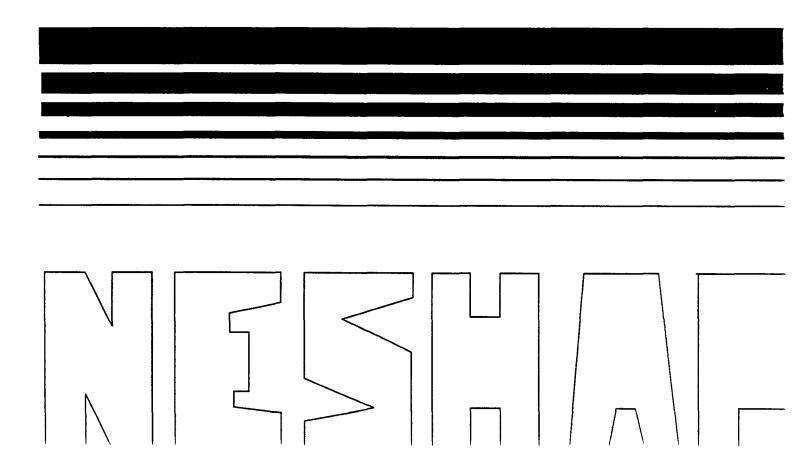
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C. 2

# **€** EPA

# Procedures for Establishing Emissions for Early Reduction Compliance Extensions

Volume 1 -- Synthetic Organic Chemical Manufacturing, Ethylene Oxide Sterilization, and Chromium Electroplating



# Procedures for Establishing Emissions for Early Reduction Compliance Extensions Volume 1

**Emissions Standards Division** 

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#### TABLE OF CONTENTS

Section				Page
1	INTR	ODUCTION	1	1-1
2	ESTA	BLISHING	G HAP EMISSIONS FROM SOCMI SOURCES	
	2.1		S Vents	2-3
		2.1.2	from Process Vents	2-4
			Emissions from Process Vents	
	2.2	Storage	e Tanks	2-7
		2.2.1	Acceptable Techniques for Establishing HAP Emissions	
		2.2.2	from Fixed Roof Storage Tanks Acceptable Techniques for	2-8
			Establishing HAP Emissions from Floating Roof Storage Tanks .	2-13
		2.2.3		
		_	Emissions from Storage Tanks	
	2.3		ent Leaks	2-30
		2.3.2	from Equipment Leaks	2-33
			Emissions from Equipment Leaks	2-37
	2.4	Transf	er Operations	
		2.4.1	Acceptable Techniques for	
			Establishing Emissions from	
			Transfer Operations	2-40
		2.4.2	Documentation of HAP	
			Emissions from Loading Operations.	2-42
	2.5		ater Collection and Treatment	2-42
		2.5.1	Acceptable Techniques for Establishing HAP Emissions	
			from Wastewater Collection and	
			Treatment	2-44
		2.5.2		
			from Wastewater Sources	2-55

## TABLE OF CONTENTS (Concluded)

<u>Section</u>		<u>Page</u>
3	ESTABLISHING CHROMIUM EMISSIONS FROM CHROMIUM ELECTROPLATING OPERATIONS	
	3.1 Control Techniques/Performance	
	Establishing Emissions	3-5
	3.2.2 Emission Factors	3-5 3-6
4	ETHYLENE OXIDE STERILIZATION	
	4.1 Techniques for Establishing Baseline HAP Emissions	4 - 3
	4.2 Techniques for Establishing 90% HAP Emission Reduction	4-3
		4-3
APPENDIX	A: CALCULATION WORKSHEETS FOR ESTABLISHING BASE YEAR AND POST-REDUCTION HAP EMISSIONS	
	FROM SOCMI SOURCES	A-1

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1	Equations for Estimating Fixed-Roof Storage Tank Emissions	2-9
2-2	Average Storage Temperature $(T_S)$ as a Function of Tank Paint Color	2-10
2-3	Paint Factors for Fixed Roof Tanks	2-11
2-4	Equations for Estimating Internal Floating Roof Storage Tank Emissions	2-14
2-5	Equations for Estimating External Floating Roof Storage Tank Emissions	2-17
2-6	Typical Number of Columns as a Function of Tank Diameter for Internal Floating Roof Tanks with Column Supported Fixed Roofs	2-20
2-7	Deck Seam Length Factors (S <sub>D</sub> ) for Typical  Deck Constructions for Internal Floating Roof Tanks	2-21
2-8	Seal Related Factors for External Floating Roof Tanks	2-22
2-9	Average Clingage Factors (C) $(bbl/1,000 \text{ ft}^2)$	2-23
2-10	Summary of Internal Floating Deck Fitting Loss Factors $(K_F)$ and Typical Number of Fittings $(N_F)$	2-24
2-11	External Roof Fitting Loss Factors (Kfa, Kfb) and Typical Number of Roof Fittings (NF)	2-26
2-12	Typical Number of Vacuum Breakers and Roof Drains	2-28
2-13	Typical Number of External Floating Roof Legs	2-29
2-14	Leaking and Non-leaking Emission Factors For Fugitive Emissions (kg/yr/source)	2-34
2-15	Stratified Emission Factors for Equipment Leaks (kg/yr/source)	2-36
2-16	Saturation (S) Factors for Calculating Organic Liquid Loading Losses	2-41
	iii	

## LIST OF TABLES (Concluded)

<u>Table</u>		Page
2-17	Emission Sources in Wastewater Collection and Treatment Systems	2-45
2-18	Compound-specific Values of $fe_i$ and $fm_i$	2-49

#### LIST OF FIGURES

<u>Figure</u>							<u>Page</u>
4-1	The Sterilization Cycle	 					4-2

#### 1. INTRODUCTION

On June 13, 1991, EPA proposed "Regulations Governing Compliance Extensions for Early Reductions of Hazardous Air Pollutants" (56 FR 27338). The proposed rule (scheduled for promulgation in March 1992) implements the provisions in Section 112(i)(5) of the Clean Air Act (Act), as amended in 1990. provisions allow an existing source of hazardous air pollutant emissions to obtain a six-year extension of compliance with an emission standard promulgated pursuant to Section 112(d) of the Act, if the source has achieved a reduction of 90 percent or more of hazardous air pollutants emitted (95 percent or more for particulate pollutants) by certain dates specified in the Act. If a source is granted a compliance extension, an alternative emission limitation will be established by permit to ensure continued achievement of the 90 (95) percent reduction. proposed rule establishes requirements and procedures for source owners and operators to follow in order to obtain compliance extensions and for reviewing agencies to follow in evaluating requests for extensions.

One requirement is that requests for a compliance extension must be submitted to a reviewing agency (EPA or a State agency with authority to implement this program) and must contain documentation that the emission reduction has been achieved. To document the reduction, the owner or operator must provide emission data for base year and post-reduction emissions of hazardous air pollutants emitted by the source. The proposed rule establishes a presumption that source test results must be used to satisfactorily document either base year or postreduction emissions. However, the rule also lists circumstances under which an owner or operator would be allowed to use methods other than source testing to document emissions for a source (for example, methods employing engineering calculations, material balances, or emission factors).

This document contains procedures for establishing emissions

for three categories of sources. The three categories covered in this document are synthetic organic chemical manufacturing, chromium electroplating and chromic acid anodizing, and ethylene oxide sterilization. Documents covering additional industries which will be regulated under Section 112(d) of the Act will be issued periodically by EPA.

The intent of this document, and additional documents in this series, is to provide methods for establishing emissions for the purposes of the early reduction program, with an emphasis on methods that can be used when source tests are not required. Owners or operators may use this document as a guide to preparing satisfactory emission reduction demonstrations for compliance extension requests. However, it is not the intent of this document to specify the only acceptable methods, other than source tests, for establishing emissions from a source. recognizes that, depending on the circumstances, there may be other ways of satisfactorily showing that hazardous air pollutants have been controlled sufficiently to qualify for a compliance extension, and owners or operators are not precluded from using them. No matter what methods are used, the emissions established for a source and submitted in a compliance extension request will undergo review to determine whether they are adequate for the purposes of the early reduction program.

### 2.0 ESTABLISHING HAP EMISSIONS FROM SOCMI SOURCES

Air emission sources in the SOCMI industry can be divided into five source types. These source types, along with a brief description, are listed below:

Process Vent Emissions - Emissions from vented process equipment such as reactors and distillation systems.

Storage Tank Emissions - Emissions from fixed roof and floating roof storage tanks.

Equipment Leak Emissions - Emissions that occur due to the escape of process materials through faulty seals in pumps, valves, compressors, flanges and other connectors, agitators, sample connections, and open-end process lines.

Transfer Emissions - Emissions that occur when loading product into tank trucks, rail cars, and marine vessels.

Wastewater Collection and Treatment Emissions - Emissions that result from the volatilization of organic hazardous air pollutants (HAP) contained in process wastewater streams.

This section describes the acceptable techniques for establishing HAP emissions from each of these emission source types. The basic approaches considered in prescribing acceptable techniques for each source type included:

- (1) Measurement Calculations based on measured concentration of the HAP in a waste stream and the flow rate of the stream.
- (2) Established EPA Protocols Engineering calculation methods presented in the US EPA publications, Compilation of Air Pollutant Emission Factors (EPA-AP-42) and Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP (450/3-88-010). These publications provide engineering calculation approaches for sources such as storage tanks, transfer operations, and equipment leaks when direct measurement is not feasible.
- (3) Engineering Calculations These are calculations based on physical properties of the HAP, an understanding of

the process, and accepted engineering relationships such as the ideal gas law. The distinction between this technique and (2) above is that the calculation procedure has not been previously published as an accepted EPA procedure for estimating source specific emissions.

- (4) Material Balance A mass balance around the entire process or piece of equipment. The amount of chemical leaving the process equals the amount entering. If input and product stream values are known and all losses are to air, then air emissions can be computed by difference. Any accumulation or depletion of the HAP by reaction must be accounted for. In general, material balances produce emission estimates with high levels of uncertainty. However, in certain situations, material balances can be used to produce accurate emission estimates. Material balance can be used, for example, where the HAP emitted is used as a process solvent and is not involved in chemical reactions.
- (5) Emission Factors Calculations based on average measured emissions at numerous facilities in the same industry. Emission factors can be expressed as a ratio of emissions to process throughput or an emission rate independent of throughput. The distinction between this technique and (2) above is that the factor has not been previously published as an accepted EPA procedure for estimating source specific emissions.

The preferred method for determining HAP emissions is measurement of the emission stream flow and HAP concentration using published EPA Methods. However, measurement can be expensive and even impractical in cases where there are large numbers of individual sources, when emissions are intermittent and highly variable or when the base year conditions no longer exist at an emission point and cannot be duplicated. When direct measurement is not feasible, the preferred approach is the use of established EPA computation methods in AP-42 and Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP (450/3-88-010). In most cases, it should be feasible to establish HAP emissions data for a source using only the first two approaches. However, certain situations may require the use of engineering calculations; and in certain situations material balances can be used to establish base year

emissions. Specific guidance on the acceptable methodologies for each source type are provided in the following subsections.

It is important to keep in mind that consistent or at least compatible methodologies must be used to establish base year and post-reduction emissions. The EPA will not allow credit for any apparent reductions achieved by using incompatible techniques for establishing base year and post-reduction emissions.

Additionally, EPA may require the applicant to demonstrate post-reduction emissions using validated EPA protocols. In many cases the validated EPA protocol may quantify more of the emissions than the technique used to establish base year emissions.

The procedures prescribed in this section are intended for continuous SOCMI processes. This is consistent with the anticipated Hazardous Organic NESHAP (HON), the 112(d) standard for continuous process chemical plants. The techniques prescribed for process vents (Section 2.1) generally are not applicable to batch processes. Another document to be released by EPA in the near future will describe emission estimating methods for batch process vents.

#### 2.1 PROCESS VENTS

Process vents are the vapor exhaust devices on process equipment in a manufacturing or processing operation. In most chemical processes, impurities and inerts contained in the raw materials necessitate the continuous or periodic venting of noncondensible gases. When released to the atmosphere, volatile HAP are carried from the process along with these noncondensible gases.

Process vents are most commonly associated with reactors and distillation systems. Direct observation of the piping and instrument diagrams should indicate if process vents exist for a given unit operation.

#### 2.1.1 <u>Acceptable Techniques for Establishing HAP</u> Emissions From Process Vents.

The preferred technique for establishing HAP emissions from process vents is direct measurement. The stream flow should be determined using EPA Methods 1 through 4; and, when possible, the HAP concentration should be determined using one of the EPA Reference methods (prescribed in 40 CFR 60, Appendix A or 40 CFR 61, Appendix A) or an EPA Conditional Method. In many cases, a validated EPA method will not exist for emissions of the subject HAP from a specific source type. In such cases, the validation protocol prescribed in EPA Method 301, Field Validation of Emission Concentrations From Stationary Sources (450/4-90-015) should be used to validate the method of choice. 1

Establishing HAP emissions for process vents is basically the same for all process vents, regardless of the unit operation. The following parameters are required through direct measurement:

- Average annual volumetric flow rate of vent gas (during operating hours),
- Vent gas discharge temperature,
- Average annual concentration of individual or aggregate HAP,
- Operating hours per year of unit operation, and
- Molecular weight of individual or aggregate HAP.

Emissions of each HAP are calculated as follows:

$$E_{U} = \frac{2.54E-09 \ O \ C \ h \ MW \ P}{T + 460}$$

where,

 $E_{U}$  = uncontrolled HAP emission rate in Mg/yr,

Q = average annual vent stream flow rate in cubic feet per minute,

C = average annual HAP concentration in ppm volume, h = annual hours of operation,

T = vent stream discharge temperature in degrees fahrenheit,

P = pressure at point of discharge in psia,

MW = HAP molecular weight, and

2.54E-09 = conversion factor to yield Mg/yr, ((60 min/hr)(Mg/2205 lb)( $10^{-6}/R$ ), where

 $R = 10.73 \text{ ft}^3 \cdot \text{psia/lb-mol} \cdot {}^{O}R)$ 

The total HAP emissions are determined by summing the calculated emissions of each HAP.

In cases where the vent emissions are intermittent or highly variable, up-front calculations of annual average flow rate and HAP concentration may be required.

In cases where there is a control device present and the control device was present prior to 1987, the control device efficiency should be accounted for in determining emissions. The control device efficiency can be accounted for by: (1) measuring the stream flow and concentration at the exit of the existing control device, or (2) using the following expression:

$$E_{B} = E_{U} (1 - eff/100)$$

where,

 $E_{R}$  = emissions in Mg/yr,

 $E_{II}$  = uncontrolled emissions in Mg/yr, and

The latter method actually requires three sets of sampling and analysis (the individual vent stream, the control device inlet, and the control device outlet), but may be necessary in situations where the vent stream is combined with other vent streams prior to control.

In cases where the control efficiency differs for individual HAP, it is necessary to perform the above calculations separately for each HAP and then sum the emissions.

In certain situations, emissions from process vents can be established by material balance, in lieu of sampling and analysis. Material balances can provide accurate determinations of emissions in cases where the HAP is used as a solvent, there is no reaction of the HAP, and all losses are to the air or can be accurately accounted for. In this case, the accuracy of computed HAP emissions can be as accurate as the determination of HAP usage. However, material balances are generally inaccurate in applications outside of the case where the HAP is a process solvent.

Calculations based on engineering principles are acceptable only in situations where:

- (1) No applicable EPA Reference Method, EPA Conditional Method, or other source test method exists;
- (2) It is not technically or economically feasible to perform source tests;
- (3) It can be demonstrated to the satisfaction of the reviewing agency that the calculation will provide emission estimates of accuracy comparable to any applicable source test method;
- (4) The base year conditions no longer exist and cannot be reproduced and testing under the current conditions and extrapolating will not produce results more accurate than an estimate base on engineering principles; or
- (5) The emissions from one or a set of emission points in the source are small compared to total source emissions and errors in estimating emissions from such points will not have a significant effect on the accuracy of estimated total emissions from the source.

The burden of adequately demonstrating one of these reasons for not source testing is placed on the source owner or operator.

## 2.1.2 <u>Documentation of HAP Emissions From Process Vents</u>

In establishing emissions, the following information should be provided with the computed emission rate:

- Stream identification;
- Vent stream flow rate, method of measurement, and date of measurement;
- Vent stream discharge temperature;
- Vent stream HAP concentration, method of measurement;
   and date of measurement;
- A detailed description of measurement methods, if EPA validated methods were not used;
- A statement that the measured flow and concentration are believed to be representative of normal operation.

A form for reporting information used to establish emissions is provided in Appendix A. In addition, detailed test data and calibration data collected during sampling and analysis of the stream should be available upon request.

#### 2.2 STORAGE TANKS

Storage tanks for organic liquids are categorized into five basic designs: fixed roof, external floating roof, internal floating roof, variable vapor space, and pressure (high and low). Procedures for establishing emissions from fixed roof, external floating roof, and internal floating roof tanks are provided in this document.

Fixed roof tanks are designed as a cylindrical steel shell with a permanent roof. The roof may be flat or shaped as a cone or dome. Fixed roof tanks have a pressure/vacuum vent which allows the tanks to operate at a slight internal pressure or vacuum. However, with significant changes in temperature, pressure, or liquid level, vapors are released through the vent. For fixed roof tanks, the vapors emitted are categorized as breathing losses and working losses. Breathing loss is the expulsion of vapor from a tank through vapor expansion and

contraction, which results from changes in temperature and barometric pressure. Breathing loss occurs regardless of the throughput of the tank. Working loss is due to emptying and filling of the tank. As the tank is filled, the increased liquid level in the tank compresses the vapor. When the pressure inside the tank exceeds the relief pressure, the pressure/vacuum vent releases vapor to the atmosphere. As the tank is emptied, air is drawn into the tank and becomes saturated with organic vapor and expands, thus exceeding the capacity of the vapor space. When the internal pressure reaches the set pressure of the pressure/vacuum vent, vapor emissions are released to the atmosphere.

Floating roof tanks have a floating deck which rests on the surface of the organic liquid. The floating deck may be the roof of the tank (external floating roof tanks) or the tank may have a permanent roof with a floating deck inside (internal floating roof). For most internal floating roof tanks, the space between the floating deck and permanent roof is vented to the atmosphere to prevent the possibility of explosion. The internal floating deck either floats directly on the liquid surface or rests on pontoons several inches above the liquid surface. The floating deck restricts the vaporization of the organic liquid. However, vaporization losses may occur from deck fittings, seams, and the space between the deck and the tank wall.

# 2.2.1 <u>Acceptable Techniques For Establishing HAP</u> <u>Emissions From Fixed Roof Storage Tanks</u>

The accepted technique for establishing HAP emissions from fixed roof storage tanks is the computation technique prescribed in AP-42.<sup>2</sup> This computation technique, along with methods for obtaining or estimating the necessary input parameters, is provided in Tables 2-1 through 2-3. As an alternate, the techniques prescribed in API publication 2518, Evaporative Loss from Fixed from Fixed Roof Tanks (second edition), may be used to establish emissions from fixed roof tanks.<sup>4</sup>

Based on initial review, the techniques prescribed in

TABLE 2-1. EQUATIONS FOR ESTIMATING FIXED-ROOF STORAGE TANK EMISSIONS<sup>a</sup>

```
L_T = L_R + L_W
L_B = 1.02 \times 10^{-5} M_{V_i} \left( \frac{P}{P_A - P} \right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.5} F_P CK_C P_i
L_W = 1.09 \times 10^{-8} M_{V_i} P_i VNK_N K_C
     where,
           L_T = total HAP emissions in Mg/yr,
           L_B = breathing loss emissions in Mg/yr,
           L_W = working loss emissions in Mg/yr,
          M_{V}, = molecular weight of HAP,
                 true vapor pressure of the material stored in psia
                 at the stored temperature (see Table 2-2),
           P<sub>i</sub> = partial pressure of the specific HAP in psia,
           P_{A} = atmospheric pressure in psia,
            D = tank diameter in feet,
            H = average vapor space height in feet (use tank
                 specific values or an assumed value of one-half
                 the tank height),
            T = average diurnal temperature change in OF (20OF can
                 be used as a typical value),
           F_p = dimensionless paint factor from Table 2-3,
            C = dimensionless tank diameter factor:
                  C = 1 for diameter \geq 30 feet
                  C = 0.0771D-0.0013D^2-0.1334 for dia. < 30 feet
           K<sub>C</sub> = product factor = 1.0 for volatile organic HAPs,
            V = tank capacity in gallons
            N = number of turnovers per year,
           K_N = dimensionless turnover factor:
                  K_{N} = 180 + N
                                   for turnovers > 36
                  K_N = 1
                                   for turnovers ≤ 36
```

aReferences 2 and 3.

TABLE 2-2. AVERAGE STORAGE TEMPERATURE ( $T_S$ ) AS A FUNCTION OF TANK PAINT COLOR<sup>a</sup>

Tank Color	Average storage temperature ${ m T}_{ m S}$
White	T <sub>A</sub> b + 0
Aluminum	T <sub>A</sub> + 2.5
Gray	$T_A + 3.5$
Black	T <sub>A</sub> + 5.0

 $<sup>^{\</sup>overline{a}}$  Reference 2.  $^{\overline{b}}T_{\overline{A}}$  is the average annual ambient temperature in degrees Fahrenheit.

TABLE 2-3. PAINT FACTORS FOR FIXED ROOF TANKS<sup>a</sup>

		Paint fa	ctors (F <sub>p</sub> )	
Tank	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	1.46	1.58b	

aReference 3.
bEstimated from the ratios of the seven preceding paint factors.

API publication 2518 appear to be more accurate for materials with low vapor pressures.

Equations for calculating losses from fixed roof tanks are provided in Table 2-1. These equations are from AP-42, but have been modified slightly to compute compound specific emissions when the HAP is part of a mixture. The equations from AP-42 have simply been multiplied by  $M_{\rm V_i}P_i/M_{\rm V}P$ , where  $M_{\rm V_i}$  is the molecular weight of the HAP,  $P_i$  is the partial pressure of the specific HAP,  $M_{\rm V}$  is the molecular weight of the mixture stored in the tank, and P is the vapor pressure of the stored mixture. The equations presented in Table 2-1 represent the product of this calculation, after the cancellation of like terms.

In cases where the HAP is part of a mixture, the vapor pressure of the material stored must be: (1) measured; or (2) calculated by summing the partial pressures of constituents. Raoult's Law and/or Henry's Law, as applicable, are recommended for calculating the partial pressure of constituents in a mixture.

The equations presented in Table 2-1 can be used to establish emissions from horizontal tanks by calculating an effective diameter for substitution in the breathing loss equation as follows:

$$D_{e} = \sqrt{LD/0.785}$$

where:

 $D_e$  = effective tank diameter (ft);

L = length of tank (ft); and

D = actual diameter of tank (ft).

For horizontal tanks, half of the diameter should be used as the average vapor space height.

For underground tanks, assume that no breathing losses occur because the insulating nature of the earth limits the diurnal

temperature change. No modification to the working loss equation is necessary for either above-ground or underground horizontal tanks.

# 2.2.2 <u>Acceptable Techniques For Establishing HAP</u> <u>Emissions From Floating Roof Storage Tanks</u>

The preferred technique for establishing HAP emissions from floating roof storage tanks are the computation techniques presented in Tables 2-4 and 2-5. These equations are essentially the techniques prescribed in AP-42, with two additions. First the equations have been modified slightly to compute compound specific emissions when the HAP is part of a mixture. The equations from AP-42 have been multiplied by  $M_{\rm V_1}P_{\rm i}/M_{\rm V}P$  to yield emissions of a specific HAP. Secondly, fitting loss calculations for external floating roofs have been added to the procedure. This additional component of the external floating roof calculations was obtained from a study recently completed by the American Petroleum Institute, Evaporative Loss From External Floating-Roof Tanks (API Publication 2517).

The equations provided in this section are applicable only to freely vented internal floating roof tanks and 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); 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. 6

Some notes and guidance for obtaining the less obvious inputs are provided in the following paragraphs.

Welded roofs. Floating roof tank emissions are the sum of rim seal, withdrawal, deck fitting, and deck seam losses. However, it should be noted that external floating roof tanks and welded internal floating roofs do not have deck seam losses. There are no procedures in AP-42 for estimating emissions from

$$L_T = L_W + L_R + L_F + L_D$$

#### where:

 $L_T$  = total loss of HAP (Mg/yr)

 $L_W$  = withdrawal loss (Mg/yr)

$$= \frac{(0.943) \ O \ C \ W}{(2205) \ D} L \ [1 + (\frac{{}^{N}C \ C}{D})] \ \frac{{}^{M}V \ P}{\underline{i} \ \underline{i}}$$

$$L_R = rim seal loss (Mg/yr) = (K_RD) P^* M_{V_i} K_C \frac{P_i}{2205 P}$$

$$L_F$$
 = fitting loss (Mg/yr) = (F<sub>F</sub>) P\* M<sub>Vi</sub> K<sub>C</sub>  $\frac{P_i}{2205 P}$ 

$$L_D = \text{deck seam loss } (Mg/yr) = (S_D K_D D^2) P^* M_{V_i} K_C \frac{P_i}{2205 P}$$

#### where:

D = tank diameter (ft)

Q = product average throughput (bbl/yr)

C = product withdrawal shell clingage factor (bbl/10<sup>3</sup> ft<sup>2</sup>), see Table 2-9

 $W_{I.}$  = density of the product (lb/gal)

 $N_C$  = number of columns (dimensionless)

 $F_C$  = effective column diameter (ft)

 $K_R$  = rim seal loss factor (lb mole/ft yr) that for an average fitting seal is as follows:

TABLE 2-4. EQUATIONS FOR ESTIMATING INTERNAL FLOATING ROOF STORAGE TANK EMISSIONS (CONTINUED)

Kp (lb mole/ft yr)

Dear System acouragement	VK-142 WOIGHTO III
Vapor-mounted primary seal only Liquid-mounted primary seal only	6.7 3.0
Vapor-mounted primary seal plus secondary seal Liquid-mounted primary seal plus	2.5
secondary seal	1.6
P* = the vapor pressure function	n (dimensionless)
$= (P/P_A)/((1 + (1 - (P/P_A))^{0.5})$	<sup>5</sup> ) <sup>2</sup> )
P = true vapor pressure of the	material stored (psia)
$P_i$ = partial pressure of the HAI	P (psia)
$P_{A}$ = atmospheric pressure (psia)	)
$M_V$ = the average molecular weight material vapor (lb/lb mole)	
$M_{V_{\dot{1}}}$ = molecular weight of the HAN	P (lb/lb-mole)
$K_C$ = the product factor (dimens:	ionless) = 1.0 for VOL
2205 = constant (lb/Mg)	

 $F_F$  = the total deck fitting loss factor (lb mole/yr)

$$= \sum_{i=1}^{n} (N_{F_{i}} K_{F_{i}}) = [(N_{F_{1}} K_{F_{1}}) + (N_{F_{2}} K_{F_{2}}) + ... + (N_{F_{n}} K_{F_{n}})]$$

where:

Seal system descriptionb

 $N_{F_i}$  = number of fittings of a particular type (dimensionless).  $N_{F_i}$  is determined for the specific tank or estimated from Tables 2-6 and 2-10.

- $K_{F_i}$  = deck fitting loss factor for a particular type fitting (lb mole/yr).  $K_{F_i}$  is determined for each fitting type from Table 2-10.
  - n = number of different types of fittings
     (dimensionless)
- $S_D$  = the deck seam length factor (ft/ft<sup>2</sup>); see Table 2-7
- KD = the deck seam loss factor (lb mole/ft yr)
  - = 0 for welded decks
  - = 0.34 for non-welded roofs

aReferences 2 and 3.

bseal emission factors are not available for mechanical shoe seals used in interval floating roof tanks. In the absence of these factors, the factors for liquid mounted seals may be used to estimate the emissions from an interval floating roof tank equipped with a mechanical shoe seal.

# TABLE 2-5. EQUATIONS FOR ESTIMATING EXTERNAL FLOATING ROOF STORAGE TANK EMISSIONS<sup>a</sup>

$$L_T = L_W + L_{SE} + L_{RF}$$

$$L_{W} = 4.28 \times 10^{-4} \underbrace{\text{OCW}_{L}}_{D} \underbrace{\frac{\text{M}_{V_{i}} \text{P}_{i}}{\text{M}_{V_{i}} \text{P}}}$$

$$L_{SE} = K_S V^N P^* DM_{V_i} K_C \frac{P_i}{2205 P}$$

$$L_{RF} = F_F P^* M_{V_i} K_C \frac{P_i}{2205 P}$$

where,

 $L_{T}$  = total loss (Mg/yr)

 $L_W$  = withdrawal loss (Mg/yr)

 $L_{RF}$  = roof fitting loss (Mg/yr)

Q = product average throughput (bbl/yr); tank
 capacity (bbl/turnover) x turnovers/yr

C = product withdrawal shell clingage factor (bbl/10<sup>3</sup> ft<sup>2</sup>); see Table 2-9

 $W_L$  = density of product (lb/gal); 7.4 to 8.0 lb/gal assumed as typical range for VOL liquids

D = tank diameter (ft)

 $K_S$  = seal factor: obtain from Table 2-8

V = average windspeed for the tank site (mph); 10 mph can be assumed as the average windspeed, if sitespecific data are not available

N = seal windspeed exponent (dimensionless): obtain from Table 2-8 P\* = the vapor pressure function (dimensionless)

 $= (P/P_A)/((1 + (1 - (P/P_A)^{0.5})^2)$ 

P = true vapor pressure of the material stored (psia)

 $P_i$  = partial pressure of the HAP (psia)

P<sub>A</sub> = atmospheric pressure (psia)

 $M_V$  = the average molecular weight of the stored material vapor (lb/lb mole)

 $MV_i$  = molecular weight of the HAP (lb/lb-mole)

 $K_C$  = product factor (dimensionless) = 1.0 for VOL

 $F_F$  = total roof fitting loss factor, lb-mol/yr

$$= \sum_{i=1}^{n} (N_{F_i} K_{F_i}) = [(N_{F_1} K_{F_1}) + (N_{F_2} K_{F_2}) + ... + (N_{F_n} K_{F_n})]$$

where:

 $N_{F_{\dot{1}}}$  = number of fittings of a particular type (see Table 2-11

 $K_{F_i}$  = deck fitting loss factor for a particular type fitting (lb mole/yr).  $K_{F_i}$  is determined for each fitting type from Table 2-11 using the equation:  $K_{F_i} = K_{F_a} + K_{F_b}$ 

n = number of different types of fittings
 (dimensionless)

aReferences 2, 3, and 5.

external floating roof tank deck fittings. However, the newly developed API procedures do include factors for deck fittings.

Number of columns. For a self-supporting fixed roof or external floating roof, no columns are used. If the number of columns is not known, Table 2-6 gives a typical number of columns based on tank diameter.

<u>Deck seam length</u>. For internal floating roof tanks with bolted decks, the deck seam length factor  $(S_D)$  may be approximated if the total length of deck seams is unknown. The factors are presented in Table 2-7. If no specific information is available, an  $S_D$  of 0.20 ft/ft<sup>2</sup> can be assumed.

Rim seal losses. For the rim seal loss, the seal factors and seal related wind speed exponents are listed in Table 2-8.

<u>Clingage factors</u>. For withdrawal loss, the shell clingage factors are presented in Table 2-9. If no shell condition information is available, the light rust condition may be assumed.

Fitting loss factors. Once the number and type of deck fittings are known for an internal floating roof tank, Table 2-10 can be used to obtain individual deck fitting loss factors. For external floating roof tanks, fitting loss factors and the typical number of roof fittings are provided in Tables 2-11, 2-12, and 2-13.

<u>Mixtures</u>. In cases where the HAP is part of a mixture, the vapor pressure of the material stored must be: (1) measured; or (2) calculated by summing the partial pressures of constituents. As stated earlier, Raoult's Law and/or Henry's Law, as applicable, are recommended for computing the partial pressure of constituents in a mixture.

#### 2.2.3 Documentation of HAP Emissions From Storage Tanks

All storage tank characteristics, tank throughput data, and HAP physical property data used to perform storage tank emission calculations should be provided for each tank. A set of forms listing the required computation inputs is provided in

TABLE 2-6. 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 7
100 < D ≤ 120	7
120 < D ≤ 135 135 < D ≤ 150	8 9
133 ( D 2 130	9
$150 < D \le 170$	16
$170 < D \le 190$	19
$190 < D \le 220$	22
220 < D ≤ 235 235 < D ≤ 270	31
235 < D ≤ 270	37
270 < D ≤ 275	43
275 < D ≤ 290	49
$290 < D \le 330$	61
330 < D ≤ 360 360 < D ≤ 400	71

aReference 2. 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 perogatives. Data in this table should not supersede information on actual tanks.

TABLE 2-7. DECK SEAM LENGTH FACTORS (SD) FOR TYPICAL DECK CONSTRUCTIONS FOR INTERNAL FLOATING ROOF TANKS<sup>a</sup>

Deck Construction	Typical deck seam length factor, S <sub>D</sub> (ft/ft <sup>2</sup> )
ontinuous sheet construction <sup>b</sup>	
5 ft wide	0.20 <sup>C</sup>
6 ft wide	0.17
7 ft wide	0.14
Panel constructiond	
5 x 7.5 ft rectangular	0.33

aReference 2. Deck seam loss applies to bolted decks only.

 $<sup>{}^{</sup>b}S_{D} = \frac{1}{w}$  , where W = sheet width (ft)

<sup>&</sup>lt;sup>C</sup>If no specific information is available, these factors can be assumed to represent the most common bolted decks currently in use.

 $ds_D = \frac{(L+W)}{LW}$ , where W = panel width (ft) and L = panel length (ft)

TABLE 2-8. SEAL RELATED FACTORS FOR EXTERNAL FLOATING ROOF TANKSab

Tank and seal type	<u>Welded</u> K <sub>S</sub>	Tank N	Riveted K <sub>S</sub>	<u>Tank</u> N
Metallic shoe seal Primary seal only With shoe mounted secondary seal With rim mounted secondary seal	1.2 0.8 0.2	1.2	1.3 1.4 0.2	
Liquid mounted resilient seal Primary seal only With weather shield With rim mounted secondary seal		1.0 0.9 0.4	NA <sup>C</sup> NA NA	NA NA NA
Vapor mounted resilient seal Primary seal only With weather shield With rim mounted secondary seal	1.2 0.9 0.2			NA NA NA

 $<sup>\</sup>overline{^a}$ 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  $K_S$  decreases in cases where the actual gaps exceed the gaps assumed during development of the correlation.

bReference 3.

<sup>&</sup>lt;sup>C</sup>NA = Not Applicable.

TABLE 2-9. AVERAGE CLINGAGE FACTORS (C) (bbl/1,000 ft<sup>2</sup>)<sup>a</sup>

		Shell conditi	on
Liquid	Light rust <sup>b</sup>	Dense rust	Gunite 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

aReference 2.
bIf no specific information is available, these values can be assumed to represent the most common condition of tanks currently in use.

TABLE 2-10. SUMMARY OF INTERNAL FLOATING DECK FITTING LOSS FACTORS (K<sub>F</sub>) AND TYPICAL NUMBER OF FITTINGS (N<sub>F</sub>) a

Deck fitting type	Deck fitting Typical number $K_F$ of fitting $K_F$ (lb-mole/yr) $K_F$	
Access hatch	1	
Bolted cover, gasketed	1.6	
Unbolted cover, gasketed	11,	
Unbolted cover, ungasketed	25 <sup>b</sup>	
Automatic gauge float well	1	
Bolted cover, gasketed	5.1	
Unbolted cover, gasketed	15	
Unbolted cover, ungasketed	28b	
Column well	(see Table 2-	-5)
Builtup column-sliding cover, ga	isketed 33	•,
Builtup column-sliding cover, ungasketed	47b	
Pipe column-flexible fabric sleev	ve seal 10	
Pipe column-sliding cover, gaske	eted 19	
Pipe column-sliding cover, ungas	sketed 32	
Ladder well	1	
Sliding cover, gasketed	56	
Sliding cover, ungasketed	76b	
Roof leg or hanger well Adjustable	$7.9b   (5 + \frac{D}{10} + \frac{D^2}{600})$	2) C
Fixed	0	
Sample pipe or well	1	
Slotted pipe, sliding cover, gas	keted 44	
Slotted pipe, sliding cover, unga		
Sample well, slit fabric seal, 10 percent open area	12 <sup>b</sup>	
Stub drain, 1 inch diameter <sup>d</sup>	1.2 $\left(\frac{D^2}{}\right)^{c}$	
	125	
Vacuum breaker	, 1	
Weighted mechanical actuation, gasketed	0.7b	
Weighted mechanical actuation, ungasketed	0.9	

aReference 2. bIf no specific information is available, this value can be assumed to represent the most common/typical deck fittings currently used.

TABLE 2-10. SUMMARY OF INTERNAL FLOATING DECK FITTING LOSS FACTORS ( $K_F$ ) AND TYPICAL NUMBER OF FITTINGS ( $N_F$ ) a (CONCLUDED)

CD = tank diameter (ft).

dNot used on welded contact internal floating decks.

TABLE 2-11. EXTERNAL ROOF FITTING LOSS FACTORS (K  $_{\rm fa}$  , K  $_{\rm fb}$  ) AND TYPICAL NUMBER OF ROOF FITTINGS (N  $_{\rm F}$  )  $^{\rm a}$ 

		Roof fitting loss factors			
		K <sub>fa</sub> lb-mole	Kfb lb-mole		
Roof fitting type and construction details		yr	(ml/h) <sup>n</sup> yr	m (dimensionless)	Typical No. of fittings, N <sub>F</sub>
	Access hatch (24-inch diameter well)				1
	a. Bolted cover, gasketed	0	0	0 <sub>p</sub>	•
	b. Unbolted cover, ungasketed	2.7	7.1	1.0	
	c. Unbolted cover, gasketed	2.9	0.41	1.0	
2.	Guide pole well (8-inch diameter unslotted pole, 21-inch diameter well)				1
	a. Ungasketed sliding cover, without float	0	67	0.98 <sup>b</sup>	
	b. Gasketed sliding cover	0	3.0	1.4	
i.	Guide pole/sample well (8-inch diameter slotted pole, 21-inch diameter well)				С
	a. Ungasketed sliding cover, without float	0	310	1.2	
	b. Ungasketed sliding cover, with float	0	29	2.0	
	c. Gasketed sliding cover, without float	0	260	1.2	
	d. Gasketed sliding cover, with float	0	8.5	2.4	
	Gauge float well (20-inch diameter well)				1
	a. Unbolted cover, ungasketed	2.3	5.9	1.0 <sup>b</sup>	•
	b. Unbolted cover, gasketed	2.4	0.34	1.0	
	c. Bolted cover, gasketed	0	0	0	
	Gauge hatch/sample well (8-inch diameter well)				1
	a. Weighted mechanical actuation, gasketed	0.95	0.14	1.0 <sup>b</sup>	•
	b. Weighted mechanical actuation, ungasketed	0.91	2.4	1.0	
	Vacuum breaker (10-inch diameter well)				See Table 2-12
	a. Weighted mechanical actuation, gasketed	1.2	0.17	1.0 <sup>b</sup>	300 Table E 12
	b. Weighted mechanical actuation, ungasketed	1.1	3.0	1.0	
	Roof drain (3-inch diameter)				See Table 2-12
	a. Open	0	7.0	1.4 <sup>e</sup>	366 18016 5-15
	b. Closed, 90 percent	0.51	0.81	1.0 <sup>e</sup>	

TABLE 2-11. EXTERNAL ROOF FITTING LOSS FACTORS ( $K_{fa}$ ,  $K_{fb}$ ) AND TYPICAL NUMBER OF ROOF FITTINGS ( $N_F$ ) a (CONCLUDED)

		<del></del>			
Roof fitting type and construction details		tb-mole (	lb-mole ( <del></del> ) [ml/h] <sup>n</sup> yr	m (dimensionless)	Typical No. of fittings, N <sub>F</sub>
8.	<ul><li>a. Adjustable, pontoon area</li><li>b. Adjustable, center area</li></ul>	1.5 0.25	0.20 0.067	1.0 <sup>b</sup>	See Table 2-13
	c. Adjustable, double-deck roofs D. Fixed	0.25 0	0.067 0	1.0 0	
	Roof leg (2 1/2 inch diameter leg)				
	e. Adjustable, pontoon area f. Adjustable, center area g. Adjustable, double-deck roofs h. Fixed	1.7 0.41 0.41 0	0 0 0 0	0 0 0 0	See Table 2-13
۶.	Rim vent (6-inch diameter)  a. Weighted mechanical actuation, gasketed  b. Weighted mechanical actuation, ungasketed	0.71 0.68	0.10 1.8	1.0 <sup>b</sup> 1.0	1.0 <sup>d</sup>

<sup>&</sup>lt;sup>a</sup>The roof fitting loss factors (K<sub>fa</sub>, K<sub>fb</sub>, m) may be used only for wind speeds from 2 to 15 ml/h.

blf no specific information is available, this value can be assumed to represent the most common or typical roof fittings currently in use.

<sup>&</sup>lt;sup>C</sup>Guide pole/sample well is an optional fitting not typically used.

dRim vents are used only with mechanical shoe primary seals.

eRoof drains that drain excess rainwater into the product are not used on pontoon floating roofs. They are, however, used on double-deck floating roofs and are typically left "open."

TANK 2-12. TYPICAL NUMBER OF VACUUM BREAKERS AND ROOF DRAINS,  $N_{\mathrm{F}}$ 

Tank	Number Vacuum Bre	of eakers, N <sub>F</sub>	Number of	
Diameter, D(feet) <sup>a</sup>	Pontoon Roof	Double-deck Roof	(Double-deck Roof)b	
50	1	1	1	
100	1	1	1	
150	2	2	2	
200	3	2	3	
250	4	3	5	
300	5	3	7	
350	6	4	-	
400	7	4	_	

<sup>&</sup>lt;sup>a</sup>If the actual diameter is between the diameters listed, the closet diameter listed should be used. If the actual diameter is midway between the diameters listed, the next larger diameter should be used.

bRoof drains that drain excess rainwater into the product are not used on pontoon floating roofs. They are, however, used on double-deck floating roofs and are typically left open.

TANK 2-13. TYPICAL NUMBER OF EXTERNAL FLOATING ROOF LEGSa

Tank	Pontoon	Roof	Double-deck
diameter, d(ft) <sup>b</sup>	Pontoon legs	Center legs	roof legs
30	4	2	6
40	4	4	7
50	6	6	8
60	9	7	10
70	13	9	13
80	15	10	16
90	16	12	20
100	17	16	25
110	18	20	29
120	19	24	34
130	20	28	40
140	21	33	46
150	23	38	52
160	26	42	58
170	27	49	66
180	28	56	74
190	29	62	82
200	30	69	90
210	31	77	98
220	32	83	107
230	33	92	115
240	34	101	127
250	35	109	138
260	36	118	149
270	36	128	162
280	37	138	173
290	38	148	186
300	38	156	200
310	39	168	213
320	39	179	226
330	40	190	240
340	41	202	255
350	42	213	270
360	44	226	285
370	45	238	300
380	46	252	315
390	47	266	330
400	48	281	345

aThis table was derived from a survey of users and manufacturers. The actual number of roof legs may vary greatly depending on age, floating roof style, loading specifications, and manufacturing prerogatives. This table should not supersede information based on actual tank data.

bIf the actual diameter is between the diameters listed, the closest diameter listed should be used. If the diameter is midway between the diameters listed, the next larger diameter should be used.

Appendix A. The appropriate form in Appendix A should be completed and submitted for each storage tank.

#### 2.3 EOUIPMENT LEAKS

Leaks occur from plant equipment that have a point of interface of the process fluid with the atmosphere. These points of interface such as seals, packings, and gaskets have a tendency to fail mechanically and thereby leak process fluid. The major sources of equipment leaks include pumps, valves, flanges and other connectors, compressors, sampling connection systems, openended lines, agitators, and pressure relief valves. Detailed discussions of these emission sources are presented in two EPA reports. 7,8 A brief discussion of these sources is presented below.

<u>Pumps</u>. Pumps are used extensively in process units for the movement of organic liquids. The centrifugal pump is the most widely used pump. However, other types, such as the positive-displacement, reciprocating and rotary action, and special canned and diaphragm pumps, are also used. Chemicals transferred by pumps can leak at the point of contact between the moving shaft and stationary casing. Consequently, all pumps except the shaftless type (canned-motor and diaphragm) require a seal at the point where the shaft penetrates the housing in order to isolate the pump's interior from the atmosphere.

Two generic types of seals, packed and mechanical, are currently in use. Packed seals can be used on both reciprocating and rotary action types of pumps. A packed seal consists of a cavity ("stuffing box") in the pump casing filled with special packing material that is compressed with a packing gland to form a seal around the shaft, Deterioration of the packing results in process liquid leaks.

Mechanical seals are limited in application to pumps with rotating shafts and can be further categorized as single and double mechanical seals. Depending on the condition and flatness

of the seal faces, the leakage rate from a mechanical seal can be quite low (as small as a drop per minute) and the flow is often not visually detectable. In order to minimize emissions due to seal leakage, an auxiliary sealing device such as packing can be employed.

<u>Valves</u>. The types of valves commonly used in organic chemical plants are globe, gate, plug, ball, relief, and check valves. All except the relief valve (to be discussed further below) and check valve are activated by a valve stem, which may have either a rotational or linear motion, depending on the specific design. This stem requires a seal to isolate the process fluid inside the valve from the atmosphere. The possibility of a leak through this seal makes it a potential source of emissions. Since a check valve has no stem or subsequent packing gland, it is not considered to be a potential source of emissions.

Compressors. Gas compressors used in process units are similar to pumps in that they can be driven by rotary or reciprocating shafts. They are also similar to pumps in their need for shaft seals to isolate the process gas from the atmosphere. As with pumps, these seals are likely to be the source of emissions from compressors.

Shaft seals for compressors may be chosen from several different types: labyrinth, restrictive carbon rings, mechanical contact, and liquid film. All of these seal types are leak restriction devices; none of them completely eliminate leakage. Many compressors may be equipped with ports in the seal area to evacuate gases collecting there.

Safety Relief Devices. Engineering codes require that pressure-relieving devices or systems be used in applications where the process pressure may exceed the maximum allowable working pressure of the vessel. The most common type of pressure-relieving device used in process units is the pressure relief valve. Typically, safety relief valves are spring-loaded and designed to open when the process pressure exceeds a set

pressure, allowing the release of vapors or liquids until the system pressure is reduced to its normal operating level. When the normal pressure is reattained, the valve reseats, and a seal is again formed. The seal is a disk on a seat, and the possibility of a leak through this seal makes the pressure relief valve a potential source of emissions. Two potential causes of leakage from safety relief valves are: "simmering or popping," a condition due to the system pressure being close to the set pressure of the valve, and improper reseating of the valve after a relieving operation.

Open-Ended Lines. Some valves are installed in a system so that they function with the downstream line open to the atmosphere. Examples are purge valves, drain valves, and vent valves. A faulty valve seat or incompletely closed valve would result in leakage through the valve and emissions to the atmosphere.

<u>Sampling Connections</u>. The operation of a process unit is checked periodically by routing analyses of feedstocks and products. To obtain representative samples for these analyses, sampling lines must first be purged prior to sampling. The purged liquid or vapor is sometimes drained onto the ground or into a sewer drain, where it can evaporate and release emissions to the atmosphere.

<u>Flanges</u>. Flanges are bolted, gasket-sealed junctions used wherever pipe or other equipment such as vessels, pumps, valves, and heat exchangers may require isolation or removal. Normally, flanges are employed for pipe diameters of 50 mm or greater and are classified by pressure and face type.

Flanges may become emission sources when leakage occurs due to improperly chosen gaskets or a poorly assembled flange. The primary cause of flange leakage is due to thermal stress that piping or flanges in some services undergo; this results in the deformation of the seal between the flange faces.

Agitators. Agitators are technologically similar to pumps and, like pumps, can be controlled using seal technology.

Although agitators have longer and larger diameter shafts than pumps and produce greater tangential shaft loadings, the emission factors used for calculating leaks from pumps are currently acceptable for use in calculating leaks from agitators, due to the lack of emissions data for agitators.

# 2.3.1 <u>Acceptable Techniques For Establishing HAP</u> <u>Emissions From Equipment Leaks</u>

There are five methods for establishing emissions from equipment leaks. These methods, in increasing order of complexity and accuracy, are:

- Average emission factor method;
- Leak/no-leak emission factor method;
- Three-strata emission factor method;
- Application of EPA correlations; and
- Development of new correlations.

A detailed discussion of the above methods is presented in the EPA report Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP. Alternatively, these methods are presented in a Chemical Manufacturers Association entitled Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment. All methods start with obtaining an accurate identification and count of equipment to be included. The equipment counts can simply be used with the EPA's previously developed emission factors. The next step in complexity and refinement is the use of a portable organic analyzer to find the number of leaking and nonleaking sources. Leaking and nonleaking emission factors developed by the EPA can then be applied to generate the emissions. These factors are presented in Table 2-14.

A final refinement is a method employing discrete emission factors. In this approach emission factors are applied to represent three different ranges of screening values. This has

TABLE 2-14. LEAKING AND NON-LEAKING EMISSION FACTORS FOR FUGITIVE EMISSIONS (kg/yr/source) a

	(>	Leaking 10,000 ppmv)	
Equipment	Service Em	ission Factor	Emission Factor
Valves	Gas/Vapor <sup>b</sup> Light liquid	0.0451 0.0852	0.00048 0.00171
	Heavy liquid	0.00023 <sup>C</sup>	0.00023
Pump Seals	Light liquid Heavy liquid		0.0120 0.0135
Compressor Sealsd	Gas/Vapor	1.608	0.0894
Pressure Relief Valves	Gas/Vapor	1.691	0.0447
Flanges	All	0.0375	0.00006
Open-Ended Lines	All	0.01195	0.00150

aReference 8.

bThe leaking and non-leaking emission factors for valves in gas/vapor service are based upon the emission factors determined for gas valves in ethylene, cumene, and vinyl acetate units during the SOCMI Maintenance Study.

CLeaking emission factor assumed equal to non-leaking emission factor since the computed leaking emission factor (0.00005 kg/hr/source) was less than the non-leaking emission factor.

dEmission factor reflects existing control level of 60 percent found in the industry; control is through the use of barrier fluid/degassing reservoir/vent-to-flare or other seal leakage capture system.

been called the stratified emission factor approach, or the three-strata approach. Applying the stratified emission factors requires more rigorous measurement of organic vapor concentrations with a portable instrument because actual concentration readings must be recorded instead of noting whether a piece of equipment is classified as leaking or not leaking. Stratified emission factors developed by the EPA can then be applied to generate the emission estimate. These factors are presented in Table 2-15.

The remaining two methods make use of correlations relating mass emissions to organic concentrations measured with a portable organic analyzer. The EPA's previously developed correlations are offered for use, and finally, if a process unit's emissions are statistically different from those represented by the EPA's correlations, provision is made for development of correlations specifically for that process unit.

The EPA will not accept the average emission factor approach for establishing base year emissions from equipment leaks, unless the EPA average emission factors for equipment leaks are also used to establish post-reduction emissions, and no reductions in equipment leak emissions are claimed as part of the reduction demonstration. The average emission factors are based on data from process units with a wide range of equipment leak frequencies. A given process unit may not have leak frequencies similar to the average leak frequencies of these process units. The application of these factors could, therefore, result in erroneous emission estimates.

The other four emission estimate methods are considered acceptable for the purpose of establishing emissions. The most accurate estimates are obviously made through development of new correlations. However, requiring the use of this method can be costly and may discourage many facilities from pursuing the early emission reduction program.

The leak/no-leak emission factor method, while a significant improvement over the average emission factor method, may yield

TABLE 2-15. STRATIFIED EMISSION FACTORS FOR EQUIPMENT LEAKSa (kg/hr/source)

		Emission Factors (kg/yr/source) for Screening Value Range, ppmv		
Source	Service	0-1,000	1,001-10,000	>10,000
Compressor Seals <sup>d</sup>	Gas/vapor	0.01132	0.264	1.608
Pump seals	Light liquid Heavy liquid	0.00198 0.00380	0.0335 0.0926	0.437 0.3885
Valves	Gas/vapor <sup>b</sup> Light liquid Heavy liquid	0.00014 0.00028 0.00023 <sup>C</sup>	0.00165 0.00963 0.00023 <sup>C</sup>	0.0451 0.0852 0.00023
Flanges, connections	All	0.00002	0.00875	0.0375
Pressure Relief devices	Gas/vapor	0.0114	0.279	1.691
Open-ended Lines	A11	0.00013	0.00876	0.01195

aReference 8.

bThe leaking and non-leaking emission factors for valves in gas/vapor service are based upon the emission factors determined for gas valves in ethylene, cumene, and vinyl acetate units during the SOCMI Maintenance Study.

CLeaking emission factor assumed equal to non-leaking emission factor since the computed leaking emission factor (0.00005 kg/hr/source) was less than the non-leaking emission factor.

dEmission factor reflects existing control level of 60 percent found in the industry; control is through the use of barrier fluid/degassing reservoir/vent-to-flare or other seal leakage capture system.

estimates that are not completely accurate. However, these estimates are considered to be within reasonable ranges of accuracy. In addition, many facilities are expected to have leak/no-leak frequency data already available which may encourage them to implement an early emission reduction program.

Regardless of the method selected to establish base year emissions, the same method must be used to establish post-reduction emissions. The EPA will not allow participants to demonstrate reductions by changing methodology.

# 2.3.2 <u>Documentation of HAP Emissions From Equipment Leaks</u>

The documentation requirements discussed in this section relate to the leak/no leak emission factor method. If a facility chooses to use one of the more refined methods, the documentation requirements will be considered on a case by case basis.

For the leak/no leak or stratified method, the following information should be provided along with the computed emissions:

- Equipment count by equipment type (i.e., vapor valves, liquid valves, etc.),
- Period during which screening was conducted,
- A description of any deviations from EPA Method 21 procedures,
- Percent of sources found leaking (by source type) or measured concentration,
- HAP content as percent of VOC,
- Number of sources in facility that were considered difficult to monitor and not screened.

Forms for reporting this information and computing baseline emissions are provided in Appendix A for both the leak/no leak approach and the stratified emission factor approach.

### 2.4 TRANSFER OPERATIONS

Loading losses are the primary source of evaporative emissions from rail tank car, tank truck and marine vessel transfer operations. Loading losses occur as organic vapors in "empty" cargo tanks are displaced to the atmosphere by the liquid being loaded into the tanks. These vapors are a composite of (1) vapors formed in the empty tank by evaporation of residual product from previous loads, (2) vapors transferred to the tank in vapor balance systems as product is being unloaded, and (3) vapors generated in the tank as the new product is being loaded. The quantity of evaporative losses from loading operations is, therefore, a function of the following parameters.

- Physical and chemical characteristics of the previous cargo,
- Method of unloading the previous cargo,
- Method of loading the new cargo, and
- Physical and chemical characteristics of the new cargo.

The three principal loading methods are splash loading, submerged loading, and vapor balance loading. In the splash loading method, the fill pipe dispensing the cargo is lowered only partway into the cargo tank. Significant turbulence and vapor/liquid contact occur during the splash loading operation, resulting in high levels of vapor generation and loss. If the turbulence is great enough, liquid droplets will be entrained in the vented vapors.

A second method of loading is submerged loading. Two types are the submerged fill pipe method and the bottom loading method. In the submerged fill pipe method, the fill pipe extends almost to the bottom of the cargo tank. In the bottom loading method, a permanent fill pipe is attached to the cargo tank bottom. The fill pipe opening is below the liquid surface level, during most of the loading operation. Liquid turbulence is controlled

significantly, resulting in much lower vapor generation than encountered during splash loading.

The recent loading history of a cargo carrier is just as important a factor in loading losses as the method of loading. If the carrier has carried a nonvolatile liquid such as fuel oil, or has just been cleaned, it will contain vapor free air. If it has just carried a volatile HAP and has not been vented, the air in the carrier tank will contain volatile organic vapors, which are expelled during the loading operation along with newly generated vapors.

Cargo carriers are sometimes designated to transport only one product, and in such cases are practicing "dedicated service". Dedicated cargo tanks return to a loading terminal containing air fully or partially saturated with vapor from the previous load. Cargo tanks may also be "switch loaded" with various products, so that a nonvolatile product being loaded may expel the vapors remaining from a previous load of a volatile product. These circumstances vary with the type of cargo tank and with the ownership of the carrier, the petroleum liquids being transported, geographic location, and season of the year.

One control measure for tank truck loading is called "vapor balance service", in which the cargo tank retrieves the vapors displaced during product unloading, and transports the vapors back to the loading terminal. A cargo tank in vapor balance service normally is saturated with organic vapors, and the presence of these vapors at the start of submerged loading results in greater loading losses than encountered during nonvapor balance, or "normal", service. Vapor balance service is usually not practiced with marine vessels, although some vessels practice emission control by means of vapor transfer within their own cargo tanks during balancing operations.

# 2.4.1 <u>Acceptable Techniques for Establishing Emissions from Transfer Operations</u>

Emissions of each HAP can be established using the following expression for each type of loading operation:<sup>2</sup>

$$L_{L} = 5.65E-06 \frac{SPMG}{T}$$

where:  $L_{I_i} = loading loss, Mg/yr,$ 

M = molecular weight of the HAP, lb/lb-mole

P = true vapor pressure of the HAP loaded, psia

G = annual volume of liquid loaded, gallons,

 $T = temperature of bulk liquid loaded, {}^{O}R ({}^{O}F + 460),$ 

S = saturation factor (see Table 2-16)

5.65E-06= constant to yield Mg/yr based on  $12.46(10^{-3} \text{ gal}) (\text{Mg}/2205 \text{ lb})$ 

The saturation factor, S, represents the expelled vapor's fractional approach to saturation, and it accounts for the variations observed in emission rates from the different unloading and loading methods. Table 2-16 lists the saturation factors for various cargo vessels and modes of operation.

When a specific HAP is loaded into a cargo tank that was previously used for a non-HAP, the clean cargo tank factor should be used.

In cases where the HAP is part of a mixture rather than a pure component, the partial pressure of the HAP should be used in place of the pure component vapor pressure. For mixtures where the HAP concentration is greater than 1 percent by volume, Raoult's Law is deemed appropriate for computing the partial pressure. For mixtures where the HAP concentration is less than 1 percent, Henry's Law is deemed appropriate for computing the partial pressure.

Total HAP emissions from loading are computed by summing the loading losses of individual HAP from each material loaded via

TABLE 2-16. SATURATION (S) FACTORS FOR CALCULATING ORGANIC LIQUID LOADING LOSSES<sup>a</sup>

Cargo Carrier	Mode of Operation	S Factor
Tank trucks and rail tank cars	Submerged loading of a clean cargo tank	0.50
	Submerged loading: dedicated normal service	0.60
	Submerged loading: dedicated vapor balance service	1.00
	Splash loading of a clean cargo tank	1.45
	Splash loading: dedicated normal service	1.45
	Splash loading: dedicated vapor balance service	1.00
Marine vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

aReference 2.

each loading method. In cases where numerous materials are loaded during the year by various loading techniques (i.e., submerged fill, splash fill, vapor balance), it is important that the HAP emissions are calculated separately for each set of conditions and then summed.

### 2.4.2 <u>Documentation of HAP Emissions From Loading</u> Operations

Loading operation characteristics, volumes loaded into each vessel type, and the HAP physical property data used to perform loading operation emission calculations should be provided for each material/vessel type. A set of forms listing the required computation inputs is provided in Appendix A. The form provided in Appendix A should be completed and submitted for each combination of material loaded, cargo carrier, and mode of operation.

#### 2.5 WASTEWATER COLLECTION AND TREATMENT

In the manufacture of chemical products, wastewater streams are generated which contain volatile organics. These wastewaters are collected and treated in a variety of ways. Some of these collection and treatment steps result in the emission of volatile organics from the wastewater into the ambient air. This subsection provides a discussion of the potential sources of emissions during wastewater collection and treatment, and techniques for establishing air emissions from wastewater sources.

The industries covered by the Hazardous Organic NESHAP differ in structure and manufacture a wide variety of products. However, many of the chemical processes employed within these industries use similar organic compounds as raw materials, solvents, catalysts, and extractants. In addition, many of these processes also generate similar organic by-products during reaction steps. Consequently, many of the wastewater streams

generated by the targeted industries are similar in their content of organic compounds. These organic compound containing wastewater streams result from both direct contact of water with organic process streams and incidental contact of water with organic compounds from leaking equipment. These wastewater streams may be either continuous or intermittent.

Water comes in direct contact with organic compounds due to many different chemical processing steps. As a result of this contact, wastewater streams are generated which must be discharged for treatment or disposal. A few sources of process wastewater are:11

- Water used to wash impurities from organic products or reactants;
- Water used to cool or quench organic vapor streams;
- Condensed steam from jet eductor systems pulling vacuum on vessels containing organics;
- Water used as a carrier for catalysts and neutralizing agents (e.g., caustic solutions); and
- Water formed as a by-product during reaction steps.

Two additional types of direct contact wastewater are landfill leachate and water used in maintenance activities such as equipment washes and spill cleanups. These two types of wastewater are normally more variable in flow and concentration than the streams previously discussed. In addition, landfill leachate and spill cleanups may be collected for treatment differently than the wastewater streams discharged from process equipment such as scrubbers, decanters, evaporators, distillation columns, reactors, and mixing vessels.

Wastewater streams which do not come in contact with organic compounds in the process equipment are defined as "indirect-contact" wastewater. However, a potential exists for organic contamination of these wastewater types. Water streams which are contaminated as a result of leaks from heat exchangers, condensers and pumps (pump seal water) are examples of non-

contact wastewater. These indirect contact wastewaters may or may not be collected and treated in the same manner as direct contact wastewaters. Pump seal water is normally collected in area drains which tie into the process wastewater collection system. This wastewater is then combined with direct contact wastewater and transported to the wastewater treatment plant. Wastewater contaminated from condenser and heat exchanger leaks are often collected in different systems and bypass some of the treatment steps used in the treatment plant.

Wastewater streams are collected and treated in a variety of ways. Generally, wastewater passes through a series of collection and treatment units before being discharged from a facility. Table 2-17 presents a list of components that may be sources of emissions in facility collection and treatment systems. Collection and treatment systems have openings, such as at junction boxes and manholes, that allow organics to escape to the atmosphere. The magnitude of emissions depends on factors such as the physical properties of the pollutants and the collection and treatment system.

# 2.5.1 <u>Acceptable Techniques for Establishing HAP</u> <u>Emissions From Wastewater Collection and Treatment</u>

The accepted approach for establishing emissions from wastewater sources is direct measurement of the volatile organic HAP content and measurement or estimation of the wastewater flow. However, considering the expense of direct measurement and the accessibility of some wastewater streams, it may not be feasible to measure the flowrate and HAP composition of all wastewater streams. A more detailed description of the accepted approach is provided below. It should be noted that the procedure described below is based on a single-phased wastewater stream passing through a typical wastewater collection and treatment system. The facility may need to make adjustments if there is a separate organic phase. Also, facilities must adjust their wastewater emissions if they currently have treatment in place prior to the

# TABLE 2-17. EMISSION SOURCES IN WASTEWATER COLLECTION AND TREATMENT SYSTEMS<sup>a</sup>

### Wastewater Collection System:

Drains
Junction Boxes
Lift Stations
Manholes
Trenches
Sumps
Surface Impoundments

### Wastewater Treatment Units:

Weirs
Oil/Water Separators
Equalization Basins or Neutralization Basins
Clarifiers
Aeration Basins
pH Adjustment Tanks
Flocculation Tanks

aReference 11.

wastewater treatment plant such as phase separation (e.g., decanters, API separators) or steam or air strippers.

Identification of wastewater sources. The first step towards establishing emissions from wastewater sources is the identification of all wastewater streams within the process or facility. As described above, there are two general types of organic containing wastewaters: direct contact and indirect contact. In general, direct contact wastewaters account for the majority of HAP loadings in facility wastewaters.

In characterizing wastewater streams, it is important to identify the wastewater stream at the point of generation. anticipated definition for point of generation under the Hazardous Organic NESHAP is as follows. Point of waste generation means the location where the waste stream exits the process unit component or product or feed storage tank prior to handling or treatment in an operation that is not an integral part of the production process, or in the case of waste management units that generate new waste after treatment, the location where the waste stream exits the waste management unit A piece of equipment is an integral part of the unit if it is essential to the operation of the process unit; i.e., removal of the equipment would result in the process unit being shut down. For example, a stripping column is part of the process unit if it produces the principle product stream and a wastewater which is discharged to the sewer. However, an identical stripper which treats a wastewater stream and recovers residual product would not be considered an integral part of the process unit. The point of generation for measurement or sampling is defined as the point where the wastewater stream exits the process unit before it is treated or mixed with other wastewater streams, and prior to exposure to the atmosphere. point of generation for landfill leachate shall be at the pump well from which the leachate is pumped out of the landfill.

Measurement of stream flow and concentration. After identifying all facility or process wastewater streams, both

continuous and intermittent, the next step is to either directly measure the annual average flowrate or estimate the annual average flowrate based on engineering calculations such as heat and material balances. This must be done for each wastewater stream, at the point of generation. It is important that the sample be taken at a time representative of normal flow. Additionally, attempts should be made to collect a sample representative of annual average concentrations. In the case of highly variable flow and concentration, a sufficient number of samples need to be taken to characterize the wastewater stream with respect to a flow-weighted annual average.

Two methods can be used to determine wastewater flowrate. These are: 1) based on historical records; or 2) using measurements that are representative of average wastewater generation rates.

It is preferable to measure the HAP concentration of each wastewater stream using draft EPA Methods 25D with Method 18 or a procedure validated by EPA Method 301. Proposed Method 25D is a method developed specifically for quantifying the organic emission potential of a wastewater stream. Proposed Method 25D is a purge and trap method that was developed for quantification of volatile organic emission potential and employs a flame ionization detector (FID) and a halogen detector. Because proposed Method 25D yields only a single volatile organic number, Method 18 is needed on the Method 25D purge stream to quantify specific HAP concentrations. The FID/halogen detector prescribed by Method 25D is replaced with a gas chromatograph and the procedures prescribed in Method 18. It is important that the sampling and purge procedures prescribed in proposed Method 25D are followed.

Alternatively, calculations based on engineering principles or material balance data are acceptable in situations where:

(1) No applicable EPA Reference Method, EPA Conditional Method, or other source test method exists;

- (2) It is not technically or economically feasible to perform source tests;
- (3) It can be demonstrated to the satisfaction of the reviewing agency that the calculation will provide emission estimates of accuracy comparable to any applicable source test method;
- (4) The base year conditions no longer exist and cannot be reproduced and testing under the current conditions and extrapolating will not produce results more accurate than an estimate base on engineering principles or material balance; or
- (5) The emissions from one or a set of emission points in the source are small compared to total source emissions and errors in estimating emissions from such points will not have a significant effect on the accuracy of estimated total emissions from the source.

The burden of adequately demonstrating one of these reasons for not source testing is placed on the source owner or operator.

If a sampling and analytical procedure other than proposed Method 25D with Method 18 is used, it should be validated with Method 301. Such measured concentrations can be adjusted using the fraction measured ( $f_m$ ) factors provided in Table 2-18 to approximate the volatile organic (VO) concentration that would be measured by Method 25D with Method 18.

<u>Compute emissions</u>. After both the annual average flow and concentration have been determined for each wastewater stream, the HAP emissions can be computed as:

$$WE_{S_i} = 5.26E-04 \ Q \ C_{VOHAP_i} \frac{fe_i}{fm_i}$$

where,

 $WE_{S_i} = HAP \text{ emissions, Mg/yr,}$ 

Q = annual average flow rate, lpm,

fei = fraction of the HAP that would be emitted
 from the wastewater (see Table 2-18),

TABLE 2-18. COMPOUND-SPECIFIC VALUES OF  $fe_i$  and  $fm_i$ 

CAS NO	COMPOUND NAME	HENRYS LAW (atm-m^3/gmol)	FM	FE
75070	Acetaldehyde	9.50E-05	0.72	0.45
60355	Acetamide	1.33E-06	0.42	0.18
75058	Acetonitrile	5.80E-06	0.74	0.27
98862	Acetophenone	1.41E-05	0.81	0.33
53963	Acetylaminofluorine-2	1.34E-06	0.43	0.18
107028	Acrolein	5.66E-05	0.85	0.42
79061	Acrylamide	5.20E-10	0.003	0.00
79107	Acrylic acid	1.20E-05	0.45	0.32
107131	Acrylonitrile	8.80E-05	0.88	0.45
107051	Allyl chloride	3.71E-01	1.00	1.00
92671	Aminobiphenyl-4	7.30E-03	0.10	0.74
62533	Aniline	2.60E-06	0.25	0.22
92159	Anisidine-o	8.20E-04	0.03	0.60
71432	Benzene (including	5.50E-03	1.00	0.72
	benzene from gasoline	)		
92875	Benzidene	1.00E-04	0.00	0.46
98077	Benzotrichloride	2.19E-03	1.00	0.66
100447	Benzyl chloride	4.33E-04	1.00	0.55
92524	Biphenyl	1.01E-01	1.00	0.91
117817	Bis(2-ethylhexyl)			
	phthalate	3.00E-07	0.97	0.08
542881	Bis(chloromethyl)ether		0.89	0.51
75252	Bromoform	5.84E-04	0.48	0.57
106990	Butadiene-1,3	1.42E-01	1.00	0.93
105602	Caprolactam	4.55E-07	0.01	0.11
75150	Carbon disulfide	1.68E-02	1.00	0.79
56235	Carbon tetrachloride	3.00E-02	1.00	0.83
463581	Carbonyl sulfide	5.76E-05	0.55	0.42
120809	Catechol	2.33E-05	0.00	0.36
79118	Chloroacetic acid	1.11E-09	0.03	0.00
532274	Chloroacetophenone-2	2.40E-04	0.84	0.52
108907	Chlorobenzene	3.93E-03	1.00	0.70
67663	Chloroform	3.39E-03	1.00	0.69
107302	Chloromethyl methylether	8.65E-05	0.84	0.45
126998	Chloroprene (2-Chloro- 1,3-Butadiene)	- 3.35E-01	1.00	0.99
108394	Cresols/Cresylic acid (isomers & mix), mix	2.13E-05	0.11	0.36
1319773	Cresols/Cresylic acid (isomers & mix), m-	4.43E-07	0.08	0.10

(continued)

TABLE 2-18. COMPOUND-SPECIFIC VALUES OF  $fe_i$  and  $fm_i$  (Continued)

CAS NO	COMPOUND NAME (	HENRYS LAW (atm-m^3/gmol)	FM	FE
95487	Cresols/Cresylic acid (isomers & mix),o-	2.60E-06	0.12	0.22
106445	Cresol/Cresylic acid (isomers & mix),p-	4.43E-07	0.06	0.10
98828	Cumene (isopropyl benzene)	1.46E-02	1.00	0.78
94757	D-2,4 Salts and esters	6.21E-02	0.75	0.88
3547044	DDE(Dichlorodiphenyl- dichloroethylene)	1.14E-01	1.00	0.92
334883	Diazomethane	3.40E-09	0.55	0.00
132649	Dibenzofuran	9.70E-05	1.00	0.46
96128	Dibromo-1,2- chloropropane-3	2.36E-05	1.00	0.36
84742	Dibutylphthalate	2.80E-07	0.32	0.07
106467	Dichlorobenzene(p) -1,4 (PDB)	1.60E-03	1.00	0.64
91941	Dichlorobenzidene-3,3'	1.00E-04	0.54	0.46
111444	Dichloroethyl ether (bis(2-chloroethyl) ether)	1.30E-05	0.94	0.32
542756	Dichloropropene-1,3	2.33E-03	1.00	0.66
111422	Diethanolamine	7.31E-03	0.00	0.74
121697	Diethylaniline-N,N	8.86E-05	1.00	0.45
64675	Diethyl sulfate	1.36E-07	0.01	0.03
119904	Dimethoxybenzidine-3,3	3' 2.44E-03	0.01	0.67
60117	Dimethyl aminoazobenzene	1.13E-04	0.32	0.47
119937	Dimethyl benzidine- 3,3'	4.40E-04	0.11	0.56
79447	Dimethyl carbamoyl chloride	8.33E-03	0.25	0.75
68122	Dimethyl formamide (DMF)	3.47E-09	0.01	0.00
57147	Dimethyl hydrazine-1,1	1.24E-04	0.49	0.47
131113	Dimethyl phthalate	2.15E-06	0.10	0.21
77781	Dimethyl sulfate	5.86E-07	0.08	0.12
534521	Dinitro-o-cresol-4,6, and salts	1.40E-05	0.04	0.33
51285	Dinitrophenol-2,4	1.53E-07	0.01	0.03
121142	Dinitrotoluene-2,4 (DNT)	1.25E-10	0.004	0.00

(continued)

TABLE 2-18. COMPOUND-SPECIFIC VALUES OF fei and fmi(Continued)

CAS NO	COMPOUND NAME	HENRYS LAW (atm-m^3/gmol)	FM	FE
123911	Dioxane-1,4 (1,4- Diethyleneoxide)	2.31E-05	0.68	0.36
122667 106898	Diphenylhydrazine-1,2 Epichlorohydrin(1-	3.50E-03 3.23E-05	1.00 0.86	0.69 0.38
	Chloro-2,3-epoxypropa			
106887	Epoxybutane-1,2	2.50E-01	0.88	0.97
140885	Ethyl acrylate	3.50E-04	0.79	0.54
100414	Ethyl benzene	6.44E-03	1.00	0.73
51796	Ethyl carbamate	5.86E-05	0.01	0.42
75003	Ethyl chloride (Chloroethane)	9.10E-03	1.00	0.75
106934	Ethylene dibromide (Dibromoethane) (EDB)		1.00	0.58
107062	Ethylene dichloride (1,2-Dichloroethane)		1.00	0.62
107211	Ethylene glycol	1.03E-07	0.004	0.01
75218	Ethylene oxide	1.42E-04	0.71	0.48
96457	Ethylene thiourea	1.60E-04	0.001	0.49
75343	Ethylidene dichloride (1,2-Dichloroethane)		1.00	0.00
50000	Formaldehyde	5.76E-05	0.53	0.42
112367	Diethylene glycol diethyl ether	2.13E-05	0.77	0.36
111966	Diethylene glycol dimethyl ether	2.48E-06	0.37	0.22
112345	Diethylene glycol monobutyl ether	3.30E-08	0.03	0.00
111900	Diethylene glycol monoethyl ether	3.38E-08	0.03	0.00
112152	Diethylene glycol monoethyl ether acetate	1.91E-07	0.12	0.05
111773	Diethylene glycol monomethyl ether	2.27E-08	0.02	0.00
110714	Ethylene glycol dimethyl ether	1.55E-05	0.68	0.34
111762	Ethylene glycol monobutyl ether	7.94E-07	0.29	0.14
112072	Ethylene glycol monobutyl ether acetate	1.64E-08	0.10	0.00

(Continued)

TABLE 2-18. COMPOUND-SPECIFIC VALUES OF  $fe_i$  and  $fm_i$  (Continued)

CAS NO	COMPOUND NAME	HENRYS LAW (atm-m^3/gmol)	FM	FE
CAS NO	COMPOUND NAME	(atm-m o/smo-/		
110805	Ethylene glycol	1.11E-06	0.38	0.16
	monoethyl ether			
111159	Ethylene glycol monoethyl ether acetate	1.49E-06	0.36	0.18
109864	Ethylene glycol monoethyl ether	6.90E-07	0.18	0.13
110496	Ethylene glycol monomethyl ether acetate	1.95E-06	0.37	0.20
122996	Ethylene glycol monophenyl ether	4.93E-08	0.03	0.00
2807309	Ethylene glycol monopropyl ether	2.74E-06	0.52	0.22
112492	Triethylene glycol	4.31E-07	0.16	0.00
118741	Hexachlorobenzene	6.80E-04	1.00	0.58
87683	Hexachlorobutadiene	2.56E-02	1.00	0.82
67721	Hexachloroethane	2.49E-06	1.00	0.22
822060	Hexamethylene-1,6- diisocyanate	1.00E-06	0.09	0.16
680319	Hexamethylphosphoramic	le 5.00E-05	0.00	0.41
110543	Hexane	1.22E-01	1.00	0.92
302012	Hydrazine	6.66E-07	0.57	0.13
123319	Hydroquinone	1.57E-07	0.00	0.04
78591	Isophorone	5.76E-06	1.00	0.27
108316	Maleic anhydride	4.00E-08	0.05	0.00
67561	Methanol	2.70E-06	0.32	0.22
74839	Methyl bromide (Bromomethane)	2.21E-01	0.54	0.96
74873	Methyl chloride (Chloromethane)	8.14E-03	1.00	0.75
71556	Methyl chloroform (1,1,1-Trichloroetham	3.00E-03 ne)	1.00	0.68
78933	Methyl ethyl ketone (2-Butanone)	4.35E-05	0.88	0.40
60344	Methyl hydrazine	3.44E-06	0.05	0.24
74884	Methyl iodide (Iodomethane)	2.53E-03	0.35	0.67
108101	Methyl isobutyl ketone (Hexone)	4.95E-05	0.95	0.41

(Continued)

TABLE 2-18. COMPOUND-SPECIFIC VALUES OF  $fe_i$  and  $fm_i$  (Continued)

	•	HENRYS LAW		
CAS NO	COMPOUND NAME	HENRYS LAW (atm-m^3/gmol)	FM	FE
624839	Methyl isocyanate	2.28E-05	0.27	0.36
80626	Methyl methacrylate	6.60E-05	0.80	0.43
1634044	Methyl tert butyl ether (MTBE)	5.01E-03	0.91	0.71
101144	<pre>4,4 Methylene bis (2- chloroaniline)</pre>	4.83E-03	0.15	0.71
75092	Methylene chloride (Dichloromethane)	3.19E-03	1.00	0.68
101688	Methylene diphenyl diisocyanate (MDI)	5.34E-03	0.47	0.72
101779	Methylene dianiline -4,4 (MDA)	2.60E-06	0.01	0.22
91203	Naphthalene	1.18E-03	1.00	0.62
98953	Nitrobenzene	1.31E-05	0.58	0.33
92933	Nitrobiphenyl-4	7.30E-03	0.45	0.74
100027	Nitrophenol-4	7.09E-07	0.001	0.13
79469	Nitropropane-4	1.21E-03	0.54	0.62
684935	N-Nitroso-N- methylurea	5.15E-05	0.38	0.42
62759	N-Nitrosodi- methylamine	5.09E-04	0.12	0.56
59892	N-Nitrosomorpholine	5.73E-05	0.06	0.42
108952	Phenol	4.54E-07	0.06	0.10
106503	Phenylenediamine-p	1.13E-08	0.001	0.00
75445	Phosgene	1.71E-01	0.87	0.95
85449	Phthalic anhydride	9.00E-07	0.10	0.15
1336363	Polychlorinated biphenyls (Aroclors)	2.94E-04	1.00	0.53
1120714	Propane sultone-1,3	1.50E-05	0.01	0.33
57578	Propiolactone (b-)	9.22E-07	0.24	0.15
123386	Propionaldehyde	1.15E-03	0.81	0.62
114261	Propoxur (Baygon)	5.00E-06	0.10	0.26
78875	Propylene dichloride	2.30E-03	1.00	0.66
75569	Propylene oxide	1.34E-03	0.84	0.63
75558	<pre>1,2-Propylenimine (2- methyl aziridine)</pre>	9.39E-06	0.81	0.30
106514	Quinone	7.20E-03	0.87	0.74
100425	Styrene	3.30E-03	1.00	0.69
96093	Styrene oxide	1.07E-04	1.00	0.46
1746016	Tetrachlorodibenzo-p- dioxin-2,3,7,8		1.00	0.66

(Continued)

TABLE 2-18. COMPOUND-SPECIFIC VALUES OF  $fe_i$  and  $fm_i$  (Concluded)

CAS NO	COMPOUND NAME (	HENRYS LAW atm-m^3/gmol)	FM	FE
79345	Tetrachloroethane- 1,1,2,2	3.80E-04	1.00	0.55
127184	Perchloroethylene (Tetrachloroethylene)	2.87E-02	1.00	0.83
108883	Toluene	6.68E-03	1.00	0.73
95807	Toluene 2,4 diamine	6.03E-08	0.001	0.00
584849	Toluene 2,4 diisocyanate	8.30E-06	0.002	0.30
95534	Toluidine (o-)	1.91E-05	0.27	0.35
120821	Trichlorobenzene (1,2,4-)	1.42E-03	1.00	0.63
79005	Trichloroethane (1,1,2-) (Vinyl Trichloride)	7.40E-04	0.97	0.59
79016	Trichloroethylene	9.10E-03	1.00	0.75
95954	Trichlorophenol-2,4,5	1.77E-05	0.29	0.34
88062	Trichlorophenol-2,4,6	1.70E-05	0.40	0.34
121448	Triethylamine	2.66E-03	0.93	0.67
1582098	Trifluralin	4.17E-06	0.74	0.25
540841	<pre>Trimethylpentane   (2,2,4-)</pre>	2.41E-03	1.00	0.67
108054	Vinyl acetate	6.20E-04	0.75	0.58
593602	Vinyl bromide	2.40E-04	0.84	0.52
75014	Vinyl chloride (Chloro Ethylene)	8.60E-02	1.00	0.90
75354	Vinylidene chloride (1,1-Dichloroethylene	1.50E-02	1.00	0.79
1330207	Xylenes (isomers and mixture) mix	5.20E-03	1.00	0.72
108383	<pre>Xylenes (isomers and mixture)-m</pre>	5.27E-03	1.00	0.72
95476	<pre>Xylenes (isomers and mixture) -o</pre>	5.27E-03	1.00	0.72
106423	<pre>Xylenes (isomers and mixture)-p</pre>	5.27E-03	1.00	0.72

<sup>---</sup> Chemical family with broad range of values, not determined.

fm<sub>i</sub> = fraction of the HAP that would be measured by proposed Method 25D/18 (see Table 2-18), and

5.26E-04 = a constant to convert to the unit Mg/yr based on  $(60 \text{ min/hr}) (8760 \text{hr/yr}) (\text{Mg/10}^9 \text{ mg})$ .

In cases where  $fe_i$  is greater than  $fm_i$ , a method other than Method 25D/18 should be used to quantify the HAP. Certain compounds cannot be quantified using proposed Method 25D with Method 18.

In cases where all of the volatile organic is a single HAP and Method 25D is performed alone, the  $fe_{\dot{1}}$  and  $fm_{\dot{1}}$  for the known HAP should be used (see Table 2-18).

If the HAP concentration is measured using Method 301, a value of 1 is to be used for  $\ensuremath{\text{fm}}_{\dot{1}}$ 

The total HAP emissions from wastewater sources is computed by simply summing the emissions of individual HAP for each streams.

#### 2.5.2 <u>Documentation of HAP Emissions From Wastewater</u> Sources

In establishing HAP emissions from wastewater sources, the following information should be provided with the computed emission rate for each stream:

- Stream identification,
- Stream flow rate, method of measurement, and date of measurement,
- Stream discharge temperature,
- Stream HAP concentration, method of measurement, and date of measurement, and
- A statement that the measured flow and concentration are believed to be representative of normal operation.

The form provided in Appendix A should be completed and submitted for each wastewater stream.

#### REFERENCES

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- 3. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. VOC Emissions from Volatile Organic Liquid Storage Tanks--Background Information for Proposed Standards. EPA-450/3-81-003a.
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- 7. U.S. Environmental Protection Agency. VOC Fugitive Emissions in Synthetic Organic Chemical Manufacturing Industry Background Information for Proposed Standards. Publication No. 450/3-80-033a. Research Triangle Park, NC. November 1980.
- 8. U.S. Environmental Protection Agency. Control of Volatile Organic Compound Leaks from Synthetic Organic Chemical and Polymer Manufacturing Equipment Guideline Series. Publication No. 450/3-83-006. Research Triangle Park, NC. March 1984.
- 9. U.S. Environmental Protection Agency. Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP. Publication No. 450/3-88-010. Research Triangle Park, NC. October 1988.

- 10. Chemical Manufacturers Association. Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment. Washington, DC. January 1989.
- 11. U.S. Environmental Protection Agency. Industrial Wastewater Volatile Organic Compound Emissions Background Information for BACT/LAER Determinations. Publication No. EPA-450/3-90-04. Research Triangle Park, N.C. January 1990. pp 3-2 through 3-6.

## 3.0 ESTABLISHING EMISSIONS FROM CHROMIUM ELECTROPLATING AND ANODIZING OPERATIONS

Chromium electroplating is the process by which chromium is electrochemically deposited from a solution of chromic acid onto a metal or plastic part. Conventional plating solutions contain 32 ounces of chromic acid per gallon of water and a small amount of sulfuric acid or fluoride compounds as a catalyst. In the chromium plating process, the part to be plated is connected as the cathode in the electrical circuit and lead alloys are used as the anode. There are two types of chromium plating processes: hard chromium plating and decorative chromium plating.

In hard chromium plating, a relatively thick layer of chromium (0.05 to 30 mils) is deposited directly on a base metal (usually steel) to provide a surface with wear resistance, a low coefficient of friction, hardness, and corrosion resistance. Hard chromium plating is typically performed in stand-alone plating tanks. Typical plating times range from one to several hours. Hard plating, also called functional plating, is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, and marine hardware.

Decorative chromium plating is performed as the last step in a series of plating and metal finishing operations. The base material is generally plated with a layer of copper, followed by a layer of nickel and then followed by a relatively thin layer (less than 0.1 mil) of chromium. The chromium provides an aesthetically pleasing, bright, tarnish resistant surface. Plating times are only a few minutes. Decorative chromium plating is used for items such as automotive trim, metal furniture, bicycles, hand tools, and plumbing fixtures.

Emissions result from the formation of mist produced by the electrodeposition reactions. The chromium plating process is highly inefficient. Only about 10 to 20 percent of the current applied is actually consumed by the deposition of chromium on the

item plated. Eighty to ninety percent of the current applied is consumed in side reactions that form hydrogen gas at the cathode and oxygen gas at the anode. The formation of these gases produces small bubbles which burst at the surface of the plating solution, which generates substantial amounts of fine mist comprised of plating solution. As more current is applied, more gassing and misting is produced.

To eliminate exposures to chromic acid mist in the workplace, plating tanks are usually equipped with local ventilation systems which effectively capture the mist at the plating tank. The ventilation air is usually treated in an air pollution control device prior to being discharged to the atmosphere. Because mists are comprised of aerosols, they are considered a particulate pollutant rather than a gas or vapor. Consequently, a 95 percent reduction would need to be achieved to qualify for an early reduction compliance extension.

Chromic acid anodizing is a process by which a film of aluminum oxide is formed on the surface of aluminum electrolytically to enhance corrosion resistance. Chromic acid anodizing is used primarily for aircraft parts that are subject to high stress and corrosive conditions. Conventional anodizing solutions contain 7 to 8 ounces of chromic acid per gallon of water. In chromic acid anodizing, the part is connected as the anode in the electrical circuit instead of the cathode as in chromium plating. Unlike the chromium plating process, the anodizing process is a voltage controlled process rather than a current controlled process. Voltage is applied to the tank in a step-wise fashion until a level of 20 or 40 volts is reached and is then maintained for the remainder of the anodizing time (about 1 hour). As in chromium plating, chromic acid emissions are formed in the anodizing tank as a result of the evolution of hydrogen and oxygen gases. The amount of gassing or misting decreases over the anodizing period as the current decreases. general, emissions from anodizing tanks are similar in magnitude to those measured at decorative chromium plating facilities.

### 3.1 CONTROL TECHNIQUES/PERFORMANCE

The principal techniques used to control emissions of chromic acid mist from chromium plating and chromic acid anodizing operations include add-on air pollution control devices, particularly mist eliminators and wet scrubbers, and chemical fume suppressants.

Mist eliminators include both chevron-blade and mesh-pad designs. Chevron-blade mist eliminators consist of one or more sets of parallel baffles that cause the gas flow to change direction several times, causing the mist droplets to impinge the blades. Mesh-pad mist eliminators consist of layers of interlocking filaments densely packed between two supporting grids. Both designs are operated dry with scheduled washdowns with water to remove accumulated chromic acid.

The packed bed scrubber is the predominant scrubber design used to control emissions of chromic acid mist from plating and anodizing operations. Designs typically include a countercurrent water spray section, a packed-bed section, and a mist elimination section. The packed-bed is usually about 12 inches thick and contains packing media made of polypropylene rings or saddles that are continuously or intermittently washed with water. Mist eliminator sections generally consist of standard chevron-blade designs.

Chemical fume suppressants are surface-active compounds that are added directly to plating and anodizing baths to inhibit misting. Fume suppressants are classified as wetting agents, foam blankets, and combinations of foam blankets and wetting agents. Wetting agents reduce misting by lowering the surface tension of the plating or anodizing solution, which substantially mitigates mist formation. Foam blankets reduce misting by entrapping the chromic acid mist as it forms at the surface of the plating bath under a blanket of foam. Combination wetting agents/foam blankets reduce misting by both methods. Fume suppressants are in wide use at decorative chromium

electroplaters and chromic acid anodizers. In contrast, fume suppressants are seldom used at hard chromium platers. Wetting agents aggravate pitting, which affects the quality of the hard chromium plate. Foam blankets in hard chromium plating tanks increase the potential for explosion due to buildups of hydrogen gas under the foam layer.

In terms of performance, all three control devices can be characterized as constant outlet devices; that is, outlet loadings are relatively constant over a wide range of inlet loadings. As a result, percent reductions achieved will vary depending on the inlet conditions encountered. Consequently, percent reduction is an uncertain indicator of performance unless comparisons are made at similar inlet conditions.

Chevron-blade mist eliminators are demonstrated to achieve outlet concentrations of 0.15 mg/dscm. This would be equivalent to about 95 percent reduction or higher at inlet concentrations typically encountered at hard chromium electroplating plants (4 mg/dscm).

Outlet concentrations of less than 0.05 mg/dscm are achievable with mesh-pad mist eliminators and packed-bed scrubbers. This would be equivalent to about a 99 percent reduction at a typical hard chromium electroplating plant.

Fume suppressants can achieve outlet concentrations of less than 0.005 mg/dscm at decorative chromium and anodizing facilities. This would be equivalent to about a 99.5 percent reduction using a typical inlet concentration at decorative chromium and anodizing plants (about 1 mg/dscm).

#### 3.2 ACCEPTABLE TECHNIQUES FOR ESTABLISHING EMISSIONS

There are two fundamental approaches available for establishing annual emissions for base year and post-reduction conditions. The first and preferred approach in most instances is the use of emissions data obtained by the direct measurement of emissions using validated test methods. The second approach,

where emission measurement is not possible or the cost of measurement is prohibitive relative to the cost of emission control, is the use of emission factors, if available.

#### 3.2.1 <u>Direct Measurement</u>

When direct measurements are made, sample locations, number of traverse points, and gas stream characteristics should be determined using EPA Methods 1, 2, and 4; and the hexavalent chromium concentration should be determined using EPA Method 5 modified for chromium measurement. Modifications include eliminating the filter and using 0.1N sodium bicarbonate in the impingers rather than water. The collected samples are then recovered and analyzed by atomic absorption to determine chromium content. A draft copy of the method for determining the concentration of chromium can be obtained by contacting the Emission Measurement Branch at (919) 541-5236.

Annual chromium emissions, base year or post-reduction, can then be calculated using the following equation:

ER = (C) (Q) (60)  $(t)/1.0 \times 10^9$ ,

where,

ER = annual chromium emissions, Mg/yr;

C = chromium concentration, mg/dscm;

Q = volumetric gas flow rate, dscmm; and

t = annual operating time, hr/yr for plating tanks.

#### 3.2.2 Emission Factors

In the case of chromium electroplaters, emissions data are sufficient in both quantity and quality to establish reliable and accurate emission factors to estimate uncontrolled emissions from hard and decorative chromium electroplaters. The emission factors are expressed in terms of weight of hexavalent chromium in milligrams (mg) divided by the electrical input in amperehours (current applied times duration). The emission factors for hard and decorative electroplaters are 10 mg/amp-hour and 2

mg/amp-hour, respectively. Providing that there exist base year records that reliably report the total amount of current consumed and hours operated, annual uncontrolled emissions can be calculated using the following equation:

 $ER = (EF) (A) (T) (10^{-9})$ 

where, ER = annual chromium emissions, Mg

EF = emission factor, mg/Ah

A = annual current consumption, amperes

T = annual operating time, hours

If base year records are incomplete, then the applicant cannot use the emission factor approach to determine base year emissions. In the case of chromic acid anodizers, currently available emissions data are too limited to establish a reliable emission factor for use in determining base year emissions.

#### 3.3 DEMONSTRATION OF EARLY REDUCTION

Regardless of the approach employed to determine base year and post-reduction annual emissions, the calculation of the percent reduction achieved is made using the following equation:

$$Reduction = (1 - \frac{ER_b}{ER_p}) 100$$

Where:  $ER_b = annual emissions in base year, Mg$ 

ER, = annual emissions after reduction, Mg

Because performance data are available in sufficient quantity and quality to support the conclusion that packed-bed scrubbers applied to hard chrome and permanent type fume suppressants added to decorative chrome and anodizers will achieve reductions in emissions of 95 percent or greater, an acceptable alternative to calculation could be the application of controls by themselves. If the base year condition is no control

and the early reduction is achieved by the installation of a packed-bed scrubber for hard chrome or a permanent type fume suppressant for decorative chrome and anodizers, the installation of the scrubber or the use of the fume suppressant alone should be considered adequate demonstration that a 95 percent reduction is achieved.

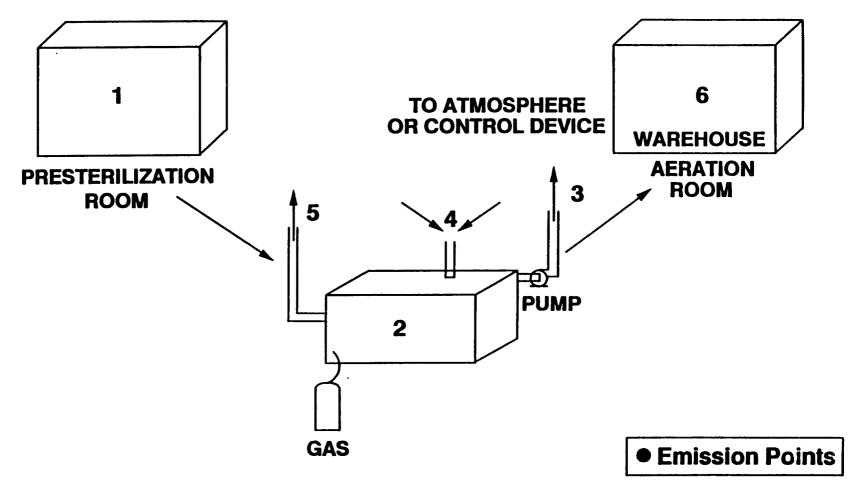
An acceptable scrubber design should include a countercurrent water spray section, a packed-bed section, and a mist elimination section. The bed should consist of an appropriate packing media, 12 inches or more in thickness, with provisions for continuous or periodic washdown. The mist eliminator section should include as a minimum a standard chevron-blade mist eliminator. The scrubber should be sized so that the face velocity across the scrubber is about 500 feet per minute. An acceptable fume suppressant is one which maintains the surface tension of a plating bath at 40 dynes/centimeter or lower.

#### 4.0 ETHYLENE OXIDE STERILIZATION

Ethylene oxide (EO) is used as a sterilant/fumigant in the production of medical equipment supplies, in miscellaneous sterilization and fumigation operations, and at hospitals. A diagram of a sterilization/fumigation cycle is presented in figure Presterilization conditioning consists of heating 4-1. humidifying the product in a separate room prior to sterilizing; this will facilitate the penetration of EO into the product. After conditioning, the product is placed in the empty sterilization chamber. The chamber is evacuated using a vacuum pump and then either pure EO or a mixture of EO and filled with chlorofluorocarbons or carbon dioxide. When sterilization is complete, the chamber vacuum pump is used to evacuate the chamber. This pumping lasts at least ten minutes. After evacuation, the chamber is filled with air or other gases, such as nitrogen or carbon dioxide, to increase the rate at which EO is diffused from the product. This "air wash" lasts from two to fifteen minutes. The evacuation and air wash steps are repeated until the desired amount of EO has been removed from the chamber. At the completion of the last evacuation, the chamber door is opened and a fan at the rear of the chamber is turned on to draw air through the chamber. This air flow protects workers by drawing EO to the rear chamber exhaust vent, which vents to the atmosphere. Chamber exhaust emissions are a function of the number of evacuation/air wash cycles.

Practically all of the EO used in the steriliztion/fumigation process is estimated to be emitted from three sources: (1) the main sterilizer exhaust (i.e., the vent from the vacuum pump/liquid separator), the aeration room or chamber, and the chamber exhaust vent. Uncontrolled emissions from these sources are assumed to be 95, 3, and 2 percent of the EO use, respectively.

Available control techniques including acid scrubbers, catalytic oxidizers, and flares can achieve emission reductions of approximately 99%. Therefore, a 90% emission reduction of total EO emissions can be achieved by controlling the main sterilizer



- 1 Presterilization Conditioning
- O 2 Sterilization
- 3 Evacuation

- ○4 Air Wash
- 5 Chamber Exhaust
- 6 Aeration; Emission Points

4

exhaust stream.

#### 4.1 TECHNIQUES FOR ESTABLISHING BASELINE HAP EMISSIONS

For facilities without add-on controls, emissions are equal to the amount of EO used in the sterilization chamber; an estimate of annual EO use can be made by using annual inventory data. Facilities with existing add-on controls must estimate the effectiveness of the existing control system and estimate emissions using the amount of EO used in the sterilization chamber.

#### 4.2 TECHNIQUES FOR ESTABLISHING 90% HAP EMISSION REDUCTION

#### Uncontrolled Facilities

An emission mass-in/mass-out approach will be used to estimate control efficiency for both catalytic oxidizers and scrubbers. Tests should be run on an empty chamber.

#### Mass-in

Mass into the control unit can be estimated by weighing the EO supply cylinders before and after use to determine the amount of EO in the chamber. Alternatively, mass in the chamber after evacuation can be calculated by using concentration and chamber volume. Concentration can be obtained by either using the ideal gas law or a gas chromatograph. Mass into the control unit is the difference between the EO charged to the chamber and the EO remaining in the chamber. The test need be run only on the first evacuation cycle.

#### Mass-out

Mass out of the control unit is estimated by measuring flow rate and EO concentration with EPA methods 2,2A,2C,or 2D and 18 respectively. For packed-bed scrubbers and catalytic oxidizers flow rate and concentration can be measured directly. However, for a reaction/detoxification tower, a flow must be induced to increase the exit flow to a measureable rate.

### Control Efficiency

The control efficiency is calculated by the following equation:

Control Efficiency =  $(1 - (MO/MI)) \times 100$ 

where MO = mass out of control device

MI = mass into control device

#### APPENDIX A

CALCULATION WORKSHEETS FOR ESTABLISHING BASE YEAR AND POST-REDUCTION HAP EMISSIONS FROM SOCMI SOURCES

Source:	

# CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM PROCESS VENTS

HAP:Year:	Date: Calculator:
Process Vent Identification: Description:	
Process Conditions/Sampling Date of flow measurement Method of flow measurement Date of concentration measurement Method of concentration measurement (if not an EPA Method give a bridescription and attach protocol) Describe any problems encountered during testing Production rate during flow determ Production rate during sampling (1) Average production rate for the year	ination (lbs/hr)
Stream Characteristics Annual average vent stream flow rate (ft <sup>3</sup> /min) Annual average HAP concentration (figure Annual hours of operation (hrs) Vent stream discharge temperature HAP molecular weight (lb/lb-mole) Pressure at point of discharge (pshap high-risk weighting factor	= Q = C = h = h = T = MW
Control Control device HAP control efficiency (%)	= eff
<u>Calculations</u> <sup>a</sup>	
Uncontrolled Emissions ( $E_U$ ) = $2.54$	E-09 Q C h MW P T + 460
Uncontrolled Emissions (E <sub>U</sub> ) = $2.54$	E-09( )( )( )( ) () + 460 Mg/yr

Source:	

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM PROCESS VENTS (CONCLUDED)

HAP Emissions (E <sub>HAE</sub>	$E_{U} = E_{U} (1 - eff/100)$
HAP Emissions (E <sub>HAE</sub>	(1/100)
	= Mg/yr
Weighted HAP Emissi	ons = $E_{HAP}$ $F_{HR}$
Weighted HAP Emissi	lons = ( ) ( )
	= Mg/yr

If the conditions during testing are not representative of base year of operation, make the appropriate extrapolation below and explain:

If the flow or concentration were not measured using an EPA reference method, EPA conditional method or validated using Method 301, provide justification and supporting calculations:

aExpression provided in "Procedures for Establishing Base Year and Post-Reduction HAP Emissions" to convert flow and concentration into an annual mass rate; the 3.94E-08 constant is based on the ideal gas law.

Source:	}		

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM FIXED ROOF STORAGE TANKS

HAP:	Date:	
Year:	Calculator:	
Tank designation:		
Product:		
Tank Characteristics  Inside diameter, (ft)  Height, (ft)  Capacity, (gal) = $\Pi \stackrel{D}{=} \frac{D^2 h}{4} * 7.48 \frac{gal}{ft^3}$ ,  if not known  Roof color		=D =H <sub>T</sub> =V
Shell color		=H
Ambient Conditions  Average atmospheric pressure (psia)   (defaults 14.7 psia)  Average ambient diurnal temperature   (°F) <sup>b</sup> Average annual ambient temperature   (°F)		$=P_{A}$ $=\Delta_{T}$ $=T_{A}$
Bulk Liquid Characteristics  Stored liquid temperature (°F)C  Total throughput per year (gal)  Number of turnovers per yeard  Molecular weight of HAP (lb/lb mole)  Vapor pressure of stored material (psi  Partial pressure of the HAP at liquid  conditions (psia)  HAP high-risk weighting factor	ia)	=TS =AN =N =MVi =P =Pi =FHR
Adjustment Factors  Paint factor (see Table 2-3)  Small diameter tank factor <sup>e</sup> Turnover factor <sup>f</sup> Product factor <sup>g</sup>		=F <sub>P</sub> =K <sub>N</sub> =K <sub>C</sub>

Source	:		

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM FIXED ROOF STORAGE TANKS (continued)

<u>Control</u>
Control device =eff
<u>Calculations</u> h
Breathing Loss $(^{Mg/yr}) =$
$L_{B} = 1.02E - 05M_{V_{\dot{1}}} \left( \frac{P}{P_{A}-P} \right)^{0.68} D^{1.73}H^{0.51}\Delta T^{0.50}F_{P}CK_{C} \frac{P}{P}i$
= 1.02E-05(
Working Loss (Mg/yr) = $L_W = 1.09E-08 M_{V_i} P_i VNK_N K_C$
= 1.09E-08 ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( )
Total Loss (Mg/yr) =
$T_L = L_B + LW = ( ) + ( ) =                          $
If a control device is employed,
HAP Emissions ( $E_{\text{HAP}}$ ) = Total Loss (1 - eff/100)
=(1/100) = Mg/yr

Source:		

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM FIXED ROOF STORAGE TANKS (continued)

			=				Mg/yr
			=	(	)	(	)
Weighted	HAP	Emissions	=	$E_{\mbox{\scriptsize HAP}}$	$F_{HR}$		

<sup>a</sup>If vapor space height is unknown or shell, assume H equals one half tank height. If tank has a cone roof, adjust vapor space height by adding 1/3 of height of cone.

bIf average ambient diurnal temperature change is unknown, assume 20°F.

CStored liquid temperature may be approximated from average annual ambient temperature. See Table 2-2.

$$d_N = \frac{AN}{V}$$
 where N = number of turnovers per year AN = total throughput per year (gal)  $V = tank \ capacity \ (gal)$ 

eFor D  $\geq$  30ft, C=1; For 6  $\leq$  D < 30ft, C=0.0771D-0.0013D2-0.1334.

fror turnovers > 36,  $K_N = (180 + N)/(6 * N)$ where  $K_N =$  turnover factor (dimensionless) N = number of turnovers per year For turnovers  $\leq$  36,  $K_N = 1$ 

 $g_{K_C} = 1.0$  for volatile organic liquids

hExpression for computing HAP emissions are from "Procedures for Establishing Base Year and Post-Reduction HAP Emissions." The calculation procedure is consistent with AP-42.

Source:	

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM INTERNAL FLOATING ROOF STORAGE TANKS

HAP:	Date:	
Year:	Calculator:	
Tank designation:	· · · · · · · · · · · · · · · · · · ·	
Product:		
Tank Characteristics		
Inside diameter, (ft)		= D
Rim Seal type: Number of columns <sup>a</sup> .	<del></del>	= N <sub>C</sub>
Effective column diameter (ft) <sup>b</sup>		= F <sub>C</sub>
Ambient Conditions		
Average atmospheric pressure (psia) Average annual ambient temperature (°	F)	= P <sub>A</sub> = T
Bulk Liquid Characteristics		
Stored liquid temperature (°F)		$= T_S$
Total throughput per year (bbl/yr)		•
[Note: 42 gal/bbl]		= Q
Vapor molecular weight of stored		$= M_V$
material (lb/lb-mole)		. = M
Molecular weight of HAP (lb/lb-mole) True vapor pressure of stored		$\cdot = M_{V_{\dot{1}}}$
material at bulk liquid		
conditions (psia)		= P
Partial pressure of HAP (psia)		$= P_{i}$
Liquid density (lb/gal)		$= W_{\mathbf{L}}^{\mathbf{L}}$
HAP high-risk weighting factor		$= F_{HR}^{-}$
Factors		
<pre>Rim seal loss factor (lb mole/ft yr);   obtain from Table 2-4</pre>		= K <sub>R</sub>
Product factor (dimensionless)		$= K_{C}$
Shell clinage factor (bbl/1000 ft <sup>2</sup> );		C
obtain from Table 2-9		= C
Deck fitting loss factor		$= F_F$
Deck seam loss factor		$=K^{D}$
(lb-mole/ft yr) <sup>d</sup>		-5
Deck seam length factor; obtain from Table 2-7		$=F_{D}$
ODERIN ITOM TRADEC 2 /		

Source:		

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM INTERNAL FLOATING ROOF STORAGE TANKS (CONTINUED)

#### Control

Control device \_\_\_\_\_\_ =ef:

### Calculationse

$$L_R = K_R D P * M_{V_{\dot{1}}} K_C \frac{P_{\dot{1}}}{2205 P} = ( ) ( ) ( ) ( ) ( ) ( ) ( ) =$$

$$L_F = F_F P * M_{v_i} K_C \frac{P_i}{2205 P} = ( ) ( ) ( ) ( ) ( ) =$$

$$L_{D} = K_{D}F_{D}D^{2} P * M_{V_{1}}K_{C} \frac{P_{1}}{2205 P} = ( )( )( )^{2}( )( )( )( )( )$$

$$= \boxed{ }$$

$$L_T = L_R + L_W + L_F + L_D = ( ) + ( ) + ( ) + ( )$$

$$= Mg/yr$$

If a control device is employed,

C			
Source:			

CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM INTERNAL FLOATING ROOF STORAGE TANKS (CONCLUDED)

aFor self-supported fixed roof or external floating roof tank,  $N_C = 0$ . If  $N_C$  is unavailable, see Table 2-6.

 $^{\mathrm{b}}$ If  $F_{\mathrm{C}}$  is unavailable;

FC = 1.1 for 9 inch by 7 inch built-up columns; 0.7 for 8 inch diameter pipe column;

1.0 if column construction details are not known

 $^{\mathrm{C}}\mathrm{F}_{\mathrm{F}}$  is determined using Table 2-10 and the following calculation

$$F_F = [N_{F_1} \ K_{F_1}] + [N_{F_2} \ K_{F_2}] + \dots + (N_{F_N} + K_{F_N})]$$

 $d_{K_{\mathrm{D}}}$  = 0.0 for welded deck and 0.34 for non-welded deck.

eExpression for computing HAP emissions are from "Procedures for Establishing Base Year and Post-Reduction HAP Emissions." The calculation procedure is consistent with AP-42.

Source:
---------

## CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM EXTERNAL FLOATING ROOF STORAGE TANK EMISSIONS

HAP: Date Year: Ca Tank Designation:	: lculator:
Product:	
Tank Characteristics	
<pre>Inside tank diameter (ft) Rim Seal Type: Tank color:</pre>	= D
Ambient Conditions	
Average atmospheric pressure Ambient temperature ( ${}^{\rm O}{\rm F}$ ) Average windspeed for the tank site (mp)	= P <sub>A</sub> h) = V
Bulk Liquid Characteristics	
Density of the material stored (lb/gal) Molecular weight of the material stored (lb/lb mole)	$= W_{L}$ $= M_{V}$
Molecular weight of HAP(lb/lb mole) True vapor pressure of the material stored (psia)	$ = M_{V_{\dot{1}}} $ $= P$
Partial pressure of HAP (psia) HAP high-risk weighting factor	$ = P_{i} $ $= F_{HR} $
<u>Factors</u>	
Seal factor; obtain from Table 2-8 Seal windspeed exponent; obtain from Table 2-8	= K <sub>S</sub>
Product withdrawal shell clingage facto obtain from Table 2-9 Product factor; 1.0 for VOL Total Roof Fitting Loss Factor <sup>a</sup>	$ \begin{array}{ccc}  & = & C \\ \hline  & 1.0 & = & K_C \\  & = & F_F \end{array} $
Calculation	
$P^* = (P/P_A)/((1 + (1 - (P/P_A))^{0.5})$	2)
= ( ) ( ) / ((1 + (1 - (	)())0.5)2)

Source:	

CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM EXTERNAL FLOATING ROOF STORAGE TANK EMISSIONS (Cont.'d)

Calculations (cont.'d)

Withdrawal Loss = 
$$L_W = 4.28E^{-0.4} \frac{OCW_L}{D} \frac{M_{V_1}P_1}{M_{V_1}P}$$
  
=  $4.28E^{-0.4} \frac{()()()}{()} \frac{()()}{()}$   
=  $Mg/yr$ 

Seal Loss = 
$$L_{SE} = K_S V^{Np}^* DM_{V_1} K_C \frac{P_1}{2205 P}$$
  
= ( )( ) ( )( )( )( )( )( )( )2205()

Roof Fitting Loss = 
$$F_F P^* M_{V_1} K_C \frac{P_1}{2205 P}$$
  
= ( ) ( ) ( ) (1.0) ( ) (2205 ( )

Total Loss = 
$$L_T = L_W + L_{SE} + L_{RF}$$
  
= ( ) + ( ) + ( )  
= Mg/yr

Sou	rce:
	FOR ESTABLISHING HAP EMISSIONS OF STORAGE TANK EMISSIONS (Cont.'d)
Calculations (cont.'d) Weighted HAP Emissions	= E <sub>HAP</sub> F <sub>HP</sub> = ( ) ( ) =

 $a_{F_F}$  is determined using Tables 2-11, 2-12, and 2-13 and the following calculation:  $F_F = [(N_{F_1} K_{F_1}) + (N_{F_2} K_{F_2}) \dots (N_{F_{n_f}} K_{F_{n_f}})]$ 

Source:	

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM EQUIPMENT LEAKS<sup>a</sup>

HAP: Year: Process:		Date: Calculator:		_	
Component ID	Component Type <sup>a</sup>	WT. % HAP of VOC	OVA Reading	Leak Emission Factor <sup>b</sup>	Emissions of HAP <sup>C</sup>
		<del></del>			
			<del></del>		<del></del>
<del></del>					
					<del></del>
			- Control of the Cont		

aRSLL = Pump Seals (Light Liquid); PSHL = Pump Seals (Heavy Liquid); VG = Valves (Gas/Vapor); VLL = Valves (Light Liquid); VHL = Valves (Heavy Liquid); PRV = Pressure Relief Valves (Gas/Vapor); OE = Open-Ended Lines; CS = Compressor Seals; SC = Samplings Connections; F = Flanges

bFrom Table 2-14, 2-15, or correlation data.

C(Wt. % HAP)/100 \* (Leak Emission Factor)

Source:	

## CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM LOADING OPERATIONS

HAP: Year:	Date: Calculator:	
	Jarouracor.	
Loading Operation:		_
Loading Parameters		
Cargo carrier (tank truck, rail car, Mode of operation (choose from Table Annual volume of liquid loaded (gal) Temperature of liquid loaded (OF) Weight percent HAP in the loaded mat True vapor pressure of the HAP loade [Note: For mixtures, use the HAP paperssure]	= 2-16) lons) = ( = cerial = ( ed (psia) = (	T
Molecular weight of the HAP (lb/lb-r Saturation factor (see Table 2-16) HAP high-risk weighting factor	= :	
<u>Control</u>		
Control device HAP control efficiency (%)	= .	eff
<u>Calculation</u> <sup>a</sup>		
Uncontrolled Loading Loss $E_u = 5.65$	E-06 <u>S P M G</u> T + 460	
Uncontrolled Loading Loss $E_u = 5.65$	E-06 ( )( )( )( () + 460	).
=	Mg/yr	
HAP Emissions $(E_{HAP}) = E_u$ (1 -	eff/100)	
= (1	- <u></u> /100)	
=	Mg/yr	

Source:	

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM LOADING OPERATIONS (CONCLUDED)

Calculation (continued)

Weighted HAP Emissions = 
$$E_{\mbox{HAP}}$$
  $F_{\mbox{HP}}$  = ( ) ( ) = Mg/yr

<sup>&</sup>lt;sup>a</sup>Calculation worksheet and procedure from "Procedures for Establishing Base Year and Post-reduction HAP Emissions." This procedure is consistent with AP-42.

Source:	
	 -

## CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM WASTEWATER SOURCES

HAP: Year:	Date: Calculator:	
Wastewater Stream Identification: Wastewater Stream Description:		
Process Conditions/Sampling		
Date of flow measurement Method of flow measurement Date of concentration measurement Method of concentration measurement Production rate during flow determ Production rate during sampling (1 Average production rate during base	mination (lbs/hr) lbs/hr)	
Stream Characteristics		
Average annual flow rate during di (1pm) Average annual HAP concentration of Fraction of HAP that would be emit (see Table 2-14) Fraction of HAP that would be measured by Method 25D/18 (see Table 2-14) HAP high-risk weighting factor	(mg/l)sured	= Q =CVOHAP = fe <sub>i</sub> = fm <sub>i</sub> = F <sub>HR</sub>
Control		
Control device HAP control efficiency (%)	<del></del>	= eff
$\frac{\text{Calculations}^{\text{a}}}{\text{Wastewater Emissions (WE}_{\text{u}})} = 5.26E$	E-04 Q C <sub>VOHAP</sub> fe <sub>i</sub>	

Source:		

### CALCULATION WORKSHEET FOR ESTABLISHING HAP EMISSIONS FROM WASTEWATER SOURCES (CONCLUDED)

Wastewater Emissions Potential (WE
$$_{\rm u}$$
) = 5.26E-04 ( ) ( )  $\frac{(}{}$  )  $\frac{(}$  )  $\frac{(}{}$  )  $\frac{(}{}$  )  $\frac{(}{}$  )  $\frac{(}{}$  )  $\frac{(}{}$  )  $\frac{($ 

<sup>&</sup>lt;sup>a</sup>Calculation worksheet and procedure from "Procedures for Establishing Base Year and Post-reduction HAP Emissions".

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#### 15. SUPPLEMENTARY NOTES

#### 16. ABSTRACT

Regulations have been proposed governing compliance extensions for Early Reductions of Hazardous Air Pollutants (HAP). The regulations allow a six year MACT standard compliance extension for sources that achieve HAP reductions of 90% (95% for particulates) from a base year of 1987 (or more recent base year). This document includes acceptable emission estimating techniques that can be used when source testing is not feasible. This document includes techniques for synthetic organic chemical manufacturing, ethylene oxide sterlization, and chromium electroplating.

17. KEY WORDS AND DOCUMENT ANALYSIS					
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