

Air Toxics Multi-Year Study

April 1994

## Study of Refinery Fugitive Emissions from Equipment Leaks

Publication 4612



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## **1993 Study of Refinery Fugitive Emissions from Equipment Leaks**

## Volume I: Data Analysis, Conclusions and Recommendations

Prepared for: American Petroleum Institute Health and Environmental Sciences Department and Western States Petroleum Association

**API PUBLICATION NUMBER 4612** 

PREPARED UNDER CONTRACT BY: RADIAN CORPORATION SACRAMENTO, CALIFORNIA

**APRIL 1994** 

American Petroleum Institute





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### ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

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This study was co-funded by the Western States Petroleum Association (WSPA). The following members of the WSPA Fugitive Emissions Project Steering Committee are recognized for their contributions of time and expertise:

Frank Giles, Ultramar

Matt Marusich, Tosco Refining Company Julian Blomley, UNOCAL

Miriam Lev-On, ARCO Products Company

Daniel Van Der Zanden, Chevron Research and Technology Company

In addition the U.S. EPA Office of Air Quality Planning and Standards, Emission Inventory Branch, Research Triangle Park, North Carolina; South Coast Air Quality Management District; Bay Area Air Quality Management District; and, California Air Resources Board are gratefully recognized for providing oversight, additional review of draft reports and concurrent QA/QC of final measurements during this study.

### ABSTRACT

The Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned this "1993 Study of Refinery Fugitive Emissions from Equipment Leaks," called the "1993 Refinery Study" in this document. The results of this study are new emission correlation equations that relate the mass of hydrocarbon emissions to specific emission rates measured by screening components with an Organic Vapor Analyzer (OVA). Emission correlation equations were developed for valves, pumps, connectors, and open-ended lines, based on established statistical methodologies recommended by the United States Environmental Protection Agency (U.S. EPA). An alternative statistical methodology called the measurement error method (MEM) was also examined. The emission correlation equations from the MEM technique account for variabilities in screening values and in the measured mass emissions. Additional evaluation of this methodology is still in progress.

The emission correlation equations from the 1993 Refinery Study result in emission calculations that are significantly lower than emission calculations based on published emission correlation equations developed from data in Radian's Assessment of Atmospheric Emissions from Petroleum Refining, called the 1980 Refinery Study in this document. However, much of the difference in emission correlation equations is based on different data collection and data analysis techniques in the two studies. Changes in equipment and operating procedures may also have contributed to the differences in emission correlation equations.

New "zero component emission factors" were developed for components that screen at background hydrocarbon levels and were compared to the zero component emission factors published in the U.S. EPA Protocols Document. Depending on the component category, the factors developed in this study were similar, higher, or lower than those in the EPA document. New emission factors were also developed for components that have screening values above the range of the screening instrument (pegged components). These factors are significantly lower than those published in the EPA document. Several special studies were also conducted as part of the 1993 Refinery Study as a quality assurance measure and to investigate the variability of factors used to develop the emission correlation equations, zero component emission factors, and pegged component emission factors. The special studies discussed in this report include:

- Effects of potentially leaking OVA probes;
- Screening variability;
- Nitrogen flow rate variability;
- Benefits of additional bagging;
- Effects of dilution probe data; and
- Effects of high screening variability data.

The results of these special studies increase the understanding of the emission correlation equations, zero component emission factors, and pegged component emission factors, but do not indicate that any changes to these equations or emission factors are required.

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### EXECUTIVE SUMMARY

Fugitive emissions from equipment leaks are a source of hydrocarbon emissions from refineries. To estimate these emissions, regulatory and industry groups have developed numerous emission factors and emission correlation equations. The primary source of emission factors and emission correlation equations for fugitive emissions from refineries has been a study that was directed by the United States Environmental Protection Agency (U.S. EPA) and conducted in the late 1970s. Therefore, the Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned this study of refinery fugitive emissions to determine how emission correlation equations have changed since the 1970s.

The primary objective of this 1993 Refinery Study was to develop new emission correlation equations for refineries and to compare these equations to those obtained in the 1980 Refinery Study. Secondary objectives were to obtain new zero component emission factors and pegged component emission factors and to assess the relationship between the vapor leak composition and the corresponding liquid stream composition.

Emission correlation equations allow conversion of hydrocarbon concentration values obtained by a portable hydrocarbon analyzer, or screening values, to a mass emission rate. The hydrocarbon analyzer used in this study was an Organic Vapor Analyzer (OVA), Model 108. The OVA 108 can measure hydrocarbon concentration values from 1 ppm to 100,000 ppm (with a dilution probe). Screening values that measure below 1 ppm or below background hydrocarbon levels often still have some mass emissions. Special emission factors, called zero component emission factors, need to be developed for this category of low-emitting components. Another set of emission factors, called pegged component emission factors, need to be developed for components with screening values >100,000 ppm.

For the 1993 Refinery Study, samples were collected from five refineries: two located in southern California, two in northern California, and one in Pennsylvania. All five refineries had inspection/maintenance (I/M) programs to reduce the number of leaking components.

ES-1

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Sampling was conducted over approximately a six-month period by two separate sampling teams. Approximately 100 components were sampled at each of the five refineries. Approximately 82% of the bag samples were used in the data analysis. The remaining 18% failed to meet the quality control objectives. At each of the five refineries the following component types were sampled:

- Valves;
- Pumps;
- Connectors; and
- Open-ended lines.

Table ES-1 shows the number of valid samples collected for each component type used in the development of the emission correlation equations (248 total), pegged component emission factors (71 total), zero component emission factors (102 total), and those used to ensure data quality (audit sample duplicates, nitrogen flow test duplicates, and accuracy checks; 119 total).

Only a few leaking compressors and pressure relief valves were found at the five refineries, therefore emission correlation equations and pegged component emission factors were not developed for these component types.

A number of special studies were also conducted as a part of the 1993 Refinery Study. These special studies were all conducted as quality assurance measures or to examine the variability of data used to develop the emission correlation equations.

### EMISSION CORRELATION EQUATIONS

The 1993 Refinery Study developed two separate sets of new emission correlation equations. The first set of emission correlation equations is based on the methodology established in the U.S. EPA document entitled *Protocol for Equipment Leak Emission Estimates* (U.S. EPA,

ES-2

# Table ES-1Number of Valid Bagged Samples and High Screening<br/>Variability Bagged Samples in 1993 Refinery Study

	Number of Samples Used for Equations	Pegged Components	Zero Components	QA/QC Components <sup>a</sup>
Connectors-Flanges	19	3	9	9
Connectors-Other	29	14	12	- 14
OEL	22	11	9	4
Pumps-Heavy liquid	10	0	5	5
Pumps-Light liquid	27	5	7	6
Valves	141	38	60 <sup>b</sup>	81
TOTALS	248	71	102	119

OEL = open-ended lines

QA/QC = quality assurance/quality control

<sup>a</sup> Includes test duplicates (20), nitrogen flow sample duplicates (60), audit samples (34), and accuracy checks (5).
 <sup>b</sup> Includes two pressure relief values

<sup>b</sup> Includes two pressure relief valves.

1993) and is shown in Table ES-2. This set of emission correlation equations follows the established, widely accepted, ordinary least-squares (OLS) statistical methodology. The second set of 1993 emission correlation equations, developed as part of this study, is based on an alternative statistical analysis technique. This alternative technique, the measurement error method (MEM), is an established statistical method, although it has not been used previously in the development of emission correlation equations. The MEM technique accounts for the variability in screening measurements as well as variability in mass emission rates, while the OLS method does not account for the variability in the screening measurements. If the screening value variability were negligible compared to the mass emission rate variability, the MEM technique would provide equations equivalent to those produced by the OLS method. Because the MEM technique accounts for emission rate and screening value variability is not negligible, the MEM technique has the potential to be superior to previously used statistical methods for use in developing emission correlation equations. Additional work is in progress to further evaluate the MEM technique. However, the general impact of using the MEM technique is noteworthy; work performed to

Component Type	Service	Number of Data Points	Emission Rate Using OLS Method
Connectors (flanges)	All	19	$ER=(1.3)(10^{-6})(SV)^{0.93}$
Connectors (non-flanges)	All	29	$ER=(2.8)(10^{-7})(SV)^{1.0}$
Open-Ended Lines	All	22	$ER=(5.3)(10^{-7})(SV)^{0.84}$
Pump Seals	HL	10	$ER=(5.6)(10^{-6})(SV)^{1.1}$
Pump Seals	LL	27	$ER=(2.3)(10^{-4})(SV)^{0.44}$
Valves	All	141	$ER=(3.7)(10^{-6})(SV)^{0.78}$

## Table ES-2 1993 Refinery Study Emission Correlation Equations

ER = SV =	Emission Rate in lbs/hr/component OVA Screening Value (in ppm) obtained at the surface of the component except for pumps. Pump seals screened at $\leq 1$ cm
ALL =	Light liquid, heavy liquid and gas service types
HL =	Heavy Liquid
LL =	Light Liquid
OLS =	Ordinary Least-Squares

date indicates that the established OLS method results in an overestimate of emissions when the variability in the screening values is not negligible.

The 1993 Refinery Study emission correlation equations, which were based on measurements made with an OVA calibrated with methane, were compared with the 1980 Refinery Study emission correlation equations, which were based on measurements made with a Threshold Limit Value Sniffer (TLV Sniffer®) calibrated with hexane. Screening with both instruments was done as close as possible to the surface of the component at the point of maximum leak. Comparisons were made based on the component type and service type categories developed for the 1980 Refinery Study. All of the 1993 Refinery Study emission correlation equations give substantially lower estimates of emissions for screening values than the 1980 Refinery Study emission correlation equations. Table ES-3 compares emission correlation equations from the 1980 and 1993 refinery studies.

A detailed analysis of the emission correlation equations for light liquid valves revealed that the majority of the differences between 1980 and 1993 can be attributed to the difference in screening instruments and calibration gases used, and also to the treatment of pegged compo-

le ES-3 Comparison of 1993 Refinery Study Emission Correlation Equation Established Emission Correlation Equations
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Companient Type	Service	1993 Refinery Fugitive Emissions Study OLS Method <sup>a,b</sup> (screened at surface)	Marketing Terminals Study <sup>a,h</sup> (screened at surface)	1980 Refinery Study <sup>a.c</sup> (screened at surface)
Connectors (Flanges)	All <sup>d</sup>	ER=(1.3)(10 <sup>-6</sup> )(OVA) <sup>0.93</sup>		
Connectors (Non-Flanges)	All <sup>e</sup>	$ER=(2.8)(10^{-7})(OVA)^{1.0}$	EK=(4, /)(10 <sup>-</sup> )(OVA) <sup></sup>	EK=(//11)(_01)(C1)=XF
Open-Ended Lines	All <sup>d</sup>	ER=(5.3)(10 <sup>-7</sup> )(OVA) <sup>0.84</sup>	$\text{ER}=(5.7)(10^{-6})(\text{OVA})^{1.0}$	c
Pump Seals	HL	ER=(5.6)(10 <sup>-6</sup> )(OVA) <sup>1.1</sup>	ده ا	ER=(1.9)(10 <sup>-5</sup> )(TLV) <sup>1.0</sup>
Pump Seals	LL	ER=(2.3)(10 <sup>-4</sup> )(OVA) <sup>0.44</sup>	$ER=(6.6)(10^{-5})(OVA)^{0.53}$	$ER=(1.8)(10^{-4})(TLV)^{0.83}$
Valves	Gas		e	$ER=(4.8)(10^{-7})(TLV)^{1.2}$
Valves	HL	$ER = (3,7)(10^{-0})(OVA)^{0.70}$	e	ə —
Valves	LL		$ER=(6.3)(10^{-6})(OVA)^{0.71}$	$ER=(3.2)(10^{-5})(TLV)^{0.80}$

Ordinary Least-Squares II OLS

ES-5

- Light liquid H ΓΓ
- Heavy liquid И ΗL
- Predicted emission rate in lbs/hr/component н
- OVA screening value (in ppm) н ER OVA
- TLV Sniffer® screening value (in ppm) 11 TLV
- Emission correlation equation developed using the ordinary least-squares (OLS) method documented in the U.S. EPA Protocols Document (1993).
- 1980 Refinery Study emission correlation equations for TLV sniffer® screening values obtained at the surface of a component except for pumps. Pump scal emission correlation equations based on screening measurements at a distance of  $\leq 1$  cm. Equations give results for non-methane Emission correlation equations developed using OVA screening values obtained at the surface of component except for pumps. Pump seal emission correlation equations based on screening measurements at a distance of < 1 cm. Equations give results for total hydrocarbon. 4 S
  - "All" services includes HL, LL, and gas services for refinery studies, and LL and Gas services only for the Marketing Terminals Study. organic compounds. <del>v</del>
    - No emission correlation equation developed. e

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nents. The 1980 Refinery Study included pegged components in the development of the emission correlation equations (pegged instrument readings were counted as if at the pegged value, [i.e., 10,000 ppm or 100,000 ppm]), whereas the 1993 Refinery Study did not include the pegged components in the development of the emission correlation equations. Figure ES-1 illustrates the result of comparing the 1980 and 1993 data sets on the same screening instrument basis and with pegged components removed. Two low screening measurement values from the 1980 Refinery Study, which would be statistical outliers if the data sets were combined, were deleted from this plot for comparison purposes. From this plot, it is apparent that much of the difference in emission correlation equations is based on different data collection and data analysis techniques rather than differences in component behavior.

The emission correlation equations in the API Study entitled *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals* (API, 1993), referred to here as the Marketing Terminals Study, are included in Table ES-3 and were also compared with the 1993 Refinery Study emission correlation equations. Comparisons were made based on the component type and service type categories developed for the Marketing Terminals Study. The emission correlation equations from the two studies are nearly identical for light liquid valves and are statistically comparable for light liquid pumps. Differences are noted for connectors and open-ended lines; however, these differences may well be a function of component sub-type (i.e. type of connector) and size (particularly for open-ended lines).

## ZERO COMPONENT EMISSION FACTORS AND PEGGED COMPONENT EMISSION FACTORS

Zero components are those components that screen at background (also called "default zeros" in previous studies). The 1993 Refinery Study factors are shown in Table ES-4.

The Marketing Terminals Study zero component emission factors are higher than those in the 1993 Refinery Study for connectors, pumps, seals, and open-ended lines. No statistically significant differences exist between the Marketing Terminals Study zero component emission factors and the 1993 Refinery Study zero component emission factors for valves.

ES-6



ES-7

Component Type	Service	Zero Component Emission Factor <sup>a</sup> (lbs/hr/component)	Pegged Component Emission Factor <sup>a</sup> (ths/hr/commonant)
Connectors (Flanges)	All	4.9 x 10 <sup>-7</sup>	2.1 x 10 <sup>.2</sup>
Connectors (Non-flanges)	All	1.7 x 10 <sup>-6</sup>	3.0 x 10 <sup>-2</sup>
Open-Ended Lines	All	5.7 x 10 <sup>-7</sup>	2.5 x 10 <sup>-2</sup>
Pressure Relief Valves	Gas	1.9 x 10 <sup>-8</sup>	9
Pump Seals	Heavy Liquid	4.3 x 10 <sup>-7</sup>	£
Pump Seals	Light Liquid	7.3 x 10 <sup>-6</sup>	64 v 10 <sup>-1</sup>
Valves	All	6.6 x 10 <sup>-6</sup>	3.6 x 10 <sup>-2</sup>
			- 01 X 0.5
<sup>a</sup> Components were screened	at the surface evo	ent for numne Dumn cool footom hoord	•

ES-8

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Table ES-4 1993 Refinery Study Zero Component and Pegged Component Emission Factors

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were screened at the surface, except for pumps. Pump seal factors based on screening measurements at a distance of  $\leq 1$  cm. ٩

No pegged component emission factor developed for this component category.

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The zero component emission factors in the 1993 Refinery Study are comparable to those presented in the U.S. EPA Protocols Document for connectors (flange and non-flange) and light liquid pumps, are significantly lower for pressure relief valves and heavy liquid pumps, and are significantly higher for valves. The zero components in the U.S. EPA Protocols Document are based on results in the chemical industry, rather than in petroleum refining.

Table ES-4 also lists the pegged component emission factors from the 1993 Refinery Study. A pegged component is a component that has a screening value above the range of the screening instrument. For the 1993 Refinery Study, a pegged component was generally a component that screened above 100,000 ppm. Pegged component emission factors could not be developed for heavy liquid pumps in the 1993 Refinery Study because no heavy liquid pumps were screened above 100,000 ppm. Pegged component emission factors are lower by more than an order of magnitude than those presented in the U.S. EPA Protocols Document.

An alternative technique to determine the mass emissions from pegged components is being considered at this time. The equation for the determination of mass emissions that is currently presented in the U.S. EPA Protocols Document and repeated in this report is based on the assumption that the volume flow of the leaking hydrocarbons into the sample bag is insignificant compared with the flow of nitrogen (and air) through the bag. For components that are not pegged, this assumption is reasonable. However, for pegged components, the volume flow of the hydrocarbon leak can be significant if the leak rate is comparable to the nitrogen flow rate. Alternative pegged component emission factors, that account for the additional contribution of the hydrocarbon flow into the bag, have been calculated and are discussed in more detail in Volume I, Section 2 of this report. Depending on the component type, these alternative factors are 12 to 115 percent greater than those computed using the standard EPA methodology.

## VAPOR LEAK COMPOSITION COMPARED WITH LIQUID STREAM COMPOSITION One of the secondary objectives of this study was to assess the relationship of the vapor leak

composition to the liquid stream composition. Fugitive emission samples (vapor leaks) were

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collected from refinery components, then analyzed by and compared with corresponding analyses of the liquid in the associated stream or line. The comparison of the vapor data to the associated liquid data was inconclusive. The scatter of the data was random and very large. Because of the scatter of the data, the collection of vapor and liquid samples and use of more involved analysis methods for this comparison were discontinued. It is currently appropriate that refiners continue to estimate emissions of individual volatile organic compound (VOC) species by assuming that the mass fractions in emitted VOCs are the same as the mass fractions in the process streams.

### SPECIAL STUDIES

The following special studies were conducted to establish the quality and variability of the data used to develop the emission correlation equations, the zero component emission factors, and the pegged component emission factors:

- Effects of potentially leaking OVA probes;
- Screening variability;
- Nitrogen flow rate variability;
- Benefits of additional bagging;
- Effects of dilution probe data; and
- Effects of high screening variability data.

Potentially leaking OVA probes were discovered during a U.S. EPA-contracted audit of the field testing process. The OVA probes were tested by blocking the end of the probe tip. In this blocked condition, air was found to be entering the OVA from an area away from the probe tip. The OVAs were calibrated with any leak already in place, thereby reducing or eliminating the potential for a leak to affect the results. Side-by-side screening measurements with inspectors from the Bay Area Air Quality Management District (BAAQMD) showed that screening measurements both before and after the potential leaks were discovered had screening variability within the anticipated range of inspector and instrument variability. All data collected before discovering that the OVA probes were potentially leaking were compared statistically to data collected after discovery. No consistent bias in screening measure-

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ments before and after discovery was found. Thus, it is believed that the impact of the potentially leaking probes was not significant.

Screening variability tests were designed to quantify the variation due to different specific OVAs and different inspectors. The combined OVA and inspector relative percent difference (RPD) was 89.4%. The variability that screening values have over time was also quantified. The average RPD within one day was 138.8%. The variability of the screening measurements taken by the refinery I/M teams and Radian was also determined. No statistically significant difference between the I/M teams and Radian paired screening value results was found at three of the four refineries tested. One refinery was found to have screening values that were higher than the Radian screening value measurements. Comparisons of the BAAQMD and South Coast Air Quality Management screening values to Radian screening values also showed no statistically significant differences between the paired screening value results.

The effect of different nitrogen flow rates on mass emissions measurements obtained by the blow-through bagging test was also investigated. Components were repeatedly bagged at different nitrogen flow rates. Nitrogen flow rate during component bagging was shown to have an insignificant effect on mass emission calculations.

Bagging of additional components would assist in developing emission correlation equations with tighter confidence intervals. However, the benefits of additional bagging depend on the number of bags already obtained for this study. The benefits are much greater for heavy liquid pumps, where only 10 bags were collected, than for valves, where 141 bags were collected. Although additional bagging would result in tighter confidence intervals, sufficient bagging was performed to meet the U.S. EPA guideline of  $\pm 50\%$  of the mean value with 95% confidence when in log space.

The impact of the dilution probe was also investigated. The dilution probe increases the range of the OVA from 10,000 ppm to 100,000 ppm. Including screening value measurements obtained with the dilution probe adds variability into the determination of emission

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correlation equations. However, plots of the data and analyses of the slopes, intercepts, and the confidence intervals of the emission correlation equations with and without the dilution probe data indicated that the impact of the dilution probe was not statistically significant in the development of the emission correlation equations.

The effects of high screening variability data were also addressed. The components that had initial screening values that varied by more than a factor of two from the final screening values were not included in the emission correlation equation development for either the OLS method or the MEM technique. These data were removed in an effort to reduce one aspect of variability from the study. Including these data, however, would improve the precision of the emission correlation equations. However, analysis of the emission correlation equations with and without using these highly variable screening value tests indicated that deletion of these tests had no significant effect on the emission correlation equations. This analysis likewise indicated that the results were not biased by eliminating these high screening variability tests.

### DATA QUALITY

A high level of attention was directed toward quality assurance and quality control (QA/QC) during this project. These QA/QC efforts extended from project planning stages, through field testing activities, and into the data analysis and reporting activities. Volume II presents the 1993 Refinery Study's test plans and QA/QC results. Protocol documents, screening guidance documents, Quality Assurance Project Plans (QAPPs) and a data analysis plan were all prepared prior to or during this project to ensure a high level of attention to quality control throughout this study.

A Regulatory Advisory Committee (originally organized in early 1992 for the 1993 Refinery Study), was included in project and test planning, test auditing, and intermediate results review. The Regulatory Advisory Committee included the following agencies:

- United States Environmental Protection Agency (U.S. EPA);
- California Air Resources Board (CARB);
- Bay Area Air Quality Management District (BAAQMD); and
- South Coast Air Quality Management District (SCAQMD).

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Representatives from each of these regulatory agencies performed audits at test sites. Research Triangle Institute (RTI) was the representative for the U.S. EPA. The other regulatory agencies sent staff members to audit test activities. The audit results indicated that the quality of data produced by the testing was sufficient to meet quality objectives. The BAAQMD and the SCAQMD also performed side-by-side screening tests with Radian; those measurements are well within the anticipated range of screening variability for different inspectors with different screening instruments. The U.S. EPA auditor, RTI, performed duplicate analysis of bagging samples and conducted audit gas testing at four of the five refineries. Results from these duplicate analyses and the audit gas testing help substantiate the quality of data produced during this study.

During auditing, recommendations were made to enhance the data quality. These enhancements were made during the project. Some of the additional analyses performed as part of this study evaluated whether data collected prior to the recommended changes were acceptable. The results of those special investigations support the inclusion of all the data collected for the development of the emission correlation equations.

Radian and its analytical laboratory subcontractor, Air Toxics Limited (ATL), also performed several QA/QC activities to validate data collection and analysis activities. These additional QA/QC tests included:

- Laboratory (method) blanks;
- Field blanks;
- Method spikes;
- Surrogate spikes;
- Laboratory duplicates;
- Field duplicates;
- Field accuracy checks;
- Multi-point calibrations; and
- Canister stability tests.

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The QA/QC results for these tests are included in Volume II, Section 4. These tests also indicated that data used for the development of emission correlation equations and pegged component emission factors were valid and within the acceptance criteria for analytical methods used. The zero component emission factors derived for this study might be over-estimated because of detection limits and the potential for a slight amount of contamination from field sampling equipment.

### DATA APPLICABILITY

Data were collected from five refineries with widely differing characteristics. One of these refineries was in Pennsylvania, two in southern California, and two in northern California. The refineries ranged in size, based on barrels of crude throughput, from approximately 50,000 barrels per day (BPD) to over 250,000 BPD. The five refineries represented five different oil companies. Sampling took place at several process units at each refinery. Components tested at some refineries had been in use for decades, while those at other refineries had been installed within the previous two years. Because of the diversity of refineries and components tested, and the validity of the data obtained, results from the 1993 Refinery Study can be used by refineries nationwide.

## Section 1 INTRODUCTION

Fugitive emissions are emissions from leaking equipment such as valves, pumps, connectors, open-ended lines, and compressors. To estimate these fugitive emissions, regulatory and industry groups have developed numerous emission factors and emission correlation equations. The primary source of emission factors and emission correlation equations for fugitive emissions from refineries has been a study funded by the United States Environmental Protection Agency (U.S. EPA) conducted in the late 1970s and published in 1980 as the Assessment of Atmospheric Emissions from Petroleum Refining (referred to here as the "1980 Refinery Study") (Radian, 1980). The Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned this study of refinery fugitive emissions to determine how the emission correlation equations have changed since the 1970s. WSPA and API believed that technology changes in equipment and changes in operating procedures could necessitate revisions to the past emission correlation equations. In the "1993 Study of Refinery Fugitive Emissions from Equipment Leaks," referred to as the "1993 Refinery Study" in this document, fugitive emissions from equipment leaks were examined and current emission correlation equations were developed. In addition, fugitive emissions were examined that were not thoroughly evaluated in the past.

### STUDY OBJECTIVES

This study's main objective was to:

• Develop quantitative correlations between screening values and mass emission rates by component type and service type, and compare the results with the 1980 Refinery Study.

The secondary objectives were to:

- Develop zero component emission factors and pegged component emission factors for different component types and service categories.
- Assess the relationship between the toxics content of the vapor leak and the corresponding toxics content of the liquid stream.

1-1

### PROJECT DESCRIPTION

For this study, sampling data were collected from five refineries, two located in southern California, two in northern California, and one in Pennsylvania. Three of the refineries were large (> 150,000 barrels crude per day [BPD]). The other two were considerably smaller (< 100,000 BPD). All five refineries had inspection/maintenance (I/M) programs to reduce the number of leaking components. Approximately 100 components were sampled/bagged at each of the five refineries. Approximately 82% of these bag results were used in the emission correlation equation, pegged emission factor, and default zero emission factor development. The remaining 18% did not meet quality assurance objectives and were not used. At each of the five refineries, the following component types were sampled:

- Valves;
- Pumps;
- Connectors; and
- Open-ended lines.

Only a few leaking compressors and pressure relief valves were found at the five refineries, therefore emission correlation equations and pegged component emission factors were not developed for these component types.

### HISTORICAL PERSPECTIVE

Information for determining fugitive emissions from refineries 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. These earlier studies are discussed below.

The 1980 Refinery Study (Radian, 1980) in this report, was one of the first programs to rigorously examine fugitive emissions from petroleum refineries. Radian screened components with a portable hydrocarbon analyzer and measured (bagged) mass emission rates for components in 13 refineries throughout the United States. In this assessment, screening value distributions, average emission factors, and correlations between screening values and mass emission rates (emission correlation equations) were developed.

1-2

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The 1980 Refinery Study results were significant, but not always easily implemented. The screening values were obtained using a Threshold Limit Value Sniffer (TLV Sniffer®) calibrated with hexane. Therefore, the emission 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 (TLV Sniffer® at the surface, OVA at 1 cm).

In 1982, the 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, 1982). This document presented average emission factors for Synthetic Organic Chemical Manufacturing Industry (SOCMI) plants. These average emission factors were developed using SOCMI screening value distributions and the refinery screening value to mass-emission rate correlation data from the 1980 Refinery 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 developed leak/no-leak emission factors. With the exception of gas/vapor service valves, the emission factors presented in this 1986 document are based largely on the data collected in the 1980 Refinery Study.

In October 1988, the 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

1-3

the same as that used in 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 Study.

In May 1993, API published a study, prepared by Radian, entitled *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals* (API, 1993), called the Marketing Terminals Study in this report. This document presented emission correlation equations for component types found in petroleum marketing terminals. Default zero emission factors, average emission factors, and stratified emission factors were developed for these component types.

In June 1993, Radian completed a revision to the 1988 Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP (U.S. EPA, 1988) entitled Protocol for Equipment Leak Emission Estimates (U.S. EPA, 1993) (U.S. EPA Protocols Document). This revision incorporates currently recommended data collection and analysis procedures. Included in this document are emission factors based on historical and recently collected data from chemical industry facilities.

### **REPORT ORGANIZATION**

This study is presented in three volumes. Volume I contains the summaries and the key data analysis results. Volume II contains the testing approach, special studies to enhance the data analysis, and documentation of quality control results. Volume III contains the appendices with raw data, in-depth discussions of calculations and statistics, and more complete independent audit results. Volumes I and II are presented in this report. Volume III is published separately as API Publication No. 4613.

Volume I is organized as follows:

• Section 2 documents the key data analysis results including the emission correlation equations, the zero component emission factors, the pegged

component emission factors, and the comparison of vapor leak compositions with liquid stream compositions;

- Section 3 discusses the conclusions and recommendations; and
- Section 4 includes the references related to Volume I.

Volume II, meant as a supplement to the data analysis, conclusions and recommendations presented in Volume I, is organized as follows:

- Section 2 explains the testing approach, including sampling procedures, analytical and calibration procedures, and quality assurance objectives and checks;
- Section 3 examines special additional studies to enhance the data analysis;
- Section 4 presents the quality assurance/quality control results; and
- Section 5 shows the references for Volume II.

Additionally, the List of Appendices from Volume III (API Publication No. 4613), which contains the appendices related to the data calculations and independent audit results, is located at the back of this report.

## Section 2 DATA ANALYSIS

The procedures used to analyze the data and the data results are explained in this section. The emission rate calculation, the development of the emission correlation equations, zero component emission factors, pegged component emission factors, and the comparison of vapor leak composition to liquid stream composition data are presented.

### EMISSION RATE CALCULATION

The methodology used to estimate the mass of hydrocarbons in hydrocarbon stream samples composed primarily of aliphatics and aromatics is illustrated in Figure 2-1. This methodology is based on the fact that, for aliphatics and aromatics, the response of a laboratory flame ionization detector (FID) is linear with respect to the mass concentration of hydrocarbons present. The same weight of any hydrocarbon will result in the same peak area (response) from the FID. This relationship holds for nearly all aliphatics and aromatics with only a minor variation among compounds. Therefore, the molar concentration of mixed hydrocarbons measured by the FID as parts per million by volume (ppmv) of a calibration gas can be converted to parts per million by weight (ppmw) using the molecular weight of the calibration gas. The result will be a relatively accurate ppmw estimate of the mixed hydrocarbon sample.

If the hydrocarbon sample were to contain significant amounts of alcohols, acids, esters, ethers, or nitrogenated or chlorinated compounds, the correlation of the response of the FID would not be linear with respect to hydrocarbon mass. However, none of the hydrocarbon samples in this study are believed to contain significant amounts of the components that would cause a non-linear response on the FID. Therefore, no response factor corrections were made to any of the data in this study.

2-1

Emission Rate 
$$(kg/hr) = \frac{1.218 \times 10^{-5} (Q) (MW) (GC) (RF)}{T+273} + \frac{(\rho)(V_L)}{16.67(t)}$$

where

$$Q = \frac{tent \ N_2 \ flow \ rate \ (liters/minute)}{1 - \frac{tent \ O_2\%}{21}} \left[ 0.06 \ \frac{m^3/hr}{l/min} \right]$$

and

Q MW T GC ppmw RF <sup>b</sup> 1.218 x 10 <sup>-5</sup> $\rho$ V <sub>L</sub>		flow rate into tent $(m^3/hr)$ molecular weight of the diluent stream ( $\approx 28 \text{ kg/kg-mol}$ ) temperature in tent (°Celsius) instrument reading minus background <sup>a</sup> reading (ppmw) instrument ppmv (MW of calibration gas)/(MW of diluent stream) response factor for leaking gas relative to calibration gas a constant that includes the gas constant and assumes a tent pressure of one atmosphere (°K 10 <sup>6</sup> kg-mol/m <sup>3</sup> ) density of organic liquid collected (g/mL) volume of liquid collected (mL) time in which liquid is collected (min)
VL	=	volume of liquid collected (mL)
t	=	time in which liquid is collected (min)
16.67	=	a conversion factor to adjust term to units of kilograms per hour (g * hr)/(kg * min)

- \* Background reading is from the OVA and is applied only to remaining fraction of air based on the oxygen analyzer reading.
- <sup>b</sup> For mixed hydrocarbon streams composed primarily of aliphatics and aromatics, RF =  $1.0 (\pm 5\%)$ . For other hydrocarbons, a mass-weighted response factor should be computed for the hydrocarbon stream.

Figure 2-1. Mass Emission Calculation Procedure for Tented Leak Rate

### EMISSION CORRELATION EQUATIONS

The data analysis procedures used to evaluate the relationship between emission rate measurements (in lbs/hr) and screening values (in ppm) are given in this subsection. First, the results of multivariate analyses to determine which factors influence the relationship between measured mass emission rates and screening values are discussed. Emission correlation equations were grouped based on the results of the multivariate analyses. Second, the emission correlation equations that were developed using the statistical procedures documented in the U.S. EPA document entitled *Protocol for Equipment Leak Emission Estimates* (U.S. EPA, 1993) (U.S. EPA Protocols Document) are presented. An alternative statistical procedure for developing the emission correlation equations was also developed and applied to the emission rate and screening value data. The equations generated using this alternative method, a measurement error method (MEM), are presented in the third part of this subsection. Finally, a comparison of the new emission correlation equations to equations developed in previous studies is given.

### Multivariate Analysis

Emission correlation equations were grouped based on the results of the multivariate analyses into the following six categories:

- Flange connectors in all services;
- Non-flanged connectors (i.e., plugs, screwed or threaded connectors, union connectors) in all services;
- Open-ended lines in all services;
- Pump seals in heavy liquid service;
- Pump seals in light liquid service; and
- Valves in all services.

Zero component emission factors and pegged component emission factors were developed for these same groupings.

2-3

No emission correlation equations or pegged component emission factors were developed for the component types of compressors or pressure relief valves because insufficient numbers of leaking compressors and pressure relief valves were found at the five refineries. A zero component emission factor, however, was developed for pressure relief valves.

Data on the following parameters collected by Radian during the field effort were evaluated in this task to determine the effects they may have on the emission correlation equations:

- Component category (connectors, open-ended lines, pump seals, valves);
- Component service (light liquid, heavy liquid, and gas/vapor);
- Component size;
- Component subcategory (gate valve, flange connector, etc.);
- Site (Refinery V, Refinery W, Refinery X, Refinery Y, Refinery Z);
- Geographic region (Pennsylvania, Bay Area Air Quality Management District [BAAQMD], and South Coast Air Quality Management District [SCAQMD]);
- Process unit (catalytic cracker, hydrocracker, alkylation, etc.);
- Ambient temperature;
- Barometric pressure;
- Windspeed;
- Organic Vapor Analyzer (OVA) screening instrument identification (ID) (Instrument 1, 2, or 3);
- Valve actuation (manual or control); and
- Pump load (on or off).

A number of different statistical procedures are available to evaluate the relationships between multiple variables. These include analysis of variance, analysis of covariance, stepwise regression, principal component analysis, and cluster analysis. These multivariate procedures were used to determine how many different emission correlation equations should be developed, whether additional factors should be incorporated into the emission correlation equations, and whether there were interdependencies (e.g, correlations) between the explana-

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tory variables. In evaluating whether additional factors should be incorporated into the emission correlation equations, the key questions were:

- Does the factor affect the relationship between emission rates and screening value measurements?
- Is adding the factor meaningful (that is, can it be physically interpreted)?
- How much more precise will the emission correlation equation be by adding the factor?

Variables that were statistically significant were evaluated for possible confounding relationships that may exist between them and other explanatory variables. In developing an emission correlation equation, it is important to know which explanatory variables may be correlated and are not independent.

One of the assumptions in performing many statistical procedures is that the errors are independent and normally distributed, and that the variances are constant for different factors or ranges. These assumptions were met by taking the natural logarithms (logs) of the emission rate and screening value measurements before performing the statistical analysis.

Screening measurements were obtained by guiding the OVA probe around the periphery of the component. The OVA probe was held as close as possible to the surface without touching the surface (referred to as "at the surface" in this report). Generally, this screening distance was very close to being on the surface, much closer than 1 cm away. The maximum reading obtained for a component was recorded. Additional measurements were taken at 90°, 180°, and 270° from the maximum reading. For the data analysis task, the relationship between emission rates and screening values was first evaluated to determine which screening value measure (i.e., the maximum screening value, the sum of the screening values, the average screening value) provided the best estimator of mass emissions. The correlation coefficients obtained for these three different screening value measures were all within 2% of each other for a given component type. Although the maximum screening value, the average

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screening values, and the sum of the screening values all provided comparable estimators of mass emissions, the maximum screening value was chosen as the most appropriate measure to be consistent with previous studies, all of which used the maximum screening values. Throughout this report, "screening value" will refer to the average of the maximum screening value before and after bagging.

Analyses of variance (ANOVAs) were first performed to determine which of the factors given above had significant effects on *log(emission rate)* after accounting for and controlling the effects of *log(screening value)*. These "ANOVAs" are the ANOVA tables given in generalized linear model procedures. The interaction between *log(screening value)* and each factor was also evaluated. Testing the significance of the main effects (or factors) and the factor multiplied by *log(screening value)* interaction in an ANOVA is analogous to testing whether separate regression equations developed for those factors will have statistically significant intercepts and slopes, respectively. These ANOVAs were performed separately for the following four component types:

- Connectors;
- Open-ended lines;
- Pump seals; and
- Valves.

Historically, separate emission correlation equations have been developed for these four component types. In addition, statistical analyses of the current data support developing different equations for these four component types.

Factors found to be statistically significant for each component type based on the ANOVA tests were further evaluated to determine whether they were correlated with other measured parameters. The  $r^2$  (i.e., the correlation coefficient squared) was also evaluated for those factors that were statistically significant to determine which factors produced emission correlation equations with the strongest correlation. The value of  $r^2$  indicates the approximate per-

2-6

centage of the total variation in the response variable (i.e., *log[emission rate]*) that can be explained by the correlating variable(s). For example, if the r (the correlation coefficient) = 0.50, then  $r^2=0.25$  and about 25% of the variation in *log(emission rates)* can be explained by the given factor(s). The remaining 75% of the variation is due to other variables and random variation.

The results of these ANOVAs are given in Table 2-1. Table 2-1 also shows the number of observations included in the analysis. For those factors that were not statistically significant at the 0.10 level, "NS" (not significant) is given in the table. For those factors that were statistically significant at the 0.10 level, the p-value, and the multiple correlation coefficient are given (i.e., the correlation coefficient for the model). Cases where both the intercepts and slopes (i.e., the main effect and the interaction with *log[screening value]*) were significant are noted in the table.

The p-value provides an indication of how significant a given factor is for a particular test. For example, in the ANOVAs performed, the null hypothesis is that a given factor does not have a significant effect on the emission correlation equation (i.e., the slopes and intercepts for the different levels of the factors being tested are not significantly different). At the outset of a hypothesis test, it is always presumed that the null hypothesis is correct. This position will change only if the sample data show that this is not true. A significance level, or alpha level, of 0.10 was used for the ANOVAs (the alpha level and the significance level are the same). Thus, the test was performed such that there is only a 10% chance of incorrectly concluding that an effect is significant when, in fact, it is not. The p-value is used to determine when the decision can be made to reject the null hypothesis that a given factor has no effect. Thus, a p-value that is greater than 0.10 (the significance level) indicates that there is not enough evidence to reject the null hypothesis. A p-value that is less than 0.10 would result in rejecting the null hypothesis that the effect is not significant (and therefore accepting the alternative hypothesis that the effect is significant). If an effect is judged to be statistically significant (i.e., the p-value is less than alpha or the significance level), the magnitude of the p-value can be used to indicate "how significant" an effect is. For example,

# Table 2-1Results of Tests to Determine Variables that Affect<br/>Log(Emission Rates) After Accounting for the Variability<br/>Explained by Log(Screening Values)

	Connectors	Open-Ended Lines	Pump Seals	Valves
Log(Screening Value): N p-value (Correlation Coefficient) <sup>a</sup>	N=48 0.0001 (0.82)	N=22 0.0001 (0.83)	N=37 0.0001 (0.74)	N=141 0.0001 (0.81)
Variables Added After Accounting for Log(Screening Value):				
Service <sup>b</sup>	N=48 NS	N=22 NS	N=37 0.01 <sup>c</sup> (0.80)	N=141 NS
Size <sup>d</sup>	N=48 0.03 <sup>f</sup> (0.84)	N=21 NS	NA*	N=141 0.0004 (0.83)
Type <sup>e</sup>	N=48 0.002 <sup>f</sup> (0.86)	NA	NA	N=141 NS
Site	N=48 NS	N=22 NS	N=37 NS	N=141 0.001 (0.83)
Region <sup>g</sup>	N=48 NS	N=22 0.05 (0.89)	N=37 NS	N=141 0.0004 (0.83)
Process Unit <sup>b</sup>	N=48 NS	N=22 0.07 (0.89)	N=37 NS	N=140 NS
Ambient Temperature	N=48 NS	N=22 NS	N=37 NS	N=141 NS
Barometric Pressure	N=23 NS	N=22 NS	N=15 0.02 (0.69)	N=70 NS
Windspeed	N=48 NS	N=22 NS	N=37 NS	N=141 0.04 (0.82)
Instrument ID	N=48 NS	N=21 0.04 (0.90)	N=37 0.02 <sup>c</sup> (0.81)	N=141 0.005 (0.83)
Valve Actuation	NA	NA	NA	N=112 0.004 (0.83)
Pump Load	NA	NA	N=32 0.0003 (0.83)	NA

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# Table 2-1 (Continued)

NS = Not statistically significant at the 0.10 significance level. The p-value is given for statistically significant effects. NA =

Not applicable (e.g., types of pumps seals and types of open-ended lines not evaluated).

а The correlation coefficient (Rxy) is given for those factors that are statistically significant. Rxy<sup>2</sup> is the variation in log(emission rate) that can be explained by the given factor and log(screening value).

b Service types evaluated are light liquid, heavy liquid, and gas services, with the exception of pump seals which are in light liquid and heavy liquid services only.

с Both the main effect and the interaction between the factor and log(screening value) have statistically significant effects on log(emission rate) [i.e., both the slopes and intercepts are statistically significant].

d Size treated as a continuous variable.

е Component types evaluated for connectors are flanges and non-flanges. Component types evaluated for valves are gate valves and non-gate valves.

- f Size and type (flange or non-flange) are confounded for connectors (i.e., the flanges tend to be larger and non-flanges tend to be smaller). Connector emission correlation equations should therefore be separated by either connector size or connector type, but not both.
- g Regions are Pennsylvania, the Bay Area Air Quality Management District (northern California), and the South Coast Air Quality Management District (southern California).
- h Process unit codes are given in Table 2-2.

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Size not tested for pump seals because of inconsistent recordings of the size variable.

a p-value that is less than 0.10, but very close to 0.10, say 0.09, could be regarded as an effect that is statistically significant at the 0.10 level, but "borderline." Furthermore, a p-value of 0.09 would be statistically significant at the 0.10 significance level but not at the 0.05 significance level. A p-value that is a lot smaller than the significance level indicates that the data strongly support the conclusion that a particular effect is significant. For example, a p-value of 0.0001 would provide strong indication that a particular effect is significant.

The focus of this analysis is to reduce the chance of including an insignificant effect. However, there is a chance some of these effects are significant, but insufficient data were available to establish significance. Therefore, we can be assured that there is less than a 10% chance of incorrectly concluding that an effect is significant when, in fact, it is not, but we cannot conclude that the effect is insignificant based on this analysis.

The first line in Table 2-1 shows the p-value and the correlation coefficient of the ANOVAs performed on log(emission rate) versus log(screening value) only. As indicated in the table, these ANOVAs had a p-value of 0.0001 for each of the component types. The correlation

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coefficients obtained for these initial analyses varied from 0.74 for pump seals to 0.83 for open-ended lines. All subsequent lines in the table are results of the ANOVAs for the given factors, after explaining the variation due to *log(screening value)*. Results presented in Table 2-1 are for the significance of each of the given variables, separately, after accounting for *log(screening value)* only. Additional tests were performed in which multiple factors and interactions were evaluated in one model. These results are not presented in Table 2-1, but significant findings are discussed in the text.

Step-wise regressions were also performed for each component type. In this type of procedure, variables are added one by one to the regression equation and each variable's contribution to the equation is determined. Variables that do not explain a significant amount of variability (at a pre-set confidence level) at a given step, are not included in the equations. In general, the results of the step-wise regression were consistent with the ANOVA results.

Analyzing the ANOVA results was only the first step in determining statistical significance. If the ANOVA tests indicated statistical significance, further analysis was performed. Frequently, the further analysis indicated that the results were inconclusive, confounded with multiple variables, of minimal significance, or based on inconsistent data recordings. Results obtained for each of the component types are explained below.

<u>Connectors</u>. The ANOVA tests indicated that connector size and connector type were both found to have statistically significant effects (alpha = 0.10) on the emission correlation equations. Connector sizes ranged from 0.5 inches to 8 inches. Connector types evaluated were flange connectors and non-flange connectors. Non-flange connectors were plugs, screwed or threaded connectors, and union connectors. Analysis of the data indicated that connector size and type were correlated (the larger connectors tended to be flanges). Thus, adding either connector size or connector type will improve the emission correlation equation, but including both factors is redundant. Table 2-1 shows that the correlation coefficient obtained by including connector type as a factor is larger than the correlation coefficient

obtained by including size as a factor. Therefore, including type as a factor for connectors provides a better model than including size as a factor.

Figure 2-2 shows a scatter plot of mass emission rates versus screening measurements for connectors. Flanged connectors are denoted with an "F" and connectors other than flanges are denoted with an "O." In examining Figure 2-2 it is apparent that the equation that would be obtained for flanges is different than the equation that would be obtained for non-flanges.

<u>Open-Ended Lines</u>. Process unit, region, and screening instrument ID (specific OVA) were initially found to have statistically significant effects on the emission correlation equations for open-ended lines (OELs) based on the ANOVA tests. Further analysis indicated that the initial results are inconclusive, of minimal significance, or based on limited data. A discussion of the effects of these factors on the emission correlation equations is given below.

As shown in Table 2-1, 22 emission rate and screening value pairs were obtained for OELs. These measurements were obtained from eight different process units (C, E, F, H, K, N, P, and Q). Process unit codes are given in Table 2-2. Only one measurement was obtained from three of the process units (H, P,and Q), two measurements were obtained from three of the other process units (F, K, and N), and four and nine measurements, respectively, were obtained from the remaining two process units (E and C). Due to the fact that only a limited number of observations were obtained from different process units, statistically significant results regarding the effects of process units should be viewed with caution. Thus, although statistically significant effects were found between process units, it would be desirable to collect additional data before making firm conclusions about the effects of process units on the emission correlation equations for OELs.

Geographic region was also initially found to have a statistically significant effect on measured mass emission rates for OELs. Three geographic regions were evaluated: BAAQMD, Pennsylvania, and SCAQMD. Further analysis of the data and plots revealed that the slopes of the regression equations for the three different regions were not statistically different from

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Code	Process Unit	
А	Crude distillation unit	
В	Alkylation (HF, sulfuric acid) unit	
С	Catalytic reforming unit	
D	Hydrocracking unit	
E	Hydrotreating/hydrorefining units	
F	Catalytic cracking (fluid and other) and CO boiler	
G	Thermal cracking (visbreaking and other)	
Н	Thermal cracking (coking)	
I	Hydrogen plant	
J	Asphalt plant	
КК	Product (liquid and gas) blending and treating units	
L	Sulfur plant	
<u>M</u>	Vacuum distillation towers	
N	Full-range distillation units (light ends, naphtha, solvent, etc.)	
0	Isomerization unit	
P	Polymerization unit	
Q	Methylethylketone dewaxing unit	
R	Other lube oil and specialties processing	
S	Interunit pipeline system	
T	Sour and other water strippers	
U	Methyltertiarybutyl ether unit	
v	Catalytic Separation Plant	
w	Product Storage and Loading	

# Table 2-2Process Unit Codes

one another. Thus, for a given change in screening value measurements, the measured rate of change in emission rates would be the same for the three different regions. Although the intercepts of the regression equations obtained for the three different regions were statistically different, they varied by less than 10% from one another (i.e., *the largest* intercept - *the smallest* intercept)/the largest intercept < 0.10). In summary, although there is statistical

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evidence that the intercepts of the equations obtained for different regions is significant, the magnitude of these differences is probably not of practical significance and does not warrant including region as a factor.

ANOVA results also indicated that the OVA screening instrument caused a statistically significant effect. However, screening instrument differences were confounded with region. Three different screening instruments (specific OVAs) were used in the field. The same OVA was always used in the SCAQMD region and a different OVA was always used in the Pennsylvania region. Roughly half of the screening value measurements collected in the BAAQMD region were obtained using the same OVA that was used in the Pennsylvania region and the remaining BAAQMD region measurements were obtained using a third OVA. Therefore, it is not known whether regional differences found for OELs can be attributed to actual differences in regions, differences between OVA used, some combination of the two, or even other factors. Therefore, statistically significant results regarding the effects of instrument screening device on the OEL mass emission correlation equation are inconclusive.

The lack of significance of component size on the current emission correlation equation for OELs deserves further discussion. In comparing the emission correlation equations developed during this 1993 Refinery Study with those presented in API's *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals* (API, 1993) (referred to here as the Marketing Terminals Study), it was found that the OEL emission correlation equation developed for the Marketing Terminals Study was roughly an order of magnitude higher than the emission correlation equation developed for the 1993 Refinery Study. It was found that the OEL sizes measured at the marketing terminals were typically > 1 inch, whereas all of the OEL sizes measured during the 1993 Refinery Study were  $\leq 1$  inch. The OELs in refineries tend to be smaller than those at marketing terminals. No leaking OELs > 1 inch were found at the refineries. Figure 2-3 shows a plot of the 1993 Refinery Study and the Marketing Terminals Study data combined. In the figure, the 1993 Refinery Study data pairs end with "-R" and the Marketing Terminals Study data pairs end with "-M."

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virtually all of the large OELs have higher emission rates than the small OELs for comparable screening values, with the exception of one of the nine large OELs. Furthermore, the data points for the small OELs for both studies were intermixed. An analysis of variance was performed on the combined data to test whether OEL size was a statistically significant factor after accounting for the variation in log(screening value). In this ANOVA, size was found to be a statistically significant factor (p-value = 0.0008).

In conclusion, although OEL size was not a statistically significant factor when evaluating only the 1993 Refinery Study OELs, this may be due to the fact that only small OELs were measured at the refineries. After combining the 1993 Refinery Study data with the Marketing Terminals Study data (which consisted of both large and small OELs), size was found to have a statistically significant effect on the combined emission correlation equation. Because the equations being presented are based on the data collected for the 1993 Refinery Study only, and because only small OELs were measured, OEL size has not been included as a factor in the emission correlation equations.

<u>Pump Seals</u>. The only factor for pump seals found to be statistically significant that did not appear to be due to any confounding factors was service type (heavy liquid or light liquid). The definition of "heavy liquid" used for this analysis is a liquid or a gas/liquid stream with a vapor pressure equal to or less than that of kerosene ( $\leq 0.1$  psia at 100°F or 689 Pa at 38°C, based on the most volatile class present at > 20% by volume). As noted in Table 2-1, both the intercept and the slope were found to be statistically significant. Figure 2-4 shows a plot of the emission rate and screening value data for pump seals. The service type is indicated by symbols (H = heavy liquid, L = light liquid). Although there is overlap between the two types of service, there tends to be more heavy liquid service types in the lower left corner (i.e., with lower emission correlation equation with a steeper slope and lower intercept than the light liquid emission correlation equation.

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The initial ANOVA tests of the data indicated several other factors also appeared to be statistically significant for pump seals. However, further analysis indicated that the preliminary results were inconclusive, or the data were based on inconsistent recordings. The factors initially found to be statistically significant for pump seals based on the ANOVA tests that were not included in the final emission correlation equation were:

- Component size;
- Barometric pressure;
- Pump load; and
- Instrument ID.

Pump size was not included in the final analysis because investigation revealed that field collection team members were not consistent in recording pump size, with the pump inlet size being used as a measure of pump size in some instances, pump outlet size being used as a measure of pump size in other instances, and pump shaft size recorded in other instances. Therefore, it would not be meaningful to perform statistical analyses on pump size.

Barometric pressure was initially found to be statistically significant for pump seals, however, inconclusive results were obtained. Note in Table 2-1 that only 15 data pairs were used in this analysis (barometric pressure was only recorded for these 15 measurements). Although barometric pressure was found to have a statistically significant effect in the ANOVAs, its effect on the correlation coefficient could not be directly determined because of the smaller sample size. The correlation coefficient for the regression performed on the 15 data pairs only was 0.39 without barometric pressure and 0.69 with barometric pressure. It is not known, however, whether the data points for which barometric pressure was recorded are representative of all 37 pump seal measurements. Due to inconclusive results, barometric pressure was not included in the emission correlation equations.

Another factor initially found to have statistically significant effects on the pump seal emission correlation equation was pump load (i.e., in service or out of service). Plots of the data showed that pump seals in service had higher emission rates than pump seals not in service.

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Discussions with field team members revealed that, for safety reasons, measurements were not obtained as close to the component when pumps were in service. Thus, it is not clear whether the effects seen for pump load are a function of the distance an inspector screened from the component or due to the fact that the pump was in service. It should be noted that during the 1980 Refinery Study, load was not found to have a statistically significant effect on measured mass emission rates. In addition, pump seal data collected during the Marketing Terminals Study was re-evaluated for the 1993 Refinery Study and no significant load effect was found. Results regarding the effects of load on the pump seal emission correlation equation are therefore inconclusive. In measuring pump seals in future work, however, it should be noted that pump load may potentially have significant effects on measured emission rates.

As with OELs, instrument ID (specific OVA) was initially found to be a statistically significant effect for pump seals. Although the region effect was not statistically significant at the 0.10 level for pump seals, it was found to be borderline (region was significant at the 0.10 level after considering the *log(screening value\*region interaction)*. As explained previously, instrument ID is confounded with region. Therefore, it is not known if statistically significant effects are due to differences between instrument screening devices or region. It should be emphasized that instrument ID was included in the multivariate analyses for the purpose of exploring possible confounding relationships only, and screening instrument has not been considered as a parameter to be included in the emission correlation equations. It would not be feasible to include screening instrument as a explanatory variable in the emission correlation equation, because every refinery uses different I/M teams, all of which use different screening instruments. The point is that screening instruments differ and part of the variability in screening values is due to differences in inspectors and differences in instruments. Detailed results of an instrument and inspector screening variability task conducted for this study are given in Volume II, Section 3.

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<u>Valves</u>. As with pump seals, a number of factors initially were found to be statistically significant for valves but were not included in the final emission correlation equation for one of two reasons:

- The relationship between the mass emission rate and the variable could not be explained physically; or
- There were confounding variables and it was uncertain which variable(s) was the "cause" of the significant effect.

The factors initially found to be statistically significant for valves that were not included in the final emission correlation equation were:

- Region;
- Instrument ID;
- Valve actuation;
- Site; and
- Size.

It is undesirable to include a variable "x" in the regression equation if the relationship between "x" and the emission rate has no physical basis. It is possible that such a variable correlates with emission rate only because of a chance relationship involving one or more other variables. The existence of this chance relationship in the data set used to develop the regression model does not guarantee that the same relationship will exist in future conditions under which the regression model is to be used to estimate emission rate. Thus, including variables not truly related to emission rate could lead to spurious estimates of emission rate in the future.

For example, the ANOVA results indicated that size was a statistically significant factor. Additional analyses and plots of the data, however, showed size groupings that could not be physically explained (i.e., small sizes were being grouped with larger sizes). For instance, cluster analyses and multiple range tests showed that the 1.5-inch sizes and the 6-inch sizes were similar, and that the 9-inch sizes and 1-inch sizes were similar. Figure 2-5 shows a plot

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of the emission rate versus screening value data for valves, with the valve size indicated. As shown in the figure, there is no apparent monotonic trend between valve size and increased emissions. In other words, for a given screening value, the larger valves did not always tend to have larger emissions and the smaller valves did not always tend to have smaller emissions. It is possible that there is a more complex relationship between mass emissions and valve size that is not obvious in the plot (e.g., certain larger valves may tend to have smaller emissions for a given screening value because of increased maintenance performed on these valves). Although size was not correlated with any of the other measured variables, it is not known whether size is confounded with some unmeasured parameter. In any case, the relationship between size and the emission rate versus screening value emission correlation equation lacked physical explanation. Therefore, size was not included as a factor in the emission correlation equation.

Site, region, instrument ID, and valve actuation also were found to be statistically significant for valves based on the initial ANOVA test. Confounding effects were found to exist for all four of these variables. The following observations can be made for valves:

- There is a statistically significant difference between instrument IDs. However, instrument ID is confounded with both site and region (i.e., different OVAs were used at different sites and regions).
- There is a statistically significant difference between regions and between sites.
- There is no statistically significant difference between sites within any one region. (Two of the regions consisted of two sites and one of the regions consisted of one site only).
- The statistically significant difference between regions and between sites was found to exist for light liquid values only (there was no evidence of a site effect for gas/vapor values or heavy liquid values).
- There is also a statistically significant difference between valve actuation (manual versus control). Manual valves have a higher intercept than control valves.
- The statistically significant difference between valve actuation was found to exist for light liquid valves only (there was no evidence of a valve actuation effect for gas/vapor valves or heavy liquid valves).

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In summary, although instrument ID was found to be statistically significant, it is confounded with site and region. And, although region, site, and valve actuation are statistically significant for valves, the driving factor for these conclusions is light liquid valves. That is, these factors are statistically significant for light liquid valves, but not for heavy liquid or gas valves. It should be noted, however, that no statistically significant service type (light liquid, heavy liquid, gas) effect was found for valves.

Figures 2-6 through 2-8 help to illustrate these statistical conclusions. Figure 2-6 shows a plot of emission rate versus screening value for valves in all service. Symbols are used to denote the phase (H=heavy liquid, L=light liquid, and G=gas/vapor). As shown in Figure 2-6, there is considerable overlap between the three phases; hence, it can be concluded statistically that phase does not have a significant effect on the valve emission correlation equations.

Because statistically significant effects were found to exist predominately for valves in light liquid service, further investigation was performed for this service type. Figures 2-7 and 2-8 show plots of the emission rate versus screening value data for light liquid valves only. In Figure 2-7, the five different refineries are identified (with codes that do not reveal the identity of any one refinery) and in Figure 2-8 the valve actuation (C=control, M=manual, '--' = missing) is identified. In the figures, the refinery effect and the valve actuation effect are apparent. It should be noted that for Refinery V valve actuation was not recorded and for Refinery Z only manual valves were measured. Further statistical tests were performed on the three remaining refineries (Refineries W, X, and Y) separately, and it was found that valve actuation did not have a statistically significant effect when evaluating these refineries individually.

In conclusion, results regarding the effects of region, site, instrument ID, and valve actuation on the valve emission rate correlation equations are inconclusive due to confounding effects between measured parameters. Although historically different equations have been developed for valves in different service types, the data collected during the current refinery study do not support separating valves into different service types.



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The similarity of emission correlation equations for valves in different services does not mean that there are comparable numbers or percentages of high leaking heavy liquid and light liquid valves at a refinery. In fact, the screening distribution (i.e. the percentage of components leaking within certain screening value ranges: 1-1000 ppm, 1001-10,000 ppm, >10,000 ppm, etc.) will almost certainly be very different for heavy liquid and light liquid valves. Far lower percentages of heavy liquid components are expected to leak at >1,000 ppm compared with light liquid components. Although a refinery with a high percentage of heavy liquid valves would use an emission correlation equation that is for all valve types, the estimated emissions from these heavy liquid valves would likely be far lower than a refinery with a higher percentage of light liquid valves because of the small number of heavy liquid valves that leak at high rates.

#### Emission Correlation Equations Using the Ordinary Least-Squares (OLS) Approach

During the 1980 Refinery Study, a statistical methodology for generating emission correlation equations that relate total hydrocarbon (THC) screening values (in ppm) to their mass emission rates (in lbs/hr) was developed. This statistical methodology, which is documented in the U.S. EPA Protocols Document (U.S. EPA, 1993), has been the accepted method for developing new emission correlation equations. These emission correlation equations are based on an OLS analysis. Equations presented in this section were generated following the methodology discussed in the U.S. EPA Protocols Document. In the next section, emission correlation equations developed using an alternative statistical methodology are presented. The alternative statistical methodology, MEM, is mathematically more accurate when there is variability in both the "x" and "y" values (i.e., the screening values and emission rate measurements). Additional work is currently being performed on the measurement error method, however, to determine how it can best be used for this application.

Emission correlation equations were developed for the following six component categories:

- Flange connectors in all services;
- Non-flanged connectors (i.e., plugs, screwed or threaded connectors, union connectors) in all services;

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- Open-ended lines in all services;
- Pump seals in heavy liquid services;
- Pump seals in light liquid services; and
- Valves in all services.

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These categories were determined based on the results of the multivariate analysis discussed earlier.

Emission correlation equations were developed for emitting components, where an "emitter" is defined as a component with a screening value above background concentrations. Separate zero component emission factors were developed for those components whose screening measurements were indistinguishable from background concentrations. Zero component emission factors are given in the third part of this subsection. Pegged components (i.e., those with screening measurements greater than the measurable range of the instrument screening device) were also not included in the emission correlation equations development. Pegged component emission factors are given in the last part of this subsection.

All of the components screened in the 1993 Refinery Study were screened using the OVA. With the exception of pump seals, all of the screening measurements obtained for this study were collected by screening each component at the highest leaking point on the component's surface. Pump seals were screened between the surface and 1 cm from the component depending on the pump accessibility and whether or not it was in service (more distance was required when the pump was in service and the shaft was rotating). To use these 1993 Refinery Study emission correlation equations, refineries should screen components (other than pumps) at the surface using an OVA. For pump seals, refineries should obtain OVA screening values between the surface and 1 cm from the component.

The complete data sets used for developing all of the emission correlation equations are given in Appendix C.

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<u>Methodology</u>. The OLS regression analyses were done for each component category, regressing the logarithm of the emission rate on the logarithm of the screening value according to the following equation:

Equation 2-1:  
Log<sub>e</sub>(Emission Rate) = 
$$\beta_o + \beta_1$$
 Log<sub>e</sub>(Screening Value)  
where:  $\beta_o$  = the intercept; and  
 $\beta_1$  = the slope.

Throughout most of this report natural logarithms (base e logarithms) are used. Common logarithms (base 10 logarithms) may also be used. However, results should be exponentiated by raising the value "10" to the appropriate power and an additional correction factor of  $\log_{e}(10)$  is needed for some equations when using common logarithms. This needless complication is avoided by using natural logarithms. Equations for both the natural and common logarithms are given in the U.S. EPA Protocols Document (U.S. EPA, 1993).

To transform these regression equations back to linear-linear space, it was necessary to incorporate a scale-bias correction factor (SBCF) into the equation. The SBCF is needed to correct for the bias inherent in performing a non-linear transformation on the mean predicted values. The need for a SBCF is best illustrated with an example of estimating means. Suppose that for a screening value of 10,000 ppm three different emission rate measurements of 0.1, 0.01, and 0.001 lbs/hr were obtained. Because the regression lines are developed in log space, and unless a SBCF is utilized, the mid-point between the three example emission rates on a log plot is not the same as the "true" average value. This is evident by taking the common logarithms of the three data points: log(0.1) = -1, log(0.01) = -2, and log(0.001) = -3. The average of these three values is -2, which exponentiated is equivalent to a mass emission rate of 0.01 lbs/hr (this is the geometric mean). However, the "true" average of these three values is actually the arithmetic average ([0.1 + 0.01 + 0.001]/3) = 0.037 lbs/hr. The arithmetic average is nearly four times greater than the geometric mean. In other words, when calculating averages in log space, simply exponentiating back will underestimate the average concentration for lognormal right-skewed distributions. A SBCF is needed to adjust

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for this low bias. More information on the SBCF can be found in the U.S. EPA Protocols Document.

The mean emission rate for a given screening value was computed as follows:

Equation 2-2:	Mean Emission Rat	te =	SBCF x $e^{(\beta_0)}$ x (Screening Value) <sup><math>\beta_1</math></sup>
		=	K x (Screening Value) <sup><math>\beta_1</math></sup>
	where:	K =	the constant of the emission correlation equation; and
		=	SBCF x $e^{(\beta_0)}$ .

A summary of the predictive emission correlation equations for THC mean emission rates is given in Table 2-3. Table 2-4 lists the emission correlation equations for non-methane organic compound (NMOC) mass emission rates. The NMOC emission correlation equations differ from the THC emission correlation equations only by the amount of methane in samples collected. In a few cases, the entire sample was methane. These samples could not be included in the NMOC emission correlation equation development. However, as Tables 2-3 and 2-4 indicate, the differences in the NMOC and THC emission correlation equations are minimal and, in some cases, the emission correlation equations are identical. In one case, for the OEL category, the NMOC emission correlation equation is slightly higher than the THC emission correlation. This statistical anomaly is caused by higher variability in the NMOC sample measurements which increased the SBCF, thereby increasing the emission correlation equation. For the 1993 Refinery Study, the majority of comparisons to other studies, the development of alternative analysis methods, and the in-depth evaluation of the data will be based on the THC emission correlation equations. Comprehensive results of the calculations are shown in Appendix C.

As stated previously, "zero" screening values were not included in the regression analyses. Substituting a screening value of zero into the emission correlation equations given in Table 2-3 would give an emission rate of zero lbs/hr. During the 1980 Refinery Study, however, several gas/vapor valves that screened at "zero" (i.e., no difference between the maximum

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Predictive Emission Correlation Equations for THC Mass Emission Rates for OVA Screening Values at the Surface of the Component Using the Ordinary Least-Squares Regression Method Table 2-3

Zero Component Screening Value (ppm)	0.36	5.6	1.1	0.09	0.0004	2.2
Correlation Coefficient	0.879	0.847	0.831	0.903	0.646	0.810
Emission Correlation Equation <sup>a</sup> (at surface)	$ER=(1.3)(10^{-6})(OVA)^{0.93}$	$ER=(2.8)(10^{-7})(OVA)^{1.0}$	ER=(5.3)(10 <sup>-7</sup> )(OVA) <sup>0.84</sup>	$ER=(5.6)(10^{-6})(OVA)^{1.1}$	ER=(2.3)(10 <sup>-4</sup> )(OVA) <sup>0.44</sup>	$ER=(3.7)(10^{-6})(OVA)^{0.78}$
Number of Data Pairs	19	29	22	10	27	141
Service	All	All	All	HL	ΓT	All
Component Type	Connectors (Flanges)	Connectors (Non-Flanges)	Open-Ended Lines	Pump Seals	Pump Seals	Valves

- Total hydrocarbon Ш
  - Light liquid II
- Heavy liquid II THC HL

All

- Light liquid, heavy liquid, and gas service types 11
  - Predicted emission rates in lbs/hr. П OVA ER
- OVA screening value (in ppm) obtained at the surface of the component. Pump seal OVA screening value obtained < 1 cm from component. 11
  - Emission correlation equation developed using the ordinary least-squares method documented in the U.S. EPA Protocols Document (1993). a

Table 2-4

the Component Using the Ordinary Least-Squares Regression **Predictive Emission Correlation Equations for NMOC Mass** Emission Rates for OVA Screening Values at the Surface of Method

Component Type	Service	Number of Data Pairs	NMOC Emission Correlation Equation <sup>a</sup> (at surface)	Correlation Coefficient
Connectors (Flanges)	All	19	ER=(1.2)(10 <sup>-6</sup> )(OVA) <sup>0.93</sup>	0.880
Connectors (Non-Flanges)	All	29	ER=(2.8)(10 <sup>-7</sup> )(OVA) <sup>1.0</sup>	0.846
Open-Ended Lines	IIA	22	ER=(5.4)(10 <sup>-7</sup> )(OVA) <sup>0.85</sup>	0.815
Pump Seals	HL	10	$ER=(5.6)(10^{-6})(OVA)^{1.1}$	0.903
Pump Seal	ΓΓ	27	$ER=(2.3)(10^{-4})(OVA)^{0.44}$	0.646
Valves	All	141	$ER=(3.7)(10^{-6})(OVA)^{0.78}$	0.796

Non-methane organic compounds NMOC =

Light liquid 11 ΓΓ HL

Heavy liquid 1

Light liquid, heavy liquid, and gas service types П HΙ

Predicted emission rates in lbs/hr. It ER

OVA screening value (in ppm) obtained at the surface of the component. Pump seal OVA screening value obtained ≤ 1 cm from component. П OVA

Emission correlation equation developed using the ordinary least-squares method documented in the U.S. EPA Protocols Document (1993).

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screening value and ambient background conditions) were bagged and found to have measurable mass emission rates. The average emission rate for these components was calculated. Because measured emission rates at zero screening values were not obtained for other component types, the average emission rate for gas valves that screened at zero was used to determine an equivalent emission correlation screening value by applying the gas valve emission correlation equation backwards (from emission rate to screening value instead of from screening value to emission rate). The results of this analysis was a "default zero" screening value of 8 ppm that the U.S. EPA had recommended be used in the component emission correlation equation to estimate emissions from all component types that screen at zero. This value of 8 ppm had been used for all components that screen at background levels, regardless of component type or service type, by "default," because nothing else was available at the time.

For this study, we have eliminated the terminology of "default" zero, because measured emission rates for each component type and service type, when appropriate, have been calculated. In the 1993 Refinery Study, "zero component emission factors" have been developed for each of the component categories, thus the development of default zero (or zero component) screening values is not necessary. In practice, to determine emissions from components that screen at background levels, the zero component emission factor in lbs/hr, not a value in ppm, will be used. For comparison, however, the zero component screening values obtained from the new "zero component emission factors" for each of the new emission correlation equations was determined. These are given in the last column of Table 2-3. The zero component screening value is calculated using the following equation:

Equation 2-3: Zero Component Screening Value (ppm) =

	(Zero Compo	nent Emission Factor $\vec{\beta}_{i}$
		<u> </u>
where:	Zero Component =	the mass emission factor in lbs/hr Emission Factor determined from bagging measurements for components that screened at background;
	К =	the constant of the emission correlation equation; and
	β <sub>1</sub> =	the slope of the emission correlation equation.

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As shown in Table 2-3 all of the zero component screening values obtained for the 1993 Refinery Study are below the U.S. EPA default zero screening value of 8 ppm that has been recommended in the past.

Figures 2-9 through 2-14 show the new emission correlation equations developed using the OLS regression method for each of the component categories, along with the 95% confidence intervals for the mean predicted values and the 95% confidence intervals for individual predicted values. The raw data are also shown in these figures. The 95% confidence intervals for the mean should be interpreted as meaning that we can expect to be correct at least 95% of the time when we state that the true mean emission rate, for a given screening value, falls within the limits computed. The 95% confidence intervals for individual values should be interpreted as meaning that we can expect at least 95% of the time when we can expect to be correct at least 95% of the time when we state that the true mean emission rate, for a given screening value, falls within the limits computed. The 95% confidence intervals for individual values should be interpreted as meaning that we can expect to be correct at least 95% of the time when we state that the individual emission rates for a given screening value fall within the limits computed.

The predicted mean values shown in Figures 2-9 through 2-14 represent the mean emission rate, assuming a log-normal distribution. Log-normal models have been found to have a better correlation between mass emissions and screening values than normal models. However, because log-normal distributions are often skewed to the right, the mean can be substantially larger than the median (i.e., the 50th percentile). Thus, it is not unusual for more data points to fall below the predicted emission correlation equation than above this line. In normal least-squares regression, the predicted mean regression line represents the mean of a normal distribution, which is typically close to the median. Therefore, one would expect roughly half of the raw data points to fall above the regression line and half of the data points to fall below the line in normal least-squares regression.

#### Emission Correlation Equations Using an Alternative Statistical Approach

The statistical methodology that has been used to develop new emission correlation equations in the past involves performing an OLS regression analysis. This OLS regression is done by regressing the logarithm of the mass emission rate on the logarithm of the screening value concentration. An important consideration in this regression analysis is that both the emission rate measurements and the screening value measurements contain measurement variability. The OLS regression methods are strictly correct if the only error is in the "y" value (i.e., the value to be predicted). In practice, OLS regression methods are often used when there is error in "y" and the error in "x" (the explanatory variable) is much smaller and assumed to be negligible.

For the 1993 Refinery Study, Radian conducted simulations to determine the potential effect that screening value variability can have on the predicted mass emission rates. The results of this work, discussed in a report entitled An Examination of the Screening Value Variation on the Prediction of Mass Emission Rates (Radian, 1993a) (Screening Value Variation Report), showed that the current method of performing an OLS regression can result in an overestimate of emissions when the errors in the screening value concentrations are not negligible. Depending on the magnitude of the errors in the screening value measurements and because of the logarithm transformation, this overestimate can be as large as an order of magnitude. Because of this overestimate, Radian was asked to develop an alternative statistical approach for predicting mass emission rates that considers errors in both the emission rates and the screening values. This approach has been developed and is referred to as the MEM because errors in both the screening value and emission rates are considered in this approach. A detailed description of the MEM technique is given in Appendix D. Appendix D also contains the results of simulations that were performed to test this method. A brief description of the MEM technique is given below. Applications of this approach to the data collected for this study and a discussion of additional work that needs to be performed for this application are also given in this subsection.

<u>Measurement Error Method</u>. In the Screening Value Variation Report, an investigation was made of the regression approach described in the U.S. EPA Protocols Document and how errors in the "x"-variable (the screening value) affect this regression method. As discussed, the regression method described in the U.S. EPA Protocols Document involves performing an OLS regression on the logarithm of the mass emission rates versus the logarithm of the

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screening values. In transforming the predicted values back to linear space it is necessary to incorporate a SBCF into the equation.

In OLS regression methods, the errors in the "x" value (the screening values) are assumed to be negligible when compared to errors in the "y" value (the emission rates). In MEM regression procedures, errors in both the "x" and "y" variables are accounted for. If there were negligible errors in the "x" values (i.e., if the screening values did not vary at all during testing or the variation in screening values was negligible compared to variation in mass emission rate) then the MEM technique would equal the OLS method.

A further elaboration of these two regression methods may help in this explanation. The method of least-squares used in OLS regression analysis chooses the parameter estimates for  $\alpha$  and  $\beta$  as those values that minimize the sum of squares of the <u>vertical</u> distances from the "y" values (i.e., of the *log(emission rates)*) to the presumed regression line. In the MEM analysis, parameter estimates are determined not simply from the vertical distance or the horizontal distances. In the MEM technique, the sum of the squares of the "x" values and "y" values are minimized for the angle that is most appropriate (i.e., horizontal distance, vertical distance, etc.) for the analysis, given the errors in the "x" and "y" values.

Simulations were performed for the 1993 Refinery Study to evaluate the two regression methods described above, as well as for a third regression method, the "inverse regression," which minimizes the sum of the squares in the <u>horizontal</u> distance. Inverse regression techniques are performed when the errors in the "y" value (in this case, the emission rate measurements) are considered negligible when compared to errors in the "x" values (i.e., the screening values), but predictive equations are needed for "y." This is performed by regressing "x" on "y" (instead of "y" on "x"), exponentiating, applying the SBCF, and then solving for "y." These simulations were performed on realistic ranges of screening value and emission rate data. All of the regressions were performed in log-log space and SBCFs were applied in the transformation back to linear space. The results of these simulations show that

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as the relative errors in the screening values become larger than the relative errors in the emission rate measurements:

- The magnitude of the biases in the inverse regression model decreases, and only a small bias exists when the relative errors in the screening values are twice those in the emission rate measurements;
- The magnitude of the biases in the OLS regression increases; and
- The MEM regression consistently produces virtually unbiased estimates of the predicted emission rates.

Detailed results of these simulations and plots illustrating these results are given in Appendix D.

In performing the MEM technique, estimates of the variability in the emission rate measurements and the screening value measurement are needed. Future work is necessary to determine the effects that uncertainty in the emission rate and screening value variability estimates have on the MEM technique equations. However, it is known that the current OLS method results in an overestimate of emissions when there is variability in both the screening values and emission rates. The next subsection below discusses the variability estimates that were used in the application of this method and the resulting emission correlation equations.

Application of the Measurement Error Method to the 1993 Refinery Study Data. An initial step in performing the MEM regression method is to determine the measurement variability in the emission rate measurements and in the screening value measurements. In order to assess the variability in emission rate measurements, field duplicate data were evaluated. To assess the screening value variability, the variability between screening measurements taken before and after bagging a component was evaluated. These variability estimates are used in the MEM regression method. A discussion of the variability estimates used in the MEM regressions is given below. Equations developed using the MEM technique are then presented.

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Emission Rate and Screening Value Variability. All components bagged had an initial and a final screening value that could be used as duplicates for screening variability analysis. Approximately 5% of the components bagged had duplicate mass emission rate measurements, called "field duplicates." Field duplicates were collected for the 1993 Refinery Study as part of the quality assurance procedures. In addition, several field duplicates were sent to Research Triangle Institute (RTI) for analysis. RTI acted as an independent auditor contracted by the U.S. EPA. Thus, for some of the bagging data there are replicates of three for a single component. For the most part, however, only duplicates were obtained. Because the field duplicates do not represent unique data points for the component being sampled, only the first sample of the duplicate pair was used in the emission correlation equation development. The second sample of the field duplicate pair was used for quality assurance/quality control purposes and in this variability assessment. Field duplicates were obtained by collecting a second canister sample from the same bagged component and do not include all sources of sampling variability. True sample duplicates would require constructing the bag and following the complete bagging procedure on a single component twice. During the Marketing Terminals Study, true sample duplicates were obtained. These variability results were used to supplement the field duplicate measurements obtained during the 1993 Refinery Study.

Field duplicates from pegged components and zero components were not included in this variability evaluation because these components were not included in the emission correlation equation development. In addition, those components that had an initial screening value and a final screening value that varied by more than a factor of two were not included in the emission correlation equation development and, therefore, were not included in this variability assessment (either for screening variability or as duplicates for emission rate variability determinations). It is also noted that the time that elapsed between duplicate screening measurements is higher than the time gap between field duplicate bagging measurements because screening values were obtained before and after bagging (at least 25 minutes apart) and typically field duplicates were taken within 10 minutes of each other.

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Table 2-5 shows the variability results for the six component categories. Variability can be quantified using a number of different statistics (e.g., the standard deviation, the relative percent difference, coefficient of variation). Because screening values are being compared to emission rates (which have different units of measure), the coefficient of variation (CV) was used for this analysis because it gives a measure of *relative* variability. The CV is calculated as a percent as follows:

Equation 2-4: 
$$CV = 100 \text{ x} \left( \frac{\text{Standard deviation}}{\text{Mean}} \right)$$

CVs were calculated for this analysis for each duplicate pair and then pooled for a particular component by squaring and then summing the CVs and dividing by the number of duplicate pairs. The square root of this measurement was then taken. Because CVs based only on two measurements are not very precise, pooling the CVs for multiple duplicate pairs provides a better estimate of the variability.

As shown in Table 2-5, CVs for the screening values varied from 16.6% for flanged connectors to 26.3% for non-flanged connectors. No significant differences in the screening value variability was observed for different component types. The overall pooled screening value CV was 21.8%. Changes in the emission rate CVs were more noticeable. The emission rate CVs, however, are not based on a very large number of duplicate pairs. It is of interest to note that the Marketing Terminals Study pooled emission rate CV was smaller than the 1993 Refinery Study pooled emission rate CV (14.5% versus 30.4%), even though the Marketing Terminals Study bagged measurements contained more potential sources of variability (recall that bags were reconstructed twice for the Marketing Terminals Study and this was not done for the 1993 Refinery Study). Emission rate CVs for the 1993 Refinery Study varied from 23.7% for open-ended lines to 55% for light liquid pump seals. Although there were differences between the emission rate variability estimates for different component types, the CVs were pooled over all component types because there were insufficient data for any one component type to adequately estimate the component-specific emission rate variability.

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# Table 2-5 Variability Estimates Obtained From Duplicate Samples<sup>a</sup>

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		Screening	Value Variability	Emissic	m Rate Measurer	nent Variabi	Ity Results
		5	(courts	1993 Refl	nery Study <sup>c</sup>	Machan	
		Number				Allhautert	ı ermual Study"
Component Type	Service	Duplicate Pairs	Variation (%) <sup>c</sup>	Number of Duplicate Pairs	Coefficient of Variation	Number of Duplicate	Coefficient of Variation
Connectors (Flanges)	All	19	16.6	f	(0) J	Pairs	(%)
Connectors (Non-	μV	ç				-	45.6
Flanges)	Ĩ	67	21.7		ــــ ا	2	0.3
Open-Ended Lines	ΠV	5					
		17	21.3	7	737	-	
Pump Seals	НL	10	263		F	4	24.3
Pump Seals	TT	36	- IC		-	-	- E
1.11		2	21.4	4	55.0	1	97.3
valves	All	136	22.3	<u>~</u>	100		
All Components <sup>§</sup>	11.4				4.07	7	3.2
		241	21.8	19	30.4	10	115
						> <b>*</b>	<b>.†</b>

B

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Not for Resale

Variability analysis performed on concentrations in linear space. ٩

1993 Refinery Study emission rate variability results obtained from duplicate samples. Duplicates obtained by extracting two Screening variability results obtained from initial and final screening values (i.e., before and after "bagging"). o

Marketing Terminals Study emission rate variability results obtained from duplicate samples. Duplicates obtained by samples from the same bagged component. ð

reconstructing the bag for a component twice and taking samples each time. e

Coefficient of variation (CV) = (100)(standard deviation)/mean.

No duplicate samples taken for this component type. CVs pooled over all component types. an

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Although it has been postulated that screening value measurements may be more variable than emission rate measurements, the data given in Table 2-5 do not support this. As already discussed, emission rate variability estimates were based on a small number of duplicate pairs. The larger relative variation seen in emission rate measurements could be partially due to the smaller sample size not being as representative or due to the fact that there are more sources of variation in obtaining an emission rate measurement than in obtaining a screening value measurement. That is, to calculate a mass emission rate in lbs/hr, a number of measurements must be obtained (e.g., temperature, nitrogen flow, oxygen, analytical results, etc.) all of which have measurement error. Furthermore, the screening value measurement variability is only an indicator of variability during a bagging test (which is desired), not an indicator of variability of screening value measurements over longer periods of time.

Table 2-5 compares the relative variability estimates for the untransformed screening value and emission rate measurements. These variability estimates are not used in the MEM regression but were given to illustrate the relative variation observed in emission rate measurements and screening value measurements. The information needed for the MEM regression is the standard deviation of the log(screening values) and the standard deviation of the log(emissionrates), because the MEM regression method is performed on the logarithms of the emission rates and the logarithms of the screening values (as the OLS regression was). Table 2-6 shows the variability estimates obtained for the log(screening values) and log(emission rates). The last column in Table 2-6 shows the ratio of the log(screening value) standard deviation to the log(emission rate) standard deviation. This ratio of screening value variability to emission rate variability varies from 0.31 to 1.05 for different component types. A ratio of 1 would indicate that the screening value measurements and the emission rate measurements are equally variable. Ratios larger than 1 indicate that the screening value data are more variable than the emission rate data, and ratios smaller than 1 indicate the screening value data are less variable than the emission rate data. As the ratio approaches zero (i.e., the emission rate data become more variable than the screening data), the MEM emission correlation equation will approach the OLS emission correlation equation. The ratio based on the pooled variability

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estimates is 0.59. This ratio of 0.59 was used in the development of the MEM emission correlation equations.

<u>MEM Emission Correlation Equations</u>. Table 2-7 shows the emission correlation equations that were developed using the MEM technique. Plots of these equations and the 95% confidence intervals for the equation are given in Figures 2-15 through 2-20. Detailed descriptions of the regression equation and confidence interval development are given in Appendix D. For comparison purposes, the emission correlation equations obtained from the OLS regression analysis (shown in Figures 2-9 through 2-14) are overlaid on the graphs. As shown in the figures, the regression lines produced by the MEM regression method are "lower" (i.e., predict lower average emission rates for a given screening value) than the regression lines produced by the OLS regression method for every component type.

Additional work is being performed to determine the effects that uncertainty in the emission rate and screening value variability estimates have on the MEM emission correlation equations. It has been shown, however, that the OLS regression method overestimates emissions by not accounting for the screening value variability. If, in fact, the screening value variability were non-existent, the MEM technique equations would be the same as the OLS equations.

To assess how well the OLS equations and the MEM equations perform in predicting actual measured emissions, a comparison of the sum of the predicted emission rates versus the sum of the measured emission rates was performed. Table 2-8 shows the results of this comparison for the OLS method and the MEM technique for each component category. As shown in the table, the MEM technique provides total emissions estimates that are closer to the actual measured total mass emissions for four of the six component categories. While the OLS method consistently overestimates the actual total measured emissions (for five of the six component categories), the MEM technique gives total measured emissions that are higher in some cases (three cases) and lower in other cases (four cases), indicating the method tends to be unbiased.

Table 2-6 Variability Estimates Used for the Measurement Error Method (MEM)<sup>a</sup>

		1	<u> </u>		T	1			
	Ratio of Screening Value Standard Deviation to Emission Rate Standard Deviation	ຍ 	ຍ 	0.92	ۍ ا	0.31	1.05	0.59	
urement ults <sup>c</sup>	Coefficient of Variation (%) <sup>d</sup>	<b>၁</b>	ວ ]	2.6	e	8.7	2.4	4.4	
n Rate Meas Hability Rest	Standard Deviation [log(ppm)]	ຍ 	ی ا	0.24	ۍ ا	0.72	0.22	0.37	
Emissio Vat	Number of Duplicate	မ 	e 	2	e 	4	13	19	
uriability	Coefficient of Variation ( <sup>0</sup> c) <sup>d</sup>	3.1	4.0	4.8	7.8	4.2	4.4	4.5	
ng Value Va Results <sup>b</sup>	Standard Deviation [log(ppm)]	0.17	0.22	0.22	0.27	0.22	0.23	0.22	-
Screeni	Number of Duplicates	19	29	21	10	26	136	241	
	Service	All	All	All	HL	ΓΓ	Gas	AII	
	Component Type	Connectors (Flanges)	Connectors (Non-Flanges)	Open-Ended Lines	Pump Seals	Pump Seals	Valves	All Components <sup>f</sup>	

Variability analysis performed on the logarithms of the concentrations.

1993 Refinery Study emission rate variability results obtained from duplicate samples. Duplicates obtained by extracting two Screening variability results obtained from initial and final screening values (i.e., before and after "bagging"). samples from the same bagged component. р. J q

Coefficient of variation (CV) = (100)(standard deviation)/mean.

No duplicate samples taken for this component type.

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CVs and standard deviations pooled over all component types.

Table 2-7 Predictive Emission Correlation Equations for THC Mass Emission Rates Using the Measurement Error Method (MEM)

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Component Type	Service	Number of Data Pairs	Measurement Error Method <sup>a,b</sup> (at surface)	Correlation Coefficient
Connectors (Flanges)	All	19	$ER=(4.0)(10^{-7})(SV)^{1.0}$	0.879
Connectors (Non-Flanges)	All	29	ER=(2.3)(10 <sup>-8</sup> )(SV) <sup>1.2</sup>	0.847
<b>Open-Ended Lines</b>	All	22	$ER=(1.2)(10^{-7})(SV)^{0.92}$	0.831
Pump Scals	HL	10	ER=(2.0)(10 <sup>-6</sup> )(SV) <sup>1.1</sup>	0.903
Pump Seals	ГГ	27	ER=(6.5)(10 <sup>-5</sup> )(SV) <sup>0.48</sup>	0.646
Valves	AII	141	$ER=(8.9)(10^{-7})(SV)^{0.86}$	0.810

Total hydrocarbon 11 THC

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- Light liquid 11 ΓΓ
- Heavy liquid 11 HL All
- Gas, light liquid, and heavy liquid services II
  - Predicted emission rates in lbs/hr 11 H

ER

- OVA screening value in ppm
- Emission correlation equation developed using the Measurement Error Method (MEM) that accounts for errors in both the emission rate and screening value measurements. đ 9
  - Emission correlation equations developed using OVA screening values obtained at the surface of the component, except for pump seals. Pump seals screened at  $\leq 1$  cm from the component.

### Predicted Using the Ordinary Least-Squares (OLS) Method and the Comparison of the Total Measured Emissions to Total Emissions **Measurement Error Method (MEM)** Table 2-8

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				Sum of Predic Ra (Dis	ted Emission tes fir)	Difference Be Predicted 4 Measured Bi	tween Sum of and Sum af nission Rates
Component Type	Service	Sample Size	Sum of Measured Emission Rates (Ibs/hr)	OLS Method	MEM Technique	0LS Method	MEM Technique
Connectors (Flanges)	All	19	0.0330	0.055	0.034	0.022	0.00039
Connectors (Non-Flanges)	All	29	0.0853	0.151	0.0451	0.0657	-0.0402
Open-Ended Lines	All	22	0.0294	0.026	0.0132	-0.0032	-0.0162
Pump Seals	HL	10	0.0392	0.120	0.0844	0.0812	0.0453
Pump Seals	ΓΓ	27	0.196	0.233	0.0997	0.0365	-0.0965
Valves	All	141	0.285	0.417	0.224	0.132	-0.0611
All Compoi	nents	248	0.668	1.00	0.500	0.334	-0.168

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Not for Resale

LL = Light liquid HL = Heavy liquid All = Gas, light liqu

= Gas, light liquid, and heavy liquid services













### Comparison to Other Studies

The newly developed THC emission correlation equations resulting from the OLS regression analysis were compared to the emission correlation equations developed during the 1980 Refinery Study and the Marketing Terminals Study. Graphical comparisons of the 1980 Refinery Study, the Marketing Terminals Study, and the 1993 Refinery Study emission correlation equations are given. In addition, an investigation was performed in order to explain the large differences observed between the 1980 Refinery Study and the 1993 Refinery Study emission correlation equations. An explanation for these differences is given below.

<u>Comparison of New Emission Correlation Equations to 1980 Refinery Study and Marketing</u> <u>Terminals Study Emission Correlation Equations</u>. In this section, graphical comparisons between the 1993 Refinery Study emission correlation equations resulting from the OLS regression analysis and the 1980 Refinery Study and Marketing Terminals Study emission correlation equations are given.

In examining discrepancies between emission correlation equations, several differences between the data collection and analysis methods used during the 1980 Refinery Study and the other two studies are noted:

- 1980 Refinery Study screening measurements were collected using a Bacharach Instrument Threshold Limit Value Sniffer (TLV Sniffer®) instrument calibrated with hexane; Marketing Terminals Study and 1993 Refinery Study screening measurements were collected using an OVA 108 instrument calibrated with methane;
- 1980 Refinery Study emission rate measurements were collected primarily using the vacuum method; Marketing Terminals Study and 1993 Refinery Study emission rate measurements were collected using the blow-through method (see U.S. EPA Protocols Document for descriptions of these methods); and
- 1980 Refinery Study emission correlation equations included data from pegged components. Data from pegged components were not included in the Marketing Terminals Study and 1993 Refinery Study emission correlation equation development. Instead, pegged component emission factors were developed separately.

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In a 1979 report entitled Valve Screening Study of Six San Francisco Bay Area Petroleum Refineries (Radian, 1979), also referred to as the Valve Screening Study, comparisons were made between side-by-side OVA and TLV Sniffer® measurements obtained at the component source for over 100 valves. The results of these comparisons showed that TLV Sniffer® measurements tended to be one-half to one-fifth the OVA measurements. Thus, one would expect the relationship between emission rates and TLV Sniffer® screening values to be different than the relationship between the same bagged emission rates and OVA screening value. If these two equations were overlaid, a given TLV Sniffer® screening value, say of 10 ppm, would result in a higher predicted emission rate than an OVA screening value of 10 ppm. This does not imply that the TLV Sniffer® screening values be used with TLV Sniffer® emission correlation equations and OVA screening values be used with OVA emission correlation equations.

All screening value measurements obtained for the Marketing Terminals Study, the 1993 Refinery Study, and the 1980 Refinery Study were obtained at the component surface with the exception of pump seals. Pump seals were screened between the surface and 1 cm from the component depending on the pump seal accessibility and whether or not it was in service (with more distance given to rotating pump shafts with the pump in service).

It is important to keep in mind the aforementioned considerations in examining differences between the 1980 Refinery Study emission correlation equations and the emission correlation equations from the other studies. The key facts to remember are that the 1980 Refinery Study emission correlation equations were based on TLV Sniffer® screening measurements and included pegged components. The 1993 Refinery Study and Marketing Terminals Study emission correlation equations were based on OVA screening measurements and did not include pegged components.

Table 2-9 gives the emission correlation equations that were developed for the 1993 Refinery Study and those developed during the 1980 Refinery Study and the Marketing Terminals

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Study. As shown in Table 2-9, the component categories developed for the 1993 Refinery Study differ from the component categories used in the 1980 Refinery Study and the Marketing Terminals Study. In order to graphically compare the 1993 Refinery Study data to data from older studies, equations and confidence intervals were developed for the 1993 Refinery Study data using the same component categories that have been used in previous studies. These component categories are:

- Connectors (flange and non-flange) in all services;
- Open-ended lines in all services;
- Pump seals in heavy liquid service;
- Pump seals in light liquid service;
- Valves in gas service; and
- Valves in light liquid service.

No equation exists from previous studies for valves in heavy liquid service.

Shown in Figures 2-21 through 2-26 are the emission correlation equations for the 1993 Refinery Study overlaid with the 95% confidence intervals for the mean. As stated previously, for some of these component categories (e.g., connectors and valves), the 1993 Refinery Study emission correlation equations are not the same as those presented in Table 2-9, but were developed specifically for these graphical comparisons. Emission correlation equations that were developed during the earlier refinery and marketing terminal studies are overlaid on these graphs. No open-ended line emission correlation equations were developed during the 1980 Refinery Study. In addition, no emission correlation equations for pump seals in heavy liquid service and for valves in gas service were developed during the Marketing Terminals Study. Screening value ranges shown in Figures 2-21 through 2-26 are the screening value ranges for which actual data were collected.

Shown in Figure 2-21 are the emission correlation equations for connectors in all services. This includes flange connectors and non-flange connectors. Although the slopes of the 1980 Refinery Study and the 1993 Refinery Study equations appear to be the same, the intercept for the 1980 Refinery Study equation is almost an order of magnitude higher than the

Table 2-9

## **Comparison of 1993 WSPA Refinery Emission Correlation Equations** With Established Emission Correlation Equations<sup>a</sup>

		1993 Refin	nery Study		
Component Type	Service	OLS Method <sup>b</sup>	MEM Technique <sup>c</sup>	Marketing Terminals Study <sup>b</sup>	1980 Refinery Study <sup>D</sup>
Connectors (Flanges)	All <sup>d</sup>	$\text{ER}=(1.3)(10^{-6})(\text{OVA})^{0.93}$	$\text{ER}=(4.0)(10^{-7})(\text{OVA})^{1.0}$	EB-(A 7)(10-5)(()(A)0.43	EP-(1 3(10-5)(TT V) <sup>0.88</sup>
Connectors	Alld	$ER=(2.8)(10^{-7})(OVA)^{1.0}$	$\text{ER}=(2.3)(10^{-8})(\text{OVA})^{1.2}$		
(Non-Flanges)					
Open-Ended Lines	Alld	$ER=(5.3)(10^{-7})(OVA)^{0.84}$	$\text{ER}=(1.2)(10^{-7})(\text{OVA})^{0.92}$	$ER=(5.7)(10^{-6})(OVA)^{1.0}$	ە 
Pump Seals	HL	$ER=(5.6)(10^{-6})(OVA)^{1.1}$	$ER=(2.0)(10^{-6})(OVA)^{1.1}$	e 	$ER=(1.9)(10^{-5})(TLV)^{1.0}$
Pump Seals	TL	ER=(2.3)(10 <sup>-4</sup> )(OVA) <sup>0.44</sup>	$\text{ER}=(6.5)(10^{-5})(\text{OVA})^{0.48}$	ER=(6.6)(10 <sup>-5</sup> )(OVA) <sup>0.53</sup>	$ER=(1.8)(10^{-4})(TLV)^{0.83}$
Valves	Gas	860 3	98 () 	e	$ER=(4.8)(10^{-7})(TLV)^{1.23}$
Valves	HL	$\left  \text{ER} = (3.7)(10^{-0})(\text{OVA})^{0.70} \right $	$ER=(8.9)(10^{-7})(OVA)^{0.00}$	9	ວ 
Valves	ΓΓ			ER=(6.3)(10 <sup>-6</sup> )(OVA) <sup>0.71</sup>	$ER=(3.2)(10^{-5})(TLV)^{0.80}$

- Ordinary Least-Squares II OLS
- Generalized Maximum Likelihood 11 GML
- Light liquid П
- Heavy liquid 11 ЦЦЦ
- Predicted emission rates in Ibs/hr. И
  - OVA screening value in ppm. Ш OVA
- TLV Sniffer® screening value in ppm. li ΠLV
- <sup>a</sup> 1980 Refinery Study emission correlation equations give results for non-methane organic compounds. The other emission correlation equations give results for total hydrocarbons.
- <sup>b</sup> Emission correlation equation developed using the ordinary least-squares method documented in the U.S. EPA Protocols Document (1993).
- <sup>c</sup> Emission correlation equation developed using the Measurement Error Method (MEM) that accounts for errors in both the emission rate and screening value measurements.
  - <sup>d</sup> "All" services includes HL, LL, and gas services for refinery studies, and LL and Gas services only for the Marketing Terminals Study. <sup>e</sup> No emission correlation equation developed.

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intercept for the 1993 Refinery Study equation. In addition, the 1980 Refinery Study equation is not contained within the 95% confidence intervals for the 1993 Refinery Study equation. There is overlap between the Marketing Terminals Study equation and the 95% confidence intervals for the 1993 Refinery Study equation. However, the slopes and the intercepts for the two equations differ dramatically. Differences between the Marketing Terminals Study and the 1993 Refinery Study equations could be due, in part, to the differences in connector sizes and connector types (i.e., flange versus non-flange). In addition, it is noted that the Marketing Terminals Study connector data contained fewer data pairs (n=36) and more variability, resulting in a correlation coefficient of only 0.41, whereas the 1993 Refinery Study equations is based on 48 data pairs and has a correlation coefficient of 0.82. It is also of interest to note that both the 1980 Refinery Study and the Marketing Terminals Study equations were based on screening values that were less than 10,000 ppm and greater than 10 ppm, whereas screening values obtained for the 1993 Refinery Study equation range from < 10 ppm to 100,000 ppm.

In Figure 2-22, the Marketing Terminals Study OEL emission correlation equation is compared to the 1993 Refinery Study OEL emission correlation equation. No OEL emission correlation equation was developed during the 1980 Refinery Study. As shown in the figure, the slopes of the two equations appear to be equivalent, but the intercepts differ by roughly an order of magnitude. Differences between these two equations are believed to be largely attributed to differences in OEL size. All of the measured 1993 Refinery Study OELs were  $\leq 1$  inch in diameter, whereas, a large number of the Marketing Terminals Study OELs were > 1 inch. The effect that differences in OEL size have on the emission correlation equations are discussed in more detail in a previous section (Multivariate Analysis Results).

Shown in Figure 2-23 are the emission correlation equations for pump seals in heavy liquid service developed during the 1980 Refinery Study and the 1993 Refinery Study. No heavy liquid pump seal emission correlation equation was developed during the Marketing Terminals Study. Again, the slopes for these two equations appear similar, whereas the intercept for the 1980 Refinery Study emission correlation equation is about five times higher. As shown in





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Figure 2-23, the 1980 Refinery Study emission correlation equation is partially contained within the 95% confidence intervals for the mean for the 1993 Refinery Study equation. However, it is noted that the 1993 Refinery Study emission correlation equation is based on only 10 data pairs, resulting in the broad confidence bands. Differences between the equations obtained for these two studies may be partially due to the limited sample size and the differences between OVA and TLV Sniffer® screening instruments. Furthermore, the 1980 Refinery Study data for heavy liquid pumps included a large percentage of pegged components (=21% pegged components). Pegged components were not included in the emission correlation equations in the 1993 Refinery Study because the exact screening values for those components, if any were found, were not known. Including pegged components at the pegged value (i.e., 100,000 ppm) would tend to attribute too much mass to a particular screening value.

Emission correlation equations for pump seals in light liquid service are given in Figure 2-24. As shown in the figure, the Marketing Terminals Study equation is lower than the 1993 Refinery Study equation, but it is contained within the 95% confidence intervals for the mean of the 1993 Refinery Study equation. Thus, there is no apparent statistical difference between the 1993 Refinery Study and Marketing Terminals Study equations. The 1980 Refinery Study equation is substantially higher than the current 1993 Refinery Study equation and appears to have a different slope. Differences between the 1980 Refinery Study equation cannot be completely explained, but may be due, in part, to fundamental differences in the data collection and analysis methods used in 1980 and 1993 as described above. It is known that, as with heavy liquid pumps, the 1980 Refinery Study included a large percentage of pegged components for light liquid pumps (~51% pegged components).

The equations for values in gas service are shown in Figure 2-25. No emission correlation equation was developed for values in gas service during the Marketing Terminals Study because there were insufficient data. The two gas value bagging measurements that were collected during the Marketing Terminals Study are plotted on the figure (the symbol "G" is

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used to denote these measurements). Although one of the measurements appears to line up with the 1993 Refinery Study equation, the other measurement is lower. It is not possible to draw any conclusions, however, based on only two measurements. As with the other figures, predictions obtained from the 1980 Refinery Study equation are one to two orders of magnitude higher than those obtained from the 1993 Refinery Study equation for high screening value ranges. This large difference may be due to the fact that pegged components were included in the 1980 equation (=57% pegged components) and that the 1980 equation was developed for TLV Sniffer® screening values instead of OVA screening values.

Shown in Figure 2-26 are the emission correlation equations for valves in light liquid service. As shown in the figure, the equation obtained during the Marketing Terminals Study and the 1993 Refinery Study are virtually identical. The differences between the 1980 and the 1993 Refinery Study light liquid valve equation are examined in detail in the next subsection.

To conclude, for valves and pump seals in light liquid service, no statistical difference was observed between the 1993 Refinery Study equations and the Marketing Terminals Study equations. Differences were observed between the 1993 Refinery Study and Marketing Terminals Study equations for connectors and OELs. These differences may be attributed, partly, to differences between components (e.g., component size, type, etc.).

The 1980 Refinery Study equations were one to two orders of magnitude higher than the 1993 Refinery Study equations for high screening value ranges, for every component type. However, there are essential differences between the 1980 Refinery Study and the 1993 Refinery Study data collection and analysis methods. As shown in the next section, the type of screening instrument used and the inclusion of pegged components in the emission correlation development accounts for a large portion of these differences.



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Comparison of 1993 Refinery Study Light Liquid Valve Data to 1980 Refinery Study Light Liquid Valve Data. In the previous subsection, it was shown that the 1980 Refinery Study emission correlation equations were consistently higher than the emission correlation equations developed for the 1993 Refinery Study. While a change in the distribution of screening values may have occurred between 1980 and 1993 (i.e., screening values may be lower due to increased I/M programs), this should not have an effect on the emission rate versus screening value relationship. There had been no obvious explanation for why the relationship between emission rate and screening value measurements for a particular component type would change. For the current study, Radian investigated why the emission rate versus screening value relationship observed in the 1980 Refinery Study is different from the relationship seen in more recent studies, and determined whether there was some difference in the methodologies used. In performing this investigation, Radian used light liquid valves as a test case because it contained the largest sample size for both studies.

The results of this investigation showed that there were two key differences between the 1980 Refinery Study equations and the 1993 Refinery Study equations. These differences, noted earlier, are:

- Data points corresponding to pegged component screening values were included in the 1980 emission correlation equations. Pegged component data were not included in the 1993 emission correlation equations.
- The 1980 Refinery Study equations were developed for TLV Sniffer® screening values. The 1993 Refinery Study equations were developed for OVA screening values. A previous study (Valve Screening Study) showed that TLV Sniffer® screening measurements could be two to five times lower than OVA screening measurements.

After correcting the 1980 Refinery Study data for these two differences, <u>no consistent</u> <u>differences were observed between the 1980 Refinery Study data and the 1993 Refinery Study</u> <u>data</u>. A description of how these adjustments were made is given below. This discussion is given in two parts:

- Adjustment of the 1980 Refinery Study light liquid valve emission correlation equation in order to compare it to the 1993 Refinery Study light liquid valve emission correlation equation; and
- Comparison of the original and revised 1980 Refinery Study emission correlation equation to the 1993 Refinery Study emission correlation equation for light liquid valves.

Throughout this discussion, unless otherwise stated, the terms OVA0, OVA1, and TLV0 are used to signify screening data gathered with an OVA at the surface of the component, with an OVA at 1 cm from the component, and with a TLV Sniffer® at the surface of the component, respectively.

### Recalculation of the 1980 Refinery Study Emission Correlation Equation Using 1993

<u>Methods</u>. For the current 1993 Refinery Study, the objective was to convert the 1980 Refinery Study light liquid valve emission correlation equation to an equation that could be more appropriately compared, for example, to the 1993 emission correlation equation. This involved two steps: removing the pegged data from the 1980 Refinery Study equation and, using the data given in the Valve Screening Study, develop an equation that relates a TLV0 screening measurement to an OVA0 screening measurement.

The raw 1980 refinery data were obtained from scatter plots of the data given in the 1980 Refinery Study. For this evaluation, these 119 light liquid valve data points were hand-keyed into a spreadsheet. The 1980 equation parameters (e.g., the slope, intercept and SBCF) were replicated using the data that were keyed in, confirming that the hand-keyed data matched the data used in the 1980 Refinery Study. Pegged component values were observed at both the 10,000 ppm and the 100,000 ppm level. These pegged component values were removed from the data set, resulting in a data set with a sample size of 79.

The only OVA versus TLV equation published in the Valve Screening Study was one which related OVA1 (i.e., an OVA measurement obtained at 1 cm from the component surface) measurements to TLV0 measurements. Although data were collected for OVA0 measure-

ments, no OVA0 to TLV0 relationship was developed for the Valve Screening Study. These data are given in Appendix B of the Valve Screening Study.

In reviewing the OVA0 and TLV0 data given in the Valve Screening Study, it was discovered that these data also included data from pegged components. Before performing the OVA0 to TLV0 regression for the current study, these pegged component values were removed. The following OVA0 to TLV0 regression was obtained:

Equation 2-5:  $Log_e(TLV0) = 0.657 + 0.792 Log_e(OVA0)$ 

Plots of this equation in linear space showed that OVA and TLV values agreed for screening values close to 20 ppm. At concentrations above 20 ppm, the OVA read higher than the TLV, with the gap widening as concentrations increased. A component that an OVA would screen at 10,000 ppm would register only 3,000 on a TLV screening instrument according to this relationship. A TLV0 screening value of 10,000 corresponds to an OVA0 screening value of 50,000 ppm.

After removing the pegged components from the 1980 Refinery Study light liquid valve data, the TLV0 to OVA0 adjustment described above was performed. It should be noted that there may be some inherent statistical biases associated with this TLV0 to OVA0 adjustment because both values contain measurement error.

Comparison of the Original and Revised 1980 Refinery Study Emission Correlation Equations to the 1993 Refinery Study Emission Correlation Equation for Light Liquid Valves. Figures 2-27 through 2-29 show the progression of the steps discussed above. Figure 2-27 shows the current 1993 Refinery Study emission correlation equation for light liquid valves overlaid with the 95% confidence intervals for the mean. The following three adjusted lines are overlaid on this plot:

• The 1980 Refinery Study emission correlation equation for valves in light liquid service. This equation was developed using TLV Sniffer® screening

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• The 1980 Refinery Study emission correlation equation after removing the pegged components. Removing the pegged components results in the 1980 Refinery Study equation being lowered roughly a half order of magnitude for the higher screening value ranges (i.e., > 1,000 ppm).

• The 1980 Refinery Study emission correlation equation for OVA after removing the pegged components. Removing the pegged components and adjusting the equation for OVA screening values results in the 1980 Refinery Study equation being lowered almost an order of magnitude for the high screening value ranges (i.e., > 1,000 ppm).

Figure 2-27 shows that even after the pegged components are removed and the equation is adjusted to be used for OVA screening values, the 1980 Refinery Study equation is still considerably higher than the 1993 Refinery Study equation for lower screening value ranges.

Figure 2-28 shows a plot of the adjusted 1980 data overlaid with the 1993 data. The symbols "O" and "N" are used to denote the old adjusted 1980 data and the new 1993 data, respectively. As shown in this figure, there does not appear to be any consistent difference between the "O's" and the "N's," with the exception of two "O" values that are in the 0.001-0.01 lbs/hr emission rate range for screening values less than 10 ppm. Although these two data points were not statistical outliers when an equation was developed based on the "O" data only, if the "O" and the "N" data are combined, these two data points are statistical outliers. Figure 2-29 shows the combined equation obtained by combining the "O" and the "N" data, after deleting the two "O" statistical outliers. The combined equation has a slope that is identical to the 1993 Refinery Study equation (slope = 0.77). The constant for the combined equation is slightly higher than the constant obtained for the 1993 Refinery Study equation (7.0 x  $10^{-6}$  versus  $4.8 \times 10^{-6}$ ).

To conclude, the 1980 Refinery Study data for light liquid valves appear to be surprisingly consistent with the 1993 Refinery Study, after adjusting the 1980 data so that it is comparable to the 1993 data. Although this exercise was performed for valves in light liquid service




only, comparable results might be expected for other valve categories, for connectors, and for OELs. Removing pegged components from the 1980 Refinery Study for pumps would also likely explain many of the differences between the 1993 Refinery Study and the 1980 Refinery Study.

#### ZERO COMPONENT EMISSION FACTORS

The average of actual emission rates associated with components whose screening values are zero parts per million (ppm) is referred to as the zero component emission factor for that type of component and service. In the U.S. EPA Protocols Document these are referred to as "default zero emission factors." In the past, zero component emission factors have been referred to as "default zero factors" because these emission factors were obtained by substituting a "default" zero screening value of 8 ppm into the component emission correlation equation. For the 1993 Refinery Study, actual emission rate measurements have been obtained for components whose screening values are zero (i.e., indistinguishable from background). Because these emission factors were determined based on measured results, they will be referred to as "zero component emission factors" instead of "default zero factors."

For this study, zero component emission factors were developed for the same component categories for which emission correlation equations were developed. These component categories are:

- Flange connectors in all services;
- Connectors (non-flanges) in all services;
- OELs in all services;
- Pump seals in heavy liquid service;
- Pump seals in light liquid service; and
- Valves in all services.

An additional zero component emission factor was obtained for pressure relief valves in gas service. The complete data set used to develop these zero component emission factors is



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given in Appendix C. Bagged emission rates obtained for components that screened at background levels were used in the zero component emission factor development.

The U.S. EPA Protocols Document recommends calculating the default zero emission factor as the mean of a lognormal distribution. The lognormal mean provides an estimate for the mean that is statistically unbiased and has the smallest error variance when the data are lognormally distributed. However, the lognormal mean gives a biased estimate of the mean if the distribution is not lognormal (Gilbert, 1987). Analysis of the emission rate data for zeroscreening components showed that the data were not lognormally distributed for four of the seven component categories. Thus, arithmetic means were used to estimate the zero component emission factors. The arithmetic mean provides a statistically unbiased estimate of the mean no matter what the underlying distributed, the arithmetic mean also has the minimum error variance property. The zero component emission factors are given in Table 2-10. The 95% confidence intervals for the mean zero component emission factors were calculated and are also shown in Table 2-10.

The new zero component emission factors range from  $1.9 \times 10^{-8}$  lbs/hr for pressure relief valves in gas service to 7.3 x  $10^{-6}$  lbs/hr for pump seals in light liquid services. Zero component emission factors for flanged connectors, non-flange connectors, OELs and valves were all based on at least nine bagged emission rates. The zero component emission factors for pump seals in heavy liquid service and light liquid service were based on five and seven data pairs, respectively. The zero component emission factor for pressure relief valves in gas service was based on only three data pairs.

# Comparison of New Zero Component Emission Factors With Established U.S. EPA Zero Component Emission Factors

Each new zero component emission factor was compared to a corresponding established zero component emission factor.

<b>Table 2-10</b>	1993 Refinery Study Zero Component THC
	<b>Emission Factors and 95% Confidence Intervals</b>

Component Type	Service	Number of Tests	Measured Zero Component Emission Factor (lbs/hr)	Lower 95% Confidence Limit (lbs/hr) <sup>2</sup>	Upper 95% Confidence Limit (lbs/hr)
Connectors (Flanges)	All	9	4.9 x 10 <sup>-7</sup>	4.4 x 10 <sup>-8</sup>	9.4 x 10 <sup>-7</sup>
Connectors (Non- Flanges)	All	12	1.7 x 10 <sup>-6</sup>	0	3.9 x 10 <sup>-6</sup>
Open-Ended Lines	All	9	5.7 x 10 <sup>-7</sup>	0	1.4 x 10 <sup>-6</sup>
Pressure Relief Valves	Gas	3	1.9 x 10 <sup>-8</sup>	7.5 x 10 <sup>-9</sup>	3.1 x 10 <sup>-8</sup>
Pump Seals	Heavy Liquid	5	4.3 x 10 <sup>-7</sup>	0	1.5 x 10 <sup>-6</sup>
Pump Seals	Light Liquid	7	7.3 x 10 <sup>-6</sup>	0	2.3 x 10 <sup>-5</sup>
Valves	All	57	6.6 x 10 <sup>-6</sup>	2.5 x 10 <sup>-6</sup>	1.1 x 10 <sup>-5</sup>

THC = Total hydrocarbon

All = Gas, light liquid, and heavy liquid services.

<sup>a</sup> Lower confidence limits of 0 represent calculated values that were negative.

Comparisons of the new and established zero component emission factors are shown in Table 2-11. If the established zero component emission factor is not contained within the 95% confidence interval for the new zero component emission factors, then the new zero component emission factor is statistically different from the established zero component emission factor. If the confidence limits for the new factor overlap with the established zero component emission factor, the new zero component emission factor is <u>not</u> statistically different from the established zero component emission factor.

The zero component emission factors published in the U.S. EPA Protocols Document are the most current factors and were therefore used for this comparison. The zero component emission factors published in the U.S. EPA Protocols Document were based on emission rates

Table 2-11 Comparison of 1993 Refinery Study Zero Component Emission Factors With Established Zero Component Emission Factors<sup>a</sup>

	•	Measured 1993 l	Refinery Stur	Iy Factors	Terminals Stu-	By Factors	Document F	actors
Component Type Serv	Er Er	Zero Component mission Factor (lbs/hr)	Lower 95% Confidence Limit (bs/hr) <sup>b</sup>	Upper 95% Confidence Limit (Ibs/hr)	Zero Component Emission Factor (lbs/hr) <sup>c</sup>	Contained within 95% Confidence Intervals?	Zero Component Emission Factor (Ibs/hr) <sup>d</sup>	Contained within 95% Confidence Intervals?
Connectors Al (Flanges)	=	4.9 x 10 <sup>-7</sup>	4.4 x 10 <sup>-8</sup>	9.4 x 10 <sup>-7</sup>	6.5 x 10 <sup>-6</sup>	No	1.3 x 10 <sup>-6</sup>	No
Connectors Al (Non-Flanges)	=	1.7 x 10 <sup>-6</sup>	0	3.9 x 10 <sup>-6</sup>		No		Yes
Open-Ended Al Lines	II	5.7 x 10 <sup>-7</sup>	0	1.4 x 10 <sup>-6</sup>	4.4 x 10 <sup>-6</sup>	No	e 	ວ 
Pressure Relief Ga Valves	gg	1.9 x 10 <sup>-8</sup>	7.5 x 10 <sup>-9</sup>	3.1 x 10 <sup>-8</sup>	e 	°	1.7 x 10 <sup>-5</sup>	No
Pump Seals HI	L L	$4.3 \times 10^{-7}$	0	1.5 x 10 <sup>-6</sup>	e 	e 	1.7 x 10 <sup>-5</sup>	No
Pump Seals LJ		7.3 x 10 <sup>-6</sup>	0	2.3 x 10 <sup>-5</sup>	3.9 x 10 <sup>-5</sup>	No	1.7 x 10 <sup>-5</sup>	Yes
Valves Gé	31S	6 4 10-6	<b>ع د ۲۵</b> -6	1 + 10-5	5.9 x 10 <sup>-6</sup>	Yes	1.4 x 10 <sup>-6</sup>	No
Valves LJ	L	01 V 0.0	01 V C'7	01 V 1.1	3.5 x 10 <sup>-6</sup>	Yes	1.1 x 10 <sup>-6</sup>	No

HL = Heavy liquid service

LL = Light liquid service

All = Gas, light liquid, and heavy liquid services

U.S. EPA Protocols Document factors give results for non-methane organic compounds. The other zero component emission factors give results for total hydrocarbons.

<sup>b</sup> Lower confidence limits of 0 represent calculated values that were negative.

- c American Petroleum Institute, 1993.
  - d U.S. EPA, 1993.
- No zero component emission factor developed for this component type and service type.

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collected from Synthetic Organic Chemical Manufacturers Industry (SOCMI) facilities. However, the U.S. EPA Protocols Document states that they can be applied for all component categories. As shown in the table, these emission factors were contained within the 95% confidence intervals for the new 1993 Refinery Study zero component emission factors for nonflange connectors and light liquid pumps. Thus, there is no statistically significant difference between the U.S. EPA emission factors and the 1993 Refinery Study emission factors for non-flange connectors and light liquid pumps. The U.S. EPA emission factors were not contained within the confidence intervals for the new emission factors for five component categories: flange-connectors, pressure relief valves, pump seals in heavy liquid service, valves in gas service, and valves in light liquid service. The new zero component emission factors from this study are significantly lower than the 1993 U.S. EPA Protocols Document zero component emission factors for pressure relief valves and heavy liquid pump seals. The U.S. EPA emission factors for valves in light liquid and gas service, however, were found to be lower than the 1993 Refinery Study emission factors. The 1993 Refinery Study zero component factors are likely to be more accurate for use in the refining industry than the U.S. EPA emission factors which were developed based on SOCMI data.

Comparisons between the 1993 Refinery Study zero component emission factors and the Marketing Terminals Study zero component emission factors were also performed. The Marketing Terminals Study zero component emission factors were found to be higher than the 1993 Refinery Study zero component emission factors for every component category with the exception of light liquid and gas valves. No statistically significant differences were found between the Marketing Terminals Study zero component emission factors for light liquid and the 1993 Refinery Study zero component emission factors for light liquid and the 1993 Refinery Study zero component emission factors and the 1993 Refinery Study zero component emission factors for light liquid and gas valves. Zero component emission factors were not developed for pressure relief valves and pump seals in heavy liquid service in the Marketing Terminals Study, and thus no comparisons could be made for these categories.

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# PEGGED COMPONENT EMISSION FACTORS

A pegged component is a component whose screening value is above the upper measurable limit of the analyzer, (i.e., usually > 10,000, or > 100,000 ppm for the OVA analyzer with a dilution probe). Under these circumstances, the actual screening value is unknown. Following the suggestion of the U.S. EPA, the estimated emission rate for such pegged components would be the average value for several components subjected to the bagging test.

For this study, bagged emission rates were obtained for the following pegged component types:

- Flange connectors in all services;
- Connectors (non-flanges) in all services;
- OELs in all services;
- Pump seals in light liquid service; and
- Valves in all services.

No pegged components were found for pump seals in heavy liquid service; thus, no pegged emission rates could be obtained for this component type.

The pegged component emission factors for the component categories listed above are given in Table 2-12. Pegged component emission factors were calculated as the arithmetic averages of the pegged emission rates in the same manner as the zero component emission factors were developed. The 95% confidence intervals for the pegged component emission factors are also given in Table 2-12.

The 1993 Refinery Study pegged component emission factors are compared to those in the 1980 Refinery Study in Table 2-12. The 1980 Refinery Study pegged component emission factors were calculated from data from the 1980 Refinery Study by the U.S. EPA after the 1980 report was issued, and are those presented in the U.S. EPA Protocols Document. The 1993 Refinery Study pegged component emission factors are more than an order of magnitude lower than the 1980 Refinery Study pegged component emission factors for each of these component categories. The reason for the magnitude of the decrease in pegged component

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Table 2-12

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Comparison of 1993 Refinery Study to 1980 Refinery Study Pegged Component Emission Factors

			16091	Refinery Study <sup>a</sup>		
Component Type	Service	Number of Tests	Measured Pegged Emission Factor (Ibs/hr)	Lower 95% Confidence Limit (lbs/hr) <sup>b</sup>	Upper 95% Confidence Limit (lhs/hr)	1980 Refinery Studyate
Connectors (Flanges & Non-Flanges)	All	q	p	p	p	8.5 x 10 <sup>-1</sup>
Connectors (Flanges)	All	3	2.1 x 10 <sup>-2</sup>	0	9.4 x 10 <sup>-2</sup>	p_
Connectors (Non- Flanges)	All	14	3.0 x 10 <sup>-2</sup>	8.3 x 10 <sup>-3</sup>	5.3 x 10 <sup>-2</sup>	P
Open-Ended Lines	IIA	11	2.5 x 10 <sup>-2</sup>	5.6 x 10 <sup>-3</sup>	4.5 x 10 <sup>-2</sup>	P
Pump Seals	Light Liquid	Ś	6.4 x 10 <sup>-1</sup>	0	2.1	6.5
Valves	All	38	3.6 x 10 <sup>-2</sup>	1.3 x 10 <sup>-2</sup>	5.9 x 10 <sup>-2</sup>	P
Valves	Gas	р	p	p	p	2.6
Valves	Light Liquid	p	p	, a	p	7.7 x 10 <sup>-1</sup>

THC = Total hydrocarbons

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All = Gas, light liquid, and heavy liquid services

All components except pumps were measured at the surface. Pumps were measured at  $\leq 1$  cm from the surface. Lower confidence limits of 0 represent calculated values that were negative. B **9** 

From U.S. EPA Protocols Document (U.S. EPA, 1993).

Not determined.

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emission factors is not fully understood at this time. The difference could be based in part on the different screening instruments used. The TLV Sniffer® can measure higher screening values than the OVA before becoming pegged. Other potential reasons for the difference in pegged factors may be related to changes in component design or the long-term impacts of I/M programs.

Not all of the pegged components pegged the instrument at > 100,000 ppm. Pegged component screening values ranged from > 40,000 ppm to > 140,000 ppm. If the component was visibly dripping liquids it was also considered a pegged component. In these cases, liquid concentrations that dripped into the bag were analyzed and added to the total mass emission rate. In addition, there were two cases where the OVA screening value was less than 10,000 ppm, but the component was visibly dripping liquids. These were also regarded as pegged components.

The pegged component emission factors range from  $2.1 \times 10^{-2}$  lbs/hr for flanged connectors in all services to 6.4 x  $10^{-1}$  lbs/hr for pump seals in light liquid services. Pegged component emission factors for non-flange connectors, OELs and valves were all based on at least 11 bagged emission rates. The pegged component emission factors for flanged connectors and pump seals in light liquid service were based on three and five data pairs, respectively.

For comparison, the emission rates that would be obtained by substituting a screening value of 100,000 ppm into the 1993 emission correlation equations were also calculated. These components could have had screening values from 100,000 ppm to 1,000,000 ppm. Therefore, it would be expected that the measured mass emission rates would be higher than those calculated only at 100,000 ppm. This calculation was performed for both the OLS emission correlation equations and the MEM emission correlation equations. These calculated values are shown in Table 2-13. For every component type, the calculated emission factor was either lower than the measured emission factor, or was contained within the 95% confidence limits for the measured emission factor. Thus, in the cases where there was a statistically significant difference between the measured emission factors and the calculated

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emission factors, the measured emission factors were higher than the calculated emission factors. Therefore, the recommended approach for handling pegged components is to use the measured pegged component emission factors in these cases.

# Table 2-13 1993 Refinery Study Pegged Component Emission Factors(THC) Comparison of Measured Emission Factors to<br/>Calculated Emission Factors

						Calculate Comp Emission	l Pegged onent Factors <sup>a</sup>
Component Type	Service	Number of Tests	Measured Pegged Component Emission Factor (lbs/hr)	Lower 95% Confidence Limit (lbs/hr) <sup>b</sup>	Upper 95% Confidence Limit (Ibs/hr)	1993 Least- Squares Equations (lbs/hr)	MEM Equations (lbs/hr)
Connectors (Flanges)	All	3	2.1 x 10 <sup>-2</sup>	0	9.4 x 10 <sup>-2</sup>	5.5 x 10 <sup>-2</sup>	3.8 x 10 <sup>-2</sup>
Connectors (Non-Flanges)	All	14	3.0 x 10 <sup>-2</sup>	8.3 x 10 <sup>-3</sup>	5.2 x 10 <sup>-2</sup>	4.2 x 10 <sup>-2</sup>	1.4 x 10 <sup>-2</sup>
Open-Ended Lines	All	11	2.5 x 10 <sup>-2</sup>	5.6 x 10 <sup>-3</sup>	4.5 x 10 <sup>-2</sup>	8.6 x 10 <sup>-3</sup>	4.8 x 10 <sup>-3</sup>
Pump Seals	Light Liquid	5	6.4 x 10 <sup>-1</sup>	0	2.1	3.5 x 10 <sup>-2</sup>	1.6 x 10 <sup>-2</sup>
Valves	All	38	3.6 x 10 <sup>-2</sup>	1.3 x 10 <sup>-2</sup>	5.9 x 10 <sup>-2</sup>	2.8 x 10 <sup>-2</sup>	1.7 x 10 <sup>-2</sup>

THC = Total hydrocarbon

All = Gas, light liquid, and heavy liquid services.

<sup>a</sup> Calculated pegged component emission factors obtained by substituting 100,000 ppm into the emission correlation equation.

<sup>b</sup> Lower confidence limits of 0 represent calculated values that were negative.

An alternative technique to determine the mass emissions from pegged components is being considered at this time. The equation for the determination of mass emissions that is currently presented in the U.S. EPA Protocols Document, and repeated in Figure 2-1 in this

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report, is based on the assumption that the volume flow of the leaking hydrocarbons into the sample bag is insignificant compared with the flow of nitrogen (and air) through the bag. For components that are not pegged, this assumption is reasonable. However, for pegged components, the volume flow of the hydrocarbon leak can be significant if the leak rate is comparable to the nitrogen flow rate. A modified method for calculating the flow rate into the bag (Q) is being considered to account for this hydrocarbon flow rate. This revised flow rate would be calculated as follows:

Equation 2-6:

$$Q = \frac{N_2, l/min}{1 - \left[\frac{O_2, \%}{21} + \left(10^{-6} * \text{ THC, ppmv} * \frac{\text{cal. gas MW}}{\text{HC MW}}\right)\right]} \left[0.06 \frac{\text{m}^3/\text{hr}}{l/\text{min}}\right]$$

Where:THC ppmv=bag hydrocarbon concentration in ppmv; and<br/>molecular weight of the calibration gas (propane in this<br/>study); andHC MW=hydrocarbon molecular weight of the leaking hydrocarbon.

This calculated flow rate (Q) could then be substituted into the equation that calculates mass emissions as shown in Figure 2-1. When the resulting mass emissions are averaged for the pegged components, the result is the alternative pegged component emission factors shown in Table 2-14. Table 2-14 compares these alternative pegged component emission factors to those calculated using the methodology in the U.S. EPA Protocols Document. Three of the five pegged component emission factors computed for the 1993 Refinery Study increase 12-17% by using this modified method of calculation compared with the U.S. EPA methodology. The alternative pegged component factor for light liquid pumps increases by approximately one-third over the factors calculated by the U.S. EPA methodology. The pegged component factor for connector-flanges approximately doubles by the alternative method. However, this particular pegged component emission factor was based on only three tests and therefore has a high degree of uncertainty. One of these three tests had a very large contribution of hydrocarbons relative to the total flow into the bag, which results in a large difference in estimated emissions.

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# Table 2-14. Comparison of Alternative Pegged Component Emission Factors that Account for Hydrocarbon Flow into Bag to Pegged **Component Emission Factors Based on U.S. EPA Methodology**

Component Type	Service Type	Number of Tests	Pegged Component Emission Factor Based on U.S. EPA Methodology (lbs/hr)	Alternative Pegged Component Emission Factor including Hydrocarbon Flow into Bag(lbs/hr)	Percent Difference (%)
Connector- Flange	All	3	2.1 x 10 <sup>-2</sup>	4.5 x 10 <sup>-2</sup>	115
Connector- Other	All	14	3.0 x 10 <sup>-2</sup>	3.6 x 10 <sup>-2</sup>	17
OEL	All	11	2.5 x 10 <sup>-2</sup>	2.8 x 10 <sup>-2</sup>	12
Pump	LL	5	6.4 x 10 <sup>-1</sup>	8.8 x 10 <sup>-1</sup>	37
Valve	All	38	3.6 x 10 <sup>-2</sup>	4.1 x 10 <sup>-2</sup>	13

All = Gas, light liquid, and heavy liquid services

LL Light liquid =

Open-ended line OEL =

As a check, this revised calculation for flow rate was also applied to the data used to calculate the emission correlation equations presented in this study. The revised flow rate had virtually no impact, within the significant figures used, on the emission correlation equations. Therefore, it was not necessary to generate alternative emission correlation equations using this alternative method of calculation.

# COMPARISON OF VAPOR LEAK COMPOSITION WITH LIQUID STREAM COMPOSITION

One of the objectives of this study was to compare the relative concentrations of selected chemical species in the vapor leaking from bagged components (i.e. fugitive emissions) with the concentrations of those same chemical species in the product flowing through the components. The chemical species evaluated were:

- Benzene;
- Ethylbenzene;
- Cumene;
- Hexane;

Isooctane:

Propylene; Xylenes.

- Toluene; and
- 2 88

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The results of the vapor leak composition analyses are summarized in Table 2-15. Typically, the computed ratios (mass fraction in vapor to mass fraction in liquid) for each species are in the range of 0.2 to 2.0. However, the selected species in some of the samples appeared to concentrate between the product and the captured leak. These anomalous values occur most commonly in canisters with low (0–15 ppmv) NMOC concentrations where there was poor agreement between the gas chromatography (GC) speciation data and the total NMOC results. Table 2-15 is limited to results from liquid streams for which the bag NMOC concentration was greater than 15 ppmv. Appendix B includes data for all components for which liquid/vapor samples were taken.

Because of the scatter in the data, the computed upper and lower 95% confidence intervals for the mean of the leak/product mass fractions were in some cases negative (not meaningful) and large positive numbers, respectively. The results for the mean values of some of the chemical species are dominated by two samples with extremely high ratios (V066, V072) that are caused by very low concentrations in one liquid stream sample used in the development of both ratios. This liquid stream was a heavy liquid, and the target analytes represented only 0.2% of the total THC in the stream. This 0.2% represents an extremely low percentage when compared with other liquid samples used in this analysis. The scatter of the data is believed to be related to the large number of variables in the testing process. Isolating variables in a field setting has proven difficult. Additional analysis in a controlled laboratory setting is recommended.

Other than the contradictory results from several of the lower concentration values, no trend was observed regarding leak rate, species vapor pressure, component type, stream composition, or stream viscosity.

Traditionally, it has been assumed that the composition of the vapor leak was the same as the liquid stream. It is assumed that the liquid in the line makes its way through the seal and vaporizes after it reaches the ambient air. The data gathered in this study are too erratic to conclusively support the theory that fugitive leaks are always of the same composition as the

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(Mass Fraction in Vanor to Mass Fraction in Liquid) Table 2-15 Refinery Fugitive Emissions vs. Stream Comparisons - Mass Fraction Basis

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Bag Sample Number	Liquid Sampla Number	OVA Screan (ppmy)	Berane	Propylene	Isooctane	Benzene	Tohene	Total Xvirnes	Ethyl Renzene		All Speciated		1
V034	V040	13	QN	QN	QN	DD	0.1	0.03	0.11	QN	0.14	H, Purge	Vomponent Type 1" Connector
V036	V041	297	1.39	QN	Q	0.7	0.2	0.03	0.05	QN	0.67	He Svstem	3/4" Valve
V047	V050	109	6.66	ND	QN	3.0	3.0	2.56	2.87	61.95	16.50	Lt Liquid	3" Gate Valve
V048	V050	3600	3.46	QN	QN	1.2	1.4	1.26	1.67	22.49	8.12	Lt Liquid	1" Connector
V049	V051	1200	3.36	QN	QN	2.1	1.7	0.98	1.35	18.70	7.98	Lt Liquid	2" Gate Valve
V065	V069	167	QN	Q	QN	QN	3.5	3.11	3.49	40.43	9.51	Hvy Liquid	3/4" Globe Valve
V066	V070	1430	QN	Ð	Q	Q	95.2	41.52	78.57	QN	180.61	Hvy Liquid	1" Threaded Conn.
V072	V070	323	QN	Q	QN	QN	26.12	25.66	36.48	DN	78.76	Hvy Liquid	Pump
X023	X029L	39000	0.89	QN	Q	0.79	0.51	QN	QN	QN	0.92	Lt Gasoline	6" Valve
X023*	X029L	39000	0.31	Q	QN	1.16	0.65	QN	QN	QN	0.48	Lt Gasoline	6" Valve
X024	X028L.	893	0.97	QN	QN	1.31	0.75	0.47	0.51	QN	0.97	Naphtha Feed	10" Valve
X027	X031L	1780	2.15	QN	DN	2.50	1.27	0.52	0.57	QN	1.57	Reactor Feed	Pump
W018	W017	8000	1.75	QN	QN	2.04	2.56	1.25	1.29	QN	2.91	Not Given	Open Ended Line
W018*	W017	8000	2.47	QN	QN	2.37	3.28	2.61	2.95	QN	2.63	Not Given	Open Ended Line
W028	W030L	184	0.74	QN	QN	0.81	0.71	0.12	0.49	QN	0.59	Crude	Pump
W028*	W030L	184	0.67	Q	QN	1.33	0.61	QN	QN	QN	0.32	Crude	Pump

NOTES:

ND = Not Detected

Bag samples flagged with \* analyzed with EPA Method TO-14 (GC/MS). All others analyzed with EPA Method TO-3 (GC/PID-FID).

Canisters with less than 15 ppmv NMOC were prone to have poor agreement between ASTM Method D-3416 NMOC and EPA Methods TO-14 and TO-3 speciated compounds. These canisters are included in Appendix B refinery-specific tables, but have been excluded from this composite table. Results are erratic and of low confidence. Therefore, it is not recommended to use these mass fraction relationships to estimate specific individual species emissions.

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Table 2-15 (Continued)

		21	S.	17	18	21	17	4	QN	17		nts	Data Poi
		34.0	57.5	18.1	10.0	16.4	1.8	1.6	DN	2.6	ence	% Confide	Upper 95
		-3.9	0.9	-2.6	-1,0	-2.7	1.1	-0.6	ΟN	1.0	ence	5% Confid	Lower 9.
		41.6	22.8	20.2	11.0	21.0	0.7	0.7	QN	1.6	eviation	Standard D	Sample 5
		15.0	29.2	7.7	4.5	6.8	1.5	0.5	QN	1.8			Mean
4" Valve	Unknown	0.89	2.42	0.77	0.42	0.91	0.87	QN	QN	0.68	75	Z035	Z033
Connection	Reg UL	0.37	QN	0.10	0.09	0.24	1.08	0.35	QN	1.22	74000	W073	W072*
Connection	Reg UL	0.17	QN	QN	0.01	0.08	0.61	0.04	QN	0.91	74000	W073	W072
Valve	Reg UL	1.10	QN	0.38	0.37	0.90	1.58	1.52	QN	2.21	23000	W071	W070*
Valve	Reg UL	0:30	QN	0.09	0.07	0.29	1.29	0.15	QN	1.08	23000	W071	W070
Component Type	Product	All Speciated Compounds	Cumene	Ethyl Benzene	Total Xylenes	Totuene	Benzene	Isooctane	Propylene	Hexane	OVA Screen (puny)	Liquid Semple Number	Rag Sample Number

Bag samples flagged with \* analyzed with EPA Method TO-14 (GC/MS). All others analyzed with EPA Method TO-3 (GC/PID-FID). ND = Not Detected NOTES:

Canisters with less than 15 ppmv NMOC were prone to have poor agreement between ASTM Method D-3416 NMOC and EPA Methods TO-14 and TO-3 speciated compounds. These canisters are included in Appendix B refinery-specific tables, but have been excluded from this composite table. Results are erratic and of low confidence. Therefore, it is not recommended to use these mass fraction relationships to estimate specific individual species emissions.

product stream. However, no hardware or chemical species-related trends are supported by these data either. Therefore, it is currently appropriate that refineries continue to estimate emissions of individual VOC species by assuming that the mass fractions in emitted VOCs are the same as the mass fractions in the process streams.

The results of the vapor leak composition analyses for all components sampled are presented in Appendix B. The analysis of the samples from each of the refineries is tabulated in a sequence of four tables presenting the analytical data and computed results. The data were processed as follows:

- Laboratory analysis of the canisters containing captured fugitive emissions from the bagged components were compiled into the first table of each refinery data set. Laboratory analyses were performed using TO-3 (GC/PID-FID) and/or TO-14 (GC/MS). These ppmv data were compiled into Table 1 of each refinery data set. Additional data, including the bagged component type and size, screening ppm level, and process stream name were also tabulated. These data were collected in order to note any correlation between these parameters and the relative leak/stream compositions.
- The ppmv values reported by the laboratory were converted to mass units (µg/L). The canister NMOC values (Method 3416 or Method 18 w/Method 3416) were also converted to µg/L units and tabulated. These µg/L canister data are recorded in Table 2 of each refinery data set.
- Product liquid stream laboratory analysis data (Method 8240 GC/MS) reported in µg/L were matched to the canister samples. Product stream densities were not recorded. Therefore, the total NMOC content of all product streams were assumed to be approximately 750,000 µg/L. Liquid speciation data are recorded in Table 3 of each refinery data set.
- The fourth table in each set lists the relative proportions of each of the selected chemical species. These tables are analogous to Table 2-14. The values in these tables were computed as follows:

Canister species µg/L Canister NMOC µg/L Equation 2–7: Product liquid stream species µg/L 750,000 µg/L NMOC in liquid

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#### Section 3

#### CONCLUSIONS AND RECOMMENDATIONS

#### EMISSION CORRELATION EQUATIONS

The 1993 Refinery Study discusses two separate sets of new emission correlation equations as shown on Table 3-1.

The Measurement Error Method (MEM) accounts for the variability in screening measurements as well as variability in mass emission rates. The OLS regression methods, which are recommended in the U.S. EPA Protocols Document, do not account for the variability in the screening measurements. The MEM technique has the potential to be superior to the previously used statistical methods for use in developing emission correlation equations. Additional work is in progress to further evaluate the MEM technique before the MEM emission correlation equations will be recommended for general use by the refineries. Work performed to date, however, indicates that the established OLS method results in an overestimate of emissions when the variability in the screening values is not negligible.

All of the 1993 Refinery Study emission correlation equations give substantially lower estimates of emissions for screening values than the 1980 Refinery Study emission correlation equations. The majority of the differences between 1980 and 1993 can be explained by two factors: the difference in screening instrument (TLV Sniffer® vs. OVA), and the inclusion of pegged components in the development of the 1980 emission correlation equations but not in 1993 equations.

The emission correlation equations from the Marketing Terminals Study and the 1993 Refinery Study were nearly identical for light liquid valves. The emission correlation equations from the two studies were statistically comparable for light liquid pumps. Differences were noted for connectors and open-ended lines; however, these differences may well be a function of component sub-type (i.e. type of connector) and size (particularly for open-ended lines).

3-1

Table 3-1 1993 Refinery Study Emission Correlation Equations

NOLS MethodMEM Technique19 $ER=(1.3)(10^{-6})(SV)^{0.93}$ $ER=(4.0)(10^{-7})(SV)^{1.0}$ 29 $ER=(2.8)(10^{-7})(SV)^{1.0}$ $ER=(2.3)(10^{-8})(SV)^{1.2}$ 22 $ER=(5.3)(10^{-7})(SV)^{0.84}$ $ER=(1.2)(10^{-7})(SV)^{0.92}$	Service         N         OI.S Method         MEM Technique           All         19 $ER=(1.3)(10^{-6})(SV)^{0.93}$ $ER=(4.0)(10^{-7})(SV)^{1.0}$ All         29 $ER=(2.8)(10^{-7})(SV)^{1.0}$ $ER=(2.3)(10^{-8})(SV)^{1.2}$ All         22 $ER=(5.3)(10^{-7})(SV)^{0.84}$ $ER=(1.2)(10^{-7})(SV)^{0.92}$
N         OLS Method           19 $ER=(1.3)(10^{-6})(SV)^{0.93}$ 29 $ER=(2.8)(10^{-7})(SV)^{1.0}$ 22 $ER=(5.3)(10^{-7})(SV)^{0.84}$	Service         N         OI S Method           All         19 $ER=(1.3)(10^{-6})(SV)^{0.93}$ All         29 $ER=(2.8)(10^{-7})(SV)^{1.0}$ All         22 $ER=(5.3)(10^{-7})(SV)^{0.84}$
N         OLS Method           19 $ER=(1.3)(10^{-5})(SV)^{0.93}$ 29 $ER=(2.8)(10^{-7})(SV)^{1.0}$ 22 $ER=(5.3)(10^{-7})(SV)^{0.84}$	Service         N         OLS Method           All         19 $ER=(1.3)(10^{-5})(SV)^{0.93}$ All         29 $ER=(2.8)(10^{-7})(SV)^{1.0}$ All         22 $ER=(5.3)(10^{-7})(SV)^{0.84}$
<b>N</b> 19 29 22	Service N All 19 All 29 All 22
	Service All All All All

- Emission rate in lbs/hr 11 ER SV
- OVA Screening value in ppm measured at the surface of the component (with pumps measured at  $\leq 1$  cm). II
  - - Hcavy Liquid R
      - Light Liquid 11
- Gas, light liquid, and heavy liquid services Ħ
  - Sample Size П
    - Ordinary Least-Squares П HL ALL N N MEM
- Measurement Error Method п

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# ZERO COMPONENT EMISSION FACTORS AND PEGGED COMPONENT EMISSION FACTORS

The Marketing Terminals Study zero component emission factors were found to be higher than the 1993 Refinery Study zero component emission factors for connectors, open-ended lines, and light liquid pump seals. No statistically significant differences were found between the Marketing Terminals Study zero component factors and the 1993 Refinery Study zero component emission factors for valves. The 1993 Refinery Study zero component emission factors are comparable to those presented in the U.S. EPA Protocols Document for the categories of connectors (flange and non-flange) and heavy liquid pumps. The 1993 Refinery Study zero component emission factors are significantly lower than the U.S. EPA Protocols Document factors for pressure relief valves and light liquid pumps, and are significantly higher for valves.

Pegged component emission factors are lower by more than an order of magnitude than those presented in the U.S. EPA Protocols Document. This is at least partly due to the differences in screening instruments (i.e., OVA vs. TLV Sniffer®).

### VAPOR LEAK COMPOSITION COMPARED WITH LIQUID STREAM COMPOSITION

The result of the comparison of fugitive emission samples (vapor leaks) with the liquid in the associated stream or line was inconclusive. The scatter of the data was random and very large. It is believed that the scatter of the data is related to the large number of variables in the testing process, for both the vapor and liquid samples. It is currently appropriate for refineries to continue to estimate emissions of individual VOC species by assuming that the mass fractions in emitted VOCs are the same as the mass fractions in the process streams.

#### SPECIAL STUDIES FOR ADDITIONAL DATA ANALYSIS

Special studies were conducted to establish the quality and variability of the data used in this study. Conclusions from these special studies are summarized below.

### Impact of Potentially Leaking OVA Probes

Side-by-side screening measurements with inspectors from the Bay Area Air Quality Management District (BAAQMD) showed that screening measurements both before and after the potential leaks were discovered had screening variability within the anticipated range of inspector and instrument variability. All data collected before discovering that the OVA probes were potentially leaking were compared statistically to data collected after discovery. Plots of emission rate versus screening value showed that the data before and after discovery were, in general, intermixed. No consistent bias in screening measurements before and after discovery was found. Thus, it is believed that the impact of the potentially leaking probes was not significant.

#### Screening Variability

The combined OVA and inspector relative percent difference (RPD) was 89.4%. The average RPD within one day was 138.8%. No statistically significant differences between the refinery inspection/maintenance (I/M) teams and Radian paired screening value results were found, with the exception of one refinery which was found to have higher screening values on the average. Comparisons of the BAAQMD and South Coast Air Quality Management District (SCAQMD) screening values to Radian screening values also showed no statistically significant differences between the paired screening value results.

#### Nitrogen Flow Rate During Component Bagging

This was shown to have an insignificant effect on mass emission calculations.

### Benefits of Additional Bagging

Bagging a larger number of components would increase the sample size and therefore would lead to the development of emission correlation equations with tighter confidence intervals. However, the benefits of additional bagging depend on the number of bags already obtained for this study. The benefits are much greater for the category of heavy liquid pumps where only 10 bags were collected than for the category of valves where 141 bags were collected. Although additional bagging would result in tighter confidence intervals, sufficient bagging

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was performed to meet the U.S. EPA guideline of  $\pm 50\%$  of the mean value with 95% confidence when in <u>log</u> space.

#### Dilution Probe Data

The use of the dilution probe, which increases the range of the OVA from 10,000 ppm to 100,000 ppm, does add variability to the determination of emission correlation equations. However, plots of the data and analysis of slopes and intercepts, and the confidence intervals of the emission correlation equations (with and without the dilution probe data) indicated that the impact of the dilution probe was not statistically significant in the development of the emission correlation equations.

#### Effects of High Screening Variability Data

The components that had initial screening values that varied by more than a factor of two from the final screening values were not included in the emission correlation equation development. Analysis of the emission correlation equations with and without using these highly variable screening value tests indicated that deletion of these tests had no significant effect on the emission correlation equations. This analysis likewise indicated that the results were not biased by eliminating these high screening variability tests.

#### DATA QUALITY

The results of the audits by the Regulatory Advisory Committee members indicated that the quality of data produced by the testing was sufficient to meet quality objectives. The BAAQMD and the SCAQMD performed side-by-side screening tests with Radian, and those measurements are well within the anticipated range of screening variability for different inspectors with different screening instruments. Staff from Research Triangle Institute (RTI), contracted by the U.S. EPA, performed duplicate analysis of bagging samples and conducted audit gas testing at four of the five refineries. Results from these duplicate analyses and the audit gas testing help substantiate the quality of data produced during this study.

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Recommendations made to enhance the data quality during auditing were implemented. The results of special investigations to evaluate data collected prior to these recommended changes support the inclusion of all the data collected for the development of the emission correlation equations.

Radian, Air Toxics Limited (ATL), and independent auditor QA/QC results indicate that data used for the development of emission correlation equations and pegged component emission factors are valid and within the acceptance criteria for analytical methods used. The zero component emission factors derived for this study might be overestimated because of detection limits and because of the potential for a slight amount of contamination from field sampling equipment.

#### DATA APPLICABILITY

Data were collected from five refineries with widely differing characteristics. One of these refineries was in Pennsylvania, two in southern California, and two in northern California. The refineries range in size, based on barrels of crude throughput per day (BPD), from approximately 50,000 BPD to over 250,000 BPD. The five refineries represented five different companies. All five had I/M programs where certain component types (primarily valves) were inspected and repaired on a quarterly or annual basis. Sampling took place at several process units at each refineries had been installed within the previous two years. Because of the diversity of refineries and components tested, and the validity of the results, findings from the 1993 Refinery Study can be used by refineries nationwide.

#### **RECOMMENDATIONS FOR FUTURE DATA ANALYSIS**

Several areas of additional research and data analysis are identified which could aid in further refining these emission correlation equations or in better understanding the mechanism by which components leak. These are:

- Evaluate component design data and stream characteristics (such as stream temperature, stream viscosity, and stream pressure) to determine if these parameters influence the emission correlation equations;
- Evaluate, in a controlled laboratory setting, the comparison of vapor leak composition to liquid stream composition;
- Reanalyze the 1980 Refinery Study data for compressors and pressure relief valves based on comparable OVA readings made at the surface and without pegged components. The revised 1980 Refinery Study data can then be used to supplement the results of the 1993 Refinery Study; and
- Perform additional research of the measurement error model (MEM) technique. This includes: further testing to obtain better estimates of the emission rate and screening value variabilities used in the MEM equations, perform a sensitivity analysis for the MEM technique to determine how it is affected by different variability estimates (i.e., of the emission rates and screening values), and perform additional simulations for the MEM technique to determine how it performs with smaller sample sizes.

These recommendations are discussed in more detail below.

#### Evaluate Component Design Data and Stream Characteristics

Numerous parameters have already been analyzed to determine the effects they have on the emission correlation equations and correlations between these parameters. Emission correlation equations were grouped based on the results of this multivariate analyses. Other parameters, such as component design data and stream characteristics (e.g., stream temperature, stream viscosity, stream pressure) could affect mass emission rates. Additional data beyond that collected in this study, would need to be collected to evaluate these additional parameters. Evaluating the effects these parameters have on mass emission rates would serve two purposes:

- More accurate emission correlation equations could be obtained by including factors that are statistically significant; and
- Evaluation of the component design data and stream characteristics data could aid in determining if there are specific component designs or process conditions that may reduce emissions.

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# Compare Vapor Leak Composition to Liquid Stream Composition in a Controlled Laboratory Setting

Traditionally, it has been assumed that the composition of the vapor leak is the same as the liquid stream, and fugitive emissions have been estimated accordingly. For example, to estimate the mass emissions for a particular chemical species (e.g., benzene) the total hydrocarbon (THC) mass emission rate is multiplied by the percent composition of that chemical species found in the stream. One of the objectives of the 1993 Refinery Study was to evaluate this assumption by comparing the relative concentrations of selected chemical species in the leaking vapor with the concentrations of those same chemical species in the product flowing through the components. The vapor results obtained from the bagged components (i.e., the fugitive emissions) were compared to liquid stream samples collected from the same component. The results of this comparison were inconclusive due to the large scatter in the data (i.e., the variability in the data was too large to detect any trends or differences). It would be beneficial to conduct this experiment in a controlled laboratory setting. Conducting this experiment in a controlled setting would eliminate some sources of variability (such as process variability) observed in the field, and meaningful trends could be detected, if in fact they do exist.

# Reanalyze the 1980 Refinery Study Data Based on Comparable OVA Readings and Without the Pegged Components

In comparing the 1980 and 1993 Refinery Studies' emission correlation equations, all of the 1993 Refinery Study emission correlation equations were found to predict substantially lower estimates of emissions for screening values than the 1980 Refinery Study emission correlation equations. A detailed analysis of the component category of light liquid valves demonstrated, however, that the majority of the differences between the 1980 and the 1993 Refinery Studies' equations can be explained by two factors. These are:

- The 1980 Refinery Study screening measurements were collected using the TLV Sniffer® instrument calibrated with hexane and the 1993 Refinery Study screening measurements were collected using an OVA 108 instrument calibrated with methane; and
- The 1980 Refinery Study emission correlation equations included data from pegged components (pegged instrument readings were counted as if

pegged value, [i.e., 10,000 ppm or 100,000 ppm]). Data from pegged components were not included in the 1993 Refinery Study emission correlation equations development. Instead, pegged component emission factors were developed separately.

It is recommended that an analysis, based on the same screening instrument and with pegged components removed, be performed for compressors and pressure relief valves, two component categories missing from the 1993 Refinery Study, but included in the 1980 Refinery Study. The revised 1980 Refinery Study emission correlation equations for these component categories could be used with the 1993 Refinery Study emission correlation equations.

#### Additional Research of the Measurement Error Method (MEM) Technique

It has been shown in this report (see Volume III, Appendix D) that the current method for developing emission correlation equations documented in the U.S. EPA Protocols Document (U.S. EPA, 1993) results in an overestimate of emissions when the screening value variability is not negligible. As a result, an alternative statistical methodology called the Measurement Error Method (MEM) was examined. The MEM technique accounts for variability in screening values and in the measured mass emissions; whereas the current U.S. EPA procedure only accounts for variability in the mass emissions. In order to perform the MEM technique, however, estimates of the screening value variability and emission rate variability must be obtained (this ratio of the screening value variability to the emission rate variability is referred to as  $\lambda$  in this report). For the 1993 Refinery Study, these estimates were obtained by evaluating duplicate screening measurements and emission rate measurements. Although there were sufficient duplicate screening measurements, the duplicate emission rate measurements were limited. It would be beneficial to perform further testing to obtain the data necessary to determine whether  $\lambda$  varies among component types and to obtain more accurate estimates of  $\lambda$ . In addition, it would also be beneficial to evaluate the sensitivity of the MEM technique to realistic errors in  $\lambda$ . If the estimate of  $\lambda$  is sufficiently accurate, the effect the uncertainty in  $\lambda$  has on the MEM emission correlation equations may not be significant. Lastly, it would be beneficial to perform additional simulations to test the MEM technique. In the simulations performed (which are discussed in Appendix D), sample sizes of 30 were assumed. It would be useful to determine if the MEM technique performs similarly for varying sample sizes.

#### Section 4

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# 1993 Study of Refinery Fugitive Emissions from Equipment Leaks

Volume II: Testing Approach, Quality Assurance and Quality Control

Prepared for: American Petroleum Institute Health and Environmental Sciences Department and Western States Petroleum Association

**API PUBLICATION NUMBER 4612** 

PREPARED UNDER CONTRACT BY: RADIAN CORPORATION SACRAMENTO, CALIFORNIA

**APRIL 1994** 

American Petroleum Institute



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# Section 1

#### INTRODUCTION

Volume II is meant as a supplement to the data analysis, conclusions and recommendations explained in Volume I of this report. Specifically, Volume II is organized as follows:

- Section 2 explains the testing approach, including sampling procedures, analytical and calibration procedures, and quality assurance objectives and checks;
- Section 3 examines special additional studies to enhance the data analysis;
- Section 4 presents the quality assurance/quality control results; and
- Section 5 shows the references for Volume II.
# Section 2 TESTING APPROACH

This section reviews the testing approach for the 1993 Refinery Study. The first part of this section discusses the quality assurance objectives. The second part of the section addresses the sampling procedures and design. The third part of this section presents the instrument analytical and calibration procedures. The fourth part of this section identifies the internal quality control checks. The fifth part of this section briefly addresses the performance and systems audits. Finally, the last part of this section discusses required corrective action.

# SAMPLING PROCEDURES AND DESIGN

This section discusses the screening, bagging, and liquid sampling procedures that were followed at the refineries.

# Screening Procedures

Screening measurements were made on all components that were bagged. The bagged components were selected based on a review of the screening value measurements from refinery inspection/maintenance (I/M) crews and also from site investigation by the Radian technicians.

The screening measurements, for use with bagging measurements, were made with the Organic Vapor Analyzer (OVA) Model 108 in accordance with the latest version of United States Environmental Protection Agency (U.S. EPA) Reference Method 21. Method 21 instrument specifications are summarized in Table 2-1. The requirements that were followed in this study exceeded the requirements of U.S. EPA Reference Method 21.

The OVA 108 is a portable, flame ionization detector (FID). The OVA 108 has a logarithmic readout which ranges between 1 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 a good choice for facilities that include a significant number of high leak rate components.

# Table 2-1 Summary of EPA Method 21 Requirements

	Determination of Volatile Organic Compound 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 3.0 L/min
5.	Intrinsically Safe
6.	Single Hole Probe with Maximum <sup>1</sup> / <sub>4</sub> -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 $\pm 2.5\%$ of Leak Definition (i.e., $\pm 500$ ppm)

Table 2-2 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 OVA probe was placed as close as possible to the surface of the leaking component where the leak occurred (referred to as screening "at the surface"). A piece of tubing was placed over the end of the metal probe tip to reduce the chance of fouling the probe.

Precision and accuracy checks were performed on the OVA 108 initially at the start of testing. They were not repeated unless poor instrument performance was suspected or maintenance was performed on the instrument. The OVA's operation continued to be evaluated by daily blank and multipoint linearity checks (at approximately 10 ppm, 100 ppm, 1,000 ppm, and 10,000 ppm), as well as leak and drift checks at every bag. If poor performance could not be corrected in the field, a backup OVA was used.

	Table 2-2         Summary of Screening Procedures						
	General Screening Procedures						
1.	Prepare analyzer for sampling.						
2.	Calibrate analyzer.						
3.	Check analyzer for leaks.						
4.	Without fouling the tip, and without restricting flow into the analyzer probe, place 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.	Record screening value on the data form.						
8.	If the reading exceeds full scale, use the dilution probe.						
9.	In addition to the maximum reading, record the screening values at three other points on the component. Multiple readings are not required for open ended lines.						
	a. Draw two circles on the back of the bagging data form, one each for both initial and final screening.						
	b. Record the highest screening value at the 12:00 position on the circle.						
	c. Also record screening values at the 3:00, 6:00, and 9:00 positions of the circle, which correspond to points going around the valve stem, connector circumference, or pump shaft.						

The dilution probe was tested after each calibration at three methane concentrations: 1,000, 10,000, and 25,000 or 35,000 ppm. The dilution probe ratio was targeted at 10:1 for each of the concentrations measured. If the ratio was easily adjusted, the dilution probe was calibrated to a 10:1 ratio at 25,000 or 35,000 ppm. If any of the three concentrations gave a dilution ratio outside of the target range of 5 to 15, then the sampler attempted to correct the dilution probe by:

Dislodging any obstructions or dirt in the probe with zero grade air;

- Replacing the carbon filter; or
- Changing the carbon tube.

When a component initially screened at >10,000 ppm, the dilution ratio was immediately checked with a sample bag of 25,000 or 35,000 ppm methane, and recorded with other QC data. The dilution ratio was checked before recording the initial screening value, which reflected the most recent ratio.

After the initial part of the field testing, the OVA pump flow rate was measured with the Mini-Buck<sup>TM</sup> before each calibration, at the end of the day, and before the battery was replaced. If battery replacement was due to a failed QC check, then the flow rate was not measured. The measured flow rate and the flow rate indicated on the OVA rotameter were recorded in the logbook. The pump flow rate was measured with the OVA probe connected with tubing to the outlet port of the Mini-Buck<sup>TM</sup>. If the Mini-Buck<sup>TM</sup> was broken, the bubble meter was used to measure flow rate.

#### **Bagging Procedures and Design**

The "bagging technique" was used to determine quantitative mass emissions from leaking 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 *Protocol for Equipment Leak Emission Estimates* (U.S. EPA, 1993b) (U.S. EPA Protocols Document) and the Chemical Manufacturers Association (CMA) *Guidance for Estimating Fugitive Emissions* (CMA, 1989).

The "Blow-Through" bagging technique, referring to the method of blowing nitrogen gas  $(N_2)$  through the bag, was used for all bagging measurements. After the bag was assembled around the component, the ultra-high purity  $N_2$  flow rate was noted, and the bag flushed with  $N_2$  until the oxygen concentration inside the bag equilibrated to below 5 percent. After the

initial bag temperature reading was taken, the vacuum gauge was attached to the end of the tubing leading from the bag. A sample of the exit gas was then analyzed by the OVA and oxygen analyzer to confirm equilibrium had been reached in the bag. For the majority of the data collection (all of the last half of field testing), the vacuum gauge was open and in place during all measuring with the oxygen analyzer and the OVA. The internal pumps in these analyzers flushed the vacuum gauge with the gas from the bagged component, ensuring that a representative sample was collected. A summary of general bagging procedures is provided in Table 2-3. The output of the bag (or tent) was used to fill an evacuated 850 milliliter summa-polished stainless steel canister. The canisters were returned to the laboratory, Air Toxics Limited, of Rancho Cordova, California, within one week of sample collection.

Bagging was performed in the usual manner, unless there was visual evidence of an aerosol or liquid leak. If the original bag had a light coating of hydrocarbon on the inside surface of the bag, but not so much that it could be collected and measured, then that fact was noted in the data sheets but not further accounted for. This procedure assumes that while there may be some condensation or adsorption of organics onto the walls of the bag, there will also be some evaporation of the condensed material back into the vapor phase. If there was no sizeable accumulation, then it was assumed that an equilibrium between condensation and evaporation had been reached and that the vapor emissions essentially represented all of the emissions from the component.

If, however, there was visible evidence of an aerosol or liquid leak before bagging, or there were drops forming and running down the inside surfaces of the bag and possibly dripping out of the bag, then a specially configured bag had to be constructed. That bag was made such that there was a distinct low point to collect the condensate, and a graduated cylinder was attached to the bag at that low point. The total mass of liquid was ascertained by the volume collected and the density of the material, and the rate was calculated by dividing the volume by the time of collection. The density was estimated as being comparable to gaso-line. If the component with a liquid leak was one which was speciated to compare leak-to-

2-5

	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 <sub>2</sub> )
6.	Initiate tent diluent gas flow.
7.	Measure tent temperature.
8.	Attach vacuum gauge to end of tubing leading from bag.
9.	Ensure tent is at $O_2 < 5\%$ .
10.	Analyze exit gas with OVA for THC to establish equilibrium.
11.	Collect canister sample.
12.	Ensure tent is at $O_2 < 5\%$ .
13.	Analyze exit gas with OVA for THC.
14.	Measure temperature.
15.	Measure diluent gas flow.
16.	Remove tent.
17.	Perform final screening tests.
18.	Record ambient conditions.
19.	Record stream parameters.

# Table 2-3 Summary of Fugitive Emissions Bagging Test

line compositions, then the collected liquid had to be transferred to a vapor-tight bottle (such as a 40 mL VOA vial with a Teflon®-lined screw cap) and sent to the lab along with liquid stream samples for analysis. The total mass leak rate for the component was the liquid mass leak rate plus the gas mass leak rate.

Radian obtained bag samples for the following categories of component and service types:

- Valves, light liquid;
- Valves, heavy liquid;
- Valves, gas/vapor;

- Connectors (flanges, union, screwed, threaded, etc.), all service types;
- Open-ended lines, all service types;
- Pumps seals, light liquid; and
- Pumps seals, heavy liquid.

Approximately 100 components were tested at each site to provide a program total of 500 bags (excluding duplicates and bags taken for special studies such as the nitrogen flow tests). Field duplicates were taken on approximately every twentieth bag. Field duplicates were taken sequentially, leaving the original tent in place when taking the second sample.

The bagging matrix included considerations for those screening value ranges which contributed most significantly to total emissions. The evaluation of screening value and emission distributions across various screening value ranges for refineries in the South Coast Air Quality Management District (SCAQMD) for the second and third quarters of 1991 is found in *The WSPA/API Revised Study Protocol* (Radian, 1992).

In addition to emphasizing those screening value ranges which contributed most significantly to total emissions, components with zero screening values and components with pegged (i.e., usually 100,000 ppm or greater) screening values deserved particular emphasis. Components with zero screening values deserved emphasis because they made up the largest percentage of components in the inventory and will make up an even larger percentage of components in future inventories. Components with pegged screening values deserved a unique approach because there were so few discovered, yet they did make up a significant percentage of the total emissions.

Based on the considerations presented above, a bagging matrix was developed and is presented in Table 2-4. This bagging matrix attempted to strike a balance between the considerations presented above in the following manner:

Targets
Matrix
. Test
Phase
Fugitives —
Refinery
WSPA/API
Table 2-4

						S	creening Val	iue Ranges		
Component	Service Type	Size (in.)	0	1.09	100.499	500-999	1,000-9.999	10,000-99,999	<b>Total Measured</b>	>100,000
Valves	gas/vapor	0-2	10	5	3	3	5	6	25	10
		>2-6	10	5	3	3	S	6	25	10
		% *	10	5	3	3	5	9	25	10
		Subtotal	30	15	6	6	15	27	75	30
	light liquid	0-2	10	5	3	3	5	9	25	10
		>2-6	10	5	3	3	5	9	25	10
	A	>6	10	5	3	3	5	6	25	10
		Subtotal	30	15	6	6	15	27	75	30
	heavy liquid	all	10	8	9	4	4	3	25	10
Con-Flange	all	all	10	5	3	3	5	9	25	10
Con-Other	all	all	10	5	3	3	5	9	25	10
OEL's	all	all	10	S	3	3	5	6	25	10
Pump Seals	light liquid	all	10	5	З	3	5	6	25	10
	heavy liquid	all	10	8	9	4	4	3	25	10
	Totals		120	66	42	38	58	96	300	120
Key: Con-Fl	lange = Conne	sctor/Flange						Ang and a second se		

Con-Flange = Con-Other = OEL =

Connector/Flange Connector/Other (screwed, tubing, union, etc.) Open Ended Line

- The bagging matrix included some measurements in each screening value range to provide accurate mass emissions in the ranges of current regulatory interest (i.e., 1,000 ppm, 500 ppm, 100 ppm).
- The bagging matrix was weighted towards those screening value ranges which contributed most significantly to total emissions in order to minimize the uncertainty in total emission estimates from fugitives.
- Components with zero and pegged screening values were given particular emphasis.

Virtually all components screening above 100,000 ppm were bagged.

Non-zero, non-pegged bags were used to develop emission correlation equations. Typically, the number of non-zero, non-pegged bags per category would total approximately 25. Assuming 10 sources with screening values of 0, and 10 components with screening values greater than 100,000 parts per million (ppm) were also bagged, then the objective was to obtain 45 components in each category.

Bagging data were entered on a form similar to that shown in Figure 2-1. These data included:

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

Sample ID	:			L	iquid Sam	ple ID:			
Plant ID:				D	ate:				
Unit ID:				В	agging Tea	m:			
Instrument	ID:			St	ream ID:				
Component	ID:			<u> </u>	omponent '	Type (valve, p	ump, etc.):		
Component	Sub-Categ	ory (gate,	globe, etc.):	V	alve Actua	tion (manual,	control):		
Component	Service (H	IL, LL, ga	s):	C	omponent :	Size (in.):			
Ambient Te	mperature	(°F):		W	indspeed (	mph):			
Barometric	Pressure (1	Hg):		Ba	ackground	(ppm):			
Stream Pres	sure (psia)	:		St	ream Tem	perature (°F):			
Unit Age:	, <u>, , , , , , , , , , , , , , , , </u>			Se	al Age:				
Stream Hyd	rocarbon (	Content (%	):	Se	al Packing	Type:			
I&M Screet	ning Value	(ppm):		18	M Screen	ing Date:	· · · · · · · · · · · · · · · · · · ·		
Time			Bagging	Data Para	meter			Value	
	Initial Sc	reening Va	alue (ppm)			· · · · · · · · · · · · · · · · · · ·			
	Initial Ni	trogen Flo	w Rate (mL/n	nin)					
	Initial Ba	ig Tempera	ature (°F)						
Bag O <sub>2</sub> Concentration at Equilibrium (%)									
	Bag THO	Concentr	ation at Equili	brium (ppr	n)				
	SAMPLE	E COLLEC	TION STAR	TED					
SAMPLE COLLECTION ENDED									
	Final Ba	g O <sub>2</sub> Conc	entration (%)						
	Final Ba	g THC Con	ncentration (pp	om)					
	Final Ba	g Tempera	ture (°F)		<u></u>				
	Final Nit	rogen Flov	v Rate (mL/mi	in)					
	Final Scr	eening Val	lue (ppm)						
			In	terim Data					
Time	OVA	02	Time	OVA	02	Time	OVA	02	

# Figure 2-1. Bagging Data Entry Form

#### Analysis of Bag Samples

All component bags were screened for total volatile organic compounds (VOCs) using the OVA. All samples were analyzed using ASTM Method D3416 for methane and by either ASTM 3416 for non-methane organic carbon (NMOC) or U.S. EPA Method 18 for total hydrocarbons (THC). All zero component bags, as determined by the OVA, were analyzed using U.S. EPA Method 18 for THC also described below.

ASTM Method D3416 consists of using a dual chromatographic system to initially separate the methane from the other hydrocarbons, followed by flame ionization detection. The sample is directly injected (one mL) into the specially constructed HP5890 and is split into two streams, one for methane separation and detection, and the other for hydrocarbons. Methane is analyzed on a 3-foot long, 1/8" diameter stainless steel column packed with molecular sieve 13X. The THC fraction is analyzed using a 6-foot long, 1/8" diameter column packed with Porapak N. The oven temperature starts at 40°C for 9 minutes followed by a temperature increase of 15°C/min to 135°C, which is held for one minute. A 5-point calibration curve is generated using certified propane standards.

All zero component bag samples and the majority of the other bag samples were analyzed for THC using U.S. EPA Method 18. The method calls for a direct injection using a gas-tight syringe of 10  $\mu$ L to 5 mL of sample into an HP 5890 gas chromatographic system equipped with a 15 m DB-5 megabore column and a flame ionization detector (FID). No attempt is made to speciate the various hydrocarbons which may have been present. The oven temperature of the gas chromatograph is ramped from 40°C to 200°C at 20°C per minute. Hydrocarbons generally boiling over this range are detected. A laboratory data system is used to integrate the total area of hydrocarbon present in the sample effluent versus a propane standard. Results are reported as ppbv THC. The minimum detectable limit is 50 ppbv.

Several bag samples were analyzed by U.S. EPA Method TO-3 for the analytes identified on Table 2-5. The method calls for concentrating up to 250 mLs of air at liquid argon temperatures. Following concentration, the sample aliquot is rapidly heated to 250°C and swept onto

2-11

List of Components
Total Non-Methane Hydrocarbons
Benzene
Ethyl Benzene
Hexane - normal
Isopropyl Benzene (Cumene)
Propylene
Toluene
2,2,4-Trimethyl Pentane (Isooctane)
Xylenes (Total)

# Table 2-5 Bagging Sample Analyte Target List

a Shimadzu 14A gas chromatographic system equipped with both a flame ionization detector (FID) and a photo ionization detector (PID) for analysis. An inlet splitter divides the sample onto a 30 m x 0.53 mm DB-5 column and a 30 m x 0.53 mm DB-624 column. The DB-624 column is connected to the PID which responds selectively to unsaturated VOCs, while the DB-5 column is connected to the FID which responds universally to VOCs. In those cases where an individual VOC responds on both detectors, the two-column system provides both analytical and confirmatory information. Reporting of THC is achieved by area summation of the DB-5/FID channel and calibration against propane. The limit of detection is 1 ppbv per speciated VOC.

Several of the samples analyzed by U.S. EPA Method TO-3 received confirmatory analysis for selected VOCs using U.S. EPA Method TO-14. The method calls for concentrating up to 250 mLs of air at liquid argon temperatures. Following concentration, the sample aliquot is rapidly heated to 250°C and swept through a hydrophobic drier prior to analysis by gas chromatography/mass spectrometry (GC/MS). Individual VOCs are speciated by a Hewlett-Packard 5971 GC/MS quadrupole using both chromatographic and mass spectral information. The GC/MS is operated in the electron impact mode scanning from 30 to 250 amu and is equipped with a jet separator. The limit of detection is 2.0 ppbv per speciated VOC. The more confirmatory analysis (TO-14) was intended to evaluate the impact of potential coelutions of compounds using the less detailed analysis (TO-3).

In addition to duplicates collected in the field, Air Toxics Limited also performed duplicate analysis on 10% of the samples.

#### Liquid Stream Samples

One of the objectives of this program was to compare measured fugitive emissions with the concentrations of compounds in the associated liquid streams. This was to be accomplished through the analyses of liquid samples collected from process lines on which bagging measurements were made. The same analytes were analyzed for the liquid samples as those for the bagging samples, as shown on Table 2-5. Table 2-6 summarizes liquid sampling procedures.

# Table 2-6 Summary of Liquid Sampling Protocol

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

The liquid samples were collected in either pre-chilled 50 mL nalgene bottles or pre-chilled 40 mL amber-colored VOA-vials. Following collection, a sample label was attached to each sample bottle identifying it by sample ID number and sample type. To minimize volatiliza-

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tion losses, the liquid samples were stored on ice or in a refrigerated cooler up to the time they were analyzed. Hold time for the liquid samples was two weeks.

Liquid stream sampling data were recorded in a master logbook. These data included:

- Sample ID number;
- Sample collection time;
- Sample location;
- Sample type; and
- Additional supportive data (temperature, process information, etc.).

Liquid samples were analyzed by a comparable analysis to U.S. EPA Method TO-14. This analysis is performed by preparing a gas sample of the liquid sample, followed by analysis of the gas sample by the TO-14 methodology. Included in this analysis is the determination of NMOC by summation of the GC/MS response for all compounds.

# Sample Custody Procedures

Each canister and vial collected during the sampling was labeled before submitting to the laboratory for analysis. Strict chain-of-custody procedures were followed in handling of samples. Process data were recorded in ink and dated. Copies of raw data, laboratory notes, and any other calibration data were maintained in a central file for future inspection.

# ANALYTICAL AND CALIBRATION PROCEDURES

This section presents information on the analytical procedures used to characterize fugitive emission components by screening and bagging. Information is also presented in this section pertaining to calibration of the analytical systems. Included in the discussion of calibration are descriptions of the procedures, the frequency, and the calibration standards used. Table 2-7 summarizes the analytical methods and their calibration requirements.

# Screening Analyses with the OVA 108

The VOC concentration of fugitive emission components was determined using the Foxboro OVA analyzer (model 108). This instrument features an FID system, a self-contained

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# Table 2-7 Analytical Calibration Requirements

Parameter	Measurement Method	Calibration	Frequency	Calibration Standards	Acceptance Criteria
Screening	OVA 108	Multipoint	Daily	CH4 in air	r ≥ 0.995
THC	EPA Method 18	Multipoint	Every 12 hours	C <sub>1</sub> H <sub>8</sub> in air	r ≥ 0.995
Methane/NMOC	ASTM D3416	Multipoint	Every 12 hours	C <sub>4</sub> H <sub>8</sub> in air	r ≥ 0.995
Gas Sample Speciations	EPA Method TO-3	Multipoint	Every 12 hours	Multicomponent blank	Initial: $\leq 20\%$ of %RSD Repeat: $\leq 30\%$ drift
Liquid Samples	EPA Method TO-14	Multipoint	Every 12 hours	Multicomponent blank	Initial: ≤ 20% of %RSD Repeat: ≤ 30% drift
Temperature	Type J T/C	Ice point and BP of water	Twice - beginning and end of project	NBS traceable thermometer	∓ 10%
Dilution Air Flow	Rotameter	Single Point	Twice/run	Mini-buck flow meter	N/A

- Boiling point
  - Methane
- Propane BP  $CH_4$   $C_3H_8$  N/A N/A
- Not applicable Organic Vapor Analyzer
- **Correlation Coefficient**
- Thermocouple Total Hydrocarbon Non-Methane Organic Carbons

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hydrogen tank, and a battery-powered sampling pump and electronics. The FID output is amplified and displayed on a hand-held meter.

The OVA 108 was calibrated in the morning of each sampling day using multi-component standard gas mixtures containing methane in hydrocarbon-free air. The standard gases were blended to an accuracy of  $\pm 2\%$  (with the exception of one 1,000 ppm standard used for less than 10% of the samples collected that was  $\pm 2.4\%$ ). Calibration gas cylinders were used, at nominal methane concentrations of 10, 100, 1,000, and 10,000 ppm for the OVA 108. Zero grade hydrocarbon-free air containing less than 0.5 ppm THC was used to check each instrument's zero response. Tedlar<sup>TM</sup> bags containing standard gases were filled and emptied with each morning calibration. If the bags leaked substantially, then this procedure was followed for each calibration.

The linearity of the OVA's four-point calibration curve (three upscale concentrations plus zero) was evaluated by linear regression analysis. A correlation coefficient of  $r \ge 0.9950$  was used as the acceptance criterion. If this criterion had not been met, the calibration would have been repeated (or instrument maintenance performed, if necessary) until an acceptable correlation value was achieved. The correlation coefficient was  $\ge 0.9950$  for each day of testing.

A dilution probe was available for the OVA 108 to allow screening values above the normal 10,000 ppm limit. Approximately a 10:1 dilution ratio was set (to permit screening up to 100,000 ppm) by adjusting the dilution air control value to achieve a 10:1 reduction in the OVA 108's response to the calibration standards. The dilution probe was calibrated with a 35,000 ppm or a 25,000 ppm standard.

#### **Bagging Sample Analyses**

All non-zero compound samples were analyzed using ASTM D3416 for methane and NMOC or U.S. EPA Method 18 for THC. Calibration was performed at five levels which bracket the linear range of the system. Samples exhibiting a response beyond the calibration range were diluted into the working range of the system. The relative standard deviation (RSD) of the five point was  $\leq 20\%$  or recalibration was performed.

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All low-level (zero component) bag samples were analyzed for THC using U.S. EPA Method 18. Multilevel calibration was achieved using a certified standard of propane in ultra-high purity (UHP) nitrogen. Calibration was performed at five levels which bracket the linear range of the system. Samples exhibiting a response beyond the calibration range were diluted into the working range of the system. The percent RSD of the five point was  $\leq 20\%$ or recalibration was performed. At the start of every shift and at 12-hour intervals, a midlevel calibration standard was analyzed and used to monitor for instrument drift. The percent recovery of the check standard versus the initial five point was  $\leq 30\%$  or recalibration was performed. A laboratory blank was analyzed at the start of every shift and after the analysis of high-level samples. The instrument demonstrated a blank level  $\leq 50$  ppbv THC prior to the analysis of samples.

A select number of bag samples were also analyzed by U.S. EPA Method TO-3. Analysis was achieved by ramping the GC oven from  $-10^{\circ}$ C to  $200^{\circ}$ C at  $10^{\circ}$ /minute. Compounds to be speciated included propylene, benzene, toluene, xylene(s), isopropyl benzene (cumene), 2,2,4-trimethylpentane (isooctane), and hexane. A five point multilevel calibration was performed using a certified gas blend of each individual VOC covering the range of 1 ppbv to 1000 ppbv. Samples exhibiting a response beyond the calibration range were diluted into the working range of the system. The percent RSD of the five point was  $\leq 20\%$  or recalibration was performed. At the start of every shift and at 12-hour intervals, a mid-level calibration standard was analyzed and used to monitor for instrument drift. The percent recovery of the check standard versus the initial five point was  $\leq 30\%$  or recalibration was performed. A laboratory blank was analyzed at the start of every shift and after the analysis of high-level samples. The instrument demonstrated a blank level  $\leq 1$  ppbv per VOC prior to the analysis of samples.

It was expected that the presence of a complex hydrocarbon matrix would result in coelutions which would affect the accurate reporting of hexane and isooctane. Inflated values could then have resulted. Methyl cyclopentane is known to coelute with benzene and could have resulted in inflated results.

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To evaluate the impact of potential coelution of compounds, a few of the speciated samples were also analyzed for selected compounds by GC/MS using U.S. EPA Method TO-14. Analysis was achieved by ramping the GC oven from  $-10^{\circ}$ C to  $200^{\circ}$ C at 5°/minute. A five point multilevel calibration was performed using a certified gas blend of each individual VOC covering the range of 1 ppbv to 100 ppbv. Samples exhibiting a response beyond the calibration range were diluted into the working range of the system. The percent RSD of the five point was  $\leq 20\%$  or recalibration was performed. The instrument was tuned at the start of every 12-hour shift by analysis of 4-bromofluorobenzene. Abundance criteria for all ions fell within the U.S. EPA-approved windows or retuning was performed. At the start of every shift and at 12-hour intervals, a midlevel calibration standard was analyzed and used to monitor for instrument drift. The percent recovery of the check standard versus the initial five point was  $\leq 30\%$  or recalibration was performed. A laboratory blank was analyzed at the start of every shift and after the analysis of high-level samples. The instrument demonstrated a blank level  $\leq 0.5$  ppbv per VOC prior to the analysis of samples.

#### Liquid Sample Analysis

All liquid samples were also analyzed for selected volatile organic hydrocarbons and NMOC using a method similar to U.S. EPA Method TO-14, as described in the previous subsection.

#### Temperature, Pressure, and Flowrate

A thermocouple with a digital readout was used to measure ambient and bag temperatures. Barometric pressure was obtained while on site on a daily basis. Diluent gas flowrate was monitored and measured by flow meters. A rotameter was used to monitor flow during testing to ensure consistent flowrate. In addition, flow at the beginning of the testing and at the end of testing of each sample was measured with an NIST-traceable flow standard.

#### QUALITY ASSURANCE OBJECTIVES

The quality assurance (QA) objectives for detection limits, precision, accuracy, completeness, representativeness, and comparability used in this study are presented in this section. These QA objectives were based upon the program requirements as well as Radian's past experience in similar projects. Detection limits, precision, accuracy and completeness objectives are defined in Table 2-8. Data representativeness and comparability are discussed at the end of this section.

Measurement	Reference	Detection Limit	Precision	Accuracy	Completeness
OVA 108/128	Instrument Manual	0.5 ppm Methane	<10% <sup>a</sup>	±20% <sup>b</sup>	NA
Screening	EPA Method 21	0.5 ppm Methane		±20% <sup>b</sup>	95% valid data
Bagging	EPA Protocol Document <sup>c</sup>	1 to 1000 ppb	<50% <sup>d</sup>	±50% <sup>e</sup>	95% valid data
ТНС	EPA Method 18	50 ppbv-C	<30%	±50%	95% valid data
Methane/NMOC	ASTM D3416	1 ppmv	<30%	±50%	95% valid data
Gas Speciation	EPA Compendium Method TO-3, TO-14 (10%)	1 ppbv	<30%	±50%	95% valid data
Liquid Samples	EPA Compendium Method TO-14	2 ppbv	<30%	±50%	95% valid data
Dilution Flow	NA	NA	<5% <sup>f</sup>	±10% FS <sup>g</sup>	NA
Temperature	NA	NA	<10% <sup>f</sup>	±5%	NA

# Table 2-8QA Objectives

<sup>a</sup> Relative Standard Deviation between duplicate analyses.

<sup>b</sup> Response to Quality Control Calibration Standard.

<sup>c</sup>, Protocol for Equipment Leak Emission Estimates (U.S. EPA, 1993b).

<sup>d</sup> Relative Standard Deviation between duplicate bagged samples.

e Response to a known, artificially induced leak rate

From manufacturer's specifications.

g FS = full scale

NA Not applicable.

THC Total Hydrocarbons NMOCNon-Methane Organic Carbons

Detection limit values, as shown in Table 2-8, are based upon manufacturers' specifications. The values for precision are defined as the relative standard deviation (ratio of the standard deviation to the mean, expressed as percent). Through duplicate screening and bagging measurements, sampling and analytical precision were assessed. Multiple bagging duplicates were taken in the field. Duplicate analyses of selected bag samples were also performed by Air Toxics, Ltd.

Accuracy is defined as the relative difference (expressed as percent) between the measured value and a known, or standard, reference value. Screening accuracy is the measured accuracy of the screening instrument, i.e., the OVA 108. Bagging accuracy was evaluated by

bagging a dummy component (such as a water valve), creating a known, artificially induced leak rate, and comparing the measured emission rate to the calculated leak rate.

Data completeness is the percentage of the total data set which are accepted as valid. For this project, the completeness objective was 95% for all screening and bagging measurements.

Data representativeness is the degree to which measurement results are representative of the conditions being measured. Data representativeness was achieved by collecting bagging and screening measurements from five different refineries with widely differing characteristics. One of the refineries was in Pennsylvania, two in southern California, and two in northern California. The refineries ranged in size, based on barrels of crude throughput, from approximately 50,000 BPD to over 250,000 BPD. The five refineries were also from five different companies and sampling took place at several process units within each refinery. The age of the components tested varied from two years to components that had been in use for decades.

To ensure data comparability, measurement results were directly comparable to standards traceable to NIST standards. Reported results were presented in a format and in consistent units to allow direct comparison with related fugitive emission studies.

Liquid stream samples and canister samples were sent to Air Toxics Limited, of Rancho Cordova, California, for analyses. Duplicate samples were analyzed to determine sampling and analytical precision. Blank samples were analyzed to ensure sampling equipment had not been contaminated. During the initial part of testing, some blanks were found to be contaminated. To ensure that there was minimal contamination in future testing, the outlet port of the vacuum gauge "tee" was screened with the OVA. If the OVA reading was not equal to or less than the zero grade air reading obtained during the multipoint linearity check run earlier that day, the gauge was cleaned either by strip cleaning with more zero grade air, with ultrapure nitrogen or a cleaning solution.

# INTERNAL QUALITY CONTROL CHECKS

This section discusses the quality control (QC) procedures that were followed in this project to control and assess sampling and analytical data quality. The specific QC checks, required frequency, acceptance criteria, and corrective action requirements are listed in Tables 2-9 and 2-10.

# <u>OVA 108</u>

Routine QC procedures for the OVA 108 analyzer consisted of several daily performance checks. These included blank analyses, precision checks, leak checks, and drift check analyses. The results of tests conducted with each sample were recorded on the bagging forms. The results of other tests were recorded in a bound laboratory notebook, along with the samplers' names. The QC checks for the OVA 108 consisted of:

- Drift Check After every bagged sample was taken, a mid-level calibration gas standard was analyzed. The response was within ±20% of the last calibration response to the same standard. Daily multipoint linearity checks at approximately 10 ppm, 100 ppm, 1,000 ppm, and 10,000 ppm were also performed.
- Leak Check After the initial part of the testing, at least once daily, with each multipoint linearity check, the end of the probe was blocked with the OVA sidepack held vertical. The pump rotameter ball hit the bottom of the rotameter column, though it possibly did not always remain at the bottom. At least a 75% reduction from normal flow was required. The pump sounded strained, and could possibly die from lack of flow.
- Blank Check Once daily, zero air was analyzed by the OVA to test for possible contamination. The response was ≤5 ppm.
- Precision Check Instrument precision was assessed by replicate analyses of a calibration standard. This was done prior to testing. Results were <20% RSD or corrective action taken.
- Accuracy Check Prior to testing, a separate QC gas standard was analyzed. The OVA's response was within ±20% of the actual concentration.

#### **Bagging Accuracy**

An accuracy check was conducted on the entire bagging measurement system. The accuracy check involved performing a pseudo-test on a component with a known emission rate to check the accuracy of the method. This was performed once at each of the sites where bagging was conducted.

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Parameter	QC Check	Frequency	Standards	Criteria	Corrective Action
OVA 108	Drift Test Blank Precision Accuracy	Each Test Daily Once Once	Mid-Span std. Zero Air Dup. Analysis of cal std QC Check std.	<20% ≤5 ppm <20% RPD <20%	<ol> <li>Repeat test.</li> <li>Recalibrate.</li> <li>Repair instrument.</li> </ol>
OVA 108	Leak	Daily Each Test		75% reduction in flow, rotameter ball hits bottom	<ol> <li>Tighten rotating barrel and filter barrel on probe tip; add Teflon® tape.</li> <li>Check nut and ferrule where umbilical cord connects to sidepack: add Teflon® tane.</li> </ol>
Oxygen Analyzer	Accuracy	Daily	Ambient Air	>24%, <18%	<ol> <li>Refresh the Tedlar<sup>TM</sup> O<sub>2</sub> bag.</li> <li>Check the analyzer battery.</li> <li>Check for leaks in the internal and external tubing leading to the pump.</li> <li>Send analyzer to the manufacturer.</li> </ol>
Bagging	Accuracy	Once	High level methane std.	Between 50% and 150% of calculated value	<ol> <li>Repeat test.</li> <li>Recalibrate.</li> <li>Repair instrument.</li> </ol>

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Not for Resale

calibration

- Duplicate cal = Dup = IDL = OVA QC = RPD = std =
- Instrument Detection Limit
  - =Organic Vapor Analyzer
    - parts per million
- Quality Control Relative Percent Difference Standard

Corrective Action	NA Check instrument; adjust if necessary	Repeat until meets specifications	Repeat until meets specifications	Check instrument; repeat until meets specification; perform new multipoint calibration	NA	Check instrument; reanalyze
Target Criteria	< 50% < 30%	± 50%	% RSD ≤ 20%	± 30% RSD	<ol> <li>ppbv TO-3</li> <li>ppbv TO-14</li> <li>assumes 250 mL</li> <li>sample volume)</li> <li>50 ppbv Method 18</li> <li>1 ppm ASTM D3416</li> </ol>	< 0.2 ppbv
Erequency	Per sample design Every analytical batch or 10%	Every analytical batch	Initially	Once per 12-hour shift	Prior to analysis of samples	Daily and after high-level samples
Method Determination	RPD of duplicate samples RPD of duplicate analyses	Laboratory and trip spike analysis	5 calibration levels 1 to 100 ppbv TO-14 1 to 1000 ppbv TO-3 50 to 1000 ppbv Method 18 1 ppm to 1000 ppm ASTM D3416	Midpoint standard	Seven replicate injections of a low-level standard	Analysis of laboratory blank
Quality Parameter	Precision	Accuracy	Multipoint calibration	Continuing calibration	Detection limits	Blank contamination

Table 2-10 Summary of Laboratory QA/QC Procedures for EPA Methods TO-3 and TO-14

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Not for Resale

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The accuracy check consisted of bagging a component with zero emissions (such as a valve serving a water line) and introducing a methane standard gas at a known flowrate. All other aspects of the bagging test were conducted normally, such as establishing the diluent flowrate, monitoring of the outlet  $O_2$  concentration, and extracting a sample for analysis by Air Toxics Limited. The results of the analysis were then compared with the calculated concentration of methane in the bag. An acceptance criteria of ±50% accuracy was acceptable.

Additional testing comparable to accuracy checks was performed by audit gases brought by the U.S. EPA contractor, Research Triangle Institute (RTI).

# Oxygen Analyzer Accuracy

The oxygen analyzer was calibrated daily. The instrument was calibrated to 5%  $O_2$  in nitrogen. The Tedlar® bag containing this standard was emptied and filled each morning before calibration. Accuracy and linearity of the analyzer was checked at ambient concentration. If the instrument measured oxygen in ambient air was greater than 24% or less than 18%, then corrective action, listed in Table 2-9, was taken.

# Laboratory Instrument QA/QC

The laboratory instrumentation consisted of a Hewlett-Packard 5890 gas chromatograph, a Shimadzu 14A gas chromatograph, and a Hewlett-Packard 5971 GC/MS. Table 2-10 contains the type and frequency of QA/QC checks for the laboratory instrumentation.

Routine quality control checks included daily blanks, blank checks after high-level samples for carry-over, and a 10% frequency of duplicate analyses. Accuracy checks were performed by analysis of laboratory standards at a frequency of one per day. A multi-point calibration was performed initially, and a one-point calibration check was performed every 12 hours.

Detection limits were determined per standard U.S. EPA methodology of replicate analysis of a low-level standard.

Assessment of QC data was performed on a continuing basis to ensure correct data.

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# PERFORMANCE AND SYSTEMS AUDITS

A system audit is an on-site inspection and review of the QA system used for the total measurement system (sample collection, sample analysis, data processing, etc.). Performance audits refer to independent checks made by an auditor to evaluate the quality of data produced by the total sampling and analysis system. The U.S. EPA sent a separate contractor, RTI, to perform system audits at several of the refineries. Performance audits of the laboratory test results and the data analysis activities were also conducted by RTI. In addition, local regulatory agencies (Bay Area Air Quality Management District and South Coast Air Quality Management District) also had representatives to audit testing activities.

# CORRECTIVE ACTION

Corrective action procedures were required anytime the project QC criteria were not met. This included the failure to achieve the precision, accuracy and completeness criteria earlier specified. Generally, Task Leaders are the first to know when a QA problem exists that may make corrective action necessary. In such cases, it was the Task Leader's responsibility to inform the Project Director. The Project Director and Program Manager then reviewed the QA and program goals to determine if the specific QA problem would prevent the achievement of the program goals.

If the QA and program goals were judged to be satisfactory, then the Project Director and Field Task Leader were responsible for seeing that the problem was resolved. When the problem was resolved, the Field Task Leader would verify the result. Following resolution of the problem, the Project Director would review all questionable data and determine if specific measurements must be repeated. Incidents of corrective action were reported by the Project Director.

# Section 3 SPECIAL STUDIES FOR ADDITIONAL DATA ANALYSIS

This section contains additional data analysis, beyond that documented in Volume I, Section 2. The studies that are discussed in this section were performed to enhance the understanding of variables associated with the development of the emission correlation equations, the zero component emission factors and the pegged component emission factors. The first part of this section examines the effect of potentially leaking OVA probes that were identified early in the field testing activities. The second part of this section evaluates the variability of screening measurements. The third part of this section addresses the effects of varying the nitrogen flow rate during the bagging measurements. The fourth part of this section discusses the potential benefits of adding more bags to the study. The fifth part of this section examines the impact of data collected with the dilution probe to determine emission correlation equations. The last part of this section identifies the impact of not including components with high screening variability in the data analysis.

# EFFECTS OF POTENTIALLY LEAKING PROBES

Ideally, if the probe tip of an OVA is completely blocked, the OVA internal pump will be unable to draw any outside air from other areas. During audits on December 4, 1992 and December 8, 1992 at two different sites, leaks were found when the probe tip of the OVA at each site (two OVAs) was completely blocked by placing a thumb over the end of the probe as part of the audit. Under blocked conditions, the OVA internal pumps were able to operate at reduced flow rates, and leaks were found around the rotating barrels and filter barrels on the probe tips and around the connections between the umbilical cord and the OVA sidepacks. To reduce the potential for leaks on one OVA, the probe with its umbilical cord and the fitting on the OVA sidepack were all replaced. For this OVA it was determined that a missing ferrule on the umbilical cord connection and possibly damaged threads on the OVA fitting could have contributed to the potential to leak. For the second OVA no replacement of any parts was deemed useful. The probe tip simply needed to be tightened into its housing. After detection, the OVAs were checked daily thereafter. It is unknown whether the OVAs had been leaking for the entire period of data collection prior to detection, or only for a short time, or even if they leaked at all when the OVA probe tip was not blocked. If the OVAs were leaking, the exact magnitude of the leaks is also unknown. The field procedure prior to December 4–8, 1993 was to check for leaks on a nonroutine basis and records of these checks generally were not made.

Leaks were discovered only by completely blocking the OVA probe tip. This is not the typical condition of the OVA during screening operations. The OVA probe tip is completely unblocked during screening for values below 10,000 ppm. Flow through the probe assembly is only slightly restrained when using the dilution probe when screening components greater than 10,000 ppm. Far less leakage is anticipated during the screening performed by Radian than observed when the probe tip was completely blocked.

It should also be noted that the OVAs were calibrated with the leaks in existence, on days when the OVAs may have leaked. This means that if some air entered the OVA analyzer from an area away from the probe tip, this effect was accounted for, in large part or completely, by adjusting the OVA to read a 100 ppm methane standard as 100 ppm. Multipoint calibrations were also performed to confirm that the adjusted OVA was reading acceptable values ( $r \ge 0.995$ ) at 10, 1,000, and 10,000 ppm as well. The dilution probe ratio was also recorded with any leak in place. Therefore, for screening values over 10,000 ppm the corresponding dilution ratio, with or without a probe leak, was accounted for by the dilution ratio determined for the instrument that day or for a particular component.

In addition to daily multipoint calibrations, a quality control check against a known hydrocarbon concentration was performed after taking every sample to confirm that the OVA had not drifted significantly. If concentrations varied by more than 20% from the calibrated value of the known hydrocarbon concentration these samples were considered invalid and results from these samples were not used in development of the emission correlation equations. This drift check confirms that no substantial change in leak occurred during the day for any component used in this study.

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After evaluating the situation, it is impossible to conclude that the potentially leaking probes had <u>no</u> effect on the data. However, this review does give strong reasons to believe that the potentially leaking probes had a minor, if not insignificant impact on the data. Radian believes that the potentially leaking probes did not bias the data analysis.

Statistical analyses were conducted to determine whether data collected before adjustment were biased. The following analyses were performed:

- For one of the instruments, data collected on the same component on the same day by both Radian inspectors and Bay Area Air Quality Management District (BAAQMD) inspectors were compared both before and after discovery of the leaks. Qualitative analyses were performed on all data, and quantitative analysis was performed on the components for which an actual screening value rather than a pegged value was recorded.
- For data collected at all sites, the relationship between emission rate and screening value that was observed after adjustment was compared to the relationship that was seen before any leaks were discovered. Plots were examined for apparent differences, and regression lines were compared statistically.

The results of these analyses are discussed in the two sections below.

# Comparison of Radian and BAAQMD Measurements

Corresponding screening value measurements obtained by BAAQMD and Radian inspectors on the same component are given in Table 3-1. The first line of data in the table shows the data collected on component one. This first line of data was not included in any quantitative analyses because the Radian measurement did not pass the quality control check (the OVA had drifted more than 20%). Also note that the Radian measurements presented in the table represent the averages of two screening measures taken on each component (i.e., before and after bagging), while it is unknown if the BAAQMD measurements represent a single measurement or the average of two screening measurements made on each component by the BAAQMD inspectors. The BAAQMD inspectors did measure components three, four and five twice, however, and for those components, two lines of data are presented. Lines 3A,

# Table 3-1 BAAQMD vs. Radian Screening Value Comparisons

Component Order Inspected	Date	Insp. Ser. (ppm) <sup>a</sup>	Radian's (ppm) <sup>b</sup>
1	12-1-92	50	170 <sup>c</sup>
2	12-1-92	100	500
3A <sup>d</sup>	12-1-92	350	2,000
3B <sup>d</sup>	12-1-92	4,500	10,000
4A <sup>d</sup>	12-1-92	3,000	5,000
4B <sup>d</sup>	12-1-92	>10,000	40,000
5A <sup>d</sup>	12-2-92	2,000	1,000
5B <sup>d</sup>	12-2-92	750	1,000
6	12-7-92	90	75
7	12-7-92	600	600
8	12-7-92	>10,000	>140,000
9	12-7-92	2,000	1,250
10	12-8-92	20	35
11	12-8-92	2	1.5
12	12-9-92	3	1
13	12-9-92	>10,000	>139,000
14	12-10-92	100	125
15	12-10-92	>10,000	49,300
16	12-10-92	300	450
17	12-10-92	800	900
18	12-10-92	2,000	2,600
19	12-10-92	>10,000	30,000
20	12-11-92	>10,000	30,000
21	12-11-92	>10,000	27,500

<sup>a</sup> BAAQMD reported all values  $\geq 10,000$  ppm as 10,000 ppm.

<sup>b</sup> Radian's values (except 3A, 3B, 4A, 4B, 5A, and 5B) represent the average of initial and final screening values.
 <sup>c</sup> Full values (except 3A, 3B, 4A, 4B, 5A, and 5B) represent the average of initial and final screening values.

<sup>c</sup> Failed QC check.

<sup>d</sup> The "A's" are the initial screening values and the "B's" are the final screening values of the same component.

 $OEL = \hat{O}pen-ended line.$ 

Component Order Inspected	Date	Insp. Scr. (ppm) <sup>a</sup>	Radian's (ppm) <sup>0</sup>
22	12-11-92	6,000	5,000
23	12-11-92	500	115
24	12-11-92	>10,000	40,000
25	12-16-92	4	2
26	12-16-92	2	2
27	12-16-92	2	1
28	1-5-93	>10,000	>75,000
29	1-5-93	>10,000	>100,000
30	1-8-93	>10,000	72,900
31	1-27-93	>10,000	>100,000
32	1-27-93	>10,000	35,000
33	1-27-93	5,000	3,250
34	1-29-93	>10,000	>100,000
35	1-29-93	>10,000	21,500
36	1-29-93	>10,000	>77,500
37	2-2-93	425	400
38	2-2-93	400	335
39	2-24-93	220	225
40	2-24-93	1,250	1,250
41	2-24-93	600	675

# Table 3-1 (Continued)

а BAAQMD reported all values ≥10,000 ppm as 10,000 ppm.

þ Radian's values (except 3A, 3B, 4A, 4B, 5A, and 5B) represent the average of initial and final screening values.

с

Failed QC check. The "A's" are the initial screening values and the "B's" are the final screening values of the same component. d OEL = Open-ended line.

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4A and 5A show the initial measurements made by both Radian and BAAQMD inspectors and lines 3B, 4B and 5B show the final measurements made by both Radian and BAAQMD inspectors. For components three and four, the Radian initial and final measurements differ by a factor greater than two, and were therefore excluded from earlier multivariate analyses and regression calculations. They are included in this comparison study. However, the point should be made that the initial and final measurements made by the BAAQMD inspectors also show a large amount of variability. One can conclude that the components were highly variable, and differences between Radian and BAAQMD measurements may be a function of the component variability as well as differences between Radian and BAAQMD inspectors.

Side-by-side histograms of the Radian and BAAQMD screening values were constructed for the measurements collected before and after adjustment of the instrument. These are shown in Figures 3-1 and 3-2. The screening values shown in the figures are not representative of refinery screening value distributions because the components were not randomly selected for screening. The BAAQMD and Radian distributions appear to be the same both before and after the potential leaks had been detected. A count revealed that, of the 13 measurements collected before detection, the Radian measurements fell into the same category as the corresponding BAAQMD measurements 11 times and into a higher category than the screening instrument had been adjusted, the Radian and BAAQMD measurements were grouped into the same category 29 times, while the BAAQMD measurement was in a higher category than the corresponding Radian measurement only once.

Side-by-side histograms are useful in showing the complete distribution of Radian and BAAQMD screening values because components that screen at zero and components that peg the instrument can be included in the histogram bins. However, the histograms do not show how individual BAAQMD and Radian screening values compare. A scatter plot was done of the BAAQMD versus Radian screening values to show how well the paired screening values compare. Screening values that screened at zero and that pegged the instrument were not included in these scatter plots. A 45° diagonal line was also drawn on the scatter diagrams, indicating the relationship that would be obtained if a perfect correlation had been obtained between the BAAQMD and Radian screening values. Points above the diagonal are



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Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS BAAQMD screening values that are higher than Radian screening values and points below the diagonal are Radian screening values that are higher than BAAQMD screening values. Data from leaking probes would tend to bias the emission correlation equations to give higher emission estimates than would emission correlation equations derived only from non-leaking probes.

Paired t-tests for the data collected before and after detection were also performed for those screening values shown in the scatter diagrams (excludes zero components and pegged components). In a paired t-test, differences between members of a matched pair are evaluated to determine if, on average, the difference is equal to zero or not, which is the appropriate analysis for dependent data. In this case, Radian and BAAQMD measurements on the same components form a matched pair, and must be treated as dependent. Determining if the *differences* between BAAQMD measurements and Radian measurements were the same before as they were after detection provides a more valid comparison of before-detection and after-detection data by controlling for the fact that components screened before detection may have differences of the logarithms of the statistical assumptions could be met. Table 3-2 presents the average differences of the logarithms of the screening values before and after adjustment of the instrument. On the basis of the t-tests, there is no evidence to conclude that the Radian screening values were different from the BAAQMD screening values either before or after adjustment.

The signed relative percent difference (RPD) between the Radian and BAAQMD screening measurements were also calculated for those components that were not pegged. The signed RPD is calculated as follows:

where: SV=OVA screening value; and

Average SV=Average of Radian and BAAQMD SV.

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# Table 3-2Paired Comparison T Test to Test for Statistically<br/>Significant Differences Between Radian and BAAQMD<br/>Screening Values<sup>a</sup>

Sample Date	Number of Paired Tests	Average Difference <sup>b</sup> (ppm)	Standard Error of Difference (ppm)	T-Statistic	P-Value	Statistical Conclusio B
Before 12/8/92	11	0.31	0.23	1.37	0.20	NS
After 12/8/92	16	-0.23	0.13	-1.76	0.09	NS
All Dates	27	-0.01	0.13	-0.06	0.95	NS

BAAQMD = Bay Area Air Quality Management District NS = Average difference between Radian screening

= Average difference between Radian screening value and the BAAQMD screening value not statistically significant at the 0.05 significance level.

<sup>a</sup> Pegged component screening values not included in quantitative comparisons.

<sup>b</sup> Average difference between Radian screening value and BAAQMD screening value.

The average signed RPD for the 11 tests before the potential probe leak was detected was +26.5% and the average signed RPD for the 16 tests after the potential probe leak was detected was -20.5%. Both of these average RPDs are less than the average RPD of 89.4% calculated in the instrument and inspector variability study (see the following subsection). Thus, the BAAQMD versus Radian variability appears to be within the range of the variability estimates obtained for the instrument and inspector screening variability study.

The data on December 8 are of particular interest because this is the only date that an OVA leak is known to have occurred (with a blocked OVA probe tip) during any of these comparison screenings. One data point was a zero component and provides little additional insight; however, the difference in OVA screening values was only 0.5 ppm. The second data point differed by 15 ppm (RPD = 55%). This level of variability is also well within the level of variability for side-by-side screening of inspectors (see the following subsection).

# Examination of the Relationship Between Emission Rate and Screening Value

Data collected at all sites were divided into two categories: data collected with a potentially leaking OVA (before detection) and data collected with a nonleaking OVA (after detection). In order to be consistent with the multivariate analysis results, analyses to determine if data collected before detection differed from data collected after detection were performed by component categories. Component categories are:

- Flange connectors in all services;
- Non-flange connectors in all services;
- Open-ended lines in all services;
- Pump seals in heavy liquid service;
- Pump seals in light liquid service; and
- Valves in all services.

For each component category, emission rate was plotted against screening value with different symbols indicating detection status (before detection or after detection). The 95% confidence bands for the means were constructed around the respective regression lines. To statistically determine if the relationships between screening value and emission rate differ by detection status, analyses of covariance were performed with log emission rate as the dependent variable and log screening value, instrument ID, detection status and the interaction between screening value and detection status as the explanatory variables. Instrument ID was included because previous analyses showed that instrument ID has a significant effect on emission rate after controlling for screening value. Including instrument ID in the analyses enables one to first control for variability between instruments before examining the effect of detection status. Testing for the main effect of detection status after controlling for other explanatory variables tests whether the intercepts of the before-detection and after-detection regression lines differ. Testing for the effect of the interaction between screening value and detection status tests the equality of the slopes.

The plots can be found in Figures 3-3 through 3-8. Conclusions drawn based on inspection of the plots generally concur with the conclusion based on the analyses of covariance, but the point should be made that the plots do not contain information on differences between instruments, while the statistical analyses do control for such differences. Notice that the confi-

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3-12





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dence bands overlap and provide no visual evidence of differences before and after detection for flange and non-flange connectors in all services and open-ended lines in all services. The analyses of covariance for these components support the visual evidence: the data do not provide significant indication of differences in the relationship between screening value before and after detection at the 95% confidence level. Note that for pump seals in heavy liquid service, only ten data points were collected, eight of which were collected after detection. There are not enough data to draw any conclusions about these components.

Although not readily apparent from the plot of pump seals in light liquid service, the analysis of covariance indicates a statistical difference in the data collected before and after detection of potential leaks. After controlling for between-instrument differences, the main effect of detection status (intercept) is not significant at a 95% confidence level; however, the p-value of 0.0666 is relatively close to the significance level of 0.05. The interaction between screening value and detection status (slope) is significant at the 95% confidence level (p-value=.0359). For valves in all services, the plot does not reveal strong evidence of a difference in intercept, but there is some indication of a difference in slope. The analysis of covariance for components in this category shows that, after controlling for between-instrument differences, both the main effect of detection status and the interaction between screening value and detection status are significant at the 95% confidence level (p-values=.0351 and .0494, respectively). However, for both light liquid pumps and valves, the data are intermixed before and after the potential for probe leaks was determined.

The statistical analysis of all the data collected before and after the potentially leaking OVAs were found gives some indication that the data collected before detection differs from data collected after detection with certain component types (pumps in light liquid service and valves in all services combined). However, no general trend is made obvious by the various analyses. For three of the component types (flange connectors, non-flange connectors, and open-ended lines), no statistically significant difference before and after the discovery of potential probe leaks is found. For valves, the data collected before detection of potential probe leaks has a higher mass emission rate per screening value than the data collected after the detection of potential probe leaks, although the 95% confidence levels overlap. Note that the "before detection" regression line for valves would be higher than the "after detection"

regression line. Therefore, if the earlier data for valves were affected by probe leaks, this would result in an overestimation of emission rates for a specific screening value. For light liquid pumps, the "before detection" and "after detection" lines would cross each other. This lack of general trend together with the overlapping confidence intervals for light liquid pumps indicates that there is no systematic bias in the data before and after potential probe leak detection.

Statistically significant differences could also be due to a number of confounding factors such as: site of testing, region of testing, instrument used in testing, and number of components in each service type.

### **Conclusion**

This analysis gives strong indication that the potentially leaking probes had a minor, if not insignificant impact on the data. Furthermore, this analysis indicates that the potentially leaking probes did not result in a systematic bias in the data analysis. There does not appear to be any reason to invalidate any data prior to the detection of potentially leaking probes. As a review:

- The probe leaks were discovered only when completely blocking the OVA probe tip during an audit procedure. The OVA probe is unobstructed when the screening measurements were made in this study. The potential to leak is dramatically reduced when the probe tip is unobstructed.
- The potentially leaking OVAs were calibrated with any probe leaks already in place and the OVAs adjusted to account for any probe leaks. The dilution ratio, with or without probe leaks, was also determined at least daily (usually with each component exceeding 10,000 ppm). No change in probe leaks could have occurred during the day that would substantially affect the data because OVA drift checks were performed after each component was bagged.
- Side-by-side screening measurements by Radian and BAAQMD inspectors indicate that both before and after December 8 both inspectors were in the same screening value ranges in nearly every case (85% before and 97% after). These side-by-side measurements both before and after also indicate differences (RPDs) well within the expected screening variability (less than the screening variability observed in other tests with two

inspectors and two different OVAs documented as having no leaks).

• Review of data collected before and after December 8 indicates no statistical difference for the categories of flange connectors, nonflange connectors, and open-ended lines. Statistically significant differences were determined for light liquid pumps and valves (all service types combined). However, statistically significant effects may be due to confounding variables. Review of the data before and after December 8 shows no general trend indicating that there is no systematic bias in the data collected before and after this date.

# SCREENING VARIABILITY TEST RESULTS

The screening value obtained for any given component fluctuates due to a number of factors. Several different screening variability studies were conducted to explore different potential sources of screening variability. The results of these screening variability studies are presented in this subsection. The first two parts of this subsection present the results of an inspector and instrument variability study, and a process variability study, respectively. Another study was conducted to examine potential differences between Radian screening value measurements and the screening measurements obtained by inspection/maintenance (I/M) teams of each California host refinery. The next two parts of this subsection compare screening value measurements collected by the Bay Area Air Quality Management District (BAAQMD) and the South Coast Air Quality Management District (SCAQMD) to screening value measurements collected by Radian on the same components.

## Inspector and Instrument Variability

Inspector and instrument variability was examined using measurements taken by two inspectors using two different Foxboro OVA 108 screening instruments. Data were collected on 45 gate valves in gas service in the same process unit at a single site. Each of the 45 components was screened twice, with the second inspector screening immediately after the first, but with no communication between the two inspectors regarding the results. Because inspector 1 used instrument 1 and inspector 2 used instrument 2 throughout the data collection period, differences in screening values cannot be attributed completely to either inspector differences or to instrument differences, but to some combination of the two, which will be referred to as inspector and instrument variability. The fact that the first inspector screened each component first may also add a confounding time factor, but this is assumed to be negligible.

Both inspector 1 and inspector 2 obtained screening values of zero for 27 of the 45 components, corresponding to an exact agreement rate of 60% (all were nonemitting components). Table 3-3 presents the screening values obtained by each inspector on the 18 remaining components for which the screening values differed. The table also shows the average of the two screening values per component as well as the signed relative percent differences (RPDs) and the coefficient of variations (CV). The RPD is calculated as:

Equation 3-2: RPD =  $\frac{100 \text{ x (inspector 1 SV - inspector 2 SV)}}{\text{Average SV}}$ 

where: SV= OVA screening value - background screening value;

Average SV=Average of inspector 1 and inspector 2 SV.

The CV is another measure of relative variability and is calculated as (100 x standard deviation)/mean. Note that, of the 18 screening values which differed by inspector, the RPD was less than 100% for 12 cases. Notice that for four of the six cases in which the RPD was greater than 100%, one of the inspectors obtained a screening value of zero, while the other inspector obtained a nonzero screening value, leading to an RPD of 200%. In these four cases, the maximum difference was only 27 ppm, which is small compared to the variability in screening values between components.

The measurement taken by inspector 1 was smaller than the second measurement for 12 of the 18 components, suggesting a possible trend in inspector and instrument differences. The plot of screening values versus component with different symbols for each inspector (see Figure 3-9), however, does not indicate a clear trend. The plot does suggest that the differences between screening values are not alarmingly large. A paired t-test supports the claim

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		Inspector Scr (p)	reening Values mi)	Summary Statistics		
Component ID	Component Type	Inspector 1 and Instrument 1	Inspector 2 and Instrument 2	Average (ppm)	Signed Relative Percent Difference (%) <sup>a</sup>	CVd (%)
1	Gate Valve	1,996	2,196	2,096.0	-9.5	6.7
2	Gate Valve	0	19	9.5	-200.0	141.4
3	Gate Valve	49,997	99,997	74,997.0	-66.7	47.1
4	Gate Valve	17	4	10.5	+123.8	87.5
5	Gate Valve	0	8	4.0	-200.0	141.4
6	Gate Valve	27	0	13.5	+200.0	141.4
7	Gate Valve	196	947	571.5	-131.4	92.9
8	Gate Valve	19,997	17,497	18,747.0	+13.3	9.4
9	Gate Valve	497	547	522.0	-9.6	6.8
10	Gate Valve	77	87	82.0	-12.2	8.6
11	Gate Valve	1,197	2,996	2,096.5	-85.8	60.7
12	Gate Valve	237	147	192.0	+46.9	33.1
13	Gate Valve	547	347	447.0	+44.7	31.6
14	Gate Valve	796	1,397	1096.5	-54.8	38.8
15	Gate Valve	346	747	546.5	-73.4	51.9
16	Gate Valve	3,998	1,497	2,747.5	+91.0	64.4
17	Gate Valve	218	346	282.0	-45.4	32.1
18	Gate Valve	0	3	1.5	-200.0	141.4
All Components					89.4 <sup>c</sup>	79.6 <sup>e</sup>

#### **Inspector and Instrument Variability Results For Non-Zero** Table 3-3 **Screening Measurements**

<sup>a</sup> Relative Percent Deviation (RPD) = 100 x (inspector 1 screening value - inspector 2 screening value)/[(inspector 1 screening + inspector 2 screening value)/2].

h

 <sup>b</sup> Average screening concentration obtained by operator.
 <sup>c</sup> Average absolute RPD. If tests that screened at background by either inspector are excluded from this analysis then the absolute RPD is 57.8.

d CV = Coefficient of variation = (100 x standard deviation)/mean.

<sup>e</sup> Pooled CV.

that differences are not substantial. The t-statistic for testing whether the mean difference in the logarithms of the screening values is zero is .60 with 14 degrees of freedom, which corresponds to a p-value of .56, leading to the conclusion that there is no statistically significant evidence of a difference in screening values. In other words, the data show no substantial inspector and instrument bias.



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### Process Variability

Following the collection of data for the inspector- and instrument- variability study, more data were gathered by inspector 1 using instrument 1 to examine process variability (or variability across time). Eighteen of the previous 45 components were rescreened seven times in a series of seven cycles during a continuous seven hour period. Because measurements of most of the components also had been made the previous day, up to nine measurements were recorded for each of the 18 components used in the study:

- One previous-day measurement (Pre-Test 1);
- One previous-study measurement (Pre-Test 2); and
- Seven process-variability measurements (Tests 1–7).

The raw data are presented in Appendix C. The 18 components have been assigned the numbers 1 through 18 so as not to identify the refinery. These do not correspond to the same component numbers assigned to the components in the inspector and instrument screening variability study.

Table 3-4 presents the average screening value as well as the smallest and the largest screening values recorded for each of the 18 components, and the coefficients of variation (CVs). Although differences in average screening values between components were observed, the focus of this study was on the variability within components across time. Analysis was performed to determine whether or not screening values tended to increase or decrease across time and to quantify the overall process variability. Note that most of the data were collected in a single day, so the conclusions drawn cannot be extended to describe the variability from one day to another.

<u>Trend Analysis</u>. Figures 3-10 and 3-11 show plots of screening values versus the consecutive test measurement. The plots do not indicate a strong overall trend that is either increasing or decreasing with time. This observation is supported by the results of the Mann-Kendall trend analysis (Gilbert, 1987) that was performed on each of the 18 components.

The Mann-Kendall trend analysis is a nonparametric analysis based on a ranking of the data. Pegged values (> 100,000 ppm) were set equal to 100,000 ppm and ranked accordingly.

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		Summary Statistics						
Component ID	Component Type	Number of Tests	Average (ppm)	Minimum (ppm)	Maximum (ppm)	CV <sup>d</sup> (%)		
01 <sup>a</sup>	Gate Valve	7	82,280.7	24,995	>100,000	31.8		
02	Gate Valve	7	837.9	595	1,195	21.6		
03 <sup>b</sup>	Gate Valve	7	>100,000	>100,000	>100,000	<sup>e</sup>		
04	Gate Valve	9	1,511.8	195	2,295	51.3		
05	Gate Valve	9	31,228.8	1,095	49,997	53.4		
06	Gate Valve	9	4.6	0	17	159.1		
07	Gate Valve	9	21.3	13	37	37.2		
08	Gate Valve	9	194.6	85	345	44.0		
09 <sup>c</sup>	Gate Valve	9	54,595.3	1,393	>100,000	71.7		
10	Gate Valve	9	397.7	15	895	62.5		
11	Gate Valve	9	78.2	50	115	29.4		
12	Gate Valve	9	928.8	295	1,295	36.3		
13	Gate Valve	9	211.0	125	295	23.0		
14	Gate Valve	8	280.9	0	695	83.1		
15	Gate Valve	9	382.8	55	797	78.0		
16	Gate Valve	9	315.2	155	495	35.0		
17	Gate Valve	9	6,995.8	1,495	29,996	124.7		
18	Gate Valve	9	132.9	0	218	54.7		
All Cor	nponents					67.9 <sup>f</sup>		

 Table 3-4 Process Variability Results

<sup>a</sup> 6 of the 7 values were recorded as > 100,000 ppm, but were set equal to 100,000 ppm for calculation of summary statistics.

<sup>b</sup> All of the values were recorded as > 100,000 ppm, but were set equal to 100,000 ppm for calculation of summary statistics.

c 3 of the 9 values were recorded as > 100,000 ppm, but were set equal to 100,000 ppm for calculation of summary statistics.

<sup>d</sup> CV = Coefficient of variation = (100 x standard deviation)/mean.

<sup>e</sup> CV could not be calculated. All components pegged.

f Pooled CV.





3-27

Fourteen of the components showed no significant trend. Components 7, 11, and 15 were found to have significant downward trends, while component 10 was found to have a significant upward trend. Thus, while some components appear to yield screening values that either increase or decrease across time, no overall time trend is evident.

<u>Overall Process Variability</u>. In addition to the trend across time, researchers were interested in quantifying the overall variability. Figures 3-12 and 3-13 display box-and-whiskers plots for each of the components. These plots show the smallest and largest screening values observed as well as the 25th, 50th, and 75th percentiles and the means for each of the 18 components. Some of the components show small amounts of spread around the mean, while others appear to be more variable.

An analysis of covariance (ANOCOVA) was conducted to determine whether the screening value measurements differed significantly across time after accounting for component differences. Data collected on the previous day (Pre-Test 1 measurements) were excluded from the analysis because these data were unique from all of the other tests that were performed on one single day. Additionally, the three components with pegged screening values were not included. The results of this analysis reveal that measurements made for components did, in fact, differ across time (p-value=.0006). It is also of interest to note that the process variability pooled CV was 67.9% which is smaller than the pooled CV obtained in the instrument and inspector variability study (CV = 79.6%).

Figures 3-12 and 3-13 illustrate the screening value variability for each component. As shown in the figures, the most consistent readings were observed for component IDs 2 and 3. For component ID 2, readings collected throughout the day consistently fell between about 600 and 1,200 ppm. For component ID 3, all 7 readings were recorded as > 100,000 ppm. Screening values that fluctuated the most appeared to be for component IDs 5, 9, and 14. Measurements for components 5 and 9 fluctuated from about 1,000 ppm to 50,000 ppm and > 100,000 ppm, respectively. Measurements from component ID 14 went from 0 ppm to about 700 ppm. It is of interest to compare these results to the results of a valve screening study conducted in 1979, entitled *Valve Screening Study of Six San Francisco Bay Area Petroleum Refineries* (Radian, 1979) (Valve Screening Study). In the Valve Screening Study,

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screening values were obtained from the same components over a period of several days. These screening values were found to have large day-to-day variability. Day-to-day variability for the "best" cases showed screening measurements that fluctuated between about 3,000 and 10,000 ppm. In one of the "worst" cases a screening value changed from > 100,000 ppm to essentially zero and back to > 100,000 ppm in a few days time.

In summary, analysis of the Western States Petroleum Association (WSPA) and American Petroleum Institute (API) data collected <u>within a single day</u> suggests that screening values are relatively constant on a given day. However, a previous study conducted by Radian (Radian, 1979), showed that the screening values collected <u>over several days</u> could differ by several orders of magnitude.

### I/M Versus Radian Screening Variability

Four out of the five refineries involved in the 1993 Refinery Study were evaluated for variability between refinery I/M screening values and Radian inspector screening values. In order to determine how well the screening values obtained by the I/M teams agreed with Radian's measurements, the Radian inspectors screened many of the same components that were to be screened by the I/M teams. Only the measurements made on the same day by both I/M inspectors and Radian inspectors were used in the analysis. Refineries were randomly assigned numbers 1 through 4 to further protect the identities of the refineries, and each refinery was analyzed separately.

When I/M teams visit a site, the standard procedure for some refineries is to immediately attempt a repair of high leaking (> 10,000 ppm) components. At two of the sites, however, the Radian team requested that no components be adjusted during this period of data collection in order to obtain meaningful comparison data. At one of these refineries, one component, for which the screening value exceeded 100,000 ppm, was adjusted by the I/M team anyway, and the data collected on this component were deleted from analyses. Discussions with operators at the other two refineries revealed that repairs of components by the I/M teams were highly unlikely on the day of comparison testing. Thus, measurements made by Radian inspectors and by I/M team inspectors were probably both made on nonrepaired com-

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ponents at all refineries. However, discrepancies between the two teams' measurements could be confounded by the possibility of adjusted components.

A further complication arises in the distance that the OVA probe tip is held from the leaking component. Radian measured leaks at all four refineries right at the point of highest concentration at the surface of the component. Refineries 2 and 3 also screened at the surface of the component. However, Refinery 1 screened at a distance of approximately 0.5 cm, and Refinery 4 screened at a distance of approximately 1 cm.

Because the refineries' I/M teams did not follow the same operating procedures for screening background as Radian's inspectors, assumptions were made and the screening values were corrected accordingly. The explanations follow:

- Refinery 1: No background screening was recorded by the refinery's I/M team. If the I/M component screening value was greater than Radian's largest background screening value (9 ppm) then background was assumed to be 9 ppm. I/M component screening values that were less than 9 ppm were assumed to be equal to background.
- Refinery 2: The I/M team recorded background screening value as 10 ppm for all components.
- Refinery 3: No component screening values less than 50 ppm were recorded, and no background screening values were recorded. For recorded component screening values (those greater than 50 ppm), background was set equal to Radian's highest background screening value (6 ppm).
- Refinery 4: No background screening was recorded by the refinery's I/M team. If the I/M component screening value was greater than Radian's largest background screening value (14 ppm) then background was assumed to be 14 ppm. I/M component screening values that were less than 14 ppm were assumed to be equal to background.

The background screening values were subtracted from the original component screening values, and these adjusted component screening values were used in all subsequent analyses. Both qualitative and quantitative analyses were performed.

<u>Qualitative Analysis</u>. Screening values were categorized as belonging to one of 5 groups: 0-50 ppm, 50-500 ppm, 500-1,000 ppm, 1,000-10,000 ppm and > 10,000 ppm. Screening values which pegged the instrument were included in the > 10,000 ppm category. Using

these categories, side-by-side histograms were constructed in order to compare the distributions of screening values obtained by the I/M teams to the distributions of those obtained by Radian (See Figures 3-14 through 3-17). Visual inspection reveals that, for all of the refineries, the distributions are quite similar to one another. One should note, however, that this does not provide evidence that the I/M screening values match the Radian screening values for individual components. Table 3-5 shows, by refinery, how many I/M measurements and Radian measurements of the same component fell into the same screening-value range, how many of Radian's measurements were in a larger screening-value range than the I/M measurement of the same component and how many of Radian's measurements were in a smaller screening-value range than the I/M measurement of the same component. One can see that most of the measurements for each of the refineries do fall into the same categories. In addition, the number of times that both the I/M team and Radian recorded corrected screening value measurements of 0 ppm is given. For each of the refineries, it should be noted that, when Radian's screening value fell into a different category than the I/M team's screening value for the same component, the two measurements were most often in one of the two lowest screening value categories. In other words, either Radian or the I/M team measured the screening value as less than 50 ppm, and the other team measured the screening value as falling between 50 and 500 ppm.

Figures 3-14 through 3-17 also show scatter plots of the I/M team screening value versus Radian's screening value for individual components. Components that screened at zero (i.e., background) and those with screening values that pegged the instrument were not included in the scatter plots. A 45° diagonal line is also shown on these plots indicating the relationship that would be obtained if there was a perfect correlation between the I/M and Radian screening values. Points above the diagonal are I/M screening values that are higher than Radian screening values and points below the diagonal are Radian screening values that are higher that I/M screening values. As shown in the figures, the agreement between the Radian and I/M screening values from Refinery 3 tended to be higher than the Radian screening values for measurements collected between 1 and 10,000 ppm. It is of interest to note that although I/M and Radian screening values between I and 10,000 ppm did not show good agreement, there was good agreement between I/M and Radian zero screening values for Refinery 3. As









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Refinery Number	Refinery Radian SV and I/M SV in Same Number Category		Radian SV in Higher Category Than I/M SV	I/M SV in Higher Category Than Radian	
	Both Screened at Background	Both Did Not Screen at Background		SV	
1	0	45	8	4	
2	191	62	8	3	
3	127	73	22	29	
4	105	57	20	7	

 Table 3-5
 Comparison of Radian and I/M Screening Value Ranges

I/M = Inspection/Maintenance.

SV = Screening Value.

shown in Table 3-5, for Refinery 3, both the I/M and Radian teams obtained zero screening values (i.e., equal to background) 51% of the time (i.e., 127 out of 251). This agreement between the zero screening values is not shown in the scatter plot because it is on a log scale and zeros cannot be shown. It is also of interest to note that although the scatter plot shows that individual screening measurements did not show good agreement for Refinery 3, the percent of screening values within each screening value range were virtually identical, as shown by the histograms.

<u>Quantitative Analysis</u>. To determine if evidence of consistently higher screening results for either the Radian or the I/M teams existed, paired t-tests were performed for each of the refineries on the differences of the logarithms of the screening values. Table 3-6 shows, for each refinery, the number of components sampled by both Radian and the I/M team, the average difference in logarithms of the screening values between the two teams, the standard error of the average difference, and the results of the t-test. The t-tests were performed to determine whether or not the data provide statistically significant evidence to conclude that the two teams differ. For Refineries 1, 2, and 4, the t-test led to the same conclusion: the data do not indicate that Radian's measurements were consistently higher or lower than the measurements made by each refinery's I/M team. For Refinery 3, the t-test results indicate that the I/M screening values were significantly higher than the Radian screening values (alpha = 0.05). This supports the visual evidence shown in the scatter plot in Figure 3-16.

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The two refineries that screen at 0.5 cm and 1 cm from the point of highest leak had screening values that were, in general, lower than the Radian screening values, as would be expected. It should be noted from the histograms in Figures 3-14 and 3-17 that for Refineries 1 and 4 (both of which did not screen at the component surface), Radian found higher numbers of components with screening values  $\geq 500$  ppm than did the I/M teams. For Refineries 2 and 3, that screen at the surface of the component (comparable to Radian's method), the number of components screened by Radian and the I/M teams at  $\geq 500$  ppm was much closer. The scatter plots of the refinery versus Radian screening values shown in Figures 3-14 and 3-17 also show a larger number of values below the diagonal line, indicating that the Radian screening values tended to be larger than the I/M screening values for Refineries 1 and 4. However, even the average differences for Refineries 1 and 4 were not statistically significant.

### BAAQMD Versus Radian Screening Variability

During the data collection period at one of the refineries, regulators from the Bay Area Air Quality Management District (BAAQMD) screened components immediately after Radian inspectors screened them in order to determine how closely the two teams agreed. Both the BAAQMD regulators and the Radian inspectors used OVA measuring instruments to screen valves, connectors, open-ended lines and pumps. The screening values detected are not representative of the true distribution of all screening values at the refinery because the components that were screened were not selected randomly. BAAQMD and Radian screening values are given in Table 3-1 of Section 3.

Because the BAAQMD measuring instrument pegged at a lower screening value (10,000 ppm) than the Radian instrument (typically 100,000–140,000 ppm), screening values were categorized as belonging to one of 5 groups: 0–50 ppm, 50–500 ppm, 500–1,000 ppm, 1,000–10,000 ppm and  $\geq$  10,000 ppm. BAAQMD screening values which pegged the instruments were classified as  $\geq$  10,000 ppm.

Figure 3-18 shows the distributions of screening values for Radian's measurements and for the BAAQMD measurements. No substantial differences between the two histograms are apparent. This does not indicate, however, whether the screening values obtained by Radian

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# Table 3-6Paired Comparison T Test to Test for Statistically<br/>Significant Differences Between Radian and I/M<br/>Screening Values<sup>a</sup>

Refinery	Number of Paired Tests	Average Log Difference (ppm)	Standard Error of Difference (ppm)	T-Statistic	P-Value	Statistical Conclusion
1°	23	0.639	0.364	1.75	0.09	NS
2	8	-0.723	0.624	-1.16	0.28	NS
3	60	-1.13	0.209	-5.39	0.0001	S
4 <sup>d</sup>	21	0.472	0.418	1.13	0.27	NS

I/M = Inspection/Maintenance.

NS = Average difference between Radian screening value and the I/M screening value not statistically significant at the 0.05 significance level.

<sup>a</sup> Pegged screening values not included in quantitative comparisons.

<sup>b</sup> Average different between Radian log(screening value) and I/M log(screening value).

<sup>c</sup> Refinery 1 screens at approximately 0.5 cm from the component.

<sup>d</sup> Refinery 4 screens at approximately 1.0 cm from the component.

inspectors agree with those obtained by BAAQMD regulators for individual components. A count revealed that, of the 44 measurements taken by both Radian inspectors and BAAQMD regulators, 40 were classified as belonging to the same category as one another. Of the four which differed, three of the Radian measurements were in a larger screening value range than the BAAQMD measurements and one was in a smaller screening value range. A scatter plot of the BAAQMD versus Radian screening values is also shown in Figure 3-18. Values that screened at zero (i.e., background levels) and values that pegged the instrument are not shown in the scatter plot. A 45° diagonal line is also drawn on the scatter plot indicating the line that would be obtained if the BAAQMD and Radian measurements agreed exactly. Points above the diagonal are BAAQMD screening values that are higher than Radian screening values and points below diagonal are Radian screening values that are higher than BAAQMD screening values above and below the diagonal line and there are no large deviations from the diagonal line.

A paired t-test was performed on the measurements depicted in the scatter diagram to determine whether Radian consistently obtained values higher or lower than BAAQMD. The difference between the logarithm of the Radian screening value and the logarithm of the BAAQMD screening value for each component was calculated, and the average difference was found to be -0.01 ppm. The t-statistic for testing whether or not the true mean difference between Radian and BAAQMD measurements is different from zero was found to be -0.06, which corresponds to a p-value of 0.95. The conclusion, then, is that the data do not provide statistically significant evidence that the Radian measurements were either consistently higher or lower than the BAAQMD measurements.

## SCAQMD Versus Radian Screening Variability

South Coast Air Quality Management District (SCAQMD) auditors were also on site at one of the refineries during the data collection efforts. SCAQMD auditors screened six of the same components that Radian screened. Both initial and final screening values (i.e., before and after bagging) were obtained by both the auditors and Radian. These results are given in Table 3-7, along with the signed relative percent difference (RPD). Component IDs ending in an "-A" are the initial screening values and component IDs ending in an "-B" are the final screening values. Both the SCAQMD inspectors and the Radian inspectors used similar OVA 108 measuring instruments. Only valves were screened. As with the BAAQMD audit results, the screening values detected are not representative of the true distribution of all screening values at the refinery because the components that were screened were not selected randomly.

During the SCAQMD audit no "zero" components (i.e, components whose screening values are indistinguishable from background) and no "pegged" components (i.e., components whose screening measurements are greater than the measurable range of the OVA instrument) were obtained. Screening values were categorized as belonging to one of the following groups: 50–500 ppm, 500–1,000 ppm, and 1,000–10,000 ppm.

Figure 3-19 shows the distributions of screening values for Radian's measurements and for the SCAQMD measurements. As with the BAAQMD results, no substantial differences between the two histograms are observed. A count of the 12 measurements taken by both Radian inspectors and SCAQMD inspectors showed that 10 of the measurements fell into the





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Component Order Inspected <sup>a</sup>	Component Type	Date	Insp. Scr. (ppm)	Radian's (ppm)	Relative Percent Difference <sup>c</sup>
1A	Valve	2-24-93	125	150	+18.2
1B	Valve	2-24-93	350	300	-15.4
2A	Valve	2-24-93	1,500	1,100 <sup>b</sup>	-30.8
2B	Valve	2-24-93	1,500	1,400	-6.9
3A	Valve	2-24-93	350	350	0.0
3B	Valve	2-24-93	1,500	1,000	-40.0
4A	Valve	2-24-93	600	600	0.0
4B	Valve	2-24-93	250	350	+33.3
5A	Valve	2-24-93	2,000	2,000	0.0
5B	Valve	2-24-93	2,000	2,200	+9.5
6A	Valve	2-25-93	1,000	750	-28.6
6B	Valve	2-25-93	1,050	850	-10.5
	16.1 <sup>d</sup>				

# Table 3-7 SCAQMD vs. Radian Screening Value Comparisons

 $a^{a}$  "A" is the initial screening value and "B" is the final screening value on the same component.

<sup>b</sup> Radian's reading was revised from 550 ppm to 1,100 ppm after a higher leak location was identified by the SCAQMD inspector.
 <sup>c</sup> Relative Percent Difference = (100) (Radian SV - Insp. SV)/average

<sup>c</sup> Relative Percent Difference = (100) (Radian SV - Insp. SV)/average.

Average absolute RPD.

same categories on the histograms. Of the two which differed, both of the SCAQMD measurements fell into a larger category than the Radian measurements. A close agreement between the SCAQMD and Radian screening values is also shown in the scatter diagram at the bottom of Figure 3-19. As would be expected, a t-test performed on the differences between the SCAQMD and Radian *log(screening values)* showed that the average difference was not statistically different from zero.

## NITROGEN FLOW RATE VARIABILITY STUDY

Nitrogen is used during bagging to establish a steady flow rate of a known gas. This flow rate is needed to determine the mass emissions as described in Volume II, Section 2. The nitrogen flow rate used in the bagging procedure is dependent on the size of the bag and the

leak rate from the component. Larger bags require higher nitrogen flow rates to ensure equilibrium takes place in an acceptable time frame for testing. Higher leak rates require higher nitrogen flow rates to allow enough dilution of the bagged contents to allow OVA measurements used to verify equilibrium. During testing only one nitrogen flow rate is established for each bag. Typically this nitrogen flow rate was between 2 and 5 l/min. However, bag samples were taken with nitrogen flow rates between 0.7 l/min and 20 l/min. This study was designed to evaluate the effect of nitrogen flow on calculated emissions.

For each of twelve components, five to seven separate baggings with varying nitrogen flow rates were performed, and emissions were sampled at each new flow rate. The entire bagging procedure was repeated for each new flow rate, except that the bag was not removed between flow rates. Nitrogen flow rates were approximately 0.5 liter/minute, 1 liter/minute, 2 liters/minute, 5 liters/minute, 10 liters/minute, and 20 liters/minute. After samples for all flow rates were taken, the first flow rate was repeated in order to address the concern that differences observed between flow rates may be a function of time rather than increasing flow rate. The components tested are listed in Table 3-8.

Test 8 differs from the other eleven tests conducted and serves as an accuracy check in this study. The component was in water service, and methane was introduced into the bag at a monitored rate to simulate a steady leak. Emissions were sampled for each new nitrogen flow rate, and all other aspects of this test were the same as those of the other eleven tests. The purpose of this accuracy check was to control for the fact that observed differences could be due to within-component variability (i.e., leak variability).

### Statistical Results

The results of the twelve nitrogen flow tests are presented graphically in Figure 3-20. From the plot, nitrogen flow rate does not appear to have a systematic impact on emission calculations. The statistical tests applied to these data support this observation. Mann-Kendall trend analyses (Gilbert, 1987) were performed for each of the twelve components. Results from these tests are shown in Table 3-9.

Test Number	Component Type	Service	Number of Flow Rates
1	Valve	light liquid	5
2	Connector	light liquid	5
3	Valve	light liquid	5
4	Connector	light liquid	5
5	Pump Seal	heavy liquid	5
6	Valve	gas	7
7	Valve	gas	7
8	Valve	water	7
9	Connector	light liquid	7
10	Valve	light liquid	5
11	Connector	light liquid	7
12	Valve	light liquid	6

# Table 3-8 Nitrogen Flow Study Components

# Table 3-9 Statistical Results of Nitrogen Study

	Mann-Kendall	Trend Analysis
Test Number	p-Value <sup>a</sup>	Conclusion <sup>b</sup>
1	0.242	NS
2	0.242	NS
3	0.117	NS
4	0.592	NS
5	0.117	NS
	0.191	NS
7	0.386	NS
8 <sup>c</sup>	0.119	NS
9	0.281	NS
10	0.242	NS
11	0.386	<u>NS</u>
12	0.500	NS

<sup>a</sup> The p-value is the probability of incorrectly concluding that there is a trend. Generally, tests with p-values above 0.05 are regarded as insignificant.
 <sup>b</sup> NS indicates results were not significant at the 95% confidence level. A p-value of 0.05 indicates a significant trend.
 <sup>c</sup> Accuracy check



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The Mann-Kendall trend analysis is a nonparametric test based on the order of the data that makes no assumptions about distribution and is not highly sensitive to outliers. These tests showed no statistically significant trend for any of the components at the 95% confidence level. Because there is no significant evidence that nitrogen flow rate is related to emission calculations, the emissions calculated for all tests in the bagging study should not be adjusted for differing nitrogen flow rates.

#### ADDITIONAL BAGGING BENEFITS

The number of components tested varied significantly by component type. In order to better understand the impact of the differences in the sample size on the development of emission correlation equations, additional statistical analysis was performed. Based on the results of the multivariate analyses, regression lines of THC emission rate on screening value were constructed separately for each of six component categories. The categories and corresponding samples sizes are:

- Flange connectors in all services (n=19);
- Nonflange connectors in all services (n=29);
- Open-ended lines in all services (n=22);
- Pump seals in heavy liquid service (n=10);
- Pump seals in light liquid service (n=27); and
- Valves in all services (n=141).

Note that samples sizes range from 10 to 141.

Figures 2-8 through 2-13 in Volume I, Section 2 of the report illustrate the effect of the sample size on the precision of the results. The figures show the regression lines for each of the six component types along with the corresponding 95% confidence bands for the means. A regression line represents the expected emission rate for a given screening value. This expected value is only an estimate based on the data. Both variability in the data and the amount of information available affect the certainty one has in such an estimate. Confidence bands are a function of the variance (variability in the data), the sample size (amount of

information), and the distribution of the data in the sample and; therefore, help to quantify the certainty in one's estimates. The 95% confidence bands for the mean can be interpreted as the boundaries within which one can be 95% certain that the true mean emission rate corresponding to a given screening value lies. Note that the confidence bands are widest for pump seals in heavy liquid service (n=10) and tightest for valves in all services (n=141). In other words, the larger the sample size, the more precise the estimates.

In the U.S. EPA Protocols Document (Radian, 1993b), it is recommended to have a sample of size of 24 to develop new emission correlation equations. This recommendation is based on previous studies. The previous version of this report, the Protocol for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP (U.S. EPA, 1988) states that if it can be shown that the estimates are "within 50% of the mean value with 95% confidence," a smaller sample size is acceptable. The total sample size in this study is 248. However, when the data are separated according to component category, the sample size for a single category becomes much smaller. Conducting separate analyses for different component categories increases the accuracy of the emission correlation equation for a given category but results in the fact that the sample of size 24 criterion is not met for three of the categories (19 for flange connectors, 22 for open-ended lines, and 10 for heavy liquid pumps). However, the 95% confidence interval for the expected mean log emission rate at the mean log screening value meets the "plus or minus 50% of the expected value" criterion for all component categories. For pump seals in heavy liquid service (n=10), the upper and lower confidence limits for the expected mean log emission rate are within 22% of the expected value at the mean log screening value. For all other component categories, the upper and lower confidence limits are within 10% or less of the expected value in log space. When this criterion is evaluated for the upper 95% confidence interval of the expected mean emission rate, at the mean screening value in linear space, the only category that met this criterion was valves. In other words, the difference between the upper 95% confidence interval for the mean and the predicted emission rates was larger than 50% for all of the component categories, except for valves.

To illustrate the change in precision that one obtains by increasing the sample size, confidence bands were recalculated based on different sample sizes assuming that the amount of

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variability in the data does not change. For all connectors, open-ended lines and pump seals, the confidence bands appeared to grow tighter as the sample sizes increased by increments as small as 20. Once sample sizes reached approximately 100, however, small increases in sample size did not appear to increase the precision of the estimates. For valves in all services, increasing the sample size by 100 or even 400 did not appear to yield substantial improvements in the precision of the estimates.

Figures 3-21 and 3-22 show the confidence bands for different sample sizes for the two most extreme cases, pump seals in heavy liquid service (smallest sample size) and valves in all services (largest sample size). Relative percent differences between the upper confidence limits for the expected mean emission rates and the expected values at the mean screening value in linear space are also examined at different sample sizes. For pump seals in heavy liquid service, the solid lines indicate the confidence band calculated using the ten observed sample points. The broken lines represent the confidence bands that would be obtained with a sample of size 30, and the dotted lines represent the confidence bands that would be obtained with a sample of size 100. Notice that the precision in one's estimates appears to increase substantially when the sample size is increased by twenty data points. Calculations show that the relative percent difference between the upper confidence limit and the expected mean emission rate at the mean screening value is 157% when n=10 and 64% when n=30. Further increases in precision are seen when the sample size is increased to 100, but the difference between a sample of size 30 and sample of size 100 does not appear as large as the difference between a sample of size 30 and a sample of size 10. The relative percent difference between the expected mean emission rate at the mean screening value and the upper confidence limit is 30% when n=100.

In contrast to the improvements that are made by increasing the sample size for pump seals, increases in precision obtained by increasing the sample size for valves appear relatively insubstantial. The solid lines, which represent the confidence bands calculated based on the 141 observed sample points are almost indistinguishable from the broken lines, which represent the confidence bands based on a sample of size 241 or from the dotted lines, which

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represent the confidence bands based on a sample of size 541. Calculations showed that the relative percent difference between the expected mean emission rate and the upper confidence limit at the mean screening value is 26% when n=141, 19% when n=241 and 12% when n=541.

Later in this section, the results of analyses with previously-excluded data points show that the inclusion of those data points would not change the slopes or intercepts of emission correlation equations substantially. The estimated increases in precision in terms of the RPD in log space and in linear space that would have been gained by including the previouslyexcluded data points were examined. For most of the component categories, including these points increases the sample size by five or less, but for valves in all services there were 28 previously-excluded data points. The largest increases in precision in both linear space and log space are seen for pumps in heavy liquid service and open-ended lines in all services. For pumps in heavy liquid service, increasing the sample size from ten to twelve corresponds to an estimated change in RPD in log space from 22% to 19% and in linear space from 157% to 131%. For open-ended lines in all services, changing the sample size from 91% to 78% in linear space. For all other component categories, the changes did not appear substantial. Additional discussion on the issue of sample size can be found in the response to comments from the regulatory agencies in Appendix F of this study.

# EMISSION CORRELATION EQUATIONS WITH AND WITHOUT DILUTION PROBE DATA

The OVA used to collect data for the fugitive emission study has a logarithmic readout which ranges from 1 ppm to 10,000 ppm. With the use of a dilution probe, the upper limit of the range can be extended to 100,000 ppm. Data used to calculate emission correlation equations included screening values above 10,000 ppm, obtained through the use of a dilution probe. In order to determine whether the dilution-probe data had a substantial impact on the observed relationship between screening value and emission rate, emission correlation equations computed both with and without the dilution-probe data were compared. Five of the six component categories discussed in the multivariate analysis section were examined separately.

Pump seals in heavy liquid service are not included in this discussion because no screening values above 10,000 ppm were obtained.

For each of the component categories, a plot was constructed that shows the emission correlation equation computed with dilution-probe data as a solid line and the emission correlation equation computed without the dilution-probe data as a dashed line. (See Figures 3-23 through 3-27.) Also included on the graphs are the data points, with asterisks representing data points collected without the use of a dilution probe and dots representing data points collected using the dilution probe. Notice that the lines computed using the dilution-probe data tend to have slopes which are slightly lower than the slopes computed without the dilution-probe data. However, the lines do not appear to differ substantially for any of the component categories.

The 95% confidence intervals for the slopes and intercepts of the line calculated with dilution-probe data were compared to the 95% confidence intervals for the slopes and intercepts of the line calculated without dilution-probe data for each of the five component categories included in this analysis. For all of the component categories, both the slope and intercept confidence intervals overlapped, lending support to the visual evidence provided by the plots that the emission correlation equations calculated using the dilution probe data do not appear to differ substantially from the emission correlation equations calculated without the dilution probe data.

#### HIGH SCREENING VARIABILITY DATA

One of the data reduction steps involved averaging the before-bagging screening value with the after-bagging screening value for each component. The average was used in all multivariate analyses as a single measure of the screening value of a component. However, if the initial and final screening values for a component differed from one another by a factor of more than two, the component was considered to have high screening variability, and all data collected for that component were excluded from analyses. This criterion was established in order to reduce the uncertainty in the screening value measurements, and resulted in the exclusion of approximately 15% of the data that could have been used in the emission correlation equations.











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Data collected from components classified as having high screening variability may have been valid, however. The emission correlation equations were re-calculated using these previously excluded data points to determine if the equations appeared to change substantially. Separate equations were calculated for each of the six component categories:

- Connectors (flanges) in all services;
- Connectors (non-flanges) in all services;
- Open-Ended Lines in all services;
- Pump Seals in heavy liquid services;
- Pump Seals in light liquid services; and
- Valves in all services.

Figures 3-28 through 3-33 show the regression lines calculated without the high-screeningvariability data (referred to as SINVs for "Screening INValid") as dashed lines and the lines calculated with the high-screening-variability data as solid lines. Note that the two regression lines do not appear to differ from one another for flange connectors, nonflange connectors, open-ended lines, valves or pump seals in light liquid service, while the lines for pump seals in heavy liquid service do appear to differ from one another. Recall, however, that the regression line calculated without the high-screening-variability data points for pump seals in heavy liquid service is based on a sample of size ten and that the confidence and prediction bands around the regression line are quite wide. Thus, not enough data are available to state with certainty whether the regression lines are substantially different from one another for these components.

The data seem to suggest that including the high-screening variability data would not have changed the results substantially, but would result in tighter confidence and prediction bands around the emission correlation equations. However, this conclusion could not have been determined before the analysis was conducted. The original decision was made to exclude these high screening variability points that could have differed from the rest of the data in potentially important ways in order to reduce one area of variability in the study.















## Section 4 QUALITY ASSURANCE/QUALITY CONTROL RESULTS

The results of the quality assurance and quality control (QA/QC) program conducted for field and laboratory activities are presented in this section. A high level of attention has been directed toward QA/QC during this project. The overall responsibility for maintaining quality control was Radian's. However, audits by a United States Environmental Protection Agency (U.S. EPA) contractor, representatives from the Bay Area Air Quality Management District (BAAQMD), and the South Coast Air Quality Management District (SCAQMD), provided additional oversight which enhanced the quality of this study.

In this section, the first part explains why some bag samples were excluded from the data analysis. The second part of this section examines the sampling and laboratory analysis QA/QC control results. The third part of this section evaluates the daily OVA multipoint calibration data. The fourth part of this section discusses a canister stability study. The fifth part of this section discusses, in part, the U.S. EPA contractor's audit results. The last part of this section discusses the BAAQMD and SCAQMD audits.

#### BAG SAMPLES NOT USED

Some of the bag samples were not used in the determination of emission correlation equations, zero component factors and pegged component factors. Most of these were not used because quality assurance objectives outlined in the Quality Assurance Project Plan (and repeated in Volume II, Section 2 of this report) were not achieved. The excluded samples are identified in the spreadsheet in Appendix A. The comments column on the spreadsheet and the codes identify the reasons these bagged samples were not used. The reasons for excluding a bag sample from analysis were generally as follows:

- Higher than acceptable variability in initial versus final screening values (higher than a factor of 2 variability);
- Higher than acceptable O<sub>2</sub> readings (above 5%);
- Leaking canisters;
- Nitrogen flow forcing hydrocarbons back into component (open-ended lines);

- Zero component sample taken following a very high concentration sample (generally a pegged component) that appeared contaminated;
- Screening distance exceeding 1 cm;
- Extreme variation in nitrogen flow rate;
- OVA instrument drift; and
- Statistical outliers.

The high screening variability bag samples are identified with a code of "SINVs." The other bag samples not used are identified with a code of "DINV" for "determined during analysis to be invalid" and "INV" for "invalidated in the field."

The QA objective for data completeness for the 1993 Refinery Study was to have 95% valid data (Volume II, Section 2); this objective was not met. The single biggest reason that this objective was not met was because of the number of components with high screening variability. Of the 502 bagged samples collected for data analysis (excluding duplicates and audit samples), 414 (82%) were accepted for this study. (Note: 7 bagged samples were used in both pegged component development and emission correlation equation development.) Of the 88 samples not used, 46 were excluded for high screening variability and 42 were excluded for one of the other reasons stated above.

The majority of the bag samples that were used in the data analysis had initial versus final screening values that differed by less than 50%. Others varied by much greater than a factor of two, meaning that the initial screening measurement was more than twice as high as the final screening measurement or the final was more than twice the initial. As shown previously, including these samples would not have changed results substantially. They were excluded in an attempt to limit the variability of the data used for analysis.

Some components were originally measured at low oxygen readings before the sample was taken, but by the time the test was completed the oxygen amount had increased substantially, indicating that a leak in the tent had occurred while testing.

A few of the canisters used to collect samples in the field leaked. The canisters were under vacuum when the sample was taken. After the sample was taken, a reading by the vacuum gauge was recorded, usually with a remaining vacuum of approximately -10 inches of mercury. The canister vacuum was also recorded when the sample arrived at the laboratory. In a few cases, the sample had leaked while in-transit allowing ambient air contamination to occur. These samples were excluded from the analysis.

In three instances it appears that nitrogen flow into tents connected to vents (open-ended lines from certain process vessels) actually entered the process vessel. These were not conventional open-ended lines from which leakage is controlled by an upstream block valve. These were vents leading directly to the vapor space of storage tanks or other atmospheric pressure vessels. Without a block valve to prevent a backflow, the hydrocarbon vapors that were being emitted prior to the bagging were forced back into the process vessel by the nitrogen. No meaningful emission rates could be determined for this type of component using the standard bagging method, so these samples were deleted from the data set used for correlations.

As discussed in more detail in the next part of this section of this volume, fairly low levels of blank contamination were discovered early in the field testing. Some lower levels of blank contamination were observed even after the primary source of contamination was discovered and steps were taken to eliminate it. This problem was particularly evident when very low concentration samples (i.e., zero components) were taken following bagging of very high concentration samples (i.e., pegged components). This was likely caused by carryover in the sampling system. Because of this concern, zero component samples indicating contamination that were taken immediately after pegged component samples were excluded from data analysis.

In one case, a pump was screened at a distance of over two inches away from the highest leaking point, instead of  $\leq 1$  cm. This was done because the probe tip could not get closer because of an obstruction. This component was excluded from analysis to control screening distance variability.

A few data points were excluded because they were statistical outliers when compared with other similar component types and service types. Statistical outlier tests were used to examine all of the data collected in the 1993 Refinery Study. However, only those components that were statistical outliers <u>and</u> had other corroborating physical evidence to question the results were excluded. For example, sample W121 was a statistical outlier when compared with other valves. This component's total hydrocarbon (THC) concentration was reported as below the detection limit of the laboratory instrument. This result was anomalous for other non-zero components. The corroborating physical evidence used to exclude this data point was the OVA measured THC readings with the bag in place in the field. These OVA readings indicated an expected concentration of approximately 30 ppm.

One component was excluded because of high variability between the initial measured nitrogen flow rate before taking the sample and the final nitrogen flow rate measured after taking the sample. The nitrogen flow rate varied by nearly two orders of magnitude. This was anomalous, because nitrogen variability measured in most/all other samples was less than 5%.

Data from three components were excluded because the QC check of the OVA at the end of the sampling period indicated that the OVA was no longer reading a methane standard within 20% of the known concentration. This phenomenon, called OVA drift, occurs when the OVA battery is discharged. Because the exact screening value cannot be assigned to the measured mass emission rate for these components, data from these components were excluded. All reasons for excluding each component are explained in the comments section of the spread-sheet in Appendix A.

## SAMPLING AND LABORATORY ANALYSIS QUALITY ASSURANCE/QUALITY CONTROL RESULTS

All field and laboratory quality control results for U.S. EPA Method 18, TO-3, TO-14, SW8240 and ASTM D3416 analyses have been assessed. The results of this assessment indicate most of the data are valid and the quality, as measured by the analytical accuracy and precision, is within the acceptance criteria for the analytical methods used. The data used for the development of emission correlation equations and pegged component emission factors are considered valid, and within the acceptance criteria for analytical methods used. The data

used for the development of zero component emission factors, because of the potential for minor sample contamination, could cause some overestimate of these factors. The contamination problem was identified when some field blank contamination was observed, indicating a high bias potential for all total hydrocarbon (THC) and methane results < 25 ppmv collected prior to December 12, 1992 due to a contaminated vacuum gauge tee used in the sample collection process. Once this problem was identified appropriate corrective action was taken. Though concentrations were reduced, some field blank contamination was still observed after the corrective action was implemented, indicating all THC results < 5 ppmv may be suspect. No additional systematic problems were indicated. A brief summary of the remaining QA/QC results are discussed below. A detailed discussion of QA/QC requirements is presented in Volume II, Section 2.

All method (laboratory) blanks were clean. All method and surrogate spike recoveries were acceptable except for two high method spike recoveries by Method TO-14 which indicate a high bias potential for xylenes by this method. Excellent analytical precision was demonstrated by the laboratory duplicate results. The field duplicate precision was also acceptable, although greater-than-expected variability occurred in 13 of the 70 field duplicate pairs. The exhibited field duplicate variability is likely due to either heterogeneous conditions or to slight variations inherent to the sample collection process. Accuracy check results were acceptable for 4 of the 5 refineries. Both Method 18 and ASTM D3416 results for the accuracy check at the fifth refinery were low because of a leaking canister. The agreement between the results for the two methods confirm that the problem was due to the sample integrity rather than the analytical process.

QC sample analyses are presented in the following order: method and field blanks; method and surrogate spikes; laboratory and field duplicates; and, accuracy checks.

#### <u>Blanks</u>

Two types of blanks, method blanks and field blanks were collected and analyzed during this sampling effort to assess the potential for contamination from various sources in the sampling and analytical process.

All method blanks were clean, indicating the analytical system was free from interferences or contamination.

Six of the fifteen field blanks were contaminated to some extent: concentrations reported range from 0.31 to 61 ppmv. All six contaminated blanks contained detectable concentrations of THC. One of the blanks from Refinery V also contained methane. Also noteworthy is that the gas chromatogram for the Refinery V blank #2 indicated the contamination of 61 ppmv detected in this sample was a heavier, less volatile compound than any of the target analytes. Field blank results are summarized in Table 4-1.

The primary source of the contamination appears to have been the connecting tee on the vacuum gauge used to control flow from the bagged component into the canister. It was observed by a member of the field crew that after collecting a sample with greater than 100,000 ppmv of THC, the OVA reading of the gauge on the following morning (the said sample was collected on the previous night) was 30 ppmv. Appropriate corrective action was taken in the field in order to reduce this source of contamination. The effect on the data is that some results from samples collected before December 12, 1992 may have been influenced by contamination and therefore may be artificially high by the amounts detected in the blanks. This is particularly true for very low concentration samples (i.e., zero components) taken immediately after very high concentration samples (i.e., pegged components). Because of this concern, zero component samples that showed high concentrations in the laboratory analysis that were taken immediately after pegged component samples were not included in the determination of zero component emission factors. In addition, two blanks collected after the corrective action was implemented contained 4.7 and 1.7 ppmv of THC, collected at Refineries W and Y, respectively. These results indicate there is a slight high bias potential due to contamination, particularly for results below 5 ppmv.

The results of an extensive study conducted by the laboratory regarding the integrity of their canister cleaning process indicate that carry-over from the canisters is not a potential source of the exhibited blank contamination.

Refinery	Sample	Method	Detection Limit (ppmv)	Concentration (ppmv)
v	Blank 1	Method 18	0.090	ND
		D3416	1.80	ND
	Blank 2	Method 18	0.095	61
		D3416	1.90	ND
	Blank 3	Method 18	0.090	22
		D3416	1.90	9.7
w	Blank 1	Method 18	0.095	ND
		D3416	1.90	ND
	Blank 2	Method 18	0.100	ND
		D3416	2.00	ND
	Blank 3	Method 18	0.095	4.7
		D3416	1.90	ND
x	Blank 1	Method 18	0.090	ND
		D3416	1.80	ND
	Blank 2	Method 18	0.095	ND
		D3416	1.90	ND
	Blank 3	Method 18	0.090	ND
		D3416	1.80	ND
Y	Blank 1	Method 18	0.10	0.31
		D3416	2.00	ND
	Blank 2	Method 18	0.10	ND
		D3416	2.00	ND
	Blank 3	Method 18	0.10	1.7
		D3416	2.00	ND
Z	Blank 1	Method 18	0.095	6.4
		D3416	1.90	ND
	Blank 2	Method 18	0.090	ND
		D3416	1.80	ND
	Blank 3	Method 18	0.095	ND
an generated the		D3416	1.90	ND

## Table 4-1 Field Blanks

D3416 ND Used for methane analysis onlyNot detected

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#### Method Spikes

A method spike is a solution of method analytes (at known concentrations) that is spiked into a method blank. The results of the analysis of these samples are then reported as percent recoveries of each spiked compound. These percent recoveries are a measure of the laboratory's ability to accurately recover analytes.

Method spikes were performed with every analytical batch. The method spike recoveries were excellent. The vast majority were in the 70–130% range indicating excellent analytical accuracy was obtained and that, in general, the analytical system was operating in control. All of the Method 18, ASTM D3416, TO-3, and SW8240 spike recoveries met the QA objective of  $\pm 50\%$  of the expected value. Two Method TO-14 xylene spikes were high (162% and 281%), indicating total xylene results obtained by Method TO-14 may be biased high.

#### Surrogate Spikes

Surrogate spikes are a group of compounds other than target analytes that have been selected because of their similarity to the target analytes. Surrogate spikes are added to samples to monitor both the performance of the analytical system and the effectiveness of the method in recovering the method analytes.

Surrogate spikes were performed on all Method TO-14 and SW8240 samples. The quality assurance objective for each was for the recoveries to be  $\pm 30\%$  of the known value. All surrogate spike recoveries for both methods met this objective indicating that these methods were performing within allowable limits and there were no systematic problems during sample analysis.

#### Laboratory Duplicates

Laboratory duplicates were samples analyzed twice. These results were used to estimate precision in the analytical portion of the sampling and analytical process. The analytical precision as demonstrated by the laboratory duplicates was excellent. All of the duplicate results meet the < 30% Relative Percent Difference (RPD) criterion. (The RPD is calculated by dividing the difference of the two results by the average, and multiplying by 100%). The laboratory duplicate results are presented, by refinery, in Tables 4-2 through 4-6.

#### Field Duplicates

Field duplicate samples are used to evaluate the precision of the total measurement system and estimate variability in the entire sampling and analytical process.

Thirty-one field duplicate pairs were collected and analyzed. Four of these were collected and analyzed in triplicate: two samples were collected and submitted to the laboratory as regular field duplicates and a third sample was sent to another laboratory for auditing purposes. Upon return of the third sample canister, Air Toxics Limited (ATL) reanalyzed the sample. Therefore, a total of 35 pairs of methane and 35 pairs of either THC or non-methane organic carbon (NMOC) results are available to evaluate precision. The results for 57 of these 70 pairs agreed quite well: either both members of the pair were "non-detects", or the detected concentrations were very close (i.e., RPDs of less than 50%). The pairs of field duplicates which did not agree as well are discussed below.

- For one THC pair and four methane pairs of field duplicate results, 12 ppmv or less of the target compounds were detected in one sample but not the other. Though this is not ideal, it is not unusual that fairly low level concentrations are not consistently present and/or detected by gas chromatography.
- One of the THC and two of the methane field duplicate pairs for which the RPDs were greater than 50% contained less than 12 ppmv of the target compounds in at least one member of the pair, once again indicating the variability associated with low level detections using gas chromatography.
- One of the THC and two of the methane field duplicate pairs for which the RPDs were greater than 50% were in samples that were originally sent to another laboratory for audit purposes. Upon return of the sample canisters to ATL, they were analyzed by ATL. Each of these samples were analyzed outside of the allowable two week holding time because of the noted transitions, which may explain some of the exhibited variability.
- One ASTM Method 3416 NMOC field duplicate pair had an RPD of 51%.

Lab ID	Method	Analyte	Reported DL	Concen- tration (ppmy)	Reported	Concen- tration (ppmy)	RPD (%)
9209091-03A	Method 18	THC	(0.092)	1600	(0.092)	1900	17.14
	D 3416	Methane	(1.8)	10	(1.8)	10	0.00
9209087-08A/B	Method 18	THC	(0.39)	35000	(0.39)	36000	2.82
	D 3416	Methane	(19)	140000	(1.9)	120000	15.38
9209098-08A	Method 18	THC	(0.095)	76	(0.095)	66	14.08
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9209111A-10A	Method 18	ТНС	(0.090)	1100	(0.090)	1000	9.52
	D 3416	Methane	(1.8)	320	(1.8)	320	0.00
9209111B-08A	Method 18	THC	(0.095)	15000	(0.095)	14000	6.90
	D 3416	Methane	(1.8)	68	(1.8)	70	2.90
9209137A-08A	Method 18	THC	(0.095)	1000	(0.095)	1100	9.52
	D 3416	Methane	(1.9)	6.2	(1.9)	6.2	0.00
9209146B-10B	D 3416	Methane	(2.7)	ND	(2.7)	ND	NC
		NMOC	(2.7)	370	(2.7)	380	2.67
9209161B-09B	D 3416	Methane	(1.9)	5.3	(1.9)	5.3	0.00
		NMOC	(1.9)	490	(1.9)	430	13.04
9210012B-08B	D 3416	Methane	(18)	110	(18)	110	0.00
		NMOC	(18)	17000	(18)	17000	0.00
9209111C-01A	TO 3	Benzene	(0.004)	ND	(0.004)	ND	NC
		Toluene	(0.004)	0.026	(0.004)	0.026	0.00
		Total Xylenes	_ (0.004)	0.011	(0.004)	0.011	0.00
		Ethylbenzene	(0.004)	0.008	(0.004)	0.009	11.76
		Cumene	(0.004)	ND	(0.004)	ND	NC
		Hexane	(0.004)	ND	(0.004)	ND	NC
		Propylene	(0.004)	ND	(0.004)	ND	NC
		Isooctane	(0.004)	ND	(0.004)	ND	NC
9209146C-07A	TO 3	Benzene	(0.052)	0.52	(0.052)	0.48	8.00
		Toluene	(0.052)	2.4	(0.052)	2.2	8.70
		Total Xylenes	(0.052)	89	(0.052)	83	6.98

Table 4-2 Laboratory Duplicates - Refinery V

THC = NMOC = DL =

Total hydrocarbons Non-methane organic carbon Detection limit Parts per million by volume Relative percent difference Not detected Not calculated =

ppmv RPD ND NC = =

= Not calculated

Lab ID	Method	Analyte	Reported	Concen- tration	Reported	Concen- tration	RPD
		Ethylbenzene	(0.052)	1.6	(0.052)	1.5	6.45
		Cumene	(0.052)	4	(0.052)	4	0.00
		Hexane	(0.052)	0.71	(0.052)	0.66	7.30
-		Propylene	(0.052)	ND	(0.052)	ND	NC
		Isooctane	(0.052)	1.3	(0.052)	1.3	0.00
9209161C-01A	TO 3	Benzene	(0.069)	ND	(0.069)	ND	NC
		Toluene	(0.069)	0.27	(0.069)	0.22	20.41
		Total Xylenes	(0.069)	1.1	(0.069)	1.2	8.70
		Ethylbenzene	(0.069)	ND	(0.069)	ND	NC
		Cumene	(0.069)	0.66	(0.069)	0.58	12.90
		Hexane	(0.069)	ND	(0.069)	ND	NC
		Propylene	(0.069)	ND	(0.069)	ND	NC
		Isooctane	(0.069)	ND	(0.069)	ND	NC

## Table 4-2 (Continued)

Total hydrocarbons Non-methane organic carbon Detection limit Parts per million by volume Relative percent difference Not detected Not calculated THC = NMOC = DL =

ppmv RPD ND NC = = =

=

Lab ID	Mathod	Ameluta	Reported	Concen- tration	Reported	Concen- tration	RPD
9211088-01A	D 3416	NMOC	(1.0)	5500	(1.0)	5500	0.00
9211088-01A	J J410	Methane	(1.9)	1600	(1.9)	4400	0.00
9211101E-06A	D 3416	NMOC	(1.9)	18000	(1.9)	18000	4.44
5211101E-00A		Methane	(2.0)	10	(2.0)	8.4	17 20
9211122A-02A	Method 18	THC	(0.000)		(0.000)	0.4 NTD	NC
9211122A-02A	D 3416	Methone	(1.8)		(1.8)		NC
9211122B-064	D 3416	NMOC	(1.0)	11	(1.0)	2.5	22.78
9211122 <b>D</b> -00A	D 5410	Mathana	(2.0)		(1.0)	<u> </u>	NC
0211153B 01A	D 3416	NMOC	(1.0)	60	(1.0)	69	1.46
9211155 <b>B</b> -01A	D 3410	Mathana	(1.0)	<u>0.9</u>	(1.0)		1.40 NC
02111624 034	Method 18	TUC	(0.005)		(0.005)		NC
9211102A-05A	D 3416	Methone	(1.0)		(1.0)		
0212104 4 04 4	Mathod 18	TUC	(0.10)	270	(0.10)	260	2 77
3212104A-04A	D 2416	Mathana	(0.10)	 ND	(0.10)	<u>200</u>	<u> </u>
0212115 4 08 4	Mathod 19	TUC	(0.15)	120	(2.0)		27.40
9212113A-00A	D 2416	Mathono	(0.13)	120	(0.15)	91 ND	27.49
0212128 4 01 4	Method 19	TUC	(0.10)		(0.10)		NC
9212120A-01A	D 2416	Mathana	(0.10)		(0.10)		NC
0212129 4 09 4	D 5410	TUC	(2.0)		(2.0)		NC NC
9212136A-06A	D 2416	Mathana	(0.10)		(0.10)		
02121274 084	10 5410	TUC	(2.0)	ND	(2.0)		NC
921213/A-08A	D 2416	Mathana	(0.10)	650	(0.10)	010	0.33
0201012 05 4	D 5410	TUC	(2.0)	22000	(2.0)	0.1	1.00
9501012-05A	D 2416	Mathema	(0.095)	32000	(0.095)	30000	0.45
9301019-07A	D 3410	TUO	(0.10)	<u>ND</u>	(1.9)	ND	<u>NC</u>
	D 2416	Mathana	(0.10)	150	(0.10)	010	0.00
0201041 104	D 3410	TUO	(2.0)		(2.0)	100	0.45
9501041-10A		IHU	(1.0)		(0.095)	ND	NC
0211101 4 01 4	TO 3	Renzene	(0.69)	<u>ND</u> 56	(0.60)	52 ND	5 50

Table 4-3 Laboratory Duplicates - Refinery W

THC Total hydrocarbons =

NMOC = Non-methane organic carbon

DL = Detection limit

= Parts per million by volume ppmv

= Relative percent difference

- ND = Not detected NC
  - Not calculated =

RPD

## Table 4-3 (Continued)

Lab ID	Method	Analyte	Reported DL	Concen- tration (ppmv)	Reported DL	Concen- tration (ppmy)	RPD (%)
		Toluene	(0.69)	64	(0.69)	58	9.84
		Total Xylenes	(0.69)	9.1	(0.69)	8.7	4.49
		Ethylbenzene	(0.69)	2.1	(0.69)	2	4.88
		Cumene	(0.69)	ND	(0.69)	ND	NC
		Hexane	(0.69)	120	(0.69)	120	0.00
		Propylene	(0.69)	ND	(0.69)	ND	NC
		Isooctane	(0.69)	97	(0.69)	97	0.00
9211153C-03A	TO 3	Benzene	(0.15)	7.3	(0.15)	7.3	0.00
		Toluene	(0.15)	2.5	(0.15)	2.5	0.00
		Total Xylenes	(0.15)	0.55	(0.15)	0.54	1.83
		Ethylbenzene	(0.15)	ND	(0.15)	ND	NC
		Cumene	(0.15)	ND	(0.15)	ND	NC
		Hexane	(0.15)	15	(0.15)	15	0.00
		Propylene	(0.15)	6,7	(0.15)	7.7	13.89
		Isooctane	(0.15)	2	(0.15)	2	0.00
9211153D-03A	TO 14	Benzene	(72)	13000	(72)	13000	0.00
		Toluene	(72)	7400	(72)	7600	2.67
		Total Xylenes	(72)	3700	(72)	3800	2.67
		Ethylbenzene	(72)	690	(72)	690	0.00
		Cumene	(72)	ND	(72)	ND	NC
		Hexane	(72)	20000	(72)	19000	5.13
		Propylene	(72)	1900	(72)	1600	17.14
		Isooctane	(72)	18000	(72)	17000	5.71
9212115B-08A	TO 14	Benzene	(6.0)	310	(6.0)	330	6.25
		Toluene	(6.0)	600	(6.0)	650	8.00
		Total Xylenes	(6.0)	640	(6.0)	680	6.06
		Ethylbenzene	(6.0)	170	(6.0)	170	0.00
		Cumene	(6.0)	17	(6.0)	19	11.11
		Hexane	(6.0)	1000	(6.0)	1100	9.52

THC = Total hydrocarbons

NMOC = Non-methane organic carbon

DL = Detection limit

ppmv =

Parts per million by volume Relative percent difference RPD =

ND Not detected =

NC Not calculated =

Lab ID	Method	Analyte	Reported	Concen- tration (ppmv)	Reported	Concen- tration (ppmv)	RPD (%)
		Propylene	(6.0)	ND	(6.0)	ND	NC
		Isooctane	(6.0)	ND	(6.0)	ND	NC
9212135-08A	8240	Benzene	(200)	10000	(200)	9200	8.33
		Toluene	(200)	38000	(200)	35000	8.22
		m,p-Xylene	(200)	9000	(200)	8600	4.55
		o-Xylene	(200)	39000	(200)	39000	0.00
		Cumene	(200)	14000	(200)	13000	7.41
		Hexane	(200)	530	(200)	410	25.53
		Propylene	(200)	12000	(200)	14000	15.38
		Isooctane	(200)	ND	(200)	ND	NC

## Table 4-3 (Continued)

THC NMOC DL 

Total hydrocarbons Non-methane organic carbon Detection limit Parts per million by volume Relative percent difference Not detected Not calculated ppmv RPD ND NC

=

=

THC	=	Total hydrocarbons
NMOC	=	Non-methane organic carbon
DL	=	Detection limit
ppmv	=	Parts per million by volume
RPD	=	Relative percent difference
ND	=	Not detected
NC	=	Not calculated

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.

					v		
Lab ID	Method	Analyte	Reported DL	Amount (ppmv)	Reported DL	Amount (ppmv)	RPD (%)
9211048A-04B	D 3416	NMOC	(18.4)	44000	(18.4)	33000	28.57
		Methane	(18.4)	240	(18.4)	180	28.57
9211063A-06A	D 3416	NMOC	(2.8)	6.6	(2.8)	6.8	2.99
		Methane	(2.8)	ND	(2.8)	ND	NC
9211099-03A	D 3416	NMOC	(1.9)	1300	(1.9)	1300	0.00
		Methane	(1.9)	ND	(1.9)	ND	NC
9211167 <b>B</b> -03A	D 3416	NMOC	(1.9)	2700	(1.9)	2700	0.00
		Methane	(1.9)	ND	(1.9)	ND	NC
9212132-03A	Method 18	THC	(0.090)	2500	(0.090)	2700	7.69
·	D 3416	Methane	(1.8)	ND	(1.8)	ND	NC
9301014-10A	Method 18	THC	(0.090)	2200	(0.090)	2000	9.52
	D 3416	Methane	(1.8)	ND	(1.0)	ND	NC
9301130-04A	Method 18	ТНС	(0.090)	2600	(0.090)	2600	0.00
	D 3416	Methane	(1.8)	ND	(1.0)	ND	NC
9301188-01A	Method 18	ТНС	(0.090)	ND	(0.090)	ND	NC
	D 3416	Methane	(1.8)	ND	(1.0)	ND	NC
9301188-11A	Method 18	THC	(0.095)	72	(0.050)	74	2.74
	D 3416	Methane	(1.9)	ND	(1.0)	ND	NC
9211153D-03A	TO 14	Benzene	(72)	13000	(72)	13000	0.00
		Toluene	(72)	7400	(72)	7600	2.67
		Total Xylenes	(72)	3700	(72)	3800	2.67
		Ethylbenzene	(72)	690	(72)	690	0.00
		Cumene	(72)	ND		ND	NC
		Hexane	(72)	20000	(72)	19000	5.13
		Propylene	(72)	1900	(72)	1600	17.14
		Isooctane	(72)	18000	(72)	17000	5.71

Table 4-4 Laboratory Duplicates - Refinery X

THC = NMOC =

Total hydrocarbons Non-methane organic carbon Detection limit

Relative percent difference Not detected

Lab ID	Method	Analyte	Reported	Amount (ppmv)	Reported DL	Amount (ppmv)	RPD (%)
9212023-03A	Method 18	THC	(0.10)	35	(0.10)	35	0.00
	D 3416	Methane	(2.0)	20	(2.0)	20	0.00
9212042A-01A	Method 18	THC	(0.095)	12	(0.095)	12	0.00
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9212073-02A	Method 18	THC	(0.10)	30	(0.10)	ND	NC
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9212090A-02A	Method 18	THC	(1.0)	23000	(1.0)	31000	29.63
	D 3416	Methane	(2.0)	ND	(2.0)	ND	NC
9301040-06A	Method 18	THC	(0.095)	320	(0.095)	320	0.00
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9301059-04A	Method 18	THC	(0.10)	27	(0.10)	30	10.53
	D 3416	Methane	(2.0)	ND	(2.0)	ND	NC
9301063-09A	Method 18	THC	(1.0)	5200	(1.0)	5300	1.90
	D 3416	Methane	(2.0)	ND	(2.0)	ND	NC
9301131-03A	Method 18	THC	(0.10)	110	(0.10)	110	0.00
	D 3416	Methane	(2.0)	ND	(2.0)	ND	NC
9301147A-01A	Method 18	ТНС	(0.10)	130	(0.10)	130	0.00
	D 3416	Methane	(2.0)	ND	(2.0)	ND	NC
9301157A-05A	Method 18	ТНС	(0.10)	1100	(0.10)	1100	0.00
	D 3416	Methane	(2.0)	ND	(2.0)	ND	NC
9212032B-02A	то з	Benzene	(0.002)	ND	(0.003)	ND	NC
		Toluene	(0.002)	ND	(0.003)	ND	NC
		Total Xylenes	(0.002)	ND	(0.003)	ND	NC
		Ethylbenzene	(0.002)	ND	(0.003)	ND	NC
		Cumene	(0.002)	ND	(0.003)	ND	NC
		Hexane	(0.002)	ND	(0.003)	ND	NC
9212032B-02A (cont.)	TO 3 (cont.)	Propylene	(0.002)	ND	(0.003)	ND	NC
,		Isooctane	(0.002)	ND	(0.003)	ND	NC
9212065B-04A	TO 3	Benzene	(0.003)	ND	(0.003)	ND	NC

Table 4-5 Laboratory Duplicates - Refinery Y

THC = Total hydrocarbons

NMOC = Non-methane organic carbon

- DL = Detection limit
- ppmv = Parts per million by volume
- RPD = Relative percent difference
- ND = Not detected
- NC = Not calculated

Lab ID	Method	Analyte	Reported DL	Amount (ppmv)	Reported DL	Amount (ppmv)	RPD (%)
		Toluene	(0.003)	ND	(0.003)	ND	NC
		Total Xylenes	(0.003)	ND	(0.003)	ND	NC
		Ethylbenzene	(0.003)	ND	(0.003)	ND	NC
		Cumene	(0.003)	ND	(0.003)	ND	NC
		Hexane	(0.003)	0.18	(0.003)	0.18	0.00
		Propylene	(0.003)	ND	(0.003)	ND	NC
		Isooctane	(0.003)	0.014	(0.003)	0.014	0.00
9301131B-01A	TO 14	Benzene	(3.8)	ND	(3.8)	ND	NC
		Toluene	(3.8)	ND	(3.8)	ND	NC
		Total Xylenes	(3.8)	ND	(3.8)	ND	NC
		Ethylbenzene	(3.8)	ND	(3.8)	ND	NC
		Cumene	(3.8)	ND	(3.8)	ND	NC
		Hexane	(3.8)	ND	(3.8)	ND	NC
		Propylene	(3.8)	ND	(3.8)	ND	NC
		Isooctane	(3.8)	ND	(3.8)	ND	NC

## Table 4-5 (Continued)

THC Total hydrocarbons = NMOC = Non-methane organic carbon DL= Detection limit Parts per million by volume ppmv = RPD = Relative percent difference ND Not detected = NC Not calculated Ξ
Lab ID	Method	Analyte	Reported	Amount (ppmv)	Reported	Amount (ppmv)	RPD (%)
9212031-06A	Method 18	THC	(0.090)	19000	(0.090)	17000	11.11
	D 3416	Methane	(1.8)	ND	(1.8)	ND	NC
9212031-16A	Method 18	THC	(0.090)	680	(0.090)	900	27.85
	D 3416	Methane	(1.8)	ND	(1,8)	ND	NC
9212033-11A	Method 18	THC	(0.10)	2200	(0.10)	2400	8.70
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9301022A-10A	Method 18	THC	(0.14)	200	(0.14)	200	0.00
	D 3416	Methane	(2.7)	11	(2.7)	14	24.00
9212064-05A	Method 18	THC	(0.095)	230	(0.095)	240	4.26
	D 3416	Methane	(1.9)	5.2	(1.9)	5.3	1.90
9212074-04A	Method 18	THC	(0.090)	14000	(0.090)	13000	7.41
	D 3416	Methane	(1.8)	140	(1.8)	140	0.00
9212084-02A	Method 18	THC	(0.090)	12000	(0.090)	12000	0.00
	D 3416	Methane	(1.8)	ND	(1.8)	ND	NC
9212084-12A	Method 18	THC	(0.090)	80	(0.090)	67	17.69
	D 3416	Methane	(1.8)	47	(1.8)	47	0.00
9301022-10A	Method 18	THC	(0.14)	200	(0.14)	200	0.00
	D 3416	Methane	(2.7)	11	(2.7)	14	24.00
9302025-01A	Method 18	THC	(0.095)	2200	(0.095)	2200	0.00
	D 3416	Methane	(1.9)	5600	(1.9)	5700	1.77
9302044-03A	Method 18	THC	(0.095)	200	(0.095)	200	0.00
	D 3416	Methane	(1.9)	480	(1.9)	490	2.06
9302079-03A	Method 18	THC	(0.090)	1500	(0.090)	1500	0.00
	D 3416	Methane	(1.8)	1.1	(1.8)	1	9.52
9302093-04A	Method 18	THC	(0.095)	ND	(0.095)	ND	NC
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9302157-04A	Method 18	THC	(0.090)	1000	(0.090)	1000	0.00
	D 3416	Methane	(1.8)	ND	(1.8)	ND	NC
9302157-20A	Method 18	THC	(0.095)	97	(0.095)	110	12.56

 Table 4-6
 Laboratory Duplicates - Refinery Z

THC = Total hydrocarbons

NMOC = Non-methane organic carbon

DL = Detection limit

ppmv = Parts per million by volume

- RPD = Relative percent difference
- ND = Not detected
- NC = Not calculated

Lah ID	Method	Analyte	Reported	Amount	Reported	Amount	RPD (%)
	D 3416	Methane	(1.9)	160	(1.9)	160	0.00
9303035-10A	Method 18	THC	(0.095)	29000	(0.095)	31000	6.67
	D 3416	Methane	(1.9)	3.1	(1.9)	3	3.28
9303035-20A	Method 18	THC	(0.095)	4300	(0.095)	4000	7.23
	D 3416	Methane	(1.9)	ND	(1.9)	ND	NC
9303060-07A	Method 18	THC	(0.095)	9900	(0.095)	9800	1.02
	D 3416	Methane	(1.9)	89	(1.9)	89	0.00
9212046B-01A	то з	Benzene	(0.005)	2	(0.005)	1.9	5.13
		Toluene	(0.005)	4.3	(0.005)	4.2	2.35
		Total Xylenes	(0.005)	3.3	(0.005)	3.2	3.08
		Ethylbenzene	(0.005)	0.66	(0.005)	0.65	1.53
		Cumene	(0.005)	0.27	(0.005)	0.26	3.77
		Hexane	(0.005)	4.9	(0.005)	4.9	0.00
		Propylene	(0.005)	ND	(0.005)	ND	NC
		Isooctane	(0.005)	4.5	(0.005)	4.5	0.00
9212084B-05A	8240	Benzene	(200)	5400	(200)	4500	18.18
		Toluene	(200)	13000	(200)	11000	16.67
		m,p-Xylene	(200)	2500	(200)	2300	8.33
		o-Xylene	(200)	9700	_(200)	8400	14.36
		Cumene	(200)	3000	(200)	2700	10.53
		Hexane	(200)	390	(200)	350	10.81
		Propylene	(200)	20000	(200)	19000	5.13
		Isooctane	(200)	ND	(200)	0.014	NC

# Table 4-6 (Continued)

THC = NMOC = DL = ppmv = RPD =

Total hydrocarbons Non-methane organic carbon Detection limit Parts per million by volume Relative percent difference Not detected Not calculated

ND NC

=

The most likely source of the lack of agreement between the above mentioned 13 pairs is a difference in concentrations of the field duplicate samples. A number of variables are involved in the sampling process which could lead to the noted slight discrepancies, including some component variability, or even small temperature, moisture or pressure changes, or slightly uneven flow of nitrogen. The excellent analytical precision demonstrated by the laboratory duplicates indicates that the analytical portion of the process was not likely a major contributor of the exhibited field duplicate variability.

Overall, the field duplicate results indicate the sampling and analytical process is reproducible. The variability exhibited in the 13 of 70 of field duplicate pairs discussed above is not unusual for this type of medium and sample collection procedure. The field duplicate results indicate the data are usable, though some of the results may not be easily reproduced. The field duplicate results are presented, by refinery, in Table 4-7.

## Accuracy Checks

The accuracy checks consisted of bagging a component with zero emissions and introducing a methane standard gas at a known flow rate. The quality assurance objective for the accuracy checks is for a reported concentration between 50 and 150% of the calculated value.

This objective was met at four of the five refineries. The methane concentrations reported for the remaining accuracy check (by both U.S. EPA Method 18 and ASTM D3416) were very low. The cause for the poor methane recoveries from this sample is attributed to a leaking canister. When this particular sample left the field, the canister pressure was -7 inches of mercury. Upon arrival at the laboratory, the canister pressure was 0 inches of mercury. Disregarding the accuracy check from Refinery V because of the canister leak, the remaining four accuracy check sample results indicate both the bagging measurement and analytical measurement systems are accurate. The accuracy check results are presented in Table 4-8.

## MULTIPOINT CALIBRATIONS

At each of the refineries, the OVA screening instruments were calibrated at least once daily at 100 ppmv methane by adjusting the OVA reading to 100 ppmv. Although U.S. EPA Method 21 dictates that OVA instruments only need to be calibrated for one hydrocarbon standard,

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Refinery	Sample	Method	Concen- tration (ppmv)	Concen- tration (ppmy)	Concen- tration (ppym)	RPD (%) (FDA/FDB)	RPD (%) (FDA/FDC)
v	Dup. 1	Method 18 - THC	54	52		3.77	
		D 3416 - Methane	< 1.8	< 1.9		NC	
	Dup. 2	Method 18 - THC	1000	1000		0.00	
		D 3416 - Methane	6.4	6.2		3.17	
	Dup. 3	D 3416 - NMOC	640	380		50.98	
		Methane	< 2.8	< 2.8		NC	
	Dup. 4	D 3416 - NMOC	2400	2400		0.00	
		Methane	1200	1200		0.00	
w	Dup. 1	D 3416 - NMOC	30000	26000		14.29	
		Methane	6.5	3.5		60.00	
	Dup. 2	Method 18 - THC	< 0.095	< 0.10		NC	
		D 3416 - Methane	< 1.9	< 2.0		NC	
	Dup. 3	Method 18 - THC	370	400	370	7.79	0.00
		D 3416 - Methane	< 1.9	< 2.0	< 2.8	NC	NC
	Dup. 4	Method 18 - THC	100		35		96.30
		D 3416 - Methane	23		25		8.33
	Dup. 5	Method 18 - THC	160	150	170	6.45	6.06
		D 3416 - Methane	< 2.0	< 2.0	< 4.2	NC	NC
	Dup. 6	Method 18 - THC	290		460		45.33
		D 3416 - Methane	< 2.0		< 2.8		NC
	Dup. 7	D 3416 - NMOC	28000	32000		13.33	
		Methane	< 1.9	< 1.9		NC	
x	Dup. 1	D 3416 - NMOC	6.5				
		Methane	< 1.9				_
		Method 18 - THC		1.8		113**	
		D 3416 - Methane		< 1.9		NC	
	Dup. 2	Method 18 - THC	< 0.090	6.8		NC	
		D 3416 - Methane	< 1.8	< 2.8		NC	

# Table 4-7 Field Duplicates

VFDA Field duplicate 'A'. =

FDB =

- Field duplicate 'B'. Field duplicate 'C'. These samples were originally sent to another laboratory for audit purposes. FDC = Upon the return of the canisters to ATL, these samples were reanalyzed by ATL.
- NC Not calculated. Ξ

RPD Relative percent difference. =

\*\*THC by Method 18 compared to NMOC by Method D-3416.

Not for Resale

Refinery	Sample	Method	Concen- tration (ppmv)	Concen- tration (ppmv)	Concen- tration (ppvm)	RPD (%) (FDA/FDB)	RPD (%) (FDA/FDC)
X (cont.)	Dup. 3	Method 18 - THC	760	670		12.59	
		D 3416 - Methane	< 1.8	< 1.8		NC	
Y	Dup. 1	Method 18 - THC	140	140		0.00	
		D 3416 - Methane	< 1.9	< 1.9		NC	
	Dup. 2	Method 18 - THC	150		190		23.53
		D 3416 - Methane	15		13		14.29
	Dup. 3	Method 18 - THC	150		190		23.53
		D 3416 - Methane	15		13		14.29
	Dup. 4	Method 18 - THC	160	97	210	49.03	27.03
		D 3416 - Methane	15	4.2	9.1	112.50	48.96
	Dup. 5	Method 18 - THC	490		720		38.02
		D 3416 - Methane	< 2.9		< 2.9		NC
	Dup. 6	Method 18 - THC	30		37		20.90
		D 3416 - Methane	< 1.9		< 2.8		NC
	Dup. 7	Method 18 - THC	19	19		0.00	
ļ		D 3416 - Methane	< 2.0	< 2.0		NC	
	Dup. 8	Method 18 - THC	3200	3200		0.00	
		D 3416 - Methane	< 2.0	< 2.0		NC	
	Dup. 9	Method 18 - THC	160	140		13.33	
		D 3416 - Methane	< 2.0	< 2.0		NC	
Z	Dup. 1	Method 18 - THC	190	160		17.14	
		D 3416 - Methane	< 1.9	< 1.9		NC	
	Dup. 2	Method 18 - THC	190		200		5.13
		D 3416 - Methane	< 1.8		11		NC
	Dup. 3	Method 18 - THC	200		200		0.00
		D 3416 - Methane	5.3		< 2.7		NC
	Dup. 4	Method 18 - THC	730		180		120.88

# Table 4-7 (Continued)

VFDA =

FDB =

Field duplicate 'A'. Field duplicate 'B'. Field duplicate 'C'. These samples were originally sent to another laboratory for audit purposes. FDC = Upon the return of the canisters to ATL, these samples were reanalyzed by ATL. NC Not calculated. =

RPD =

Relative percent difference.

\*\*THC by Method 18 compared to NMOC by Method D-3416.

Refinery	Sample	Method	Concen- tration (ppmv)	Concen- tration (ppmv)	Concen- tration (ppvm)	RPD (%) (FDA/FDB)	RPD (%) (FDA/FDC)
Z (cont.)		D 3416 - Methane	< 1.8		12		NC
	Dup. 5	Method 18 - THC	230		700		101.08
		D 3416 - Methane	5.2		< 2.6		NC
	Dup. 6	Method 18 - THC	610		530		14.04
		D 3416 - Methane	< 1.9		< 2.7		NC
	Dup. 7	Method 18 - THC	830	910	990	9.20	17.58
		D 3416 - Methane	720	730	1400	1.38	64.15
	Dup. 8	Method 18 - THC	1500	1500		0.00	
		D 3416 - Methane	1.1	1.1		0.00	

# Table 4-7 (Continued)

VFDA =

FDB = FDC

Field duplicate 'A'. Field duplicate 'B'. Field duplicate 'C'. These samples were originally sent to another laboratory for audit purposes. Upon the return of the canisters to ATL, these samples were reanalyzed by ATL. ==

NC Not calculated. =

RPD

RPD = Relative percent difference. \*\*THC by Method 18 compared to NMOC by Method D-3416.

Refinery	Method	Analyte	True Value (ppmy)	Conc. Reported	Percent Recovery
v	Method 18	THC <sup>a</sup>	1127	770	68%
	D 3416	Methane	1127	1200	106%
$\mathrm{W}^{b}$	Method 18	THC <sup>a</sup>	927	96	10%
	D 3416	Methane	927	260	28%
Х	D 3416	NMOC	0	5.8	NC
		Methane	758	660	87%
Y	Method 18	THC <sup>a</sup>	841	1072	128%
	D 3416	Methane	841	900	107%
Z	Method 18	THC <sup>a</sup>	981	1238	126%
	D 3416	Methane	981	770	78%

# **Table 4-8 Accuracy Checks**

NC = Not calculated NMOC = Non-methane hydrocarbons THC = Total Hydrocarbons (including methane) <sup>a</sup> Results have been multiplied by a factor of 2.75 (mol. wt. of propane/mol. wt. of methane) to account for the <sup>b</sup> fact that the THC results are quantitated using propane only. <sup>b</sup> This sample had a leaking canister and is invalid for comparison.

and this is typically what is done by I/M teams in the field, Radian performed multipoint calibrations as an additional quality assurance check. Additional calibration checks were made at 0, 10, 1000 and 10,000 ppmv methane. The results of each calibration were evaluated to ensure that the correlation coefficient between the standards and recorded values was greater than .995. Screening values read in the field were not adjusted by a calibration factor.

A total of 189 calibration sets were performed in the field. Three of the sets of calibrations included only one or two standards, so a least-squares regression could not be performed. A least-squares regression line was computed for each of the remaining 186 multipoint calibrations performed at the refineries, and tests were performed to determine whether or not the slopes and intercepts differed from one and zero at the 95% confidence level. This was performed because a sufficiently high correlation coefficient does not indicate whether the slope of the calibration regression line is one or whether the intercept is zero. A slope of one means that a one unit change in the standard corresponds to a one unit change in the reading. An intercept of zero means that, when the standard is zero, the measured screening value is also zero.

The results for the slopes are:

- 32.3% (60 of 186) of the regression lines had slopes that were not different from one at the 95% confidence level. For these 60 cases, the expected change in reading per one unit change in standard was one.
- 18.3% (34 of 186) of the regression lines had slopes that were less than one at the 95% confidence level. The average slope for these 34 cases was .92 and the average signed percent difference was -7.9% [signed percent difference = 100\*((slope-1)/1)]. Slopes ranged from .794 to .998, corresponding to signed percent differences as high as 20.6% and as low as .2%.
- 49.5% (92 of 186) of the regression lines had slopes that were greater than one at the 95% confidence level. The average slope for these 92 cases was 1.10, and the average signed percent difference was 10.3%. Slopes ranged from 1.003 to 1.810, corresponding to signed percent differences from .3% to 81.0%.

The results for the intercepts are:

- 95.7% (178 of 186) of the regression lines had intercepts that were not different from zero at the 95% confidence level. The expected reading is zero when the standard is zero for these 178 cases.
- 4.3% (8 of 186) of the regression lines had intercepts that were significantly higher than zero. The average intercept for these 8 cases was 6.18 and intercepts ranges from 1.7 to 21.3.

In addition to evaluating the slopes and intercepts, Radian evaluated individual differences between the calibration standards and the readings in order to determine the OVA response variability at each point of the multipoint calibration. The signed percent difference [signed percent difference = ((standard-OVA reading)/standard)\*100] at each calibration point for each of the 186 calibrations was calculated. The average methane concentrations of the 186 recorded standards and of the 186 recorded OVA readings at each of the calibration points were also calculated in addition to the average signed percent difference. Screening values that were recorded as < 1 ppm were examined in two ways:

- The cases were excluded from the analysis; and
- The cases were included and a value of 1 ppm was used.

Screening values that were recorded as > 10,000 ppm were excluded from all analyses.

The average standard concentration and average OVA reading for each calibration point are shown in Table 4-9. In addition, the average signed percent difference, the standard deviation of the signed percent difference, and the minimum and maximum signed percent differences are shown for each calibration point. The largest average percent difference occurs when the standard is set at 10 ppm (28.87%). Average percent differences for all other points are less than 3.3% in magnitude. Note also that the variability among percent differences at the 10 ppm calibration point is much greater than the variability at other calibration points. For eight of the calibrations, the signed percent difference at the 10 ppm point was between 100% and 200%, and for five of the calibrations, the signed percent differences obtained at the 10 ppm standard were the largest, this is not believed to greatly affect the field measurements because most field measurements were not in the 10 ppm OVA screening value range. Many of the readings close to 10 ppm were indistinguishable from background concentrations, and were recorded as measurements of zero ppm.

The results of the multipoint calibration appear acceptable for a portable field analyzer such as the OVA. The data in this study were not corrected or modified in any way based on this analysis of the multipoint calibration results. Test results from this study need to be consistent with results field I/M teams would obtain. No modifications were made because these tests are not conducted by field I/M teams. Field I/M teams calibrate their OVAs with only one hydrocarbon standard rather than the four hydrocarbons standard used in this study. However, this information does provide insight into the variability of OVA readings.

## CANISTER STABILITY STUDY

The 1993 Refinery Study used a two week hold time criteria for development of emission correlation equations, zero component emission factors, and pegged component emission factors to reduce any potential for sample degradation. This two week hold time was met for all data used to develop emission correlation equations, zero component emission factors, and pegged component emission factors. Only those samples sent to RTI's laboratory for analysis and subsequently sent to ATL laboratory for reanalysis, and certain samples that were held intentionally for an evaluation of the speciation methods exceeded this two-week hold time criteria. The samples sent to both laboratories were only used to establish interlaboratory comparisons and were not used for further data analysis. The samples held for an evaluation of speciation methods (TO-3 and TO-14) were used in the analysis of vapor leak species concentration versus liquid stream species concentration. All samples analyzed were analyzed within 30 days.

To confirm that hold times up to two weeks do not result in substantial degradation of samples, a stability study was conducted by ATL Laboratories to examine the stability of the target analytes in Summa canisters.

#### Summa Passivation

Most containers used to collect and store air samples are specially treated or passivated to ensure an inert surface. The metal surfaces used in these containers range from stainless steel

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Variability	Standards
A Response	Calibration
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able	or I

	Maximum Percent Difference (%)	22.0	22.0	-26.3	-18.4	-25.0	-20.0
ity Results	Minimum Percent Difference (%)	0.8	0.8	+268.4	+17.3	+80.0	+20.0
Summary of Variabil	Standard Deviation of Percent Difference (%)	3.2	2.4	48.6	3.7	12.6	6.3
	Average Percent Difference <sup>4</sup> (%)	3.3	2.0	-28.9	-1.2	-1.3	-1.4
	Average OVA Reading (ppm)	3.3 <sup>b</sup>	2.0 <sup>c</sup>	12.5	99.8	1,012	9,993 <sup>d</sup>
	Average Standard Concentration (ppm)	0.0	0.0	9.7	98.6	999.5	9,861.8
	Number of Calibration Standards	79	180	188	179	177	140
	Calibration Standard Range (ppm)	$0^{\mathrm{p}}$	0°	10	100	1,000	10,000 <sup>d</sup>

- Percent difference =  $100 \times (OVA reading calibration standard)/calibration standard.$ Percent difference not calculated for the 0 ppm standard. 69
- Summary statistics given for the 0 ppm standards are for the OVA readings only. Readings of < 1 ppm not included in analysis. p.
  - υP
  - Readings of < 1 ppm set equal to 1 ppm for analysis. Pegged values (i.e., readings > 10,000 ppm) not included in analysis.

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to aluminum. Within those metal surfaces are active sites of high polarity that enhance adsorption and facilitate decomposition. Surface treatments attempt to eliminate those active sites to promote inertness of the surface. Examples of these treatments are the Summa polishing process, by Molectrics Corporation, or Aculife by Scott Gases. The Summa passivation process was recommended by U.S. EPA as the surface of choice for maximum stability of typical air samples. In addition, the presence of water vapor greatly enhances stability due to its layering ability, thereby forming a protective layer(s) on the metal surface.

### Canister Hold Time

While the ostensible "hold time" for canisters has generally been set at two weeks, there is an abundance of evidence that shows hydrocarbons to be extremely stable for periods of up to several months at low pressure and several years at higher pressure. While TO-14 and many other air sampling methods do not specify hold times, the two week hold time has evolved into an industry standard, mainly due to a desire to be very conservative and not endanger the integrity of any field samples. In addition, it has been recognized that not all canister samples would consist of the relatively "clean" (i.e., ambient air with no acid gases, etc. that could enhance degradation) matrix in which the stability studies were conducted, so the shorter hold time would also encompass any uncertainties from that eventuality.

The U.S. EPA has conducted several formal hold time studies in order to make recommendations regarding this question for the canister-based Compendium Method TO-14 (Oliver, 1986; Pleil, 1985). The approach is generally the same, i.e., several humidified canisters were repeatedly analyzed over a period of time, in this case, 30 days. These data show that the VOC concentrations in canisters were stable to an average of  $\pm 3.2\%$  over a seven-day period. Hydrocarbon concentrations showed changes on the order of less than 1% change per day over 30 days for three canisters, which is within the observable variability of the analytical method.

Research Triangle Institute (RTI) conducted a study of stability of several VOCs in cylinders, which showed hydrocarbons to be stable over a period of 18 months (Jayanty, 1986). Two other studies show the same results. Miller et al. (Miller, 1990), shows at low concentrations, the change over nine months is less than 1%. The work of Harrell, et al. (Harrell, 1990)

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which compares the relative stability of various compounds in canisters from different manufacturers shows that except for two canisters, hydrocarbons were stable up to 38 weeks. Even in two brands with poor stability, the concentration for some compounds did not start to change significantly until after week 20.

Therefore, no degradation of collected target analytes is expected within the two week laboratory hold time.

### Laboratory Study

The ATL Laboratory study was conducted by setting aside two normal field samples, and subjecting them to each type of analysis on a periodic basis. Three analyses were conducted: the Method 18 (THC), ASTM D3416 (methane) analysis, and TO-14 (8 target species). The THC and methane analyses were conducted over a period of 18 days, and the TO-14 analyses were conducted over a period of 37 days.

The data were analyzed in two ways. First, because stability implies no change over time, the coefficient of variation (%CV) was calculated to determine the agreement of the three analyses with each other. This calculation is conducted by dividing the mean of the values into the standard deviation. A small value shows better agreement between the data points. A reasonable criterion is to use the standard laboratory agreement factor of a %CV of less than or equal to 30%. The second analysis was a graphical plot and linear regression. In this case, the plots may imply more change than is actually occurring, which can lead to erroneous interpretations. In both cases, a general understanding of inherent laboratory variability is essential to make correct interpretations of the data.

The ATL Laboratory followed U.S. EPA Contract Laboratory Program guidelines, which state that calibration curves and duplicate analyses must agree within  $\pm 30\%$ . This factor recognizes the inherent variability in all measurements due to an accumulation of many small factors which cannot be easily controlled in a production environment. The sum of these factors is the normal laboratory variability. This suggests that two consecutive analyses producing values within a 30% agreement are within specification. For the stability data, any tighter factor would ignore the normal variability of the process. More sophisticated

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statistical analyses of the data to break out smaller variability factors require much more data and are beyond the scope of this study.

Table 4-10 lists the results of the THC and methane analyses. For both the THC and methane, it is seen that the %CV indicates good agreement over time for the three analyses, confirming that the samples are stable over the 18 day study period.

Figures 4-1 and 4-2 show the plots of the data from Table 4-10. The linear regression lines show that within the laboratory uncertainty, the concentrations are stable.

Table 4-11 shows the data from the TO-14 analyses. The %CV values again show that the data are stable over the study period of 38 days. Toluene shows a %CV of 27%, which is within the specifications, but is somewhat larger than for most of the other analytes. This higher value appears to be an anomaly, because most of the other analytes are in much better agreement.

Figures 4-3 and 4-4 show the plots and linear regression for these data. Again in this case, the plots may exaggerate the difference in the three analyses. The error bars for the regression curves would encompass all the data points, thereby confirming the conclusion of no degradation occurring.

Two events which may have affected the last two data points are a change in analytical column and the cleaning of the mass spectrometer ion source. Both these events caused a recalibration of the instrument, which may induce a small change in individual responses. It appears that the observed changes do not significantly affect the conclusion that the target analytes are stable over the nominal two week hold time.

# Table 4-10 Total Hydrocarbons (THC) and Methane Stability Results

Sample Number	Date	THC <sup>a</sup> (ppmv)	Methane (ppmv)
Z085	2/5/93	310	620
	2/11/93	310	560
	2/20/93	330	650
	Average	317	610
	%CV	4	8
Z088	2/5/93	530	ND
	2/11/93	550	ND
	2/20/93	630	ND
	Average	570	NA
	%CV	9	NA

<sup>a</sup> THC based on propane







Date	Benzene	Toluene	Xylenes	Ethylbenzene	Cumene	Hexane	Propylene	Isooctane
Z085			<u></u>					
2/5/93	140	60	7	ND	ND	310	ND	ND
3/2/93	110	43	ND	ND	ND	340	ND	ND
3/11/93	96	36	ND	ND	ND	270	ND	ND
Average	115	46	7	NA	NA	307	NA	NA
%CV	19	27	NA	NA	NA	11	NA	NA
Z088								
2/5/93	11,000	40,000	35,000	5,400	450	16,000	ND	ND
3/2/93	9,900	34,000	27,000	4,000	760	18,000	ND	ND
3/11/93	8,000	27,000	23,000	3,700	660	14,000	ND	ND
Average	9,633	33,667	28,333	4,367	623	16,000	NA	NA
%CV	16	19	22	21	25	13	NA	NA

# Table 4-11 TO-14 Stability Data



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### **Conclusion**

The results of the stability study show that the target analyte list is stable over the two week hold time period, and that the analytes are stable longer than this two week period. There were no differences between high and low level samples. Actual hold times for all samples used in the development of emission correlation equations, zero component emission factors, and pegged component emission factors were always less than two weeks. Therefore, canister stability for the 1993 Refinery Study is not considered an issue.

### U.S. EPA AUDIT RESULTS

An audit program was conducted by the U.S. EPA in order to verify the integrity of the analytical data collected for this project. This section is Radian's assessment of the audit results.

There were two parts to the U.S. EPA audit, a system audit and a performance audit. A system audit is an on-site inspection and review of the quality assurance system used for the total measurement system (sample collection, sample analysis, data processing, etc.). The U.S. EPA contracted RTI to conduct two separate sample collection audits at two different refineries with each audit (a total of four site visits). The RTI preliminary observations from the first audit and Radian's response to these observations are found in Appendix E. A Draft Audit Report of all of the RTI audits was issued on June 9, 1993. Radian's response to this Draft Audit Report is also in Appendix E. A Final Audit Report was released by the U.S. EPA in September, 1993 (U.S. EPA, 1993a) that revised the Draft Audit Report based, in part, on Radian's earlier response. In Radian's opinion, nothing was found in these audits that would invalidate results of this study. However, some items were identified that could enhance the study accuracy and/or defensibility, such as purging the vacuum gauge tee and eliminating potential probe leaks. All items of enhancement were changed immediately after the first audit. The impacts of one of the observations, that of probe leaks on the OVAs, was thoroughly analyzed and discussed in earlier sections of this report.

A performance audit refers to independent checks made by an auditor to evaluate the quality of data produced by the total sampling and analysis program. The performance audits were also conducted by the U.S. EPA contractor RTI throughout the testing period for four of the

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five refineries. The audit consisted of submitting audit gas samples containing known amounts of THC to the primary laboratory (ATL), and to the audit laboratory (RTI). In addition, a set of field duplicate samples were split between these two laboratories.

The performance audit results indicate ATL is capable of accurately identifying and quantitating THC in vapor samples using U.S. EPA Method 18. ATL's ability to accurately identify methane in vapor samples by ASTM Method 3416 was also confirmed. The concentrations of methane reported by the two laboratories do not agree. However, RTI used a different method for the analysis of methane. Because the actual concentrations of methane (and THC) present in the field duplicate samples are unknown, and because the audit gas samples did not contain methane, it was not possible to evaluate the ability of either laboratory to accurately quantify methane. The remainder of this section addresses the detailed results of the performance audit.

### Audit Gas Results

<u>Accuracy</u>. Fifteen audit gas samples containing known amounts of total hydrocarbons were collected and analyzed by ATL. Seven of these samples were also sent to RTI for comparison. All audit gas results met the accuracy objective of an RPD of  $\pm 50\%$ . The majority of audit gas samples analyzed by ATL were recovered within 70-130% of the certified values, indicating the analytical data are accurate. Recoveries of the seven audit gas samples analyzed by RTI were excellent, ranging from 88–106% of the certified values.

Both ATL and RTI test results help substantiate the accuracy of the laboratory analysis and also, for those measured with the bag in place (through tent), help establish the accuracy of the bagging method. In fact, RTI has concluded that, "Based on the results of the QA gas flow-through tests, sampling (testing) appeared to have been done with little leakage or loss of material. No statistically significant difference was found between the results from the canister analyses for QA gas introduced through the tent or directly into the canister" (U.S. EPA, 1993a). The audit gas accuracy results are presented in Table 4-12.

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Refinery	Sample	Certified Value (ppmv)	ATL Result (ppmv)	ATL Percent Recovered	RTI Result (ppmy)	RTI Percent Recovered
W - Direct	1	170	190	112%	NA	NC
	2	690	720	104%	NA	NC
W - Through Tent	3-FDA	170	170	100%	NA	NC
	3-FDB	170	180	106%	NA	NC
	4	690	690	100%	NA	NC
X - Direct	1	170	170	100%	NA	NC
	2	690	590	86%	NA	NC
X - Through Tent	3-FDA	690	760	110%	NA	NC
	3-FDB	690	670	97%	NA	NC
	4	170	200	118%	NA	NC
Y - Direct	1-FDA	170	160	94%	170	100%
	1-FDB	170		57%	NA	NC
	1-FDC*	170	210	124%	NA	NC
	2-FDA	690	490	71%	660	96%
	2-FDB*	690	720	104%	NA	NC
Y - Through Tent	3-FDA	170	150	88%	170	100%
	3-FDB*	170	190	112%	NA	NC
	4-FDA	690	450	65%	660	96%
	4-FDB*	690	750	109%	NA	NC
Z - Direct	1-FDA	170	230	135%	180	106%
	1-FDB	170	240	141%	NA	NC
	1-FDC*	170	180	106%	NA	NC
Z - Through Tent	2-FDA	170	200	118%	150	88%
	2-FDB*	170	200	118%	NA	NC
	3-FDA	690	730	106%	.640	93%
	3-FDB*	690	700	101%	NA	NC

Table 4-12 Audit Gas THC Results - Accuracy

\* These "duplicate" samples were reanalyses by ATL of the samples originally sent to RTI. FDA - Field Duplicate A. Duplicates submitted to ATL only. FDB - Field Duplicate B. Duplicates submitted to ATL only. NA - Not Analyzed NC - Not Calculated

<u>Precision</u>. Three sets of audit gas sample duplicates are available to assess precision:

- Nine of the fifteen audit gas samples sent to ATL were collected for and analyzed by ATL as field duplicates;
- Seven of the fifteen samples were sent to both ATL and RTI; and
- Two of the seven audit gas samples sent to RTI were subsequently reanalyzed by ATL (though because of the amount of time for the transition, the ATL analysis of the RTI samples took place after the two week holding time had expired).

The RPDs between all pairs were less than 50%, indicating both the sampling and analytical processes are reproducible. In addition, the interlaboratory agreement attained was quite good, providing further indication that both laboratories are capable of accurately performing THC analysis. The audit gas precision results are presented in Table 4-13.

### Interlaboratory Field Duplicate Results

<u>THC</u>. Seventeen pairs of field duplicate samples were collected; one member of each sample was sent to ATL and the other to RTI in order to provide further information regarding interlaboratory precision and to validate ATL's analytical processes. In addition, at four of the locations samples were collected in triplicate so that two samples were sent to ATL and one to RTI, all from the same sampling locale.

Of the 21 pairs of THC results, the RPDs for 17 of these pairs were less than 50%, indicating that excellent overall interlaboratory agreement was achieved and validating ATL's ability to analyze for THC by U.S. EPA Method 18. Of the four THC pairs which did not agree as well, one low level THC detection (0.9 ppmv) was not replicated by ATL. The THC concentrations for the remaining three pairs agreed by a factor of four at the most (RPDs up to 112%). Though the concentrations were not precisely duplicated, the results agreed well enough for the data to be considered usable.

<u>Methane</u>. RTI reported methane results for eight samples only. Of these eight samples, the presence or absence of methane reported by ATL was confirmed by RTI in all but one. The exception (from Refinery Y) was for a methane result of 3.4 ppmv reported by ATL. RTI did not detect methane in the field duplicate member they analyzed. (RTI did not provide detection limits to Radian.) The interlaboratory field duplicate results are presented in Table 4-14.

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Table 4-13 Audit Gas Total Hydrocarbons (THC) Results - Precision

Refinery	Sample	Certified Value (ppmv)	ATL Result (ppmv)	ATL RPD	RTI Result (ppmy)	RTI RPD
W - Direct	1	170	190		NA	
	2	690	720		NA	
W - Through Tent	3-FDA	170	170		NA	
	3-FDB	170	180	5.71	NA	
	4	690	690		NA	
X - Direct	1	170	170		NA	
	2	690	590		NA	
X - Through Tent	3-FDA	690	760		NA	
	3-FDB	690	670	12.59	NA	
	4	170	200		NA	
Y - Direct	1-FDA	170	160		170	0
	1-FDB	170	97	49.03	NA	
	1-FDC*	170	210	27.03	NA	
	2-FDA	690	490		660	4.4
	2-FDB*	690	720	38.02	NA	
Y - Through Tent	3-FDA	170	150		170	0
	3-FDB*	170	190	23.53	NA	
	4-FDA	690	450		660	4.4
	4-FDB*	690	750	50.00	NA	
Z - Direct	1-FDA	170	230		180	5.7
	1-FDB	170	240	4.26	NA	
	1-FDC*	170	180	24.39	NA	
Z - Through Tent	2-FDA	170	200		150	12.5
	2-FDB*	170	200	0.00	NA	
	3-FDA	690	730		640	7.5
	3-FDB*	690	700	4.20	NA	

\* These "duplicate" samples were reanalyses by ATL of the samples originally sent to RTI.

FDA - Field Duplicate A. Duplicates submitted to ATL only.

FDB - Field Duplicate B. Duplicates submitted to ATL only.

NA - Not Analyzed

NC - Not Calculated

RPD - Relative percent difference.

ATL - Air Toxics, Limited.

RTI - Research Triangle Institute.

Refinery	Sample	ATL THC Result (ppmy)	RTI THC Result (ppmv)	THC RPD	ATL Methane Result (ppmv)	RTI Methane Result (ppmy)	Methane RPD (%)
W	1-FDA	370	450	19.51	< 1.9	NR	NC
	1-FDB	400	NA	11.76	< 2.0	NA	NC
	2	100	28	112.50	23	NR	NC
	3-FDA	160	140	13.33	< 2.0	NR	NC
	3-FDB	150	NA	6.90	< 2.0	NA	NC
	4	290	360	21.54	< 2.0	NR	NC
x	1	< 0.090	0.9	NC	< 1.8	NR	NC
	2	18000	14000	25.00	< 1.8	ND	NC
Y	1	30	16	60.87	< 1.9	NR	NC
	2	660	350	61.39	280	95.2	98.51
	3-FDA	950	1100	14.63	< 2.0	ND	NC
	3-FDB	960	NA	13.59	< 2.0	NA	NC
	4	1700	2000	16.22	3.4	ND	NC
	5	140	160	13.33	< 2.0	ND	NC
Z	1	190	220	14.63	< 1.8	NR	NC
	2	610	430	34.62	< 1.9	NR	NC
	3-FDA	830	990	17.58	720	NR	NC
	3-FDB	910	NA	8.42	730	NA	NC
	4	2200	2400	8.70	5600	1820	101.89
	5	25	16	43.90	22	6.7	106.62
	6	140000	140000	0.00	1800	9.4	197.92

## **Table 4-14 Interlaboratory Duplicates**

- FDA Field Duplicate A. Duplicates submitted to ATL only. FDB Field Duplicate B. Duplicates submitted to ATL only. LDA Laboratory Duplicate A, performed by ATL only.
- LDB Laboratory Duplicate B, performed by ATL only.
  RPD Relative percent difference.
  RTI Research Triangle Institute.

 $\mathbf{N}\mathbf{A}$ 

Not ApplicableNot Calculated NC

- ND - Not Detected (RTI did not supply detection limits).
- NR Not Reported ATL Air Toxics, Limited.

Overall, the methane results are inconclusive. The identification of methane is generally consistent between the two laboratories, though the quantitation is not. As previously mentioned, RTI used a different method to analyze for methane and therefore greater variability in reported concentrations would be expected. The limited methane field duplicate data set does not allow for an assessment of ATL's ability to accurately analyze for methane using ASTM Method 3416. However, it is notable that the methane concentrations reported by ATL are significantly higher than those reported by RTI.

## BAAQMD AND SCAQMD AUDITS

The BAAQMD and SCAQMD also conducted audits of the testing activities for the 1993 Refinery Study. The differences between screening values obtained by the BAAQMD and Radian, and the differences between screening values obtained by the SCAQMD and Radian are discussed in detail in Volume II, Sections 3. The differences in screening value measurements are well within the anticipated range of screening variability for different inspectors with different instruments.

The BAAQMD observed much of the testing at two refineries. No particular problems were communicated to Radian during, or as a result of, the BAAQMD audits. The BAAQMD obtained some duplicate samples from components tested at both refineries that they audited. However, results of the analysis of the BAAQMD duplicates are not known by Radian at this time.

In general, the SCAQMD auditors appeared favorably impressed with the testing procedures and quality controls used during the audit. However, the audit by the SCAQMD also highlighted some areas of potential concern to this agency. These areas of potential concern were addressed fully in Radian's letter to the Western States Petroleum Association (WSPA) dated April 27, 1993 (see Appendix E). Radian does not believe that any issue raised as a result of the SCAQMD has a significant impact on the data quality of this study.

## Section 5

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Order No. 841-46120

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