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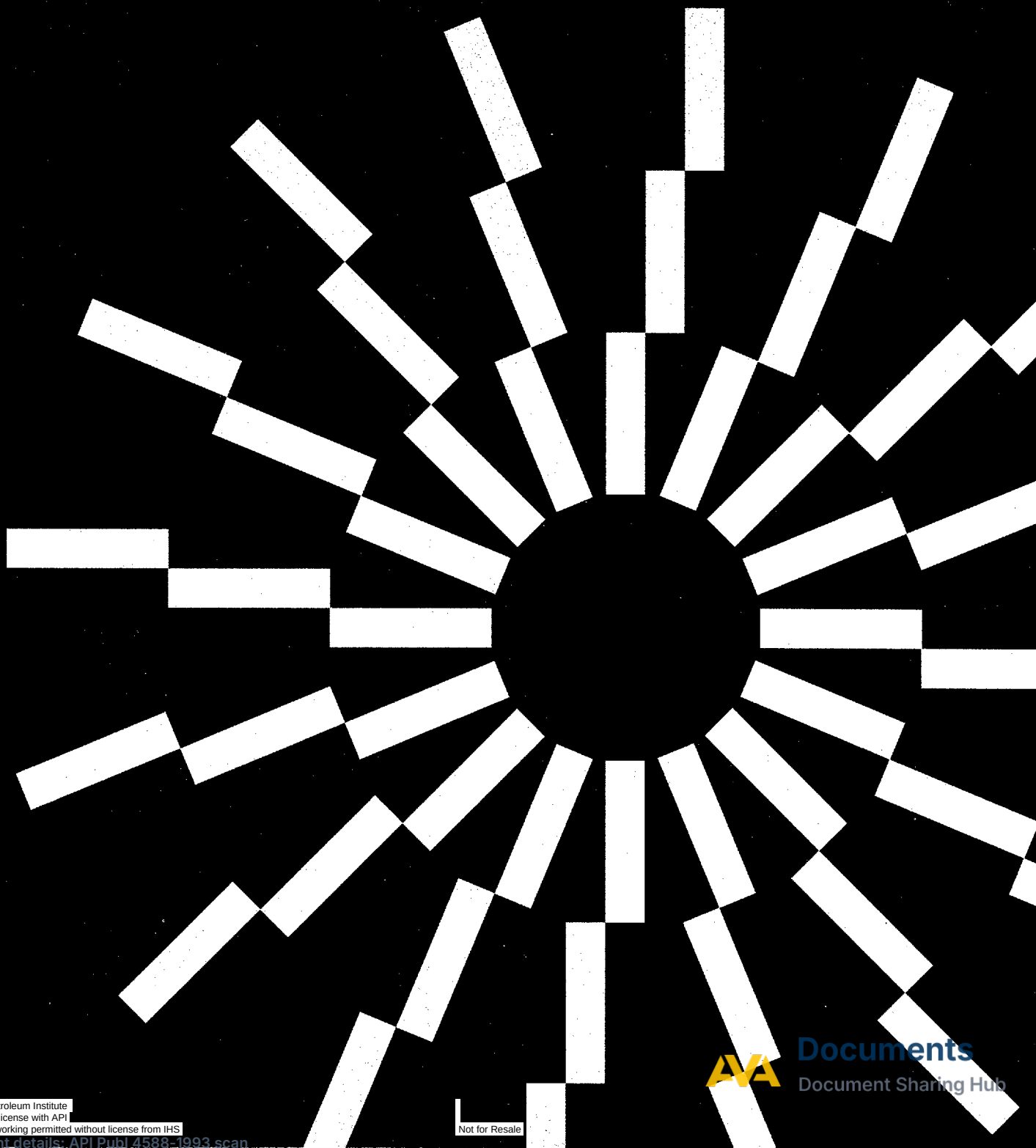
Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals



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Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals

Volume I: Text

Health and Environmental Sciences Department

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ABSTRACT

The American Petroleum Institute (API) commissioned this study to "Develop Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals" by screening and/or bagging components at three marketing terminals. The United States Environmental Protection Agency (U.S. EPA) separately funded the same test contractor (Radian) to test an additional terminal. The results for all four marketing terminals are presented in this report.

New average emission factors, new default zero emission factors, and new emission correlation equations were developed for the majority of the component types found in petroleum marketing terminals. In almost all cases the new average emission factors, new default zero emission factors and new emission correlation equations predict substantially lower emissions than those factors and equations determined in previous studies of the chemical and petroleum refinery industries. These emission factors are lower because of lower leak distributions and lower correlations between mass emissions and screening values.

In addition to screening and bagging, a test was performed to determine the quantities of liquid gasoline that leaked out of loading arms after filling the gasoline tank trucks. These drips occur immediately after the trucks have been loaded and the liquid loading arms released from the trucks. In almost all cases the measured drip volumes per loading arm were below the detection limit of the measuring instrument (0.1 mL per truck loading event), indicating that these drips result in minimal emissions.

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EXECUTIVE SUMMARY

The American Petroleum Institute (API) commissioned this study to "Develop Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals" by screening and/or bagging components at three marketing terminals. The United States Environmental Protection Agency (U.S. EPA) separately funded the same test contractor (Radian) to test an additional terminal. The results for all four marketing terminals are presented in this report. The study's main objective was to:

- Determine emission factors and fugitive emission correlation equations for components (e.g., valves, pumps, etc.) in light liquid and gas services¹ specifically related to the petroleum marketing terminals.²

The secondary objectives were to:

- Develop correlations between chemical composition of the liquids in the lines and the chemical composition of the fugitive emissions.
- Compare the physical characteristics of the petroleum marketing terminals and the effect of these characteristics on the levels of fugitive emissions.

In this study, components analyzed for fugitive emissions were:

- Valves (ball, plug, butterfly, gate, check, diaphragm, globe, etc.).
- Connectors (flanges, screwed connectors, tubing connectors, union connectors, etc.).
- Pumps (centrifugal).
- Open-ended lines.

¹ Gas service in this study is defined as the vapor phase of the liquid product.

² The U.S. EPA's primary objective was the development of emission correlation equations and stratified emission factors (but not average emission factors) specific to marketing terminals.

- Pressure relief valves.
- Tank truck loading arm valves (check valves on lines that connect to trucks including liquid loading arms and gas/vapor return arms).

Components at four marketing terminals were studied. The locations of the marketing terminals are:

- Los Angeles, California.
- Bridgeport, Connecticut.
- Providence, Rhode Island.
- Irving, Texas.

Leak rate data were gathered from components at all four marketing terminals with an organic vapor analyzer (OVA). Bagging data were gathered from three of the four terminals. Liquid stream composition and fugitive emission composition data were obtained at the three locations bagged.

New average emission factors, new default zero emission factors, and new emission correlation equations were developed for the majority of the components found in petroleum marketing terminals. In almost all cases the new average emission factors, new default zero emission factors, and new emission correlation equations predict substantially lower emissions than the factors and equations developed in previous studies of the chemical and petroleum refinery industries. Table 1 shows the new default zero emission factors. Table 2 shows the new emission correlation equations. Table 3 shows the new average and stratified (<1,000 parts per million [ppm] and $\geq 1,000$ ppm) emission factors.

The distribution of leaking components from the petroleum marketing terminals showed significantly fewer components with high screening values than the distribution observed in the 1980 Refinery Assessment Study. Marketing terminals were not included in the refinery study; however, that study was used as a comparison because refinery component character-

Table 1

Default Zero Emission Factors (Total Hydrocarbons)

Component Type	Service	Number of Tests	Default Zero Emission Rate (lbs/hr)	Lower 95% Confidence Limit (lbs/hr)	Upper 95% Confidence Limit (lbs/hr)
Connectors ^a	Light Liquid	12	6.5×10^{-6}	3.9×10^{-6}	1.1×10^{-5}
Valves	Gas	8	5.9×10^{-6}	3.8×10^{-6}	9.3×10^{-6}
Valves	Light Liquid	11	3.5×10^{-6}	2.4×10^{-6}	5.2×10^{-6}
Open-Ended Lines ^b	Light Liquid and Gas Combined	8	4.5×10^{-6}	2.6×10^{-6}	7.7×10^{-6}
Pumps	Light Liquid	8	3.9×10^{-5}	2.1×10^{-5}	7.4×10^{-5}

^a Also recommended for Gas Connectors and "Other" (gas, LL) component types such as hatches, covers, manholes, thermal wells, and pressure relief valves.

^b Also recommended for Loading Arm Valves (gas, LL).

Table 2
Predictive Emission Correlation Equations for Total Hydrocarbon Mass Emission Rates

Component Type	Service	Number of Data Pairs	Emission Correlation Equation ^{a,b}	Correlation Coefficient	Standard Deviation of Regression	Default Zero Screening Value (ppm)
Connectors ^c	Light Liquid and Gas Combined	36	$ER = (4.65 \times 10^{-5}) \times (SV)^{0.426}$	0.412	0.604	0.01 ^d
Valves	Light Liquid	46	$ER = (6.34 \times 10^{-6}) \times (SV)^{0.708}$	0.845	0.460	0.44
Loading Arms Valves/ Open-Ended Lines ^e	Light Liquid and Gas Combined	40	$ER = (7.66 \times 10^{-6}) \times (SV)^{0.959}$	0.838	0.632	0.57
Pumps	Light Liquid	12	$ER = (6.57 \times 10^{-5}) \times (SV)^{0.534}$	0.757	0.667	0.38

^a ER = Emission Rate (lbs/hr).

^b SV = Screening value (ppm) using the OVA calibrated with methane.

^c Also use for "other" component types (Gas, LL).

^d The default zero screening value for this category is based only on connectors in light liquid service.

^e Used the default zero emission factor for open-ended lines (light liquid and gas services combined) to estimate the default zero screening value.

ES-4



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Table 3

**Petroleum Marketing Terminal Average and
Stratified Total Hydrocarbon Emission Factors**

Component Type	Service	Average Emission Factor (lbs/hr)	Stratified Emission Factor (lbs/hr)	
			0 – 999 ppm	≥1000 ppm
Connectors	Gas	0.000067	0.000030	0.0020
	Light Liquid	0.000023	0.000020	0.0010
Valves	Gas ^a	0.00016	0.000084	0.0090 ^b
	Light Liquid	0.00015	0.000026	0.0046
Loading Arm Valves	Gas	0.045	0.00066	0.15
	Light Liquid	0.00087	0.00047	0.015
Open-Ended Lines	Gas	0.0067	0.00022	0.037
	Light Liquid	0.0065	0.00017	0.097
Pump Seals	Light Liquid	0.00093	0.00015	0.011
"Other" ^c	Gas	0.0014	0.00062	0.0025
	Light Liquid	0.00025	0.000073	0.0021

^a Based on refinery correlation equation (Radian, 1989).

^b Emission factor based on only one screening value.

^c "Other" includes components such as hatches, covers, manholes, thermal wells, and pressure relief valves.

istics were believed to be similar to marketing terminals in many respects. Figure 1 shows the distribution of the screening values of all component types and service types combined for the 1980 Refinery Assessment Study and the current petroleum marketing terminals study.

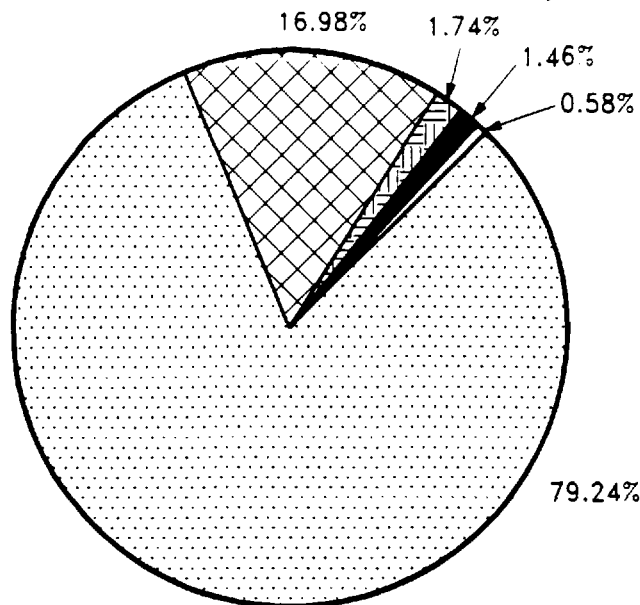
The physical characteristics of the petroleum marketing terminals, such as size, age, and throughput, did not show conclusive ties to screening value distributions.

- Traditionally, it has been assumed that the composition in the vapor leak was the same as in the liquid stream. The mechanism for this assumption is that the liquid in the line leaks through the component seal as a liquid and then vaporizes after reaching ambient air.
- As an alternative, Raoult's Law could be applied to determine the speciated vapor fraction based on liquid stream composition if the mechanism is identified as liquid vaporizing in the line with a pocket of gas trapped below a seal area.
- In this study, an attempt was made to determine the relationship between the composition of air toxics in the vapor (fugitive emissions) and the composition in associated liquid. However, the results were inconclusive.

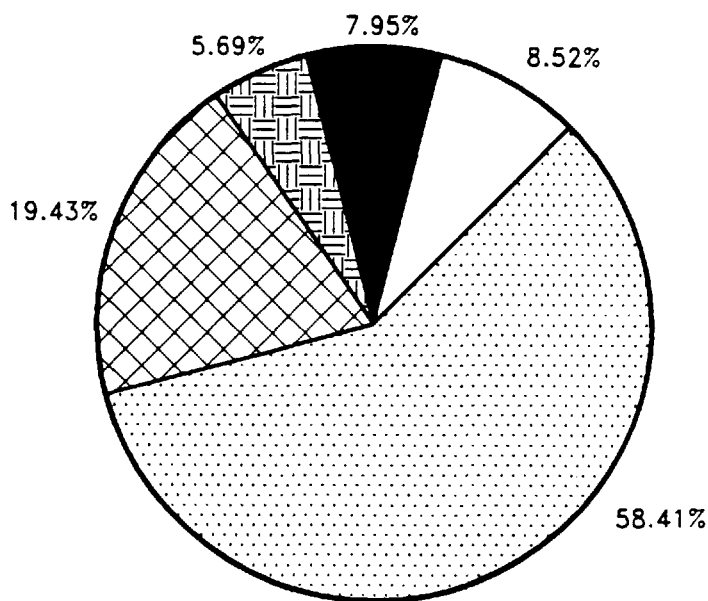
No satisfactory physical explanation of the results has yet been determined. The results do not follow pre-study or traditional expectations. The limited data set may not have been sufficient to overcome random data scatter. It should be noted that the stringent QA/QC objectives defined at the start of this study were not fully met for the speciation of the liquids and vapors at two of the marketing terminals. However, the data indicate that even with improved precision and accuracy, the results would still be inconclusive. Without an explanation of the results that fits the physical principles, we do not recommend that these results be used to estimate individual species fractions of the total hydrocarbon emissions from marketing terminals.

In addition to screening and bagging, Radian performed a test at two marketing terminals to determine the quantities of liquid gasoline that leaked out of loading arms after filling the gasoline tank trucks. These drips occur immediately after the trucks have been loaded and the liquid loading arms are disconnected from the tank trucks. In almost all cases the measured volume of the drips per loading arm release were below the detection limit of the measuring instrument (0.1 mL per truck loading event), indicating that these drips result in minimal emissions.

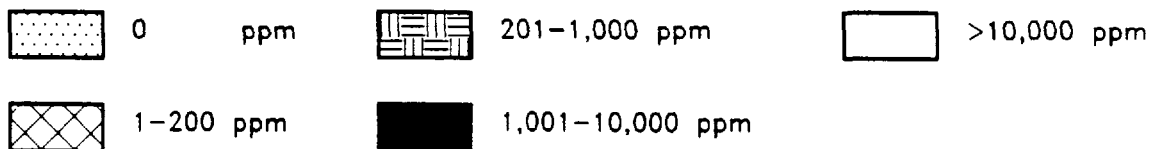
PETROLEUM MARKETING TERMINALS STUDY, 1992



REFINERY ASSESSMENT STUDY, 1980



LEGEND



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Figure 1. Comparison of Screening Value Distributions (LL, HL, and Gas) Between Petroleum Marketing Terminals Study (1992) and Refinery Assessment Study (1980).

1.0 INTRODUCTION

Fugitive emission factors that are specific to petroleum marketing terminals have not existed to date. Therefore, fugitive emission estimates for petroleum marketing terminals have typically been based on average emission factors derived from petroleum refining or chemical industries. Furthermore, the average emission factors for these industries were primarily developed more than 10 years ago and may no longer reflect current technology or operating procedures. To improve the accuracy of fugitive emission estimates for petroleum marketing terminals, the American Petroleum Institute (API) commissioned this study to "Develop Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals." The United States Environmental Protection Agency (U.S. EPA) separately funded the same contractor (Radian) to test at one terminal.

1.1 STUDY OBJECTIVES

This study's main objective was to:

- Determine average emission factors and fugitive emission correlation equations for components in light liquid and gas services specifically related to the petroleum marketing terminals.³

The secondary objectives were to:

- Develop correlations between chemical composition of the liquids in the lines and tanks and the chemical composition of the fugitive emissions.
- Compare the physical characteristics of the petroleum marketing terminals and the effect of these characteristics on the levels of fugitive emissions.

³ The U.S. EPA's primary objective was the development of emission correlation equations and stratified emission factors (but not average emission factors) specific to marketing terminals.

1.2 HISTORICAL PERSPECTIVE

In the past, those attempting to estimate fugitive emissions from petroleum marketing terminals used information prepared for the petroleum refining or chemical industries. Information for these industries was primarily gathered during the late 1970s and early 1980s. In this report, comparisons are made to some of these study results. Other studies, that discuss fugitive emission protocols, are also referred to in this report. This section discusses earlier studies.

The *Assessment of Atmospheric Emissions from Petroleum Refining* (Radian, 1980), also called the 1980 Refinery Assessment Study, was one of the first programs to rigorously examine fugitive emissions from petroleum refineries. Components were screened with a portable hydrocarbon analyzer and mass emission rates for components were measured (bagged) in 13 refineries throughout the United States (U.S.). The assessment developed screening value distributions, average emission factors, and correlations between screening values and mass emission rates (emission correlation equations).

The 1980 Refinery Assessment Study results were significant, but not always easily implemented. The screening values were obtained using a Threshold Limit Value (TLV®) Sniffer, calibrated with hexane. Therefore, the correlation equations developed could only be used when the screening value measurements were done using a TLV® Sniffer. Many refineries, however, obtain screening values with an organic vapor analyzer (OVA), calibrated with methane. In a screening study conducted in 1979, a correlation analysis was performed between screening values obtained with a TLV® Sniffer, calibrated with hexane, and an OVA, calibrated with methane (Radian, 1979). One of the results of this analysis was an equation that related these two types of screening values.

In 1982, the U.S. Environmental Protection Agency (U.S. EPA) published a document entitled *Fugitive Emission Sources of Organic Compounds -- Additional Information on Emissions, Emissions Reductions, and Costs (AID)* (U.S. EPA, 1982a). This document presented average emission factors for Synthetic Organic Chemical Manufacturing Industry (SOCMI) plants,

developed using SOCM I screening value distributions and supplemented with refinery screening value to mass-emission rate correlation data from the 1980 Refinery Assessment Study.

In January 1986, the U.S. EPA published a document entitled *Emission Factors for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1986). In this document, U.S. EPA explained the development of the average emission factors presented in AID, and the procedures for developing leak/no-leak emission factors. With the exception of gas/vapor service valves, these emission factors are based largely on the data collected in the 1980 Refinery Assessment Study.

In October 1988, U.S. EPA published a document entitled *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1988). In this document, the emission factors were extended from two categories (leak/no-leak) to three categories (stratified emission factors). The basis for these emission factors continued to be the same as the previous studies. Therefore, with the exception of gas/vapor service valves, the stratified emission factors were based largely on the data collected in the 1980 Refinery Assessment Study.

In 1989, API contracted with Radian Corporation to complete the development of leak/no-leak and stratified emission factors for all component and service types that existed in the 1980 Refinery Assessment Study. This included the development of emission factors for gas/vapor service valves, as well as emission factors for components in hydrogen service. The emission factors, and corresponding emission correlation equations, developed during the study (API, 1989 Draft Report) are the most accurate and appropriate for refineries currently available. As a result, they are used as comparisons to the emission factors, and emission correlation equations determined in the current study of petroleum marketing terminals.

1.3 REPORT ORGANIZATION

Section 2.0 identifies characteristics of the four marketing terminals tested. Section 3.0 outlines the testing methodology. Section 4.0 presents the quality control results. Section 5.0 describes the data analysis procedures and results. Section 6.0 summarizes the conclusions and recommendations. References are shown in Section 7.0.

2.0 CHARACTERISTICS OF MARKETING TERMINALS TESTED AND HOW THESE CHARACTERISTICS AFFECT EMISSIONS

Fugitive emission screening value data were collected at four petroleum marketing terminals. At three of these marketing terminals, bagging and speciation of liquid streams and fugitive emissions were conducted. At two terminals, a test of the amount of liquid leaking from liquid loading arms (after tank truck loading) was conducted. A general description of each terminal and testing condition is provided in Table 2-1.

It was not possible within the scope of this study to determine the exact impact of the variables identified on Table 2-1. However, several of the variables are believed to have some impact on the distribution of screening values obtained while testing. The distribution of screening values by facility for all components combined is provided on Table 2-2. The variables identified on Table 2-1 and, in some cases, their relationship to the screening value distribution shown in Table 2-2 are discussed briefly in this section.

The age of the facility, or at least the age of the components, may have some relationship to the screening value distribution. In general, newer facilities had slightly lower percentages of components with screening values over 100 ppm. However, the age of each component, or the age of the packing or seal of each component was not determined. It seems reasonable to believe that increased component age increases the chance that seals no longer hold as well as they did when new. If so, and if older facilities have, in general, older components, then the relationship of slightly higher screening values for older facilities can be readily understood. The volume throughput, number of loading racks, and number of tank trucks per day tends to impact the overall emissions from each facility. Higher throughput increases the number of tank trucks loaded per day and the potential for drip leaks after loading a tank truck. In general, higher volume throughput also means increased numbers of components, which means higher fugitive emissions. However, no information gathered would indicate that the higher throughput means a change of screening value distribution. The marketing terminal

Table 2-1

Comparison of Selected Petroleum Marketing Terminal Characteristics

Terminal Description	Terminal A	Terminal B	Terminal C	Terminal D
Age of Facility (yrs.)	>40. Major modifications in late 1970s on loading racks.	>50. Major modifications in late 1970s on loading racks.	>80. Major modifications in late 1970s on loading racks.	>45. Major modifications in early 1970s on loading racks.
Average Throughput (All Products) (Gal./Day)	>900,000 (100,000 gallons of which is piped to airport).	>2,500,000	>1,300,000	>650,000
Number of Loading Racks	7 (bottom load)	8 (bottom load)	10 (7 bottom load, 3 top load)	4 (bottom load)
Number of Trucks per Day (Avg.)	90	>300	>180	12 ^c
Type of Vapor Recovery System	Carbon adsorption	Refrigeration	Carbon adsorption	Carbon adsorption
Product Types	Motor gasolines; Jet A; Distillates; Solvent	Motor gasolines; Distillates	Motor gasolines; Aviation gas; Distillates	Motor gasolines; Environmental gasoline; Distillates
Approximate Ambient Temperature While Testing (°F) ^a	66	78	70	74
Approximate Wind Speed While Testing (mph) ^b	7	2	2	4
Approximate Number of Light Liquid and Gas Fugitive Components	3,600	6,800	5,800	4,300
Have Marine Terminal?	No	No	Yes	Yes
Routine I/M Program?	No	Yes	No	No
Type of Vapor Return Line Controls	Check valves (single and dual)	Posts and check valves (single)	Posts and check valves (single)	Posts and check valves (single)

^a Temperature estimates based on the averaged measured data while bagging at three terminals, and on a rough estimate at the terminal not bagged.

^b Wind speed estimates based on estimated and recorded data while bagging of three terminals, and on a rough estimate at the terminal not bagged.

^c Terminal D also loads 150 barges per year.

mph = miles per hour

I/M = inspection/maintenance

Table 2-2
Distribution of Screened Values Per Facility For Components
in Light Liquid and Gas Services

Screening Value Range (ppm)	Terminal A		Terminal B		Terminal C		Terminal D	
	Number of Components	Percent of Total (%)	Number of Components	Percent of Total (%)	Number of Components	Percent of Total (%)	Number of Components	Percent of Total (%)
$X < 1$	1,148	85.8	1,201	78.8	898	71.6	1,114	77.3
$1 \leq X < 100$	168	12.6	237	15.6	230	18.3	262	18.2
$100 \leq X < 500$	10	0.7	50	3.3	56	4.5	24	1.7
$500 \leq X < 1,000$	4	0.3	9	0.6	14	1.1	8	0.6
$1,000 \leq X < 10,000$	5	0.4	17	1.1	40	3.2	26	1.8
$10,000 \leq X < 100,000$	3	0.2	8	0.5	13	1.0	5	0.3
$X \geq 100,000$	0	0.0	2	0.1	3	0.2	2	0.1
Total Components Screened*	1,338	100.00	1,524	100.00	1,254	100.00	1,441	100.00

* In most cases only every tenth connector was screened; therefore, total components screened will not equal the total components of each terminal.

with the highest number of components with screening values >1000 parts per million (ppm) was not the marketing terminal with the highest volume throughput.

The type of vapor recovery system may impact the emission rates from the facility. The number of leaking components from each type of vapor recovery system was analyzed. The number of higher leaking components from the vapor recovery system in the marketing terminal with the refrigeration system was greater than in the three marketing terminals with carbon adsorption systems. Some of the leaking areas of the refrigeration system did not fall easily within the traditional categories of components and have been included in the "other" category. For example, some hatch covers to boxes associated with the refrigeration unit, which is in the "other" category, had hydrocarbon emissions that exceeded 100,000 ppm.

The product type (within the light liquid and gas service categories) at each marketing terminal influenced the screening value distribution at each terminal. The definition of "heavy liquid" used for this analysis is a liquid or gas/liquid stream with a vapor pressure equal to or less than that of kerosene (≤ 0.1 psia at 100°F or 689 Pa at 38°C), based on the most volatile class present at >20% by volume. Heavy liquids include diesel, fuel oil, and jet fuels. Components carrying heavy liquids had fewer higher leaking components than components carrying light liquids or gases. Because not all components in heavy liquid service were screened, they are not included in the screening distributions shown in Table 2-2. Gasoline additives are not a heavy liquid by the definition used in this study, but have a relatively low vapor pressures compared with gasolines. Components carrying gasoline additives at each loading rack also showed lower screening values than those carrying liquids with higher vapor pressures. In contrast, components carrying aviation gasoline, a particularly light liquid, had a high number of components leaking over 1,000 ppm. The numbers of components carrying gasoline additives or aviation gasoline will influence the screening value distribution at each terminal.

The effects of ambient temperature and wind speed on measured emission rates are inconclusive. There are too many competing variables to isolate the effects of ambient

temperature and wind speed data. Ambient temperature and windspeed were based on measured data and estimated data gathered while on site. These data are based on temperatures and wind speeds while bagging or screening, and not the average daily temperatures or wind speed.

One of the marketing terminals had marine loading and unloading facilities. Marine loading and unloading of petroleum products could impact the total emissions from such a terminal. The marine environment has the potential to affect fugitive components differently than in nonmarine environments; however, too few components were available to be measured at the marketing terminal with marine loading and unloading facilities to reach any conclusions on screening value distribution.

Available literature strongly supports that inspection/maintenance (I/M) programs are effective in reducing fugitive emissions (U.S. EPA, 1982b). Interestingly, Terminal B was the only terminal with an I/M program (quarterly inspections, 1,000 ppm leak definition), but it was not the terminal with the lowest percentage of leaking components. This result may be anomalous, with other factors outweighing the contributions of the I/M program. Some of the other factors that may outweigh the contribution of the I/M program are the age of the facility, age of the component or seal, temperature while testing, temperature changes during the year, type of products handled, or specific types of components within a component category (i.e., more gate valves than butterfly valves, etc.). None of these potential factors was studied in enough detail to reach conclusions on their impact.

One of the highest sources of emissions, on a mass emitted per component basis, at the marketing terminals was from the gas loading arm valves (vapor return valves). The vapor return valves are check valves in the vapor return lines that connect to the trucks during loading. A schematic drawing of the vapor return line system is shown as Figure 2-1. The vapor return arms allow the hydrocarbon vapors in the tank trucks to be displaced to a collection and recovery system while the tank truck is loaded with the product. The check valves in these vapor return arms have as a primary purpose the prevention of liquids that can

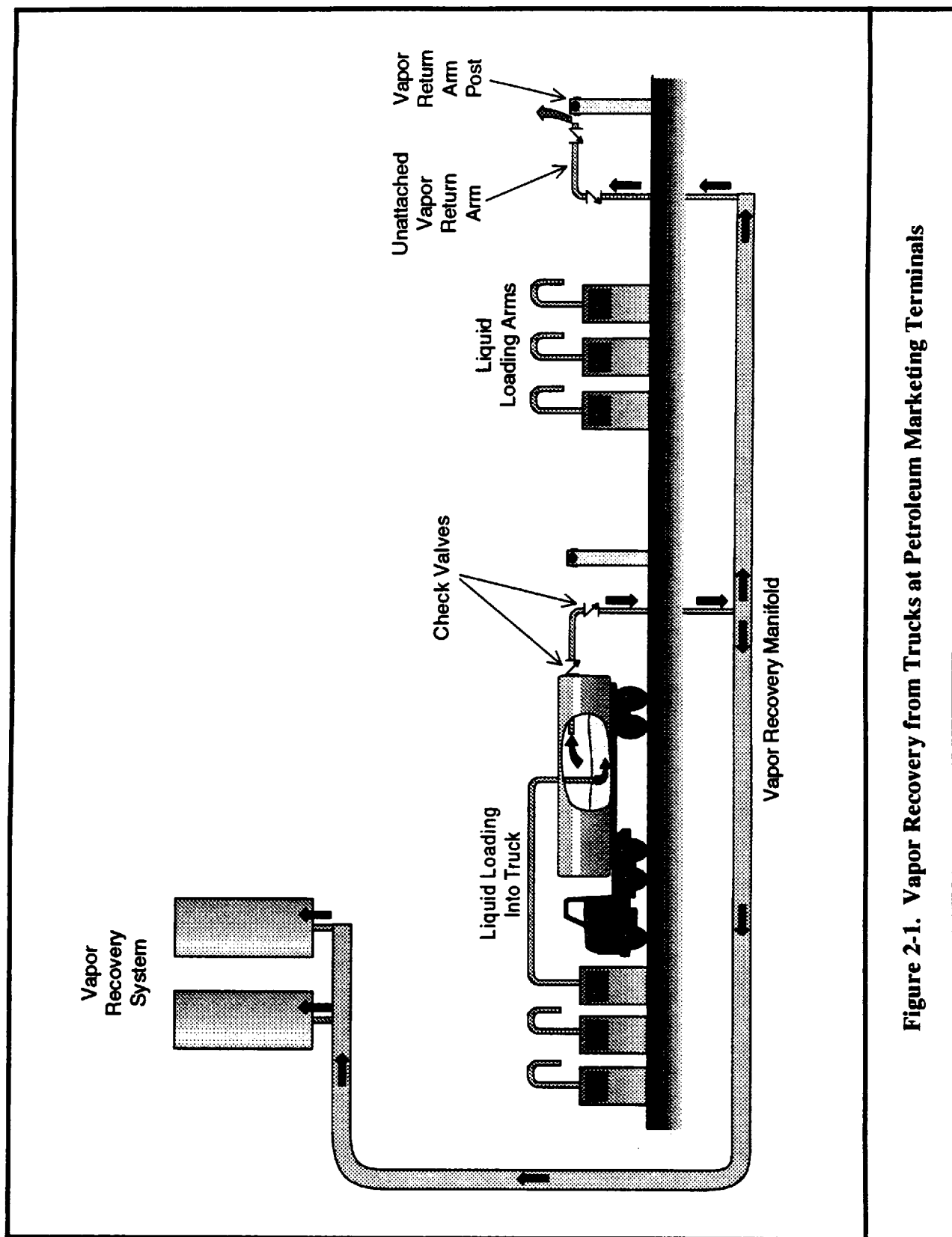


Figure 2-1. Vapor Recovery from Trucks at Petroleum Marketing Terminals

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accumulate in the lines and in the vapor recovery unit from coming back up the vapor return lines. One reason for the high leak rates from these vapor return arms is that all of the loading rack vapor return lines are connected to a common underground header. Vapors recovered from one truck are often emitted from vapor return valves several rows away. For instance, while a truck was loading at one loading rack, emissions from an idle vapor return valve exceeded 100,000 ppm. In summary, the check valves frequently do not stop vapors from being released through idle vapor return arms.

Some terminals solved the problem of backflowing vapors by installing blinds on posts to attach idle vapor return arms. The blinds, when latched or fastened to the idle vapor return arm, prevent vapors from backflowing. When blinds were properly attached, the emissions from these vapor return arms were very small. The vapor return arms were frequently not correctly fastened in place, with either one latch or two not secured. In at least one observed case the vapor return arm was not attached to the blind at all. Emissions from unsecured vapor return arms were very high. From earlier studies the U.S. EPA estimated that 10 to 30% of the displaced vapors from tank truck loading do not reach the vapor control device. Emissions from unsecured vapor return arms may account for part of these losses.

Terminal C did not use vapor return arms while top loading trucks with fuel oil. Vapors from the trucks were emitted to the atmosphere while top loading. Screening values at the open hatch cover for these trucks while loading were approximately 2,500 ppm.

3.0 TECHNICAL APPROACH

This section discusses the screening, soap-scoring, bagging, and liquid sampling procedures that were followed at the four petroleum marketing terminals. Also discussed are the quality control procedures and the data analysis techniques.

3.1 SCREENING PROCEDURES

Screening measurements were made on safely accessible components carrying gasoline, gas, gasoline additives, diesel, Jet A and fuel oil. The focus of this study was on the gas/vapor and light liquid components. Components in heavy liquid service (Jet A, fuel oil, diesel) were occasionally screened, but results were not included in the development of emission correlation equations or emission factors. Over 1,400 components (heavy liquid, light liquid, and gas services) at each marketing terminal were screened. The screening measurements were made with the Foxboro Organic Vapor Analyzer (OVA) Model 108, in accordance with the latest version of U.S. Environmental Protection Agency (U.S. EPA) Reference Method 21. Method 21 instrument specifications are summarized in Table 3-1.

The OVA 108 is a portable, flame ionization detector (FID). The Model 108 has a logarithmic readout which ranges between 1 part per million (ppm) to 10,000 ppm. Through the use of a dilution probe, the range of the OVA 108 can be extended to 100,000 ppm. Because of its broad range, the OVA 108 was selected for this testing.

Table 3-2 outlines the general screening procedures that were followed using the OVA 108. These procedures closely follow the guidelines discussed in U.S. EPA Method 21. The following component categories were screened at each facility:

- Valves (ball, plug, butterfly, gate, check, diaphragm, globe, etc.).
- Connectors (flanges, screwed connectors, tubing connectors, union connectors, etc.).
- Pumps (centrifugal).

Table 3-1**Summary of EPA Method 21 Requirements**

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS LEAKS (Including Proposed Revisions Published May 30, 1989)	
1.	Analyzer Response Factor <10
2.	Analyzer Response Time ≤ 30 Seconds
3.	Calibration Precision ≤ 10% of Calibration Gas
4.	Internal Pump Capable of Pulling 0.1 to 3 L/min
5.	Intrinsically Safe
6.	Single Hole Probe with Maximum ¼-Inch OD
7.	Linear and Measuring Ranges Must Include Leak Definition Value (May Include Dilution Probe)
8.	Instrument Readable to ±2.5% of Leak Definition
9.	No Detectable Emissions (NDE) Value Defined as ±2.5% of Leak Definition (i.e., ±500 ppm)

Table 3-2

Summary of Screening Procedures

GENERAL SCREENING PROCEDURES	
1.	Prepare analyzer for sampling.
2.	Calibrate analyzer.
3.	Complete top portion of screening data sheet.
4.	Place analyzer probe as close as possible and approximately perpendicular to the component surface or seam where leakage could occur.
5.	Move the probe slowly along the line of potential leakage to obtain the maximum reading.
6.	Leave the probe tip at the maximum reading location for approximately two times the instrument response time.
7.	If the reading exceeds full scale use the dilution probe.

- Open-ended lines.
- Pressure relief valves.
- Tank truck loading arm valves (check valves on lines that connect to trucks including liquid loading arms and gas/vapor return arms).

Components were screened while moving liquid products through the lines (load) and while the lines were full of liquid but the liquid was not moving (no-load).

During the screening process, the following data were recorded:

- Component identification number.
- Component type.
- Service (i.e., light liquid, heavy liquid, gas/vapor) of material flowing through the component.
- Screening value of the component in ppm.
- Additional supportive data (temperature, background volatile organic compound [VOC] concentration, etc.).

3.2 SOAP SCORING PROCEDURES

Soap scoring procedures were applied to nearly all of the components at the first terminal tested. Soap testing of components is a relatively simple and inexpensive strategy that may be used on potential leak sources that:

- Have no continuously moving parts.
- Have a surface temperature less than the boiling point and greater than the freezing point of the soap solution.
- Do not have open areas to the atmosphere the soap cannot bridge (the solution must cover all holes).
- Are not leaking liquid.

Table 3-3 summarizes general soap scoring procedures.

Table 3-3

Summary of Soap Scoring Procedures

GENERAL SOAP SCORING PROCEDURES	
1.	Obtain a commercial soap solution or prepare one.
2.	Spray a soap solution over the selected component. The solution may be applied with either a squeeze bottle or pressure sprayer.
3.	Observe the component and record whether or not bubbles are formed.
4.	If no bubbles are formed, the component is assumed to have no detectable emissions or leaks.
5.	If any bubbles are formed, measure the rate of bubble formation and apply existing correlations to determine emission rate or measure the VOC concentration directly with the OVA.

Because only two components out of over 1,500 measured showed any response to soap scoring at the first terminal tested, soap scoring was not conducted at the remaining sites. Please note that all components of Marketing Terminal A were also screened with the OVA. It is hypothesized that the lack of effectiveness of soap scoring at marketing terminals is due to the lower volatility of the products tested. Soap scoring has been used successfully in gas production and gas plants, even in very volatile liquid services. The apparent mechanism at the terminals is that a small leak of liquid gasoline would appear at the surface of the seal and below a layer of soap film. Instead of vaporizing and bubbling up through the soap film, however, the gasoline liquid would float to the top of the soap film, since gasoline is less dense than water. The gasoline would then evaporate slowly from the surface of the soap without causing any bubbling. This would explain the apparent lack of sensitivity of the soap scoring on components that showed elevated OVA readings.

3.3 BAGGING PROCEDURES

In this section both the sampling techniques for bagging and the analytical techniques for bagging are discussed.

3.3.1 Bagging Sampling Techniques

The "bagging technique" was used at three of the four sites to determine quantitative mass emissions from gasoline components. Bagging refers to a sampling method in which the component is completely enclosed in an impermeable plastic "bag." The internal atmosphere of the bag is allowed to equilibrate and then a sample of the gas within the enclosure is collected for analysis. Although there is not an official reference method for bagging, the technique is well established and documented in both the U.S. EPA *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP* (U.S. EPA, 1988) and the Chemical Manufacturers Association (CMA) *Guidance for Estimating Fugitive Emissions* (CMA, 1989).

The "Blow-Through" bagging technique, referring to the method of flowing nitrogen gas (N₂) through the bag, was used for all bagging measurements. After the bag was assembled

around the component, it was flushed with N_2 until the oxygen concentration inside the bag equilibrated to below 5%. A sample of the exit gas was then collected for expeditious analysis by a laboratory gas chromatograph (GC) brought to the site. During the bagging process, the diluent gas (N_2) flow rate was noted, along with the internal bag temperature. A summary of general bagging procedures is provided in Table 3-4.

To collect samples for GC analysis from a bagged component, a small air sampling pump was temporarily connected to the sample port of the bag. The pump flow rate was set well below the flow of the diluent gas to ensure that ambient air was not drawn into the bag. The output of the pump was used to fill a 2-liter Tedlar® bag. The Tedlar® bag was delivered to the on-site analyst who injected the sample into a Byron 301 (Byron) and Tracor Model 540 GC (Tracor GC) for analysis.

Bagging data recorded include:

- Component identification number.
- Component type.
- Initial screening value.
- Dilution gas flow rate.
- Bag temperature.
- Bag concentration.
- Final screening value.
- Additional supportive data (temperature, background VOC concentration, etc.).

A thermocouple with a digital readout was used to measure ambient and bag temperatures. The thermocouple and readout were calibrated before and after each site visit using icepoint and boiling water temperatures as well as NIST-traceable thermometers.

Table 3-4

Summary of Fugitive Emissions Bagging Test Protocol

GENERAL BAGGING PROCEDURES	
1.	Perform accuracy test (once per site).
2.	Record component data.
3.	Perform initial screening tests.
4.	Install tent enclosure.
5.	Measure diluent gas flow (N_2).
6.	Initiate tent diluent gas flow and measure tent temperature.
7.	Ensure tent concentration equilibrium ($O_2 < 5\%$, THC reading steady on OVA).
8.	Collect bag sample (THC, VOC).
9.	Check to ensure O_2 still $< 5\%$.
10.	Check THC reading on OVA.
11.	Measure tent temperature.
12.	Measure diluent gas flow.
13.	Remove tent.
14.	Perform final screening tests.
15.	Record ambient conditions.
16.	Record stream parameters.

Barometric pressure was obtained from the local National Weather Service office or from on-site equipment.

Diluent gas flowrate was measured prior to and after each bagging run with a Mini-Buck® flow calibrator. The Mini-Buck® is a primary flow calibrator with a rated accuracy of ± 1 percent.

Additional procedures had been planned if any bagged component had a liquid leak or emitted a liquid aerosol. However, no liquid leaking or liquid aerosol leaking components were found. Therefore, these planned additional bagging procedures are not discussed in this text.

3.3.2 Analysis of Bag Samples

The bagging samples were analyzed on-site by a Byron 301 and a Tracor Model 540 GC. Total hydrocarbon concentration (THC), as methane and nonmethane were provided by the Byron 301. The Tracor GC was used for sample compound speciation. Table 3-5 identifies the compounds for speciation from bag samples.

Samples were introduced to both the Byron 301 and the Tracor GC by connecting the Tedlar® sample bag to the instrument inlet and pressurizing the bag (by squeezing the bag) for 20 to 30 seconds to fill the GC injection loop. The bag was then removed and the sample injected into the chromatographic column. All samples and calibration standards were introduced to the analyzers from bags in a consistent fashion in order to account for surface effects or other errors and interferences.

Table 3-5**Bagging Sample Analyte Target List**

LIST OF COMPOUNDS
Total Hydrocarbons (Methane & Non-Methane)
Benzene
Cumene
Ethyl Benzene
Hexane
Methyl Tertiary Butyl Ether (MTBE)
Toluene
2,2,4 Trimethyl Pentane (isooctane)
Xylenes (p, m, o)

3.4 LIQUID STREAM SAMPLES

One of the objectives of this program was to compare measured fugitive emissions with the concentrations of gasoline compounds in the associated bulk streams. To achieve this objective, liquid samples were collected and analyzed from process lines that bagging measurements were made on. Ten types of analyses were performed on each liquid sample. Table 3-6 summarizes general liquid sampling procedures. Liquid samples were taken by petroleum marketing terminal operations staff.

Analysis of the liquid samples was performed on-site using the Byron 301 and Tracor GC. Liquid stream sampling data were recorded in a Master Logbook.

After sampling had been concluded, a revised procedure for the liquid sampling was developed and is recommended for future liquid stream sampling projects. The revised procedure is to chill the sample bottles prior to collecting the sample. Chilling will reduce the potential for the most volatile components to be lost during sample collection. Of course, the samples should be kept refrigerated until laboratory analysis is performed.

3.5 INTERNAL QUALITY CONTROL CHECKS

This section discusses the quality control (QC) procedures that were followed in this project to assess and control sampling and analytical data quality. The specific QC checks, required frequency, acceptance criteria, and corrective action requirements are listed in Table 3-7. The QC data results are presented in Section 4.0 and Appendix D. Much of the quality assurance (QA) and QC was conducted in the field. If instruments failed QA/QC tests, repeat testing was typically performed.

Review of these quality control checks at the conclusion of this study suggests that some of these QA/QC objectives were probably overly stringent and unrealistic. In particular, there was difficulty in meeting the precision and accuracy objectives for the Tracor GC.

Table 3-6**Summary of Liquid Sampling Protocol**

GENERAL LIQUID SAMPLING PROCEDURES	
1.	Fill two sample bottles completely with sample liquid.
2.	Cap bottles and turn upside down to check for bubbles. If bubbles appear in either bottle, empty that bottle and refill.
3.	Complete a sample ID label. Wipe dry the outside of the sample bottles and attach the labels to them.
4.	Package samples in double Zip-Lock bags and store on ice or in a cooler.
5.	Record sample information in Master Logbook.
6.	Complete sample chain-of-custody form.

Table 3-7
QC Checks

Parameter/ Instrument	QC Check	Frequency	Calibration Standards	Criteria	Corrective Action
OVA 108	Drift Test	Daily	Mid-Span std.	$\pm 20\%$	- Repeat Test - Recalibrate - Repair Instrument
	Blank	Daily	Zero Air	≤ 5 ppm	
	Precision	Daily	Mid-Span std.	$\pm 20\%$	
	Accuracy	Daily	Multi-Point Calibration	—	
Byron 301	Drift Test	Daily	Mid-Span std.	$\pm 20\%$	- Repeat Test - Recalibrate - Repair Instrument
	Blank	Daily	Zero Air	≤ 1 ppm	
	Precision	Every 10-20 Samples	Dup. Analyses	$\pm 30\%$	
	Accuracy	Daily	QC Check std.	$\pm 25\%$	
Tracor 540	Drift Test	Daily	Mid-Span std.	$\pm 20\%$	- Repeat Test - Recalibrate - Repair Instrument
	Blank	Daily	Zero Air	≤ 1 ppm	
	Precision	Every 10-20 Samples	Dup. Analyses	$\pm 50\%$	
	Accuracy	Daily	QC Check std.	$\pm 35\%$	
Bagging	Accuracy	Twice	Mid-Span std.	$\pm 50\%$	