State of California
AIR RESOURCES BOARD
Technical Support Division

Technical Guidance Document for the Emission Inventory Criteria and Guidelines Regulation for AB 2588 (Air Toxics "Hot Spots" Information and Assessment Act of 1987)

Prepared By

Technical Support Division
With the Participation of the
AB 2588 Technical Advisory Committee

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CHAPTER I
INTRODUCTION

THE PURPOSE OF THIS DOCUMENT

The purpose of this Technical Guidance Document is to provide California facility operators with additional technical guidance in implementing the inventory plans required by the Air Toxics "Hot Spots" Information and Assessment Act of 1987 (Health and Safety Code Sections 44300 et seq.) (the "Act"). These inventory plans must meet requirements of the Emission Inventory Criteria and Guidelines Regulation, (the "Regulation") California Code of Regulations, Subchapter 7.6, Sections 93300 through 93347. The Technical Guidance Document focuses on emission estimation methods the facility operator may use to quantify listed substances when source testing or other measurement is not required. An adjunct to the Regulation, this document is not regulatory. The estimation methods included are suggestions, and facility operators should refer to the Regulation as well as consult with their local air pollution control district or air quality management district when implementing their plans. (Copies of the Regulation are available from the districts.)

In developing this document, the ARB staff received assistance from a technical advisory committee which included representatives from several air pollution control districts and air quality management districts, the Department of Health Services, and the California Air Pollution Control Officers Association. The public also provided comments and suggestions at two sets of public consultation meetings held in Sacramento and Los Angeles during February and July of 1989.

Periodic updates to this report are planned as time and staff resources permit. Updates will incorporate new information and additional technical guidance for facility operators to use to comply with the Regulation. A high priority of the ARB staff is developing process-specific estimation techniques for facility operators to use to comply with the Regulation. As required by the Act, emission data derived from the AB 2588 process are to be used to support the ARB's Toxic Air Contaminants Identification and Control Program, commonly referred to as the AB 1807 process (Health and Safety Code, Sections 39650 et seq.). Facility operators should check with the air pollution control districts for the most current version of the Technical Guidance Document.

THE EMISSION INVENTORY CRITERIA AND GUIDELINES REGULATION

On April 14, 1989, the Air Resources Board approved the Emission Inventory Criteria and Guidelines Regulation, California Code of Regulations, Subchapter 7.6, Sections 93300 through 93347. The Regulation provides facility operators with criteria and guidelines to use in completing their emission inventory plans and emission inventory reports required by the Air Toxics "Hot Spots" Information and Assessment Act of 1987 (AB 2588 or the "Act"). The Regulation was adopted by the

ARB Executive Officer on May 23, 1989, and became effective on June 1, 1989, as an emergency regulation.

Beginning July 1, 1988, the Act applies to any California facility that meets one of the following criteria: (1) manufactures, formulates, uses, or releases any listed substance, and releases 25 tons per year or more of total organic gases, particulate matter, nitrogen oxides, or sulfur oxides; or (2) is listed in any current toxics use or toxics air emission survey, inventory, or report released or compiled by an air pollution control district or air quality management district and referenced in Appendix B of Title 17, California Code of Regulations, Sections 90700 through 90704. In addition, beginning July 1, 1989, this Act also applies to any facility which manufactures, formulates, uses, or releases any listed substance and releases 10 or more but less than 25 tons per year of total organic gases, particulate matter, nitrogen oxides, or sulfur oxides.

Facilities subject to the Act in 1988 were to submit an emission inventory plan to their appropriate district by August 1, 1989. Those facilities subject to the Act in 1989 must submit their plans to the appropriate district by August 1, 1990. The plan must present a comprehensive and detailed description of the methods the facility operator proposes to use to quantify air releases or potential air releases from all points of release of substances listed in Appendix A-I of the Regulation. That Appendix is contained in Attachment A-I of this document.

The Regulation sets forth the requirements for quantifying emissions. Source testing and other measurement requirements are found in Appendix D of the Regulation, and are incorporated in Attachment A of this report as Appendix D. The Regulation also specifies the acceptable estimation methods to quantify substances for which source testing or other measurement is not required. Under the Regulation, the plan must also account for the effects of control equipment on emissions, and justify the use of any proposed control efficiencies to the district.

Facility operators should work with their districts as they develop their plans. Once the district approves the plan, the facility operator is committed to using that plan, and has 180 days to implement the plan by completing and submitting an emission inventory report to the district. The emission inventory report must include the results of all required source tests, material analyses, and any other measurement performed to quantify specific substances as well as emission estimation methods used to quantify substances not requiring actual measurement.

The Regulation contains the reporting forms facility operators must use to complete the emission inventory report; these are available at local district offices and will be provided upon request (see Appendix B of the Regulation for "Reporting Forms and Instructions"). However, if the district requires, facility operators will use an alternative format.

Attachment B of this document contains a more detailed summary of the Emission Inventory Criteria and Guidelines Regulation.

CHAPTER II
WHERE TO FIND INFORMATION

This Chapter provides facility operators with guidance on where to locate the necessary information to implement the emission inventory plan. These plans must be prepared in accordance with the requirements set forth in the Emission Inventory Criteria and Guidelines Regulation. Facility operators must familiarize themselves with the Regulation. To assist operators in doing this, Table 1 in this Chapter references key sections in the Regulation, and Attachment A contains the following sections from the Regulation:

- "Summary of Requirements for Measurement and Alternatives"
- "Substances for Which Emissions Must Be Quantified"
- "Substances for Which Production, Use, or Other Presence Must Be Reported"

Table 2 of this Chapter contains a series of questions and answers to guide the operator to the information in this document needed for estimating emissions when source testing is not required. Table 3 lists those ARB publications available to facility operators at the district office.

TABLE 1
KEY SECTIONS IN THE EMISSION INVENTORY CRITERIA AND GUIDELINES REGULATION

Subject Under the Regulation	References In the Regulation	References In this Document
Substances for Which Emissions Must Be Quantified	Appendix A-I	Attachment A
Substances for Which Production, Use or Other Presence Must Be Reported	Appendix A-II	Attachment A
Requirements for Source Testing and Measurement	Sections 93336 through 93340 and Appendix D	Attachment A
Specifications for Identifying Emission Points and Substances Emitted ("Facility Look-Up Table")	Section 93332 and Appendix C	
Specifications for Acceptable Estimation Methods and Emission Factors	Section 93345	
Specifications for Emission Quantification and Degree of Accuracy	Section 93334	
Specifications for Reporting Period and Averaging Intervals	Section 93331	
Reporting Forms	Section 93322	
Instructions for Completing Reporting Forms	Appendix B	
Exempted Uses	Section 93333	

TABLE _

GUIDE TO CHAPTERS AND ATTACHMENTS
IN THE TECHNICAL GUIDANCE DOCUMENT

Questions	Answers	Reference in Document
o What substances must I quantify?	The Emission Inventory Criteria and Guidelines Regulation specifies what substances must be quantified. A copy of that list has been reproduced in this document.	Attachment A
o Am I required to source test?	In specific cases, source testing is required by the Emission Inventory Criteria and Guidelines Regulation. These requirements are included in this document.	Attachment A
o Does the ARB have a specific emission estimation technique (EET) for my facility's emitting process?	The ARB has developed 9 EETs. An additional EET was developed independently.	Chapter V
o If no EET exists, what other methods can I use to estimate emissions of listed substances?	Chapter III provides discussion and examples of generic emission estimation methods: emission factors, mass balance, engineering calculations, and speciation profiles. The facility operator should review the material in Chapter III before going to the Attachments.	Chapter III
o If no EET exists and the generic methods in Chapter III are not applicable, how do I estimate emissions?	Some EETs may be adaptable to your facility's process.	Chapter V

TABLE 2 Continued

Questions	Answers	Reference in Document
o Where do I find emission factors?	Facility operators will find AB 1807 Emission Factors in Attachment E-I, and Other Emission Factors in Attachment E-II. Facility operators are required by the Regulation to use AB 1807 emission factors.	Attachments E-I and E-II
o Where do I find a speciation profile?	ARB-published speciation profiles are available at the district office.	
o How do I account for control efficiencies?	Chapter IV provides a general discussion of control efficiencies. The engineering calculations in Chapter III provide an example calculation with a control efficiency	Chapter IV
o Where do I find control efficiencies?	See Chapter IV or consult your district.	Chapter IV Tables 4, 5, 6, 7

TABLE 3
ARB PUBLICATIONS AVAILABLE THROUGH DISTRICT OFFICES

- The Emission Inventory Criteria and Guidelines Regulation
- Emission Inventory Reporting Forms
- The Technical Guidance Document for The Emission Inventory Criteria and Guidelines Regulation
- ARB Speciation Profiles
  (Source Classification Codes and ARB profiles are cross referenced.)

CHAPTER III
GENERIC EMISSION ESTIMATION METHODS

INTRODUCTION

The purpose of this Chapter is to provide facility operators with information about general emission estimation methods that are available for facility operators to use in preparing emission inventory reports. Where source testing is not required but listed substances must be quantified, facility operators may use emission estimation methods such as emission factors, mass balance, engineering calculations, and speciation profiles. These methods are suggestions only. Operators need to determine the method that applies to their facility's process and the substances being emitted.

This Chapter provides specific examples of the general estimation methods to demonstrate how a facility operator would calculate emissions using one of these methods. Each example presents emission estimates from one process and substance, but does not account for facility-wide emissions. Facility operators must account for all the sources of emissions of any substance listed in Appendix A-I of the Regulation (reproduced in Attachment A-I of this document.) In addition, the numbers representing the process rates and emission factors used in these examples may not be representative of the operator's facility, and should not be used without independent verification.

To comply with the reporting requirements in the Regulation, facility operators must report emissions of listed substances as an **annual average** and a **maximum one-hour emission** during the reporting year and must also meet the **degree of accuracy** requirements set forth in the Regulation. These terms are defined below for the purposes of this document and the Regulation.

Annual average emissions are defined as the total emissions (expressed in pounds) of listed substances released under normal operating conditions during the reporting calendar year.

Maximum hourly emissions are defined as those emissions (expressed in pounds) of listed substances occurring in one hour, which are allowable under normal operating conditions, and which are expected to result in the worst emissions of those substances. In calculating maximum hourly emissions, the facility operator should use those process conditions resulting in the worst emissions within the range of allowable conditions, under routine operation or predictable upset, but not including conditions reflecting atypical shut-down or malfunction of control equipment.

If the facility operator is unable to determine the <u>hourly</u> process parameters used to calculate "maximum hourly emissions," then the daily maximum emissions divided by the number of operating hours in the day may be used. If this second approach is not possible, the facility operator should consult with the district to determine the appropriate options. In some cases, the operator may be able to use the design

value or maximum capacity of the piece of equipment to determine maximum hourly emissions.

The **Degree of Accuracy** for emission quantification is specified in Section 93334 of the Regulation. The emission results from source testing, where required, must be reported to within the detection and accuracy levels of the ARB-adopted source test method used. The total emissions of listed substances from processes not requiring source testing must meet the degree of accuracy specified in Section 93334 (d) and (e). If a facility's emissions of a substance fall below the required degree of accuracy, the facility operator shall report only the presence of that substance on the use/production form provided in the Regulation.

ESTIMATION METHODS

Emission Factors

Emission factors can be used to estimate emissions of listed substances from a wide range of sources. An emission factor expresses air emissions as a ratio of the amount of a pollutant released to a process-related parameter or measurement ("process unit"), frequently expressed as the amount of pollutant emitted per throughput of a process or piece of equipment, or per quantity produced or processed, (for example, pounds of a particular substance emitted per pounds of product produced).

When using emission factors, Section 93345 (a) (3) (B) of the Regulation requires facility operators to use published AB 1807 emission factors to estimate emissions where applicable to the facility's emitting process. Attachment E-I contains the published AB 1807 emission factors. If an appropriate factor is not in Attachment E-I, facility operators may use other available emission factors which are found in Attachment E-II. The emission factors included in Attachment E-II were developed from source test data and mass balance calculations.

If operators find no applicable emission factor listed, they should explore the following alternatives. Operators should check with the district staff for an emission factor applicable to the facility's process. If the district does not have an acceptable emission factor, then operators will need to use some other method of estimating emissions, such as mass balance, engineering calculations, and speciation profiles. These other methods are described later in this chapter.

<u>Examples Using Emission Factors</u>

1. Estimating Emissions of Chloroform From a Pulp and Paper Mill Using An Emission Factor

A mill uses wood chips and recycled paper to produce approximately 35,000 tons of bleached kraft pulp and 52,500 tons of tissue paper pulp per year by chemical pulping process. The facility's maximum process rates are 122 tons of bleached kraft pulp and 157 tons of tissue paper pulp per day. The mill operates 10 hours per day, 350 days a year. Other days are

reserved for maintenance. To estimate annual average and maximum hourly chloroform emissions from the pulping process, the facility operator should use the following method.

Using Attachment E-II, the operator finds that the uncontrolled emission factor for bleached kraft pulp is 0.00022 lb of chloroform per lb of pulp produced (or 0.00022 ton of chloroform per ton of pulp produced), and the uncontrolled emission factor for tissue paper pulp is 0.00016 lb chloroform per lb of pulp produced.

Using these emission factors and the calculated process rates, the facility operator estimates chloroform emissions as follows:

$$EMS = PR \times EF \qquad (1)$$

Where:

EMS = Annual average chloroform emissions, tons/yr
PR = Annual process rate, tons/yr
EF = Emission factor, ton chloroform emitted/ton pulp produced

A. Annual Average Emissions

For bleached kraft pulp:

EMS = 35,000 tons/yr x 0.00022 ton chloroform/ton pulp produced

= 7.7 tons of chloroform emitted per year
= 15,400 lbs chloroform emitted per year

For tissue paper pulp:

EMS = 52,500 tons/yr x 0.00016 ton chloroform/ton pulp produced

= 8.4 tons of chloroform emitted per year
= 16,800 lbs chloroform emitted per year

Total annual chloroform emissions from the pulping process for the facility:

= 15,400 lbs/yr + 16,800 lb/yr
= 32,200 lbs/yr

B. Maximum Hourly Emissions

In this example, the operator cannot estimate maximum hourly emissions directly because the maximum hourly process rates are not available. However, the maximum daily process rates and the daily hours of operation are known.

To calculate the maximum hourly process rates, the operator uses the maximum daily process rate and the daily hours of operation as follows:

$$HPR_{max} = DPR_{max} \div DHO \qquad (2)$$

Where:

HPR_{max} = Maximum hourly process rate, tons/hour

DPR_{max} = Maximum daily process rate, tons/day

DHO = Average daily hours of operation, hours/day

For bleached kraft pulp:

HPR_{max} = 122 tons of bleached kraft pulp/day ÷ 10 hours/day

= 12.2 tons of bleached kraft pulp produced/hour

For tissue paper pulp:

HPR_{max} = 157 tons tissue paper produced/day ÷ 10 hours/day

= 15.7 tons tissue paper pulp produced/hour

To estimate maximum hourly emissions, the facility operator uses Equation (2), and follows a procedure similar to the one used for calculating annual average emissions. In this case, maximum hourly parameters replace all the annual ones.

$$HEMS_{max} = HPR_{max} \times EF \qquad (3)$$

Where:

$HEMS_{max}$ = Maximum hourly chloroform emissions, lbs/hour

HPR_{max} = Maximum hourly process rate, tons/hour

EF = Emission factor, ton chloroform/ton pulp produced

For bleached kraft pulp:

$HEMS_{max}$ = 12.2 tons/hr x 0.00022 ton chloroform/ton pulp produced

= 0.00268 tons chloroform emitted per hour

The maximum hourly emissions must be expressed in pounds, so to convert tons of chloroform to pounds, the operator does the following:

$HEMS_{max}$ = 0.00268 tons/hr x 2,000 lbs/ton

= 5.4 lbs of chloroform emitted per hour

For tissue paper pulp:

$HEMS_{max}$ = 15.7 tons/hour x 0.00016 ton chloroform/ton pulp produced x 2,000 lbs/ton

= 5.0 lbs chloroform emitted per hour

Total maximum hourly chloroform emissions from the facility's pulping process:

5.4 lbs/hour + 5.0 lbs/hour
= 10.4 lbs/hour.

2. Estimating Emissions of Nitrobenzene From Nitrobenzene Production Using An Emission Factor

Facility "P" produces 5,000 gallons of nitrobenzene per year for use in manufacturing benzidine and quinoline. The facility operates 16 hours per day, 250 days per year. The maximum quantity of nitrobenzene produced daily in this process is 28 gallons. The facility operator knows that nitrobenzene weighs approximately 10 pounds per gallon. (The density of the solvent is used to convert from gallons of solvent to pounds of solvent in the emissions calculation.) The facility operator calculates the annual average and maximum hourly pounds of nitrobenzene emitted during this process using the following method:

Calculate the activity level or process-related parameter:

$$PR = PRV \times D_N \qquad (4)$$

Where:

PR = Amount of nitrobenzene produced through the wash and neutralization phase in mass units, lbs/year
PRV = Amount of nitrobenzene produced through the wash and neutralization phase in volumetric units, gallons/year
D_N = Density of nitrobenzene, lbs/gallon

PR = 5,000 gallons produced/year x 10 lbs/gallon
= 50,000 lbs of nitrobenzene produced/year

Using Attachment E-II, the facility operator finds that the emission factor for nitrobenzene during its production is 8.0×10^{-6} lb of nitrobenzene per 1.0 lb of nitrobenzene produced, which represents

uncontrolled fugitive emissions. Thus, the facility operator estimates nitrobenzene emissions as follows:

A. Annual Average Emissions

Using Equation (1) again: (1)

$$EMS = PR \times EF$$

Where:

EMS = Annual nitrobenzene emissions, lbs/yr
PR = Amount of nitrobenzene produced during the wash and neutralization phase in mass units, lbs/yr
EF = Emission factor, lbs nitrobenzene/lbs of nitrobenzene produced

EMS = 50,000 lbs/yr x (8.0×10^{-6}) lb nitrobenzene/ lbs nitrobenzene produced

= 0.4 lb nitrobenzene emitted per year

B. Maximum Hourly Emissions

To estimate the maximum hourly emissions, the facility operator must estimate the maximum hourly process rate. The operator inserts the maximum daily process rate and the daily hours of operation into Equation (2).

Using Equation (2) again: (2)

$$HPR_{max} = DPR_{max} \div DHO$$

Where:

HPR_{max} = Maximum hourly process rate, lbs/hour

DPR_{max} = Maximum daily process rate, lbs/day

DHO = Average daily hours of operation, hours/day

DPR_{max} = 28 gallons/day x 10 lbs/gallon (density of nitrobenzene)

DPR_{max} = 280 lbs/day

HPR_{max} = 280 lbs/day ÷ 16 hours/day

= 17.5 lbs of nitrobenzene produced per hour

After calculating the maximum hourly emissions, the operator uses Equation (3) and the previous emission factor for nitrobenzene to estimate the maximum hourly nitrobenzene emissions as follows:

$$HEMS_{max} = HPR_{max} \times EF \qquad (3)$$

Where:

$HEMS_{max}$ = Maximum hourly nitrobenzene emissions, lbs/hour

$HEMS_{max}$ = 17.5 lbs/hour x (8.0×10^{-6}) lbs of nitrobenzene/lb nitrobenzene produced

= 0.00014 lbs nitrobenzene/hour for this process

Mass Balance

Mass balance can be used to estimate emissions when emission factors are unavailable, or when mass balance would provide a more accurate estimate than the use of emission factors. Mass balance is a method which equates the input of material to the consumption, accumulation, and loss of that material. All mass balance calculations must account for all routes of inflow and outflow, as well as any accumulation or depletion of the substance in the equipment, including control devices, and through any chemical reaction.

Examples Using Mass Balance

1. Estimating Emissions Using Mass Balance with a Single Component

In one process, facility "Z" uses a solvent bath to clean its product, widgets. The solvent density is 7.7 lbs per gallon. (The density of the solvent is used to convert from gallons of solvent to pounds of solvent in the emissions calculation.) Substance A is the only substance in the solvent for which emissions must be quantified, and it constitutes 87% of the solvent by weight. At the beginning of 1989, the facility had 7,500 lbs of this solvent in storage and purchased another nine tons over the year. At the end of 1989, the facility has 10,000 lbs in storage.

A. Annual Average Emissions

Assumptions:

a. Solvents are typically volatile, and the total volume is usually emitted to the atmosphere. Thus, emissions equal amount of solvent used.
b. No control device is used to reduce the emissions of solvent.

Because emissions equal the amount of solvent used, emissions (EMS) are determined using the following equation:

$$EMS = (SB + SI - SE) \times F \qquad (5)$$

Where:

EMS	=	Annual emissions of substance A, lbs/yr
SB	=	Amount of solvent in storage at the beginning of the year, lbs
SI	=	Amount of solvent purchased during the year, lbs
SE	=	Amount of solvent left in storage at the end of the year, lbs
F	=	Fraction of substance A in the solvent, lbs A/lb solvent

EMS = [7,500 lbs + (9 tons x 2,000 lbs/ton) - 10,000 lbs] x 0.87 lb A/lb solvent

= 15,500 lbs x 0.87 lb A/lb solvent

= 13,485 lbs of substance A emitted in 1989

B. Maximum Hourly Emissions

The facility operator reviews the facility's production records for the maximum amount of solvent used in the tank in a one-hour period, and uses the following equation to determine the maximum solvent used in an hour.

Assume other process parameters remain the same throughout the year.

$$HEMS_{max} = [(SBH + SIH - SEH) \times D] \times F \qquad (6)$$

Where:

$HEMS_{max}$	=	Maximum hourly emissions of substance A, lbs/hour
SBH	=	Amount of solvent in bath at start of hour, gallons
SIH	=	Amount of solvent added throughout the hour, gallons
SEH	=	Amount of solvent remaining in bath at the end of hour, gallons
D	=	Density of solvent, lbs/gallon
F	=	Fraction of substance A in solvent, lbs A/lb solvent

The facility operator determines the parameters of the facility's maximum hourly emissions, and inserts these values into Equation (6) to estimate maximum hourly emissions. There are 10 gallons of solvent in the widget cleaning tank at the beginning of the hour. At the

end of the hour, there are 9.03 gallons of solvent left in the tank. No solvent was added during the hour.

$$HEMS_{max} = (10 \text{ gals} + 0 \text{ gals} - 9.03 \text{ gals})\text{hr} \times 7.7 \text{ lbs/gal} \times 0.87 \text{ lb A/lb solvent}$$

$$= 6.5 \text{ lbs of substance A emitted/hour (rounded off)}$$

2. Estimating Emissions Using Mass Balance With Multiple Components

A facility uses a solvent "B" that is 16% perchloroethylene (PERC), 28% methyl chloroform (1,1,1-trichloroethane or TCA), and 45% xylenes by weight. The remaining 11% consists of components not found on the list of substances to be quantified. The facility began 1989 with 1,250 lbs of solvent "B" in storage. The facility purchased 1,500 lbs that year, and when 1989 ended had 875 lbs of solvent "B" in storage. The facility operates 8 hours per day, 260 days per year. Although the facility operator does not keep count of hourly production rates, purchase records indicate that the maximum daily amount of solvent "B" used is 7.88 lbs.

Assumptions:

a. No solvent is reclaimed.
b. All solvent used is eventually emitted to the atmosphere.

The facility operator estimates the annual average and maximum hourly emissions of PERC, TCA, and xylenes as follows (Remember: input = output):

A. Annual Average Emissions

Equation (5) is also applicable in this example, and is repeated here. In the calculation, emissions of each substance is rounded off.

$$EMS = (SB + SI - SE) \times F \qquad (5)$$

Where:

EMS = Annual emissions of listed substance, lbs/yr
SB = Amount of solvent in storage in the beginning of the year, lbs
SI = Amount of solvent purchased during the year, lbs
SE = Amount of solvent left in storage at the end of the year, lbs
F = Fraction of listed substance in the solvent, lbs of listed substance/lb of solvent

<u>Emissions of PERC</u>

$$EMS = (1{,}250 \text{ lbs} + 1{,}500 \text{ lbs} - 875 \text{ lbs}) \times (0.16 \text{ lb PERC/lb solvent "B"})$$

$$= 1{,}875 \text{ lbs} \times 0.16 \text{ lb/lb}$$

$$= 300 \text{ lbs of PERC emitted in 1989}$$

Emissions of TCA

EMS = (1,250 lbs + 1,500 lbs - 875 lbs) x
(0.28 lb methyl chloroform/lb solvent "B")

= 1,875 lbs x 0.28 lb/lb

= 525 lbs of methyl chloroform emitted in 1989

Emissions of Xylenes

EMS = (1,250 lbs + 1,500 lbs - 875 lbs) x
(0.45 lb xylene/lb solvent "B")

= 1,875 lbs x 0.45 lb/lb

= 844 lbs of xylenes emitted in 1989

For a quick check on whether or not the annual average calculations are correct, add the individual quantities of each listed substance emitted to determine whether the total equals the percentage of listed substances to be quantified.

In this example, the individual quantities of substances emitted are:

300 lbs/yr + 525 lbs/yr + 844 lbs/yr

= 1,669 lbs of three quantified substances in solvent "B" emitted/year

The operator needs to quantify 89% of solvent "B."

1,875 lbs/yr x .89 lb to quantify/lb "B"

= 1,669 lbs of PERC, TCA, and Xylenes emitted in 1989

The calculation is correct.

B. Maximum Hourly Emissions

In this example, the maximum daily emission rates of each listed substance have been determined. The facility operator estimates the maximum daily emissions for each listed substance as follows:

$$DEMS_{max} = DS_{max} \times F \qquad (7)$$

Where:

$DEMS_{max}$ = Maximum daily emissions of a listed substance, lbs/day

DS_{max} = Maximum daily emissions of solvent "B", lbs/day

F = Fraction of listed substance in solvent "B", lbs/lb

The facility operator estimates the maximum hourly emissions of each listed substance as follows:

$$HEMS_{max} = DEMS_{max} \div DHO \qquad (8)$$

Where:

$HEMS_{max}$ = Maximum hourly emission of a listed substance, lbs/hr

$DEMS_{max}$ = Maximum daily emissions of solvent "B", lbs/day

DHO = Daily hours of operation, hours/day

The operator uses Equations (7) and (8) together to calculate the maximum hourly emissions of the three listed substances in solvent "B" as follows:

<u>Emissions of Perchloroethylene</u>

$DEMS_{max}$ = 7.88 lbs solvent "B"/day x .16 lb PERC/lb solvent "B"

= 1.26 lbs PERC/day

$HEMS_{max}$ = 1.26 lbs/day ÷ 8 hours/day

= 0.16 lbs of perchloroethylene emitted/hour

<u>Emissions of Methyl Chloroform</u>

$DEMS_{max}$ = 7.88 lbs solvent "B"/day x .28 lb methyl chloroform/ lb solvent "B"

= 2.21 lbs methyl chloroform/day

$HEMS_{max}$ = 2.21 lbs/day ÷ 8 hours/day

= 0.28 lbs of methyl chloroform emitted/hour

<u>Emissions of Xylenes</u>

$DEMS_{max}$ = 7.88 lbs solvent "B" emitted/day x .45 lbs xylenes/lb of solvent "B"

= 3.55 lbs xylenes/day

$HEMS_{max}$ = 3.55 lbs/day ÷ 8 hours/day

= 0.44 lbs of xylenes emitted/hour

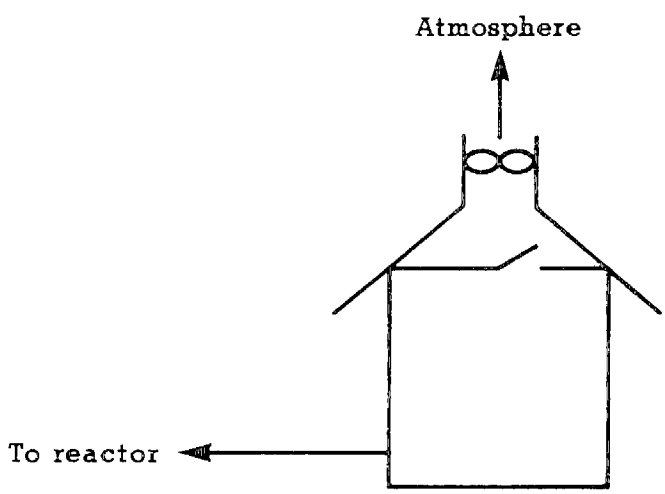
Engineering Calculations

Engineering calculations involve the use of principles of chemistry and physics to estimate emissions. (For example, information derived from the ideal gas law is frequently used to establish gaseous concentrations of a particular substance.) Engineering calculations generally provide "fill-in" information needed for another emission estimation method when emissions cannot be directly estimated. Information about the design of the unit of operation, equipment design, or emission information from similar processes are used to calculate emissions.

Examples Using Engineering Calculations

1. Estimating Releases From a Process Vent

A facility withdraws liquid from a process tank to feed a reactor. The mixture in the tank contains 5 percent by weight of substance A, 15 percent by weight of substance B, and 80 percent by weight of substance C. To prevent possible explosion, the vessel is vented at the top of the tank under a hood. A fan is used to draw the vapor to the atmosphere at the rate of 0.5 cubic feet per minute (measured at 70°F). This fan is operated continuously for 200 days per year. The process is simplified in the following figure:



Assumptions:

a. Vapor above the liquid in the tank is continuously emitted to the atmosphere at the exhaust rate of the vent.
b. The substance content vapor is constant in composition.

The facility operator estimates emissions of any species from the tank as follows (any component in the mixture is denoted the "ith" species):

$$EMS_i = [ER \times Y_i \times (K_v)^{-1}] \times MW_i \quad (9)$$

Where:

EMS_i = Emissions of the ith species, lbs/yr

ER = Exhaust rate, ft^3/yr

Y_i = Mole fraction or volume fraction of the ith species in vapor phase, dimensionless

K_v = Conversion factor from molar unit to volumetric unit, ft^3/lb-mole

MW_i = Molecular weight of the ith species, lb/lb-mole

The facility operator calculates the exhaust rate, ER, from the vent rate and the operation rate as follows:

$$ER = 0.5\ ft^3/min \times 60\ min/hr \times 24\ hr/day \times 200\ days/yr$$

$$= 1.44 \times 10^5 ft^3/yr$$

Assume equilibrium exists between vapor and liquid in the tank. For an ideal solution, the relationship (also known as Raoult's Law) among the partial pressure, the liquid mole fraction, and the vapor pressure of any component in the mixture is:

$$p_i = X_i \times p_i^o \quad (10)$$

Where:

p_i = Partial pressure of component i, atmosphere

X_i = Mole fraction of the ith species in the liquid, dimensionless

p_i^o = Vapor pressure of pure component i, atmosphere

For an ideal gas, partial pressure of any component (also known as Dalton's Law) is expressed as:

$$p_i = Y_i \times P_T \quad (11)$$

Where:

Y_i = Mole fraction of component i in the gas, dimensionless

P_T = Total pressure of the vapor, atmosphere

By setting Equation (10) equal to Equation (11), the facility operator determines the mole fraction in the vapor.

$$Y_i = (P_i^o \div P_T) \times X_i \qquad (12)$$

Assume the vapor is exposed to air; therefore the total pressure is equal to 1.0 atmosphere.

Note: Raoult's Law works best if the liquid and the gas are ideal solutions. For ideal solutions, the components in the liquid mixture are very similar chemically and physically, and the pressure of the gas is relatively low (approximately less than 3 atm). A more rigorous approach to estimating the gaseous mole fraction requires the Henry's Law constants in place of the pressure ratios. Henry's Law is applicable to non-ideal solutions, and these constants must be determined experimentally for each substance.

Only weight percents of the liquid components are provided; therefore the liquid mole fraction, X_i, is estimated as follows:

$$X_i = [\, Wt_i \div MW_i \,] \div \Sigma\, [\, Wt_i \div MW_i \,] \qquad (13)$$

Where:

Wt_i = Fraction by weight, dimensionless
MW_i = Molecular weight, lb/lb-mole

The symbol Σ represents the summation of all species in the solution. As an example, the facility operator calculates the liquid mole fraction of A in the mixture as follows:

$$\text{Mole fraction of A} = \frac{\dfrac{Wt\ A}{MW_A}}{\dfrac{Wt\ A}{MW_A} + \dfrac{Wt\ B}{MW_B} + \dfrac{Wt\ C}{MW_C}}$$

To calculate the liquid mole fraction, X_i, and the vapor mole fraction, Y_i, the facility operator needs the physical properties of the substances A, B, and C. The Handbook of Chemistry and Physics is one source. Some other sources that provide information on the physical properties of substances include the Chemical Engineering Handbook and the Handbook of Environmental Data on Organic Chemicals. In this example, the data for A, B, and C are:

Substances	Molecular Weight	Vapor Pressure (atm)
A	78	0.10
B	92	0.03
C	106	0.01

From the above properties, the facility operator uses Equation (13) to calculate the liquid mole fraction of X_A, of substance A:

$$X_A = [.05 \div 78] \div [(.05 \div 78) + (.15 \div 92) + (.80 \div 106]$$

$$X_A = 0.065$$

Similarly, the facility operator calculates X_B and X_C as 0.166 and 0.769, respectively.

Using Equation (12) and the calculated liquid mole fraction of A, X_A, the facility operator calculates the vapor mole fraction of A, Y_A, as follows:

$$Y_A = (0.10 \div 1.0) \times 0.065$$

$$= 0.0065$$

The vapor mole fractions Y_B and Y_C are 0.005 and 0.00769, respectively. Because the total of vapor mole fractions equals 1.0, the balance of 0.922 is air.

To estimate the conversion factor, K_v, from molar unit to volumetric unit, the facility operator would use Equation (14) as follows:

$$K_v = 359 \text{ ft}^3/\text{lb-mole} \times [(T_a + 460)\ ^oR \div (32 + 460)\ ^oR\ ] \qquad (14)$$

Where:

T_a = Measured temperature of the vent exhaust, ^oF

Assume the vapor follows the ideal gas relationship. Therefore, one lb/mole of gas at standard temperature and pressure (32^oF and 1 atmosphere) occupies 359 ft^3/lb-mole. In this case, T_a is 70^oF; therefore the conversion factor is corrected to the actual temperature T_a. In this example, K_v is calculated as follows:

$$K_v = 359 \text{ ft}^3/\text{lb-mole} \times (70 + 460)\ ^oR \div (32 + 460)\ ^oR$$

$$= 387 \text{ ft}^3/\text{lb-mole}$$

With all the available data, the facility operator uses Equation (9) to estimate emissions of any substance as follows:

$$EMS_A = 1.44 \times 10^5 \text{ ft}^3/\text{yr} \times 0.0065 \times (387 \text{ ft}^3/\text{lb-mole})^{-1} \times 78 \text{ lb/lb-mole}$$

$$= 189 \text{ lbs/yr}$$

Emissions of species B are 171 lbs/yr and emissions of species C are 303 lbs/yr.

2. Estimating Emissions of Trace Metals Using Engineering Calculations, with a Control Efficiency

Facility A burns 5 million gallons of distillate oil a year in its boilers. The facility's boilers operate 12 hours per day, 300 days a year. The maximum amount of distillate oil the facility's boiler can burn is 2,000 gallons/hr. The facility hires a contractor to analyze its oil, and the contractor provides the following average trace metal composition from all the storage tanks in the facility as follows:

Metals	Concentration (ppmw)
Arsenic	0.01
Beryllium	0.003
Copper	0.01
Cadmium	0.20
Chromium	0.01
Lead	1.10
Mercury	0.04
Manganese	0.30
Nickel	5.2
Selenium	0.20
Zinc	0.02

The ppmw is the part per million by weight, or one unit mass of the substance per million unit masses of the fluid.

Assume all metals in the oil are emitted upon combustion.

The facility operator estimates the trace metal emissions resulting from burning the oil as follows:

$$EMS_i = (1 - CNTL_i) \times PR \times D \times C_i \qquad (15)$$

Where:

EMS_i = Annual emissions of the ith trace metal, lbs/yr

$CNTL_i$ = Control efficiency for the ith substance (expressed as fraction), dimensionless

PR = Amount of distillate oil burned per year, gals/yr

D = Density of distillate oil, lbs/gallon

C_i = Concentration of the ith element in distillate oil, ppmw or $lb/10^6$ lbs

Given that Facility A uses a baghouse (fabric filter) with an 85% control efficiency for trace metals except mercury. Assume the average density of distillate oil equals 7.2 lb/gal.

Using the nickel concentration of distillate oil, the facility operator estimates the annual average and maximum hourly emissions of nickel as follows:

A. Annual Average Emissions

Using Equation 15: (15)

$$EMS_i = (1 - .85) \times 5 \times 10^6 \text{ gals/yr} \times 7.2 \text{ lb/gal} \times 5.2 \text{ lb}/ 10^6 \text{lb}$$

$$EMS_i = 28 \text{ lb of nickel emitted per year}$$

Similarly, emissions for other trace contaminants are estimated by substituting their concentrations in distillate oil as reported. However, the operator knows that mercury behaves like a gas under these conditions and escapes through the baghouse. Therefore, for mercury, the control efficiency of the baghouse is zero.

B. Maximum Hourly Emissions

The maximum hourly process rate is available, and the operator uses Equation (15) to estimate maximum hourly emissions of nickel:

$$HEMS_{max} = (1 - .85) \times 2{,}000 \text{ gals/hr} \times 7.2 \text{ lbs/gal} \times 5.2 \text{ lbs}/10^6 \text{lbs}$$

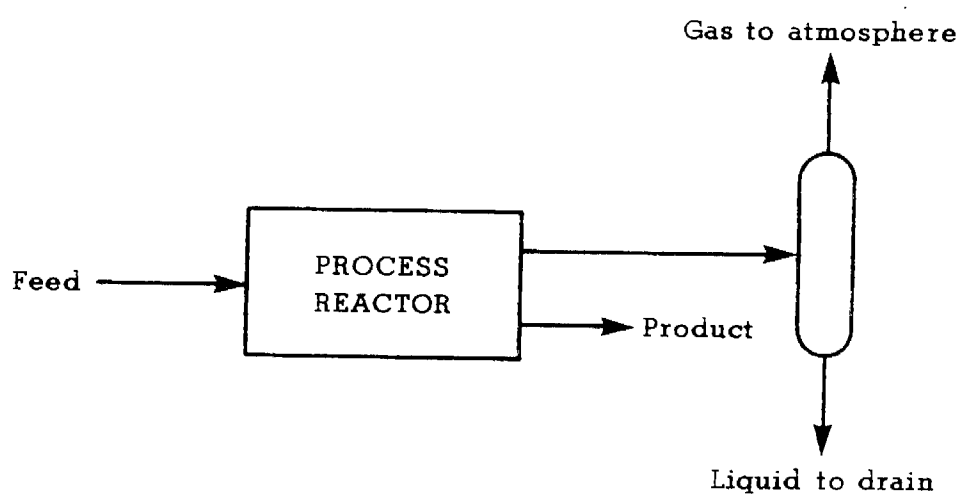
$$HEMS_{max} = .011 \text{ lbs of nickel emitted per hour}$$

<u>Note</u>: The calculation(s) in the above section apply to trace metals. Emission factors or source testing should be used to estimate emissions for organic gases such as benzene and formaldehyde.

3. Estimating Emissions of Carbon Tetrachloride Using Engineering Calculations Based on the Conversion of a Chemical Reaction

A facility manufactures a specific drug which uses 5,000 lbs per year of carbon tetrachloride as an intermediate. The operator determines that 90% of carbon tetrachloride is converted to the manufacturer's product, and only 10% of carbon tetrachloride is lost at the end of the process. The effluent of this process is 85% liquid and 15% gas by weight. The gas is vented to the atmosphere and the liquid is drained into the sewer. (The POTW accounts for the emissions from the sewer.) The maximum hourly usage at any given time is approximately 2 pounds. The weight ratio between carbon tetrachloride and other processed materials is 1:4.

To simplify the emission estimation, the process is diagrammed as follows:



Using the available information, the facility operator estimates carbon tetrachloride emissions as follows:

The calculation for emissions vented directly to the atmosphere at the plant is:

$$EMS_1 = [(R \times PR) \times (1 - x_c)] \times (1 - L) \qquad (16)$$

Where:

EMS_1	=	Emissions of carbon tetrachloride from exhaust, lbs/yr
R	=	Weight ratio of carbon tetrachloride to feed material, dimensionless
PR	=	Amount of feed materials, lbs/year
x_c	=	Fraction of conversion, carbon tetrachloride, dimensionless
L	=	Fraction of liquid discharged into the sewage, dimensionless

A. Annual Average Emissions

Using Equation (16) and the information provided about the process, the operator estimates carbon tetrachloride emissions directly at the plant as:

$$EMS_1 = (.20) \times 5{,}000 \text{ lbs/yr} \times (1 - .90) \times (1 - 0.85)$$
$$= 15 \text{ lbs/yr}$$

B. Maximum Hourly Emissions

To estimate maximum hourly emissions, the operator uses Equation (16) along with the facility's hourly process rate of 2 lbs/hour:

$$HEMS_{max} = [(.20) \times 2 \text{ lbs/hour} \times (1-0.90) \times (1-0.85)$$
$$= 0.006 \text{ lb/hour}$$

Speciation Profiles

A speciation profile lists the chemical composition of total organic gases (TOG) or particulate matter (PM) by specific device/process. These profiles are developed from a variety of sources including actual measurements and engineering judgments. Speciation profiles do not always provide an accurate method for estimating emissions, and may not include all AB 2588 substances that need to be quantified. Therefore, facility operators should use one of the other methods discussed in this chapter, if that method gives a more accurate estimate of emissions.

To determine emissions using a speciation profile, the operator must use the TOG or PM emissions and then multiply the TOG or PM emissions by the the fraction(s) of the substance(s) to be quantified in the speciation profile. TOG or PM emissions can be obtained by measurement or by the use of methods similar to those in this chapter. Where emission factors for TOG or PM are needed, the operator should consult the appropriate district. In addition, the Compilation of Air Pollution Emission Factors, Volume I: Stationary Point and Area Sources, (EPA AP-42) can be used to find emission factors. However, when looking for factors for total organic gases, the operator needs to obtain the emission factor for total organics and not just the reactive gases.

Once the operator has the TOG or the PM emissions, the operator finds the speciation profile in the ARB manual entitled Identification of Volatile Organic Compounds Series Profiles, (ARB Speciation Manual). This manual contains approximately 500 speciation profiles for TOG and approximately 70 profiles for PM emissions. Copies of this manual are available at the district office. If no ARB speciation profile is available, the EPA Air Emissions Species Manual Volume I: Volatile Organic Compound Series Profiles is another reference for speciation profiles.

Example Using Speciation Profile

1. Estimating Emissions from an External Combustion Boiler Using an ARB Speciation Profile

Facility "W" uses an external combustion boiler which burns natural gas. The facility operates 300 days per year, 12 hours per day, and emits 1,500 lbs of TOG daily from this natural gas combustion. After reviewing this document, the facility operator realizes that the the EETs in Chapter V and the generic methods in Chapter III are not appropriate for the facility's emitting process, and the operator considers using a speciation profile.

The facility operator knows that the facility's Source Classification Code is 1-03-006-03. Using the ARB Speciation Manual with the Source Classification Code, the operator finds the ARB speciation profile code is #3. This profile lists several substances, but emissions of only three of these substances must be quantified: formaldehyde, benzene, and toluene. The weight fraction of each substance in the exhaust gas is 0.0768 for formaldehyde, 0.0325 for benzene, and 0.0164 for toluene.

Although the facility does not keep account of the hourly production rates, the operator does know that the maximum daily emissions of TOG are 1,750 lb a day, and then estimates emissions of the listed substances using the following equations:

$$EMS = PR \times F \qquad (17)$$

Where:

EMS = Emissions of a listed substance, lb/yr
F = Fraction of the listed substance in the exhaust gas, dimensionless (wt/wt)
PR = 300 days/yr x 1,500 lbs/day of TOG
= 450,000 lbs/year of TOG

A. Annual Average Emissions

Emissions of Formaldehyde

EMS = 450,000 lbs/year x 0.0768

EMS = 34,560 lbs of formaldehyde emitted/year

Emissions of Benzene

EMS = 450,000 lbs/year x 0.0325

EMS = 14,625 lb of benzene emitted/year

Emission of Toluene

EMS = 450,000 lbs/year x 0.0164

EMS = 7,380 lb of toluene emitted/year

B. Maximum Hourly Emissions

$$HEMS_{max} = (DPR_{max} \times F) \div DHO \qquad (18)$$

Where:

$HEMS_{max}$ = Maximum hourly emissions, lb/hr

DPR_{max} = Maximum daily emissions of TOG, lb/day

F = Fraction of listed substance in the exhaust gas, dimensionless

DHO = Daily hours of operation, hr/day

Emissions of Formaldehyde

$HEMS_{max}$ = (1,750 lb of TOG/day x 0.0768) ÷ 12 hr/day

$HEMS_{max}$ = 134.4 lbs/day ÷ 12 hr/day

$HEMS_{max}$ = 11.2 lbs of formaldehyde emitted/hour

Emission of Benzene

$HEMS_{max}$ = (1,750 lb of TOG/day x 0.0325) ÷ 12 hr/day

$HEMS_{max}$ = 56.87 lbs/day ÷ 12 hr/day

$HEMS_{max}$ = 4.74 lbs of benzene emitted/hour

Emission of Toluene

$HEMS_{max}$ = (1,750 lb of TOG/day x 0.0164) ÷ 12 hr/day

$HEMS_{max}$ = 28.7 lbs/day ÷ 12 hr/day

$HEMS_{max}$ = 2.39 lbs of toluene emitted/hour

REFERENCES

California Air Resources Board. May 1986. Improvement of the Emission Inventory For Reactive Organic Gases and Oxides of Nitrogen in the South Coast Air Basin, Volume I. Sacramento, California.

U.S. Environmental Protection Agency. December 1987. Compilation of Air Pollutant Emission Factors Volume I: Stationary Point and Area Sources. AP-42. 4th Edition. Research Triangle Park, North Carolina.

U.S. Environmental Protection Agency. December 1987. Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form. EPA-560/4-88-002. Washington D.C.

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CHAPTER IV
CONTROL DEVICE EFFICIENCIES

This Chapter provides facility operators with basic information on control device efficiencies. For the purposes of this document, control efficiency is defined as the fraction of the uncontrolled emissions collected and/or eliminated by the control device. Control devices are an essential part of the emission inventory plan and report, and facility operators must account for any depletion or accumulation of listed substances which pass through the control device(s). In Chapter III, the second sample engineering calculation "Estimating Emissions of Trace Metals Using Engineering Calculations, With A Control Efficiency" demonstrates the use of control efficiencies in the calculation of emissions.

To determine the exact control efficiency of a control device for any particular substance, the emissions of the substance at the inlet and outlet of the device must be directly measured. In cases where the operator is not using direct measurement, a control efficiency must be used from another source such as the manufacturer's performance tests. If the facility operator has substance/device-specific control efficiencies, he or she should submit them, with the appropriate justification, to the district for approval.

Few control efficiencies are available from the literature for the listed substances. Table 4 is a compilation of substance/device control efficiencies found in the literature which may be useful for the facility operator. These control efficiencies should be used under the conditions specified in the table.

If the facility operator cannot find substance/device control efficiencies, it **may** be possible to use control efficiencies for TOG or PM in determining emissions of listed substances. However, this method is **not** the preferred method of estimating emissions because it introduces a significant degree of uncertainty. Table 5 lists control efficiencies for TOG and PM. In many cases, ranges of efficiencies are given; the operator should use the lower end of the range unless the higher range can be justified.

There are numerous factors which affect the control efficiency of a control device. These include the substances emitted and their potential for chemical interaction. Particle size is another factor affecting control efficiency. Table 6 demonstrates the relationship between particle size and control efficiency, and shows the broad range of control of emissions of PM a facility operator might expect from a control device. The variation seen is based solely on particle size. Table 6 is a starting point for facility operators who use those types of control devices listed and have knowledge of the range of size of the PM the facility emits.

TABLE 4

CONTROL EFFICIENCIES FOR SPECIFIC DEVICES AND SUBSTANCES

Few specific control efficiencies exist for the substances on the AB 2588 list which must be quantified. The specific control efficiencies that exist are provided below.

Substance	Process/Device	Control Technology	Control Efficiency
Chlorine	General	Absorption in an alkali solution	90%
Hydrogen fluoride	General	Water absorption	95%
Hydrogen sulfide	General	Absorption in a sodium carbonate/water solution	98%
Hydrogen sulfide	General	Adsorption on ammonia-impregnated activated carbon	100%
Mercury	General	Absorption in a brine/hypochlorite solution	95%
Mercury	General	Adsorption on sulfur-impregnated activated carbon	90%
Perchloroethylene	Drycleaning-dryer exhaust	Carbon adsorber- packed bed, fluidized bed	95%
Phthalic anhydride	Production-main process vent	Wet scrubber	99%

TABLE 5: CONTROL EFFICIENCIES FOR TOTAL ORGANIC GASES AND PARTICULATE MATTER

Control Device/Method	Percent Efficiency Range By Substance Type	
	Particulate Matter (PM)	Total Organic Gases (TOG)
No control equipment	0	0
Wet Scrubber- High Efficiency	95 - 99.9	
Wet Scrubber- Medium Efficiency	80 - 95.0	
Wet Scrubber- Low Efficiency	70 - 80.0	
Gravity Collector- High Efficiency	95 - 99.9	
Gravity Collector- Medium Efficiency	80 - 95.0	
Gravity Collector- Low Efficiency	20 - 80.0	
Centrifugal Collector High Efficiency-	95 - 99.9	
Centrifugal Collector Medium Efficiency-	80 - 95.0	
Centrifugal Collector Low Efficiency-	20 - 80.0	
Electrostatic Precipitator High Efficiency-	95 - 99.9	
Electrostatic Precipitator Medium Efficiency-	80 - 95.0	
Electrostatic Precipitator Low Efficiency-	60 - 80.0	
Gas Scrubber (general, not classified)		70 - 99.0
Mist Eliminator, High Velocity (v > 250 ft/min)-	70 - 99.0	
Mist Eliminator, Low Velocity (v < 250 ft/min)-	50 - 99.9	
Fabric Filter, High Temp. (T > 250 F)-	75 - 99.9	
Fabric Filter, Medium Temp. (180 F < T < 250 F)-	80 - 99.9	

TABLE 5: CONTROL EFFICIENCIES FOR TOTAL ORGANIC GASES AND PARTICULATE MATTER Cont.

Control Device/Method	Percent Efficiency Range By Substance Type	
	Particulate Matter (PM)	Total Organic Gases (TOG)
Fabric Filter, Low Temp. (T < 180 F)-	80 - 99.9	
Catalytic Afterburner-	80 - 95.0	90 - 99.0
Catalytic Afterburner (with Heat Exchanger)-	80 - 95.0	90 - 99.0
Direct Flame Afterburner-	25 - 70.0	94 - 99.9
Direct Flame Afterburner (with Heat Exchanger)-	25 - 70.0	94 - 99.9
Flaring-	25 - 98.0	90 - 99.9
Process Change-	10 - 90.0	10 - 90.0
Vapor Recovery System (including condensers, hooding, and other enclosures)-		85 - 90.0
Activated Carbon Adsorption-		85 - 99.0
Liquid Filtration System-	50 - 99.9	
Packed-Gas Absorption Column-	70 - 99.0	70 - 99.0
Tray-Type Gas Absorption Column-	70 - 99.0	70 - 99.0
Spray Tower-	90 - 99.0	70 - 99.0
Venturi Scrubber-	90 - 99.0	70 - 99.0
Process Enclosure-	50 - 99.0	
Impingement Plate Scrubber-	20 - 99.0	20 - 99.0
Dynamic Separator (Dry)-	20 - 99.9	
Dynamic Separator (Wet)-	20 - 99.9	
Mat or Panel Filter-	10 - 95.0	
Metal Fabric Filter-	50 - 99.0	
Process Gas Recovery-		95 - 99.9
Dust Suppression By Water Sprays-	0 - 99.9	
Dust Suppression By Chemical Stabilizers or Wetting Agents-	0 - 99.9	
Gravel Bed Filter-	90 - 99.9	
Annular Ring Filter-	90 - 99.9	

TABLE 5: CONTROL EFFICIENCIES FOR TOTAL ORGANIC GASES AND PARTICULATE MATTER Cont.

Control Device/Method	Percent Efficiency Range By Substance Type	
	Particulate Matter (PM)	Total Organic Gases (TOG)
Fluid Bed Dry Scrubber-	90 - 99.9	
Tube and Shell Condenser-		20 - 99.9
Refrigerated Condenser-		20 - 99.9
Barometric Condenser-		20 - 99.9
Single Cyclone-	25 - 99.0	
Multiple Cyclone w/o Fly Ash Reinjection-	50 - 99.9	
Multiple Cyclone w/ Fly Ash Reinjection-	50 - 99.9	
Chemical Oxidation-	20 - 99.9	20 - 99.9
Ozonation-		10 - 99.9
Chemical Neutralization-	10 - 99.9	10 - 99.9
Activated Clay Adsorption-		20 - 99.9
Wet Cyclonic Separator-	20 - 99.9	
Water Curtain-	10 - 95.0	10 - 95.0
Nitrogen Blanket-		10 - 99.0
Conservation Vent-		10 - 99.9

TABLE 6: CONTROL EFFICIENCIES RELATED TO PARTICLE SIZE

Device	Particle Diameter (μm)	Control Efficiency
High Efficiency Cyclone	0.4	5%
	2.5	50%
Venturi Scrubber*		
P = 10 inches H2O	0.4	20%
	1.2	99%
P = 20 inches H2O	0.1	15%
	1.0	99%
P = 100 inches H2O	0.28	99%
	1.1	99.9%
Filter Fabric	0.10	99.8%
	0.35	99.2%
	4.0	99.9%
	10.0	99.6%
Electrostatic Precipitators (ESPs)		
Hot	0.05	99.2%
	0.50	97.0%
	7.0	99.95%
Cold	0.015	80%
	0.10	96%
	0.40	92%
	7.0	99.9%
Calvert Collision Scrubber		55.2 - 99.8%

*P = Pressure

REFERENCES: CHAPTER IV

California Air Resources Board. January 1988. Instructions For the Emission Data System Review and Update Report: Appendix III Source Classification Codes and EPA/NEDS Emission Factors. Sacramento, California.

California Air Resources Board. 1982. Air Pollution Technology: Controls for Fine Particle Emissions from Industrial Sources in California. Sacramento, California.

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U.S. Environmental Protection Agency. September 1986. Control Technologies for Hazardous Air Pollutants. EPA-625/6-86-014. Research Triangle Park, North Carolina.

CHAPTER V
SPECIFIC EMISSION ESTIMATION TECHNIQUES

This Chapter contains process/device-specific emission estimation techniques (EETs). This first set of EETs was developed with technical review from the technical advisory committee identified in Chapter I. The ARB initiated the development process by requesting district representatives to submit a list of those processes/devices with significant toxic emissions in their respective districts. These lists were then compiled and evaluated by the ARB staff to form a prioritized list of processes/devices for the Air Toxics "Hot Spots" program.

Time constraints did not allow the ARB staff to develop an EET for each process/device on the prioritized list. As the "Hot Spots" program progresses, more EETs will be developed and included in this Technical Guidance Document.

If an operator has not been able to utilize a generic emission estimation method and an EET has not been developed for the facility's process, the ARB staff recommends that the operator review the available EETs in this Chapter. While process-specific, each EET explains the use of one or more of the general methods described in Chapter III. A process described in an EET may be sufficiently similar to the process at the operator's facility to allow the operator to use the estimation method in that particular EET. If the operator is still in doubt as to whether an estimation method described in Chapter III or in an EET is appropriate, the operator should contact the appropriate air pollution control district or air quality management district. Table 7 below lists the general methods used in each EET.

TABLE 7

GUIDE TO GENERIC ESTIMATION METHODS DISCUSSED IN THE EMISSION ESTIMATION TECHNIQUES (EETs)

Emission Estimation Technique	Generic Estimation Method(s)
Chrome Electroplating	Emission Factor Mass Balance
Combustion of Petrolemm Derivatives	Emission Factor Engineering Calculation
Incineration	Emission Factor
Oil and Gas Production	Engineering Calculation
Oil Refinery	Engineering Calculation
Perchloroethylene Production	Emission Factor
Smelters and Secondary Foundries	Mass Balance Emission Factor Engineering Calculation (With Examples of Control Efficiencies)
Storage Tank	Engineering Calculation
Surface Coating	Mass Balance (Estimation of solvents emitted by evaporation)
Wood-Fired Boilers	Engineering Calculations

EMISSION ESTIMATION TECHNIQUE: CHROME ELECTROPLATING

CHROME ELECTROPLATING
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique (EET), developed by the Air Resources Board staff in accordance with the Air Toxic "Hot Spots" Information and Assessment Act of 1987 (the Act). Specifically this report describes the processes used in the electroplating of metals. This process results in the air emission of toxic substances listed pursuant to the Act. This report specifies the method(s) a facility operator would use to calculate resulting emissions of these listed substances.

A number of different industries use electrolytic deposition (electroplating) to decorate and coat a variety of industrial and consumer goods, resulting in emissions of listed substances such as chromium (VI) as well as methyl chloroform (1,1,1-trichloroethane), trichloroethylene, perchloroethylene, methylene chloride, and fluorocarbon-113. The focus of this EET is quantifying emissions of chromium (VI) as well as other listed substances.

The listed substance chromium (VI) is very toxic. The cancer unit risk value, 1.5×10^{-1} (ug/m^3), for chromium (VI) is the highest among commonly used industrial substances such as benzene, carbon tetrachloride, methylene chloride, or perchloroethylene. (A cancer unit risk value relates the possibility that one person in a million, exposed over seventy years, will get cancer).

II. PROCESS DESCRIPTION FOR ELECTROPLATING WITH CHROME

The process(es) used in chrome electroplating depend upon the function of the plating and the composition of the work piece. Generally, a workpiece must be cleaned prior to electroplating.

A. Cleaning

Several cleaning steps are possible including physically removing loose dirt and scale from the workpiece with a wire brush or wire wheel, or soaking it in a solvent bath to remove paint or grease.

Possible intermediate steps include: soaking the work piece in an alkaline bath, electrocleaning, and pickling. In electrocleaning, a current is passed through the alkaline bath, mechanically and chemically removing dirt. A final intermediate step is pickling, soaking the work piece in an acid bath and possibly passing an electric current through it. Once cleaned, the work piece is ready for electroplating.

Thirty percent of chrome electroplating is for decorative purposes while seventy percent is for wear- and corrosion-resistance purposes.

However, of that seventy percent, ten percent involves chromic acid anodizing.

B. Decorative and Hard Electroplating

Although differing in their function, decorative and hard plating are similar in that the workpiece is placed in a chromic acid bath as a cathode of an electrolytic cell.

Typically, a layer of chrome with a thickness of 0.25 microns

(10^{-5} inches) is applied as a protective and decorative coating to such items as auto parts, furniture, and plumbing fixtures. In hard

plating, a layer of chrome with a thickness of 10-300 microns (10^{-4} to .01 inch) is applied to such workpieces as tools, rollers, and pump shafts.

Decorative and hard electroplating occur in tanks containing chromic acid and a catalyst, generally sulfuric acid. A workpiece is placed in a chromic acid bath as a cathode of an electrolytic cell; then a low voltage, direct current is applied across the cell. Positively charged, chromium (VI) is drawn to the work piece and the metal is deposited on it.

During this process, electrolysis occurs; water is broken down into hydrogen and oxygen, and with these bubbling gases, chromium can be dispersed into the air. Eighty to ninety percent of the current that is consumed results in the breakdown of water into hydrogen and oxygen. The remaining 10 to 20 percent of current is used for the actual electroplating process. Any remaining chromium (VI) must be reduced to trivalent chromium (a much less toxic substance than chromium (VI)). Substances such as ferrous sulfate, iron, sodium bisulfate, and sulfur dioxide may be used to facilitate reduction.

C. Anodizing

Unlike decorative and hard plating, in anodizing an aluminum or magnesium workpiece is placed in a bath of chromic acid as the anode of an electrolytic cell (positive electrode); then a low voltage, direct current is passed through the bath. In the process, chromium (VI) is reduced and the surface oxidized (adds free oxygen) to form a protective finish.

III. POTENTIAL SOURCES OF EMISSIONS

Cleaning

As discussed in Section II, five steps are generally taken to clean a workpiece prior to electroplating, and within each step emissions of toxic listed substances are possible. During the cleaning process, several solvents are used that contain listed substances including 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, methylene chloride, and fluorocarbon-113.

a) Emissions of potentially toxic particulate matter are of primary concern when dirt and scale are physically removed.

b) Emissions of potentially toxic vapors and mists, especially in the work area, are of primary concern during the the soaking process.

c) Emissions from caustic aerosols, especially in the work area, are of primary concern during the alkaline bath and during electrocleaning.

d) Emissions from caustic aerosols, especially in the work area, are of primary concern during electrocleaning.

e) Emissions of toxic substances during pickling and electropickling are possible.

Chrome Electroplating

The electroplating process itself is a primary source of toxic emissions. The bubbling of the plating bath, due to electrolysis, disperses chromium (VI) as an aerosol or mist. If there is no control equipment or if such equipment is not working properly, the chromium (VI) can reach the ambient air. Workplace emissions may reach the ambient air through the vents for the exhaust fans in the plant's circulation system.

IV. CONTROL DEVICES

An emission control device may greatly reduce air pollutants leaving a device relative to those entering a device. Any one of the following possibilities, or combinations of them, exist when an air pollutant enters a control device. The pollutant may be transferred from the air stream to another medium, be modified to a less toxic state, destroyed through combustion and/or dissociation, or it may pass through untreated. When a pollutant is transferred into another medium, the medium is a potential source of emissions. If the medium has any emissions while located anywhere on the facility site, the emissions must be accounted for. Emission estimates must take into account the effect of the control device(s) used. Usually the efficiency of the control device must be known. The data used

should reflect the efficiency achieved during typical day-to-day operations, not the theoretical optimum efficiency. The control efficiency used in estimating emissions of each listed substance must be justified by the facility operator, and the justification must be cited.

The ARB has determined that in the electroplating process, the following control devices are applicable: a ventilation system channeled through a system of scrubbers is the principle method used to control emissions from the plating system. The most common type of scrubbers utilized are water misting/recycling systems. These scrubbers are associated with slot vents by the tank sides. These slot vents remove toxic mists and vapors prior to those mists and vapors entering the breathing zone of the plant employees. There are other scrubbers that utilize an alkaline solution that neutralizes the vapors and mists produced during the electroplating process. Source tests in California have shown that a control efficiency of 75% can be achieved for chromium (VI) when such a ventilation system is used.

Other control devices for electroplating emissions include foams applied to the surface of the plating tanks. The EPA has estimated the control efficiency of foams to be 90 to 99 percen$in reducing emissions of chromium (VI). For the purposes of developing emission factors for use by electroplating pursuant to the control phase of the Toxic Air Contaminant Identification and Control Program (the AB 1807 Program), a control efficiency of 95% has been used (1988 Technical Support Document to Proposed Hexavalent Chromium Control Plan.)

V. EMISSION ESTIMATES

Source testing is the preferred method of accurately determining toxic emissions of listed substances when testing is feasible and when approved, reliable methods exist. Although source testing is available for the chrome electroplating processes, the Air Toxics "Hot Spots" Emission Inventory Criteria and Guidelines Regulation accompanying this document does not require any new source testing for determining toxic emissions at this time. The regulation does require, however, that source test results be reported from all source testing performed pursuant to district regulations adopted to implement the ARB airborne toxic control measure for hexavalent chromium, which was adopted pursuant to the AB 1807 program.

Generally, for chrome electroplating operations, emission factors are used to quantify emissions of chromium (VI). The emission estimate must account for control devices used. Several emission estimation methods are discussed on the next several pages.

A. Mass Balance

In general terms, a mass balance procedure accounts for all input and output streams of a chemical in a whole process or subprocess. This procedure is useful for estimating emissions when emission data have not been measured, but input and output streams have been either measured or estimated.

The emissions can be calculated as the difference between the input and output streams. Any accumulation or depletion of the chemical in the equipment such as by reaction must also be accounted for. Individual operations within the mass balance usually must be evaluated.

Example Using a Mass Balance

Mass balance is appropriately used to estimate emissions of listed substances from cleaning solvent solutions. Plating Shop "A" uses a solvent bath that is 95% perchloroethylene. At the beginning of 1989, Plating Shop "A" had 4,000 pounds of this material in storage. The shop purchased 15,000 pounds; 7,000 pounds were left in storage when the year ended. Assuming no solvent is reclaimed, the emissions of perchloroethylene for that year are calculated as follows (remember: input = output):

(4,000 lbs. + 15,000 lbs.- 7,000 lbs.)(0.95) = Emissions of PERC, lbs/year

(12,000 lbs.)(0.95) = emissions of PERC, lbs/year

11,400 lbs. = lbs of perchloroethylene emitted in 1989

B. Emission Factors

Emission factors usually express air emissions as a ratio of the amount released of a pollutant to a process-related parameter or measurement ("usage unit"), frequently expressed as the amount of pollutant per throughput of a process or piece of equipment, or as the amount of pollutant per quantity produced or processed. The throughput must be quantified to use this type of emission factor. Emission factors for air emissions are commonly based on averages measured at several facilities within the same type of industry. The applicability and accuracy of emission factors are dependent on whether the chemical substances, processes, and equipment are substantially equivalent between those tested and those to which the emission factor is to be applied.

For chrome electroplating, the appropriate measure of throughput is the current applied to the plating bath.

To calculate chromium (VI) emissions, an operator must know the current applied to the plating bath (in amps), the emission factors for chromium (VI), and whether emission control equipment is in use.

Chromium (VI) Emission Factors For Uncontrolled Systems
Hard plating/anodizing: 5.2 mg/amp-hour
Decorative plating: 0.50 mg/amp-hour

Chromium (VI) Emission Factors For Controlled Systems
Hard plating/anodizing (scrubber): 1.3 mg/amp-hour

Hard plating/anodizing (foam)[1]: 0.26 mg/amp-hour
Decorative plating (scrubber): 0.13 mg/amp-hour

Decorative plating (foam)[1]: 0.025 mg/amp-hour

1- foam or foam plus scrubber

(Emission factor information was taken from ARB, 1988, Technical Support Document to Proposed Hexavalent Chromium Control Plan.)

Using the current (in amps) and these emission factors, an operator would calculate chromium (VI) emissions using the following equation:

$$\text{Emission factor (mg/amp-hours)} \times \frac{\text{gram}}{1000\text{ mg}} \times \frac{\text{lb}}{453.6\text{ grams}} \times \text{\# Amps} = \text{lb/hour}$$

Amps= the current used (in amperes)

The above hourly estimate is converted to annual emissions by multiplying by the number of hours of operation per year.

Example Using Emission Factors

Plating Shop "A" plates industrial equipment in a tank that is operated at an average current of 10,500 amps over the year. This shop also operates at a maximum of 12,000 amps. On an annual basis, shop "A" operates the chrome plating tank approximately 4,000 hours. Facility "A" currently has no emission control devices associated with its chrome electroplating operation. The chromium (VI) emissions are calculated as follows:

1. Annual Average Emissions of Chromium (VI) from Plating Shop A

Ems = 5.2 mg/amp-hour x gram/1,000 mg x pound/453.6 grams

X 10,500 amps x 4,000 hours/year

= 481.48 pounds/year

2. Maximum Hourly Emissions of Chromium (VI) from Plating Shop A

Ems = 5.2 mg/amp-hour x gram/1,000 mg x pound/453.6 grams

x 12,000 amps

= 0.138 pounds/hour

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EMISSION ESTIMATION TECHNIQUE: COMBUSTION OF PETROLEUM DERIVATIVES

COMBUSTION OF PETROLEUM DERIVATIVES
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

Many facilities in California use combustion processes to generate heat and/or power for various purposes, such as utility electrical generation, industrial mechanical power, and commercial or residential space heat. Although this EET only covers combustion of petroleum derivatives, every combustion process emits listed substances that should be reported. If the primary purpose of a combustion process is hazardous waste incineration, the incineration EET should be used. If the process is primarily for energy generation, and if relatively small amounts of hazardous waste are cofired (burned together) with oil or gas, or if waste fuel is used, this combustion EET should be used. The incineration EET may be helpful in estimating emissions from some waste fuels. This EET may also provide some general background for combustion processes which aren't specifically addressed herein.

Fuels which are petroleum derivatives include (but aren't limited to) all the standard liquid fuels such as fuel oils (residual, distillates and diesel), gasoline, kerosene, jet fuel, and light distillate gas turbine fuel. Also included are gaseous petroleum derivatives such as methane (natural gas), propane and butane, in gas or liquid form. In addition, there are the non-standard fuels such as crude oils, waste oils, waste solvents, and waste gasses, as well as process-derived fuels similar to those listed above, such as may be used in oil extraction and refining. Typically, process-derived fuels result from some process within a facility which yields a non-standard fuel which nevertheless has significant heating value.

Since combustion is such a complicated process, its toxic emissions are more difficult to estimate than those from most other processes. Combustion emissions typically include more listed substances than other process emissions, many of which (both organic and inorganic) can be emitted in gaseous and particulate form, simultaneously. A flow chart of the basic procedure to follow for each substance has been included for your reference. (See Fig. 1 in Section IV of this EET.)

The Facility Look-up Table (App. C of the Regulation) includes most of the listed substances which could be emitted. In addition, they are categorized in Table I of this EET. Given the complex nature of the combustion process, these tables may not include every listed substance which is being emitted, if the substances haven't actually been researched, tested, and mentioned in the literature. It should be noted, however, that facilities are still responsible for reporting known or suspected emissions of any listed substances. Also, the diversity of fuels and devices which are currently used appears to exceed the presently available information on emission factors and contaminant concentrations. Thus, this EET includes a general discussion of combustion (Section II) for reference when adjustment of existing information for a special situation is appropriate. Those readers only interested in the emission calculations should go directly to Sections IV and V.

The outline of the rest of the EET is given below, to assist you in finding the topic you need at any particular time.

I. Introduction (p. 1)
II. General Aspects of Combustion Processes (p. 2)
  A. Combustion Emissions
  B. Fuels
  C. Devices
  D. Control Devices
    1. Particulate Matter
    2. Gas/Vapor
III. Potential Emission Sources (p. 6)
IV. Emission Estimation (p. 6)
  A. Source Tests
  B. Fuel Analysis
  C. Emission Factors
  D. Control Efficiencies
V. Sample Calculations (p. 8)
VI. References (p. 17)
Attachment I (Table I)
Attachment II (Table II)
Attachment III (Table III)

II. GENERAL ASPECTS OF COMBUSTION PROCESSES

The main reason combustion is so complicated is the number and interactions of the variables involved. In addition to chemistry, heat and mass transfer play a very important role in theoretical descriptions of the process. On a practical level, the most important factors affecting combustion processes are:

Equivalence Ratio
Combustion Temperature
Residence Time
Quenching Effects
Design of Combustion Chamber & Air-Fuel Mixing Devices

The Equivalence Ratio (usually denoted by $\varnothing$) is defined as a ratio of ratios. Specifically, it is the ratio of the actual fuel-to-air ratio to the stoichiometric (chemically exact) fuel-to-air ratio. Thus, if $\varnothing = 1$ then the actual process provides exactly the number of oxygen molecules required to convert the fuel completely to CO_2. If $\varnothing < 1$, one has lean combustion, with excess air. If $\varnothing > 1$, one has rich combustion, with excess fuel. Lean combustion often gives rise to high NOx emissions, whereas rich combustion is associated with high emissions of CO and products of incomplete combustion (PICs). Generally, automobile engines have higher equivalence ratios than other combustion devices.

Combustion temperature also affects combustion efficiency, often in conjunction with residence time. Higher temperatures mean faster combustion, while lower combustion temperatures require longer residence times for complete combustion. Sometimes the situation is more complicated; combustion temperatures of 900-1450 deg. F have been found to promote dioxin formation, while higher temperatures promote its destruction (assuming of course the presence of chlorine in the fuel). (EPA 1984 Dioxin)

Quenching refers to rapid cooling of combustion products (or intermediates) such as would occur near a boiler's heat transfer surfaces, and is associated with formation/retention of PICs and with particulate matter condensation.

Efficiency of air-fuel mixing is a major factor in combustion chamber design as well as in fuel atomization and/or vaporization by means of special fuel injection and/or burner designs. Mixing is more important than often realized, since chemical oxidation can only occur if oxygen and fuel molecules come in contact. Such designs, many of them for energy efficiency purposes, also tend to reduce PIC formation. Gaseous fuels, such as natural gas, have a distinct advantage over oil in this respect, since it is much easier to mix two gasses on a molecular level than air and liquids or solids.

Secondary combustion is a fairly common pollution-control strategy which illustrates the interrelationship of several of these factors. It is an integral part of the combustion process whereby the PICs from first-stage combustion are mixed with additional air, for more complete combustion. While the temperature range is typically 1200-1700 deg. F, both oxygen concentration and residence time are apparently more important than temperature in promoting complete combustion. Complete oxidation of organic particulate is especially sensitive to residence time. (Edwards) Thorough mixing is very important since if oxygen and fuel molecules never meet, they cannot react chemically.

Combustion emissions will be minimized by well-tuned, steady-state combustion processes. Predictable process upsets or transients such as start-up and shut-down, load variations, and air or fuel feed variations, will result in higher emissions. While these may be part of normal operations, they will likely result in maximum emissions from combustion processes. Poor maintenance or poor operating practices will also typically result in increased emissions.

A. COMBUSTION EMISSIONS

These emissions include particulate matter (PM) and total organic gas (TOG), which together are expected to contain virtually all of the listed substances which combustion would be expected to produce. (Exceptions include H_2S, HCl, HF, phosgene and Hg.) Both of these categories give rise to a "species profile," which is the set of particle types or volatile organics and the fractions of each individual substance which make up the whole. For PM, both the particle sizes and the type and amount of substances present are defined by the profile. For TOG, only type and amount matter. Different devices and different fuels both lead to variations in these profiles. For example, destruction efficiencies have been found to be lower for more volatile organics in small commerical boilers. (EPA 1984 Waste Oils) All fuels can lead to both of these types of emissions, even natural gas in poor combustion conditions such as insufficient air or flaring.

In addition to benzene, toluene, xylene, aldehydes, and other common combustion emissions of listed substances, almost all combustion processes also emit polycyclic organic matter (POM), which includes polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Depending on the source, POM may include substances containing nitrogen, sulfur, chlorine, and oxygen, as well as hydrogen and carbon. POM formation correlates with poor combustion conditions as well as with high C/H ratios and high aromatic and oxygen concentrations in fuels. (EPA 1983 POM)

In cases of combustion of waste fuels or other sources of principal organic hazardous constituents (POHCs), there will be emissions of toxic products of incomplete combustion (PICs) which are formed during combustion and which would be considered POHCs if present in the fuel prior to combustion. This is of course in addition to the breakthrough emissions of POHCs. Mass emission ratios of toxic PICs to POHCs range from 5 to 20, with lower values in this range typical for incinerators and higher values typical for boilers. (Castaldini, Acurex/EPA, EPA 1985 Haz Waste) See Table III for default breakthrough factors for POHCs and formation factors for toxic PICs. While this table only includes conservative averages derived from the literature for boilers and flares, other values for other situations can be proposed in facility plans, based on the general discussion herein.

In 13 field emission tests of 8 industrial boilers, the most common halogenated toxic PICs were chlorinated methanes such as chloroform, dichloromethane, and chloromethane, and the most common non-halogenated toxic PICs were toluene and benzene. (Castaldini)

B. FUELS

Many listed substances (such as formaldehyde, PAHs, and other PICs) are formed from fuel components during the combustion process, while others (such as benzene and nickel) are present in the new fuel. All other combustion parameters being equal, fuels with higher molecular weight and higher carbon/hydrogen ratios lead to increased emission of heavier organics and of particulate. Also, the presence of chlorinated organics can promote PIC formation, and metals can catalyze certain reactions. (EPA 1984 Waste Oil Risk) Also, the presence of chlorine may lead to finer particulate matter. (CARB 1981)

New fuels can also contain a bewildering variety of additives, some of which contain metals, organometallics and/or complex organic compounds which may include listed substances. Waste fuels such as used oils and solvents typically contain more kinds and greater amounts of listed substances (particularly chlorinated organics, as well as PAHs and higher metal concentrations) than do new fuels. On the other hand, new fuels are only relatively clean. Residual oil ends up with many of the original crude oil contaminants, while others may contain additives (such as ethylene dibromide (EDB) in gasoline or metal additives in boiler fuel) which can lead to emissions of listed substances. Natural gas typically contains no metals, but its combustion will always lead to emissions of some PICs. Landfill gas may contain vinyl chloride, benzene, EDB, EDC, methylene chloride, perchloroethylene, carbon tetrachloride, chloroform, methyl chloroform, and TCE. (CARB 1986)

Particulate matter from oil combustion differs from particulate matter emitted from coal combustion. Coal particulate is characterized by "enrichment," whereby metals with low boiling points (particularly As, Cd, and Hg, and also to some extent Be, Cr, Cu, Mn and Ni) are partially or completely volatilized during combustion, and then tend to condense more on smaller particles which have a greater surface-to-volume ratio. Oil particulate has a different structure such that surface area may be less strongly related to particle size, resulting in less enrichment. (Radian 1986) ARB staff believes a conservative approach might be to assume that enrichment of oil PM is 80% of that of coal PM.

C. DEVICES

There are many combustion devices currently used, each of which is characterized by its own specific emissions. In general, these devices emit many of the same overall set of combustion products and contaminants, but typically in differing proportions. Combustion devices capable of burning petroleum derivatives include the following:

Boilers	Miscellaneous	
Firetube	Furnaces	Ovens
Watertube	Heaters	Flares (can be control devices in certain situations--see Section II.D.2 below)
Cast Iron	Dryers	
	Kilns	

Internal Combustion Engines
- Reciprocating Engines
  - Spark Ignition (gasoline)
  - Compression Ignition (diesel)
- Turbines (light distillate oil & natural gas)

For institutional and commercial space heat, firetube and cast iron boilers are typically used. Industrial boilers are usually either firetube or watertube. These devices use various designs for fuel atomization, such as mechanical, rotary cup, pressurized-air, and steam-atomized. Burner position(s) also vary, and include tangential (typical for utility boilers), front wall, and horizontally opposed. Many of the larger boilers also now incorporate various devices for NOx control, which are often an integral part of the combustion device and process, and can affect emissions of listed substances.

For combustion of waste fuels, firetube and cast iron boilers have been found to work better than watertube boilers (EPA 1984 Waste Oil Risk), possibly due to quenching considerations. (See above discussion of quenching.) For boilers larger than 1 MBtuh (M = 1E6), one study found no correlation between boiler size, firing method, and destruction efficiency. (EPA 1984 Waste Oils) Combustion of waste fuels in cement kilns works fairly well, since in addition to high temperatures and ample residence time, the alkali from the cement neutralizes the hydrochloric acid which is formed from the chlorinated organic contaminants. (CARB 1981) The Incineration EET also includes a discussion of boiler types.

D. CONTROL DEVICES

In general, pollution control devices are designed primarily for removal of either particulate matter or gasses and vapors. However, in some cases, a device which is intended to control one type of pollutant may also, as a side effect, remove some portion of the other type of pollutant when the two types occur together as in combustion. For example, a fabric filter (baghouse) which is installed for particulate removal may, through adsorption by, or chemical reaction with, the previously collected particles, retain a portion of NOx (which is known to react with organic particles). Similarly, organic vapors may adsorb onto particulate matter, especially organic particulate; in the case of dioxins and furans this apparently leads to decreased toxicity. (CARB 1981) Then there are devices such as wet scrubbers which may have been selected primarily for one or the other, but typically remove both. Another control

strategy with dual effectiveness is water injection. Although not very common except in gas turbines, it can reduce both NOx and soot formation.

Remember, though, that the efficiency rating given by the manufacturer or other reference is usually a general efficiency describing overall gas/vapor or particulate removal. Such overall efficiency ratings cannot be assumed to be equal to removal efficiencies for individual listed substances. Another important aspect of actual control device efficiency is the quality of operation and maintenance procedures. Many control devices need regular and careful attention if they are to continue to work as well as they did when recently installed. (Some control devices take a little time after installation to achieve maximum efficiency.)

The exact location of a given control device, with respect to the combustion chamber, can affect its efficiency. As combustion products travel away from the combustion chamber, they cool off, and an increasing portion of the gaseous exhaust condenses, into or onto particulate. A fair number of metals (such as mercury, arsenic and cadmium) and organic compounds (such as PAHs and other organics of intermediate molecular weight) can be affected in this way. Thus, a particulate control device should have a greater efficiency when installed further away from the combustion chamber, where temperatures are lower. Devices for vapor pollutant control would typically not be greatly affected by this phenomenon, although some such as carbon adsorption units may suffer from uneven or over-saturation.

1. Particulate Matter Control

The 5 main types of particulate control devices are:

Gravity Settlers (momentum separators, gravity spray towers)
Centrifugal Separators or Collectors (cyclones)
Electrostatic Precipitators (ESPs)
Scrubbers (spray towers, packed-bed unit, venturi scrubbers)
Filters (baghouses)

The selection of a specific particulate control device typically depends on the flow rate, temperature, the type of pollutant, the particle size distribution, and the particle concentration. Efficiency can be based on either the weight or the number of particles removed; for reporting purposes, efficiency in terms of weight should be used. Remember that overall efficiencies cannot be used for individual listed substances. Two kinds of information are needed to accurately estimate actual control efficiency for a specific particulate substance: 1) the particle size distribution of that substance and 2) the variation of control device efficiency with particle size. Gravity and centrifugal settlers typically aren't very good at collecting smaller particles (less than than 5-10 um in diameter). Venturi scrubbers and (especially) baghouses are more efficient than settlers at removing small particles. ESPs, on the other hand, are less efficient with particles having high or low electrical resistivities, but can be quite efficient at sub-micron particle removal. (Theodore) For particle sizes between 0.1-1 um, at least 95% efficiency is typical, with 98-99% for other sizes. (Pedco)

2. Gas/Vapor Controls

The 4 main types of gas-phase pollutant control are:

Condensation (contact & surface condensers)
Adsorption (with activated carbon or alumina, silica gel)
Absorption (packed or plate columns)
Incineration (flaring, thermal or catalytic oxidation)

The selection of a particular method and device depends on the type of pollutant and characteristics of the gas stream such as flow rate, temperature, pressure, humidity, and chemical reactivity. As with particulate control devices, the overall efficiency rating will differ from the efficiencies for individual listed substances. (Theodore)

Flares as control devices are most often found in the chemical, petroleum, and metallurgical industries. While exact flare efficiencies will probably never be available, some useful generalizations can be made. Flare stability is limited by insufficient gas exit velocities (i.e., insufficient heating value) and by excessively windy conditions. (The flare stability information below and in Table III cannot be assumed to be relevant when ambient breezes exceed about 5-10 mph.) For a given flare gas mixture, stability can be described by a ratio of actual gas exit velocity to the minimum exit velocity necessary to avoid flame extinction. For ratios exceeding 1.2 (1.5 for toluene), flares studied have shown combustion and destruction efficiencies of at least 98%. For ratios near 1, 90% is typical, but may decline as low as 50%. Particulate matter emissions are likely to occur in these transient unstable regions. (E&ERC 1986 & 1984, Eng'g-Science, EPA 1986 Flares)

The presence of chlorinated organic gasses in flares tends to inhibit combustion. For methyl chloride, flare flame stability correlated with H/Cl ratios. Also, excessive amounts of chlorine are likely to increase soot and POM emissions. (E&ERC 1986) On the other hand, H2S appears to burn more readily than some hydrocarbon gasses. Pilots will of course enhance stability, though at the expense of additional emissions. (EPA 1986 Flares) Steam injection can suppress significant soot and particulate matter formation unless too much results in quenching and decreased combustion efficiency. (E&ERC 1984, Eng'g-Science)

III. POTENTIAL EMISSION SOURCES

Combustion devices emit the majority of toxic air pollutants associated with combustion processes. The most common types are listed in section II.C of this EET. Virtually every indoor combustion device (except a residential gas stove) is required by code, if not by the local Air Pollution Control District or Air Quality Management District, to be vented to the outdoors through some sort of stack or flue, which represents the primary emission point source associated with combustion. Devices which are outdoors may also exhaust through stacks or flues. Some of these have only an exhaust pipe or short flue which is part of the combustion device.

Combustion devices which have been burning waste fuels or other toxic substances typically collect some portion of these substances and of related toxic products of incomplete combustion (PICs) on their interior surfaces, and

continue to emit such toxics after waste fuel has been replaced by standard fuels. (Acurex/EPA 1987)

If there are control devices which retain some of the substances which would otherwise be emitted at the time of combustion, the possibility of particulate or gaseous fugitives being emitted from a scrubber cake, from a saturated carbon adsorption unit, from baghouse dust, etc., should be considered. Such fugitives should be reported. Also, any leaking of combustion exhaust upstream of the control device would result in fugitive emissions of uncontrolled exhaust. (If a combustion source test is required, any leaks in the combustion device upstream of the sampling point would result in fugitive emissions. If an emission factor is used, facility operators may assume all emissions exit through the stack or flue.) Some control devices use listed substances as part of the control mechanism (such as ammonia for NOx control); these may emit traces of listed substances.

Sometimes combustion exhaust gasses are used directly for product drying. This creates the possibility of physical entrainment (in the combustion exhaust) of product vapors or particles, as well as chemical reactions (due to heating or to the specific substances present) between the products of combustion and any substances which may arise from the product itself, such as occurs in cement kilns. For reporting purposes, such dual processes as co-firing and combustion of in-process fuel should be reported separately if possible and/or if required. (See Section 93311(b) in the Regulation.)

Although one often thinks of combustion devices as the source of emissions, in actual fact they all originate in the fuel(s) used. Devices can only transform the fuel constituents, physically and/or chemically. Most petroleum fuels contain and emit a wide variety of compounds. Most organic emissions which contain carbon, hydrogen, nitrogen, oxygen, sulfur, and/or chlorine can be emitted from liquid or gaseous fuels, while metals or metallic compounds are only emitted from oil (or coal) combustion.

Fuel storage and transfer can also lead to fugitive emissions from evaporation. The EET for storage tanks can be used to estimate these fugitives. Lubricating oil vents on combustion devices may also emit fugitives from evaporation.

IV. EMISSION ESTIMATION

The flowchart in Fig. 1 summarizes the general estimation procedure which is implicit in this EET.

The complexity of the combustion process largely precludes use of estimation methods other than source tests, fuel analysis and emission factors. While mass balance techniques are mostly irrelevant (due to the theoretical complexity of combustion) they can however be used to keep track of Cl partitioning (distribution) into HCl and various chlorinated hydrocarbons (perhaps in conjunction with Table III), or partitioning of metal into particulate and vapor phases. Engineering calculations, while theoretically possible, have yet to be developed and verified.

Procedure for
Estimating Combustion Emissions
of a Listed Substance

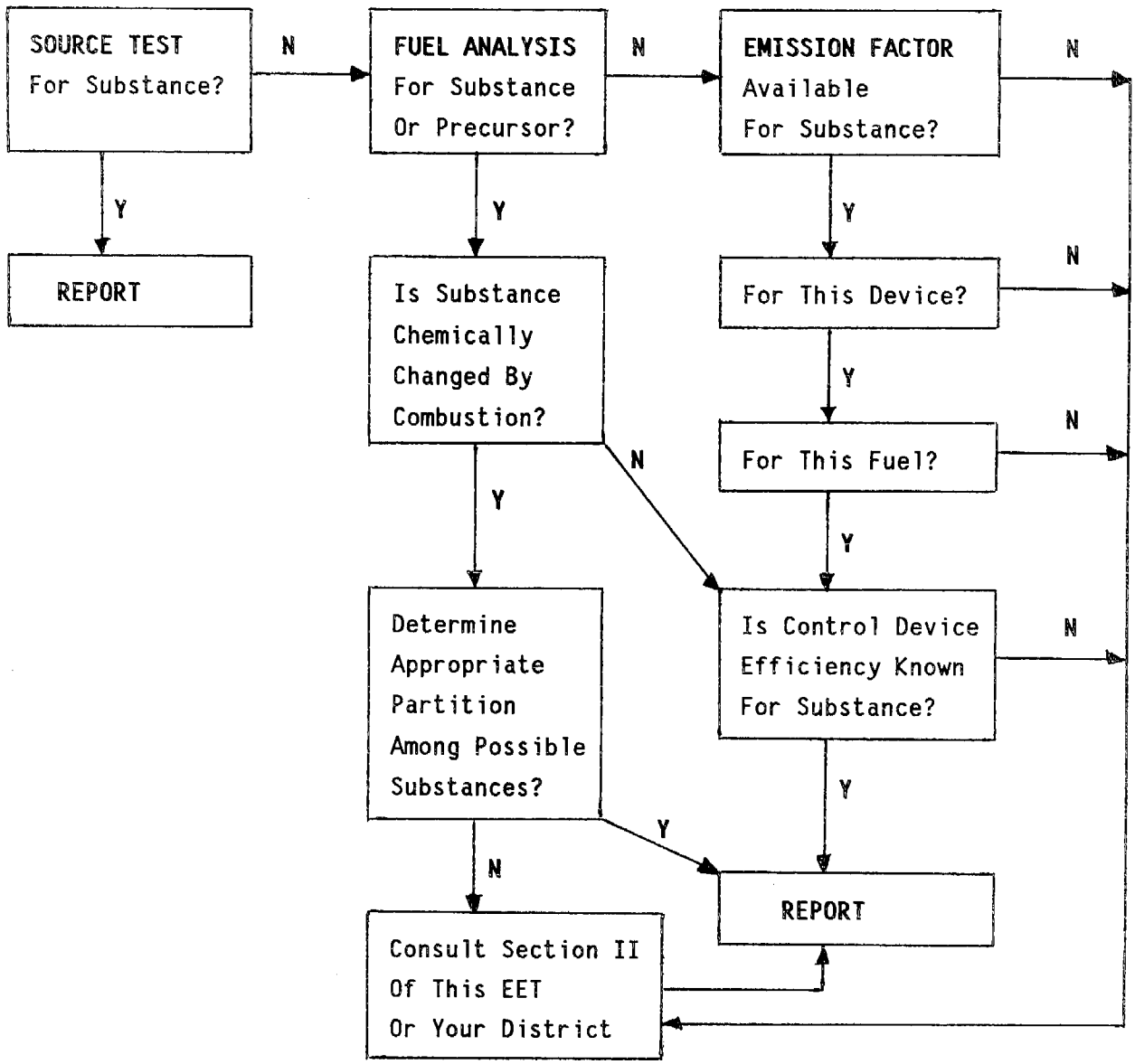

Figure 1

Table I summarizes two kinds of information about individual substances, 1) the availability of the most common estimation methods, and 2) how each substance fits into the overall combustion context. Reporting facilities can thus more easily see how to use the flowchart and sample calculations to estimate emissions of each substance. Table II summarizes information about typical concentrations of various listed substances in various fuels. Table III summarizes information about default toxic destruction efficiencies. None of these tables is definitive or complete, due to time constraints.

The Air Toxics "Hot Spots" program requires reporting of total annual emissions and maximum hourly emissions. Unless otherwise noted, simply apply the best available information (whether it is based on a source test, fuel analysis, or emission factor) to the maximum hourly and total annual fuel use. If this seems inappropriate for some reason (such as occurrence of predictable combustion upsets such as start-up), the general discussion of combustion (and/or the references thereto) included in this EET can be used as a basis for proposing adjustments to existing information. Such adjustments would be subject to district review.

A. SOURCE TESTS

Refer to Section 93336 and Appendix D of the Regulation to determine the source test and/or fuel analysis requirements for the combustion processes at your type of facility. (Appendix I of the Technical Guidance Document is the same as Appendix D of the Regulation.) Also, source test methodologies can be found in Appendix IV of the Technical Guidance Document. (To determine if your facility is a small business, see Government Code Section 11342(e), or consult your local district.) If your facility wishes to use pooled source testing, you should coordinate such pooling with your district.

If any source tests are required for your facility, the source test methods may be obtained from the Monitoring & Laboratory Division of the ARB, located in Sacramento.

B. FUEL ANALYSIS

If fuel analysis is used for estimating emissions from combustion at your facility, the ASTM methods referenced in the Regulation can be found in The Annual Book of ASTM Standards, available at larger libraries. Emission estimates based on fuel analysis should assume that all of each of the metals and other elements found in the fuel are emitted. (Sometimes, fuel is filtered or allowed to settle before combustion. It should then be analyzed after filtration or sedimentation, as some portion of some metals can be removed this way.)

A particular fuel can be analyzed for metals and other non-organic contaminants, and for organic constituents and contaminants. In both cases, default average concentrations (see Attachment II) can be used if lab fuel analysis is not required or not available. Many fuels contain additives for purposes such as improved fuel handling, soot/particulate suppression, or corrosion prevention. Your fuel supplier or refiner should be able to provide information on additives which are listed substances or precursors.

Sometimes more than one fuel is used for one device during a reporting year. In that case, the differences in emissions must be accounted for, either by reporting several processes during the year for that device, or by calculating a weighted (by fuel proportion) average of emissions for the year. Maximum hourly emissions of a given substance would be based on both the fuel and the process conditions which led to the highest emissions of that substance.

C. EMISSION FACTORS

There are 2 categories of emission factors for combustion: 1) those which estimate emissions of substances which can be source tested and/or analyzed in the fuel, and 2) those which would be used by all facilities in the absence of any approved source tests or fuel analyses. Typical units for combustion emission factors are mass of pollutant per unit mass of fuel, mass of pollutant per unit of fuel energy (higher heating value), and mass of pollutant per unit time, such as ppmw, ng/J, and gm/hr, respectively. Some factors have been tabulated for your use in Appendix V.

Where no reliable emission factors are available, TOG or PM speciation profiles may be used. In such cases, emission factors should be calculated by multiplying TOG or PM emission factors by the fraction of the listed substance specified in the profile. An example of this type of calculation can be found in Section III of the TGD.

Selection of an emission factor for a particular combustion process should be based on the same SIC (standard industrial classification) category, device, fuel and control device as the process for which emissions are being estimated. If there is no emission factor for the specific type of combustion process used in your facility, the general discussion of combustion included in this EET can serve as a basis for extrapolation of existing information, in conjunction with consultation with your district.

D. CONTROL EFFICIENCIES

The ranges of efficiencies for various devices can be found in Table IV-A of the overall Technical Guidance Document (TGD). Please read section II.D. of this EET for general discussion about actual efficiencies for particular substances. Appendix VIII of the TGD lists ARB-approved ranges for efficiencies of various control devices.

V. SAMPLE CALCULATIONS

NB: These samples are intended for illustration only. Any numbers such as concentrations of listed substances, emission factors, or fuel consumption may not be realistic and should not be used for facility calculations without independent verification.

A variety of assumptions are used as a basis for these sample calculations, some of which are listed at the beginning of the example, and some of which are mentioned in the middle. While every effort has been made to use reasonably realistic numbers, none of them may be used in an inventory plan or report without independent verification, either elsewhere in this document or in the literature. Also, these calculations don't include the effects of control devices in reducing

emissions; this aspect is illustrated in Section III of the overall Technical Guidance Document.

The use of identical emission factors for average annual and maximum hourly emissions will not be accurate in all cases. Any device which experiences predictable combustion process upsets lasting more than 10-15 minutes will have higher toxic emission rates unless these transients are NOT characterized by any of the poor combustion conditions discussed in Section II of this EET.

Although each example is different, the same average annual and maximum hourly process rate (157,400 gal/hr and 60 gal/hr, respectively) has been used in each case. Based on a hypothetical operating schedule of 24 hours a day, 50 weeks a year, the average hourly process rate is about 19 gal/hr, much less than the maximum hourly rate of 60 gal/hr which is assumed.

Throughout the combustion example calculations, engineering notation is used for exponentials. When you see a number followed by "E" followed by a positive or negative integer, the "E" means you should multiply the first number by the power of ten indicated by the second number. Thus, 5.25 E-8 means 5.25 times 10 to the minus 8 power. This type of notation is used in Fortran, and also appears on some pocket calculators.

A. Calculation of Chromium VI Emissions Based On Fuel Analysis or Default Chromium Concentration.

Given: Chromium concentration = 0.14 ppmw (parts-per-million by weight)
Chromium VI is 5% by weight of total Chromium in combustion products
Density of Fuel (Oil) = 7.5 lb/gal

1. Calculate the amount of Cr-VI emitted per unit of fuel used. This number is the emission factor for the process and substance.

EF = Emission factor
[Cr]F = Chromium concentration in fuel
[Cr-VI]Cr = Chromium VI concentration in total chromium, after combustion
DF = Fuel density

$$[Cr]F \times [Cr\text{-}VI]Cr \times DF = EF \qquad (1)$$

$$\left(\frac{0.14 \text{ lb Cr}}{1 \text{ E } 6 \text{ lb fuel}}\right)\left(\frac{0.05 \text{ lb Cr-VI}}{1 \text{ lb Cr}}\right)\left(\frac{7.5 \text{ lb fuel}}{\text{gallon fuel}}\right) = 5.25 \text{ E-8} \frac{\text{lb Cr-VI}}{\text{gallon fuel}}$$

2. Calculate emissions from total annual and maximum hourly process rates. For combustion processes, the process rate is almost always fuel consumption.

EMS = Emissions
PR = Process Rate
EF = Emission Factor

$$PR \times EF = EMS \qquad (2)$$

Annual Emissions from 157,400 gallons of fuel used per year

(157,400 gal/yr)(5.25 E-8 lb Cr-VI/gallon) = 0.008266 lb Cr-VI/year

Maximum Hourly Emissions from 60 gallons of fuel used per hour

(60 gal/hr)(5.25 E-8 lb Cr-VI/gallon) = 3.15 E-6 lb Cr-VI/hour

B. <u>Calculation of Emissions of Chlorine-Containing Compounds Based on Fuel Analysis of Chlorine Concentration and Manufacturer's Specification</u>

Given: 30 ppmw Chlorine based on fuel (gasoline) analysis
20 ppmv (parts-per-million by volume) Ethylene Dichloride (EDC) based on refinery specification
Density of Fuel (Gasoline) 6.0 lb/gal

1. Calculate the amount of chlorine present per unit of fuel based on fuel analysis and on refinery specification.

[EDC]F = Concentration of EDC in fuel
[Cl]F = Concentration of chlorine in fuel
D-EDC = Density of EDC
MW-Cl = Atomic weight of chlorine
MW-EDC = Molecular weight of EDC

$$[EDC]F \times D\text{-}EDC \times 2(MW\text{-}Cl) / MW\text{-}EDC = [Cl]F \qquad (3)$$

$$\left(\frac{20 \text{ gal EDC}}{1 \text{ E } 6 \text{ gal gas}}\right)\left(10.4 \frac{\text{lb EDC}}{\text{gal EDC}}\right)\left(\frac{71 \text{ lb Cl/lb-mol EDC}}{99 \text{ lb EDC/lb-mol EDC}}\right) = 1.49 \text{ E-4} \frac{\text{lb Cl}}{\text{gal gas}}$$

Convert units of fuel from pounds to gallons using fuel density.

$$\left(\frac{30 \text{ lb Cl}}{1 \text{ E } 6 \text{ lb gas}}\right)\left(6.0 \frac{\text{lb gas}}{\text{gal gas}}\right) = 1.80 \text{ E-4} \frac{\text{lb Cl}}{\text{gal gas}}$$

Clearly, 1.49 does not equal 1.80.

When such a discrepancy occurs, the reporting facility must make some assumptions before proceeding. The refinery specification is probably an average process concentration, with some uncertainty, whereas the fuel analysis is an exact measurement of a specific sample. On the other hand, the analyzed sample is a very small portion of the total fuel use for which emissions are being reported. For purposes of this calculation, and in the absence of analysis of another fuel sample, the measured value is assumed to be correct. Dilemmas such as this should

be discussed with local districts, and, if necessary, with CARB. Of course, the magnitude of the discrepancy is a factor; in this case there is roughly a 20% difference. If it were only 1-2%, the decision would not be as important.

Assumptions must also be made as to the identity of the compounds containing the 'extra' chlorine. If they are listed halogenated organics, as much as 1% could be emitted in the original form. If they are inorganic chlorides, listed halogenated organics are likely to be formed during combustion. In either case, 99% of the total chlorine may be assumed to be emitted as HCl, hydrogen chloride. In actual fact, most of the chlorine in this case would be emitted as PbCl rather than HCl, since EDC is added to leaded gasoline specifically for lead scavenging. In general, however, most of any chlorine present (see Table III) would be emitted as HCl in the absence of specific preempting chemical reactions such as lead scavenging.

2. Calculate the emission factor for hydrogen chloride (HCl).

EF-HCl = Emission factor for HCl
MW-HCl = Molecular weight of HCl

$$[Cl]F \times 0.99 \times MW\text{-}HCl / MW\text{-}Cl = EF\text{-}HCl \qquad (4)$$

$$\left(1.80\ E\text{-}4\ \frac{lb\ Cl}{gal\ gas}\right)\left(0.99\right)\left(\frac{36.5\ lb\ HCl/lbmol\ HCl}{35.5\ lb\ Cl/lbmol\ HCl}\right) = 1.83\ E\text{-}4\ \frac{lb\ HCl}{gal\ gas}$$

3. Calculate the emission factor for EDC. In the absence of a source test, assume 1% of the EDC is emitted rather than being destroyed by combustion.

EF-EDC = Emission factor for EDC

$$[EDC]F \times D\text{-}EDC \times 0.01 = EF\text{-}EDC \qquad (5)$$

$$\left(\frac{20\ gal\ EDC}{1\ E\ 6\ gal\ gas}\right)\left(10.4\ \frac{lb\ EDC}{gal\ EDC}\right)\left(0.01\right) = 2.08\ E\text{-}6\ \frac{lb\ EDC}{gal\ gas}$$

4. Calculate total annual and maximum hourly emissions of HCl and EDC, based on process rates.

$$PR \times EF = EMS \qquad (2)$$

Annual HCl Emissions from 157,400 gallons of fuel used per year

(157,400 gal/yr)(1.83 E-4 lb HCl/gal) = 28.8 lb HCl/year

Maximum Hourly EDC Emissions from 60 gallons of fuel used per hour

(60 gal/hr)(2.08 E-6 lb EDC/gal) = 0.000125 lb EDC/hr

5. Calculate the amount of Cl which remains to be accounted for. One percent (1%) of the difference between the values from fuel analysis and refinery specification is left, since 99% of the higher amount has been allocated to HCl emission, and 1% of the smaller amount has been allocated to EDC emission.

$$\left[(1.80\ E\text{-}4 - 1.49\ E\text{-}4)\ \frac{\text{lb Cl}}{\text{gal gas}}\right](0.01) = 3.1\ E\text{-}7\ \frac{\text{lb Cl}}{\text{gal gas}}$$

Possible PICs which may result include chloroform, carbon tetrachloride, chlorobenzene, ethylene dichloride, methylene chloride, benzyl chloride, etc. In the absence of source tests, a conservative approach would be to assume emissions of those possible substances which have the highest unit risk values, such as chloroform, carbon tetrachloride, or benzyl chloride.

C. Calculation of Some of the Emissions From an Industrial Boiler Burning Waste-Derived Fuel

Given:	Fuel Composition: (by volume)	47.5% Fuel Oil 47.5% Waste Crankcase Oil 5.0% Waste Degreasing Solvent
	Waste Oil Analysis:	1600 ppmw Cl
	Fuel Oil Analysis:	1.3 ppmw Cl
	Solvent Composition: (by volume)	97% TCA 3% 1-4 Dioxane (a typical impurity)
	Densities: Oil	7.5 lb/gal
	TCA	11.024 lb/gal
	1,4-D.	8.61 lb/gal

(In cases where a facility varies the composition of the fuel used for a particular device, ingredient analysis would be necessary for accurate reporting.) In addition to the emissions calculated here, the emissions of various listed metals and organic substances typically present in oil and waste oil should also be calculated.

1. Calculate overall fuel density (eqn. 6) and amount of listed substances or precursors present per unit of fuel (eqns. 7-11)

D-F = Fuel density
D-O = Oil density
D-TCA = TCA density
D-D = 1,4-Dioxane density
[O]F = Concentration of oil in fuel
[TCA]F = Concentration of TCA in fuel
[D]F = Concentration of 1,4-Dioxane in fuel

[Cl]O = Concentration of chlorine in oil
[Cl]TCA = Concentration of chlorine in TCA
W-O = Weight fraction of oil in fuel
W-TCA = Weight fraction of TCA in fuel
W-D = Weight fraction of 1,4-Dioxane in fuel
W-Cl = Weight fraction of chlorine in fuel
MW-Cl = Atomic weight of chlorine
MW-TCA = Molecular weight of TCA
EF-HCl = Emission factor for HCl
EF-TCA = Emission factor for TCA
EF-D = Emission factor for 1,4-Dioxane

$$[O]F \times D\text{-}O + [TCA]F \times D\text{-}TCA + [D]F \times D\text{-}D = D\text{-}F \qquad (6)$$

$$\left(0.95 \frac{\text{gal oil}}{\text{gal fuel}}\right)\left(7.5 \frac{\text{lb oil}}{\text{gal oil}}\right) + \left(0.05 \frac{\text{gal solvent}}{\text{gal fuel}}\right)\left(0.97 \frac{\text{gal TCA}}{\text{gal solvent}}\right)\left(11.024 \frac{\text{lb TCA}}{\text{gal TCA}}\right)$$

$$+ \left(0.05 \frac{\text{gal solvent}}{\text{gal fuel}}\right)\left(0.03 \frac{\text{gal 1,4-dioxane}}{\text{gal solvent}}\right)\left(8.61 \frac{\text{lb 1,4-dioxane}}{\text{gal 1,4-dioxane}}\right)$$

$$= 7.125 \frac{\text{lb oil}}{\text{gal fuel}} + 0.5347 \frac{\text{lb TCA}}{\text{gal fuel}} + 0.0129 \frac{\text{lb 1,4-dioxane}}{\text{gal fuel}} = 7.67 \frac{\text{lb fuel}}{\text{gal fuel}}$$

$$[O]F \times D\text{-}O \;/\; D\text{-}F = W\text{-}O \qquad (7)$$

$$\frac{7.125 \text{ lb oil/gal fuel}}{7.67 \text{ lb fuel/gal fuel}} = 0.9289 \frac{\text{lb oil}}{\text{lb fuel}}$$

$$[TCA]F \times D\text{-}TCA \;/\; D\text{-}F = W\text{-}TCA(\qquad (8)$$

$$\frac{0.5347 \text{ lb TCA/gal fuel}}{7.67 \text{ lb fuel/gal fuel}} = 0.0697 \frac{\text{lb TCA}}{\text{lb fuel}}$$

$$[D]F \times D\text{-}D \;/\; D\text{-}F = W\text{-}D \qquad (9)$$

$$\frac{0.0129 \text{ lb 1,4-diox./gal fuel}}{7.67 \text{ lb fuel/gal fuel}} = 0.00168 \frac{\text{lb 1,4-dioxane}}{\text{lb fuel}}$$

$$3(\text{MW-Cl}) \;/\; \text{MW-TCA} = [\text{Cl}]\text{TCA} \qquad (10)$$

$$\frac{106.5 \dfrac{\text{lb Cl}}{\text{lbmol TCA}}}{133.5 \dfrac{\text{lb TCA}}{\text{lbmol TCA}}} = 0.7978 \frac{\text{lb Cl}}{\text{lb TCA}}$$

$$[\text{Cl}]\text{O} \times \text{W-O} + \text{W-TCA} \times [\text{Cl}]\text{TCA} = \text{W-Cl} \qquad (11)$$

$$\left[\frac{1600 \text{ lb Cl}}{1 \text{ E } 6 \text{ lb w. oil}} + \frac{1.3 \text{ lb Cl}}{1 \text{ E } 6 \text{ lb oil}}\right]\left(0.9289 \frac{\text{lb oil}}{\text{lb fuel}}\right) + \left(0.0697 \frac{\text{lb TCA}}{\text{lb fuel}}\right)\left(0.7978 \frac{\text{lb Cl}}{\text{lb TCA}}\right)$$

$$= 0.0563 \frac{\text{lb Cl}}{\text{lb fuel}}$$

With so many fuel ingredients, things can get confusing. Summarizing your intermediate results can be helpful.

Fuel Components	Vol.%	Density (lb/gal)	Wt.%
Fuel	100.0	7.67	100.0
Oil	95.0	7.5	92.89
Solvent	5.0		
TCA	4.85	11.024	6.97
1,4-Dioxane	0.15	8.61	0.168
Chlorine (from TCA & Waste Oil)			5.63

2. Calculate emission factors for HCl, TCA and 1,4-Dioxane. In default of a source test, 99% of the total chlorine is assumed to be emitted as hydrogen chloride.

$$\text{W-Cl} \times \text{D-F} \times 0.99 \times \text{MW-HCl} \;/\; \text{MW-Cl} = \text{EF-HCl} \qquad (12)$$

$$\left(0.0563 \frac{\text{lb Cl}}{\text{lb fuel}}\right)\left(7.67 \frac{\text{lb fuel}}{\text{gal fuel}}\right)(0.99)\left(\frac{36.5 \text{ lb HCl/lbmol HCl}}{35.5 \text{ lb Cl/lbmol HCl}}\right) = 0.440 \frac{\text{lb HCl}}{\text{gal fuel}}$$

$$\text{W-TCA} \times \text{D-F} \times 0.01 = \text{EF-TCA} \qquad (13)$$

$$\left(0.0697 \frac{\text{lb TCA}}{\text{lb fuel}}\right)\left(7.67 \frac{\text{lb fuel}}{\text{gal fuel}}\right)(0.01) = 0.005346 \frac{\text{lb TCA}}{\text{gal fuel}}$$

Similarly,

W-D x D-F x 0.01 = EF-D (14)

3. Calculate emissions of HCl, TCA and 1,4-Dioxane based on total annual and maximum hourly fuel use.

PR x EF = EMS (2)

Annual Emissions of TCA from 157,400 gallons of fuel used per year

(157,400 gal/yr)(0.005346 lb/gal) = 841.5 lb/yr

Maximum Hourly Emissions of HCl from 60 gallons of fuel used per hour

(60 gal/hr)(0.440 lb/gal) = 26.4 lb/hr

D. Calculation of PAH Emissions For Combustion Process Described in C. Above

Given: PAHs: 530 ppmw default concentration in waste oil
2.6 E-12 lb/Btu emission factor for fuel oil in industrial boilers
143,500 Btu/gal fuel heating value

1. Calculate amount of PAH present in waste oil which is emitted rather than destroyed during combustion. In default of a source test, assume 1% of the PAHs are emitted rather than destroyed.

[PAH]-O = Concentration of PAHs in waste oil
W-W = Weight fraction of waste oil in fuel (see eqn. 7; 0.9289/2=0.464)
D-F = Fuel density
EF-1 = Emission factor due to PAHs in fuel
EF-2 = Emission factor due to PAHs formed in combustion
EF-PAH = Overall PAH emission factor

[PAH]-O x W-W x D-F x 0.01 = EF-1 (15)

$$\left(\frac{530 \text{ lb PAHs}}{1 \text{ E } 6 \text{ lb w. oil}}\right)\left(\frac{0.464 \text{ lb w. oil}}{1 \text{ lb fuel}}\right)\left(7.67 \frac{\text{lb fuel}}{\text{gal fuel}}\right)\left(0.01\right) = 1.888 \text{ E-5} \frac{\text{lb PAHs}}{\text{gal fuel}}$$

2. Additional PAHs will be formed as reflected by the emission factor. Convert this emission factor into consistent units.

$$\left(2.6 \text{ E-12} \frac{\text{lb PAHs}}{\text{Btu fuel}}\right)\left(143{,}500 \frac{\text{Btu}}{\text{gal}}\right) = 3.73 \text{ E-7} \frac{\text{lb PAHs}}{\text{gal fuel}}$$

3. Calculate overall PAH emission factor.

EF-1 + EF-2 = EF-PAH (16)

$$\left[(3.73\ E\text{-}7 + 1.888\ E\text{-}5)\ \frac{\text{lb PAHs}}{\text{gal fuel}}\right] = 1.93\ E\text{-}5\ \frac{\text{lb PAHs}}{\text{gal fuel}}$$

4. Calculate total annual and maximum hourly emissions based on appropriate process rates.

PR x EF = EMS (2)

Annual Emissions from 157,400 gallons of fuel used per year

(157,400 gal/yr)(1.93 E-5 lb/gal) = 3.04 lb/yr

Maximum Hourly Emissions from 60 gallons of fuel used per your

(60 gal/hr)(1.93 E-5 lb/gal) = 0.00116 lb/hr

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ATTACHMENT I

TABLE I

SUMMARY OF

AVAILABILITY OF ESTIMATION METHODS AND

ROLE(S) OF LISTED SUBSTANCES IN COMBUSTION PROCESSES

EXPLANATION OF TABLE I

The first 4 columns indicate (with an 'x') the availability of approved source tests, fuel analysis methods, ARB-approved (AB 1807) emission factors, and other uncertified (non-1807) emission factors for each individual listed substance which is a possible emission from any combustion process. (Lack of availability is thus shown by a blank space.) For availability of emission factors for a specific type of combustion (device, fuel, control, etc.) see Appendix V.

The next 3 columns define for each substance the type of combustion product it is. Organic combustion products are defined as PICs only if they are thought to be actually formed during combustion. Those that are thought to be strictly residual amounts of organic fuel additives or hazardous contaminants are defined as POHCs (principle organic hazardous components). Many organic substances fall into both categories.

The last 2 columns indicate which substances (organic or not) may be present as fuel contaminants prior to combustion. Waste fuels include waste oils and waste solvents.

The non-organic substances are subdivided into 2 categories, elements (mostly metals), and miscellaneous. Although metals aren't involved in basic combustion chemistry, they can affect combustion emissions; hence their use as fuel additives. During combustion, the energy involved may cause them to form compounds such as zinc oxide or mercuric chloride. Thus, while you should assume that the total amount of each metal found in the fuel is emitted, there may be some leeway in the exact distribution of a particular element among the various substances in which it is found. For example, a given amount of zinc in the fuel could be emitted as zinc oxide as well as in the simple elemental form. Of course, such allocation must be consistent with approved measurement methods and emission factors.

Compounds which are listed in Appendix A-II are indicated with an asterisk (*), while those which are chlorinated organics are indicated with a number sign (#).

TABLE I NON-ORGANIC SUBSTANCES	ARB ST	ARB FA	ARB EF	ARB EF	Combustion Products PICs	Combustion Products POHCs	Combustion Products Non-Org.	Fuel Contaminants New Fuel	Fuel Contaminants Waste
Elements									
Arsenic	x	x	x				x	x	x
Beryllium	x	x					x	x	x
Bromine		x						x	x
Cadmium		x	x				x	x	x
Chlorine	x	x						x	x
Chromium VI	x	x	x				x	x	x
Copper		x					x	x	x
Lead	x	x					x	x	x
Manganese		x					x	x	x
Mercury	x	x					x	x	x
Nickel	x	x	x				x	x	x
Phosphorus		x					x	x	x
Radionuclides		x					x		
Selenium		x					x	x	x
Sulfur								x	x
Zinc		x					x	x	x
Miscellaneous									
Hydrogen Sulfide	x						x		
Hydrogen Chloride #	x						x		
Hydrogen Fluoride	x						x		
Mercuric Chloride #							?		
Phosgene #							x		
Zinc Oxide							x		
ORGANIC SUBSTANCES									
Acetaldehyde				?	x				
Acrolein									
Benzene	x		x			x		x	x
Benzyl Chloride #	x								
1,3-Butadiene					x	x			x
Carbon Tetrachloride #	x					x			x
Chloroform #	x				x	x			x
Chlorobenzene #	x				x	x			x
Chlorophenols #	x								
Cresols									
Di(2-ethylhexyl)-phthalate									x
1-4 Dioxane									x
Dioxins (PCDDs) #	x				x	x			x
Epichlorohydrin #	x								
Ethyl Chloride #	x								
Ethylene Dibromide	x					x		gasoline	x

	ST	FA	ARB EF	EF	Combustion Products PICs	POHCs	Non-Org.	Fuel Contaminants New Fuel	Waste
Ethylene Dichloride #	x						x	gasoline	x
Ethylene Oxide	x								
Fluorocarbons, (chlorinated & brominated) #	x						x		x
Formaldehyde	x			x	x				
Furans (PCDFs) #	x				x		x		x
Glycol Ethers								x	
Methyl Bromide	x								
Methyl Mercury					x				
Methylene Chloride #	x				x				x
Nitrosomorpholine								x	x
N-nitrosodiphenylamine									x
Perchloroethylene #	x						x		x
PCBs #	x						x		x
Phenol									x
Propylene									
Propylene Oxide									
Styrene									x
Styrene Oxide									
Toluene								x	x
Trichloroethane #	x								x
Trichloroethylene #	x								x
Trichlorophenol #									x
Vinyl Chloride #	x								x
Xylene								x	x
PAHs				x	x		x		x
Benz(a)anthracene	x								x
Benz(a)pyrene	x			x					x
Benzo(b)fluoranthene		x							
*Benzo(j)fluoranthene									
Benzo(k)fluoranthene	x								
*Dibenzo(a,h)acridine									
*Dibenzo(a,j)acridine									
Dibenzo(a,h)anthracene		x							
*7H-Dibenzo(c,g)cabazole									
*Dibenzo(a,e)pyrene									
*Dibenzo(a,h)pyrene									
*Dibenzo(a,i)pyrene									
*Dibenzo(a,l)pyrene									
Indeno(1,2,3-cd)pyrene	x								
Naphthalene	x								x

* Appendix A-II
\# Contains Chlorine

ATTACHMENT II

TABLE II

SUMMARY OF

AVAILABLE INFORMATION ON

CONCENTRATION OF LISTED SUBSTANCES IN VARIOUS TYPES OF OIL

NB: This table currently contains the best available information. Most of these concentrations are ranges rather than single default numbers, because there is so much variation in the literature. In most cases, there is no clear justification for selecting a single value.

Any feedback as to reasonably accurate and unique values for these default concentrations is very welcome.

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U.S. Environmental Protection Agency. 1980. Trace Metals & Stationary Conventional Combustion Processes. EPA 600/7-80-155a

U.S. Environmental Protection Agency. 1978. Environmental Assessment of Coal- & Oil--Firing in a Controlled Industrial Boiler. EPA 600/7-78-164b & 600/7-78-164c

TABLE II

NON-ORGANIC SUBSTANCES	OILS (ppmw) CA Crude	Residual	Distillate	Fuel	Waste
Elements					
Arsenic	0.14-0.66	0.2-0.7		0.0006-2	11-14
Beryllium				<0.05	
Bromine	0.29				50-4000
Cadmium		0.003-1		< 3.5	1-2, <100
Chlorine	1.47	12.0			500-14,000
Chromium	0.64	0.045-6.2	<0.01-1.15	0.002-2.2	10-25
Copper	0.93	2.8		1.4	
Lead		1-4, 3.5		2.6	220-13,000
Manganese	1.2	0.16, 1.33	<0.01	0.001-6	
Mercury	23.1	0.002-0.4		0.02-30	
Nickel	98.4	18-50, 42.2	"a few"	14-68	
Phosphorus		1.1			
Radionuclides		1			
Selenium	0.364	0.7		0.03-1	
Sulfur	9.9, 1-2%	< 0.5%	< 0.5%	0.25-0.5 %	0.5%
Zinc	9.76	0.4-2, 1.26		3.0	470-900
Miscellaneous					
Hydrogen Sulfide					
Hydrogen Chloride #					
Hydrogen Fluoride					
Mercuric Chloride #					
Phosgene #					
Zinc Oxide					
ORGANIC SUBSTANCES					
Acetaldehyde +					
Acrolein					
Benzene					46-100
Benzyl Chloride #					
1,3-Butadiene +					
Carbon Tetrachloride # +					
Chloroform # +					
Chlorobenzene #					
Chlorophenols #					
Cresols					
Di(2-ethylhexyl)-phthalate (DEHP)					
1-4 Dioxane					
Dioxins (PCDDs) # +					
Epichlorohydrin # +					
Ethyl Chloride # +					
Ethylene Dibromide +					

	OILS				
	Crude	Residual	Distillate	Fuel	Waste
Ethylene Dichloride # +					
Ethylene Oxide +					
Fluorocarbons, (chlor-inated & brominated # +					20-200 (CFC-12) <1-33 (CFC-113)
Formaldehyde +					
Furans (PCDFs) #					
Glycol Ethers +					
Methyl Bromide +					
Methyl Mercury					
Methylene Chloride #					
Nitrosomorpholine					
N-nitrosodiphenylamine					
Perchloroethylene # +					120-750
PCBs # +					9-100
Phenol					
Propylene +					
Propylene Oxide +					
Styrene					
Styrene Oxide					
Toluene					190-2000
Trichloroethane # +					270-2500
Trichloroethylene # +					50-500
Trichlorophenol # +					60-490
Vinyl Chloride # +					
Xylene					36-7000
PAHs					
Benz(a)anthracene					9-60
Benz(a)pyrene					16-26
Benzo(b)fluoranthene					
*Benzo(j)fluoranthene					
Benzo(k)fluoranthene					
*Dibenzo(a,h)acridine					
*Dibenzo(a,j)acridine					
Dibenzo(a,h)anthracene					
*7H-Dibenzo(c,g)cabazole					
*Dibenzo(a,e)pyrene					
*Dibenzo(a,h)pyrene					
*Dibenzo(a,i)pyrene					
*Dibenzo(a,l)pyrene					
Indeno(1,2,3-cd)pyrene					
Naphthalene					290-500

* Appendix A-II
\# Contains Chlorine
\+ Presence likely only in waste oil

ATTACHMENT III

TABLE III

DEFAULT POHC & TOXIC PIC EMISSION PERCENTAGES

FOR INDUSTRIAL BOILERS AND FLARES

BOILERS

Operating Conditions	Emissions as Weight Percent of Fuel POHCs		Wt. Pct. Cl ** Emitted as HCl
	% Toxic PIC *	% Toxic POHC	
FAIR (with combustion transients in load, fuel, air, operation, or with poor maintenance) or low comb'n temps or high H/Cl fuel ratio)	1 %	0.1 %	~ 99 %
GOOD (steady-state operation)	0.1 %	0.01 %	~ 99.9 %

FLARES

1.2 Stability Ratio @	2 %	0.2 %	~ 98 %
1.0 Stability Ratio	10 %	1 %	~ 90 %

Note: Breakthrough percentages tend to be higher for volatiles. (EPA 1984 Waste Oils)

* Toxic PICs are compounds which would be considered POHCs if present in the fuel prior to combustion.

** In the even that the POHC is a chlorinated organic

@ See Section II.D.2 of this EET
Not applicable to flares in ambient wind conditions above 5-10 mph.

EMISSION ESTIMATION TECHNIQUE: INCINERATION

INCINERATION
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique (EET), developed by the Air Resources Board staff in accordance with the Air Toxic "Hot Spots" Information and Assessment Act of 1987 (the Act). Specifically this report describes the process of using combustion as a method to reduce waste products. This process results in the air emission of toxic substances listed pursuant to the Act. This report specifies the method(s) a facility operator would use to calculate resulting emissions of these listed substances.

Dibenzofurans, dibenzo-p-dioxins, metals, and other products of incomplete production (PIC, including formaldehyde and polycyclic aromatic hydrocarbons) are the principal listed substances of concern during the incineration of solid waste, hazardous waste, wire reclamation, hospital waste, and biomass. The polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) are particularly significant because these are potentially highly toxic substances and may be associated with many combustion processes.

PCDFs and PCDDs are potentially produced under one, or more, of the following conditions:

a) Trace PCDF and PCDD contamination in the product or process;

b) High temperature chemical reactions of chlorinated aromatic compounds such as polychlorinated biphenyls (PCBs) and chlorophenols which have chemical structures closely related to PCDD, and

c) High temperature free radical reactions combining organic matter and chlorine to form PCDFs and PCDDs.

Though there have been no known cases of death in humans caused by PCDF/PCDD, these groups of substances are considered a very dangerous threat to human health. The significance placed on these substances is demanded by their extreme biological potency and potential chronic effects. The toxicity of these compounds is related to the specific placement of the chlorines, with 2,3,7,8-TetraCDD (TCDD) probably being the most toxic. TCDD has been found to be carcinogenic to animals and should be considered a potential human carcinogen. The California Department of Health Services has also concluded that isomers of PCDFs and PCDDs containing four, five, six, and seven chlorines should be considered potential human carcinogens.

Although source testing should be used to determine emissions of the most toxic and variable substances, such as PCDDs and PCDFs (see Section V), this EET will provide methods to estimate emissions of other listed substances including a number of organic compounds. Emissions of PCDDs,

PCDFs, and other products of incomplete combustion appear to be related to the type of combustor used and its operating efficiency. Generally, PCDDs and PCDFs are inversely related to combustion temperature. That is, the higher the combustion temperature, the lower the emissions of PCDDs and PCDFs. In general, the waste used needs to have a net heat content of 8,000 Btu per pound; blending with supplemental fuels can be done to achieve that value. In addition to maintaining high temperatures, the chlorine content of the waste needs to be controlled by blending. Although chlorine content can be as high as 70 percent, most operators limit chlorine content to 10 percent or less.

In 1986, numerous types of facilities in California used incineration to dispose of waste or generate energy. These facilities include municipal waste incinerators (in 1986, there was one facility in the state and 35 proposed facilities); hazardous waste incinerators (in 1986, there were 17 facilities in the state and 3 proposed facilities); wire reclamation incinerators (in 1986, there were 76 facilities in the state); hospital incinerators (in 1986, there were 311 facilities in the state); and cement kilns co-firing wastes (in 1986, there was one such facility). Because of the potentially toxic emissions and the number of facilities which may be emitting them, the potential health risks must be assessed.

The types of incinerators used to thermally destroy waste include: liquid injection, rotary kilns, fluidized bed, modular units (or fixed hearth), acid regeneration, and multiple hearth furnaces. Two types of boilers that are generally used are the watertube and firetube. These two types of boilers can each have a variety of firing modes.

II. PROCESS DESCRIPTIONS OF INCINERATORS

The processes involved in using combustion to reduce waste depend on the fuel preparation and feeding along with the type of combustion chamber.

A. Fuel Preparation and Feeding

Liquids

Liquids are generally blended, then pumped into the combustion chamber(s) through nozzles or via specially designed atomizing burners.

Sludges

Sludges are generally fed using progressive gravity pumps or water cooled lances.

Bulk Solids

Bulk solids may require some alteration to control particle size; they can be fed using rams, gravity feed, air lock feeders, screw or vibratory feeders, or belt feeders.

Containerized Waste

Containerized waste is usually fed using gravity or rams.

B. Combustion Chamber(s)

Most incineration systems derive their name from the type of combustion chamber used.(Most of the following information on incinerator types was taken from the U.S. EPA 1986 Permit Writers Guide to Test Burn Data: Hazardous Waste Incineration and the IJAPCWM 1988 "Hospital Waste Disposal by Incineration: Waste Streams, Technologies, and State Requirements").

Liquid Injection Incinerators

Liquid injection incinerators are used almost exclusively for pumpable liquid wastes. They are usually simple, refractory-lined cylinders equipped with one or more burners.

Rotary Kilns

Rotary kilns can be used to incinerate solids, slurries, and containerized waste as well as liquids. This combustion chamber type is incorporated most frequently into a commercial off-site incineration facility because it is versatile. It is a cylindrical, refractory-lined shell mounted at a slight angle. Rotation of this shell allows movement of the fuel through the kiln and also enhances the mixing of the waste. Most rotary kilns have afterburners associated with them to reduce potential emissions.

Fixed-Hearth Incinerators

Fixed-hearth incinerators employ a two-stage combustion process. These incinerators are smaller, so they have lower relative capital costs, and are the most attractive choice for a small on-site facility.

Fluidized Bed Incinerators

Fluidized bed incinerators can be either circulating or bubbling bed designs. Both types are single refractory-type combustion vessels partially filled with sand, alumina, sodium carbonate, or other materials. Fluidized bed incinerators are used primarily for sludges or shredded solid materials.

Multiple-Hearth (Herreshoff Furnace)

Generally, multiple-hearth incinerators are used to burn chemical sludges, oil refinery sludges, and still bottoms. A multiple hearth is made up of several hearths assembled vertically in a refractory-lined cylindrical shell.

Boilers

There are two principle types of boilers: watertube and firetube.

Watertube

In the watertube boiler, hot gas passes over water- or steam-filled tubes that line the combustion chamber walls. Most boilers with heating capacities greater than 30 x

10^6 Btu/hour are watertube boilers, utilizing a high pressure steam.

Firetube

In a firetube boiler, hot gas flows directly through tubes submerged in water. Firetube units are usually packaged with

capacities less than 30 x 10^6 Btu/hour, utilizing a low pressure steam. Watertube and firetube boilers can be fueled with coal, oil, gas, or process waste (such as sawdust, black liqueur from paper pulping, or hazardous waste). The main distinction among these boilers is the type of fuel-firing mode, including:

Single- or opposed-wall
Tangential
Cyclone
Stoker

Each of the major firing modes, except stoker firing, can be used in boilers burning gas, oil, or pulverized coal. Stoker firing units can only burn solid fuels (that is, coal) that will remain on the stoker grate until burned. Stoker firing boilers need to be retrofitted with burners to fire other fuels (such as hazardous waste).

III. POTENTIAL SOURCES OF EMISSIONS

A number of operations using combustion to reduce waste may result in toxic emissions of listed substances. The actual substances emitted depend on the feed, equipment, and processes used.

Exhaust Stack

Historically, the exhaust stack has been the central focus of sampling and emission estimation calculations. While quantifying emissions from the exhaust stack is an important focus, calculating fugitive emissions is also.

Fugitive Emissions

There are several potential sources of fugative emissions including from dump stacks, fuel storage, and during the handling of residues and ash.

Dump Stacks

Dump stacks are used only in emergencies, and should be properly sealed to ensure that inadvertent emissions do not occur.

Fuel Storage

Fuel storage is of particular concern in facilities that use solid waste, hazardous waste, or biomass as fuel, or that use liquid supplemental fuels.

Residue/Ash Handling

When the residue or ash that results from the incineration process is classified as a hazardous waste (as defined by Article 9. of Division 4. of Title 22. of the California Administrative Code), emissions of listed substances may occur during its transfer and disposal.

IV. CONTROL DEVICES

An emission control device may greatly reduce air pollutants leaving a device, relative to those entering a device. Any one of the following possibilities, or combinations of, exist when an air pollutant enters a control device. The pollutant may be transferred from the air stream to another medium, may be modified to a less toxic state, and/or dissociation, or it may pass through untreated. When a pollutant is transferred into another medium, any emissions while located anywhere on the facility site must be accounted for. There is a broad spectrum of emission control devices that can be used in conjunction with an incinerator, including (Most of the following information on control devices was taken from the IJAPCWM 1987 "Incineration of Hazardous Waste, A Critical Review"):

Dry Cyclonic Separator

Dry cyclonic separators are inertial separators.

Dry Scrubber

Dry scrubbers are generally used to remove acid gas components, operating as an absorbent system rather than the washing system inherent in wet scrubbers.

Wet Scrubber

Wet scrubbers are used primarily to control gaseous emissions (such as oxides of sulfur) and other acid gases, and to some extent particulate matter. Examples of wet scrubbers include: venturi, spray tower, packed-bed, and tray scrubber.

Wet Ionizing Scrubber

A wet ionizing scrubber consists of a packed-bed scrubber preceded by an ionizer that imparts a charge on the entering particulate matter.

Electrostatic Precipitators (ESPs)

There are two primary types of ESPs: dry ESPs and wet ESPs.

Dry ESP

In a dry ESP, the gas stream passes through a series of negatively charged electrodes which collect particulate matter.

Wet ESP

In a wet ESP, the gas stream is flushed with a continuous sheet of water, over each collection surface, to flush away any collected particulate matter.

When water is integral to the scrubber or an ESP control device, water collects at the bottom of the device, is pumped to a tank where particulate matter settles out, and the water may be reused.

Fabric Filters (Baghouses)

Fabric filters generally consist of a series of permeable bags which allow the passage of gas, but catch particulate matter. The gases are pushed or pulled through the fabric. Particles already captured help to catch still smaller particles.

Emission estimates must take into account the effect of the control device(s) used. Usually the efficiency of the control device must be known. Efficiency is expressed as a percentage. The data used should reflect the efficiency achieved during typical day-to-day operations, not the theoretical optimum efficiency. The control device efficiency used in estimating emissions of each listed substance must be justified by the facility operator, and the justification must be cited.

V. EMISSION ESTIMATION

Source testing is the preferred method of accurately determining toxic emissions of listed substances when testing is feasible and when approved, reliable methods exist. Some types of incinerators will be required to perform source testing for specific substances pursuant to the Air Toxics "Hot Spots" Emission Inventory Criteria and Guidelines Regulation. However, when source testing is not required, several emission factors have been developed to estimate air emissions of specific listed substances from specific incinerator types.

The regulation associated with this document identifies the incinerators for which source tests are required, and explains why those particular types of source tests are required (refer to the Air Toxics "Hot Spots" Emission Inventory Criteria and Guideline Regulation for the specific requirements). This document addresses the devices, processes and the listed substances for which emission estimation techniques, rather than measurement techniques, are appropriate.

A. Emission Factors

Several specific emission factors are useful in quantifying toxic emissions of listed substances for which emissions must be quantified, but for which no source testing is required. Emission factors usually express air emissions as a ratio of the amount released of a pollutant to a process-related parameter or measurement ("usage unit"), frequently expressed as the amount of pollutant per throughput of a process or piece of equipment, or the amount of pollutant per quantity produced or processed. The throughput must be quantified to use this type of emission factor. Emission factors for air emissions are commonly based on averages measured at several facilities within the same type of industry. The applicability and accuracy of emission factors are dependent on whether the chemical substances, processes, and equipment are substantially equivalent between those tested and those to which the emission factor is to be applied.

An operator would use the following equation to estimate emissions:

(feed rate of fuel) x (fraction of listed substance in fuel) x emission factor = emissions of that listed substance

The emission factors to use in this equation are as follows (The units are: unit mass of listed substance per unit mass of listed substance in the waste)(the following emission factors were developed from CARB source test data and data found in the U.S. EPA 1986 <u>Permit Writers Guide to Test Burn Data: Hazardous Waste Incineration</u>):

	Controlled (using a venturi scrubber)	Uncontrolled
Two-chamber Incinerator (fixed hearth incinerator)		
-Carbon tetrachloride-	2.37×10^{-5}	no information
-Chlorobenzene-	7.18×10^{-4}	1.39×10^{-3}
-Methyl chloroform- (1,1,1-trichloroethane)	2.52×10^{-4}	no information
-Toluene-	1.15×10^{-4}	1.21×10^{-4}
-Trichloroethylene-	3.86×10^{-4}	4.34×10^{-4}
Rotary-kiln		
-Carbon tetrachloride-	8.15×10^{-6}	no information

The emission factors listed are derived from information found in: U.S. EPA, 1986, "Permit Writers Guide to Test Burn Data, Hazardous Waste Incineration". The "controlled" emission factors are for specific substances emitted from specific incinerator types with venturi scrubbers, which are one of the most commonly used control devices. **If a facility does not utilize a venturi scrubber, the operator should use the uncontrolled emission factors and apply the control efficiency for the specific listed substance of the control device utilized.** The control efficiency used should reflect the efficiency achieved during typical day-to-day operations, not the theoretical optimum efficiency. The control device efficiency used in estimating emissions of each listed substance must be justified by the facility operator and the justification must be cited.

"No information" indicates that all the incineration systems reviewed provided only data gathered under controlled conditions.

Example Using Emission Factors

Facility "A" utilizes a two-chamber, fixed hearth incinerator to destroy waste material produced on-site, with a Venturi scrubber for control equipment. The waste material is fed into the incinerator at a rate of 3,000 lbs per hour. The facility operator knows that the maximum feed rate per hour is 3,900 lbs. per hour. The waste contains 6.5% carbon tetrachloride. Facility "A" operates 4,000 hours per year. Facility "A" wants to calculate the maximum hourly and average annual emissions of carbon tetrachloride. Utilizing the emission factor for carbon tetrachloride and the equation provided, facility "A" can estimate the emissions of carbon tetrachloride:

A. Annual Average Emissions

EMS = PR x F x Emfac

Where:

EMS = Emissions of Carbon tetrachloride, lbs./year
PR = Process rate, lbs./hour
F = Fraction of Carbon tetrachloride in waste stream, dimensionless
Emfac = Emission factor, dimensionless

Calculate PR:

PR = FR x DOH

Where:

FR = Waste stream feed rate, lbs./hour
DOH = Hours of operation, hours/year

PR = 3,000 lbs./hour x 4,000 hrs/year
PR = 12,000,000 lbs. of waste incinerated per year

EMS = (1.2×10^{7}) lbs./year x .065 x (2.37×10^{-5})

EMS = 18.49 lbs. of carbon tetrachloride emitted per year

B. Maximum Hourly Emissions

$HEMS_{max}$ = HFR_{max} x F x Emfac

Where:

$HEMS_{max}$ = Maximum hourly carbon tetrachloride emissions, lbs/hour

HFR_{max} = Maximum Hourly Feed Rate, lbs/hour

F = Fraction of Carbon tetrachloride in waste, dimensionless
Emfac = Emission factor, dimensionless

$HEMS_{max}$ = 3,900 lbs/hour x .065 x (2.37×10^{-5})

$HEMS_{max}$ = 0.006 lbs of carbon tetrachloride emitted per hour

B. Control Device Efficiencies

Control Efficiencies (particulate matter and inorganics)

Particulate Matter

Control Equipment	Approximate Particle Size (micrometers) 0.01	0.10	0.5	1.0	5.0	10.0
1) High efficiency cyclone			5%		50%	
2) Venturi scrubbers						
p= 10 to 20 in. H20		20%			99%	
p= 100 in. H20		99%				99.9%
3) ESP (cold)	80%					99.9%
4) ESP (hot)		99%		95%		99.9%
5) Fabric filter		99.8%		99%		99.9%

A facility operator must know the particle size that a specific listed substance is associated with prior to utilizing the above chart. The association of particle size and listed substance must be justified and the justification must be cited.

SO2/HCl Controls

Wet Scrubbers-	95+% for SO2 99+% for HCl
Dry Scrubbers-	80% for SO2 80% for HCl
Ionizing Wet Scrubber-	99% for HCl

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EMISSION ESTIMATION TECHNIQUE: OIL AND GAS PRODUCTION

OIL AND GAS PRODUCTION
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique (EET) for oil and gas production and transmission. It does not cover flares, fuel combustion, drilling fluids, and marketing operations. Specifically, estimation methods are given for valves, fittings, pumps, compressors, sumps and tanks. This document was written for the facility operator who is already familiar with the oil and gas production industry and who needs assistance with estimating emissions of listed substances from onshore and offshore crude oil production and natural gas processing operations. Descriptive information on oil and gas production is not included.

The examples in this EET focus on calculating the emissions of benzene because benzene is photochemically active and remains stable in ambient air, producing widespread emissions. In addition, benzene is a known human carcinogen, and prolonged exposure to even trace levels can have mutagenic effects. However, the information provided can be modified, using the appropriate weight fraction, and used to estimate emissions of other listed substances associated with natural gas and crude oil production such as toluene, xylene, hydrogen sulfide, and mercaptans. Other listed substances possibly emitted during oil and gas production operations include: formaldehyde, ammonia, and others.

II. SOURCES OF POTENTIAL EMISSIONS

To estimate emissions from oil and gas production, the field operator must account for all sources of toxic emissions both on-shore and off-shore. Table 1.1 shows the potential sources of emissions from crude oil production operations by activity and major subsystems. Table 1.2 shows the source of potential emissions from on-shore and off-shore production operations.

Operators should take into account differences in general operations when applying the methods in this EET. For example, the hydrocarbons fraction is generally released from crude oil more rapidly during thermal enhanced recovery than conventional production and transfer of crude oil because the oil from thermal recovery is at a higher temperature. In most cases, the estimation of total hydrocarbons will suffice because the specific hydrocarbon composition can easily be deduced from the distillation curve of the crude oil and applied to the calculation of emission estimates of specific components.

Although oil production involves a closed system, hydrocarbons can be released from values or flanges in the drill pipe or casing, and from steam

drive wells. An open valve on a casing vent can also result in emissions. When crude oil is pumped up the tubing, hydrocarbon gases may escape into the atmosphere.

TABLE 1.1

POTENTIAL EMISSION SOURCES

Exploratory/Development Drilling

Subsystems:

- Power Generation
- Mud Conditioning
  - Mud tanks/pits
  - Degasser
  - Shaker
- Fuel Storage
- Deck Sumps (offshore)

Well Completion Test

Subsystems:

- Power Generation
- Wellhead

Production

Subsystems:

- Production
- Energy Source-Lifting
  - Natural or Primary
  - Electric Submersible Pumps
  - Gas Lift Systems
  - Power Oil/Water Systems
- Pressure Maintenance or Secondary Recovery
  - Gas Injection
  - Water Injection
- Power Generation
  - Turbines
  - Gas Engines
  - Diesels
- Processing-Separation
  - Free Water Knockout
  - Two Phase/Three Phase Separator
  - Pressure Stage separators
  - Test Separator

TABLE 1.1 (Cont.)

POTENTIAL EMISSION SOURCES

Production (Cont.)

Subsystems:

Gas Preparation

- Glycol Dehydrator
- Amine Systems (H_2S)

Gas Compression

- Combustion Turbine
- Gas-Fired Reciprocating
- Electric Motor
- Diesel

Oil Preparation

- Treater

Oil Shipment

- Storage

Pumping

- Electric/Diesel
- Charge Pumps/Valves
- Turbine
- Gas

Water Cleanup (for Disposal/Injection)

- Skim Tank
- Flotation Cell
- Skim Pile
- Floor Drain System (offshore)
- Injection Pump

  Electric Pump
  Gas Turbine
  Diesel

TABLE 1.2

POLLUTANTS EMITTED BY SOURCES

SOURCE	POLLUTANTS
Power Generation - Drilling	NO_x, SO_2, HC, CO, Particulates
Mud Degassing	HC (BTX etc.)
Mud Tanks/Pits	HC (BTX etc.)
Fuel Storage	HC (Benzene, Toluene, Xylenes)
Power Generation - Production	NO_x, SO_2, HC, CO, H_2S, Part.
Gas Drying	NO_x, SO_2, CO, H_2S, Particulates
Gas Processing Vents	HC, H_2S
Oil Treaters	NO_x, SO_2, CO, H_2S, Particulates
Oil Storage/Surge Tanks	HC, H_2S
Water Treating	HC
Valves, Pump Seals, Compressor Seals	HC, H_2S

BTX = Benzene, Toluene, Xylene

Part. = Particulates

III. EMISSION CONTROL MEASURES

Emission estimates must take into account control device(s) used to reduce potentially toxic pollutants. Usually the efficiency of the control device must be known. The data used should reflect the efficiency achieved during typical day-to-day operations, not the theoretical optimum efficiency. The control efficiency used in estimating emissions of each listed substance must be justified by the facility operator and the justification must be cited in the emission inventory plan.

Efficiency is expressed as a percentage:

$$\text{Efficiency} = \frac{M_i - M_o}{M_i} \qquad (1)$$

Where:

M_i = Mass of potential 'Toxic Pollutant' flowing into the control device per period of time.

M_o = Mass of potential 'Toxic Pollutant' flowing out of the control device per period of time.

A valid efficiency estimate can be based on source tests or measurement, a mass balance calculation, or a combination of the two. Actual measurement is the best way to determine efficiency.

A number of control measures can be used in oil production operations. For example, vapor recovery and internal floating roofs can be used for storage tanks. Various treatment processes (Claus and Beavon gas treatment processes) can be used to reduce hydrogen sulfide in natural gas.

IV. EMISSION ESTIMATES

Emissions of benzene and other toxic substances from oil and gas production processes can be estimated by multiplying total organic gas (TOG) or volatile organic gas (VOC) in the facility's emission inventory data system by the product of applicable emission factor and estimates of the weight fraction that is benzene (or specific listed toxic substance).

Fugitive emissions are defined as emissions that escape from a component (valve, flange, pump seal, compressor seal, etc.) without control of flowrate, direction or composition. This description includes all emissions that are not intentional or not vented through a stack or duct.

Emissions from drilling operations, for example, are associated with gas, LPG and liquid fuel lines. In addition, emissions emanate from the drilling fluid during degassing. During the vast majority of drilling time, no entrained gases are present in the water base drilling fluid. However,

the use of oil base drilling fluids may emit small amount of toxic substances.

Besides the fugitive and combustion emissions associated with oil producing operations, there are often emissions which are intentionally vented and not necessarily associated with stack. Relief valves and valves actuated by the build-up and release of field gas pressure would fall into this category. Valves used to bleed down a system pressure to atmosphere rather than to low pressure collection lines are other sources of vented emissions. The vented emitters noted here are of intermittent nature.

Virtually all storage tanks associated with oil production operations are of fixed roof type. These tanks have many fittings in common with the oil producing flow lines and, in addition, have specialized pressure-relief vents.

Significant emissions can be observed from storage and there is a significant number of such tanks used in production operations in California. The contribution of these emissions to the total toxic emissions observed, however, will depend on the number of tanks not under vapor recovery.

A. Fugitive Losses From Valves And Fittings

The emissions from valves and fittings are largely the result of leakage due to frictional wear and tear of valves, fittings and pumps, corrosion or improper connection.

For emission estimation purposes, fittings are classified as threaded and flanged connections. The emission factors for these categories are based upon general oil production emission factors calculated by Rockwell International and the California specific emission factors generated by KVB Inc. The emission factors generated by Rockwell are based on empirical valve and fitting fugitive data. KVB based its emission factors on a 1980 field study to develop composite emission factors specifically for the valve and fitting components of oil production operations in California. KVB study was based on detailed counts of the numbers of valves and fittings in actual operation at a lease.

The following correlations will calculate the toxic emission rates of specific Volatile Organic Compounds, for example benzene, based on Total Organic Gas (TOG) and Reactive Organic Gas (ROG) emissions from valves and fittings. In order to estimate benzene emissions from total reactive organic hydrocarbon emissions, a conversion factor based on the benzene content of the liquid, the vapor pressure of the liquid, and Raoult's Law needed to be calculated. The benzene emissions, for example, can be estimated by multiplying the ROG emissions by the weight fraction of benzene, $[(Wt)_i]$.

The detailed per well emission factors for valves, fittings, pumps, compressors, well heads, and sumps are presented in the tables in Appendix D.

It has been determined that both valve and fitting emissions can be calculated based upon the following equation:

$$\text{Emissions} = (\text{Active Wells on a lease}) \times (\text{Per well E.F}) \times (Wt)_i \quad (2)$$

$$(Wt)_i = \frac{Y_i (Mw)_i}{\Sigma (Mw)_i (Y)_i} \quad (3)$$

Where Y_i = Vapor-phase mole fraction of specific toxic substance (lb/lb-mole)

NOTE:

A common approach to calculating the concentration of a substance in the vapor phase over a liquid is to determine its partial pressure. The partial pressure of the substance divided by the total pressure of the gas stream is equal to the mole fraction, Y_i, of the substance in the stream.

Calculation of mole fractions in a liquid

The mole fractions of components in a liquid must be calculated in order to estimate the vapor pressure of the liquid using Raoult's Law:

The partial pressure of each component is the liquid mole fraction (X_i) times the vapor pressure of the component (P_i)

$$P_i X_i = P_a \quad (4)$$

The liquid phase mole fractions sum to 1.00 .

Calculation of mole fraction in a Vapor

The mole fractions of a vapor phase are based on the the partial pressure that each component exerts:

$$Y_i = \frac{P_{partial}}{P_{total}} \quad (5)$$

The vapor phase mole fractions sum to 1.00.

Calculation of molecular weight of vapor

The molecular weight of the vapor is dependent upon the mole fractions of the components in the vapor:

$$M_v = \Sigma (Mw)_i (Y)_i \quad (6)$$

Calculation of the weight fraction of the vapor

The weight fraction of each component in a mixture is the pounds of that component divided by the total pounds of the mixture.

The weight fraction, Wt_i, of the vapor are needed to calculate the amount (in pounds) of each component emitted from a storage tank, valve, sump, process unit etc. The weight fractions are related to mole fractions in the vapor phase. Weight fractions calculated are valid no matter how many moles actually are present.

Calculation of the amount of each component emitted from a Tank

The amount of each component emitted is the weight fraction of that component in the vapor multiplied by the total amount of VOC emitted from the storage tank, sump or valves.

Assumptions:

1) For wells in a similar lease, the physical and mechanical properties of the wells along with the improvement and maintenance programs are identical. This will allow one composite set of emission factors to be developed and used for each lease.

2) The process rate unit, "number of active wells," is used for these emission categories in place of the more commonly used throughput units. This choice is based on the assumption that emissions depend not on the amount of oil or gas produced, but on the number of leak points (values/fittings), which is proportional to the number of wells in operation.

$$\text{(Total ROG Emissions Rates (Valves))} = (\text{Valve Em})_{gas} + (\text{Valve Em})_{oil} \quad (7)$$

$$(\text{Valve Emissions})_{gas} = (\text{\# of Active Wells}) \times (\text{Applicable E.F}) \times (Wt)_i \quad (8)$$

$$(\text{Valve Emissions})_{oil} = (\text{\# of Active Wells}) \times (\text{Applicable E.F})_{oil} \times (Wt)_i \quad (9)$$

$$\text{Total ROG Fitting Emissions} = (\text{Fitting Emissions})_{gas} + (\text{Fitting Emission})_{oil} \quad (10)$$

$$(\text{Fitting Emissions})_{gas} = (\text{\# of Active Wells}) \times (\text{Applicable E.F})_{gas} \times (Wt)_i \quad (11)$$

$$(\text{Fitting Emissions})_{oil} = (\text{\# of Active Wells}) \times (\text{Applicable E.F})_{oil} \times (Wt)_i \quad (12)$$

B. Fugitive Losses From Sumps and Pits

Before a detailed presentation of the emission factor equation for sumps is made, an explanation of some of the oil industry developed terms relating to oil production sumps is essential. In general terms, a sump is defined as a lined or unlined excavated depression in the ground that is in more or less continuous use for separating oil, water, and sand in oil and gas production operations. There are three basic classification of sumps which must be differentiated when applying the emission factor equation: primary, secondary and tertiary production sumps.

1. **Primary Production Sump**

A primary production sump is a sump that receives a generally continuous stream of oil and produced water directly from oil production wells and/or field gathering systems.

2. **Secondary Production Sump**

A secondary production sump receives a generally continuous waste water stream from one or more first stage separators (including a first stage sump and/or tank).

3. **Tertiary Production Sump**

A tertiary production sump receives a generally continuous waste water stream from second stage separation processes (sumps and tanks) upstream of the sump and in general has only a small amount of oil present. Sumps are classified as serving light oil or heavy oil. Light oil service sumps are those which contain crude oil having API gravity of 30 or greater, and heavy oil srvice sumps are those which contain crude oil having API gravity less than 30.

4. **Pit**

A pit is classified as a lined or unlined excavated depression in the ground used for emergencies or to receive intermittent flows of waste products from drilling and oil production processes which may contain toxic hydrocarbon materials.

Estimating Emissions From Sumps

It has been empirically determined that toxic emissions from sumps can be estimated using the following equation:

$$\text{Emissions} = (\text{Sump Surface Area}) \times (\text{Emission Factor}) \times (\text{Wt})_i \quad (13)$$

The ROG emission factors listed in Appendix D-1 for heavy crude were obtained from ARB testings between 1983 and 1987. The listed emission factors for light crudes (Appendix D-1) were extrapolated from API/Rockwell and ARB test results.

The emission rate of a specific toxic substance can be estimated by multiplying equation 13 by the weight fraction of the specific toxic substance (for example benzene).

C. <u>Methods of Estimating Toxic Emissions From Crude Oil Storage Tanks</u>

The following emission estimation techniques for crude oil storage tanks were derived from equations in section 4.3 of <u>Compilation of Air Pollutant Emission Factors: Volume 1 Stationary Point and Area Sources</u>, AP-42 (4th Edition, September, 1985). These equations estimate total VOC emissions from storage tanks, and can be modified to estimate chemical-specific emissions directly. The correlations in this emission estimation techniques reflect these modifications.

1. Estimation of Toxic Emissions From Floating Roof Tanks

The total loss from external floating roof tanks can be estimated from the following equations:

$$L_T = L_S + L_W \quad (14)$$

Where:

L_T = Total loss

L_S = Storage loss

L_W = Withdrawal loss

Storage loss, L_S, can be determined by the following equations:

$$L_S = K_S V^N P^* D M_V K_C E_F (Wt)_i \quad (15)$$

$$P^* = \frac{P/Pa}{[1 + (1 - P/Pa)^{0.5}]^2} \quad (16)$$

Where:

L_S = Standing storage loss (lbs/yr)

K_S = Seal Factor (lb-mole/(ft(mile/hr)^{N}yr)) (See Table 4.3-4, Appendix C).

V = Average wind speed at tank site (mile/hr) (See Table A-6, Appendix F).

$(Wt)_i$ = Weight fraction of listed substance i, in the crude (Wt. % in vapor/Wt. % in liquid)

N = Seal related wind speed exponent (dimensionless) (See Table 4.3-4, Appendix C).

P^* = Vapor pressure function (dimensionless) (See Figure 4.3-9, Appendix F).

D = Tank diameter (feet)

P = True vapor pressure at average actual organic liquid storage temperature (psia)

P_a = Average atmospheric pressure at tank location (psia)

M_V = Average molecular weight of vapor (lb/lb-mole) (See Table 4.3-2, Appendix F).

K_C = Product factor (dimensionless)

E_F = Secondary seal factor

Notes:

(a) If average actual organic liquid storage temperature, T_S, is unknown, the average storage temperature can be estimated from the average ambient temperature, T_A(^oF) (See Table A-4, Appendix F). This information, T_A, is available from the local weather service data, and needs to be adjusted to the tank paint color factor.

(b) A typical value of 60 lb/lb-mole can be assumed for the molecular weight of all hydrocarbon vapors (reflecting typical California data) and a value of 50 lb/lb-mole can be assumed for United States midcontinental crude oils. The diurnal temperature change can be assigned a value of 25^oF, while the atmospheric pressure term, P_A, can be set at 14.7 psia.

(c) For all Volatile Organic Liquids: K_C = 1.0

For crude oil: K_C = 0.4

(d) For petroleum liquid storage with any seal system: E_F = 1.0

For volatile organic liquid storage with a primary only seal system: E_F = 1.0

With a primary/secondary seal system: E_F = 0.07 to 0.45

(A value of 0.25 is recommended for tanks and seals in good condition.) Standing storage loss emissions from internal floating roof tanks was estimated using equation 15.

(e) K_S = 0.7 for all seal systems

(f) N = 0.4 for all seal systems

The working loss from external floating roof and internal floating roof tanks can be estimated using Equation 17.

$$L_W = \frac{(0.943)\ QCW_L}{D} \left[1 + \left(\frac{N\ F}{D} \right) \right] (Wt)_i \qquad (17)$$

Where:

L_W = Working loss (lb/yr)

Q = Throughput (bbl/year) (tank capacity [bbl] times annual turnover rate)

C = Shell clingage factor (bbl/1,000 ft^2) (See Table 4.3-5, Appendix F).

W_L = Average organic liquid density (lb/gal) (See Table 4.3-2, Appendix F).

D = Tank diameter (ft)

N = Number of columns (dimensionless)

F = Effective column diameter (ft) [column perimeter (ft)/pi] (pi = 3.142)

Notes:

(a) If W_L is unknown, an average value of 5.6 lb/gallon can be assumed for gasoline. An average value cannot be assumed for crude oil, since densities are highly variable.

(b) The constant, 0.943, has dimensions of (1,000 ft^3 x gal/bbl^2).

(c) For self-supporting fixed roof or an external floating roof tank:

N = 0.

For column supported fixed roof:

N = Use tank specific information

(d) Use tank effective column diameter, or F = 1.1 for 9 inch by 7 inch built-up columns, 0.7 for 8 inch diameter pipe columns, and 1.0 if column construction details are not known.

(e) For round tanks, the diameter is measured and recorded in feet. For rectangular tanks, the equivalent diameter (in feet) is found by applying the following equation:

$$\text{Equivalent Diameter} = (1.13) \times (\text{Length} \times \text{Width})^{0.5} \qquad (18)$$

2. Estimation of Toxic Emissions from Fixed Roof Tanks

The two major sources of emissions from fixed roof tanks are classified as occurring from either breathing losses or working losses. The term breathing loss refers to those emissions that result without any significant change in the liquid level within the tank. These types of emission are the expected results from hydrocarbon vapors that are released from the tanks by expansion or contraction caused by changes in either temperature or pressure. Working loss, on the other hand, represents those emissions that occur due to changes in liquid level caused by either filling or emptying the tank itself.

The total hydrocarbon loss from a fixed roof tank is the sum of: $L_B + L_W$ multiplied by operational percentage vapor recovery factor for the system used.

$$L_T = L_B + L_W \qquad (19)$$

Where:

L_T = Total loss (lb/yr)

L_B = Breathing loss (lb/yr)

L_W = Working or withdrawal loss

If the tank is vented to a vapor recovery system, multiply equation (19) by 0.05. If vented to thermal oxidizer, multiply equation (19) by 0.01.

a. Calculating Breathing loss from a Fixed Roof Tank:

$$L_B = 0.0226 \times M_V \left(\frac{P}{P_A - P}\right)^{0.68} \times D^{1.73} \times H^{0.51} \times \Delta T^{0.50} \times F_P C K_C \, (Wt)_i \qquad (20)$$

$$M_V = M_a \frac{(P_a X_a)}{P_t} + M_b \frac{(P_b X_b)}{P_t} \cdots\cdots + M_n \frac{(P_n X_n)}{P_t} \qquad (21)$$

P_t by Raoult's law is:

$$P_t = P_a X_a + P_b X_b \ldots\ldots + P_n X_n \quad (22)$$

Where:

M_V = Molecular weight of vapor in storage tank, lb/lb-mole, (See Table 4.3-2, Appendix F OR use Equation 21).

P_A = Average atmospheric pressure at tank location, psia

P = True vapor pressure at bulk liquid conditions, psia

P_t = True vapor pressure, psia (See Table 4.3-2 or Figure 4.3-5, Appendix F).

D = Tank diameter, ft

H = Average vapor space height, including roof volume correction, ft

ΔT = Average ambient diurnal temperature change, ^oF.

F_P = Paint factor, dimensionless (See Table C-1, Appendix C)

C = Adjustment factor for small diameter tanks, dimensionless (See figure 4.3-4, Appendix F)

K_C = Product factor, dimensionless

M_a = Molecular weight of pure component, a

M_b = Molecular weight of pure component, b

P_a = Vapor pressure of pure component, a (See Cox Chart in Appendix B)

P_b = Vapor pressure of pure component, b (See Cox Chart in Appendix B)

X_a = Mole fraction of component, a

X_b = Mole fraction of component, b

1. **Average Vapor Space Height (H)**

The average vapor space height refers to the typical height of hydrocarbon vapor that is in the tank, and can be calculated by the application of the following equation:

$$H = 0.5 \text{ (Height of tank)} \quad (23)$$

2. **Paint Factor (F_p)**

Hydrocarbon emissions from tanks depend on the tank color, the condition of the paint itself, and whether or not there is an insulation present. The paint factor is the term that takes into account the effects that these three variables have on overall breathing loss emissions. Values of the paint factor for different conditions are tabulated Appendix C.

3. **Adjustment Factor for Small Diameter Tanks (C)**

Tank emissions also depend on the tank diameter, with small diameter tanks emitting proportionally less pollutants than larger diameter tanks. The breakpoint between small and large diameter tanks was set at 30 feet. At values greater than or equal to 30 feet, the emissions were considered to be independent of tank diameter and the adjustment factor was set equal to 1.0. If the tank diameter was less than 30 feet, the following equation can be applied to calculate the adjustment factor:

$$C = (0.0771) \times \text{(Diameter)} - (0.0013) \times \text{(Diameter)}^2 - 0.1334 \quad (24)$$

4. **Control Factor (CONTROL)**

Certain types of control measures have been devised which considerably reduce theoretical tank emissions. To quantify the corresponding emissions reductions that result from the implementation of these measures, control factor terms have been developed. These terms are applied directly to the emission calculation equations in other to obtain controlled emission estimates. Table C-4 in Appendix C lists several storage tank types along with their corresponding acceptable control factors. A control factor of 1.00 means that no emissions reductions are achieved by the use of this type of tank.

5. **True Vapor Pressure (TVP)**

True vapor pressure, the equilibrium partial pressure exerted by a volatile liquid, is perhaps the most difficult term in the breathing loss equation to calculate. A nomograph (included in Appendix E) relates TVP to both the Reid Vapor Pressure (RVP) and the storage temperature (T_s). RVP is

the absolute vapor pressure of volatile crude oil and nonviscuous petroleum liquids. Numerically, the relationship between TVP, RVP and temperature can be expressed by the following equation:

$$TVP = (RVP)\ e^{[C_0(IRTEMP - ITEMP)]} \qquad (25)$$

Where:

C_0 = Constant dependent upon the value of RVP

ITEMP = $(1/559.69\ ^oR)$

IRTEMP = $(1/(T_S + 459.69^oR))$

T_S = Temperature of the stored fluid

The value of the constant term C_0 depends upon the given value of RVP. Values of C_0 for different RVP numbers are tabulated in Appendix C. It should be noted, however, that an error was discovered in the API nomograph calculated values of TVP so that the RVP was not equal to TVP at 100^oF as was expected given the general definition of RVP. Using linear regression techniques, correction factors (C_F) were developed and should be added to the calculated values of TVP in order to obtain reasonable TVP numbers. The relationship between the three values is given as follows:

$$\text{Corrected TVP} = \text{Calculated TVP} + C_F \qquad (26)$$

The correction factor was found to be dependent upon RVP according to the following equations:

If RVP < 3 ,

$$C_F = (0.04) \times (RVP) + 0.1 \qquad (27)$$

If RVP > 3

$$C_F = e^{[(2.3452061 \log (RVP)) - 4.132622]} \qquad (28)$$

Notes:

(All tables and figures referenced/listed below can be found in EPA AP-42, Section 4.3, Fourth Edition, September 1985.)

(1) The molecular weight of the vapor, M_V, can be determined from Table 4.3-2 (See Appendix E) for selected petroleum liquids and volatile organic liquids or by analysis of vapor samples. Where mixtures of organic liquids are stored in a tank, M_V can be estimated from the liquid composition using equation (6) or (21).

(2) For crude oil: $K_C = 0.65$.

For all other organic liquids: $K_C = 1.0$.

(3) The vapor space in a cone roof is equal in volume to a cylinder, which has the same base diameter as the cone and is one third the height of the cone. If information is not available, assume H equals one half tank height.

(4) True vapor pressures for organic liquids can be determined from Figures 4.3-5 or 4.3-6 (See Appendix F), or Table 4.3-2 (See Appendix E). In order to use Figures 4.3-5 or 4.3-6, the stored liquid temperature, T_S, must be determined in degrees Fahrenheit. T_S is determined from Table C-2 in Appendix C, given the average annual ambient temperature, T_A, in degrees Fahrenheit. True vapor pressure is the equilibrium partial pressure exerted by a volatile organic liquid, as defined by ASTM-D-2879 or as obtained from standard reference texts. Reid Vapor Pressure is the absolute vapor pressure of volatile crude oil and volatile nonviscuous petroleum liquids, except liquified petroleum gases, as determined by ASTM-D-323.

B. Calculating Working Losses from a Fixed Roof Tank

Working losses from fixed roof tanks can be estimated using the following equation:

$$L_W = 2.40 \times 10^{-5} M_V \; P \; V \; N \; K_N \; K_C \; (Wt)_i \qquad (29)$$

Where:

L_W = Fixed roof working loss (lb/year)

M_V = Molecular weight of vapor in storage tank (lb/lb-mole) (See Table 4.3-2, Appendix F).

P = True vapor pressure at bulk liquid temperature (psia)
V = Tank capacity (gal)
N = Number of turnovers per year (dimensionless)

$$= \frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, V (gal)}} \qquad (30)$$

Equation (29) can be modified to reflect the actual conditions as they exist in California fields. Control measures are common place in California and should be reflected in the working loss equation. Thus, the resulting working loss equation can be expressed as follows:

$$L_W = (0.00144) \times P\ V\ N\ K_C K_N\ (\text{CONTROL})\ (Wt)_i \qquad (31)$$

3. Estimating Toxic Emissions from Bulk Loading Operations

Toxic emissions from loading petroleum liquid can be estimated using the following equation:

$$L_L = 523.32\ \frac{SPM}{T}\ (1.00 - \frac{eff.}{100})\ (Wt)_i \qquad (32)$$

Where:

L_L = Loading loss (lb HC/1000 bbl. loaded)

S = Saturation factor (EPA AP-42, Table 4.4-1,
$(Wt)_i$ = Weight fraction of the listed substance

P = Vapor pressure, psia (See Cox Chart, Appendix B)
M = Molecular weight of condensed vapors (lb/lb-mole) (See Table 4.3-2)
T = Loading temperature, ^oR (^oF + 460)
eff. = Typical efficiency (%)
99 - vapor recovery to fuel gas system
92 - vapor recovery to recovery unit
0 - uncontrolled

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APPENDIX A
SAMPLE CALCULATIONS

SAMPLE CALCULATIONS - TOXIC EMISSIONS FROM VALVES

The following example illustrates the calculation of TOG and ROG valve and fitting emissions for Union Oil's Polvadero Lease located in Fresno County. It has been determined that four active wells are in operation at the lease and that the GOR is 877. This data places the lease in Lease Model #4 for toxic emission estimation purposes.

Total ROG = $(\text{Valve Emission})_{gas} + (\text{Valve Emission})_{oil}$

$(\text{Valve Emission})_{gas}$ = (# of Active Wells) x $(\text{Emission Factor})_{gas}$

$(\text{Valve Emissions})_{gas}$ = (4 wells) x (4.617 lbs/day-well)

= (18.47 lbs/day) (365 days/year) (1 ton/2000 lbs)
= 3.37 tons/year

$(\text{Valve Emissions})_{oil}$ = (# of Active Wells) x $(\text{Emission Factor})_{oil}$

= (4 wells) ($1.253 \times 10^{-4} + 3.129 \times 10^{-2}$ lbs/day-well)
= (0.126 lbs/day) (365 days/year) (1 ton/2000 lbs)
= 0.02 tons/year

Total Valve Emissions = 3.37 tons/year + 0.02 tons/year
= 3.39 tons/year

Note: The **weight fraction of each component is the pounds of that component divided by the pounds of the mixture.**

ASSUMPTION: Weight $\text{fraction}_{benzene}$ in the oil/gas that passed through the valves, Wt._i = 0.25 **(HYPOTHETICAL)**

Therefore, $(\text{Toxic}_{benzene}\ \text{Emission})_{valves}$ = (0.25) (3.39 tons/year)

= 0.85 ton/year Benzene

APPENDIX B
ANTOINE'S EQUATION CONSTANTS
AND
COX CHART FOR ESTIMATING VAPOR PRESSURE

APPENDIX B-ANTOINE'S EQUATION CONSTANTS

Antoine equation correlates vapor pressure-temperature data extremely well. Clausius-Clapeyron equation OR Cox Charts can also estimate vapor pressure.

$$\log_{10} p^* = A - \frac{B}{T + C} \quad ; \quad p^* \text{ in mm Hg} \quad ; \quad T \text{ in } ^oC$$

Substance	Formula	Range, ^oC	A	B	C
Acetaldehyde	C_2H_4O	-45 to +70	6.81089	992.0	230
Acetic Acid	$C_2H_4O_2$	0 to +36	7.80307	1651.2	225
		+36 to +170	7.18807	1416.7	211
Acetone	C_3H_6O	—	7.02447	1161.0	224
Ammonia	NH_3	-83 to +60	7.55466	1002.711	247.885
Benzene	C_6H_6	—	6.90565	1211.033	220.790
Carbon tetrachloride	CCl_4	—	6.93390	1242.43	230.0
Chlorobenzene	C_6H_5Cl	0 to +42	7.10690	1500.0	224.0
		+42 to +230	6.94504	1413.12	216.0
Chloroform	$CHCl_3$	-30 to +150	6.90328	1163.03	227.4
Cyclohexane	C_6H_{12}	-50 to +200	6.84498	1203.526	222.863
Ethyl Acetate	$C_4H_8O_2$	-20 to +150	7.09808	1238.71	217.0
Ethyl alcohol	C_2H_5OH	—	8.04494	1554.3	222.65
Ethylbenzene	C_8H_{10}	—	6.95719	1424.255	213.206
n-Heptane	C_7H_{16}	—	6.90240	1268.115	216.900
n-Hexane	C_6H_{14}	—	6.87776	1171.530	224.366
Methyl alcohol	CH_3OH	-20 to +140	7.87863	1473.11	230.0
Methyl ethyl ketone	C_4H_8O	—	6.97421	1209.6	216
n-Pentane	C_5H_{12}	—	6.85221	1064.63	232.000
Isopentane	C_5H_{12}	—	6.78967	1020.012	233.097
Styrene	C_8H_8	—	6.92409	1420.0	206.
Toluene	C_7H_8	—	6.95334	1343.943	219.377
Water	H_2O	0 to 60	8.10765	1750.286	235.0
		60 to 150	7.96681	1668.21	228.0

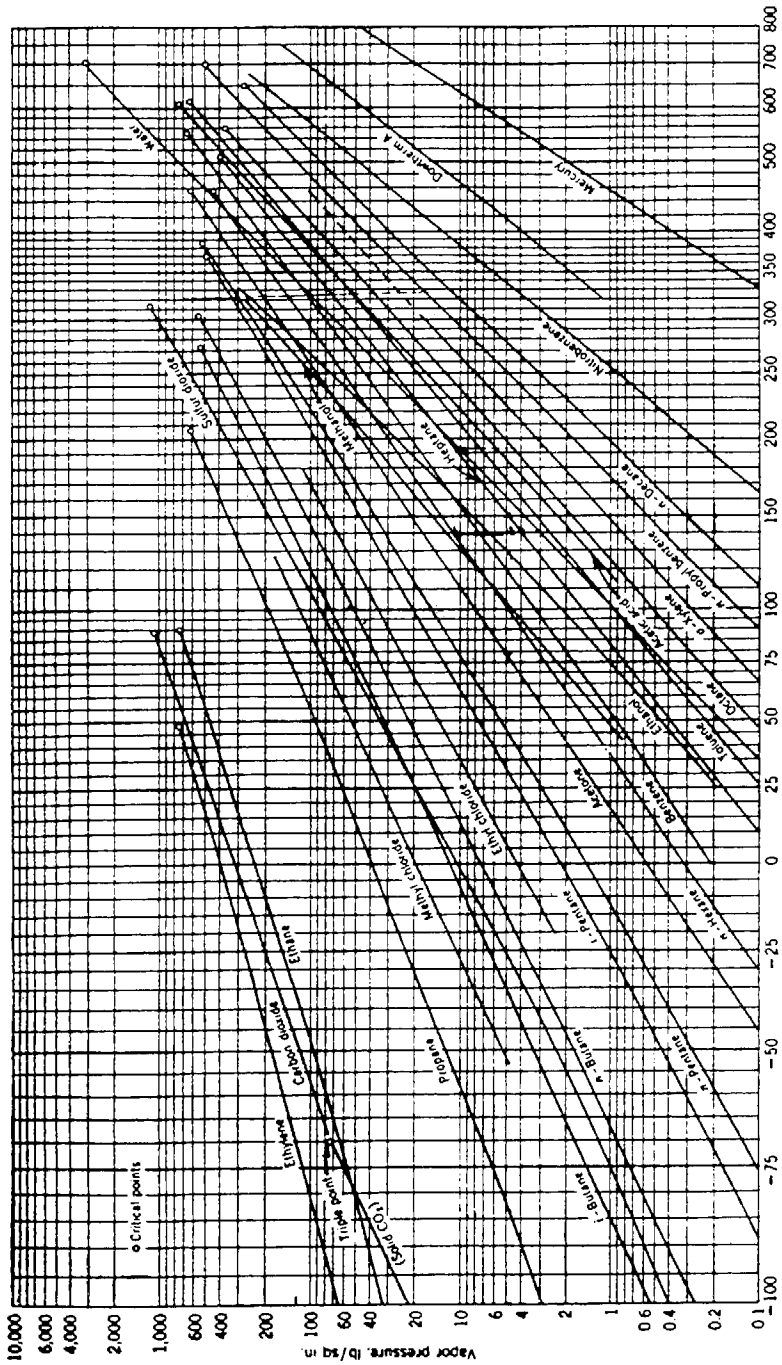


FIGURE 7.1-4. Cox chart vapor pressure plots. From A. S. Foust *et al.*, *Principles of Unit Operations*, Wiley, New York, 1960, p. 550.

(Source: Richard M. Felder, Donald W. Rousseau, 1978, Elementary Principles of Chemical Processes, John Wiley and Sons, Inc.)

APPENDIX C
FACTORS FOR CRUDE OIL STORAGE TANK CALCULATIONS

FACTORS FOR FIXED ROOF TANK CALCULATIONS

TABLE C-1 PAINT FACTOR FOR FIXED ROOF TANKS

Tank color		Paint factors (F_p)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44
Medium gray	Medium gray	1.40	1.58[a]

[a]Estimated from the ratios of the seven preceding paint factors.

TABLE C-2. AVERAGE STORAGE TEMPERATURE (T_S) AS A FUNCTION OF TANK PAINT COLOR

Tank Color	Average Storage Temperature, T_S (^oF)
White	T_A^* + 0
Aluminum	T_A + 2.5
Gray	T_A + 3.5
Black	T_A + 5.0

*T_A is average ambient temperature in degrees farenheit.

(Compiled from: U.S. EPA, 1985, Compilation of Air Pollutant Emission Factors: Volume 1 Stationary Point and Area Sources, AP-42, 4th Edition, September).

TABLE C-3 VALUES OF C_0 FOR DIFFERENT RVP NUMBERS

RVP	C_0
0<RVP<2	-6622.5
2<RVP<3	-6439.2
RVP = 3	-6255.9
3<RVP<4	-6212.1
RVP = 4	-6169.2
4<RVP<5	-6177.9
RVP = 5	-6186.5
5<RVP<6	-6220.4
RVP = 6	-6254.3
6<RVP<7	-6182.1
RVP = 7	-6109.8
7<RVP<8	-6238.9
RVP = 8	-6367.9
8<RVP<9	-6477.5
RVP = 9	-6587.9
9<RVP<10	-6910.5
RVP = 10	-7234.0
10<RVP<15	-8178.0
RVP > 15	-9123.2

TABLE C-4 CONTROL FACTORS

TANK TYPE	CONTROL FACTOR
Open top tank (no fixed or floating roof)	1.00
Fixed roof tank with roof openings (open vents, holes), but no vapor controls	1.00
Fixed roof tank with functional p.v. valve on the roof, but no open vents and no vapor controls	0.90
Fixed roof tank with internal floating roof and p.v. valve on roof	0.05
Fixed roof tank with vapor balance type emission control system	0.10
Fixed roof tank with compression, refrigeration or combustion type vapor control or recovery system	0.02
External floating roof tank	0.05

TABLE 4.3-4. SEAL RELATED FACTORS FOR FLOATING ROOF TANKS[a]

Tank and seal type	Welded Tank K_S	Welded Tank n	Riveted Tank K_S	Riveted Tank n
External floating roof tanks[b]				
Metallic shoe seal				
Primary seal only	1.2	1.5	1.3	1.5
With shoe mounted secondary seal	0.8	1.2	1.4	1.2
With rim mounted secondary seal	0.2	1.0	0.2	1.6
Liquid mounted resilient seal				
Primary seal only	1.1	1.0	NA[c]	NA
With weather shield	0.8	0.9	NA	NA
With rim mounted secondary seal	0.7	0.4	NA	NA
Vapor mounted resilient seal				
Primary seal only	1.2	2.3	NA	NA
With weather shield	0.9	2.2	NA	NA
With rim mounted secondary seal	0.2	2.6	NA	NA
Internal floating roof tanks[d]				
Liquid mounted resilient seal				
Primary seal only	3.0	0	NA	NA
With rim mounted secondary seal[e]	1.6	0	NA	NA
Vapor mounted resilient seal				
Primary seal only	6.7	0	NA	NA
With rim mounted secondary seal[e]	2.5	0	NA	NA

[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.
[b]Reference 5.
[c]NA = Not Applicable.
[d]Reference 6.
[e]If tank specific information is not available about the secondary seal on an internal floating roof tank, then assume only a primary seal is present.

APPENDIX D
APPLICABLE EMISSION FACTORS FOR VARIOUS OIL AND GAS PRODUCTION OPERATIONS

TABLE D-1

CATEGORY	EMISSION FACTORS
Well Cellars	Same as sump
Oil/Water Separators **(SOURCE: BAAQMD TEST RESULTS)**	925 lbs VOC/MM Gallon Wastewater (uncontrolled) (85% control efficiency with cover)
SUMPS	
Light Crude[a]	
Primary Sumps	0.142 lbs ROG/sq ft -day
Secondary	0.019 lbs ROG/sq ft -day
Tertiary	0.009 " "
Heavy Crude[b]	
Primary Sumps	0.097 " "
Secondary	0.013 " "
Tertiary	0.006 " "
Pumps	0.004 lb ROG/well-day
Compressors	0.07 lb ROG/well-day
Well Heads	0.01 lb ROG/well-day
Steam Drive Wells	3610 lb ROG/well-year (Controlled)
Steam Drive wells (VOC)	220 lbs/well/day (Uncontrolled)
Cyclic Steam Wells (VOC)	3.6 lbs/well/day (Uncontrolled)
Cyclic Wells	1210 lb ROG/well-year (Controlled)
"Pseudocyclic" wells (Tertiary)	110 lb/day/well

a Extrapolated from API/Rockwell and ARB test results.
b Results obtained from ARB testing between 1983 - 1986.

TABLE D-2
VALVE EMISSION FACTORS

LEASE MODEL	SERVICE	TOG EMISSION FACTOR (lbs/day-well) x 10^{-4}	ROG EMISSION FACTOR (lbs/day-well) x 10^{-4}
MODEL #1	GAS	36250.000	14610.000
	LIQUID	2.511	1.012
	MIXTURE	1914.000	771.500
	CONDENSATE	0.000	0.000
MODEL #2	GAS	17410.000	7018.000
	LIQUID	2.484	1.001
	MIXTURE	488.600	196.900
	CONDENSATE	0.000	0.000
MODEL #3	GAS	159.100	64.100
	LIQUID	0.666	0.268
	MIXTURE	394.800	159.100
	CONDENSATE	0.000	0.000
MODEL #4	GAS	114600.000	46170.000
	LIQUID	3.109	1.253
	MIXTURE	776.400	312.900
	CONDENSATE	0.000	0.000
MODEL #5	GAS	21220.000	8550.000
	LIQUID	1.302	0.525
	MIXTURE	855.300	344.700
	CONDENSATE	0.000	0.000
MODEL #6	GAS	43080.000	17360.000
	LIQUID	0.216	0.087
	MIXTURE	613.900	247.400
	CONDENSATE	0.000	0.000

MODEL #1: Number of wells on the lease is less than 10 and the GOR is less than 500.
MODEL #2: Number of wells on the lease is between 10 and 50 and the GOR is less than 500.
MODEL #3: Number of wells on the lease is greater than 50 and the GOR is less than 500.
MODEL #4: Number of wells on the lease is less than 10 and GOR is greater than 500.
MODEL #5: Number of wells on the lease is between 10 and 50 and the GOR is greater than 500.
MODEL #6: Number of wells on the lease is greater than 50 and the GOR is greater than 500.
NOTE: GOR is Gas/Oil ratio.

TABLE D-3
FITTING EMISSION FACTORS

LEASE MODEL	SERVICE	TOG EMISSION FACTOR (lbs/day-well) x 10^{-4}	ROG EMISSION FACTOR (lbs/day-well) x 10^{-4}
MODEL #1	GAS	21700.000	8746.000
	LIQUID	827.500	333.500
	MIXTURE	2916.000	1175.000
	CONDENSATE	0.000	0.000
MODEL #2	GAS	14810.000	5968.000
	LIQUID	0.001	0.000
	MIXTURE	312.200	1258.000
	CONDENSATE	0.000	0.000
MODEL #3	GAS	426.600	171.900
	LIQUID	24.860	10.020
	MIXTURE	1271.000	512.200
	CONDENSATE	0.102	0.410
MODEL #4	GAS	52180.000	21030.000
	LIQUID	0.002	0.001
	MIXTURE	2354.000	948.600
	CONDENSATE	0.000	0.000
MODEL #5	GAS	44890.000	18090.000
	LIQUID	74.320	29.950
	MIXTURE	4727.000	1905.000
	CONDENSATE	0.000	0.000
MODEL #6	GAS	63670.000	25660.000
	LIQUID	0.000	0.000
	MIXTURE	294.500	118.700
	CONDENSATE	0.621	0.250

MODEL #1: Number of wells on the lease is less than 10 and the GOR is less than 500.
MODEL #2: Number of wells on the lease is between 10 and 50 and the GOR is less than 500.
MODEL #3: Number of wells on the lease is greater than 50 and GOR is less than 500.
MODEL #4: Number of wells on the lease is less than 10 and the GOR is greater than 500.
MODEL #5: Number of wells on the lease is between 10 and 50 and the GOR is greater than 500.
MODEL #6: Number of wells on the lease is greater than 50 and the GOR is greater than 500.

APPENDIX F
FIGURES AND TABLES

TABLE 4.3-1. PAINT FACTORS FOR FIXED ROOF TANKS[a]

Tank color		Paint factors (F_p)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44[b]
Medium gray	Medium gray	1.40	1.58[b]

[a]Reference 2.
[b]Estimated from the ratios of the seven preceding paint factors.

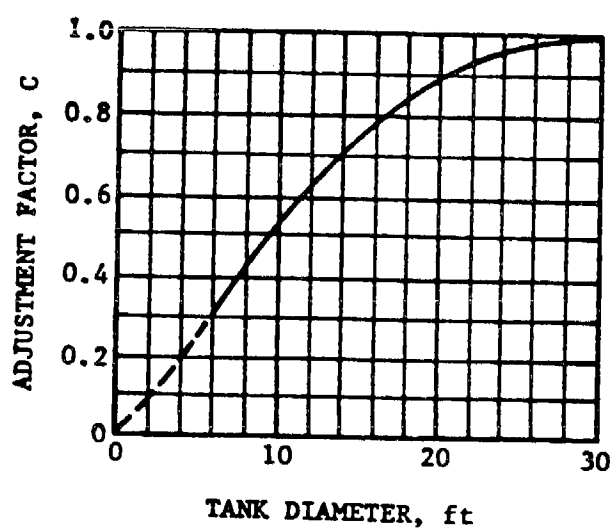


Figure 4.3-4. Adjustment factor (C) for small diameter tanks.[2]

TABLE 4.3-5. AVERAGE CLINGAGE FACTORS (C) (bbl/1,000 ft^2)[a]

Liquid	Shell condition		
	Light rust[b]	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

[a]Reference 5.
[b]If no specific information is available, these values can be assumed to represent the most common condition of tanks currently in use.

TABLE 4.3-6. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETER FOR INTERNAL FLOATING ROOF TANKS WITH COLUMN SUPPORTED FIXED ROOFS[a]

Tank diameter range D (ft)	Typical number of columns, N_C
$0 < D \leqq 85$	1
$85 < D \leqq 100$	6
$100 < D \leqq 120$	7
$120 < D \leqq 135$	8
$135 < D \leqq 150$	9
$150 < D \leqq 170$	16
$170 < D \leqq 190$	19
$190 < D \leqq 220$	22
$220 < D \leqq 235$	31
$235 < D \leqq 270$	37
$270 < D \leqq 275$	43
$275 < D \leqq 290$	49
$290 < D \leqq 330$	61
$330 < D \leqq 360$	71
$360 < D \leqq 400$	81

[a]Reference 1. This table was derived from a survey of users and manufacturers. The actual number of columns in a particular tank may vary greatly with age, fixed roof style, loading specifications, and manufacturing perogatives. Data in this table should not supersede information on actual tanks.

TABLE 4.3-2. PHYSICAL PROPERTIES OF TYPICAL ORGANIC LIQUIDS[a]

Organic liquid[b]	Vapor molecular weight @ 60°F	Product density (d), lb/gal @ 60°F	Condensed vapor density (w), lb/gal @ 60°F	True vapor pressure in psia at: 40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum Liquids[c]										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel no. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil no. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Volatile Organic Liquids										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1,2-Dichloroethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methylethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
1,1,1-Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

[a] References 3-4.
[b] For a more comprehensive listing of volatile organic liquids, see Reference 3.
[c] RVP = Reid vapor pressure in psia.

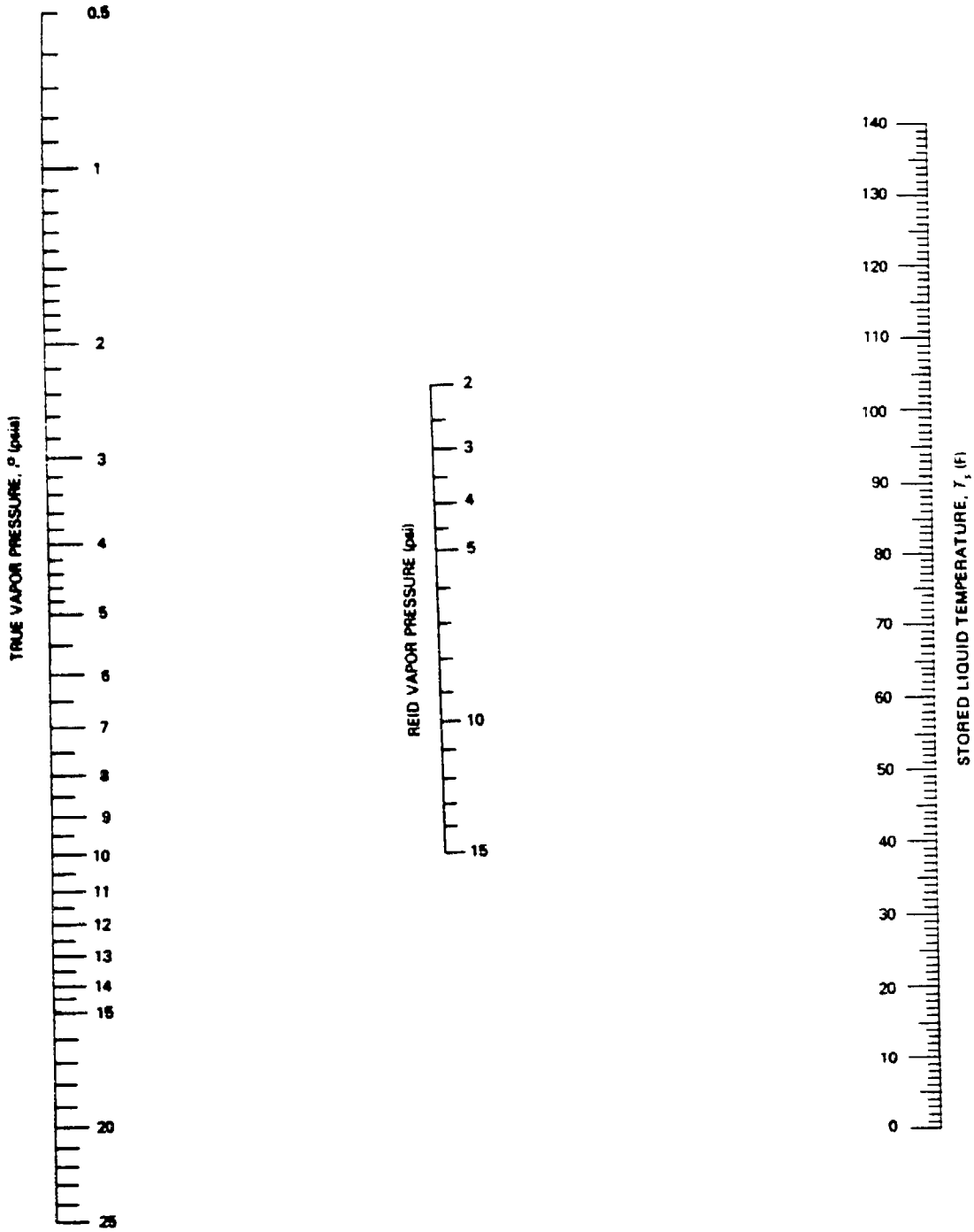
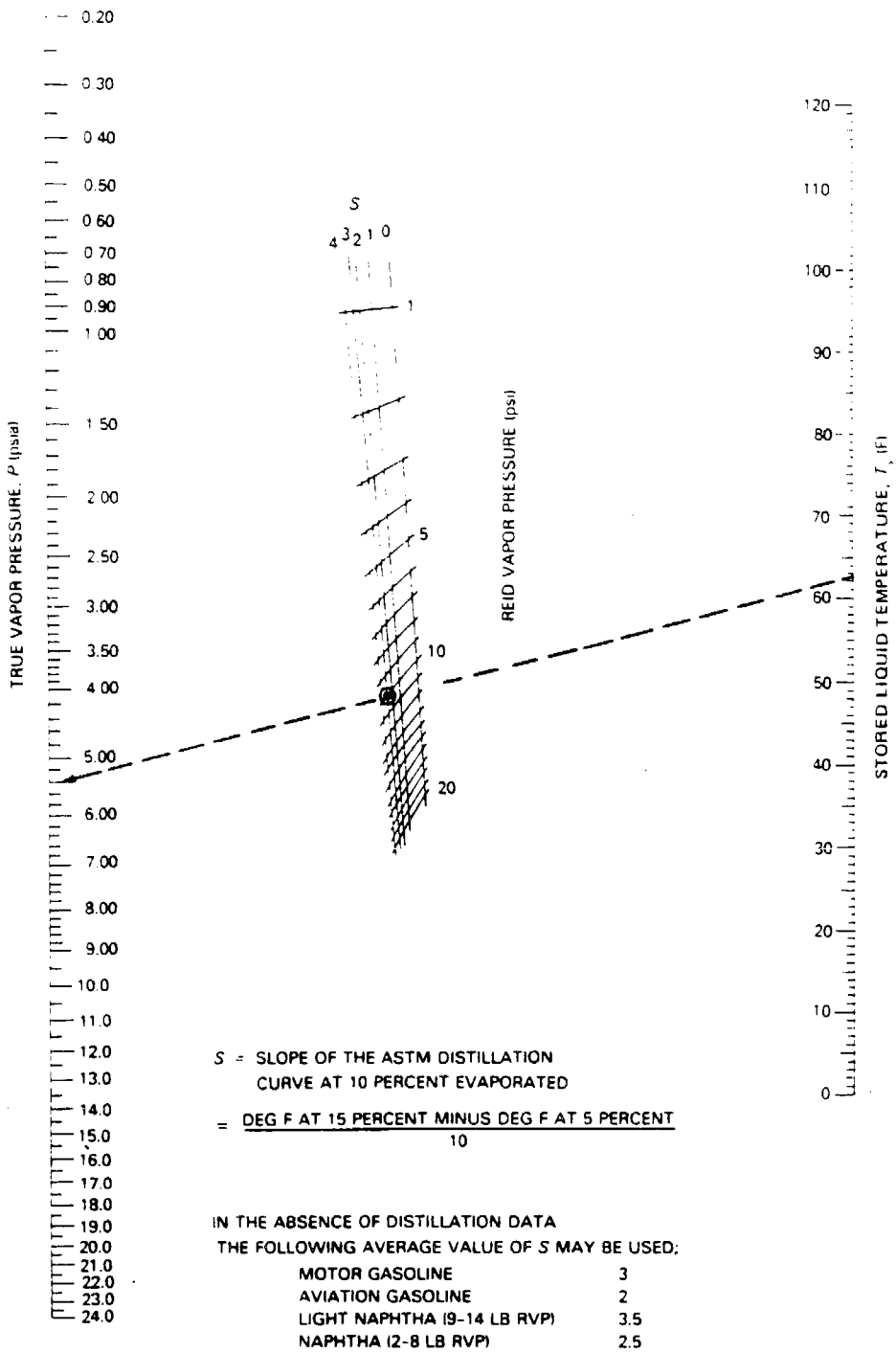
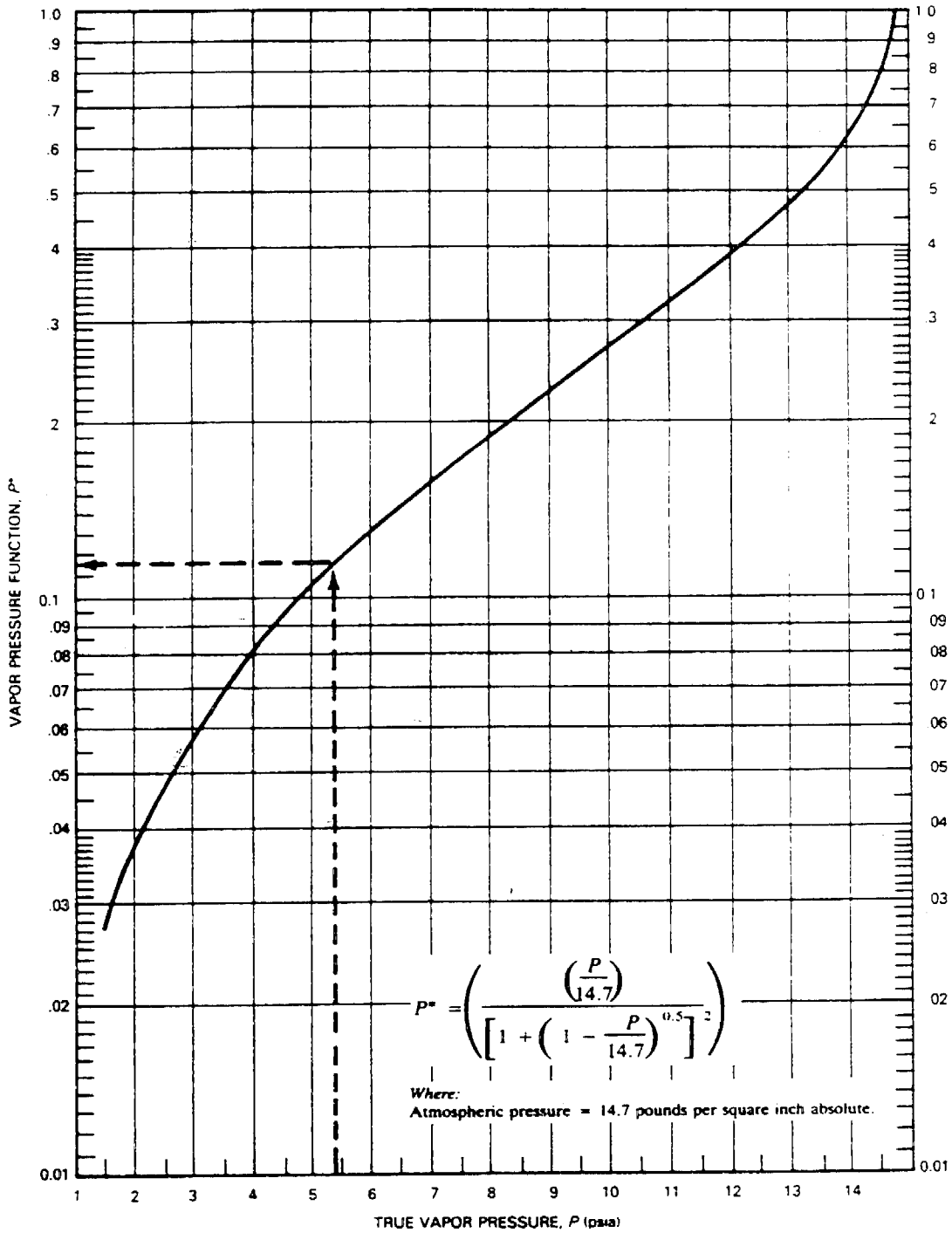


Figure 4.3-5. True vapor pressure (P) of crude oils (2-15 psi RVP).[6]



NOTE: Dashed line illustrates sample problem for RVP = 10 pounds per square inch, gasoline (S = 3), and T_s = 62.5°F
SOURCE: Nomograph drawn from the data of the National Bureau of Standards.

Figure 4.3-6. True vapor presure (P) of refined petroleum liquids like gasoline and napththas (1-20 psi RVP).[6]



NOTE: Dashed line illustrates sample problem for P = 5.4 pounds per square inch absolute.

Figure 4.3-9. Vapor pressure function (P*).[5]

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 4.4-1 lists suggested saturation factors.

TABLE 4.4-1. SATURATION (S) FACTORS FOR CALCULATING PETROLEUM LIQUID LOADING LOSSES

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[a]	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

[a]For products other than gasoline and crude oil. Use factors from Table 4.4-2 for marine loading of gasoline. Use Equations 2 and 3 and Table 4.4-3 for marine loading of crude oil.

Emissions from controlled loading operations can be calculated by multiplying the uncontrolled emission rate calculated in Equation 1 by the control efficiency term:

$$\left(1 - \frac{eff}{100}\right).$$

Measures to reduce loading emissions include selection of alternate loading methods and application of vapor recovery equipment. The latter captures organic vapors displaced during loading operations and recovers

TABLE 4.4-2. VOLATILE ORGANIC COMPOUND EMISSION FACTORS FOR GASOLINE LOADING OPERATIONS AT MARINE TERMINALS[a]

Vessel tank condition	Previous cargo	Total organic emission factors: Ships/ocean barges[b] mg/liter transferred	Ships/ocean barges[b] lb/10^3 gal transferred	Barges[b] mg/liter transferred	Barges[b] lb/10^3 gal transferred
Uncleaned	Volatile[c]	315	2.6	465	3.9
Ballasted	Volatile	205	1.7	d	d
Cleaned	Volatile	180	1.5	e	e
Gas-freed	Volatile	85	0.7	e	e
Any condition	Nonvolatile	85	0.7	e	e
Gas-freed	Any cargo	e	e	245	2.0
Typical overall situation[f]	Any cargo	215	1.8	410	3.4

[a]References 2, 8. Factors represent nonmethane-nonethane VOC emissions because methane and ethane have been found to constitute a negligible weight fraction of the evaporative emissions from gasoline.
[b]Ocean barges (tank compartment depth about 40 feet) exhibit emission levels similar to tank ships. Shallow draft barges (compartment depth 10 to 12 feet) exhibit higher emission levels.
[c]Volatile cargoes are those with a true vapor pressure greater than 1.5 psia.
[d]Barges are not usually ballasted.
[e]Unavailable.
[f]Based on observation that 41% of tested ship compartments were uncleaned, 11% ballasted, 24% cleaned, and 24% gas-freed. For barges, 76% were uncleaned.

TABLE 4.4-3. AVERAGE ARRIVAL EMISSION FACTORS, C_A, FOR CRUDE OIL LOADING EMISSION EQUATION[a]

Ship/ocean barge tank condition	Previous cargo	Arrival emission factor, lb/10^3 gal
Uncleaned	Volatile[b]	0.86
Ballasted	Volatile	0.46
Cleaned or gas-freed	Volatile	0.33
Any condition	Nonvolatile	0.33

[a]Arrival emission factors (C_A) to be added to generated emission factors calculated in Equation 3 to produce total crude oil loading loss. These factors represent total organic compounds; nonmethane-nonethane VOC emission factors average about 15% lower.
[b]Volatile cargoes are those with a true vapor pressure greater than 1.5 psia.

TABLE A-4. AVERAGE ANNUAL AMBIENT TEMPERATURE (T_a, °F) FOR SELECTED U.S. LOCATIONS

Birmingham, Ala.	62.0
Huntsville, Ala.	60.6
Mobile, Ala.	67.5
Montgomery, Ala.	64.9
Anchorage, Alaska	35.3
Annette, Alaska	45.4
Barrow, Alaska	9.1
Barter Island, Alaska	9.6
Bethel, Alaska	28.4
Bettles, Alaska	21.2
Big Delta, Alaska	27.4
Cold Bay, Alaska	37.9
Fairbanks, Alaska	23.9
Gulkana, Alaska	26.5
Homer, Alaska	36.6
Juneau, Alaska	40.0
King Salmon, Alaska	32.8
Kodiak, Alaska	40.7
Kotzebue, Alaska	20.9
McGrath, Alaska	25.0
Nome, Alaska	25.5
St. Paul Island, Alaska	34.3
Talkeetna, Alaska	32.6
Unalakleet, Alaska	26.4
Valdez, Alaska	38.3
Yakutat, Alaska	38.6
Flagstaff, Ariz.	45.4
Phoenix, Ariz.	71.2
Tucson, Ariz.	68.0
Winslow, Ariz.	54.9
Yuma, Ariz.	73.8
Fort Smith, Ariz.	60.8
Little Rock, Ark.	61.9
North Little Rock, Ark.	61.7
Bakersfield, Calif.	65.5
Bishop, Calif.	56.0
Blue Canyon, Calif.	50.4
Eureka, Calif.	52.0
Fresno, Calif.	62.6
Long Beach, Calif.	63.9
Los Angeles, Calif.— International Airport	62.6
Los Angeles, Calif.	65.3
Mount Shasta, Calif.	49.5
Red Bluff, Calif.	62.9
Sacramento, Calif.	60.6
San Diego, Calif.	63.8
San Francisco, Calif.— International Airport	56.6
San Francisco, Calif.--City	56.8
Santa Barbara, Calif.	58.9
Santa Maria, Calif.	56.8
Stockton, Calif.	61.6
Alasosa, Colo.	41.2
Colorado Springs, Colo.	48.9
Denver, Colo.	50.3
Grand Junction, Colo.	52.7
Pueblo, Colo.	52.8
Bridgeport, Conn.	51.8
Hartford, Conn.	49.8
Wilmington, Del.	54.0
Wash., D.C.-Dulles Airport	53.9
Wash. D.C.-National Airport	57.5
Apalachicola, Fla.	68.2
Daytona Beach, Fla	70.3
Fort Myers, Fla.	~~73.9~~
Gainsville, Fla.	68.6
Jacksonville, Fla.	68.0
Key West, Fla.	77.7
Miami, Fla.	75.7
Orlando, Fla.	72.4
Pensacola, Fla.	68.0
Tallahassee, Fla.	67.2
Tampa, Fla.	72.0
Vero Beach, Fla.	72.4
West Palm Beach, Fla.	74.6
Athens, Ga.	61.4
Atlanta, Ga.	61.2
Augusta, Ga.	63.2
Columbus, Ga.	64.3
Macon, Ga.	64.7
Savannah, Ga.	65.9
Hilo, Hawaii	73.6
Honolulu, Hawaii	77.0
Kahului, Hawaii	75.5
Lihua, Hawaii	75.2
Boise, Idaho	51.1
Lewiston, Idaho	52.1
Pocatello, Idaho	46.6
Cairo, Ill.	59.1
O'Hare Airport, Chicago, Ill.	49.2
Moline, Ill.	49.5
Peoria, Ill.	50.4
Rockford, Ill.	47.8
Springfield, Ill.	52.6
Evanville, Ind.	55.7
Fort Wayne, Ind.	49.7
Indianapolis, Ind.	52.1
South Bend, Ind.	49.4
Des Moines, Iowa	49.7
Dubuque, Iowa	46.3
Sioux City, Iowa	48.4
Waterloo, Iowa	46.1
Concordia, Kans.	53.2
Dodge City, Kans.	55.1
Goodland, Kans.	50.7
Topeka, Kans.	54.1

(continued)

(Source: U. S. EPA, 1988, Estimating Air Toxics Emissions from Organic Liquid Storage Tanks. EPA-450/4-88-004 October)

TABLE A-6. AVERAGE ANNUAL WIND SPEED (v, mi/h) FOR SELECTED U.S. LOCATIONS

Birmingham, Ala.	7.3
Huntsville, Ala.	8.1
Mobile, Ala.	9.0
Montgomery, Ala.	6.7
Anchorage, Alaska	6.8
Annette, Alaska	10.6
Barrow, Alaska	11.8
Barter Alaska	13.2
Bethel, Alaska	12.8
Bettles, Alaska	6.7
Big Delta, Alaska	8.2
Gold Bay, Alaska	16.9
Fairbanks, Alaska	5.4
Gulkana, Alaska	6.8
Homer, Alaska	7.2
Juneau, Alaska	8.4
King Salmon, Alaska	10.7
Kodiak, Alaska	10.6
Kotzebue, Alaska	13.0
McGrath, Alaska	5.1
Nome, Alaska	10.7
St. Paul Island, Alaska	18.3
Talkeetna, Alaska	4.5
Valdez, Alaska	6.0
Yakutat, Alaska	7.4
Flagstaff, Ariz.	7.3
Phoenix, Ariz.	6.3
Tucson, Ariz.	8.2
Winslow, Ariz.	8.9
Yuma, Ariz.	7.8
Fort Smith, Ark.	7.6
Little Rock, Ark.	8.0
Bakersfield, Calif.	6.4
Blue Canyon, Calif.	7.7
Eureka, Calif.	6.8
Fresno, Calif.	6.4
Long Beach, Calif.	6.4
Los Angeles, Calif.—International Airport	7.5
Los Angeles, Calif.	6.2
Mount Shasta, Calif.	5.1
Oakland, Calif.	8.2
Red Bluff, Calif.	8.6
Sacramento, Calif.	8.1
San Diego, Calif.	6.8
San Francisco, Calif.—International Airport	10.5
San Francisco, Calif.—City	8.7
Santa Maria, Calif.	7.0
Stockton, Calif.	7.5
Colorado Springs, Colo.	10.1
Denver, Colo.	8.8
Grand Junction, Colo.	8.1
Pueblo, Colo.	8.7
Bridgeport, Conn.	12.0
Hartford, Conn.	8.5
Wilmington, Del.	9.2
Wash., D.C.-Dulles Airport	7.5
Wash. D.C.-National Airport	9.3
Apalachicola, Fla.	7.9
Daytona Beach, Fla.	8.8
Fort Myers, Fla.	8.2
Jacksonville, Fla.	8.2
Key West, Fla.	11.2
Miami, Fla.	9.2
Orlando, Fla.	8.6
Pensacola, Fla.	8.4
Tallahassee, Fla.	6.5
Tampa, Fla.	8.6
West Palm Beach, Fla.	9.5
Athens, Ga.	7.4
Atlanta, Ga.	9.1
Augusta, Ga.	6.5
Columbus, Ga.	6.7
Macon, Ga.	7.7
Savannah, Ga.	7.9
Hilo, Hawaii	7.1
Honolulu, Hawaii	11.6
Kahului, Hawaii	12.8
Lihua, Hawaii	11.9
Boise, Idaho	8.9
Pocatello, Idaho	10.2
Cairo, Ill.	8.5
Chicago, Ill.	10.3
Moline, Ill.	10.0
Peoria, Ill.	10.1
Rockford, Ill.	9.9
Springfield, Ill.	11.3
Evansville, Ind.	8.2
Fort Wayne, Ind.	10.2
Indianapolis, Ind.	9.6
South Bend, Ind.	10.4
Des Moines, Iowa	10.9
Sioux City, Iowa	11.0
Waterloo, Iowa	10.7
Concordia, Kans.	12.3
Dodge City, Kans.	13.9
Goodland, Kans.	12.6
Topeka, Kans.	10.2
Wichita, Kans.	12.4
Cincinnati, Ky.—Airport	9.1
Jackson, Ky.	7.0
Lexington, Ky.	9.5
Louisville, Ky.	8.3
Baton Rouge, La.	7.7
Lake Charles, La.	8.7
New Orleans, La.	8.2

(continued)

EMISSION ESTIMATION TECHNIQUE: OIL REFINERY

OIL REFINERY
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique developed by the Air Resources Board staff in accordance with the Air Toxic "Hot Spots" Information and Assessment Act of 1987 (the Act). Specifically this report describes the processes used at an oil refinery that result in the emission of air toxic substances listed pursuant to the Act. This report specifies the methods a facility operator would use to calculate resulting emissions of the listed substances.

This EET focuses on the listed substance benzene, but the information provided in this report can be used to estimate emissions of other listed substances at an oil refinery such as toluene and xylene. Other listed substances possibly emitted during refinery operations include: formaldehyde, chromium, ethylene dichloride, ammonia, nickel, hydrogen sulfide and others.

Benzene is a volatile, aromatic, unsaturated hydrocarbon occurring naturally in crude oil. Benzene is formed during gasoline production, and is emitted as a by-product when petroleum is refined. Benzene is the focus of this EET because it is a known human carcinogen. It remains stable in ambient air, and its emissions are widespread.

II. PROCESS DESCRIPTION OF OIL REFINERIES

An oil refinery is an integrated system of pumps, valves, cooling towers, process heaters, storage tanks, and other equipment and operations. Four major operations characterize refinery processes: separation, blending, treating, and conversion. Emissions of listed substances are possible from most of the equipment and at most of the stages in the operations.

This document focuses primarily on oil refineries that handle LPG, gasoline, or other highly volatile products with high process pressures and temperatures. These refineries will have a higher hydrocarbon emission rate than refineries that handle less volatile products. Other important factors affecting refinery emissions include crude oil capacity, fuel type, air pollution control measures in effect, general level of maintenance and good housekeeping in the refinery, and the processing scheme(s) employed. In addition, the vapor pressure of the crude oil itself may affect emissions of listed substances.

During the treating operation, catalyst regeneration and air agitation in mixing tanks are potential sources of listed substances. Trace quantities of malodorous substances may escape from numerous sources throughout the treatment area including settling tank vents, surge tanks, water treatment units, waste water drains, valves and pump seals. These substances may include hydrogen sulfide and mercaptans.

III. SOURCES OF POTENTIAL EMISSIONS

Assessing potential sources of toxic emissions in a modern oil refinery is difficult for a number of reasons: the unique nature of any refinery, the complexity of the refining process, the variety of emissions, the large number and the wide distribution of possible sources, the inaccessibility of some sources, and the difficulties in identifying some emissions. In addition, measuring emissions, in particular fugitive emissions, requires specialized technology.

The possible sources of emissions in a refinery range from stacks on combustion units (confined or ducted sources) to pipeline flanges and valves (fugitive emission sources). The following provides an assessment of possible sources.

Emissions From Cracking Operations

Cracking operations are significant sources of emissions because the by-product, coke, must be removed. Deposits on the catalyst or in the reactor tubes occurring during operations may contain sulfur and other impurities. Deposits are usually removed by a controlled combustion process with a resulting discharge of combustion gases including catalyst fines, unburned hydrocarbons, sulfur oxides, carbon monoxide, ammonia, and nitrogen oxides.

Emissions From Process Heaters and Boilers

Many processes in refineries necessitate high pressure steam or elevated temperatures. Various boilers and process heaters may be used, although conventional boilers are generally used. Heaters are usually the box-type cylinder although they may be unique. The fuel used varies, including refined or natural gas, heavy fuel oil, or combinations.

Emissions From Storage Tanks

Tanks used to store crude oil and other petroleum distillates are a possible source of emissions. Several factors may affect emissions such as changes in diurnal temperatures, filling operations, and volatilization.

Hydrocarbon (Fugitive) Emissions From Valves and Flanges

An oil refinery has numerous valves and flanges, which are potential sources of fugitive emissions. Under the influence of heat, pressure, vibration, friction, and corrosion, valves and flanges may develop leaks. Leaks may be liquid, vapor, or both. Although individual leaks may be small, the cumulative amount can be high.

Hydrocarbon (Fugitive) Emissions From Pumps and Compressors

Pumps and compressors can leak product at the contact between the moving shaft and stationary casing. (Packing and mechanical seals are almost universally used to retard leakage.) Pumps and compressors can contribute significantly to fugitive emissions.

Emissions From Cooling Towers

Refineries use large quantities of water for cooling purposes. Before the water can be reused, the heat absorbed must be removed. The heat is usually removed by passing the water through a series of decks and slat-type grids in a cooling tower. Some of the water evaporates, removing sensible heat. However, the water may contain particles or aerosols of listed substances that can escape to the atmosphere.

Emissions From Wastewater Separators and Process Drains

Some equipment and a number of refinery operations may allow hydrocarbons to reach drains and wastewater. For example, sampling operations, leaks in process equipment, and actual spills may occur. In addition, the water reaching the drains may already be contaminated from various operations and processes. As the hydrocarbon-water mixture reaches the drains, hydrocarbons may evaporate and escape into the atmosphere.

NOTE:

Flares: Flares are probably the largest unknown sources of emissions of listed toxic substances. Flares have high potential for toxic emissions because of their vast usage throughout the refinery, their large flowrates and obvious efficiency swings. Although little information is available at this time, research is underway to find appropriate methods to estimate flare emissions.

IV. CONTROL DEVICES

An emission control device may greatly reduce air pollutants leaving the device relative to those entering the device. Any one of the following possibilities, or combinations of them, exist when an air pollutant enters a control device. The pollutant may be transferred from the air stream to another medium, be modified to a less toxic state, destroyed through combustion and/or dissociation, or it may pass through untreated. When a pollutant is transferred into another medium, the medium is a potential source of emissions. If the medium has any air emissions while located anywhere on the facility site, the emissions must be accounted for. Emission estimates must take into account the effect of the control device(s) used. Usually the efficiency of the control device must be known. The data used should reflect the efficiency achieved during typical day-to-day operations, not the the theoretical optimum efficiency. The control efficiency used in estimating emissions of each listed substance must be justified by the facility operator and the justification must be cited.

Controlling emissions of toxic listed substances can be accomplished by changing processes, installing control equipment, improving housekeeping as well as maintaining equipment. Some combination of these is often the most effective solution. A brief description of some applicable control equipment follows.

Air pollution control equipment for oil refinery operation includes combustion devices such as thermal or catalytic incinerators, or flares. These devices reduce emissions of combustible organic substances by destroying organic matter through oxidation; other substances in the mixture are then emitted as oxides or acid gases.

A. Combustion Devices

1. Thermal incinerators rely on high temperature, sufficient pollutant residence time, and adequate turbulence to ensure high destructive efficiencies.

2. Catalytic incinerators operate at somewhat lower temperature as a catalyst promotes the oxidation. Most volatile organic compounds are rapidly destroyed at temperatures over 1400 ^{o}F; some volatile organic compounds, however (for example halogenated hydrocarbons), require higher temperatures.

Several other devices can be used to control emissions of listed substances including the following.

B. Wet Scrubbers

Wet scrubbers are used to collect organic and inorganic matter and reactive gases. These scrubbers often use water as their medium, and have the potential to create toxic emissions in the liquid medium.

C. Floating Roof Tank

This type of tank consists of a cylindrical steel shell, equipped with a roof which floats on the surface of the stored liquid, rising and falling with the liquid level. The floating roof and the seal system help reduce evaporation loss of the stored liquid.

D. Vapor Recovery Systems

The vapor recovery system collects emissions from storage vessels and converts them to liquid product. Several vapor recovery procedures may be used, including vapor/liquid absorption, vapor compression, vapor cooling, vapor/solid adsorption, or a combination of these. The overall control efficiencies of vapor recovery systems are as high as 90 to 98 percent, depending on the method used, the design of the unit, the composition of vapors recovered, and the mechanical condition of the system.

V. EMISSION ESTIMATES

Source testing is the preferred method of accurately determining toxic emissions of listed substances when testing is feasible and when approved, reliable methods exist. Source testing is required by the Emission Inventory Criteria and Guideline Regulations for some refinery operations. However, when source testing is not required, several methods are available for quantifying toxic air emissions: mass balance, emission factors, engineering calculations, and hybrids of mass balance and emission factors. An emission estimate for a listed toxic substance may involve the use of more than one of these methods. Additionally, the estimate must account for the control device(s) used.

Applicable emission factors, valid estimates of control effectiveness and percentage (allowable) adjustments for inspection and maintenance programs are subject to district approval.

A. Background Information on Reforming and Aromatics

As noted in Section III, this document focuses on the toxic emissions in an oil refinery, typified by the aromatic hydrocarbon, benzene. Benzene can be derived from hydrodealkylation of toluene, transalkylation of toluene by disproportionate reaction, and catalytic reforming of petroleum:

n-Paraffin <======> Alkylcyclohexanes <======> Aromatics.

Most of these reactions are reversible, indicating the importance of reaction equilibrium.

The octane rating of the various classes of reformer feeds is in the order of:

Aromatics > Cycloparaffins > Isoparaffins > n-Paraffins.

Thus gasoline refiners and BTX producers need to increase the proportion of aromatics to produce high octane gasoline.

Currently there is little specific information on benzene so that it becomes necessary to rely on information gathered from literature searches and emission factors published by credible study groups to estimate emissions from various refinery sources.

B. Equations

1. Fugitive Emissions of Toxic Substances from Refinery Operations

Fugitive emissions are those emissions not released through a stack, chimney, vent, or other confined vent stream. These emissions include process leaks and evaporation from open processes and spills. Whenever possible, fugitive emissions should be calculated by the use of data available from direct measurement. Fugitive emissions, however, often have to be estimated by the use of emission factors or engineering calculations because they are too diffuse or dilute to be measured directly, or they are too small relative to the amounts of material processed to permit the use of a mass balance. This is particularly true of toxic air pollutants at an oil refinery.

Various emission factors (See Appendix D, Tables D-1, D-2, D-3 and D-4) are available to estimate emissions from leaks in process streams carrying hydrocarbon vapors, light liquids (lighter than diesel or more volatile than kerosene, that is, a vapor pressure greater than 0.1 psia at 100°F), or heavy liquids (equal to or less volatile than kerosene). These factors can also be used to estimate fugitive emissions in other industries that process hydrocarbon streams.

Fugitive Emission Estimation Method For a Specific Stream Containing a Listed Substance, "A"

Assumption: The concentration of "A" material in the liquid phase (in "the pipe") is equal to the toxic concentration in the vapor emitted to the air.

Toxic Emission Rate = (Equipment count) x (AP-42 emission factor for the device handling the toxic substance) x (Stream "A" material concentration)

NOTE:

(Stream "A" material concentration or the weight fraction of a specific substance in a vapor can be obtained from laboratory analysis of all incoming crude or feed. The weight fraction (Wt_i) of each specific substance is the pounds of that substance divided by the total pounds of the mixture. The weight fractions of a vapor are needed to calculate the amount (in pounds) of each component emitted from a tank.)

A common approach to calculating the concentration of a substance in the vapor phase over a liquid is to determine its partial pressure. The partial pressure of a compound divided by the total pressure of the gas stream is equal to the mole fraction of the compound in the stream. The weight fractions are related to the mole fractions.

Methods of Estimating Toxic Emissions from Storage of Organic Liquids

The following emission estimation techniques for organic liquid storage tanks were derived from equations in section 4.3 of "Compilation of Air Pollutant Emission Factors: Volume 1 Stationary Point and Area Sources", AP-42 (4th Edition, September, 1985). The equations in AP-42 estimate total VOC emissions from storage tanks. These equations can be modified to estimate chemical-specific emissions directly. The correlations in this emission estimation techniques reflect these modifications.

NOTE:

(The following equations demonstrate calculation of annual emissions. The final document will also demonstrate calculation of hourly emissions.)

2. Estimation of Toxic Emissions from Floating Roof Tanks

The total loss from external floating roof tanks can be estimated from the following equations:

$$L_T = L_S + L_W \qquad (1)$$

$$L_S = K_S V^N P^* D M_V K_C E_F (Wt_i) \qquad (2)$$

$$P^* = \frac{P/Pa}{[1 + (1 - P/Pa)^{0.5}]^2} \quad (3)$$

Where:

L_T = Total loss (lbs/yr)

L_S = Standing storage loss (lbs/yr)

L_W = Withdrawal loss (lbs/yr)

K_S = Seal factor (lb-mole/(ft(mile/hr)^{N}yr)).

V = Average wind speed at tank site (mile/hr).

X_i = Liquid-phase mole fraction of listed substance i, in the stock being stored, (lb-mole i/lb-mole stock).

N = Seal related wind speed exponent (dimensionless).

P^* = Vapor pressure function (dimensionless).

D = Tank diameter (feet)

P = True vapor pressure at average actual organic liquid storage temperature (psia)

P_a = Average atmospheric pressure at tank location (psia)

M_V = Average molecular weight (lb/lb-mole)

K_C = Product factor (dimensionless).

E_F = Secondary seal factor.

T_S = Organic liquid storage temperature (^oF)

NOTES:

(a) If average actual organic liquid storage temperature, T_S, is unknown, the average storage temperature can be estimated from the average ambient temperature T_A(^oF). This information, T_A, is available from the

local weather service data, and needs to be adjusted by the tank paint color factor.

(b) A typical value of 64 lb/lb-mole can be assumed for the molecular weight of gasoline vapor, and a value of 50 lb/lb-mole can be assumed for United States midcontinental crude oils.

(c) For all other organic liquids : $K_C = 1.0$

For crude oil: $K_C = 0.4$

(d) For petroleum liquid storage with any seal system: $E_F = 1.0$

For volatile organic liquid storage with a primary only seal system:

$E_F = 1.0$

With a primary/secondary seal system : $E_F = .07$ to 0.45

(A value of 0.25 is recommended for tanks and seals in good condition.) Standing storage loss emissions from internal floating roof tanks was estimated using Equation 2.

Where:

K_S = 0.7 for all seal systems

N = 0.4 for all seal systems

K_C = 0.4 for crude oil

K_C = 1.0 for all other organic liquids

E_F = 1.0 for primary only seal systems

E_F = 0.07 - 0.45 for primary/secondary seal systems (A value of 0.25 is recommended for tanks and seals in good condition.)

The withdrawal loss from external floating roof and internal floating roof tanks can be estimated using Equation 4.

$$L_W = \frac{(0.943)\ QC_F W_L}{D} \left[1 + \left(\frac{N\ F}{D} \right) \right] (Wt_i) \qquad (4)$$

Where:

L_W = withdrawal loss (lb/yr)

Q = throughput (bbl/year) (tank capacity [bbl] times annual turnover rate)

C_F = shell clingage factor (bbl/1,000 ft^2) see table

W_L = average organic liquid density (lb/gal)

D = tank diameter (ft)

N = number of columns (dimensionless)

F = effective column diameter (ft) [column perimeter (ft)/pi]

Notes: (1) If W_L is unknown, an average value of 5.6 lb/gallon can be assumed for gasoline. An average value cannot be assumed for crude oil, since densities are highly variable.

(2) The constant, 0.943, has dimensions of (1,000 ft^3 x gal/bbl^2).

(3) For self-supporting fixed roof or an external floating roof tank :

N = 0.
For column supported fixed roof :

N = use tank specific information

(4) Use tank effective column diameter; or

F = 1.1 for 9 inch by 7 inch built-up columns, 0.7 for 8 inch diameter pipe columns, and 1.0 if column construction details are not known

3. <u>Estimation of Toxic Emissions from Fixed Roof Tanks</u>

A. Calculating Breathing Loss from a Fixed Roof Tank

The total hydrocarbon loss from a fixed roof tank is the sum of : $L_B + L_W$ multiplied by operational percentage vapor recovery factor for the system used.

$$L_T = L_B + L_W \qquad (5)$$

If the tank is vented to a vapor recovery system, multiply equation (5) by 0.05. If vented to thermal oxidizer, multiply equation (5) by 0.01 .

$$L_B = 0.0226 \times M_V \left(\frac{P}{P_A - P}\right)^{0.68} \times D^{1.73} \times H^{0.51} \times \Delta T^{0.50} \times F_P C K_C (Wt_i) \quad (6)$$

The tank diameter factor (C) is calculated using the equation below:

$$C = 0.0771 \times D - 0.0013 \times D^2 - 0.1334 \quad (7)$$

If this tank were located underground, then the breathing losses could be assumed to be negligible because the diurnal temperature change, ΔT, would be close to zero .

$$M_V = M_a \frac{(P_a X_a)}{P_t} + M_b \frac{(P_b X_b)}{P_t} \ldots\ldots + M_n \frac{(P_n X_n)}{P_t} \quad (8)$$

And P_t, by Raoult's law is:

$$P_t = P_a X_a + P_b X_b \ldots\ldots + P_n X_n \quad (9)$$

Where:

L_T = Total loss (lb/yr)

L_B = Breathing loss (lb/yr)

M_V = Molecular weight of vapor in storage tank, lb/lb-mole

P_A = Average atmospheric pressure at tank location, psia

P = True vapor pressure at bulk liquid conditions, psia

P_t = True vapor pressure (psia)

X_i = Liquid-phase mole fraction of the listed substance

D = Tank diameter, ft

H = Average vapor space height, including roof volume correction, ft

ΔT = Average ambient diurnal temperature change, F^o

F_P = Paint factor, dimensionless (See Appendix C, Table C-1)

C = Adjustment factor for small diameter tanks, dimensionless (See Appendix F, figure 4.3-4)

K_C = Product factor, dimensionless

M_a = Molecular weight of pure component, a

M_b = Molecular weight of pure component, b

P_a = Vapor pressure of pure component, a

P_b = Vapor pressure of pure component, b

X_a = Mole fraction of component, a

X_b = Mole fraction of component, b

NOTES

(All tables and figures referenced/listed below can be found in EPA AP-42, Section 4.3, Fourth Edition, September 1985.)

(1) The molecular weight of the vapor, M_V, can be determined from table 4.3-2 (See Appendix E) for selected petroleum liquids and volatile organic liquids or by analysis of vapor samples. Where mixtures of organic liquids are stored in a tank, M_V can be estimated from the liquid composition using equation (8).

(2) For crude oil, K_C = 0.65. For all other organic liquids, K_C = 1.0 .

(3) The vapor space in a cone roof is equal in volume to a cylinder, which has the same base diameter as the cone and is one third the height of the cone. If information is not available, assume H equals one half tank height.

(4) True vapor pressures for organic liquids can be determined from figures 4.3-5 or 4.3-6 (See Appendix F), or table 4.3-2 (See Appendix E). In order to use figures 4.3-5 or 4.3-6, the stored liquid temperature, T_S, must be determined in degrees Fahrenheit. T_S is determined from Table C-2 in Appendix C, given the average annual ambient temperature, T_A, in degrees

Fahrenheit. True vapor pressure is the equilibrium partial pressure exerted by a volatile organic liquid, as defined by ASTM-D-2879 or as obtained from standard reference texts. Reid Vapor Pressure is the absolute vapor pressure of volatile crude oil and volatile nonviscous petroleum liquids, except liquified petroleum gases, as determined by ASTM-D-323.

B. Estimating Working Losses from Fixed Roof Tanks

Working losses from fixed roof tanks can be estimated using the following equation:

$$L_W = 2.40 \times 10^{-5} M_V \; P \; V \; N \; K_N \; K_C \; (Wt_i) \qquad (10)$$

Where:

L_W = Fixed roof working loss (lb/year)

M_V = Molecular weight of vapor in storage tank (lb/lb-mole)

P = True vapor pressure at bulk liquid temperature (psia)

V = Tank capacity (gal)

N = Number of turnovers per year (dimensionless)

$$= \frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, V (gal)}} \qquad (11)$$

III. Estimating Toxic Emissions from Bulk Loading Operations

Toxic emissions from loading petroleum liquid can be estimated using the following equation:

$$L_L = 523.32 \frac{SPM}{T} \left(1.00 - \frac{eff.}{100}\right) (Wt_i) \qquad (12)$$

Where:

L_L = Loading loss (lb HC/1000 bbl. loaded)

S = saturation factor (AP-42, Table 4.4-1, see Appendix E)
P = vapor pressure, psia
M = molecular weight of condensed vapors (lb/lb-mole)

T = loading temperature, ^oR (^oF + 460)

eff. = Typical efficiency (%)
99 - vapor recovery to fuel gas system
92 - vapor recovery to recovery unit
0 - uncontrolled

Emission estimates must take into account control device(s) used to reduce toxic pollutants. Usually the efficiency of the control device must be known. The data used should reflect the efficiency achieved during typical day-to-day operations, not the theoretical optimum efficiency. The control efficiency used in estimating emissions of each listed substance must be justified by the facility operator and the justification must be cited.

Efficiency is expressed as a percentage:

$$\text{Efficiency} = \frac{M_i - M_o}{M_i} \times 100 \qquad (13)$$

Where:

M_i is the mass of 'Toxic Pollutant' flowing into the control device per period of time.

M_o is the mass of 'Toxic Pollutant' flowing out of the control device per period of time.

A valid efficiency estimate can be based on source tests or measurement, a mass balance calculation, or a combination of the two. It is important to use data that reflect efficiency achieved during typical operations, not the theoretical optimum efficiency. Actual measurement is the best way to determine efficiency.

NOMENCLATURE

BTX	=	Benzene , Toluene , Xylene
>	=	Greater than
<===>	=	Reversible reaction
lb	=	Pounds
#	=	Number
yr	=	Year
pi	=	3.14
gal	=	gallons

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APPENDIX A
SAMPLE CALCULATIONS

APPENDIX A: BENZENE EMISSION FACTOR WITH SAMPLE CALCULATIONS

Emissions from Refineries

A. From Crude Storage and Handling

1. Emissions From Refineries

EPA Emission Factor	=	4.7×10^{-3} lbs/1000 gals crude
Crude Capacity (15 Refineries)	=	805.9×10^{6} bbls/yr or $21,247 \times 10^{6}$ gals/yr

Assume all refineries operated at 75% of their design capacities in 1989, the revised crude capacity becomes:

$$= 21,247 \times 10^{6} \times 0.75$$
$$= 15,935.3 \times 10^{6} \text{ gals/yr}$$

$$\text{Emissions} = \frac{4.7 \times 10^{-3}}{1,000} \times \frac{15,935.3 \times 10^{6}}{2,000} = 37.5 \text{ tons/yr}$$

2. From Refinery Operations

EPA Emission Factor = 0.01 lbs/1000 gals crude

$$\text{Emissions} = \frac{0.01}{1,000} \times \frac{15,935.3 \times 10^{6}}{2,000} = 79.7 \text{ tons/yr.}$$

APPENDIX B
ANTOINE'S EQUATION CONSTANTS

APPENDIX B-ANTOINE'S EQUATION CONSTANTS

Antoine equation correlates vapor pressure-temperature data extremely well. Clausius-Clapeyron equation OR Cox Charts can also estimate vapor pressure.

$$\log_{10} p^* = A - \frac{B}{T + C} \quad ; \quad p^* \text{ in mm Hg} \quad ; \quad T \text{ in } ^oC$$

Substance	Formula	Range, ^oC	A	B	C
Acetaldehyde	C_2H_4O	-45 to +70	6.81089	992.0	230
Acetic Acid	$C_2H_4O_2$	0 to +36	7.80307	1651.2	225
		+36 to +170	7.18807	1416.7	211
Acetone	C_3H_6O	—	7.02447	1161.0	224
Ammonia	NH_3	-83 to +60	7.55466	1002.711	247.885
Benzene	C_6H_6	—	6.90565	1211.033	220.790
Carbon tetrachloride	CCl_4	—	6.93390	1242.43	230.0
Chlorobenzene	C_6H_5Cl	0 to +42	7.10690	1500.0	224.0
		+42 to +230	6.94504	1413.12	216.0
Chloroform	$CHCl_3$	-30 to +150	6.90328	1163.03	227.4
Cyclohexane	C_6H_{12}	-50 to +200	6.84498	1203.526	222.863
Ethyl Acetate	$C_4H_8O_2$	-20 to +150	7.09808	1238.71	217.0
Ethyl alcohol	C_2H_5OH	—	8.04494	1554.3	222.65
Ethylbenzene	C_8H_{10}	—	6.95719	1424.255	213.206
n-Heptane	C_7H_{16}	—	6.90240	1268.115	216.900
n-Hexane	C_6H_{14}	—	6.87776	1171.530	224.366
Methyl alcohol	CH_3OH	-20 to +140	7.87863	1473.11	230.0
Methyl ethyl ketone	C_4H_8O	—	6.97421	1209.6	216
n-Pentane	C_5H_{12}	—	6.85221	1064.63	232.000
Isopentane	C_5H_{12}	—	6.78967	1020.012	233.097
Styrene	C_8H_8	—	6.92409	1420.0	206.
Toluene	C_7H_8	—	6.95334	1343.943	219.377
Water	H_2O	0 to 60	8.10765	1750.286	235.0
		60 to 150	7.96681	1668.21	228.0

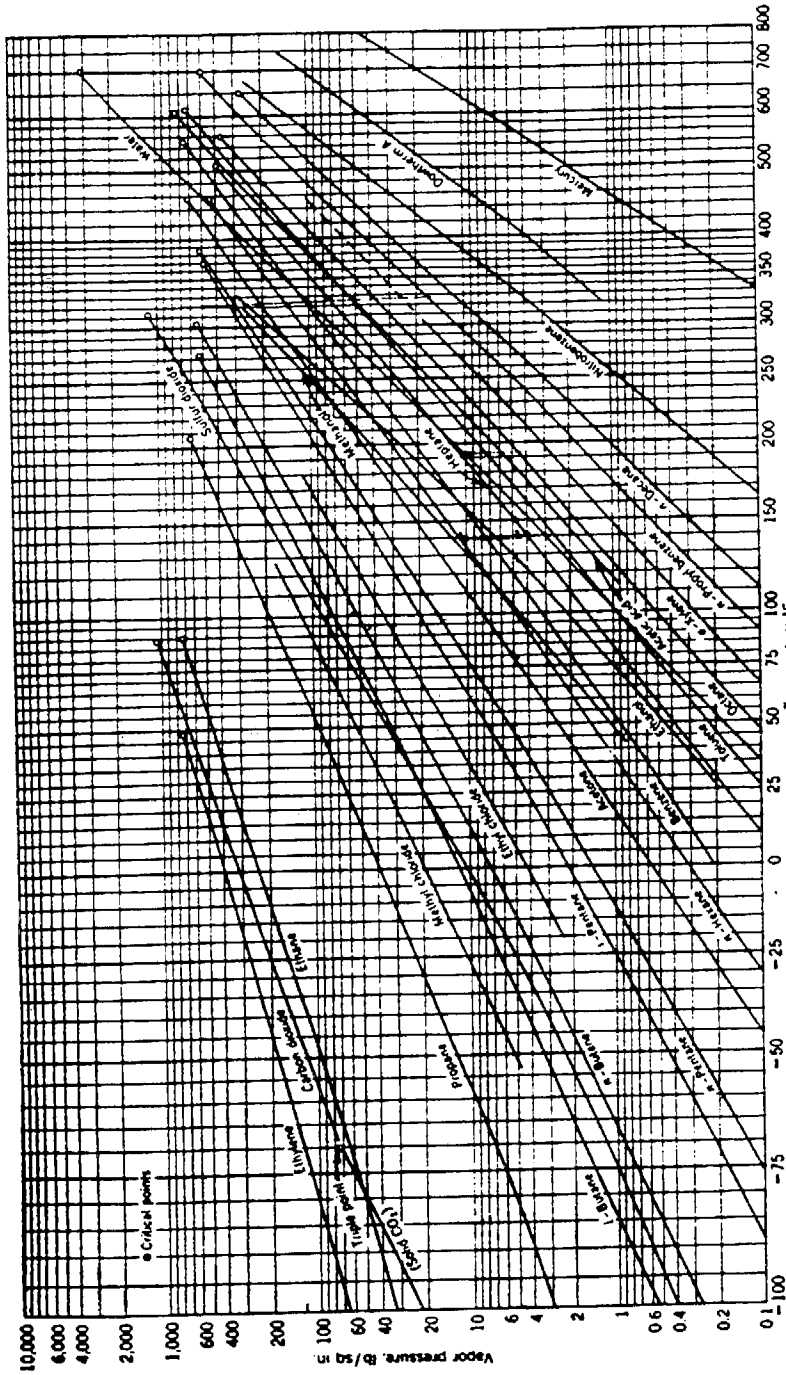


FIGURE 7.1-4. Cox chart vapor pressure plots. From A. S. Foust *et al.*, *Principles of Unit Operations*,, Wiley, New York, 1960, p. 550.

(Source; Richard M. Felder, Donald W. Rousseau, 1978, Elementary Principles of Chemical Processes, John Wiley and Sons, Inc.)

APPENDIX C
FACTORS FOR FIXED ROOF TANK CALCULATIONS

FACTORS FOR FIXED ROOF TANK CALCULATIONS

TABLE C-1 PAINT FACTOR FOR FIXED ROOF TANKS

Tank color		Paint factors (F_p)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44
Medium gray	Medium gray	1.40	1.58[a]

[a]Estimated from the ratios of the seven preceding paint factors.

TABLE C-2. AVERAGE STORAGE TEMPERATURE (T_S) AS A FUNCTION OF TANK PAINT COLOR*

Tank Color	Average Storage Temperature, T_S (^oF)
White	T_A^* + 0
Aluminum	T_A + 2.5
Gray	T_A + 3.5
Black	T_A + 5.0

*T_A is average ambient temperature in degrees farenheit.

(Compiled from: U.S. EPA, 1985, Compilation of Air Pollutant Emission Factors: Volume 1 Stationary Point and Area Sources, AP-42, 4th Edition, September).

TABLE 4.3-4. SEAL RELATED FACTORS FOR FLOATING ROOF TANKS[a]

Tank and seal type	Welded Tank K_S	Welded Tank n	Riveted Tank K_S	Riveted Tank n
External floating roof tanks[b]				
Metallic shoe seal				
Primary seal only	1.2	1.5	1.3	1.5
With shoe mounted secondary seal	0.8	1.2	1.4	1.2
With rim mounted secondary seal	0.2	1.0	0.2	1.6
Liquid mounted resilient seal				
Primary seal only	1.1	1.0	NA[c]	NA
With weather shield	0.8	0.9	NA	NA
With rim mounted secondary seal	0.7	0.4	NA	NA
Vapor mounted resilient seal				
Primary seal only	1.2	2.3	NA	NA
With weather shield	0.9	2.2	NA	NA
With rim mounted secondary seal	0.2	2.6	NA	NA
Internal floating roof tanks[d]				
Liquid mounted resilient seal				
Primary seal only	3.0	0	NA	NA
With rim mounted secondary seal[e]	1.6	0	NA	NA
Vapor mounted resilient seal				
Primary seal only	6.7	0	NA	NA
With rim mounted secondary seal[e]	2.5	0	NA	NA

[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.
[b]Reference 5.
[c]NA = Not Applicable.
[d]Reference 6.
[e]If tank specific information is not available about the secondary seal on an internal floating roof tank, then assume only a primary seal is present.

APPENDIX D

APPLICABLE EMISSION FACTORS FOR VARIOUS REFINERY PROCESSES

TABLE D-1, AVERAGE FUGITIVE EMISSION FACTORS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY (SOCMI)[a]

Fugitive-emission source	Emission factor (lb/hr)
Pump seals	
Light liquids	0.11
Heavy liquids	0.047
Valves (in-line)	
Gas	0.012
Light liquid	0.016
Heavy Liquid	0.00051
Gas safety-relief valves	0.23
Open-ended lines	0.0037
Flanges	0.0018
Sampling connections	0.033
Compressor seals	0.55

[a]Emission Factors for Equipment Leaks of VOC and HAP, EPA-450/3-86-002, January 1986, Table 3.4. These (uncontrolled) factors take into account a leak frequency determined from field studies in the synthetic organic chemicals manufacturing industry. Light liquids have a vapor pressure greater than 0.1 psia at 100°F .

Compiled from: U.S. EPA, 1987, Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form, EPA-560/4-88-002, December).

TABLE D-2. LEAKING AND NONLEAKING AVERAGE FUGITIVE EMISSION FACTORS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY (SOCMI)[a]

Fugitive-emission source	Leaking (>10,000 ppm) emission factor (lb/hr)	Nonleaking (10,000 ppm) emission factor (lb/hr)
Pump seals		
Light liquids	0.96	0.026
Heavy liquids	0.85	0.030
Valves (in-line)		
Gas	0.099	0.0011
Light liquid	0.19	0.0038
Heavy liquid	0.00051	0.00051
Gas safety-relief valves	3.72	0.098
Open-ended lines	0.0263	0.0033
Flanges	0.083	0.00013
Compressor seals	3.54	0.20

[a]Emission Factors for Equipment Leaks of VOC and HAP, EPA-450/3-86-002, January 1986, Table 3-3. These (**uncontrolled**) factors take into account a leak frequency determined from field studies in the synthetic organic chemicals manufacturing industry. Light liquids have a vapor pressure greater than 0.1 psia at 100°F.

(Compiled from: U.S. EPA, 1987, Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form, EPA-560/4-88-002, December.)

TABLE D-3. **STRATIFIED EMISSION FACTORS FOR EQUIPMENT LEAKS (kg/hr/source)**

Source	Service	Emission Factors (kg/hr/source) for Screening Value Ranges, ppmv		
		0 - 1,000	1,001 - 10,000	Over 10,000
Compressor seals	Gas/vapor	0.01132	0.264	1.608
Pump seals	Light liquid	0.00198	0.0335	0.437
	Heavy liquid	0.00380	0.0926	0.3885
Valves	Gas/vapor	0.00014	0.00165	0.0451
	Light liquid	0.00028	0.00963	0.0852
	Heavy liquid	0.00023	0.00023	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	All	0.00013	0.00876	0.01195

Source: Chemical Manufacturers Association, 1989, Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment

Note:

The stratified emission factor approach is based on several population and emission factors spanning several discrete screening value ranges. Screening values in the EPA SOCMI data base are distributed widely from 0 ppmv to over 100,000 ppmv. The mass emissions are correspondingly distributed. The stratified emission factor approach for estimating emissions segments this distribution into discrete intervals to account for different ranges of screening values.

TABLE D-4 EMISSION FACTORS FOR TOXIC AIR POLLUTANTS

Pollutant	Process	Emission Factor	Notes
Ammonia	Petroleum refinery		
	Reciprocating compressor engines	3.2 kg/1000 m^3 gas burned	
	fluidized catalytic cracking unit	0.155 kg/m^3 fresh feed	Uncontrolled
	fluidized catalytic cracking unit	Negligible	Controlled by ESP and CO boiler
Benzene	Petroleum refinery		
Benzene	Without cracking/reforming (fugitives)	0.72 lb/ton total HC	Assumes benzene is 0.036% of total HC
	Fixed roof, working loss	0.2 mg/year tank of gasoline	Based on terminal with 950,000 liters/day and four storage tanks for gasoline.
	Fixed roof, breathing loss	0.05 mg/year tank of gasoline	Based on terminal with 950,000 liters/day and four storage tanks for gasoline
	Petroleum refinery with catalytic/reforming	7.2 lb/ton total HC (fugitives)	Assumes fugitives are 0.36% benzene
	Aromatics Rheniformer.	0.0025 lb/day flange	Radian factor for

(TABLE D-4 CONTD.)

	Gasoline Fractionating Unit.	0.0025 lb/day flange	Flanges assuming 75% emission reduction due to Rule 466.1
	Crude storage/handling Refinery operations Gasoline marketing	4.7×10^{-3} lb/1000 gal crude 0.01 lb/1000 gal crude 0.184 lb/1000 gal gasoline	
	Flocculation Sumps/Tanks	0.0004 lb VOC/1000 gal wastewater	
	API Separation Effluent Channels and Ponds (Uncovered)	0.4 lb VOC/10^6 gallons wastewater	
	Covered API Separators	4.5 lb VOC/10^6 gallons wastewater	Assume 85% cover efficiency
	Dissolved-Air Flotation (D-A-F) Unit	0.004 lb/1000 gallons wastewater	
Chromium	Fresh water utility cooling tower.		Factors expressed as weight of pollutant per thermal energy input to the plant associated with the cooling tower. Emissions expressed as total chromium.
	Drift loss range of 0.1 to 0.2% (fraction of recirculating water emitted by design as draft)	2.5 pg/J	

(TABLE D-4 CONTD.)	Drift loss range of 0.002 to 0.0005%	0.06 pg/J	
Formaldehyde	Petroleum refining FCC generator	2.2 kg/1000 bbl fresh feed (Derived from emission test data for total aldehydes)	Controlled with CO boiler/ESP
	Moving bed (TCC) generator	1.0 kg/1000 bbl fresh feed	Controlled with CO boiler/ESP
	Fluid Coker burner	0.54 kg/1000 bbl fresh feed	Controlled with CO boiler/ESP

(SOURCES:
1. U.S. EPA, 1986, Compiling Air Toxics Emission Inventories, EPA-450/4-86-010, July.
2. JR Witherspoon, May 12, 1988, Toxic Fugitive Emissions From The Bay Area Refineries BAAQMD Waste Water Treatment study-All refineries with D-A-F Units.)
3. U.S. EPA, 1988, Toxic Air Pollutant Emission Factors- A Compilation For Selected Air Toxic Compounds And Sources

APPENDIX E

TABLES OF PHYSICAL CONSTANTS FOR VARIOUS POLLUTANTS

TABLE 4.3-2. PHYSICAL PROPERTIES OF TYPICAL ORGANIC LIQUIDS[a]

Organic liquid[b]	Vapor molecular weight @ 60°F	Product density (d), lb/gal @ 60°F	Condensed vapor density (w), lb/gal @ 60°F	True vapor pressure in psia at: 40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum Liquids[c]										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel no. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil no. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Volatile Organic Liquids										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1,2-Dichloroethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methylethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
1,1,1-Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

[a]References 3-4.
[b]For a more comprehensive listing of volatile organic liquids, see Reference 3.
[c]RVP = Reid vapor pressure in psia.

TABLE 4.3-5. AVERAGE CLINGAGE FACTORS (C) (bbl/1,000 ft^2)[a]

Liquid	Shell condition		
	Light rust[b]	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

[a]Reference 5.
[b]If no specific information is available, these values can be assumed to represent the most common condition of tanks currently in use.

TABLE 4.3-6. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETER FOR INTERNAL FLOATING ROOF TANKS WITH COLUMN SUPPORTED FIXED ROOFS[a]

Tank diameter range D (ft)	Typical number of columns, N_C
$0 < D \leqq 85$	1
$85 < D \leqq 100$	6
$100 < D \leqq 120$	7
$120 < D \leqq 135$	8
$135 < D \leqq 150$	9
$150 < D \leqq 170$	16
$170 < D \leqq 190$	19
$190 < D \leqq 220$	22
$220 < D \leqq 235$	31
$235 < D \leqq 270$	37
$270 < D \leqq 275$	43
$275 < D \leqq 290$	49
$290 < D \leqq 330$	61
$330 < D \leqq 360$	71
$360 < D \leqq 400$	81

[a]Reference 1. This table was derived from a survey of users and manufacturers. The actual number of columns in a particular tank may vary greatly with age, fixed roof style, loading specifications, and manufacturing perogatives. Data in this table should not supersede information on actual tanks.

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 4.4-1 lists suggested saturation factors.

TABLE 4.4-1. SATURATION (S) FACTORS FOR CALCULATING PETROLEUM LIQUID LOADING LOSSES

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[a]	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

[a]For products other than gasoline and crude oil. Use factors from Table 4.4-2 for marine loading of gasoline. Use Equations 2 and 3 and Table 4.4-3 for marine loading of crude oil.

Emissions from controlled loading operations can be calculated by multiplying the uncontrolled emission rate calculated in Equation 1 by the control efficiency term:

$$\left(1 - \frac{eff}{100}\right).$$

Measures to reduce loading emissions include selection of alternate loading methods and application of vapor recovery equipment. The latter captures organic vapors displaced during loading operations and recovers

TABLE 4.4-2. VOLATILE ORGANIC COMPOUND EMISSION FACTORS FOR GASOLINE LOADING OPERATIONS AT MARINE TERMINALS[a]

Vessel tank condition	Previous cargo	Total organic emission factors: Ships/ocean barges[b] mg/liter transferred	Ships/ocean barges[b] lb/10^3 gal transferred	Barges[b] mg/liter transferred	Barges[b] lb/10^3 gal transferred
Uncleaned	Volatile[c]	315	2.6	465	3.9
Ballasted	Volatile	205	1.7	d	d
Cleaned	Volatile	180	1.5	e	e
Gas-freed	Volatile	85	0.7	e	e
Any condition	Nonvolatile	85	0.7	e	e
Gas-freed	Any cargo	e	e	245	2.0
Typical overall situation[f]	Any cargo	215	1.8	410	3.4

[a]References 2, 8. Factors represent nonmethane-nonethane VOC emissions because methane and ethane have been found to constitute a negligible weight fraction of the evaporative emissions from gasoline.
[b]Ocean barges (tank compartment depth about 40 feet) exhibit emission levels similar to tank ships. Shallow draft barges (compartment depth 10 to 12 feet) exhibit higher emission levels.
[c]Volatile cargoes are those with a true vapor pressure greater than 1.5 psia.
[d]Barges are not usually ballasted.
[e]Unavailable.
[f]Based on observation that 41% of tested ship compartments were uncleaned, 11% ballasted, 24% cleaned, and 24% gas-freed. For barges, 76% were uncleaned.

TABLE 4.4-3. AVERAGE ARRIVAL EMISSION FACTORS, C_A, FOR CRUDE OIL LOADING EMISSION EQUATION[a]

Ship/ocean barge tank condition	Previous cargo	Arrival emission factor, lb/10^3 gal
Uncleaned	Volatile[b]	0.86
Ballasted	Volatile	0.46
Cleaned or gas-freed	Volatile	0.33
Any condition	Nonvolatile	0.33

[a]Arrival emission factors (C_A) to be added to generated emission factors calculated in Equation 3 to produce total crude oil loading loss. These factors represent total organic compounds; nonmethane-nonethane VOC emission factors average about 15% lower.
[b]Volatile cargoes are those with a true vapor pressure greater than 1.5 psia.

APPENDIX F

GRAPHS

TABLE 4.3-1. PAINT FACTORS FOR FIXED ROOF TANKS[a]

Tank color		Paint factors (F_P)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44[b]
Medium gray	Medium gray	1.40	1.58[b]

[a]Reference 2.
[b]Estimated from the ratios of the seven preceding paint factors.

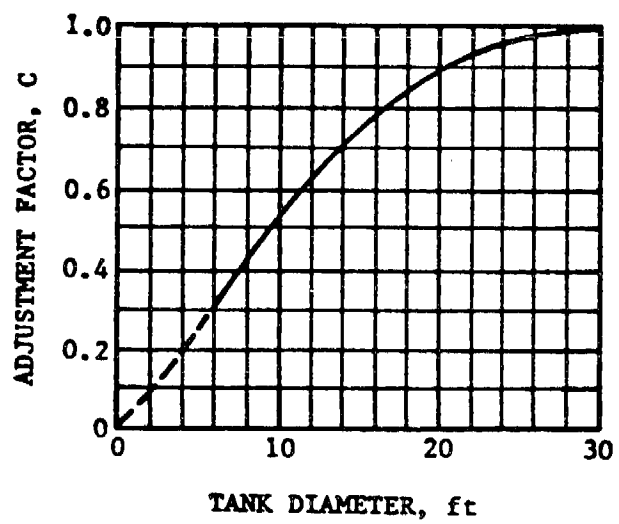


Figure 4.3-4. Adjustment factor (C) for small diameter tanks.[2]

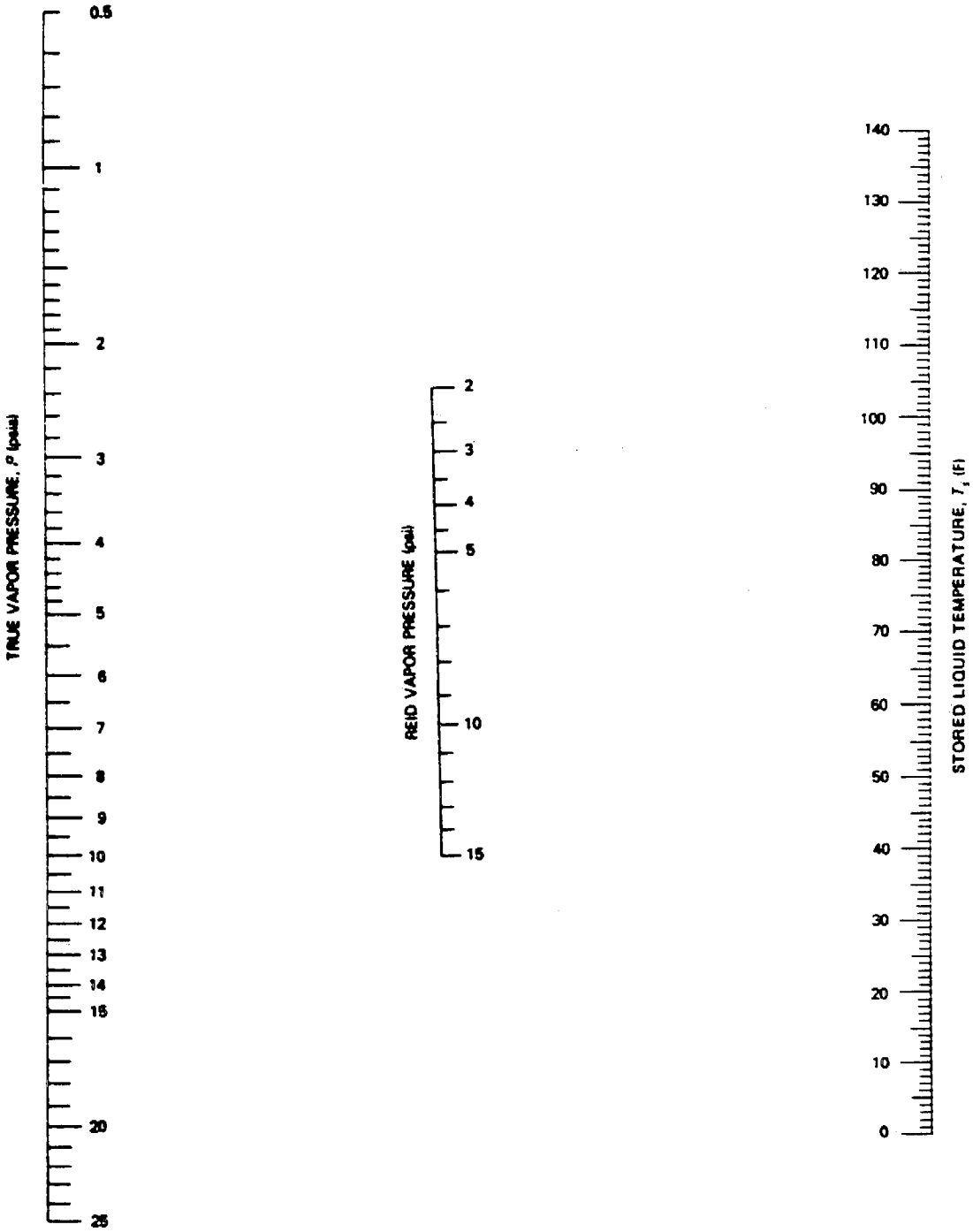
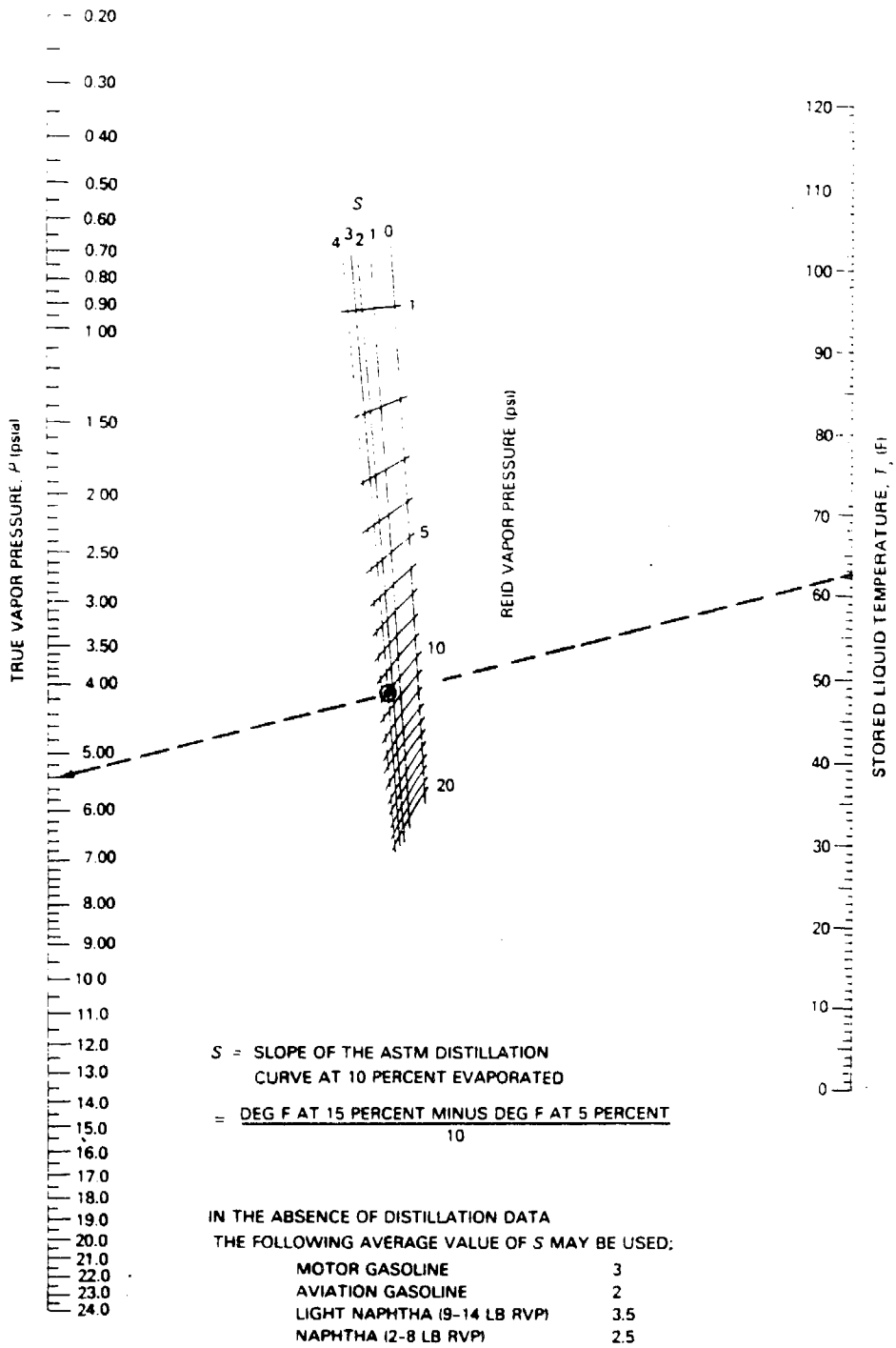
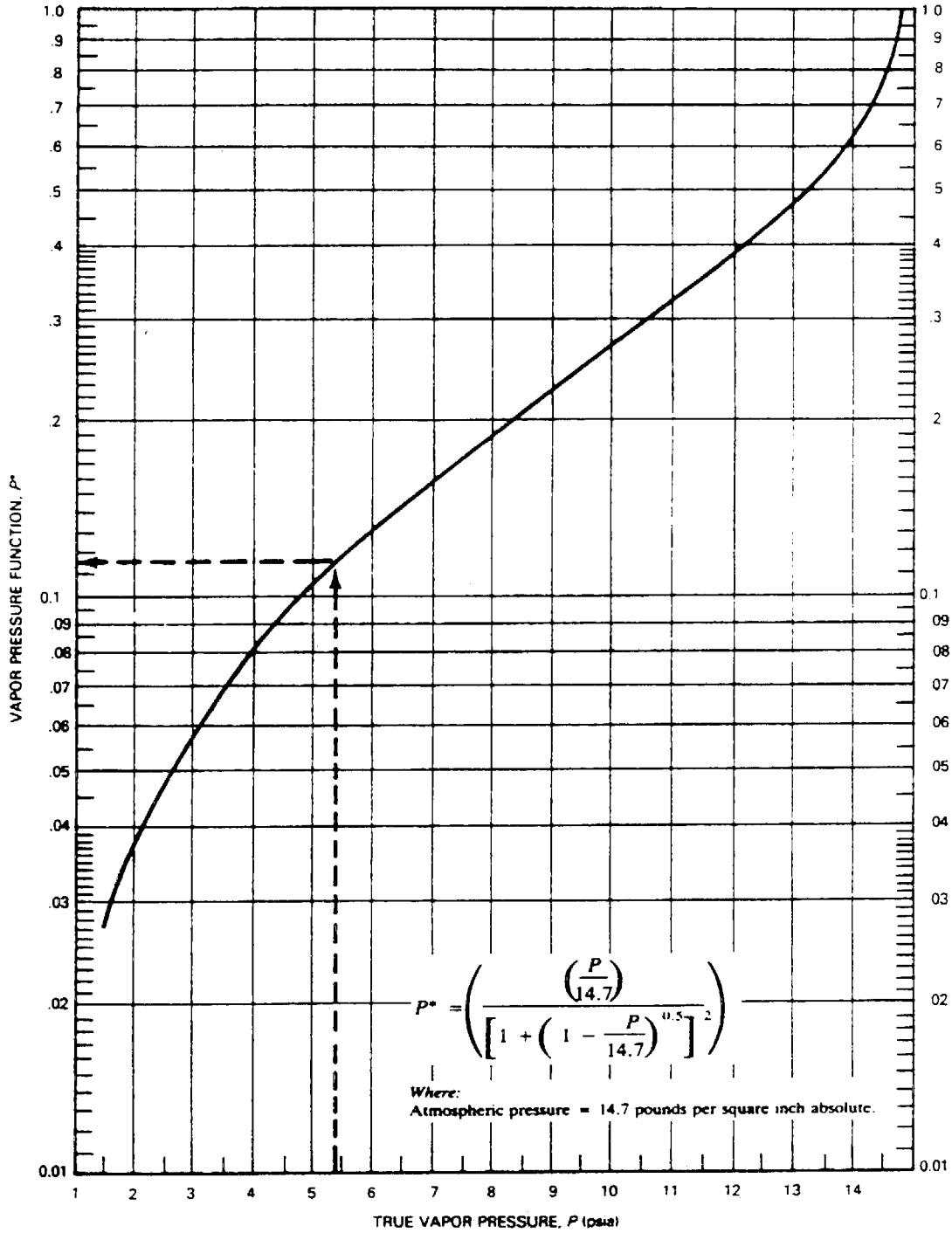


Figure 4.3-5. True vapor pressure (P) of crude oils (2-15 psi RVP).[6]



NOTE: Dashed line illustrates sample problem for RVP = 10 pounds per square inch, gasoline (S = 3), and T_s = 62.5°F
SOURCE: Nomograph drawn from the data of the National Bureau of Standards.

Figure 4.3-6. True vapor presure (P) of refined petroleum liquids like gasoline and napththas (1-20 psi RVP).[6]



NOTE: Dashed line illustrates sample problem for P = 5.4 pounds per square inch absolute.

Figure 4.3-9. Vapor pressure function (P^*).[5]

TABLE A-4. AVERAGE ANNUAL AMBIENT TEMPERATURE (T_a, °F) FOR SELECTED U.S. LOCATIONS

Birmingham, Ala.	62.0
Huntsville, Ala.	60.6
Mobile, Ala.	67.5
Montgomery, Ala.	64.9
Anchorage, Alaska	35.3
Annette, Alaska	45.4
Barrow, Alaska	9.1
Barter Island, Alaska	9.6
Bethel, Alaska	28.4
Bettles, Alaska	21.2
Big Delta, Alaska	27.4
Cold Bay, Alaska	37.9
Fairbanks, Alaska	23.9
Gulkana, Alaska	26.5
Homer, Alaska	36.6
Juneau, Alaska	40.0
King Salmon, Alaska	32.8
Kodiak, Alaska	40.7
Kotzebue, Alaska	20.9
McGrath, Alaska	25.0
Nome, Alaska	25.5
St. Paul Island, Alaska	34.3
Talkeetna, Alaska	32.6
Unalakleet, Alaska	26.4
Valdez, Alaska	38.3
Yakutat, Alaska	38.6
Flagstaff, Ariz.	45.4
Phoenix, Ariz.	71.2
Tucson, Ariz.	68.0
Winslow, Ariz.	54.9
Yuma, Ariz.	73.8
Fort Smith, Ariz.	60.8
Little Rock, Ark.	61.9
North Little Rock, Ark.	61.7
Bakersfield, Calif.	65.5
Bishop, Calif.	56.0
Blue Canyon, Calif.	50.4
Eureka, Calif.	52.0
Fresno, Calif.	62.6
Long Beach, Calif.	63.9
Los Angeles, Calif.— International Airport	62.6
Los Angeles, Calif.	65.3
Mount Shasta, Calif.	49.5
Red Bluff, Calif.	62.9
Sacramento, Calif.	60.6
San Diego, Calif.	63.8
San Francisco, Calif.— International Airport	56.6
San Francisco, Calif.—City	56.8
Santa Barbara, Calif.	58.9
Santa Maria, Calif.	56.8
Stockton, Calif.	61.6
Alamosa, Colo.	41.2
Colorado Springs, Colo.	48.9
Denver, Colo.	50.3
Grand Junction, Colo.	52.7
Pueblo, Colo.	52.8
Bridgeport, Conn.	51.8
Hartford, Conn.	49.8
Wilmington, Del.	54.0
Wash., D.C.-Dulles Airport	53.9
Wash. D.C.-National Airport	57.5
Apalachicola, Fla.	68.2
Daytona Beach, Fla.	70.3
Fort Myers, Fla.	73.8
Gainsville, Fla.	68.6
Jacksonville, Fla.	68.0
Key West, Fla.	77.7
Miami, Fla.	75.7
Orlando, Fla.	72.4
Pensacola, Fla.	68.0
Tallahassee, Fla.	67.2
Tampa, Fla.	72.0
Vero Beach, Fla.	72.4
West Palm Beach, Fla.	74.6
Athens, Ga.	61.4
Atlanta, Ga.	61.2
Augusta, Ga.	63.2
Columbus, Ga.	64.3
Macon, Ga.	64.7
Savannah, Ga.	65.9
Hilo, Hawaii	73.6
Honolulu, Hawaii	77.0
Kahului, Hawaii	75.5
Lihua, Hawaii	75.2
Boise, Idaho	51.1
Lewiston, Idaho	52.1
Pocatello, Idaho	46.6
Cairo, Ill.	59.1
O'Hare Airport, Chicago, Ill.	49.2
Moline, Ill.	49.5
Peoria, Ill.	50.4
Rockford, Ill.	47.8
Springfield, Ill.	52.6
Evansville, Ind.	55.7
Fort Wayne, Ind.	49.7
Indianapolis, Ind.	52.1
South Bend, Ind.	49.4
Des Moines, Iowa	49.7
Dubuque, Iowa	46.3
Sioux City, Iowa	48.4
Waterloo, Iowa	46.1
Concordia, Kans.	53.2
Dodge City, Kans.	55.1
Goodland, Kans.	50.7
Topeka, Kans.	54.1

(continued)

(Source: U. S. EPA, 1988, Estimating Air Toxics Emissions from Organic Liquid Storage Tanks. EPA-450/4-88-004 October)

TABLE A-6. AVERAGE ANNUAL WIND SPEED (v, mi/h) FOR SELECTED U.S. LOCATIONS

Birmingham, Ala.	7.3
Huntsville, Ala.	8.1
Mobile, Ala.	9.0
Montgomery, Ala.	6.7
Anchorage, Alaska	6.8
Annette, Alaska	10.6
Barrow, Alaska	11.8
Barter Alaska	13.2
Bethel, Alaska	12.8
Bettles, Alaska	6.7
Big Delta, Alaska	8.2
Gold Bay, Alaska	16.9
Fairbanks, Alaska	5.4
Gulkana, Alaska	6.8
Homer, Alaska	7.2
Juneau, Alaska	8.4
King Salmon, Alaska	10.7
Kodiak, Alaska	10.6
Kotzebue, Alaska	13.0
McGrath, Alaska	5.1
Nome, Alaska	10.7
St. Paul Island, Alaska	18.3
Talkeetna, Alaska	4.5
Valdez, Alaska	6.0
Yakutat, Alaska	7.4
Flagstaff, Ariz.	7.3
Phoenix, Ariz.	6.3
Tucson, Ariz.	8.2
Winslow, Ariz.	8.9
Yuma, Ariz.	7.8
Fort Smith, Ark.	7.6
Little Rock, Ark.	8.0
Bakersfield, Calif.	6.4
Blue Canyon, Calif.	7.7
Eureka, Calif.	6.8
Fresno, Calif.	6.4
Long Beach, Calif.	6.4
Los Angeles, Calif.—International Airport	7.5
Los Angeles, Calif.	6.2
Mount Shasta, Calif.	5.1
Oakland, Calif.	8.2
Red Bluff, Calif.	8.6
Sacramento, Calif.	8.1
San Diego, Calif.	6.8
San Francisco, Calif.—International Airport	10.5
San Francisco, Calif.—City	8.7
Santa Maria, Calif.	7.0
Stockton, Calif.	7.5
Colorado Springs, Colo.	10.1
Denver, Colo.	8.8
Grand Junction, Colo.	8.1
Pueblo, Colo.	8.7
Bridgeport, Conn.	12.0
Hartford, Conn.	8.5
Wilmington, Del.	9.2
Wash., D.C.-Dulles Airport	7.5
Wash. D.C.-National Airport	9.3
Apalachicola, Fla.	7.9
Daytona Beach, Fla.	8.8
Fort Myers, Fla.	8.2
Jacksonville, Fla.	8.2
Key West, Fla.	11.2
Miami, Fla.	9.2
Orlando, Fla.	8.6
Pensacola, Fla.	8.4
Tallahassee, Fla.	6.5
Tampa, Fla.	8.6
West Palm Beach, Fla.	9.5
Athens, Ga.	7.4
Atlanta, Ga.	9.1
Auguata, Ga.	6.5
Columbus, Ga.	6.7
Macon, Ga.	7.7
Savannah, Ga.	7.9
Hilo, Hawaii	7.1
Honolulu, Hawaii	11.6
Kahului, Hawaii	12.8
Lihua, Hawaii	11.9
Boise, Idaho	8.9
Pocatello, Idaho	10.2
Cairo, Ill.	8.5
Chicago, Ill.	10.3
Moline, Ill.	10.0
Peoria, Ill.	10.1
Rockford, Ill.	9.9
Springfield, Ill.	11.3
Evansville, Ind.	8.2
Fort Wayne, Ind.	10.2
Indianapolis, Ind.	9.6
South Bend, Ind.	10.4
Des Moines, Iowa	10.9
Sioux City, Iowa	11.0
Waterloo, Iowa	10.7
Concordia, Kans.	12.3
Dodge City, Kans.	13.9
Goodland, Kans.	12.6
Topeka, Kans.	10.2
Wichita, Kans.	12.4
Cincinnati, Ky.--Airport	9.1
Jackson, Ky.	7.0
Lexington, Ky.	9.5
Louisville, Ky.	8.3
Baton Rouge, La.	7.7
Lake Charles, La.	8.7
New Orleans, La.	8.2

(continued)

EMISSION ESTIMATION TECHNIQUE: PERCHLOROETHYLENE PRODUCTION

PERCHLOROETHYLENE PRODUCTION
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique (EET) developed by the Air Resources Board staff in accordance with the Emission Inventory Criteria and Guidelines Regulation for the Administration of AB 2588, the Air Toxics "Hot Spots" Information and Assessment Act of 1987 (the "Act"). Specifically, this report describes the processes used in the production of perchloroethylene. These processes result in the air emission of toxic substances listed pursuant to the Act and the Regulation. The purpose of this report is to describe and recommend a method that a facility operator should use to calculate emissions of these listed substances.

Perchloroethylene (PERC) is an organic solvent which is also called tetrachloroethylene, tetrachloroethene, or PCE. PERC is widely and primarily used in the dry cleaning and textile-processing industries. Other uses include use as a solvent in vapor degreasing and industrial metal cleaning operations, and as a chemical intermediate in chlorofluorocarbon production.

PERC was once manufactured by the chlorination of acetylene. Today, PERC is produced separately or as a coproduct with trichloroethylene (TCE) by the chlorination and oxychlorination of ethylene dichloride (EDC). The raw material ratios determine the proportions of PERC and TCE produced by these processes.

PERC is also produced as a coproduct with carbon tetrachloride by the chlorinolysis of hydrocarbons (e.g., methane, ethane, propane, or propylene). There is only one facility in California that produces PERC. This facility uses the hydrocarbon chlorinolysis process.

Various grades of PERC are produced, including those listed below:

PERC Grade	Use
Purified	Dry Cleaning
Technical	Technical
USP	Industrial
Spectrometric	Vapor Degreasing

There are four producers of PERC at six locations in the United States, including the one facility in California. Some PERC is also imported. It is believed that in the long term, U.S. PERC production demand will remain about the same or will experience a minor decline.

II. PROCESS DESCRIPTIONS FOR PERCHLOROETHYLENE PRODUCTION

As mentioned above, perchloroethylene is produced in the U.S. by three processes: 1) ethylene dichloride chlorination, 2) ethylene dichloride oxychlorination, and 3) hydrocarbon chlorinolysis.

A. Ethylene Dichloride Chlorination Process

In the direct chlorination process, EDC reacts with chlorine to produce a crude product which is then distilled and purified to marketable-grade PERC and TCE. The proportions of EDC and chlorine determine how much PERC and TCE are produced. Hydrogen chloride is also produced in this process.

B. Ethylene Dichloride Oxychlorination Process

In the oxychlorination process, EDC reacts with chlorine and/or hydrogen chloride, and oxygen to form PERC, TCE, and water. The proportions of PERC and TCE produced depend on the EDC to hydrogen chloride/chlorine ratio.

C. Hydrocarbon Chlorinolysis Process

As stated earlier, in California, PERC is produced by the hydrocarbon chlorinolysis process. Most of the PERC produced in the United States is also produced by this process.

In hydrocarbon chlorinolysis, chlorine is reacted with chlorinated hydrocarbon derivatives or with a hydrocarbon (such as methane, ethane, propane, or propylene) to produce PERC, carbon tetrachloride, and hydrogen chloride. This process produces a crude product which is distilled and purified to marketable-grade PERC and carbon tetrachloride.

The following briefly summarizes the hydrocarbon chlorinolysis process (as described in the EPA revised draft report, "Locating and Estimating Air Emissions from Sources of Perchloroethylene and Trichloroethylene", April 4, 1989):

Preheated hydrocarbon feed material and chlorine are fed to a fluid-bed chlorinolysis reactor. The reaction products pass through a cyclone for removal of entrained catalyst and then are sent to a condenser. Uncondensed materials, consisting of hydrogen chloride, unreacted chlorine, and some carbon tetrachloride, are removed to the hydrogen chloride purification system. The condensed material is fed to a hydrogen chloride and chlorine removal column, with the overheads from this column going to hydrogen chloride purification. The bottoms from the column are transferred to a crude storage tank and the crude material is fed to a distillation column, which recovers carbon tetrachloride as overheads. The bottoms from the carbon tetrachloride distillation column are fed to a PERC distillation column. The overheads from the PERC distillation column are taken to PERC storage and loading, and the bottoms are incinerated.

III. POTENTIAL SOURCES OF EMISSIONS

Possible substances which may be emitted from the production of PERC by the hydrocarbon chlorinolysis process, and which require quantification in accordance with the Emission Inventory Criteria and Guidelines Regulation, include PERC, carbon tetrachloride, and hydrogen chloride. In addition, ethylene dichloride, vinylidene chloride, chloroform, and chlorine must also be quantified if emitted.

A. Perchloroethylene and Carbon Tetrachloride Emissions

Most of the PERC and carbon tetrachloride process emissions originate from fugitive sources. Some fugitive sources are the process pumps, valves, and compressors. Chlorine and hydrogen chloride may cause corrosion and contribute to these fugitive emissions. The PERC and carbon tetrachloride distillation condensers and caustic scrubber are other process emission sources. Other sources of PERC and carbon tetrachloride emissions are the crude and final product storage tanks. Still other emissions originate from handling and loading of the products into drums, tank trucks, tank cars, barges, or ships. Secondary PERC and carbon tetrachloride emissions result from the handling and disposal of process waste liquids, the bottoms of the PERC distillation column (hex wastes), and the waste caustic from the caustic scrubber.

B. Ethylene Dichloride, Vinylidene Chloride Emissions

Ethylene dichloride and vinylidene chloride are produced in the chlorinolysis reaction. Emissions of these substances may result from the handling and disposal of hex wastes from the PERC distillation column.

C. Chloroform Emissions

Chloroform emissions may originate from wastewater stripping.

D. Chlorine, Hydrogen Chloride Emissions

Chlorine emissions may originate from fugitive sources such as pumps and valves. Other possible sources of chlorine emissions are condensers, the hydrogen chloride/chlorine removal column, chlorine absorption column, and caustic scrubber. Hydrochloric acid is formed when uncondensed overheads from the chlorine absorption column mix with water to produce a hydrochloric acid solution. Hydrogen chloride emissions may originate from hydrochloric acid storage tanks.

IV. CONTROL DEVICES

The emission points and control devices used in PERC production vary among facilities in the United States. As described in the EPA's revised draft report, "Locating and Estimating Air Emissions from Sources of Perchloroethylene and Trichloroethylene", April 4, 1989, emissions from

process vents may be controlled by scrubbers; fixed roof tanks by installation of internal floating roofs with primary and/or secondary seals and addition of refrigerated condenser system; handling by use of submerged fill pipe technology; equipment openings by purging/washing/cleaning prior to openings; fugitive sources by employing an inspection and maintenance program; and secondary sources by steam stripping and incineration.

Emission sources, substances, possible controls, control efficiencies (where available), and emission factors (where available) are presented in Appendices A, B, and C of this EET, as well as in Attachment E of the Technical Guidance Document. All control efficiencies and emission factors proposed to be used in emissions calculations by a facility operator must be justified in the emission inventory plan to the appropriate Air Pollution Control District or Air Quality Management District.

V. EMISSION ESTIMATES

When source testing is feasible, and when reliable, ARB-approved methods exist, then source testing is the preferred method of accurately determining toxic emissions of listed substances. Although source testing is available for emissions from the perchloroethylene production processes, the Air Toxics "Hot Spots" Emission Inventory Criteria and Guidelines Regulation does not require any source testing at this time to determine toxic emissions from PERC production.

A source test and/or mass balance is considered to be the best means to determine air emissions directly from perchloroethylene production. Test Method 422 for gaseous halogenated organics is described in the Air Resources Board's Stationary Source Test Methods, Volume III: Methods for Determining Emissions of Toxic Air Contaminants from Stationary Sources, Stationary Source Division, March 1988. When using a mass balance, the facility operator must account for all routes of inflow and outflow of a substance, including any accumulation or depletion of the substance in the equipment, control devices, or through chemical reaction. Published emission factors are available for some toxic emissions from PERC production (see Appendices A, B, and C of this EET and Attachment E of the Technical Guidance Document). However, the accuracy and reliability of currently published emission factors are not established. Order-of-magnitude differences could result between actual and calculated emissions in a worst-case scenario, due to differences in a facility's emission points, control devices, and specific operating procedures.

A. Sample Calculation Using An Emission Factor

Calculate annual PERC emissions from storage tanks if annual PERC production is 25,000 tons:

$$2.5 \times 10^4 \text{ tons} \times .907 \text{ Mg/ton} \times .4 \text{ kg/Mg}^* = 9.07 \times 10^3 \text{ kg PERC}$$

$$9.07 \times 10^3 \text{ kg} \times 2.205 \text{ lb/kg} = 19{,}999 \quad \text{or} \quad 2 \times 10^4 \text{ lb PERC}$$

* Assume emission factor used (0.4 kilogram of PERC emitted per megagram of PERC produced) has been determined to be reliable and applicable for the specific conditions in the facility.

B. Sample Calculation Using An Emission Factor

Calculate annual carbon tetrachloride emissions from hex waste handling and disposal if annual carbon tetrachloride production is 30,000 Mg/yr:

Uncontrolled Emissions

$$3 \times 10^4 \text{ Mg} \times 4.6 \times 10^{-3} \text{ kg/Mg}^{**} = 138 \text{ kg}$$

$$138 \text{ kg} \times 2.205 \text{ lb/kg} = 304$$

or 300 lb CCl_4 (uncontrolled)

Controlled Emissions

$$300 \text{ lb} \times (1 - .99)^{***} = 3 \text{ lb } CCl_4 \text{ (controlled)}$$

** Assume emission factor used (4.6×10^{-3} kilogram of carbon tetrachloride emitted per megagram of carbon tetrachloride produced) has been determined to be reliable and applicable for the specific conditions in the facility.

*** The control efficiency of the vapor balance system and refrigerated condenser for hex waste handling and disposal is 99 percent.

APPENDICES

APPENDIX A. Controlled and Uncontrolled Emission Factor Ranges for the Release of Perchloroethylene From Perchloroethylene Production by Hydrocarbon Chlorinolysis

APPENDIX B. Emission Factors for the Release of Carbon Tetrachloride From Perchloroethylene and Carbon Tetrachloride Production by Hydrocarbon Chlorinolysis

APPENDIX C. Emission Factors for the Release of Ethylene Dichloride, Vinylidene Chloride, Chloroform, Hydrogen Chloride, and Chlorine From Perchloroethylene Production by Hydrocarbon Chlorinolysis

APPENDIX A

Controlled and Uncontrolled Emission Factor Ranges for the Release of Perchloroethylene From Perchloroethylene Production by Hydrocarbon Chlorinolysis

Emission Source	Substance	Possible Control	% Reduction	Emission Factor Range[1]
Process Fugitives	PERC	I & M Program	-----	0.41 - 60 Mg/yr
Storage Tanks	PERC	Internal Floating Roofs; Refrigerated Condenser System	-----	0.013 - 0.69 kg/Mg
Process Vents	PERC	Scrubbers	-----	$< 4 \times 10^{-5}$ - 0.20 kg/Mg
Handling	PERC	Submerged Fill Pipe Technology	-----	0.03 - 0.89 kg/Mg
Equipment Openings	PERC	Purging/Washing/ Cleaning Prior to Openings	-----	6×10^{-5} - 0.054 kg/Mg
Secondary[2]	PERC	Steam Stripping/ Incineration	-----	2.5×10^{-3} - 0.013 kg/Mg

1 Emission factors in terms of kg/Mg refer to kilograms of PERC emitted per megagram of PERC production capacity. The emission factor ranges were taken from Table 7 of the EPA revised draft report "Locating and Estimating Air Emissions from Sources of Perchloroethylene and Trichloroethylene", April 4, 1989. The ranges were based on emission factors calculated for five facilities in 1983, and reflect emissions from both uncontrolled and controlled sources. Emission factor ranges given are for guidance only. The facility operator must default to the high end of a range unless he/she can justify otherwise to the District.

2 Secondary emissions result from handling and disposal of process waste liquids, from hex wastes from the PERC distillation column, and from the waste caustic from the caustic scrubber.

APPENDIX B

Emission Factors for the Release of Carbon Tetrachloride (CT)
From Perchloroethylene and Carbon Tetrachloride Production by Hydrocarbon Chlorinolysis

Emission Source	Substance	Possible Control	% Reduction	Emission Factor[1] Uncontrolled	Emission Factor[1] Controlled
Process Fugitives	CT	Quarterly I/M of Pumps and Valves	48	1.5 kg/hr	0.78 kg/hr
		Monthly I/M of Pumps and Valves	64	1.5 kg/hr	0.54 kg/hr
		Monthly I/M of Valves; double mechanical seals on pumps; rupture disks on relief valves	73	1.5 kg/hr	0.41 kg/hr
Storage					
Crude Tank	CT	Refrigerated[2] Condenser	87	0.098 kg/Mg	0.013 kg/Mg
CT Tank	CT	Refrigerated[2] Condenser	85	0.58 kg/Mg	0.087 kg/Mg
Distillation Column	CT	-----	-----	0.008 kg/Mg	-----
Handling	CT	Refrigerated[2] Condenser	85	0.24 kg/Mg	0.036 kg/Mg
Secondary	CT				
Hex Waste Handling and Disposal and Waste Hydrocarbon Storage		Vapor Balance & Refrigerated Condenser	99	4.6×10^{-3} kg/Mg	4.6×10^{-5} kg/Mg
Waste Caustic		Steam Stripper	96	2.9×10^{-3} kg/Mg	1.2×10^{-4} kg/Mg

1 Emission factors in terms of kg/Mg refer to kilograms of carbon tetrachloride emitted per megagram of carbon tetrachloride produced. The emission factors were taken from Table 2 of the EPA report "Locating and Estimating Air Emissions From Sources of Carbon Tetrachloride", March 1984. The emission factors are for a hypothetical facility with a total production capacity of 80,000 Mg and a product mix of 37.5 percent carbon tetrachloride and 62.5 percent perchloroethylene. Any given facility may vary in configuration and level of control from this hypothetical facility.

2 For refrigerated condensers, removal efficiency is based on a condenser operating temperature of -15°C and uncontrolled emission temperatures of 20°C for product storage and handling, and of 38°C for crude storage. Greater removal efficiency can be achieved by using lower operating temperatures.

APPENDIX C

Emission Factors for the Release of Ethylene Dichloride, Vinylidene Chloride, Chloroform, Hydrogen Chloride, and Chlorine from Perchloroethylene Production by Hydrocarbon Chlorinolysis

Emission Source	Substance	Possible Control	% Reduction	Emission Factors[1] Uncontrolled	Controlled
Hex Waste Handling	Ethylene Dichloride	Vapor Balance System/Carbon Adsorption	99	0.026 kg/Mg PERC & carbon tet. produced	2.6×10^{-4} kg/Mg PERC & carbon tet. produced
Hex Waste Handling	Vinylidene Chloride	Vapor Balance System/Carbon Adsorption	99	0.013 kg/Mg PERC & carbon tet. produced	1.3×10^{-4} kg/Mg PERC & carbon tet. produced
Wastewater Stripper	Chloroform	Condensers	-----	-----	-----
Entire Process, By-Product HCL Manufacturing	Hydrogen Chloride	-----	-----	0 - 8.5 lbs/ton by-product acid produced	
Entire Process	Chlorine	Uncertain	-----	----- Based on tests and mass balance	-----

1 Emission factors are from EPA's "Toxic Air Pollutant Emission Factors--A Compilation for Selected Air Toxic Compounds and Sources", October 1988. Emission factors for ethylene dichloride and vinylidene chloride are based on a hypothetical facility producing 50,000 Mg/yr PERC and 30,000 Mg/yr carbon tetrachloride.

REFERENCES

U.S. EPA, April 4, 1989. Locating and Estimating Air Emissions from Sources of Perchloroethylene and Trichloroethylene. Revised Draft Report. Research Triangle Park, North Carolina.

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EMISSION ESTIMATION TECHNIQUE: SECONDARY SMELTER AND FOUNDRY

SECONDARY SMELTER AND FOUNDRY EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique (EET), developed by the Air Resources Board staff in accordance with the Air Toxic "Hot Spots" Information and Assessment Act of 1987 (The Act). Specifically this report describes the processes used in metallurgical industrial operations involving furnaces that result in the emission of toxic substances listed pursuant to the Act, and specifies the method(s) a facility operator would use to calculate resulting emissions of these listed substances.

The two basic types of metallurgical industrial operations in California involving furnaces are secondary smelters and foundries. (As California has no primary smelters, this report focuses on secondary smelters and foundries.) Secondary smelters and foundries are similar except that foundries generally use cleaner scrap (or ingots) than do secondary smelters; in addition metallurgical operations at foundries generally do not result in a chemical change in the material charged. Foundries are involved in the production and use of cores and molds.

In secondary smelting, scrap metal mixtures are heated, accompanied by a chemical change that results in the formation of slag, and eventually results in usable metals and metal alloys. In foundry operations, the material charged is generally heated without an accompanying chemical change.

In California, secondary smelters and foundries operations may produce emissions of numerous listed toxic substances. The nature and amount produced depend on the feed, processes, and equipment used. In addition, metal scrap subjected to sorting and treating processes prior to undergoing smelting or melting may also create toxic emissions of listed substances.

Pollutants emitted may consist of organic or inorganic substances. Organic substances include acrolein, acetaldehyde, formaldehyde, phenol, toluene, and xylene vapors. Other substances are polycyclic organic matter (POM) which include polycyclic aromatic hydrocarbons (PAH). Inorganic substances include arsenic, fluoride, and zinc vapors. Inorganic particulate matter (PM) may include arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, vanadium, zinc, and other trace metals (U.S. EPA, 1986).

II. PROCESS DESCRIPTION OF SECONDARY SMELTERS AND FOUNDRIES

The processes in metallurgical industrial operations depend on the types of feed and furnaces used; hence not every step of every process described below will be used in a particular facility. These steps can be combined or reordered, depending on furnace design, scrap quality, process inputs, and product specifications.

Inspecting, Sorting, and Treating

In the inspection process, scrap metal is received; scrap requiring no sorting or treatment may be stored or charged directly to the furnace. Other scrap may require manual sorting to remove undesirable and oversized materials. Once sorted, the scrap will usually require treatment.

In the treating process, scrap metal is processed to remove contaminants and prepare it for the furnace. Grease, oil, or any combustible material is removed to prevent explosion. Scrap metal is also concentrated before entering the furnace to avoid backcharging. Treatment may include mechanical, pyrometallurgical, and hydrometallurgical methods, or a combination of these techniques (U.S. EPA, 1977).

Mechanical

Mechanical methods include stripping, shredding, crushing, and separating contaminants through magnetic attraction.

Pyrometallurgical

Pyrometallurgical methods include sweating, burning, and drying.

Hydrometallurgical

Hyrdrometallurgical methods include leaching and flotation.

Once treated, the scrap is usually first charged by mechanical means. Often the furnace is designed so that chips and light scrap are fed below the surface of a previous charge. The smelting/melting process may involve a number of processes including the following.

Smelting/Melting

Charging

The scrap metal is fed into the furnace. The load added constitutes a charge.

Batch Processing

Scrap is fed into the furnace continuously.

Smelting/Melting

The charge is heated to a molten metal.

Backcharging

More metal and possibly alloys or fluxes are added to the furnace.

Fluxing

A mineral is added to a charge to promote the fusion of metals or prevent the formation of oxides. Cover fluxes prevent the air from reaching and oxidizing the melt. Solvent fluxes react with non-metals and form insolubles which float to the surface as part of the slag. Air or oxygen may be blown through to adjust the composition of the charge.

Skimming

Contaminated semi-sold fluxes (dross, slag, or skimmings) are ladled from the surface of the melt and removed.

Alloying

Metals are added to a charge to form a compound (two or more metals) to attain the composition of the final product.

Refining

The content of molten metal is adjusted to attain a specified composition. Alloys and other chemicals may be used to treat the metal.

Tapping

The melt is allowed to enter a ladle or mold.

Casting

Casting is the act of forming a particular shape by pouring molten metal into a mold or over a core.

Mold and Core Production

Cores are forms used to make the internal voids in castings, and molds are forms used to shape the casting exterior. Cores may be made of sand with organic binders, molded into an internal void in the casting and baked in an oven. Molds are commonly made of wet sand with clay and organic additives, dried with hot air. Increasingly cold setting binders are being used in core and mold production. Used sand from castings shakeout operations is recycled to the sand preparation area to be cleaned, screened, and reused (U.S. EPA, 1985).

Finishing Operations

Finishing operations include the removal of burrs and other unwanted appendages as well as abrasive blast cleaning to remove any remaining sand or scale.

In addition to the processes, several different types of furnaces used in secondary smelters and foundries can affect emission of toxics.

(Most of the following information on furnaces was taken from the U.S. EPA, 1977 Emissions Factors and Emission Source Information for Primary and Secondary Copper Smelters).

Furnaces

Reverberatory Furnace

In a reverberatory furnace, the charge is heated by radiating heat from the furnace's burner flame, roof, and walls, with fuel combustion occurring directly above the molten bath. Commonly used to smelt and refine aluminum scrap metals, the largest reverberatory furnaces are
open-hearth furnaces, with a capacity of 40 to 500 metric tons.

Cupola Furnace

A cupola furnace, often considered a smaller variety of a blast furnace, is essentially a vertical, refractory-lined cylinder. (The terms blast and cupola are sometimes used interchangeably.) The furnace is open at the top and is equipped with airports at the bottom, which supply air by a down draft blower. Alternate charges of scrap metal, coke and flux, are added through the top of the furnace onto a bed of coke. The molten metal is drawn off through a tap-hole and spout at the bottom of the furnace. Cupolas are commonly used in foundries to remelt iron before casting. Typical capacity is 55 to 65 metric tons.

Rotary Furnace

A rotary furnace is a more elaborate type of a cylindrical reverberatory furnace; the rotary furnace not only tilts for charging and pouring, but can be rotated about on its horizontal cylindrical axis. Rotation during the melting period improves heat transfer.

Converter Furnace

A converter furnace is basically a cylindrical reverberatory furnace, which is mounted to tilt on it longitudinal axis and is modified to permit blowing air through the melt.

Crucible

A crucible is a refractory vessel or pot made of graphite or porcelain. An indirect-fired furnace, a crucible is used to melt materials with melting points not above 1400°C (2500°F). With a capacity of 10 to 1000 kg, the crucible is used to melt small batches of aluminum scrap.

Pot Furnaces

Pot furnaces are an indirect-fired furnace, which are used for metals with melting points not above 800°C (1400°F). These furnaces may be cylindrical or rectangular, and consist of an outer shell lined

with refractory material, combustion chamber, and a pot. The pots are made of pressed steel, cast steel, or cast iron with flanged tops. The flange rests on the furnace wall, holds the pot above the furnace floor, and seals the contents of the pot from the products of combustion of the fuel used. The shape of the pot depends upon the operation.

Some furnaces are electrical; a major advantage with these is atmosphere control and higher temperatures.

Direct-arc Furnace

A direct-arc furnace can heat scrap in a number of ways. The principal heating method is radiation which uses electrodes spaced below the surface of slag cover. The current is passed from the cathode through the slag, to the metal charge, to the slag, and then back to the anode. Sometimes the current is carried from the metal charge to the earth.

Indirect-arc Furnace

In an indirect-arc furnace, the metal charge is placed below the electrodes, forming an arc between the electrodes and charge. The furnace is commonly used in the steel industry.

Electric Induction Furnace

An electric induction furnace consists of a crucible within a water-cooled, copper coil. An alternating current, in the coil and around the crucible, induces currents in the charge. Heating is rapid and uniform, with accurate control possible. This furnace is commonly used to blend pure aluminum and hardening agents to produce hardened aluminum.

III. POTENTIAL SOURCES OF EMISSIONS

A number of metallurgical operations result in emissions which may include particulate matter, carbon monoxide, organic compounds, sulfur dioxide, nitrogen oxides as well as chloride and fluoride compounds. The actual compounds emitted depend upon the feed, equipment, and processes used.

Typical emissions from secondary aluminum smelters include inorganic fluoride and nickel particles and fluoride vapor. Emissions from secondary copper smelters and brass and bronze foundries include particles of cadmium, copper, lead, nickel, selenium, and zinc. Secondary lead smelting can potentially produce emissions of arsenic, lead, manganese, and selenium particulate matter (U.S. EPA, 1986).

Gray iron foundries may produce emissions of inorganic arsenic, barium, beryllium, cadmium, chromium, copper, lead, mercury, manganese, nickel, and zinc particulate matter. Steel foundries may produce emissions of arsenic, chromium, beryllium, manganese, and nickel particles (U.S. EPA, 1986).

In secondary smelters and foundries, significant emissions may be released from the furnace during the smelting/melting process. These fumes are generally captured through a hood and routed to the furnace stack. The stack is then connected to a control device.

Fugitive emissions may result from a number of processes including the sorting and treating processes, (crushing and screening, shredding and classifying, burning and drying) as well as the smelting/melting processes. Emissions of particulate matter and gases may occur when raw materials are handled, especially during receiving, unloading, storing, and conveying processes. Chlorides and fluorides can be generated from the incomplete combustion of coke, carbon and flux additives, dirt, and some gases may be released from burning contaminants such as insulation.

Significant emissions occur when furnace lids and doors are opened during charging, backcharging, alloying, skimming slag, tapping, and pouring processes. For example, during backcharging, fugitive emissions may occur when the amount of scrap being processed is not sufficiently compact to allow a full charge to fit into the furnace prior to heating. Subsequently introducing additional material onto the liquid metal surface produces significant amounts of volatile and combustible materials and smoke that may escape through the charging doors (U.S. EPA, 1977).

Other processes where emissions of listed substances are potentially released include reclaiming, preparing, and mixing sand for the production of cores and molds. Listed substances may be emitted from core baking and organic emissions from mold drying.

During pouring processes, toxic emissions of listed substances result from mold and core materials contacting the molten metal. Emissions continue as the molds cool. A significant quantity of particulate matter is also generated during the casting shakeout operations. During finishing and blast cleaning operations, large, coarse particles are emitted when burrs and other unwanted appendages are removed.

IV. CONTROL DEVICES

In general, escaping furnace gases and fumes are collected and vented through roof openings to air pollution control devices. Controls for fugitive furnace emissions include canopy hoods or special hoods near the furnace doors, and tapping hoods to capture emissions and route them to emission control systems. (The following information on control devices is taken from the U.S. EPA 1987 Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release inventory Form.)

Air pollution control equipment includes combustion devices such as thermal or catalytic incinerators, boiler or process heaters, or flares. These devices reduce emissions of combustible organic compounds by destroying organic particulate matter through oxidation; other components in the mixture are then emitted as an oxide or acid gas.

Thermal Incinerators

Thermal incinerators achieve efficiency through the use of high temperature, sufficient pollutant residence time, and adequate turbulence.

Catalytic Incinerators

Catalytic incinerators operate at lower temperatures relying on catalyst to promote oxidation. While one pollutant may be destroyed, another pollutant may be created requiring other steps to remove it from flue gases.

Control devices commonly used to remove particular matter include, fabric filters or baghouses, cyclones, electrostatic precipitators, wet scrubbers, and afterburners. Gaseous pollutants must be absorbed onto a solid particle or react with water in a scrubber to be removed.

Fabric Filters (Also known as baghouse)

Fabric filters are efficient control devices even for small particles. Variations in processes that affect gas streams as well as temperature and gas dew point affect efficiency of these devices. Chemical properties of particulate matter do not usually affect control efficiency. Cooling systems are needed to prevent the hot exhaust gases from damaging or destroying the fabric filters.

Cyclones

Cyclones are used in the finishing operations of foundries. The chemical properties of the particulate matter do not usually affect the control efficiency of cyclones.

Electrostatic Precipitators (ESP)

Electrostatic precipitators remove electrically charged gas stream particles, but are not used to collect organic solids as these are potentially combustible. Efficiency depends on the physical characteristics of the particulate matter, gas stream, and electrical resistivity of pollutant. Temperature can affect pollutant resistivity. Because of a low collection efficiency, electrostatic precipitators are not as well suited to the collection of dense particulate matter such as lead and zinc oxides.

Wet Scrubbers

Wet scrubbers are used to collect organic and inorganic particulate matter and reactive gases. Water is often used as the medium, with efficiency based on physical parameters and scrubber pressure drop. Wet scrubbers are useful only when particulate matter is larger than one micron. Wet scrubbers are used to reduce sulfur dioxide emissions.

Afterburners

Afterburners are generally used to convert unburned Volatile Organic Carbons (VOC) to carbon dioxide and water from burning/drying insulation and other contaminants of scrap metal.

V. EMISSION ESTIMATES

Source testing is the preferred method of accurately determining toxic emissions of listed substances when testing is feasible and approved, reliable methods exist. Some secondary smeltering and foundry operations may be required to perform source testing. However, when source testing is not feasible, there are several methods available for quantifying air emissions: mass balance, emission factors, engineering calculations, and hybrids of mass balance and emission factors. An emission estimate may involve the use of more than one of these methods; in addition, the estimate must account for the control device(s) used. (Refer to the Air Toxics "Hots Spots" Emission Inventory Criteria and Guideline Regulation for definitions of these terms and criteria for their use and for when source testing will be required.)

Air emissions may be either from a process source or a fugitive source. Process source emissions are typically those from a confined vent stream. Fugitive source emissions include process leaks, evaporation from open processes and spills, and loading and unloading losses of raw materials and product. It is preferable to calculate fugitive emission using direct measurement data.

MASS BALANCE

In general terms, a mass balance procedure accounts for all input and output streams of a chemical in a whole process or subprocess. This procedure is useful for estimating emissions when release data has not been measured but input and output streams have been either measured or estimated.

The emissions released can be calculated as the difference between the input and output streams. Any accumulation or depletion of the chemical in the equipment, eg. by reaction, must also be accounted for. Individual operations within the mass balance usually must be evaluated.

Example Using A Mass Balance

A company processes 1000 tons of secondary iron scrap per year containing 1% by weight of the listed toxic substance manganese. The company annually produces 600 tons of a cast iron product containing .5% by weight of manganese from the scrap. 375 tons of sold waste is produced annually, containing 1.5%, by weight, of manganese. Quantify the emissions of manganese.

Consider the quantities of manganese in all streams that enter or leave the process. The amount of manganese released can be calculated as follows:

Input = Manganese in scrap metal (1000 tons X 1%) = 10 tons
Output = Manganese in final product (600 tons X .5%) +
Waste (375 tons X 1.5%) + Emissions (unknown)
Input = Output

10 tons of Manganese = 3 + 5.63 + Emissions

Emissions = 10 - 3 - 5.63 = 1.37 tons of manganese is released per year.

To use the mass balance method, the composition of the iron scrap, any metal or flux added, and final product must be known. In addition, the composition and amount of any slag, skimmings, or dross removed must be considered and included in the output side of the mass balance. The particulate matter removed using a control device must also be taken into account on the output side of the mass balance. Some of the numbers may be calculated or estimated, but the most accurate method would include a measurement technique on the composition analysis of each input and output.

EMISSION FACTORS

It may not always be feasible to estimate fugitive emissions by the mass balance technique because the amounts emitted are sometimes too small, relative to the amount of material processed, especially for hazardous and toxic air pollutants present at low concentrations. Fugitive emissions are also generally to diffuse and dilute to be measured directly; therefore, emission factor calculations are often most appropriate to estimate fugitives.

Emission factors usually express air emissions as a ratio of the amount released of a pollutant to a process-related parameter or measurement, frequently expressed as the amount of pollutant per throughput of a process or piece of equipment, or the amount of pollutant per quantity produced or processed. The throughput must be quantified to use this type of emission factor. Emission factors for air emissions are commonly based on averages measured at several facilities within the same type of industry. The applicability and accuracy of emission factors are dependent on whether the chemical substances, processes, and equipment are substantially equivalent.

Example Using Emission Factors

A secondary lead smelter uses a blast furnace to process 100,000 tons of scrap metal per year. Calculate the controlled emissions of lead for this process on an annual basis.

The emission factor for this process is 0.29 lb of lead (Appendix A, Table 7) emitted per ton of scrap processed so that:

$$\frac{100{,}000 \text{ tons metal processed}}{\text{year}} \times \frac{0.29 \text{ lb of lead}}{\text{ton of metal}} = \frac{29{,}000 \text{ lb lead}}{\text{year}}$$

Air emission factors may also be expressed in terms of total volatile organic compounds (VOC) per throughput or total particulate matter per throughput instead of a single chemical substance per throughput.

Once the total VOC or particulate matter for the process is calculated, the totals may be used to estimate emissions of a specific substance. Reports are available that provide information on the composition of numerous air emission sources, which allows emission estimates of specific substances to be made based on total amount of VOC (U.S. EPA, 1988a) or particulate matter (U.S. EPA, 1988b) from a particular source.

Example Using Emission Factors With Species Profiles

Calculate the toxic air releases from a steel foundry using an electric arc furnace for the melting process. A baghouse is used to control emissions. The foundry processes 5,000 tons of metal annually.

The emission factor for the melting operation is given as 13 lb of particulate matter (PM) per ton of metal processed (Appendix A, Table 3). For total particulate matter the control efficiency of a baghouse used on an electric arc furnace in a steel foundry is given as 98.5% (Appendix A, Table 4) such that:

Uncontrolled emissions

$$5{,}000 \text{ tons metal processed} \times \frac{13 \text{ lb PM}}{\text{ton metal processed}} = 65{,}000 \text{ lb PM}$$

Controlled Emissions (Baghouse)

$$65{,}000 \text{ lb PM} \times (1-.985) = 975.00 \text{ lb PM}$$

Listed substances to be included for the Air Toxics "Hot Spots" Information and Assessment Act of 1987 include the following:

Compound	% of PM	Annual Emissions To Be Reported (lb)
Chlorine	1.850	18.04
Manganese	8.700	84.83
Nickel	0.700	6.83
Copper	.280	2.73
Zinc	1.2	11.70
Lead	.760	7.41

Fugitive emissions may be estimated by using appropriate emission factors, especially for estimating releases from leaks in pipes and vessels.

ENGINEERING CALCULATIONS

Engineering calculations based on engineering judgement is another technique of estimating air emissions. When emission-related

parameters cannot be directly measured, emissions may be estimated or deduced through engineering calculations and/or the measurement of other secondary parameters.

The secondary parameters may be the physical and chemical properties of the materials involved, design information on the equipment for which the estimate is being made, or information from similar processes. Engineering calculations are generally used to obtain information required for one of the other emission estimation techniques.

Information acquired from the equipment design such as capacities, operating temperatures and pressures can be used to estimate gaseous flow rates. Engineering principles including physical and chemical properties can be used to estimate gaseous concentrations of a particular substance.

EMISSION CONTROL DEVICE EFFICIENCIES

An emission control device may greatly reduce air pollutants entering the device. Any one of the following possibilities, or combinations of, exist when an air pollutant enters a control device. The pollutant may be transferred from the air stream to another medium, be modified to a less toxic state, destroyed through combustion and/or dissociation, or it may pass through untreated. When a pollutant is transferred into another medium, the medium is a potential source of emissions. If the medium has any emissions while located anywhere on the facility site, the emissions must be accounted for.

Emission estimates must take into account the effect of the control device(s) used. Usually the efficiency of the control device must be known.

Efficiency is expressed as a percentage:

$$\text{Efficiency} = \frac{X_i - X_o}{X_i} \times 100$$

Where:

X_i is the mass of 'Pollutant X' flowing into the control device per period of time.

X_o is the mass of 'Pollutant X' flowing out of the control device per period of time.

A measurement or test, a mass balance calculation, or a combination of the two is the preferred basis for estimating efficiency. If these data are not available, engineering calculations, data on the operating parameters of the control device, or vendor data that reflects actual operating conditions may be used to estimate the device's efficiency. The data used should reflect the efficiency achieved during typical day-to-day operations, not the theoretical optimum efficiency. The control efficiency used in estimating emissions of each listed substance must be justified and the justification must be cited.

Appendix A is a list of emission factors that may be used to estimate emissions and control efficiencies of equipment (U.S. EPA, 1985). These emission factors are to be used only in the absence of specific information or data regarding a process or control device for which an emission estimate is being made. There are certain limitations in using emission factors that should be taken into account; these factors depend on many variables including, feed material, furnace type, melting/smelting process and control equipment. Hence the estimate might not accurately represent emissions at any particular facility. In this case a source test may be more appropriate. Appendix B contains species profiles of particulate matter (U.S. EPA, 1988b).

APPENDIX A

Table 1 Secondary Aluminum Smelters
Table 2 Gray Iron Foundry
Table 3 Steel Foundries
Table 4 Steel Foundries (Control Efficiencies)
Table 5 Secondary Copper Smelting and Alloying (Brass & Bronze Foundry)
Table 6 Copper Smelting and Alloying
Table 7 Secondary Lead Smelting
Table 8 Secondary Lead Smelting (Control Efficiencies)

The listed emission factors & control efficiencies are for total particulate matter. To report individual listed substances an appropriate species profile must be applied. (Source of information: U.S. EPA, 1985)

TABLE 1

SECONDARY ALUMINUM SMELTERS

Total Particulate Matter Emissions

Operation	Uncontrolled		Baghouse		ESP	
	kg/mg	lb/ton	kg/mg	lb/ton	kg/mg	lb/ton
Sweating Furnace	7.25	14.5	1.65	3.3	---	---
Smelting Furnace						
-Crucible	.95	1.9	---	---	---	---
-Reverberatory	2.15	4.3	.65	1.3	.65	1.3
Chlorine Demagging	500	1000	25	50	---	---

TABLE 2

GRAY IRON FOUNDRY

Total Particulate Matter (PM) Emissions

	Control Device	kg/mg	lb/ton
Cupola Furnace:	Uncontrolled	6.91	13.8
	Scrubber	1.6	3.1
	Venturi Scrubber	1.5	3.0
	Baghouse	.3	.7
	Single Wet Cap	4.0	8.0
	Impingement Scrubber	2.5	5.0
	High Energy Scrubber	0.4	0.8

TABLE 3

STEEL FOUNDRIES

	Total PM		Nitrogen Oxides	
Melting	kg/mg	lb/ton	kg/mg	lb/ton
-Electric Arc	6.5	13	0.1	0.2
-Open Hearth	5.5	11	0.005	0.01
-Open Hearth & oxygen lanced	5	10	---	---
-Electric induction	0.05	0.1	---	---

TABLE 4

STEEL FOUNDRIES

Total Particulate Matter Control Efficiencies

Control Device	Electric Arc	Open Hearth	Open-Hearth & Lanced
ESP	95.0	96.7	96.5
Baghouse	98.5	99.9	99.0
Venturi Scrubber	96.0	97.5	96.5

NOTE: Electric induction furnaces are not usually pollution controlled.

The listed emission factors & control efficiencies are for total particulate matter. To report individual listed substances an appropriate species profile must be applied. (Source of information: U.S. EPA, 1985)

TABLE 5

SECONDARY COPPER SMELTING AND ALLOYING (BRASS & BRONZE FOUNDRY)

Furnace and charge type	Control Equipment	Total PM kg/mg	Total PM lb/ton
Cupola			
-Scrap iron	none	0.002	0.003
-Insulated copper wire	none	120	230
	esp	5	10
-Scrap copper and brass	none	35	70
	ESP	1.2	2.4
Reverberatory			
-Copper	none	2.6	5.1
	Baghouse	0.2	0.4
-Brass and bronze	none	18	36
	Baghouse	1.3	2.6
Rotary			
-Brass and bronze	none	150	300
	ESP	7	13
Crucible and pot			
-Brass and bronze	none	11	21
	ESP	0.5	1
Electric Arc			
-Copper	none	2.5	5
	Baghouse	0.5	1
-Brass and bronze	None	5.5	11
	Baghouse	3	6
Electric induction			
-Copper	none	3.5	7
	Baghouse	0.25	0.5
-Brass and bronze	None	10	20
	Baghouse	0.35	0.7

TABLE 6

COPPER SMELTING AND ALLOYING

Furnace and charge type	Lead* kg/mg	Lead* lb/ton
Reverberatory Furnace		
-High lead alloy (58% lead)	25	50
-Red/yellow brass (15% lead)	6.6	13.2
-Other alloys (7% lead)	2.5	5.0

*NOTE: Factors are based on unit weight produced.

The listed emission factors & control efficiencies are for total particulate matter. To report individual listed substances an appropriate species profile must be applied. (Source of information: U.S. EPA, 1985)

TABLE 7

SECONDARY LEAD SMELTING

	Total PM		Lead	
	kg/mg	lb/ton	kg/mg	lb/ton
Reverberatory				
-Smelting uncontrolled	162	323	32	65
-Smelting controlled	0.50	1.01	---	---
Blast				
-Smelting uncontrolled	153	307	52	104
-Smelting controlled	1.12	2.24	0.15	0.29
Kettle				
-Refining uncontrolled	.02	.03	0.006	.01
-Refining controlled	Neg	Neg	Neg	Neg
Casting				
-Uncontrolled	.02	.04	.007	.01
-controlled	Neg	Neg	Neg	Neg

TABLE 8

SECONDARY LEAD SMELTING

Total Particulate Matter Control Efficiencies

Control Equipment	Furnace Type	Control Efficiency %
Fabric Filter	Blast	98.4
	Reverberatory	99.2
Dry cyclone plus Fabric Filter	Blast	99.0
Wet cyclone plus Fabric Filter	Reverberatory	99.7
Settling chamber plus dry cyclone plus fabric filter	Reverberatory	99.8
Venturi scrubber plus demister	Blast	99.3

(Source of information: U.S. EPA, 1988b)

APPENDIX B

Table 1 Cast Iron-Cupola Furnace
Table 2 Steel-Electric Arc Furnace

TABLE 1 CAST IRON Foundry-CUPOLA Furnace

Substance			%*
13	Al	Aluminum	1.100
14	Si	Silicon	24.000
16	S	Sulphur	2.300
17	Cl	Chlorine	0.890
19	K	Potassium	3.000
20	Ca	Calcium	1.000
22	Ti	Titanium	0.060
23	V	Vanadium	0.009
24	Cr	Chromium	0.052
25	Mn	Manganese	4.500
26	Fe	Iron	15.00
27	Co	Cobalt	0.004
28	Ni	Nickel	0.035
29	Cu	Copper	0.260
30	Zn	Zinc	0.830
33	As	Arsenic	0.013
34	Se	Selenium	0.002
35	Br	Bromine	0.009
37	Rb	Rubidium	0.022
51	Sb	Antimony	0.370
82	Pb	Lead	0.230

TABLE 2 STEEL FOUNDRY-ELECTRIC ARC FURNACE

Substance			%*
11	Na	Sodium	1.260
12	Mg	Magnesium	6.500
13	Al	Aluminum	0.650
14	Si	Silicon	5.000
16	S	Sulphur	1.960
17	Cl	Chlorine	1.850
19	K	Potassium	0.920
20	Ca	Calcium	6.200
22	Ti	Titanium	0.200
23	V	Vanadium	0.060
24	Cr	Chromium	2.100
25	Mn	Manganese	8.700
26	Fe	Iron	32.000
28	Ni	Nickel	0.700
29	Cu	Copper	0.280
30	Zn	Zinc	1.200
82	Pb	Lead	0.760

*NOTE: Expressed as a percentage of total PM by weight.

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EMISSION ESTIMATION TECHNIQUE: STORAGE TANKS

STORAGE TANK
EMISSION ESTIMATION TECHNIQUE (EET)

I. INTRODUCTION

This document is an Emission Estimation Technique (EET) developed by the ARB staff in accordance with the Emission Inventory Criteria and Guidelines Regulation (the "Regulation") for the administration of AB 2588, the Air Toxics "Hot Spots" Information and Assessment Act of 1987 (the "Act"). Specifically, facility operators can use this EET to estimate emissions of listed substances from floating roof, fixed roofs, variable vapor space, and bulk loading storage tanks. The "Oil and Gas EET," also included in the Technical Guidance Document, provides more specific equations for estimating storage tank emissions in the petroleum industry. Facility operators in the petroleum industry should use the "Oil and Gas EET" to estimate their emissions.

The equations for calculating storage tank emissions are complex and lengthy. The ARB staff has provided both the complete equations for estimating tank emissions and alternate equations which are based on assumptions about the variables in the equations. The alternate equations provide much of the data that facility operators need to make the calculations. However, operators should be aware that these alternative values represent the upper range of possible values and may result in an overestimation of their emissions. Operators will need to work with their respective districts to determine the most appropriate approach for their facility.

II. HOW TO LOCATE INFORMATION IN THIS DOCUMENT

Section II of this document presents a series of tables to assist facility operators in locating information in this EET. Table 1 lists the detailed and the alternate equation(s) by tank type along with the page in this document where the equation is found. Table 2 lists the steps a facility operator needs to take to estimate storage tank emissions if the detailed equations are used. If the alternate equations are used, the operators may not need to use all of these steps. Table 3 presents additional variables and parameters facility operators may need to use to calculate the equations. (Facility operators will find these variables and parameters in alphabetical order in Section IV of this EET.)

TABLE 1: GUIDE TO LOCATING TANK TYPE AND EQUATION(S) IN SECTION III OF THIS EET

Tank Type*	Equation(s) Type	Equation Number
A. Floating Roof Tank		
Total Emissions		(1)
Standing Loss	Detailed	(2)
	Alternate	(3)
Working Loss	Detailed	(4)
	Alternate	(5)
B. Fixed Roof Tank		
Total Emissions		(6)
Breathing Loss	Detailed	(7)
	Alternate	(8)
Working Loss	Detailed	(9)
	Alternate	(10)
Horizontal Tanks	Adapt Fixed Roof Equations see page	
C. Variable Vapor Space Tank		
Total Emissions		
Vapor Loss	Detailed	(11)
	Alternate	(12)
D. Bulk Loading	Detailed	(13)
	Alternate	(14)

*Pressure tanks are not discussed in this EET.

TABLE 2: STEPS TO ESTIMATING EMISSIONS FROM STORAGE TANKS

1. Determine tank type
2. Determine estimating methodology
3. Select equations to be used
4. Identify parameters to be calculated or determined from tables
5. Calculate mole fractions in the liquid
6. Calculate partial pressures and total vapor pressure of the liquid
7. Calculate mole fractions in the vapor
8. Calculate molecular weight of the vapor
9. Calculate weight fractions of the vapor
10. Calculate total VOC emitted from the tank
11. Calculate amount of each toxic substance emitted from the tank

TABLE 3: ADDITIONAL PARAMETERS

	Variable or Parameter	Equation in EET
1.	Control factor (CONTROL)	(15)
2.	Diameter adjustment for small tanks (C)	(16)
3.	Mole fraction in liquid (X_i)	(17)
4.	Mole fraction in vapor (Y_i)	(18)
5.	Molecular weight in vapor (M_V)	(19)
6.	Paint factor (F_P)	(See page 24)
7.	Temperature (T)	(Table A-4, App. F)
8.	True vapor pressure (P)	(20) through (25)
9.	Turnover Factor (K_N)	(26)
10.	Vapor pressure function (P^*)	(27)
11.	Vapor space height (H)	(28)
12.	Weight fraction in vapor $(Wt)_i$	(29) & (30)
13.	Wind Speed (V)	(Table A-6, App. F)

III. METHODS FOR ESTIMATING EMISSIONS FROM STORAGE TANKS

The emission estimation methods used in this EET for storage tanks were derived from the EPA's Compilation of Air Pollutant Emission Factors: Volume 1, (EPA AP-42). These equations estimate **total** VOC emissions from storage tanks, but can be modified to estimate chemical-specific emissions directly. To estimate emissions of AB 2588 listed substances from storage tanks using these equations, the facility operator needs to multiply the total amount (in pounds) of VOC emitted by the weight fraction of that substance in the vapor. The weight fractions are related to mole fractions in the vapor phase. Weight fractions calculated are valid no matter how many moles actually are present.

A. Estimation of Emissions from Floating Roof Tanks

The major source of emissions for floating roof tanks come from standing storage losses and working losses. The total loss from external and internal floating roof tanks can be estimated from the following equations:

$$L_T = L_S + L_W \qquad (1)$$

Where:

L_T = Total Loss (lbs/yr)

L_S = Standing storage loss (lbs/yr)

L_W = Working loss (lbs/yr)

1. Standing Storage Loss From Floating Roof Tanks

To determine the standing storage loss, L_S, facility operators may use equation (2) or the alternate equation (3).

$$L_S = K_S V^N P^* D M_V K_C E_F (Wt)_i \qquad (2)$$

Where:

L_S = Total loss (lbs/yr)

K_S = Seal factor (lb-mole) ÷ [ft (mile/hr) yr] ^{N}

V = Average wind speed at tank site (mile/hr) (See Table A-6, Appendix F).

N = Seal related wind speed exponent (dimensionless). (See Table 4.3-4, Appendix C).

P^* = Vapor pressure function, dimensionless (See Equation 26 or figure 4.3-9, Appendix F).

D = Tank diameter (feet)

M_V = Average molecular weight (lb/lb-mole). (Use Table 4.3-2. Appendix F or Equation (19)).

K_C = Product factor, dimensionless

E_F = Secondary seal factor

$(Wt)_i$ = Weight fraction of listed substance i (See Equation (29)).

Alternate Equation for Standing Storage Loss

$$L_S = 0.008\ X_i\ P_i^2\ (Mw_i)\ D \qquad (3)$$

Equation (3) is based on Equation (2) and the following assumptions:

K_S = 0.7 for all seal systems

V = 10.5 mi/hr (or use Table 6).

N = Exponent 0.4 for all seal systems

M_V = 60 lb/lb-mole

K_C = 1.0

E_F = 1.0

P^* = P_i/P_{total} (See Equation (27)).

P_{total} = 14.71 (psia)

Wt_i = $0.001\ X_i\ P_i\ (Mw)_i$ (See Equation (30)).

2. Working Loss from Floating Roof Tanks

The working loss from external floating roof and internal floating roof tanks can be estimated using Equation (4) **OR** the alternate equation (5).

$$L_W = (0.943) \frac{QCW_L}{D} \times \left[1 + \frac{N_c F}{D}\right] (Wt)_i \qquad (4)$$

Where:

L_W = Working loss (lb/yr)

0.943 is a constant which has the dimensions of (1000 ft^3 x gal/bbl^2)

Q = Throughput (bbl/year) (tank capacity [bbl] times annual turnover rate)

C = Shell clingage factor (bbl/1,000 ft^2), (See Table 4.3-5, Appendix F).

W_L = Average organic liquid density (lb/gal) (See Table 4.3-2, Appendix F).

N_c = Number of columns, dimensionless (See Table 4.3-6, Appendix F).

D = Tank diameter (ft)

F = Effective column diameter (ft) [column perimeter (ft)/Π]

$(Wt)_i$ = Weight fraction of listed substance (See Equation (29))

Alternate Equation for Working Loss

$$L_W = \frac{0.0100343\ Q\ X_i\ P_i (Mw)_i\ (1 + N_c)}{D} \qquad (5)$$

Equation (5) is derived from Equation (4) based on the following assumptions:

Where:

C = 1.0

W_L = 8.3 lbs/gal

F = Tank diameter, D in feet, can be used for the alternate equation

$(Wt)_i$ = 0.001 $X_i P_i (Mw)_i$ (See Equation (30))

B. Estimation of Emissions from Fixed Roof Tanks

The two major sources of emissions from fixed roof tanks are breathing losses and working losses. The term breathing loss refers to those emissions that result without any significant change in the liquid level

within the tank. Breathing losses are caused by changes in the ambient temperature or pressure, which cause the vapor to expand or contract, resulting in the release of emissions. Working losses, on the other hand, occur when the tank is filled or emptied.

The total loss from a fixed roof tank is the sum of breathing losses plus working losses multiplied by the operational percentage vapor recovery factor for the system used.

$$L_T = L_B + L_W \qquad (6)$$

Where:

L_T = Total loss

L_B = Breathing loss

L_W = Working loss

If the tank is vented to a vapor recovery system, the operator multiplies Equation (7) by 0.05 (which assumes 95 percent control). If vented to a thermal oxidizer, the operator multiplies Equation (7) by 0.01 (assumes 99% control).

1. <u>Calculating Breathing Loss from a Fixed Roof Tank</u>

$$L_B = 0.0226 \times M_V \left(\frac{P}{P_A - P}\right)^{0.68} \times D^{1.73} \times H^{0.51} \times \Delta T^{0.50} \times F_P C K_C \, (Wt)_i \qquad (7)$$

Where:

L_B = Breathing loss (lbs/yr)

M_V = Molecular weight of vapor in storage tank, lb/lb-mole (See Equation (19))

P_A = Average atmospheric pressure at tank location, psia

P = True vapor pressure at bulk liquid conditions, psia (See Equations (21) through (26))

D = Tank diameter, ft

H = Average vapor space height, including roof volume correction, ft (See Equation (28))

ΔT = Average ambient diurnal temperature change in degrees F .

F_P = Paint factor, dimensionless (See Table C-1, Appendix C)

C = Adjustment factor for small diameter tanks, dimensionless (See Equation (16))

K_C = Product factor, dimensionless

$(Wt)_i$ = Weight fraction of substance i (See Equation (29))

Alternate Equation for Breathing Loss

$$L_B = 0.27\left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} (H)^{.51} (X_i) P_i (Mw)_i \qquad (8)$$

Equation (8) can be derived from Equation (7) with the following assumptions:

Where:

M_V = 60 lb/lb-mole

P_A = 14.7 psia

H = 0.5 (h) (h = height of the tank).

ΔT = 25 ^oF

F_p = 1.6

C = 1

K_C = 1

$(Wt)_i$ = $0.001\ X_i P_i (Mw)_i$ (See Equation (29)).

2. Calculating Working Losses from a Fixed Roof Tank

Working losses from a fixed roof tank can be estimated using the following equation:

$$L_W = 2.40 \times 10^{-5}\ M_V\ P\ Q\ K_N\ K_C\ (Wt)_i \qquad (9)$$

Where:

L_W = Fixed roof working loss (lbs/year)

M_V = Molecular weight of vapor in storage tank (lb/lb-mole)

P = True vapor pressure at bulk liquid temperature (psia) (See Equation (20)).

Q = Discharge in (gals/yr) or bbls/yr (42 U.S. gals = bbl)

$$\frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, V (gal)}}$$

K_N = Turnover factor, dimensionless (See Figure 4.3-7, Appendix F or Equation (26)).

K_C = product factor, dimensionless

$(Wt)_i$ = Weight fraction of substance i. (See Equation (29)).

Equation (9) can be modified to reflect actual conditions as they exist at facilities in California. For example, control measures are commonplace in California and should be reflected in the working loss equation. Thus, the resulting working loss equation can be expressed as follows:

$$L_W = 2.40 \times 10^{-5} M_V P Q K_N K_C (CONTROL) (Wt)_i \qquad (9a)$$

<u>Alternative Equation for Working Loss</u>

$$L_W = 1.44 \times 10^{-6} P_i (Mw)_i Q X_i (Control) P \qquad (10)$$

Equation (10) can be obtained from Equation (9) based on the following assumptions:

M_V = 60 lb/lb-mole

K_C = 1

$(Wt)_i$ = $0.001 X_i P_i (Mw)_i$ (See Equation (29)).

K_N = 1

3. **Calculating Emissions for Horizontal Tanks**

Horizontal tanks are typically small, with their volume rarely exceeding 30,000 gallons. To calculate emissions from horizontal tanks, the facility operator adapts the equations and parameters for fixed roof tanks, which were developed for vertical fixed roof tanks.

Assumptions:

(a) The tank is one-half filled, and the surface area of the liquid in the tank is approximately equal to the length of the tank times the diameter of the tank.

(b) This area represents a circle (i.e., that the liquid is in an upright cylinder). The effective diameter of the tank is

$(1.13) \times (\text{length} \times \text{width})^{0.5}$.

C. **Estimation of Emissions from Variable Vapor Space Tanks**

Variable vapor space filling losses occur during filling operations. Since the variable vapor space tank has an expandable vapor storage

capacity, this loss is not as large as the filling loss associated with fixed roof tanks. Loss of vapor occurs only when the tank's vapor storage capacity is exceeded. Variable vapor space system filling losses can be estimated from:

$$L_V = (2.40 \times 10^{-5})\, M_V P \left[(Q) - \frac{(0.25\, V_1 N_2)}{V}\right] \qquad (11)$$

Where:

L_V = Variable vapor space filling loss (lb/10^3 gal throughput)

M_V = Molecular weight of vapor in storage tank (lb/lb-mole)

P = True vapor pressure at bulk liquid conditions (psia) (See Equations (20 through 25)).

Q = Volume of liquid pumped into system, throughput (bbl)

V_1 = Volume expansion capacity of system (bbl)

V = Tank volume

N_2 = Number of transfers into system (dimensionless)

Alternate Equation for Variable Space Tanks

$$L_V = 0.0014\, P\, (Q - 0.125\, N_2) \qquad (12)$$

Equation (12) can be derived from Equation (11) with the following assumptions:

M_V = 60 lb/lb-mole

V_1/V = 0.5

Note: Although not developed for use with heavier petroleum liquids such as kerosenes and fuel oils, equation (12) is recommended for use with heavier petroleum liquids in the absence of better data.

D. Estimation of Emissions from Bulk Loading Operations

Emissions from liquid bulk loading operations can be estimated using the following equation:

$$L_L = 523.32 \frac{SPM}{T} (1.00 - \frac{eff.}{100}) (Wt)_i \quad (13)$$

Where:

L_L = Loading loss (lb HC/1000 bbl. loaded)

S = Saturation factor (EPA AP-42, Table 4.4-1 in Appendix F)

P = Vapor pressure, psia

M = Molecular weight of condensed vapors (lb/lb-mole)

T = Loading temperature, ^oR (^oF + 460)

eff. = Typical control efficiency (%)
99% - vapor recovery to fuel gas system
92% - vapor recovery to recovery unit
0 - uncontrolled

$(Wt)_i$ = Weight fraction of the listed substance (See Equation (29))

Alternate Equation for Bulk Storage Tanks

$$L_L = 0.056 P X_i P_i (Mw)_i (1.00 - \frac{eff.}{100}) \quad (14)$$

Equation (14) can be derived from Equation (13) with the following assumptions:

S = 1.0

M_V = 60 lb/lb-mole

T_L = 530

$(Wt)_i = 0.001 X_i P_i (Mw)_i$ (See Equation (30).)

IV. EQUATIONS AND VALUES FOR CALCULATING ADDITIONAL PARAMETERS FOR EMISSION ESTIMATION

Section IV provides facility operators with the parameters and equations to calculate the chemical and physical properties of listed substances which are needed to complete the emission estimate from storage tanks.

Control Efficiency

Emission estimates must take into account control device(s) used to reduce toxic pollutants. Usually, the efficiency of the control device must be known. The data used should reflect the efficiency achieved during

typical day-to-day operations, and not the theoretical optimum efficiency. The control efficiency used in estimating emissions of each listed substance must be justified by the facility operator and the justification must be cited in the emission inventory plan. For additional information on control efficiencies, facility operators should consult Chapter IV, "Control Efficiencies," of the Technical Guidance Document for AB 2588.

Efficiency is expressed as a percentage:

$$\text{Efficiency} = \frac{M_i - M_o}{M_i} \times 100 \qquad (15)$$

Where:

M_i = Mass of 'Toxic Pollutant' flowing into the control device per period of time

M_o = Mass of 'Toxic Pollutant' flowing out of the control device per period of time.

A valid efficiency estimate can be based on source tests or other measurement, a mass balance calculation, or a combination of the two. The data should reflect efficiency achieved during typical operations, and not the theoretical optimum efficiency. Actual measurement is the best way to determine efficiency.

Diameter Adjustment for Small Tanks

Tank emissions also depend upon the tank diameter. Small diameter tanks emit proportionally less pollutants than larger diameter tanks. The breakpoint between small and large diameter tanks is set at 30 feet. At values greater than or equal to 30 feet, the emissions are independent of tank diameter and the adjustment factor is 1.0. If the tank diameter is less than 30 feet, the following equation is used to calculate the adjustment factor:

$$C = (0.0771) \times (\text{Diameter}) - (0.0013) \times (\text{Diameter})^2 - 0.1334 \qquad (16)$$

Mole fraction in Liquid

The mole fractions of toxic substances in a liquid must be calculated in order to estimate the vapor pressure of the liquid using Raoult's Law. The partial pressure, X_i, of each substance equals the liquid mole fraction, X_i, times the vapor pressure of the pure substance, P_i.

$$X_i = \frac{P_i}{P_T} \qquad (17)$$

The liquid phase mole fractions sum is 1.00.

Mole Fraction in Vapor

The mole fraction of a substance in a vapor phase (Y_i) is based on the partial pressure the substance exerts:

Where:

$$Y_i = P_{partial} / P_{total} \quad (18)$$

$$P_{total} = P_1 X_1 + P_2 X_2 + \ldots P_n X_n$$

$P_{partial}$ = Pure vapor pressure x mole fraction of liquid (Rauolt's Law)

P_i = Vapor pressure of pure component, i

X_i = Mole fraction of component, i

n = Total components in vapor

Molecular Weight in Vapor

The molecular weight of the vapor (M_v) is dependent upon the mole fractions of the substance in the vapor:

$$M_v = \Sigma (Mw)_i (Y)_i \quad (19)$$

The molecular weight of the vapor can be calculated using Equation (3) or by looking up the molecular weight on Table 4.3-2, Appendix F.

Paint Factor

Emissions from tanks also depend upon the tank color, the condition of the paint itself, and whether or not insulation is present. The paint factor takes into account the effects these three variables have on overall

breathing loss emissions. Values for the paint factor for different conditions are tabulated in Table 4.3-1.

True Vapor Pressure

True vapor pressure (P) is the equilibrium partial pressure exerted by a volatile liquid, and is perhaps the most difficult term in the breathing loss equation to calculate. A monograph (included in Appendix F Figure 4.3-6) relates P to both the Reid Vapor Pressure (RVP) and the storage temperature (T_s). RVP is the absolute vapor pressure of volatile crude oil and nonviscuous petroleum liquids. Numerically, the relationship between P, RVP, and temperature is expressed in the following equations:

$$P = (RVP)\, e^{[C_0(IRTEMP - ITEMP)]} \qquad (20)$$

Where:

C_0 = constant dependent upon the value of RVP

$$ITEMP = (1/560\ ^{o}R) \qquad (21)$$

$$IRTEMP = [1/(T_S + 460^{o}\ R)] \qquad (22)$$

T_S = temperature of the stored fluid in Fahrenheit

The value of the constant term C_0 depends upon the given value of RVP. Values of C_0 for different RVP numbers are tabulated in Table C-3, Appendix C) . However an error was discovered in the API monograph calculated values of P. The RVP is not equal to P at 100°F, given the general definition of RVP. Using linear regression techniques, correction factors (C_F) were developed and should be added to the calculated values of TVP in order to obtain reasonable P numbers. The relationship between the three values is given as follows:

$$\text{Corrected P} = \text{Calculated P} + C_F \qquad (23)$$

The correction factor was found to be dependent upon RVP according to the following equations:

If RVP < 3,

$$C_F = (0.04) \times (RVP) + 0.1 \quad (24)$$

If RVP > 3,

$$C_F = e^{[(2.3452061 \log_{10}(RVP)) - 4.132622]} \quad (25)$$

Turnover Pressure Function

$$K_N = \frac{180 + N}{6N} \quad \text{if N is greater than 36} \quad (26)$$

$$K_N = 1 \quad \text{if N is equal to or less that 36}$$

N = number of turnovers

Vapor Pressure Function

$$P^* = \frac{P / P_a}{[1 + (1-P/P_a)^{0.5}]^2} \quad (27)$$

Where:

P = True vapor pressure at average actual organic liquid storage temperature (psia)

P_a = Average atmospheric pressure at tank location (psia)

Vapor Space Height (H) (Average)

The average vapor space height refers to the typical height of the vapor in the tank, and can be calculated using the following equation:

$$H = 0.5 \text{ (height of tank)} \tag{28}$$

Weight Fraction of the Vapor

The weight fraction (Wt_i) of each component in a fluid mixture is the unit weight of that component divided by the total unit weight of the mixture.

$$(Wt)_i = \frac{Y_i (Mw)_i}{\Sigma\ (Mw)_i (Y\ )_i} \tag{29}$$

Where Y_i = Vapor-phase mole fraction of specific substance (lb/lb-mole)

For alternate equations, use the following:

$$Y_i = \frac{X_i\ P_i}{P_T}$$

$$\text{then } (Wt)_i = X_i\ \frac{P_i}{P_T}\ \frac{(Mw)_i}{(Mw)_{Total}}$$

assume:

$$P_T = 14.7$$

$(Mw)_{Total} =$ 60 lb/lb-mole

then $(Wt)_i = 0.001\ X_i\ P_i\ (Mw)_i$ (30)

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APPENDIX B
ANTOINE'S EQUATION CONSTANTS
AND
COX CHART FOR ESTIMATING VAPOR PRESSURE

APPENDIX B-ANTOINE'S EQUATION CONSTANTS

Antoine equation correlates vapor pressure-temperature data extremely well. Clausius-Clapeyron equation OR Cox Charts can also estimate vapor pressure.

$$\log_{10} p^* = A - \frac{B}{T + C} \quad ; \quad p^* \text{ in mm Hg} \quad ; \quad T \text{ in } ^oC$$

Substance	Formula	Range, ^oC	A	B	C
Acetaldehyde	C_2H_4O	-45 to +70	6.81089	992.0	230
Acetic Acid	$C_2H_4O_2$	0 to +36	7.80307	1651.2	225
		+36 to +170	7.18807	1416.7	211
Acetone	C_3H_6O	—	7.02447	1161.0	224
Ammonia	NH_3	-83 to +60	7.55466	1002.711	247.885
Benzene	C_6H_6	—	6.90565	1211.033	220.790
Carbon tetrachloride	CCl_4	—	6.93390	1242.43	230.0
Chlorobenzene	C_6H_5Cl	0 to +42	7.10690	1500.0	224.0
		+42 to +230	6.94504	1413.12	216.0
Chloroform	$CHCl_3$	-30 to +150	6.90328	1163.03	227.4
Cyclohexane	C_6H_{12}	-50 to +200	6.84498	1203.526	222.863
Ethyl Acetate	$C_4H_8O_2$	-20 to +150	7.09808	1238.71	217.0
Ethyl alcohol	C_2H_5OH	—	8.04494	1554.3	222.65
Ethylbenzene	C_8H_{10}	—	6.95719	1424.255	213.206
n-Heptane	C_7H_{16}	—	6.90240	1268.115	216.900
n-Hexane	C_6H_{14}	—	6.87776	1171.530	224.366
Methyl alcohol	CH_3OH	-20 to +140	7.87863	1473.11	230.0
Methyl ethyl ketone	C_4H_8O	—	6.97421	1209.6	216
n-Pentane	C_5H_{12}	—	6.85221	1064.63	232.000
Isopentane	C_5H_{12}	—	6.78967	1020.012	233.097
Styrene	C_8H_8	—	6.92409	1420.0	206.
Toluene	C_7H_8	—	6.95334	1343.943	219.377
Water	H_2O	0 to 60	8.10765	1750.286	235.0
		60 to 150	7.96681	1668.21	228.0

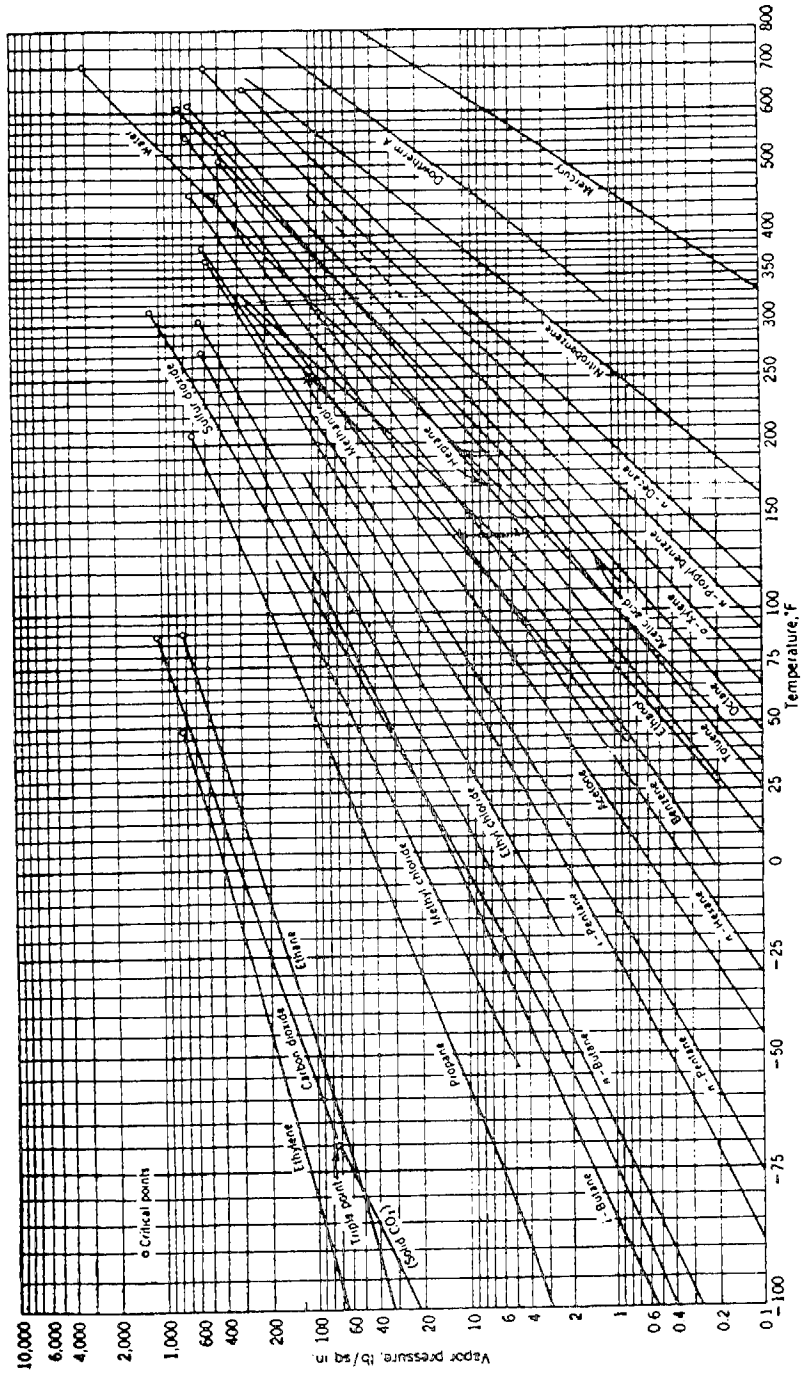


FIGURE 7.1-4. Cox chart vapor pressure plots. From A. S. Foust *et al.*, *Principles of Unit Operations*,, Wiley, New York, 1960, p. 550.

APPENDIX C
FACTORS FOR CRUDE OIL STORAGE TANK CALCULATIONS

FACTORS FOR FIXED ROOF TANK CALCULATIONS

TABLE C-1 PAINT FACTOR FOR FIXED ROOF TANKS

Tank color		Paint factors (F_p)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44
Medium gray	Medium gray	1.40	1.58[a]

[a]Estimated from the ratios of the seven preceding paint factors.

TABLE C-2. AVERAGE STORAGE TEMPERATURE (T_S) AS A FUNCTION OF TANK PAINT COLOR

Tank Color	Average Storage Temperature, T_S (^oF)
White	T_A^* + 0
Aluminum	T_A + 2.5
Gray	T_A + 3.5
Black	T_A + 5.0

*T_A is average ambient temperature in degrees farenheit.

(Compiled from: U.S. EPA, 1985, Compilation of Air Pollutant Emission Factors: Volume 1 Stationary Point and Area Sources, AP-42, 4th Edition, September).

TABLE C-3 VALUES OF C_0 FOR DIFFERENT RVP NUMBERS

RVP	C_0
0<RVP<2	-6622.5
2<RVP<3	-6439.2
RVP = 3	-6255.9
3<RVP<4	-6212.1
RVP = 4	-6169.2
4<RVP<5	-6177.9
RVP = 5	-6186.5
5<RVP<6	-6220.4
RVP = 6	-6254.3
6<RVP<7	-6182.1
RVP = 7	-6109.8
7<RVP<8	-6238.9
RVP = 8	-6367.9
8<RVP<9	-6477.5
RVP = 9	-6587.9
9<RVP<10	-6910.5
RVP = 10	-7234.0
10<RVP<15	-8178.0
RVP > 15	-9123.2

TABLE C-4 CONTROL FACTORS

TANK TYPE	CONTROL FACTOR
Open top tank (no fixed or floating roof)	1.00
Fixed roof tank with roof openings (open vents, holes), but no vapor controls	1.00
Fixed roof tank with functional p.v. valve on the roof, but no open vents and no vapor controls	0.90
Fixed roof tank with internal floating roof and p.v. valve on roof	0.05
Fixed roof tank with vapor balance type emission control system	0.10
Fixed roof tank with compression, refrigeration or combustion type vapor control or recovery system	0.02
External floating roof tank	0.05

APPENDIX F
FIGURES AND TABLES

TABLE 4.3-2. PHYSICAL PROPERTIES OF TYPICAL ORGANIC LIQUIDS[a]

Organic liquid[b]	Vapor molecular weight @ 60°F	Product density (d), lb/gal @ 60°F	Condensed vapor density (w), lb/gal @ 60°F	True vapor pressure in psia at: 40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum Liquids[c]										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel no. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil no. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Volatile Organic Liquids										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1,2-Dichloroethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methylethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
1,1,1-Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

[a]References 3-4.
[b]For a more comprehensive listing of volatile organic liquids, see Reference 3.
[c]RVP = Reid vapor pressure in psia.

TABLE 4.3-5. AVERAGE CLINGAGE FACTORS (C) (bbl/1,000 ft^2)[a]

Liquid	Shell condition		
	Light rust[b]	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

[a]Reference 5.
[b]If no specific information is available, these values can be assumed to represent the most common condition of tanks currently in use.

TABLE 4.3-6. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETER FOR INTERNAL FLOATING ROOF TANKS WITH COLUMN SUPPORTED FIXED ROOFS[a]

Tank diameter range D (ft)	Typical number of columns, N_C
$0 < D \leqq 85$	1
$85 < D \leqq 100$	6
$100 < D \leqq 120$	7
$120 < D \leqq 135$	8
$135 < D \leqq 150$	9
$150 < D \leqq 170$	16
$170 < D \leqq 190$	19
$190 < D \leqq 220$	22
$220 < D \leqq 235$	31
$235 < D \leqq 270$	37
$270 < D \leqq 275$	43
$275 < D \leqq 290$	49
$290 < D \leqq 330$	61
$330 < D \leqq 360$	71
$360 < D \leqq 400$	81

[a]Reference 1. This table was derived from a survey of users and manufacturers. The actual number of columns in a particular tank may vary greatly with age, fixed roof style, loading specifications, and manufacturing perogatives. Data in this table should not supersede information on actual tanks.

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 4.4-1 lists suggested saturation factors.

TABLE 4.4-1. SATURATION (S) FACTORS FOR CALCULATING PETROLEUM LIQUID LOADING LOSSES

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[a]	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

[a]For products other than gasoline and crude oil. Use factors from Table 4.4-2 for marine loading of gasoline. Use Equations 2 and 3 and Table 4.4-3 for marine loading of crude oil.

Emissions from controlled loading operations can be calculated by multiplying the uncontrolled emission rate calculated in Equation 1 by the control efficiency term:

$$\left(1 - \frac{\text{eff}}{100}\right).$$

Measures to reduce loading emissions include selection of alternate loading methods and application of vapor recovery equipment. The latter captures organic vapors displaced during loading operations and recovers

TABLE 4.4-2. VOLATILE ORGANIC COMPOUND EMISSION FACTORS FOR GASOLINE LOADING OPERATIONS AT MARINE TERMINALS[a]

Vessel tank condition	Previous cargo	Total organic emission factors: Ships/ocean barges[b] mg/liter transferred	Ships/ocean barges[b] lb/10^3 gal transferred	Barges[b] mg/liter transferred	Barges[b] lb/10^3 gal transferred
Uncleaned	Volatile[c]	315	2.6	465	3.9
Ballasted	Volatile	205	1.7	d	d
Cleaned	Volatile	180	1.5	e	e
Gas-freed	Volatile	85	0.7	e	e
Any condition	Nonvolatile	85	0.7	e	e
Gas-freed	Any cargo	e	e	245	2.0
Typical overall situation[f]	Any cargo	215	1.8	410	3.4

[a]References 2, 8. Factors represent nonmethane-nonethane VOC emissions because methane and ethane have been found to constitute a negligible weight fraction of the evaporative emissions from gasoline.
[b]Ocean barges (tank compartment depth about 40 feet) exhibit emission levels similar to tank ships. Shallow draft barges (compartment depth 10 to 12 feet) exhibit higher emission levels.
[c]Volatile cargoes are those with a true vapor pressure greater than 1.5 psia.
[d]Barges are not usually ballasted.
[e]Unavailable.
[f]Based on observation that 41% of tested ship compartments were uncleaned, 11% ballasted, 24% cleaned, and 24% gas-freed. For barges, 76% were uncleaned.

TABLE 4.4-3. AVERAGE ARRIVAL EMISSION FACTORS, C_A, FOR CRUDE OIL LOADING EMISSION EQUATION[a]

Ship/ocean barge tank condition	Previous cargo	Arrival emission factor, lb/10^3 gal
Uncleaned	Volatile[b]	0.86
Ballasted	Volatile	0.46
Cleaned or gas-freed	Volatile	0.33
Any condition	Nonvolatile	0.33

[a]Arrival emission factors (C_A) to be added to generated emission factors calculated in Equation 3 to produce total crude oil loading loss. These factors represent total organic compounds; nonmethane-nonethane VOC emission factors average about 15% lower.
[b]Volatile cargoes are those with a true vapor pressure greater than 1.5 psia.

TABLE 4.3-1. PAINT FACTORS FOR FIXED ROOF TANKS[a]

Tank color		Paint factors (F_P)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44[b]
Medium gray	Medium gray	1.40	1.58[b]

[a]Reference 2.
[b]Estimated from the ratios of the seven preceding paint factors.

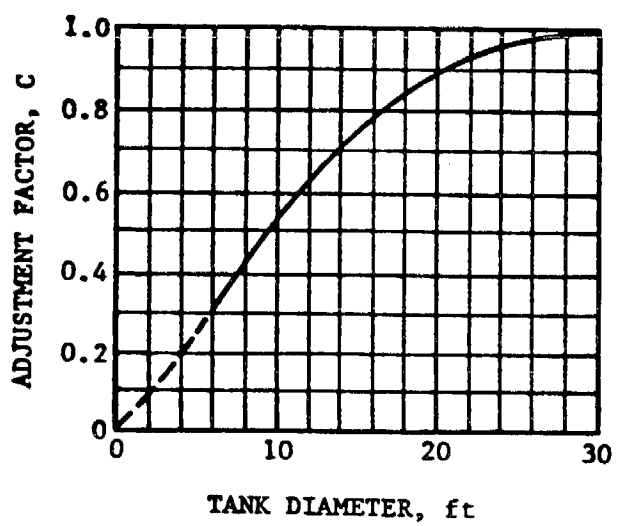


Figure 4.3-4. Adjustment factor (C) for small diameter tanks.[2]

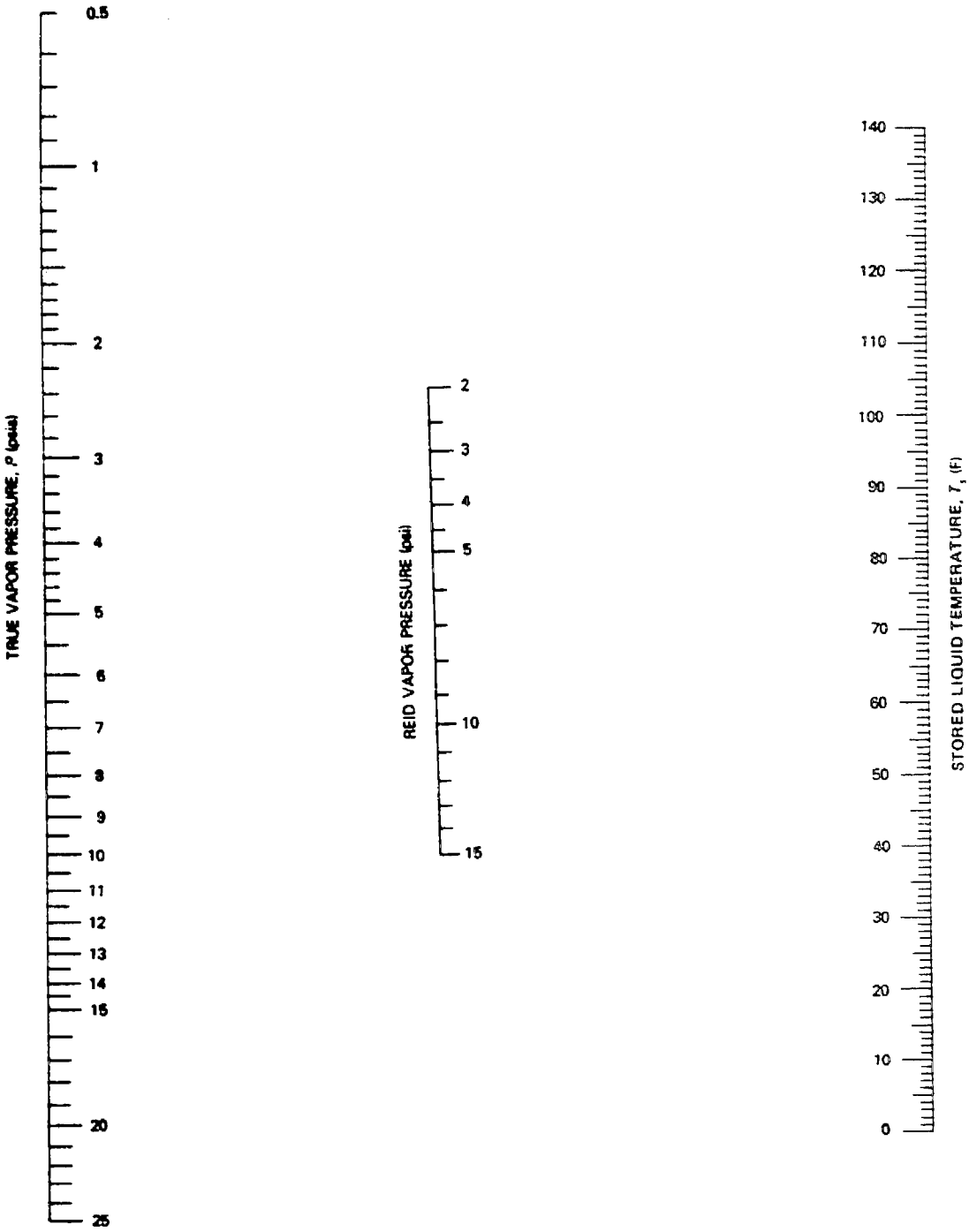
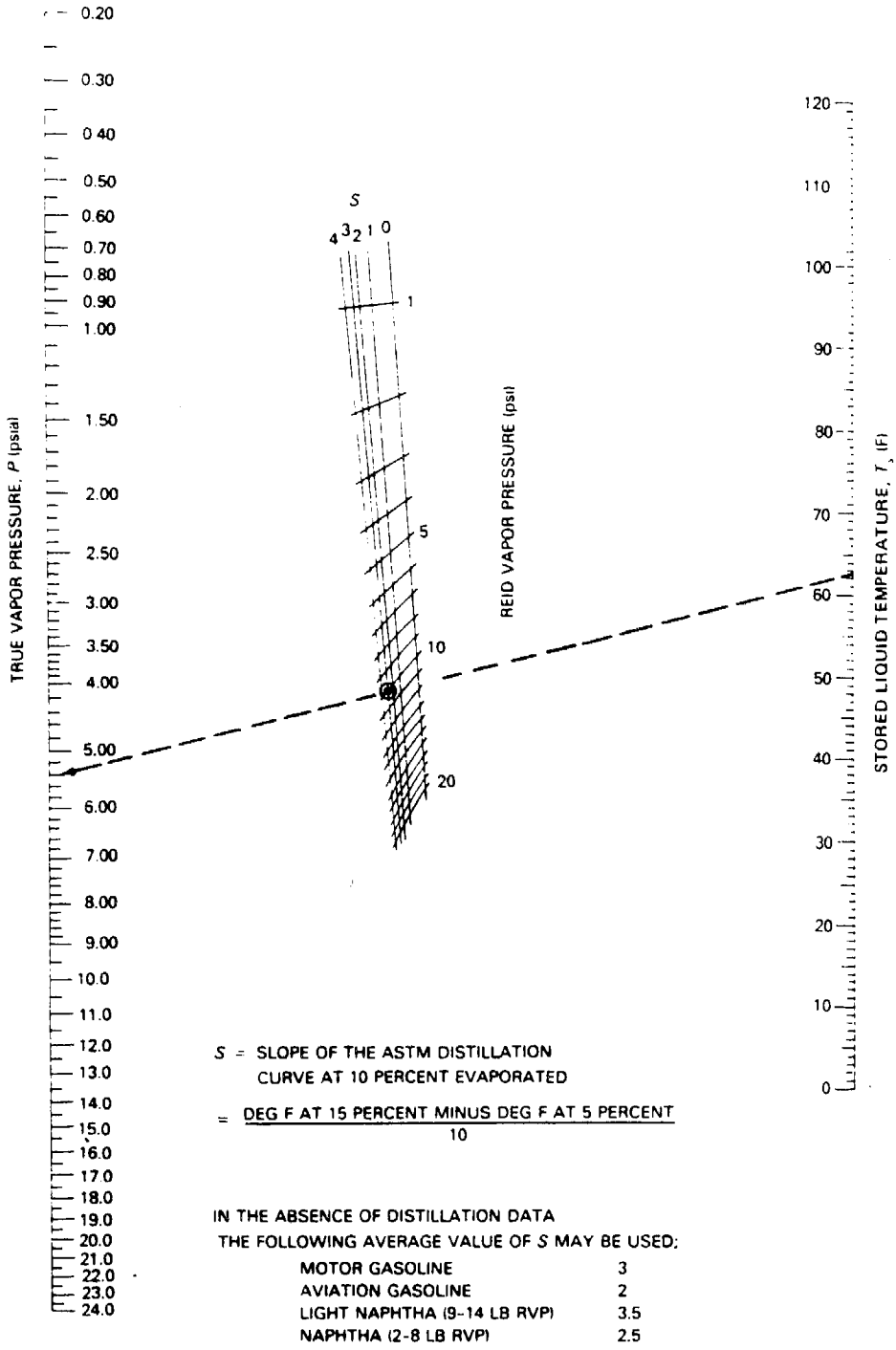
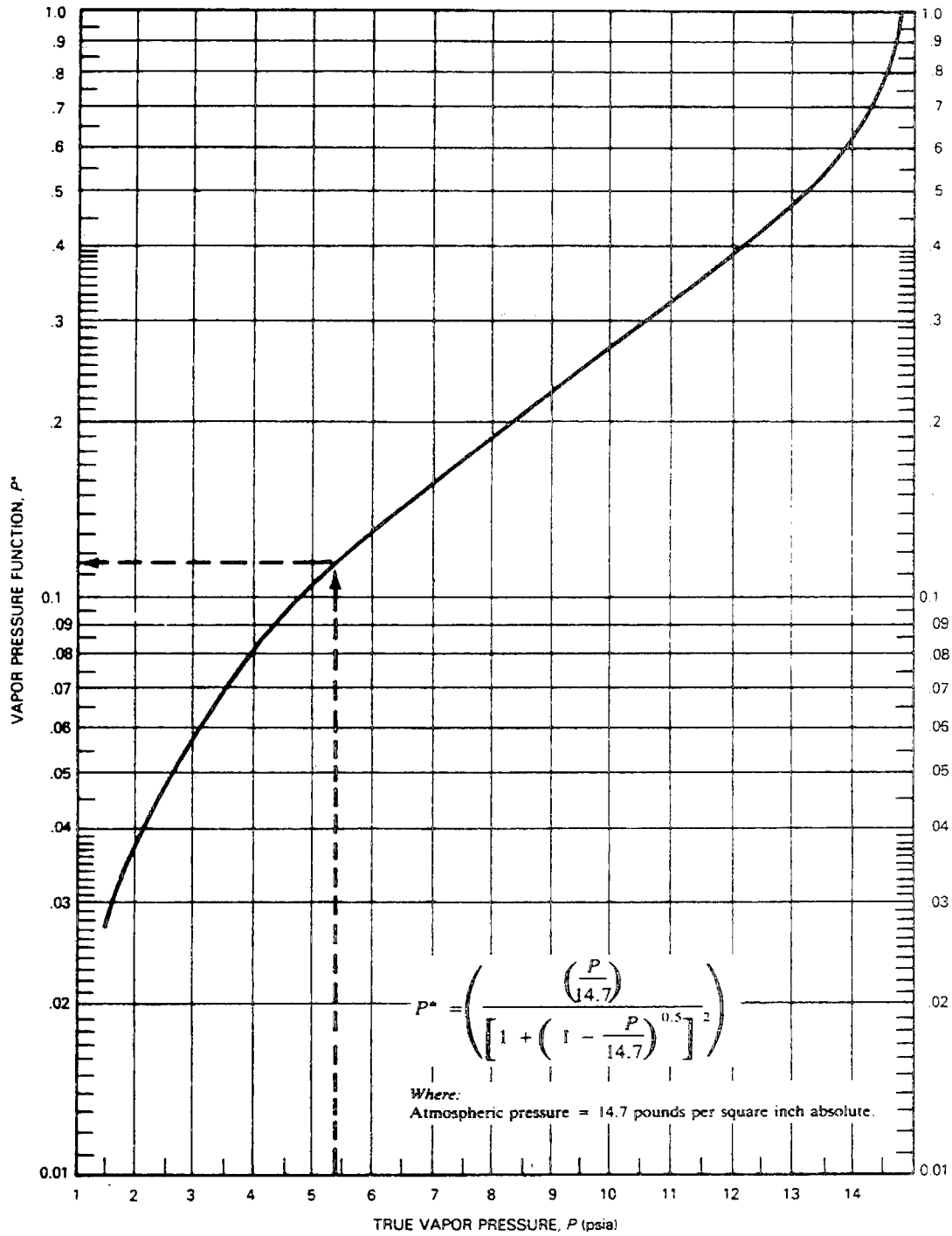


Figure 4.3-5. True vapor pressure (P) of crude oils (2-15 psi RVP).[6]



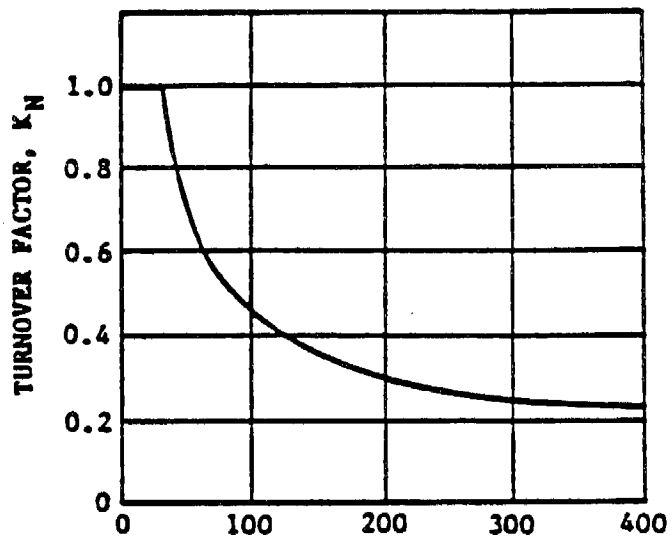
NOTE: Dashed line illustrates sample problem for RVP = 10 pounds per square inch, gasoline (S = 3), and T_s = 62.5°F
SOURCE: Nomograph drawn from the data of the National Bureau of Standards.

Figure 4.3-6. True vapor presure (P) of refined petroleum liquids like gasoline and napththas (1-20 psi RVP).[6]



NOTE: Dashed line illustrates sample problem for P = 5.4 pounds per square inch absolute.

Figure 4.3-9. Vapor pressure function (P*).[5]



$$\text{TURNOVERS PER YEAR, } N = \frac{\text{ANNUAL THROUGHPUT}}{\text{TANK CAPACITY}}$$

NOTE: FOR 36 TURNOVERS PER YEAR OR LESS, $K_N = 1.0$

FOR 36 TURNOVERS OR MORE PER YEAR,

$$K_N = \frac{180+N}{6N}$$

Figure A-2. Turnover factor (K_N) for fixed roof tanks.

TABLE A-6. AVERAGE ANNUAL WIND SPEED (v, mi/h) FOR SELECTED U.S. LOCATIONS

Birmingham, Ala.	7.3	Grand Junction, Colo.	8.1
Huntsville, Ala.	8.1	Pueblo, Colo.	8.7
Mobile, Ala.	9.0	Bridgeport, Conn.	12.0
Montgomery, Ala.	6.7	Hartford, Conn.	8.5
Anchorage, Alaska	6.8	Wilmington, Del.	9.2
Annette, Alaska	10.6	Wash., D.C.-Dulles Airport	7.5
Barrow, Alaska	11.8	Wash. D.C.-National Airport	9.3
Barter Alaska	13.2	Apalachicola, Fla.	7.9
Bethel, Alaska	12.8	Daytona Beach, Fla.	8.8
Bettles, Alaska	6.7	Fort Myers, Fla.	8.2
Big Delta, Alaska	8.2	Jacksonville, Fla.	8.2
Gold Bay, Alaska	16.9	Key West, Fla.	11.2
Fairbanks, Alaska	5.4	Miami, Fla.	9.2
Gulkana, Alaska	6.8	Orlando, Fla.	8.6
Homer, Alaska	7.2	Pensacola, Fla.	8.4
Juneau, Alaska	8.4	Tallahassee, Fla.	6.5
King Salmon, Alaska	10.7	Tampa, Fla.	8.6
Kodiak, Alaska	10.6	West Palm Beach, Fla.	9.5
Kotzebue, Alaska	13.0	Athens, Ga.	7.4
McGrath, Alaska	5.1	Atlanta, Ga.	9.1
Nome, Alaska	10.7	Auguata, Ga.	6.5
St. Paul Island, Alaska	18.3	Columbus, Ga.	6.7
Talkeetna, Alaska	4.5	Macon, Ga.	7.7
Valdez, Alaska	6.0	Savannah, Ga.	7.9
Yakutat, Alaska	7.4	Hilo, Hawaii	7.1
Flagstaff, Ariz.	7.3	Honolulu, Hawaii	11.6
Phoenix, Ariz.	6.3	Kahului, Hawaii	12.8
Tucson, Ariz.	8.2	Lihue, Hawaii	11.9
Winslow, Ariz.	8.9	Boise, Idaho	8.9
Yuma, Ariz.	7.8	Pocatello, Idaho	10.2
Fort Saith, Ark.	7.6	Cairo, Ill.	8.5
Little Rock, Ark.	8.0	Chicago, Ill.	10.3
Bakersfield, Calif.	6.4	Moline, Ill.	10.0
Blue Canyon, Calif.	7.7	Peoria, Ill.	10.1
Eureka, Calif.	6.8	Rockford, Ill.	9.9
Fresno, Calif.	6.4	Springfield, Ill.	11.3
Long Beach, Calif.	6.4	Evansville, Ind.	8.2
Los Angeles, Calif.--International Airport	7.5	Fort Wayne, Ind.	10.2
		Indianapolis, Ind.	9.6
Los Angeles, Calif.	6.2	South Bend, Ind.	10.4
Mount Shasta, Calif.	5.1		
		Des Moines, Iowa	10.9
Oakland, Calif.	8.2	Sioux City, Iowa	11.0
Red Bluff, Calif.	8.6	Waterloo, Iowa	10.7
Sacramento, Calif.	8.1	Concordia, Kans.	12.3
San Diego, Calif.	6.8	Dodge City, Kans.	13.9
San Francisco, Calif.--International Airport	10.5	Goodland, Kans.	12.6
		Topeka, Kans.	10.2
San Francisco, Calif.--City	8.7	Wichita, Kans.	12.4
Santa Maria, Calif.	7.0	Cincinnati, Ky.--Airport	9.1
Stockton, Calif.	7.5	Jackson, Ky.	7.0
Colorado Springs, Colo.	10.1		
Denver, Colo.	8.8	Lexington, Ky.	9.5
		Louisville, Ky.	8.3
		Baton Rouge, La.	7.7
		Lake Charles, La.	8.7
		New Orleans, La.	8.2

(continued)

TABLE A-4. AVERAGE ANNUAL AMBIENT TEMPERATURE (T_a, °F) FOR SELECTED U.S. LOCATIONS

Birmingham, Ala.	62.0
Huntsville, Ala.	60.6
Mobile, Ala.	67.5
Montgomery, Ala.	64.9
Anchorage, Alaska	35.3
Annette, Alaska	45.4
Barrow, Alaska	9.1
Barter Island, Alaska	9.6
Bethel, Alaska	28.4
Bettles, Alaska	21.2
Big Delta, Alaska	27.4
Cold Bay, Alaska	37.9
Fairbanks, Alaska	23.9
Gulkana, Alaska	26.5
Homer, Alaska	36.6
Juneau, Alaska	40.0
King Salmon, Alaska	32.8
Kodiak, Alaska	40.7
Kotzebue, Alaska	20.9
McGrath, Alaska	25.0
Nome, Alaska	25.5
St. Paul Island, Alaska	34.3
Talkeetna, Alaska	32.6
Unalakleet, Alaska	26.4
Valdez, Alaska	38.3
Yakutat, Alaska	38.6
Flagstaff, Ariz.	45.4
Phoenix, Ariz.	71.2
Tucson, Ariz.	68.0
Winslow, Ariz.	54.9
Yuma, Ariz.	73.8
Fort Smith, Ariz.	60.8
Little Rock, Ark.	61.9
North Little Rock, Ark.	61.7
Bakersfield, Calif.	65.5
Bishop, Calif.	56.0
Blue Canyon, Calif.	50.4
Eureka, Calif.	52.0
Fresno, Calif.	62.6
Long Beach, Calif.	63.9
Los Angeles, Calif.—International Airport	62.6
Los Angeles, Calif.	65.3
Mount Shasta, Calif.	49.5
Red Bluff, Calif.	62.9
Sacramento, Calif.	60.6
San Diego, Calif.	63.8
San Francisco, Calif.—International Airport	56.6
San Francisco, Calif.—City	56.8
Santa Barbara, Calif.	58.9
Santa Maria, Calif.	56.8
Stockton, Calif.	61.6
Alasosa, Colo.	41.2
Colorado Springs, Colo.	48.9
Denver, Colo.	50.3
Grand Junction, Colo.	52.7
Pueblo, Colo.	52.8
Bridgeport, Conn.	51.8
Hartford, Conn.	49.8
Wilmington, Del.	54.0
Wash., D.C.-Dulles Airport	53.9
Wash. D.C.-National Airport	57.5
Apalachicola, Fla.	68.2
Daytona Beach, Fla	70.3
Fort Myers, Fla.	73.9
Gainsville, Fla.	68.6
Jacksonville, Fla.	68.0
Key West, Fla.	77.7
Miami, Fla.	75.7
Orlando, Fla.	72.4
Pensacola, Fla.	68.0
Tallahassee, Fla.	67.2
Tampa, Fla.	72.0
Vero Beach, Fla.	72.4
West Palm Beach, Fla.	74.6
Athens, Ga.	61.4
Atlanta, Ga.	61.2
Augusta, Ga.	63.2
Columbus, Ga.	64.3
Macon, Ga.	64.7
Savannah, Ga.	65.9
Hilo, Hawaii	73.6
Honolulu, Hawaii	77.0
Kahului, Hawaii	75.5
Lihua, Hawaii	75.2
Boise, Idaho	51.1
Lewiston, Idaho	52.1
Pocatello, Idaho	46.6
Cairo, Ill.	59.1
O'Hare Airport, Chicago, Ill.	49.2
Moline, Ill.	49.5
Peoria, Ill.	50.4
Rockford, Ill.	47.8
Springfield, Ill.	52.6
Evanville, Ind.	55.7
Fort Wayne, Ind.	49.7
Indianapolis, Ind.	52.1
South Bend, Ind.	49.4
Des Moines, Iowa	49.7
Dubuque, Iowa	46.3
Sioux City, Iowa	48.4
Waterloo, Iowa	46.1
Concordia, Kans.	53.2
Dodge City, Kans.	55.1
Goodland, Kans.	50.7
Topeka, Kans.	54.1

(continued)

(Source: U. S. EPA, 1988, Estimating Air Toxics Emissions from Organic Liquid Storage Tanks. EPA-450/4-88-004 October)