 Hours)**

### **EQUIPMENT MAINTENANCE (0.25 to 0.5 Hour)**

- o Clean and Store Safety Equipment
- o Recharge and Store VOC Analyzers  
(Level 3 Inspection Only)

## PORTABLE VOC INSTRUMENT PROBLEMS

WEAK BATTERIES

AIR INFILTRATION

CONTAMINATION AND GAS FLOW BLOCKAGE

POOR LEAK PLUME CAPTURE

GROSS CONTAMINATION

- o Flame Ionization Detectors - Flameout
- o Photoionization Detectors - Optical Surface Deposits
- o Catalytic Detectors - Sensor Volatilization

NOTE: ESSENTIALLY ALL INSTRUMENT PROBLEMS RESULTS  
IN UNDETECTED LEAKS

## PORTABLE VOC EQUIPMENT LIST

FLAME IONIZATION DETECTOR

with,

- o Spare Battery
- o Spare Charger
- o Spare Probe
- o Particulate Filters
- o Precision Rotameter
- o 5-Liter Tedlar Bag
- o Calibration Gas Kit
- o Cylinder Mounting Equipment

PHOTOIONIZATION ANALYZER

with,

- o Spare Lamp
- o Spare Intrinsically Safe Battery
- o Spare Charger
- o Soap Bubble Flow Meter
- o 5-Liter Tedlar Bags
- o Calibration Gas Kit
- o Lamp Cleaning Compound
- o Lamp Cleaning Cloth

CATALYTIC COMBUSTION ANALYZER

with,

- o Spare Sensor
- o Spare Intrinsically Safe Battery
- o Spare Recharger
- o Spare Particulate Filters
- o Spare Rotameter

LABORATORY/SHOP FACILITIES

- o Ventilated Hoods
- o Cylinder Racks
- o Bench Space

**SAFETY EQUIPMENT - VOC INSPECTIONS**  
(OTHER EQUIPMENT MAY ALSO BE NEEDED  
IN SPECIAL CIRCUMSTANCES)

**TRIPLE GAS DOSIMETER**

**RESPIRATORS**

- o Full- and Half-Face Respirators  
(Check with Agency Safety Officer)
- o Respirator Carrying Pouches
- o Spare Cartridges or Canisters
- o Emergency Respirators

**EYEWEAR**

**SAFETY SHOES**

(Several Types of Shoes May be Required)

**EXPLOSION PROOF FLASHLIGHT**

**EAR PROTECTION**

**PROTECTIVE CLOTHING**

### **Note from the Editor**

The information contained in this document has been assembled solely for the purpose of general instruction in the emissions, control and inspection of VOC sources. Nothing in this document should be construed as representing official policy or guidance. Readers are advised to contact either their state agency or the USEPA regional office for official policies and rules and their interpretation.

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# VOC Properties

# Organic Chemistry Review

## Lesson Goal and Objectives

### *Goal*

To familiarize you with the concepts and terminology of organic chemistry that will prepare you for the technical literature associated with the measurement of organic compounds.

### *Objectives*

Upon completing this lesson, you should be able to:

1. classify organic compounds into the following groups:
  - a. aliphatic hydrocarbons (alkanes, alkenes, alkynes)
  - b. aromatic hydrocarbons
  - c. oxygenated compounds (ethanols, ethers, ketones, aldehydes, esters, acids)
  - d. amines, mercaptans
2. describe the difference between a straight chain hydrocarbon compound and an aromatic hydrocarbon compound.
3. recognize the structure of problem organic pollutants, such as dioxin, benzo alpha-pyrene, and polychlorinated biphenyls, that are frequently discussed in the popular and technical literature.
4. identify the importance of chemical properties of organic compounds, such as reactivity, for developing air pollution control regulations.

## Introduction

Organic chemistry is the study of carbon compounds. Carbon has the property of being able to bind with itself to form long chains, rings, and other chemical structures. Carbon can also bind with other elements to yield an almost endless number of compounds. This combining power, and the number of compounds produced as a result, makes organic chemistry so important to modern society.

Although many organic compounds occur in natural products, others have been made solely in the laboratory. Modern technology can produce large quantities of naturally occurring compounds and new, synthesized compounds for a large number of useful purposes. This has resulted in the introduction of materials into the environment which may sometimes have other than beneficial effects. The inability

of the environment to accommodate large quantities of organic compounds in the atmosphere can result in the production of smog. Also, a simple compound produced in quantity for plastics manufacturing may be discovered to cause toxic effects in the people handling it.

The importance of measuring organic compound emissions to the environment has become clear over the past decade. A better understanding of their role in photochemical oxidant generation and an increasing awareness of their direct effects on human health has necessitated the improvement and standardization of monitoring techniques. Because of the large number of different organic species, finding a "best" measurement method has been difficult; some methods work better for one class of compounds than for another. To understand the applicability and limitations of the various measurement techniques, we must first review some of the basic terminology of organic chemistry. This lesson will review the classification schemes of this field and will discuss some important chemical concepts associated with it.

## The Combining Power of Carbon

Elements combine with other elements to form compounds. The compounds produced depend principally on the electronic configurations of the elements. Carbon, for example, is composed of a positively charged central nucleus and twelve negatively charged electrons outside of it. Four of these electrons are available in carbon to form chemical bonds. Let us take an example of one of the simplest organic compounds, methane, which is composed of one carbon and four hydrogen atoms and is given the symbol,  $\text{CH}_4$ . The left side of Figure 2-1, gives a representation of the carbon atom, and its four available electrons. Hydrogen, also shown in the figure, differs from carbon since it has only one electron available for bonding.

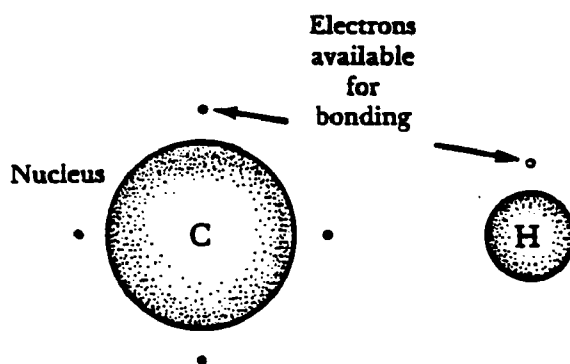


Figure 2-1. Carbon and hydrogen atoms.

To form the chemical bonds necessary to make methane, the hydrogen atoms must first come close to the carbon atom. When this happens, the hydrogen nuclei and the carbon nucleus will share electrons between each other. This is shown for

methane schematically in Figure 2-2a. The bonds, called *covalent bonds*, are actually an electronic arrangement between the two types of elements. The positive charge of a hydrogen nucleus would normally be repelled by a positive charge in a carbon nucleus. However, the two negatively charged electrons, one from the hydrogen and one from the carbon, mediate between the two nuclei to contribute to the glue of the chemical bond. The negative charge of the shared electron pair attracts both nuclei and holds them together in a bond (Figure 2-2b).

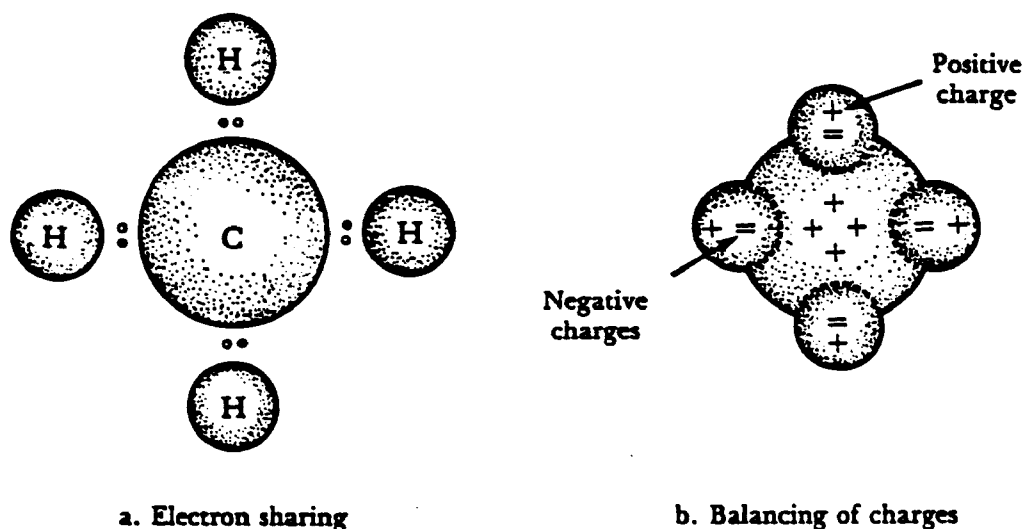


Figure 2-2. Methane.

Methane can be represented in a number of ways, as can all organic compounds. Figure 2-3 shows the common symbol, the electron-dot formula, a figure with stick bonds representing the electron pair, and the actual three-dimensional structure of methane.

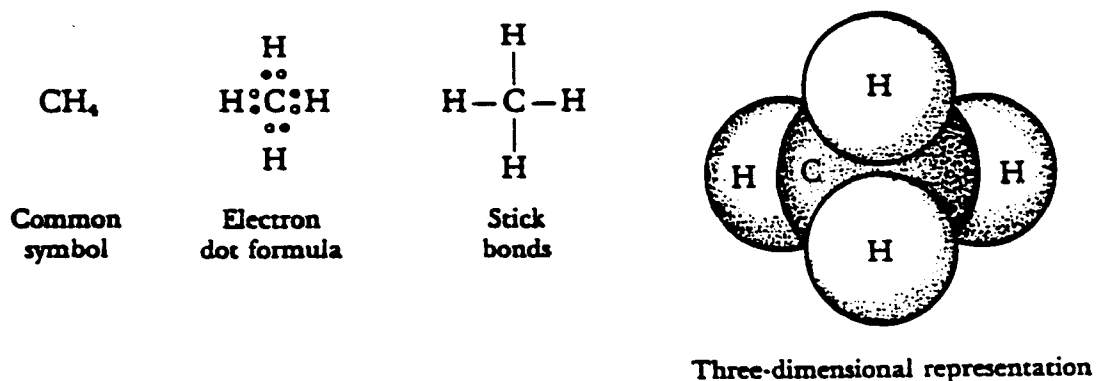


Figure 2-3. Representations for methane.

## Straight Chain Hydrocarbons

One of the most important properties of carbon is its ability to form covalent bonds with other carbon atoms. As a result, chains of carbon can be produced. These chains can be either straight or branched, as shown in Figure 2-4 for a number of hydrocarbons (compounds composed of just carbon and hydrogen). Isooctane is a branched form of the straight octane chain shown.

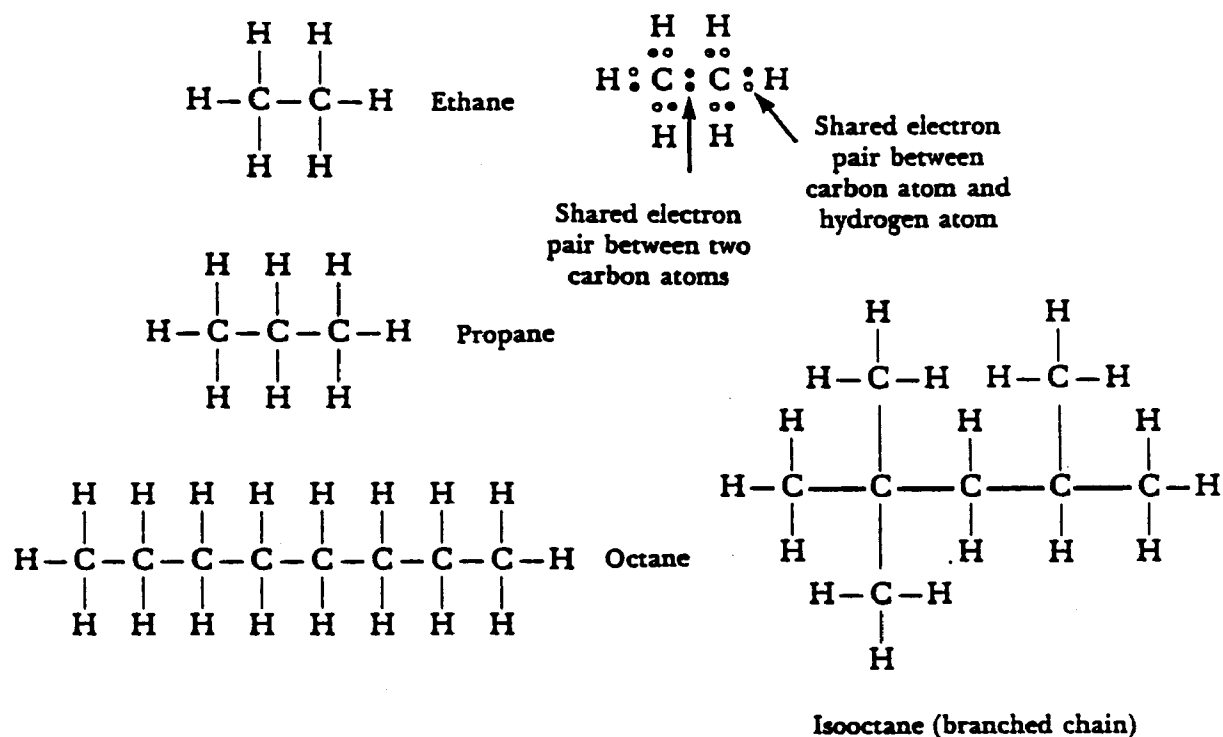


Figure 2-4. Bonding between carbon atoms—straight and branched chains.

The number of possibilities associated with branching results in different compounds with identical elements, but with different structures. These compounds are called isomers of each other. In Figure 2-4, octane and isooctane are isomers. A simpler example is that of the isomers of butane,  $\text{C}_4\text{H}_{10}$  (Figure 2-5).

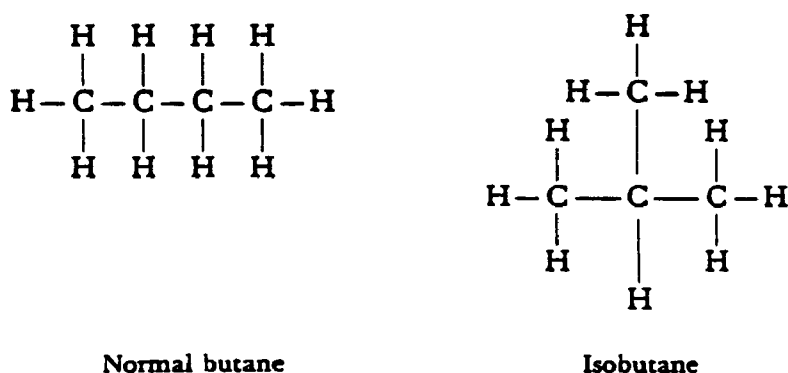


Figure 2-5. Isomers of butane.

Another special property of carbon is that it can share more than one electron with another element. In other words, a carbon can form either single or multiple bonds. The simplest example is that of the double-bonded compound, ethylene,  $C_2H_4$  (Figure 2-6).

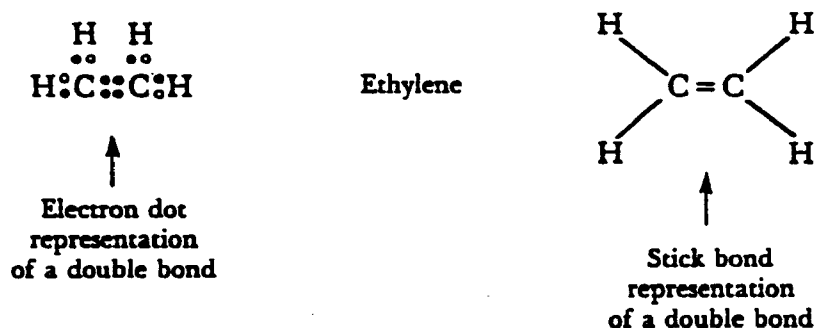


Figure 2-6. The double bond of ethylene.

Acetylene,  $H-C\equiv C-H$ , is an example of a triple-bonded hydrocarbon. Carbon can also form multiple bonds with other elements such as oxygen, sulfur, and nitrogen. Double-bonded compounds are quite important reactants in the generation sequences for photochemical oxidants. The double bond provides a reactive site where the molecule can be broken apart or formed into other species.

### Ring Structures

Another special property of carbon is the ability of carbon chains to turn back on themselves to form rings. Rings may be either singly or multiply-bonded. For example, consider the ring structures of cyclohexane and benzene (Figure 2-7).

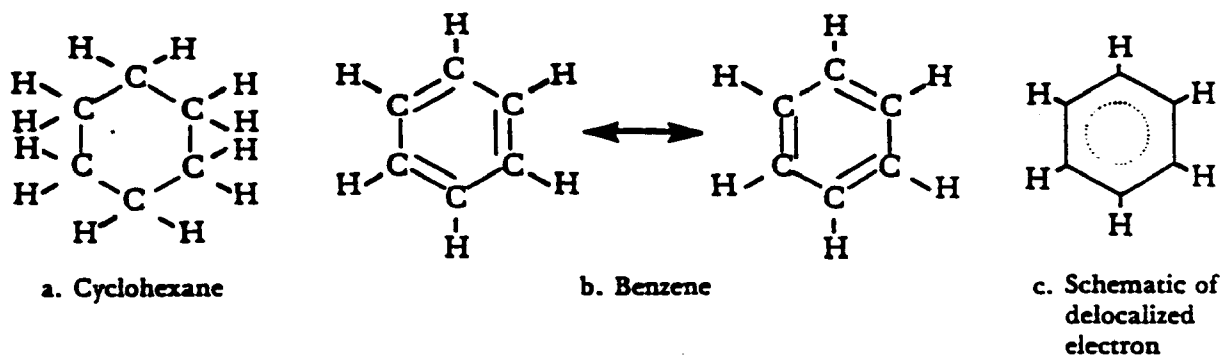


Figure 2-7. Ring structures.

Cyclohexane contains two less hydrogen atoms than its corresponding straight chain hydrocarbon containing the same number of carbon atoms. Benzene, on the other hand, contains three double bonds and even fewer hydrogens. As shown in the figure, the double bonds can be thought of as shifting between different carbon

atoms. In actuality, the electrons associated with the bonds are spread evenly around the ring as shown in Figure 2-7c. This "delocalization" of electrons creates a very stable structure with very special properties. Ring compounds containing delocalized electrons are classified in a group known as aromatic compounds because many of them have a pronounced odor. The properties of aromatic compounds can vary quite considerably. For example, because benzene has been found to be carcinogenic, NESHAPs are currently being developed for its control. On the other hand, toluene, which has the structure in Figure 2-8

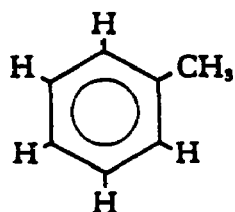


Figure 2-8. Toluene.

has been found not to be a toxic material and will not be regulated under NESHAPs. The xylenes (Figure 2-9) are, however, still being evaluated.

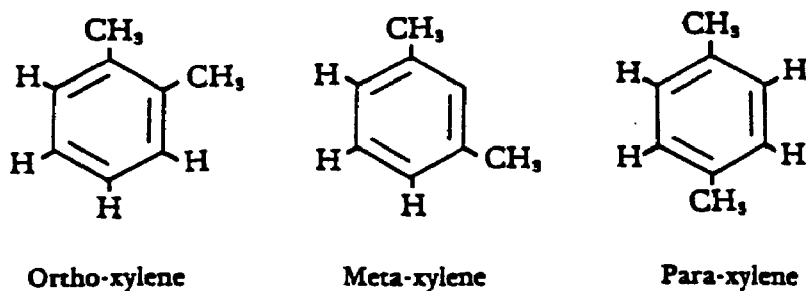


Figure 2-9. Xylene.

Benzene rings can also be combined to each other. One way of doing this is to join two carbons of two benzene rings by a single bond to obtain a biphenyl (Figure 2-10). (The term *phenyl* is often used to refer to benzene rings.)

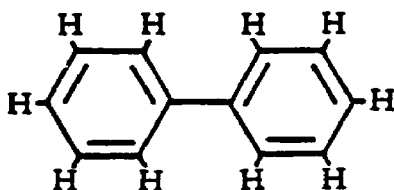


Figure 2-10. Biphenyl.

Another way to combine benzene rings is to produce networks of ring structures such as that shown in Figure 2-11.

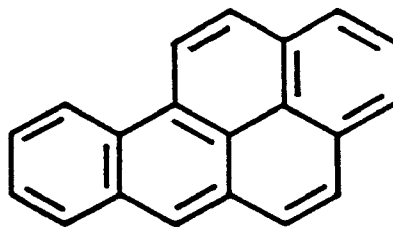


Figure 2-11. Benzo[α]pyrene (BaP).

(Note: It is common practice not to show the hydrogen atoms in the aromatic structures.) These are called polynuclear aromatics (PNA—an older acronym), or polycyclic aromatic hydrocarbons (PAHs—acronym currently popular). The electrons in such structures are delocalized as they are in benzene. Some of these compounds can contribute to the formation of cancer.

Hydrocarbons are commonly divided into two major groups, aliphatic hydrocarbons and aromatic hydrocarbons. Compounds having an open-chain structure are known as aliphatic compounds and are further subdivided into alkanes or paraffinic hydrocarbons (single-bonded carbon compounds), alkenes or olefins (hydrocarbons containing a double bond between two carbons), and the alkynes or acetylenes (hydrocarbons containing a carbon-carbon triple bond). These classifications are summarized in Figure 2-12.

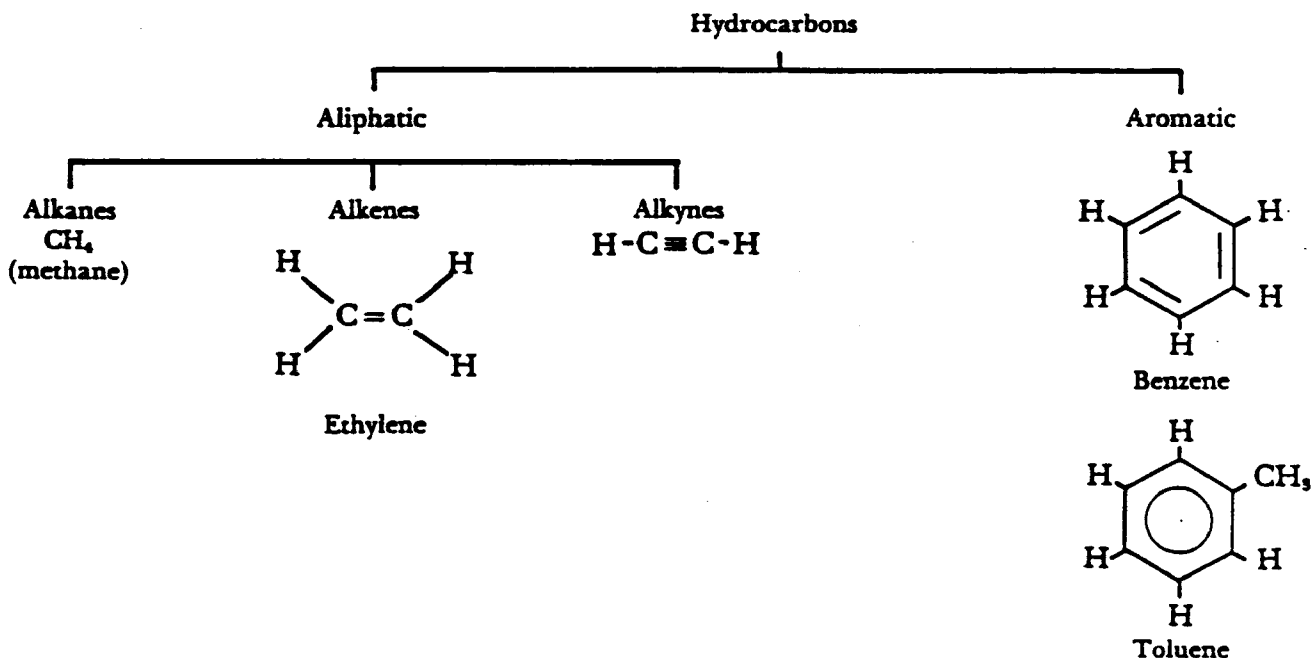


Figure 2-12. Classification of hydrocarbons with examples.



Ring compounds such as cyclohexane are classified in a different category known as alicyclics.

The nomenclature associated with aliphatic compounds forms the basis for naming more complicated materials. For example, prefixes have been established for aliphatics, based on the number of carbon atoms they contain (Table 2-1).

Table 2-1. Prefixes for aliphatics.

Prefix	Number of carbon atoms	Examples
meth-	1	methane
eth-	2	ethylene
prop-	3	propane
but-	4	butane
pent-	5	pentyne
hex-	6	cyclohexane
hept-	7	heptane
oct-	8	octane

For further information on standard nomenclature systems for organic compounds, see IUPAC 1960.

Air pollution programs that address the control and measurement of organic compounds have also developed a number of terms and acronyms which appear in the literature. Among these are:

HC Hydrocarbon

THC Total Hydrocarbon—A term applied to measurements that report the total amount of hydrocarbons in the sample.

NMHC Nonmethane Hydrocarbons—A term applied to measurements that report the amount of hydrocarbons, excluding methane. This acronym has been popular since methane is not regarded as a precursor to the generation of photochemical smog.

Unfortunately, many documents and publications have misapplied these definitions. For example, one such document has stated: "for the purposes of this report, the term *hydrocarbon* sometimes refers to other organic materials also." This is clearly incorrect in terms of scientific practice and a more concerted effort has been made in current programs to correctly identify the larger class of organic compounds which are regulated. This has led to another set of definitions and acronyms including:

TGNMO Total Gaseous Nonmethane Organics—The total measure of gaseous organic compounds in a sample, excluding methane.

NMOC Nonmethane Organic Compound—A measure of organic compounds in a sample, excluding methane.

VOC Volatile Organic Compound—Any organic compound that, when released into the atmosphere, can remain long enough to participate in photochemical reactions. Almost all organics that can be considered VOCs have vapor pressures greater than 0.1 mm Hg at 20°C and 760 mm Hg; a typical regulatory definition.

## The Classification of Organic Compounds

The study of organic chemistry would be simple indeed if it incorporated only compounds composed of carbon and hydrogen. Instead, other elements and groups of elements can be attached to hydrocarbon chains and rings to provide wide-ranging types of compounds. Organic chemists talk about these compounds by using a short-hand notation.

First, hydrocarbons that join to other elements or groups of elements are often called radicals. For example, when a group consisting of oxygen and hydrogen attaches to a single carbon atom to form methyl alcohol,  $\text{CH}_3\text{—OH}$ . Figure 2-13 represents the methyl radical.

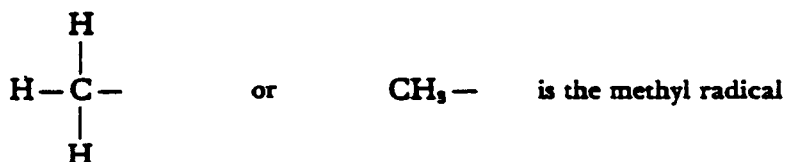


Figure 2-13. Methyl radicals.

(The dash, —, corresponds to the covalent bond of the stick figures.) In ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{—OH}$ , the hydrocarbon group  $\text{CH}_3\text{CH}_2\text{—}$  is called the ethyl radical.

Secondly, the elements or groups of elements attached to the hydrocarbon radicals are known as functional groups. Some examples of functional groups are the —OH group which is characteristic of organic alcohols, the —NH<sub>2</sub> group for amines, the —SH group for mercaptans, and —Cl for organic chlorides. The functional groups located on a hydrocarbon chain or ring determine the principle chemical properties of the molecule. For this reason the study of organic chemistry is often divided into a series of studies of compounds classified by their functional group. When a discussion centers around the properties of the functional group and not of the hydrocarbon radical, the radical is often merely represented by the symbol R— (the dash again stands for a bond). The symbol R—OH or ROH, thus stands as a general expression for alcohols.

We will discuss a number of these classes in this lesson. Of primary importance to the environmental scientist are the classes associated with compounds that contain oxygen, chlorine, nitrogen, or sulfur.

## Organic Compounds Containing Oxygen

Let us examine first, the functional groups associated with the oxygen molecule. These are:

Group	Compound class
$\text{—O—H}$	Alcohols
$\text{—O—}$	Ethers
$\begin{array}{c} \text{O} \\   \\ \text{—C—H} \end{array}$	Aldehydes
$\begin{array}{c} \text{O} \\   \\ \text{—C—} \end{array}$	Ketones
$\begin{array}{c} \text{O} \\   \\ \text{—C—O—H} \end{array}$	Organic acids
$\begin{array}{c} \text{O} \\   \\ \text{—C—O—} \end{array}$	Esters

Oxygen has the property of being able to share two electrons with other elements. (From the first part of this lesson, we have seen that carbon will share four electrons and hydrogen shares one electron.) Alcohols are composed of an  $\text{—OH}$  group, where one electron is shared with a hydrogen and the other with a carbon. Common alcohols are shown in Figure 2-14.

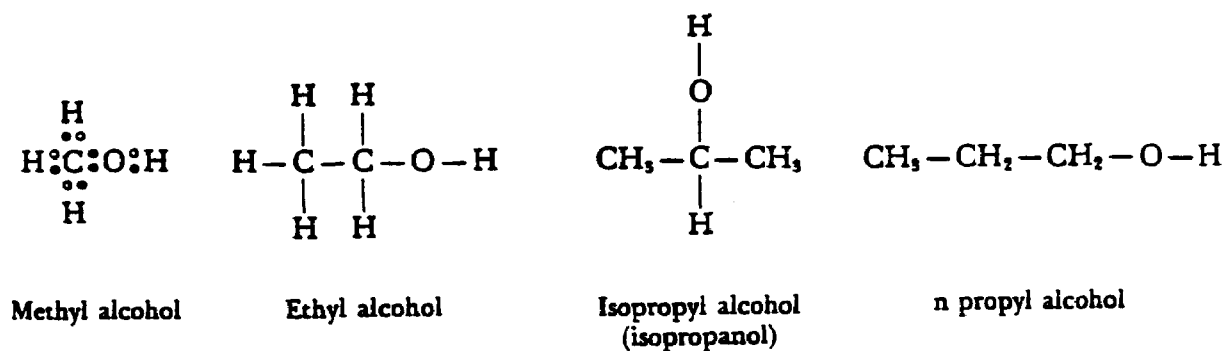


Figure 2-14. Common alcohols.

Aromatic alcohols can also be made, and are called phenols (Figure 2-15). Phenols tend to behave more like acids than alcohols because of the properties of the benzene ring.

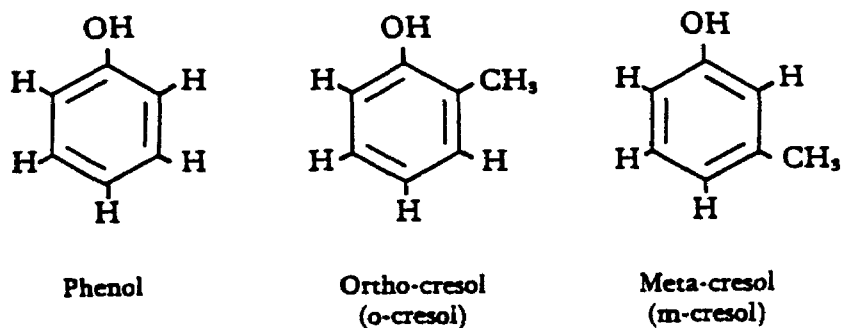


Figure 2-15. Phenols.

Ethers form a class of compounds where the oxygen atom shares each of its electrons with a different carbon atom. They have the general formula  $R-O-R$ , where the radicals,  $R$ , may be different. Diethyl ether,  $CH_3CH_2-O-CH_2CH_3$ , is an ether well known as an anesthetic. A special group of ethers known as *cyclic ethers* are important in the plastics industry for making epoxides and other compounds. Two compounds representative of this group are ethylene oxide and propylene oxide (Figure 2-16).

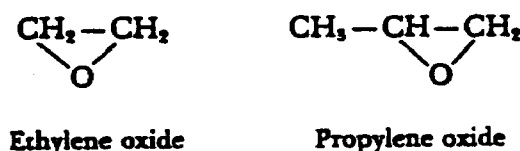
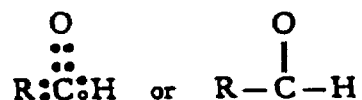


Figure 2-16. Cyclic ethers.

Aldehydes compose a group of compounds that contribute significantly to the generation of photochemical oxidants. By being either emitted into the atmosphere or produced in the oxidant reaction sequences, aldehydes provide numerous reaction pathways for the generation of photochemical oxidants. The aldehyde group is composed of an oxygen atom sharing two electrons in a double bond with a carbon atom, with a hydrogen atom sharing an additional electron.



The simplest aldehyde is formaldehyde,  $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H}$ , a compound which has caused some problem in urea-formaldehyde foam insulation products. A methyl radical attached to the aldehyde functional group gives acetaldehyde or ethanol (Figure 2-17). A more complicated aldehyde, acrolein, is found in photochemical smog and is quite reactive.

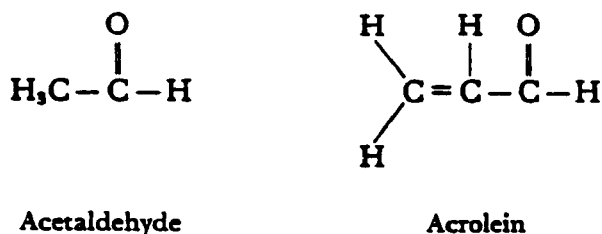


Figure 2-17. Acetaldehyde and acrolein.

Ketones are widely used as solvents in industry. Acetone, the simplest ketone, characterizes this classification, where a carbon double-bonded to an oxygen atom is bonded with two other carbons (Figure 2-18).

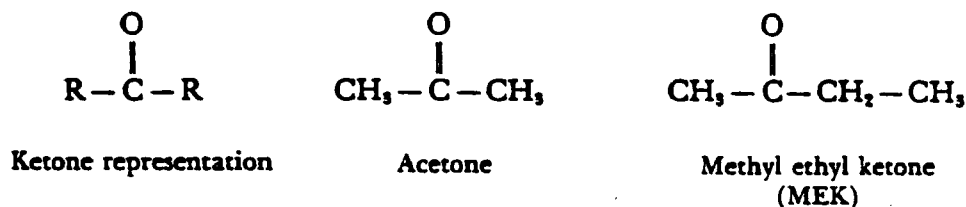


Figure 2-18. Ketones.

Methyl ethyl ketone is widely used as a solvent in the coatings industry and is popularly known as MEK. The ketones differ from the aldehydes by the replacement of the aldehyde hydrogen with a carbon group. Ketones are also reactive and contribute to smog generation.

Some other oxygen-containing compounds are the organic acids, esters, and acid anhydrides. Acids have the structure shown in Figure 2-19a and are often represented by the form  $\text{RCOOH}$ . Acetic acid, found in vinegar, has the structure shown in 2-19b. Another type of acid, the peroxyacids, have an extra oxygen to give the form in 2-19c. The peroxyacids are generated in photochemical smog and are extremely reactive, being able to break apart and initiate chain reactions.

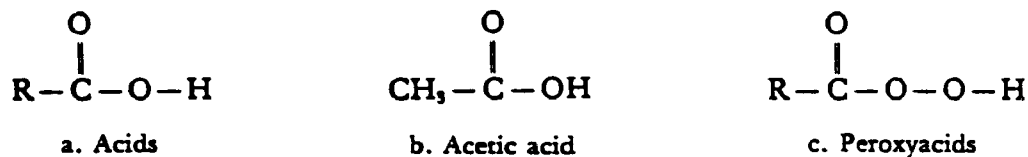


Figure 2-19. Acids.

Acid anhydrides are derivatives of organic acids. Basically, they are a combination of two acids with the removal of a water molecule (hence the term *anhydride*). They have the structure shown in Figure 2-20a.

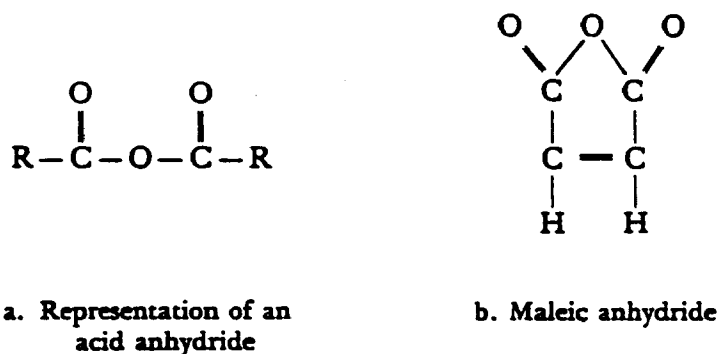


Figure 2-20. Acid anhydrides.

Maleic anhydride (Figure 2-20b) is the special case of a cyclic anhydride used in the production of chemicals and plastics. It may have toxic effects.

Lastly, another type of derivative of organic acids is the ester (Figure 2-21) often represented by  $\text{RCOOR}$ .

Here the hydrogen of the acid is replaced by a hydrocarbon radical. These compounds are generally sweet smelling. They are generally formed by reacting acids with alcohols.

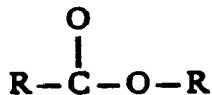


Figure 2-21. Ester.

## Organic Compounds Containing Chlorine

Organic compounds containing chlorine are used widely in industry as solvents and as starting compounds for producing other chemicals. Unfortunately, many of them may cause serious environmental problems. In addition to contributing to toxicological problems, some compounds in this class have been implicated in the problem of the depletion of the stratospheric ozone layer. Although many of the compounds do not react in the photochemical oxidant cycles, the Environmental Protection Agency recommends that emissions of these compounds be reduced because of their possible toxic effects. Figure 2-21 illustrates some of the organic chlorides which are currently of concern to the EPA.

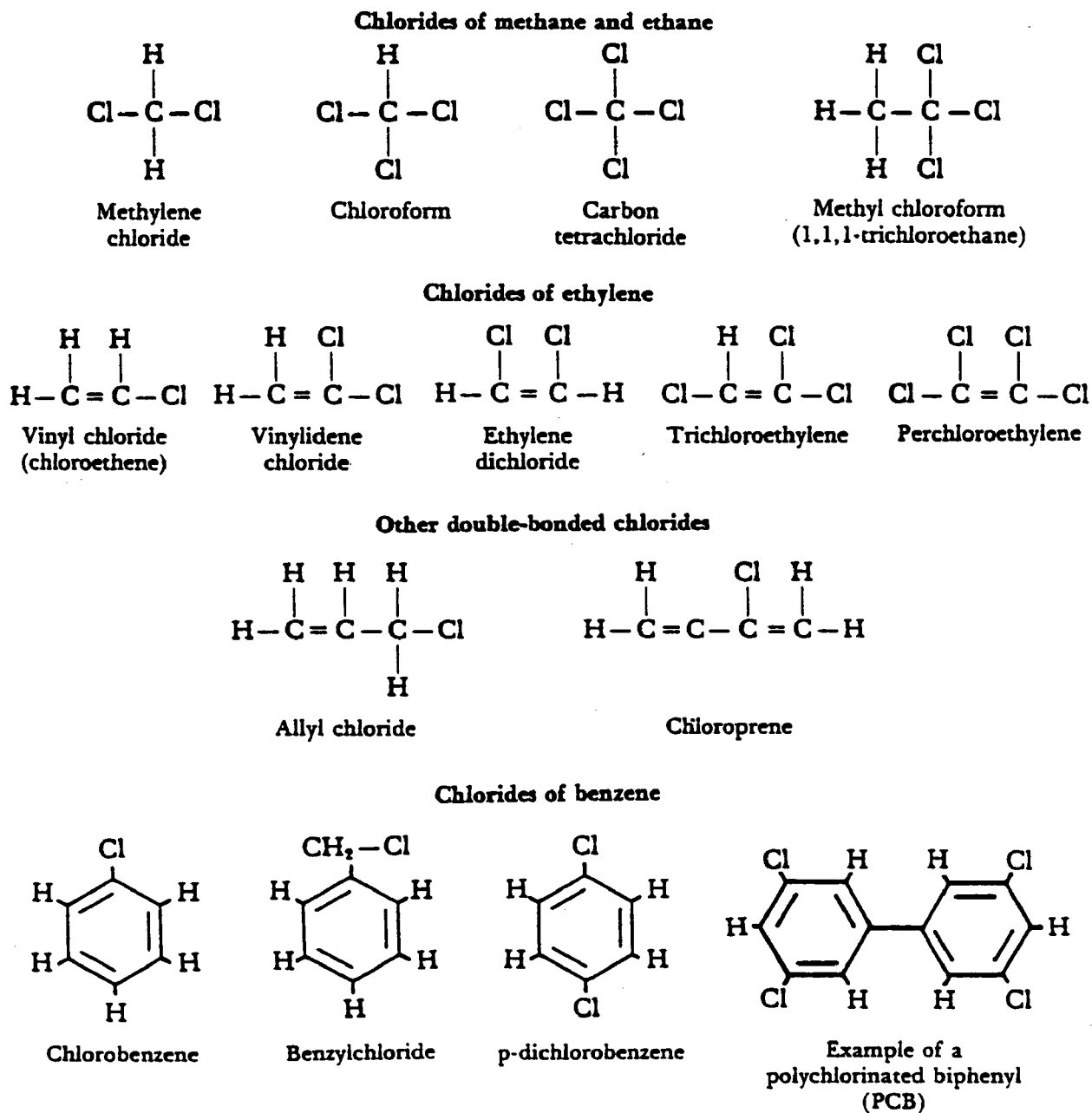
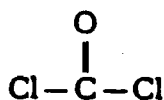
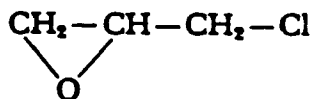


Figure 2-21. Organic chlorides or chlorocarbon.

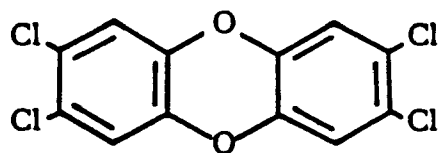
Compounds that contain combinations of carbon, hydrogen, oxygen, and chlorine can also be prepared. Figure 2-22 presents examples of some which are of serious concern.



Phosgene



Epichlorohydrin



Example of a  
dioxin (TCDD)  
2,3,7,8 tetrachlorodibenzo-p-dioxin

Figure 2-22. Compounds containing both oxygen and chlorine.

### Organic Compounds Containing Nitrogen

Organic compounds that contain nitrogen constitute another important class of substances for the environmental scientist. The organic nitrates are end products in the photochemical oxidant reaction sequences. Amines are odorous materials and have often been the subject of nuisance complaints. Other combinations of nitrogen with carbon, oxygen, and hydrocarbon result in chemicals which may be toxic.

Nitrogen has the capability of sharing either three or five electrons with other atoms. The simplest nitrogen compounds are the amines. These compounds share three electrons with either carbon or hydrogen, having the general structures illustrated in Figure 2-23.

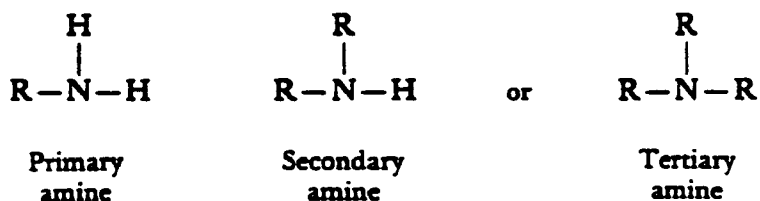


Figure 2-23. Amines.

Methyl amine,  $\text{CH}_3-\text{NH}_2$  is an example of a primary amine. The organic *nitrites* also have a nitrogen that shares three electrons, but these are shared with oxygen atoms instead of carbon and hydrogen:  $\text{R}-\text{O}-\text{N}=\text{O}$ .

The more complicated nitrogen compounds are those where the nitrogen atom shares five electrons with other atoms. The organic nitro compounds are an example here:  $\text{R}-\text{NO}_2$ . Other compounds in this group are the nitrates:  $\text{R}-\text{ONO}_2$ . Nitroethane,  $\text{CH}_3-\text{CH}_2-\text{NO}_2$  and ethyl nitrate,  $\text{CH}_3-\text{CH}_2-\text{ONO}_2$



are materials formed in photochemical smog. One quite active group of compound

called peroxyacetyl nitrates (PAN),  $\text{R}_3\text{C}(\text{O})\text{OONO}_2$ , is responsible for many of the adverse effects of photochemical smog.

### *Organic Compounds Containing Sulfur*

Kraft pulp mills produce a large number of by-product chemicals in the paper-making process. The sodium sulfide used in these operations reacts with the organic matter in wood chips to produce organic compounds that contain sulfur. One group of these, the mercaptans, have the structure  $\text{R-SH}$ , which is similar to that of alcohols. Methyl mercaptan,  $\text{CH}_3\text{-SH}$ , has a distinctive, unpleasant odor at very low concentration levels. Dimethyl sulfide  $\text{CH}_3\text{-S-CH}_3$  also is a malodorous product of this process. These compounds cause more of a nuisance problem than a problem to public health.

## Organic Chemistry—Reactivity

Organic compounds exhibit large differences in their ability to react with other chemicals. For example, the double-bonded hydrocarbons will be more reactive than the single-bonded hydrocarbons. Aldehydes will readily participate in the photochemical oxidant sequences; aromatic hydrocarbons will not. However, reactivity in the atmosphere is not the only concern of the environmental scientist. The toxic effects of organic chemicals or the nuisance problem of odorous materials also call for control of atmospheric emissions.

An early policy for emission control of organic compounds was that developed by the State of California, known as Rule 66. This was based on the differences of reactivity of compounds with sunlight. In these so-called "photochemical reactions," light energy interacts with a molecule to cause it to dissociate and produce *free radicals*. Look at this example of an aldehyde (Figure 2-24).

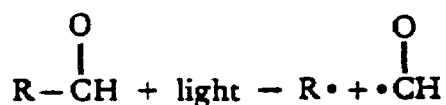


Figure 2-24. Free radical generation.

Note that the products of this reaction have unshared electrons. These materials are known as free radicals. They are extremely reactive and will attack other compounds so that they can share their electrons again. Complicated sequences of reactions involving free radicals are involved in the development of photochemical smog. Rule 66 attempted to control the emission of compounds that react readily in this process. The rule essentially required industry to replace reactive compounds with less reactive compounds.

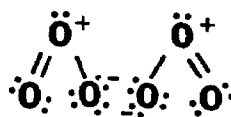
Although Rule 66 had some validity, it was not very effective in reducing ambient oxidant levels. The replacement compounds may not have been as reactive, but they were found to react with sunlight nevertheless; at a later time and at a location more distant from the area of the emission. In addition to this, EPA viewed the increased emissions of "nonreactive" chlorinated hydrocarbons used as replacement materials, as a threat to the stratospheric ozone. Other compounds with less reactivity were also suspected of having carcinogenic, mutagenic, or teratogenic effects on humans.

As a result of these problems, EPA adopted a policy of "positive emissions reduction." This EPA reactivity policy expressed in the *Federal Register* of July 8, 1977, 40 FR 35314, called for the reduction of organic emissions by the use of new technological processes or the application of control equipment. This policy has been incorporated in State Implementation Plans designed to bring ozone non-attainment areas into attainment status and has been extended to the New Source Performance Standards established for emission sources of organic compounds.

The policy of emissions reduction necessitates emissions monitoring. Progress in controlling toxic emissions or precursors to ozone formation is monitored by a variety of analytical methods. Because of the large difference in organic chemicals, methods often have to be designed for specific groups of compounds. Some methods, such as gas chromatography, can give the general information necessary for monitoring overall emissions. In subsequent lessons we will be examining a number of monitoring techniques and their application to the many groups of organic chemicals discussed here.

# PHOTOCHEMICAL OXIDANTS

## Ozone



## Peroxyacylnitrates

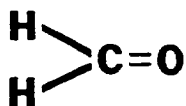
### PAN



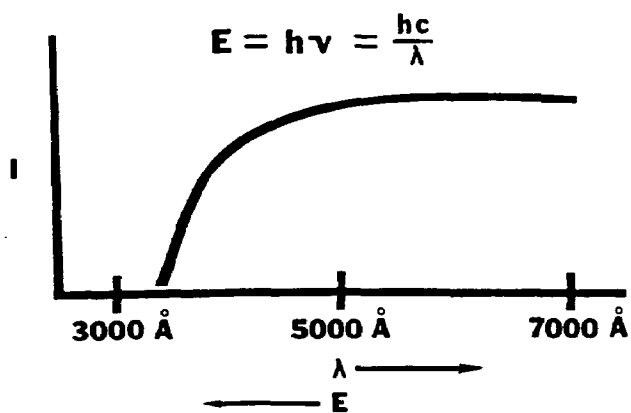
### PBzN

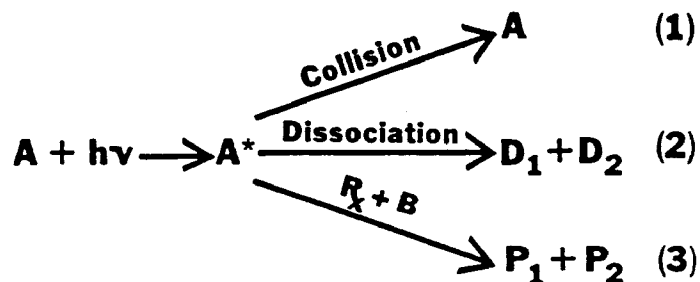


## ■ FORMALDEHYDE



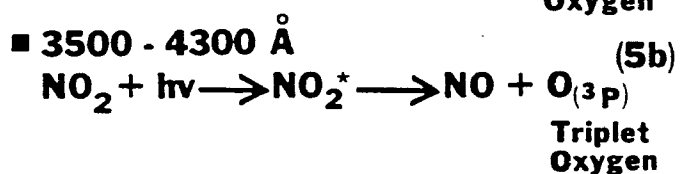
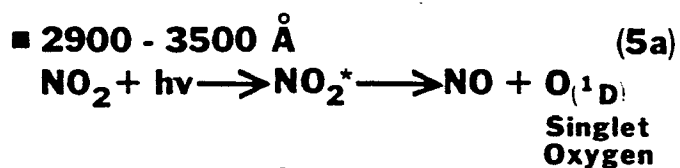
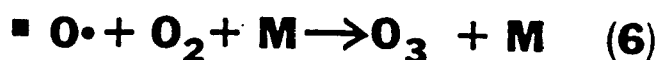
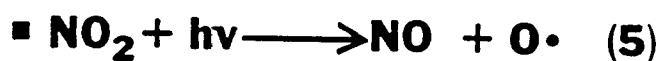
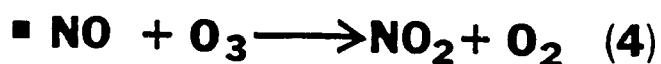
## ■ ACROLEIN





### "PHOTOSTATIONARY STATE"

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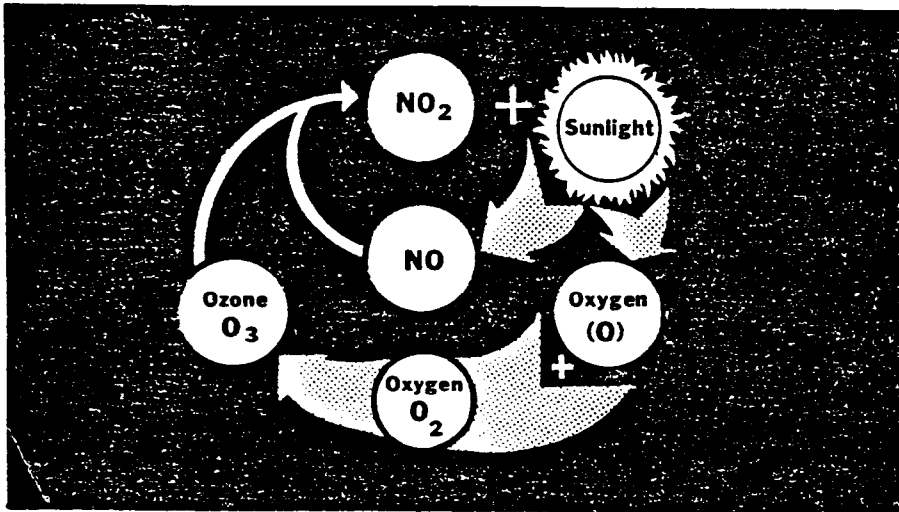


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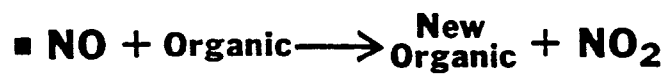
$$\blacksquare [O_3] = k \frac{[NO_2]}{[NO]}$$

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(7)



## NET $[O_3]$ INCREASED

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- Ozone not destroyed



- New organic species are formed which continue to reduce  $[NO]$

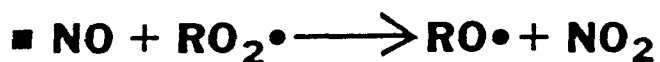
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## PEROXY RADICALS

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(7a)

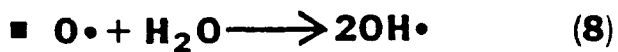


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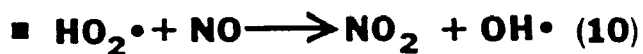
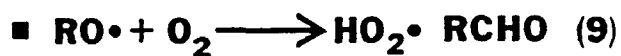
## PEROXY RADICAL FORMATION

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### STEP 1: Hydroxyl Radical Formation

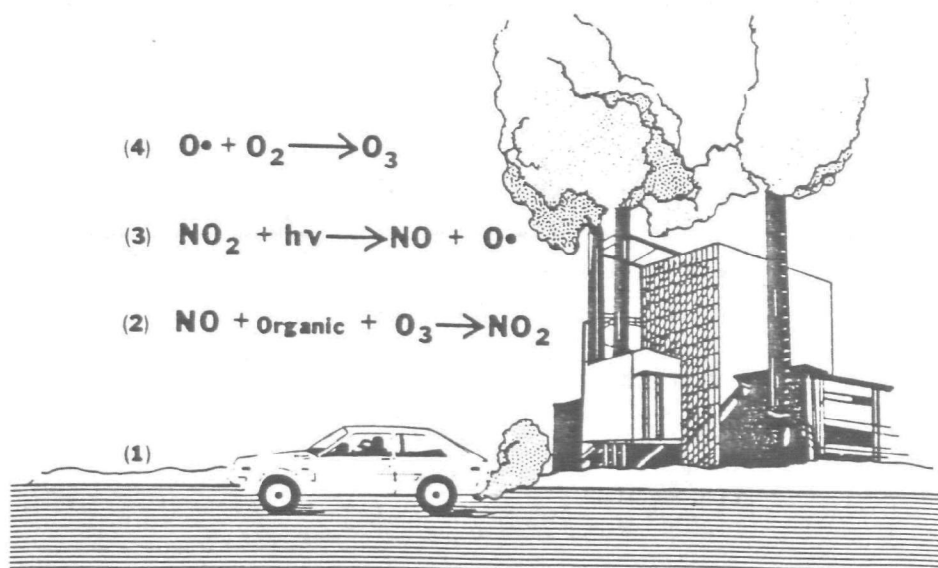
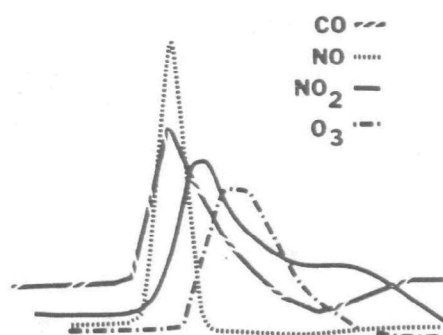
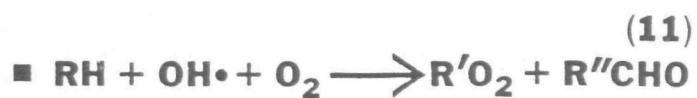


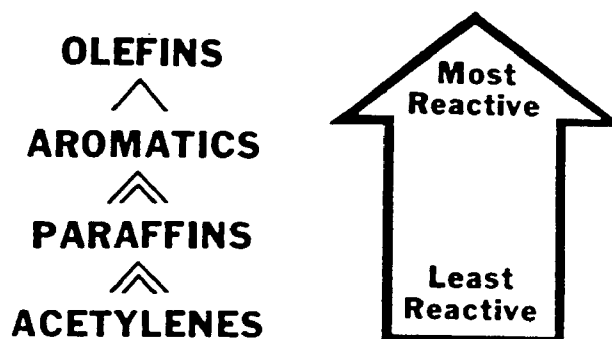
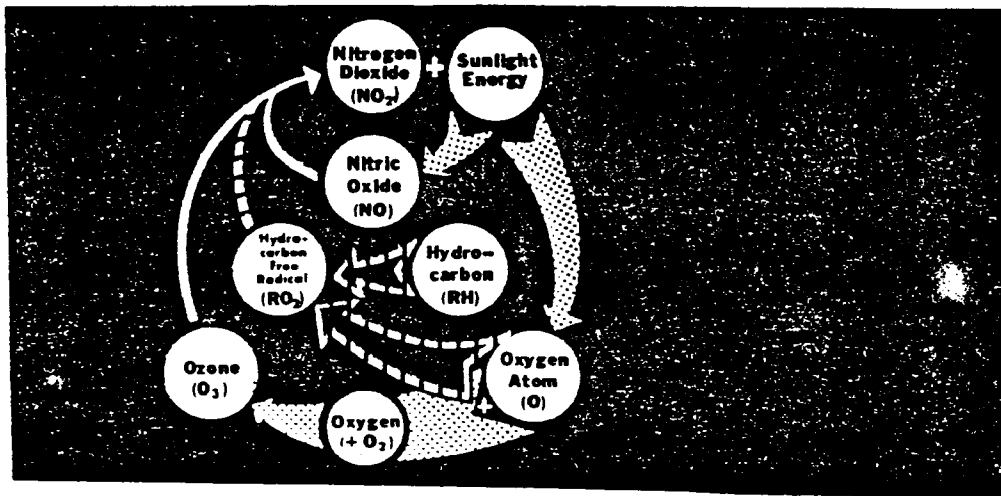
or



# PEROXY RADICAL FORMATION

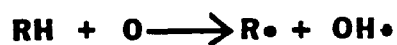
## STEP 2: Radical Formation





### R<sub>x</sub>n WITH ATOMIC OXYGEN

#### ■ Paraffins



#### ■ Aromatics

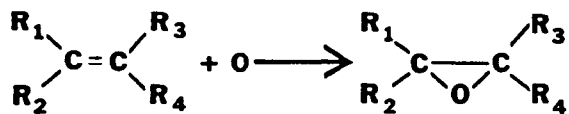




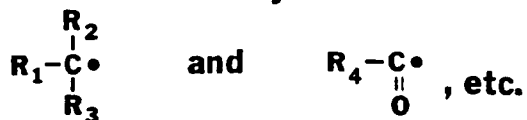
## $R_xn$ WITH ATOMIC OXYGEN

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### ■ Olefin



which yields

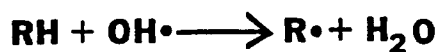



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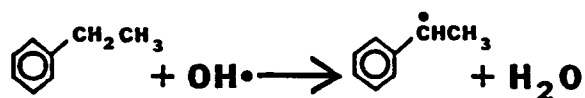
## $R_xn$ WITH $OH^\bullet$ RADICALS

---

### ■ Paraffins



### ■ Aromatics

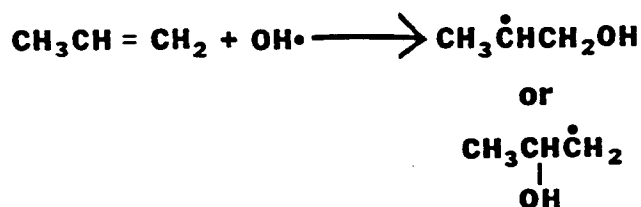



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## $R_xn$ WITH $OH^\bullet$ RADICAL

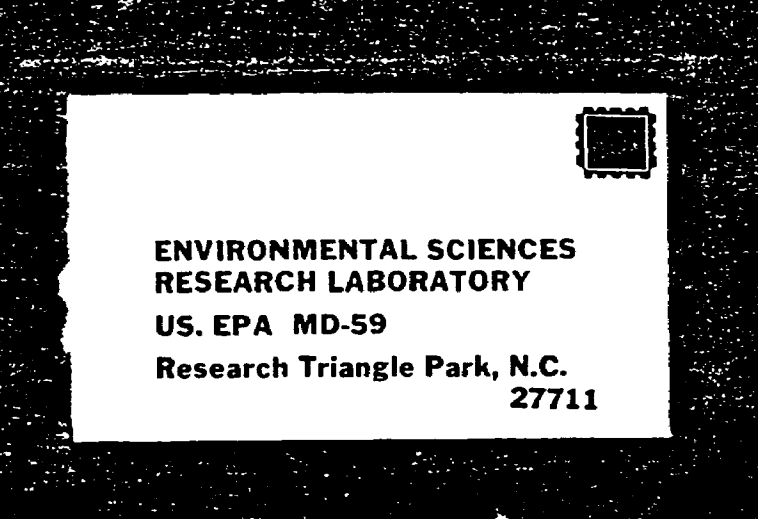
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### ■ Olefins





- [illegible]



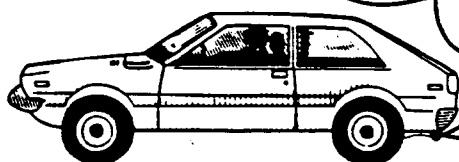
**ENVIRONMENTAL SCIENCES  
RESEARCH LABORATORY  
US. EPA MD-59  
Research Triangle Park, N.C.  
27711**

## HYDROCARBON COMPONENTS OF ATMOSPHERE

	Los Angeles	Kenosha, Wisc.
Paraffins	53 %	60%
Aromatics	20%	30%
Olefins	16 %	10%
Acetylenes	10%	neg

### MOBILE SOURCE CONTRIBUTION

Leaded Gas	Unleaded Gas	
38%	36%	Paraffins
13%	21%	Aromatics
36%	31%	Olefins
13%	10%	Acetylenes
1%	2%	Other

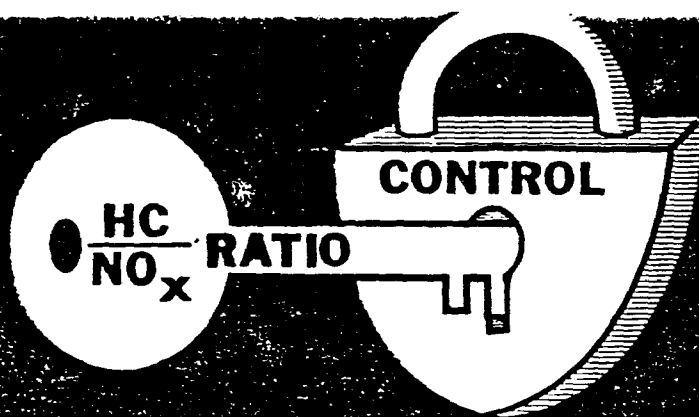


### ■ EPA-600/3-77-109 a & b

#### “Effect of Hydrocarbon Composition on Oxidant- Hydrocarbon Relationships”

#### PHASE I - Mobile Sources

#### PHASE II - Mobile and Stationary Sources



## **OZONE PRODUCTION DEPENDS ON:**

---

- Organics involved
  - Light intensity and duration
  - Temperature
- 

### ■ 6 HR IRRADIATION

Max  $[O_3]$  results at  $\frac{HC}{NO_x}$  ratio

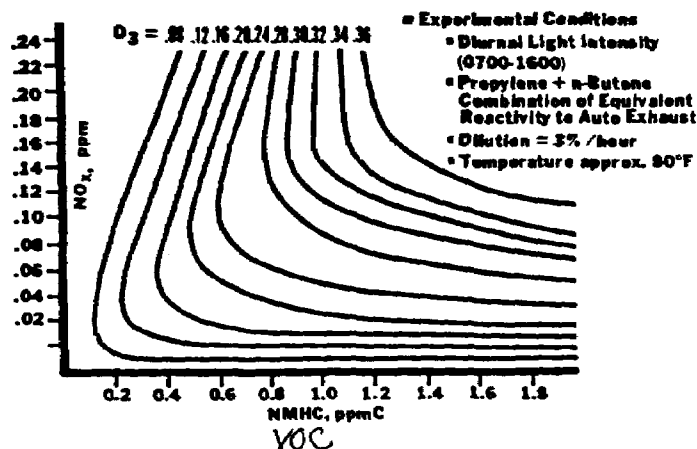
between  $\frac{10}{1}$  to  $\frac{15}{1}$

### ■ 10 HR IRRADIATION

Max  $[O_3]$  results at  $\frac{HC}{NO_x}$  ratio

$$= \frac{7}{1}$$

## OZONE VS INITIAL PRECURSOR LEVELS - MODELED RESULTS



## EKMA DOCUMENTS

- EPA-450/2-77-021 a & b  
November 1977

**“Use, Limitations, and Technical Basis of Procedures for Quantifying Relationships between Photochemical Oxidants and Precursors”**

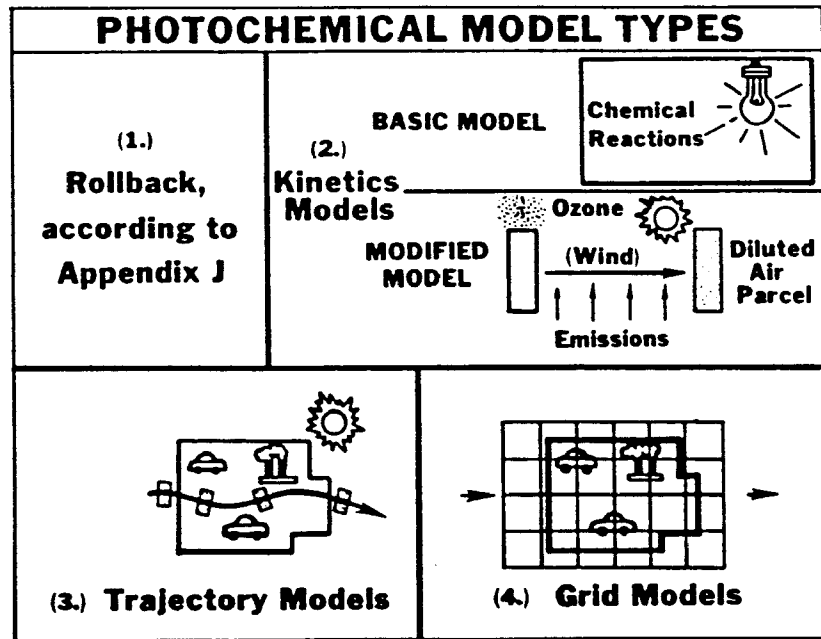
- EPA-450/3-77-022 a, b, c

**“Relation of Oxidant Levels to Precursor Emissions and Meteorological Features”**

**VOL. I: Analysis and Findings**  
**VOL. II: Review of Available Research Results and Monitoring Data**  
**VOL. III: Appendices**

**“International Conference  
on Photochemical  
Pollution and Its Control”**

The principal  
drawback to modeling  
is the possible inaccuracy  
in representing reality.



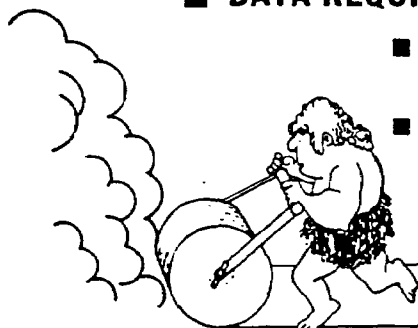
## AVAILABLE OXIDANT MODELS

MODEL TYPE	MODEL NAME AND/OR DEVELOPER
ROLLBACK	■ Rollback/Appendix J
BOX	■ Hanna and Gifford ■ EPA Box Model
KINETICS	■ Model for EKMA (EPA)
TRAJECTORY	■ Diffkin* (Environmental Research & Technological Technology) ■ REM (Pacific Environmental Services)
GRID	■ "SAI Model" (Systems Applications Inc.) ■ LIRAQ (Lawrence Livermore Labs)

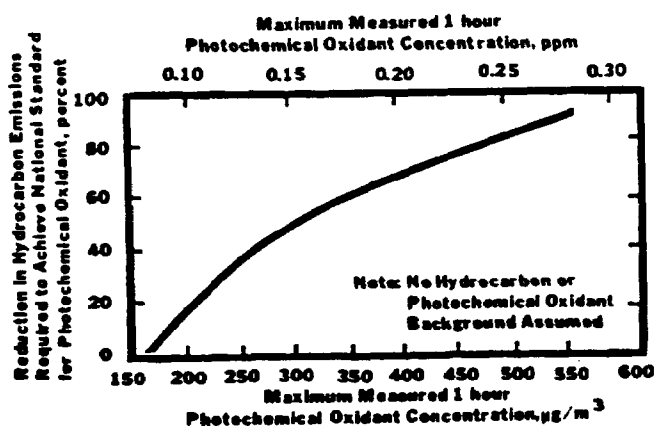
## ROLLBACK

### ■ DATA REQUIREMENTS:

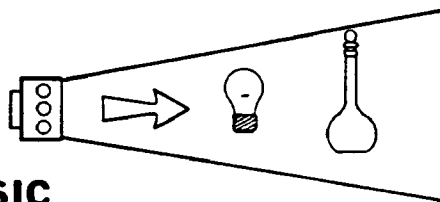
- Present  $O_x$  Concentration
- Area-wide Emissions



### REQUIRED HYDROCARBON EMISSION CONTROL AS A FUNCTION OF PHOTOCHEMICAL OXIDANT CONCENTRATION



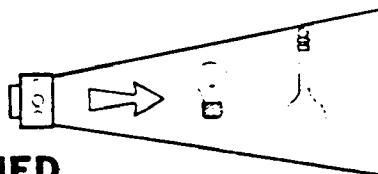
## KINETICS MODEL



### BASIC

- Present  $O_x$  Concentration Morning  
HC/ $NO_x$  Ratio Area-wide Emissions

## KINETICS MODEL



### MODIFIED

- Estimates are also required for
  - light intensity parameters
  - morning and afternoon mixing heights
  - appropriate spatial emissions distribution
  - transported ozone concentration, if possible

■ EPA 600/8-78-014a

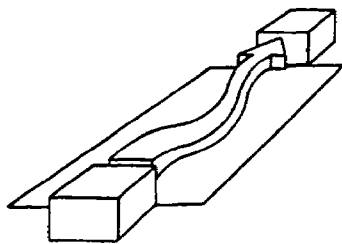
July, 1978

**“User’s Manual for Kinetics  
Model and Ozone Isopleth  
Plotting Package”**



## TRAJECTORY MODEL

---

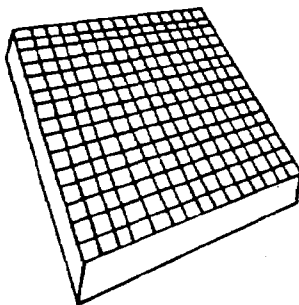


- Sufficient wind data (possibly including upper air data) to determine trajectories
- Initial concentrations in air parcels
- Hourly mixing heights
- Insolation
- Emission rates for the areas traversed by the air parcel

---

## GRID MODEL DATA REQUIREMENTS

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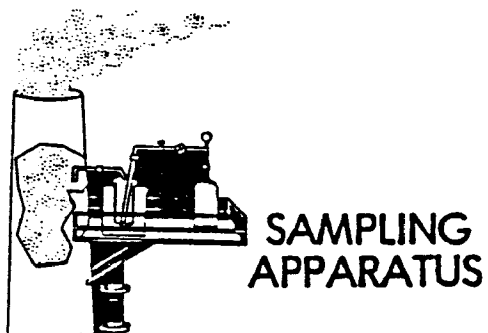
### ■ TYPICAL RESOLUTION

- SPATIAL : (a few miles)<sup>2</sup>  
e.g. 2 miles × 2 miles
- TEMPORAL : Hourly
- SPECIES : 4 Classes of HC—  
Paraffins, Olefins,  
Aromatics, Aldehydes  
Also NO, NO<sub>2</sub>, O<sub>3</sub>, CO, etc.

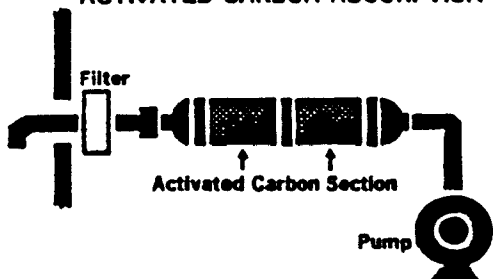
QAQPS 12-080  
**GUIDELINE ON  
AIR QUALITY MODELS**  
APRIL 1978



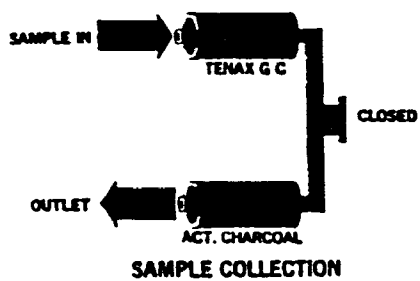
# Emission Measuring Techniques



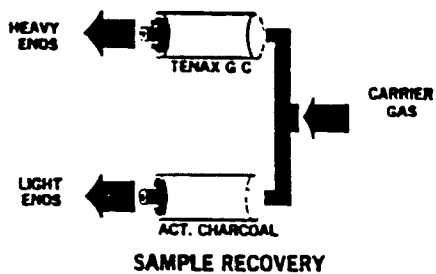
**ACTIVATED CARBON ADSORPTION**



**UNIVERSAL COLLECTOR**

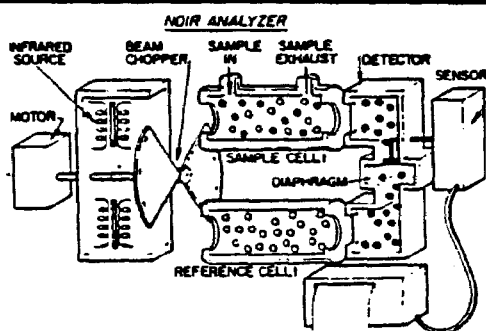
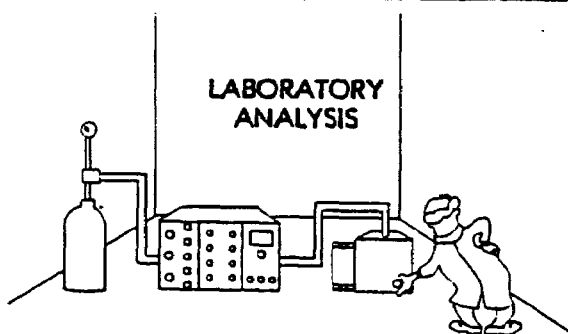
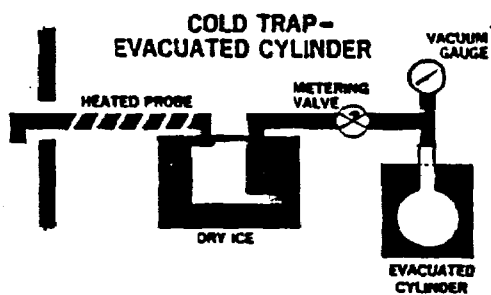
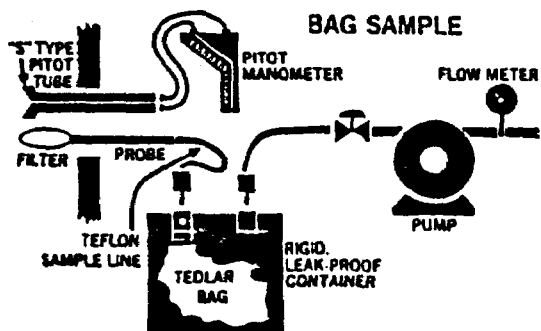


**UNIVERSAL COLLECTOR**





AND



The strengths and weaknesses for the allowed sampling techniques are as follows:

### **Direct Interface or Dilution Interface**

**Strengths:**

1. Samples collected are in a form that approximates the form in stack emissions.
2. No loss or alteration in compounds due to sampling since a sample collection media (bag or adsorbent) is not used.
3. Method of choice for steady state sources when duct temperature is below 100°C and organic concentrations are suitable for the GC detector.

**Weaknesses:**

1. GC must be located at the sampling site.
2. GC cannot be operated at a sampling site if the presence of the H<sub>2</sub> flame will be hazardous.
3. Cannot sample proportionally or obtain a time integrated sample.
4. Results represent only grab samples and should not be used for non steady state processes.

### **Tedlar Bag**

**Strengths:**

1. Samples collected are in a form that approximates the form in stack emissions.
2. Samples may be returned to the laboratory for GC analysis.
3. Multiple analyses, if necessary, may be performed on each collected sample.
4. Samples can be collected proportionally.

**Weaknesses:**

1. Unless protected, Tedlar bags are awkward and bulky for shipping back to the laboratory. Caution must be taken to prevent bag leaks.
2. Stability of compound(s) of interest in Tedlar bags must be known and sample storage time is generally less than 24 hours.
3. Polar compounds should not be collected due to bag absorption. Direct interface or dilution interface is the method of choice for polar compounds.

### **Adsorbent Tubes**

**Strengths:**

1. Samples collected are compact and easy to return to the laboratory for analysis.
2. Samples may be returned to the laboratory for GC analysis.
3. Sample storage time generally can be extended to a week by keeping samples at 0°C.

**Weaknesses:**

1. Quantitative recovery of organic compounds from the adsorbent material must be known.
2. Breakthrough sample gas volume for organic compounds for the adsorbent material must be known.
3. Any effect of moisture (in the stack gas) on the adsorbent material collection capacity must be known. Moisture in the sample above 2 to 3 percent may severely reduce the adsorptive capacity.
4. Generally, samples are collected at a constant rate.

# Review of Analytical Methods for Identifying Organic Compounds

## Lesson Goal and Objectives

### *Goal*

To provide a background in gas chromatography sufficient for understanding the EPA measurement methods for organic compounds.

### *Objectives*

Upon completing this lesson, you should be able to:

1. illustrate the separation of gaseous mixtures by the partitioning process of a chromatograph column,
2. identify the components of a gas chromatograph,
3. list at least three techniques used to introduce samples into the gas chromatograph, and
4. list and describe two types of chromatograph detectors.

## Introduction

The measurement of organic compound emissions is not as straightforward a procedure as the measurement of inorganic gases such as  $\text{SO}_2$  and  $\text{NO}$ . Because of the wide variation of properties associated with the different classes of organic materials, developing one single analytical method for this category of pollutant has been difficult. Instead, analytical approaches vary from the relatively simple measurement of materials evaporated from a painted plate to sophisticated mass spectroscopic techniques.

The degree of complexity in the sampling and analytical procedures also depends on what the information is needed for. Testing for leaky valves at a petroleum refinery is much simpler than identifying and quantifying the emissions of toxic materials from a hazardous waste incinerator. However, what is required in any sampling and analytical procedure for organic compounds, is a knowledge of the limitations of the procedure and careful attention to experimental details.

One technique does stand out as being common to many of the field methods used for characterizing organic compounds. That technique is gas chromatography. The detectors used in gas chromatographs are also used in the small, portable leak

checkers. Chromatographic separation principles are used in EPA Reference Method 25 for measurement of Total Gaseous Nonmethane Organics (TGNMO) and a detailed gas chromatographic procedure is specified in EPA Method 106 for vinyl chloride. Ultimately in the analytical laboratory, a gas chromatographic system tied in with a mass spectrometer, provides a powerful tool for identifying organic species.

This lesson will provide a review of the chromatographic method. It will discuss types of columns, detectors, and special techniques used for identifying organic air pollutants. The lesson will provide a basis for our further study in this course on the EPA reference methods for organic compounds.

## Chromatography—Definition

Chromatography is used to isolate the individual components of a mixture of organic compounds from each other for subsequent identification and quantitative analysis. The term, *chromatography* (color-writing) derives from an earlier technique used to separate colored compounds found in plants. It has since been applied to a variety of techniques, the two most important today being gas chromatography and liquid chromatography.

All types of chromatography are based on the selective distribution of compounds between a stationary material and a moving material. Figure 3-1 shows such a distribution, or *partitioning*, for the example of gas chromatography.

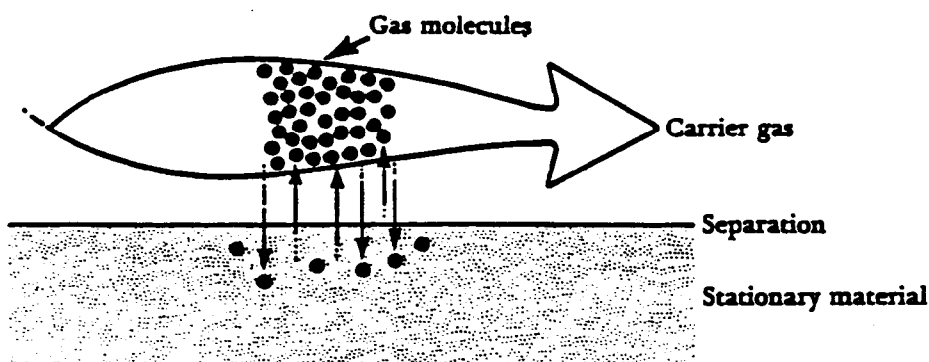


Figure 3-1. Partitioning in gas chromatography.

Here, the moving gas phase passes over a stationary material which is chosen to either absorb or adsorb the organic molecules contained in the gas. In gas chromatography, the stationary material or *phase* can be either a liquid or a solid. A phase is defined as a part of the system which is marked off by a boundary at which physical properties (e.g., gas phase and liquid phase) suddenly change. If the stationary phase is a liquid, the technique is called gas-liquid chromatography (GLC); if a solid, it is called gas-solid chromatography (GSC). Liquids are chosen in the GLC method for their ability to dissolve (absorb) the organic molecules to be



separated. In liquid chromatography, the *moving* phase is a liquid and the *stationary* phase is either a liquid or a solid. Adsorption, the attraction of molecules to the surface of a solid, is the predominant effect in the GSC technique. These types of chromatographic techniques are summarized in Figure 3-2.

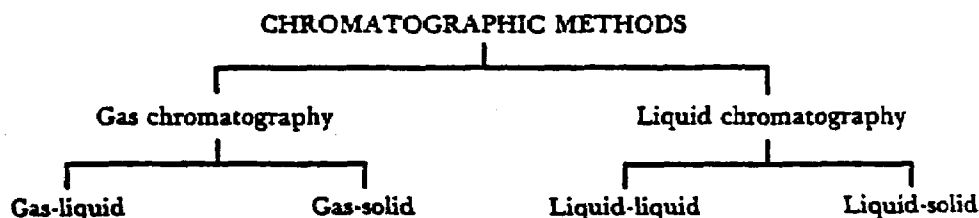


Figure 3-2. Types of chromatographic methods.

### ***Physical Basis of Gas-Liquid Chromatography***

When a gas dissolves in a liquid, a certain equilibrium occurs. Some of the gas molecules will not stay dissolved, but will evaporate to escape the surface of this liquid. They may reenter the liquid again, but at constant temperature and pressure, a steady-state condition results in the number of gas molecules entering equaling the number leaving the liquid (Figure 3-3).

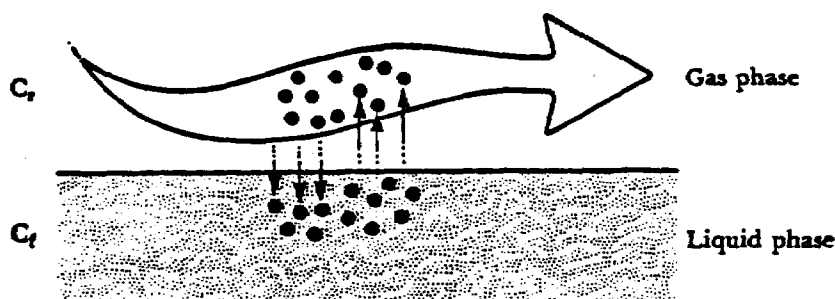


Figure 3-3. Equilibrium condition for a gas absorbed in a liquid.

The organic molecules will have a different concentration in the liquid,  $C_l$ , than in the gas ( $C_g$ ). By definition, the ratio of the quantity of the material dissolved in 1 ml liquid to the quantity in 1 ml of carrier gas is known as the partition coefficient  $K$ , shown in Equation 3-1.

(Eq. 3-1) 
$$K = \frac{C_l}{C_g}$$

Different organic compounds have different solubilities in a given liquid. High solubility means that the molecules stay longer in the liquid phase. At equilibrium, the rate of the molecules entering and leaving the liquid are equal. However, if the compound is not very soluble in the liquid, that rate is small and most of the

molecules will remain in the gas phase. If the compound is highly soluble, the rate will be higher and at any given instant, more molecules will be found dissolved in the liquid. So  $C_l$  and  $K$  would be larger than the corresponding values for the poorly dissolving substance (Figure 3-4).

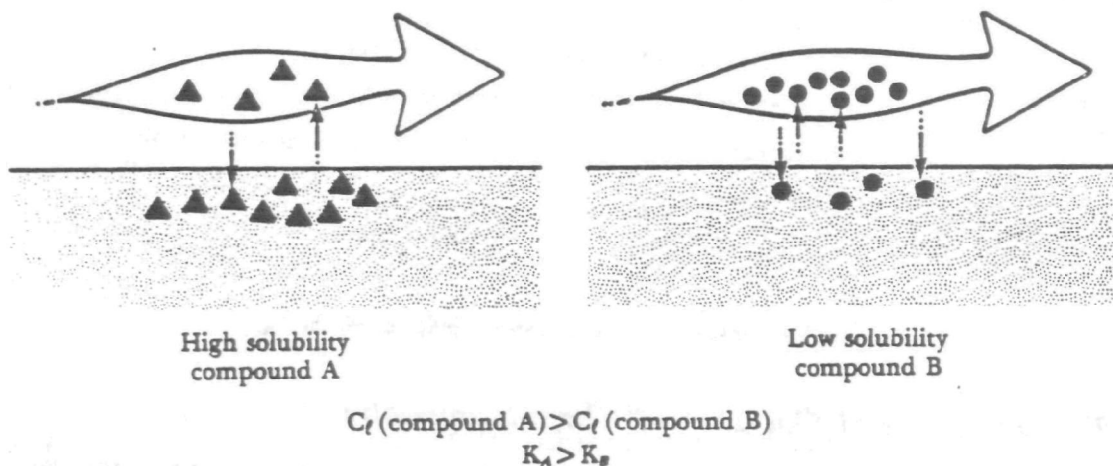


Figure 3-4. Differences in solubility.

This difference in partition coefficients causes the separation of compounds in chromatography. Let us see how the chromatographic method does this.

A simple gas-liquid chromatograph system is composed of the following:

- carrier gas,
- injection area,
- column, and
- detector.

A carrier gas, such as helium or nitrogen, sweeps a sample from the injection area into the heart of the system, the column. The column is a tube which contains the absorbing liquid. The liquid may be coated on a solid support such as powdered firebrick packed in the tube as shown in Figure 3-5a, or it may coat a support attached to the wall of the tube as shown in Figure 3-5b.

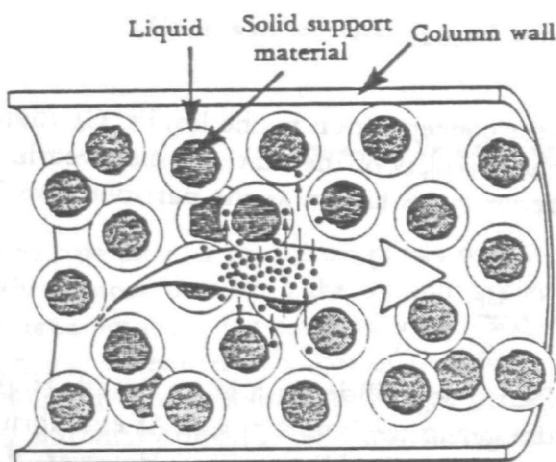


Figure 3-5a. Packed GLC column.

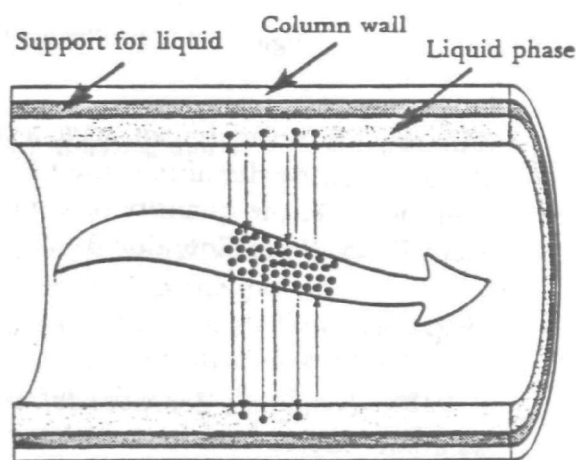


Figure 3-5b. Open-tubular GLC column (capillary).

A detector located at the end of the column is designed to sense the organic molecules in the sample when the carrier gas sweeps them to that point.

To understand the separation process, let us first divide the column into a number of imaginary segments. Then suppose that the sample contains two types of organic molecules, molecules A and molecules B. Let us assume that the A molecules are equally soluble in both the gas and liquid. Let us also assume that the B molecules are insoluble in the liquid. The sample containing organic molecules is injected and the carrier gas sweeps it into the first segment (Figure 3-6).

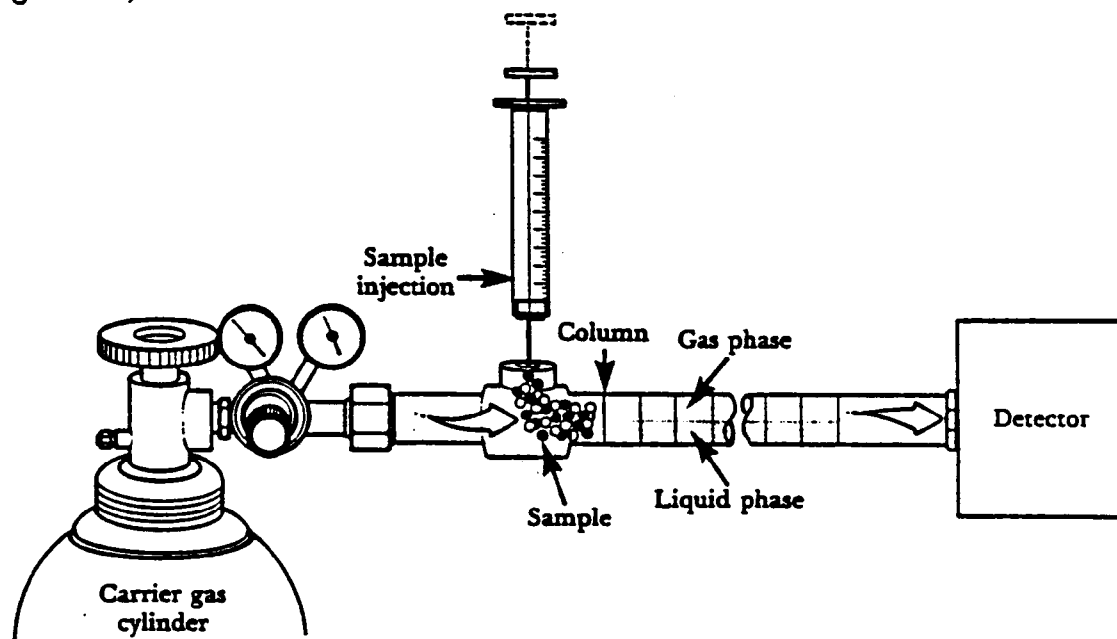


Figure 3-6. GLC separation process—injection.

After a short period of time, an equilibrium will be reached over the first segment. Since the A molecules have equal solubility in both phases, half will remain in the gas phase and the other half will dissolve in the liquid. The B molecules will not enter the liquid. The equilibrium result will be as shown in Figure 3-7.

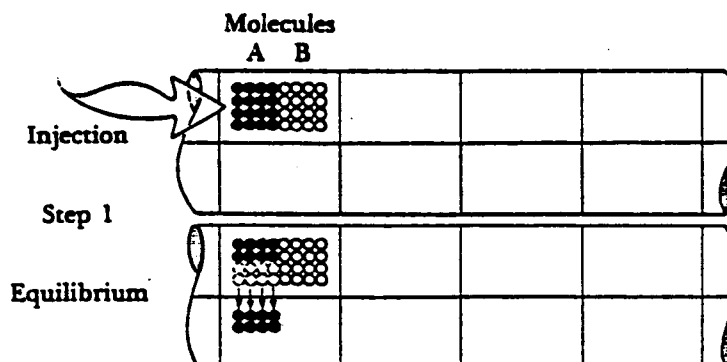


Figure 3-7. The GLC separation process—equilibrium at the first segment.

The carrier gas, however, will then propel the molecules in the gas phase on to the next segments. All of the B molecules will be transported there, but half of the A molecules will remain in the liquid since they only travel down the column when they are in the gas phase (Figure 3-8).

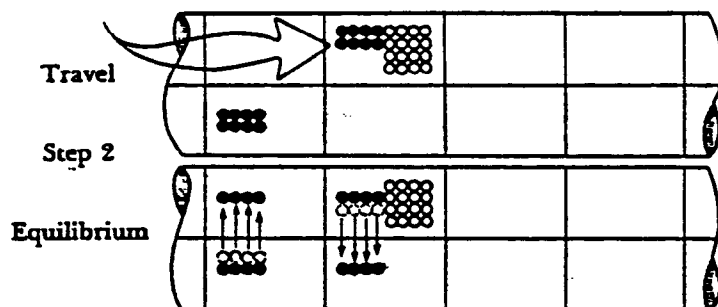


Figure 3-8. Travel of gas to the second segment and equilibrium in first and second segments.

A new equilibrium will then be established. The molecules of A equilibrate both the first and second section as shown in Figure 3-9.

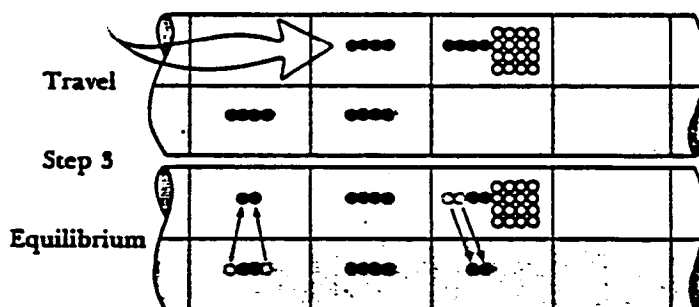


Figure 3-9. Travel to the third segment and equilibrium in first through third segments.

This process of gas travel and equilibrium will proceed down the column at each segment. Note the equilibrium of the A molecules down the column for its remaining segments (Figure 3-10).

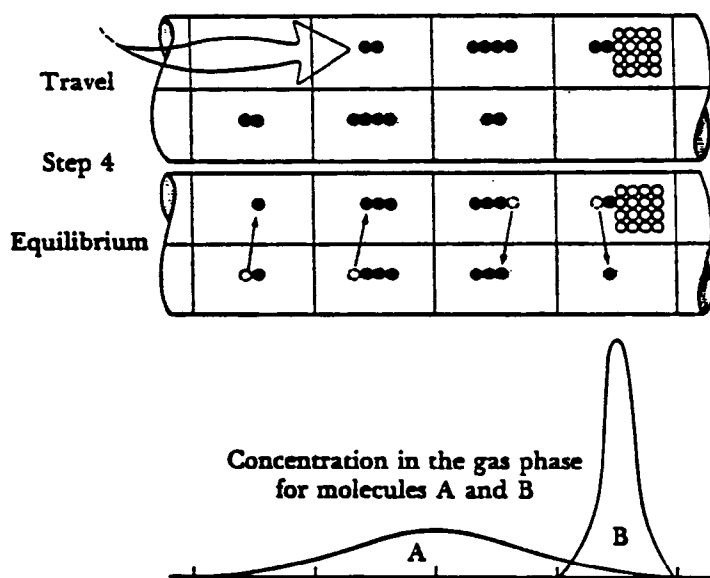


Figure 3-10. Travel and equilibrium continuing through column.

At the fourth step we can see that the A molecules have almost separated from the B molecules. Similarly, another organic compound with a different solubility and partition coefficient will move through the column at a different rate and likewise be separated from the other two. This constant movement between the gas and liquid phase is the fundamental mechanism of the gas chromatographic process.

## The Chromatogram

Organic compounds swept to the chromatograph detector produce an electrical signal proportional to the quantity of molecules present. Also, compounds separated before they reach the detector produce signals at different times. Because of the nature of the equilibrium processes just described and because of various random diffusion processes that occur in the column, all molecules of a given liquid will not arrive at the same time. This will give a distribution of signals at the detector. This distribution corresponds to a normal probability curve and is shown in what is called a chromatogram for our two compounds, A and B in Figure 3-11.

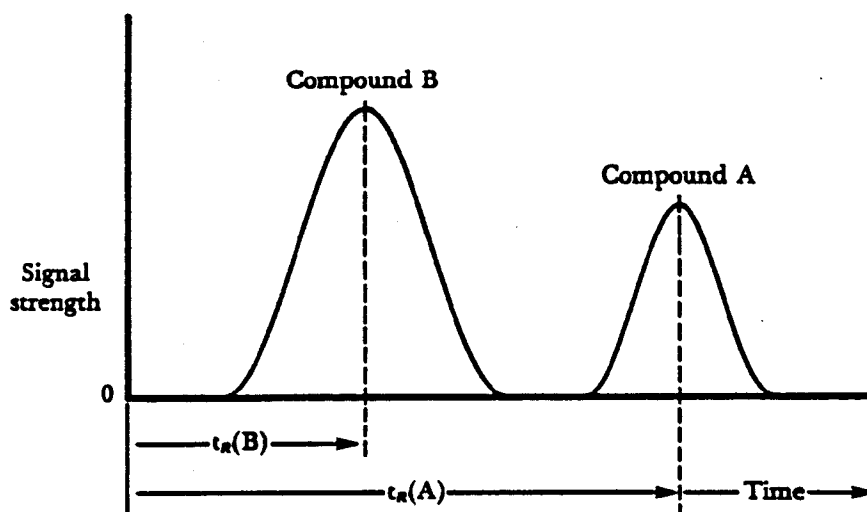


Figure 3-11. Chromatogram for two organic compounds, A and B.

By operating the chromatograph, data are obtained in the form of chromatograms. Peaks in the chromatogram give information about the identity of the compounds in the injected sample and also provide information about their concentration. The time taken for a compound to travel to the detector after the sample has been injected is known as the retention time,  $t_R$ . This time depends on the type of column, the temperature of the column, the carrier gas velocity, and the properties of the molecules themselves. The determination of retention times is used to identify the organic species present in a sample. Different compounds are separated by choosing a set of experimental conditions that will produce non-overlapping elution curves with different retention times. In terms of the partition coefficient for each compound, a large *relative retention* is desired for good separations (Equation 3-2).

(Eq. 3-2)

$$\alpha = \frac{\bar{K}_A}{\bar{K}_B} = \frac{t_R(A) - t_0}{t_R(B) - t_0}$$

where  $t_0$  is the sample injection time (usually determined by a small peak due to air injected with the sample). The resolution of compounds into separate peaks is one of the most important problems in chromatography. This will be discussed further in this lesson in the section on chromatographic columns.

Once separate peaks are obtained for the components of a sample mixture, their identity can be determined by running known standards through the column under the same set of experimental conditions. The object is to inject known compounds that will produce retention times corresponding to those of the unknown components in the sample. Matching known standards with unknowns then assists in the sample identification. However, a rigorous identification of an unknown cannot be made by a comparison of retention times since other materials may elute similarly. Experience and the wealth of scientific literature on chromatography can also assist in these efforts. Retention times for specific columns, compounds, and experimental conditions are documented in a large volume of literature for this purpose. Lastly, where standards or literature are not available, the compounds corresponding to each peak can be collected or further analyzed for identification. The coupling of mass-spectrometer systems to gas chromatographs is the principle example of this identification technique.

The concentration of each component in a mixture can be determined from the area defined by the elution curve. The area of each peak is compared to the total area of all the peaks to obtain the relative proportion of each component in the sample. This can be done crudely by manually measuring the areas, but today microprocessor techniques have been applied to perform this operation automatically.

## Gas Chromatograph—Components

Gas-chromatographic instrumentation may be simple or quite complex. Basic early systems have led to today's microprocessor controlled units that provide the analytical chemist with powerful tools for sample separation and identification. Behind even the most complex systems, however, lie the basic components required for gas chromatography (Figure 3-12).

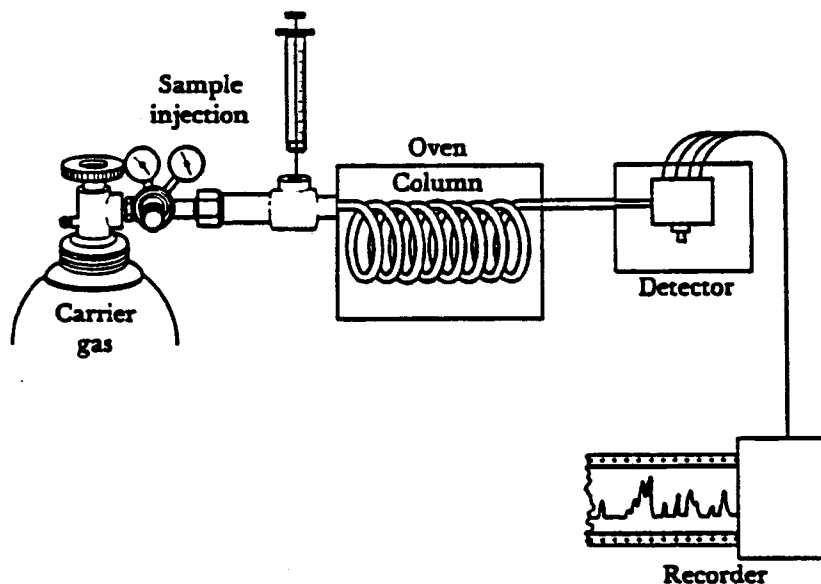


Figure 3-12. Block diagram.

A source of high pressure gas, such as a cylinder of nitrogen, helium, or argon provides the moving gas phase. Gas regulators on these cylinders generally provide a pressure ranging from 30 to 100 psi (200–700 kPa) for the carrier gas in the chromatograph. The sample is introduced to the system by the *injection system*. For gas samples, this system may consist of specially designed valves that allow carefully measured amounts of the sample gas to enter the column. Liquid samples are normally injected by a syringe into a heated chamber. The liquid sample is vaporized in the chamber to be subsequently carried into the column.

The gas stream containing the sample introduced by the injection system is carried to the *column*, which is housed in an oven. As discussed earlier, the primary purpose of the column is to separate the individual components of the sample. To choose a column, the analytical chemist must consider the following variables:

- column: packed or open-tubular (capillary),
- column length and diameter,
- solid support material,
- liquid phase, and
- column operating temperature.



For completely unknown samples, experience in chromatography and experimental technique are needed to resolve the individual components. In industries, where a compound such as benzene or vinyl chloride is to be monitored, sufficient experience has been attained to specify column types in EPA reference method procedures. This, for example, has been done in EPA Reference Method 106, for vinyl chloride which gives two types of columns for the analysis:

Column A: Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102® at column temperature of 100°C

Column B: Stainless steel, 2.0 m by 3.2 mm, containing 20% GE SF-96 on 60/80-mesh at column temperature 100°C

Chromasorb P-AW (to be used when acetaldehyde is present)

The column operating temperature is chosen so that all of the components in the sample mixture will remain vaporized. If the retention times of the components differ greatly, the column temperature may be varied or "programmed" by progressive increases. Compounds of low volatility can be eluted faster by this technique, therefore reducing the analysis time.

Sample components eluted from the column are subsequently sensed at the *detector*. Many detectors are available today, but the two most widely used are the flame ionization detector (FID) and the electron capture detector (ECD). The sensitivity of a detector generally depends on the characteristics of the molecules being measured. For example, the ECD is highly selective and sensitive to halogenated compounds. The FID, on the other hand, has a relatively constant response for different compounds, but is not as sensitive as the ECD. Other detectors especially sensitive to nitrogen compounds or sulfur containing compounds have been designed. These are often used in special studies and in some experimental programs; two or even three types of detectors have been combined for the analysis of complex environmental mixtures.

The *recorder*, of course, documents the results of the analysis in the form of chromatograms. Modern microprocessor systems are used to provide additional information on integrated peak areas, and hence provide the concentration of the individual components.

This part of Lesson 3 will examine the components of the gas chromatograph in more detail. The options available for injection systems, columns, and detectors will be provided along with a discussion of the principles of operation and performance for a number of the systems.

### ***Sample Collection and Injection Systems***

The GC injection method used for organic air pollutant samples depends on the manner in which the sample is collected. A number of collection techniques are common to both ambient and source sampling. Among these are:

- collection of whole air samples,
- condensation in cryogenic (low temperature) traps,
- adsorption on resin or charcoal columns, and
- absorption in liquids.

Whole air samples are collected by using either evacuated flasks or gas sampling bags. By first evacuating a flask and then opening it into the atmosphere being tested, samples can be obtained at the site for subsequent analysis in the laboratory. Tedlar® bags or their equivalent are similarly evacuated, but the air is pumped into the bag to obtain a sample integrated over longer time periods. Several methods are used to inject such whole air samples into the chromatograph. One of the simplest methods is to use a gas-tight syringe. An example of a familiar design is shown in Figure 3-13.



Figure 3-13. Gas syringe.

The sample withdrawn from the flask or bag is then injected into the gas chromatograph through a rubber septum. The gas is expelled into the carrier gas stream and the needle withdrawn from the rubber cap, which seals itself off again (Figure 3-14).

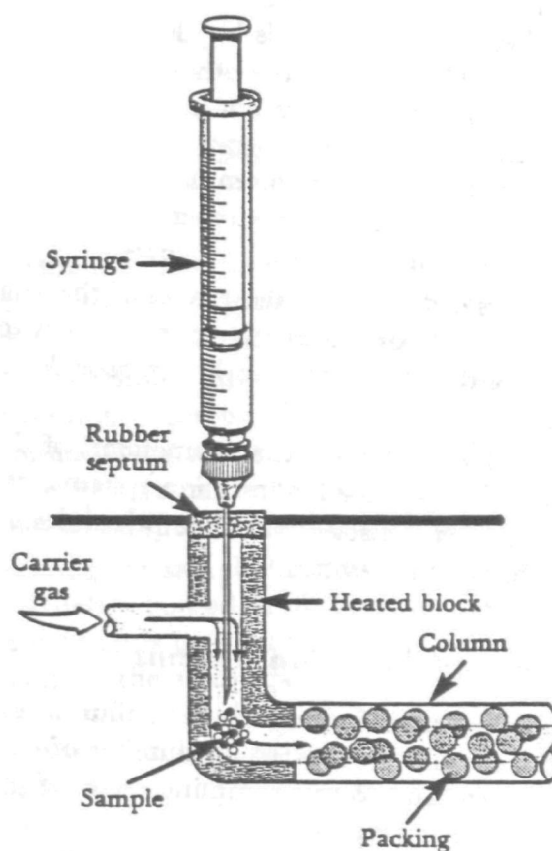


Figure 3-14. Sample injection using syringe.

Such gas syringes can have volumes of 0.1  $\mu\text{l}$  to 50 ccs. The accuracy of such injections is about 1% for the volume.

Another method of injecting whole air samples is to use special sampling valves. A pump draws the gas from the flask or bag into a sample valve containing a sample loop of known volume. The loop is closed off and carrier gas then sweeps the gas in the loop into the column. Two basic designs of gas-sampling valves are the rotary and linear valves.

The rotary valve shown in Figure 3-15 determines the size of the gas sample as it passes through ports in the valve to a loop of tubing with a known volume. The loop serves as a reservoir for the sample until the valve is turned to the inject position where the internal valve passages A, B, and C are rotated 45° to align with a new set of ports. As a result, the carrier gas pushes the sample out of the loop and into the column.

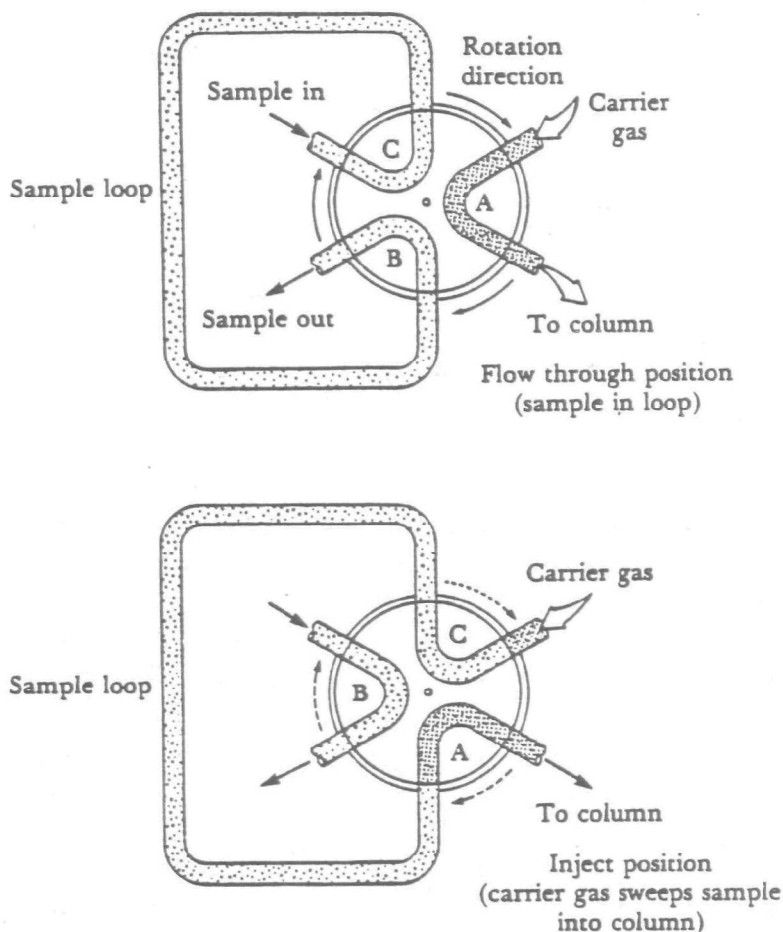


Figure 3-15. Rotary valve.

In the linear valve shown in Figure 3-16, sample gas passes through a loop of known volume as carrier gas passes through another port to enter the column. By pushing the valve into the inject position, the gas flow is changed by cutting off the sample gas and sweeping the known amount in the loop on into the column. Unlike the syringe method, systems with sampling valves can be automated to provide a semi-continuous analysis. They can be designed to pull in a sample using vacuum methods or can accept it under pressure.

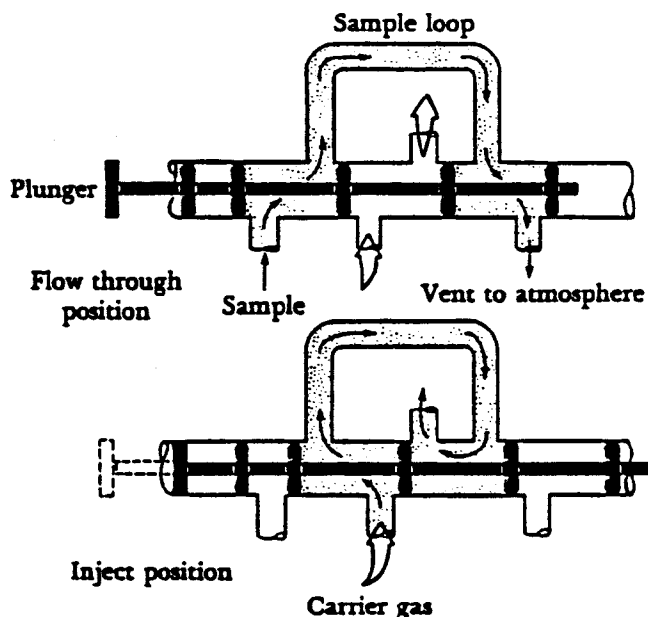


Figure 3-16. Linear valve.

In many field studies, the concentration levels of organic compounds in whole air samples are too low to be conveniently analyzed. This is particularly true in ambient air sampling, although the problem is still an important one when looking for trace levels of pollutants in industrial source emissions. Many preconcentration techniques have been developed to overcome this problem. The two most common techniques are cryogenic trapping and adsorption.

In cryogenic trapping the sample gas is passed through a system, such as stainless steel U-tube filled with glass beads, which is cooled with liquid oxygen or liquid argon. Liquid nitrogen is generally not used for this purpose since it will liquefy oxygen and make the chromatographic analysis more difficult. After the sample is collected, the U-tube can be attached directly to the chromatograph. The tube can then be flash heated and the sample subsequently injected into the column using an appropriate sampling-valve system.

Another method of collecting a concentrated sample is by using a solid adsorbent. Tubes packed with solid adsorbents such as Tenax-GC<sup>®</sup>, silica gel, or

activated charcoal are often used for this purpose. Tenax-GC<sup>®</sup> is a polydiphenyl ether having the structure shown in Figure 3-17.

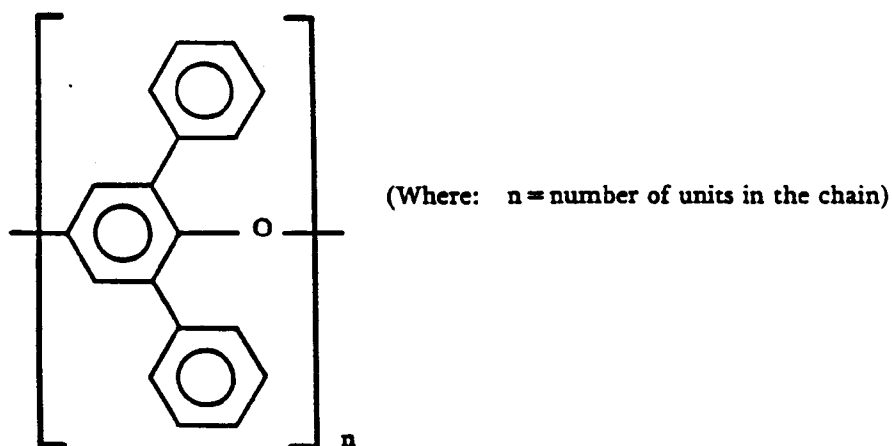


Figure 3-17. Tenax-GC<sup>®</sup>

Sample gas is pulled through a tube or specially designed cartridge containing the adsorbent. After a sufficient period of time, the tube is capped and stored for laboratory analysis. Various techniques have been developed to desorb such sampling tubes. A common technique is to heat the tubes and collect the desorbed materials in a cryogenic trap. The concentrated sample is then flash evaporated to provide a sample for the chromatograph.

Problems do exist in using such adsorbents because their affinities for different classes of organic compounds vary. For example, Tenax-GC<sup>®</sup> has poor adsorptive capability for low molecular weight compounds. Tubes containing activated charcoal, which does attract the lower molecular weight compounds, are often combined in series as a back-up for Tenax-GC<sup>®</sup>. Amborsorb<sup>®</sup> is another material commonly used for this purpose. Much research is presently being conducted on the adsorption characteristics of solid adsorbents. New adsorbents are also being developed which avoid some of the problems associated with those now in use.

Lastly, organic compounds may be collected by bubbling the sample gas through liquids which either absorb or react with them. A liquid syringe can then be used to inject the sample into the chromatograph.

We have seen great differences between the methods for the introduction of gaseous samples. The method chosen depends on how the sample was acquired and the concentration levels of the components being measured. In all cases, however, three conditions must be fulfilled when a substance is introduced.

1. Gas or liquid samples should reach the column as a vapor. After introduction, the sample should be carried by the carrier gas to the column in as short a time as possible. This is to minimize diffusion of the sample which may excessively broaden the peak.
2. The volume of sample injected should not overload the capacity of the column or change its temperature.
3. Both the quantity of substance introduced and the manner in which it is introduced must be reproducible with a high degree of precision.

In short, the type and manner of sample injection influence the gas chromatographic result. For quantitative analysis the injection conditions must be reproducible if a high degree of accuracy is required.

## **Columns**

The column is the central component of the chromatograph. The actual separation of the organic compounds is achieved here, so the choice of column type and column materials are important to any analysis. Two types of GC columns are widely used, the packed column and the open-tubular, or capillary column. As discussed in the first part of this lesson, packed columns consist of a tube containing near-spherically shaped particles coated with a liquid. The open-tubular columns are open tubes of small diameter with a thin liquid film on the wall or on a solid support coated on the wall. Packed columns are easier to prepare and have a higher capacity than the capillary columns. However, capillary columns offer less resistance to gas flow and can resolve complex mixtures using very small samples. Choosing between these two types of columns will generally influence the design of the other chromatograph components if optimum performance is to be achieved. The small samples associated with capillary columns may require both special injection and detection methods.

Packed columns can vary from less than 1 meter in length to over 20 meters in length with diameters varying from 1.5 mm to 2 mm. Capillary columns can vary from 0.25 mm to 1.25 mm in diameter, with lengths ranging beyond 100 meters. The column tubes can be stainless steel, glass, aluminum, or copper and are either U-shaped or wound in coils to fit in the chromatograph oven.

Several types of columns have been suggested by EPA for use in the agency source assessment program (Harris, 1979). These recommendations include specifications for column material, column length and diameter, and the materials to be used for the liquid phase and solid support material. These are given in Table 3-1.

Table 3-1. Suggested columns for environmental source assessment activities.

Column (liquid/solid phases)	Applications
Oxypropionitrile/Porasil C on 2 mm x 2 m glass column	Hydrocarbons boiling between -161 °C and 68 °C
Methyl phenyl silicone (SP 2250 or OV-17)/Supelcoport 2 mm x 2 m glass column	For compounds of moderate volatility (can be used up to 375 °C)
Dexsil 400/Supelcoport (2 mm x 2 m glass column)	For high boiling compounds, good for polycyclic aromatic hydrocarbons
Carbowax 20M (SP 1000)/Supelcoport (2 m x 2 m glass on stainless steel)	Ethers, carbonyls, alcohols—other moderately volatile compounds

## Solid Supports

The purpose of the solid phase is to provide a support for the liquid film. (Note: In gas-solid chromatography, solid materials are used to partition the sample primarily by adsorption processes.) Solids used for packed columns should have a large specific surface area, a pore structure with uniform pore diameter, thermal stability, mechanical strength, uniformly shaped particles, and an inertness to the sample being measured. They, of course, should be wettable by the liquid phase so that uniform film can coat the surface.

Diatomaceous earth is commonly used as a support and is available in many forms under a variety of commercial trade-names. The Chromasorb® series is widely used and has been applied to solve numerous analytical problems. Chromasorb-W® is a white support treated with sodium carbonate. Chromasorb-P® is a pink material obtained from crushed diatomaceous earth firebrick. Glass beads, Teflon®, Fluoropak®, Chromosorb-T®, and metals tend to be more inert than the diatomaceous earth supports, but they are more difficult to wet.

## The Liquid Phase

The liquid phase is chosen to match the compounds being separated and measured. The choice of a proper liquid phase or liquid phase/solid support combination may be a trial and error procedure in the case of complex unknown samples. The most important characteristic of a good liquid phase is that the partition coefficient (the K value) be appropriate for the components in the sample; it should be neither too small nor too large. In other words, the liquid should be a good solvent for the sample components, but it should not hold them so tightly that they can't get back into the gas stream. The components should also have varying solubilities in the liquid so that they can be correspondingly separated on the column. The liquid should also be nonvolatile, thermally stable at column temperatures, and should not react with the sample. Some commonly used liquid phases used in ambient air monitoring and their applications are given in Table 3-2 (EPA, 1983).

Table 3-2. Commonly used GC liquid phases in ambient monitoring.

Liquid phase	Applications
SE-30, OV-1 (methyl silicones)	Hydrocarbons, chlorinated hydrocarbons
OV-17, SE-54 (methyl/phenyl silicones)	PAHs, chlorinated pesticides, hydrocarbons
Carbowax 20M (polyethylene glycol)	Polar compounds; esters, alcohols, etc.
FFAP, SP-1000 (polyethylene glycol terephthalate)	Phenols, volatile acids

Several methods are used for coating the solid support with the liquid. In general, the liquid is dissolved in a solvent and the solid particles are mixed in with the solution. The solvent is then allowed to evaporate either under vacuum or by adding heat. The amount of liquid used must be carefully calculated so that a thin film will coat the particles without creating excess pools of liquid.

Packing columns is a process which must be carefully done, but is still more of an art than a technically defined procedure. For good column efficiency and reproducibility, air pockets and channels need to be avoided. It is often convenient to purchase prepared columns from vendors who are able to exercise quality control methods in their production.

### Column Performance

The ability of a column to separate the components of a sample depends on many variables. The choices of liquid and solid phases, column material and dimensions, column temperatures, and flow rates, provide a wide range of possibilities when approaching an analysis problem. To help the analytical chemist, several mathematical methods have been developed that can be used to compare the effectiveness of one column over another. In your reading of the literature associated with gas chromatography, you will see a number of expressions characterizing column performance. In the first part of this lesson, we discussed the partition coefficient,  $K$ , and the relative retention,  $\alpha$ . Here, we will introduce the concept of plate number and plate height.

Earlier, we divided up an example column and showed how two types of molecules behaved as they traveled along its length. The soluble molecules became distributed in each segment, or were "partitioned" between the gas and liquid phases at each segment under equilibrium conditions. As a result of this process, we could visualize how two components could separate and produce signal peaks at the detector. In a similar fashion, a theory, called *plate theory*, has been developed to help explain the factors that influence the operation of a column.

Plate theory imagines that a column can be divided into a finite number of identical segments,  $n$ , each with a plate height,  $H$ , where  $H = L/n$ , and  $L$  is the length of the column (Figure 3-18).

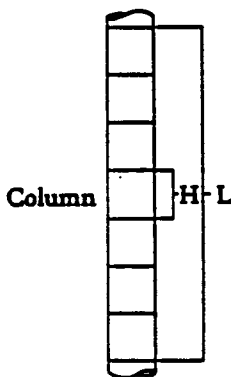


Figure 3-18. Plate height.



The characteristic feature of each segment of "height H," is that the sample component studied will need that amount of column in order to come into equilibrium with the system. For example in Figure 3-19,

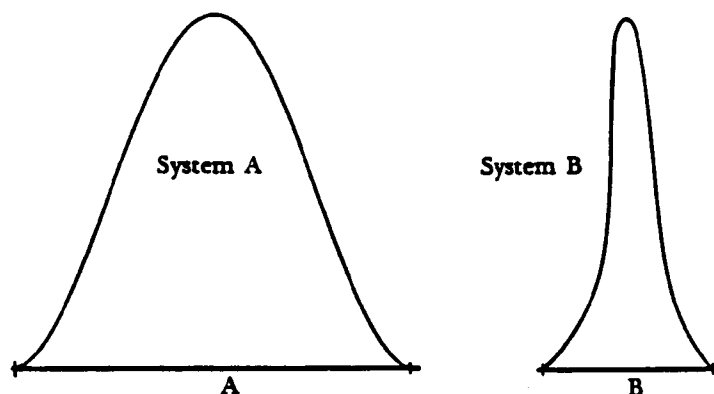


Figure 3-19. Molecules exhibiting different plate heights.

the peak shown for system A requires a longer length of column before it resolves into an equilibrium distribution than does system B. As a result, the peak observed for system B will be sharper than that for system A.

The number of plates,  $n$ , can be calculated from the chromatogram by using the formula shown in Figure 3-20.

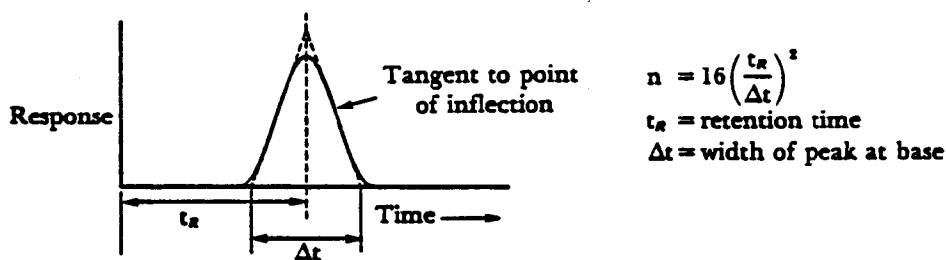


Figure 3-20. Schematic chromatogram.

This expression is derived from statistical consideration of the chromatogram curve (see Nogare, 1966 for the best discussion). A high number of plates for a given length of column implies high efficiency, or sharp peaks. The number of plates can be increased by lengthening the column or by improving the column without changing its length. The expression is useful when comparing similar columns or setting standards for packing techniques.

The plate height,  $H$ , is also useful for characterizing columns. It is a better term to use than the plate number when comparing columns of different length. The plate height is also called the *Height Equivalent to a Theoretical Plate* (HETP), since the plates themselves are imaginary, theoretical constructs.

"This means that one HETP is the length of column in which the equivalent of one simple equilibration step occurs. Thus the length of column divided by the HETP is the effective number of partitions a compound undergoes in its passage through the column" (Moore, 1971).

Plate theory does not address the experimental factors that determine the HETP; it only tells how to calculate it after you have obtained a chromatogram. However, another theory has been developed that relates column conditions to the HETP.

The HETP can be calculated from the "rate theory" for column performance. A theoretical expression derived from basic principles expresses the plate height as depending on three primary factors: 1) The path the gas must take when traveling through the packing, 2) the diffusion of the organic components in the carrier gas, and 3) the time it takes the molecules to reach equilibrium between the gas and liquid phases. An abbreviated form of this expression is given in the Van Deemter Equation, Equation 3-3.

$$\text{(Eq. 3-3)} \qquad \text{HETP} = A + \frac{B}{u} + Cu$$

Here, A, B, and C are constant and u is the carrier gas velocity. The A term is called the eddy diffusion term, related to the path of the gas; B is the longitudinal diffusion term; and C is the mass transfer term which expresses the equilibrium characteristics of the column. The carrier gas velocity is the independent variable in this simplified expression since it is the experimental parameter most easily varied after the column is constructed. If the velocity is increased, there will be less time for a band of adsorbing molecules to spread in the column (i.e.,  $\Delta t$  would decrease). This is reflected in the reciprocal form of the second term, B/u, so the HETP would decrease.

However, if the velocity is increased, the carrier gas will rush the molecules through the column at a faster rate and there will be less time available for them to reach equilibrium with the adsorbent. You would therefore need a longer length of column for the molecules to come into equilibrium with the adsorbent and the HETP would increase. This is reflected in the third term Cu, which will increase as the carrier gas velocity increases. The last two terms compete against each other since the HETP decreases as the diffusion term decreases, but increases when the third term increases. This is shown graphically in what is known as a Van Deemter

plot (Figure 3-21). The figure illustrates the effect on the HETP for each term in the Van Deemter expression. Each of the terms is plotted separately against the velocity of the carrier gas. The sum of the three terms at any velocity gives the HETP.

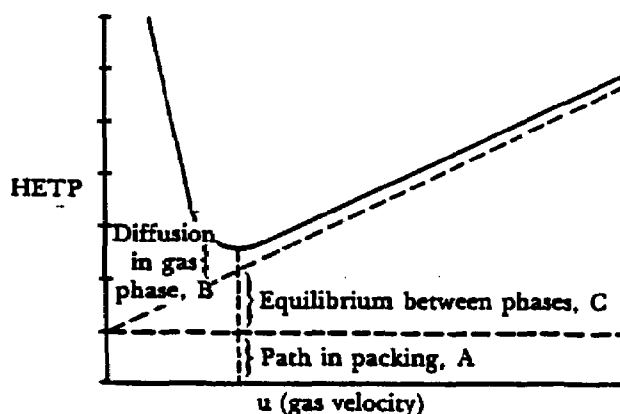


Figure 3-21. Plot of HETP against gas velocity.

Columns can be characterized for their effectiveness in separating an organic compound by specifying a number of terms. These are  $t_R$ , the retention time; the plate number,  $n$ ; and the plate height,  $H$  or HETP. When comparing how well two different compounds are separated by the liquid phase, one can use the relative retention,  $\alpha$ , discussed earlier.

The choice of a column is essentially a problem in optimizing the values for  $n$ ,  $H$ , and  $\alpha$ . In the complex mixtures involved in environmental monitoring, the selection of the proper column is important if all of the components are to be adequately resolved. The scientific literature is well-documented with various approaches taken towards the analysis of specific environmental samples. A study of this extensive literature should precede the development of new monitoring programs.

## Detectors

The separation performed in the column must in some way be sensed and recorded. The sample components will generally be eluted at very low concentrations and will pass through the detector at a rapid rate depending on the velocity of the carrier gas. Any detector designed for use in a gas chromatograph system must have a high sensitivity for low concentration of organic molecules and a rapid response time. Many detectors are available which meet these requirements; the two most commonly used in environmental analysis are the Flame Ionization Detector (FID) and the Electron Capture Detector (ECD).

### Flame Ionization Detector

Ionization refers to the process where charged atoms or molecules (ions) are formed from an electrically neutral compound. Ionization detectors supply energy to the sample to ionize the organic compounds contained in it. The number of ions

produced by this process are then counted through a measurement of their electric charge. Electronic circuitry can then convert this measurement to produce the chromatogram.

The flame ionization detector provides energy to the gases eluted from the column by burning hydrogen in the presence of oxygen (Figure 3-22).

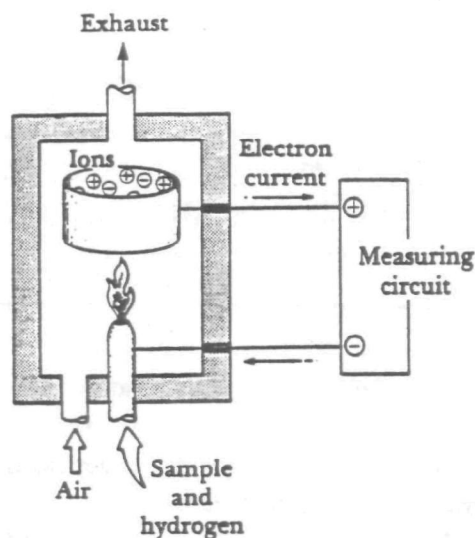


Figure 3-22. Flame ionization detector.

The hydrogen flame produced in turn burns the organic vapors in the eluted gas. In doing this, both positively and negatively charged ions are formed. These ions make the gap between the two electrodes (anode and cathode) conductive. An electric current can then flow through this part of the circuit. The current is approximately proportional to the number of carbon atoms entering the flame. The response of the detector is, however, slightly different for different types of organic compounds. As a result, the detector must be calibrated for the compounds being studied if accurate results are to be obtained.

The flame ionization detector is convenient to use in many source sampling situations since it does not respond appreciably to gases such as  $O_2$ ,  $N_2$ ,  $H_2O$ ,  $CO$ ,  $SO_2$ , and  $NO$ . Performance depends on the carrier gas flow rate, but the FID is still one of the most sensitive detectors available.

#### Electron Capture Detector

The electron capture detector is selective towards certain groups of organic compounds such as those containing halogen atoms or nitro groups. In this method, a carrier gas such as nitrogen is ionized by a radioactive material such as  $Ni^{63}$  or tritium ( $H^3$ ) to produce a large number of free electrons. These electrons move to a

positively charged anode as shown in Figure 3-23 to generate a current through the system.

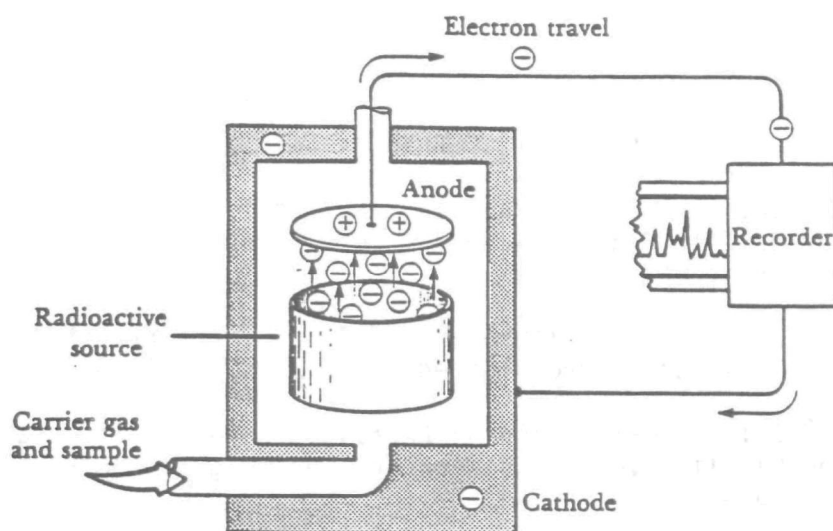


Figure 3-23. Electron capture detector.

When the nitrogen carrier gas contains electron-absorbing molecules such as halocarbons, the electric current will be reduced since the flow of free electrons is reduced. The ECD is more sensitive for specific groups of compounds than is the FID, but the response can vary from compound to compound.

#### Other Detectors

Other types of detectors are used in chromatographs applied to environmental monitoring. Many of these are species selective like the ECD. Among these are the Hall Electrolytic Conductivity Detector (HECD) used for halogen, sulfur, or nitrogen compounds; the Flame Photometric Detector (FPD) used for sulfur or phosphorous compounds; and the Alkalai Flame Detector (AFD), used for nitrogen and phosphorous compounds. Systems that will detect a range of organic compounds are the thermal conductivity detector (TCD), and the Mass Spectrometer (MS). Thermal conductivity was a technique used in early chromatographs but it has less sensitivity than does the flame ionization method. It is, consequently, not widely used for trace level analysis of environmental samples. The photoionization detector (PID) uses high energy UV radiation to ionize organic molecules. This highly sensitive detector is becoming popular in both field and laboratory applications.

With the increasing demands for the analysis of trace levels of toxic materials, unique approaches are being taken to increase the resolving power and sensitivity of chromatographic systems. Dual detector systems such as the combination of PID/ECD, HECD/FID, and even FID/ECD/MS have been used for a variety of applications (EPA, 1983) (Fox, 1983). Combining the gas chromatograph with the mass spectrometer is useful in many applications where identifying the sample components is paramount. This GC/MS combination has become very popular for such analyses and is in widespread use in industry and university laboratories.

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40 CFR PART 61 - APPENDIX C - QUALITY ASSURANCE PROCEDURES

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APPLICABLE STANDARDS TEST METHODS

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ASTM-D2369-81. Volatile Content of Coatings D2369-1

ASTM-D3792-79. Water Content of Water-Reducible Paints  
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ASTM-D4017-81. Water in Paints and Paint Materials by  
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METHOD 18. MEASUREMENT OF GASEOUS ORGANIC  
COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

INTRODUCTION

[This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.]

1. Applicability and Principle

1.1 Applicability. This method applies to approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources.

This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.2 Principle. This method is based on separating the major components of a gas mixture with a gas chromatograph (GC) and measuring the separated components with a suitable detector.

The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.



## **2. Range and Sensitivity**

**2.1 Range.** The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

**2.2 Sensitivity.** The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

## **3. Precision and Accuracy**

Gas chromatography techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Duplicate analyses are within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

METHOD 21. DETERMINATION OF VOLATILE  
ORGANIC COMPOUND LEAKS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

DRAFT  
DO NOT QUOTE OR CITE

METHOD 23. DETERMINATION OF HALOGENATED  
ORGANICS FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, and trichlorotrifluoroethane in stack gases from sources as specified in the regulations. The method does not measure halogenated organics contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

2. Range and Sensitivity

The range of this method is 0.1 to 200 ppm. The upper limit may be extended by extending the calibration range or by diluting the sample.

METHOD 24--DETERMINATION OF VOLATILE MATTER CONTENT, WATER  
CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D 1475-60 (Reapproved 1980). Standard Test Method for Density of Paint, Lacquer, and Related Products (incorporated by reference - see §60.17).

2.2 ASTM D 2369-81. Standard Test Method for Volatile Content of Paints (incorporated by reference - see §60.17).

2.3 ASTM D 3792-79. Standard Test Method for Water Content in Water Reducible Paint by Direct Injection into a Gas Chromatograph (incorporated by reference - see §60.17).

2.4 ASTM D 4017-81. Standard Test Method for Water in Paints or Paint Materials by the Karl Fischer Titration Method (incorporated by reference - see §60.17).

METHOD 24A--DETERMINATION OF VOLATILE MATTER CONTENT  
AND DENSITY OF PRINTING INKS AND RELATED COATINGS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.

1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

METHOD 25 - DETERMINATION OF TOTAL GASEOUS NONMETHANE  
ORGANIC EMISSIONS AS CARBON

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the

detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide ( $\text{CO}_2$ ) which is quantitatively collected in an evacuated vessel; then a portion of the  $\text{CO}_2$  is reduced to methane ( $\text{CH}_4$ ) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide ( $\text{CO}$ ),  $\text{CO}_2$  and  $\text{CH}_4$ ; the nonmethane organics (NMO) are oxidized to  $\text{CO}_2$ , reduced to  $\text{CH}_4$ , and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.



METHOD 25A - DETERMINATION OF TOTAL GASEOUS ORGANIC  
CONCENTRATION USING A FLAME IONIZATION ANALYZER

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

METHOD 25B DETERMINATION OF TOTAL GASEOUS ORGANIC  
CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes. (Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.) The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

METHOD 27-DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE  
DELIVERY TANK USING PRESSURE-VACUUM TEST

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery tank which is equipped with vapor collection equipment.

1.2 Principle. Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

METHOD 106--DETERMINATION OF VINYL CHLORIDE  
FROM STATIONARY SOURCES

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle

1.1 Applicability. The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. The method does not measure vinyl chloride contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to GC analysis using a flame ionization detector (FID).

2. Range and Sensitivity

This method is designed for the 0.1 to 50 ppm range. However, common GC instruments are capable of detecting 0.02 ppm vinyl chloride. With proper calibration, the upper limit may be extended as needed.

DRAFT  
DO NOT QUOTE OR CITE

METHOD 110. DETERMINATION OF BENZENE  
FROM STATIONARY SOURCES

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to benzene, a carcinogen.

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of benzene in stack gases from processes as specified in the regulations. The method does not measure benzene contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

2. Range and Sensitivity

The range of this method is 0.1 to 70 ppm. The upper limit may be extended by extending the calibration range or by diluting the sample.



# Emission Inventories

## Emission Inventories For Volatile Organic Compounds

### 1. Introduction: (482-5-1) (482-5-1A)

Organic compounds are found or produced in nature, but many more have been synthetically produced by man. Gasoline obtained from oil is a natural product, but the plastic produced from oil do not occur in nature. Over 30,000 new compounds are synthesized each year, adding to a list exceeding 1,000,000 that are registered. Two important facts are known about the environmental effects of these organic materials: (482-5-2)

1. Organic compounds volatile enough to be emitted into the atmosphere can contribute to the generation of photochemical oxidants (smog). (482-5-2A)
2. Organic compounds can have toxic effects on plants and animals. In dealing with the problem of photochemical oxidant generation, control programs have been established to limit the emission of organic compounds into the atmosphere.

Regulation of toxic organic compounds are just now beginning to characterize what compounds are toxic and to what degree they pose a threat to public health and welfare when emitted into the atmosphere.

National emissions of volatile organic compounds (VOC) are shown in Table 5-1, classified by source category from the years 1970, 1975, and 1980. During the past 10 years the total amount of VOC's emitted from industrial processes has remained relatively constant VOC emissions from some individual industrial categories have increase slightly but have decreased slightly in others. (482-5-3) (482-5-3A) (482-5-3B)

### 2. Overview Of Inventory Procedures (482-5-4)

Four basic steps are involved in the preparation of a VOC emission inventory. The first is planning. The agency should define the need for the VOC inventory as well as the constraints that limit the ability of the agency to produce it. The various planning aspects discussed in the following sections of this chapter should all be considered prior to initiation of the actual data gathering phases of the inventory effort. All proposed procedures and data sources should be documented at the outset and be subjected to review by all potential users of the final inventory, including the management and technical staff of the inventory agency.

The second basic step is data collection. A major distinction involves which sources should be considered point sources in the inventory and which should be considered area sources. Fundamentally different data collection procedures are used for these two source types. Individual plant contacts are used to collect point source data, whereas collective information is generally used to estimate area source activity. Much more



Table 5-1 National Estimates Of Volatile Organic Compound (VOC) Emissions

Source Category	12 Teragrams(10 <sup>12</sup> ) per year		
	1970	1975	1980
Transportation			
Highway vehicles	10.5	8.8	6.8
Aircraft	0.2	0.2	0.2
Railroads	0.2	0.2	0.2
Vessels	0.4	0.4	0.5
Other off-highway vehicles	0.5	0.5	0.5
<u>Transportation total</u>	<u>11.8</u>	<u>10.1</u>	<u>8.2</u>
Stationary Source Fuel Combustion			
Electric utilities	0.0	0.0	0.0
Industrial	0.1	0.1	0.1
Commercial-institutional	0.0	0.0	0.0
Residential	0.5	0.5	0.8
<u>Fuel combustion total</u>	<u>0.6</u>	<u>0.6</u>	<u>0.9</u>
<u>Industrial processes</u>	<u>9.8</u>	<u>9.3</u>	<u>10.7</u>
Solid waste disposal			
Incineration	0.3	0.4	0.3
Open burning	1.3	0.5	0.3
<u>Solid waste total</u>	<u>1.8</u>	<u>0.9</u>	<u>0.6</u>
Miscellaneous			
Forest fires	0.7	0.5	0.9
Other burning	0.3	0.1	0.1
Miscellaneous organic solvent	2.2	1.7	1.6
<u>Miscellaneous total</u>	<u>3.2</u>	<u>2.3</u>	<u>2.6</u>
<u>Total</u>	<u>27.2</u>	<u>23.2</u>	<u>23.0</u>

The third basic step in the inventory compilation effort involves an analysis of data collected and the development of emission estimates for each source. Emissions will be determined individually for each point source, whereas emissions will generally be determined collectively for each area source category. Source test data, material balances, and emission factors are all used to make these estimates. Adjustments are required to exclude nonreactive VOC and to make the resulting emission totals representative of the ozone season. A special adjustment called "scaling up" is necessary in some cases to account for sources not covered in the point source inventory. Estimates of projected emissions must also be made as part of this step.

The fourth step is reporting. Basically, reporting involves presenting the inventory data in a format that serves the agency in the development and implementation of an ozone control program or other regulatory effort. Depending on the capabilities of the inventory data handling system many kinds of reports can be developed that will be useful in numerous facets of the agency's ozone control effort.

An important consideration affecting emission accuracy is whether the agency has included all sources of VOC in its inventory. Table 5-2 presents those major sources of VOC that, at a minimum, should be considered in the inventory. Some sources in this table are generally considered point sources, some are generally handled collectively as area sources, while others, such as drycleaners, can be either point or area sources, depending on the size of each operation and the particular cutoff made between point and area sources. (482-5-5) (482-5-6) (482-5-7) (482-5-8) (482-5-9) (482-5-10) (482-5-11)

The entries in Table 5-2 describe general source categories and do not list all of the emitting points that may be associated with any of the particular source categories. For example, petroleum refining operations actually include many emitting points ranging from process heaters to individuals seals and pumps.

Those stationary sources of VOC for which EPA has published or will publish Control Techniques Guidelines (CTG) are included in the categories listed in Table 5-2.

Table 5-3 shows industrial source category's VOC atmospheric emissions by amounts and percentage for all of the industries listed on Table 5-1. (482-5-12)

### 3. Point/Area Source Distinctions (482-5-13)

A major distinction typically made in inventories is between point and area sources. Point sources are those facilities/plants/activities for individual source records are maintained in the inventory. Under ideal circumstances, all sources would be considered point sources. In practical applications, only sources that emit (or have the potential to emit) more than some specified cutoff level of VOC are considered point sources.

Table 5.2 VOLATILE ORGANIC COMPOUND (VOC) EMISSION SOURCES

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STORAGE, TRANSPORTATION AND MARKETING OF VOC

Oil and Gas Production & Processing  
Gasoline and Crude Oil Storage  
Synthetic Organic Chemical Storage & Transfer  
Ship and Barge Transfer of VOC  
Barge and Tanker Cleaning  
Bulk Gasoline Terminals  
Gasoline Bulk Plants  
Service Station Loading (Stage I)  
Service Station Unloading (Stage II)  
Others

INDUSTRIAL PROCESSES

Petroleum Refineries  
Lube Oil Manufacture  
Organic Chemical Manufacture  
Inorganic Chemical Manufacture  
Fermentation Processes  
Vegetable Oil Processing  
Pharmaceutical Manufacture  
Rubber Tire Manufacture  
Plastic Products Manufacture  
SBR Rubber Manufacture  
Textile Polymers & Resin Manufacture  
Synthetic Fiber Manufacture  
Iron and Steel Manufacture  
Others

INDUSTRIAL SURFACE COATING

Large Appliances  
Magnet Wire  
Automobiles  
Cans  
Metal Coils  
Paper  
Fabric  
Metal Wood Products  
Miscellaneous Metal Products  
Plastic Parts Painting  
Large Ships  
Large Aircraft  
Others

NON-INDUSTRIAL SURFACE COATING

Architectural Coatings  
Auto Refinishing  
Others

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Table 5.2 (cont)

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**OTHER SOLVENT USE**

Degreasing  
Dry Cleaning  
Graphic Arts  
Adhesives  
Cutback Asphalt  
Solvent Extraction processes  
Consumer/Commercial Solvent Use  
Other .

**OTHER MISCELLANEOUS SOURCES**

Fuel Combustion  
Solid Waste Disposal  
Forest, Agricultural, and Other Open Burning  
Pesticide Application  
Waste Solvent Recovery Processes  
Stationary Internal Combustion  
Engines

**MOBILE SOURCES**

Highway Vehicles  
a. Light duty automobiles  
b. Light duty trucks  
c. Heavy duty gasoline trucks  
d. Heavy duty diesel trucks  
e. Motorcycles

**OFF HIGHWAY VEHICLES**

Rail  
Aircraft  
Vessels

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Table 5.3 VOLATILE ORGANIC COMPOUND EMISSION FROM INDUSTRIAL PROCESSES

Industrial Source Category	Gigagrams per year				Percent of Total for 1981
	1970	1975	1980	1981	
Crude Oil Production, Storage, and transfer (1311,4463)	550	530	560	540	5.5
Food and beverage (20)	120	130	150	150	1.5
Textiles (22)	180	170	190	170	1.7
Graphic arts (27)	280	240	330	250	2.6
Plastics (2821,3079)	400	390	550	490	5.0
Organic chemicals(286)	570	690	710	760	7.8
Other chemicals (28)	520	330	370	380	3.9
Petroleum refining (2911)	720	880	970	950	9.7
Rubber tires (3011)	100	90	80	90	0.9
Glass (321,322)	50	50	60	60	0.6
Iron and steel (3312)	110	90	80	70	0.7
Petroleum produce storage and transfer (5171,5541)	1,570	1,740	1,500	1,450	14.9
Dry cleaning (721)	280	250	320	240	2.5
Adhesives	460	400	540	420	4.3
Degreasing	560	400	440	350	3.6
Solvent extraction processes	230	190	250	200	2.1
Surface coating	1,730	1,470	2,070	1,800	18.4
Other organic solvent use	1,370	1,210	1,560	1,460	14.9
Total	9,790	9,250	10,730	9,770	

The Standard Industrial Classification (SIC) code is given in the parenthesis where appropriate.

This is a general category which includes process emissions from organic solvent use in a wide variety of industries. Thus no specific SIC is given.

NOTE: One Gigagram equal  $10^9$  grams or  $10^3$  metric tons ( $1.1 \times 10^3$  short tons). total may differ slightly from sum of source category totals due to independent founding of data.

Depending on the needs of and resources available to the agency, this cutoff level will vary. Area sources, in contrast, are those activities for which aggregated source and emission information is maintained for entire source categories rather than for each source therein. Sources that are not treated as point sources must be included as area sources. The cutoff level distinction is especially important in the VOC inventory because there are so many more small sources of VOC than of most other pollutants.

If too high a cutoff level is chosen, many facilities will not be considered individually as point sources, and if care is not taken, emissions from these sources may not be included in the inventory at all.

If too low a cutoff level is chosen, the result will be a significant increase (1) in the number of plant contacts of various sorts that must be made and (2) in the size of the point source file that must be maintained. While a low cutoff level may increase the accuracy of the inventory, the tradeoff is that many more resources are needed to compile and maintain the inventory.

The choice of a point source cutoff level will not only determine how many point sources will be contained in the inventory, but also will impact on the kinds of sources included. As a rule, the lower this cutoff is (1) the greater the cost of the inventory, (2) the more confidence users will have in the source and emissions data, and (3) the more applications that can be made of the inventory. At a minimum, all facilities exceeding 100 tons of VOC per year should be inventoried as point sources and each process emission point should be identified. If possible, a point source cutoff level of less than 100 tons per year should be selected to avoid handling the myriad of medium size VOC emitters found in most urban areas as area sources. In some cases, the agency may decide to pursue lower cutoff levels or to simply include all of a certain type of source in the point source inventory, regardless of size. This may be desirable, for example, if all sources in a certain category and subject to control regulations such as RACT

At a minimum, every source category shown in Table 5.2 should be considered for inclusion, with an emphasis on those RACT categories for which controls are anticipated in the ozone control program.

4. Exclusion of Nonreactive Compounds and Consideration of Species Information (482-5-14)

While most volatile organic compounds ultimately engage in photochemical reactions, some are considered nonreactive under atmospheric conditions. Therefore, controls on the emissions of these nonreactive compounds do not contribute to the attainment and maintenance of the national ambient air quality standard for ozone.

These nonreactive compounds are listed below:

Methane  
1,1,1-Trichloroethane (Methyl Chloroform)  
Methylene Chloride

Dichlorodifluoromethane (CFC 12)  
Chlorodifluoromethane (CFC 22)  
Trifluoromethane (FC 23)  
Trichlorotrifluoroethane (CFC 113)  
Dichlorotetrafluoroethane (CFC 114)  
Chloropentafluoroethane (CFC 115)

These compounds should be excluded from emission inventories used for ozone control strategy purposes. Because this list may change as additional information becomes available, the inventory agency should remain aware of EPA policy on reactivity considerations.

## 5. Emission Calculations (482-5-15)

After planning and data collection, the third basic step in the inventory is the calculation of emissions. This involves (1) an analysis of the point and area source data collected by the procedures outlined in the proceeding two chapters and (2) the development of emissions estimates for each source. In some cases, test data will be supplied by the source. However, in most instances the agency will have to compute emissions using emission factors or material balance considerations. The following three sections discuss the making of emission estimates based on source test data, material balances, and emission factors.

### a. Source Test Data (482-5-15A)

In many cases, the most accurate method of estimating a source's emissions is to use test data obtained by the agency or supplied by the plant itself. The use of source test data reduces the number of assumptions that need be made by the agency regarding the applicability of generalized emission factors, control device efficiencies, equipment variations, or fuel characteristics. A single source test or series of tests, taken over a sufficiently long time to produce results representative of conditions that would prevail during the time period inventoried, will normally account for most of these variables. The most nearly complete type of source testing is continuous monitoring.

Most source test reports summarize emissions for each pollutant by expressing them in terms of (1) a mass loading rate (weight of pollutant emitted per unit time), (2) an emission factor (weight of pollutant emitted per unit of process activity), or (3) in terms of a flue gas concentration (weight or number of moles of pollutant per some weight or volume of flue gas). Generally, when a mass loading rate or emission factor is provided, the resulting emission estimates can be easily calculated. For example, if the average VOC emission rate for the time period tested was 12 lbs/hr, and the source operated for 16 hrs/day, 350 days/year, daily emission would be  $12 \times 16$ , or 192 lbs, and the annual emission would be  $192 \times 350$ , or 67,200 lbs (34 tons). Or, if an emission factor of 5 lbs. of VOC per ton of product was given and the plant produced 160 tons of product per day for 200 days per year, annual emission would be  $5 \times 1600 \times 200$ , or 160,000 lbs (80 tons).

If the source test results are expressed in terms of VOC concentrations the emission calculations are more detailed. As an example, assume that volatile organic compound emissions are expressed as parts per million, as shown in Table 5.3. In this case, the concentration measurements and the flow rate measurements are used to obtain mass loading rates. (A formula for determining mass loading rates is shown as part of the calculations in Table 5-4. Note that in this example, the results are expressed as methane, and molecular weight of 16 lbs/lb -mole is used in the mass loading rate formula. If the concentration was expressed in terms of another organic reference compound, the appropriate molecular weight would be used. Upon determining the mass loading rate 0.3 lbs/hr, in this example), this rate can be divided by the production rate at the time of testing to yield an emission factor of 0.1 lbs VOC emitted per ton of production. After averaging the individual mass loading rates and emission factors determined for all runs of the source test, the resulting average mass loading rate or emission factor can be multiplied by the annual operating time or annual production, respectively, to determine annual emissions. Emissions can be calculated similarly for other time periods. (482-5-16) (482-5-17)

Two points should be noted when using source test data to calculate emissions. First, because source tests are generally only conducted over several hours or days, at most, caution is urged when using these data to estimate emissions over longer time intervals or for conditions different from those under which the tests were performed. Adjustments may be needed to account for differing conditions. Second, a source test supplied by a plant may not adequately describe a given facility's annual or seasonal operating pattern. In cases where such data are not included in the test reports, an operating rate will have to be obtained in order to make reliable annual or seasonal emission estimates. This is best done by contracting the plant and obtaining operating information for the period the test was conducted. Such information could be obtained from questionnaire data but may not be as accurate.



Table 5-4 EXAMPLE SOURCE TEST DATA AND EMISSION CALCULATIONS

SOURCE TEST RESULTS

RUN NUMBER	1	2	3
Date	8-5-71	8-6-71	8-7-71
Stack flow rate	9840	8510	10290
% Excess air	225	227	366
CO Emissions (ppm, by volume)	2.5	6.4	4.6
VOC Emission (ppm by volume, as CH <sub>4</sub> )	11.9	6.8	10.9
<u>Process Conditions</u>			
Production rate (tons/hour)	3.0	3.2	3.1

CALCULATION OF VOC EMISSIONS

CONVERSION FORMULA:

$$\text{LB VOC/HR} = 1.58 \times M \times 10^{-7} \times \text{ppm} \times \text{SCFM}$$

where M = Molecular weight of reference VOC

CALCULATION FOR RUN 1:

$$\text{Mass Loading Rate} = 1.58 \times 16 \times 10^{-7} \times 11.9 \times 9840 = 0.3 \text{ lb/hr}$$

$$\begin{aligned} \text{Emission Factor} &= 0.3 \text{ lb/hr} \times 1 \text{ hr/3 tons production} \\ &= 0.1 \text{ lb/VOC/TON Production} \end{aligned}$$

6. MATERIAL BALANCE (482-5-18)

If source test results are not available, the agency can, in some cases, use material balance considerations to estimate emissions. In fact, for some sources, a material balance is the only practical method to estimate VOC emissions accurately. Source testing of low level, intermittent, or fugitive VOC exhaust streams can be very difficult and costly in many instances. Emissions from solvent evaporation sources are most commonly determined by the use of material balances.

Use of a material balance involves the examination of a process to determine if emission can be estimated solely on knowledge of specific operating parameters and material compositions. Although the material balance is a valuable tool in estimating emissions from many sources, its use requires that a measure of the material being "balanced" be known at each point throughout the process. If such knowledge is not available, and is therefore assumed, serious errors may result.

In the VOC emission inventory, a material balance is generally used to estimate emissions from solvent evaporation sources. This technique is equally applicable to both point and area sources. The simplest form of material balance is to assume that all solvent consumed by a source process will be evaporated during that process. For instance, the assumption is reasonable that, during many surface coating operations, all of the solvent in the coating evaporates to the atmosphere during the drying process. In such cases, emissions simply are equal to the amount of solvent applied in the surface coating (and added thinners) as a function of time. As another example, consider a dry cleaning plant that uses Stoddard solvent as the cleaning agent. To estimate emissions, the agency needs only to elicit from each plant the amount of solvent purchased during the time interval of concern, because emissions are assumed equal to the quantity of solvent purchased.

Several other situations can complicate the material balance. First, not all of the solvent losses from certain operations such as drycleaning or degreasing occur at the plant site. Significant quantities of solvent may be evaporated, instead, from the waste solvent disposal site, unless the waste solvent is incinerated or disposed of in a manner, such as deep well injection, that precludes subsequent evaporation to the atmosphere. Generally, one can assume that much of the solvent sent to disposal sites will evaporate. The fact that some solvent associated with various operations evaporates at the point of disposal rather than at the point of use should be determined, as these losses may occur outside of the area covered by the inventory.

Material balances cannot be employed in some evaporation processes because the amount of material lost is too small to be determined accurately by conventional measurement procedures. As an example, applying material balances to petroleum product storage tanks is not generally feasible, because the breathing and working losses are small, relative to the total average capacity or throughout, to be determined readily from changes in the amount of material stored in each tank. In these cases, AP-42 emission factors developed by

special procedures, will have to be applied.

7. EMISSION FACTORS (482-5-19)

One of the most useful tools available for estimating emissions from both point, and area sources is the emission factor. An emission factor is an estimate of the quantity of pollutant released to the atmosphere as a result of some activity, such as combustion or industrial production, divided by level of that activity. In most cases emission factors are expressed simply as a single number, with the underlying assumption being that a linear relationship exists between emissions and the specified activity level over the probable range of application. Empirical formulas have been developed for several source categories that allow the agency to base its emission estimates on a number of variables instead of just one. The most important VOC emitters for which a number of variables are needed to calculate emissions are highway vehicles and petroleum product storage and handling operations. As a rule, the most reliable emission factors are those based on numerous and representative source tests or on accurate material balances.

The use of an emission factor to estimate VOC emissions from a source necessitates that the agency have complete source and control device information.

Tables 5-5 and 5-6 are examples of metal furniture surface coating for determining VOC emissions from a surface coating operation, using AP-42 emission factors. (482-5-20) (482-5-21)

8. Reporting Formats (482-5-21A)

In addition to required reporting formats, wide variety of tables and graphic displays can be employed to present inventory data via personal computer programs. Pie charts, tables and graphs can quickly convey to the reader emission breakdowns by industries, geographical areas, or source size. Emission trends and the effects of control programs can also be tabulated or graphed. Several examples of tables and graphs are included here to provide some ideas on how data can be presented. (482-5-22) (482-5-23)

Table 5-5 OPERATING PARAMETERS FOR COATING OPERATIONS

Plant size	Operating Schedule (hr/yr)	Number of lines	Line speed (m/min)	Surface area coated/yr (m <sup>2</sup> )	Liters of coating used
Small	2,000	1 ( 1 spray booth )	2.5	45,000	5,000
Medium	2,000	2 ( 3 booths/line )	2.4	780,000	87,100
Large	2,000	10 ( 3 booths/line )	4.6	4,000,000	446,600

Line speed is not used to calculate emissions, only to characterize plant operations.

Using 35 volume & solids coating, applied by electrostatic spray at 65 % transfer efficiency.

Table 5-6 EMISSION FACTORS FOR VOC FROM SURFACE COATING OPERATIONS

Plant Size and Control Techniques	VOC Emissions		
	kg/m coated	kg/year	kg/hour
Small			
Uncontrolled emissions	.064	2,875	1.44
65 Volume % high solids coating	.019	835	.42
Waterborne coating	.012	520	.26
Medium			
Uncontrolled emissions	.064	49,815	24.91
65 Volume % high solids coating	.019	14,445	7.2
Waterborne coating	.012	8,970	4.4
Large			
Uncontrolled emissions	.064	225,450	127.7
65 Volume % high solids coating	.019	74,080	37.0
Waterborne coating	.012	46,000	23.0

Calculated using the parameters given in Table 4.2.2.12-2 and the following equation. Values have been rounded off.

How the inventory data can most efficiently be summarized will depend on time and manpower available to assemble a report. Tabular reports are the most common kind of report, as they can be readily generated from computerized inventory systems.



# Concepts of VOC Control

# Organic Compounds and Air Pollution Regulations

## Lesson Goal and Objectives

### *Goal*

To review air pollution control programs that address the emission of organic compounds from industrial sources.

### *Objectives*

Upon completing this lesson, you should be able to:

1. state two reasons for developing emission control programs for organic compounds,
2. identify common acronyms used in the regulatory documents associated with the control of organic compounds,
3. describe control options for volatile organic compounds and control options associated with trading policies, and
4. define *air toxics* and state the rationale behind regulatory programs for their control.

## Introduction

Organic compounds constitute the largest class of chemicals described in the field of chemistry. Organic compounds are composed of carbon and other elements such as hydrogen, oxygen, chlorine, and nitrogen, and exist as solids, liquids, or gases. As a result of their wide diversity, they are the products and waste products from many of today's industries.

Organic compounds are found or produced in nature, but many more have been synthetically developed to serve some need, whether practical or out of scientific curiosity. Gasoline obtained from oil is a natural product, but the plastics produced from oil do not occur in nature. Over 30,000 new compounds are synthesized each year, adding to a list exceeding over 1,000,000 that are registered (Ref. 1983). The environmental effects of these materials are difficult to assess, but two important facts are known.

1. Organic compounds volatile enough to be emitted into the atmosphere can contribute to the generation of photochemical oxidants (smog).
2. Organic compounds can have toxic effects on plants and animals.



The U.S. Environmental Protection Agency (EPA), under the requirements of the Clean Air Act, is responsible for protecting and enhancing air quality. In dealing with the problem of photochemical oxidant generation, control programs have been established to limit the emission of organic compounds into the atmosphere. In the regulation of toxic organic compounds, programs are just now beginning to characterize what compounds are toxic and to what degree they pose a threat to public health and welfare when emitted into the atmosphere.

This lesson will review the programs developed by the Federal government and individual States to limit the emission of organic compounds. The lesson will provide a rationale for characterizing these materials and for monitoring them.

## **The Photochemical Oxidant Problem\***

Photochemical oxidants are contained in the atmospheric chemical mix known as smog. A principal photochemical oxidant in this mix is ozone. Ozone is defined a criteria pollutant, and a National Ambient Air Quality Standard (NAAQS) has been set for it of 0.12 ppm (235  $\mu\text{g}/\text{m}^3$ ). Volatile organic compounds (VOCs) emitted into the atmosphere have been found to contribute to the formation of ozone. Through a series of complex chemical reactions involving nitrogen oxides and light, organic compounds lead to buildups of photochemical oxidants. As a result of this, control strategies for ozone emphasize the control of these emissions. Hopefully, by controlling these reaction precursors, the oxidant levels will in turn be controlled.

Typical sources of volatile organic compounds are highway vehicles and industrial sources associated with

- petroleum refining, distribution, and marketing,
- fuel combustion and solid waste incineration,
- evaporation of organic solvents,
- chemical manufacturing, and
- miscellaneous industrial processes.

Emissions of these compounds have ranged to about 25 million metric tons per year. National estimates for these are given in Table 1-1.

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\*This section has been adapted from G. T. Joseph, D. S. Beachler, and W. F. Dimmick 1983. VOC Emission Regulations Promulgated and Proposed. Paper presented at AIChE Meeting, Houston, Texas March 1983.

Table 1-1. National estimates of volatile organic compound (VOC) emissions.

Source category	Teragrams (10 <sup>12</sup> ) per year		
	1970	1975	1980
Transportation			
Highway vehicles	10.5	8.8	6.8
Aircraft	0.2	0.2	0.2
Railroads	0.2	0.2	0.2
Vessels	0.4	0.4	0.5
Other off-highway vehicles	0.5	0.5	0.5
Transportation total	11.8	10.1	8.2
Stationary source fuel combustion			
Electric utilities	0.0	0.0	0.0
Industrial	0.1	0.1	0.1
Commercial-institutional	0.0	0.0	0.0
Residential	0.5	0.5	0.8
Fuel combustion total	0.6	0.6	0.9
Industrial processes	9.8	9.3	10.7
Solid waste disposal			
Incineration	0.5	0.4	0.3
Open burning	1.3	0.5	0.3
Solid waste total	1.8	0.9	0.6
Miscellaneous			
Forest fires	0.7	0.5	0.9
Other burning	0.3	0.1	0.1
Miscellaneous organic solvent	2.2	1.7	1.6
Miscellaneous total	3.2	2.3	2.6
Total	27.2	23.2	23.0

Source: Joseph et al. 1983.

During the past 10 years the total amount of VOCs emitted from industrial processes has remained relatively constant. VOC emissions from some individual industrial source categories have increased slightly, but have decreased slightly from other source categories (Table 1-2). Therefore, in order to meet the ambient ozone standards, industrial source emission standards have been adopted.

Table 1-2. Volatile organic compound emissions from industrial processes.

Industrial source category	Gigagrams per year			
	1970	1975	1980	1981
Crude oil production, storage, and transfer (1311,4463)	550	530	560	540
Food and beverages (20)	120	130	150	150
Textiles (22)	180	170	190	170
Graphic arts (27)	280	240	330	250
Plastics (2821,3079)	400	390	550	490
Organic chemicals (286)	570	690	710	760
Other chemicals (28)	520	330	370	380
Petroleum refining (2911)	720	880	970	950
Rubber tires (3011)	100	90	80	90
Glass (321,322)	50	50	60	60
Iron and steel (3312)	110	90	80	70
Petroleum product storage and transfer (5171,5541)	1,570	1,740	1,500	1,460
Dry cleaning (721)	280	250	320	240
Adhesives	460	400	540	420
Degreasing	560	400	440	350
Solvent extraction processes	230	190	250	200
Surface coating	1,730	1,470	2,070	1,800
Other organic solvent use*	1,370	1,210	1,560	1,460
Total	9,790	9,250	10,730	9,770

The Standard Industrial Classification (SIC) code is given in the parenthesis where appropriate.

\*This is a general category which includes process emissions from organic solvent use in a wide variety of industries. Thus no specific SIC is given.

Note: One gigagram equals  $10^9$  grams or  $10^6$  metric tons ( $1.1 \times 10^6$  short tons). Total may differ slightly from sum of source category totals due to independent rounding of data.

Source: Joseph et al. 1983.

States must set regulations, as required by the Clean Air Act, to limit the amount of VOCs that can be emitted by sources of VOCs. The U.S. Environmental Protection Agency (EPA) must set New Source Performance Standards (NSPS), as required by the Clean Air Act, for major sources of pollutants such as VOCs.

In order to understand source emission standards, it is necessary to become familiar with a few regulatory terms. The following definitions are from the U.S. Code of Federal Regulations:

A *new source* is one which is contracted and installed at a facility after the date emission standards are proposed for that industry.

*Modification* is any physical change or operational change of an existing facility that increases the amount of an air pollutant emitted, or results in the emission of an air pollutant not previously emitted into the atmosphere to which a standard applies.

*Existing source* refers to an air pollution source constructed before the proposal date of the emission standard.

An *attainment area* is an air quality control region that actually meets the NAAQS.

A *nonattainment area* is an area or region where the NAAQS for a particular pollutant is being violated.

The Clean Air Act, as amended in 1977, mandates that all States develop control plans, referred to as State Implementation Plans (SIPs), describing their enforcement strategy for meeting and maintaining the NAAQS. The SIPs, which must be approved by the EPA, list the State regulations aimed at

1. bringing *nonattainment* areas into attainment status, and
2. ensuring that clean air in *attainment* areas will be maintained. (Prevention of Significant Deterioration—PSD)

The Clean Air Act, as amended in 1977, also defines three classes of control technology aimed at reducing emissions from both existing sources and new or modified sources. These are Reasonably Available Control Technology (RACT), Best Available Control Technology (BACT), and controls that reflect the Lowest Achievable Emission Rate (LAER). Each of these classes describes technological methods that are applied to industrial sources to reduce air pollution emissions.

RACT is generally defined as the lowest emission limit that an existing source is capable of meeting by applying control technology that is reasonably available. RACT considers both availability and economic feasibility of the control methods.

The section of a SIP covering VOC emission control must contain regulations for industrial categories identified as major VOC sources. Regulations aimed at existing sources in nonattainment areas (for ozone) must reflect the application of RACT. In order to give the States guidance in setting RACT emission standards, EPA has published and is continuing to develop a series of documents referred to as Control Technique Guidelines (CTG). The guideline documents are not regulations, but only serve as an information base from which State and local agencies can develop their own regulations.

EPA has prepared CTG documents for many of the major sources of VOC emissions. For each source, a CTG describes the source or industry, identifies the VOC emission points, discusses the applicable control methods, analyzes the costs required to implement the control methods, and recommends an emission limit.

Tables 1-3 through 1-5 list the stationary source categories for which a CTG has been or is currently being developed. Table 1-3 lists the 11 CTG documents published prior to January 1978. This first group of CTG documents is referred to as Group I. Table 1-4 lists the 10 CTG documents (called Group II) that were published in 1978. Table 1-5 lists the Group III CTG documents that are currently being developed. The NTIS ordering number is given in the table.

Table 1-3. Group I—Control Technique Guideline documents.

Source category	EPA reference number	NTIS number*
Surface coating of cans, coils, paper, fabric, automobiles, and light-duty trucks	EPA 450/2-77-008	PB 272 445/8BE
Surface coating of metal furniture	EPA 450/2-77-032	PB 278 257/1BE
Surface coating for insulation of magnetic wire	EPA 450/2-77-033	PB 278 258/9BE
Surface coating of large appliances	EPA 450/2-77-034	PB 278 259/7BE
Storage of petroleum liquids in fixed roof tanks	EPA 450/2-77-036	PB 276 749/9BE
Bulk gasoline plants	EPA 450/2-77-035	PB 276 722/6BE
Solvent metal cleaning	EPA 450/2-77-022	PB 274 557/8BE
Use of cutback asphalt	EPA 450/2-77-037	PB 278 185/4BE
Refinery vacuum producing systems, wastewater separators, and process unit turnarounds	EPA 450/2-77-025	PB 275 662/5BE
Hydrocarbons from tank truck gasoline loading terminals	EPA 450/2-77-026	PB 275 060/2BE
Design criteria for stage I vapor control systems, gasoline service stations, U.S. EPA, OAQPS, November 1975	—	—

\*Documents can be ordered from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

Source: Joseph et al. 1983.

Table 1-4. Group II—Control Technique Guideline documents.

Source category	EPA reference number	NTIS number
Leaks from petroleum refinery equipment	EPA 450/2-78-036	PB 286 158/1BE
Surface coating of miscellaneous metal parts and products	EPA 450/2-78-015	PB 286 157/3BE
Manufacture of vegetable oil	EPA 450/2-78-035	PB 286 307/4BE
Surface coating of flat wood paneling	EPA 450/2-78-032	PB 286 199/5BE
Manufacture of synthesized pharmaceutical products	EPA 450/2-78-029	PB 290 580/0BE
Manufacture of pneumatic rubber tires	EPA 450/2-78-030	PB 290 557/8BE
Graphic arts—rotogravure and flexography	EPA 450/2-78-033	PB 292 490/0BE
Petroleum liquid storage in external floating roof tanks	EPA 450/2-78-047	PB 290 579/2BE
Perchloroethylene dry cleaning systems	EPA 450/2-78-050	PB 290 613/9BE
Leaks from gasoline tank trucks and vapor collection systems	EPA 450/2-78-051	PB 290 568/5BE

Source: Joseph et al. 1983.

Table 1-5. Group III—Control Technique Guideline documents.

Source category	Status
Control of volatile organic compound emissions from the manufacture of high-density polyethylene, polypropylene, and polystyrene resins	Draft, May 1982
Control of volatile organic compound emissions from volatile organic liquid storage and floating and fixed roof tanks	Draft, August 1981
Control of VOC fugitive emissions from synthetic organic chemical, polymer, and resin manufacturing equipment	Draft, August 1981
Control of volatile organic emissions from large petroleum dry cleaners	Finalized EPA 450/3-82-009
Control of volatile organic compound emissions from air oxidation processes—synthetic organic chemical manufacturing industry	Draft, July 1981
Control of volatile organic compound equipment leaks from natural gas/gasoline processing plants	Draft, December 1981

Source: Joseph et al. 1983.

The States are required to apply other control strategies in order to bring non-attainment areas into attainment status. As a consequence of the Clean Air Act amendments of 1977, they are required to institute a permit system for industrial construction in either attainment or nonattainment areas. The States were also required to develop a Reasonable Further Progress (RFP) schedule to provide a timetable of activities for nonattainment areas leading to attainment status by 1982. The amendments gave the option, however, that an extension to 1987 could be granted in meeting ambient air standards if (among other requirements) an Inspection/Maintenance (I/M) program for motor vehicles were instituted for those areas exceeding the standards. Failure to reach attainment by 1982 and to institute such an I/M program could result in the application of *sanctions* to that area—withholding of Federal highway and other grant funds and the prohibition of new industrial construction.

A flexible policy of "controlled trading" has also been established as a method for VOC control. Controlled trading incorporates essentially three types of policies:

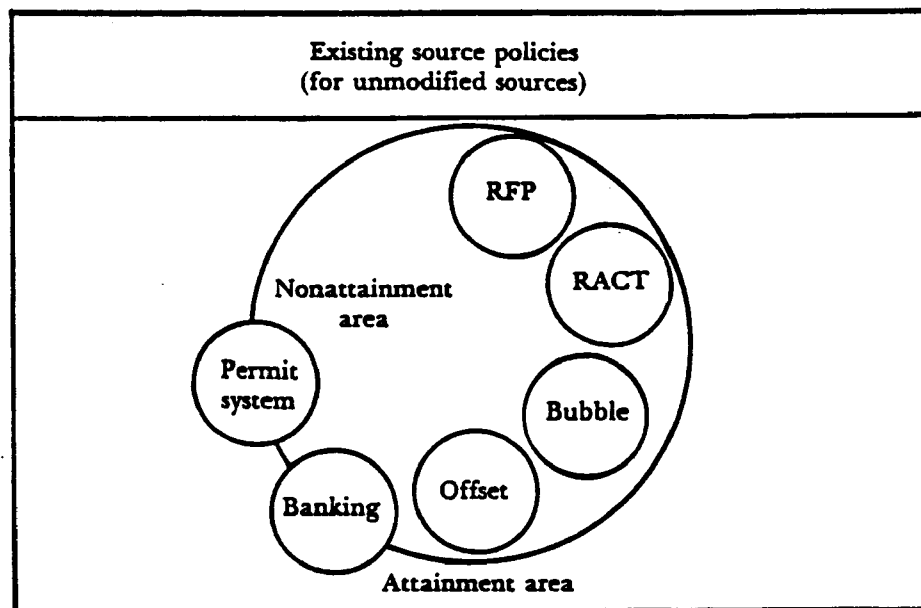
- offset,
- bubble, and
- banking.

The *offset policy* allows the trade-off of emissions between different sources so that a new source can be allowed to locate in a nonattainment area. For example, if an auto assembly plant is to be constructed in a nonattainment area, the manufacturer might only be allowed to do so if a petroleum refinery or some other industry in the area is willing to reduce their emissions to a level that will compensate for the new emissions from the auto plant.

The *bubble policy* applies to existing sources in nonattainment areas. The policy treats a plant as if an imaginary bubble were placed over it. Changes can be made in different plant operations so long as overall VOC emissions from the bubble are reduced. For example, a can coating operation may wish to increase emission controls on two coating lines so that controls need not be placed on an older line.

*Banking policies* allow sources to reduce emissions and *bank* the reductions for future expansion in attainment or nonattainment areas.

All of these policies are used by the States to limit the emission of volatile organic compounds into the atmosphere. Figure 1-1 provides a summary of these existing source policies.



**Figure 1-1. Direct impact of Federal policies on stationary sources.**

The large circle represents a nonattainment area and the space outside of it, an attainment area. The smaller circles illustrate how the different control policies apply and overlap between the two areas. For example, an existing source located in a nonattainment area must apply RACT so that the area can reach attainment status according to the RFP schedule developed in the State program. By reducing emissions more than required, an existing source may provide an *offset* for a new source wishing to locate in a nonattainment area, or it may bank them for future expansion.

# New Source Performance Standards for VOC Sources

In addition to State regulations, direct Federal regulations also affect industrial sources. Section 111 of the Clean Air Act provides the regulatory authority for establishing New Source Performance Standards (NSPS). NSPS apply to all new or modified sources that are constructed after the standards have been proposed. NSPS are set for a number of industrial source categories and specify emission limits, emission monitoring requirements, and occasionally the type of control equipment that must be installed on various industrial sources.

Categories of major sources of emissions which may affect public health and welfare have been identified and placed on a priority list. EPA is required to perform an analysis for each source category on the list. Based on this analysis, EPA may then set an NSPS for that source category. Presently, there are six NSPS for VOC emission sources. Table 1-6 lists the stationary source categories for which NSPS have been promulgated. Table 1-7 lists the source categories for which an NSPS has been proposed in the Federal Register.

**Table 1-6. Promulgated NSPS for VOC sources.**

Affected facility	Proposed date	Promulgated date	Background information document number
Petroleum liquid storage vessels (40,000 gallons or larger)	6/11/73 5/11/78	3/08/74 4/04/80	APTD-1352 A, B & C EPA 450/2-74-003
Industrial surface coating:			
• automotive and light duty trucks	10/05/79	12/24/80	EPA 450/3-79-030 A & B
• metal furniture	11/20/80	10/29/82	EPA 450/3-80-007 A & B
• large appliances	12/24/80	10/27/82	EPA 450/3-80-037 A & B
• metal coils	1/05/81	11/01/82	EPA 450/3-80-035 A & B
Rotogravure printing	10/28/80	11/08/82	EPA 450/3-80-031 A & B

Proposed date: All sources whose construction "commenced" after this date are subject to the NSPS.

Promulgated: Date the final rule appeared in the Federal Register.

Source: Joseph et al. 1983.



Table 1-7. Recommended and proposed NSPS for VOC sources.

Affected facility	Proposed date	Date of final rule
Organic solvent cleaners (metal cleaning and degreasing)	6/11/80	Undetermined
Perchloroethylene dry cleaning	11/25/80	12/82*
Industrial surface coating: <ul style="list-style-type: none"> <li>• pressure sensitive tapes and labels</li> <li>• cans</li> <li>• vinyl coating and printing</li> <li>• metal furniture</li> <li>• metal coil</li> <li>• automobile and light duty truck</li> <li>• large appliances</li> </ul>	12/30/80 11/26/80 11/18/83 11/28/80 1/15/81 10/05/79 12/24/80	10/18/83 8/25/83 9/83* 10/29/82 11/01/82 12/24/80 10/27/82
Synthetic organic chemical manufacturing: <ul style="list-style-type: none"> <li>• fugitive emissions</li> <li>• air oxidation processes</li> </ul>	1/05/81 12/82*	10/18/83 12/83*
Bulk gasoline terminals	12/17/80	8/18/83
Volatile organic liquid storage (40,000 gallons or more)	Undetermined	Undetermined
Rubber products industry—tire manufacturing	1/20/83	Undetermined
Refining fugitive emissions	1/04/83	12/83*
Synthetic fibers (solvent spinning)	12/82*	12/83*
Petroleum solvent dry cleaning	12/82*	12/83*
Solvent degreasing	Undetermined	Undetermined
On shore production (natural gas/gasoline)	10/82*	12/83*
Distillation operations (for both refineries and chemical manufacturing)	2/83*	9/83*
Polymer and resins manufacturing	9/83*	9/84*
Graphic arts rotogravure	10/28/80	11/08/82

\*Estimated

The control policies for new and modified sources are generally more stringent than for existing sources. In order to maintain and improve air quality, the PSD program, BACT, and NSPS are applied to the attainment areas. All of this is overseen by the New Source Review (NSR) program. New sources wishing to locate in nonattainment areas are affected by even more stringent policies such as LAER and the requirement to obtain offsets. The application of these policies is summarized in Figure 1-2.

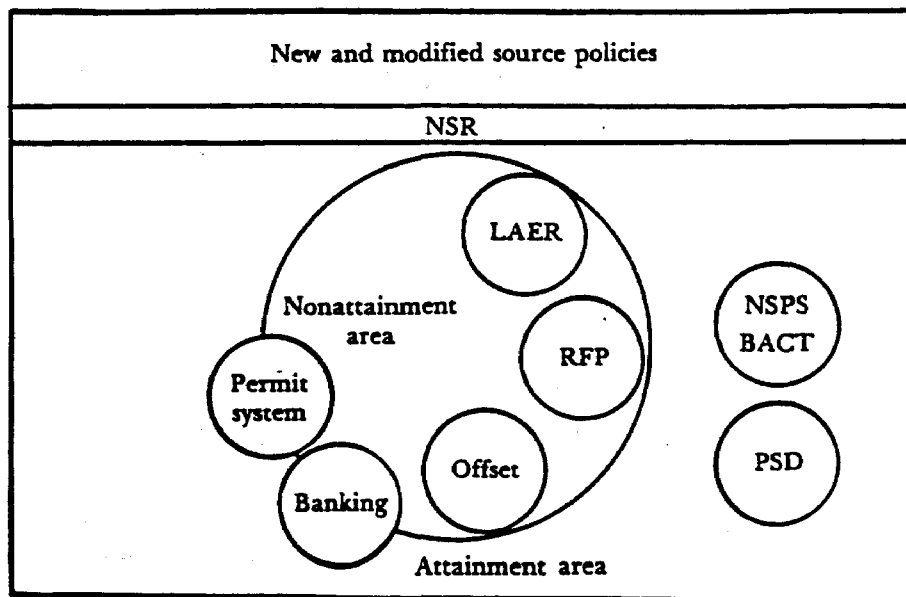


Figure 1-2. Direct impact of Federal policies on stationary sources.

For example, a new source locating in an attainment area must comply with PSD regulations, apply BACT, and meet NSPS. If it wishes to locate in a non-attainment area, it must meet LAER, fit in with the RFP schedule, and obtain offsets.

Table 6-2

## Group I CTGs Limits, Control Options &amp; Affected Facilities

Industry	CTG Emission Limit	Applicable Control Options	Number of Affected Facilities
<u>SURFACE COATING OF CANS</u>	<p>The recommended voc emission limits are:</p> <p>a. Sheet coating, two-piece exterior 0.34 Kg/l (2.8 Lb/gal)*</p> <p>b. Two- and three-piece interior 0.51 Kg/l (4.2 Lb/gal)*</p> <p>c. Two-piece end exterior 0.51 Kg/l (4.2 Lb/gal)*</p> <p>d. Three-piece side seam 0.66 Kg/l (5.5 Lb/gal)*</p> <p>e. End seal compound 0.44 Kg/l (3.7 Lb/gal)*</p>	<p>Low solvent Coatings</p> <p>Add-on Controls</p>	460
<u>SURFACE COATING OF METAL COILS</u>	<p>The recommended voc emission limit is 0.31 Kg per liter of coating minus water (2.6 Lb/gal).</p>	<p>Low solvent Coatings</p> <p>Add on Controls</p>	180
<u>SURFACE COATING OF FABRICS</u>	<p>The recommend voc emission limits are:</p> <p>a. Fabric coating 0.35 Kg per liter of coating minus water (2.9 Lb/gal).</p> <p>b. Vinyl coating 0.45 Kg per liter of coating minus water (3.8 Lb/gal).</p>	<p>Low solvent Coatings</p> <p>Add on Controls</p>	130
<u>SURFACE COATING OF PAPER PRODUCTS</u>	<p>The recommended voc emission limit is 0.34 Kg per liter of coating minus water (2.9 Lb/gal).</p>	<p>Low Solvent Coatings</p> <p>Add on Controls</p>	290

Table 6-2 (cont)

## GROUP I CTGS LIMITS, CONTROL OPTIONS &amp; AFFECTED FACILITIES

<u>TANK TRUCK GASOLINE LOADING TERMINALS</u>	The recommended emission limit is 80 mg/liter (0.67 Lb/1,000 gal) of gasoline loaded. This limit is based on submerged fill and vapor recovery/control systems. No leaks in the vapor collection system during operation is a requirement.	Add on Controls	600
<u>BULK GASOLINE PLANTS</u>	<p>Alternative 1 - submerged filling of of tank trucks.</p> <p>Alternative 2 - alternative 1 plus a vapor balance (displacement) system to control voc emissions from filling of bulk plant storage tanks. The vapors displaced from the storage tank are transferred to the tank truck being unloaded. Ultimately, the vapors are recovered when the tank truck returns to the terminal.</p> <p>Alternative 3 - alternative 2 plus a vapor balance system to control voc emissions from filling of account tank truck are transferred to the storage tank.</p>	Vapor Balance System Equipment Specifications and Operating Procedures	1800
<u>GASOLINE SERVICE STATIONS-STAGE I</u>	Emission limits recommended in terms of specifications. Recommended controls are submerged fill of storage tanks, vapor balance between truck and tank, and a leak between truck and tank, and a leak free truck and vapor transfer system.	Equipment Specification and Operating Procedures Vapor Balance System	340000
<u>FIXED-ROOF PETROLEUM STORAGE TANKS</u>	Emission limits recommended in terms of equipment specifications: installation of internal floating roofs or alternative controls are not specified in the CTG document.	Equipment Specifications and Maintenance Requirements Internal Floating Roof	300 5

Table 6-2 (cont)

## GROUP I CTGS LIMITS, CONTROL OPTIONS &amp; AFFECTED FACILITIES

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<u>PETROLEUM REFINERY PROCESSES</u>	Emission limits recommend a. VPS - incineration of VOC emissions from con- densers b. ws - covering separator forebays c. PUT - combustion of vapor Vented from vessels	Various Equipment Specification and Operating Procedures	285
<u>CUTBACK ASPHALT</u>	Substitute water and non- volatile emulsifier for petroleum distillate blending stock.	Water Emission	n/a
		Emulsion Solvent Content	
<u>SOLVENT METAL CLEANING</u>	The VOC emission limit is recommended in terms of equipment specifications and operation procedures. Required control equipment can be adsorp- tion system depending on the type, size, and design of the degreaser.	Equipment Specifications and Operating Procedures	1,245,000
		Add-on Carbon Absorber	

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Table 6-3  
Group II CTGS Limits, Control Options

INDUSTRY	CTG EMISSION LIMIT	APPLICABLE CONTROL OPTIONS	NUMBER OF AFFECTED FACILITIES
Petroleum refinery Fugitive emissions (Leaks)	If a leaking component has a voc concentration of over 10,000 ppm at the potential leak source, it should be scheduled for maintenance and repaired within 15 days.	Inspection monitoring maintenance	311
Surface Coating Miscellaneous Metal Parts	<u>Coating method</u> a. Air or forced dried items b. Clear coat c. No or infrequent color change or small number of color applied 1. Powder coatings 2. Other d. Outdoor, harsh exposure or extreme performance characteristics e. Frequent color change, large number of colors applied, or first coat on untreated ferrous substrate	<u>Recommended limitation wt. VOC vol. Coating</u> 0.42 Kg/l (3.5 lb/gal) 0.52 Kg/l (4.3 lb/gal) 0.05 Kg/l (0.4 lb/gal) 0.36 Kg/l (3.0 lb/gal) 0.42 Kg/l (1.5 lb/gal) 0.36 Kg/l (3.0 lb/gal)	low solvent coatings 9600 add on
FACTORY SURFACE COATING FLATWOOD	Printed hardwood plywood and partteleboard Natural finish hardwood Clean II Finishes for boarding paneling	<u>Recommended limitation</u> 2 2.9 Kg VOC/100 m <sup>2</sup> (6.0 lb VOC/1000 ft <sup>2</sup> ) 2 5.8 Kg VOC/100 m <sup>2</sup> (12.0 lb VOC/1000 ft <sup>2</sup> ) 2 4.8 Kg VOC/100 m <sup>2</sup> (10.0 lb VOC/100 ft <sup>2</sup> )	Low Solvent COATING 300 Add on

Table 6.3 (cont)

INDUSTRY	CTG EMISSION LIMIT	APPLICABLE CONTROL OPTIONS	NUMBE OF AFFECTED FACILITIES
Pharmaceutical Manufacture	1. a. Surface condensers or equivalent control on vents from reactors, distillation operations, crystallizers, centrifuges, and vacuum dryers that emit 6.8 Kg/day (15 lb/day) or more voc.	Maintenance and Operation	800
	b. Surface condensers must meet certain temperature versus VOC vapor pressure criteria.	Add-on	
	2. Additional specific emission reductions are required for air dryers, production equipment exhaust system, and storage and transfer of VOC.		
	3. Enclosures or covers are recommended for rotary vacuum filters, processing liquid containing VOC and in-process tanks.		
	4. Repair of components leaking liquids containing VOC.		
RUBBER TIRE MANUFACTURE	VOC emissions reduction from the affected operations is recommended through use of carbon adsorption of incineration. Water-based coatings may be used for green tire spraying.	Add-on	62
GRAPHIC ARTS ROTOGRAVURE AND FLEXOGRAPHY	Of water-borne or high solids inks meeting certain composition criteria or the use of capture and control equipment which provides:	Low Sol-vent Inks,	53000 units
	a. 75 Percent overall voc reduction where a publication rotogravure process is employed;		
	b. 65 Percent overall voc reduction where a packaging rotogravure process is employed; or,	add-on	
	c. 60 Percent overall voc reduction where a flexographic printing process is employed.		

Table 6.3 (cont)

INDUSTRY	CTG EMISSION LIMIT	APPLICABLE CONTROL OPTIONS	NUMBER OF AFFECTED FACILITIES
External Floating Roof Tanks	A continuous secondary seal or equivalent closure on all affected storage tanks, plus certain inspection and record-keeping requirements.	Inspection Maintenance Monitoring	13,800
*Drycleaning Perchloroethylene	<p>a. Reduction of dryer outlet concentration to less than 100 ppm voc, by means of carbon adsorption. (Facilities with inadequate space or steam capacity for adsorbers are excluded.)</p> <p>B. Reduction of voc emissions from filter and distillation wastes.</p> <p>C. Eliminate liquid and vapor leaks.</p>	<p>Operation and Maintenance</p> <p>Add-on Carbon Adsorption</p>	60,000
Gasoline Tank Trucks	<p>The control approach is a combination of testing, monitoring, and equipment design to ensure that good maintenance practices are employed to prevent leaks from truck tanks or tank compartments and vapor collection systems during gasoline transfer at bulk plants, bulk terminals, and service stations. A leak is a reading greater than or equal to 100 percent of the lel at 2.5 Cm from a potential leak source as detected by a combustible gas detector.</p>	<p>Pressure-Vacuum Test</p> <p>Inspection, Monitoring, Maintenance</p>	N/A
Manufacture of Vegetable Oil	<p>Recommended VOC emission limits:</p> <p>a. Limit extractor vent exhaust to 9000 ppm</p> <p>b. Limit desolventizer, dryer cooler and pneumatic conveyer emission to 207 lb/ton of flake</p>	<p>Add-on Inspection, Monitoring and Maintenance</p>	N/A



Table 6-4. GROUP III GTC'S LIMITS AND CONTROL OPTIONS

<u>INDUSTRY</u>	<u>CTG DOCUMENT NUMBER</u>	<u>APPLICABLE CONTROL OPTIONS</u>	<u>CTG EMISSION LIMIT</u>
Large Petroleum Dry Cleaners	EPA-450/3-82-009	Operation and Main- nance	Solvent recover dryer to reduce emissions by 81%, a cartridge filtration system in place of existing diatomite filtration system and improved operation of stillls with leak detect ion and repair program
Natural Gas/ Gasoline Processing Plants	EPA-450/3-83-007	Inspection Monitoring Maintenance	Weekly visual inspection of pumps and quarterly instrument monitoring of pumps, valves, compres- sors and relief valves. Leaking components >10,000 ppm should be repaired within fifteen (15) days.
SOCMI-Fugitive	EPA-450/3-83-006	Inspection Moni- toring Maintenance	Same as CTG for natural gas/gasoline processing plant except process streams must be >10% VOC and no small plant ex- ception
Manufacture of High Density Poly- ethylene Polypropy- styrene	EPA-450/3-83-008	Add-On	Reduction to 20 ppm for continuous voc emissions is recommended or a 98% reduction for poly propylene plants and an emissions limit of 0.12 Kg voc/1000 kg product for polystyrene plants
VOL STORAGE	CTG not issued as of 9/1/84		Recommended RACT requires affected facilities to reduce VOC emission by 98% or to 20 ppm which is even less stringent.
SOCMI Air Oxidation	EPA-450/3-84-015		

Pollutants, airflows, and, to a limited extent, pollutant concentrations in the atmospheric discharge are described. The reports also identify emission controls for each site and provides cost estimates for carbon adsorption and catalytic incineration for VOC control.

Call the **CTC HOTLINE** to order these reports or to obtain additional information.

ctc

## **NEW VOC CTG's, ACT's and RULES**

By Bob Blaszcak  
CTC Co-chair  
U.S. EPA, OAQPS

The EPA has recently begun, or is about to begin, work on 15 new VOC control techniques guidelines (CTG'S), alternative control techniques documents (ACT's), or rules. The following source categories are included in this new effort:

1. Synthetic Organic Chemical Manufacturing Industry (SOCMI) Distillation Processes
2. SOCMI Reactor Processes
3. SOCMI Batch Processes
4. Wood Furniture Manufacturing
5. Coating of Plastic Parts - Business Machines
6. Coating of Plastic Parts - Other

7. Web Offset Lithography
8. Autobody Refinishing
9. Clean-up Solvents
10. Industrial Adhesives
11. Pesticides Application
12. Petroleum Wastewater
13. Consumer & Commercial Products
14. Architectural & Industrial Coatings
15. Marine Vessel Loading and Unloading

If you have any questions concerning the status or schedule for developing CTG's/ACT's/rules for any of these categories, call the CTC HOTLINE.

ctc

## **INDUSTRIAL WASTEWATER TREATMENT EMISSIONS**

By Bob Blaszcak,  
CTC Co-chair  
and Penny Lassiter,  
U.S. EPA, OAQPS

The CTC recently completed its report on industrial wastewater treatment emissions and controls. This document, "Industrial Wastewater Volatile Organic Compound Emissions - Background Information For BACT/LAER Determinations," provides tech-

nical information on 1) estimating emissions of VOC from the collection and treatment of industrial wastewater, and 2) determining the control technology for VOC emissions from this category.

The document applies to four types of industries: the organic chemicals, plastics, and synthetic fibers industry; the pesticides industry; the pharmaceutical industry; and the hazardous waste treatment, storage, disposal facilities industry. This list, however, could be expanded to include additional industries as new information becomes available. Sources within the four listed categories have the potential to generate wastewater containing high concentrations of volatile organic compounds. Wastewater typically passes through a series of collection and treatment units prior to its discharge. Many of these collection and treatment units are open to the atmosphere. This allows organic-containing wastewater to contact ambient air which results in significant VOC emissions from the wastewater.

Three different control strategies are available for the reduction of VOC emissions. The most effective strategy involves the implementation of pollution prevention or waste minimization techniques to reduce or eliminate the generation of wastewater or to reduce the organic concentration of the wastewater. The second control strategy involves the identification of potentially significant VOC-emitting wastewater streams, management of these

*(continued page 4)*

## **CTC ASSISTANCE**

No-cost assistance to staff of State and local agencies and EPA Regional Offices on air pollution control technology issues.

**CTC HOTLINE:** CALL (919) 541-0800 or (FTS) 629-0800 to access EPA expert staff for consultations, references to pertinent literature, or access to EPA technical data and analyses. No question is too simple!

**ENGINEERING ASSISTANCE PROJECTS:** If you need in-depth assistance concerning a specific control tech-

nology problem, call the HOTLINE or write the CTC. The EPA staff and contractors are available for short-term projects such as review of proposed or existing control technology applications. Projects are subject to CTC Steering Committee approval.

**TECHNICAL GUIDANCE PROJECTS:** If the CTC receives several similar HOTLINE calls or a joint request from a group of agencies, the CTC Steering Committee may undertake broad, long-term projects of national or regional interest. The result may be a control technology document for a particular type of source, microcomputer software, or seminars and workshops.

# Control by Incineration

# Chapter 3

## Combustion

### Introduction

The process of combustion is most often used to control the emissions of volatile organic compounds from process industries. At a sufficiently high temperature and adequate residence time, any organic vapor can be oxidized to carbon dioxide and water by the combustion process. Combustion systems are often relatively simple devices capable of achieving very high removal efficiencies. They consist of: burners, which ignite the fuel and organic vapors; and a chamber, which provides appropriate residence time for the oxidation process. Due to the high cost and decreasing supply of fuels, combustion systems are designed to include some type of heat recovery. If heat recovery can be used, combustion can be a very effective control technique. For example, pollutant emissions from paint bake ovens can be reduced by 99.9+ % using incineration while heat recovered from the incinerator flue gases can be fed back to the oven. Combustion can also be used for serious emission problems which require high destruction efficiencies, such as odor problems or the emission of toxic gases.

There are, however, some problems that may occur when using combustion to control gaseous pollutants. Incomplete combustion of many organic compounds results in the formation of aldehydes and organic acids which may create an additional pollution problem. Oxidizing organic compounds containing sulfur or halogens produce unwanted pollutants such as sulfur dioxide, hydrochloric acid, hydrofluoric acid or phosgene. If present, these pollutants would require a scrubber to remove them prior to release into the atmosphere.

Four basic combustion systems can be used to control combustible gaseous emissions. They are *flares*, *thermal oxidizers*, *catalytic oxidizers*, and *process boilers*. Although these devices are physically similar, the parameters under which they operate are markedly different. Choosing the proper device depends on many factors including: concentration of combustibles in the gas stream, process flow rate, control requirements, presence of contaminants in the waste stream, and an economic evaluation. This chapter will examine the principles of combustion, simple combustion calculations, and the design and operating parameters of each combustion device.

### Combustion Principles

Combustion is a chemical process occurring from the rapid combination of oxygen with various elements or chemical compounds, resulting in the release of heat. The process of combustion is also referred to as *oxidation*. Most fuels used for combus-

tion are composed essentially of carbon and hydrogen, but can include other elements such as sulfur. Simplified reactions for the oxidation of carbon and hydrogen are given as:



Equations 3-1 and 3-2 show that the final products of combustion from an organic fuel are carbon dioxide and water vapor. Although combustion seems to be a very simple process that is well understood, in reality it is not. The exact manner in which a fuel is oxidized does not occur exactly as given in the above equations, but rather in a series of complex, free radical chain reactions. The precise set of reactions by which combustion occurs is termed the *mechanism* of combustion. By analyzing the mechanism of combustion, the rate at which the reaction proceeds and the variables affecting the rate can be predicted. For most combustion devices, the rate of reaction proceeds extremely fast compared to the mechanical operation of the device. Maintaining efficient and complete combustion is somewhat of an art rather than a science, as anyone who has built a campfire can attest to. Therefore, this chapter will focus on the factors which influence the completeness of combustion, rather than analyzing the mechanisms involved.

To achieve complete combustion once the air (oxygen) and fuel have been brought into contact, the following conditions must be provided: a *temperature* high enough to ignite the air and fuel mixture; *turbulent mixing* of the air and fuel; and sufficient *residence time* for the reaction to occur. These three conditions are referred to as the "three T's of combustion". Time, temperature, and turbulence govern the speed and completeness of reaction. They are not independent variables since changing one affects the other two.

### ***Temperature***

The rate at which a combustible compound is oxidized is greatly affected by temperature. The higher the temperature, the faster the oxidation reaction will proceed. The chemical reactions involved in the combination of a fuel and oxygen can occur even at room temperature, but very slowly. For this reason, a pile of oily rags can be a fire hazard. Small amounts of heat are liberated by the slow oxidation of the oils. This in turn raises the temperature of the rags and increases the oxidation rate, liberating more heat. Eventually a full-fledged fire can break out.

For combustion processes, ignition is accomplished by adding heat to speed up the oxidation process. Heat is needed to combust any mixture of air and fuel until the *ignition temperature* of the mixture is reached. By gradually heating a mixture of fuel and air, the rate of reaction and energy released will gradually increase until the reaction no longer depends on the outside heat source. More heat is being generated than is lost to the surroundings. The ignition temperature must be reached or exceeded to ensure complete combustion.

The ignition temperature of various fuels and compounds can be found in combustion handbooks such as the North American Combustion Handbook (1965). These temperatures are dependent on combustion conditions and therefore should be used only as a guide. Ignition depends on (EPA, 1972):

1. concentration of combustibles in the waste stream
2. inlet temperature of the waste stream
3. rate of heat loss from combustion chamber
4. residence time and flow pattern of the waste stream
5. combustion chamber geometry and materials of construction.

Most incinerators operate at higher temperatures than the ignition temperature which is a minimum temperature. Thermal destruction of most organic compounds occurs between 590 and 650°C (1100 and 1200°F). However, most incinerators are operated at 700 to 820°C (1300 to 1500°F) to convert CO to CO<sub>2</sub>; which occurs only at these higher temperatures.

### *Time*

Time and temperature affect combustion in much the same manner as temperature and pressure affect the volume of a gas. When one variable is increased, the other may be decreased with the same end result. With a higher temperature, a shorter residence time can achieve the same degree of oxidation. The reverse is also true, a higher residence time allows the use of a lower temperature. In describing incinerator operation, these two terms are always mentioned together. One has little meaning without specifying the other.

The choice between higher temperature or longer residence time is based on economic considerations. Increasing residence time involves using a larger combustion chamber resulting in a higher capital cost. Raising the operating temperature increases fuel usage which also adds to the operating costs. Fuel costs are the major operating expense for most incinerators. Within certain limits, lowering the temperature and adding volume to increase residence time can be a cost effective alternative method of operation.

The residence time of gases in the combustion chamber may be calculated from:

(Eq. 3-3) 
$$\Theta = \frac{V}{Q}$$

Where:  $\Theta$  = residence time, s

$V$  = chamber volume, m<sup>3</sup>

$Q$  = gas volumetric flow rate at combustion conditions, m<sup>3</sup>/s

$Q$  is the total flow of hot gases in the combustion chamber. Adjustments to the flow rate must include any outside air added for combustion. Example 3-1 shows the determination of residence time from the volumetric flow rate of gases.

## ***Turbulence***

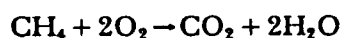
Proper mixing is important in combustion processes for two reasons. First, for complete combustion to occur, every particle of fuel must come in contact with air (oxygen). If not, unreacted fuel will be exhausted from the stack. Second, not all of the fuel or waste gas stream is able to be in direct contact with the burner flame. In most incinerators a portion of the waste stream bypasses the flame and is mixed at some point downstream of the burner with the hot products of combustion. If the two streams are not completely mixed, a portion of the waste stream will not react at the required temperature and incomplete combustion will occur.

A number of methods are available to improve mixing the air and combustion streams. Some of these include the use of refractory baffles, swirl fired burners, and baffle plates. These devices are discussed in more detail in the equipment section of this chapter. The problem of obtaining complete mixing is not easily solved. Unless properly designed, many of these mixing devices may create "dead spots" and reduce operating temperatures. Merely inserting obstructions to increase turbulence is not the answer. According to one study of afterburner systems, "the process of mixing flame and fume stream to obtain a uniform temperature for decomposition of pollutants is the most difficult part in the design of the afterburner" (EPA, 1972).

## ***Oxygen Requirements***

Oxygen is necessary for combustion to occur. To achieve complete combustion of a compound, a sufficient supply of oxygen must be present to convert all of the carbon to CO<sub>2</sub>. This quantity of oxygen is referred to as the *stoichiometric* or *theoretical amount*. The stoichiometric amount of oxygen is determined from a balanced chemical equation summarizing the oxidation reactions. For example, from Equation 3-4, 1 mole of methane requires 2 moles of oxygen for complete combustion.

(Eq. 3-4)



If an insufficient amount of oxygen is supplied, the mixture is referred to as *rich*. There is not enough oxygen to combine with all the fuel so that incomplete combustion occurs. This condition results in black smoke being exhausted. If more than the stoichiometric amount of oxygen is supplied, the mixture is referred to as *lean*. The added oxygen plays no part in the oxidation reaction and passes through the incinerator.

Oxygen for combustion processes is supplied by using air. Since air is essentially 79% nitrogen and 21% oxygen, a larger volume of air is required than if pure oxygen were used. To balance Equation 3-4, 9.53 moles of air would be required to completely combust the 1 mole of methane. The stoichiometric calculations for this are presented in Appendix D. A listing of theoretical air requirements is given in Table 3-1.

Table 3-1. Combustion constants and approximate limits of flammability of gases and vapors in air.

Substance	Lb/ft <sup>3</sup>	Ft <sup>3</sup> /lb	Heat of combustion				For 100% total air (mol/mol of combustible) (ft <sup>3</sup> /ft <sup>3</sup> of combustible)						For 100% total air (lb/lb of combustible)						Flammability limits (% by volume)	
			(Btu/ft <sup>3</sup> )		(Btu/lb)		Required for combustion			Flue products			Required for combustion			Flue products			Lower	Upper
			Gross (high)	Net (low)	Gross (high)	Net (low)	O <sub>2</sub>	N <sub>2</sub>	Air	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Air	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>		
Carbon, C*	—	—	—	—	14,093	14,093	1.0	3.76	4.76	1.0	—	3.76	2.66	8.86	11.53	3.66	—	8.86	—	—
Hydrogen, H <sub>2</sub>	0.0053	187.723	325	275	61,100	51,623	0.5	1.88	2.38	—	1.0	1.88	7.94	26.41	34.34	—	8.94	26.41	4.00	74.20
Oxygen, O <sub>2</sub>	0.0846	11.819	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nitrogen (atm), N <sub>2</sub>	0.0744	13.443	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Carbon monoxide, CO	0.0740	13.506	322	322	4,347	4,347	0.5	1.88	2.38	1.0	—	1.88	0.57	1.90	2.47	1.57	—	1.90	12.50	74.20
Carbon dioxide, CO <sub>2</sub>	0.1170	8.548	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Paraffin series																				
Methane, CH <sub>4</sub>	0.0424	23.565	1013	913	23,879	21,520	2.0	7.53	9.53	1.0	2.0	7.53	3.99	13.28	17.27	2.74	2.25	13.28	5.00	15.00
Ethane, C <sub>2</sub> H <sub>6</sub>	0.0803	12.455	1792	1641	22,320	20,432	3.5	13.18	16.68	2.0	3.0	13.18	3.73	12.39	16.12	2.93	1.80	12.39	3.00	12.50
Propane, C <sub>3</sub> H <sub>8</sub>	0.1196	8.365	2590	2385	21,661	19,944	5.0	18.82	23.82	3.0	4.0	18.82	3.63	12.07	15.70	2.99	1.68	12.07	2.12	9.35
n-Butane, C <sub>4</sub> H <sub>10</sub>	0.1582	6.321	3370	3113	21,308	19,680	6.5	24.47	30.97	4.0	5.0	24.47	3.58	11.91	15.49	3.03	1.55	11.91	1.86	8.41
Isobutane, C <sub>4</sub> H <sub>10</sub>	0.1582	6.321	3363	3105	21,257	19,629	6.5	24.47	30.97	4.0	5.0	24.47	3.58	11.91	15.49	3.03	1.55	11.91	1.80	8.44
n-Pentane, C <sub>5</sub> H <sub>12</sub>	0.1904	5.252	4016	3709	21,091	19,517	8.0	30.11	38.11	5.0	6.0	30.11	3.55	11.81	15.35	3.05	1.50	11.81	—	—
Isopentane, C <sub>5</sub> H <sub>12</sub>	0.1904	5.252	4008	3716	21,052	19,478	8.0	30.11	38.11	5.0	6.0	30.11	3.55	11.81	15.35	3.05	1.50	11.81	—	—
Neopentane, C <sub>5</sub> H <sub>12</sub>	0.1904	5.252	3993	3693	20,970	19,396	8.0	30.11	38.11	5.0	6.0	30.11	3.55	11.81	15.35	3.05	1.50	11.81	—	—
n-Hexane, C <sub>6</sub> H <sub>14</sub>	0.2274	4.398	4762	4412	20,940	19,403	9.5	35.76	45.26	6.0	7.0	35.76	3.53	11.74	15.27	3.06	1.46	11.74	1.18	7.40
Olefin series																				
Ethylene, C <sub>2</sub> H <sub>4</sub>	0.0746	13.412	1614	1513	21,644	20,295	3.0	11.29	14.29	2.0	2.0	11.29	3.42	11.39	14.81	3.14	1.29	11.39	2.75	28.60
Propylene, C <sub>3</sub> H <sub>6</sub>	0.1110	9.007	2336	2186	21,041	19,691	4.5	16.94	21.44	3.0	3.0	16.94	3.42	11.39	14.81	3.14	1.29	11.39	2.00	11.10
n-Butene, C <sub>4</sub> H <sub>8</sub>	0.1480	6.756	3084	2885	20,840	19,496	6.0	22.59	28.59	4.0	4.0	22.59	3.42	11.39	14.81	3.14	1.29	11.39	1.75	9.70
Isobutene, C <sub>4</sub> H <sub>8</sub>	0.1480	6.756	3068	2869	20,730	19,382	6.0	22.59	28.59	4.0	4.0	22.59	3.42	11.39	14.81	3.14	1.29	11.39	—	—
n-Pentene, C <sub>5</sub> H <sub>10</sub>	0.1852	5.400	3836	3586	20,712	19,363	7.5	28.23	35.73	5.0	5.0	28.23	3.42	11.39	14.81	3.14	1.29	11.39	—	—
Aromatic series																				
Benzene, C <sub>6</sub> H <sub>6</sub>	0.2060	4.852	3751	3601	18,210	17,480	7.5	28.23	35.73	6.0	3.0	28.23	3.07	10.22	13.30	3.38	0.69	10.22	1.40	7.10
Toluene, C <sub>7</sub> H <sub>8</sub>	0.2431	4.113	4484	4284	18,440	17,620	9.0	33.88	42.88	7.0	4.0	33.88	3.13	10.40	13.53	3.34	0.78	10.40	1.27	6.75
Xylene, C <sub>8</sub> H <sub>10</sub>	0.2803	3.567	5230	4980	18,650	17,760	10.5	39.52	50.02	8.0	5.0	39.52	3.17	10.53	13.70	3.32	0.85	10.53	1.00	6.00
Miscellaneous gases																				
Acetylene, C <sub>2</sub> H <sub>2</sub>	0.0697	14.344	1499	1448	21,500	20,776	2.5	9.41	11.91	2.0	1.0	9.41	3.07	10.22	13.30	3.38	0.69	10.22	—	—
Napthalene, C <sub>10</sub> H <sub>8</sub>	0.3384	2.955	5854	5654	17,298	16,708	12.0	45.17	57.17	10.0	4.0	45.17	3.00	9.97	12.96	3.43	0.56	9.97	—	—
Methyl alcohol, CH <sub>3</sub> OH	0.0846	11.820	868	768	10,259	9,078	1.5	5.65	7.15	1.0	2.0	5.65	1.50	4.98	6.48	1.37	1.13	4.98	6.72	36.50
Ethyl alcohol, C <sub>2</sub> H <sub>5</sub> OH	0.1216	8.221	1600	1451	13,161	11,929	3.0	11.29	14.29	2.0	3.0	11.29	2.08	6.93	9.02	1.92	1.17	6.93	3.28	18.95
Ammonia, NH <sub>3</sub>	0.0456	21.914	441	365	9,668	8,001	0.75	2.82	3.57	—	1.5	3.32	1.41	4.69	6.10	—	1.59	5.51	15.50	27.00
Sulfur and sulfur compounds																				
Sulfur, S*	0.0911	10.979	—	—	3,983	3,983	1.0	3.76	4.76	SO <sub>2</sub> 1.0	—	3.76	1.00	3.29	4.29	2.00	—	3.29	—	—
Hydrogen sulfide, H <sub>2</sub> S	0.1733	5.770	647	596	7,100	6,545	1.5	5.65	7.15	1.0	1.0	5.65	1.41	4.69	6.10	1.88	0.53	4.69	4.30	45.50
Sulfur dioxide, SO <sub>2</sub>	0.0476	21.017	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Water vapor, H <sub>2</sub> O	0.0766	13.063	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Air	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Gasoline	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.40	7.60

\*Carbon and sulfur are considered as gases for molal calculations only.

Sources: Adapted from *Fuel Flue Gases*, American Gas Association.  
*Combustion Flame and Explosions of Gases*, 1951.



In industrial applications, more than the stoichiometric amount of air is used to ensure complete combustion. This extra volume is referred to as *excess air*. If ideal mixing were achievable, no excess air would be necessary. However, most combustion devices are not capable of achieving ideal mixing of the fuel and air streams. The amount of excess air is held to a minimum in order to reduce heat losses. Excess air takes no part in the reaction but does absorb some of the heat produced. To raise the excess air to the combustion temperature, additional fuel must be used to make up for this loss of heat. Operating at a high volume of excess air can be very costly in terms of the added fuel required. Equations to calculate excess air are also listed in Appendix D.

In addition to the theoretical air required, Table 3-1 also lists the *volume of combustion products produced* from oxidizing a substance. This is an important term used to determine the size of the combustion chamber. Example 3-1 illustrates how these values are used. The values in Table 3-1 are given in *volume percent* and *weight percent*. Volume percent is the more important term for combustion of gaseous substances since gas flows are measured in cubic meters per second instead of weight units. For example, from Table 3-1, when 1 m<sup>3</sup> of methane is combusted with the theoretical amount of air, 10.53 m<sup>3</sup> of flue gas is produced. Table 3-1 is given in English units. Since these are volume ratios (ft<sup>3</sup>/ft<sup>3</sup>), metric units and English units are interchangeable.

Natural gas is not listed in Table 3-1 since its chemical composition can vary. When 1 m<sup>3</sup> of natural gas is burned with a stoichiometric amount of air, it produces approximately 11.5 m<sup>3</sup> (average value) of flue gas.

### **Combustion Limits**

Not all mixtures of fuel and air are able to support combustion. The flammable or explosive limits for a mixture are the maximum and minimum concentrations of fuel in air that will support combustion. The *upper explosive limit* (UEL) is defined as the concentration of fuel which produces a nonburning mixture due to a lack of oxygen. The *lower explosive limit* (LEL) is defined as the concentration of fuel below which combustion will not be self-sustaining. Table 3-1 lists the flammability limits (LEL and UEL) for common fuels and solvents.

For example, consider that a mixture of gasoline vapors and air is at atmospheric conditions. From Table 3-1 the LEL is 1.4% by volume of gasoline vapors and the UEL is 7.6%. Any concentration of gasoline in air within these limits will support combustion. That is, once a flame has been ignited it will continue to burn. Concentrations of gasoline in air below or above these limits will not burn and can quench the flame. The lower explosive limit is the more important of the two terms in describing gas streams with combustible contaminants. Industrial processes which handle combustible vapors, such as paint or solvent vapors, are usually required by insurance companies to operate at less than 25% of the LEL of the vapor in the ducts to minimize fire hazards. By using gas analyzers and an alarm system, the concentration of vapor may be allowed to be as high as 50% of the LEL by an insurance company covering the plant.

Flammability limits are not absolute values, but are affected by temperature,

pressure, geometry of the chamber, and presence of other contaminants. The higher the temperature, the greater the activation energy of combustion is. Thus, there is a greater probability that the flame will propagate. At high enough temperatures even vapor concentrations within 25% of their LEL can propagate a flame. This high degree of flammability limits the temperature to which some waste streams can be preheated prior to oxidation. Pressure also changes vapor flammability by its effect on gas densities. The higher the pressure, the closer the gas molecules are to one another. This decreases the distance a flame or spark must jump from one combustible point to another (Bethea, 1978).

The size and geometry of the combustion chamber also affect the flammability limits. The smaller the diameter of the chamber, the narrower the flammability range will become. Increased surface-to-volume ratio promotes rapid cooling and flame quenching, limiting flammability. Some flame arresters are designed on this principle of large surface-to-air volume ratio to eliminate fire hazards. The presence of other compounds can also affect flammability limits. The flammability range of a mixture can be either increased or decreased depending on the properties of the contaminant.

### ***Flame Combustion***

When mixing fuel and air, two different mechanisms of combustion can occur. A luminous (yellow) flame results when air and fuel flowing through separate ports are ignited at the burner nozzle. The yellow flame results from thermal cracking of the fuel. Cracking occurs when hydrocarbons are intensely heated before they have a chance to combine with oxygen. The cracking releases both hydrogen and carbon which diffuse to the flame to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The carbon particles give the flame the yellow appearance. If incomplete combustion occurs from flame temperature cooling or if there is insufficient oxygen, soot and black smoke will form.

Blue flame combustion occurs when the fuel and air are premixed in front of the burner nozzle. This produces a short, intense, blue flame. The reason for the different flame is that the fuel-air mixture is gradually heated. The hydrocarbon molecules are slowly oxidized, going from aldehydes and ketones to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . No cracking occurs and no carbon particles are formed. Incomplete combustion results in the release of the intermediate, partially oxidized compounds. Blue haze and odors are emitted from the stack.

## Combustion Equipment Used for Control of Gaseous Emissions

### *Introduction*

Afterburning, incineration, or thermal oxidation are interchangeable terms used to describe the combustion process used to control gaseous emissions. Although not technically correct, this nomenclature is generally accepted. Afterburners and incinerators perform different functions even though both are forms of *thermal oxidation*. The term afterburner is appropriate only to describe a thermal oxidizer used to control gases coming from a process where combustion was not complete (Ross, 1977). An example of an afterburner in use would be an application on a copper wire reclaiming source which **incompletely** burns off the rubber coating. Incineration or thermal oxidation are **not** necessarily afterburning. Each is a primary burning process that is installed to control effluent pollutants which are combustible. Incinerators are used to combust solid, liquid and gaseous materials. When used in this manual, the term incinerator will refer to controlling gaseous emissions of organic vapors. Examples of sources using incineration are curing and drying ovens, chemical processes, petroleum refining processes, and food processing plants. In this chapter the terms incinerator and thermal oxidizer will be used interchangeably.

Equipment used to control waste gases by combustion can be divided into three categories: *direct combustion* or *flaring*, *thermal oxidation*, and *catalytic oxidation*. A *direct combustor* or *flare* is a device in which air and all the combustible waste gases react at the burner. Complete combustion must occur instantaneously since there is no residence chamber. Therefore, the flame temperature is the most important variable in flaring waste gases. In contrast, in *thermal oxidation*, the combustible waste gases pass over or around a burner flame into a residence chamber where oxidation of the waste gases is completed. *Catalytic oxidation* is

very similar to thermal oxidation. The main difference is that after passing through the flame area, the gases pass over a catalyst bed which promotes oxidation at a lower temperature than does thermal oxidation.

### ***Direct Combustion or Flaring***

Direct combustion or flaring is used for the disposal of intermittent or emergency emissions of combustible gases from industrial sources. Safety and health hazards at or near the plant can be eliminated by using flares to prevent the direct venting of these emissions. Flares have been used mainly at oil refineries and chemical plants which handle large volumes of combustible gases.

Flares are simply burners that have been designed to handle varying rates of fuel while burning smokelessly. In general, flares can be classified as either *elevated* or *ground level*. The reason for elevating a flare is to eliminate any potential fire hazard at ground level. Ground level flares must be completely enclosed to conceal the flame. Either type of flare must be capable of operating over a wide range of flow rates in order to handle all plant emergencies. The range of waste gas flows within which a flare can operate and still burn efficiently is referred to as the turndown ratio. Flares are expected to handle turndown ratios of 1000:1, while most industrial boilers seldom handle more than a 10:1 turndown ratio (Gottschlich, 1977). For example, a flare should be capable of maintaining complete combustion for waste gas flow rates ranging from 20,000 m<sup>3</sup>/h to 20 m<sup>3</sup>/h.

Although the flare is designed to eliminate waste gas stream disposal problems, it can present safety and operational problems of its own. Some of the problems associated with operation of a flare system are:

1. Thermal radiation: Heat given off to the surrounding area may be unacceptable.
2. Light: Luminescence from the flame may be a nuisance if the plant is located in an urban area.
3. Noise: Mixing at the flare tip is done by jet venturis which can cause excess noise levels in nearby neighborhoods.
4. Smoke: Incomplete combustion can result in toxic or obnoxious emissions.
5. Energy consumption: Flares waste energy in two ways. First by keeping the pilot flame constantly lit and secondly, by the potential recovery value of the waste gas being flared.

For flaring to be economically feasible, the waste gas usually must supply at least 50% of the fuel value to combust the mixture. When the heat content of the waste gas is below  $4.28 \times 10^3$  kJ/m<sup>3</sup> (115 Btu/ft<sup>3</sup>), injecting an additional gas with a higher heating value is necessary to achieve complete combustion. This type of system is referred to as a *fired* or *endothermic* flare. The cost of the additional fuel for endothermic flaring can be considerable. To conserve energy, some companies have used other waste gases in place of conventional fuels.

## Elevated Flares

A typical elevated flare is composed of a system which first collects the waste gases and passes them through a knockout drum to remove any liquids. Water seals or other safety devices are placed between the knockout drum and the flare stack to prevent a flashback of flames into the collection system. The flare stack is essentially a hollow pipe that may extend to a height of 100 meters or more. The diameter of the flare stack determines the volume of waste gases that can be handled. At the top of the stack is the flare tip which is comprised of the burners and a system to mix the air and fuel.

*Smokeless* combustion is accomplished by proper design of the flare tip. Smokeless flares require a system allowing for intimate mixing of waste gases and air. A number of flare tip designs provide good mixing characteristics over a wide range of waste gas flow values and still have excellent flame holding capabilities. Steam jets have proved to be one of the most effective ways to mix air and waste gases. An example of a flare tip designed for steam injection is illustrated in Figure 3-4. In addition to increasing turbulence, steam injection reduces the partial pressure of the waste gas, thus reducing polymerization reactions. The steam also reacts with the gases to produce oxygenated compounds which readily burn at lower temperatures. Other devices used to reduce smoke are high pressure fuel gases, water sprays, high velocity swirl fired burners, and electric air blowers (Straitz, 1980). In addition to these devices, shields are also used on elevated flares to protect the flame zone from atmospheric conditions. This shield also helps reduce noise and visibility problems associated with flares.

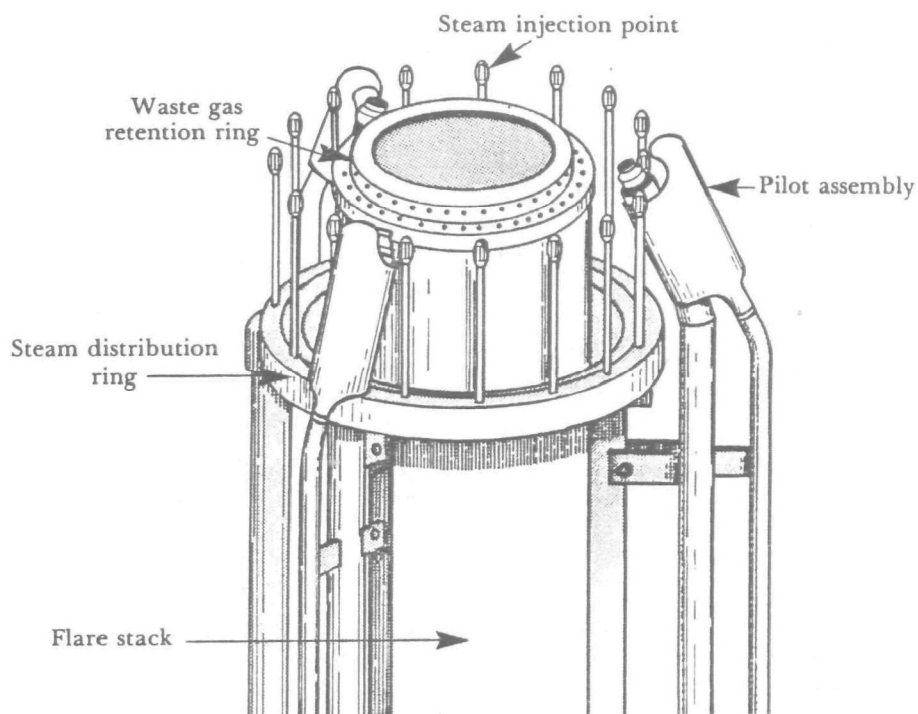
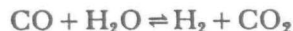


Figure 3-4. Smokeless flare tip.

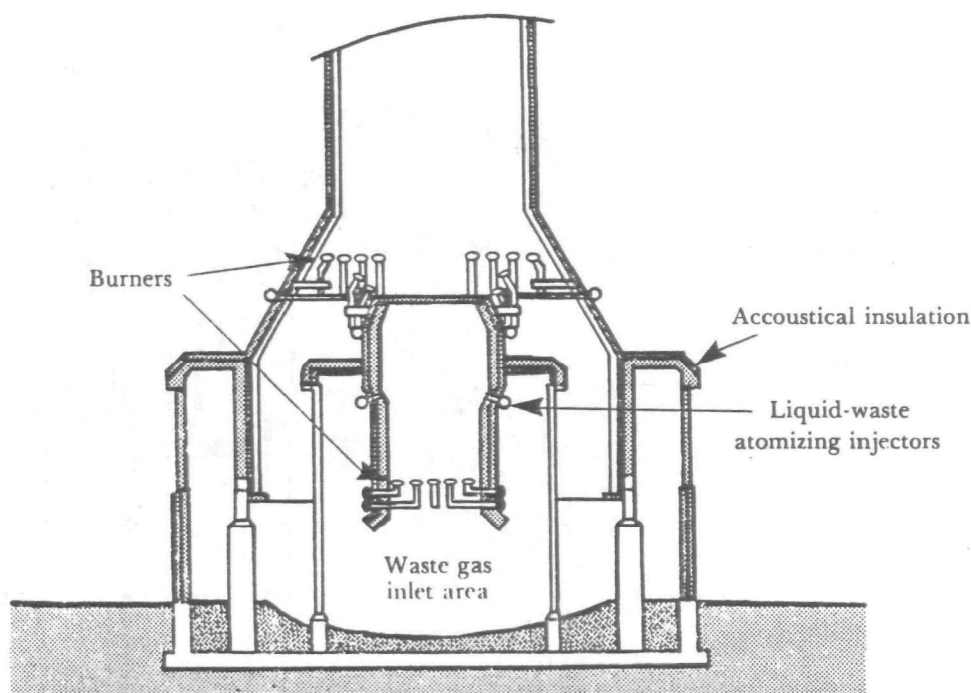
As previously mentioned, steam reacts with intermediate combustion products to form compounds that burn readily at lower temperatures. One of the main reactions taking place is a hydrolysis reaction referred to as the *water-gas reaction*. This reaction produces hydrogen gas which helps flare operation. The simplified water-gas shift can be written as:



Steam-to-hydrocarbon mass ratios are usually determined by the molecular weight and concentration of the unsaturated organic compounds (alkenes and alkynes) in the waste gas. Steam requirements generally range between 0.05 and 0.30 kg of steam per kg of waste gas (Gottschlich, 1977). The steam is automatically injected proportionally to the flow rate of the waste gases.

### Enclosed Ground Flares

Manufacturers design a number of different ground flares. Most ground flares consist of multiple burners enclosed within a refractory shell. The shell encloses the flame to eliminate noise, luminescence, and safety hazards. The waste gas is introduced through a jet or venturi to provide turbulent mixing. The term *ground flare* refers to locating the flare tip at ground level. The flare system still requires a stack for proper release of the effluent gases. Figure 3-5 shows a ground flare installed at Nippon Steel Company in Oita City, Japan (Straitz, 1980). The flare is composed of two chambers designed to combust eight different gases and a liquid-waste stream.



Source: Straitz, 1980.

Figure 3-5. Ground flare.

Ground level flares normally have a much higher capital cost than elevated flares. The cost of a ground flare depends on the size of the enclosure. The size of a ground flare is directly proportional to the volume of vapors it must handle. Ground flares can be designed for efficient combustion without steam injection. Eliminating the use of steam injection can significantly lower operating costs as compared to elevated systems (Straitz, 1980). Some plants have incorporated both designs. A ground flare is used for normal or intermittent operation and a large elevated flare is only used to control emergency releases of large quantities of gases.

### *Incinerators*

Thermal oxidizers or organic vapor incinerators refer to any device that uses a flame (temperature) combined with a chamber (time and turbulence) to convert combustible material to carbon dioxide and water. An incinerator usually consists of a refractory-lined chamber that is equipped with one or more sets of burners. A typical incinerator is depicted in Figure 3-6. The contaminant-laden stream is passed through the burners where it is heated above its ignition temperature. The hot gases then pass through one or more residence chambers where they are held for a certain length of time to ensure complete combustion. Depending on the particular needs of the system, additional fuel and/or excess air can be added through the burners. Also, since the flue gases are discharged at elevated temperatures, a system to recover the heat may be included. With the rising costs of fuel and solvents, heat recovery devices are becoming an integral part of many incineration systems.

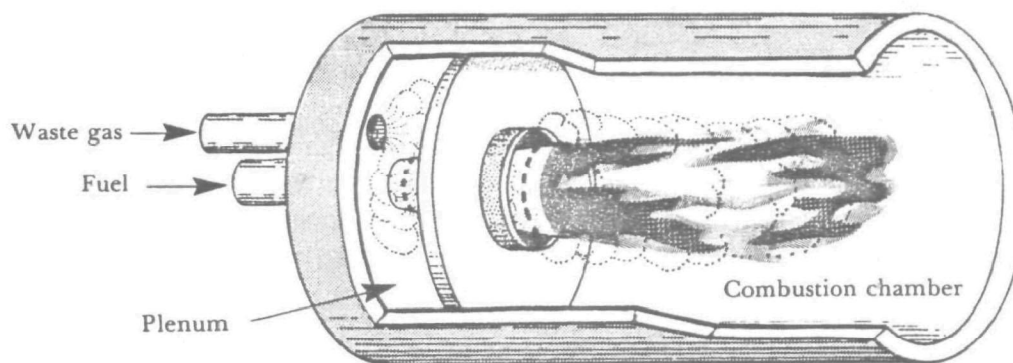


Figure 3-6. Typical thermal incinerator (UOP raw gas burner).

Incinerators on industrial processes are most often used to control gas streams with a **low concentration** of organic vapors. The concentration of vapors delivered to an incinerator through process ductwork is limited by the LEL of the mixture. Safety codes usually limit combustible vapor concentrations in ducts to a maximum of 25% of the LEL. By using process control monitors and alarm systems, some plants have been allowed to go up to 50% of the LEL. Supplemental fuel is required to ignite the waste gas stream and bring it up to the proper operating

temperature. The amount of fuel is then decreased proportionally to the heating value supplied by the waste gas stream. Ideally, after initial startup, little or no auxiliary fuel would be needed.

Incinerators operate at temperatures between 700 and 800°C (1300 and 1500°F) with a residence time of 0.1 to 0.5 seconds. The residence time is determined by the size of the combustion chamber and is measured after the required temperature has been reached. Typical operating temperatures of thermal oxidizers for various processes are listed in Table 3-3 (EPA, 1972). As noted previously, temperature and residence must be discussed together since changing one affects the other. By raising the temperature, the residence time for complete combustion is reduced and vice versa. However, temperature is the more important process variable. Figure 3-7 illustrates the effect of both temperature and residence time on the percent destruction of pollutants (oxidation rate). Depending on the initial temperature, small increases in temperature can bring dramatic increases in pollutant destruction. For example, for a 0.01 second residence time increasing the temperature from 1200 to 1400°F, the percent destruction is doubled from approximately 50 to 100%. At 1200°F, the residence time must be increased ten times (from 0.01 second to over 0.1 second) for the same increase in percent pollutant destruction.

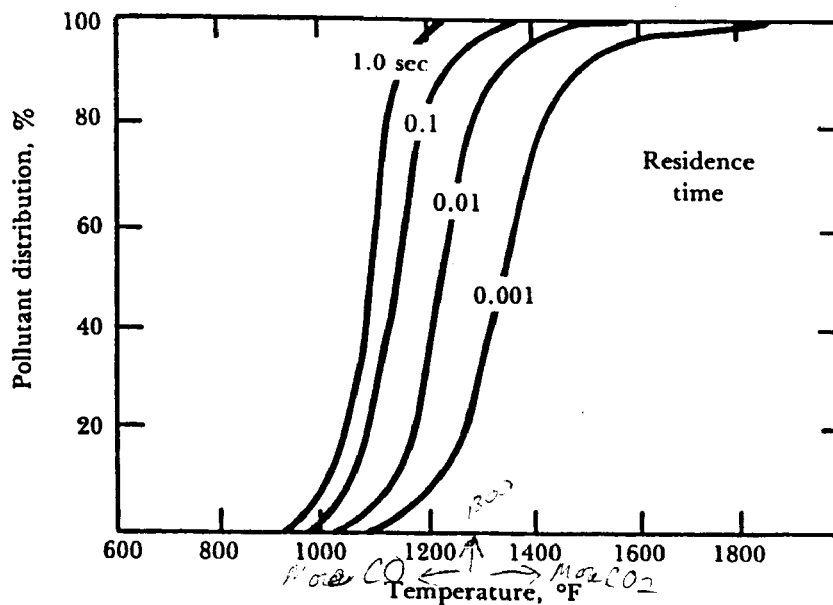
Table 3-3. Typical waste gas incinerators' operating temperatures (°F).

Industry	LAAPCD** recommendation	Survey data	Literature
Asphalt blowing	—	1000-2000	—
Biological control, fermentation	—	110-1250	—
Carpet laminating	1200-1400	—	—
Coffee roasting	—	1200-1500	1050
Coil coating, sheet coating, metal decorating	—	1200-1500	1300
Core ovens, foundry	1400	2000	—
Coating, engraving	—	1000*-1450	—
Cloth carbonization	1800	—	—
Deep fat fryers	1200	—	—
Gum label drying oven	—	—	1250
Mineral wool, fiberglass curing	—	1000*	1310
Odor control (general) sludge off-gas	1300-1500	1100-1250	1300-1425
Hardboard tempering	—	1200	1200
Oil and grease smoke (metal chip recovery, heat quench baths, tempering)	1200-1400	900*-1600	—
Paint bake ovens	1200-1500	1100-1500	1240
Paper manufacture—sulfite digester off-gas	—	—	1350
Pipe wrapping	1400	—	—
Rendering plants	1200	1200-1300	1200
Rubber products	—	1300-1400	1300
Petroleum refining and products	—	1300-2000	—
Printing, lithographing	—	1300-1500	—
Smelting, refining, metal recovery, wire burnoff	—	1300-1650	—
Smokehouse operation	1200	800*-1200	—
Solvent control	1300-1500	—	—
Varnish cookers, resin kettles	1200	1000*-1500	1200-1400
Vinyl plastisol curing	1200-1400	1200	900*
Wood milling	—	—	1200
Wire enameling	—	—	1300-1350, 1400
Phthalic anhydride	—	1250-1440	—
Textile drying oven	—	1350	—

\*Low temperature generally for odor, smoke control, not true organic vapor destruction.

\*\*LAAPCD is the Los Angeles Air Pollution Control District.





Source: Rolke, 1972.

Figure 3-7. Effects of temperature and residence time on rate of pollutant oxidation.

Besides temperature and residence time, the concentration of the pollutant in the waste gas stream also affects operation of the incinerator. First, the concentration of the contaminant dictates the amount of supplemental fuel required. Initially, supplemental fuel must be added to start the oxidation reaction. As the temperature rises, the rate of oxidation of the contaminant increases until the reaction becomes self-sustaining. The amount of fuel can then be decreased. A certain amount of fuel is normally burned to ensure stable operation. Secondly, there is a problem of flame quenching. To avoid noncombustible mixtures, the entire amount of waste gas and fuel cannot usually be mixed at the burner. It would require an inordinate amount of fuel to bring the entire waste gas stream within combustible limits. Only part (about one-half) of the waste gas stream is mixed with the fuel at the burner. The remainder of the waste gas stream must be mixed with the hot products of combustion downstream of the flame to avoid quenching the flame. Unless adequate mixing of the waste gas stream and hot products of combustion is accomplished, incomplete combustion products will be exhausted.

### Types of Burner Arrangements

The design of an incinerator must allow adequate mixing of the fuel and waste gas streams. A number of different burner designs provide the required mixing without quenching the flame. Burners are classified as either *discrete* or *distributed* (EPA, 1973). The main distinction between the two types of burners is the number and size of flames in each type. The discrete burner produces a single large flame plume into which the waste gas stream must be blended. The distributed burner system produces an array of smaller flames. The waste gas stream is divided and then flows around these flames. In distributed burners more of the waste gas stream is passed over or around the flame. This allows distributed burners to complete mixing of the waste gases and hot products of combustion in shorter distances than in discrete burners. Distributed burners also utilize the oxygen in the waste gas stream more efficiently, reducing the amount of oxygen supplied through the burner. This in turn reduces the need for additional fuel to heat the air/waste gas mixture to the required oxidation temperature.

Three types of distributed burner systems are the *line burner*, the *multijet*, and the *grid* burner. All three of these systems are comprised of a manifold system, to inject the fuel, and a mixing or profile plate which regulates air flow to the flame area. Fuel (usually natural gas) enters the burner area of the line burner (Figure 3-8) through holes in manifold pipes. The pipes are placed across the duct at 0.3 meters (1.0 foot) intervals (EPA, 1972). Waste gas enters the burner area through holes in the profile plate. The plate allows only a portion of the waste gas, usually 50%, to directly contact the flame. The remaining portion of the gas bypasses the flame area and is mixed with the hot combustion gases downstream of the flame. Figure 3-9 illustrates an example of one type of mixing plate. The plate is attached to the manifold pipes and forms a "v" shaped trough; part of the waste gas enters the flame area through the holes, while the remaining portion of waste gas passes around the plate.

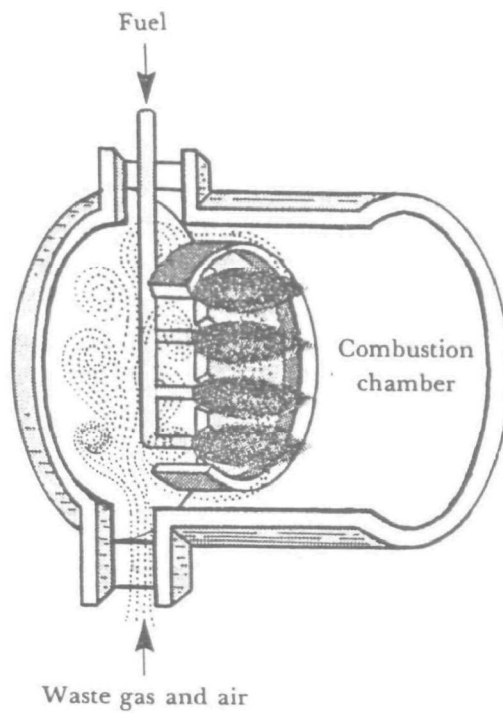


Figure 3-8. Distributed (line) burner.

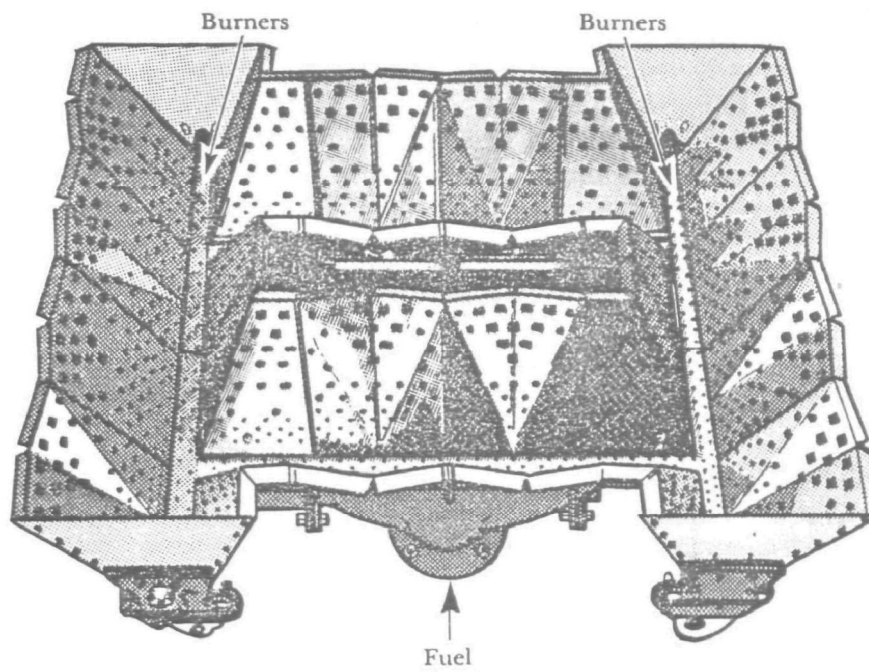


Figure 3-9. Mixing plate for waste gas and hot combustion products.

Multijet burners are very similar to line burners. Multijet burners have a single fuel inlet which is manifolded to produce numerous individual flames. Figure 3-10 shows the Hirt multijet burner system. In this system, waste gases flowing to the flame area are controlled by a profile or mixing plate. The profile plate allows a portion of the waste gas stream to flow behind it and mix with the fuel to supply the combustion area. The remaining gases must pass around in front of the profile plate. Air flow to the burner flame area is adjusted by moving the profile plate either closer or further away from the burners. Adjusting the profile plate on the multijet system is relatively simple and can be accomplished while the unit is still in service. Adjusting the mixing plate on the line burner is not as simple, because the unit must be taken off line. The line burner, however, has the advantage of being much smaller. The line burner accomplishes mixing over a relatively short distance, a few inches, as compared to the multijet which requires several feet.

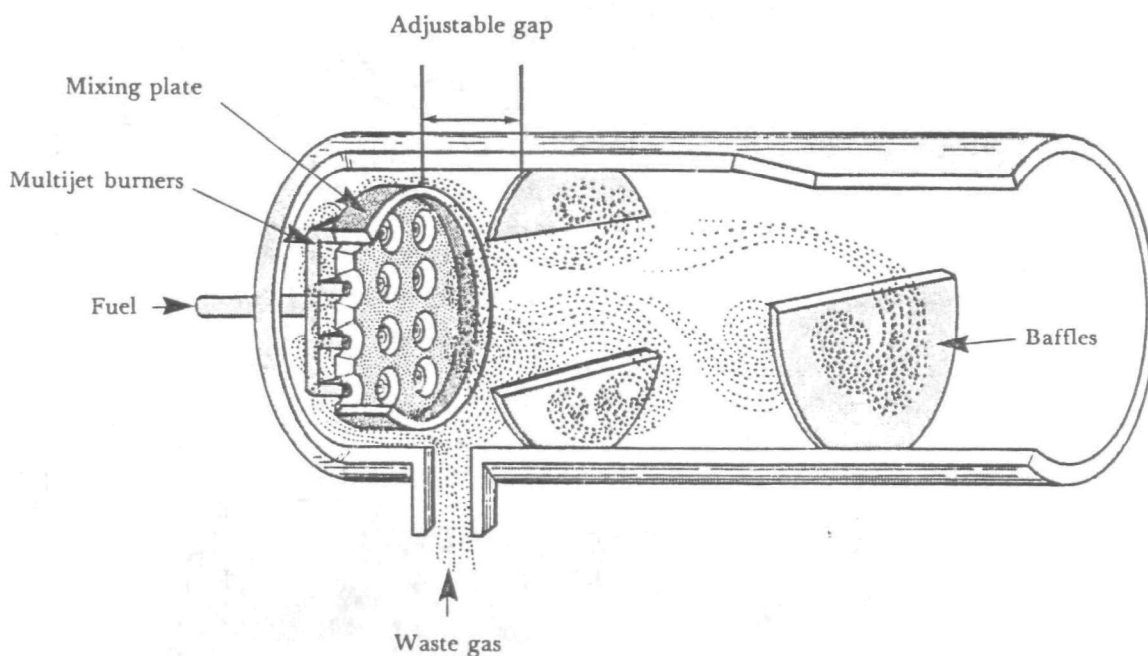


Figure 3-10. Multijet burner.

The grid burner also uses a manifold system to introduce the fuel. Mixing is accomplished by passing the waste gas stream through a slotted grid as shown in Figure 3-11. The slots are approximately 2.5 by 7.5 cm (1 by 3 in.) (EPA, 1972). The grid allows for extremely fast mixing of the fuel and waste gas. There is, however, very little control to allow for adjusting flow rates since the grid is stationary. Grid burners are best suited for applications where waste gas flow ratios are relatively constant.

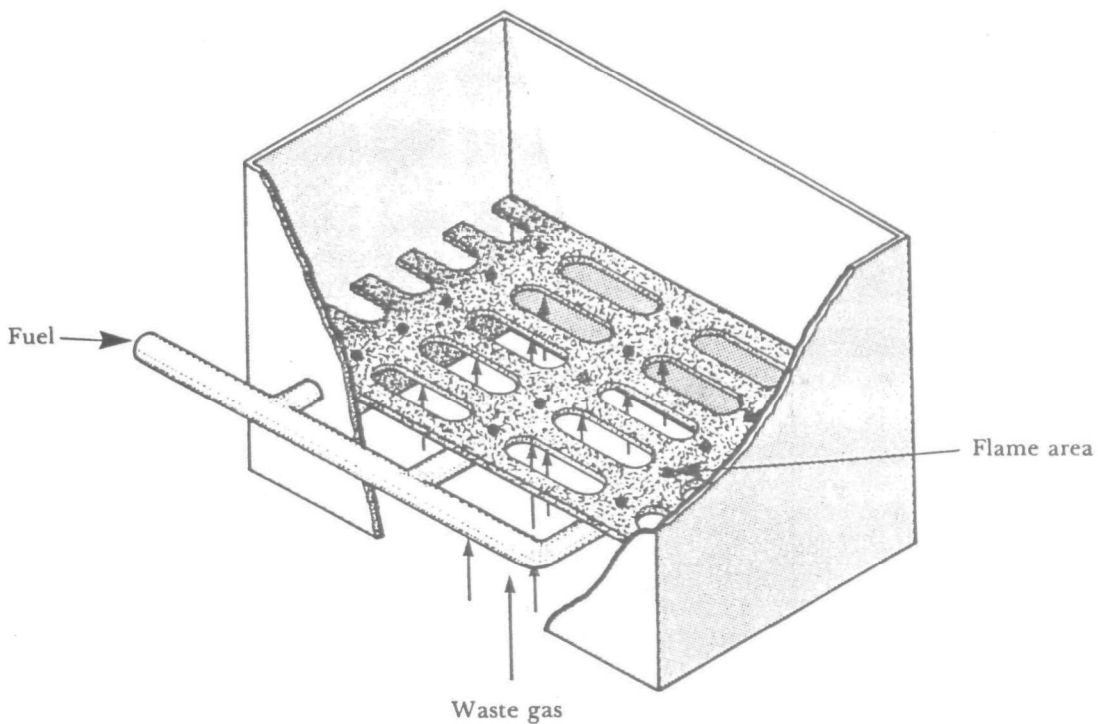


Figure 3-11. North American flame grid burner.

Problems can arise using any of the three types of distributed systems. Some of these are:

1. Natural gas is the only fuel source that can be used. If solid or liquid particles are present or formed during combustion, they can plug the tiny holes in the fuel manifold system. This is known as *burner fouling*.
2. The oxygen content of the waste gas stream must be at least 16%. Oxygen for combustion is supplied by the waste gas stream. If the oxygen content is not 16% or greater, incomplete combustion can occur.
3. Mixing, profile, and grid plates must be able to withstand high temperatures. This adds to the capital equipment costs.

To avoid some of the problems associated with distributed burners, especially fouling, discrete burners are sometimes used. The discrete burner is simply one large burner (Figure 3-12). Many other burner arrangements are classified as discrete burners. They can range from a simple gas ring, comparable to those used on home stoves, to a torch burner (Figure 3-6). In this illustration, mixing the process waste gas and hot products of combustion is accomplished by using a conical mixing plate.

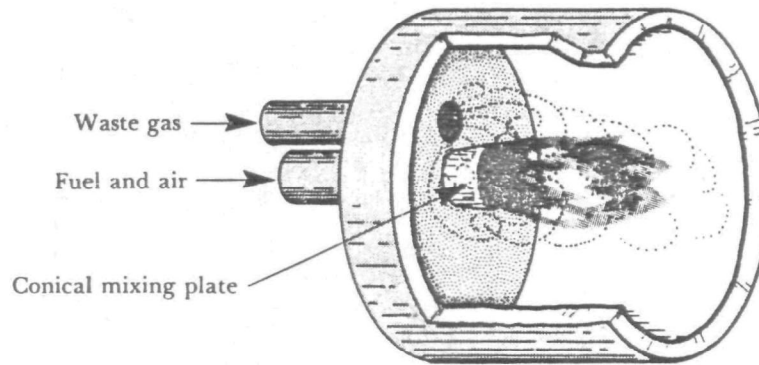


Figure 3-12. Discrete burner.

In most discrete burners, mixing must usually be provided downstream of the flame. Baffles are most commonly used to provide the required turbulence. However, baffles increase the pressure drop across the incinerator. Unless installed correctly, baffles can cause *dead zones* which actually decrease the degree of mixing. Two main types used in incinerators are the *bridge wall baffle* and the *ring and disc baffle* illustrated in Figure 3-13 and Figure 3-14. The bridge wall baffle is a wall placed across the combustion chamber. The bridge wall technique is most effective when pairs of baffles are used. The ring and disc baffles consist of a series of rings inserted in the middle along with discs on the side walls of the chamber.

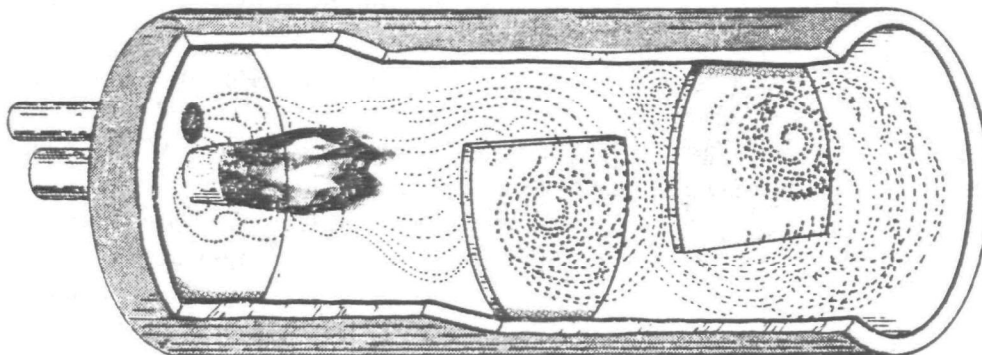


Figure 3-13. Bridge wall baffle.

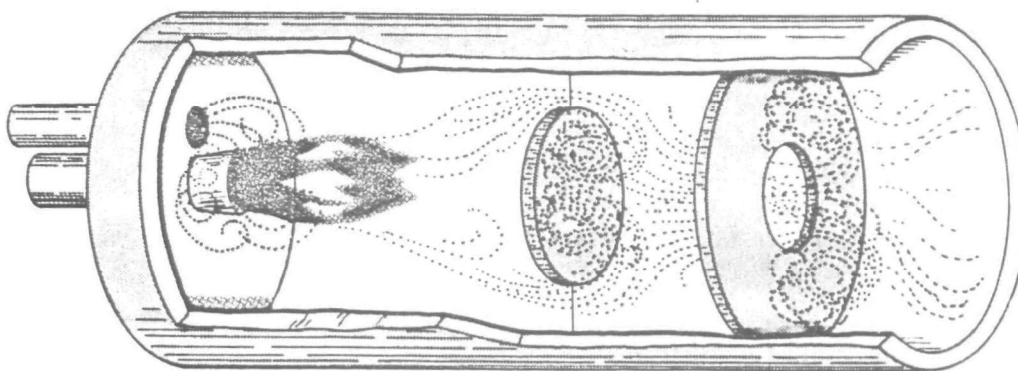


Figure 3-14. Ring and disc baffle.

### Catalytic Oxidation

A *catalyst* is a substance which causes or speeds a chemical reaction without itself undergoing a change. In catalytic incineration, a waste gas is passed through a layer of catalyst known as the *catalyst bed*. The catalyst causes the oxidation reaction to proceed at a **faster rate and lower temperature** than is capable in thermal oxidation. Catalytic incinerators operating in a 370 to 480°C (700 to 900°F) range can achieve the same efficiency as a thermal incinerator operating between 700 and 820°C (1300 and 1500°F). This can result in a 40 to 60% fuel savings.

Catalytic reactions can be classified as either homogeneous or heterogeneous. Homogeneous reactions occur throughout the bulk of the catalyst, while heterogeneous reactions occur only on the surface of the catalytic material. In air pollution control applications, all reactions are heterogeneous. The oxidation reaction of the organic vapors occurs only on the surface of the catalyst. It should be noted that catalytic reactions produce the same end products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) and liberate the same heat of combustion as does thermal incineration.

A heterogeneous catalyst reaction proceeds through a series of five basic steps:

1. Organic compounds in the waste gas must first *diffuse* from the bulk of the vapor to the surface of the catalyst.
2. Organic compounds then *adsorb* onto the surface of the catalyst.
3. Organic compounds then *react* (oxidize).
4. New compounds then *desorb* after reacting.
5. New compounds then *diffuse* and mix back into the bulk of the exhaust air stream.

The most effective and commonly used catalysts for oxidation reactions come from the noble metals group. *Platinum* either alone or in combination with other noble metals is by far the most commonly used. Desirable characteristics of platinum are that it gives a high oxidation activity at low temperatures, is stable at high temperatures, and is chemically inert. *Palladium* is another noble metal which exhibits these properties and is sometimes used in catalytic incinerators.

Since catalytic oxidation is a surface reaction, the noble metal is coated onto the surface of a cheaper support material. The support material can be made of a ceramic or a metal such as *alumina*, *silica-alumina* or *nickel-chromium*. The support material is arranged in a matrix shape to provide: high geometric surface area; low pressure drop; uniform flow of the waste gas through the catalyst bed; and a structurally stable surface (EPA, 1972). Structures which provide these characteristics are pellets, a honeycomb matrix, or a mesh matrix. Figure 3-15 shows a typical honeycomb catalyst module which is the most common. The support material for these is usually ceramic, but can be metal.

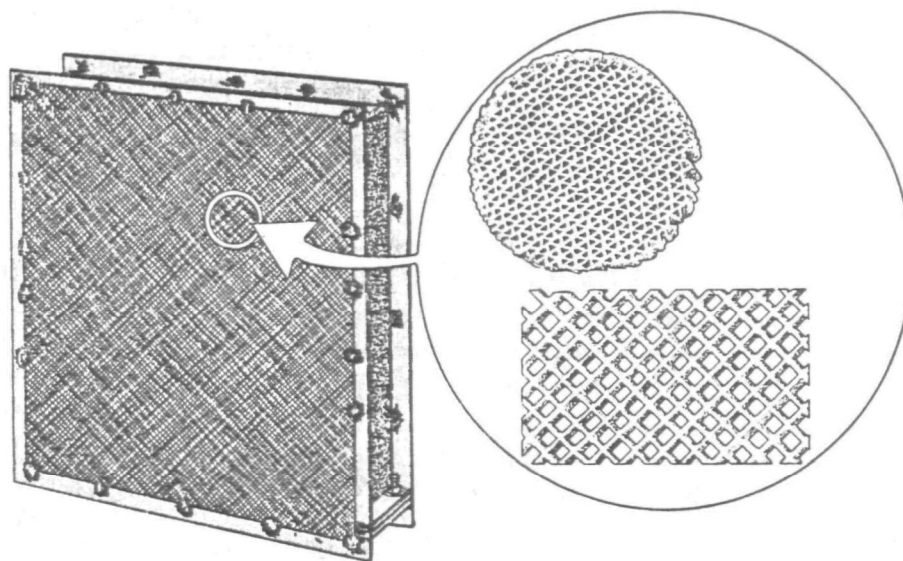


Figure 3-15. Typical honeycomb catalysts (metallic or ceramic).

A schematic of a catalytic incinerator is shown in Figure 3-16. Catalytic incinerators consist of a preheat section (burner area), where part of the waste gas is raised to operating temperature. The burners are the same as those used for thermal incineration, with the majority being distributed burners. The remaining portion of the waste gas is mixed with the hot products of combustion before passing over the catalyst bed. This ensures a homogenous waste gas and temperature mixture as it passes over the bed. After passing over the bed, the hot flue gases may be sent to a heat recovery system.



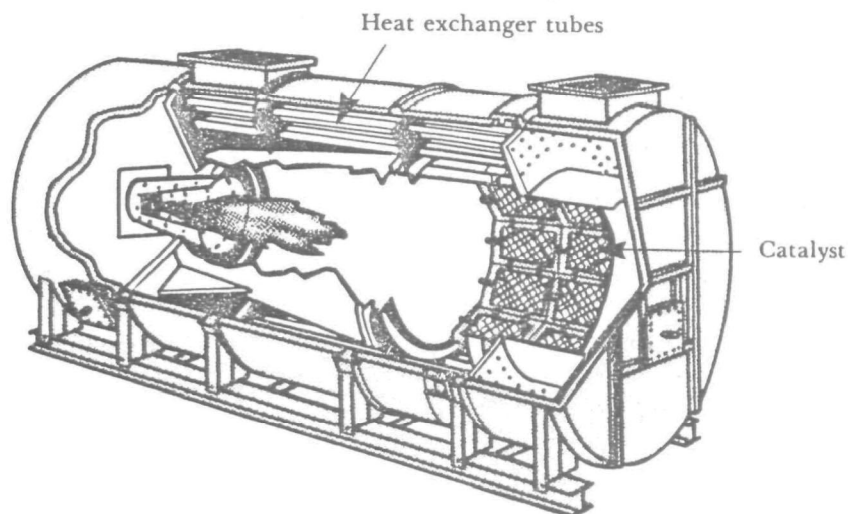


Figure 3-16. Catalytic incinerator.

Catalyst bed depth controls the pressure drop across the incinerator. Typically, the volume of catalyst required for 85 to 95% conversion of all organic compounds in 0.01 to 0.05 seconds is between 0.03 to 0.14 m<sup>3</sup> of catalyst per 1000 m<sup>3</sup>/s of waste gas (0.5 to 2.0 ft<sup>3</sup> of catalyst per 1000 cfm of waste gas). As a general rule, the higher the molecular weight of the compound, the more readily it is oxidized. Normal pressure drops through catalytic incinerators are between 62 and 125 Pa (0.25 and 0.5 in. H<sub>2</sub>O). If the exhaust does not have sufficient draft to overcome this pressure drop, a blower may have to be installed.

To ensure proper operation, the inlet and outlet temperatures to the catalyst section are monitored. This verifies that the temperature is sufficient to achieve the required conversion and also ensures protection of the catalyst from excessive temperatures. Since catalytic incinerators operate at lower temperatures than thermal units, less refractory brick and small chamber volumes can be used. This reduction in size of the device reduces installation costs.

### Operating Limitations of Catalytic Incinerators

Catalytic incinerators usually cannot be used effectively on waste gas streams which contain particulate matter. Particulate matter that deposits on the surface of the catalyst prohibits the organic compounds from being adsorbed. Coating of the catalyst surface in this manner is referred to as *fouling* of the catalyst. Oil droplets can also foul the catalyst bed unless they are vaporized in the preheat section. By periodically cleaning and washing the catalyst, 90% of its activity can be restored (EPA, 1972). Maintenance of this type, however, adds significantly to the cost of operating the unit.

Certain metals can chemically combine with or alloy to the catalyst, thereby making it useless. Deactivation in this manner is called catalyst *poisoning*. Catalyst poisons can be divided into two categories: fast acting poisons which include

phosphorus, bismuth, arsenic, antimony, and mercury; and slow acting poisons which include zinc, lead and tin. Catalysts are more tolerant of the slow acting poisons, particularly at temperatures below 540°C (1000°F). At sufficiently high temperatures (>590°C), even copper and iron are capable of alloying to platinum, reducing its activity.

Sulfur and halogen compounds act as poisons, but not to the extent of the metals. They are essentially reaction inhibitors called *suppressants*. Their chemical interaction with the catalyst is reversible. Once the halogen or sulfur compound is removed, catalyst activity is restored to normal.

All catalysts deteriorate with normal use. Gradual loss of the catalyst material can occur from erosion, attrition, and vaporization. High temperatures can also accelerate catalyst deactivation. Loss of catalyst activity due to high temperature is known as *thermal aging*, and causes very rapid catalyst deterioration. Even short term temperatures above 820°C (1500°F) can cause a near total loss of catalyst activity. With proper monitoring of operating temperatures, a catalyst bed can be expected to last from three to five years before it must be replaced. The percent destruction of pollutants decreases with increasing thermal aging. Adjustment to operating conditions (temperature, residence time, etc.) may need to be made to ensure that the exhaust continues to meet emission limits.

### **Comparison of Thermal vs. Catalytic Incinerators**

The major difference between thermal and catalytic incinerators is that complete combustion can be achieved at much lower temperatures in a catalytic incinerator. The reduced temperatures cut the cost of fuel usage by 40 to 60%. Operation at lower temperatures also decreases the construction costs. Lighter materials of construction can be used in catalytic units. This also makes installation easier and less costly. In terms of overall equipment costs, for small capacity units, up to 4.7 or 5.7 m<sup>3</sup>/s (10,000 or 12,000 cfm), the purchase costs for either unit is essentially equal (EPA, 1972). For larger units that must be custom designed, thermal incinerators are usually less expensive, but this depends on the type of heat recovery system.

The main problem in catalytic incineration is the reduction or loss of catalyst activity. Loss of catalyst activity occurs due to fouling by particulate matter or suppression or poisoning due to other contaminants in the waste gas stream. In order to effectively use catalytic incineration, these contaminants must be removed from the waste gas stream. Removing these contaminants would require additional equipment which adds greatly to the cost of the system. Finally, all catalysts must periodically be replaced due to thermal aging.

### ***Process Boilers Used as Incinerators***

An alternative to installing a thermal or catalytic incinerator would be to combust the waste gases in an existing plant or process boiler. This would avoid the capital cost of new equipment and may help to reduce present fuel consumption. Process and plant boilers are normally designed to operate in excess of 980°C (1800°F)

with a flue gas residence time of 0.5 to 3.0 seconds. These conditions exceed those recommended for thermal incinerators. However, a number of additional conditions must be satisfied before waste gases can be properly disposed of in this manner.

The following criteria must be considered before a process boiler can be used as an incinerator (EPA, 1977):

1. The waste gases must be almost completely combustible. If solid particles are present in the waste gases, or formed by incomplete combustion, they can foul heat exchanger surfaces in the boiler, thus reducing boiler efficiency. Particulate matter may also cause boiler emissions to exceed applicable emission regulations. The costs of increased maintenance of the boiler and/or control of particulate matter may well exceed the purchase price of an incinerator.
2. The waste gas should, preferably, constitute only a small fraction of the air requirements of the boiler. If the volume of the waste gas is large, special attention must be paid to the oxygen balance, mixing, and continuation of the air flow in the boiler when the process is shut down.
3. The oxygen concentration of the contaminated gas stream should be close to that of air to avoid incomplete combustion. Incomplete combustion produces tars that coat heat exchanger surfaces, reducing boiler efficiency.
4. The boiler must operate at all times when incineration is required.
5. The waste gas must be free of compounds, such as halogenated hydrocarbons, that accelerate corrosion of the boiler.
6. Baffling may be required in the combustion chamber to ensure adequate mixing and combustion of the waste gas.
7. If the boiler-firing rate varies greatly, it may be necessary to install a small auxiliary boiler that will operate under steady load conditions.

To date, not many industries have been successful in using plant or process boilers as incinerators. Petroleum refineries, which have numerous waste gas streams and process boilers, are one of the few industries which have been able to incinerate waste gases in process boilers.

THERMAL AND CATALYTIC INCINERATORS  
Inspection Summaries

7.3 Inspection Summaries

7.3.1 Level 1 Inspections - Not Applicable

7.3.2 Level 2 Inspections

Basic Inspection Points

- Stack
  - Visible emissions
- Bypass Stack
  - Vapor refraction lines
- Incinerator
  - Heat recovery outlet gas temperature
  - Incinerator outlet temperature
  - Temperature rise across catalyst bed
  - Audible air infiltration
  - Obvious corrosion
- Process Equipment
  - Process operating rate

Follow-up

- Incinerator
  - Fan motor current
  - Hood static pressure

7.3.3 Level 3 Inspections

- Stack
  - All elements of a Level 2 Inspection
- Incinerator
  - All elements of a Level 2 Inspection
  - Inlet gas temperature
  - Inlet VOC concentration
  - Outlet VOC concentration
- Process
  - All elements of a Level 2 Inspection
  - Coatings compositions

INSPECTION OF THERMAL AND CATALYTIC INCINERATORS  
Inspection Summaries

7.3.4 Level 4 Inspections

Stack

- All elements of a Level 3 inspection

Incinerator

- All elements of a Level 3 inspection
- Locations for measurement ports
- Potential inspection safety problems

Process Equipment

- All elements of a Level 3 inspection
- Basic flowchart of process
- Potential inspection safety problems

## THERMAL AND CATALYTIC INCINERATORS

### Inspection Procedures

#### 7.4. Inspection Procedures

The inspection procedures for incinerators can be classified as Level 2 and Level 3 inspections. The Level 2 inspection is a detailed walkthrough inspection utilizing the on-site incinerator and process instrumentation. The Level 3 inspection includes all of the Level 2 steps and also includes the limited use of portable instruments to verify incinerator performance. The instruments generally used are the portable VOC detectors and portable thermocouple thermometers. Instrument measurement procedures and safety considerations are discussed in another section of this notebook.

##### 7.4.1 Basic Level 2 Inspections

###### Observe the Incinerator Exhaust.

There should be no visible soot or particulate emissions from the exhaust. Visible emissions are generally due to improper burner operation or condensation of unburned organic compounds.

###### Observe the incinerator bypass stack.

Incinerators generally must have bypass stacks so that the process equipment can be safely vented in the event of incinerator malfunction. However, during routine operation, there should be no significant leakage of VOC contaminated gas through the bypass stack dampers. The leakage of high VOC concentration gas can often be identified by the wavy light refraction lines at the stack mouth.

###### Record the incinerator operating temperature.

For thermal incinerators, the combustion chamber exhaust gas temperature should be recorded. This is generally monitored by a thermocouple that is used to adjust the main burner firing rate. A reduction in the operating temperature could result in a reduced VOC oxidation efficiency.

For catalytic incinerators, the inlet and outlet gas temperatures to the catalyst bed should be recorded. The inlet gas temperature is the temperature after the preheat burner and immediately ahead of the catalyst bed. The bed

## INSPECTION OF THERMAL AND CATALYTIC INCINERATORS

### Basic Level 2 Inspection Procedures

Record the incinerator operating temperature. (Continued)  
outlet temperature is the temperature before the gas stream enters any of the heat recovery equipment. Smaller than normal temperature increases across the catalyst bed are due to either catalyst inhibition or to a reduced VOC concentration in the inlet gas stream.

Listen for air infiltration into the incinerator system.

Air infiltration into incinerators under negative pressure (fan downstream of the incinerator) can lead to localized cooling of the gas stream. Incomplete VOC oxidation can occur in these areas. Severe air infiltration into the inlet duct could prevent proper incinerator operating temperatures since this reduces the sensible heat and the heating value of the inlet gas stream. Infiltration also reduces the VOC capture effectiveness at the process source.

Check the incinerator shell, outlet ductwork, and stack for obvious corrosion.

Hydrochloric acid vapor can be formed in incinerators due to the oxidation of chlorinated hydrocarbons. This can lead to corrosion of the incinerator shell and downstream gas handling equipment.

Review the process operating records.

Confirm that the incinerator was operated whenever high-solvent materials were being used.

#### 7.4.2 Follow-up Level 2 Inspection Steps

Evaluate the fan motor current.

A decrease in the fan motor current as compared to the baseline levels indicates a decrease in the total gas flow from the process equipment. A flow rate decrease could be due to a decrease in the process operating rate or a change in the process operating conditions. Fugitive emissions should be evaluated to the extent possible when there has been a significant decrease in the fan motor currents without process operating changes.

INSPECTION OF THERMAL AND CATALYTIC INCINERATORS  
Follow-up Level 2 Inspection Procedures

Measure the hood static pressure.

The hood static pressure provides a general indication of the gas flow rate from the process equipment. This data is useful to confirm that there are no significant fugitive VOC emissions.

7.4.3 Level 3 Inspections

Measure the VOC outlet concentration.

The effluent gas concentration should be measured if there is safe and convenient access to the effluent gas duct. The port should be located downstream of the heat recovery equipment so that the gas temperature is as low as possible. A glass-lined probe is usually advisable to minimize losses of organic vapor to the surfaces of the probe. If the gas temperature is greater than 300 °F, it will probably be necessary to include a condensor and knock-out trap in the sample line in order to protect the VOC detectors.

The VOC detector (and its portable recorder, if any) should be certified as intrinsically safe for the type of hazardous location prevailing in the vicinity of the incinerator. No electrically powered equipment should be used that could ignite fugitive VOC vapors.

The observed concentration should be less than 5 to 10% of the inlet concentration if the incinerator is operating properly.

Measure the inlet VOC concentration.

The inlet gas stream VOC concentration can usually be measured using the same VOC instrument used for the outlet port. A dilution probe will often be necessary for photoionization instruments and flame ionization instruments limited to 1000 to 2000 ppm. The condensor and knock-out trap are rarely necessary since the gas stream temperatures are normally less than 250 °F. As in the case with the outlet measurements, the measurement of the inlet concentration should be done only when all safety requirements are satisfied.



INSPECTION OF THERMAL AND CATALYTIC INCINERATORS  
Level 3 Inspection Procedures

Measure the incinerator outlet temperature.

The measurement of the incinerator outlet temperature is attempted whenever the on-site gauge does not appear to be providing accurate data. However, measurement of the outlet temperature using portable gauges is subject to a number of significant possible errors. These include the following.

- ° Higher than actual values due to exposure of the probe to radiant energy from the burner.
- ° Lower than actual values due to shielding of the probe behind refractory baffles in the combustion chamber.
- ° Non-representative values due to spatial variations of gas temperature immediately downstream of the incinerator.

For these reasons, the independent measurement of the incinerator outlet temperature is rarely done by regulatory agency inspectors. Also, battery powered thermocouple thermometers are not intrinsically safe and can therefore not be used in certain areas.

Measure the hood static pressure.

The hood static pressure provides a general indication of the gas flow rate from the process equipment. This data is useful to confirm that there are no significant fugitive VOC emissions.

## INSPECTION OF THERMAL AND CATALYTIC INCINERATORS

### Level 4 Inspection Procedures

#### 7.4.4 Level 4 Inspection Procedures

The Level 4 inspection includes many inspection steps performed during Level 2 and 3 inspections. These are described in earlier sections. The unique inspection steps of Level 4 inspections are described below.

##### Evaluate locations for measurement ports.

Many existing fabric filters do not have convenient and safe ports that can be used for static pressure, gas temperature, and gas oxygen measurements. One purpose of Level 4 inspections is to select (with the assistance of plant personnel) locations for ports to be installed at a later date to facilitate Level 3 inspections.

##### Evaluate potential safety problems.

Agency management personnel and/or senior inspectors should identify any potential safety problems involved in standard Level 2 or Level 3 inspections at this site. To the extent possible, the system owner/operators should eliminate these hazards. For those hazards that can not be eliminated, agency personnel should prepare notes on how future inspections should be limited and should prepare a list of the necessary personal safety equipment. A partial list of common health and safety hazards includes the following.

- ° Hot exhaust duct surfaces
- ° Inhalation hazards due to low stack discharge points
- ° Weak catwalk and ladder supports
- ° Fugitive emissions from process equipment
- ° Inhalation hazards from adjacent stacks and vents
- ° Weak roofs or catwalks

INSPECTION OF THERMAL AND CATALYTIC INCINERATORS  
Level 4 Inspection Procedures

Prepare a system flowchart.

A relatively simple flowchart is very helpful in conducting a complete and effective Level 2 or Level 3 inspection. This should be prepared by agency management personnel or senior inspectors during a Level 4 inspection. This should consist of a simple block diagram that includes the following elements.

- ° Source(s) of emissions controlled by a single incinerator
- ° Location(s) of any fans used for gas movement through the system (used to evaluate inhalation problems due to positive static pressures)
- ° Locations of any main stacks and bypass stacks
- ° Location of incinerator
- ° Locations of major instruments (static pressure gauges, thermocouples)

Evaluate potential safety problems in the process area.

The agency management personnel and/or senior inspectors should evaluate potential safety problems in the areas which may be visited by agency inspectors during Level 2 and/or Level 3 inspections. They should prepare a list of the activities that should not be performed and locations to which an inspector should not go as part of these inspections. The purpose of this review is to minimize inspector risk and to minimize the liability concerns of plant personnel.



# Control by Adsorption

# Chapter 5

## Adsorption

### Introduction

During adsorption, one or more gaseous components are removed from an effluent gas stream by adhering to the surface of a solid. The gas molecules being removed are referred to as the *adsorbate*, while the solid doing the adsorbing is called the *adsorbent*. Adsorbents are highly porous particles. Adsorption occurs on the internal surfaces of the particles as illustrated in Figure 5-1.

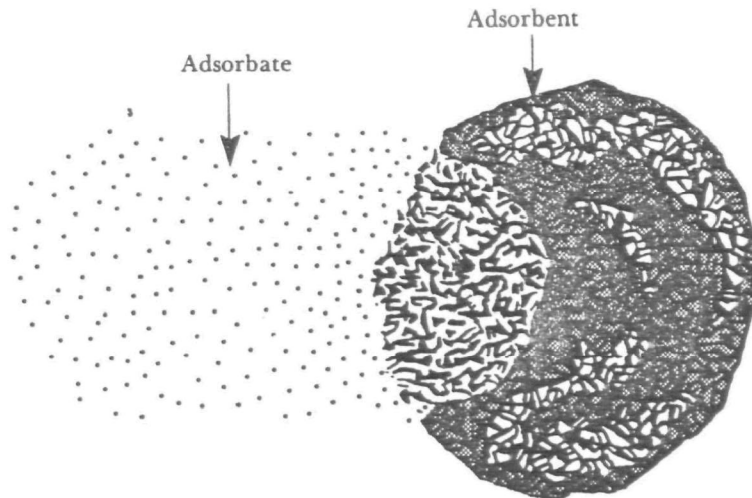


Figure 5-1. Vapor adsorbed into pores of activated carbon.

The attractive forces which hold the gas to the surface of the solid are the same that cause vapors to condense (van der Waals' forces). All gas-solid interfaces exhibit this attraction, some more than others. Adsorption systems use materials which are highly attracted to each other to separate these gases from the non-adsorbing components of an air stream. For air pollution control purposes, adsorption is not a final control process. The contaminant gas is merely **stored** on the surface of the adsorbent. After it becomes saturated with adsorbate, the adsorbent must either be disposed of and replaced, or the vapors must be **desorbed**. Desorbed vapors are highly concentrated and may be recovered more easily and more economically than before the adsorption step.

Traditionally, adsorption has been used for **air purification** and **solvent recovery**. Air purification processes are those in which the contaminant is present in trace quantities (less than 1.0 ppm) but is highly odorous or toxic. Systems used

for air purification are small *thin bed* adsorbers. When the bed becomes saturated with contaminant, it is taken out and replaced. Solvent recovery processes require much larger systems and are usually designed to control organic emissions whose concentrations are greater than 1000 ppm. This has been the point where the recovery value of the solvent could justify the expense of the large adsorption-desorption system. Currently, adsorption is used as a method of recovering valuable organic vapors from flue gases at all concentration levels. This is due to present regulations limiting volatile organic emissions and the higher costs of solvents.

## Theory of Adsorption

### *Mechanism of Adsorption*

Adsorption occurs by a series of three steps. In the first step, the contaminant diffuses from the major body of the air stream to the external surface of the adsorbent particle. In the second step, the contaminant molecule migrates from the relatively small area of the external surface (a few  $\text{m}^2/\text{g}$ ) to the pores within each adsorbent particle. The bulk of adsorption occurs in these pores because the majority of available surface area is there (hundreds of  $\text{m}^2/\text{g}$ ). In the third step, the contaminant molecule adheres to the surface in the pore. Figure 5-2 illustrates this overall diffusion and adsorption process.

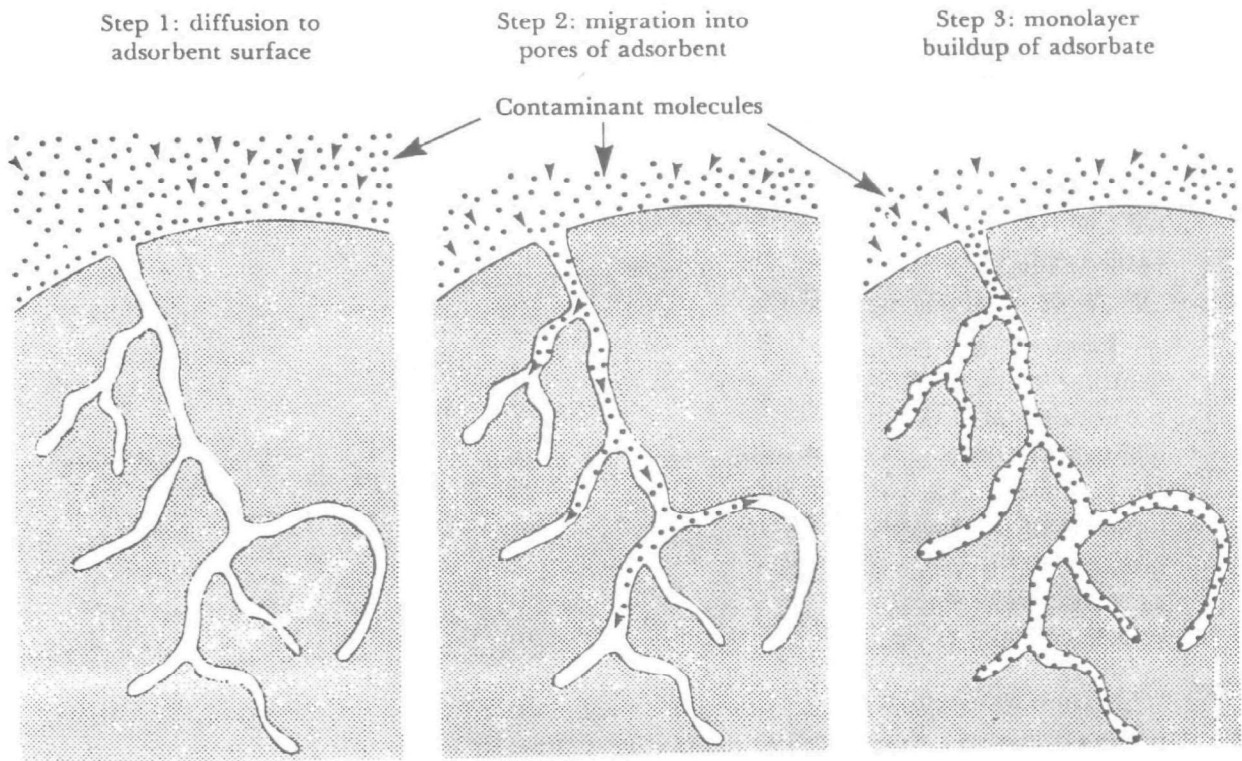


Figure 5-2. Mechanism of adsorption.

The purpose of analyzing the mechanism of adsorption is to determine which step controls the overall process. By describing this step mathematically, adsorber performance can be predicted from physical data. The actual adsorption of a molecule, step 3, proceeds relatively quickly compared to steps 1 or 2. Therefore, step 3 can be ignored when developing design equations. Steps 1 and 2 are both diffusional processes. They involve the transport of the adsorbate through a carrier gas phase to an adsorption site. In the first step, diffusion occurs because of a concentration difference. The rate of mass transferred by this type of diffusion can be predicted from Equation 5-1.

Equation 5-1 is based on a film resistance theory of bulk diffusion as presented in Chapter 4 on absorption. Bulk diffusion assumes that the only resistance a gas molecule encounters in movement through the carrier gas stream occurs during collisions with other gas molecules.

$$\text{(Eq. 5-1)} \quad N_A = \frac{k_g A \beta (p - p_i)}{\rho_B}$$

Where:  $N_A$  = rate of mass transfer, kg mol/s  
 $k_g$  = local mass transfer coefficient, kg mol/s·m<sup>2</sup>·Pa  
 $\beta$  = void area between adsorbent granules, m<sup>3</sup>/m<sup>3</sup>  
 $A$  = surface area of adsorbent, m<sup>2</sup>/kg  
 $p$  = partial pressure of adsorbate in gas phase, Pa  
 $p_i$  = partial pressure of adsorbate at the gas-solid interface, Pa  
 $\rho_B$  = bulk density of adsorbent, kg/m<sup>3</sup>

The mass transfer coefficient ( $k_g$ ) is a function of the velocity, viscosity, and density of the carrier gas stream; the diffusivity of the gas molecule that is being adsorbed; and the diameter of the adsorbent. Equations to estimate the transfer coefficient based on these parameters can be found in Perry (1973).

Once the gas molecule has reached the external surface of the adsorbent, it must diffuse (move) into the pores. Diffusion in the pores of the adsorbent can occur by a number of different diffusion mechanisms depending on the size of the pore. When the pores are large, bulk diffusion predominates. As the pores begin to narrow, collisions with the wall of the adsorbate become more likely than inter-molecular collisions. The gas molecules strike the wall, remain for a short time, then return to the gas phase. This is termed Knudsen (or molecular) diffusion and occurs much more slowly than does bulk diffusion for a given pore length. Finally, in the smallest pores, surface diffusion is the predominant mechanism of gas transport. Gas molecules can either migrate along the surface of the solid or jump between adsorption sites.

Due to these varied mechanisms by which diffusion occurs, mass transfer rates in the pores are extremely difficult to predict. Unless extensive data are available concerning the specific adsorption application, determining the rate-controlling step (step 1 or step 2) is impossible.



One approach to determining the mass transfer rate is to rewrite Equation 5-1 in terms of an overall mass transfer coefficient.

$$(Eq. 5-2) \quad N_A = K_{OG}a(p - p^*)$$

Where:  $a$  = external adsorbent area,  $m^2/m^3$

$p^*$  = partial pressure in equilibrium with the surface concentration of adsorbate, Pa

$p$  = partial pressure of adsorbate in the gas phase, Pa

$K_{OG}$  = overall mass transfer coefficient,  $kg \text{ mol}/h \cdot m^2 \cdot Pa$

The overall mass transfer coefficient represents the resistance to molecular motion encountered both outside and inside the pore.

$$(Eq. 5-3) \quad \frac{1}{K_{OG}} = \frac{1}{k_s} + \frac{1}{k_p}$$

Where:  $k_s$  = local mass transfer coefficient for combined surface migration and pore diffusion,  $kg \text{ mol}/h \cdot m^2 \cdot Pa$

The local mass transfer coefficient cannot be satisfactorily predicted from basic theory at the present time. However, it (and therefore  $K_{OG}$ ) can be determined with some certainty from experimental data. Therefore, Equation 5-2 still does not give a simple and accurate means of predicting adsorber performance from physical data. What Equation 5-2 does show is that the equilibrium partial pressure of the adsorbate ( $p^*$ ) determines the theoretical minimum adsorber bed size. Empirical design procedures based on adsorption equilibrium conditions are the easiest and most common methods used to predict adsorber size and performance. These methods will be discussed later.

### Adsorption Forces—Physical and Chemical

The adsorption process is classified as either physical or chemical. The basic difference between physical and chemical adsorption is the manner in which the gas molecule is bonded to the adsorbent. In physical adsorption the gas molecule is bonded to the solid surface by weak forces of intermolecular cohesion. The chemical nature of the adsorbed gas remains unchanged; therefore, physical adsorption is a readily reversible process. In chemical adsorption a much stronger bond is formed between the gas molecule and adsorbent. A sharing or exchange of electrons takes place—as happens in a chemical bond. Chemical adsorption is not easily reversible.

The forces active in physical adsorption are electrostatic in nature. These forces are present in all states of matter: gas, liquid, and solid. They are the same forces of attraction which cause gases to condense and real gases to deviate from ideal behavior. This electrostatic force can be measured by the constant “ $a$ ” in van der Waals’ equation describing nonideal gas behavior. Physical adsorption is sometimes also referred to as van der Waals’ adsorption. The electrostatic effect which produces the van der Waals’ forces depends on the polarity of both the gas and solid molecules. Molecules in any state are either polar or nonpolar depending on their

chemical structure. **Polar** substances are those which exhibit a separation of positive and negative charges within the compound. This separation of positive and negative charges is referred to as a permanent dipole. Water is a prime example of a polar substance. **Nonpolar** substances have both their positive and negative charges in one center so they have no permanent dipole. Most organic compounds, because of their symmetry, are nonpolar.

Physical, or van der Waals' adsorption can occur from three different effects: an orientation effect, dispersion effects, or induction effects (Figure 5-3). For polar molecules, attraction to each other occurs because of the orientation effect. The orientation effect describes the attraction which occurs between the dipoles of two polar molecules. The negative area of one is attracted to the positive area of the other. An example of this type of adsorption would be the removal of water vapor (polar) from an exhaust stream by using silica gel (polar).

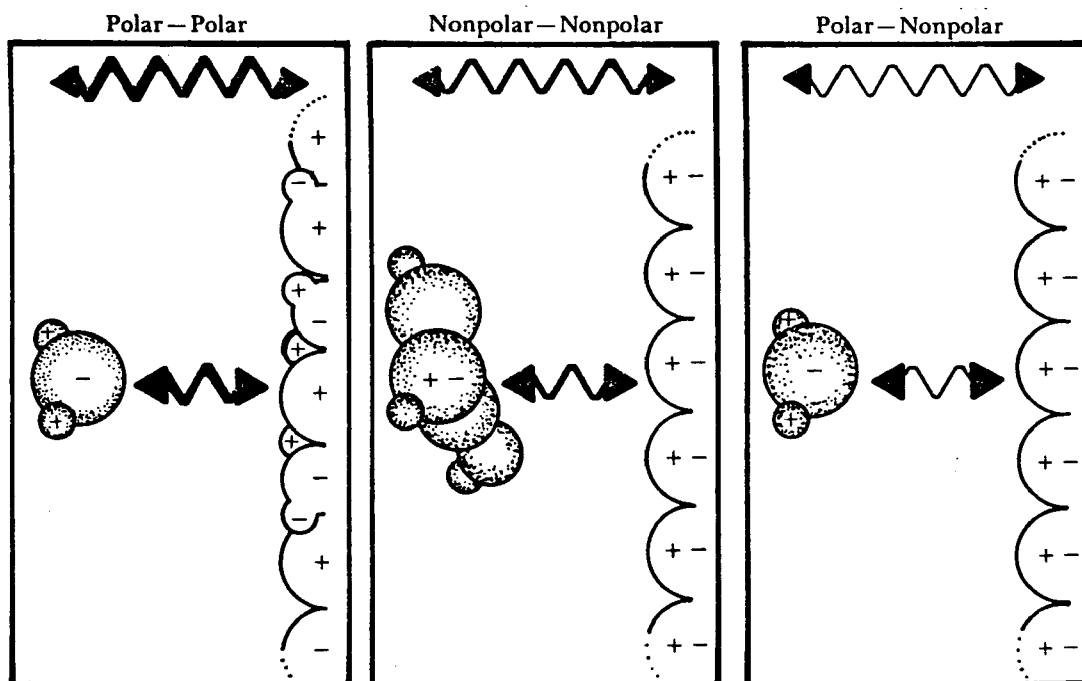


Figure 5-3. Physical forces causing adsorption.

The adsorption of a nonpolar gas molecule onto a nonpolar surface is accounted for by the dispersion effect. The dispersion effect is based on the fact that although nonpolar substances do not possess a permanent dipole, they do have a fluctuating or oscillating dipole. Fluctuating dipoles are a result of momentary changes in electron distribution around the atomic nuclei. In a nonpolar substance, when two fluctuating dipoles come close to one another, their total energy decreases, and they fluctuate in phase with each other. Oscillating dipoles disperse light. Consequently, this is where the name dispersion effect comes from. The adsorption of organic vapors onto activated carbon is an example of nonpolar molecular attraction.

The attraction between a molecule with a permanent dipole (polar molecule) and a nonpolar molecule is caused by the induction effect. A molecule with a permanent dipole can induce or polarize a nonpolar molecule when they come in close contact. The energy of this effect is determined by the polarizability of the nonpolar molecules. The induction effect is, however, very small when compared to the orientation or dispersion effects. Therefore, adsorption systems use polar adsorbents to remove polar contaminants and nonpolar adsorbents to remove nonpolar contaminants. This ensures that the intermolecular forces of attraction between the gas and solid will be greater than those between similar molecules in the gas phase.

Chemical adsorption or chemisorption results from the chemical interaction between the gas and the solid. The gas is held to the surface of the adsorbate by the formation of a chemical bond. Adsorbents used in chemisorption can be either pure substances or chemicals deposited on an inert carrier material. One example is using pure iron oxide chips to adsorb  $H_2S$  gases. Another example is using activated carbon which has been impregnated with sulfur to remove mercury vapors.

All adsorption processes are *exothermic*, whether adsorption occurs from chemical or physical forces. In adsorption, molecules are transferred from the gas to the surface of a solid. The fast-moving gas molecules lose their kinetic energy of motion to the adsorbent in the form of heat.

In chemisorption, the heat of adsorption is comparable to the heat evolved from a chemical reaction, usually over 10 kcal/mol. The heat given off by physical adsorption is much lower, approximately 100 cal/mol, which is comparable to the heat of condensation. Some additional general differences between physical adsorption and chemisorption which make physical adsorption more desirable for air pollution control are:

1. Molecules that are adsorbed by chemisorption are very difficult (and in some cases, impossible) to remove from the adsorbent bed. Physically adsorbed molecules can usually be removed by either increasing the operating temperature or reducing the pressure of the adsorbent bed.
2. Chemisorption is a highly selective process. A gas molecule must be capable of forming a chemical bond with the adsorbent surface for chemisorption to occur. Physical adsorption occurs under suitable conditions in most gas-solid systems. For industrial purposes specific solids are chosen which enhance the rate of adsorption.
3. Chemisorption stops when all the reactive sites on the surface of the adsorbent have reacted. Chemisorption forms only a monolayer of adsorbate molecules on the surface. Because of van der Waals' forces, physical adsorption can form multilayers of adsorbate molecules—one atop another.
4. The chemisorption rate increases with increasing temperature. For physical adsorption the exact opposite is true: the rate decreases with increasing temperature.

For these and other reasons, chemisorption is not used extensively in air pollution control systems. A summary of the characteristics of physical versus chemical adsorption is presented in Table 5-1.

Table 5-1. Summary of characteristics of chemisorption and physical adsorption.

Chemisorption	Physical adsorption
Releases high heat 10,000 cal/mol	Releases low energy 100 cal/mol
Forms a chemical compound	Dipolar interaction
Desorption is difficult	Desorption is easy
Impossible adsorbate recovery	Easy adsorbate recovery

## Adsorbent Materials

Several materials are used effectively as adsorbing agents. The most common adsorbents used industrially are *activated carbon*, *silica gel*, *activated alumina* (alumina oxide), and *zeolites* (molecular sieves). Adsorbents are characterized by their chemical nature, extent of their surface area, pore size distribution, and particle size. In physical adsorption the most important characteristic in distinguishing between adsorbents is their surface polarity. As discussed previously, the surface polarity determines the type of vapors a particular adsorbent will have the greatest affinity for. Of the above adsorbents, activated carbon is the primary nonpolar adsorbent. It is possible to manufacture other adsorbing material having nonpolar surfaces. Since their surface area is much less than that of activated carbon, they are not used commercially. Polar adsorbents will preferentially adsorb any water vapor that may be present in a gas stream. Since moisture is present in most pollutant air streams, the use of polar adsorbents is severely limited for an air pollution system. Therefore, in further discussion, the emphasis is placed on the use of activated carbon, although some of the information is applicable to polar adsorption systems.

### *Activated Carbon*

Activated carbon can be produced from a variety of feedstocks such as wood, coal, coconut, nutshells, and petroleum-based products. The activation process takes place in two steps. First, the feedstock is carbonized. Carbonization involves heating

usually in the absence of air) the material to a temperature high enough ( $600^{\circ}\text{C}$ ) to drive off all volatile material. Thus, carbon is essentially all that is left. To increase the surface area, the carbon is then "activated" by using steam, air, or carbon dioxide at higher temperatures. These gases attack the carbon and increase the pore structure. The temperatures involved, the amount of oxygen present, and the type of feedstock, all greatly affect the adsorption qualities of the carbon. Manufacturers vary these parameters to produce activated carbons suitable for specific purposes. In sales literature, the activity and retentivity of carbons are based on their ability to adsorb a standard solvent, such as carbon tetrachloride ( $\text{CCl}_4$ ).

Because of its nonpolar surface, activated carbon is used to control emission of organic solvents, odors, toxic gases, and gasoline vapors. Carbons used in gas phase adsorption systems are manufactured in granular form, usually between  $4 \times 6$  to  $4 \times 20$  mesh in size. Bulk density of the packed bed can range from 0.08 to  $0.5 \text{ g/cm}^3$  ( $5$  to  $30 \text{ lb/ft}^3$ ) depending on the internal porosity of the carbon. Surface area of the carbon can range from 600 to  $1600 \text{ m}^2/\text{g}$  ( $2.9 \times 10^6$  to  $7.8 \times 10^6 \text{ ft}^2/\text{lb}$ ). This is equivalent to having the surface area of 2 to 5 football fields in one gram of carbon.

### ***Silica Gel***

Silica gels are made from sodium silicate. Sodium silicate is mixed with sulfuric acid, resulting in a jellylike precipitant from where the "gel" name comes. The precipitant is then dried and roasted. Depending on the processes used in manufacturing the gel, different grades varying in activity can be produced. Silica gels have surface areas of approximately  $750 \text{ m}^2/\text{g}$  ( $3.7 \times 10^6 \text{ ft}^2/\text{lb}$ ). Silica gels are used primarily to remove moisture from exhaust streams, but are ineffective at temperatures above  $260^{\circ}\text{C}$  ( $500^{\circ}\text{F}$ ).

### ***Molecular Sieves***

Unlike the other adsorbents, which are amorphous (not crystalline) in nature, molecular sieves have a crystalline structure. The pores are, therefore, uniform in diameter. Molecular sieves can be used to capture or separate gases on the basis of molecular size and shape. An example of this are refining processes which sometimes use molecular sieves to separate straight chained paraffins from branched and cyclic compounds. However, the main use of molecular sieves is in the removal of moisture from exhaust streams. The surface area of molecular sieves range from 600 to  $700 \text{ m}^2/\text{g}$  ( $2.9 \times 10^6$  to  $3.4 \times 10^6 \text{ ft}^2/\text{lb}$ ).

### ***Aluminum Oxide (Activated Alumina)***

Aluminum oxides are manufactured by thermally activated alumina or bauxite. This is accomplished by heating the alumina in an inert atmosphere to produce a porous aluminum oxide pellet. Aluminum oxides are not commonly used in air pollution applications. They are primarily used for the drying of gases, especially

under high pressures, and as support material in catalytic reactions. A prime example is the impregnating of the alumina with platinum or palladium for use in catalytic incineration. Activated alumina's surface areas can range from 200 to 300 m<sup>2</sup>/g ( $0.98 \times 10^6$  to  $1.5 \times 10^6$  ft<sup>2</sup>/lb).

### ***Pore Size Distribution***

The physical properties of the adsorbent affect the adsorption capacity, rate, and pressure drop across the adsorber bed. Table 5-2 summarizes these properties for the above adsorbents. Since adsorption occurs at the gas-solid interface, the surface area available to the vapor molecules determines the effectiveness of the adsorbent. Generally, the larger the surface area, the higher the adsorbent's capacity. However, the surface area must be available in certain pore sizes if it is to be effective as a vapor adsorber. Dubinin (1936) classified the pores in activated carbon as micropores, transitional pores, or macropores. Micropores are openings whose radii are 200 nanometers (20 Å) or less. Pores larger than 2000 nanometers (200 Å) are macropores. Transitional pores are those with radii between 200 and 2000 nanometers.

Table 5-2. Physical properties of major types of adsorbents.

Adsorbent	Internal porosity (%)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Bulk dry density (g/cm <sup>3</sup> )	Mean pore diameter (nm)
Activated carbon	55-75	600-1600	0.80-1.20	0.35-0.50	150-200
Activated alumina	30-40	200-300	0.29-0.37	0.90-1.00	180-200*
Molecular sieves	40-55	600-700	0.27-0.38	0.80	30-90
Silica gel	70	750	0.40	0.70	220

\*The 150-200 nanometer average is for the micropores only; since 95% of the surface area is associated with them.

Most gaseous air pollutant molecules are in the 40 to 90 nanometer size range. If a large portion of an adsorbent's surface area is in pores smaller than 40 nanometers, many contaminant molecules will be unable to reach these active sites. Figure 5-7 illustrates molecule movement in the pores. In addition, the larger pore sizes (macro and transitional) contribute little to molecule capture. The vapor pressure of the contaminant in these larger areas is too low to be effectively removed. These larger pores serve mainly as passageways to the smaller micropore area where the adsorption forces are strongest. Adsorption forces are strongest in pores that are not more than approximately twice the size of the contaminant molecule. These strong adsorption forces result from the overlapping attraction of the closely spaced walls.

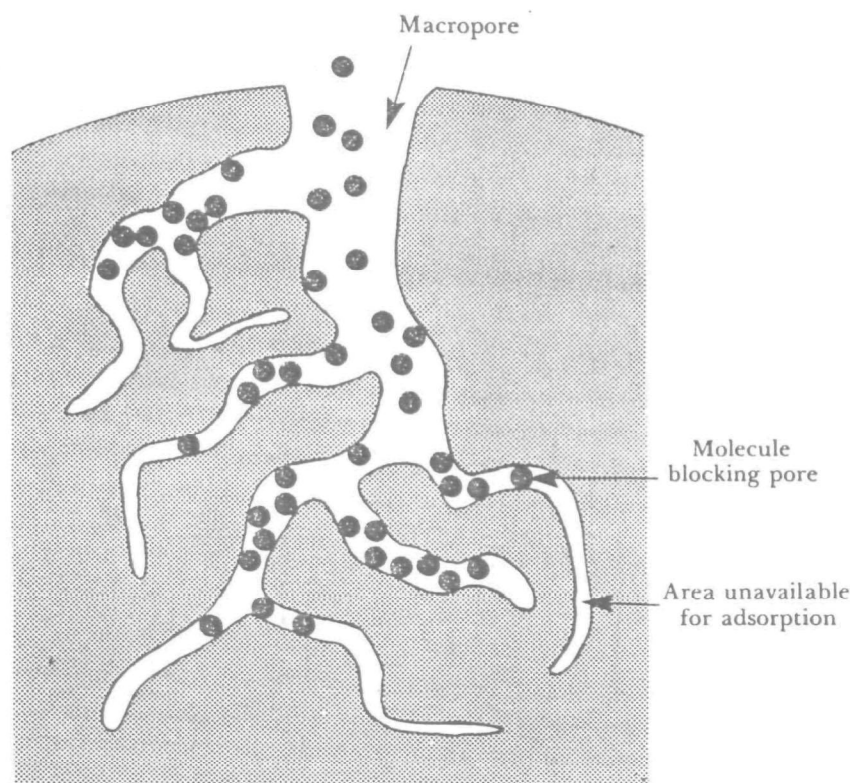


Figure 5-7. Molecular screening in pores of activated carbon.

Another phenomenon, *capillary condensation* usually only occurs in the micropores. Capillary condensation occurs when multilayers of adsorbed contaminant molecules build up from both sides of the pore wall, totally packing the pore and condensing in the pore. The amount of contaminant that is removed increases since additional molecules condense on the surface of the liquid which has formed. Contaminant molecules can also be removed at lower vapor pressures (more dilute concentrations) since capture forces are now acting from three sides instead of just one. However, desorption is not as complete if capillary condensation occurs, since the forces that hold a liquid together are much stronger than the physical adsorption forces.

Air pollution control involves removing contaminant vapors at low partial pressures. Therefore, the micropore structure of an adsorbent plays an important role in determining the overall efficiency. Another reason for the wide use of activated carbon is that 90 to 95% of its surface area is in the micropore size range.

## Dynamic Adsorption Process

The movement of vapors through an adsorbent bed is often referred to as a dynamic process. The term dynamic refers to motion both in the movement of air through the adsorbent bed and change in vapor concentration as it moves through the bed. There are a variety of configurations in which the contaminant air stream and adsorbent are brought into contact. The most common configuration is to pass the air stream down through a fixed volume or bed of adsorbent. Figure 5-8 illustrates how adsorption (mass transfer) occurs as vapors pass down through the bed.

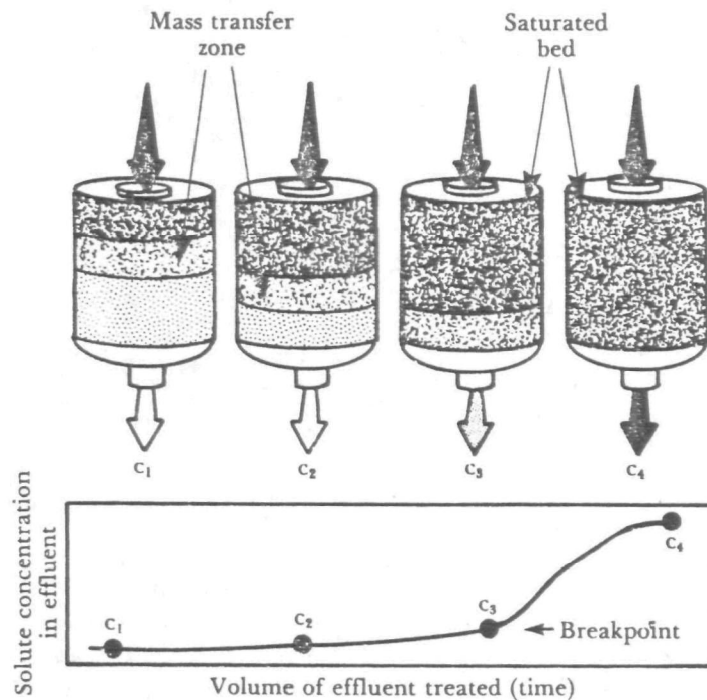


Figure 5-8. Breakthrough curve.

The gas stream containing the pollutant, at an initial concentration,  $c_i$ , is passed down through a deep bed of adsorbent material which is free of any contaminant. Most of the contaminant is readily adsorbed by the top portion of the bed. The small amount of contaminant that is left is easily adsorbed in the remaining section of the bed. The effluent from the bottom of the bed is essentially pollutant free, denoted at  $c_1$ .

After a period of time the top layer of the adsorbent bed becomes saturated with contaminant. The majority of adsorption (approximately 95%) now occurs in a narrow portion of the bed directly below this saturated section. The narrow zone of adsorption is referred to as the *mass transfer zone* (MTZ). As additional contaminant vapors pass through the bed, the saturated section of the bed becomes larger and the MTZ moves further down the length of the adsorber. The actual length of



the MTZ remains fairly constant as it travels through the adsorbent bed. Additional adsorption occurs as the vapors pass through the "unused" portion of the bed. The effluent concentration at  $c_2$  is essentially still zero since there is still an unsaturated section of the bed.

Finally, when the lower portion of the MTZ reaches the bottom of the bed, the concentration of contaminant in the effluent suddenly begins to rise. This is referred to as the *breakthrough point*—where untreated vapors are being exhausted from the adsorber. If the contaminated air stream is not switched to a fresh bed, the concentration of contaminant in the outlet will quickly rise until it equals the initial concentration, illustrated at point  $c_4$ .

In most air pollution control systems even trace amounts of contaminants in the effluent stream are undesirable. To achieve continuous operation, adsorbers must be either replaced or cycled from adsorption to desorption before breakthrough occurs. In *desorption* or *regeneration*, the contaminant vapors are removed from the used bed in preparation for the next cycle. Most commercial adsorption systems are the regenerable type.

In regard to regenerable adsorption systems, three important terms are used to describe the *capacity* of the adsorbent bed. All the capacities are measured in lb of vapor per lb of adsorbent. First, the *breakthrough capacity* is defined as the capacity of the bed at which unreacted vapors begin to be exhausted. The *saturation capacity* is the maximum amount of vapors that can be adsorbed per unit weight of carbon. (This is the capacity read from the adsorption isotherm). The *working capacity* is the actual amount of adsorbent used in an adsorber. The working capacity is a certain fraction of the saturation capacity. Working capacities can range from 0.1 to 0.5 of the saturation capacity. (Note: a smaller capacity increases the amount of carbon required.) This fraction is set by the designer for individual systems by balancing the cost of carbon and adsorber operation versus preventing breakthrough allowing for an adequate cycle time.

Another factor in determining the working capacity is that it is uneconomical to desorb all the vapors from the adsorber bed. The small amount of residual vapors left on the bed is referred to as the *heel*. This heel accounts for a large portion of the difference between the saturation and the working capacity. In some cases the working capacity can be estimated by assuming it is equal to the saturation capacity minus the heel (Turk, 1977). The following example illustrates one method of estimating the working capacity. In all the examples in this manual and the accompanying workbook, a design factor of 0.5 of the saturation capacity is used. This is the same as assuming the working amount of carbon is twice the amount required at saturation.

## **Factors Affecting Adsorption**

A number of factors or system variables influence the performance of an adsorption system. These variables and their effects on the adsorption process are discussed in the following section.

### ***Temperature***

For physical adsorption processes, the capacity of an adsorbent decreases as the temperature of the system increases. Figure 5-9 illustrates this concept. As the temperature increases the vapor pressure of the adsorbate increases, raising the energy level of the adsorbed molecules. Adsorbed molecules now have sufficient energy to overcome the van der Waals' attraction and migrate back to the gas phase. Molecules already in the gas phase tend to stay there due to their high

vapor pressure. As a general rule, adsorber temperatures are kept below 55°C (130°F) to ensure adequate bed capacities. Temperatures above this limit can be avoided by cooling the exhaust stream that is to be treated.

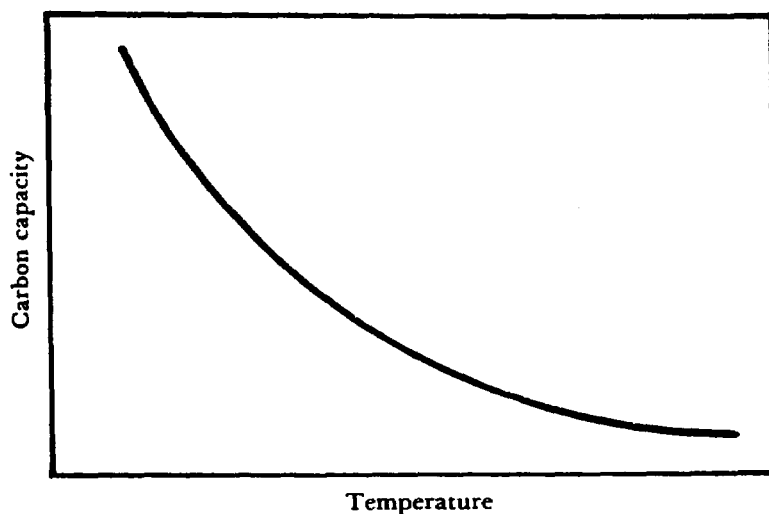


Figure 5-9. Carbon capacity vs. temperature.

Adsorption is an exothermic process with the heat released for physical adsorption approximately equal to the heat of condensation. At low concentrations (below 100 ppm) the heat release is minimal and is quickly dissipated by the air flow through the bed. At higher concentrations (approximately 5000 ppm) considerable heating of the bed can occur, which if not removed can cause the adsorber efficiency to rapidly decrease. In addition, granular carbon is a good insulator, which inhibits heat dissipation from the interior of the bed. In some cases, especially ketone recovery, the temperature rise can cause auto-ignition of the carbon bed. Monitoring of bed temperatures and leaving the bed slightly wet after steam regeneration are techniques used to avoid bed fires.

### ***Pressure***

Adsorption capacity increases with an increase in the partial pressure of the vapor. The partial pressure of a vapor is proportional to the total pressure of the system. Any increase in pressure will increase the adsorption capacity of a system (see Figure 5-4). The increase in capacity occurs because of a decrease in the mean free path of vapors at higher pressures. Simply, the molecules are packed more tightly together. More molecules have a chance to "hit" the available adsorption sites, increasing the number of molecules adsorbed.

## Gas Velocity

The contact or residence time between the contaminant stream and adsorbent is determined by the gas velocity through the adsorber. The residence time directly affects capture efficiency. The slower the contaminant stream flows through the adsorbent bed, the greater the probability of a contaminant molecule hitting an available site. Once a molecule has been captured it will stay on the surface until the physical conditions of the system are changed. To achieve 90% + capture efficiency most carbon adsorption systems are designed for a maximum air flow velocity of 30 m/min (100 ft/min) through the adsorber. A lower limit of at least 6 m/min (20 ft/min) is maintained to avoid flow distribution problems, such as channeling.

Gas velocity through the adsorber is a function of the diameter of the adsorber for a given volume of contaminant gas. By specifying a maximum velocity through the adsorber, the minimum diameter is also specified. For example, if 300 m<sup>3</sup>/min of contaminant gas is to be treated, and the maximum velocity through the adsorber is to be 30 m/min, then the adsorber must have a cross sectional area of at least 10 m<sup>2</sup>.

The gas flow rate through the adsorber also affects the pressure drop. Increasing the flow rate increases the pressure drop. Within the above stated maximum and minimum flow rates, the allowable pressure drop usually dictates the required tower diameter and flow rate. The pressure drop across the bed also depends on the depth of adsorbent. This will be discussed in the following section.

## Bed Depth - affects pressure drop

Providing a sufficient depth of adsorbent is very important in achieving efficient gas removal. If the adsorber bed depth is shorter than the required mass transfer zone, breakthrough will immediately occur rendering the system ineffective. Computing the length of the MTZ is very difficult since it depends upon six factors: the adsorbent particle size, gas velocity, adsorbate concentration, fluid properties of the gas stream, temperature, and pressure of the system. The MTZ can be estimated from experimental data using Equation 5-6 (Kovach, 1978). To obtain the necessary data, vendors will usually test a small portion of the exhaust stream on a pilot adsorber column.

$$(Eq. 5-6) \quad MTZ = \frac{1}{1 - X_s} D \left( 1 - \frac{C_B}{C_s} \right)$$

Where: D = bed depth, m

C<sub>B</sub> = breakthrough capacity, %

C<sub>s</sub> = saturation capacity, %

X<sub>s</sub> = degree of saturation in the MTZ, % (usually assumed to be 50%)

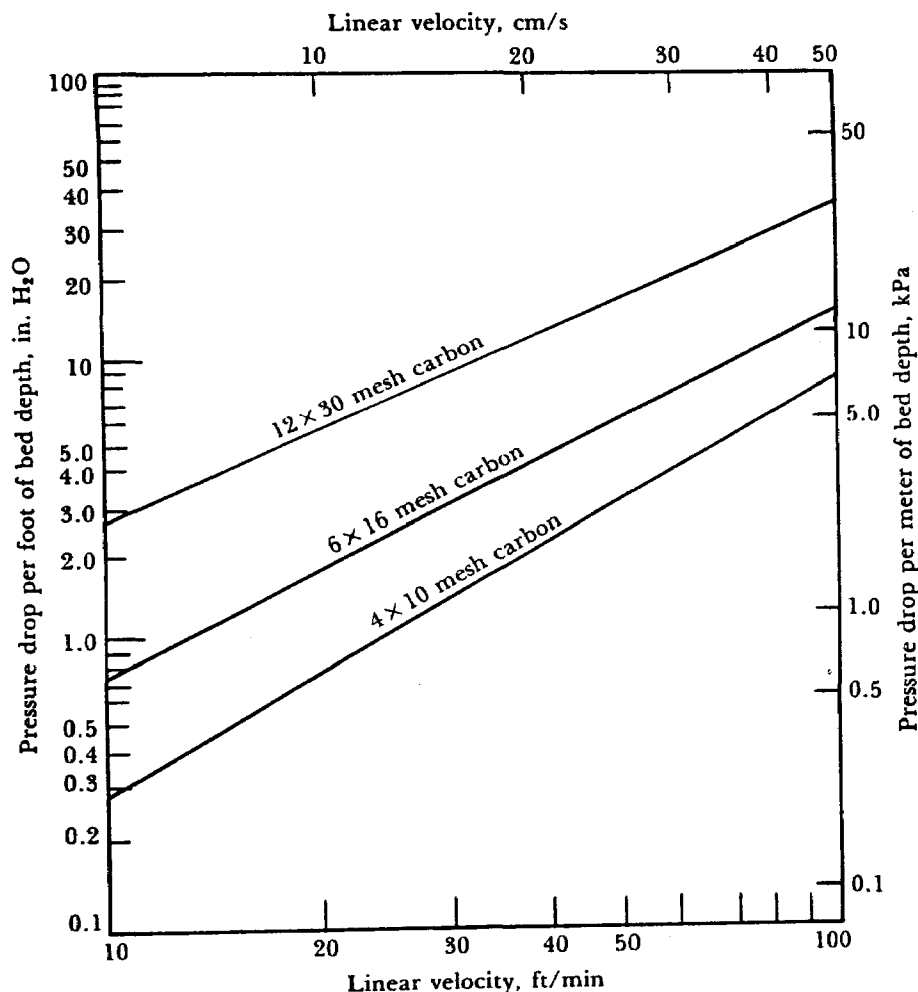
MTZ = length of MTZ, m

The above equation is used mainly as a check to ensure that the proposed bed depth is longer than the MTZ. Actual bed depths are usually many times longer than the length of the MTZ. The additional bed depth allows for adequate cycle times. Equation 5-6 can be rearranged to solve for the breakthrough capacity:

(Eq. 5-7)

$$C_B = \frac{(X_s)(C_s)(MTZ) + C_s(D - MTZ)}{D}$$

The total amount of adsorbent required is usually determined from the adsorption isotherm, as illustrated in Example 5-2. Once this has been set, the bed depth can then be estimated by knowing the tower diameter and density of the adsorbent. Example 5-3 illustrates how this is done. Generally, the adsorbent bed is sized to the maximum length allowed by the pressure drop across the bed. Data on the pressure drop per meter of bed depth for typical carbons is presented in Figure 5-10 (Turk, 1977). The pressure drop per meter of bed depth is plotted versus the gas flow rate, with the carbon mesh size as a parameter. From the figure, an adsorber with a flow rate of 40 cm/s (80 ft/min) using  $4 \times 10$  mesh carbon will have a pressure drop of approximately 5 kPa per meter (6 in. H<sub>2</sub>O per foot) of bed depth. Therefore, if the pressure drop across the bed is limited to 4.5 kPa (18 in. H<sub>2</sub>O) then the total bed depth should not exceed 0.9 meters (3 ft).



Source: From *Air Pollution*, 3rd ed., Vol IV, Engineering Control of Air Pollution, Chapter 8 - Adsorption by Amos Turk, A.C. Stern editor. ©1977. Used with the permission of Academic Press, Inc.

Figure 5-10. Pressure drop vs. flow rate through granular carbon beds.

## ***Humidity***

As stated previously activated carbon will preferentially adsorb nonpolar hydrocarbons over polar water vapor. The water vapor molecules in the exhaust stream exhibit strong attractions for each other rather than the adsorbent. At high relative humidities, over 50%, the number of water molecules increases such that they begin to compete with the hydrocarbon molecules for active adsorption sites. This reduces the capacity and the efficiency of the adsorption system. Exhaust streams with humidities greater than 50% may require installation of additional equipment to remove some of the moisture. Coolers to remove the water are one solution. Dilution air with significantly less moisture in it than the process stream has also been used. Also, the contaminant stream may be heated to reduce the humidity as long as the increase in temperature does not greatly affect adsorption efficiency.

## ***Contaminants***

In addition to humidity; particulate matter, entrained liquid droplets, and organic compounds which have high boiling points can also reduce adsorber efficiency if present in the air stream. Any micron-sized particle of dust or lint which is not filtered can cover the surface of the adsorbent. This greatly reduces the surface area of the adsorbent available to the gas molecule for adsorption. Covering of active adsorption sites by an inert material is referred to as *blinding* or *deactivation*. To avoid this situation almost all industrial adsorption systems are equipped with some type of particulate matter removal device.

Entrained liquid droplets can also cause operational problems. Liquid droplets that are nonadsorbing act the same as particulate matter. The liquid covers the surface, blinding the bed. If the liquid is the same as the adsorbate, high heats of adsorption occur. This is especially a problem in activated carbon systems where liquid organic droplets carried over from the process can cause bed fires from the heat released. Some type of entrainment separator may be required when liquid droplets are present.

For activated carbon systems, other contaminants are high boiling point organic compounds, usually in excess of 260°C (500°F). High boiling point (high molecular weight) compounds have such an affinity for the carbon that it is extremely difficult to remove them by standard desorption practices. These compounds also tend to react chemically on the carbon surface forming solids or polymerization products which are extremely difficult to desorb. Loss of carbon activity in this manner is called *chemical deactivation*.

## **Adsorbent Regeneration Methods**

Periodic replacement or regeneration of the adsorbent bed is mandatory in order to maintain continuous operation. When the adsorbate concentration is high and/or cycle time is short (less than 12 hours) replacement of the adsorbent is not feasible

and in-situ regeneration is required. Regeneration is accomplished by reversing the adsorption process, usually by increasing the temperature or decreasing the pressure. Commercially, four methods are used in regeneration:

*Thermal swing:* The bed is heated so that the adsorption capacity is reduced to a lower level. The adsorbate leaves the surface of the carbon and is removed from the vessel by a stream of purge gas. Cooling must be provided before the subsequent adsorption cycle begins. Steam regeneration is an example of thermal swing regeneration.

*Pressure swing:* The pressure is lowered at a constant temperature to reduce the adsorbent capacity.

*Inert purge gas stripping:* The stripping action is caused by an inert gas that reduces the partial pressure of the contaminant in the gas phase, reversing the concentration gradient. Molecules migrate from the surface into the gas stream.

*Displacement cycle:* The adsorbates are displaced by some preferentially adsorbed material. This method is usually a last resort for situations in which the adsorbate is both valuable and is heat sensitive, and for which pressure swing regeneration is ineffective (Bethea, 1978).

Table 5-3 compares the effectiveness of the various regeneration methods (Wood, 1964). As can be seen from this table, steam regeneration was most effective for the test conditions. This is also true for most industrial applications.

Table 5-3. Regeneration of one pound of activated carbon loaded with 20% ether.

Regeneration method	Regeneration conditions	Expelled ether (%)
Thermal swing	Heating at 100°C (212°F) for 20 min	15
Pressure swing	Vacuum of 50 mm Hg at 20°C (68°F) for 20 min	25
Combination	Gas circulation at 130°C (266°F) for 20 min	45
Thermal swing	Direct steam at 100°C (212°F) for 20 min	98

### ***Thermal Swing—Steam Stripping***

Because it is simple and relatively inexpensive, steam stripping is the most common desorption technique. Several additional advantages to using steam for desorption are:

- At high pressure, the steam's temperature (100°C) is high enough to desorb most solvents of interest without damaging the carbon or the desorbed vapors. Desorbed vapors can be polymerized or cracked, sometimes forming undesirable compounds.
- Steam readily condenses in the adsorber bed releasing its (the steam) heat of condensation, aiding in desorption.
- Many organic compounds can be easily separated and recovered from the effluent stream by condensation or distillation.

- Residual moisture in the bed is removed easily by a stream of cool dry air (either pure or process effluent).
- Steam is a more concentrated source of heat than hot air so it is very effective in raising the temperature of the adsorber bed very quickly.

The amount of steam required for regeneration depends on the adsorbate loading of the bed. The longer a carbon bed is steamed, the more adsorbate will be desorbed. It is usually not cost effective to try to desorb all of the adsorbed vapors from the bed. Acceptable working capacities can be achieved by using less steam and leaving a small portion of adsorbate in the bed. During the initial heating period no vapors are desorbed. This is because a fixed amount of steam is first required to raise the temperature of the cold bed to the desorption temperature. After this initial period a substantial amount of adsorbate vapor is released, until a plateau is reached. The plateau represents the optimum steam requirement, usually in the range 0.25 to 0.35 kg of steam/kg of carbon (Parmele, 1979). In these systems, steam is usually supplied at pressures ranging from 21 to 103 kPa (3 to 15 psig).

A typical two bed adsorption system is shown in Figure 5-11. Regeneration steam usually passes up through the bed countercurrent to the flow of solvent laden vapors. Since the bed is switched to the desorption mode before breakthrough, the outlet end of the bed remains adsorbate free, providing a safety margin for subsequent cycles. The steam usage can range anywhere from 0.3 to 10 kg of steam per kg of solvent removed.

Some disadvantages are associated with steam regeneration. Problems arising are:

- The effluent from the condenser could pose a water pollution problem unless the condensate is sent to a waste water treatment facility.
- Some organic compounds are subject to hydrolysis and/or other reactions with water which may produce corrosive substances. Corrosive substances can greatly reduce the life of the adsorption equipment unless expensive corrosive resistant materials are used.
- A hot wet carbon bed will not effectively remove organic vapors. Cooling and drying of the bed may be needed to ensure adequate removal efficiencies at the beginning of a subsequent cycle.



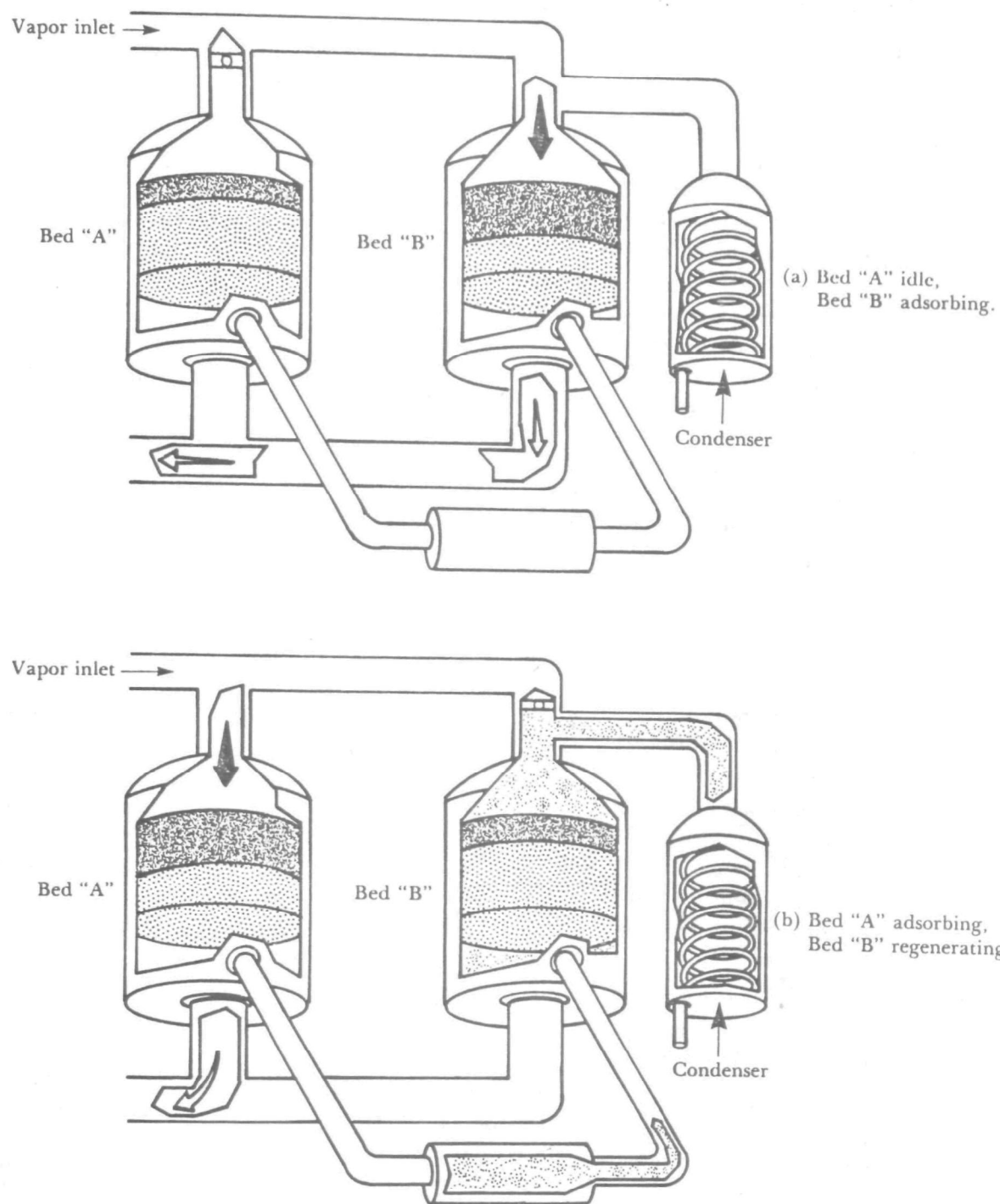


Figure 5-11. Two bed adsorption system.

### ***Pressure Swing—Vacuum Desorption***

Pressure swing or vacuum desorption has one primary advantage over thermal desorption. Desorption is accomplished by a change in pressure rather than temperature so no time is required to initially heat up or cool the carbon bed. This adiabatic (no change in temperature) pressure swing allows the bed to be in the adsorbing cycle longer. Units may also be sized smaller since there is no increase in air volume due to heating of the bed. Both of these conditions allow for higher throughputs or smaller adsorber designs than can be accommodated by thermal swing desorption systems. In addition, the desorbed vapors may be recovered directly without the need for additional downstream processing equipment.

The principle disadvantages of a pure pressure swing cycle are the high operating and construction costs. In pressure/vacuum systems the adsorber vessel and valving must be constructed of materials capable of withstanding vacuums of 9.5 kPa (28 in. Hg). Unless the adsorber is initially operated at elevated pressures (so that the pressure swing can be accomplished by reducing the vessel to atmospheric pressures) a vacuum producing system is required. Vacuum systems that operate cyclically may require more operating attention than other regeneration systems. To be effective, pressure regeneration systems must be designed so that a small decrease in pressure will result in a drastic shift in the direction of mass transfer.

## **Adsorption Control Systems**

Adsorption control systems can be classified as either regenerable or non-regenerable. Nonregenerable systems are normally used to control exhaust streams with low pollutant concentrations, below 1.0 ppm. Generally these pollutants are highly odorous or to some degree toxic. When these systems reach the breakthrough point the bed is taken off stream and replaced with a fresh bed. The used carbon can then be sent back to the manufacturer for reactivation. Regenerable systems are used for higher pollutant concentrations such as in solvent recovery operations. Once the bed reaches the breakthrough point in a regenerable system, the pollutant vapors are directed to a second bed while the first has the vapors desorbed.

### ***Nonregenerable Adsorption Systems***

Nonregenerable adsorption systems are manufactured in a variety of configurations. Bed areas are sized to control the air flow through them at between 6.0 to 18 m/min (20 to 60 ft/min). They usually consist of thin adsorbent bed depth, ranging in thickness from 1.25 to 10.0 cm (0.5 to 4.0 inches). These thin beds have a low pressure drop, normally below 62 Pa (0.25 in. H<sub>2</sub>O) dependent on the bed thickness, gas velocity, and particle size of the adsorbent. Service time for these units can range from 6 months for "heavy" odor concentrations to up to 2 years for

trace concentrations or intermittent operations (EPA, 1973). They are used mainly as air purification devices for small air flows in offices, laboratory exhaust, and other small exhaust streams.

The shapes of these thin bed adsorbers are flat, cylindrical, or pleated. The granules of activated carbon are retained by porous support material, usually perforated sheet metal. An adsorber system usually consists of a number of *retainers* or *panels* placed in one frame. Figure 5-12 shows a nine panel thin bed adsorber. The panels are similar to home air filters except that instead of containing steel wool they contain activated carbon as the filter. Figure 5-13 illustrates a pleated cell adsorber. The pleated cell is one continuous retainer of activated carbon, rather than individual panels. The cylindrical canisters (Figure 5-14) are usually small units designed to handle low flow rates of approximately 0.12 m/s (25 cfm). Cylindrical canisters are made of the same materials as the panel and pleated adsorbers except their shape is round rather than square. Panel and pleated beds are dimensionally about the same size, normally 0.6 meters square (2 ft by 2 ft) with the carbon depth ranging from 0.2 to 0.6 m (8 in. to 2 ft). Flat panel beds are sized to handle higher exhaust flow rates, approximately 9.4 m/s (2000 cfm), while pleated beds are limited to flow rates of 4.7 m/s (1000 cfm). Typical flow rate values are listed in Table 5-4.

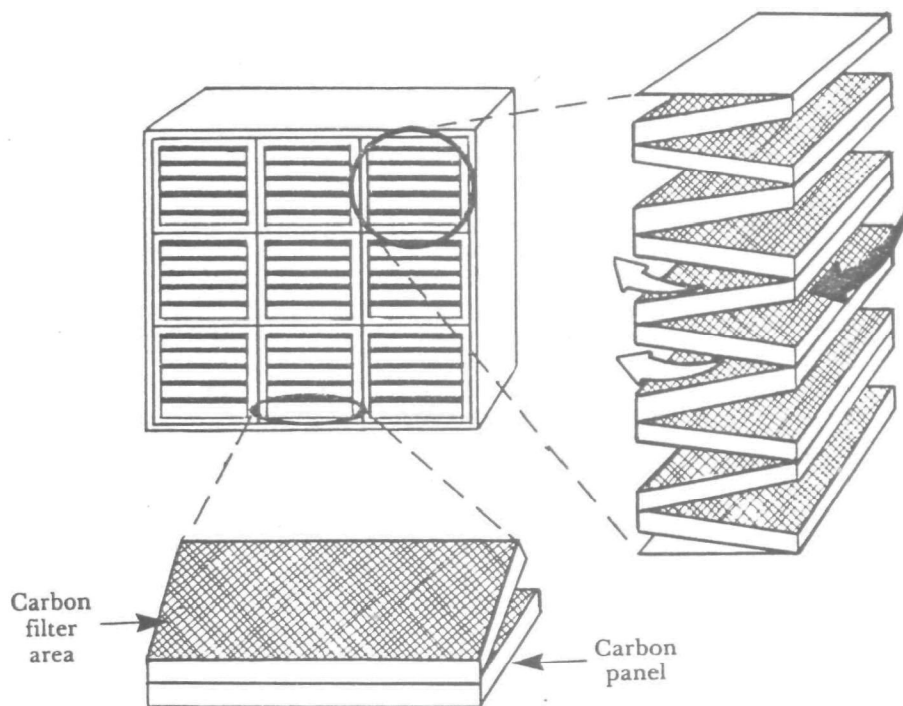


Figure 5-12. Thin bed adsorber: nine cell system.

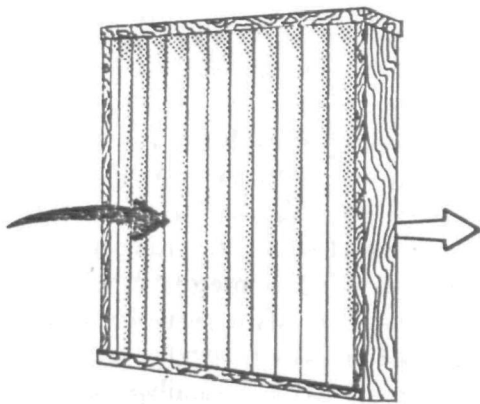


Figure 5-13. Pleated thin bed.

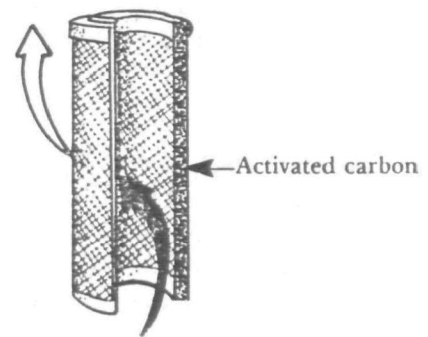


Figure 5-14. Canister.

Table 5-4. Adsorption filters.

Filter shape	Size	Flow rate
Multiple panel cell	$\sim 0.6 \text{ m}^2$	9.4 m/s
Pleated cell	$\sim 0.6 \text{ m}^2$	4.7 m/s
Cylindrical canister	$\sim 0.002 \text{ m}$ diameter $\sim 0.005 \text{ m}$ length	0.12 m/s

In addition to thin bed systems, thick bed nonregenerable systems are also available. One system that can be used is essentially just a 55-gallon drum. The bottom of the drum is filled with gravel to support a bed of activated carbon weighing approximately 330 kg (150 lb). A typical unit is shown in Figure 5-15. These units are used to treat small flow rates (0.5 m/s or 100 cfm) from laboratory hoods, chemical storage tank vents, and chemical reactors.

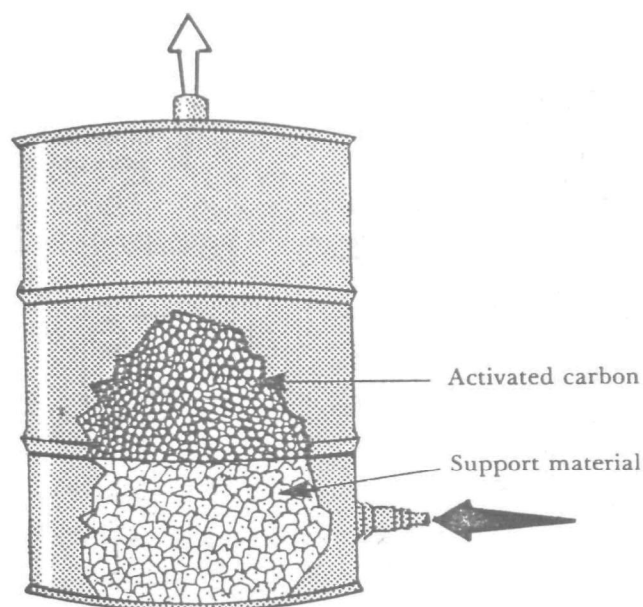


Figure 5-15. Canister.

### *Regenerable Adsorption Systems*

A large regenerable adsorption system can be categorized as a fixed, moving or fluidized bed. The name refers to the manner in which the vapor stream and adsorbent are brought into contact. The choice of a particular system depends on the pollutants to be controlled and the recovery requirements. The most common adsorption system for controlling air pollutants is the fixed carbon bed. These systems are used to control a variety of organic vapors and are usually regenerated by direct steaming of the bed. The organic compounds may be recovered by condensing the exhaust from the regeneration step and separating out the water and solvent.

### Fixed Bed Adsorbers

Fixed bed adsorption systems generally involve multiple beds. One or more beds treat the process exhaust while the other beds are either being regenerated or cooled. A typical three bed adsorption system is shown in Figure 5-16. The solvent-laden air stream is first pretreated to remove any solid or liquid particles which could blind the carbon bed and decrease its efficiency. The solvent-laden air stream then usually passes down through the fixed carbon bed. Upward flow through the bed is usually avoided (unless flow rates are low ( $<500$  cfm) to eliminate the risk of entraining carbon particles in the exhaust stream).

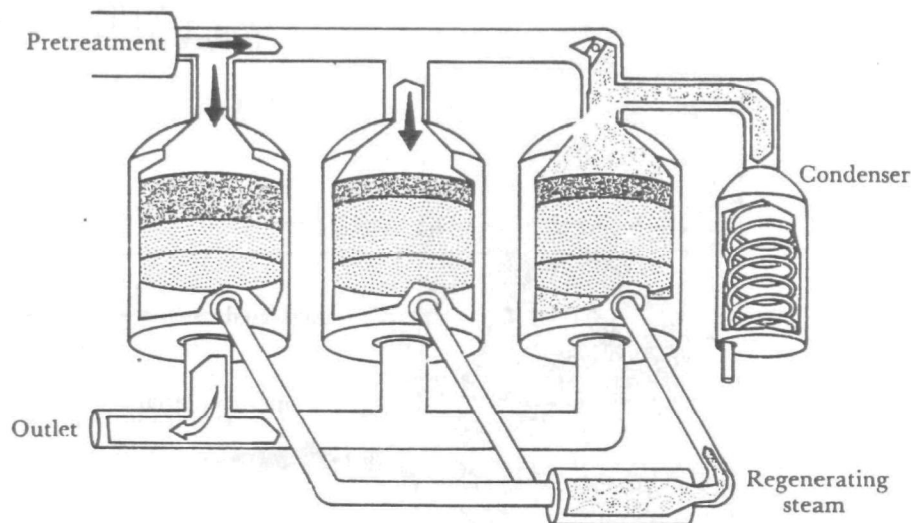


Figure 5-16. Three bed system.

After a predetermined length of time, referred to as the cycle time, the solvent-laden air stream is directed to the second adsorber by a series of valves. Steam is then injected into the first bed to remove the adsorbed vapors. The steam and desorbed vapors are then usually sent to a recovery system. If the solvents are immiscible in water, they can be separated by condensing the exhaust and decanting off the solvent. If the solvents are miscible in water, distillation may be required. Before the first adsorber is returned to service, cooling and drying of the carbon should be provided. This will ensure against immediate breakthrough occurring from the "hot, wet" carbon bed. This can be accomplished by venting the solvent-laden air stream through the hot, wet adsorber, then to the on-line adsorber to maintain a high removal efficiency.

Regenerable fixed carbon beds are usually between 0.3 and 1.2 m (1 to 4 ft) thick. The maximum adsorbent depth of 1.2 m is based on pressure drop considerations (Vic Mfg. Co.). Superficial gas velocities through the adsorber range from 6.0 to 30.0 m/min (20 to 100 ft/min) with 30.0 m/min being a maximum

permissible flow rate. Pressure drops normally range from 750 to 3730 Pa (3 to 15 in.  $\text{H}_2\text{O}$ ) depending on the gas velocity, bed depth and carbon particle size (Bethea, 1978). For specific applications, graphs similar to that in Figure 5-11 are supplied by the carbon manufacturer to compute the pressure drop.

The two types of fixed bed adsorbers are distinguished by bed orientation in relation to air flow. The first is referred to as a *vertical flow adsorber*. The bed length is vertical as is the direction of air flow. The air stream usually flows downward. This system is shown in Figure 5-16. These units are suited to handle flows up to 1.4 to 2.0  $\text{m}^3/\text{s}$  (3000 to 4000 cfm) per adsorber. Figure 5-17 shows a three bed vertical system used to recover 34 kg/m (75 lbs/hr) of trichloroethylene from a vapor degreasing operation. Each vessel is 1.2 m (48 in.) in diameter, contains 255 kg (560 lbs) of carbon approximately 10 cm (4 in.) deep and handles 1.7  $\text{m}^3/\text{s}$  (3500 scfm) air flow. One vessel is being desorbed each hour using 102 kg (225 lbs) of steam at 103 kPa (15 psig). The pressure drop across the system is approximately 3 kPa (12 in.  $\text{H}_2\text{O}$ ) (Vic Mfg. Co. with permission).

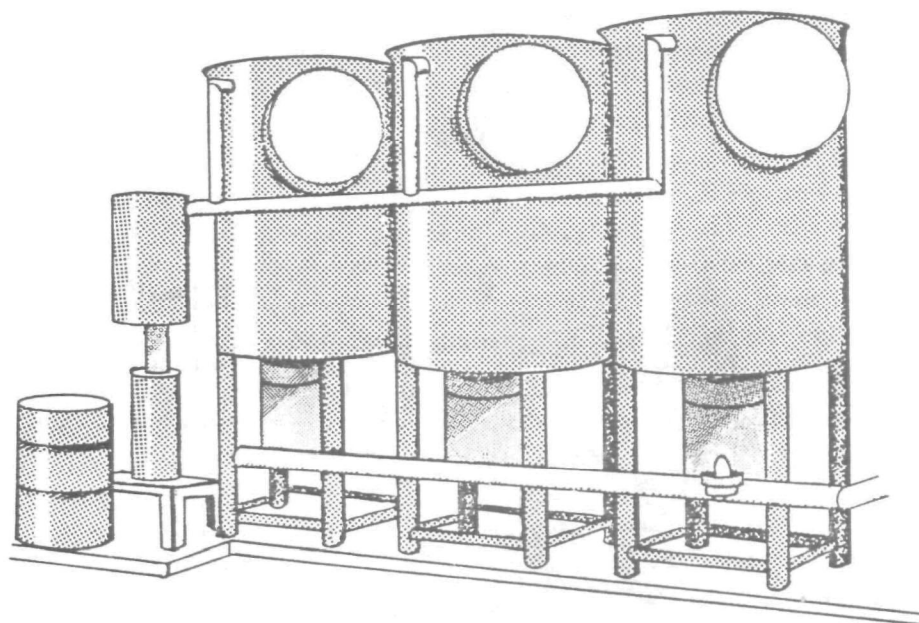


Figure 5-17. Three bed vertical system.

For larger flow rates, *horizontal flow adsorbers* are used. Structurally they are more suited to handle the larger air volumes. In horizontal flow units, the bed length is horizontal as is the direction of the incoming air stream. The air stream flows across the bed and down. This system is illustrated in Figure 5-18. Adsorbers of this type are manufactured as a package system capable of handling flow rates up to 1150 m<sup>3</sup>/s (40,000 cfm). Larger units must be engineered and fabricated for the specific application. Figure 5-19 shows a three bed horizontal system used to recover 1180 kg/hr (2600 lb/hr) of toluene from a rotogravure operation. Each vessel is 7 m (22 ft) long and 3 m (10 ft) in diameter and contains 9000 kg (20,000 lbs) of carbon packed to a 1 m (3 ft) bed depth. The system handles 21 m<sup>3</sup>/s (44,000 scfm) air flow with a pressure drop of 6 kPa (24 in. H<sub>2</sub>O). One vessel is desorbed each 45 minutes using 3600 kg/hr (8000 lbs/hr) of steam at 103 kPa (15 psig) pressure (Vic Mfg. Co. with permission).

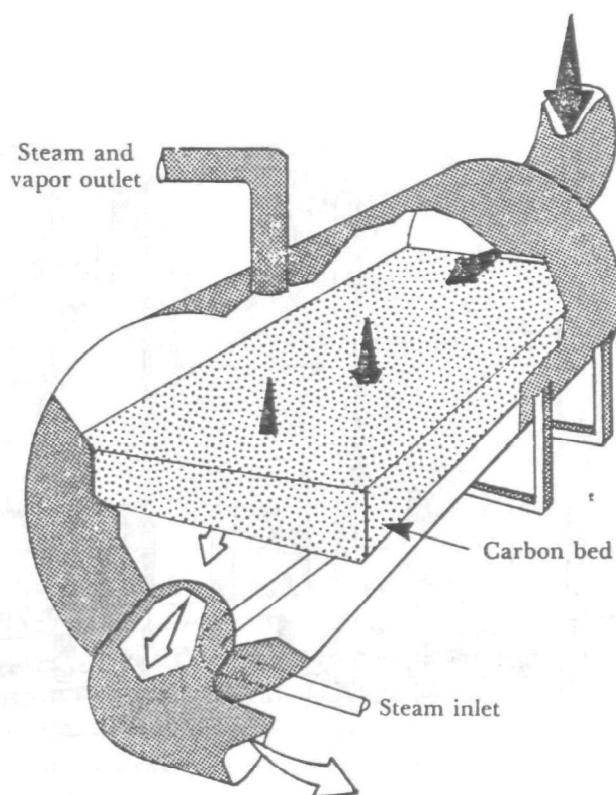


Figure 5-18. Horizontal bed.



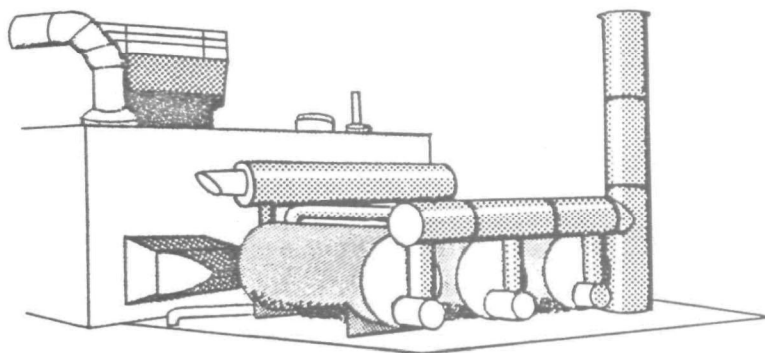


Figure 5-19. Three bed horizontal system.

### Moving Bed Adsorbers

Moving bed systems can also be used to obtain a higher degree of utilization of the carbon bed than is possible with a fixed bed. In moving bed systems, the solvent-laden vapor stream passes only through the unsaturated portion of the carbon bed. This reduces the distance (thus pressure drop) the air stream travels through the bed.

One design of a moving (rotary) bed system is illustrated in Figure 5-20 (Sutcliffe Speakman Co., 1963). The device consists of four cylinders which are in constant rotation. The granular carbon is held in place between two cylinders made of steel screening or perforated sheet metal. This bed is placed between inner and outer cylinders which are impervious to air flow except at slots near their ends.

The slots on the outer cylinder act as solvent-laden inlets. They permit the air stream to pass into the annular section where the carbon is located. The solvent-laden air stream passes through the carbon bed and purified air exits out the inner slots. The carbon bed is broken into sections. The cylinders rotate such that when the proper degree of saturation is reached the bed is desorbed. Desorption occurs by injecting steam in through the slots on the inner cylinder. Steam and desorbed vapors exit through the slots on the outer cylinder. During each rotation of the cylinder, each segment of the carbon bed undergoes both an adsorption and desorption cycle.

Because of the continuous adsorbing and desorbing process, bed utilization is improved. The air stream is no longer required to pass through the top, saturated portion; or the bottom, idle portion of the bed. The air stream passes only through the active, mass transfer portion of the bed. Therefore, shorter and more compact beds may be used which reduce the pressure drop. The disadvantages are wear on moving parts and maintaining air tight seals on moving parts.

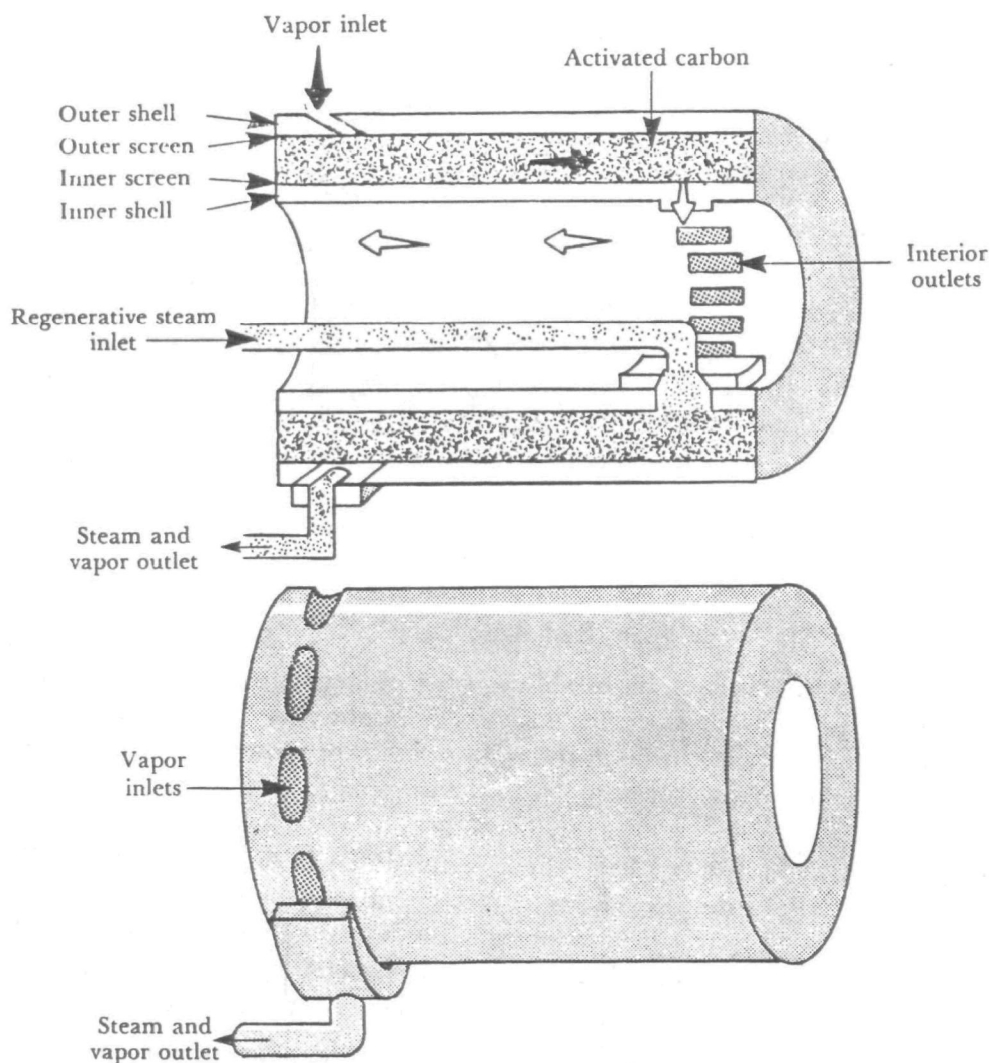


Figure 5-20. Rotary bed system.

### Fluidized Bed Adsorbers

A fluidized bed adsorption system operates in the same physical manner as a tray scrubber. Instead of liquid flowing down the column from tray to tray, granular activated carbon is used. Figure 5-21 shows one recently developed fluidized bed system which is being marketed by Union Carbide. The solvent-laden air stream is introduced at the middle of the tower. Then it passes up through the tower fluidizing the activated carbon in a series of trays. The carbon then flows down through the vessel from tray to tray until it reaches the desorption section. Regeneration is accomplished in the bottom half of the vessel and the activated carbon is air conveyed back to the top of the tower.

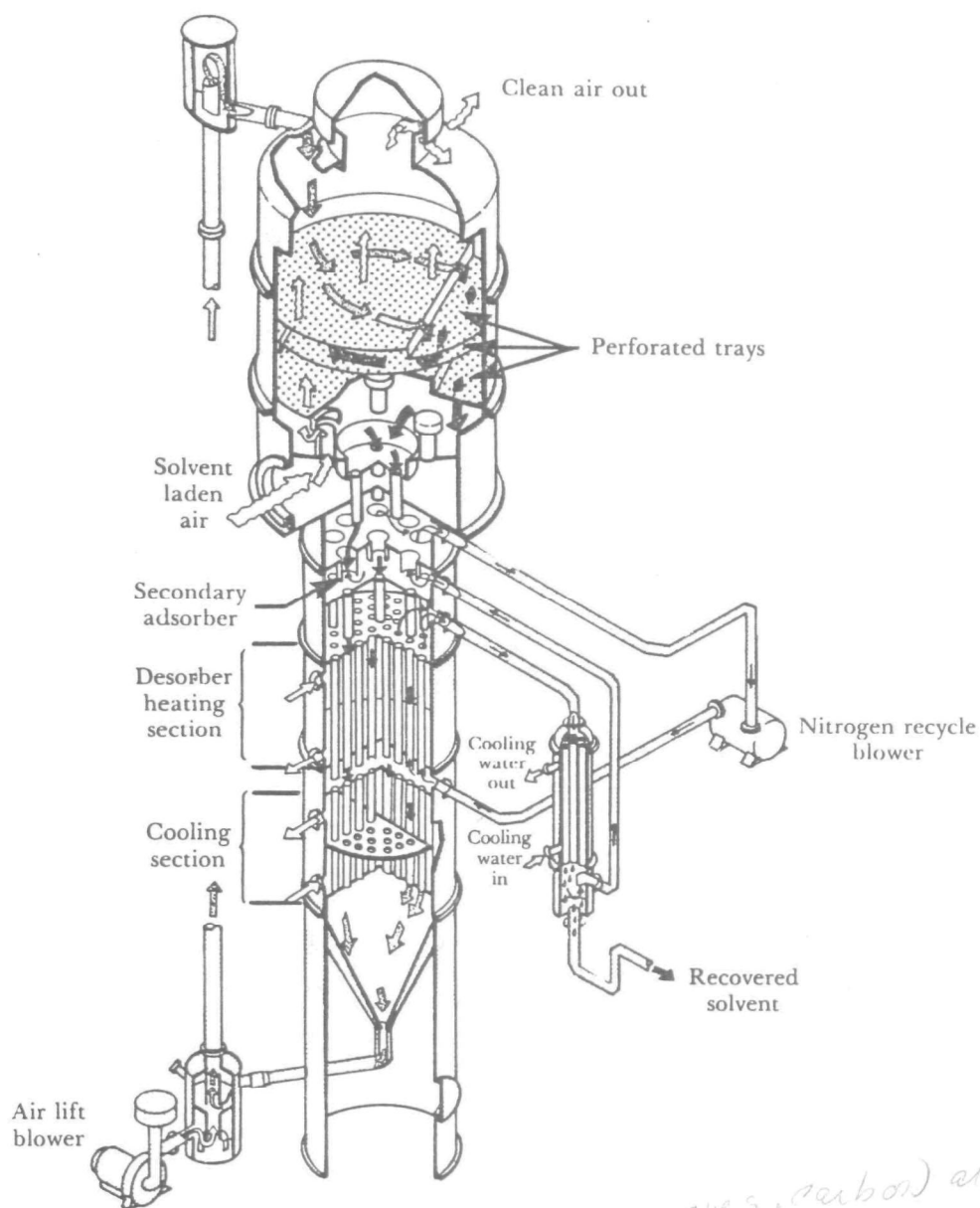


Figure 5-21. Fluidized bed adsorber.

*By Union Carbide*

As with the moving bed, the fluidized bed also provides continuous operation and more efficient utilization of the adsorbent. The need for multiple vessels is eliminated, which can greatly reduce the cost of the system. Gas velocities around 1 m/s (196 ft/min) are needed to fluidize the bed. These are 2 to 4 times the velocities achieved in fixed bed systems. This allows for use of a much smaller vessel for comparable air flow and helps to achieve uniform gas distribution.

The main disadvantage with fluidized bed adsorption systems is the high attrition (wear) losses of the granular activated carbon. Recently a new "beaded" activated carbon was developed in Japan. The beaded shape is inherently stronger and has better fluidity properties than granular carbon. The beaded carbon has been used in a number of installations (mostly in Japan) and is reported to reduce the attrition losses to 2 to 5% per year as compared to 10% for fluidized granular carbon (Union Carbide).

The following example illustrates the use of the principles and general rules of practice discussed in this chapter in designing an adsorption system.

INSPECTION OF CARBON BED ADSORBERS  
Inspection Summaries

6.3 Inspection Summaries

6.3.1 Level 1 Inspections - No Inspection Steps

6.3.2 Level 2 Inspections

Basic Level 2 Inspection Steps

Stack/Exhaust

- Exhaust VOC concentration for 10 - 15 minutes near the end of the adsorption cycle\*

Carbon Bed Adsorber

- Obvious corrosion on the adsorber shell
- Adsorption/desorption cycle times
- Steam pressure and temperature during desorption

Process Equipment

- Obvious fugitive emissions\*

Follow-up Level 2 Inspection Steps

Carbon Bed Adsorber

- Inlet gas temperature
- Inlet and outlet static pressures
- Outlet detector calibration and maintenance
- Quantity of solvent in recovered solvent tank

Process Equipment

- Maximum production rate during the last 6 months
- Average production rate during the last 12 months
- Types of solvents used
- Quantities of solvents purchased
- Quantities of solvents sold/discarded

INSPECTION OF CARBON BED ADSORBERS  
Inspection Summaries

6.3.3 Level 3 Inspections

Stack/Exhaust

- Exhaust VOC concentration for 10 - 15 minutes near the end of the adsorption cycle\*
- Outlet gas temperature\*

Carbon Bed Adsorber

- Inlet gas temperature \*
- Obvious corrosion on the adsorber shell\*
- Adsorption/desorption cycle times\*
- Inlet and outlet static pressures\*
- Outlet detector calibration and maintenance\*
- Quantity of solvent in recovered solvent tank\*
- Measure the outlet VOC concentration
- Measure the inlet gas temperature
- Measure the static pressure drop

*esp. prior to  
cleaning  
cycle* →

Process Equipment

- Obvious fugitive emissions\*
- Maximum production rate for last 6 months\*
- Average production rate for last 12 months\*
- Types of solvents used\*
- Quantities of solvents purchased\*
- Quantities of solvents sold/discarded\*
- Hood static pressure

6.3.4 Level 4 Inspection Procedures

Exhaust Stack

- All elements of a Level 3 inspection

Carbon Adsorber

- All elements of a Level 3 inspection
- Locations for measurement ports
- Potential inspection safety problems

Process Equipment

- All elements of a Level 3 inspection
- Basic flowchart of process
- Potential inspection safety problems

\* Refer to Level 2 Inspection Procedures

INSPECTION OF CARBON BED ADSORBERS  
Basic Level 2 Inspection Procedures

6.4 Inspection Procedures

Techniques for the inspection of carbon bed adsorbers can be classified as Level 2 or Level 3. The Level 2 inspections primarily involve a walkthrough evaluation of the carbon bed adsorber system and process equipment using on-site gauges. The Level 3 inspection incorporates all of the inspection points of the Level 2 inspection and includes independent measurements of the adsorber operating conditions.

6.4.1 Basic Level 2 Inspections

Evaluate the VOC outlet detector.

The VOC detectors often used at the outlet of the carbon bed systems are relatively sophisticated instruments which require frequent maintenance. Confirm that they are working properly by reviewing the calibration records since the previous inspection. Maintenance work orders should also be briefly reviewed to determine if the instruments have been operational most of the time.

Check carbon bed shell for obvious corrosion.

Some organic compounds collected in carbon bed systems can react during steam regeneration. This leads to severe corrosion of the screens retaining the carbon beds and of the unit shell.

Observe the adsorption/desorption cycles.

Determine the time interval between bed regenerations and compare this with previously observed values. An increase in this time interval could mean that breakthrough is occurring if the quantities of organic vapor entering the carbon bed have remained unchanged. Systems in which the cycle frequency is controlled by a timer rather than an outlet organic vapor detector are especially prone to emission problems due to longer than desirable cycle times.

Check the regeneration steam line pressure.

Any decrease in the steam line pressure from previously recorded levels could indicate less than necessary steam flow for regeneration of the carbon beds.

INSPECTION OF CARBON BED ADSORBERS  
Follow-up Level 2 Inspection Procedures

6.4.2 Follow-up Level 2 Inspection Procedures

Evaluate carbon bed system static pressure drop.

If there are on-site gauges, evaluate any changes in the static pressure drop. A decrease could mean deterioration of the carbon bed to the point that channeling of the gas stream is affecting gas-solid contact. Higher than normal static pressure could mean partial pluggage of the carbon bed due to fines formation or due to material entering with the gas stream. However, gas flow changes could also be responsible for changes in the static pressure drop.

Prepare solvent material balances.

For some processes, the effectiveness of the carbon bed system can be evaluated by preparing a solvent material balance around the facility for a period of several weeks to a month. The information needed for the calculations includes solvent quantities purchased, changes in solvent storage tank levels, and solvent quantities transferred from the system.

Evaluate ventilation system.

To the extent safely possible, gas flow rates from process equipment to the carbon bed system should be evaluated. Record hood static pressures (if monitored) and look for any holes or gaps in the ductwork.

6.4.3 Level 3 Inspections

Measure the VOC outlet concentrations.

The effluent concentration from each bed should be measured if there is safe and convenient access to the effluent ductwork. The measurements should be made with an organic vapor analyzer that is calibrated for 50 to 2000 ppm.

The instrument (and its portable recorder, if any) should be certified as intrinsically safe for Class I, Group C and D locations. This means simply that the instrument is incapable of initiating an explosion when used properly. A small port is adequate to draw a 0.5 to 3.0 liter per minute sample into the instrument. An observed VOC concentration greater than 500 ppm (v/v) is a sign that the bed is not performing properly.



INSPECTION OF CARBON BED ADSORBERS  
Level 3 Inspection Procedures

Measure the VOC outlet concentration (continued).

It is important to determine the approximate desorption cycle of multi-bed systems. Outlet VOC measurements conducted earlier in the adsorption cycle of a bed may appear adequate even when the bed activity is severely reduced. Breakthrough usually does not occur until late in the operating cycle unless the condition of the carbon is extremely poor. Therefore, an effort should be made to measure the outlet VOC concentration of each bed at a time when it is approaching the end of the adsorption mode. The adsorption/desorption cycle is normally controlled by a timer and this can be used to determine the approximate status of each bed.

In some commercial multi-bed units there is only poor accessibility to the effluent ducts from each unit. In this case, the VOC concentration in the combined duct should be measured at the exhaust point. Obviously, this measurement should be attempted only when there is safe and convenient access to the exhaust. It is especially important to avoid areas where high VOC concentrations could accumulate.

Measure the inlet gas temperature.

Adsorption is inversely related to the gas temperature entering the carbon bed adsorbers. An increase in the gas temperature from the baseline period could result in a decreased capacity for organic vapors. The gas temperature should be measured in the inlet ductwork, immediately ahead of the carbon bed.

Measure the static pressure drop.

A change in the static pressure drop since the baseline period is usually due to either a change in the gas flow rate through the carbon bed or due to the physical deterioration of the bed itself.

INSPECTION OF CARBON BED ADSORBERS  
Level 3 Inspection Procedures

Measure the static pressure drop (continued).

Measurement taps on the adsorber shell should be used, if available. Alternatively, the static pressure drop can be measured using ports in the inlet ductwork to the adsorber system and the outlet duct from the adsorber. Obviously, the static pressure drop should be determined while the adsorber is on-line.

Check/measure the hood static pressure.

At the hood, the gas stream is accelerated to the velocity of 1200 to 2000 feet per minute. The static pressure in the hood is a useful indicator of the total gas flow rate. A drop in the hood static pressure from previously recorded levels means that the gas flow has decreased.

The relationship between gas flow rate and hood static pressure is indicated below. The equation simply illustrates that the gas flow rate is proportional to the square root of the hood static pressure. If the hood static pressure decreases by a factor of 2, the gas flow rate has decreased by approximately a factor of 1.41.

$$G = C\sqrt{Sph}$$

Where: G = Gas flow rate, ACFM

C = Proportionality constant, ACFM/(Inches W.C.)

Sph = Hood static pressure

INSPECTION OF CARBON BED ADSORBERS  
Level 4 Inspection Procedures

6.4.4 Level 4 Inspection Procedures

The Level 4 inspection includes many inspection steps performed during Level 2 and Level 3 inspections. These are described in earlier sections. The unique inspection steps of Level 4 inspections are described below.

Evaluate locations for measurement ports.

Many existing carbon bed adsorbers do not have safe and convenient ports that can be used for volatile organic compound concentration, static pressure, and gas temperature measurements. One purpose of the Level 4 inspection is to select (with the assistance of plant personnel) locations for ports to be installed at a later date to facilitate Level 3 inspections.

Evaluate potential safety problems.

Agency management personnel and/or senior inspectors should identify any potential safety problems involved in standard Level 2 or Level 3 inspections at this site. To the extent possible, the system owner/operators should eliminate these hazards. For those hazards that can not be eliminated, agency personnel should prepare notes on how future inspections should be limited and should prepare a list of the necessary personnel safety equipment. A partial list of common health and safety hazards includes the following.

- ° Inhalation hazards due to low stack discharge points
- ° Fugitive emissions from process equipment system
- ° Inhalation hazards from adjacent stacks and vents
- ° Access to system components only available by means of weak roofs or catwalks

## INSPECTION OF CARBON BED ADSORBERS

### Level 4 Inspection Procedures

#### Prepare a system flowchart.

A relatively simple flowchart is very helpful in conducting a complete and effective Level 2 or Level 3 inspection. This should be prepared by agency management personnel or senior inspectors during a Level 4 inspection. It should consist of a simple block diagram that includes the following elements.

- ° Source(s) of emissions controlled by a single carbon bed adsorber
- ° Location(s) of any fans used for gas movement through the system (used to evaluate inhalation problems due to positive static pressures)
- ° Locations of any main stacks and bypass stacks
- ° Location of any prefilters for particulate removal
- ° Location of carbon bed adsorbers
- ° Locations of major instruments (VOC concentration, static pressure gauges, thermocouples)

#### Evaluate potential safety problems in the process area.

The agency management personnel and/or senior inspectors should evaluate potential safety problems in the areas that may be visited by agency inspectors during Level 2 and/or Level 3 inspections. They should prepare a list of the activities that should not be performed and locations to which an inspector should not go as part of these inspections. The purpose of this review is to minimize inspector risk and to minimize the liability concerns of plant personnel.

# Control by Condensation

# Chapter 6

## Condensation

### Introduction

Condensation is the process of reducing a gas or vapor to a liquid. Any gas can be reduced to a liquid by lowering its temperature and/or increasing its pressure. The most common approach is to reduce the temperature of the gas stream, since increasing the pressure of a gas is very costly (EPA, 1973).

Condensers are simple, relatively inexpensive devices that normally use water or air to cool and condense a vapor stream. Since these devices are usually not capable of reaching low temperatures (below 80°F), high removal efficiencies of most gaseous pollutants are not obtained unless the vapors will condense at high temperatures. Condensers are typically used as pretreatment devices. They are used ahead of incinerators, absorbers, or adsorbers to reduce the total gas volume to be treated by more expensive control equipment. Used in this manner, they help reduce the overall cost of the control system.

### Condensation Principles

When a hot vapor stream contacts a cooler surface, heat is transferred from the hot gases to the cooler surface. As the temperature of the vapor stream is cooled, the average kinetic energy of the gas molecules is reduced. Also, the volume that these vapors occupy is reduced. Ultimately the gas molecules are slowed down and crowded together so closely that the attractive forces (van de Waals' forces) between the molecules cause them to condense to a liquid.

The two conditions which aid condensation are: low temperatures so that the kinetic energy of the gas molecules are low; and high pressures so that the molecules are brought close together. The actual conditions at which a particular gas molecule will condense depends on its physical and chemical properties.

Condensation occurs when the partial pressure of the pollutant in the gas stream equals its vapor pressure as a pure substance at operating conditions.

Condensation of a gas can occur in three ways: first, at a given temperature, the system pressure is increased (compressing the gas volume) until the partial pressure of the gas equals its vapor pressure; second, at a fixed pressure, the gas is cooled until the partial pressure equals its vapor pressure; or third, by using a combina-

tion of compression and cooling of the gas until its partial pressure equals its vapor pressure. These processes are illustrated in Figure 6-1, a typical vapor pressure diagram for a pure substance.

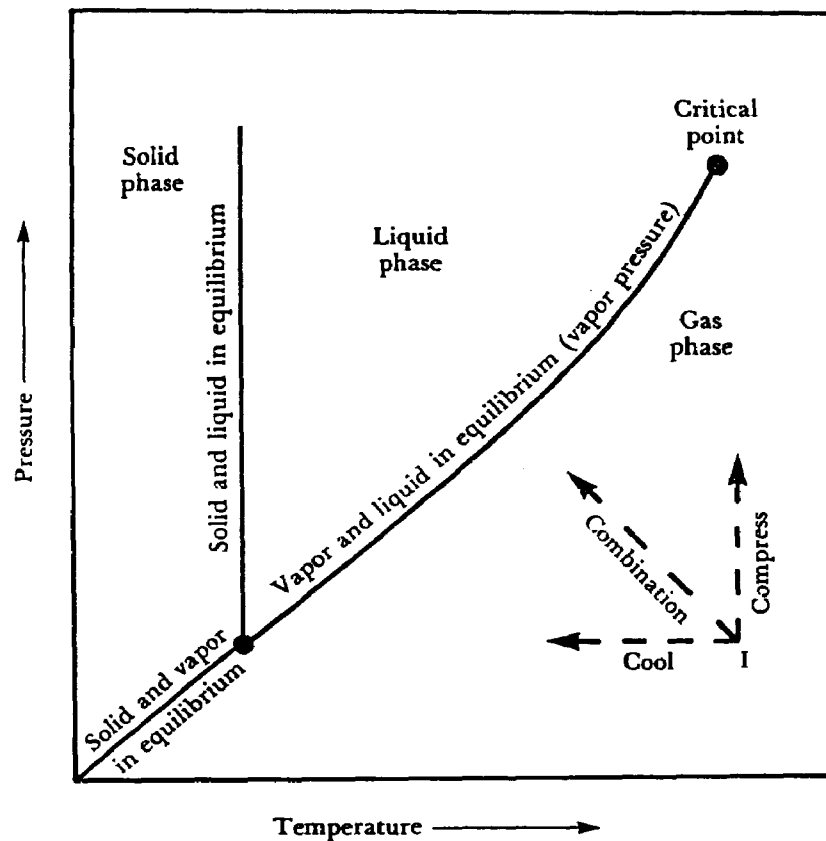


Figure 6-1. Typical vapor pressure curve.

In Figure 6-1, point I is the initial temperature and pressure of a gas. The dotted lines indicate the paths a quantity of gas would follow to reach the vapor pressure curve. Points on the vapor pressure curve are also referred to as *dew points*. The dew point is defined as the condition at which gas is ready to condense into the first drop of liquid.

Also on Figure 6-1, the critical point is plotted. Each substance has a critical temperature and critical pressure. The critical temperature is important in that it is a maximum temperature above which the gas will not condense, no matter how great a pressure is applied. The pressure required to liquify a gas at its critical temperature is the critical pressure.

Once the gas conditions (temperature, pressure, and volume) equal those on the vapor pressure line, liquid begins to condense. From this point on, the gas-liquid mixture follows the vapor pressure line. If the mixture is cooled continuously, the partial pressure of the remaining gas will always equal the vapor pressure. This is

important since even though the contaminated gas is being condensed, it still has a certain partial pressure indicating that uncontrolled vapors are being emitted from the condenser. For most practical applications, the vapor-liquid equilibrium restricts the use of condensers as primary air pollution control devices. Unless very low temperatures or high pressures are attained, condensers are not capable of reducing the pollutant concentration to within acceptable emission limits.

Practically, temperature is the only process variable which governs the effectiveness of a condenser. In industrial applications, increasing the system pressure is very costly and therefore rarely used for condensation. At the operating pressure of the system, the outlet temperature from the condenser determines the maximum removal efficiency. Therefore, condensers cannot be used in the same manner as other gaseous pollutant control devices. For example, condensers cannot be used in series like adsorbers or absorbers to further reduce outlet concentration unless the outlet temperature of the second condenser is lower than the previous one. Increasing gas residence time or decreasing flow rates in the condenser does not add to the theoretical achievable efficiency as these operations do in incinerators, adsorbers, and absorbers.

## Condensers

Condensers fall into two basic categories; *contact* and *surface condensers*. In a contact condenser the coolant and vapor stream are physically mixed. They leave the condenser as a single exhaust stream. In a surface condenser, the coolant is separated from the vapors by tubular heat transfer surfaces. The coolant and condensed vapors leave the device by separate exits. Surface condensers are commonly called *shell-and-tube heat exchangers*. The temperature of the coolant is increased, so these devices also act as heaters.



### ***Direct Contact Condensers***

Contact condensers are simple devices such as *spray towers*, *steam or water jet ejectors*, and *barometric condensers*. These devices bring the coolant, usually water, into direct contact with the vapors as illustrated in Figure 6-2. The liquid stream leaving the condenser contains the coolant plus the condensed vapors. If the vapor is soluble in the coolant then absorption also occurs. Absorption increases the amount of contaminant that can be removed at the given conditions.

(a) spray contact condenser

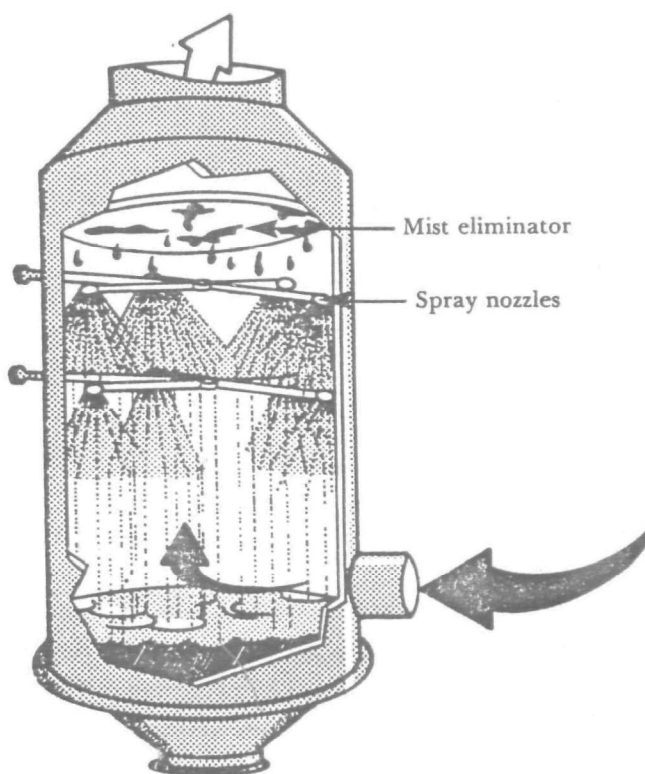
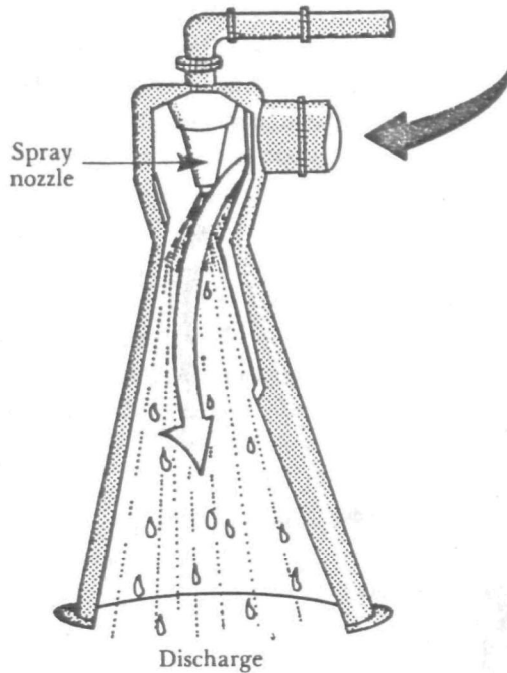
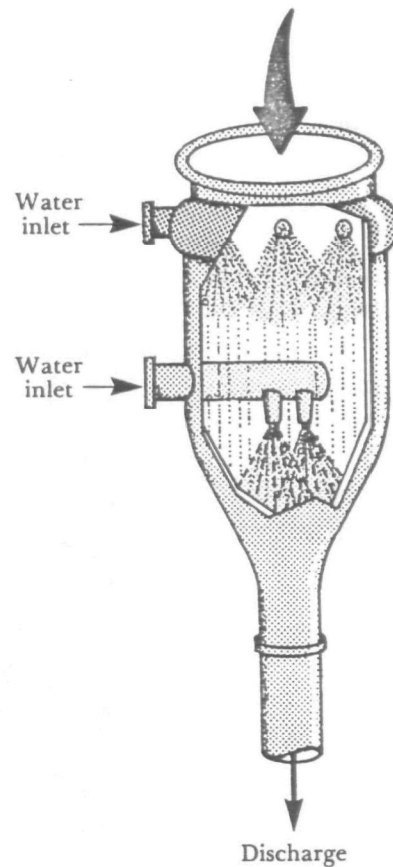


Figure 6-2. Direct contact condensers:  
(a) spray, (b) jet ejector, and (c) barometric.

(b) jet ejector condenser



(c) barometric condenser



Spray tower condensers (Figure 6-2a) are normally the same as the spray absorbers discussed in Chapter 4. The vapors enter the bottom of the tower while coolant is sprayed down over them. Baffles are usually added to ensure adequate contact between coolant and vapors. Ejectors (Figure 6-2b) and barometric condensers (Figure 6-2c) operate in a similar manner. The difference being that they use liquid sprays to move the vapor stream. In both of these devices the coolant is sprayed into a venturi throat creating a vacuum which moves the vapor stream through the condenser.

## Surface Condensers

Surface condensers are usually in the form of *shell-and-tube heat exchangers* (Figure 6-3). The device consists of a circular or oval cylindrical shell into which the vapor stream flows. Inside the shell are numerous small tubes through which the coolant flows. Vapors contact the cool surface of the tubes, condense, and are collected, while noncondensed vapors are sent for further treatment.

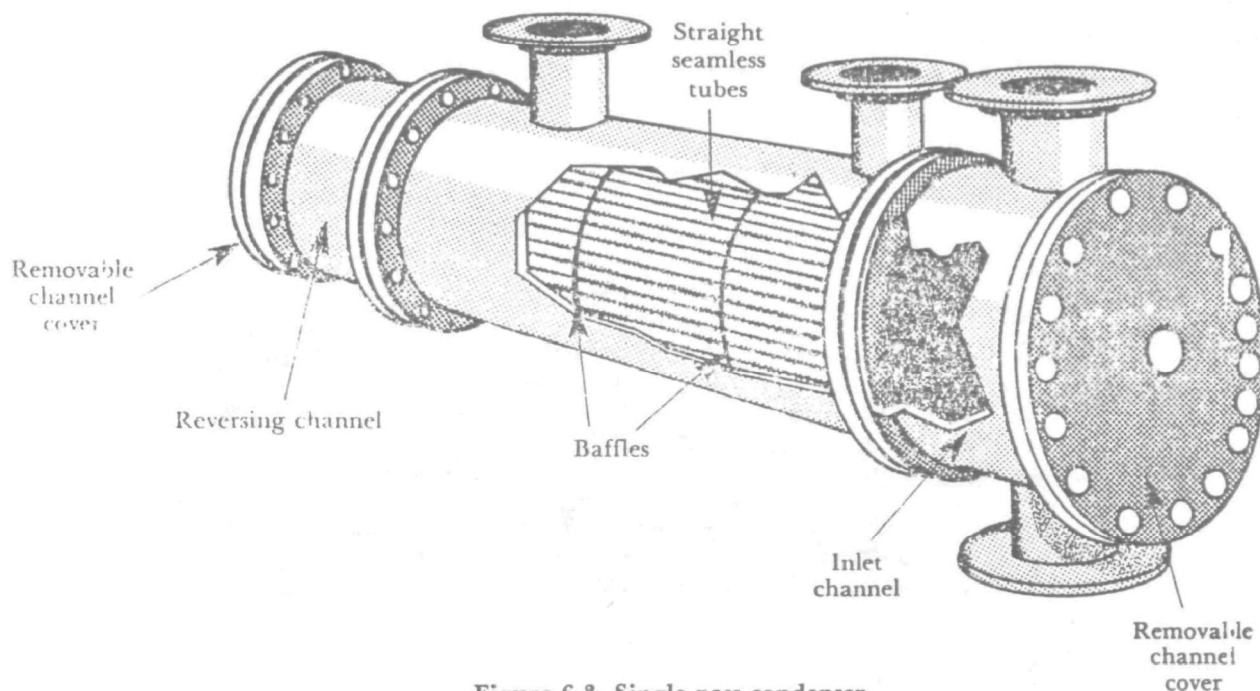


Figure 6-3. Single-pass condenser.

Figure 6-3 is a diagram of a *single-pass heat exchanger*, where the entire stream of coolant flows through all the parallel tubes. The cooling liquid enters and makes **one pass** through the tubes or **tube side** of the exchanger. The uncondensed vapor stream enters and makes one pass on the **shell side** of the exchanger. The single pass exchanger is limited in that it requires a large number of tubes and low gas velocities through the exchanger to provide adequate heat transfer. By using a *multipass system*, shorter tube lengths, higher gas velocities through the exchanger, and improved heat transfer can be achieved (McCabe, 1967).

Figure 6-4 illustrates two types of multipass heat exchangers, referred to as 1-2 and 2-4 heat exchangers. The first digit refers to the number of passes the vapor makes on the shell side, while the second digit indicates the number of tube side passes. Both of these designs give improved performance over the single-pass exchanger. The 2-4 heat exchanger is capable of higher gas velocities and better heat transfer than the 1-2 heat exchanger. Adding more passes does have disadvantages however. These disadvantages are: the exchanger construction is more complicated; friction losses are increased due to the higher velocities; and exit and entrance losses are multiplied.

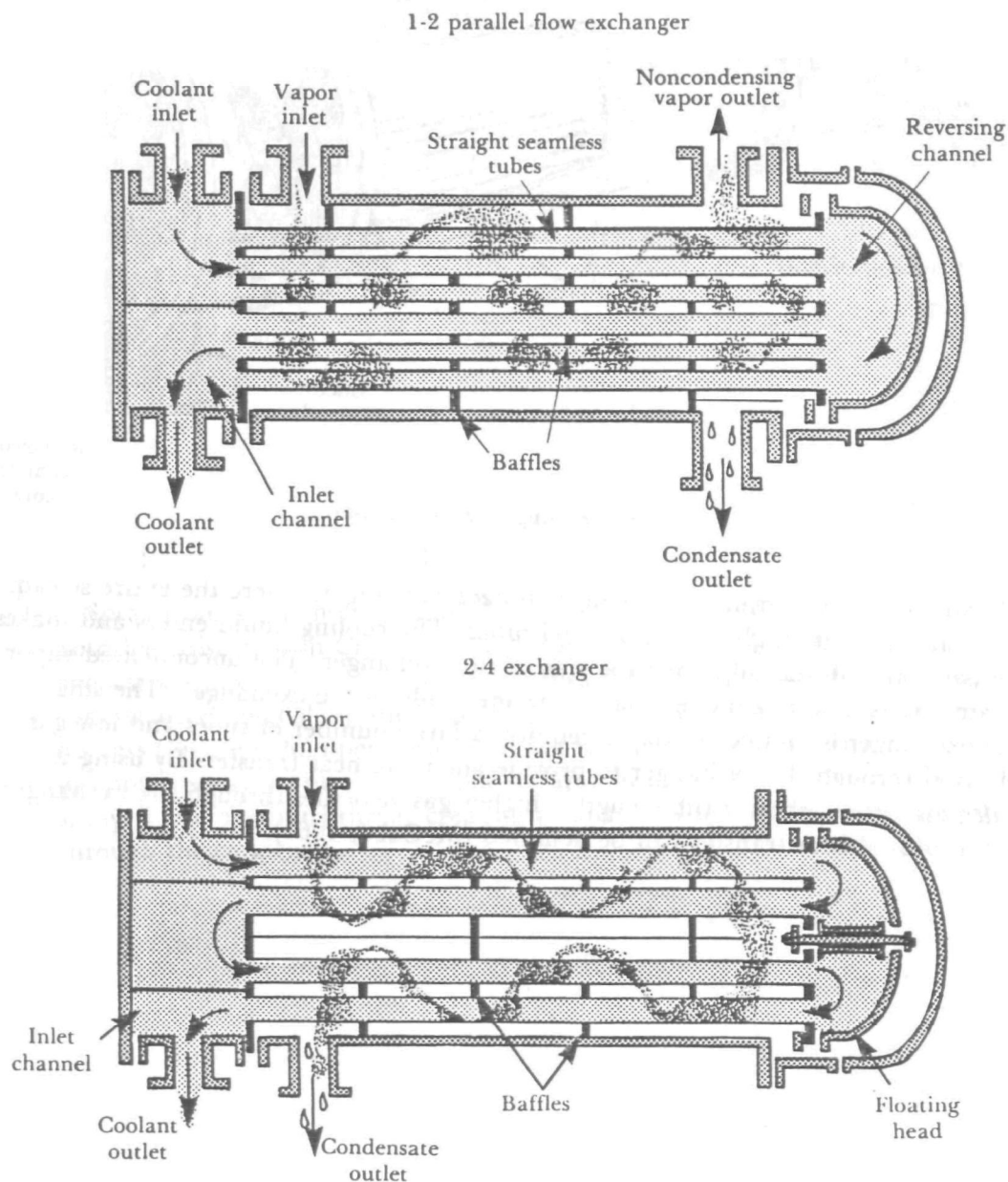


Figure 6-4. Simplified air flow in multipass exchangers.

Condensation applications normally require large temperature differentials between vapor and coolant. These temperature variances can cause the tubes to expand or contract. This expansion stress can eventually cause the tubes to buckle or pull loose from the shell, destroying the condenser. Floating head construction is commonly used to avoid condenser expansion stress damage. In a floating head, one end of the tube bundle is mounted so that it is structurally independent from the shell as shown in Figure 6-4. This allows the tubes to expand and contract within the shell.

Water is generally the coolant used in condensers. However, short supply and expense to treat water make it an uneconomical choice in some cases. In these cases, air-coolers are used. The specific heat of air is only about 0.25 Btu/lb•°F, approximately one-fourth that of water. Therefore, air condensers must be very large compared to water condensers.

To conserve space and reduce the cost of equipment in these cases, heat exchangers with *extended surfaces* can be used. In these devices, the outside area of the tube is multiplied or extended by adding *fins* or *disks*. Figure 6-5 illustrates two types of finned tubes. In extended surface condensers, the vapor is condensed inside the tube while air flows around the outside contacting the extended surfaces.

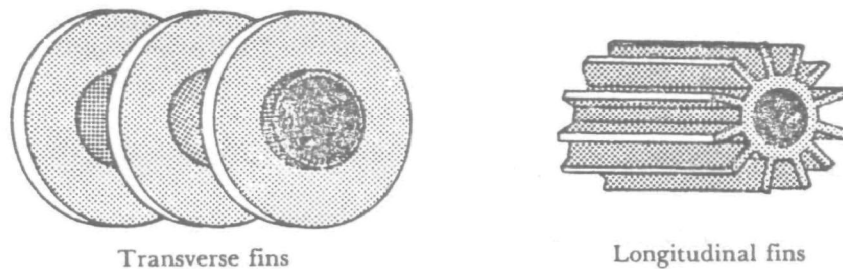


Figure 6-5. Extended surface tubes.

### ***Comparison of Contact and Surface Condensers***

Since in contact condensers coolant is merely sprayed on the vapors, these systems are simpler in design, less expensive, and more flexible in application than surface condensers. However, contact condensers require more coolant, and due to direct mixing, produce 10 to 20 times the amount of wastewater (condensate) than surface condensers. Since the wastewater from a contact condenser is contaminated with vapors, it cannot be reused posing a water disposal problem. If the condensed vapors have a recovery value, surface condensers are usually used since the condensate can be recovered directly.

## Condensers

Condensers remove vaporous contaminants from a gas stream by cooling it and converting the vapor into a liquid. In some instances, control of volatile contaminants can be satisfactorily achieved entirely by condensation. However, most applications require additional control methods. In such cases, the use of a condenser reduces the concentration load on downstream control equipment. The two most common types of condensers are:

- a. **Contact or barometric condensers**, where a direct spray contacts the vapors to cause condensation (see Figure 13-15). The liquid leaving the condenser contains the coolant plus the condensed vapors.
- b. **Surface condensers**, such as the shell-and-tube heat exchanger (see Figure 13-16). This device consists of a shell into which the vapor stream flows. Inside the shell are numerous small tubes through which the coolant flows. Vapors contact the cool surface of the tubes, condense and are collected without contamination by the coolant.

### Basic Level 2 Inspection Points

- a. **Physical condition:** indications of corrosion or physical damage.
- \* b. **Outlet temperature:** increased temperature may mean reduced condensation efficiency.
- c. **Inlet liquid pressure:** provides an indirect indication of the liquid flow rate and nozzle condition; increases may indicate nozzle pluggage and lower coolant flow rates; decreases may indicate nozzle erosion and higher flow rates (contact-type only).
- d. **Liquid turbidity and settling rate:** high settling rate indicates coarse solids that could plug nozzles (contact-type only).
- e. **Droplet re-entrainment:** droplet rainout or a mud-lip on the stack indicates a significant demister problem.

# Surface Coating Fundamentals

## SECTION 1

### OVERVIEW

#### 1.0 Scope and Objective

This manual was developed to assist compliance officers with determining the compliance status of surface coating and graphic arts operations with volatile organic carbon (VOC) regulations. It is designed as an advanced level manual where the user has already had some exposure to pertinent regulation terminology and process configurations. The material presented will focus on (1) determinations of coating formulations, (2) compliance determination calculations, and (3) process and add-on control equipment evaluations. The information presented here is in a condensed form; more detail on these industries can be found through other sources (4,5,6). A complete listing of reference materials used to develop this manual is given in Section 6.

Examples and case studies are presented for typical industries. This manual should assist inspectors to thoroughly evaluate a source and to assess its compliance with Federal, State, and Local regulations.

#### 1.1 Terminology

Many of the terms used to describe materials, processes, emissions and controls in the surface coating and graphic arts facilities have been defined in the EPA glossary document entitled, Glossary for Air Pollution Control of Industrial Coating Operations, Second Edition (With Graphical Aids for Rapid Estimation of Acceptable Compliance Alternatives), EPA-450/3-83-013R, December 1983. This glossary can be found in Appendix A and defines the most common terms, both technical and regulatory, needed to be effective in carrying out VOC regulatory compliance activities for surface coating and graphic arts operations.

#### 1.2 Surface Coating Operations - Overview

Surface coating operations involve the application of paint, primer, varnish, and a variety of other coatings to surfaces for both protection and decoration. Application methods include brushing, rolling, spraying, dipping and flow coating. Coatings are air or heat dried to drive off volatile solvents and produce a hard surface film. Industrial surface coating operations generally are categorized by the type of product coated because specific coatings, application and control methods, etc., will vary somewhat with product category. The categories addressed here are as follows:

- |                       |                            |
|-----------------------|----------------------------|
| * Can coating         | * Flat wood interior panel |
| * Metal coil          | * Paper coating            |
| * Magnet wire         | * Fabric coating           |
| * Large appliance     | * Vinyl and urethane       |
| * Metal furniture     | * Auto/Light-duty truck    |
| * Miscellaneous metal | * Large aircraft           |

A more detailed description is given for each category in Section 2.



### 1.2.1 Coating Operations

There are both "toll" (independent) and "captive" surface coating operations. Toll operations fill orders to various manufacturer specifications, and thus change coating and solvent conditions frequently. Captive companies fabricate and coat products within a single facility, and might operate continuously with the same coatings.

Although the details of coating operations vary among companies and for the different product categories, the typical components of a coating line can be described as follows. Fabricated parts are first cleaned to remove grease, dust and other contamination. The most common coating application methods are spray, dip and flow coating, usually in some type of booth or enclosure to contain overspray and evaporated solvents. Parts are either air or oven dried. Parts may be conveyed to a "flashoff zone" before entering a bake oven so that some of the solvent can evaporate before the 120 to 230°C (250 to 450°F) oven heat is applied. Ovens are either single or multipass.

Depending on product requirements and the material being coated, a surface may have one or more layers of coating applied. The first coat (primer) is applied to provide corrosion protection, cover surface imperfections and/or assure adhesion of subsequent coats. The intermediate coats usually provide the required color, texture or print, and a clear protective topcoat is often added.

### 1.2.2 Coating Formulations

Coatings consist of finely divided solid materials (pigments and binders) dispersed in a liquid medium (the volatile portion). The volatiles generally consist of a mixture of organic solvents, and may also contain water. The organic solvent mixture may contain both regulated (VOC) and exempt solvents, but the great majority of solvents used are considered VOC's. Conventional (solvent borne) coatings contain at least 30 percent by volume of solvents to permit easy handling and application, but can contain up to 70 to 85 volume percent solvents. Typical paint solvents are acetone, methyl ethyl ketone, cellosolves, toluene, xylene and mineral spirits. Coatings with 30 volume percent or less of solvent are referred to as low solvent, or high solids, coatings (solids contents are greater than 70 volume percent).

Waterborne coatings, whose use is continually increasing, are of several types: water emulsions, water soluble and colloidal dispersion, and electrocoat. Common ratios of water to solvent organics in emulsion and dispersion coatings are 80/20 and 70/30.

Two-part catalyzed coatings, powder coatings, hot melts, and radiation cured (electromagnetic and electron beam) coatings contain essentially no VOC, although some monomers and other lower molecular weight organics may volatilize during curing (cure volatiles).

### 1.2.3 Application Methods

Spray methods may consist of conventional air spray, airless, air-assisted airless, or high volume-low pressure (HVLP) spraying. Electrostatic assist is sometimes added to improve the transfer efficiency<sup>1</sup>. Air spray is versatile and can produce a very high quality finish, but consumes a large amount (8 to 30 scfm) of high pressure air and suffers from low transfer efficiency. Airless spray uses hydrostatic pressure (about 2,000 psi) to atomize the

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1. Ratio of solids applied to solids used. This concept is discussed in more detail in Section 3.

coating into slightly larger particles. Air-assisted airless technology combines these two techniques, but can use lower pressures and air and fluid rates, and is more manageable for an operator.

In hot airless spray, warm pressurized paint is forced through an atomizing nozzle. Volumetric flow is less, and so overspray is reduced. Also, less solvent is required to maintain viscosity, thus reducing VOC emissions. Electrostatic spray, in which charged paint particles are attracted to an oppositely charged surface, is most efficient for low viscosity paints. Spray guns, spinning discs or bell shaped atomizers can be used to atomize the paint.

Roller coating is used to apply coatings and inks to flat surfaces. If the cylindrical rollers move in the same direction as the surface to be coated, the system is called a direct roll coater. If they rotate in the opposite direction, the system is a reverse roll coater. Coatings can be applied to any flat surface efficiently and uniformly, and at high speeds. Printing and decorative graining are applied with direct rollers. Reverse rollers are used to apply fillers to porous or imperfect substrates, including papers and fabrics, to give a smooth, uniform surface.

Brush coating is best suited for application of slow-drying coatings to uneven surfaces, such as a rough fiber panels. Brush coating machines have been largely replaced by air-knife coaters.

Knife coating is relatively inexpensive, but it is not appropriate for coating unstable materials, such as some knit goods, or when a high degree of accuracy in the coating thickness is required.

Dip coating requires that the object be immersed in a bath of paint. Dipping is effective for coating irregularly shaped or bulky items, and for priming. All surfaces are covered, but coating thickness varies, edge blistering can occur, and a good appearance is not always achieved.

In flow coating, materials to be coated are conveyed through a flow, or stream, of paint. Paint flow is directed, without atomization, toward the surface through multiple nozzles, then is caught in a trough and recycled. For flat surfaces, close control of film thickness can be maintained by passing the surface through a constantly flowing curtain of paint at a controlled rate.

### **1.3 Graphic Arts Operations - Overview**

The term "graphic arts" has come to encompass the various sectors of the printing and publishing industry, including the production of books, newspapers, magazines and other reading materials, as well as packaging and many types of specialty items. The four basic printing processes are web offset lithography, web letterpress, gravure printing and flexography. These four high volume processes are similar in that the image to be printed is placed on a cylinder that rotates in contact with a paper "web", or continuous roll. Gravure printing performed this way is termed "rotogravure." Other, lower production processes using more manual (such as sheet fed) techniques often are used by smaller firms. The discussion here is limited to the three graphic arts source categories covered by the Control Technology Guidelines (5,6):

1. Publication rotogravure
2. Packaging rotogravure
3. Flexography

Printing can be performed on coated or uncoated paper, and also on other substrates such as metals, plastics and fabrics. Printing operations involve the transfer of an image, using a transfer device that maintains a fixed position with respect to the substrate as contact is made. Coating operations, on the other hand, strive for uniform total coverage with the coating material. From an emissions standpoint, however, printing and coating are very similar.

Printing inks vary widely in composition, but all of them consist of three major components. Pigments, which provide the ink's color, are composed of finely divided organic and inorganic materials. Binders, which lock the pigments to the substrate, are composed of organic resins and polymers or oils and resins. Solvents dissolve and disperse the solids, and usually consist of volatile organic liquids. As in coatings, the volatile portion evaporates and leaves the visible solids behind in the form of the desired image.

Both rotogravure and flexographic printing use very fluid inks of about 75 volume percent organic solvent. Rotogravure solvents include alcohols, aliphatic naphthas, aromatic hydrocarbons, esters, glycol ethers, ketones and nitroparaffins. Flexography solvents include glycols, ketones and ethers. Water base inks generally are used only in certain packaging or specialty applications. A more detailed discussion of the individual printing categories is presented in Section 2 of this manual.

## **1.4 Control Techniques - Overview**

Most of these regulations of the surface coating and graphic arts industries have been aimed at limiting the amount of VOC that is released in order to limit the formation of ozone in the ambient air. It usually is assumed that all of the VOC content of a coating evaporates after application to become potential emissions. Control strategies at reducing VOC content are threefold: 1) reformulation to reduce the amount of VOC in the coatings, 2) improved application methods, and the use of add-on controls to remove the VOC before emissions are vented to the atmosphere. All of the evaporated solvent that is not in turn recovered or destroyed in control equipment becomes actual emissions. This section provides an overview of the principal control techniques used to limit VOC emissions from surface coating facilities.

### **1.4.1 Coating Formulation and Application**

In cases where it is technically feasible, the substitution of exempt solvents (solvents which have been determined to have negligible photoreactivity<sup>2</sup>) for VOC solvents in a coating can be used to reduce emissions. The degree of reduction is equal to the percentage of the VOC solvent that is replaced. Exempt solvents appear to have limited application in the surface coating and printing industries, although 1,1,1-trichloroethane has been used as a principal solvent in various applications ranging from specialty coatings for aerospace parts to lacquers for wood furniture and two-component urethanes for coating plastics.

High solids coatings generally contain at least 70 weight percent of solids, and so the solvent fraction, and VOC emissions, are dramatically reduced. Since the viscosity of such coatings is higher than that of conventional coatings, handling problems with high solids

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2. Negligible photoreactive compounds include methane, ethane, 1,1,1-trichloroethane (Methyl chloroform), Methylene chloride, Trichlorotrifluoroethane (CFC-113), Trichlorofluoromethane (CFC 11), Dichlorodifluoromethane (CFC-12), Chlorodifluoromethane (CFC-22), Trifluoromethane (CFC-23), Dichlorotetrafluoroethane (CFC-114), and Chloropentafluoroethane (CFC-115).

principal solvent in various applications ranging from specialty coatings for aerospace parts to lacquers for wood furniture and two-component urethanes for coating plastics.

High solids coatings generally contain at least 70 weight percent of solids, and so the solvent fraction, and VOC emissions, are dramatically reduced. Since the viscosity of such coatings is higher than that of conventional coatings, handling problems with high solids coatings have been common. The resin binder component and solvents must be carefully selected or developed specifically for a given application to create acceptable handling and finish quality. A solvent-based coating containing 30 volume percent solids that was switched to 75 volume percent solids would have a reduction in its VOC emission potential of 87 percent.

Waterborne coatings enlist water as the principal solids carrier in order to reduce the VOC content. Most such coatings contain some organic solvent to provide desired properties such as solubility, evaporation rate and film coalescence. Applications for these coatings are growing, particularly in the aircraft, appliance, metal coil and wood panel categories. A 75/25 ratio of water to organic solvent is common. Waterborne inks have not received wide acceptance in the printing industry.

Powder coatings represent perhaps the greatest potential for emissions reduction of any type of coating reformulation. A powder coating is a collection of resin, pigments and various additives that has been thoroughly mixed and broken down into a fine powder. These coatings usually are applied by electrostatic spray or fluidized bed dipping (electrocoating). The application of heat fuses the powder coating into a hard film. Only very small amounts of volatile organics are emitted during curing, and thus the emission reduction achievable by switching to a powder coating can approach 100 percent. Powder coatings can be used in can coating operations without cemented seams.(4)

A high transfer efficiency helps to limit VOC emissions by reducing the amount of coating that must be used (all of the coating used will emit its total volatile content whether it coats the part or is wasted as overspray). Electrostatic coating is very efficient because paint particles are attracted preferentially to a part maintained at a different electric potential. This method is used widely in conjunction with various types of spraying techniques, including powder application. When electrostatic methods are used in conjunction with dip coating, it is usually termed electrocoating.

#### 1.4.2 Add-on Controls

In addition to changes to the materials in surface coating and printing, various types of control equipment are used to limit VOC emissions from these facilities. In these systems, the generated vapors are delivered to the control device using a system that captures them near the points of origin. The capture system may consist of hoods, partial enclosures and/or total enclosures which are adjacent to, or enclose, the process equipment, and pull vapor-laden air into ducting using one or more fans. The overall control efficiency is a function of the capture efficiency and the efficiency of add-on controls.

There are three basic types of Add-on controls; incinerators, carbon absorbers and refrigeration systems. Incinerators oxidize organic vapors into nonphotoreactive compounds by thermal or catalytic combustion. The catalytic incinerator system utilizes a catalyst, such as platinum or cobalt, to oxidize at a lower temperature (600 to 1,200°F) than is required for thermal incineration (about 1,500°F). High destruction efficiencies (over 95 percent) are possible if adequate combustion temperatures are maintained in the system.

Incinerators generally have been applied in most coating categories where the VOC concentrations were sufficient to support combustion without using excessive amounts of auxiliary fuel. Heat recovery, using combustion heat to pre-heat incoming vapors, is used to reduce auxiliary fuel requirements. Incineration is used to some extent in the graphic arts industry, but solvent recovery is the preferred approach in most applications.

Carbon adsorption systems exploit the high adsorptivity of organics onto activated carbon to collect and recover volatile solvents in exhaust gas streams. Carbon beds are exposed to organic vapors until the beds are nearly saturated, and then the organics are desorbed by steam heat or vacuum and the solvents recovered. Systems contain two or more beds so that one bed can be adsorbing vapors while another is being desorbed, in a continuous adsorption/desorption cycle. Carbon beds are either fixed, moving or fluidized. Solvents and water are collected after desorption and separated by gravity decantation or distillation, or the mixture may be incinerated. These systems are subject to operating problems due to the presence of certain organics in the inlet stream. High boiling point compounds can be difficult to remove from the carbon, reducing the available surface area for adsorption and lowering the control efficiency. Some other organics may be difficult to collect or may have high heats of adsorption, raising the bed temperature excessively.

Carbon-adsorption systems are widely used in several surface coating and printing categories where it is economical to recover solvents or where VOC concentrations are too low to justify incineration. In painting operations, exhaust containing sticky particulate must be filtered before entering the control system. Carbon systems are widely applied in the publication printing categories, and less so in smaller specialty printing operations (6). A more detailed discussion of control techniques and equipment is presented in Section 3.

## **1.5 Inspection Procedures**

Finally, an on-site inspection is often required in order to determine and verify compliance. The primary activity of an on-site inspection is the compilation and verification of coating/ink composition data and then the calculation of emissions. Section 5 contains a description of the steps that are necessary to conduct a thorough on-site inspection.

Although the surface coating and graphic arts industry is quite diverse there are areas and operations that are common between them. Determining compliance through calculation can also be complex. Compliance Calculation examples are given in Section 4. It is hoped that the material contained in this manual will allow the compliance officer to work within this complexity and provide him/her with the necessary understanding to conduct a compliance determination.

## SECTION 2

### INDIVIDUAL PROCESS DESCRIPTIONS

#### 2.0 Summary

In this section a brief description of each surface coating and graphic arts process is given. Process flow sheets are also given. These descriptions have been developed from the EPA Guideline Series for the surface coating and graphic arts industries. (4,5,6)

#### 2.1 Can Coating

Cans may be made from a rectangular sheet (body blank) and two circular ends (three piece cans), or they can be drawn and wall ironed from a shallow cup to which an end is attached after the can is filled (two piece cans). There are major differences in coating practices, depending on the type of can and the product packaged in it. Figure 2.1 depicts a three piece can sheet printing operation.

There are both "toll" and "captive" can coating operations. The former fill orders to customer specifications, and the latter coat the metal for products fabricated within one facility. Some can coating operations do both toll and captive work, and some plants fabricate just can ends.

Three piece can manufacturing involves sheet coating and can fabricating. Sheet coating includes base coating and printing or lithographing, followed by curing at temperatures of up to 220°C (425°F). When the sheets have been formed into cylinders, the seam is sprayed, usually with a lacquer, to protect the exposed metal. If they are to contain an edible product, the interiors are spray coated, and the cans are baked at up to 220°C.

Two piece cans are used largely by beer and other beverage industries. The exteriors may be reverse roll coated in white and cured at 170 to 200°C (325 to 400°F). Several colors of ink are then transferred (sometimes by lithographic printing) to the cans as they rotate on a mandrel. A protective varnish may be roll coated over the inks. The coating is then cured in a single or multipass oven at temperatures of 180 to 200°C (350 to 400°F). The cans are spray coated on the interior and spray and/or roll coated on the exterior of the bottom end. A final baking at 110 to 200°C (225 to 400°F) completes the process.

#### 2.2 Metal Coil

Metal coil surface coating (coil coating) is the linear process by which protective or decorative organic coatings are applied to flat metal sheet or strip packaged in rolls or coils. Although the physical configurations of coil coating lines differ from one installation to another, the operations generally follow a set pattern. Metal strip is uncoiled at the entry to a coating line and is passed through a wet sections, where the metal is thoroughly cleaned and given a chemical treatment to inhibit rust and to promote coating adhesion to the metal surface. In some installations, the wet section contains an electrogalvanizing operation. Then the metal strip is dried and sent through a coating application station, where rollers coat one or both sides of the metal strip. The strip then passes through an oven where the coatings are dried and cured. As the strip exits the oven, it is cooled by a water spray in a quench chamber and

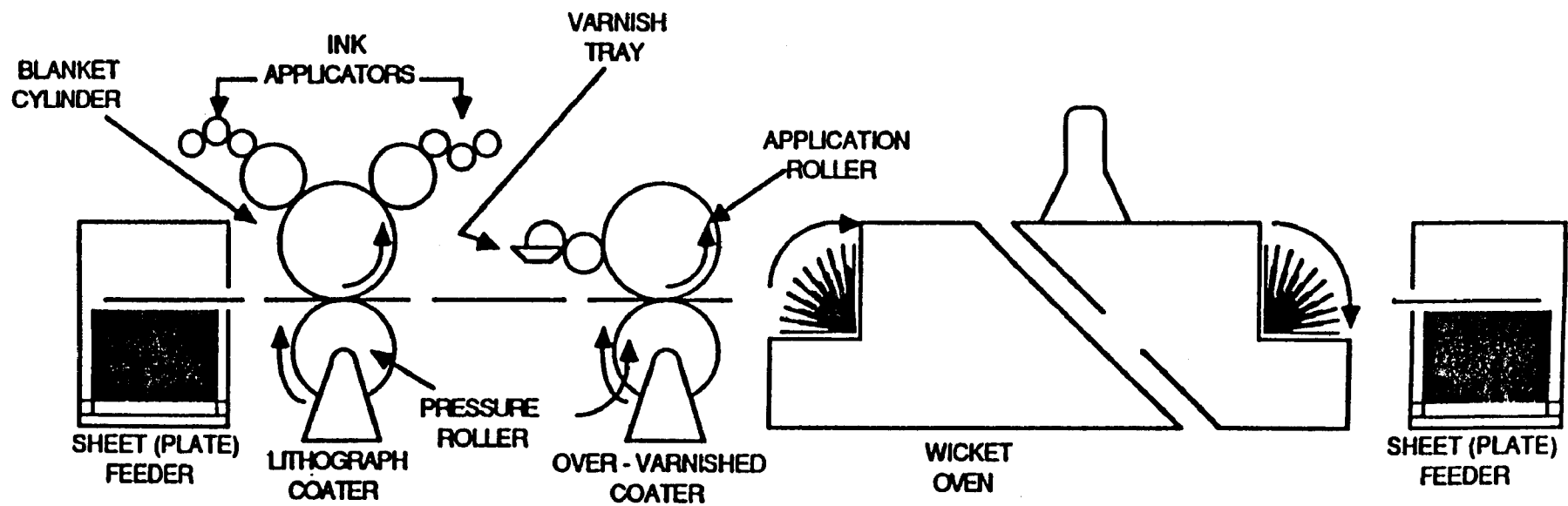


Figure 2.1 Three piece can sheet coating operation

again dried. If the line is a tandem line, there is first the application of a prime coat, followed by another of top or finish coat. The second coat is also dried and cured in an oven, and the strip is again cooled and dried before being rewound into a coil and packaged for shipment or further processing. Most coil coating lines have accumulators at the entry and exit that permit continuous metal strip movement through the coating process while a new coil is mounted at the entry or a full coil removed at the exit. Figure 2.2 is a flow diagram of a coil coating line.

Coil coating lines process metal in widths ranging from a few centimeters to 183 centimeters (72 inches), and in thickness of from 0.018 to 0.229 centimeter (0.007 to 0.090 inch). The speed of the metal strip through the line is as high as 3.6 meters per second (700 feet per minute) on some of the newer lines.

A wide variety of coating formulations is used by the coil coating industry. The more prevalent coating types include polyesters, acrylics, polyfluorocarbons, alkyds, vinyls and plastisols. About 85 percent of the coatings used are organic solvent base and have solvent contents ranging from near 0 to 80 volume percent, with the prevalent range being 40 to 60 volume percent. Most of the remaining 15 percent of coatings are waterborne, but they contain organic solvent in the range of 2 to 15 volume percent. High solids coatings, in the form of plastisols, organosols and powders, also are used to some extent by the industry, but the hardware is different for powder applications.

The solvents most often used in the coil coating industry include xylene, toluene, methyl ethyl ketone, Cellosolve Acetate (TM), butanol, diacetone alcohol, Cellosolve (TM), Butyl Cellosolve (TM), Solvesso 100 and 150 (TM), isophorone, butyl carbinol, mineral spirits, ethanol, nitropropane, tetrahydrofuran, Panasolve (TM), methyl isobutyl ketone, Hisol 100 (TM), Tenneco T-125 (TM), isopropanol, and diisoamyl ketone.

There are both toll and captive coil coating operations. Toll coaters normally use mostly organic-solvent base coatings. Major markets for toll coating operations include the transportation and construction industries, and appliance, furniture and container manufacturers. The captive coater is normally one operation in a manufacturing process. Many steel and aluminum companies have their own coil coating operations, where the metal they produce is coated and then formed into end products. Captive coaters are much more likely to use water-base coatings because the metal coated is often used for only a few end products. Building products such as aluminum siding are one of the more important uses for waterborne metal coatings.



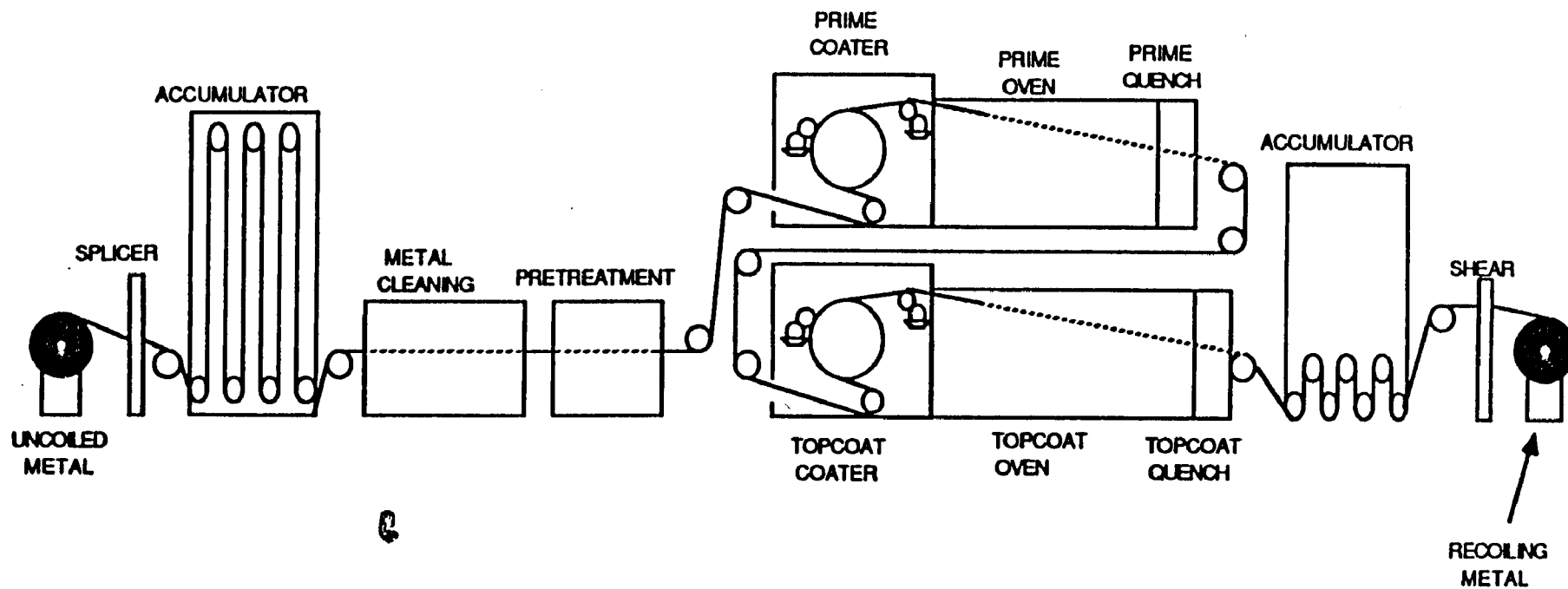


Figure 2.2 Metal coil coating line

## 2.4 Large Appliance

Large appliance surface coating is the application of protective or decorative organic coatings to preformed large appliance parts. For this discussion, large appliances are defined as any metal range, oven, microwave oven, refrigerator, freezer, washing machine, dryer, dishwasher, water heater or trash compactor.

Regardless of the appliance, similar manufacturing operations are involved. Coiled or sheet metal is cut and stamped into the proper shapes, and the major parts welded together. The welded parts are cleaned with organic degreasers or a caustic detergent (or both) to remove grease and mill scale accumulated during handling, and the parts are then rinsed in one or more water rinses. This is often followed by a process to improve the grain of the metal before treatment in a phosphate bath. Iron or zinc phosphate is commonly used to deposit a microscopic matrix of crystalline phosphate on the surface of the metal. This process provides corrosion resistance and increases the surface area of the part, thereby allowing superior coating adhesion. Often the highly reactive metal is protected with a rust inhibitor to prevent rusting prior to painting.

Two separate coatings have traditionally been applied to these prepared appliance parts; a protective prime coating that also covers surface imperfections and contributes to total coating thickness, and a final, decorative top coat. Single coat systems, where only a prime coat or only a top coat is applied, are becoming more common. For parts not exposed to customer view, a prime coat alone may suffice. For exposed parts, a protective coating may be formulated and applied so as to act as the top coat. There are many different application techniques in the large appliance industry, including manual, automatic and electrostatic spray operations, and several dipping methods. Selection of a particular method depends largely upon the geometry and use of the part, the production rate, and the type of coating being used. Typical application of these coating methods is shown in Figure 2.4.

A wide variety of coating formulations is used by the large appliance industry. The prevalent coating types include epoxies, epoxy/acrylics, acrylics and polyester enamels. Liquid coatings may use either an organic solvent or water as the main carrier for the paint solids.

Waterborne coatings are of three major classes, water solution, water emulsions and water dispersions. All of the waterborne coatings, however, contain a small amount (up to 20 volume percent) of organic solvent that acts as a stabilizing, dispersion or emulsifying agent. Waterborne systems offer some advantages over organic solvent systems. They do not exhibit as great an increase in viscosity with increasing molecular weight of solids, they are nonflammable, and they have limited toxicity. However, because of the relatively slow evaporation rate of water, it is difficult to achieve a smooth finish with waterborne coatings. A bumpy "orange peel" surface often results. For this reason, their main use in the large appliance industry is as prime coats.

While conventional organic solventborne coatings also are used for prime coats, they predominate as top coats. This is due in large part to the controllability of the finish and the amenability of these materials to application by electrostatic spray techniques. The most common organic solvents are ketones, esters, ethers, aromatics and alcohols. To obtain or maintain certain application characteristics, solvents often are added to coatings at the plant. The use of powder coatings for top coats is gaining acceptance in the industry. These coatings, which are applied as a dry powder and then fused into a continuous coating film through the use of heat, yield negligible emissions.

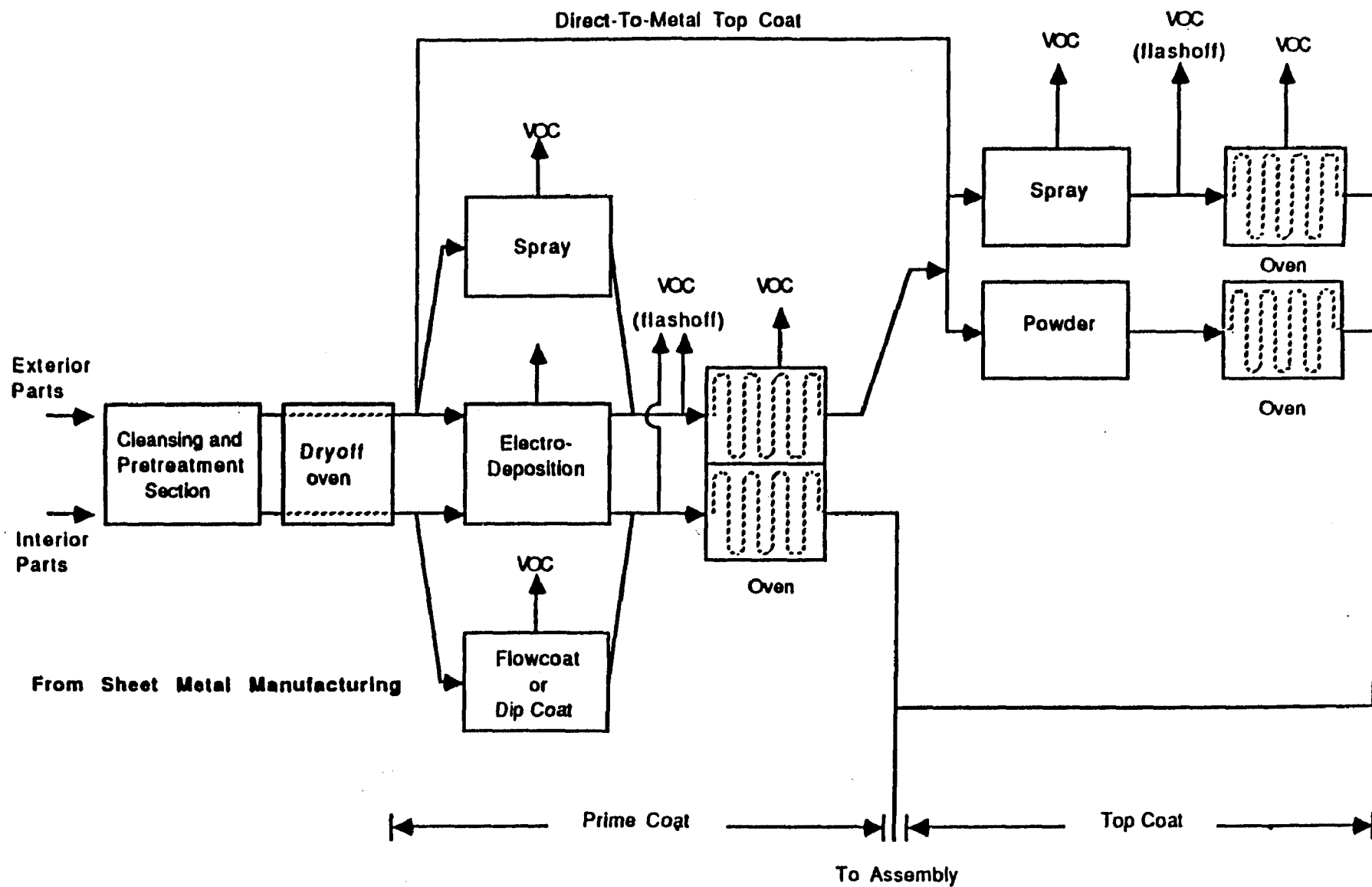


Figure 2.4 Typical large appliance coating methods.

## 2.8 Paper Coating

Paper is coated for various decorative and functional purposes with waterborne, organic solventborne, or solvent free extruded materials. Paper coating differs from printing in that coating involves the application of a uniform layer of coating material across the paper, whereas printing involves the transfer of an illustration, design or script in a contrasting color on the paper.

Waterborne coatings improve printability and gloss but cannot compete with organic solventborne coatings in resistance to weather, scuff and chemicals. Solventborne coatings, as an added advantage, permit a wide range of surface textures. Most solvent borne coating is done by paper converting companies that buy paper from mills and apply coatings to produce a final product. Among the many products that are coated with solvent borne materials are adhesive tapes and labels, decorated paper, book covers, zinc oxide coated office copier paper, carbon paper, typewriter ribbons and photographic film.

Organic solvent formulations generally used are made up of film forming materials, plasticizers, pigments and solvents. The main classes of film formers used in paper coating are cellulose derivatives (usually nitrocellulose) and vinyl resins (usually the copolymer of vinyl chloride and vinyl acetate). Three common plasticizers are dioctyl phthalate, tricresyl phosphate and castor oil. The major solvents used are toluene, xylene, methyl ethyl ketone, isopropyl alcohol, methanol, acetone and ethanol. Although a single solvent is frequently used, a mixture is often necessary to obtain the optimum drying rate, flexibility, toughness and abrasion resistance.

A variety of low solvent coatings, with negligible emissions, has been developed for some uses to form organic resin films equal to those of conventional solventborne coatings. They can be applied up to 1/8-inch thick (usually by reverse roller coating) to products like artificial leather goods, book covers and carbon paper. Smooth hot melt finishes can be applied over rough textured paper by heated gravure or roll coaters at temperatures from 65 to 230°C (150 to 450°F).

Plastic extrusion coating is a type of hot-melt coating in which a molten thermoplastic sheet (usually low or medium density polyethylene) is extruded from a slotted die at temperature up to 315°C (600°F). The substrate and the molten plastic coat are united by pressure between a rubber roll and a chill roll which solidifies the plastic. Many products, such as the polyethylene coated milk carton, are coated with solvent-free extrusion coatings.

Figure 2.8 shows a typical paper coating line that uses organic solventborne formulations. The application device is usually a reverse roller, a knife or a rotogravure printer. Knife coaters can apply solutions of much higher viscosity than roll coaters can, thus emitting less solvent per pound of solids applied. The gravure printer can print patterns or coat a solid sheet of color on a paper web.

Ovens may be divided into from two to five temperature zones. The first zone is usually at about 43°C (110°F), and other zones have progressively higher temperatures to cure the coating after most solvent has evaporated. The typical curing temperature is 120°C (250°F), and ovens are generally limited to 200°C (400°F) to avoid damage to the paper. Natural gas is the fuel most often used in direct fired ovens, but fuel oil is sometimes used. Some of the heavier grades of fuel oil can create problems, because sulfur oxides and particulate may contaminate the paper coating. Distillate fuel oil usually can be used satisfactorily. Steam

produced from burning solvent retrieved from an absorber or vented to an incinerator may also be used to curing ovens.

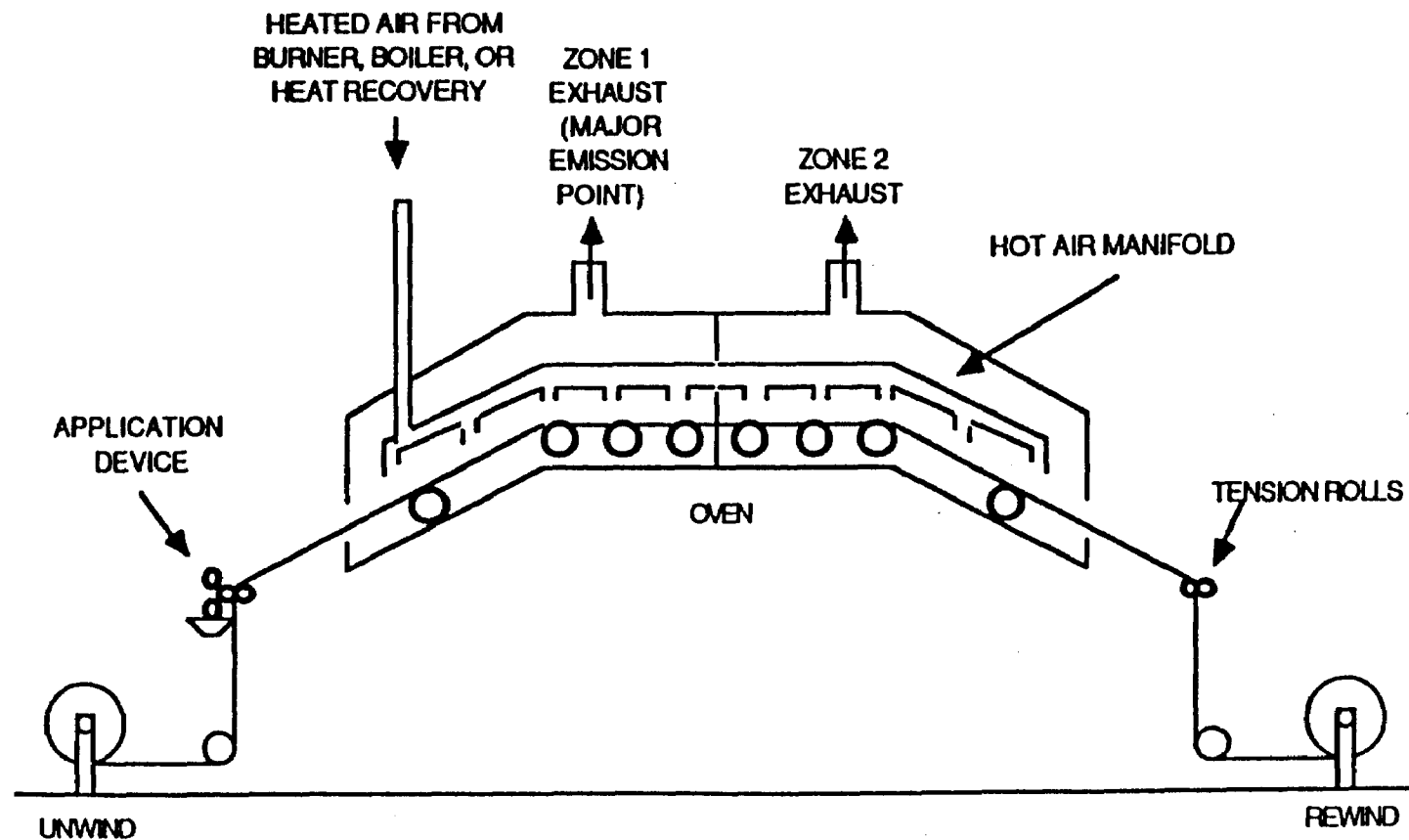
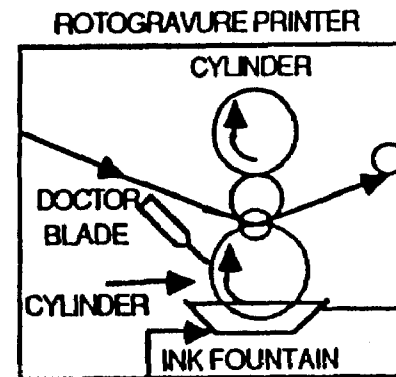
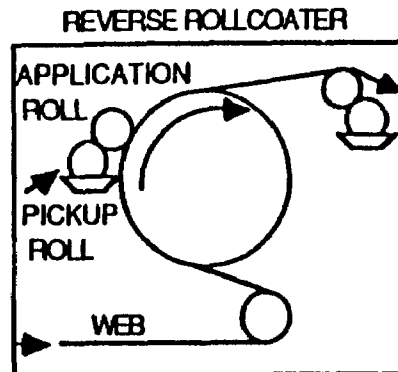
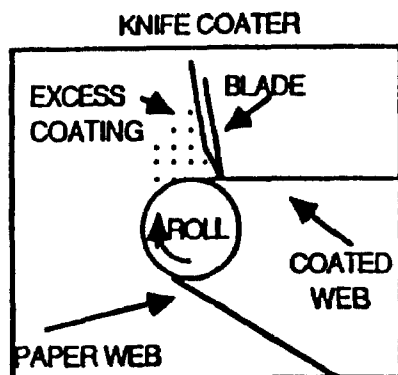


Figure 2.8 Paper coating line

### **2.13 Publication Gravure Printing**

Publication gravure printing is the printing by the rotogravure process of a variety of paper products such as magazines, catalogs, newspaper supplements and preprinted inserts, and advertisements. Publication printing is the largest sector involved in gravure printing, representing over 37 percent of the total gravure product sales value in a 1976 study.

The rotogravure press is designed to operate as a continuous printing facility. However, normal press operation experiences numerous shutdowns caused by web breaks and mechanical problems. Each rotogravure press generally consists of 8 to 16 individual printing units, with an 8 unit press the most common. In publication printing, only four colors of ink are used: yellow, red, blue and black. Each unit prints one ink color on one side of the web, and colors other than these four are produced by printing one color over another.

In the rotogravure printing process, a web from a continuous roll is passed over the image surface of a revolving gravure cylinder. For publication printing, only paper webs are used. the printing images are formed by many tiny recesses or cells etched or engraved into the surface of the gravure cylinder. The cylinder is about one-fourth submerged in a fountain of low viscosity mixed ink. Raw ink is solvent diluted at the press and is sometimes mixed with related coatings, usually referred to as extenders or varnishes. The ink, as applied, is a mixture of pigments, binders, varnish and solvent. The mixed ink is picked up by the cells on the revolving cylinder surface and is continuously applied to the paper web. After the impression is made, the web travels through an enclosed heated air dryer to evaporate the volatile solvent. The web is then guided along a series of rollers to the next printing unit. Figure 2.12 illustrates this printing process by an end (or side) view of a single printing unit.

At present, only solventborne inks are used on a large scale for publication printing. Waterborne inks are still in research and development states, but some are now being used in a few limited cases. Pigments, binders and varnishes are the nonvolatile solid components of the mixed ink. For publication printing, only aliphatic and aromatic organic liquids are used as solvents. Presently, two basic types of solvents, toluene and a toluene-xylene-naphtha mixture, are used. The naphtha base solvent is the more common. Benzene is present in both solvent types as an impurity, in concentrations up to about 0.3 volume percent. Raw inks, as purchased, have 40 to 60 volume percent solvent, and the related coatings typically contain about 60 to 80 volume percent solvent. The applied mixed ink consists of 75 to 80 volume percent solvent, required to achieve the proper fluidity for rotogravure printing.

## **2.14 Packaging and Specialty Rotogravure**

In addition to the publishing rotogravure industry, which prints newspapers and supplements, magazines, catalogs and advertisements, the remaining segment of gravure printing produces packaging products and a miscellaneous group of "specialty" products. the packaging products include cigarette cartons and labels, can labels, and detergent and many other folding cartons. In the specialty field, gravure is used for wall coverings and decorative household paper products such as towels, tissue and shelf paper. Other products include floor coverings, vinyl upholstery and items with woodgrain effects.

While the basic rotogravure printing process is very similar for publications, packaging and specialties, packaging and specialty plants are generally much smaller and there are many more of them than there are publication facilities.

## **2.15 Flexographic Printing**

In flexographic printing, the image area is above the surface of the plate, as opposed to the etched image used in rotogravure. Flexography uses a rubber image carrier and alcohol-base inks. The process is usually web fed and is employed for medium or long multicolor runs on a variety of substrates, including heavy paper, fiberboard, and metal and plastic foil. The major categories of the flexography market are flexible packaging and laminates, multiwall bags, milk cartons, gift wrap, folding cartons, corrugated paperboard (which is sheet fed), paper cups and plates, labels, tapes and envelopes. Almost all milk cartons and multiwall bags, and half of all flexible packaging are printed by this process.

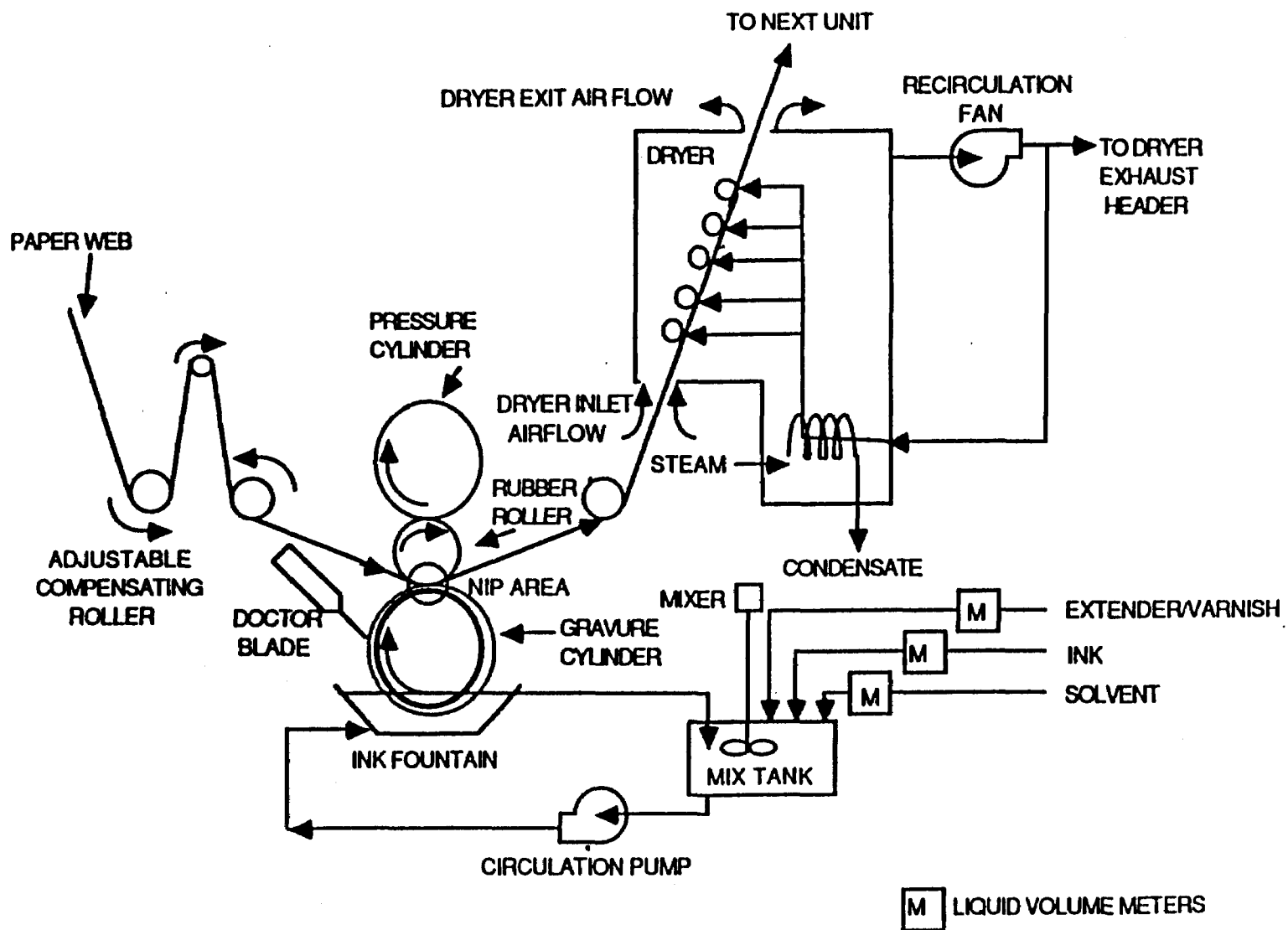


Figure 2.12 Schematic of rotogravure printing unit



Steam set inks, employed in the "water flexo" or "steam set flexo" process, are low viscosity inks of a paste consistency that are gelled by water or steam. Steam set inks are used for paper bag printing, and they product no significant emissions. Water-base inks, usually pigmented suspensions in water, also are available for some flexographic operations, such as the printing of multiwall bags.

Solvent base inks are used primarily in publication printing (see Figure 2.13). As with rotogravure, flexography publication printing uses very fluid inks of about 75 volume percent organic solvent. The solvent, which must be rubber compatible, is straight alcohol or alcohol mixed with an aliphatic hydrocarbon or ester. Typical solvents also include glycols, ketones and ethers. The inks dry by solvent absorption into the web and by evaporation, usually in high velocity steam drum or hot air dryers, at temperatures below 120° C (250° F). As in rotogravure publishing, the web is printed on only one side at a time, but passes over chill rolls after drying.

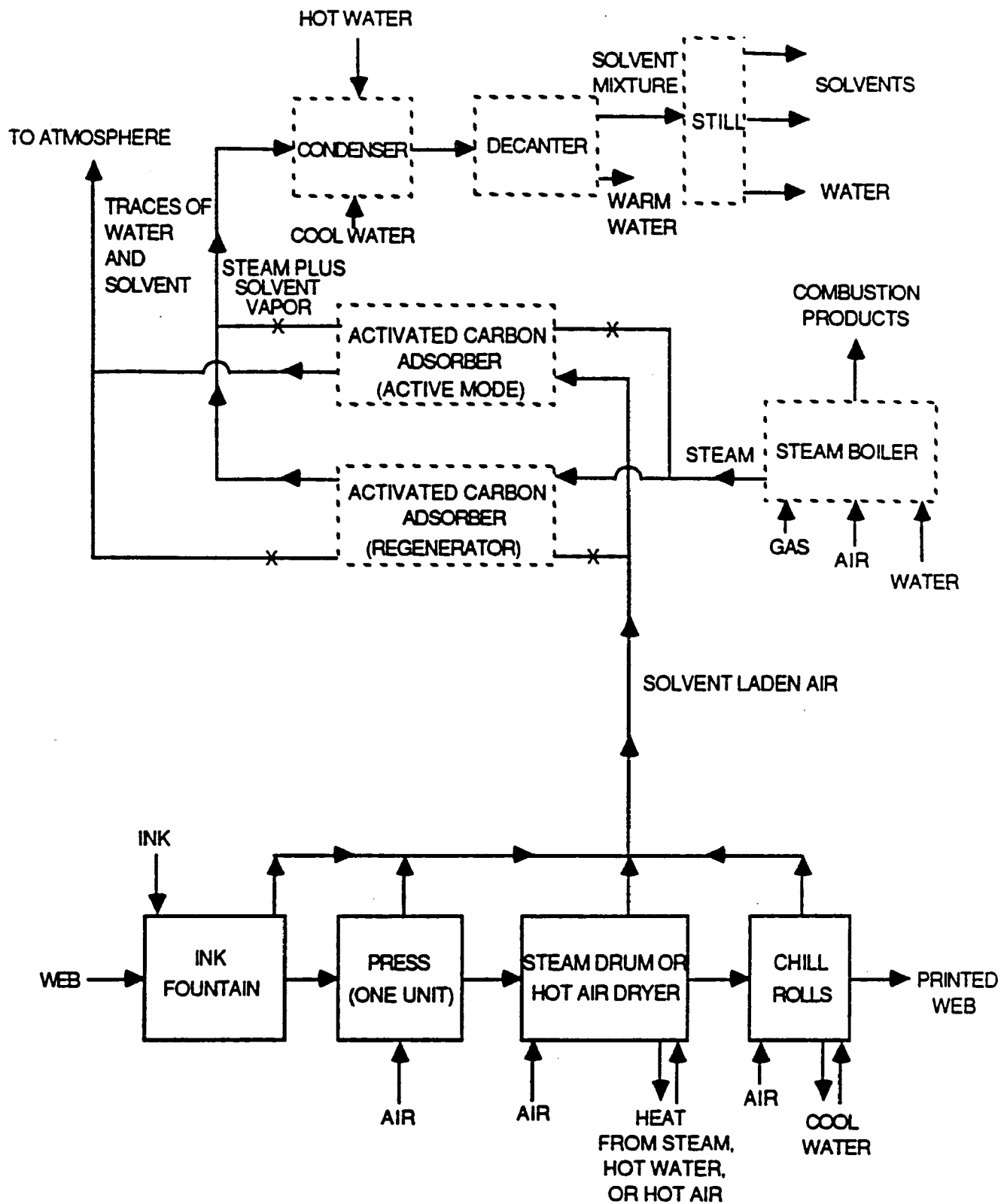


Figure 2.13 Flexography printing line VOC emissions points

## **SECTION 3.0**

### **EMISSION CONTROL STRATEGIES**

#### **3.0 Introduction**

It is generally assumed that the entire VOC content of a coating evaporates after application to become potential emissions. That portion of the evaporated solvent which is not subsequently recovered or destroyed in control equipment becomes actual emissions. The VOC content of all coatings applied, together with capture and control efficiencies for the vapor-control system, determines the net VOC emissions from the process.

The VOC emissions at a facility can also result from on-site dilution of coatings with solvents, from makeup solvents, and from solvents used for cleanup. Makeup solvents may be added to a coating to compensate for standing losses and to restore the working specifications of the coating. These types of solvent emissions should be added to VOC emissions from coatings to get total emissions from a facility. Note that improved housekeeping efforts can help prevent VOC emissions by minimizing the exposure of solvents to the air.

In Section 3.1, probable sources of VOC emissions from surface coating processes are examined. Section 3.2 then discusses the principal methods used in the coating industry to limit VOC emissions from surface coating facilities. A detailed description of several representative coating processes was presented earlier in Section 2.0 of this Manual.

#### **3.1 Process Emissions**

Each plant has its own unique combination of coating formulations, application equipment, and operating parameters. The emission points discussed, however, are fairly typical of coating and graphic arts operations. Process emissions points include the application area, floor grates, ovens, hoods and enclosures. The process examples and data given herein have been developed from the EPA Control Technology Guideline Series.(2,4,5,6) Plant-specific data should be used for emission estimates whenever possible.

Emissions from coating operations depend on the composition of the coating, the coated area, the coating thickness, and the efficiency of application. Post-application chemical changes, and nonsolvent contaminants such as oven fuel combustion products, can also affect the composition of emissions. All solvent used and not recovered is considered to be potential emissions.

In can-coating processes, sources of VOC emissions include the coating area and the oven area of the sheet base and lithographic coating lines, the three piece can side seam and interior spray coating processes, and the two piece can coating and end sealing compound lines. Emission rates vary with line speed, can or sheet size, and coating type. On sheet coating lines, where the coating is applied by rollers, most solvent evaporates in the oven. For other coating processes, the coating operation itself is the major source.

In metal coil surface-coating operations, VOC are emitted from the coating application station, the curing oven, and the quench area. VOC emissions result from the evaporation of organic solvents in the coating. The percentage of total VOC emissions given off at each emission point varies from one installation to another, but on the average, about 8 percent is given off at the coating application station, 90 percent at the oven, and 2 percent at the quench area. On most coating lines, the coating application station is enclosed or hooded to capture fugitive emissions and direct them into the oven. The quench area is an enclosed operation located immediately adjacent to the oven exit so that a large fraction of the quench emissions are drawn into the oven by the oven ventilating air. In operations such as these, approximately 95 percent of the total emissions is exhausted by the oven, and the remaining 5 percent escapes as fugitive emissions.

The oven exhaust is also the most important source of solvent emissions in wire-coating plants. Emissions from the applicator are comparatively low, because a dip coating technique is used.

In surface coating of large appliances, VOC from evaporation of organic solvents in the coating are emitted in the application station and flashoff area (80 percent), and from the oven (20 percent).

Surface coating of metal furniture results in the evaporation of organic solvents as VOC emissions. Specific operations that emit VOC are the coating application process, the flashoff area, and the baking oven. The percentage of total VOC emissions given off at each emission point varies from one installation to another, but on the average spray coating line, about 40 percent is given off at the application station, 30 percent in the flashoff area, and 30 percent in the baking oven.

Emissions of VOC at flat-wood coating plants occur primarily from reverse roll coating of filler, direct roll coating of sealer and basecoat, printing of wood-grain patterns, direct roll or curtain coating of topcoat(s), and oven drying after one or more of these operations.

The main emission points from paper coating lines are the coating applicator and the oven. In a typical paper coating plant, about 70 percent of solvent emissions come from the coating lines, chiefly from the first zone of the oven. The remaining 30 percent of the emissions result from solvent transfer, storage, and mixing operations. A negligible amount of the solvent used (i.e., less than 5 percent) is typically retained in the product.

The VOC emissions in a fabric coating plant originate at the mixer, the coating applicator, and the oven. Emissions from these three areas are from 10 to 25 percent, 20 to 30 percent, and 40 to 65 percent, respectively. Fugitive losses, amounting to a few percent, escape during solvent transfer, storage tank breathing, agitation of mixing tanks, waste solvent disposal, various stages of cleanup, and evaporation from the coated fabric after it leaves the line.

In auto surface coating operations, the application and curing of the prime coat, guide coat, and top coat account for 50 to 80 percent of the VOC emitted from assembly plants. Final topcoat repair, cleanup, and miscellaneous sources such as the coating of small component parts and application of sealants, account for the remaining 20 percent. Approximately 75 to 90 percent of the VOC emitted during the application and curing process is emitted from the spray booth and flashoff area, and 10 to 25 percent from the bake oven.

In printing operations, VOC solvent and traces of aerosol emissions occur at several points in the finishing steps. Most of the emissions occur when the wet web is heated in the drying ovens. Approximately 80 percent of the solvent entering a print station is evaporated in the associated oven. The balance of the solvent is emitted as fugitive emissions in the area of the cylinders and coating reservoirs.

In publication rotogravure printing, the sources of VOC emissions are the solvent components in the raw inks, the coatings used at the printing presses, and the solvent added for dilution and press cleaning. In uncontrolled presses, emissions occur from the dryer exhaust vents and the evaporation of solvent retained in the printed product. About 75 to 90 percent of the VOC emissions occur from the dryer exhausts, depending on press operating speed, press shutdown frequency, ink and solvent composition, product printed, and dryer design. The amount of solvent retained by the various rotogravure printed products is about 3 to 4 percent of the total solvent in the ink. The retained solvent eventually evaporates after the printed product leaves the press.

There are numerous points around a printing press from which fugitive emissions occur. Most of the fugitive vapors result from solvent evaporation in the ink fountain, exposed parts of the gravure cylinder, the paper path at the dryer inlet, and the paper web after exiting the dryers between printing units.

### 3.2 Process Control Techniques

In this section, techniques are presented for lowering VOC emissions:

- (1) coating reformulations;
- (2) improved application methods; and
- (3) add-on control devices such as incineration and carbon adsorption.

The emission reduction potential of some of the strategies discussed in this section are given below:

Table 3.1. Control Efficiencies for Surface Coating Operations	
Control Option	Reduction <sup>a</sup> (%)
Substitute waterborne coatings	60-95
Substitute low solvent coatings	40-80
Substitute powder coatings	92-98
Add afterburner/incinerator <sup>b</sup>	95-98
Add carbon adsorber <sup>b</sup>	95

<sup>a</sup> Expressed as % of total uncontrolled VOC load.

<sup>b</sup> Reduction efficiency applies to control device only.

#### 3.2.1 Coating Reformulations

Conventional coatings consist of finely divided solid materials (pigments and binders) dispersed in a liquid medium (the volatile portion). The volatiles generally consist of a mixture of organic solvents, and can also contain water. The organic solvent

mixture may contain both regulated (VOC) and exempt solvents, but the great majority of solvents are VOC. Solventborne coatings contain at least 30 percent by volume of solvents to permit easy handling and application, and can contain up to 85 volume percent solvents.

Most emission reduction efforts in the coating industry today are focused on lowering the VOC content of coatings. Four principal methods are available: solvent substitution, high solids (low solvent) conventional coatings, waterborne coatings, and powder coatings. Some low-VOC coating formulations, when introduced as replacements for conventional coatings, may eliminate the need for capture and control devices in some situations. Table 3.2 shows recent trends in the use of some coating formulations:

In cases where it is technically feasible, the substitution of exempt solvents for VOC solvents can, in principle, be used to reduce coating emissions. Exempt solvents, however, appear to have limited application in the surface coating and printing industries. An example of solvent replacement is the use of 1,1,1-trichloroethane as a primary solvent in specialty coatings for aerospace parts and in lacquers for wood furniture.

Table 3.2. Percent Usage of Various Coating Formulations

Coating Type	Year	
	1985(%)	1988(%)
Conventional solventborne	57.4	41.5
High solids	12.9	17.6
Waterborne	9.8	14.4
Powder	8.3	14.5
Two-component	4.5	4.4
Radiation cure	1.3	1.5
Other	5.8	6.1

High-solids coatings generally contain at least 70 weight percent solids, which dramatically reduces the solvent fraction and the VOC emissions. For example, if a conventional solvent-based coating containing 30 volume percent solids is reformulated to contain 75 volume percent solids, it will exhibit a 64 percent reduction in its VOC emission potential. Because the viscosity of high-solids coatings is higher than that of conventional coatings, handling problems are common. The resin binder component and solvents must be selected carefully to create acceptable handling characteristics and product quality.

Waterborne coatings use water as the principal solids carrier (e.g., solvent) to reduce the VOC content. Most coatings of this type still contain some organic solvent to provide desired properties such as solubility, evaporation rate, and film coalescence. A 75/25 ratio of water to organic solvent is typical. For example using this water-to-solvent ratio, a conventional solvent-based coating originally containing 30 volume percent solids (and 70 percent solvent) will exhibit a 75 percent reduction in its VOC emission potential. Applications for waterborne coatings are growing, particularly in the aircraft, appliance, metal coil, and wood panel categories. Waterborne inks, however, have not

received wide acceptance in the printing industry due to slower drying and lower product quality in some applications.

Powder coatings, which contain almost no VOC, represent perhaps the greatest potential for emissions reduction of any type of coating reformulation. A powder coating is a collection of resin, pigments, and various additives that has been thoroughly mixed into a fine powder. These coatings are usually applied manually, by electrostatic spray, or fluidized bed dipping (electrocoating). The application of heat then fuses the powder coating into a hard film. Only very small amounts of volatile organics are emitted during curing, enabling the emission reduction achievable by switching to a powder coating to approach 100 percent .

Powder coatings are applied as single coats on some large appliance interior parts and as topcoat for kitchen ranges. They are also used on metal bed and chair frames, shelving, and stadium seating. Other single coat applications include small appliances, small farm machinery, fabricated metal product parts, and industrial machinery components (4).

### 3.2.1 Coating Application / Transfer Efficiency

The transfer efficiency is defined as the fraction of solids in the total consumed coating that remains on the product, and it varies with the type of application technique. A high transfer efficiency helps to limit VOC emissions by reducing the amount of coating that must be used to achieve a given film thickness (or to cover a given surface area). Spraying equipment produces a mist of overspray with a large surface area for solvent evaporation. A transfer efficiency of 60 percent means that 60 percent of the coating solids consumed is deposited usefully onto the product. The other 40 percent is wasted overspray. Because not every application method can be used with all parts and types of coating, transfer efficiencies in the surface coating industry range widely.

Note that the total volatile content of a coating is emitted whether the part is coated or the coating is wasted as overspray. By using low-VOC coatings and an application system with a high transfer efficiency (such as electrostatic spraying), VOC emission reductions can approach those achieved with control devices.

Powder coating systems are designed to capture and recirculate overspray material, and are characterized in terms of a "utilization rate" rather than a transfer efficiency. Most facilities achieve a powder utilization rate of 90 to 95 percent.

## **SECTION 5**

### **INSPECTION PROCEDURES**

#### **5.0 Summary**

The primary focus of this section is on-site inspection procedures. The purpose of an inspection is to confirm that the coatings and solvents used are in compliance with regulatory requirements. Procedures are presented which inform inspectors as to why, where, how, and what to look for so a thorough inspection of a source can be conducted. A description of some basic, often encountered equipment and instruments is presented. Checklists are provided in the text for field use to guide and aid the inspector in observing and noting the condition and operation of the capture and control systems. This section also provides guidance on preparing for an inspection, and procedures for conducting general plant inspections and inspections of surface coating process operations.

The material presented herein has been purposely written in a simple and general manner that might mask the true complexity of VOC capture and control at surface coating operations. Therefore, throughout this guide, references are made to documents that provide further technical data.

#### **5.1 Preparation**

A certain amount of preparation prior to an inspection is always advisable. The preinspection procedures suggested here are intended as general guidelines on how to prepare for and begin the inspection of a surface coating operation. However, the procedures are only suggestions; the inspector must become familiar with and follow the procedures established by the regulatory agency at all times.

These procedures are for continuing compliance inspections; inspections of sources which have previously proved initial compliance with regulatory emission limits by installing air pollution control systems and/or modifying processes. A properly conducted continuing compliance inspection will, at a minimum, allow a qualitative comparison of present equipment operation and condition to the initially permitted conditions.

##### **5.1.1 File Review**

The first step in preparing for an inspection is a review of all information available in the regulatory agency's files on the operation that will be inspected. Efforts invested in reviewing the available information will reduce onsite field time because the information that must be collected and verified will be known.

First, a general review of the documents on file should be conducted. The file review should include items such as permit applications, approved permits, reports of violations or enforcement actions, and annual coating or emissions inventory. Records of citizen complaints, previous inspection reports, and equipment malfunctions should also be noted. Plot plans showing the layout of the source, the location of equipment, and identification of emission points should be examined. Documents should be available that provide specific design and operational data for processes and control equipment.



During the review of the source file, the control strategy should be examined. Specific references to regulations that apply to the emission points at the source may be incorporated. These regulations should be reviewed thoroughly and the type of emission limitation noted. For each emission point, the source should have either done something (process modification, control equipment installation) or submitted something (stack test/coating/ink composition data) that would establish initial compliance with emission limits. In addition to regulations that establish emission limits, there are also requirements for certain operation, maintenance, recordkeeping, or reporting activities (See Section 4.4).

In addition, some sources may have a non-standard compliance method incorporated as a source specific SIP revision. This is true for sources with approved bubbles or alternate control strategy. The inspector should note any deviations from the standard compliance procedures and become familiar with any such methods prior to the on-site inspection. The type of data to be obtained in order to verify compliance with these requirements will be discussed in Section 5.3.

Finally, the regulatory agency may have negotiated certain legally-binding agreements with the subject source. These agreements are likely to be in regard to issues unique to the activities at the source. They may allow the source some leniency from the strict interpretation of a regulation, or they may have established requirements more stringent than a regulation. These agreements are sometimes called variances, consent decrees, or compliance schedules. It is important to fully understand any such agreements before the inspection.

The documentation that the source submitted to support its claim of compliance along with records the source is required to maintain related to compliance should contain the detailed information needed to become familiar with the process and control equipment. It may be helpful to summarize some of the data or previous inspection information so that it will be available during the inspection. Examples of inspection forms/checklists are provided in Section 5.3..

At the end of the file review, the inspector should be aware of the following information.

1. The emission points and the relative magnitude of their emissions.
2. The specific steps the source has taken at each emission point to comply with emission limits.
3. The key parameters that affect emissions from each emission point.
4. The processes or process areas at the source.
5. The results, recommendations, or conclusions of previous inspections.
6. The history of citizen complaints against the source.
7. The history of process or control-equipment malfunctions that have caused increased emissions.

An outline of detailed information is presented in Table 5.1. If any of these items of information are not available from the file, an effort should be made to obtain them during the inspection.

#### **5.1.2 Preliminary Data Verification**

As mentioned in Section 4.4, each source is required to maintain records of coatings and process variables. Occasionally these records will be reviewed to verify their accuracy as part of determining compliance or developing a case for enforcement action. The review and verification for enforcement purposes will be fairly extensive but a spot check of this recordkeeping data is recommended for compliance review also. This is a way for the inspector to become familiar with the compliance methods and calculations for the specific source and potentially uncover areas to focus the on-site inspection.

### **5.2. Plant Inspection**

Due to the variety and complexity of surface coating processes, a detailed description of the inspection methods that would provide a basis for quantifying emission rate changes that would result from process changes is beyond the scope of this manual. However, some basic guidelines are presented below.

#### **5.2.1 Field Inspection**

The inspection can (and should) begin before entering the plant. The observations outlined here can also be conducted after the in-plant inspection.

The perimeter of the plant should be circumnavigated, being careful not to trespass on either the company's or other people's property. Visible emissions from stacks in the plant, and fugitive emissions and odors leaving the plant property can legally be read without obtaining permission from the company as long as they are not done on the company's property. The noise levels around the plant boundary should be noted as well as the proximity of homes, schools, and businesses to the plant property line.

#### **5.2.2 On-site Inspection**

A brief meeting with plant personnel should be conducted before the actual inspection is begun unless the inspector has good reason to suspect that violations will be corrected during the meeting. The following topics are suggested for discussion during this meeting.

1. The purpose of the inspection, the equipment to be inspected, the data and samples desired.
2. The confidentiality requirements and procedures of the company as they will apply to the data collection or inspection needs.
3. The process and control equipment plot plans and flow sheets to confirm the understanding of current operational equipment and to identify any changes or modifications in plant operations since the last inspection.
4. The safety procedures, required safety equipment, and hazard potential of areas covered in the inspection.

**TABLE 5.1**

**SPECIFIC DATA FROM FILE REVIEW**

**I. GENERAL**

- A. Number of coating lines at plant
- B. Number of control systems at plant
- C. Major noncoating line-related emission sources at plant

**II. SURFACE COATING PROCESS**

- A. Material being coated
- B. Production rate
- C. Coating applied
- D. Coating application method
- E. Coating application rate
- F. Drying/curing method
- G. Drying/curing temperature

**III. REGULATIONS**

- A. Emission Limitation and Expression
- B. Control Strategy Description
- C. Permit Conditions
- D. Variances

**IV. CAPTURE SYSTEM**

- A. Total number of hoods in each system
- B. Type of hoods
- C. Distance of each hood from source
- D. Design capture/face velocity at each hood
- E. Location of filters
- F. Location of dampers
- G. Type and location of fan(s) in system
- H. Type of fan drive (direct, belt)
- I. Design flow rate of system

**V. CONTROL DEVICE**

- A. Type of control device
- B. Inlet pollutant concentration
- C. Outlet pollutant concentration
- D. Air flow through device
- E. Design efficiency
- F. Disposal or recovery procedure for pollutant removed from control device.

In addition to these topics, the inspector should be prepared to discuss areas of concern with the plant management, such as:

1. The agency's authority to conduct the inspection.
2. The specific applicability of regulatory requirements to the source.
3. The purpose of uses for information collected during the inspection.

Any noise, odor, or fugitive emission problems noted during the pre-inspection circumnavigation of the source should be investigated. The inspector should note the location of the raw material and finished product storage areas, noise-producing processes or operations, their proximity to the source property line, the potential for the noise to reach the nearest off-site receptor, operations that are odorous or dust-producing and that have the potential for odors or dust from these sources to leave the plant property should be evaluated.

If the plant operates a boiler, it should be inspected for obvious signs of improper operation or malfunction. Other guidance documents are available that provide detailed inspection procedures. However, obvious signs of boiler problems are a smoky stack or erratic boiler temperature. Finally, if during the preinspection file review, a recurring emission problem or citizen complaint was noticed, that equipment should be inspected and note if the plant is taking steps to eliminate recurrence of the past problems.

### **5.3 Process Inspection**

Changes in emission rates can result from changes in the surface coating process operation. Changes that can affect emission rate are:

- ♦ changes in coating compositions
- ♦ changes in coating application methods
- ♦ changes in coating application rates
- ♦ changes in coating drying/curing methods or rates
- ♦ changes in the material being coated.

#### **5.3.1 Coating Formulation**

The inspection of the surface coating process begins at the point where the coating is prepared for application. The company escort can be questioned about the composition, preparation and application methods. Does the coating require cut or diluent solvents? Is it necessary to clean the preparation or application area with solvents? Do they change the types of coatings applied by the applicator? How often are they changed? What are the differences between coatings? Do they buy the coatings from various suppliers? How is coating consumption tracked?

Regulatory requirements often dictate that coating/ink composition data be maintained by the source and submitted to the State agency on a quarterly or semiannual basis. These data records should, at a minimum, include the following for all coatings used in the process during the previous year's time:

- ♦ volume percent solids
- ♦ weight percent solvent
- ♦ weight percent water
- ♦ coating density (pounds per gallon)
- ♦ solvent density (pounds per gallon)

### 5.3.2 Sample Coatings

During the walk through inspection of the plant, the inspector may collect samples of the individual "as applied" coatings being used at that time for EPA Reference Method 24 analysis. The inspector may choose to sample coatings which may not be compliant based on the file and recordkeeping review or to sample coatings to verify the claim that they are compliant. The samples should be handled in a consistent manner with a chain- of- custody record. Duplicate samples should also be taken for analysis by an EPA laboratory or EPA consultant laboratory and by the source. It is the responsibility of the field inspector to determine the following when attempting to obtain a sample of the coating or ink:

1. Can the sample be obtained safely?
2. Can the sample be handled and shipped safely?
3. Is the sample representative of the coating at the sample location or do non-homogeneous conditions introduce significant error?
4. Is the sample representative of the coating(s) used at the source or does normal process variability introduce significant error?

### 5.3.3 Sampling Location

To the extent possible, the sample should be obtained at the point of coating application. In this way, the sample will adequately represent the "As Applied" coating which may have been diluted by volatile organic solvents. However, it should be noted that there can be numerous significant safety hazards involved in sampling coatings and inks near the applicators. It is often impossible to obtain samples at the point of application. In this case, inspectors should determine if it is possible to obtain meaningful "As Supplied" samples from a storage or mixing vessel. Sampling safety is also important when obtaining these samples.

Regulatory agency personnel should not attempt to take samples themselves. This should be done only by plant personnel. The inspectors should note how the sample was obtained and record on the data label the following information:

- ♦ Sample identification number
- ♦ Date and time
- ♦ Source name
- ♦ Sampling location
- ♦ Type of coating (color, generic type)
- ♦ Inspector's signature
- ♦ Plant representative signature
- ♦ Availability of "As Applied" formulation (yes or no)
- ♦ Availability of "As Supplied" formulation (yes or no).

A VOC sampling checklist should be completed for each sample. It should supply pertinent information regarding sampling location and type of coating.

Coating equipment is generally cleaned using a VOC solvent. These solvents and waste coatings are generally collected in 55-gallon drums for off-site disposal. If waste coatings are disposed of as hazardous waste and the source is claiming the right to subtract significant amounts of VOCs contained in the waste coatings from its emissions estimates, samples of the waste coatings should be obtained for Reference Method 24 analysis.

#### **5.3.4 Type of Sampling Container**

All field inspectors should carefully consider the type of container to be used before attempting to obtain any samples of coatings or inks. Metal cans with a bonding cable back to the source of sample are generally preferred since they can be properly grounded while obtaining the sample. Also, the main coating or ink source should be properly grounded.

Another advantage of metal cans is that they usually will not break when dropped. Slight contamination of the sample due to the soldered joint in the metal can is usually not a problem because the analytical methods are all gravimetric.

Glass sample containers are not recommended because they break while being carried or during shipping back to the agency laboratory. Metal and plastic containers are virtually immune to breakage, but are especially prone to static charge accumulation.

#### **5.4 Coating Processes.**

The coating application method (spray, flow, dip, etc.) and the shape of the material being coated (chairs, fenders, discs, springs, etc.) should be observed. Plant personnel can be questioned if they have made any changes to the application method recently. Have they changed the rate at which they apply the coating? Can they coat other shapes on the same line? Do they change shapes often? Do they change the application rate for different shapes? What adjustments do they make to the applicator when they change shapes? Do they adjust the control system when they make adjustments to the applicator?

Next, the drying/curing area of the line should be observed and the way the coating is dried/cured onto the material (gas-fired oven, infrared heaters, stacked in room) noted. Many ovens operate continuously with material moved through them on some type of conveyor system. Can the conveyor speed be changed? What circumstances cause it to be changed? Is the temperature of the drying/curing operation monitored? Is it necessary to vary the temperature frequently? The physical integrity of the ovens should be checked. When ovens are totally enclosed, the capture system will often evacuate them directly. Thus, they should be under negative pressure and fumes should not be observed leaking from the entrance or exit of the ovens. However, a crack or space between oven panels may allow too much air into the oven and overload the capture system. The drying/curing process is important to the quality of the coating and, therefore, the drying/curing equipment is likely to be well maintained.

Due to the diversity of coating process equipment, a suggested checklist is not presented--one that would cover all possibilities would be too cumbersome and a general one would be of little practical value. Instead, the preceding discussion is

intended to inform you of the changes to the surface coating process that can be made and the fact that these changes can influence the control system's ability to perform as originally designed. Plant personnel may, in some cases, be genuinely unaware of the influence that process changes can have on the control system. By asking about process changes, potential changes in emission rates may be identified when the inspection information is compared to the original permit conditions.

## **5.7 Post Inspection Procedures**

After an on-site inspection, the inspector may find that the data collected and contained in the file is not sufficient. Deficiencies could include:

1. Additional data on coatings if the recordkeeping data do not include all coatings or diluents.
2. Destruction or removal efficiency test results especially if there is reason to believe that the control equipment has deteriorated.
3. Capture efficiency test results.
4. EPA Reference Method test results for "as applied" coatings or coatings in which the data are suspect.

The inspector may choose to initiate procedures under Section 114 which allows the regulatory agency to request information for use in determining compliance or to request a new performance tests for the control and capture systems.



# Surface Coating Calculations

## **SECTION 4**

### **COMPLIANCE DETERMINATION CALCULATIONS**

#### **4.0 Summary**

Basic calculations for determining compliance with surface coating and graphic arts regulations require four types of information. First the form of the emission limitation must be known. The second is data on the physical and chemical properties and compositions of the coatings or inks. Performance specifications for add-on controls and finally production rates and usages must also be known. In this section, the regulatory basis for emission limitations is presented along with a description of the sources of data necessary for compliance determinations. Equations and methods for calculating emissions including example calculations are also provided.

#### **4.1 Expressions of Emission Limitations**

The first piece of information that is needed to determine the compliance status of a source in the surface coating or graphic arts industry is the emission limitation or limitations which the source is required to meet. A number of Federal programs, such as Reasonably available control technology, new source performance standards among others, apply to surface coating and graphic arts industries, and States have a certain latitude in developing specific control programs to reduce VOC emissions. It is beyond the scope of this manual to present a complete description of the various regulatory programs that apply to these industries. The brief description is designed to provide the reader with sufficient understanding of the regulatory bases to interpret emission limitations. It is not meant as a guide for determining emission limitations for sources.

The form in which the emission limit is expressed depends in part on the establishing regulatory program. Common forms of emission limitations expressions for the surface coating industry are (7):

- ♦ Weight VOC per volume of coating minus water,
- ♦ Weight VOC per square foot (flat wood coating) or
- ♦ Weight VOC per volume solids content
- ♦ Weight VOC per volume solids, as applied.

Emission limitations for graphic arts industry are on a different basis and common ones are (3):

- ♦ Volume % VOC in volatile fraction for waterborne ink,
- ♦ Volume % Water in volatile fraction for waterborne ink,
- ♦ Volume % Solids in ink.

The regulatory basis for many of the emissions units is the reasonably available control technologies (RACT) as issued by EPA and defined in the Control Techniques Guidelines (CTG). Many States have adopted these limits into their SIP's. Appendix B contains a copy of the CTG limits for surface coating and graphic arts. Emission limits developed from New Source Performance Standards (NSPS) are also listed in Appendix B, and they are typically expressed on a solids basis.

The SIP's generally require continuous compliance on a line-by-line over some period of time, either a daily or hourly rate. Water and exempt solvents are not included in the basis or unit of the emission limitation. The emission limits may also be set "as applied," as actually used in the process which would be calculated from the "as supplied" by the manufacturer plus any diluent solvents or cutting solvents.

Compliance determination calculations are typically done in the units or basis of the emission limitation. Calculations for sources which are complying by reformulating the coatings, compliant coatings, are typically done on a weight of VOC per gallon of coating. It may be necessary to convert the coatings "as supplied," as received from the manufacturer, to "as applied" in the compliance determinations.

It is sometimes necessary to compare compliant coatings with other forms of emission limitations. These types of calculations are called Equivalency calculations and are done on a solids basis. The reason for this is the amount of solids it takes to coat a surface to a particular film thickness is the same regardless of coating formulation or application method.

Solids basis or Solids applied basis are used when add-on controls or improved transfer efficiencies are used for the same reasons as equivalency calculations. Occasionally, a source may wish to use a combination of over-compliant and non-compliant coatings and add-on controls on a plant wide basis. This is termed an alternative control strategy or "Bubble". In these cases the emission limits are expressed on a solids basis. Bubbles must provide an additional 20% emissions reduction, be approved by the State and EPA, and must specify the method used to determine compliance.

Equations for determining compliance are given in Section 4.5 for each emission limitation expression. Samples of each type of calculations are also provided in Section 4.6

## **4.2 Physical and Chemical Data Sources**

The second set of information that is needed to conduct a compliance determination calculation is physical and chemical data including densities, VOC contents, and solids content, for the coating. Common methods and sources for obtaining the necessary data are presented below. The sample calculations in Section 4.6 use data from these sources.

### **4.2.1 Standard Methods**

The EPA has promulgated standard methods (Reference Methods 24 and 24A) for determining the VOC content and densities of coatings and inks. Method 24 is used to determine:

- (1) the volatile matter content (weight fraction or weight %),
- (2) water content (weight fraction or weight %),
- (3) coating density (kg per Liter), and
- (4) solids content (volume fraction).

of paint, varnish, lacquer, or related surface coatings. Although Method 24 is suitable for most coatings, Method 24A is more applicable to publication rotogravure printing inks which contain high volatile fraction inks. Method 24A specifies a gravimetric procedure to determine:

- (1) the VOC weight fraction of the coating,
- (2) coating density, and
- (3) solvent densities.

Both methods rely on American Society of Testing Materials (ASTM) procedures, and are presented in Appendix C. Other methods may be used only if approved by the State and EPA.

#### **4.2.2. Data Sheets**

In an attempt to simplify the process for determining compliant coatings, EPA prepared a manual, Recordkeeping Guidance Document for Surface Coating Operations and the Graphic Arts Industry (10) which identifies the data to be maintained by coating manufacturers and users and suggests a format in which the data be presented. Other formats may also be used.(8) Example data sheets are illustrated in Appendix D.

#### **4.2.3 Materials Data Sheets**

Materials Safety Data Sheets (MSDS) may also be used to supplement physical or chemical data from the data sheets. MSDS are supplied by the manufacturer and contain physical and chemical properties such as densities and composition of the manufacturer's product. This may not be sufficient information to determine the VOC content of a coating in a process setting. The MSDS data sheets however can be especially useful as a source of data on diluents or cut solvents.

### **4.3 Transfer Efficiencies**

The third piece of information that is necessary to determine the compliance status of a specific source is the degree of emission reduction which can be expected of certain add-on or alternative controls.

Certain minimum or baseline transfer efficiencies have been established in the CTG's for the following four surface coating applications:

- ♦ spray applications in automotive assembly plants,
- ♦ surface coating of large appliances, and
- ♦ surface coating of metal furniture.

Transfer efficiencies have also been established in certain NSPS. These values can be used in compliance determination calculations for NSPS sources. Many sources, however, can take advantage of improved or enhanced transfer efficiencies (greater than baseline).(9) The enhanced transfer efficiency is established under plant conditions and included in the SIP along with the baseline transfer efficiency. When enhanced transfer efficiency is used, compliance is determined by comparing the VOC emission from a baseline case and enhanced transfer efficiency case. Example 4.7 is an example of the use of enhanced transfer efficiencies.

Minimum performance criteria may be specified in the regulations for add-on control equipment. The efficiency of capture and control equipment is determined by a performance test for a specific source. EPA recommends that sources keep records of performance data as part of recordkeeping requirements.

### **4.4 Recordkeeping Requirements**

The fourth piece of information that is necessary for compliance determinations is information on coating usage and process conditions. Most SIP's require sources to maintain

a record of coatings used and other process data. Although recordkeeping requirements can vary from State to State, generally the minimum information that must be maintained is:

- ♦ Coating formulation and analytical data,
- ♦ Coating consumption data,
- ♦ Capture and control equipment performance data,
- ♦ Spray applicator transfer efficiency data, and
- ♦ Process information.

Sources are only required to submit data applicable to their operation. For instance, if a source uses only compliant coatings to meet emissions limitations, it need not maintain records related to transfer efficiencies or control equipment performance. Sources subject to NSPS or construction or operating permits may have other recordkeeping requirements specific to those programs.

Sources are required to maintain records in a format consistent with the emission limitations and time frame. Information on the method for determining compliance must also be maintained if the source is subject to a bubble.

Examples of standard forms for recordkeeping purposes were illustrated in Section 4.2 above. Sources are not required to use these specific forms but they must provide the same data. These recordkeeping forms should contain all the information that is necessary to determine the compliance status of a source.

#### **4.5 Compliance Calculations**

As seen in Section 4.2, the regulations are expressed in different basis units and different data can be required. A summary of applicable surface coating or graphic arts regulations and corresponding data requirements are summarized in Table 4.1. On first inspection, it appears to be a formidable task to calculate compliance. It is not as difficult as it may seem if one keeps in mind some basic facts. Equations for determining compliance are provided below.

Examples of basic calculations for determining compliance with regulations are presented in the following material beginning with volume and weight percent conversions. Up to this point, emissions limits have been discussed in terms of weight per volume. Most emissions limitations will be codified in English units, i.e., pounds, gallons rather than metric, kilograms, Liters. The examples are all presented in English units.

**TABLE 4.1**  
**BASIC DATA REQUIREMENTS FOR COMPLIANCE DETERMINATIONS**

Emission Source Limitation Expression	Basic Data Required
<b><u>SURFACE COATING</u></b>	
1a. lbs VOC/gal coating (less water) as supplied <sup>1</sup>	a. coating density (lbs coating/gal coating) b. weight % volatiles (lbs volatiles/lb coating) c. weight % water (lbs water/lb coating <sup>2</sup> )
	or
	d. coating density (lbs coating/gallon coating) e. VOC density (lbs VOC/gallon VOC) f. volume % volatiles g. volume % water
1b. lbs VOC/gal coating (less water) as applied <sup>1</sup>	h. a through c (or d through g) above i. cut solvent density (lbs VOC/gallon VOC) j. ratio of cut solvent to coating (gallon of cut solvent per gallon of coating as supplied)
2. lbs VOC/gal solids as applied <sup>2</sup>	k. coating density (lbs coating/gallon coating) l. weight % VOC (lbs VOC/lb coating) m. volume % solids (gal solids/gal coating) n. transfer efficiency <sup>3</sup> (amount of solids applied <sup>4</sup> /amount of solids used)

**TABLE 4.1 (continued)**  
**BASIC DATA REQUIREMENTS FOR COMPLIANCE DETERMINATIONS**

**Emission Source  
Limitation Expression**

**Basic Data Required**

**SURFACE COATING (continued)**

3. lbs VOC/1,000 ft<sup>2</sup> flatwood

- o. coating usage rate  
(gallons of coating applied/unit of time)
- p. weight % VOC (lb VOC/lb gal as applied)
- q. flat wood production rate (1,000 ft<sup>2</sup>/unit of time)

**GRAPHIC ARTS**

4. gal VOC/(gal VOC + gal water)  
  
and  
  
gal water/(gal VOC + gal water)

- r. ink density (lbs ink/gal ink)
- s. weight % VOC (lbs VOC/lb ink)
- t. weight % water (lbs water/lb ink)
- u. volume % solids (gal solids/gal ink)
- v. ratio of ink as supplied to cut solvent  
added (gal ink supplied:gal cut solvent added)
- w. cut solvent density (lbs VOC/gal VOC)

5. gal solids/gal ink as applied

- x. volume % solids (gal solids/gal ink)
- y. ratio of ink as supplied to cut solvent added  
(gal ink supplied: gal cut solvent added)
- z. volume % water (gal water/gal ink)

**TABLE 4.1 (conclusion)**  
**BASIC DATA REQUIREMENTS FOR COMPLIANCE DETERMINATIONS**

Emission Source Limitation Expression	Basic Data Required
<b>GRAPHIC ARTS (continued)</b>	
6. Overall capture and abatement reduction percentage	aa. capture efficiency (lb VOC captured/lbs VOC released) bb. destruction efficiency (lb VOC destroyed/lb VOC entering control device)

240

- <sup>1</sup> The composition and characteristics of these coatings and inks just delivered from the manufacturer and before the user opens the containers are termed "as supplied". Before a coating or ink is applied to a substrate, the user may add dilution of "cut" solvent to the coating in order to obtain desired characteristics (e.g., lower viscosity) or otherwise alter the coating after delivery. The composition and characteristics of the coating or ink that is actually applied to the substrate are termed "as applied".
- <sup>2</sup> Once weight % water is known, the volume % water can be calculated by dividing the weight % water by the density of water, which can be considered a constant (= 8.33 lb/gal water).
- <sup>3</sup> The ratio of the amount of solids applied to the amount of solids used represents the transfer efficiency of the application technique. For example, if 8 lbs of solids are applied but 10 lbs of solids are used (vis., sprayed), the ratio is 8:10 or 0.8, and the application technique is said to have a transfer efficiency of 80%.
- <sup>4</sup> The solid portion of a coating that lands on and sticks to the substrate is the "solids applied". The amount of solids applied, however, will most likely not be the same as the amount of "solids used". That is, in most cases, some portion of the solids in the coating will not end up on the substrate, but will either miss it altogether or bounce off it.



## CTG Compliant Coating Equations

If the emission limitation is expressed as LBS PER GALLON OF COATING (LESS WATER) , then the following equations can be used. Note that Volume and Weight %'s are used in these equations. If Volume and Weight fraction are used substitute 1 for 100.

### EQUATION 4.1

$$\frac{\text{LBS VOC}}{\text{GAL COATING LESS WATER}} = \frac{\text{COATING DENSITY} \times (\text{WEIGHT \% VOLATILES} - \text{WEIGHT \% WATER})}{(100 - \text{VOLUME \% WATER})}$$

### EQUATION 4.2

$$\frac{\text{LBS VOC}}{\text{GAL COATING LESS WATER}} = \frac{(\text{VOC DENSITY} \times (\text{VOLUME \% VOLATILES} - \text{VOLUME \% WATER}))}{(100 \% - \text{VOLUME \% WATER})}$$

If there is no water in the coating, % Volatiles = % VOC and both Weight % Water, and Volume % water become 0, the equations reduce to the following:

### EQUATION 4.1(A)

$$\frac{\text{LBS VOC}}{\text{GAL COATING LESS WATER}} = \text{COATING DENSITY} \times \frac{\text{WEIGHT \% VOC}}{100 \%}$$

### EQUATION 4.2(A)

$$\frac{\text{LBS VOC}}{\text{GAL COATING LESS WATER}} = \text{VOC DENSITY} \times \frac{\text{VOLUME \%}}{100 \%}$$

## CTG Compliant Coating Equations - As Applied

If the coating limit is expressed as - - lbs VOC per gallon of coating (less water) as applied, then the addition of cut solvent has to be taken into account during calculations. Solvent densities may be obtained from Manufacturer's Data Sheets or EPA Data Sheets.

If Method 24 data is available use Equation 4.3:

EQUATION 4.3

$$\frac{\text{LBS VOC}}{\text{GAL COATING}} = \left( \text{COATING DENSITY AS SUPPLIED} \times \text{WT FRACTION VOC} \times \frac{\text{GAL COATING SUPPLIED}}{\text{GAL COATING APPLIED}} \right) + \frac{\text{SOLVENT DENSITY} \times \frac{\text{GAL SOLVENT}}{\text{GAL COATING APPLIED}}}{(1 - \text{VOL FRACTION WATER AS APPLIED})}$$

Note that if the volume fraction of water is given "as supplied", the denominator for the second term of the equation becomes:

EQUATION 4.3 (A)

$$((1 - \text{VOLUME FRACTION WATER AS SUPPLIED}) \times \frac{\text{GAL COATING SUPPLIED}}{\text{GAL COATING APPLIED}})$$

## CTG Compliant Coating Equations - As Applied Continued

If Method 24 data is not available, Equation 4.4 may serve as an alternative. If the volume % of water is given "as supplied" the denominator must be adjusted as in Equation 4.3 (A).

### EQUATION 4.4

$$\frac{\text{LBS VOC}}{\text{GAL COATING LESS WATER AS APPLIED}} = \left( \text{VOC DENSITY} \times \text{VOLUME FRACTION VOC} \times \frac{\text{GAL COATING AS SUPPLIED}}{\text{GAL COATING AS APPLIED}} \right) + \frac{\text{DENSITY OF CUT SOLVENT} \times \frac{\text{GAL CUT SOLVENT}}{\text{GAL COATING AS APPLIED}}}{(100\% - \text{VOLUME \% WATER AS APPLIED})}$$

## CTG Compliant Coating Equations: Solids Basis

If the coating limit is expressed in terms of solids, such as - lb VOC per gallon of solids applied, use Equation 4.5 or Equation 4.6. Note that the data may need to be converted into the variables used in these equations.

When the VOC content of a coating less water is known Equation 4.5 is appropriate:

EQUATION 4.5

$$\frac{\text{LB VOC}}{\text{GAL SOLIDS}} = \frac{\text{VOC CONTENT OF COATING LESS WATER}}{\frac{\text{VOLUME \% SOLIDS}}{(100 - \text{VOLUME \% WATER})}}$$

When the VOC content of a coating with water is known or when no water is present, Equation 4.5 reduces to:

EQUATION 4.5 (A)

$$\frac{\text{LB VOC}}{\text{GAL SOLIDS}} = \frac{\text{VOC CONTENT OF COATING} \times 100\%}{\text{VOLUME \% SOLIDS}}$$

Equation 4.6 may also be used when the data is presented as follows:

EQUATION 4.6

$$\frac{\text{LB VOC}}{\text{GAL SOLIDS}} = \frac{\text{COATING DENSITY} \times \text{WEIGHT \% VOC}}{\text{VOLUME \% SOLIDS}}$$

## Graphic Arts Compliance Equations

If the graphic arts limitation is expressed as --VOC solvent volume % of the volatile fraction  
Equation 4.7 applies:

### EQUATION 4.7

$$\frac{\text{GAL VOC}}{\text{GAL VOLATILE FRACTION AS APPLIED}} = \frac{\left( \text{VOL \% VOC AS SUPPLIED} \times \frac{\text{GAL INK AS SUPPLIED}}{\text{GAL INK AS APPLIED}} \right) + \frac{\text{GAL SOLVENT}}{\text{GAL INK APPLIED}}}{\left( 1 - \frac{\text{GAL SOLIDS}}{\text{GAL INK AS APPLIED}} \right) \times \frac{\text{GAL INK SUPPLIED}}{\text{GAL INK APPLIED}} + \frac{\text{GAL SOLVENT}}{\text{GAL INK APPLIED}}}$$

When there is no diluent or cut solvent added the equation reduces to Equation 4.7 (A):

### EQUATION 4.7 (A)

$$\frac{\text{GAL VOC}}{\text{GAL VOLATILE FRACTION AS APPLIED}} = \frac{\text{VOL \% VOC}}{(100 - \text{VOL \% SOLIDS})}$$

If the graphic arts limitation is expressed as -- water volume % of the volatile fraction  
Equation 4.8 applies:

### EQUATION 4.8

$$\frac{\text{GAL WATER}}{\text{GAL VOLATILE FRACTION AS APPLIED}} = \frac{\left( \text{VOL\% WATER IN INK AS SUPPLIED} \times \frac{\text{GAL INK AS SUPPLIED}}{\text{GAL INK AS APPLIED}} \right) + \frac{\text{GAL SOLVENT}}{\text{GAL INK APPLIED}}}{\left( \left( 1 - \frac{\text{GAL SOLIDS}}{\text{GAL INK AS APPLIED}} \right) \times \frac{\text{GAL INK SUPPLIED}}{\text{GAL INK APPLIED}} \right) + \frac{\text{GAL SOLVENT}}{\text{GAL INK APPLIED}}}$$

## Graphic Arts Compliance Equations Cont.

When no diluent or cut solvent is used Equation 4.8 reduces to Equation 4.8 (A) as below:

### EQUATION 4.8 (A)

$$\frac{\text{GAL WATER}}{\text{GAL VOLATILE FRACTION AS APPLIED}} = \frac{\text{VOLUME \% WATER IN INK}}{(100 \% - \text{VOLUME \% SOLIDS})}$$

If the graphic arts regulation is expressed as-- volume % of nonvolatiles (i.e., gallons of solids per gallons of ink) less water, as applied: use the Equation 4.9:

### EQUATION 4.9

$$\text{VOLUME \% SOLIDS IN INK,} = \frac{\text{VOLUME \% SOLIDS}}{\left( 1 + \frac{\text{GAL OF DILUTION SOLVENT}}{\text{GAL OF INK AS SUPPLIED}} - \frac{\text{GAL OF WATER}}{\text{GAL OF INK AS SUPPLIED}} \right)}$$

Volume % have been used in all of the above equations for ease of presentation. If the data is presented in Weight % it must be converted to Volume %. Example 4.1 illustrates the conversions between weight and volume percent calculations. Note that the diluent solvent is assumed to be 100 % VOC. This is not always the case. If the diluent solvent contains water it must be subtracted out. Example 4.11 shows how the calculation is completed.

## Graphic Arts Compliance Equations Add- On Controls

If the graphic arts regulation requires calculation of -- overall VOC capture and abatement reduction, use Equations 4.10, through 4.12:

### EQUATION 4.10

% OVERALL VOC CONTROL EFFICIENCY = CAPTURE EFFICIENCY(%) X DESTRUCTION EFFICIENCY(%)

where:

### EQUATION 4.11

CAPTURE EFFICIENCY =  $\frac{\text{LB OF VOC DUCTED TO CONTROL DEVICE}}{\text{LB OF VOC EMITTED DURING OPERATION}} \times 100 \%$

### EQUATION 4.12

DESTRUCTION EFFICIENCY =  $\frac{\text{LB OF VOC DUCTED TO CONTROL DEVICE} - \text{LB OF VOC EMITTED TO ATMOSPHERE}}{\text{LB OF VOC DUCTED TO CONTROL DEVICE}} \times 100 \%$





# Dry Cleaning

## INTRODUCTION

Dry cleaning is the process of cleaning fabric by washing in a substantially non-aqueous solvent. Two classes of organic solvents are used most frequently by the dry cleaning industry. One class includes petroleum solvents, which are mixtures of paraffins and aromatic hydrocarbons. The other class includes chlorinated hydrocarbon solvents, called "synthetic solvents" in the industry, consisting almost exclusively of perchloroethylene, also known as tetrachloroethylene.

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### The Dry Cleaning Industry

The dry cleaning industry is divided into 3 segments based on the types of services offered. The 3 categories are coin operated systems, commercial systems, and industrial systems. Coin operated dry cleaning facilities are usually part of a laundromat and generally process about 16,000 pounds of clothes per year per store. Commercial facilities include neighborhood dry cleaning shops and specialty cleaners. A typical commercial facility processes approximately 60,000 pounds of clothes per year. Industrial cleaning plants

typically supply uniform cleaning and rental services and process from 600,000 to 1,500,000 pounds of clothes annually.

Nationwide perc emissions are 21,400 metric tons for coin-op, 123,000 metric tons for commercial and 13,600 metric tons for industry dry cleaners. The major use of perchloroethylene dry cleaning machine is in commercial dry cleaning establishments.

### The Dry Cleaning Process

Figure 1 is a diagram of a typical perchloroethylene dry cleaning plant. Clothes and perchloroethylene are loaded into a washer and agitated by the turning motion of a paddle or wheel. After washing, the solvent is extracted from the clothes by spinning as in a conventional washer spin cycle. After extraction the used solvent is filtered and distilled to remove impurities and is then returned to the system for reuse. The filtered solids, or "muck", contain solvent which is usually removed by heating and condensed for reuse. Drying may occur in the same unit as did the washing (a dry-to-dry machine) or it may occur in a different machine (transfer machine system). During the drying cycle, the perchloroethylene recovery dryer operates through a closed loop system with much of the evaporated solvent recovered and is then returned to the system through a water cooled condenser. A final process called aeration or deodorization reduces the amount of any solvent remaining in the clothes. This is done by venting ambient air through the clothes in the dryer and then sending the exhaust to the atmosphere.

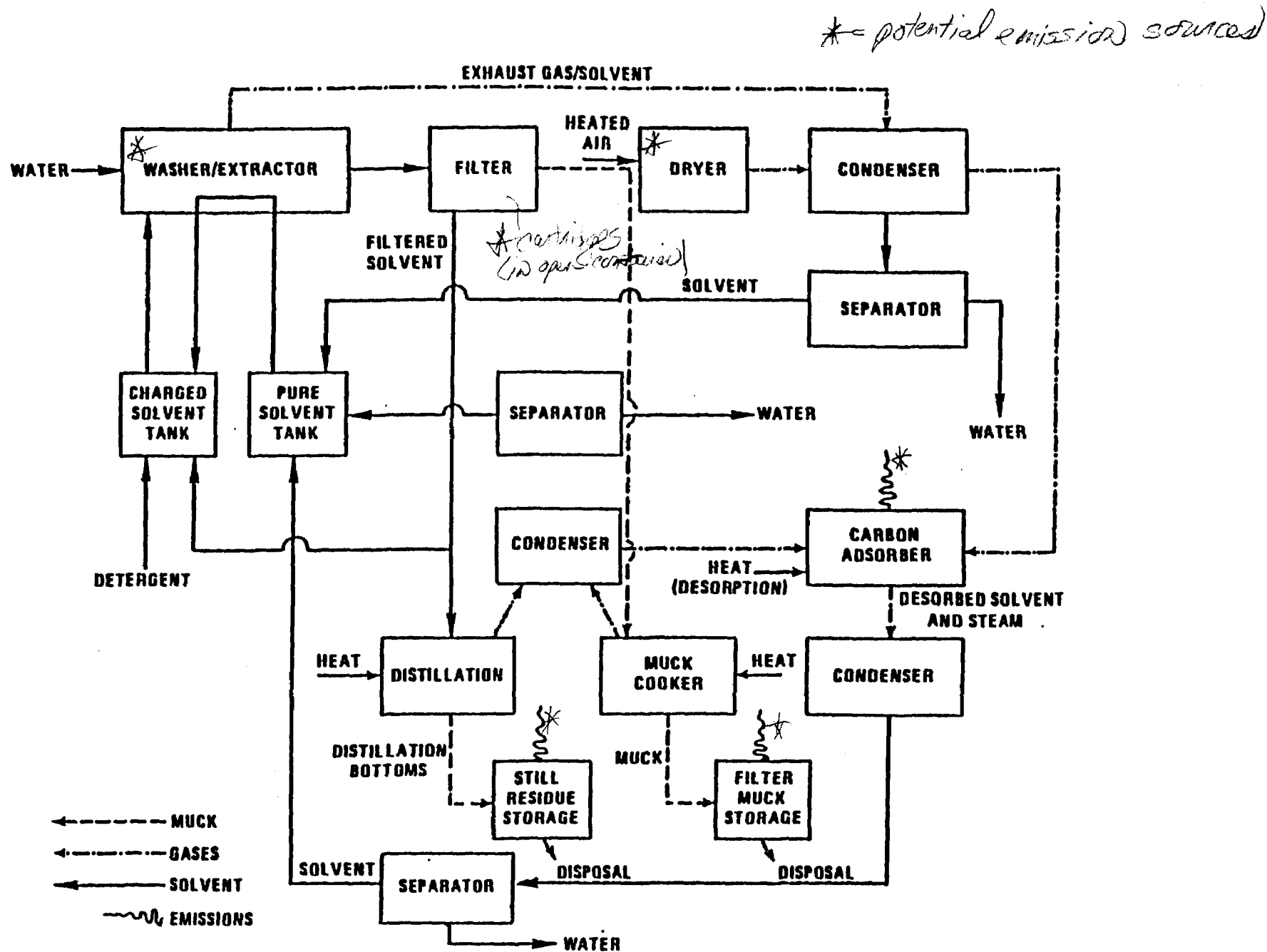


Figure 1. Perchloroethylene dry cleaning plant flow diagram.

## Solvent Characteristics

Although other chlorinated hydrocarbon solvents have been used for dry cleaning in the United States, perchloroethylene is the only chlorinated solvent seeing significant use at this time. An estimated 346 million pounds of perc are used annually for dry cleaning purposes. The solvent may be generally characterized as follows: non flammable, very high vapor density and high cost. Table I lists the properties of dry cleaning solvents.

## Emission Sources

The primary source of perchloroethylene emissions from a dry cleaning plant is the dryer exhaust during the aeration cycle. After washing and extraction, dry-cleaned goods still contain approximately 20-25 kg of solvent per 100 kg of clothes. During the drying cycle, this solvent is vented to a water condenser which typically reduces these potential losses to 3-6 kg per 100 kg of clothes. In the absence of additional abatement equipment, this un-extracted perchloroethylene is vented to the atmosphere.

A second significant source of perchloroethylene emissions from dry cleaning plants is associated with solvent contained in disposed filtrate. This waste solvent is generated in the form of distillation bottoms and filter muck. As previously discussed, solvent extracted from the clothes is filtered and then distilled for reuse. For the distillation unit, the EPA recommends that the residue from the solvent still contain not more than 60 kg of solvent per 100 kg of wet waste material. This is to be considered a state-of-the-art operating

**TABLE I - PROPERTIES OF DRY CLEANING SOLVENTS**

Property	140-F	Typical 140-F, R 66	Stoddard	Typical Stoddard, R 66	Perchloro ethylene
Flash point (TCC), °F	138.2	143	100	108	Extinguish fire
Initial boiling point, °F	357.8	366	305	316	250
Dry end point, °F	396	400	350	356	254
API gravity	47.9	44.0	50.1	48.1	
Specific gravity at 60 °F	0.789	0.8063	0.779	0.788	1.62
Weight, lb/gal	6.57	6.604	6.49	6.56	13.55
Paraffins, volume %	45.7	82.5	46.5	88.3	
Aromatics, volume %	12.1	7.0	11.6	5.9	
Naphthenes, volume %	42.2		41.9		
Olefins, volume %		0.5		0.8	
Toluene/ethylbenzene, volume %				5.0	
Corrosiveness	None	None	None	None	Slight on n
Caution	Flammable	Flammable	Flammable	Flammable	Toxic
Odor	Mild	Mild	Sweet	Sweet	Ether li
Color	Water white	Water white	Water white	Water white	Colorle
Cost (average size plant), \$/gal	0.29	0.30	0.28	0.29	2.05

procedure. During extraction, solvent is filtered with either regenerable filter materials (usually diatomaceous earth) or paper cartridge filters. RACT (reasonably available control technology) is defined in the CTG as "the residue from any diatomaceous earth filter shall be cooked or treated so that wastes shall not contain more than 25 kg of solvent per 100 kg of wet waste material". For filtration cartridges, RACT was defined as follows: "Filtration cartridges must be drained in the filter housing for at least 24 hours before being discarded. The drained cartridges should be dried in the dryer tumbler if at all possible".

A third source of solvent emissions is associated with liquid and vapor leakage from various components of the dry cleaning system.

#### Types of Control Devices

##### Carbon Adsorption System

A typical carbon adsorption system used in a commercial dry cleaning facility consists of one carbon canister which is usually desorbed with steam once a day.

Large industrial units, however, usually consist of multiple canisters so that one can be used to control emissions while the others is being regenerated. In many plants, other sources in addition to the dryer are vented to the carbon adsorption unit. A current of fresh air is often required at the operator's face when loading & unloading the washer or dryer for occupational health reasons. An internal fan, activated by opening the door, draws air through a duct at the machine door lip. This air containing perchloroethylene vapor should, if at all possible, be vented to the adsorber rather than

directly to the atmosphere. Floor vents installed to control fugitive vapors around the machines and to remove vapors from solvent spills may also be ducted to the adsorber. Additionally, vents from the distillation unit, muck treating units, perchloroethylene separators, and storage tanks may also be controlled by the adsorber.

Government supervised tests show over 99 % removal efficiency and average emission is less than 0.1 pounds per hour.

Carbon should be changed every 6-12 months.

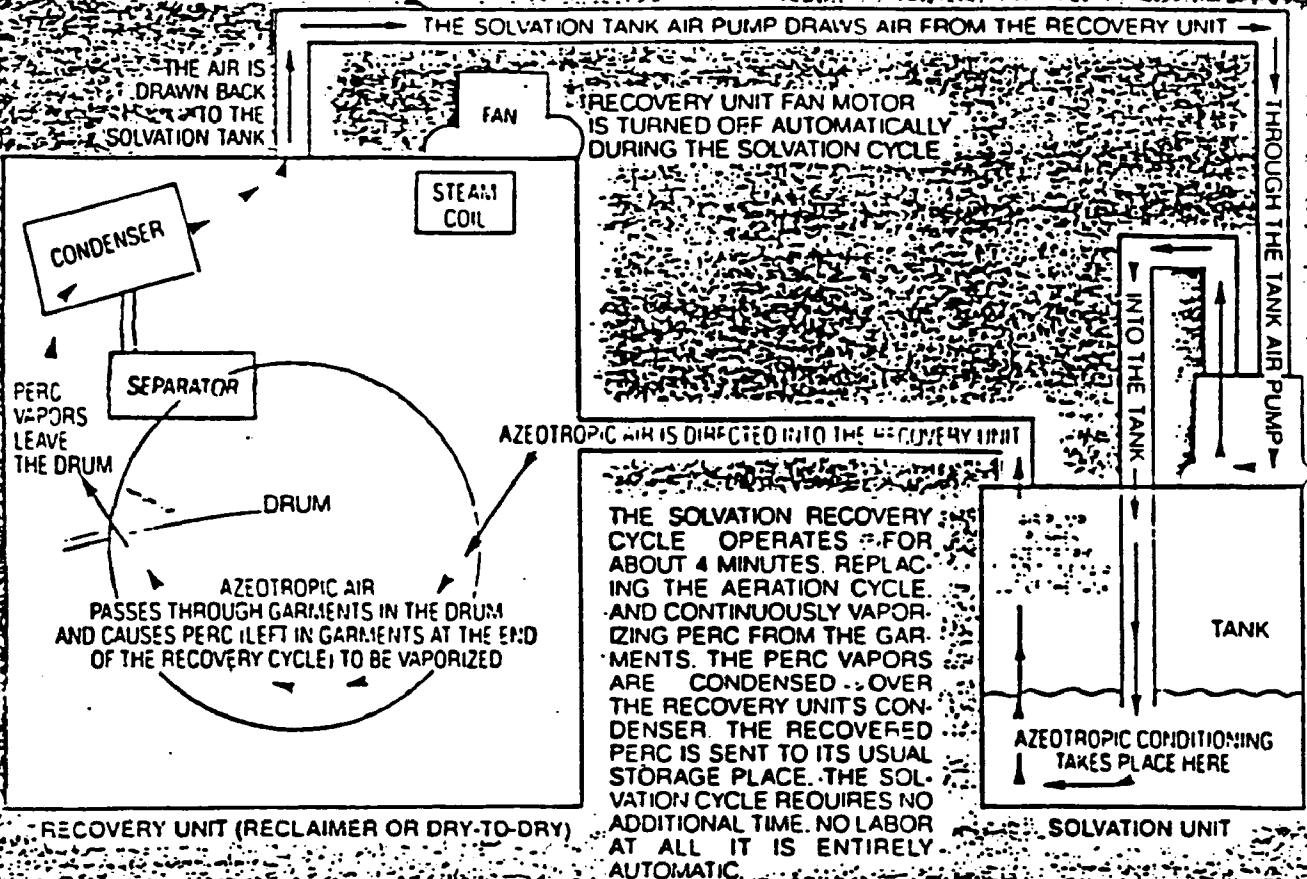
### Solvation System

The solvation process is azeotropic, and it replaces the aeration cycle of a conventional dry cleaning system. In the solvation process, the warm dryer air laden with perc is passed through water, where it is cooled due to evaporation of the water. The resulting gas stream, saturated with water vapor, is returned to the dryer as a low boiling, perchloroethylene-water azeotrope. Perc has a normal boiling point of 189°F. In this way, more perc is vaporized at a lower temperature and ultimately recovered. Perc recovery is also enhanced due to the fact that the materials dry cleaned have a greater affinity for water than perc. At the end of the drying cycle, materials still contain a residual amount of perc. When the air conditioned, humidified stream passes through the materials, they absorb humidity which displaces the residual perc, thus allowing the perc previously absorbed into the materials to be recovered. Figure 3 presents an flow diagram of a solvation system. Government supervised test show 99.98% removal efficiency and only 12 ppm average emissions.



# HOW SOLVATION CLOSES THE SYSTEM

START HERE:  
WHEN THE RECOVERY CYCLE STOPS  
THE SOLVATION CYCLE STARTS  
AND ELIMINATES THE NEED  
FOR AN AERATION CYCLE



## EQUIPMENT SELECTION CHART

EQUIPMENT	SOLVATION MODEL
1 Dry-to-Dry	1022-A 2253-FA
1 Reclaimer	1022-B 2253-FB
1 Reclaimer and 1 Washer	2253-FBW
2 Dry-to-Dry	315-AA 325-F2A
2 Reclaimers	315-BB 325-F2B
1 Dry-to-Dry and 1 Reclaimer	315-AB 325-FAB
1 Dry-to-Dry and 1 Reclaimer and 1 Washer	325-FABW
2 Reclaimers and 1 Washer	325-F2BW
2 Reclaimers and 2 Washers	325-F2B2W
3 Reclaimers	426-F3B
3 Dry-to-Dry	426-F3A
2 Dry-to-Dry and 1 Reclaimer	426-F2AB
2 Reclaimers and 1 Dry-to-Dry	426-FA2B
3 Reclaimers and 2 Washers	426-F3B2W
2 Dry-to-Dry 1 Reclaimer and 1 Washer	426-F2ABW
2 Reclaimers and 1 Dry-to-Dry and 2 Washers	426-FA2B2W
1 Dry-to-Dry Unit Capacity to 240 Lbs	1044-A

## BASIC MODEL SPECIFICATIONS

Dimensions: 72" high x 30" wide x 12" deep  
 Floor Space: 12" x 30"  
 Electrical Requirements: 230/115 VAC; 60 hz  
 Tank Air Pump: Rated power: 2.5/5.0 amp  
 AOP Motor: Rated power: 5/10 amp  
 Components: UL Yellow Card /CSA  
 Water Connections: None  
 Location: Generally, to within 30 ft. of equipment  
 Construction: Aluminum  
 Operation: Automatic, as interconnect equipment  
 Limited Warranty: 10 years, tank  
 other components 90 days  
 Optional Equipment: Spill vapor pick-ups, cartridge cabinet pick-ups

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## Refrigeration System

The vapor condenser operates by modification of the dry cleaning process to reduce solvent emissions. A dry cleaning device modified with a vapor condenser does not include an aeration cycle.

The vapor condenser principle of operation can be summarized in the following way. The vapor condenser is placed into the air stream in conjunction with the water cooled condenser near the end of the drying cycle. This effectively reduces the air stream temperatures, thereby condensing the solvent vapors. Under normal conditions, the temperature of recirculated air is approximately 100°F. However, with the vapor condenser, this recirculated air temperature is reduced to approximately 45°F.

The vapor condensers are 95% efficient in reducing dryer emissions, as compared to a normally operated dryer. This efficiency is dependent on:

1. The dryer/condenser system must not vent to the atmosphere until the air-vapor stream temperature on the outlet side of the refrigerated condenser is equal to or less than 45°F.
2. The dryer/condenser system must be closed to the atmosphere at all times except when articles are being loaded or unloaded through the door of the machine. The refrigerated condenser will be bypassed when

the dryer door is open because perchloroethylene may be evaporated from the frozen coils resulting in increased emissions.

#### 4. ENVIRONMENTAL ANALYSIS OF RACT

The installation of RACT equipment and the implementation of RACT procedures in a typical dry cleaning plant involve the replacement of existing dryers with recovery dryers, the replacement of existing diatomite filtration systems with a cartridge filtration system, and improved operating and maintenance procedures to identify and repair liquid and vapor leaks.

The environmental impacts of RACT implementation on air, water, and solid-waste disposal are discussed in this section. In addition, the effects of RACT equipment operation on overall energy consumption are detailed, based on the two model plants that were discussed in Chapter 2, and these values are compared with those of uncontrolled model plants. Finally, beneficial and adverse effects from the installation of RACT equipment are assessed in relation to emissions and energy consumption in these model plants.

##### 4.1 AIR POLLUTION

Table 4-1 lists the estimated uncontrolled VOC emissions for each emission point and indicates the range (or nominal value) of controlled emissions per 100 kg of articles cleaned. Because the uncontrolled dryer provides from 60 to 80 percent of the total emissions, effective control and reduction (81 percent) of VOC emissions from this source provides the greatest direct impact on overall plant emissions.

Filtration system VOC emissions in dry cleaning facilities with existing non-RACT diatomite filters account for about 25 percent of the total uncontrolled emissions. Filtration emissions in these facilities will be reduced by as much as 88 percent as a direct result of cartridge filter installation. However, RACT will provide no reduction in filtration system VOC emissions in facilities that have existing settling tanks or

Table 4-1. NOMINAL EMISSIONS FACTORS FOR EXISTING AND RACT EQUIPMENT  
(in kg VOC emitted per 100 kg dry weight of articles cleaned)

Source	Existing equipment emissions	RACT equipment emissions	VOC emission reduction	Percent reduction
Dryer	18	3.5	14.5	81
Filter				
Diatomite	8	1	7	88
Cartridge	1	1	0	0
Still	3	3	0	0
Fugitive sources	<u>1</u>	<u>1</u>	<u>b</u>	<u>b</u>
Total	22-30	7.5-8.5	14.5-21.5	

<sup>a</sup>Existing equipment emission estimates are based on industry association data and EPA plant tests, and represent approximate midrange for most sources. See Section 2.0 for complete explanations of controlled emissions sources and levels.

<sup>b</sup>Indeterminate quantity.

cartridge filters. In addition, the VOC emissions resulting from fugitive sources could be directly reduced by improvements in maintenance and operating procedures. Thus, RACT equipment and procedures would produce average VOC emissions reductions ranging from 66 to 72 percent.

Table 4-2 illustrates the VOC emissions reductions that result from the installation of RACT equipment and the adoption of RACT operating and maintenance procedures in two model plants. Based on three uncontrolled emissions rates representing the three filtration alternatives in model plant I and two RACT emissions rates, the model plants show a 66 to 70 percent reduction in model plant I and a 66 percent reduction in VOC emissions in the model plant II. The specific reductions in VOC emissions range from 26 Mg to 39 Mg per year in a model plant I and approximately 92 Mg per year in a large model plant.

#### 4.2 WATER POLLUTION

Increases in water pollution, due to RACT implementation in petroleum dry cleaning plants, would result primarily from inefficient separation of condensed solvent and water. Recovery dryers employ gravimetric separators to remove water from the reclaimed solvent. This unit uses the difference in density between petroleum solvent and water to separate and divert them. Typically, water collected in this manner is dumped into a sewer. The leveling of the separator is critical to the optimization of its performance. If it is not level at installation or is bumped during maintenance, the quantity of solvent in the sewered water could increase to the point of becoming a significant source of water pollution.

Insufficient drainage of RACT filter cartridges could prove to be a source of groundwater pollution, especially if the cartridges were buried in an improperly located or maintained landfill or dump. RACT procedures for cartridge drainage would decrease the overall volume of solvent exposed to groundwater and would, therefore, reduce water pollution by petroleum solvent. Furthermore, based on a maximum solubility of 100 kg (Saary, 1981) of petroleum solvent in 1,000,000 kg of recovered water and an average recovery dryer water recovery rate of 3.4 kg water per 100 kg of articles dried (Plaisance et al., 1981),

**Table 4-2. NOMINAL ANNUAL VOC EMISSIONS FOR TWO MODEL PLANTS  
EMPLOYING EXISTING AND RACT EQUIPMENT AND PROCEDURES**

Type of plant	Plant throughput, kg/yr (lb/yr)	Nominal emission factors in kg VOC emitted per 100 kg dry weight of articles cleaned		Nominal VOC emissions, megagrams/yr (tons/yr)		Nominal annual VOC emission reductions resulting from RACT implementation, megagrams/yr (tons/yr)
		Existing equipment	RACT equipment	Existing equipment	RACT equipment	
Model plant I	182,000 (400,000)					
with existing:						
Diatomite filter		30	8.5	55 (60)	16 (17)	39 (43)
Cartridge filter		23	8.5	42 (46)	16 (17)	26 (29)
Settling tank		22	7.5	41 (45)	14 (15)	27 (30)
Model plant II	635,000 (1,400,000)	22	7.5	140 (154)	48 (53)	92 (101)

model plant I and model plant II would lose about 0.5 kg and 1.5 kg per year, respectively, from solvent dissolved in the recovered water.

#### 4.3 SOLID-WASTE DISPOSAL

Implementation of RACT in existing petroleum dry cleaning facilities would result in a net reduction in both the mass and solvent content of solid wastes. Installation of RACT cartridge filters would produce a dramatic decrease in emissions from solid wastes in petroleum dry cleaning plants. Cartridge filters, when compared with diatomite filters, have been shown to reduce solvent content of disposed filter wastes by 80 to 90 percent (Plaisance, 1981), thereby decreasing the overall quantity of solvent-laden solids introduced to the environment. In addition, the replacement of diatomite with cartridge filters will reduce the mass of solid waste generated by 60 percent, based on an average industry estimate of 3.57 kg of waste generated per 100 kg of throughput with a diatomite filter (Fisher, 1975) and 1.47 kg solid waste per 100 kg of throughput for a cartridge filter (Plaisance, 1981).

#### 4.4 ENERGY

Energy savings result from the implementation of RACT guidelines in both model plants. With the installation of RACT recovery dryers and cartridge filters in the model plants, annual expenditures for both steam and electricity are reduced by a combined average of 70 percent over utility costs for existing standard dryers and diatomite filters (see Section 5.2 and 5.3).

The energy value of recovered solvent is included in the overall analysis of petroleum dry cleaning plant energy consumption. One approach to this analysis that would be meaningful to the dry cleaning industry is to assume that all recovered solvent is resold at its current market value (\$0.53 per kg) and that the proceeds are used to purchase electricity at its current market value of \$0.0603 per kilowatt-hour (Vatavuk, 1980). This approach to energy conservation by solvent recovery illustrates a savings of energy accrued directly to the individual petroleum dry cleaning plant.

Table 4-3 delineates the impact of RACT implementation on model plant energy consumption per year based on the previously discussed



Table 4-3. ENERGY IMPACT OF EXISTING AND RACT EQUIPMENT<sup>a</sup>  
(in Gigajoules per year)

Model plant	Existing equipment	RACT equipment	Percent reduction
Model plant I	1,865	(660) <sup>b</sup>	135
Model plant II	6,070	(1,040)	120

<sup>a</sup>Based on 0.00314 GJ/kg steam and 0.0036 GJ/kWh electricity (Baumeister et al., 1978), and utility consumption and solvent recovery values calculated in Chapter 5.

<sup>b</sup>Numbers in parenthesis represent overall energy savings, based on savings from solvent recovery (at \$0.53 per kg) to purchase electricity at a cost of \$0.0603 per kWh.

approach. Considerable energy savings (over 140 percent for both model plants) arise from the installation of RACT equipment. A maximum annual energy savings of 6,260 GJ takes place in the model plant II, where solvent recovery in the dryers is optimized by the plant's high throughput without the additional solvent recovery due to the installation of cartridge filters. Model plant I shows an annual energy savings of 2,460 GJ, due to the combined effects of solvent recovery on energy consumption.

#### 4.5 REFERENCES FOR CHAPTER 4

Chevron Oil Co., 1980. Sales Brochure: Chevron Thinners and Solvents. EL Segundo, California.

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Baumeister, T., E. Avallone, and T. Baumeister, III. 1978. Marks' Standard Handbook for Mechanical Engineers. McGraw-Hill. New York, New York.

Plaisance, S. 1981. A Study of Solvent Drainage and Retention in Discarded Petroleum Dry Cleaning Cartridge Filter Elements. TRW Inc., Research Triangle Park, North Carolina (EPA Contract No. 68-02-3063).

Plaisance, S., J. Jernigan, G. May, and C. Chatlynnne. 1981. TRW Inc. Evaluation of petroleum solvent concentrations, emissions, and recovery in a solvent recovery dryer (EPA Contract No. 68-02-3063).

Saary, Z. 1981. Chevron Research Laboratory, Telecon with S. Plaisance, TRW Inc., July 20. Maximum solubility of Chevron petroleum solvent in water.

Vatavuk, W. 1980. Factors for Developing CTG Costs. Cost and Energy Analysis Section, Economic Analysis Branch. EPA/OAQPS. Research Triangle Park, North Carolina (Draft Document).

E. Determining compliance (482-18-35)

1. Visual inspection
2. VOC detector
3. EPA Method 25 or 25A
4. Alternatives

F. Visual Inspection points (482-18-36)

1. Hose connections, unions, couplings, and valves
2. Machine door gaskets and seatings
3. Filter head gaskets and seatings
4. Pumps
5. Base tanks and storage containers
6. Water separators
7. Filter sludge recovery
8. Distillation unit
9. Diverter valves
10. Cartridge filters
11. Saturated lint and basket

G. Information to be gathered for each dry cleaning establishment visited (482-18-37)

1. Dry cleaning equipment:
  - o Types (dry-to-dry, transfer)
  - o Capacity
2. Flow diagram for perc liquid/vapors
3. Pounds of clothes cleaned per load, day, month
4. Amount of solvent used per day, week, month (482-18-38)

5. Carbon adsorption/condensing (refrigeration)/scrubber equipment:
  - o Manufacturer
  - o Model number
  - o Year of installation
  - o New/retrofit
6. Frequency and time of steam out (carbon adsorbers)
7. Is the steamed carbon bed allowed to dry out (carbon adsorbers)? (482-18-39)
8. How much perc is recovered per steam out (carbon adsorbers)?
9. Does the amount of recovered perc vary? (are records available?)
10. Frequency of use of perc removal system (during dryer aeration cycle only, continuously, etc.) (482-18-40)
11. Sources at dry cleaning facility that are vented through the perc removal system
12. Cooling water temperature into and out of condenser (used during drying)
13. System operating (manpower) requirements.
14. Steam pressure to adsorber (carbon adsorbers) (482-18-41)
- \* 15. Has the carbon ever been replaced?
16. Describe any problems.
17. Is muck cooked properly? (482-18-42)
18. How long are cartridge drained?
19. Are cartridges dried?
- H. Inspection items for dry cleaning facilities with perc removal equipment (482-18-43)
  1. Inspect following for vapor leaks:
    - o Ductwork
    - o Improper gasket seating
    - o Other

2. Inspect following for liquid perc leaks:

- o Hose connections, unions, couplings, and valves
- o Machine door gaskets and seatings
- o Filter head gasket and seating (482-18-44)
- o pumps
- o Base tanks and storage containers
- o Water separators
- o Filter sludge recovery
- o Distillation unit
- o Diverter valves
- o Saturated lint from lint basket
- o Cartridge filters

3. Observe location of control system vent

4. Observe the following equipment to see where vented (482-18-45)

- o Perc removal system
- o Still
- o Muck cooler
- o Separators
- o Dry cleaning machine(s)
- o Other sources vented through perc removal system

5. Inspect perc removal system for lint buildup and corrosion problems (482-18-46)

6. Inspect floor pickup points for proper operation and for lint accumulation

7. Obtain samples of muck cooker and still bottoms if possible

8. Observe general housekeeping



# Degreasing

## 1.2 EPA's POLICY ON RACT REGULATIONS FOR DEGREASERS

EPA's guidelines for RACT as applied to degreasers are contained in Appendix B to this manual. Separate guidelines were issued for cold cleaners, open top vapor degreasers, and conveyORIZED degreasers. Each guideline is divided into two levels of control. Control System A consists of operating practices and simple, inexpensive control equipment. Control System B consists of System A plus additional requirements to improve the effectiveness of control.

### 1.2.1 Application of Control Systems A and B

An approvable State Implementation Plan (SIP) must require the application of Control System B throughout urban nonattainment areas (>200,000 population) seeking an extension and to all facilities emitting VOC's in excess of 100 tons per year in other nonattainment areas. Facilities emitting 100 tons per year or less of VOC's in other nonattainment areas must apply Control System A as a minimum. However, EPA encourages states to control all degreasers in nonattainment areas to the Control System B level.

### 1.2.2 EPA's Policy on Exemptions

The CTG recommends two exemptions for solvent metal cleaning processes. First, conveyORIZED degreasers with an air/vapor interface of less than 2.0 square meters should be exempted from the requirement for a major control device. Requirements for controlling these smaller units would not be cost effective and would tend to move the small conveyORIZED degreaser users to open top vapor degreasers which emit more solvent per unit of work. Second, open top vapor degreasers with an open area of less than 1.0 square meter of open area should be exempt from the application of refrigerated chillers and carbon adsorbers since these controls would not be cost effective. These two exemptions are the only ones EPA will approve in urban nonattainment areas. Blanket exemptions such as a 3 pound per day cutoff or exemptions for cold cleaners will not be approved.

In rural nonattainment areas EPA will approve exemptions for sources emitting less than 100 tons per year of VOC's. This would allow a blanket exemption for cold cleaners since a typical cold cleaner emits approximately 0.3 tons per year. However, SIP's will not be approved that exempt all open top vapor degreasers and conveyORIZED degreasers that individually emit



less than 100 tons per year in rural nonattainment areas because large scale users may have over 100 separate degreasing operations at one plant location. If a State chooses to exempt open top or conveyORIZED degreasing operations in rural nonattainment areas, the limitation should be 100 tons or less on a facility-wide basis based on annual solvent purchase records. Further, any exemption which distinguishes between open top vapor degreasers and conveyORIZED degreasers will not be approved because of the potential of switching between equipment types. Although conveyORIZED degreasers are larger emitters, they emit significantly less solvent than do open top vapor degreasers for an equivalent workload. Thus, it would not be advantageous to encourage degreaser operators to choose open top vapor degreasers in order to avoid regulations on conveyORIZED degreasers.

### 1.3 DEGREASING SOLVENTS

Degreasing solvents are organic chemicals derived principally from petroleum. They commonly include (i) petroleum distillates such as Stoddard, kerosene, heptane and cyclohexane, (ii) halogenated hydrocarbons such as methylene chloride, perchloroethylene, 1,1,1-trichloroethane, trichloroethylene and trichlorotrifluoroethane (FC-113), (iv) oxygenated organics such as acetone, methyl ethyl ketone, isopropyl alcohol and ethers, and (v) aromatics such as toluene, turpentine and xylene. Table 1-1 summarizes some of the important properties of common metal cleaning solvents.

Selection of a solvent for a particular application depends on the type of cleaning to be done (cold or vapor), the nature of the grease and other soil to be removed, and the level of cleanliness required. The purpose of the solvent is to dissolve oils, grease, waxes, tars, and in some cases, water. When these materials have been removed from the work, insoluble material such as sand, metal chips, buffing abrasives and so forth are flushed away at the same time. Consideration must be given to nonmetallic portions of the work to be cleaned. For example plastic may be dissolved or otherwise deteriorated by certain solvents. Other materials may not be able to stand the heat necessary to boil high boiling solvents in vapor degreasers.

Halogenated hydrocarbons are used universally in vapor degreasers for two reasons. A very important consideration in solvent selection is its flammability especially if the solvent must be heated to create a vapor zone. The halogenated hydrocarbons used commonly in vapor degreasers are nonflammable. Second, the vapors of halogenated hydrocarbons are approximately four times more dense than air. This property enhances the stability of the solvent vapor zone and thus reduces diffusion and convection losses. Petroleum solvents are among the most widely used in cold cleaners, especially in maintenance cleaners. If petroleum solvents are not adequate for a particular cleaning application, the operator may turn to any of the various alcohols, ketones, aromatics or halogenated hydrocarbons that are capable of doing the job.

TABLE 1-1

## COMMON METAL CLEANING SOLVENTS\*\*\*\*

Type of Solvent/ Solvent	Solvency for Metal Working Soils	TLV (ppm)	Flash Point	Evaporation Rate**	Water Solubility (% wt.)	Boiling Point (Range)	Pounds Per Gal.	Price Per Gal.
Alcohols								
Ethanol (95%)	poor	1000*	60°F	24.7	∞	165-176°F	6.76	\$ 1.59
Isopropanol	poor	400*	55°F	19	∞	179-181°F	6.55	\$ 1.26
Methanol	poor	200*	58°F	45	∞	147-149°F	6.60	\$ 1.11
Aliphatic Hydrocarbons								
Heptane	good	500*	<20°F	26	<0.1	201-207°F	5.79	\$ 0.86
Kerosene	good	500	149°F	0.63	<0.1	354-525°F	6.74	\$ 0.66
Stoddard	good	200	105°F	2.2	<0.1	313-380°F	6.38	\$ 0.62
Mineral Spirits 66	good	200	107°F	1.5	<0.1	318-382°F	6.40	\$ 06.2
Aromatic Hydrocarbons								
Benzene***	good	10*	10°F	132	<0.1	176-177°F	7.36	--
SC 150	good	200	151°F	0.48	<0.1	370-410°F	7.42	\$ 1.06
Toluene	good	200*	45°F	17	<0.1	230-232°F	7.26	\$ 0.90
Turpentine	good	100*	91°F	2.9	<0.1	314-327°F	7.17	\$ 2.40
Xylene	good	100*	81°F	4.7	<0.1	281-284°F	7.23	\$ 0.96
Chlorinated Solvents								
Carbon Tetrachloride***	excellent	10*	none	111	<0.1	170-172°F	13.22	\$ 3.70
Methylene Chloride	excellent	500*	none	363	0.2	104-105.5°F	10.98	\$ 2.83
Perchloroethylene	excellent	100*	none	16	<0.1	250-254°F	13.47	\$ 3.33
1,1,1-Trichloroethane	excellent	350*	none	103	<0.1	165-194°F	10.97	\$ 2.78
Trichloroethylene	excellent	100*	none	62.4	<0.1	188-190°F	12.14	\$ 3.13
Fluorinated Solvents								
Trichlorotrifluoro- ethane (FC-113)	good	1000*	none	439	<0.1	117°F	13.16	\$ 7.84
Ketones								
Acetone	good	1000*	<0°F	122	∞	132-134°F	6.59	\$ 1.45
Methyl ethyl ketone	good	200*	28°F	45	27	174-176°F	6.71	\$ 1.74

\*Federal Register, June 27, 1974, Vol. 39, No. 125.

\*\*Evaporation Rate determined by weight loss of 50 mls in a 125 ml beaker on an analytical balance. (ml/dm<sup>2</sup>/min) (Dow Chemical Co., method).

\*\*\*Not recommended or sold for metal cleaning (formerly standards in industry).

\*\*\*\*Primary source from The Solvents and Chemicals Companies "Physical Properties of Common Organic Solvents" and Price List (July 1, 1975).

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## CHAPTER 2

### COLD CLEANERS

#### 2.1 PROCESS DESCRIPTION

##### 2.1.1 Unit Operation

Manually operated cold cleaners provide solvent degreasing for low volume workloads of small, variably shaped automotive and general plant maintenance parts, and for fabricated metal products. The basic steps involved in degreasing with a cold cleaner include soaking with solvent in the dip tank, and drying the work of solvent after cleaning.

The solvent dissolves the dirt/grease on the part to be cleaned as it is immersed. The part is usually lowered into the solvent bath in a metal basket. The cleaning action is often enhanced by agitation of the solvent and by spraying solvent on the part. After cleaning the part is dried by allowing evaporation and drainage of the solvent on drying racks which are located inside the cleaner or on external racks which route the drainage back into the cleaner.

Many cold cleaners which are equipped with sprayers or pump agitation utilize filters in the pump piping system to remove sludge and dirt thus extending the useful life of the solvent.

##### 2.1.2 Types of Cold Cleaner Degreasers

Cold cleaners can be generally classified as maintenance and manufacturing degreasers. Maintenance cold cleaners are by far more common and are used for automotive and plant maintenance cleaning. Maintenance cold cleaners are usually smaller, simpler and less expensive than manufacturing cleaners. A typical size of maintenance cold cleaners is approximately  $0.4 \text{ m}^2$  ( $4 \text{ ft}^2$ ) of opening and  $0.1 \text{ m}^3$  (30 gallon) solvent capacity.

Manufacturing cold cleaners are employed in applications where a larger volume workload, a higher degree of cleaning and larger parts to be cleaned dictate the use of larger more specialized degreasers. Manufacturing cold cleaners are usually found in metal fabrication facilities. The larger size, greater workload and higher solvency needed to achieve the degree of cleaning required of manufacturing cold cleaners result in more solvent emissions than is usually released by maintenance cold cleaners.

The variety of specific applications for cold cleaners offers a method for more accurately classifying cold cleaners by agitation technique and tank design.

The two basic designs are the dip tank and the spray sink, although many cold cleaners employ both cleaning methods. Dip tank cleaners (Figure 2-1) allow for more thorough cleaning by providing for soaking dirty parts in the liquid solvent bath. The spray sink (Figure 2-2) is simple, inexpensive and used when a relatively low degree of cleanliness is required. As can be seen from Figure 2-2, the liquid solvent tank is not accessible for soaking parts; however, solvent losses due to bath evaporation are insignificant with this arrangement.

### 2.1.3 Operation of Degreaser Components

Agitation of the liquid solvent in dip tanks further improves cleaning efficiency and can be provided by pumping, compressed air, vertical motion or ultrasonic vibration. Pump agitation rapidly circulates solvent through the tank. Compressed air is dispersed from the bottom of the tank in air agitation. The rising bubbles scrub the surface of the work. Vertically agitated cold cleaners vibrate the dirty parts up and down in the tank with a motor driven, cam actuated device usually operated at 60-70 cycles per minute. Ultrasonic agitation vibrates the solvent with high frequency sound waves. This vibration causes cavitation, the implosion of bubbles of vaporized solvent on the surface of the parts, which breaks down the dirt film. To optimize cavitation, the solvent is usually heated to a specific temperature.

Other degreaser components that are discussed in this chapter include the cover, spray pump and hose, internal and external drain boards and the parts basket.

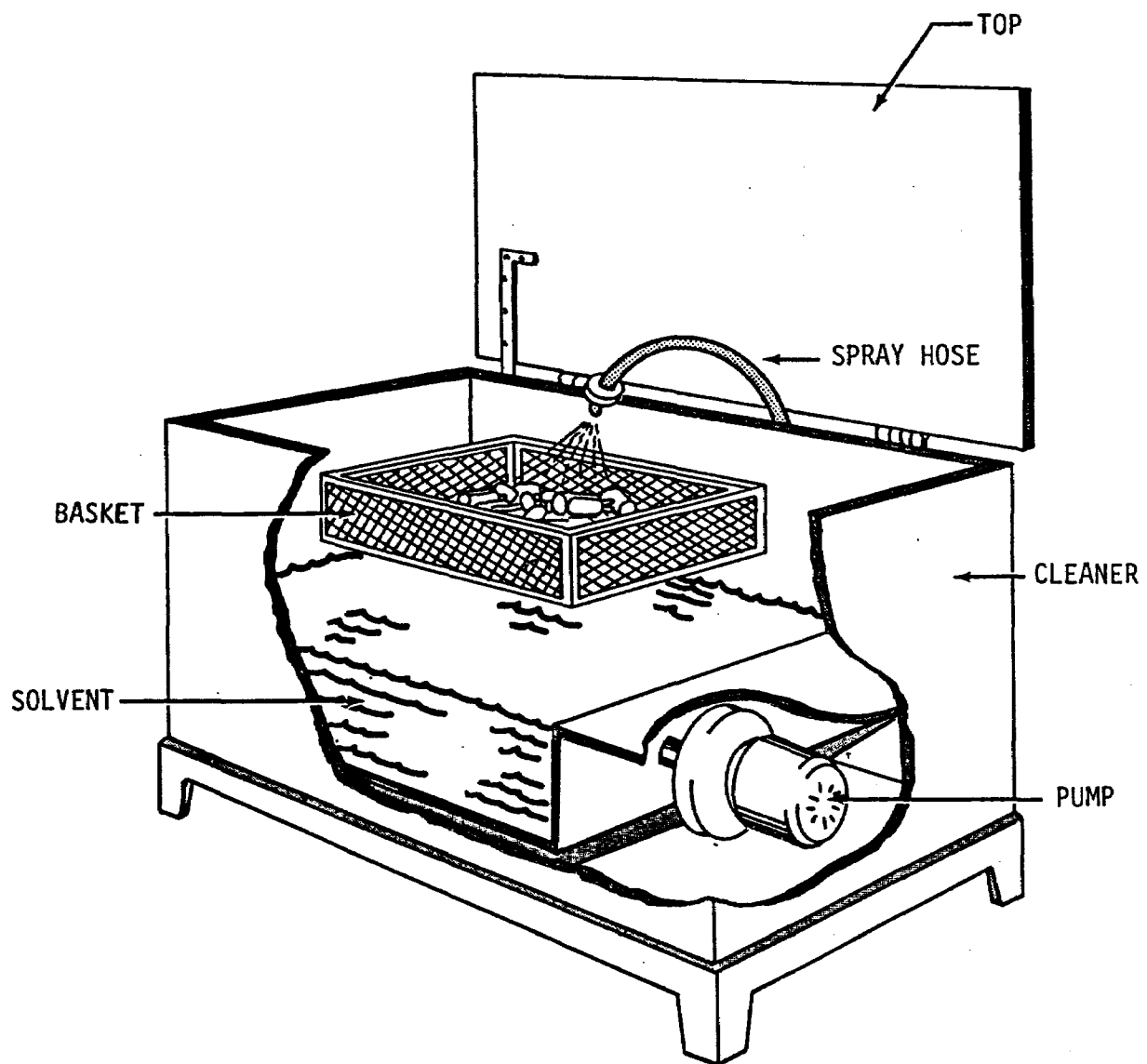
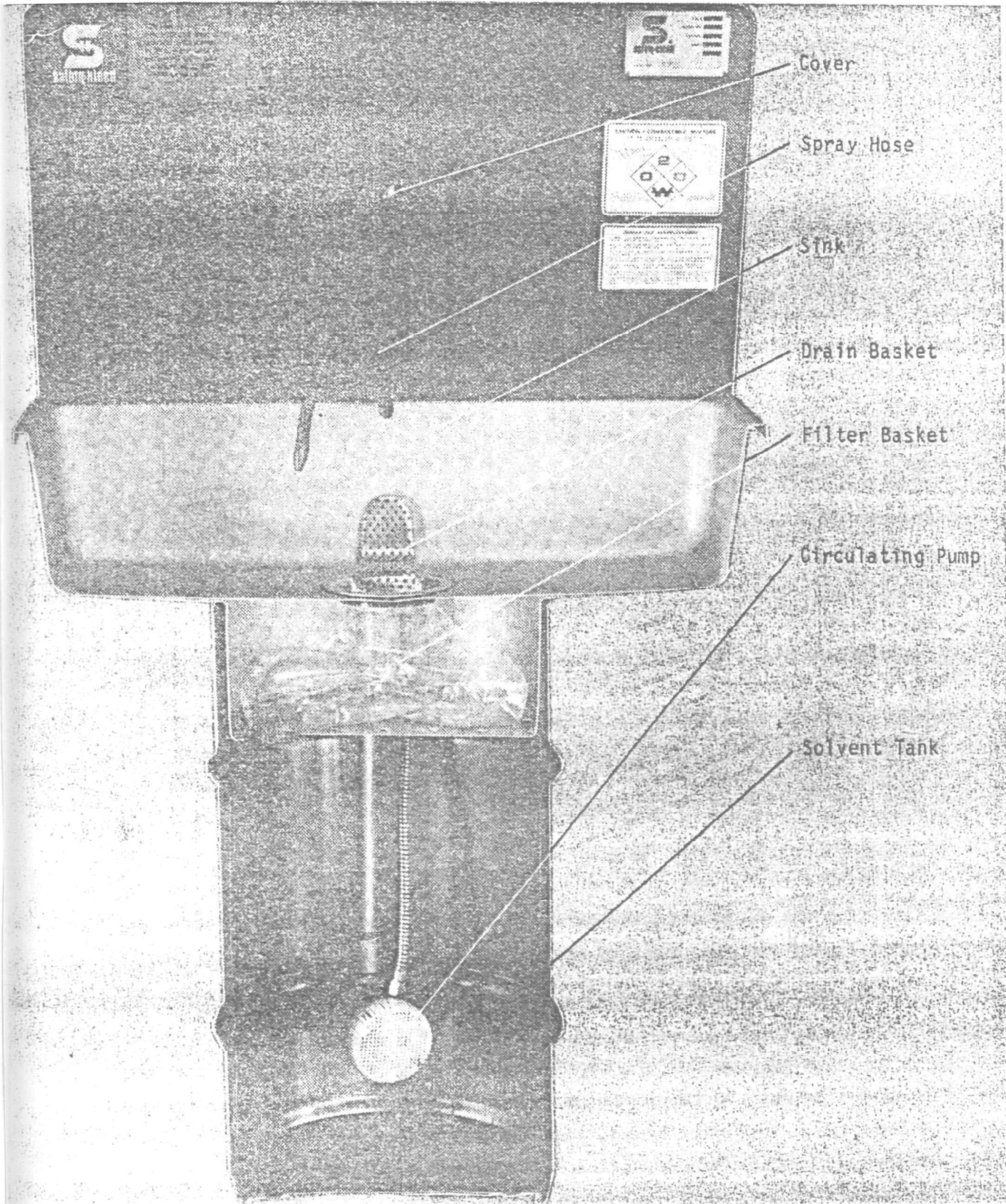


Figure 2-1. Cold Cleaner

Figure 2-2  
**SPRAY SINK**



(Safety-Kleen, New Berlin, Wisconsin)

## 2.2 ATMOSPHERIC EMISSIONS

### 2.2.1 Emission Points

Solvent evaporation is the basic emission mechanism for cold cleaners and the emission rates vary with size, frequency of use, and manner of their operation. Based on national consumption data, cold cleaners each emit an average of 0.3 metric tons of solvent vapor per year. Maintenance cold cleaners emit an average of 0.25 metric tons per year and manufacturing cold cleaners emit an average of 0.5 metric tons per year. Emissions from manufacturing cleaners are larger primarily because their units are used more steadily in the course of a work day than maintenance cleaners.

There are several means by which organic solvent vapors can be emitted to the atmosphere from a cold cleaner. These are illustrated in Figure 2-3. Cold cleaners are very rarely hooded or vented to the outside. Thus, an obvious emission point is the direct evaporation of solvent from the tank to the atmosphere (Location 1). Carry out emissions (Location 2) result from liquid solvent that is physically carried out of the degreaser on the cleaned parts and subsequently evaporates. Mechanical agitation of the solvent bath (Location 3) increases evaporative losses. Turbulence from spraying (Location 4) increases emissions as does overspraying (spraying outside the tank), and excessive spray velocity. Finally, the emissions from the disposal of waste solvent (Location 5) can vary significantly, depending on the techniques employed.

### 2.2.2 Parameters Affecting Rate of VOC Emissions

Bath evaporation occurs whenever the degreaser's hood is open but is increased by air movement such as drafts or ventilation and is directly related to the evaporation rate of the solvent used. The solvents most commonly used by cold cleaners are Stoddard solvents, safety solvents (blends of chlorinated hydrocarbons and petroleum solvents), ketones and fluorinated solvents.

Bath evaporation can be minimized during operation when adequate freeboard height (distance from solvent level to top of the cold cleaner) is employed. Freeboard height requirements are often expressed as freeboard ratio, which is the ratio of freeboard height to the width of the degreaser.



Bath evaporation emissions can be further reduced by keeping the degreaser cover closed during degreasing operations except when parts are removed from or added to the degreaser. Various types of covers are available. Sliding plastic covers which roll up on a rotating shaft at one end of the degreaser when not in use are the most simple and easy to use. Some large degreaser covers use counterweights. Electrically or pneumatically powered covers are also used. Guillotine covers are another easily operated type found on many degreasers. Generally, the amount of effort required will dictate the frequency of use of the cover and therefore dictate the amount of bath evaporation. Hatch type covers such as the one shown in Figure 2-3 usually have a fusible link support arm so that they will slam shut in the event that a fire breaks out. Local fire and safety codes often require such devices.

Air flow into the tank also influences solvent evaporation. The degreaser should be located to minimize evaporative losses due to work fans and ventilation ducts. Partitions, curtains or baffles help create a still air zone around the degreaser and can reduce bath evaporation emissions.

Control devices are required for cold cleaners with heated ( $>50^{\circ}\text{C}$ ) or highly volatile (volatility  $>4.3$  Kpa measured at  $38^{\circ}\text{C}$ ) solvent. (The term "cold cleaner" applies even if the solvent is heated, as long as the objective is not to create a vapor zone.) The control devices which comply with the RACT guidelines are refrigerated chillers, freeboard ratios  $>0.7$ , carbon adsorption and water blankets. If properly applied, maintained and operated, these control devices can significantly reduce solvent emissions.

Refrigerated chillers are condensing coils located peripherally along the freeboard, which condense the solvent vapor before escaping from the degreaser. Carbon adsorption is a device which reclaims solvent from the air/vapor mixture escaping the cleaner. These are rarely used on cold cleaners.

A water blanket is a layer of water in the dip tank on top of the solvent which provides a vapor barrier between the solvent and the atmosphere. The solvent must be heavier than and insoluble in water.

Carry-out emissions occur when wet parts are removed from the degreaser and are influenced by: drying procedure, location and type of drying racks, size of the parts being cleaned, and the volume of the workload.

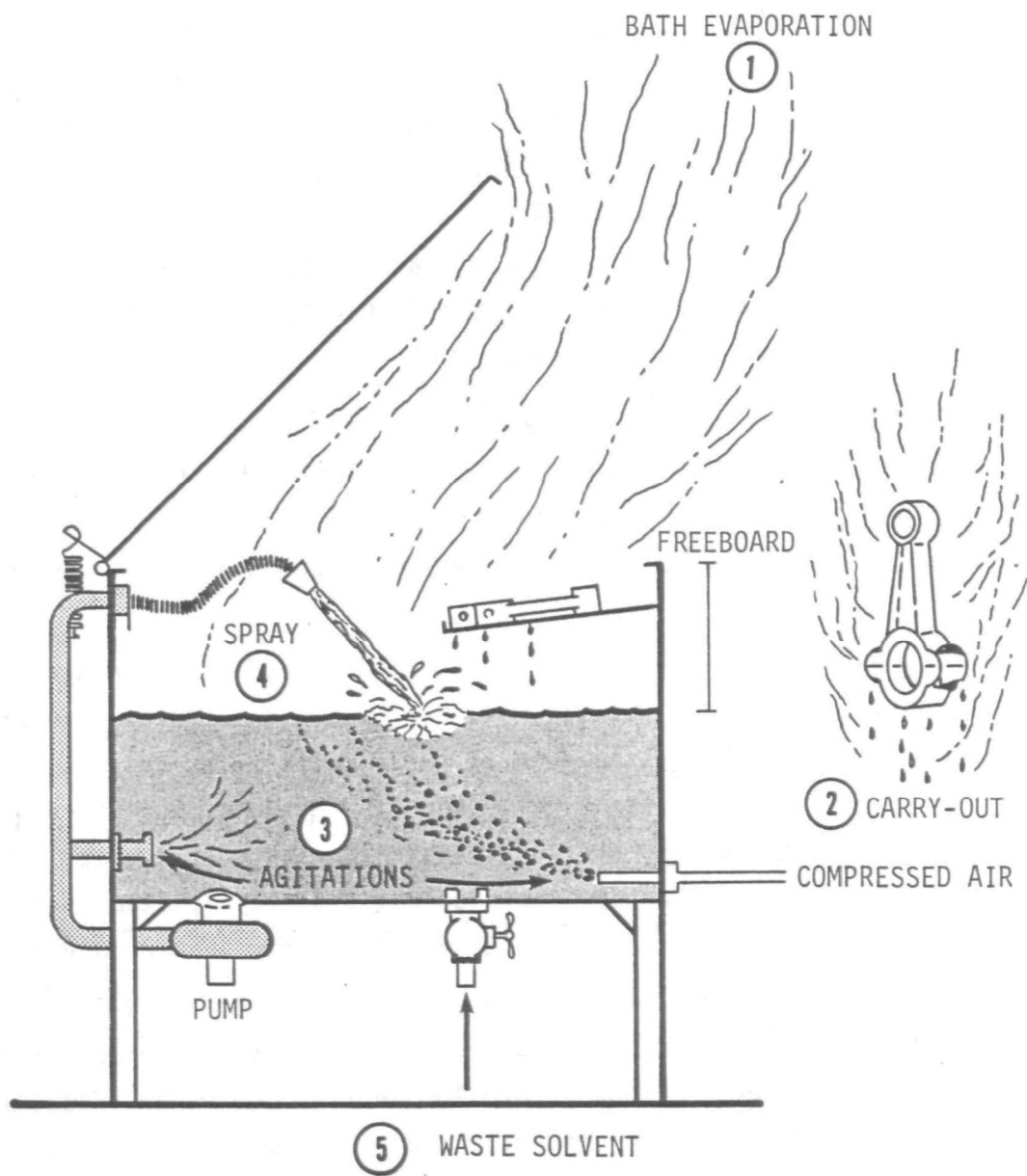


Figure 2-3. Cold Cleaner Emission Points

Drainage of any solvent entrained in crevices or depressions in the parts prior to moving them to external drying racks, and closing the hood during drying if internal racks are used, minimizes carry-out emissions. If external racks are employed, drains which return the carried-out solvent to the degreaser tank reduce solvent loss. As recommended from ASTM D-26, cleaned parts should be drained for 15 seconds.

The surface area of the parts workload affects carry-out since the mass-transfer of solvent by evaporation is directly proportional to the amount of solvent-laden surface area.

Agitation increases emissions. Agitation intensity, amount of heat input, if any, and solvent volatility all affect VOC emissions from cold cleaners. Proper operating procedures can minimize emission during agitation. Emissions are insignificant if the cover is closed during agitation and the bath should be agitated only during cleaning. If air or pump agitation is used, the flow rate should be adjusted to the minimum amount required to achieve the desired degree of cleaning. Air flow rate should not exceed 0.01 to 0.03 m<sup>3</sup> per minute per square meter of opening.

Evaporation from spraying will vary with spray pressure, spray droplet size and distribution, amount of overspray which splashes from the sink, solvent volatility and amount of time the spray is in use.

Spray operating techniques can lower emissions. Care to eliminate overspray, adjusting spray to a solid fluid stream and limiting spray fluid pressure to a maximum of 10 psig will reduce solvent losses by evaporation.

Waste solvent evaporation is the single largest mechanism for solvent emissions from cold cleaning. The amount of solvent disposed by a single degreaser is dependent upon the degreaser size, frequency of operation, degree of cleanliness required and amount of oil and dirt to be removed. If a cold cleaner spray system is equipped with a filter, the frequency of disposal is reduced.

Leaks in spray lines and agitation pump discharge lines which are under pressure can cause significant solvent emissions. Pipe flanges, drain valves, corroded tanks (especially when using an acidic solvent or if water is present in the solvent) can also leak if not properly maintained.

Acceptable methods of disposal include recycling by distillation, proper incineration, distillation (recovery of solvent for re-use) and chemical landfilling if waste is enclosed in sealed containers and surrounded by impermeable soil.

Disposal by flushing solvent into sewers, spreading solvent for dust control and landfilling without proper containers or prevention of leaching all result in complete evaporative emissions of waste solvent to the atmosphere.

Solvent emissions are greatly influenced by the type of solvent. Obviously volatility and operating temperatures are significant parameters affecting emissions. Highly toxic solvents are more conscientiously controlled to protect workers and comply with OSHA regulations. Solvent costs often determine the care with which degreasers are operated. More expensive solvents are usually conserved by the same procedures which reduce emissions and are more likely to be recycled.

## 2.3 EMISSION CONTROL METHODS

The EPA Control Technology Guideline (CTG) document for solvent metal cleaning identifies a number of control strategies for reducing volatile organic emissions from cold cleaning degreaser operations. These form the basis of defining RACT for the cold cleaning degreasers and should therefore be the focal point of a field inspection. The CTG suggests two levels of control. (See Table 2-1). Level A could reduce cold cleaning emissions by 50% (+20%) and Level B may achieve a reduction of 53% (+20%). The range represents the limits of reduction for poor operating procedure (-20%) and good operating procedure (+20%). The estimated benefit from Level B only slightly exceeds that from Level A, assuming low volatility solvents. This is because the additional devices required in Level B generally control only bath evaporation which represents only 20% to 30% of the total emissions from an average cold cleaner. For cold cleaners using highly volatile solvents, bath evaporation may constitute 50% of the total emissions, and it is estimated that Level B would then achieve an emissions reduction of 69% (+20%) and a 55% (+20%) reduction for Level A.

The preceding discussion on the parameters affecting the rate of VOC emissions (Section 2.2.2) explicitly identifies the equipment and operating procedures necessary to implement the RACT control strategies except for the disposal of waste solvent. Dirt, grease, oil, metal chips and the like slowly build up in the liquid solvent over a period of time and eventually severely affects its ability as a cleaning agent. This usually occurs when the solvent contamination level reaches about 10 percent by volume. It is fairly common for the small operator to secure a service contract that provides for reclaiming the spent solvent. The contractor distills the spent solvent and returns it to users for a fee. One organization rents the cold cleaner and provides the solvent reclamation service as a package deal. Large operations that use scores of manufacturing cold cleaners sometimes operate stills on-site to reclaim the solvent. Distillation, proper landfilling, and incineration (which is not commonly used) will meet the RACT operating requirements ("not greater than 20 percent can evaporate into the atmosphere"). Disposal of the waste solvent (and still bottoms) at landfills may be subject to hazardous waste disposal regulations. EPA has proposed regulations governing the disposal of such material in the Federal Register at 43FR58946 (December 18, 1978).

TABLE 2-1

CONTROL SYSTEMS FOR COLD CLEANING

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Control System A

Control Equipment

1. Cover
2. Facility for draining cleaned parts
3. Permanent, conspicuous label, summarizing the operating requirements

Operating Requirements:

1. Do not dispose of waste solvent or transfer it to another party, such that greater than 20 percent of the waste (by weight) can evaporate into the atmosphere.\* Store waste solvent only in covered containers.
2. Close degreaser cover whenever not handling parts in the cleaner.
3. Drain cleaned parts for at least 15 seconds or until dripping ceases.

Control System B

Control Equipment:

1. Cover: Same as in System A, except if (a) solvent volatility is greater than 2 kPa (15 mm Hg or 0.3 psi) measured at 38°C (100°F),\*\* (b) solvent is agitated, or (c) solvent is heated, then the cover must be designed so that it can be easily operated with one hand. (Covers for larger degreasers may require mechanical assistance, by spring loading, counterweighting or powered systems.)
2. Drainage facility: Same as in System A, except that if solvent volatility is greater than about 4.3 kPa (32 mm Hg or 0.6 psi) measured at 38°C (100°F), then the drainage facility must be internal, so that parts are enclosed under the cover while draining. The drainage facility may be external for applications where an internal type cannot fit into the cleaning system.
3. Label: Same as in System A
4. If used, the solvent spray must be a solid, fluid stream (not a fine, atomized or shower type spray) and at a pressure which does not cause excessive splashing.
5. Major control device for highly volatile solvents: If the solvent volatility is > 4.3 kPa (33 mm Hg or 0.6 psi) measured at 38°C (100°F), or if solvent is heated above 50°C (120°F), then one of the following control devices must be used:
  - a. Freeboard that gives a freeboard ratio\*\*\*  $\geq 0.7$
  - b. Water cover (solvent must be insoluble in and heavier than water)
  - c. Other systems of equivalent control, such as a refrigerated chiller or carbon adsorption.

Operating Requirements:

Same as in System A

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\*Water and solid waste regulations must also be complied with.

\*\*Generally solvents consisting primarily of mineral spirits (Stoddard) have volatilities - 2 kPa.

\*\*\*Freeboard ratio is defined as the freeboard height divided by the width of the degreaser.

FIGURE 2-4

EXAMPLE WORKSHEET FOR FIELD INSPECTION OF

COLD CLEANERS

1. BUSINESS LICENSE NAME OF CORPORATION, COMPANY, OR INDIVIDUAL OWNER OR GOVERNMENTAL AGENCY:		
2a. MAILING ADDRESS:	2b. PLANT ADDRESS WHERE THIS DEGREASER IS LOCATED:	
3. SOURCE NO. (PERMIT NUMBER, NEDS ID, ETC.):		
4. NAME AND TITLE OF COMPANY REPRESENTATIVE:		
5. TELEPHONE NO.:		
6. NAME OF OFFICIAL CONDUCTING INSPECTION:		
7. DEGREASER		
MANUFACTURER: _____ MODEL NO. _____ SERIAL NO. _____		
INSIDE DIMENSIONS OF TANK (FT.): _____ WIDE X _____ LONG X _____ DEEP		
TYPE OF DEGREASER: SPRAY SINK <input type="checkbox"/> DIP TANK <input type="checkbox"/>		
8. TITLE AND CODE NUMBERS OF DRAWINGS, SPECIFICATIONS, STANDARDS, CODES, PROCEDURES AND DOCUMENTS USED WITH THE INSPECTION		
9. TYPE OF SOLVENT IN USE (SPECIFIC NAME AND MANUFACTURER):		
INSPECTION OBSERVATIONS		
RACT REQUIREMENT	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATION
<u>CONTROL EQUIPMENT</u>		
1. Cover	o Observe if a cover is installed and if it is closed when parts are not being handled in the degreaser.	
2. Cover must be easily operated with one hand if: - Solvent volatility >2 kPa (measured at 38°C) - Solvent is agitated - Solvent is heated	o Observe if cover can be operated with one hand. Observe if solvent is heated or agitated. If degreaser cover is large, check for mechanical assistance for operation. Determine the solvent type and its volatility. Vapor pressures for common solvents can be found in Chapter 1 of this manual.	
3. Drainage Facility	o Observe if drainage racks are provided. If drainage racks are external to the degreaser, observe if drainage is routed to the solvent bath.	
4. Internal drainage facility is required if: - Solvent volatility > 4.6 kPa (measured at 38°C)	o Observe if drainage racks are internal. Determine solvent volatility.	

FIGURE 2-4

(Continued)

RACT REQUIREMENT	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATION
5. Solvent spray must be a solid fluid stream and at a pressure that does not cause splashing.	o Observe if spray forms a mist or shower type consistency. Check for splashing above degreaser freeboard	
6. Permanent conspicuous label summarizing operating requirements.	o Observe if label is clearly displayed, complete and permanently fastened to degreaser	
7. If solvent volatility >4.3 kPa measured at 38°C, or solvent temperature is > 50°C then one of the following control measures must be used.  a. Freeboard Ratio $\geq 0.7$  b. Water Cover  c. Other systems of equivalent control such as chiller or carbon adsorption	o Determine if requirement is applicable  o Measure solvent temperature (if heated) with thermometer  o Calculate from degreaser dimensions. Freeboard ratio = $\frac{\text{Freeboard}}{\text{Width}}$  o Observe if the solvent is covered with water.  o Determine if appropriate device is installed and operational	
<u>OPERATING REQUIREMENTS</u>		
1. Do not dispose of waste solvent or transfer it to another party such that greater than 20% (by weight) can evaporate to the atmosphere. Store waste solvent only in covered containers.	o Determine if source has inhouse reclamation facility (i.e. still) or a service contract with a solvent reclamation firm.  o Confirm that storage is done with covered containers. Note whether containers leak.	
2. Close degreaser cover whenever not handling parts in the cleaner.	o Observe the operation	
3. Drain parts for at least 15 seconds or until parts are dry.	o Observe this operation. Time if necessary, or determine if parts are dry when removed from drying rack.	



## CHAPTER 3

### OPEN TOP VAPOR DEGREASERS

#### 3.1 PROCESS DESCRIPTION

##### 3.1.1 Unit Operation

Open top vapor degreasers provide an efficient and economical method for preparing clean, dry articles for subsequent finishing or fabricating. There are several configurations in use for open top degreasers; all are similar in basic design. In the simple vapor method, cleaning results from the condensation of solvent vapors on the cool surface of the article; the dissolving and flushing action of the condensate removes the soil. When the article reaches the temperature of the solvent vapor, no more condensation (or cleansing) occurs and the article is removed from the vapor zone. Other cleaning methods involve various combinations of the simple vapor method with immersion and spray-ind with liquid solvent.

Open top vapor degreasers utilize nonflammable solvent contained in the lower area of the degreaser, referred to as the boiling sump. The solvent is boiled to produce a vapor zone, the height of which is controlled by cooling coils installed above the vapor zone. The "cold work" introduced into the vapor space of the degreaser must be at a temperature lower than the vapor zone in order to cause the solvent vapors to condense on the work surfaces and flush the oil and other foreign matter off with the liquid condensate. The removed material accumulates in the boiling sump and only the pure vapor comes in contact with the work load. In either case, flushing is often followed by pure solvent spray and/or liquid immersion. The cool, pure liquid solvent reduces the temperature of the work surface below the vapor temperature, producing a second vapor condensation flushing action on the work surfaces. When the work pieces are removed from the degreaser, they should be clean, dry, and ready for further processing.

##### 3.1.2 Types of Open Top Vapor Degreasers

Open top vapor degreasers are most suitable in situations where the work flow is variable or intermittent. Otherwise, a conveyORIZED degreaser might be the equipment preferred. Essentially, there are three variations of vapor degreasing: (1) straight vapor, (2) liquid immersion-vapor, and (3) vapor-spray-vapor degreasing.

- o Straight Vapor: In this unit, the article to be cleaned is lowered into the vapor zone and held there until it reaches the vapor temperature, at which point vapors cease condensing on the article. It is gently agitated to enhance drainage of trapped liquid solvent. Then, it is brought into the freeboard area and allowed to dry for a moment before being removed from the degreaser. Figure 3-1 is a cut away sketch of a straight vapor degreaser. As with any open top arrangement, the work to be cleaned may be lowered manually or with an overhead hoist with hooks or long handle baskets. Hands should never be placed below the vapor line.
  
- o Liquid Immersion - Vapor: Immersion of the work in the hot or boiling solvent is preferred; (i) for closely nested work, (ii) for excessive soil levels (iii) for light gauge work, (iv) when ultrasonics is necessary, and (v) for parts with intricate patterns. Figures 3-2 to 3-4 show various equipment configurations for this technique. Typically, the work is lowered into the vapor zone for a straight vapor rinse, then lowered into the liquid immersion chamber to be rinsed. This will cool the work slightly. Then, the work is raised into the vapor zone for a second vapor rinse. The 2-compartment unit shown in Figure 3-3 may be operated in this fashion or, if necessary for proper cleaning, the work may be lowered directly into the boiling sump, then rinsed in the condensate reservoir. (Care should be taken not to drag dirty solvent from the boiling liquid tank to the rinse tank). After the liquid rinse the work is given a vapor rinse above the condensate reservoir. The reservoir is often heated to ensure that the liquid rinse is warm. Similarly, the 3-compartment unit depicted in Figure 3-4 may be outfitted to operate with two or three liquid immersions.
  
- o Vapor - Spray - Vapor: This is similar to straight vapor degreasing except that as soon as the work is below the vapor level, it is sprayed with cool condensate. After spraying is complete the work should remain in the vapor zone until it reaches the vapor temperature and condensation has stopped. Figure 3-5 is a schematic of a spray unit with an offset condenser. Spraying should be done as far below the top of the vapor line as possible so that evaporative losses due to spraying are minimized.

Some units, especially larger ones, are equipped with a lip exhaust. A lip exhaust draws air laterally across the top of the degreaser and vents the air directly to the roof or to a carbon adsorption unit. Figure 3-6 is a schematic of one of these units. The primary purpose of a lip exhaust is to limit worker exposure to solvent vapors.

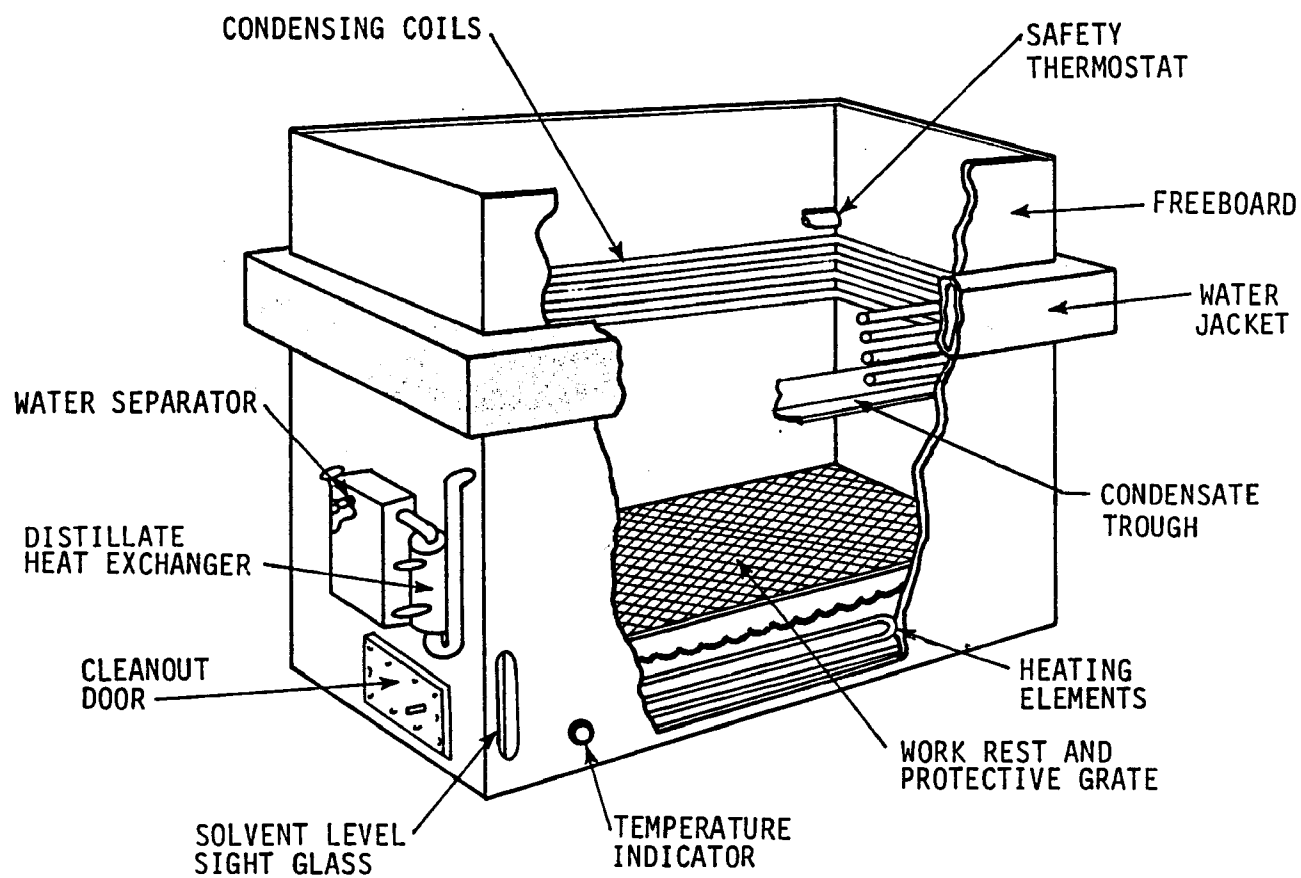


Figure 3-1. Single Compartment Vapor Degreaser

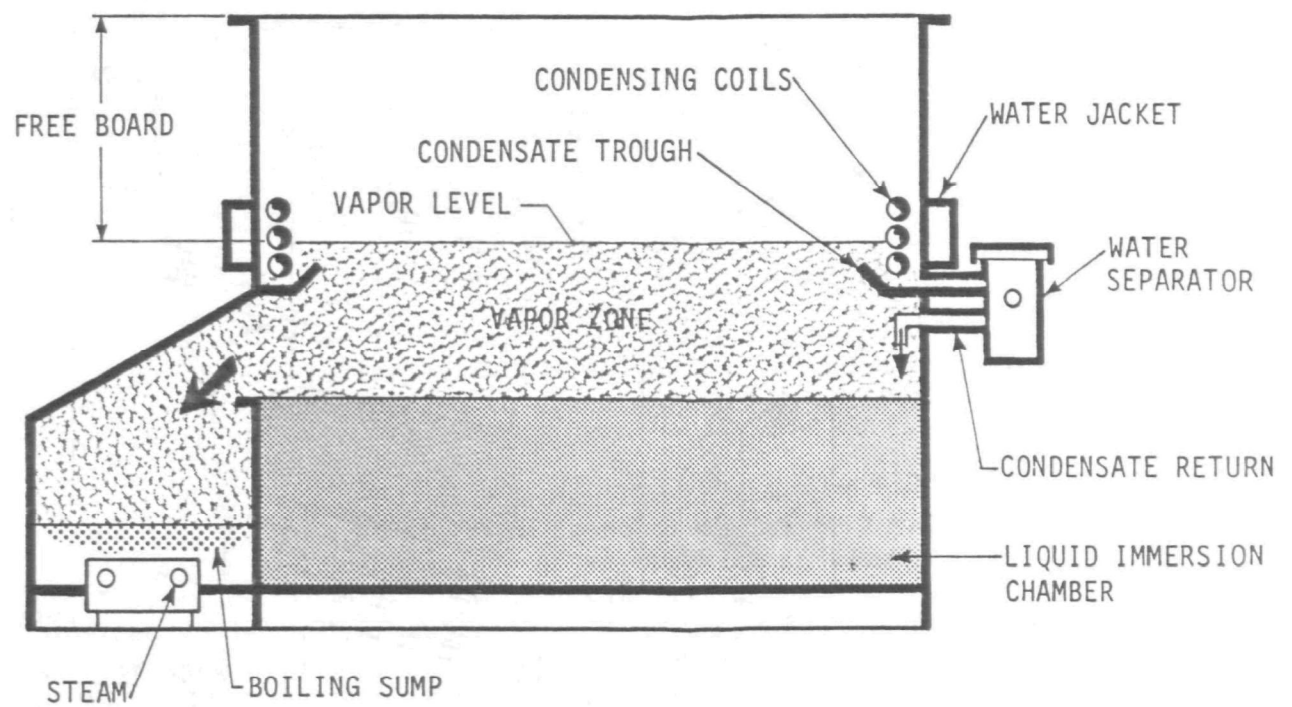


Figure 3-2. Liquid-Vapor Degreaser

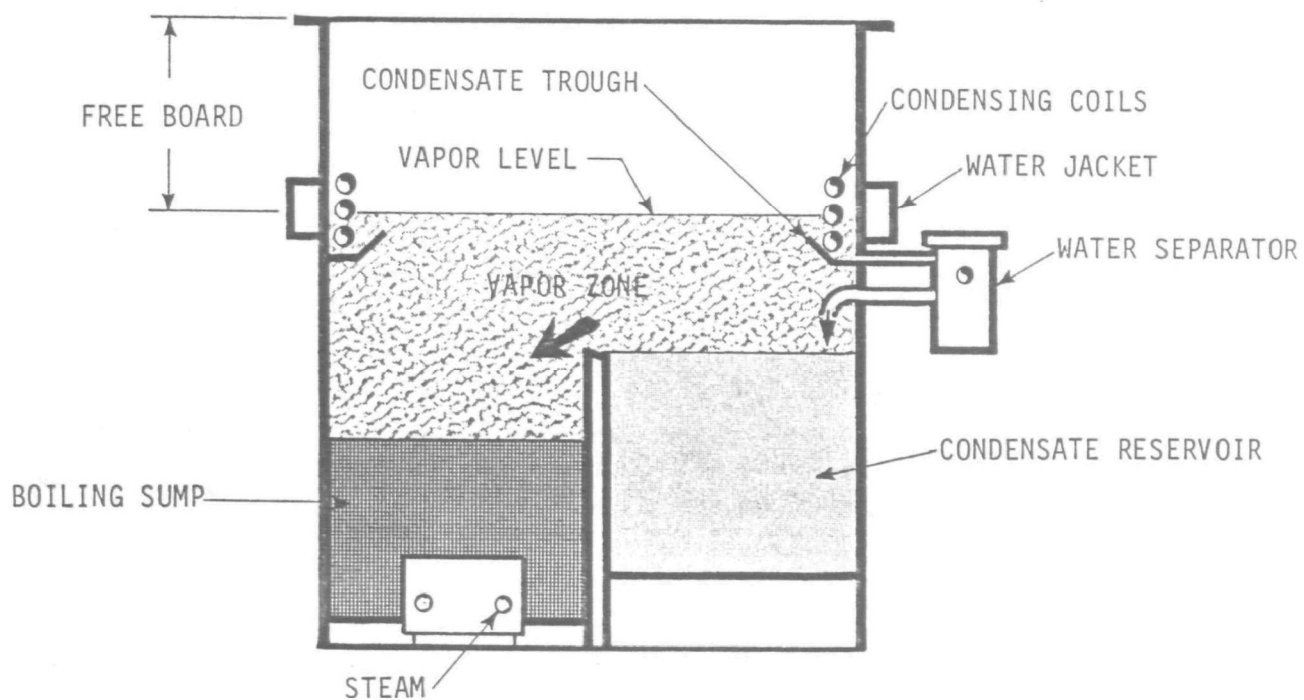


Figure 3-3. Liquid-Liquid-Vapor Degreaser 2 Compartment

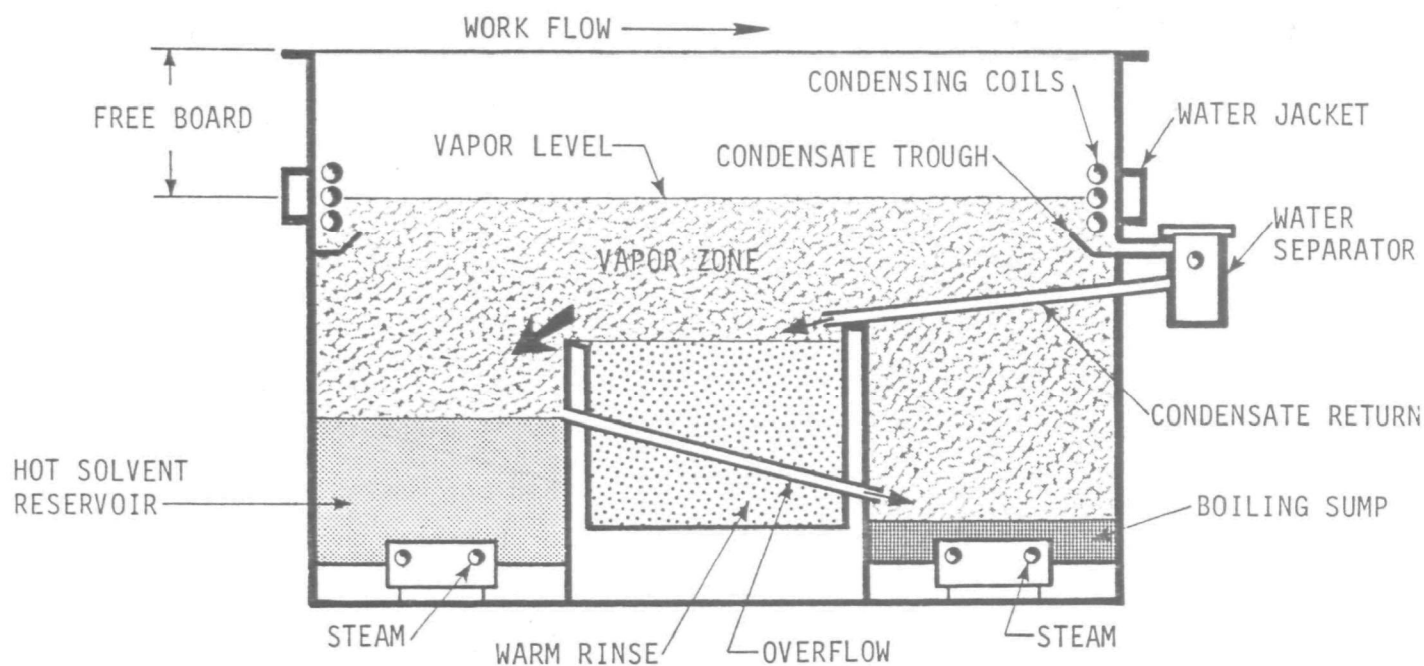


Figure 3-4. Liquid-Liquid-Vapor Degreaser 3 Compartment

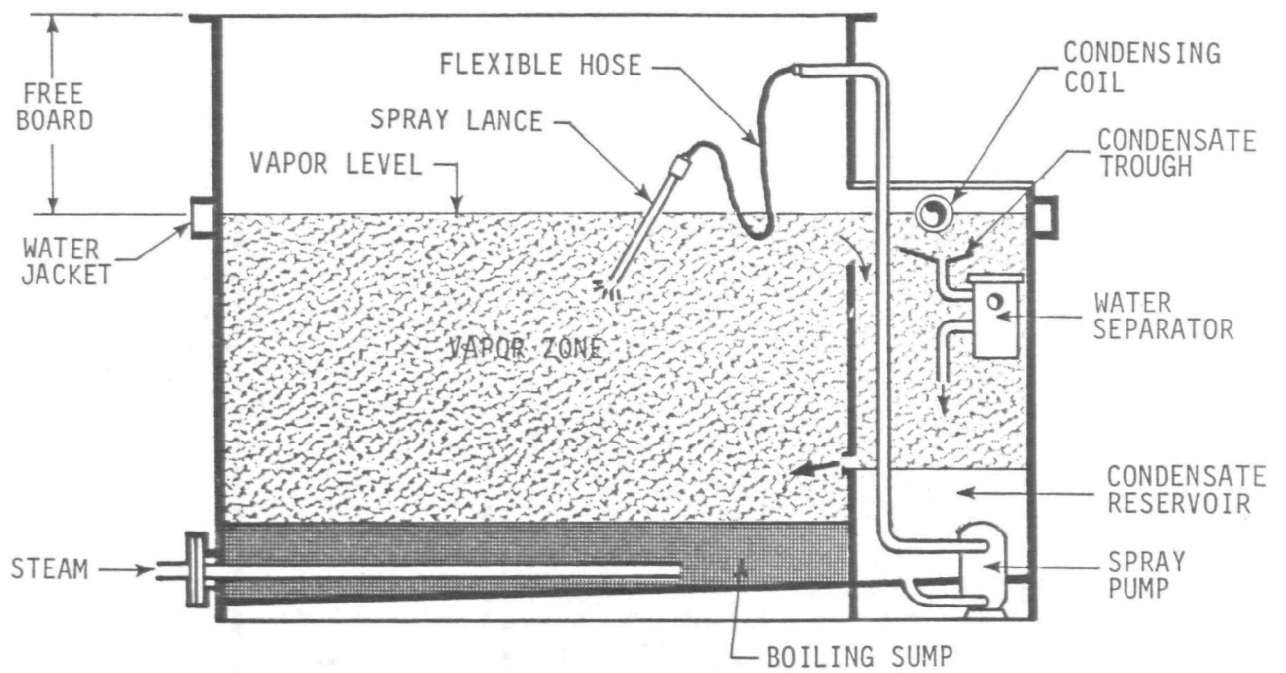


Figure 3-5. Offset Condenser Vapor-Spray-Vapor Degreaser

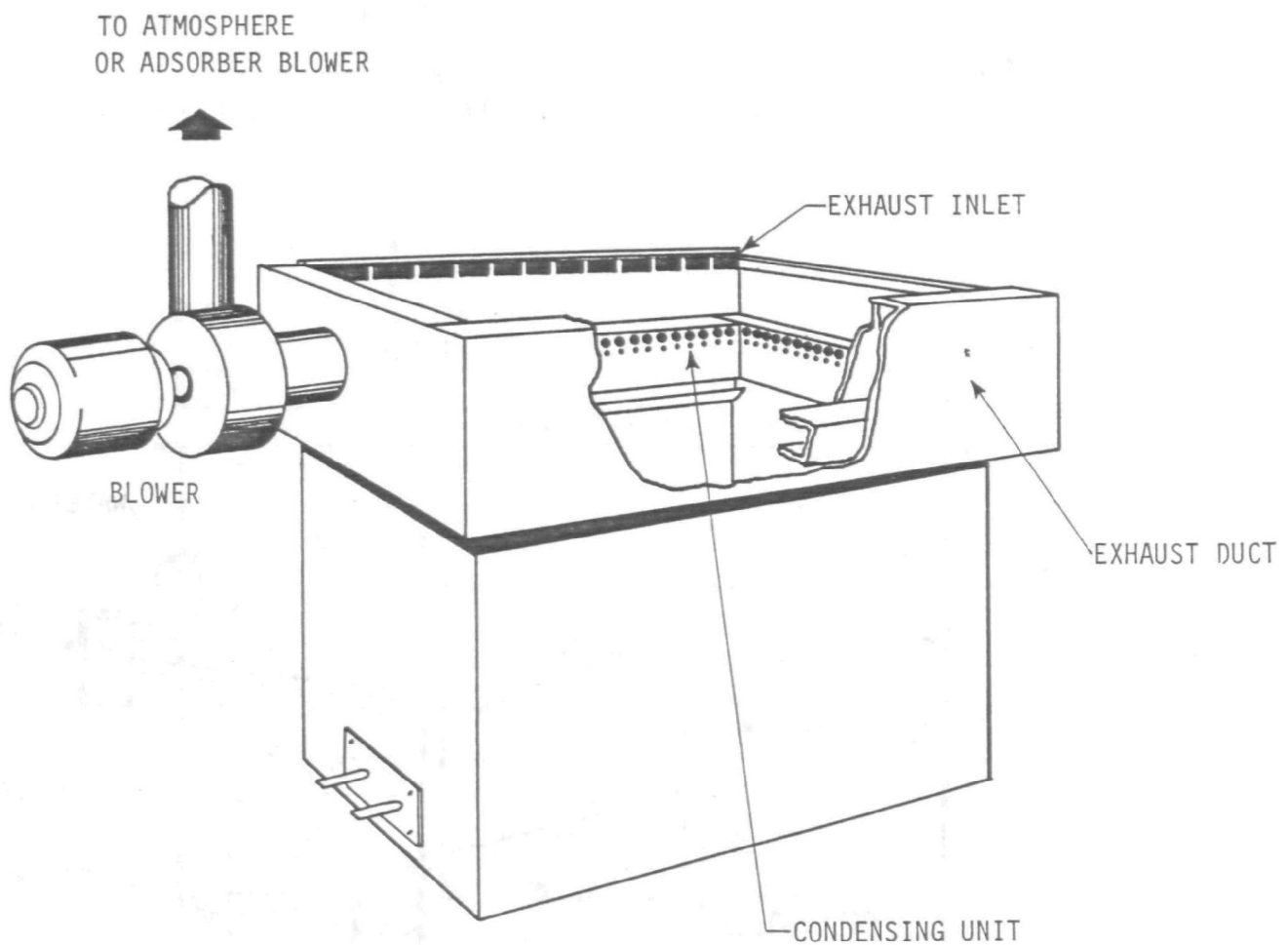


Figure 3-6. Degreaser with Lip Exhaust

## 3.2 ATMOSPHERIC EMISSIONS

### 3.2.1 Emission Points

There are several means by which organic solvent vapors can be emitted to the atmosphere in an open top vapor degreaser. These are identified in Figure 3-10. In general, open top units are not hooded or vented to the outside. Thus, an obvious emission point is the direct diffusion and convection of vapors from the vapor zone to the atmosphere (Location 1). If a lip exhaust is installed some of these vapors can be directed to a roof vent (Location 2). If not properly designed, these systems can actually increase solvent evaporation, especially if the exhaust rate is excessive, causing disruption of the air/vapor interface. The use of lip (or lateral) exhausts is usually limited to larger than average degreasers where the primary objective is to limit worker exposure to solvent vapors. A rule of thumb used by degreaser and control systems manufacturers is to set the exhaust rate at 50 cubic feet per minute per square foot of degreaser opening. If this exhaust rate is not adequate to protect the workers, higher rates may be encountered.

Carry-out emissions result from solvent that has condensed on the work and has not fully evaporated before being removed from the degreaser (Location 3). Also, solvent vapors may be entrained by the motion of removing the work from the vapor zone or by convection due to the hot work heating the solvent laden air as it is removed from the vapor zone. Porous or adsorbant materials such as cloth, leather, wood or rope will adsorb and trap condensed solvent and thus such materials should never enter a degreaser.

As the solvent material is spent and itself becomes contaminated with impurities its usefulness decreases. To reduce the volume of waste material some degreasers are used as a simple still during downtime where the solvent in the sump is boiled off as much as feasible and the pure condensed vapors are piped off to a storage tank, rather than back to the sump. Other degreasers, especially the larger ones, may be used with an external still that may run on a continuous or batch basis. Nevertheless, a significant volume of waste material will remain to be disposed of and depending on the method of disposal, waste solvents may enter the atmosphere (Location 4).

Fugitive emissions can occur at any of the piping connection or pump seals that may have loosened, or become worn or corroded (Location 5). These emission points are usually eliminated fairly quickly because they are detectable by visual observation and represent a correctable loss of valuable material, and create a potentially unhealthy work environment.

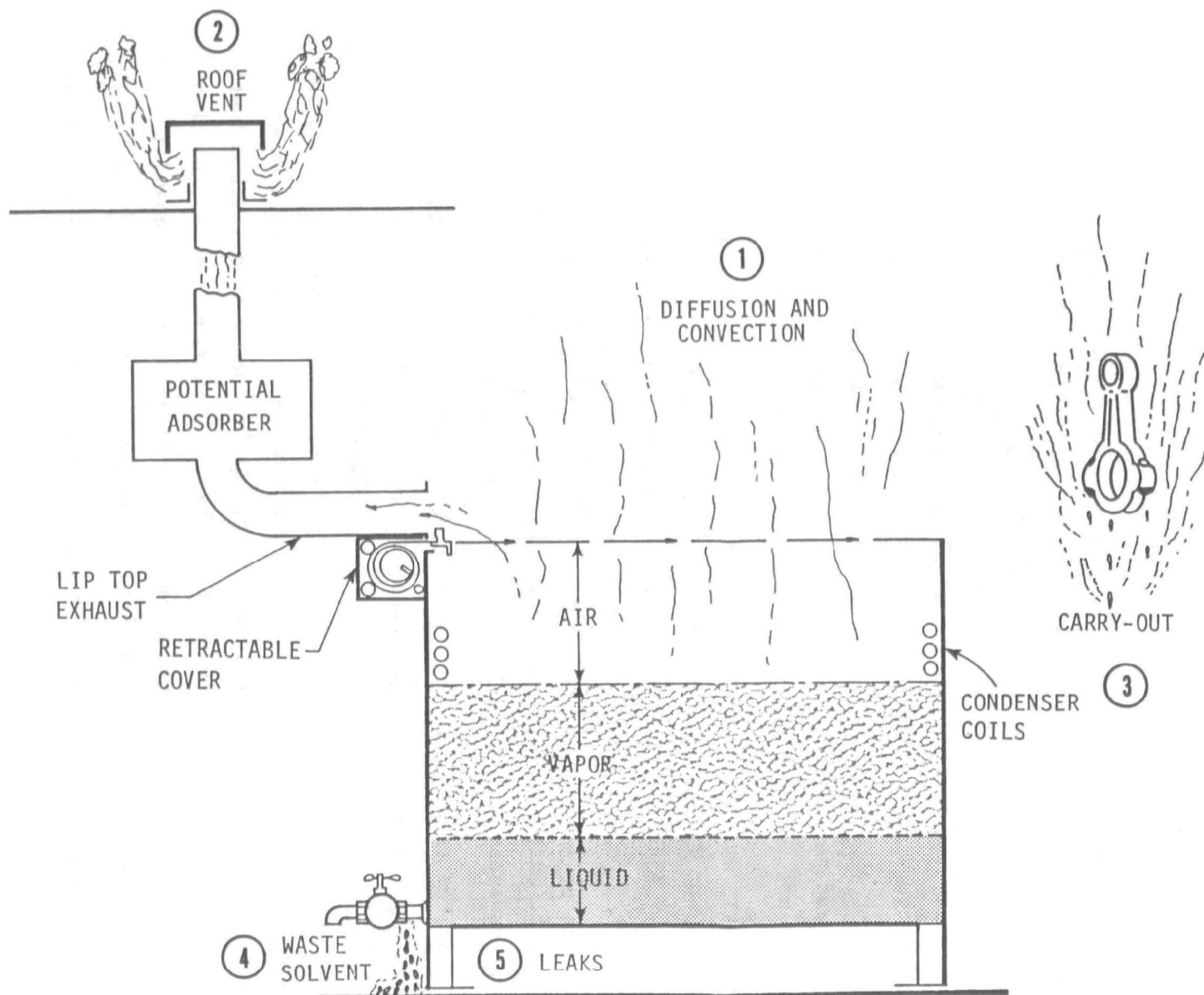


Figure 3-10. Open Top Degreaser Emission Points



### 3.2.2 Parameters Affecting Rate of VOC Emissions

The rate of vapor emissions emanating from the various points previously discussed is dependent on a variety of operating and design parameters. Emissions can be minimized by attempting to achieve certain optimum conditions; however, it is important to understand the cause and effect relationship. The following parameters significantly affect VOC emissions from open top vapor degreasers:

- o Freeboard Ratio - The freeboard ratio is the ratio of the freeboard height to the width (not the length) of the degreaser. Manufacturers of degreasers generally size the equipment so that this ratio is at least 0.5 for the higher boiling solvents. For solvents with lower boiling points, such as methylene chloride and trichlorotrifluoroethane, this ratio should be at least 0.75.
- o Drafts - A fan or other air moving devices located in the work area near the degreaser can cause a draft to enter the freeboard area of the degreaser housing, thereby upsetting the interface and drawing vapors into the ambient air.
- o Type of Work Load - Atmospheric emissions increase when the parts being processed in the degreaser contain numerous pockets or liquid traps that allow liquids to be carried from the degreaser chamber.
- o Size of Work Load - If the cross-sectional area of the work is substantial compared to the cross-sectional area of the vapor chamber, moving the work in and out of the degreaser will have a piston effect on the surrounding vapors; the resulting turbulence will cause excessive emissions.
- o Mass of Work Load - If the work load is especially massive the heat required to bring the work to vapor temperature will be excessive. This will cause the vapor zone to collapse resulting in turbulence that will increase emissions.
- o Solvent Heat Input - Once the solvent's boiling temperature has been achieved, increasing the heat input to the solvent will increase the rate of solvent vaporization. If continued, the cool air blanket generated by the condenser coils may not be sufficient to retain the increased vapors and breakthrough could occur, resulting in greater emissions.
- o Temperature and Flow Rate of the Cooling Water - The function of a condensing coil is to limit the upper level of the vapor zone. A condenser consisting of a coil of pipe through which cooling water flows, creates a blanket of cool air. The flow rate and temperature of the water affect the efficiency of a given set of coils with a given heat input rate. Increasing flow increases efficiency. Decreasing the temperature of the water will also increase the efficiency of the coils in supporting the vapor layer.

- o Work Rate - Moving the work into and out of the degreaser creates turbulence that will result in the emission of vapors. Turbulence and the resulting emissions increase as the speed of the work increases.
- o Location of Spraying - If spraying is conducted in a manner that disrupts the vapor/air interface, emissions will increase. Spraying should be done below the vapor line; the spray should never be pointed to allow liquid to be sprayed above the vapor line.
- o Water in the Solvent - If water is allowed to accumulate in the boiling sump emissions may be increased in three ways: (i) the water/solvent vapor mixture has a lower density than pure solvent vapor and thus has a greater tendency to be lost by diffusion, (ii) water combines with the solvent to form a low boiling azeotrope that results in a higher vaporization rate, and (iii) water is corrosive to degreaser surfaces and piping, thus making leaks a serious problem. Water has a tendency to form acidic by-products with certain solvents, especially 1,1,1 - trichloroethane and methylene chloride, further exacerbating the corrosion problem.
- o Covers - The use of a cover during idle and down time virtually eliminates diffusion losses during these periods.
- o Drying Time - After the work has been removed from the vapor zone it may carry some condensed solvent out of the degreaser. To minimize these emissions the work should be allowed to dry for a brief time (about 15 seconds) in the freeboard area. Note, however, that when the hot part rests just above the vapor level, it will cause solvent laden air to heat up and rise, so the drying time should not become excessive.
- o Lip Exhaust - If the degreaser is equipped with a lip exhaust, the ventilation rate should not be excessive; otherwise, the exhaust system may disrupt the air/vapor interface and actually increase emissions.

### 3.3 EMISSION CONTROL METHODS

The EPA Control Technology Guideline document for solvent metal cleaning identifies a number of control strategies for reducing volatile organic emissions from open top vapor degreasers. These form the basis for defining RACT for these degreasers and should therefore be the focal point of a field investigation. The CTG document suggests two alternative control schemes. Level A represents a relatively low efficiency system consisting primarily of operating procedures and has an estimated efficiency of 45 (+15) percent. Level B consists of Level A plus additional control and has a control efficiency estimated at 60 (+15) percent. These control methods are presented in Table 3-1. EPA's policy regarding the application of these control levels is discussed in Chapter 1. EPA suggests that open top vapor degreasers with an open area of less than one square meter be exempt from the application of refrigerated chillers or carbon adsorbers because these devices would not be cost effective on such small units.

The safety switches and thermostat recommended in Control System B are the spray safety switch, the condenser flow switch and thermostat. The vapor level thermostat is not included because it is already required by OSHA on "open surface vapor degreasing tanks". The sump thermostat and solvent level control discussed in Section 3.1.3 are used primarily to prevent solvent degradation and protection of the equipment rather than to prevent solvent emissions.

Refrigerated chillers should not be confused with the condenser coils or water jacket; rather, the chillers are an optional, additional control device designed to minimize solvent losses. The refrigerated chiller consists of a second set of condenser coils located slightly above the primary coils. Figure 3-11 depicts a unit with finned chiller coils. The function of the primary coils remains as in units without freeboard chillers, i.e. to control the upper limit of the vapor zone. The refrigerated freeboard chiller creates a sharper temperature gradient than would otherwise exist. The resulting cold air blanket reduces diffusion losses and the stable inversion layer created by the increased temperature gradient decreases upward convection of solvent laden air.

Two types of chiller designs are commercially available; one that operates below 0°C and one that operates above that temperature. Most manufacturers of degreasing equipment offer both types, although there is a patent\* on the sub-zero design.

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\*U.S. Patent 3,375,177 issued to Autosonics, Inc., March 26, 1968

TABLE 3-1

COMPLETE CONTROL SYSTEMS FOR OPEN TOP VAPOR DEGREASERS

---

Control System A

Control Equipment:

1. Cover that can be opened and closed easily without disturbing the vapor zone.

Operating Requirements:

1. Keep cover closed at all times except when processing work loads through the degreaser.
2. Minimize solvent carry-out by the following measures:
  - a. Rack parts to allow full drainage.
  - b. Move parts in and out of the degreaser at less than 3.3 m/sec. (11 ft/min).
  - c. Degrease the work load in the vapor zone at least 30 sec. or until condensation ceases.
  - d. Tip out any pools of solvent on the cleaned parts before removal.
  - e. Allow parts to dry within the degreaser for at least 15 sec. or until visually dry.
3. Do not degrease porous or absorbent materials, such as cloth, leather, wood or rope.
4. Work loads should not occupy more than half of the degreaser's open top area.
5. The vapor level should not drop more than 10 cm (4 in.) when the work load enters the vapor zone.
6. Never spray above the vapor level.
7. Repair solvent leaks immediately, or shutdown the degreaser.
8. Do not dispose of waste solvent or transfer it to another party such that greater than 20 percent of the waste (by weight) will evaporate into the atmosphere. Store waste solvent only in closed containers.
9. Exhaust ventilation should not exceed  $20 \text{ m}^3/\text{min. per m}^2$  (65 cfm per  $\text{ft}^2$ ) of degreaser open area, unless necessary to meet OSHA requirements. Ventilation fans should not be used near the degreaser opening.
10. Water should not be visually detectable in solvent exiting the water separator.

Control System B

Control Equipment:

1. Cover (same as in system A).
2. Safety switches.
  - a. Condenser flow switch and thermostat - (shuts off sump heat if condenser coolant is either not circulating or too warm).
  - b. Spray safety switch - (shuts off spray pump if the vapor level drops excessively, about 10 cm (4 in)).

3. Major Control Device:

- Either:
- a. Freeboard ratio greater than or equal to 0.75, and if the degreaser opening is  $>1\text{m}^2$  (10  $\text{ft}^2$ ), the cover must be powered,
  - b. Refrigerated chiller,
  - c. Enclosed design (cover or door opens only when the dry part is actually entering or exiting the degreaser),
  - d. Carbon adsorption system, with ventilation  $>15 \text{ m}^3/\text{min per m}^2$  (50 cfm/ $\text{ft}^2$ ) of air/vapor area (when cover is open), and exhausting  $<25$  ppm solvent averaged over one complete adsorption cycle, or
  - e. Control system, demonstrated to have control efficiency, equivalent to or better than any of the above.

4. Permanent, conspicuous label, summarizing operating procedures #1 to #6.

Operating Requirements:

Same as in System A

The recommended operating temperature for below freezing chillers is -30 to -25°C. The cold coils attract moisture as does a dehumidifier. Therefore, the designs include a defrost cycle to remove frost from the coils and restore heat exchange efficiency. The defrost cycle operates approximately hourly, requiring only a few minutes to melt the accumulated ice and slush, which is collected in the condensate trough and poured through the water separator. Water contamination of the solvent can have an adverse affect on water soluable stabilizer systems and can contribute to equipment corrosion. Therefore, on some units, the material condensed from the chiller coils may be diverted to a different water separater.

The operating temperature of above freezing chillers should not exceed 5°C. These units are normally designed to achieve a minimum of 500 Btu/hr cooling capacity per foot of air/vapor interface perimeter. The sub-freezing units are normally designed in the range of 200-600 Btu/hr per foot of perimeter, depending on the width of the degreaser.

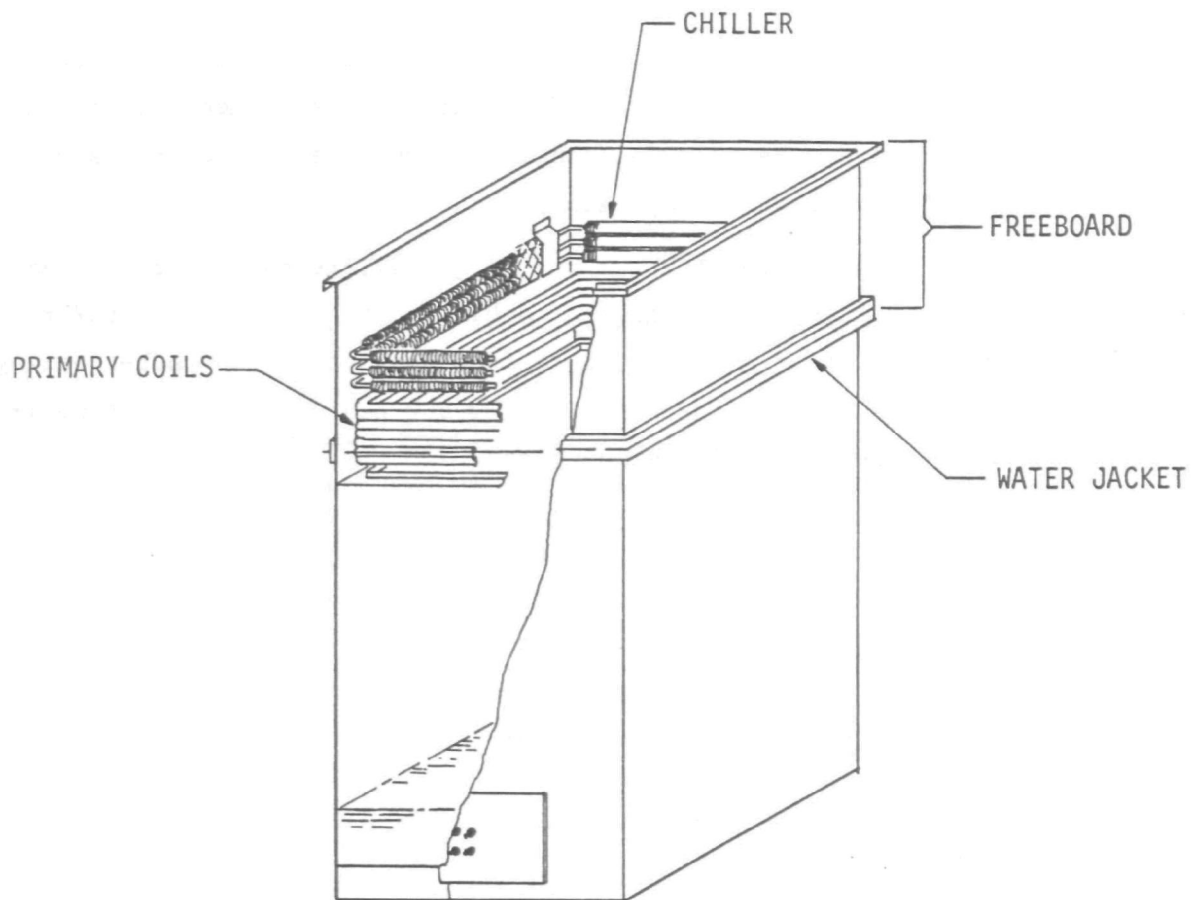


Figure 3-11. Refrigerated Freeboard Chiller

FIGURE 3-12

## EXAMPLE WORKSHEET FOR FIELD INSPECTION OF

## OPEN TOP VAPOR DEGREASERS

1. BUSINESS LICENSE NAME OF CORPORATION, COMPANY, OR INDIVIDUAL OWNER OR GOVERNMENTAL AGENCY:		
2a. MAILING ADDRESS:	2b. PLANT ADDRESS WHERE THIS DEGREASER IS LOCATED:	
3. SOURCE NO. (PERMIT NUMBER, NEDS ID, ETC.)		
4. NAME AND TITLE OF COMPANY REPRESENTATIVE:		
5. TELEPHONE NO.:		
6. NAME OF OFFICIAL CONDUCTING INSPECTION:		
7. DEGREASER		
MANUFACTURER: _____ MODEL NO. _____ SERIAL NO. _____ INSIDE DIMENSIONS OF TANK (FT.): _____ WIDE X _____ LONG X _____ DEEP		
8. TITLE AND CODE NUMBERS OF DRAWINGS, SPECIFICATIONS, STANDARDS, CODES, PROCEDURES AND DOCUMENTS USED WITH THE INSPECTION		
9. TYPE OF SOLVENTS IN USE (SPECIFIC NAME AND MANUFACTURER):		
INSPECTION OBSERVATIONS		
RACT REQUIREMENTS	- SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
<u>CONTROL EQUIPMENT</u>		
1. Lid	<ul style="list-style-type: none"> <li>o Observe if a lid is installed and if it is used during idling and downtime. Observe if opening and closing the lid disturbs the vapor zone.</li> </ul>	
2. Safety Switches a. Condenser flow switch & thermostat	<ul style="list-style-type: none"> <li>o Confirm that the switch and thermostat have been installed.</li> <li>o If available, check readings of flow and temperature indicators. For high boiling solvents, the temperature should be about 8° to 11°C (15° to 20°F) above dewpoint of surrounding atmosphere or 32° to 46°C (90° to 115°F). For low boiling solvents (methylene chloride and fluorocarbon 113) the exit temperature should be less than 29°C (85°F). Many installations may not have a temperature indicator at the cooling coil exit. A rough estimate of the temperature may be made if a bleed valve is available at the exit end of the coils. Bleed a sample of coolant into a small vessel and measure the temperature with a portable thermometer.</li> <li>o If plant is agreeable, interrupt flow of coolant and determine if switch is tripped.</li> </ul>	

FIGURE 3-12

(Continued)

RACT REQUIREMENTS	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
b. Spray safety switch	o Confirm that the switch has been installed.	
<p>3. Major Control Devices</p> <p>a. Freeboard ratio greater than 0.75.</p> <p>b. If the degreaser area is greater than 1.0m<sup>2</sup> the cover must be powered.</p> <p>c. Refrigerated Chiller</p> <p>d. Enclosed Design</p>	<p>o Measure the height of the freeboard and the width of the tank; calculate the ratio.</p> <p>o (Measurements usually can be made externally to avoid creating emissions and breathing solvent vapors. Otherwise, obtain the measurements from shop drawings). Measure the length of the tank and calculate the degreaser area. Observe if the cover is powered.</p> <p>o Unless observed during the defrost cycle, sub-zero chillers should be coated with frost or slush. The indicated temperature of the coolant should not exceed -25°C (-13°F). Do <u>not</u> attempt to extract a sample of coolant from a refrigerated chiller.</p> <p>o For above freezing chillers the coolant temperature should not exceed 5°C (40°F).</p> <p>o Determine the cooling capacity from the design specifications.</p> <p>oo For subzero chillers the minimum cooling capacity should be as follows for each degreaser width: (The cooling units are Btu's per hour per foot of perimeter.)</p> <p>&lt;3.5 ft - 200</p> <p>&gt;3.5 ft - 300</p> <p>&gt;6 ft - 400</p> <p>&gt;8 ft - 500</p> <p>&gt;10 ft - 600</p> <p>oo For above freezing chillers the cooling capacity should be at least 500 Btu/hr per foot of perimeter.</p> <p>o Observe that the cover or doors are open only when the dry part is entering or exiting the degreaser.</p>	



(Continued)

RACT REQUIREMENTS	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
e. Carbon Adsorber	<ul style="list-style-type: none"> <li>o If the degreaser is equipped with an adsorber solvent odors should not be detectable on the roof downwind from the stack.</li> <li>o See the source testing section in this manual.</li> </ul>	
<u>OPERATING REQUIREMENTS</u>		
1. Keep cover closed except while processing work loads.  2. Minimize solvent carry-out by the following measures: <ul style="list-style-type: none"> <li>a. Rack parts to allow full drainage.</li> <li>b. Move parts in and out of degreaser at less than 3.3 m/sec (11 ft/min).</li> <li>c. Degrease parts for at least 30 seconds or until condensation stops.</li> <li>d. Tip out pools of solvent on the cleaned parts before removal.</li> <li>e. Allow parts to dry within the degreaser for at least 15 seconds or until visually dry.</li> </ul>	<ul style="list-style-type: none"> <li>o Observe the operation.</li> <li>o Observe how the parts are racked.</li> <li>o Using a stopwatch, time the vertical movement of parts over a measured distance.</li> <li>o Observe this operation and time it if necessary.</li> <li>o Observe this operation.</li> <li>o Observe this operation, time it if necessary.</li> </ul>	
3. Do not degrease porous or absorbant materials.	<ul style="list-style-type: none"> <li>o Note the nature of the materials being cleaned. Baskets should not have rope or leather handles.</li> </ul>	
4. Work loads should not occupy more than half of the degreasers open top area.	<ul style="list-style-type: none"> <li>o Observe the size of the work load. Measure it if necessary and compare it to the open top area.</li> </ul>	
5. The vapor level should not drop more than 10 cm (4 inches) when the work load enters the vapor zone.	<ul style="list-style-type: none"> <li>o Observe this operation and estimate the drop in the vapor level.</li> </ul>	
6. Never spray above the vapor line.	<ul style="list-style-type: none"> <li>o Observe this operation.</li> </ul>	
7. Repair solvent leaks immediately or shut down the operation.	<ul style="list-style-type: none"> <li>o Look for leaks around the degreaser. Note especially the solvent spray pump and line, piping, the external sump drain valve (if so equipped) and the water separator.</li> </ul>	

FIGURE 3-12

(Continued)

RACT REQUIREMENTS	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
<p>8. Do not dispose of waste solvent or transfer it to another party such that greater than 20 percent of the waste (by weight) can evaporate into atmosphere. Store waste solvent only in covered containers.</p>	<ul style="list-style-type: none"> <li>o Determine if source has inhouse reclamation facilities (i.e. still) or a service contract with a solvent reclamation firm.</li> <li>o Confirm that storage is done with covered containers by visual inspection. Note whether containers leak.</li> </ul>	
<p>9. a. Exhaust ventilation should not exceed <math>20\text{m}^3/\text{min per m}^2</math> (65 cfm per <math>\text{ft}^2</math>) of degreaser open area unless necessary to meet OSHA requirements.</p> <p>b. Ventilation fans should not be used near degreaser opening.</p>	<ul style="list-style-type: none"> <li>o Determine the air handling capacity of the fan, -or- If sampling ports are available, the velocity of the exhaust gases may be measured with a swinging vane velocity meter. Also determine the cross-sectional area of the duct, then calculate the cfm.</li> <li>o After the air volume is determined from either of the above methods, obtain the area of the degreaser opening and calculate the cfm per square foot of degreaser opening.</li> <li>o Note the location of ventilation fans near the degreaser.</li> </ul>	
<p>10. Water should not be visually detectable in solvent exiting the water separator.</p>	<ul style="list-style-type: none"> <li>o This solvent is normally returned to the degreaser sump, or if so equipped, to the warm rinse tank. This solvent should be clear.</li> </ul>	
<p>11. Permanent, conspicuous label, summarizing operating procedures #1 to #6 above.</p>	<ul style="list-style-type: none"> <li>o Confirm the presence of this label.</li> </ul>	

## CHAPTER 4

### CONVEYORIZED DEGREASERS

#### 4.1 PROCESS DESCRIPTION

##### 4.1.1 Unit Operation

Conveyor operated solvent degreasers provide an efficient and economical method for preparing clean, dry articles for subsequent finishing or fabricating. There are several types of conveyORIZED degreasers and each can operate with either cold or vaporized solvents. The basic steps found in the typical conveyORIZED vapor degreaser include a vapor rinse upon entry to the degreaser vapor space section, liquid immersion, liquid spray, vapor rinse, and, finally, a slow withdrawal through a cold air space drying area.

A nonflammable solvent contained in the lower area of the degreaser, referred to as the boiling sump, is boiled to produce a vapor zone, the height of which is controlled by cooling coils installed above the vapor zone. The "cold work" introduced into the vapor space of the degreaser must be at a temperature lower than the vapor zone, in order to cause the solvent vapors to condense on the work surfaces and flush the oil and other foreign matter off with the liquid condensate. The removed material accumulates in the boiling sump and only the pure vapor comes in contact with the work load. Vapor flushing is followed by pure solvent spray and/or liquid immersion. The cool, pure solvent reduces the temperature of the work surface below the vapor temperature, producing a second vapor condensation flushing action on the work surfaces. When the work pieces are removed from the vapor zone, they should be clean, dry, and ready for further processing.

A well-operated conveyORIZED vapor degreaser should provide the required cleansing action and confine the solvent and solvent vapors, thereby maintaining a healthful working environment.

##### 4.1.2 Types of ConveyORIZED Degreasers

ConveyORIZED degreasers are generally large, automatic units designed to handle a high volume of work in either a straight-through process or a return type process in which the work pieces enter and leave the degreaser unit from the same end. Their use minimizes the human element and produces consistently high quality cleaning with minimum solvent losses. As indicated earlier, there are several basic designs which are termed conveyORIZED degreasers: gyro, vibra, monorail, cross-rod, mesh belt and strip cleaners. Figures 4-1 to 4-4 present a sketch of each design (with the excep-

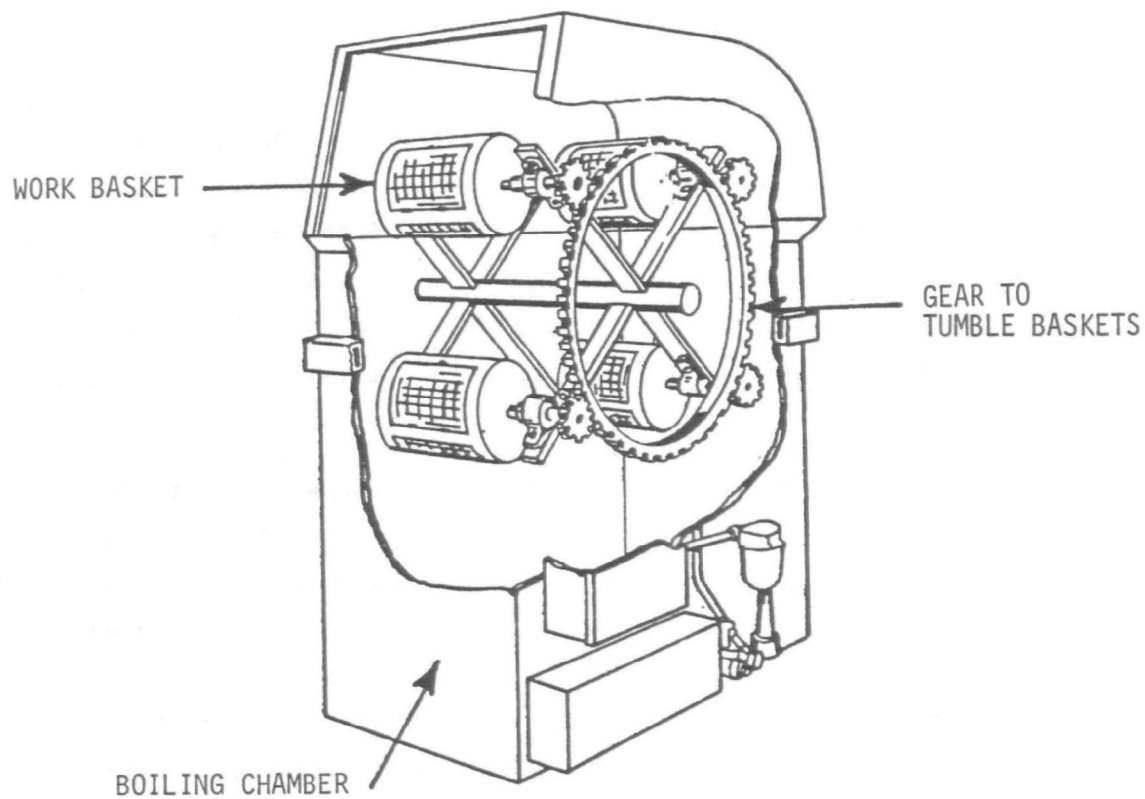


Figure 4-1a. Gyro Degreaser

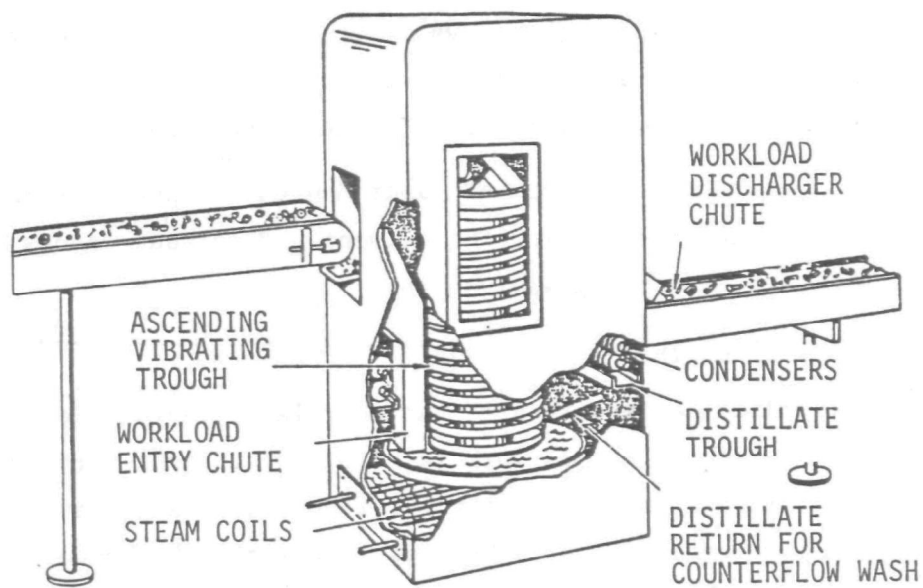


Figure 4-1b. Vibra Degreaser

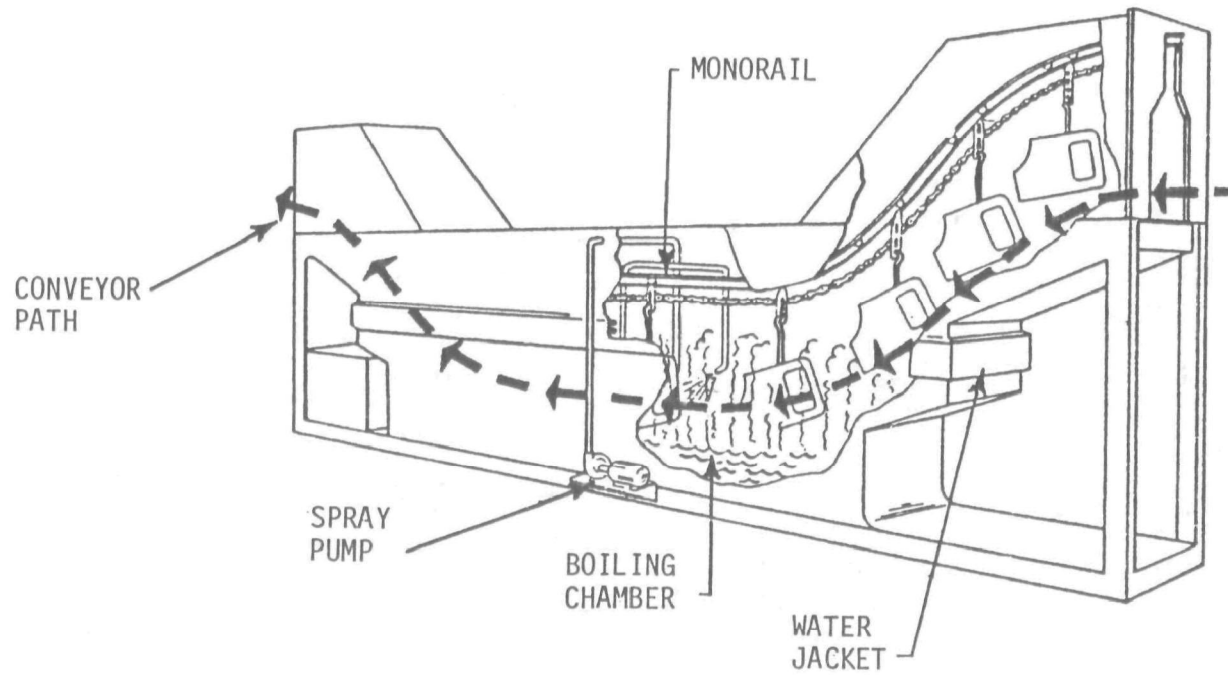


Figure 4-2. Monorail Degreaser

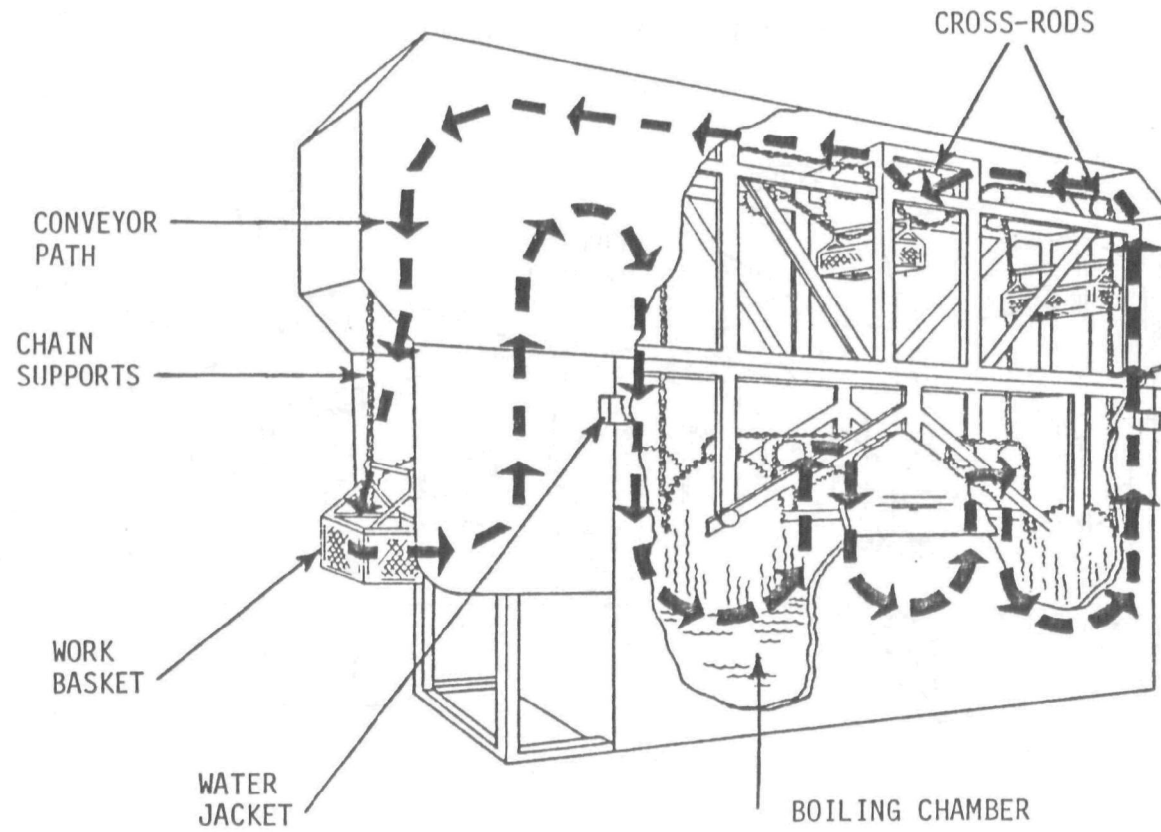


Figure 4-3. Cross-Rod Degreaser

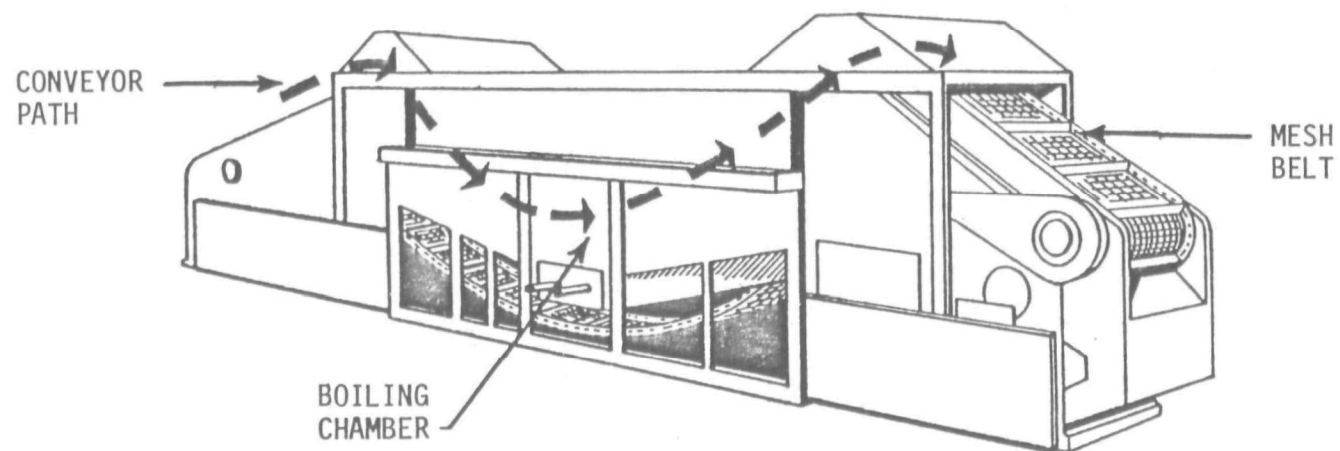


Figure 4-4. Mesh Belt Conveyorized Degreaser

tion of the strip cleaner type). A brief discussion of the rationale for each system follows:

- o Gyro (ferris wheel) type degreasers permit the operator to load and unload the baskets from one work station. The design is similar to the cross-rod degreaser. It is one of the smallest conveyORIZED degreasers available.
  - o Vibra type degreasers are used for high production rate applications where the work pieces are small. The work piece is dipped into solvent, and rises on a spiral vibrating elevator through a counter-flow rinsing action of clean solvent vapor. Cleaning action is accomplished by the combination of vibration, solvent dip, and solvent vapor condensation.
  - o Monorail conveyor systems are used for high production of standardized work pieces and are generally found in facilities that use monorail systems to transport materials within the plant. The monorail can be a straight through type, carrying parts in one side and out the other, or can turn 180° and exit the material through a duct that is parallel and adjacent to the entrance.
  - o Cross-rod conveyORIZED units are generally used for processing small or irregular parts. A rod placed between two power-driven chains carries parts within suspended pendant baskets or perforated cylinders. The cylinders are rotated to provide the tumbling action required to clean and drain the crevices in the work pieces. The pendant baskets do not rotate and are used to carry small parts that do not require this action for cleaning and draining.
  - o Mesh belt and strip cleaner degreasers are similar in design; however, the mesh belt degreaser carries the material to be cleaned while the other draws the material through. The latter design is used for sheet metal products. A continuous strip of material is drawn through the unit for cleaning prior to coating or fabrication processes. Mesh belt degreasers are used for smaller parts and allow for rapid loading and unloading of material.
-



## 4.2 ATMOSPHERIC EMISSIONS

### 4.2.1 Emission Points

There are several locations in a conveyORIZED degreaser that may allow organic liquid or vapor to escape to the atmosphere. These are identified in Figure 4-6. In general, conveyORIZED degreasers are hooded and vented to the outside. Therefore, an emission point is the vent line and subsequent exhaust. In most instances, a control device such as a carbon adsorption system is placed in the line to remove organic vapors. Although constant ventilation of the hood should create a negative pressure and prevent vapors from escaping from the work openings, ventilation rates are kept to a minimum level ( $< 65$  cfm per ft<sup>2</sup> of degreaser opening) to prevent disruption of the vapor-level boundary and corresponding increased emissions. However, in minimizing the ventilation rate, the opportunity for vapors to escape from the work openings increases at the inlet (Location 2) and exit (Location 3) of the degreaser. In addition, at the exit of the unit the cleaned material may be carrying out liquid organic material which condensed on its surface but did not totally dry or drip off while in the degreaser.

As the solvent material is spent and itself becomes contaminated with impurities, its usefulness decreases. Most conveyORIZED degreasers are designed to distill and recycle this material on a continuous basis through the use of external stills. However, these stills will eventually accumulate wastes and, depending on the method of disposal, waste solvents may enter the atmosphere at this point.

Fugitive emissions can occur at any of the piping connections or sump seals that may have loosened or become worn because of continuous operation. Where good housekeeping practices are followed, these emission points are eliminated fairly quickly because they are detectable by visual observation, represent a correctable loss of valuable material, and create a potentially unhealthy work environment.

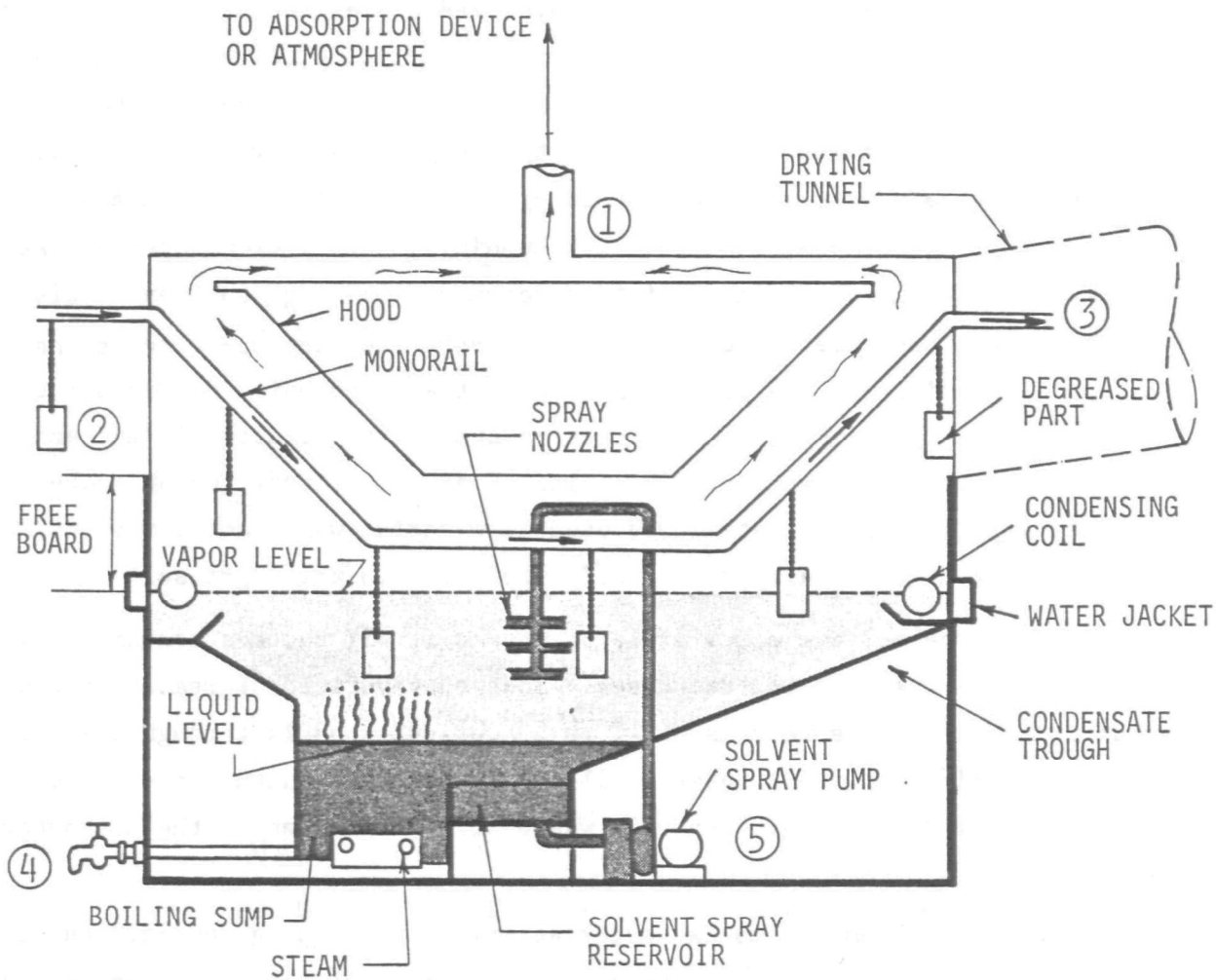


Figure 4-6. Typical Emission Points

The rate of vapor emissions emanating from the various points previously discussed is dependent on a variety of operating and design parameters. Emissions can be minimized by attempting to achieve certain optimum conditions; however, it is important to understand the cause and effect relationship. The following parameters significantly affect VOC emissions from conveyORIZED degreasers:

- o Drafts - A fan or other air-moving devices located in the work area near the degreaser can cause a draft to enter the freeboard area of the degreaser housing, thereby upsetting the balance of the air/vapor interface.
- o Size of Work Opening - Although conveyORIZED degreasers are generally covered, the size of the opening allowing work loads to enter and exit should be kept to a minimum to reduce the opportunity for vapors to escape. The term "average silhouette clearance" is used to define the distance from the edge of the degreaser opening to the part or the basket or cage conveying the part. Where hoods are exhausted, the smaller the opening the greater the capture velocity of the room air traveling through the area and the greater the control of vapors escaping at this point.
- o Exhaust Rate - The greater the exhaust rate, the greater the control of vapor escaping from the work openings; however, an excessive exhaust rate also produces greater emissions because it disturbs the vapor and air interface within the degreaser, thereby exhausting high concentrations of organic vapors into the exhaust gas stream. To achieve both goals the exhaust rate should not exceed  $20 \text{ m}^3/\text{min per m}^2$  ( $65 \text{ cfm per ft}^2$ ) of degreaser opening.
- o Conveyor Speed - As the conveyor speed increases, emissions increase. Increased speeds represent less time for the material to dry. Therefore, evaporation of the liquid droplets that originally condensed on the cold material will take place outside the hooded portion of the degreaser and will increase emissions. Too rapid a conveyor speed may also induce drafts that will create vapor loss at the outlet work opening. Conveyor speeds must be maintained below  $3.3 \text{ m/min}$  ( $11 \text{ ft/min}$ ) to minimize losses.
- o Type and Magnitude of Load - Atmospheric emissions increase when the parts being processed in the conveyORIZED degreaser contain numerous pockets or liquid traps that allow liquids to be carried from the degreaser chamber. Liquid trapped in pockets can be removed by placing the working pieces in baskets which are rotated and tumbled as they move through the degreaser so that they drain liquid solvent back to the sump. Increases in the magnitude of the work load will cool the vapor area. A massive load may cause a collapse of the vapor space and increase emissions. When the vapor space collapses two situations arise, (1) the vapor/air

layers mix and organic vapors escape and (2) the working pieces spend less time within the collapsed vapor space and therefore have less time to evaporate the condensed solvent, resulting in greater carry out and subsequent emissions.

- o Solvent Heat Input - Once the solvent's boiling temperature has been achieved, increasing the heat input to the solvent will increase the rate of solvent vaporization. If continued, the cool air blanket generated by the condenser coils may not be sufficient to retain the increased vapors and breakthrough could occur, resulting in greater emissions.
- o Temperature and Flow Rate of the Condensing Coils - The function of a condensing coil is to limit the upper level of the vapor zone. A condenser consisting of a coil of pipe through which cooling water flows, creates a blanket of cool air. The flow rate and temperature of the water affect the efficiency of a given set of coils with a given heat input rate. Increasing flow increases efficiency. Decreasing the temperature of the water will also increase the efficiency of the coils in supporting the vapor layer.

The EPA Control Technology Guideline (CTG) document for solvent metal cleaning identifies a number of control strategies for reducing volatile organic emissions from conveyORIZED degreasing operation. These form the basis of defining RACT for the conveyORIZED degreaser and should therefore be the focal point of a field inspection. The CTG document suggests two levels of control. EPA's policy regarding the application of these control levels is discussed in Chapter 1. Level A represents a relatively low efficiency system, estimated at  $25 \pm 5$  percent. Level B, consisting of Level A plus additional requirements represents a higher efficiency system, estimated at  $60 \pm 10$  percent. The following discussion will address these and other control measures found in the CTG document. However, the organization is slightly different. It is divided into three areas: process equipment design, operating requirements, and control equipment requirements. In addition, a second series of suggested controls is offered which do not appear in the CTG document. These controls should be considered by the inspector as additional means of reducing emissions.

It should be noted that a given control strategy will not provide equal results for similar degreasers or degreasers used in different applications. Therefore, each degreaser should be evaluated individually.

#### 4.3.1 RACT Controls

##### o Process Equipment Design

- oo Minimum entrance and exit openings should be provided by silhouetting the work load. The average silhouette clearance (distance between the edge of the openings and the part) should be  $< 10$  percent of the opening width.
- oo Safety switches should be included in the design to prevent emissions during malfunctions and abnormal operation.
  - a. Condenser flow switch and thermostat shut off sump heat if coolant is either not circulating or becomes too hot.
  - b. Spray safety switch shuts off spray pump or conveyor if vapor level drops excessively.
  - c. Vapor level control thermostat shuts off sump heat when vapor level rises too high.

o Operating Requirements

- oo Conveyor speed should be  $< 3.3$  m/min (11 ft/min) to minimize solvent carry-out emissions.
- oo Exhaust ventilation should not exceed  $20 \text{ m}^3/\text{min}$  per  $\text{m}^2$  (65 cfm per  $\text{ft}^2$ ) of degreaser opening unless necessary to meet Occupational Safety and Health Administration (OSHA) requirements or the degreaser is vented to a carbon adsorber.
- oo Work place fans should not be used near the degreaser opening because they will induce mixing of the air/vapor layer, thereby increasing emissions.
- oo Solvent leaks should be repaired immediately, or the degreaser should be shut down, until repairs can be made.
- oo Water should not be visibly detected in the solvent exiting the water separator. For chlorinated solvents, water contributes to vapor loss because the mixture of water and solvent has a lower density than that of dry solvent. In addition, water contributes to corrosion and creates a low boiling azeotrope with the solvent in the boiling sump.
- oo Down-time covers must be placed over entrances and exits of conveyorized degreasers immediately after the conveyor and exhaust are shut down and removed just before they are started.
- oo Disposal or transfer of waste solvents should be performed in a manner that will not allow greater than 20 percent of the waste (by weight) to evaporate to the atmosphere. Waste solvents should be stored in covered containers.
- oo Racking parts to allow maximum drainage should be implemented to minimize carry-out emissions.

o Control Equipment Requirements

- oo Rotating baskets, trays, etc., and/or a drying tunnel should be provided to prevent solvent drag-out. Such carry-out is most likely to occur from solvent hold up in recesses or pockets in the work being degreased.
- oo Covers must be provided for the entrance and exit in order to close these openings immediately after shutting down the degreaser. These covers should close off at least 80 to 90 percent of the opening to effectively prevent solvent emissions.

- oo Refrigerated chillers can be used to control the upper limit of the vapor zone; or carbon adsorption systems should be used to control emissions in the exhaust line of the degreaser. The ventilation rate (when down-time covers are open) should be  $\geq 15 \text{ m}^3/\text{min}$  per  $\text{m}^2$  (50 cfm/ft<sup>2</sup>) of air /vapor area for adsorbers.
- oo The exhaust gas from the adsorption system must contain < 25 ppm solvent by volume averaged over a complete adsorption cycle.
- oo Alternate control systems may be used if they demonstrate control efficiencies equal to or greater than the refrigerated chiller or carbon adsorption units.

#### 4.3.2 Other Controls

Several control techniques are discussed in the literature that deserve mention although they are not recommended by EPA as RACT requirements.

- o The unit is capable of being hooded or covered without affecting its operation. The enclosure of a degreaser diminishes solvent losses from the system that result from the movement of air within the plant.
- o Sprays should be designed or adjusted so they do not cause turbulence at the air/vapor interface; spraying must be conducted below the vapor line. Spray pressure should be the minimum necessary for adequate cleansing.
- o Overloading work baskets may reduce the vapor temperature and collapse the vapor zone, thereby increasing the air/vapor mixing and subsequent emissions. This situation can be avoided by following equipment specifications for the allowable work load as determined by a system heat balance.
- o A solvent reclaimer-still to recycle and return a purified solvent to the solvent sump. This will tend to stabilize vaporization rates and eliminate emission due to improper waste disposal methods.
- o Where work being degreased contains acidic cutting oils or other acidic products, acid acceptance and pH determination should be made to determine the quality of the solvent.
- o Absorbent materials such as wood and fabric materials should not be degreased or used in the basket construction.
- o A "good housekeeping" and maintenance program should be in effect. Clean out doors, line connections, pumps, water separator, etc., should be checked frequently.
- o For large users of solvent, bulk storage may prove more economical than purchases by individual drums. Where bulk storage is used, a submerged fill pipe from the top of the tank should be included in the design of the storage tank. Alternate controls such as a return vent line to a recovery still should be investigated.

Figure 4-7. Example Worksheet for Field Inspection of

Conveyorized Degreasers

1. BUSINESS LICENSE NAME OF CORPORATION, COMPANY, OR INDIVIDUAL OWNER OR GOVERNMENTAL AGENCY:		
2a. MAILING ADDRESS:	2b. PLANT ADDRESS WHERE THIS DEGREASER IS LOCATED:	
3. SOURCE NO. (PERMIT NUMBER, NEDS ID, ETC.)		
4. NAME AND TITLE OF COMPANY REPRESENTATIVE:		
5. TELEPHONE NO.:		
6. NAME OF OFFICIAL CONDUCTING INSPECTION:		
7. DEGREASER  MANUFACTURER: _____ MODEL NO. _____ SERIAL NO. _____ INSIDE DIMENSIONS OF TANK (FT.): _____ WIDE X _____ LONG X _____ DEEP TYPE OF DEGREASING: COLD SOLVENT CLEANING <input type="checkbox"/> VAPOR DEGREASING <input type="checkbox"/> TYPE OF CONVEYOR _____		
8. TITLE AND CODE NUMBERS OF DRAWINGS, SPECIFICATIONS, STANDARDS, CODES, PROCEDURES AND DOCUMENTS USED WITH THE INSPECTION _____		
9. TYPE OF SOLVENT IN USE (SPECIFIC NAME AND MANUFACTURER): _____		
<b>INSPECTION OBSERVATIONS</b>		
<b>FACT REQUIREMENTS</b>	<b>SUGGESTED INSPECTION PROCEDURE</b>	<b>FIELD OBSERVATIONS</b>
<u>CONTROL EQUIPMENT</u>  1. Safety Switches a. Condenser flow switch & thermostat	<ul style="list-style-type: none"> <li>o Confirm that the switch and thermostat have been installed.</li> <li>o If available, check readings of flow and temperature indicators. For high boiling solvents, the temperature should be about 8° to 11°C (15° to 20°F) above dewpoint of surrounding atmosphere or 32° to 46°C (90° to 115°F). For low boiling solvents (methylene chloride and fluorocarbon 113) the exit temperature should be less than 29°C (85°F). Many installations may not have a temperature indicator at the cooling coil exit. A rough estimate of the temperature may be made if a bleed valve is available at the exit end of the coils. Bleed a sample of coolant into a small vessel and measure the temperature with a portable thermometer.</li> </ul>	



FIGURE 4-7

(Continued)

RACT REQUIREMENTS	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
<p>1. (continued)</p> <p>b. Spray Safety Switch</p> <p>c. Vapor level control thermostats</p>	<ul style="list-style-type: none"> <li>o If plant is agreeable, interrupt flow of coolant and determine if switch is tripped.</li> <li>o Confirm that the switch has been installed.</li> <li>o Confirm that vapor level control thermostat is located just above cooling coil or jacket.</li> <li>o Suggested thermostat settings for four types of solvents: <ul style="list-style-type: none"> <li>-Perchloroethylene 82°C (180°F)</li> <li>-Trichloroethylene - 68°C (155°F)</li> <li>-1,1,1-Trichloroethane 60°C (140°F)</li> <li>-Methylene Chloride 32°C (90°F) or about 6°C (10°F) lower than boiling point of solvent-water azeotrope</li> </ul> </li> <li>o Read temp. on indicators</li> </ul>	
<p>2. Minimized openings at entrance and exit of conveyor</p>	<ul style="list-style-type: none"> <li>o Determine with a tape measure that the average silhouette is less than 10 cm (4 in.) or less than 10 percent of the width of the opening.</li> </ul>	
<p>3. Drying tunnel or rotating baskets</p>	<ul style="list-style-type: none"> <li>o Observe whether the degreaser is equipped with either of these devices. Observe whether parts are wet or have liquid in crevices when exiting the degreaser.</li> </ul>	
<p>4. Refrigerated chiller</p>	<ul style="list-style-type: none"> <li>o Observe indicated coolant temperature. <ul style="list-style-type: none"> <li>oo For subzero chillers the temperature should not exceed -25°C (-13°F).</li> <li>oo For above freezing chillers the temperature should not exceed 5°C (40°F).</li> <li>oo Do <u>not</u> attempt to extract a sample of coolant from a refrigerated chiller.</li> </ul> </li> <li>o Determine the cooling capacity from the design specifications.</li> </ul>	

FIGURE 4-7

(Continued)

RACT REQUIREMENTS	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
	<ul style="list-style-type: none"> <li>oo For subzero chillers the minimum cooling capacity should be as follows for each degreaser width: (The cooling units are Btu's per hour per foot of perimeter.) <ul style="list-style-type: none"> <li>&lt;3.5 ft - 200</li> <li>&gt;3.5 ft - 300</li> <li>&gt;6 ft - 400</li> <li>&gt;8 ft - 500</li> <li>&gt;10 ft - 600</li> </ul> </li> <li>oo For above freezing chillers the cooling capacity should be at least 500 Btu/hr per foot of perimeter.</li> </ul>	
<p>5. Carbon adsorption system with ventilation &gt;15 m<sup>3</sup>/min per m<sup>2</sup> (50 cfm/ft<sup>2</sup>) of air/vapor area.</p>	<ul style="list-style-type: none"> <li>o Solvent odors should not be detectable on the roof downwind from the stack.</li> <li>o Determine the air handling capacity of the fan, -or- If sampling ports are available, the velocity of the exhaust gases may be measured with a swinging vane velocity meter. Also determine the cross-sectional area of the duct, then calculate the cfm.</li> <li>o After the air volume is determined from either of the above methods, obtain the area of the air/vapor opening and calculate the cfm per square foot of opening.</li> <li>o See the source testing chapter of this manual.</li> </ul>	
<p><u>OPERATING REQUIREMENTS</u></p> <p>1. a. Exhaust ventilation should not exceed 20m<sup>3</sup>/min per m<sup>2</sup> (65 cfm per ft<sup>2</sup>) of degreaser open area unless necessary to meet OSHA requirements. (This ventilation rate is applicable if a carbon adsorber is not installed.)</p> <p>b. Work place fans should not be used near degreaser opening.</p>	<ul style="list-style-type: none"> <li>o Determine the air handling capacity of the fan, -or- If sampling ports are available, the velocity of the exhaust gases may be measured with a swinging vane velocity meter. Also determine the cross-sectional area of the duct, then calculate the cfm.</li> <li>o After the air volume is determined from either of the above methods, obtain the area of the degreaser opening and calculate the cfm per square foot of degreaser opening.</li> <li>o Note the location of ventilation fans near the degreaser.</li> </ul>	

FIGURE 4-7

(Continued)

RACT REQUIREMENTS	SUGGESTED INSPECTION PROCEDURE	FIELD OBSERVATIONS
2. Water should not be visually detectable in solvent exiting the water separator.	o Observe any water present in the sight glass on the separator.	
3. Conveyor speed should not exceed 3.3 m/min. (11 ft/min).	o Check conveyor speed with stop watch.	
4. Rack parts for best drainage.	o Observe whether parts are racked in a manner that allows liquid solvent to collect in pockets and crevices.	
5. Repair solvent leaks immediately.	o Inspect for wetted areas around pump seals, sight glass, pipes, etc.	
6. Downtime covers	o If the unit is not in operation, observe whether they are in place.	
7. a. Do not dispose of waste solvent or transfer it to another party such that greater than 20 percent of the waste (by weight) can evaporate into atmosphere.  b. Store water solvent only in covered containers.	o Determine if source has inhouse reclamation facilities (i.e. still) or a service contract with a solvent reclamation firm.  o Confirm that storage is done with covered containers by visual inspection.  o Check for container leakage.	



# Petroleum Refining

## SECTION 2

### PETROLEUM REFINING - OVERVIEW

#### 2.1 INTRODUCTION

##### 2.1.1 Petroleum

Petroleum, usually called crude oil, is a complex mixture of hydrocarbons, with small amounts of other substances, that occurs as an oily liquid in many places in the upper strata of the earth. Many crude oils, such as those from Arabia and Iraq, have a strong odor of hydrogen sulfide and sulfur compounds; others, such as those from Nigeria and Indonesia, contain very little sulfur and do not have any unpleasant odor. The color of crude oil ranges from clear to black.

Crude oil in the ground is associated with hydrocarbon gases, of which substantial quantities are dissolved in the oil under pressure. Methane and ethane constitute by far the greatest proportion of the gases associated with crude oil.

It has been estimated that crude oil contains over 3000 different chemical compounds, and the chemical composition varies with the source. Hydrocarbons are the predominant components; the remainder consists chiefly of organic compounds containing oxygen, nitrogen, sulfur, and traces of inorganic compounds containing iron, nickel, vanadium, and arsenic.

The molecular weight of the hydrocarbons in crude oil varies widely because they contain different numbers of carbon atoms per molecule. The chemical structure of these hydrocarbons also differs greatly. The types of hydrocarbons present in crude oil are paraffins (alkanes), naphthenes (cycloparaffins), and aromatics.

Crude oil is separated by distillation into fractions designated as (1) light ends; (2) straight-run gasolines, with boiling points that range up to about 204°C (400°F); (3) middle distillates, boiling at about 185° to 343°C (365° to 650°F), from which are obtained kerosene, heating oils, and fuels for diesel, jet, rocket, and gas turbine engines; (4) wide-cut gas oil, boiling at 343° to 538°C (650° to 1000°F), from which are obtained waxes, lubricating oils, and feedstock for catalytic cracking operations that produce gasoline; and (5) residual oil, from which asphalt, coke, and tar may be obtained.

### 2.1.2 Petroleum Refining

The refining sector of the petroleum industry converts crude oils, various semifinished petroleum fractions, and hydrocarbon gases into useful products. These products are refined by various physical, thermal, catalytic, and chemical processes, into the wide range of products mentioned earlier. Refinery products generally are not pure chemical compounds but are mixtures of chemical compounds. Table 2-1 characterizes many of these products. In each case the boiling range, rather than a single boiling point, is due to the fractions being a mixture of chemical compounds.

Because refining processes are complex and are specific to each refinery, intermediate storage may be needed for certain fractions that will be returned to various units for further processing. Since each refinery is designed, engineered, and constructed to handle specific crude oils and to produce specific refined or semirefined products, there is no "typical" refinery. Additionally, the processing parameters change with the type of crude oil to be refined. For example, an increase in the refining of Alaska's North Slope crude has led to expanded use of catalytic reformers and fluid-bed catalytic cracking units.

Even though there is no typical refinery, most U.S. refineries are designed to maximize the production of light distillates, i.e., gasoline. The following operations (Figure 2-1) are basic:

TABLE 2-1. CHARACTERIZATION OF FRACTIONS OBTAINED FROM CRUDE OIL

Fraction	Carbon atoms	Molecular weight	API gravity	Boiling range, °F <sup>a</sup>
Gas	1 to 4	16 to 58		-259 to 31
Gasoline	5 to 12	72 to 170	58 to 62	31 to 400
Jet fuel	10 to 16	156 to 226	40 to 46	356 to 525
Gas oil	15 to 22	212 to 294	34 to 38	500 to 700
Lube oil	19 to 35	268 to 492	24 to 30	640 to 875
Residuum	36 to 90	492 to 1262	8 to 18	875+

$$^{\circ}\text{F} = 5/9 (^{\circ}\text{C}) + 32$$



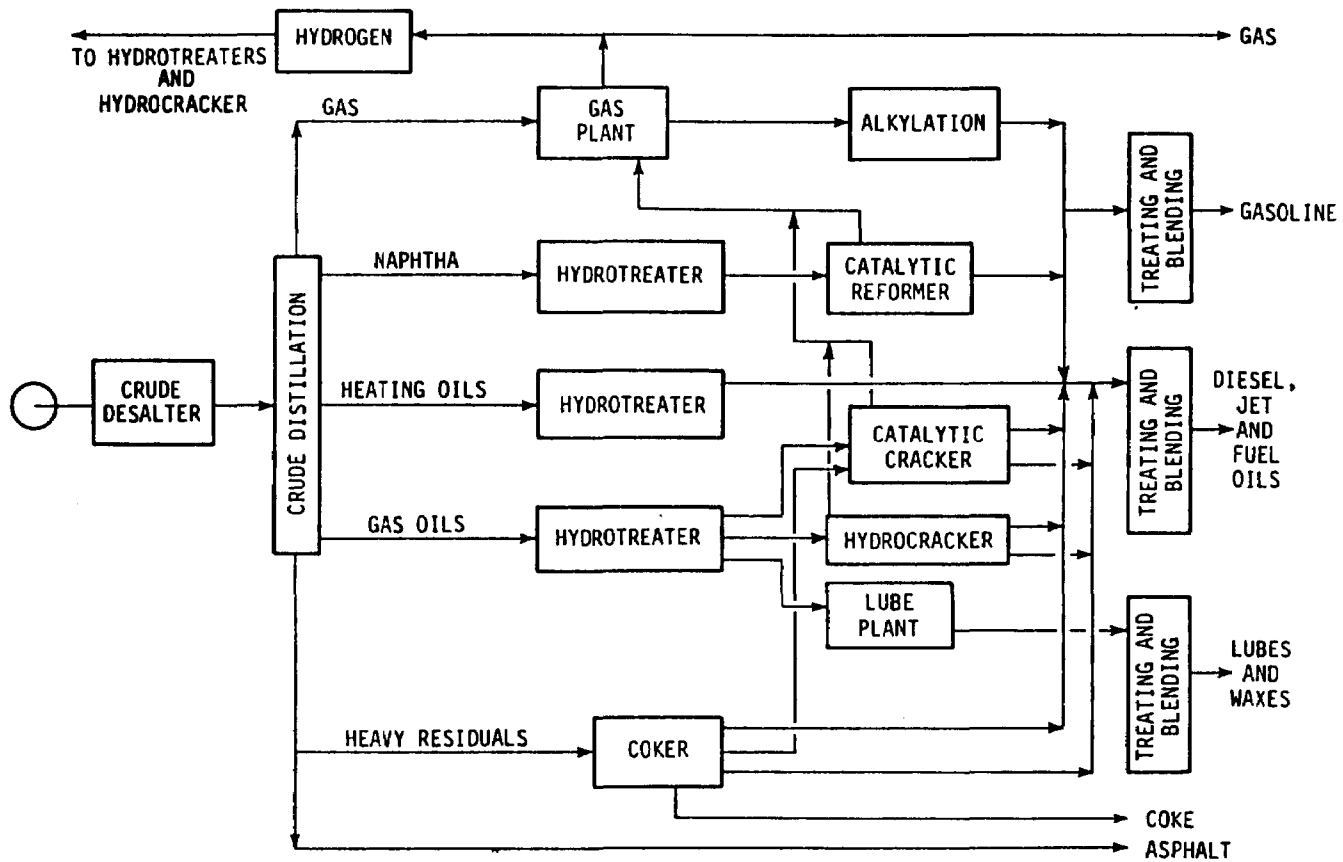


Figure 2-1. Typical processing steps in a petroleum refinery.

(1) separation processes, separating the crude oils to isolate the desired products (e.g., distillation); (2) decomposition processes, breaking large hydrocarbon chains into smaller ones by cracking (e.g., catalytic cracking, coking); (3) formation processes, building the products by chemical reaction (e.g., reforming, alkylation, isomerization); (4) treating processes, removing impurities or compounds that are detrimental to operation of the refinery; (5) recovery operations (e.g., sulfur recovery, fuel gas recovery); (6) storage; and (7) auxiliary facilities. Figure 2-1 shows the interrelationships of these processes, which are described in the following subsections.

## 2.2 SEPARATION PROCESSES

### 2.2.1 Desalting

Crude oil is a mixture of hydrocarbon compounds contaminated by water, salt, and sand. Although most of the water and sand settle out and separate during storage, the crude is saturated with water, dissolved salts, and minerals. Crude oil desalting is a combination separation/reaction operation, in which an impressed electrical current field and/or chemical additives are used to coalesce the salt particles, which are then washed away with water.

Electrical desalting, the most common technique, involves the addition of water to crude under pressure and at 71° to 149°C (160° to 300°F). This mixture is emulsified and introduced into a high-potential electrostatic field, which causes the impurities to associate with the water phase and at the same time causes the water phase to agglomerate so that it can be removed. The desalted crude proceeds to the distillation units.

Chemical desalting of crude is accomplished by adding water to the heated [93° to 149°C (200° to 300°F)] and pressurized oil. The pressure must be high enough to prevent vaporization of the water. The mixture is emulsified, and the salt enters the water phase. Chemical additives may be used to break the emulsion and

allow the water phase to settle. The water containing the salt is discharged from the system.

### 2.2.2 Crude Distillation

The first major separation operation in refining is crude oil distillation. In distillation towers (columns) various constant-boiling-range fractions are separated, the lowest boiling fraction leaving the top of the tower and the highest boiling fraction leaving the bottom. Products may be withdrawn as side-streams at appropriate points on the tower. The sidestreams are further processed in small towers called strippers, in which steam is used to free the sidestream (cut) from its more volatile components so that the boiling point of the product can be adjusted to a specified value. There are three major types of distillation systems: single-stage, two-stage, and two-stage with a vacuum tower.

#### Single-Stage Distillation--

The crude feed is preheated by outgoing streams before entering a direct-fired, furnace-type heater, from which it goes to a distillation column for separation into gas, gasoline, naphtha, kerosene, gas oil, fuel oil, and residuum. These side-streams are steam-stripped and then routed to storage. Topping plants use single-stage distillation, usually separating the crude into five or six sidestreams. Very little additional treating is performed at these plants. The number and type of fractions that result from distillation depend on the crude base and on operating conditions.

#### Two-Stage Distillation--

Two-stage distillation provides more cuts than the single-stage system. The process includes a primary tower (preflash tower), which operates at above atmospheric pressure, and a secondary tower (atmospheric tower), which operates at atmospheric pressure. These units, together with a stabilizer (stabilizing

tower), are used to separate the crude into light ends, depropa-  
nized light gasoline, light kerosene, naphtha, kerosene, light  
diesel, heavy diesel, and residuum.

The preflash overhead is fed to the stabilizer for removal  
of the lighter hydrocarbons (usually dissolved gaseous hydrocar-  
bons such as propane). In the stabilizer, the light hydrocarbons  
are removed overhead, and the stabilized product is removed at  
the bottom.

The preflash bottoms feed the atmospheric tower, where again  
side cuts are taken and steam stripped to remove the light ends.

#### Two-Stage Distillation with Vacuum Tower--

This system incorporates the two-stage arrangement and adds  
to it a vacuum tower. The bottoms from the atmospheric tower  
feed the vacuum distillation tower, which operates at below  
atmospheric pressure. Operation under a vacuum allows the reduc-  
tion of operating temperatures and thus prevents coking in the  
heater tubes or on trays and thermal degradation, which may occur  
in high-temperature operations.

The petroleum refinery uses vacuum distillation to produce  
light and heavy gas oils, heavy fuel oil, vacuum gas oil, lubri-  
cating oil fractions, and vacuum bottoms. A refinery that prod-  
uces lubricating oils may use two separate vacuum towers, one  
especially designed to recover lube oil fractions and the other  
designed for fuel oil fractions.

Although steam is not usually injected into the vacuum unit,  
in some wet vacuum units steam is added to the distillation  
column operating under a vacuum. The dry vacuum process has the  
advantage of using smaller towers and smaller condensing equip-  
ment for a given throughput and also is more economical and  
energy efficient than the wet process.

A vacuum is usually created by steam jet ejectors discharg-  
ing to surface condensers (shell and tube), which limits air  
pollution. Alternatively, direct contact condensers are used, in  
which case, water, steam, and hydrocarbon vapors are mixed. This  
type of condenser can generate air pollutants; however, the

noncondensables from these units usually are vented to the refinery flare system as a means of controlling hydrocarbon emissions.

Appendix C provides more details of the principles of fractionation. Literature references and definition of terms are given in the Bibliography and Glossary at the end of this manual.

### 2.2.3 Deasphalting

Deasphalting separates asphalts or resins from more viscous fractions. Refineries and chemical plants commonly accomplish such separation by liquid-liquid extraction. In this operation, a mixture is separated into two components by means of a selective solvent, the separation being due to differences in solubility. For ease of separation, the solvent must yield a two-phase mixture with appreciable difference in densities of the two phases.

In deasphalting, residuum from the vacuum tower and liquid propane are heated to a controlled temperature and mixed at a controlled ratio as feed to the deasphalting tower. The two phases that result are separated, and propane is removed from the deasphalted oil phase by a two-stage evaporation process and steam stripping. The asphalt phase is heated and steam stripped for removal of residual propane. The propane is then condensed and recycled. Overhead from both strippers is water washed, compressed, and condensed before being recycled as propane extractant.

## 2.3 DECOMPOSITION PROCESSES

### 2.3.1 Catalytic Cracking

Catalytic cracking is a relatively inexpensive method of breaking down heavier distillate fractions into lighter gasoline material and thus increasing the overall gasoline yield from crude oil. The variety of catalysts and system designs provide a

wide range of operating flexibility for the catalytic cracking process.

Two well-known catalytic processes are in use today--the fluid catalytic cracker (FCC) and the Thermoform catalytic cracker (TCC). The FCC uses a powdered catalyst and the TCC or Houdriflow, no longer generally manufactured, uses a bead catalyst.

In the FCC, finely powdered catalyst is lifted into the reaction zone by the incoming oil, which vaporizes immediately upon contact with the hot catalyst. When the reaction is complete, the product and catalyst are lifted into a regeneration zone by air. In the reaction and regeneration zones, the catalyst powder is held in a suspended state by the passage of gases through it, and a small amount of catalyst is moved from the reactor to the regenerator and vice versa. Oil tends to saturate the enormous volume of pulverized catalyst in the reactor, and hence the catalyst must be steam stripped before it enters the regenerator.

The TCC is a moving-bed system with catalyst in the form of beads or pellets. The catalyst is lifted by air, or in old plants by bucket elevators, to a high position so that it can flow downward by the force of gravity. It moves through the oil zone, causing reaction, and then through a regeneration zone.

In both the FCC and TCC processes the catalyst must be regenerated. Coke that forms on the catalyst particles during the reaction must be continuously removed to maintain catalyst activity. In the regenerator, a controlled stream of air is added to burn off the coke. The resulting combustion gases flow through a series of cyclones for removal of the entrained catalyst. The regenerator gases (often rich in carbon monoxide, CO) may be burned as fuel in a CO boiler to generate refinery steam and eliminate CO emissions.

Reactor products are condensed and stabilized in a large distillation tower, where several streams are taken off. The lightest streams are sent to a gas recovery unit, and the heaviest streams are recycled to the catalytic cracker. The recycle

ratio and the ratio of catalyst to oil depend on the type of feedstock and the desired product.

More detailed explanations of the fluid unit are given in Section 4.2 and Appendix B.

### 2.3.2 Hydrocracking

Hydrocracking units perform both cracking and hydrogenation. Products from hydrocracking are essentially saturated materials with high concentrations of isoparaffins and naphthenes.

The hydrocracker functions in a manner similar to the catalytic cracker but operates over a wider range of feedstock boiling points. Because of their great flexibility, hydrocracking processes may be operated to produce high-quality motor gasoline, petrochemical naphtha, jet fuel, and diesel oils. With the new catalysts available, a single hydrocracking unit can be used to convert feedstocks as heavy as vacuum gas oils into either naphtha or high yields of middle distillates, simply by regulation of the fractionation cut points and reactor temperatures. Hydrocracking is also used to desulfurize high-sulfur crude oils while upgrading the heavier fractions into lighter fuel oils. The inherent flexibility of the process will allow a gradual increase in yield of motor gasoline to meet current market demand.

The fixed-bed hydrocracking catalysts maintain high activity in the presence of nitrogen and sulfur compounds. Various process configurations and catalyst systems can be combined to yield the optimum product spectrum for a particular feedstock.

The feedstock undergoes heat exchange with the second reactor product, combined with preheated recycle and makeup hydrogen, and introduced into the first reactor. The first reactor product is combined with preheated recycle and additional liquid recycle and introduced into the second reactor. The product is exchanged with feedstock, condensed, and separated to recover recycle hydrogen. A second flash stage removes gases, and the liquid product enters the fractionator, from which various product streams are taken for blending or further processing. The bottom

product is recycled to the second reactor. Because this process consumes hydrogen (200 to 350 volumes of hydrogen per volume of feedstock), refineries often operate a hydrogen production facility onsite.

In the United States, about one-third of the hydrocracking capacity is on the West Coast, where it is used to upgrade heavy fuels to motor gasoline and jet fuel. Another one-third is on the Gulf Coast, where it is used to alternate production of motor gasoline and light distillates according to market demands.

### 2.3.3 Coking

Coking is a severe form of thermal cracking; it is an ultimate-yield destructive distillation process that produces gas, distillate, and coke from residuals that may resist cracking by other methods. Although coke was earlier considered a low-value byproduct, it is now used in electrode manufacture when sulfur and metals contents are low enough. Coke with intermediate-range sulfur content may be used as fuel for steam generator boilers.

There are two principal coking processes, delayed and fluid. Delayed coking is the more widely used, and very few fluid coking units are in service.

In the delayed coking process, the feedstock goes directly to the fractionator. The lighter material is vaporized and leaves the fractionator overhead. It is cooled and separated, and the vapor phase is sent to the refinery fuel gas system. Various sidestreams from the fractionator include naphtha and light and heavy gas oils, which may be further processed. The bottoms from the fractionator are pumped through a furnace to the coking drums. Overhead from the coking drums flows back to the fractionator and is recycled.

Coke forms on the coking drum walls and eventually fills the drum. After a purging with steam, the drum is isolated and opened; coke is broken free by high-pressure water jets. At least two coking drums are provided so that one may be mechanically or hydraulically decoked while the other is filling. These



drums are usually sized so that they can be decoked and returned to service during one work shift. The coke particles are washed out with water and separated from the water on vibrating screens.

In the fluid coking process, the feedstock enters the reactor, where it is mixed with a fluidized bed of preheated recycled coke particles. The hydrocarbons in the liquid feed crack and vaporize, while the nonvolatile material is deposited on the suspended coke particles. The coke particles thus grow larger, sink to the bottom of the reactor, and flow to the burner. In the burner, the particles are fluidized with air, partially burned, and recycled to the reactor. A portion of the coke produced in the reactor is withdrawn as product. The overhead vapor can be desulfurized to yield fuel gas suitable for process heaters or steam/power generation.

#### 2.3.4 Visbreaking

Viscosity breaking, or "visbreaking," is a milder form of thermal cracking than coking; it is used to reduce the viscosity of some residual fractions so that they may be blended into fuel oils. It is applied when the demand for middle distillates exceeds that for motor gasoline.

The atmospheric or vacuum-reduced crude is preheated by heat exchange with visbroken fuel oil and fed to a furnace. Mild cracking in furnace tubes produces a mixture of residual oil, naphtha, and gas. The reaction products are quenched with a recycle stream and sent to a fractionator, in which the visbreaker bottoms accumulate in the lower portion. A simple pump system in the tower allows fractionation of the flashed vapors into gas, gasoline, and light and heavy gas oils. The gas oil sidestream normally flows through a steam-stripping tower for separation of the motor gasoline fraction.

## 2.4 FORMATION PROCESSES

### 2.4.1 Catalytic Reforming

Catalytic reforming is used to alter the structure of saturated straight-chain paraffins, which have very low octane numbers, to yield a different kind of molecule with much higher octane characteristics. The process converts straight-carbon-chain naphtha to a ring or branch-structured gasoline. Catalytic reforming is also called platforming (when a platinum catalyst is used), ultraforming, or magnaforming.

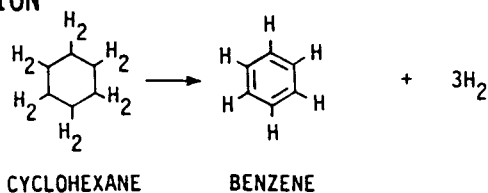
Catalytic reforming is a high-temperature, low-pressure, fixed-bed process using a bimetallic catalyst. The most important property of the catalyst is that which causes ring formation and permits ring preservation in molecules that have just undergone partial dehydrogenation (aromatization). As would be expected with a substance as complex as crude oil, the process reactions are numerous and complex. (A basic organic chemistry text will explain these reactions in detail.) Table 2-2 presents the major types of reactions that occur in catalytic reforming units. Naphthene dehydrogenation, naphthene dehydroisomerization, and paraffin isomerization are the predominant reactions. The other reactions may become significant at high temperatures, high pressures, and low-space velocities. Avoidance of hydrocracking is particularly important since it can lead to excessive coke deposition, which deactivates the catalyst.

Compared with the feed, the final product contains a high percentage of aromatic compounds and a small quantity of aliphatic hydrocarbons. Some of the aromatics (benzene, toluene, and xylenes) may be isolated to become petrochemical feedstock, but the major portion becomes motor gasoline blending stock.

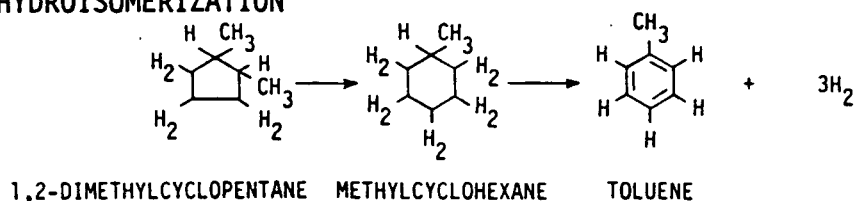
Catalytic reforming units are regenerative or nonregenerative. Regenerative reformers are the most common since they operate at the low pressures that produce larger yields of high-octane gasoline and also produce more hydrogen.

TABLE 2-2. MAJOR REACTIONS OCCURRING IN CATALYTIC REFORMING<sup>1</sup>

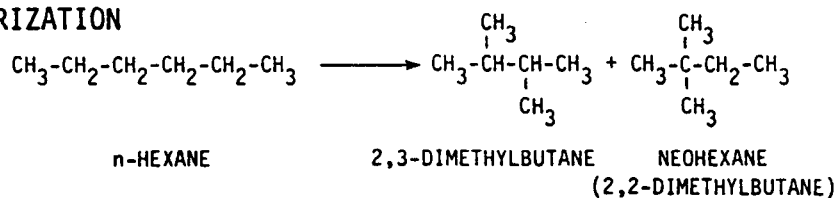
## NAPHTHENE DEHYDROGENATION



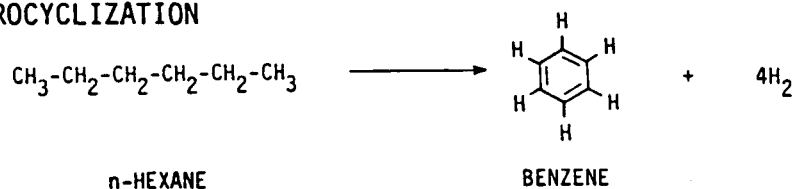
## NAPHTHENE DEHYDROISOMERIZATION



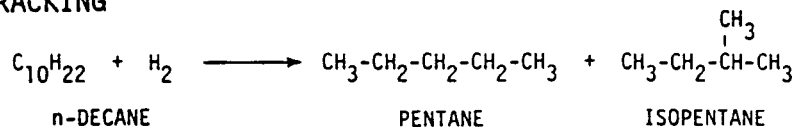
## PARAFFIN ISOMERIZATION



## PARAFFIN DEHYDROCYCLIZATION



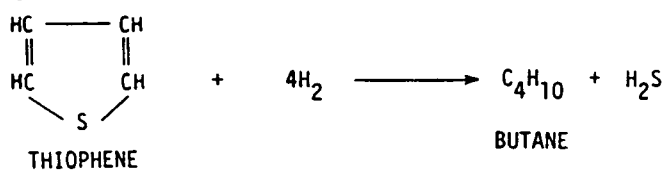
## PARAFFIN HYDROCRACKING



## OLEFIN HYDROGENATION



## HYDRODESULFURIZATION



Before entering the reforming unit, the naphtha feed is hydrotreated to remove elements that may poison the reforming catalyst. The hydrotreated naphtha is mixed with hydrogen from the reformat<sup>s</sup> stabilizer, exchanged with product streams, and heated in a furnace. This feed mixture then passes through several reactors. The charge is heated before entering each reactor to compensate for the endothermic reactions that occur. The final reactor effluent is cooled, and the gases are separated from the liquid products. The gases may be recycled, sent to the hydrogen recovery system, or sent to the plant fuel system.

The liquid products are sent to a stabilizer (tower). The noncondensable overhead from the stabilizer goes to the fuel gas system, and the condensable liquids are treated for recovery of light ends. Bottoms from the stabilizer are the reformat<sup>s</sup> product, which is usually sent to gasoline blending.

So that a reactor may be regenerated, most reforming units contain a spare ("swing") reactor, which is periodically placed in service during the regeneration cycle. During regeneration, the coke deposited on the catalyst is burned off by a carefully controlled stream of inert gases and a limited amount of air.

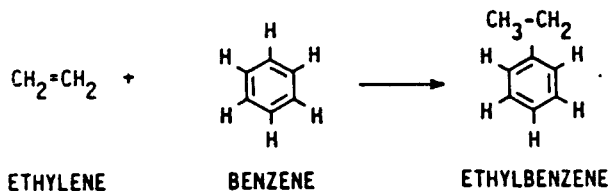
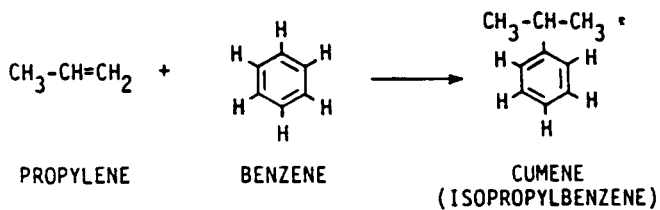
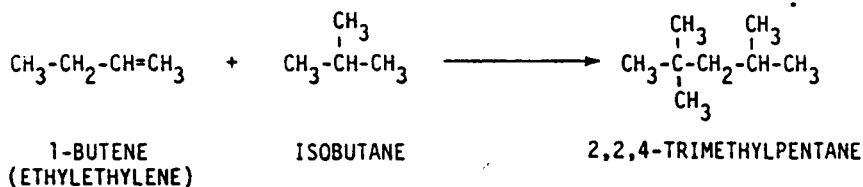
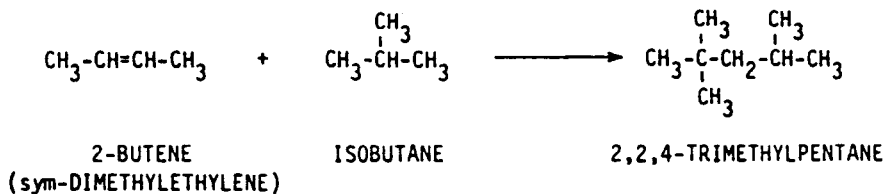
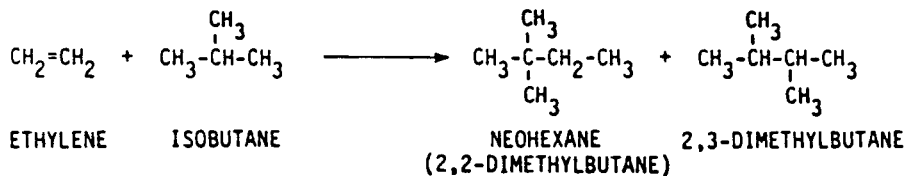
The nonregenerative systems do not have a spare reactor; instead, the unit is shut down when the catalyst is deactivated, and the catalyst is replaced. In other respects operation of these units is similar to that of regenerative reformers.

#### 2.4.2 Alkylation

The alkylation process for production of high-octane gasoline resulted from the discovery that isoparaffin hydrocarbons unite with olefins in the presence of a catalyst. The process may involve isobutane and olefins, which produce high-octane dimers or trimers. Table 2-3 summarizes some of the alkylation reactions.

Sulfuric acids or hydrofluoric acid is used to catalyze the alkylation reaction. The reactants are combined with rapid and violent mixing into refrigerated liquid acid. The resultant vapors are separated from the acid mixture, caustic washed, water

TABLE 2-3. SUMMARY OF REACTIONS OCCURRING IN ALKYLATION



washed, and stabilized in a fractionation tower (debutanizer). The tower bottoms are taken as alkylate, and the overhead vapors are condensed and recycled. The tower also yields a normal butane fraction.

#### 2.4.3 Isomerization

As in catalytic reforming, the isomerization processes rearrange the molecular structure of the feedstock while reducing losses that normally occur in cracking or condensation reactions. In the isomerization reactions nothing is added to or taken away from the material. Formation of branched-chain compounds from straight-chain compounds increases the octane number. The main types of isomerization are butane, pentane, hexane, and xylene isomerization.

Butane isomerization is closely linked with alkylation when alkylate is required and isobutane is in short supply. Isobutane is produced to provide feedstock for the alkylation unit. Building alkylation and isomerization units together permits sharing of common distillation equipment. Isomerization of butanes is increasing as a means of supplying petrochemical feedstock. Isomerization of pentane and hexane yields products more suited for motor gasoline blending stocks because they have desirable antiknock properties. If a refinery is extracting paraxylene from the catalytic reformat, the remaining orthoxylene and metaxylene may be fed to an isomerization unit to produce paraxylene. (Details of this type of isomerization are given in Reference 2).

The butane isomerization process converts normal butane into isobutane over a catalyst in the presence of hydrogen. A mixed butane feedstock is fed into the deisobutanizer tower (distillation tower) from which isobutane product is taken overhead. The bottoms undergo heat exchange with the reactor product after recycle, and makeup hydrogen is added. The mixture is heated to the reaction temperature in a furnace. Vaporized butanes enter the fixed-bed catalytic reactor, undergo heat exchange with the

reactor feed, and are condensed; the reactor effluent flows to the separator for recovery of recycle hydrogen. Separator liquid is sent to the stabilizer, where overheads are condensed and noncondensables flow to the refinery gas system. Stabilizer bottoms go to the deisobutanizer, where the overhead is the product isobutane.

#### 2.4.4 Polymerization

Polymerization is the combining of monomers. In a refinery operation, propylene (olefin; monomer) would be polymerized to yield dimer (2-propylenes), trimer (3-propylenes), tetramer (4-propylenes) and perhaps higher order polymers.

This process is used very rarely in refineries today. It was first introduced to provide a motor gasoline blending stock when octane levels were very low. The octane gain from blending of polymer (poly) gasoline was soon replaced by blending of alkylate from alkylation units. Polymers are valuable in some applications, however, such as additives for motor oil.

A refinery stream of propylene and butylenes is mixed with recycle propane and water, subjected to heat exchange with reactor product, preheated, and introduced into the top of a multiple-fixed-bed reactor. Solid phosphoric acid deposited on an inert carrier is the catalyst. Water is injected between the several fixed beds for temperature control. The reactor product is cooled by heat exchange with feed and sent to the depropanizer (distillation tower). The overhead product is recycled to the reactor feed. Bottom material is debutanized in a distillation tower, from which butane goes overhead and polymer gasoline is taken as bottoms.

### 2.5 TREATING PROCESSES

The objective of all petroleum refinery treatment of intermediate fractions or products is to remove or render inactive

compounds that would otherwise reduce the quality of these fractions or products. Treating is particularly important for removing sulfur, nitrogen, and metal compounds from feed for a catalytic cracker or catalytic reformer. If these compounds were not removed, they would attack the catalyst. Therefore, this treatment both improves performance and lengthens catalyst life.

Refinery treating processes can be classified as catalytic or chemical. Several processes can be applied, depending upon the content of undesirable compounds and the required severity of the treatment. The vent or waste gas streams from the treating processes usually contain the hydrogenated form of the undesirable compound. These streams can be sent to the sulfur recovery process or the refinery fuel system.

#### 2.5.1 Catalytic Treating

Hydrotreating is the most widely used process for all types of petroleum products. With the appropriate catalyst and operating conditions, hydrotreating can desulfurize, eliminate other impurities such as nitrogen and oxygen, decolorize and stabilize, and correct odor problems and many other product deficiencies.

Hydrodesulfurization processes convert the sulfur in sulfur compounds into more easily removed hydrogen sulfide ( $H_2S$ ) by use of rugged catalysts and hydrogen. The processes also convert some nitrogen compounds into ammonia.

Other hydrogenation or hydrotreating processes (not intended primarily to attack sulfur) saturate olefinic materials, which are undesirable in many refinery products. For example, certain cracked gasoline stocks contain hydrocarbons that tend to polymerize (form gums) upon exposure to air. These can be stabilized by a mild catalytic hydrotreating process.

#### 2.5.2 Chemical Processes

Chemical treating processes scrub fractions with inorganic acids such as sulfuric acid ( $H_2SO_4$ ) and bases such as sodium hydroxide ( $NaOH$ ) to remove undesirable acids and sulfur compounds. Certain chemical treating processes use proprietary



chemicals to remove specific impurities and improve the quality and/or performance of petroleum products.

Acid gas removal processes bring feed streams into contact with a selective solvent or absorbent. These materials absorb the acid gases (normally hydrogen sulfide); they are regenerated by stripping and then recycled. The stripped acid gases are disposed of either in the sulfur recovery unit or by incineration. The sulfur recovery process (Claus unit) is preferred because it minimizes emissions.

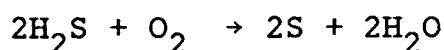
Many processes are commercially available to perform all types of treating operations. The Bibliography gives literature references in the categories of acid gas removal, chemical sweetening, hydrotreating, and hydrodesulfurization processes.

## 2.6 RECOVERY OPERATIONS

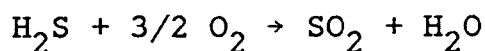
### 2.6.1 Sulfur Recovery

Sulfur compounds in petroleum fractions are converted into  $\text{H}_2\text{S}$  by treating processes. This  $\text{H}_2\text{S}$  is collected and sent to the sulfur recovery plant (Claus unit).

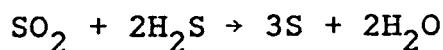
In the Claus unit,  $\text{H}_2\text{S}$  is burned with air to form elemental sulfur. The overall chemical reaction is:



The reaction is normally conducted in stages in which part of the  $\text{H}_2\text{S}$  is oxidized with air to form  $\text{SO}_2$ , as follows:



This  $\text{SO}_2$  is combined with the remaining  $\text{H}_2\text{S}$  over a fixed-bed catalyst to complete the reaction:



A number of catalytic stages can be used to increase the sulfur recovery and reduce  $\text{SO}_2$  emissions.

Final exhaust gases may contain sulfur carbonyls, carbon disulfide ( $\text{CS}_2$ ),  $\text{H}_2\text{S}$ , and some elemental sulfur. These are

normally incinerated at high temperature in a tail gas unit, and the exhaust gas contains only small quantities of  $\text{SO}_2$ .

#### 2.6.2 Fuel Gas Recovery

The fuel gas plant incorporates a system of operations for recovering useful hydrocarbon vapor mixtures from the crude oil distillation unit and other refinery processes. While adding value to the overall refinery process, the recovery process also prevents hydrocarbon losses and emissions. A well-operated gas recovery system is essential to the overall economics of petroleum refining.

Vapors (noncondensable gases) from the crude distillation towers, the reformers, and the catalytic cracking units are collected and sent to the gas processing unit for light-ends recovery. The gases are compressed, condensed, and distilled (separated) into various mixtures having constant vapor pressure. These mixtures may be used as refinery fuel (burned in fired heaters and boilers), sold as liquefied petroleum gases, used as feedstock for hydrogen production, used as alkylation feedstock, or sold as petrochemical feedstock.

### 2.7 STORAGE

All refineries use tanks and vessels for storage of feedstocks (crude oil, pressurized liquid hydrocarbons, etc.) and of intermediate products awaiting further processing and/or blending. A certain amount of lower volume storage within the processing area is referred to as "rundown tankage." Tankage is also provided for finished products awaiting shipment and for use in loading and unloading operations.

### 2.8 AUXILIARY FACILITIES

A refinery requires many auxiliary facilities, which can include those for steam generation, production of electrical power, wastewater treatment, and hydrogen production, as well as

cooling towers and blowdown systems (including flares and liquid incineration).

Many large refineries now generate some of their own electrical power. Steam leaving turbines goes into refinery steam systems at various pressure levels.

Wastewater treatment systems can range from a simple API separator to very elaborate biological treatment systems. All water streams are treated to meet environmental standards as well as to recover various products.

Process water is recirculated and cooled to the specified temperatures in cooling towers. Air coolers are being used with increasing frequency to reduce requirements for cooling water.

Because product treating processes require hydrogen, the hydrogen production facilities are often considered as auxiliary or utility systems.

Blowdown systems receive releases of liquid and gaseous streams from emergency vents and safety valves. These systems entail collection, separation, and disposition by a flare or incinerator.

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## SECTION 5

### ENFORCEMENT PROCEDURES

Each petroleum refinery is designed, engineered, constructed, and operated to process specific crude oils and produce specific products. This results in each petroleum refinery being unique in the complexity and number of processes employed. Since there is no typical refinery, a standard procedure for conducting the inspection does not exist. This section describes approaches to conducting an inspection rather than describing a standard procedure for the inspector to follow.

#### 5.1 INTRODUCTION

This section describes the various levels of enforcement inspections and lists the process units and other emission sources that are to be inspected on those levels.

A thorough search should be conducted of the file for the refinery to be inspected to determine what process units are there, to note compliance history and trends, and to collect other pertinent data. The inspection checklists (which are given in Appendixes J through M) should be filled out as much as possible from file data. The data can then be verified and additional data collected during the inspection. The checklists are merely a means of organizing data; they are not official forms.

The inspector should be as informed as possible before entering the refinery, and one way to accomplish this is to review the descriptions of the various refining processes (Section 4). The inspector should review the subsections pertaining to those units that will be inspected. Appendix B and Appendix C

provide additional background on the chemical engineering principles applicable to petroleum refining. The more an inspector knows about an industry he is inspecting, the better he will be able to communicate with plant personnel and the better the inspection will be. The inspector is cautioned not to appear to possess more knowledge of a subject than he actually has; by doing so, he may miss getting important information or discredit himself if plant personnel detect an area of ignorance. An honest, questioning approach is generally the most effective.

It is important that the inspector be assertive in order to assess compliance. The inspector should guide the course of the inspection and be persistent in getting and verifying important data. For example, the inspector may have a list of process units and their feed rates. Rather than accepting the word of the plant personnel aiding in the inspection, the inspector should ask to see production sheets or a logbook that will verify these data. An inspector should be confident that correct data are collected. This approach, although time consuming, is effective in uncovering additional compliance problems.

The following subsections describe three levels of inspection, which increase in degree of intensity and follow different time schedules. The Level I inspection is aimed at obtaining continuing compliance of a limited number of units. These units are the most likely to cause emission problems. The purpose of a Level II inspection is to obtain compliance with particulate, sulfur oxide, nitrous oxide, and some hydrocarbon emission regulations. In a Level II inspection more units are investigated than on a Level I inspection. The Level III inspection is aimed at obtaining strict compliance with hydrocarbon emission regulations. The number of fugitive emission sources monitored on a Level III inspection is much greater than the number monitored on a Level II inspection. Level II and III inspections are similar in the number of sources investigated for compliance with particulate, sulfur oxide, and nitrous oxide emission regulations. In the future, a fourth or very detailed inspection may be added.

This manual does not rule out that possibility, which would result from new state and Federal policies.

## 5.2 LEVEL I INSPECTION

It is recommended that a Level I inspection be performed once every 2 to 4 months. The actual frequency depends on the workload and manpower available at local, state and Federal offices. The duration of the inspection depends on the size of the refinery and the number of inspectors. A two-man inspection team can investigate a 30,000 barrel per day refinery in 2 to 3 hours.

Note the overall condition of the refinery during this inspection. Dust from the unpaved roads is a source of particulate emissions, and pools of oily water are a source of hydrocarbon emissions. Observe all heater and boiler stacks to monitor opacity. When a heater or a boiler stack is out of compliance with the state visible emission standard, complete the the visible emission observation form.

Review and investigate the following units:

<u>Unit</u>	<u>Pollutant</u>
Fluid catalytic cracking	Particulates; sulfur dioxide
Sulfur recovery	Sulfur dioxide

The pollution control equipment that may be present at the Fluid Catalytic Cracking (FCC) unit includes a CO boiler, an electrostatic precipitator (ESP), and internal and external cyclones. Note the type of control equipment that is used and also note whether the CO boiler or ESP is bypassed during the inspection. (A refinery that does not have a flare, bypasses the CO boiler to the FCC sump stack.)

Sulfur dioxide emissions from a sulfur plant are continuously monitored at incinerator stacks by recording the incinerator temperature. The usual incinerator temperature is about

1204°C (2200°F). This temperature increases, however, to about 1427°C (2600°F) when the acid gas feed bypasses the Claus and tail gas unit and is routed directly to the incinerator, thus increasing SO<sub>2</sub> emissions at the stack. The incinerator temperature is a good indicator of the amount of acid gas being bypassed.

Completion of the Level I checklist is further discussed in Section 5.7.

### 5.3 LEVEL II INSPECTION

It is recommended that a Level II inspection be performed once every 6 to 9 months. The actual frequency depends on the workload and manpower available at the agency. The duration of the inspection depends on the size of the refinery and the number of inspectors. It takes a two-man team 1 to 2 days to inspect a 30,000 barrel per day integrated refinery. Before the inspection, obtain the data listed below for the units being inspected; during the inspection, review the data with refinery personnel.

Process flow diagram

Process information

Heater and boiler data (type of fuel, heater duty, exit temperature, and stack data)

Storage tank data

Wastewater separator data (type of separator, type of cover, condition of cover)

Some fugitive emissions are monitored by a hydrocarbon detector, in addition to the monitoring of particulates and SO<sub>2</sub> emissions.

Review and investigate the following units:

<u>Unit</u>	<u>Pollutant</u>
Fluid catalytic cracking	Hydrocarbon vapors; particulates; sulfur dioxide
Sulfur recovery	Sulfur dioxide
Wastewater treatment	Hydrocarbon vapors

(continued)

<u>Unit</u>	<u>Pollutant</u>
Isomerization	Hydrocarbon vapors, particulates
Alkylation	Hydrocarbon vapors, particulates
Storage	Hydrocarbon vapors
Loading	Hydrocarbon vapors
Light-ends/gas processing	Hydrocarbon vapors

The survey of oil refineries by the California Air Resources Board in April 1978 showed that isomerization, alkylation, storage, loading, light ends/gas processing, and FCC units accounted for about 40 percent of the fugitive hydrocarbon emissions. The CARB study also identified the items that contributed most to fugitive emissions: valves, pump seals, and compressor seals. For each process unit listed, use a hydrocarbon detector to inspect a certain number of the key emission contributors (Table 5-1). A screening procedure for monitoring fugitive emissions is provided in Appendix H. Appendix G contains operating instructions for a Century Organic Vapor Analyzer, hydrocarbon detector.

#### 5.4 LEVEL III INSPECTION

It is recommended that a Level III inspection be performed once every 12 to 18 months. The frequency and duration depends on the workload and manpower available at the agency. The duration of the inspection depends on the size and complexity of the refinery. It takes a four-man team about one week to inspect a 30,000 barrel per day integrated refinery. It is a very detailed inspection of the following units:



TABLE 5-1. LEVEL II LEAK DETECTION PROGRAM

Process unit	Valves (in gas service)		Pump seals		Compressor seals	
	Sample size	Accept No.*	Sample size	Accept No.*	Sample size	Accept No.*
Isomerization	20	5				
Alkylation	20	5	5	1		
Storage	20	5	8	2	2	1
Loading	20	5	8	2		
Gas processing	20	5	8	2	2	1
FCC	8	2	5	1	2	1

\*The accept number is the maximum number of leaks detected in the sample size that results in statistically approving the sample. This number is based on varying quality levels and statistics. Appendix E explains the derivation of these numbers.

<u>Unit</u>	<u>Pollutant</u>
Fluid catalytic cracking	Hydrocarbon vapors; particulates, sulfur dioxide
Sulfur recovery	Sulfur dioxide
Wastewater treatment	Hydrocarbon vapors
Distillation: Vacuum	Hydrocarbon vapors; particulates
Distillation: Atmospheric	Hydrocarbon vapors; particulates
Isomerization	Hydrocarbon vapors; particulates
Alkylation	Hydrocarbon vapors; particulates
Storage	Hydrocarbon vapors
Loading	Hydrocarbon vapors
Light-ends/gas processing	Hydrocarbon vapors
Hydrocracking	Hydrocarbon vapors; particulates
Reforming	Hydrocarbon vapors; particulates
Visbreaking	Hydrocarbon vapors
Hydrotreating (Hydrodesulfurization, or HDS)	Hydrocarbon vapors

Again, the CARB study determined that the process units listed above comprise about 52 percent of the fugitive hydrocarbon emissions. For each process unit listed, use a hydrocarbon sniffer to inspect a certain number of the key emission contributors (Table 5-2). The operating instructions for using a Century Organic Vapor Analyzer to monitor fugitive emissions is provided in Appendix G. Appendix H contains a screening procedure for monitoring fugitive emissions.

TABLE 5-2 LEVEL III LEAK DETECTION PROGRAM

Process unit	Valves (in gas service)		Pump seals		Compressor seals	
	Sample size	Accept No.	Sample size	Accept No.	Sample size	Accept No.
Isomerization	20	2				
Alkylation	50	5	8	1		
Storage	50	5	20	2	3	0
Loading	50	5	20	2		
Gas Processing	50	5	20	2	3	0
FCC	20	2	8	1	3	0
Visbreaking	20	2	8	1	3	0
Hydrotreating* (HDS)	20	2	8	1	3	0
Hydrocracking	20	2	8	1	3	0
Reformer	20	2	8	1	3	0
Distillation: Atmospheric	20	2	8	1		
Distillation: Vacuum	20	2	8	1		

\*A refinery has hydrotreating units for several feedstreams, some of which are listed below:

HDS--reformer feed  
HDS--light gas oil  
HDS--heavy gas oil  
Vacuum--(Residue) gas oil  
Coker--Naphtha



# Petroleum Product Storage and Distribution

## 4.3 STORAGE OF ORGANIC LIQUIDS

### 4.3.1 Process Description

Storage vessels containing organic liquids can be found in many industries, including (1) petroleum producing and refining, (2) petrochemical and chemical manufacturing, (3) bulk storage and transfer operations, and (4) other industries consuming or producing organic liquids. Organic liquids in the petroleum industry, usually called petroleum liquids, generally are mixtures of hydrocarbons having dissimilar true vapor pressures (for example, gasoline and crude oil). Organic liquids in the chemical industry, usually called volatile organic liquids, are composed of pure chemicals or mixtures of chemicals with similar true vapor pressures (for example, benzene or a mixture of isopropyl and butyl alcohols).

Five basic tank designs are used for organic liquid storage vessels, fixed roof, external floating roof, internal floating roof, variable vapor space, and pressure (low and high).

**Fixed Roof Tanks** - A typical fixed roof tank is shown in Figure 4.3-1. This type of tank consists of a cylindrical steel shell with a permanently affixed roof, which may vary in design from cone or dome shaped to flat.

Fixed roof tanks are commonly equipped with a pressure/vacuum vent that allows them to operate at a slight internal pressure or vacuum to prevent the release of vapors during very small changes in temperature, pressure or liquid level. Of current tank designs, the fixed roof tank is the least expensive to construct and is generally considered the minimum acceptable equipment for storage of organic liquids.

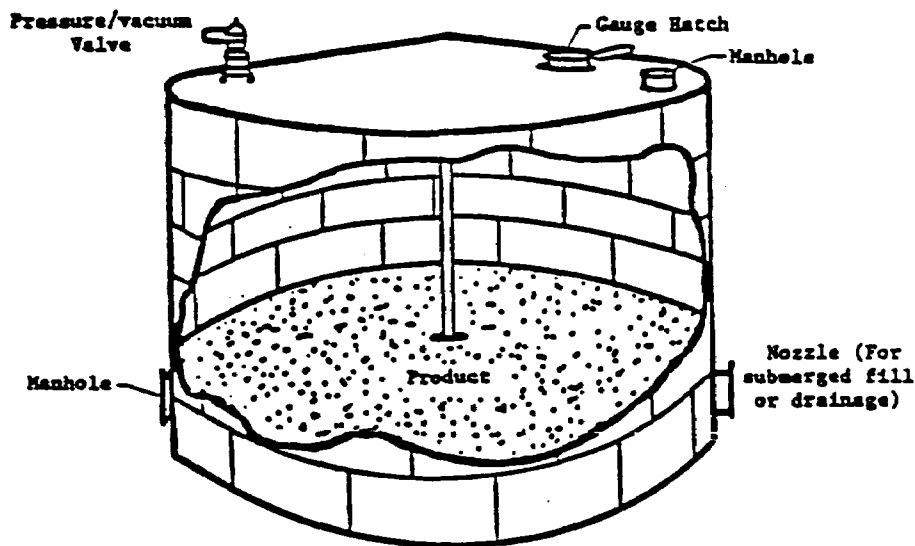


Figure 4.3-1. Typical fixed roof tank.<sup>1</sup>

External Floating Roof Tanks - A typical external floating roof tank is shown in Figure 4.3-2. This type of tank consists of a cylindrical steel shell equipped with a roof which floats on the surface of the stored liquid, rising and falling with the liquid level. The liquid surface is completely covered by the floating roof, except at the small annular space between the roof and the tank wall. A seal (or seal system) attached to the roof contacts the tank wall (with small gaps, in some cases) and covers the annular space. The seal slides against the tank wall as the roof is raised or lowered. The purpose of the floating roof and the seal (or seal system) is to reduce the evaporation loss of the stored liquid.

Internal Floating Roof Tanks - An internal floating roof tank has both a permanent fixed roof and a deck inside. The deck rises and falls with the liquid level and either floats directly on the liquid surface (contact deck) or rests on pontoons several inches above the liquid surface (non-contact deck). The terms "deck" and "floating roof" can be used interchangeably in reference to the structure floating on the liquid inside the tank. There are two basic types of internal floating roof tanks, tanks in which the fixed roof is supported by vertical columns within the tank, and tanks with a self-supporting fixed roof and no internal support columns. Fixed roof tanks that have been retrofitted to employ a floating deck are typically of the first type, while external floating roof tanks typically have a self-supporting roof when converted to an internal floating roof tank. Tanks initially constructed with both a fixed roof and a floating deck may be of either type.

The deck serves to restrict evaporation of the organic liquid stock. Evaporation losses from decks may come from deck fittings, nonwelded deck seams, and the annular space between the deck and tank wall. Typical contact deck and noncontact deck internal floating roof tanks are shown in

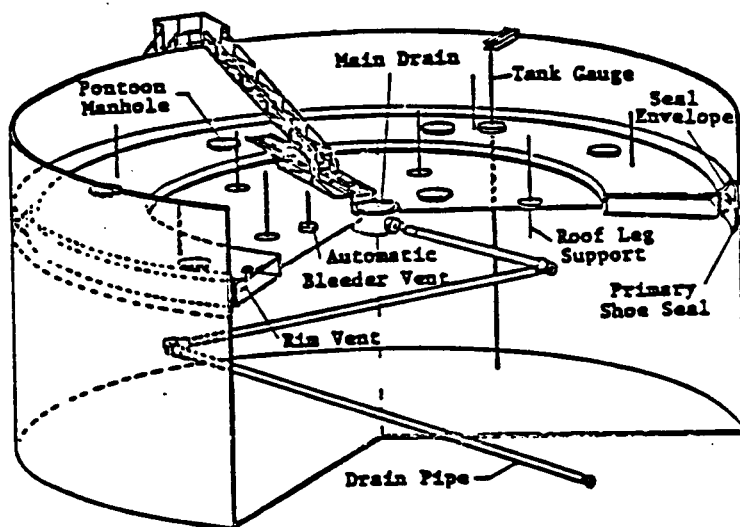


Figure 4.3-2. External floating roof tank.<sup>1</sup>

Figure 4.3-3. Contact decks can be aluminum sandwich panels with a honeycomb aluminum core floating in contact with the liquid, or pan steel decks floating in contact with the liquid, with or without pontoons. Typical noncontact decks have an aluminum deck or an aluminum grid framework supported above the liquid surface by tubular aluminum pontoons or other bouyant structures. Both types of deck incorporate rim seals, which slide against the tank wall as the deck moves up and down. In addition, these tanks are freely vented by circulation vents at the top of the fixed roof. The vents minimize the possibility of organic vapor accumulation in concentrations approaching the flammable range. An internal floating roof tank not freely vented is considered a pressure tank.

Pressure Tanks - There are two classes of pressure tanks in general use, low pressure (2.5 to 15 psig) and high pressure (higher than 15 psig). Pressure tanks generally are used for storage of organic liquids and gases with high vapor pressures and are found in many sizes and shapes, depending on the operating pressure of the tank. Pressure tanks are equipped with a pressure/vacuum vent that is set to prevent venting loss from boiling and breathing loss from daily temperature or barometric pressure changes. High pressure storage tanks can be operated so that virtually no evaporative or working losses occur. In low pressure tanks, working losses can occur with atmospheric venting of the tank during filling operations.

Variable Vapor Space Tanks - Variable vapor space tanks are equipped with expandable vapor reservoirs to accomodate vapor volume fluctuations attributable to temperature and barometric pressure changes. Although variable vapor space tanks are sometimes used independently, they are normally connected to the vapor spaces of one or more fixed roof tanks. The two most common types of variable vapor space tanks are lifter roof tanks and flexible diaphragm tanks.

Lifter roof tanks have a telescoping roof that fits loosely around the outside of the main tank wall. The space between the roof and the wall is closed by either a wet seal, which is a trough filled with liquid, or a dry seal, which uses a flexible coated fabric.

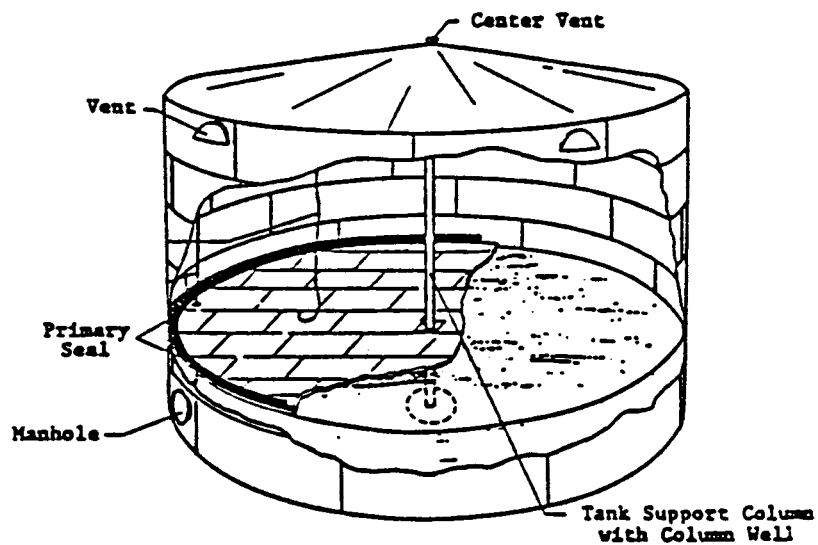
Flexible diaphragm tanks use flexible membranes to provide expandable volume. They may be either separate gasholder units or integral units mounted atop fixed roof tanks.

#### 4.3.2 Emissions And Controls

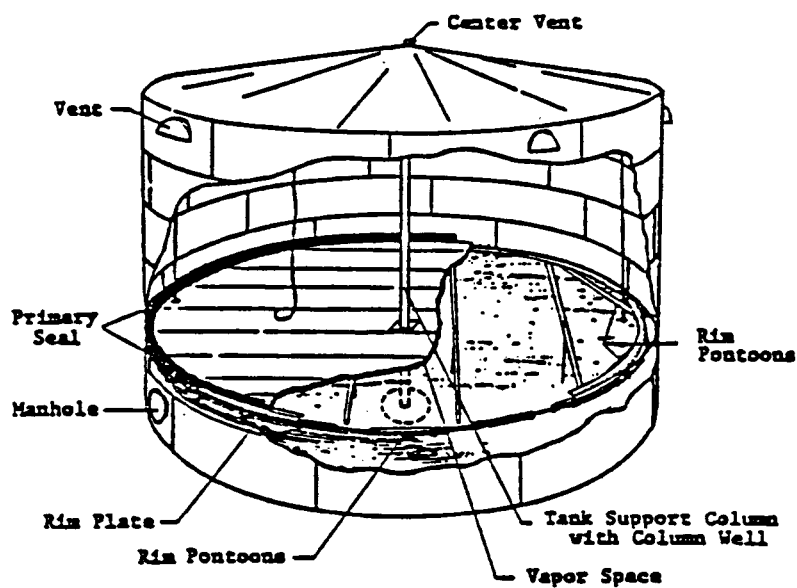
Emission sources from organic liquids in storage depend upon the tank type. Fixed roof tank emission sources are breathing loss and working loss. External or internal floating roof tank emission sources are standing storage loss and withdrawal loss. Standing storage loss includes rim seal loss, deck fitting loss and deck seam loss. Pressure tanks and variable vapor space tanks are also emission sources.

Fixed Roof Tanks - Two significant types of emissions from fixed roof tanks are breathing loss and working loss. Breathing loss is the expulsion of vapor from a tank through vapor expansion and contraction, which are the results of changes in temperature and barometric pressure. This loss occurs without any liquid level change in the tank.





Contact Deck Type



Noncontact Deck Type

Figure 4.3-3. Internal floating roof tanks.<sup>1</sup>

The combined loss from filling and emptying is called working loss. Filling loss comes with an increase of the liquid level in the tank, when the pressure inside the tank exceeds the relief pressure and vapors are expelled from the tank. Emptying loss occurs when air drawn into the tank during liquid removal becomes saturated with organic vapor and expands, thus exceeding the capacity of the vapor space.

The following equations, provided to estimate emissions, are applicable to tanks with vertical cylindrical shells and fixed roofs. These tanks must be substantially liquid and vapor tight and must operate approximately at atmospheric pressure. Fixed roof tank breathing losses can be estimated from<sup>2</sup>:

$$L_B = 2.26 \times 10^{-2} M_V \left( \frac{P}{P_A - P} \right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_P C K_C \quad (1)$$

where:

$L_B$  = fixed roof breathing loss (lb/yr)

$M_V$  = molecular weight of vapor in storage tank (lb/lb mole), see Note 1

$P_A$  = average atmospheric pressure at tank location (psia)

$P$  = true vapor pressure at bulk liquid conditions (psia), see Note 2

$D$  = tank diameter (ft)

$H$  = average vapor space height, including roof volume correction (ft), see Note 3

$\Delta T$  = average ambient diurnal temperature change (°F)

$F_P$  = paint factor (dimensionless), see Table 4.3-1

$C$  = adjustment factor for small diameter tanks (dimensionless), see Figure 4.3-4

$K_C$  = product factor (dimensionless), see Note 4

Notes: (1) The molecular weight of the vapor,  $M_V$ , can be determined by Table 4.3-2. for selected petroleum liquids and volatile organic liquids or by analysis of vapor samples. Where mixtures of organic liquids are stored in a tank,  $M_V$  can be estimated from the liquid composition. As an example of the latter calculation, consider a liquid known to be composed of components A and B with mole fractions in the liquid  $X_a$  and  $X_b$ , respectively. Given the vapor pressures of the pure

TABLE 4.3-1. PAINT FACTORS FOR FIXED ROOF TANKS<sup>a</sup>

Tank color		Paint factors ( $F_p$ )	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44 <sup>b</sup>
Medium gray	Medium gray	1.40	1.58 <sup>b</sup>

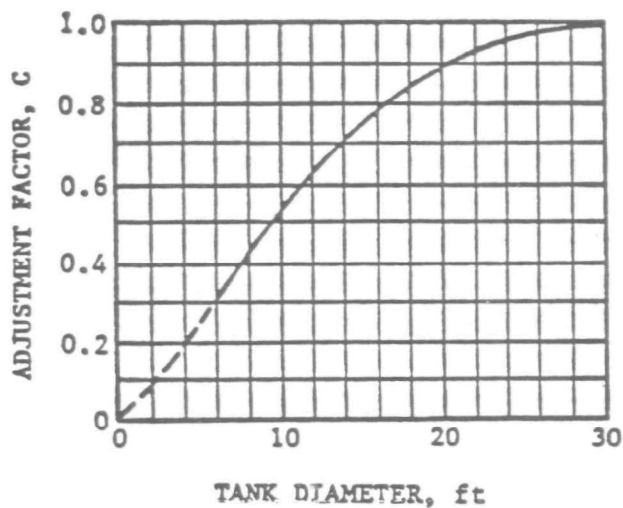
<sup>a</sup>Reference 2.<sup>b</sup>Estimated from the ratios of the seven preceding paint factors.Figure 4.3-4. Adjustment factor (C) for small diameter tanks.<sup>2</sup>

TABLE 4.3-2. PHYSICAL PROPERTIES OF TYPICAL ORGANIC LIQUIDS<sup>a</sup>

Organic liquid <sup>b</sup>	Vapor molecular weight @ 60°F	Product density (d), lb/gal @ 60°F	Condensed vapor density (w), lb/gal @ 60°F	True vapor pressure in psia at:						
				40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum Liquids <sup>c</sup>										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel no. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil no. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Volatile Organic Liquids										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1,2-Dichloroethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methylethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
1,1,1-Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

<sup>a</sup> References 3-4.<sup>b</sup> For a more comprehensive listing of volatile organic liquids, see Reference 3.<sup>c</sup> RVP = Reid vapor pressure in psia.

components,  $P_a$  and  $P_b$ , and the molecular weights of the pure components,  $M_a$  and  $M_b$ ,  $M_v$  is calculated:

$$M_v = M_a \left( \frac{P_a X_a}{P_t} \right) + M_b \left( \frac{P_b X_b}{P_t} \right)$$

where:  $P_t$ , by Raoult's law, is:

$$P_t = P_a X_a + P_b X_b$$

- (2) True vapor pressures for organic liquids can be determined from Figures 4.3-5 or 4.3-6, or Table 4.3-2. In order to use Figures 4.3-5 or 4.3-6, the stored liquid temperature,  $T_S$ , must be determined in degrees Fahrenheit.  $T_S$  is determined from Table 4.3-3, given the average annual ambient temperature,  $T_A$ , in degrees Fahrenheit. True vapor pressure is the equilibrium partial pressure exerted by a volatile organic liquid, as defined by ASTM-D-2879 or as obtained from standard reference texts. Reid vapor pressure is the absolute vapor pressure of volatile crude oil and volatile nonviscous petroleum liquids, except liquified petroleum gases, as determined by ASTM-D-323.
- (3) The vapor space in a cone roof is equal in volume to a cylinder, which has the same base diameter as the cone and is one third the height of the cone. If information is not available, assume  $H$  equals one half tank height.
- (4) For crude oil,  $K_C = 0.65$ . For all other organic liquids,  $K_C = 1.0$ .

Fixed roof tank working losses can be estimated from<sup>2</sup>:

$$L_w = 2.40 \times 10^{-5} M_v P V N K_N K_C \quad (2)$$

where:

$L_w$  = fixed roof working loss (lb/year)

$M_v$  = molecular weight of vapor in storage tank (lb/lb mole), see Note 1 to Equation 1

$P$  = true vapor pressure at bulk liquid temperature (psia), see Note 2 to Equation 1

$V$  = tank capacity (gal)

$N$  = number of turnovers per year (dimensionless)

$$N = \frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, } V \text{ (gal)}}$$

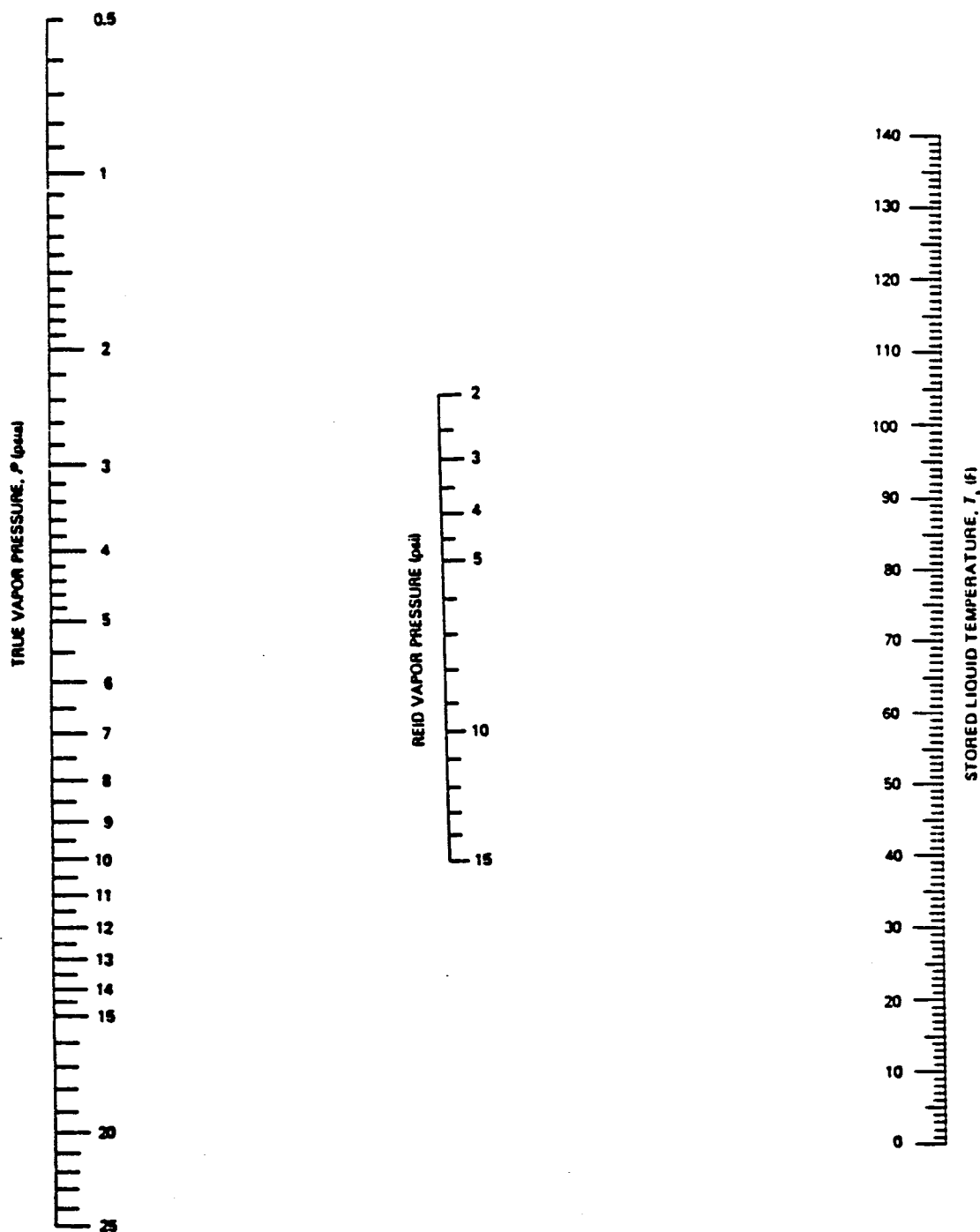
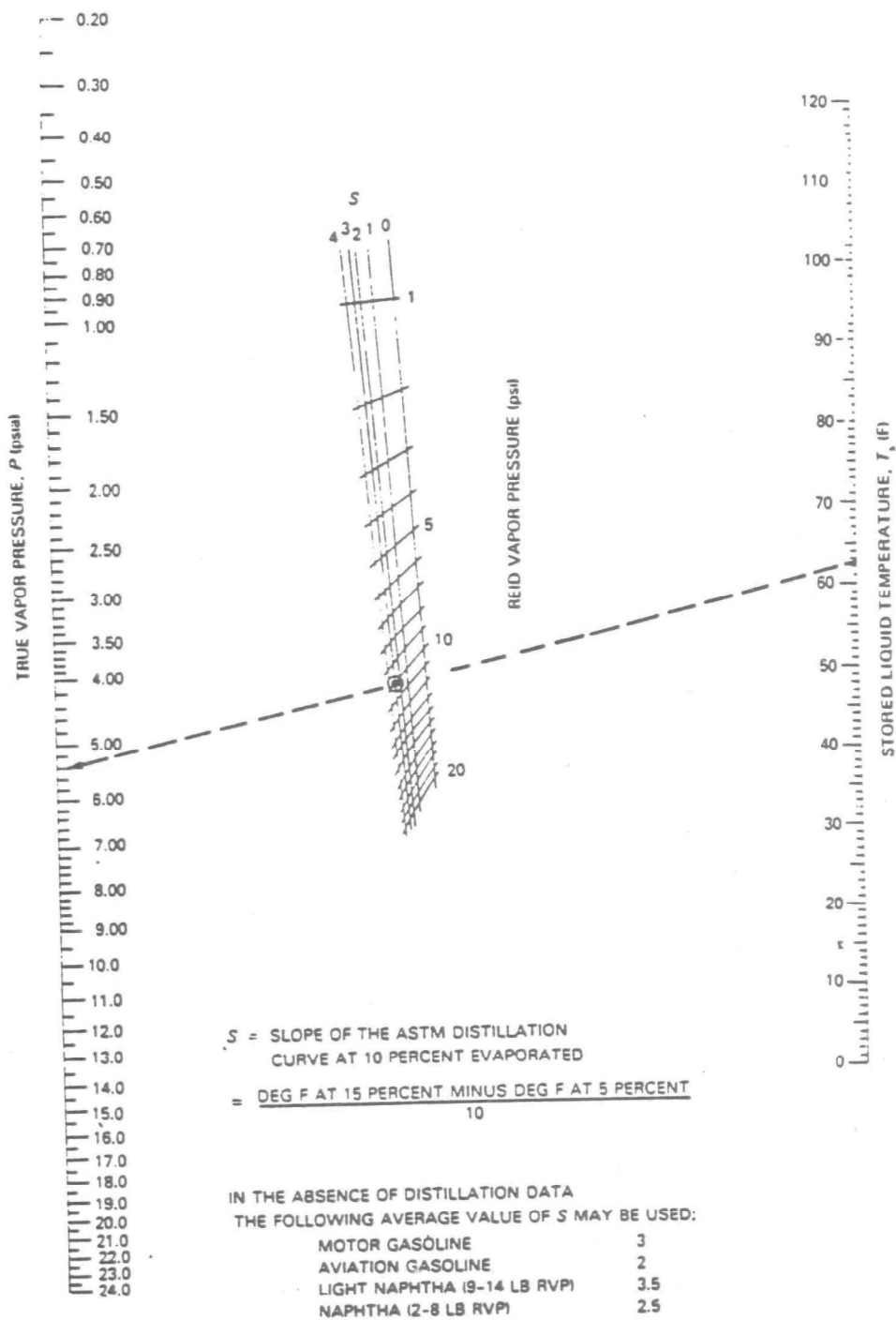


Figure 4.3-5. True vapor pressure ( $P$ ) of crude oils (2-15 psi RVP).<sup>6</sup>



NOTE: Dashed line illustrates sample problem for RVP = 10 pounds per square inch, gasoline ( $S = 3$ ), and  $T = 62.5^\circ\text{F}$ .  
 SOURCE: Nomograph drawn from the data of the National Bureau of Standards.

Figure 4.3-6. True vapor pressure ( $P$ ) of refined petroleum liquids like gasoline and naphthas (1-20 psi RVP).<sup>6</sup>

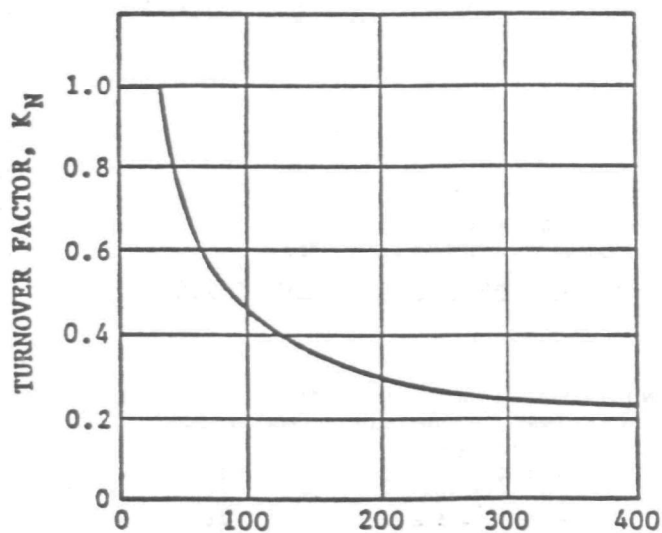
- $K_N$  = turnover factor (dimensionless), see Figure 4.3-7
- $K_C$  = product factor (dimensionless), see Note 1
- Note: (1) For crude oil,  $K_C = 0.84$ . For all other organic liquids,  $K_C = 1.0$ .

TABLE 4.3-3. AVERAGE STORAGE TEMPERATURE ( $T_S$ )  
AS A FUNCTION OF TANK PAINT COLOR<sup>a</sup>

Tank color	Average storage temperature, $T_S$
White	$T_A^b + 0$
Aluminum	$T_A + 2.5$
Gray	$T_A + 3.5$
Black	$T_A + 5.0$

<sup>a</sup>Reference 5.

<sup>b</sup> $T_A$  is the average annual ambient temperature in degrees Fahrenheit.



$$\text{TURNS PER YEAR} = \frac{\text{ANNUAL THROUGHPUT}}{\text{TANK CAPACITY}}$$

Note: For 36 turnovers per year or less,  $K_N = 1.0$

Figure 4.3-7. Turnover factor ( $K_N$ ) for fixed roof tanks.



Several methods are used to control emissions from fixed roof tanks. Emissions from fixed roof tanks can be controlled by the installation of an internal floating roof and seals to minimize evaporation of the product being stored. The control efficiency of this method ranges from 60 to 99 percent, depending on the type of roof and seals installed and on the type of organic liquid stored.

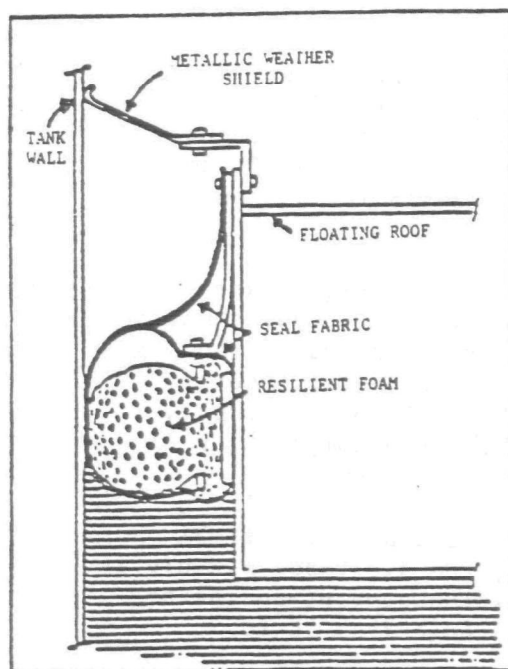
The vapor recovery system collects emissions from storage vessels and converts them to liquid product. Several vapor recovery procedures may be used, including vapor/liquid absorption, vapor compression, vapor cooling, vapor/solid adsorption, or a combination of these. The overall control efficiencies of vapor recovery systems are as high as 90 to 98 percent, depending on the method used, the design of the unit, the composition of vapors recovered, and the mechanical condition of the system.

Another method of emission control on fixed roof tanks is thermal oxidation. In a typical thermal oxidation system, the air/vapor mixture is injected through a burner manifold into the combustion area of an incinerator. Control efficiencies for this system can range from 96 to 99 percent.

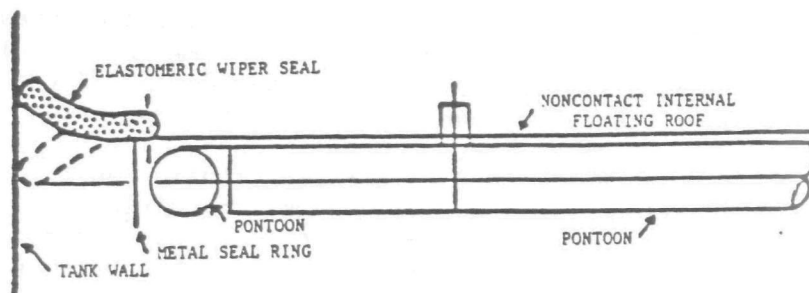
External And Internal Floating Roof Tanks - Total emissions from floating roof tanks are the sum of standing storage losses and withdrawal losses. Standing storage loss from internal floating roof tanks includes rim seal, deck fitting, and deck seam losses. Standing storage loss from external floating roof tanks, as discussed here, includes only rim seal loss, since deck fitting loss equations have not been developed. There is no deck seam loss, because the decks have welded sections.

Standing storage loss from external floating roof tanks, the major element of evaporative loss, results from wind induced mechanisms as air flows across the top of an external floating roof tank. These mechanisms may vary, depending upon the type of seals used to close the annular vapor space between the floating roof and the tank wall. Standing storage emissions from external floating roof tanks are controlled by one or two separate seals. The first seal is called the primary seal, and the other, mounted above the primary seal, is called the secondary seal. There are three basic types of primary seals used on external floating roofs, mechanical (metallic shoe), resilient (nonmetallic), and flexible wiper. The resilient seal can be mounted to eliminate the vapor space between the seal and liquid surface (liquid mounted), or to allow a vapor space between the seal and liquid surface (vapor mounted). A primary seal serves as a vapor conservation device by closing the annular space between the edge of the floating roof and the tank wall. Some primary seals are protected by a metallic weather shield. Additional evaporative loss may be controlled by a secondary seal. Secondary seals can be either flexible wiper seals or resilient filled seals. Two configurations of secondary seal are currently available, shoe mounted and rim mounted. Although there are other seal system designs, the systems described here compose the majority in use today. See Figure 4.3-8 for examples of primary and secondary seal configurations.

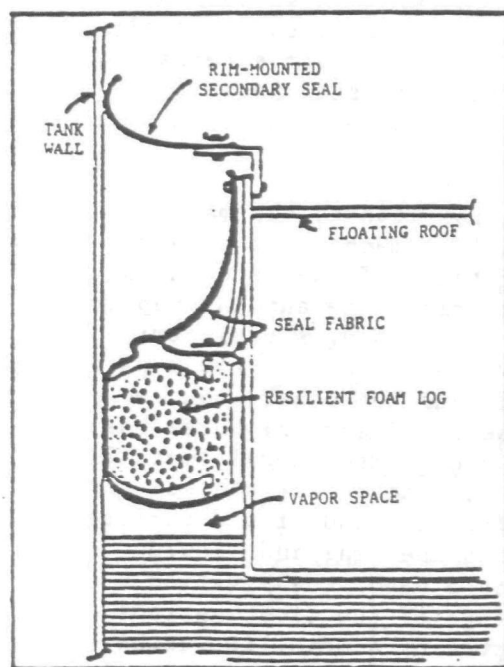
Typical internal floating roofs generally incorporate two types of primary seals, resilient foam filled seals and wipers. Similar in design



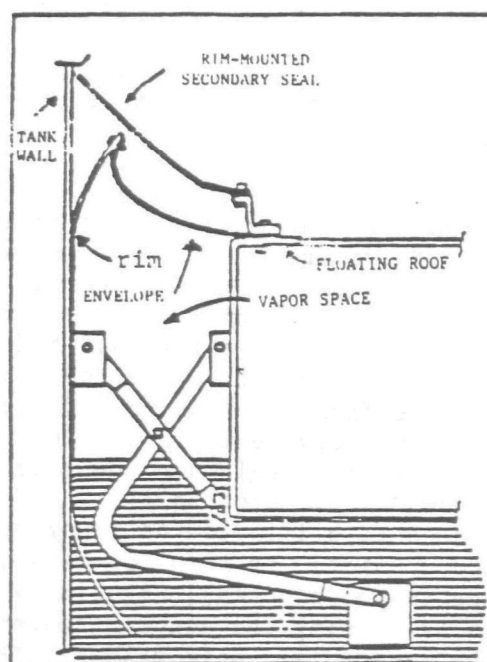
a. Liquid mounted seal with weather shield.



b. Elastomeric wiper seal.



c. Vapor mounted seal with rim mounted secondary seal.



d. Metallic shoe seal with shoe mounted secondary seal.

Figure 4.3-8. Primary and secondary seal configurations.<sup>1</sup>

to those in external floating roof tanks, these seals close the annular vapor space between the edge of the floating roof and the tank wall. Secondary seals are not commonly used with internal floating roof tanks.

Deck fitting loss emissions from internal floating roof tanks result from penetrations in the roof by deck fittings, fixed roof column supports or other openings. There are no procedures for estimating emissions from external roof tank deck fittings. The most common fittings with relevance to controllable vapor losses are described as follows:<sup>1</sup>

1. Access Hatch. An access hatch is an opening in the deck with a peripheral vertical well that is large enough to provide passage of workers and materials through the deck for construction or servicing. Attached to the opening is a removable cover which may be bolted and/or gasketed to reduce evaporative loss. On noncontact decks, the well should extend down into the liquid to seal off the vapor space below the deck.

2. Automatic Gauge Float Well. A gauge float is used to indicate the level of liquid within the tank. The float rests on the liquid surface, inside a well that is closed by a cover. The cover may be bolted and/or gasketed to reduce evaporation loss. As with other similar deck penetrations, the well extends fixed into the liquid on noncontact decks.

3. Column Well. For fixed roofs that are column-supported, the columns pass through deck openings with peripheral vertical wells. On noncontact decks, the well should extend down into the liquid. The wells are equipped with closure devices to reduce evaporative loss and may be gasketed or ungasketed to further reduce the loss. Closure devices are typically sliding covers or flexible fabric sleeve seals.

4. Ladder Well. Some tanks are equipped with internal ladders that extend from a manhole in the fixed roof to the tank bottom. The deck opening through which the ladder passes has a peripheral vertical well. On noncontact decks, the well should extend down into the liquid. The wells are typically covered with a gasketed or ungasketed sliding cover.

5. Roof Leg or Hanger Well. To prevent damage to fittings underneath the deck and to allow for tank cleaning or repair, supports are provided to hold the deck a predetermined distance off the tank bottom. These supports consist of adjustable or fixed legs attached to the floating deck or hangers suspended from the fixed roof. For adjustable legs or hangers, the load-carrying element passes through a well or sleeve into the deck. With noncontact decks, the well should extend into the liquid.

6. Sample Pipe or Well. A funnel-shaped sample well may be provided to allow for sampling of the liquid with a sample thief. A closure is typically located at the lower end of the funnel and frequently consists of a horizontal piece of fabric slit radially to allow thief entry. The well should extend into the liquid on noncontact decks. Alternatively, a sample well may consist of a slotted pipe extending into the liquid, equipped with a gasketed or ungasketed sliding cover.

7. Vacuum Breaker. A vacuum breaker equalizes the pressure of the vapor space across the deck as the deck is either being landed on or floated off its legs. The vacuum breaker consists of a well with a cover. Attached to the underside of the cover is a guided leg of such length that it contacts the tank bottom as the internal floating deck approaches. When in contact with the tank bottom, the guided leg mechanically opens the breaker by lifting the cover off the well; otherwise, the cover closes the well. The closure may be gasketed or ungasketed. Because the purpose of the vacuum breaker is to allow the free exchange of air and/or vapor, the well does not extend appreciably below the deck.

The decks of internal floating roofs typically are made by joining several sections of deck material, resulting in seams in the deck. To the extent that these seams are not completely vapor tight, they become a source of emissions. It should be noted that external floating roof tanks and welded internal floating roofs do not have deck seam losses.

Withdrawal loss is another source of emissions from floating roof tanks. This loss is the vaporization of liquid that clings to the tank wall and is exposed to the atmosphere when a floating roof is lowered by withdrawal of liquid. There is also clingage of liquid to columns in internal floating roof tanks which have a column supported fixed roof.

Total Losses From Floating Roof Tanks - Total floating roof tank emissions are the sum of rim seal, withdrawal, deck fitting, and deck seam losses. It should be noted that external floating roof tanks and welded internal floating roofs do not have deck seam losses. Also, there are no procedures for estimating emissions from external floating roof tank deck fittings. The equations provided in this Section are applicable only to freely vented internal floating roof tanks or external floating roof tanks. The equations are not intended to be used in the following applications: to estimate losses from closed internal floating roof tanks (tanks vented only through a pressure-vacuum vent); to estimate losses from unstabilized or boiling stocks or from mixtures of hydrocarbons or petrochemicals for which the vapor pressure is not known or cannot be readily predicted; or to estimate losses from tanks in which the materials used in the seal system and/or deck construction are either deteriorated or significantly permeated by the stored liquid.<sup>6</sup> Total losses may be written as:

$$L_T = L_R + L_W + L_F + L_D \quad (3)$$

where:

$L_T$  = total loss (lb/yr)

$L_R$  = rim seal loss (see Equation 4)

$L_W$  = withdrawal loss (see Equation 5)

$L_F$  = deck fitting loss (see Equation 6)

$L_D$  = deck seam loss (see Equation 7)

Rim Seal Loss - Rim seal loss from floating roof tanks can be estimated by the following equation<sup>5-6</sup>:

$$L_R = K_S V^n P^* D M_V K_C \quad (4)$$

where:

$L_R$  = rim seal loss (lb/yr)

$K_S$  = seal factor (lb-mole/(ft (mi/hr)<sup>n</sup> yr)), see Table 4.3-4

$V$  = average wind speed at tank site (mi/hr), see Note 1

$n$  = seal related wind speed exponent (dimensionless), see Table 4.3-4

$P^*$  = vapor pressure function (dimensionless), see Note 2

$$P^* = \frac{\frac{P}{P_A}}{\left[ 1 + \left( 1 - \frac{P}{P_A} \right)^{0.5} \right]^2}$$

where:

$P$  = true vapor pressure at average actual liquid storage temperature (psia), see Note 2 to Equation 1

$P_A$  = average atmospheric pressure at tank location (psia)

$D$  = tank diameter (ft)

$M_V$  = average vapor molecular weight (lb/lb-mole), see Note 1 to Equation 1

$K_C$  = product factor (dimensionless), see Note 3

Notes: (1) If the wind speed at the tank site is not available, wind speed data from the nearest local weather station may be used as an approximation.

(2)  $P^*$  can be calculated or read directly from Figure 4.3-9.

(3) For all organic liquids except crude oil,  $K_C = 1.0$ . For crude oil,  $K_C = 0.4$ .

Withdrawal Loss - The withdrawal loss from floating roof storage tanks can be estimated using Equation 5.<sup>5-6</sup>

$$L_W = \frac{(0.943) Q C W_L}{D} \cdot \left[ 1 + \left( \frac{N_C F_C}{D} \right) \right] \quad (5)$$

TABLE 4.3-4. SEAL RELATED FACTORS FOR FLOATING ROOF TANKS<sup>a</sup>

Tank and seal type	Welded Tank		Riveted Tank	
	K <sub>S</sub>	n	K <sub>S</sub>	n
External floating roof tanks <sup>b</sup>				
Metallic shoe seal				
Primary seal only	1.2	1.5	1.3	1.5
With shoe mounted secondary seal	0.8	1.2	1.4	1.2
With rim mounted secondary seal	0.2	1.0	0.2	1.6
Liquid mounted resilient seal				
Primary seal only	1.1	1.0	NA <sup>c</sup>	NA
With weather shield	0.8	0.9	NA	NA
With rim mounted secondary seal	0.7	0.4	NA	NA
Vapor mounted resilient seal				
Primary seal only	1.2	2.3	NA	NA
With weather shield	0.9	2.2	NA	NA
With rim mounted secondary seal	0.2	2.6	NA	NA
Internal floating roof tanks <sup>d</sup>				
Liquid mounted resilient seal				
Primary seal only	3.0	0	NA	NA
With rim mounted secondary seal <sup>e</sup>	1.6	0	NA	NA
Vapor mounted resilient seal				
Primary seal only	6.7	0	NA	NA
With rim mounted secondary seal <sup>e</sup>	2.5	0	NA	NA

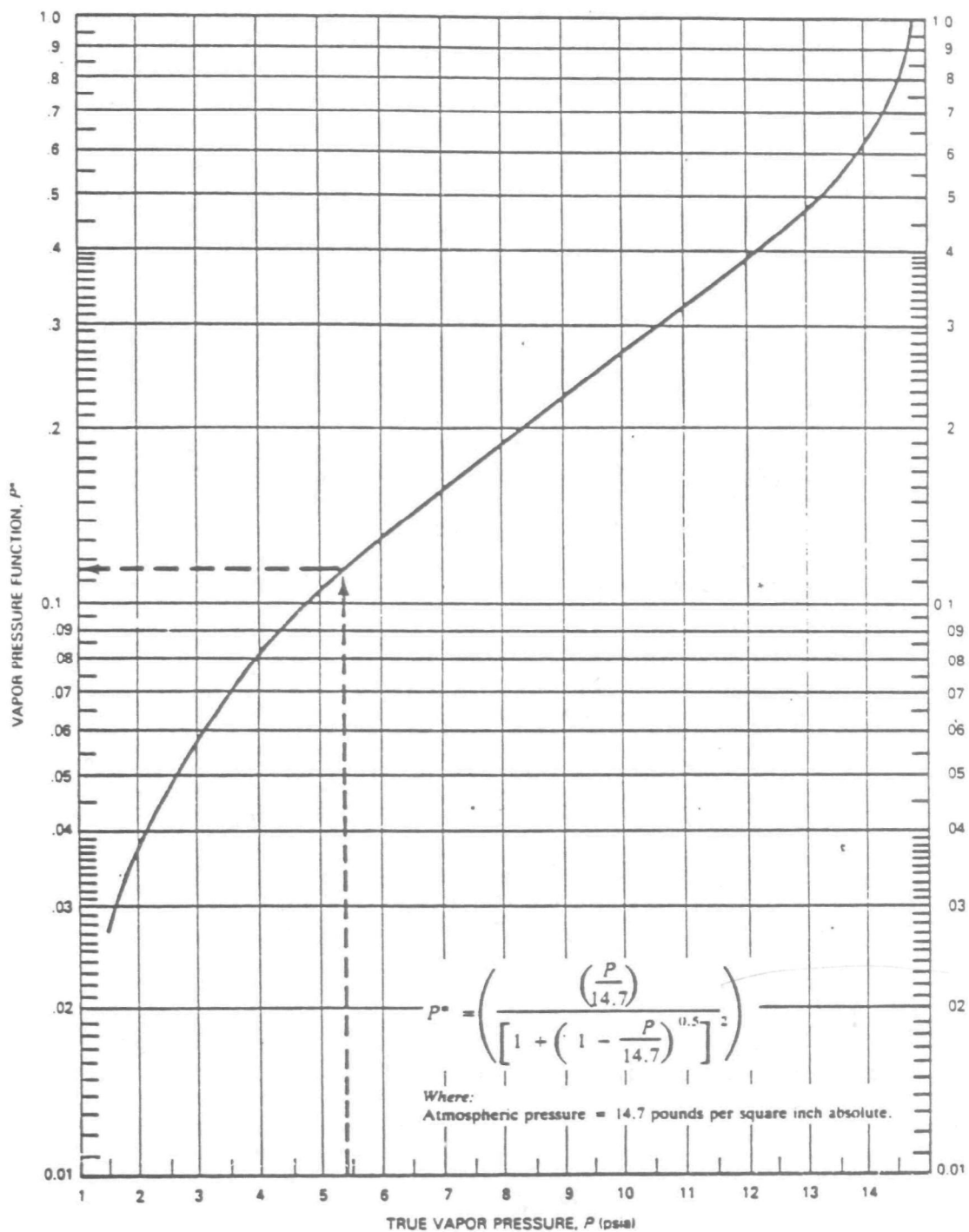
<sup>a</sup>Based on emissions from tank seal systems in reasonably good working condition, no visible holes, tears, or unusually large gaps between the seals and the tank wall. The applicability of K<sub>S</sub> decreases in cases where the actual gaps exceed the gaps assumed during development of the correlation.

<sup>b</sup>Reference 5.

<sup>c</sup>NA = Not Applicable.

<sup>d</sup>Reference 6.

<sup>e</sup>If tank specific information is not available about the secondary seal on an internal floating roof tank, then assume only a primary seal is present.



NOTE. Dashed line illustrates sample problem for  $P = 5.4$  pounds per square inch absolute.

Figure 4.3-9. Vapor pressure function ( $P^*$ ).<sup>5</sup>

where:

$L_W$  = withdrawal loss (lb/yr) ·

$Q$  = throughput (bbl/year) (tank capacity [bbl] times annual turnover rate)

$C$  = shell clingage factor (bbl/1,000 ft<sup>2</sup>), see Table 4.3-5

$W_L$  = average organic liquid density (lb/gal), see Note 1

$D$  = tank diameter (ft)

$N_C$  = number of columns (dimensionless), see Note 3

$F_C$  = effective column diameter (ft) [column perimeter (ft)/ $\pi$ ], see Note 4

Notes: (1) If  $W_L$  is not known, an average value of 5.6 lb/gallon can be assumed for gasoline. An average value cannot be assumed for crude oil, since densities are highly variable.

(2) The constant, 0.943, has dimensions of (1,000 ft<sup>3</sup> x gal/bbl<sup>2</sup>).

(3) For self-supporting fixed roof or an external floating roof tank:

$$N_C = 0.$$

For column supported fixed roof:

$N_C$  = use tank specific information, or see Table 4.3-6.

(4) Use tank specific effective column diameter; or

$F_C$  = 1.1 for 9 inch by 7 inch builtup columns,  
0.7 for 8 inch diameter pipe columns, and  
1.0 if column construction details are not known.

Deck Fitting Loss - Deck fitting loss estimation procedures for external floating roof tanks are not available. Therefore, the following procedure applies only to internal floating roof tanks.

Fitting losses from internal floating roof tanks can be estimated by the following equation<sup>6</sup>:

$$L_F = F_F P^* M_V K_C \quad (6)$$



TABLE 4.3-5. AVERAGE CLINGAGE FACTORS (C) (bbl/1,000 ft<sup>2</sup>)<sup>a</sup>

Liquid	Shell condition		
	Light rust <sup>b</sup>	Dense rust	Gunitite lined
Gasoline	0.0015	0.0075	0.15
Single component stocks	0.0015	0.0075	0.15
Crude oil	0.0060	0.030	0.60

<sup>a</sup>Reference 5.<sup>b</sup>If no specific information is available, these values can be assumed to represent the most common condition of tanks currently in use.TABLE 4.3-6. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETER FOR INTERNAL FLOATING ROOF TANKS WITH COLUMN SUPPORTED FIXED ROOFS<sup>a</sup>

Tank diameter range D (ft)	Typical number of columns, N <sub>C</sub>
0 < D ≤ 85	1
85 < D ≤ 100	6
100 < D ≤ 120	7
120 < D ≤ 135	8
135 < D ≤ 150	9
150 < D ≤ 170	16
170 < D ≤ 190	19
190 < D ≤ 220	22
220 < D ≤ 235	31
235 < D ≤ 270	37
270 < D ≤ 275	43
275 < D ≤ 290	49
290 < D ≤ 330	61
330 < D ≤ 360	71
360 < D ≤ 400	81

<sup>a</sup>Reference 1. This table was derived from a survey of users and manufacturers. The actual number of columns in a particular tank may vary greatly with age, fixed roof style, loading specifications, and manufacturing prerogatives. Data in this table should not supersede information on actual tanks.

where:

$L_F$  = the fitting loss in pounds per year

$F_F$  = total deck fitting loss factor (lb-mole/yr)

$$= [(N_{F_1} K_{F_1}) + N_{F_2} K_{F_2} + \dots + (N_{F_n} K_{F_n})]$$

where:

$N_{F_i}$  = number of deck fittings of a particular type  
( $i = 0, 1, 2, \dots, n$ ) (dimensionless)

$K_{F_i}$  = deck fitting loss factor for a particular type fitting  
( $i = 0, 1, 2, \dots, n$ ) (lb-mole/yr)

$n$  = total number of different types of fittings  
(dimensionless)

$P^*, M_V, K_C$  = as defined for Equation 4

The value of  $F_F$  may be calculated by using actual tank specific data for the number of each fitting type ( $N_F$ ) and then multiplying by the fitting loss factor for each fitting ( $K_F$ ).<sup>1</sup> Values of fitting loss factors and typical number of fittings are presented in Table 4.3-7. Where tank specific data for the number and kind of deck fittings are unavailable, then  $F_F$  can be approximated according to tank diameter. Figures 4.3-10 and 4.3-11 present  $F_F$  plotted against tank diameter for column supported fixed roofs and self-supporting fixed roofs, respectively.

**Deck Seam Loss** - Deck seam loss applies only to internal floating roof tanks with bolted decks. External floating roofs have welded decks and, therefore, no deck seam loss. Deck seam loss can be estimated by the following equation:<sup>6</sup>

$$L_D = K_D S_D D^2 P^* M_V K_C \quad (7)$$

where

$L_D$  = deck seam losses (lb/yr)

$K_D$  = deck seam loss per unit seam length factor (lb-mole/ft yr)

= 0.0 for welded deck and external floating roof tanks,  
0.34 for bolted deck

$S_D$  = deck seam length factor (ft/ft<sup>2</sup>)

$$= \frac{L_{\text{seam}}}{A_{\text{deck}}}$$

TABLE 4.3-7. SUMMARY OF INTERNAL FLOATING DECK FITTING LOSS FACTORS ( $K_F$ ) AND TYPICAL NUMBER OF FITTINGS ( $N_F$ )<sup>a</sup>

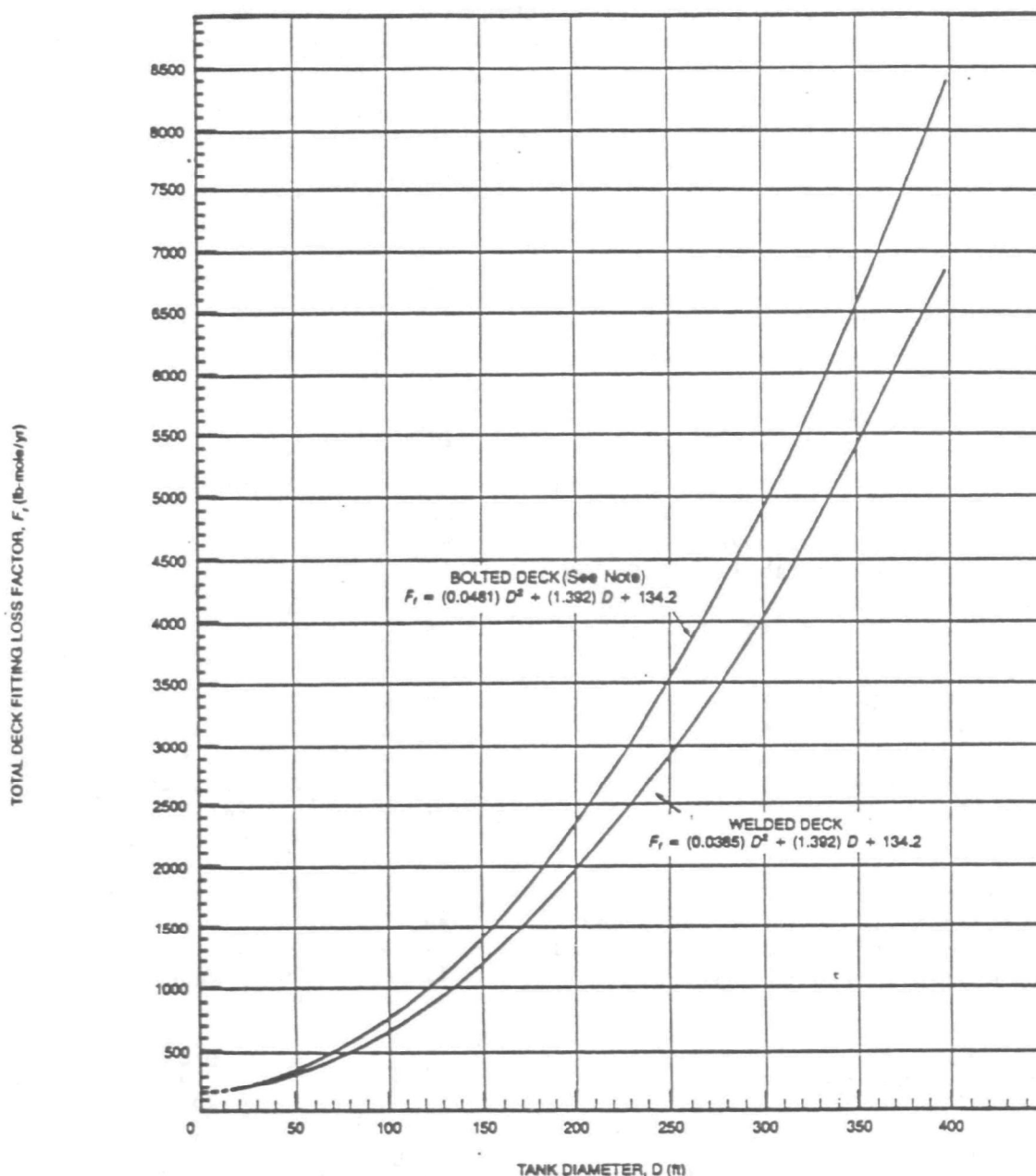
Deck fitting type	Deck fitting loss factor, $K_F$ (lb-mole/yr)	Typical number of fittings, $N_F$
Access hatch		1
Bolted cover, gasketed	1.6	
Unbolted cover, gasketed	11 <sub>b</sub>	
Unbolted cover, ungasketed	25 <sub>b</sub>	
Automatic gauge float well		1
Bolted cover, gasketed	5.1	
Unbolted cover, gasketed	15 <sub>b</sub>	
Unbolted cover, ungasketed	28 <sub>b</sub>	
Column well		(see Table 4.3-6)
Builtup column-sliding cover, gasketed	33 <sub>b</sub>	
Builtup column-sliding cover, ungasketed	47 <sub>b</sub>	
Pipe column-flexible fabric sleeve seal	10	
Pipe column-sliding cover, gasketed	19	
Pipe column-sliding cover, ungasketed	32	
Ladder well		1
Sliding cover, gasketed	56 <sub>b</sub>	
Sliding cover, ungasketed	76 <sub>b</sub>	
Roof leg or hanger well		$(5 + \frac{D}{10} + \frac{D^2}{600})^c$
Adjustable	7.9 <sub>b</sub>	
Fixed	0	
Sample pipe or well		1
Slotted pipe-sliding cover, gasketed	44	
Slotted pipe-sliding cover, ungasketed	57 <sub>b</sub>	
Sample well-slit fabric seal, 10% open area	12 <sub>b</sub>	
Stub drain, 1 inch diameter <sup>d</sup>	1.2	$(\frac{D^2}{125})^c$
Vacuum breaker		1
Weighted mechanical actuation, gasketed	0.7 <sub>b</sub>	
Weighted mechanical actuation, ungasketed	0.9	

<sup>a</sup>Reference 1.

<sup>b</sup>If no specific information is available, this value can be assumed to represent the most common/typical deck fittings currently used.

<sup>c</sup>D = tank diameter (ft).

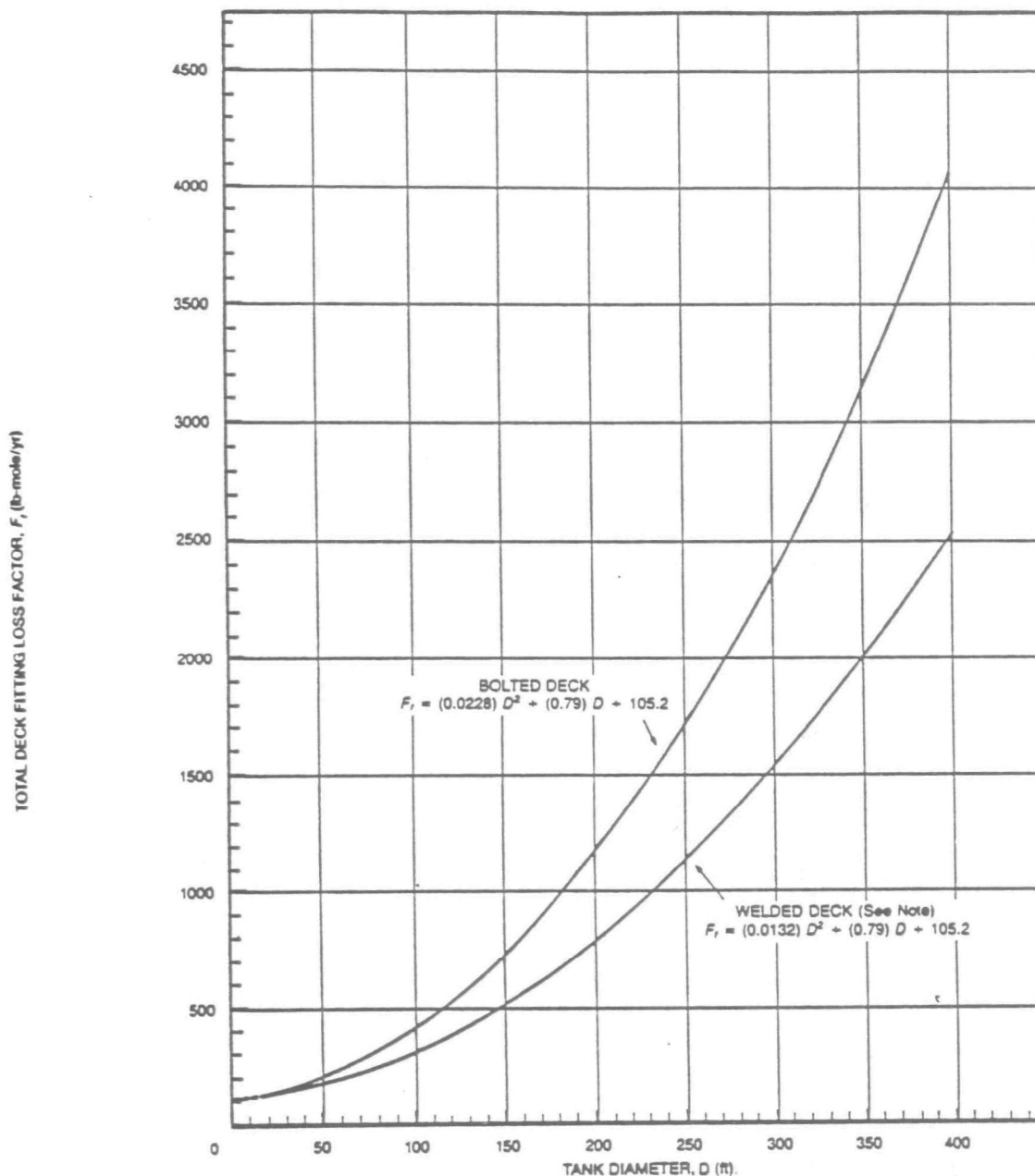
<sup>d</sup>Not used on welded contact internal floating decks.



Basis: Fittings include: (1) access hatch, with ungasketed, unbolted cover; (2) built-up column wells, with ungasketed, sliding cover; (3) adjustable deck legs; (4) gauge float well, with ungasketed, unbolted cover; (5) ladder well, with ungasketed sliding cover; (6) sample well, with slit fabric seal (10 percent open area); (7) 1-inch diameter stub drains (only on bolted deck); and (8) vacuum breaker, with gasketed weighted mechanical actuation. This basis was derived from a survey of users and manufacturers. Other fittings may be typically used within particular companies or organizations to reflect standards and/or specifications of that group. This figure should not supersede information based on actual tank data.

NOTE: If no specific information is available, assume bolted decks are the most common/typical type currently in use in tanks with column-supported fixed roofs.

Figure 4.3-10. Approximated total deck fitting loss factors ( $F_f$ ) for typical fittings in tanks with column supported fixed roofs and either a bolted deck or a welded deck.<sup>6</sup> This figure is to be used only when tank specific data on the number and kind of deck fittings are unavailable.



Basis: Fittings include: (1) access hatch, with ungasketed, unbolted cover; (2) adjustable deck legs; (3) gauge float well, with ungasketed, unbolted cover; (4) sample well, with slit fabric seal (10 percent open area); (5) 1-inch diameter stub drains (only on bolted deck); and (6) vacuum breaker, with gasketed weighted mechanical actuation. This basis was derived from a survey of users and manufacturers. Other fittings may be typically used within particular companies or organizations to reflect standards and/or specifications of that group. This figure should not supersede information based on actual tank data.

Notes: If no specific information is available, assume welded decks are the most common/typical type currently in use in tanks with self-supporting fixed roofs.

Figure 4.3-11. Approximated total deck fitting loss factors ( $F_f$ ) for typical deck fittings in tanks with self-supporting fixed roofs and either a bolted deck or a welded deck.<sup>6</sup> This figure is to be used only when tank specific data on the number and kind of deck fittings are unavailable.

where:

$L_{\text{seam}}$  = total length of deck seams (ft)

$A_{\text{deck}}$  = area of deck (ft<sup>2</sup>) =  $\pi D^2/4$

$D$ ,  $P^*$ ,  $M_V$ ,  $K_C$  = as defined for Equation 4

If the total length of the deck seam is not known, Table 4.3-8 can be used to determine  $S_D$ . Where tank specific data concerning width of deck sheets or size of deck panels are unavailable, a default value for  $S_D$  can be assigned. A value of 0.20 (ft/ft<sup>2</sup>) can be assumed to represent the most common bolted decks currently in use.

TABLE 4.3-8. DECK SEAM LENGTH FACTORS ( $S_D$ ) FOR TYPICAL DECK CONSTRUCTIONS FOR INTERNAL FLOATING ROOF TANKS<sup>a</sup>

Deck construction	Typical deck seam length factor, $S_D$ (ft/ft <sup>2</sup> )
Continuous sheet construction <sup>b</sup>	
5 ft wide	0.20 <sup>c</sup>
6 ft wide	0.17
7 ft wide	0.14
Panel construction <sup>d</sup>	
5 x 7.5 ft rectangular	0.33
5 x 12 ft rectangular	0.28

<sup>a</sup>Reference 6. Deck seam loss applies to bolted decks only.

<sup>b</sup> $S_D = \frac{1}{W}$ , where  $W$  = sheet width (ft)

<sup>c</sup>If no specific information is available, these factors can be assumed to represent the most common bolted decks currently in use.

<sup>d</sup> $S_D = \frac{(L+W)}{LW}$ , where  $W$  = panel width (ft) and  $L$  = panel length (ft)

#### 4.5.4 STORAGE TANK INSPECTION

A storage tank inspection form is shown in Table 4-20. The RACT for fixed roof tanks is an internal floating cover, but other equivalent technology may be used on approval. Except for special installations where vapor recovery or incineration is used, only inspections at Levels 1 and 2 are required for storage tanks. Special systems may require a Level 3 inspection analogous to the one for loading terminals described in Appendix D. The RACT requirements apply to storage tanks of capacities greater than 150,000 liters (39,600 gal) storing liquids whose true vapor pressure is greater than 10.5 kiloPascals (1.5 psia).

Once every year or two, when they are empty, most storage tanks are checked by their owners for corrosion, malfunctioning seals, and so on. It is also recommended that they be examined

Table 4-17. STORAGE TANK INSPECTION FORM

Facility Name/Company _____ Facility Address _____ Company Contact Name _____ Title _____ Mail Address _____ _____ Phone _____ Inspector _____ Representing _____ Phone _____ Inspection Date _____ Time _____ Temperature _____ (Attach diagram or map of facility)						
	1	2	3	4	5	6
Tank ID						
Records in order						
Date last inspection						
Agency last inspection						
Maximum temperature						
Temperature during inspection						
Tank contents						
True vapor pressure, psia						
Tank dimensions						
Tank capacity, gallons						
Liquid level, % of capacity						
Type of vapor control (roof type)						
Fixed roof tank openings covered						
Seal defects, location clockwise from ladder, o'clock (Describe defect)						
Explosimeter readings, Location and percent LEL						
Comments						

384  
4-56



visually as part of Level 2 terminal and bulk plant inspections (refer to Sections 4.5.1 and 4.5.2). The following guidelines summarize the procedures to be followed and may duplicate portions of those sections.

#### 4.5.4.1 Storage Tank Inspection, Level 1

Table 4-18 shows a Level 1 storage tank inspection checklist. Equipment maintenance and product records should be checked to learn whether they are adequately kept and whether the required visual and internal inspections have been performed by the owners. Visual examination of a selected tank through the roof hatch may be desirable if plant records are not adequate (refer to Section 4.5.4.2 for the method).

To ascertain whether or not the control device installed to meet RACT requirements maintains its control efficiency, records must be kept by the facility management and made available upon request to EPA representatives. Records should be kept of the inspections through roof hatches, recording evidence of any malfunction. These roof hatch inspections should be performed at intervals of 6 months or less. If the tank is emptied for maintenance, or for other nonoperational reasons, records of a complete inspection of the cover and seal must be maintained. The jurisdictional control agency (EPA, state, or local) should be notified prior to a complete inspection so that inspectors from that agency may be present.

A record of the average monthly storage temperature and true vapor pressure of the petroleum liquid stored should be maintained if the product has a stored vapor pressure greater than 7.0 kPa (1.0 psia) and is stored in a fixed roof tank not equipped with an internal floating roof or alternative equivalent control device.

Table 4-18. STORAGE TANK INSPECTION CHECKLIST, LEVEL 1

[For Tanks Larger Than 150,000 Liters (40,000 gal) Storing  
Liquids With True Vapor Pressure Greater Than 10.5 kPa]

Key	Inspection Point	RACT Requirements	Inspection Procedure	Quick Key	Inspection Findings					
1	Records	Inspection through roof hatches at least twice yearly. Whenever tank empty for maintenance or other non-operational reason, make internal inspection of cover and seal. If no vapor control, maintain record of average monthly storage temperature and true vapor pressure, if latter is greater than 7.0 kPa.	Examine records	TANK ID						
			Examine records  Examine records	RECORDS						

The true vapor pressure may be determined by the typical Reid vapor pressure of the stored product, using the average monthly storage temperature and standard tables, nomographs, or equations.

Each of these records should be kept by the facility management and made available upon request of the inspector. If a question arises on the values reported for a product, analytical data may be requested of the facility.

If other equivalent means of control are used, such as vapor recovery, it may be necessary to record the amount of vapor captured, flow rates, and operating parameters (such as temperatures and pressures) to establish the day-to-day operating efficiencies. It should not be anticipated that this type of information on vapor recovery systems will be available on the facility's first inspection.

#### 4.5.4.2 Storage Tank Inspection, Level 2

In addition to the record check performed for Level 1, each fixed roof tank should be inspected and the checklist given in Table 4-19 should be completed. Inspectors should, if possible, climb to the tank roof and visually inspect the roof seals and note any vents. Under no circumstances should the inspector make such a climb or perform any other act if plant personnel believe it to be unsafe or if instrument readings indicate dangerously high levels of organic vapors or hydrogen sulfide. Concentrations at vents, flanges, valves, pumps, and relief valves in the tank may be measured with instruments. Locations with significant concentrations should be recorded.

If the tank has an internal floating cover, the seal should be visually inspected from the roof hatch to identify any obvious

Table 4-19. STORAGE TANK INSPECTION CHECKLIST, LEVEL 2

[For Tanks Larger Than 150,000 Liters (40,000 gal) Storing  
Liquids With True Vapor Pressure Greater Than 10.5 kPa]

Key	Inspection Point	RACT Requirements	Inspection Procedure	Quick Key	Inspection Findings					
1	Records	Inspection through roof hatches at least twice yearly. Whenever tank empty for maintenance or other non-operational reason, make internal inspection of cover and seal. If no vapor control, maintain record of average monthly storage temperature and true vapor pressure, if latter is greater than 7.0 kPa.	Examine records	TANK ID						
			Examine records	RECORDS						
			Examine records							
2	Internal floating roof	Internal floating roof with a closure seal, or approved alternate control. Roof uniformly floating on or above liquid.	Brief visual examination through roof hatches Brief visual examination through roof hatches	FLOATING ROOF						
3	Floating roof seal	No visible gaps in seal; no liquid on cover	Brief visual examination through roof hatches for obvious damage or malfunction.	SEAL						
7	Openings in floating roof	All openings except stub drain equipped with lids. Lids closed except when roof is floated off or landed on leg supports.	Brief visual examination through roof hatches Brief visual examination through roof hatches	VENTS						

damage such as gaps, tears, or other openings that have a potential for emission. The inspector should visually inspect whether the internal roof is floating on or above the liquid and whether there are visible defects in the surface of the roof or liquid accumulated on it. The seal should be inspected along the entire circumference to assure that it fits tightly to the tank wall and that no gaps are visible. Conditions of the roof and seal should be recorded.

## 2. PROCESS DESCRIPTION

### 2.1 BULK GASOLINE TERMINAL DEFINITION

The distribution of gasoline and other petroleum liquids is accomplished by a network of pipelines and tank vehicle transfer routes that transport these products from refineries to consumer outlets. Intermediate storage locations are used to transfer the gasoline to progressively smaller points of distribution. Bulk terminals are wholesale marketing facilities that receive gasoline from refineries by pipeline, ship, or barge; store it in large aboveground tanks; and load it into tank trucks for delivery to bulk plants or retail accounts. Terminals handle several petroleum products in addition to gasoline, including diesel fuel, kerosene, and heating oil. Figure 2.1 depicts the marketing network.

Bulk terminals are distinguished from bulk plants largely by their higher gasoline throughputs (greater than 20,000 gallons, or 75,700 liters, per day) and storage capacities. Another difference is that incoming product at a bulk plant generally is delivered by means of tank vehicles from refineries or bulk terminals.

### 2.2 LOADING RACKS

Loading racks consist of the equipment necessary to meter and deliver the various liquid products into delivery tank trucks. A typical loading rack contains fuel loading arms, pumps, meters, shutoff valves, relief valves, check valves, electrical grounding, and lighting. Terminals generally utilize two to four rack positions (loading lanes) for gasoline, each having one to four loading arms. Gasoline is loaded through an arm at about 600 gallons (2,270 liters) per minute.

Tank truck loading is performed using either top splash, top submerged, or bottom loading, although essentially all NSPS terminals use bottom loading. Top loading is divided into top splash loading, with or without vapor collection, top submerged, and top tight submerged

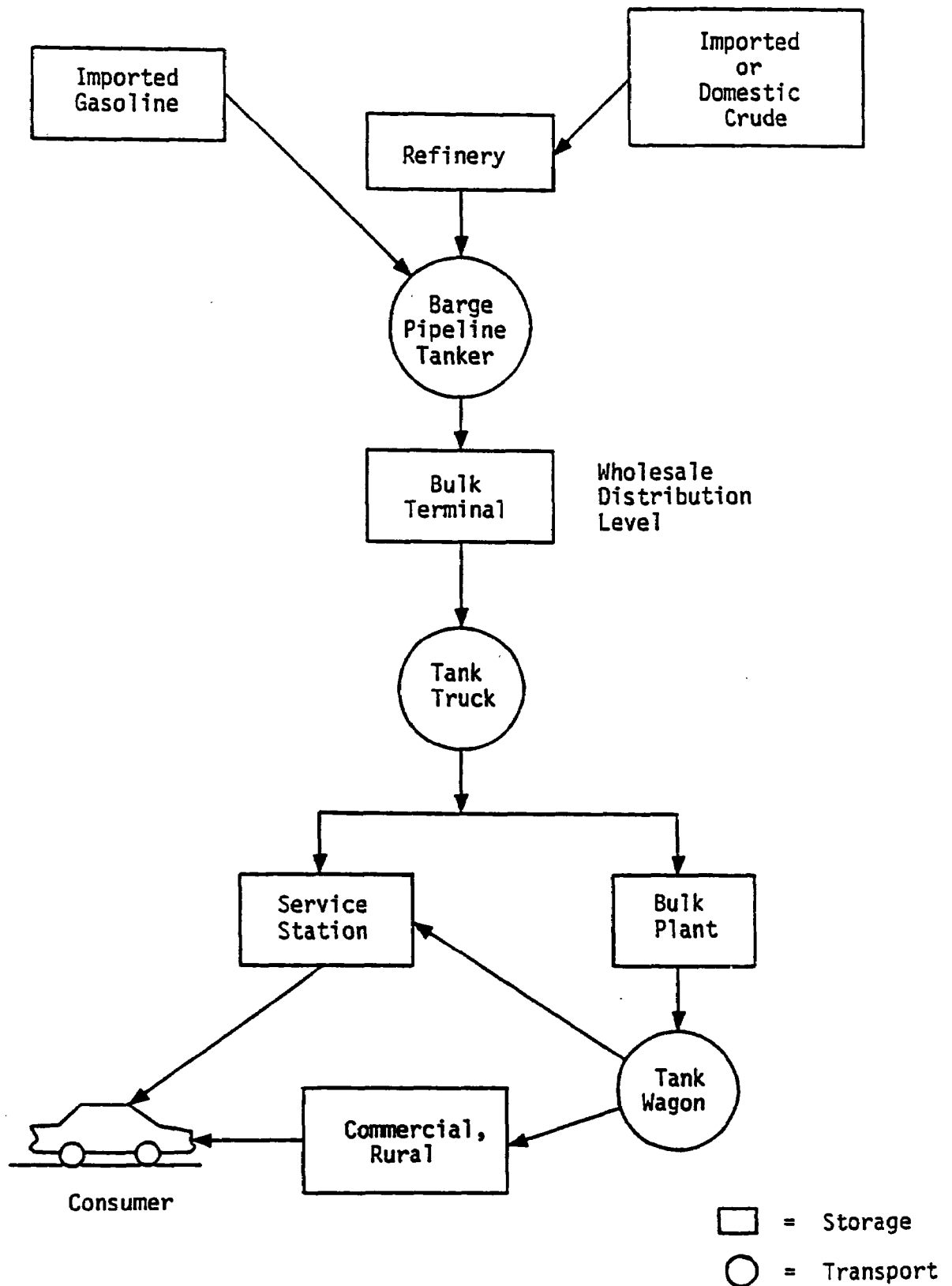


Figure 2.1 Gasoline distribution in the U.S.

loading (top submerged with vapor collection). Top loading involves loading of products into the tank via the hatchway located at the top of each compartment. Gasoline is loaded directly into the compartment through a top loading fill pipe (splash fill). Attachment of a fixed or extensible downspout to the fill pipe provides a means of introducing the product near the bottom of the tank (submerged fill), creating less turbulence and vapor mist generation than splash filling. Top loading can also be designed for vapor collection, but a bulk terminal required to comply with the NSPS is not likely to install (or retain) top loading equipment.

Bottom loading refers simply to the loading of products into the cargo tank through adapters located at the bottom. Submerged loading occurs naturally using this method and turbulence is again held to a minimum. Some of the advantages of bottom loading include: (1) improved safety, (2) faster loading, and (3) better emission control (because of the leakage often associated with top loading systems). The loading arms are attached to each compartment's loading adapter using dry-break couplers so that liquid loss is minimized during connecting and disconnecting. For vapor collection, a flexible hose or swing-type arm is connected to a vapor collection line on the truck. This line routes gasoline vapors displaced during the loading operation to vapor collection and processing systems. Figure 2.2 depicts the three basic types of tank truck loading described above.

### 2.3 TANK TRUCKS

Oil companies operating bulk terminals typically operate from 3 to 20 "branded" gasoline tank trucks out of one or more terminals, although many terminals are served exclusively by "for-hire" tank trucks operated by other companies. These tank trucks range in size from 4,000 to 10,000 gallons (15,140 to 37,850 liters), averaging about 8,500 gallons (32,170 liters) capacity. They are divided into four or five individual compartments, allowing various products (leaded and unleaded gasolines, diesel, etc.) to be transported in the same cargo tank.

During a bottom loading operation, an internal valve is opened to allow product flow, and tank vents open to permit the exit of vapors which are displaced by the incoming product. Vapor collection systems on tank trucks incorporating bottom loading equipment collect vapors



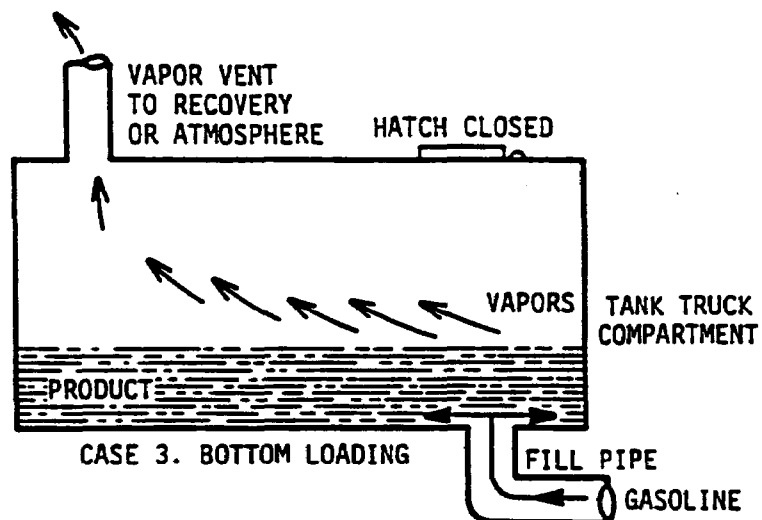
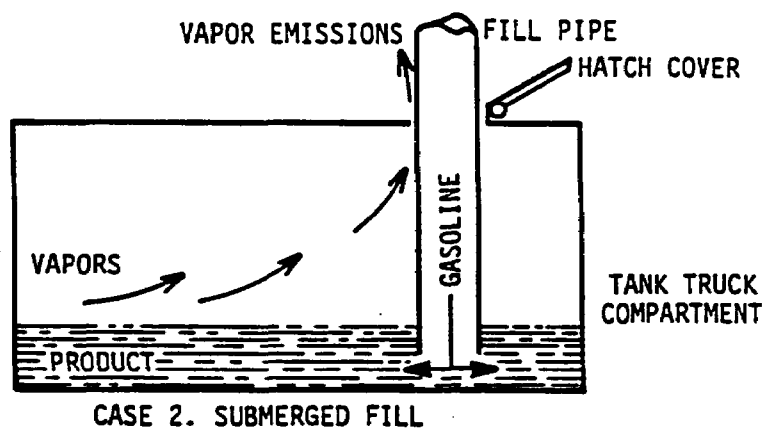
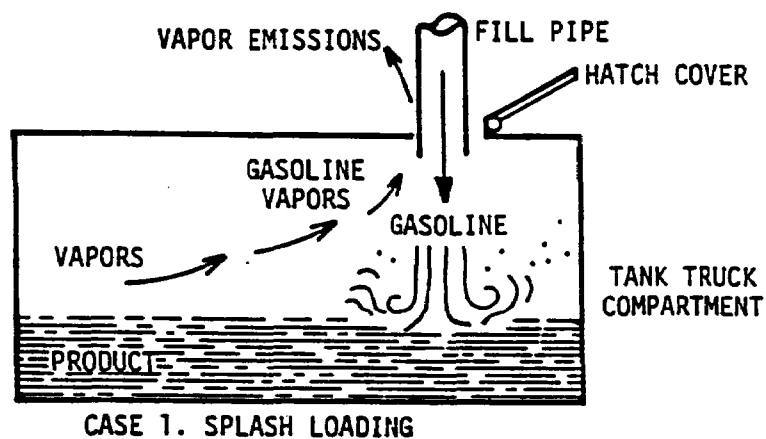


Figure 2.2 Basic types of tank truck loading.

from the compartment vents through a common vapor manifold, which is usually one of the two overturn rails running along the top of the tank. This vapor line terminates at an adapter at the rear (and also sometimes on the side center) of the tank truck. This adapter allows the driver to hook up vapor recovery as part of the loading procedure while standing on the ground. A coupler on the terminal's vapor return line is compatible with and connects tightly to the truck's vapor fitting.

In order to measure the quantity of gasoline delivered during bottom loading and to provide protection against overfilling, set-stop meters are used to shut off the flow of gasoline when a preset amount has been delivered. Liquid level sensing devices, electrically connected to close flow control valves and shut off the delivery pumps if the level approaches the top of the tank, are also commonly used to provide secondary control in the event of a malfunction or human error. This overfill protection may consist of fiber optics systems, electric probe, or float switches.

It was mentioned earlier (Section 2.1) that bulk gasoline terminals may also handle liquid petroleum products other than gasoline. VOC emissions from the dedicated loading of fuel oil, diesel, and jet fuel are essentially negligible compared to emissions from gasoline, because of the lower volatilities of these products. At many terminals, "switch loading" of delivery tank trucks is practiced. Switch loading involves the transport, in a single tank compartment on successive deliveries, of one or more other products in addition to gasoline. Gasoline vapors can be displaced from the delivery tank either by incoming gasoline or by any other liquid product when vapors from a previous load of gasoline are left in the tank. Thus, VOC emissions can occur at gasoline loading racks or at product loading racks that switch load into tank trucks that transport gasoline.

The effectiveness of vapor control systems at bulk terminals is dependent upon the minimization of leaks in the vapor-containing equipment. Some gasoline delivery tank trucks have been demonstrated to be major sources of fugitive vapor leakage during loading operations. Tank trucks in areas having no tank vapor tightness requirements have been found to leak approximately 30 percent of the displaced vapors to the atmosphere, and some of these tanks may lose essentially all of the

displaced vapors due to leakage. In contrast, the average leakage in areas requiring vapor tightness certification averages about 10 percent.<sup>2</sup> Sources of leakage include hatch covers and gaskets, pressure-vacuum (P-V) vents, and other components of the tank truck's vapor collection system. Figure 2.3 shows some common vapor leakage points on a tank truck.

## 2.4 VAPOR COLLECTION SYSTEM

The flexible hoses or swing-type arms at the loading racks, which collect air-vapor mixture from loading tank trucks, are manifolded together and all of the collected vapors are piped to a single vapor processor (or, occasionally, to a main processor plus add-on device). In the case where two tank trucks are loading simultaneously at different racks, it is possible for the vapors displaced from one tank truck to pass through the manifold and escape through the other tank. To avoid this problem, terminals often install check valves to isolate individual lines and ensure that vapors are routed to the processor.

There are three types of equipment often used in the collection system between the loading racks and the vapor processor: liquid knockout tank, saturator tank, and vapor holder. The liquid knockout tank removes any liquid gasoline that may have entered the vapor line due to overfilling, condensation, etc. Saturator tanks contain gasoline spray nozzles to raise the vapor concentration above the explosive range, and sometimes serve as a preconditioner for certain less-used types of processors. Vapor holders store air-vapor mixture until some preset capacity is reached, and then release it to the control system for processing. This intermittent form of processing minimizes fluctuations in the vapor load and allows some processors to operate more efficiently. Generally, a vapor holder consists of a large tank containing a flexible bladder or lifter roof.

## 2.5 VAPOR CONTROL SYSTEM

The function of the vapor control system (VCS) is to receive air-vapor mixture from the collection system and process it in some way so that emissions to the atmosphere are reduced. These systems are often referred to as vapor recovery units (VRU) or vapor processors. Systems

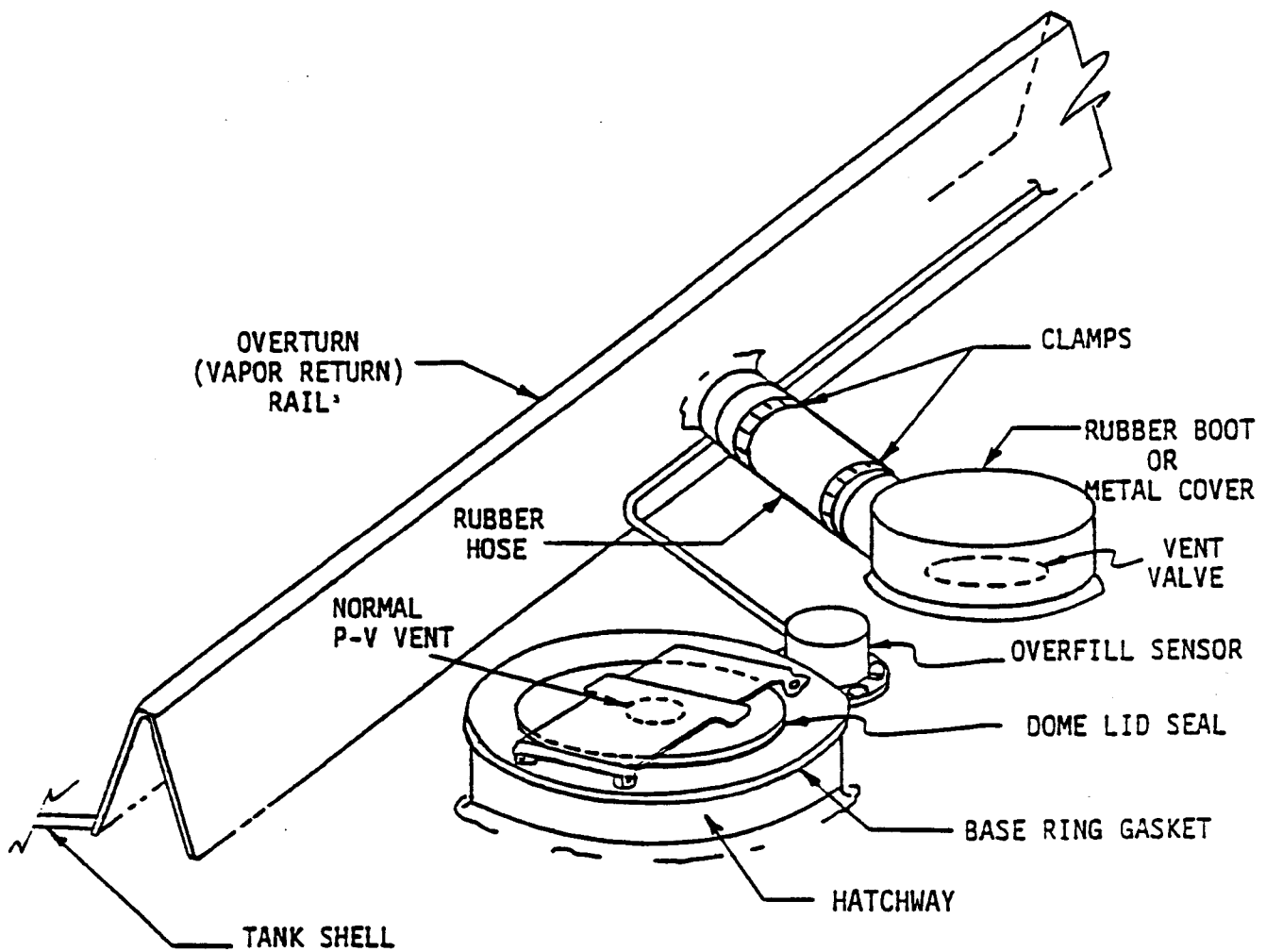


Figure 2.3 Vapor leakage points on a tank truck compartment (bottom loading only).

that process vapors into recoverable liquid product include carbon adsorption and refrigeration systems, as well as various hybrid systems that operate on the principles of compression and absorption. Thermal oxidation, or combustion, systems are also in widespread use. These systems, in the form of either incinerators or flares, do not recover any product from the vapors. Processor types are described in detail in Section 4. Figure 2.4 demonstrates the recovery of vapors during tank truck loading.

## 2.6 EMISSION POINTS

At a bulk terminal without vapor collection and control systems, hydrocarbon vapors are displaced directly to the atmosphere during product loading, the emission rate being determined largely by the type of loading. Top splash loading creates a turbulent liquid surface that causes the entrainment of gasoline mist and droplets into the vapor space. In submerged fill or bottom loading, there is much less turbulence and entrainment, and emissions are reduced. In response to State regulations, tank trucks are often unloaded at bulk plants and service stations using a closed piping system to contain the storage tank's vapors and transfer them to the tank truck as it is emptied of liquid product. Using this system, the VOC vapors that would otherwise have been emitted are "balanced" into the tank truck. Tank trucks practicing vapor balance (also termed Stage I control) return to the terminal with a high concentration of vapors that can approach saturation, which increases the emission rate over that without vapor balance. Bulk terminal vapor control and Stage I are generally used together in the same area to form a complete emission control program.

The emissions from controlled loading operations depend on the control efficiency of the vapor processor and on the amount of leakage (fugitive losses) from the vapor collection system. Fugitive leakage from tank trucks during loading was discussed earlier (Section 2.3). Such leaks can occur from any of the vapor-containing components installed at the top of each compartment, including hatch covers and vent valve covers. Another source of leakage is the interface between the tank truck's vapor adapter and the terminal's vapor return line coupler.

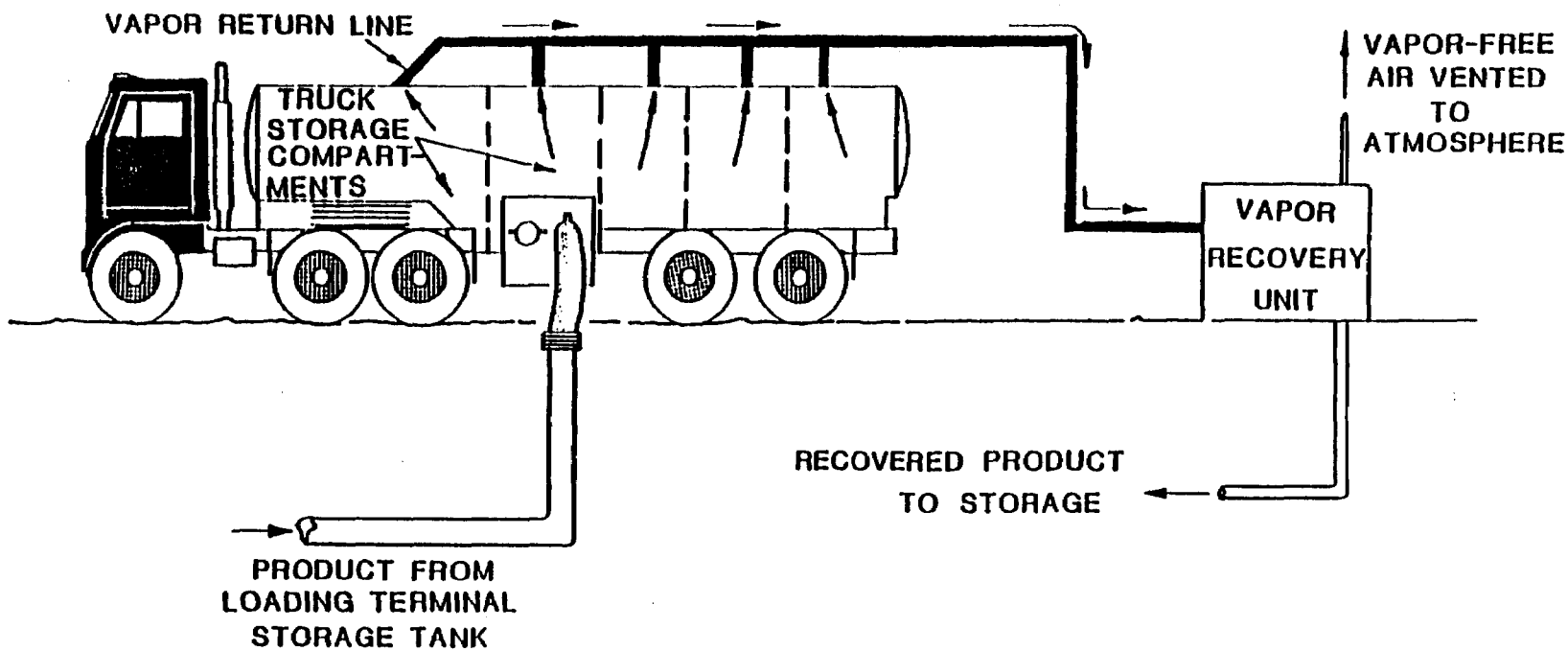


Figure 2.4 Tank truck loading with vapor collection and recovery.

In top loading vapor collection systems, a significant potential source of leakage is the interface between the top loading vapor head and the tank truck hatch. The vapor heads are designed to seal at the hatch through the compression of a cone-shaped rubber ring. However, these seals can develop flaws and a complete seal is often difficult to achieve. The terminal's flexible vapor return lines may develop leaks through damage or gradual wear, or can leak at the clamps that attach them to the vapor manifold line. P-V vents on knockout (condensate) tanks and vapor holders are leakage sources if they do not close fully due to dirt or damage. The bladder in a vapor holder may eventually crack or tear and can become a serious source of leakage.

The vapor processor itself is not often a source of fugitive leakage emissions. However, any piping joint in the collection system, including flanges where the processor is connected, can leak due to improper installation or a damaged gasket. Process emissions consist of the control system exhaust emission rate as measured in the most recent performance test, although for calculation purposes it is often assumed to be the applicable regulatory limit of either 80 or 35 milligrams of total organic compounds (or of VOC) per liter of gasoline loaded (see Section 3.3)

The EPA's Office of Air Quality Planning and Standards (OAQPS) has prepared two Control Techniques Guidelines (CTG) documents<sup>3,4</sup>, which discuss reasonably available control technology (RACT) for bulk terminal process emissions and for tank trucks and vapor collection systems. The bulk terminal CTG prescribes a vapor processor that will achieve emissions of 80 mg/liter. The tank truck CTG restricts the amount of fugitive vapor and liquid leakage allowable from tank trucks and collection systems, as indicated by a tank truck pressure/vacuum test and monitoring of potential leak sources using a combustible gas detector.

The bulk terminal NSPS uses the CTG recommendations as a starting point, and then builds on them to create a scheme that employs the best controls available, considering all other impacts. Therefore, many of the NSPS requirements are very similar to those contained in State regulations, and the NSPS inspection will parallel the inspections traditionally performed by State and local agency personnel to enforce the RACT-based rules.

INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS  
Baseline and Diagnostic Data

3.2. Baseline and Diagnostic Inspection Data

3.2.1 General Information

- ° Method of refueling facility (e.g. pipeline, truck)
- ° Gasoline throughput, annual total and daily maximum
- ° Number of loading racks and loading arms
- ° Types of loading arms
- ° Average number of trucks loaded per day
- ° Fraction of trucks returning with vapor
- ° Types and capacities of storage tanks
- ° Presence of vapor holding tank

3.2.2 Carbon Bed Vapor Recovery System

- ° Maximum vacuum
- ° On-line carbon bed temperatures
- ° Gasoline supply temperature
- ° Absorption gasoline supply pump pressure
- ° Absorption gasoline return pump pressure
- ° Carbon bed cycle times
- ° Carbon bed outlet VOC concentrations

3.2.3 Refrigeration Vapor Recovery Systems

- ° Second stage chamber temperature
- ° Brine, coolant, and defrost pump pressures

3.2.4 Thermal Incinerator Vapor Recovery Systems

- ° Outlet gas temperature
- ° Presence of visible emissions



INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS  
Routine Inspection Data

3.3 Routine Inspection Data

3.3.1 General Information

- ° Type of products being handled
- ° Fill rates
- ° Vapor recovery system outages since last inspection

3.3.2 Level 2 Inspections

Fugitive Leaks (during loading of one or more trucks)

- ° Presence of any visible, odorous, or audible vapor leaks or spills
- ° Vapor line is connected to truck during loading
- ° Unconnected vapor lines at other loading racks ~~not~~ not in service are closed
- ° Truck relief valves do not open during loading
- ° Top-loading nozzle grommet in good physical condition and is seated properly against filling port
- ° Top seal remains tight during loading and truck settling
- ° Truck tank fill sensor is connected to automatic shutoff
- ° Loading of distillate fuels into trucks previously containing gasoline is not being done at loading racks not connected to vapor recovery system.

Inspection of Vapor Recovery Systems - General

- ° Confirm that vapor recovery system is operating during truck loading or when vapor accumulator is full
- ° Confirm that accumulator pressure relief valve is not stuck open and emitting VOC materials
- ° Confirm that level indicator is rising during truck loading, if the vapor recovery system is not operating.

Carbon Bed Vapor Recovery Systems

- ° Maximum vacuum during operation of each bed
- ° On-line carbon bed temperatures
- ° Absorption gasoline supply pump pressure
- ° Absorption gasoline return pump pressure
- ° Gasoline supply temperature
- ° Verify that unit operates during truck loading or when vapor accumulator is full

INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS  
Routine Inspection Data (Continued)

Thermal Incinerator Vapor Recovery Systems

- ° Outlet gas temperatures
- ° Verify that unit operates during truck loading or when holding tank is full

Refrigeration Vapor Recovery Systems

- ° Temperature readings for second stage chamber.
- ° Brine, coolant, and defrost pump pressures

Storage Tanks (Inspect one or more)

- ° Examine internal floating roofs through roof hatch to determine obvious damage or malfunctions.

3.3.3 Level 3 Inspections

Fugitive Leaks (during loading of one or more trucks)

- ° All inspection points listed under Section 3.3.2
- ° Measure VOC concentrations near (1 cm.) top-loading seal and loading arm joints
- ° Measure VOC concentration near (1" cm.) vapor line connections.
- ° Measure VOC concentration near (1' cm.) near truck pressure-relief valve
- ° Measure VOC concentration near (1" cm.) all truck top hatches

Vapor Recovery System - General

- ° All inspection points listed in Section 3.3.2
- ° Measure VOC concentration near (1 cm.) accumulator pressure relief valve
- ° Measure VOC concentration near (1 cm.) all flanges and joints in vapor line to accumulator and to vapor recovery system

Carbon Bed Adsorber Vapor Recovery Systems

- ° All inspection points listed in Section 3.3.2
- ° Measure VOC concentration (1 to 2 cm.) at outlet of each bed near the end of the adsorption cycle

Refrigeration Systems and Thermal Incinerator Vapor Recovery Systems

- ° All inspection points listed in Section 3.3.2.

## INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS

### Inspection Procedures

#### 3.4. Inspection Procedures

There are two levels of inspection for Gasoline distribution terminals and bulk plants. A Level 2 inspection consists primarily of a walk through inspection to confirm that all engineering controls necessary to minimize visible emissions are being used. Also, an evaluation of the vapor recovery systems is performed using on-site gauges. The Level 3 inspection involves the use of portable VOC monitoring instruments to determine if there are any measureable fugitive emissions and if the VOC emissions from the vapor recovery systems are the within normal range.

##### 3.4.1 General Information

###### Review the facilities operating records.

- ° Determine the types of products being loaded into trucks during the inspection. Compare this with the types of products loaded since the last inspection to confirm that operating conditions during the inspection are actually representative of normal conditions.
- ° Determine the peak loading rates to determine if the vapor recovery system is potentially being overloaded.
- ° Examine operating logs and maintenance records to determine the extent of vapor recovery system downtime since the last inspection. All organic vapors are emitted when the vapor recovery system is not operated.

###### Check for any facility modifications.

- ° Check for modifications to loading racks
- ° Check for modifications to storage tanks

##### 3.4.2 Level 2 Inspections

###### Fugitive Emissions from Trucks and Loading Racks

###### Check vapor return line connections

Inspect and verify the presence of a vapor collection line at the account truck vapor port, the connection pipe at the loading rack, and the inlet lines to stationary storage tanks.

## INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS

### Inspection Procedures

#### Note any potential gasoline vapors leak sources.

Carefully observe one or more truck loadings to determine if there are any potential leak sources. The most common sources include:

- (1) unconnected vapor return lines from trucks
- (2) open vapor lines at other loading racks
- (3) open truck pressure-relief lines
- (4) poor top-loading truck nozzle seals
- (5) poor truck hatch covers

Leaks at any of these locations when allow gasoline vapor to escape to the atmosphere rather than being pushed to the vapor recovery system. Since the static pressures throughout the vapor balance system is 2 to 16 inches W.C., even small leaks can result in substantial emissions. Note all odors, visual leaks, and audible leaks.

#### Check top-loading fill pipe extension.

Verify that the discharge is within 6 inches of the bottom.

#### Check diameter of vapor return line to recovery system.

Locate and observe the use of an adequately sized vapor return line. This should be properly sized properly for the number of trucks loaded at peak periods.

#### Vapor Recovery System - General

#### Check the operation of the vapor accumulator (if present).

The level indicator should increase whenever the vapor recovery system is not operating and one or more trucks are being loaded.

#### Check the pressure-relief valve the accumulator.

Look for any visible emissions (vapor light refraction lines) which indicate that this valve is stuck in the open position. The presence of emissions also indicates that there is leakage through the diaphragm of the accumulator.

#### Check for visible symptoms of emissions

Check for vapors light refraction lines from emergency vent stacks and from holding/knockout tank vent.

INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS  
Inspection Procedures

Carbon Bed Vapor Recovery System

Check for system activation during truck loading.

For facilities without vapor accumulators (hold tanks), the carbon bed system should be running during gasoline transfer operations. For facilities with the accumulators, the carbon bed system should run whenever the tank level is within a preset range.

Check for visible symptoms of vapor emission.

Observe the exhaust ports from both beds during the end of the absorption cycle (usually 15 to 20 minutes duration). Visible light refraction lines suggest higher than normal VOC emissions and carbon bed operating problems.

Verify regeneration vacuum of 27 to 28 inches of mercury.

The regeneration vacuum should gradually reach 27 to 28 inches of mercury during desorption of each bed. Lower levels of vacuum indicate that less than the necessary amount of the adsorbed gasoline is being removed from the bed. During the next adsorption cycle, there may be insufficient active sites available to adequately remove organic vapors.

Check carbon bed operating temperatures during adsorption.

Record dial-type thermometer readings near the end of each adsorption cycle and during the air stripping of the carbon beds during regeneration. If the bed temperatures during adsorption are low (very close to ambient temperatures), there is probably very little removal of organic vapor. Adsorption is an exothermic process and is indicated by slightly increased temperature.

Check gasoline supply temperature to absorber tower.

Verify that the gasoline supply temperature to the absorption tower is less than 100 °F. This is necessary to ensure adequate absorption of the gasoline vapors stream removed from the carbon beds.

## INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS

### Inspection Procedures

#### Verify that the gasoline absorption cycle is operational.

Verify operation of the gasoline absorption cycle by recording the gasoline supply pump and gasoline return pump pressures. Measurable pressures indicate that the absorption cycle is working. The flow of gasoline to the absorption tower is inversely related to the pressure for a given pump.

#### Note any system warning lights.

All warning lights should be noted since these indicate system malfunction. Ask the facility manager to explain the possible impact of the indicated malfunction on the system VOC collection efficiency.

#### Record Clock meter readings.

The total operating time of the vapor recovery system should be compared with previously recorded values observed in earlier inspections. This data is used to determine if the system has had excessive downtime.

### Refrigeration Vapor Recovery Systems

#### Check the present operating temperature of the system.

This is checked using the system temperature recorder. If the unit is operating in the previously observed temperature range (usually -90 to -120 °F), then other refrigeration system components are probably operating properly. The removal of VOC materials is directly proportional to the operating temperature - the colder the better.

#### Evaluate temperature strip charts.

These are evaluated to identify any chronic high temperature conditions. Ask the facility manager to explain any problems which are preventing proper operating temperatures in the refrigeration system.

#### Evaluate defrosting practices.

Confirm that the units are being defrosted on at least a daily basis. All refrigeration units are subject to frost problems which can ultimately have an adverse impact on the VOC removal efficiency and the system availability.

## INSPECTION OF GASOLINE MARKETING AND BULK PLANTS

### Inspection Procedures

#### Note any system warning lights.

These are indications of system malfunctions and should be carefully noted. Ask the facility manager to explain the potential impact of the indicated problem on system efficiency and downtime.

#### Thermal Incinerators

##### Check system activation.

Confirm that the burner is ignited whenever the accumulator is full and/or a truck is being loaded.

##### Check the outlet temperature.

The outlet temperature is generally 1400 °F. This can be confirmed by use of the thermocouple installed either in the stack or in the combustion chamber. Low outlet temperatures indicate low efficiency combustion or flame out of the burner.

##### Check for visible emissions.

Black smoke indicates severe burner maladjustment or fouling. Poor VOC destruction and objectionable smoke result from the poor burner maintenance.

#### Storage Tanks

##### Examine internal floating roofs.

Examine internal floating roof in one or more fixed roof storage tanks to determine the the presence of any physical damage or malfunctions. It is important that inspectors avoid inhalation of high concentrations of organic vapor during this step.

##### Examine pressure-relief valves and vents.

Note any visible symptoms of VOC emission from these vents.

### 3.4.2 Level 3 Inspections

Level 3 inspections include all of the inspection described above for Level 2 inspections. In addition, portable VOC monitors are used to evaluate fugitive emissions and to evaluate the performance of vapor recovery systems.

## INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS

### Inspection Procedures

The types of instruments generally used at gasoline terminals and bulk plants include: (1) explosimeters, (2) catalytic combustion instruments, and (3) flame ionization detectors. Since these have different VOC concentration units, care is necessary in determining what is and is not a leak in accordance with the applicable regulation.

#### Instrument Check-out

##### Check-out Instrument(s) Before Leaving for Inspection Site.

All VOC detectors to be used during the inspection should be fully checked before arriving at the facility. The checks include:

- ° Batteries or battery packs are fully charged
- ° All probe assemblies are complete
- ° All flame arrestors are present and in good physical condition
- ° All instruments are intrinsically safe
- ° All necessary spare parts are packed

##### Calibrate instruments.

VOC detectors used for gasoline terminals and bulk plants are generally calibrated using propane or butane. These are most similar to the compounds emitted.

#### Evaluation of Fugitive Emissions

##### Measure VOC concentrations of potential truck leaks.

Measure VOC concentrations near (1 cm.) all truck pressure-relief valves, vapor line connections, top-loading hatch seals (if present), bottom-loading connections (if present), and truck hatches. Measure emissions from pressure-relief valves in the approximate center of the valve outlet. All hatch and connection measurements should be made by traversing the entire circumference. Complete all measurements before each compartment of the truck is filled in case the automatic shutoff is not working properly.

##### Measure VOC concentration on loading racks.

Measure VOC concentrations near (1 cm.) all loading rack line joints/connections and on all vapor return line joints/connections.



INSPECTION OF GASOLINE TERMINALS AND BULK PLANTS  
Inspection Procedures

Evaluation of Vapor Recovery Systems - General  
Measure the VOC concentrations from potential leak sources on the vapor accumulator.

Measure the VOC concentrations from all pressure-relief valves and vents on the vapor accumulator.

Evaluate Carbon Bed Adsorber System Performance  
Measure the VOC concentration from each bed.

The VOC concentration of the exhaust from each bed should be less than 1000 ppm (explosimeter: 0.05 to 0.10). Higher concentrations indicate that the bed(s) is not removing organic vapors at the efficiency intended. Possible problems include inadequate regeneration and/or gradual accumulation of high molecular weight materials which can not be desorbed.

Evaluation of Refrigeration System Performance  
VOC instruments are generally not applicable.

The VOC concentrations from refrigeration systems are usually in the range of 10,000 ppm to 30,000 ppm which is equivalent to approximately 90 to 95% control efficiency. These concentrations are above the normal operating range of VOC detectors.

Evaluation of Thermal Incinerator Performance  
VOC instruments are generally not applicable.

The exhaust temperatures from incinerators are several hundred degrees Fahrenheit above the allowable maximum temperatures for the VOC instrument probes.