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Air



**INDEPENDENT
QUALITY ASSURANCE OF
REFINERY FUGITIVES TESTING
BY WESTERN STATES
PETROLEUM ASSOCIATION
FINAL AUDIT REPORT**



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Office Of Air Quality Planning And Standards
Office Of Air And Radiation

U. S. Environmental Protection Agency
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EPA-454/R-93-033

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EXECUTIVE SUMMARY

Research Triangle Institute (RTI) undertook this task for the U.S. Environmental Protection Agency's (EPA's) Office of Air Quality Planning and Standards to provide third-party Quality Assurance (QA) support to a Western States' Petroleum Association (WSPA) program to measure fugitive emissions at petroleum refineries. Conduct of the WSPA program was contracted to Radian Corporation, and analytical work was subcontracted to Air Toxics, Ltd. (ATL) of Rancho Cordoba, CA. Work at one refinery in the eastern U.S. had been completed and work at two others had begun when the QA effort conducted the first field audit in December 1992. A second field audit was conducted in early January 1993. Each audit involved visits to two different refineries so that all four of the California refineries were visited. The field sampling program concluded in late February.

Fugitive emissions are an important source of potentially controllable air pollutants, and both the industry and EPA have an interest in accurate quantification. Emissions estimates are difficult to make because of the unconfined and diffuse nature of the sources. The primary objectives of the WSPA study were to determine the correlation between screening values and true mass emission rates and to develop a relationship between liquid and gas composition. EPA's QA effort, however, focused only on the correlation objective because the number of leaking components in the California refineries cannot be expected to be representative of refineries in general. The number of components leaking at a given screening value is used in conjunction with the mass correlations to derive the average emission factors.

The number of components leaking at a given screening value is used with the mass correlations to derive the average emission factors. Emissions of concern to EPA include non-methane organic compounds (NMOCs), which can react in the atmosphere to create ozone; methane, a potent greenhouse gas; and hazardous air pollutants (air toxics), which can be harmful to health and the environment.

The screening values consist of peak ambient air concentrations of total hydrocarbons in the vicinity of a leaking component. Screening measurements are made using a hand-held Organic Vapor Analyzer (OVA). Mass emission rates from a selected subset of individual components are determined by completely enclosing each component with a "tent" of Mylar plastic and sealing it with tape. Zero-grade nitrogen flows from a pressurized cylinder into the tent at a known rate controlled by a rotameter, and samples are drawn from the tent into passivated stainless-steel canisters which are sent to the laboratory for analysis using gas chromatography.

RTI used several different approaches to assess and characterize the quality of data obtained from this effort:

- Technical systems audits (TSAs) were performed on-site while the Radian technicians were obtaining screening measurements and collecting samples. The objectives of these audits were to determine compliance with applicable methods and the QA Project Plan (QAPjP), and to look for any potential problems with technique, QC practices, etc.
- During the performance evaluation audits (PEAs), certified gas cylinders were provided to challenge both the screening instruments and the laboratory's results. Some of the PEAs were used to determine the total measurement error, including components attributable to both sampling and analysis.
- RTI's laboratory performed analyses that duplicated those performed by Air Toxics, Limited (ATL). These analyses provided information on interlaboratory variability.
- For the audit of data quality (ADQ), selected raw data obtained from the analytical laboratory were examined for obvious errors. Data for the PEA samples were examined closely since the "correct" value was known.

After field audits at two refineries in December 1992, RTI issued a memorandum of findings and recommendations based on the TSAs. The auditors found that screening measurements, the tenting procedures, and other field

measurements were performed in general accordance with established methods and guidelines, but insufficient attention was being paid to preventing leakage at the OVA probe and in preventing cross-contamination of equipment used for filling the canisters. The dilution probe also appeared to be giving erratic results.

A second set of audits (TSAs and PEAs) were performed in early January 1993, and a second memorandum of findings was issued, showing that the most significant findings from the first audit had been addressed. Assuming that these corrective actions continued to be observed, the screening data taken after mid-December should be of acceptable quality. Data taken before that time should be screened for any indication that the OVA probe was not sealed tightly, or that the dilution probe was not performing consistently. Because field checks were performed immediately before the OVAs were used, errors in screening measurements are expected to be minimal. Any screening measurements for which the actual concentration was >10,000 may be suspect if the dilution probe gave inconsistent results during that day's calibration.

Examination of laboratory results for PEA samples provided by RTI during the December audits and analyzed by ATL revealed that the two most serious discrepancies were due to simple calculation or dilution errors that could be fully explained by the raw data.

The main conclusions regarding the usability of the data set generated by the project are as follows:

- Based on the results of the QA gas flow-through tests, sampling (tenting) 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.
- Precision for repeated measurements of the QA cylinders by ATL was generally less than 30%. This component of error is probably small relative to other uncertainties in the measurement system, particularly screening measurements of the fugitive emissions made with the OVA; however, the latter source of uncertainty could not be characterized within the scope of this project.

- Users of the data should take care to convert data into appropriate units for their applications. Data are variously reported to Radian and ATL as parts per million (ppm) by volume "as propane," and by volume "as methane." Scott Specialty Gases and RTI reported some results in ppm "as carbon." Emission factors ultimately derived from this data will be in units of weight per unit time. This can lead to confusion where the units are not clearly specified.
- OVA (screening) data acquired before the first audit in December should be scrutinized by Radian for possible anomalies due to probe leakage. This leakage is most likely to be evident as inconsistent dilution factor measurements. After the audit, additional measures implemented by Radian to detect and prevent probe leakage appear to have reduced the dilution factor variations.
- Use of the emission factors or correlations calculated in this project should be limited to the specific type of instrument and offset distances used to acquire the screening measurements; i.e. the OVA Model 108 at zero cm and operating at approximately 800 mL/min. Other instruments could have different response characteristics due to inlet flow rate, probe offset distance, or other factors.

1.0 INTRODUCTION

From December 3 through 8, 1992, and January 4 through 8, 1993, Research Triangle Institute (RTI), under sub-contract to the Midwest Research Institute (MRI), provided external quality assurance support to the Western States Petroleum Association (WSPA) project on behalf of the U.S. Environmental Protection Agency (EPA) and Office of Air Quality Planning and Standards (OAQPS). WSPA contracted Radian Corporation to perform field testing at five oil refineries in the U.S.: ARCO, Pacific, Chevron, Ultramar, and British Petroleum. The MRI/RTI team was contracted by EPA to provide quality assurance (QA) support to the project. WSPA's primary project objectives were (1) to correlate screening measurements (leak concentrations) for total hydrocarbons (THCs) and emission rates and (2) to correlate between liquid and gas composition. The latter objective was not achieved due to technical difficulties in relating product composition with the fugitive emissions.

1.1 QA PROJECT OBJECTIVES

QA audits were conducted at the ARCO Oil Refinery in Carson, CA, and the Pacific Oil Refinery in Hercules, CA, during December 3 through 8, 1992. The Chevron Oil Refinery in Richmond, CA, and the Ultramar Oil Refinery in Wilmington, CA, were audited during the week of January 4, 1993. The project schedule also included field testing at a fifth refinery, British Petroleum in Marcus Hook, PA; because the project had a late start, however, field testing at this site had already been completed. A field testing and audit schedule is shown in Figure 1-1. The overriding QA objectives were (1) assessment of compliance with guidelines and the Quality Assurance Project Plan (QAPjP) and (2) assessment of data usability. QA support included performance evaluation audits (PEAs), technical systems audits (TSAs), and an audit of data quality (ADQ).

Refinery	September	October	November	December	January
BP; Marcus Hook, PA	██████████				
Ultramar; Wilmington, CA			██████████	██████████	
ARCO; Los Angeles, CA				██████████	
Chevron; Richmond, CA		██████████	██████████	██████████	
Pacific; Hercules, CA			██████████	██████████ ██████████	
Field Audits				██████████	

Figure 1-1. Tentative field testing schedule.

1.2 QA PROJECT DESCRIPTION

1.2.1 QAPjP Review and Comparison with EPA Guidance Documents

The first step in assessing Radian's compliance with the QAPjP and with EPA guideline documents was to conduct a thorough review of the QAPjP and to compare the plans for the project as projected in the QAPjP and as required by the provision of applicable guideline documents. The review report was prepared on December 11, 1992, by Shirley J. Wasson and James B. Flanagan and is provided in Appendix A. Part 1 of the report offers comments in the interest of improving the quality of data for the project. Part 2 presents comments that, if acted upon, would result in a clearer and more understandable QA plan and test plan. Part 3 contains a comparison of the sampling and data reduction procedures in three documents:

- 1) Radian Corporation's Quality Assurance and Test Plan for WSPA/API Refinery Fugitive Emissions Study, Phase III
- 2) Suggested Guidelines for a QA/QC Protocol to Determine Volatile Organic Compound Emission Rates from Equipment Components (QA/QC Guidelines for Screening and Bagging)
- 3) Protocols for Emission Estimates of Equipment Leaks of VOC and VHAP, OAQPS, October 1992 (draft).

Some of the differences between the three documents were in the sampling containers, the calculation of response factors, the frequency of certain measurements, the analysis of blind standards, and the calculation of emissions factors.

Each document provided for response factors somewhat differently. Radian used the response factors generated with the OVA for methane. Document 2 indicated that the response factors should be generated in the laboratory. Document 3 provided a list of response factors.

There were also significant differences among the three documents regarding how the emission factors were to be calculated. Radian intended to report the FID response in units of concentration by weight (ppmw), a method which automatically compensates for the mass of the calibration gas used. This method of calculation is acceptable for refinery emissions that are simple hydrocarbons because FID response is proportional to carbon number. The Agency guideline documents' equations refer to the concentrations of VOCs in units of concentration by volume. This approach would have required explicit values for relative response factors for each compound found. This would have been impractical for the complex mixture of hydrocarbons encountered in petroleum refining. Radian's method was simpler and allowed direct use of the raw data in its emission equation.

1.2.2 Technical Systems Audits

A technical systems audit (TSA) is a qualitative assessment of a measurement system. The audit is conducted at the measurement site so that equipment and documentation can be observed in use by project personnel. In order for corrective actions to be taken on a timely basis, TSAs are conducted as soon as possible after a project is initiated. The auditors examine equipment and records and speak with key project personnel. TSAs are also qualitative assessments of the likelihood that the project will produce data of known and acceptable quality. For this project, auditors conducted site visits at four oil refineries where OVA screening and bagging measurements were being performed. The TSAs performed for this project included the following specific areas and activities:

- Project Organization and Personnel--The organizational structure of the project was given in Figure 2-1, Management Organization Plan, of the QAPjP. Since the plan did not include a QA coordinator from Radian for the project, the auditors coordinated their efforts through the Assistant Project Director, Ronald Ricks.

- Facilities and Equipment--Field equipment and facilities were reviewed at each of the refinery sites. Instrument care and condition were verified. Each site was examined for adequate working space.
- Calibration Procedures--The OVAs, oxygen meters, and flow rate meters were examined for evidence of recent and suitable calibration. The calibration logs were examined. Auditors observed preparation of the calibration standards and the calibrations of the instruments as performed by project personnel.
- Sampling and Sample Handling System--Sampling procedures were defined in the QAPjP and test plan. The auditors observed Radian following these sampling procedures and noted any deviations. Sampling was examined for adherence to the plan and for uniformity of action among the personnel on each of the four sites audited. The auditors also examined the sample logs, custody sheets, and procedures for storing and shipping the samples to the analytical laboratory.
- Analytical Procedures--RTI was not permitted to conduct a TSA of the analytical laboratory. Thus assess analytical accuracy and precision, selected raw data generated by the laboratory for the QA and duplicate samples were examined in detail.
- Quality Control Procedures--The auditors observed the reference materials used by Radian in the field. A midrange calibration standard was routinely checked before and after each "bagging" (tenting) procedure to determine how well the OVA was maintaining its calibration. The observed frequency with which blanks and duplicates were taken was compared with that required by the QAPjP and the guideline documents.
- Preventive Maintenance and Maintenance Records--The auditors observed the Method 21 preventive checks which precede each day's sampling. After the first two audits, several suggestions made by the auditors were implemented to improve the quality of the OVA screening data. Among these were conducting leak detection procedures, checking the OVA flow rates, changing the oxygen meter calibration procedure, and purging the Tedlar bags prior to filling them with calibration gases. Records of the OVA checks were examined. Maintenance notes were kept in the daily log.

- Data Processing and Validation Procedures--Raw calibration data of the OVA were tested by linear regression. The correlation coefficient (r^2) was to be 0.995 or better. Calibration of the oxygen meter was performed at first on room air (20.9% oxygen) and then validated with 5% oxygen from a certified cylinder. After the first audit, this procedure was reversed since oxygen measurement was being conducted below the 5% level.

Dilution factors were checked with the dilution probe in place using two or three different calibration gas concentrations.

Data processing and validation in the analytical laboratories was not examined on-site, but as part of the audit of data quality on the selected records received by the auditors.

- Recordkeeping--The auditors observed all field records including the daily master log, daily notes, OVA and oxygen calibration records, dilution factors, custody sheets, and the field sheets titled "Bagging Data Entry Forms."

To prepare for the audit, the auditors became familiar with Radian's QAPjP and test plan. They then prepared project-specific questions and generated a checklist which became the basis of every site visit. During the audit, the auditors used the checklist as one of the primary audit tools. Queries from the checklist often led to discussions of project matters outside the checklist. Where appropriate, the auditors asked to see evidence in support of Radian's responses to questions.

The TSAs did not provide a quantitative assessment of data quality, nor were they vehicles for data validation. Two other types of audits, performance evaluation audits and an audit of data quality, were performed to provide those assessments. Additionally the TSAs only touched upon the management roles of the Radian team. No attempt was made to conduct a management system review for this project.

1.2.3 Performance Evaluation Audits

Audit materials were obtained from Scott Specialty Gases and used for audits of both the field equipment and the laboratory analyses. Materials consisted of the following:

- Two cylinders, each containing three different hazardous air pollutants (HAPs) listed in the Radian QAPjP. These cylinders were used primarily for preparing QA samples for the laboratory, but readings were also made in the field using the OVA.
- Three cylinders containing methane at known levels for the OVA challenge. By using a different method of supplying the gas (a simple gas manifold arrangement instead of the transfer bag arrangement used by Radian) any artifacts due to the use of transfer bags could be detected.
- One cylinder containing methane and ethane for OVA challenge. The concentrations in this cylinder were known to RTI through repeated analyses, and provided a measure of OVA response factor variability when the challenge gas was not pure methane.
- One cylinder of 5% oxygen in nitrogen for oxygen meter challenge. This cylinder was also used to provide a source of pressurized gas for the flow rate audit.

1.2.4 Audit of Data Quality

The audit of data quality consisted of reviews of the following data packages:

- The Interim Final Report, consisting of a spreadsheet of Radian's complete data set (received by RTI in May 1993)
- Copies of Air Toxics, Limited's laboratory logs and instrumental raw data for samples specified by RTI
- Copies of Radian's field notebooks for all five refinery sites.

1.2.5 Review of Final Report

The WSPA/Radian Draft Final Report was expected to be available by mid-August, 1993 for review as part of this QA report. It was not available by the end of August, and thus only the spreadsheet data set provided by Radian in May was included in the data audit.

2.0 AUDIT DESCRIPTION AND RESULTS

RTI auditors conducted PEAs and TSAs at each of the four refineries visited. PEAs were conducted to evaluate sampling and analysis precision and accuracy. The TSAs involved the observation and evaluation of field operators. After specific data were requested and obtained from Radian and Air Toxics, Ltd., the data were reviewed and evaluated by RTI personnel for an ADQ. Activities for each audit are described in this section.

2.1 TECHNICAL SYSTEMS AUDITS (TSAs)

For the TSAs at each refinery, auditors observed the following:

- calibration procedures for the oxygen analyzer and the OVA
- routine instrument checks performed on the OVA
- dilution probe operation
- tenting and sampling procedures
- field documentation.

The field operating procedures were observed and compared to specified procedures in Radian Corporation's QAPjP, Method 21, and the videotape documentary, "VOC Fugitive Emissions Procedures and Equipment," by E.J. Richards.

2.1.1 Preparations for Audits (Including Dates and Personnel)

A schedule of the two audit trips is as follows:

<u>Auditors</u>	<u>Sites</u>	<u>Dates</u>
<u>First Audit</u>		
J. Flanagan/L. Pearce	ARCO Oil Refinery, Carson, CA	12/3-4/92
	Pacific Oil Refinery, Hercules, CA	12/7-8/92
<u>Second Audit</u>		
S. Wasson/L. Pearce	Chevron Oil Refinery, Richmond, CA	1/4-5/93
	Ultramar Oil Refinery, Wilmington, CA	1/7-8/93

The audits were arranged in consultation with individuals from the host refineries and with Radian Corporation prior to each trip. The following personnel were consulted in preparation for the first audit:

- Ron Ricks - Radian Corporation
- Miriam Lev-On - WSPA (ARCO Corporation)
- Dennis Rood, Bill Zobel, James Jeeter - ARCO Refinery
- Frank Bly, Mat Marusich - Pacific Refinery

Consultations prior to the second audit included:

- Ron Ricks - Radian Corporation
- John Knoblock - Chevron Refinery
- Frank Giles - Ultramar Refinery

Other preparations included reviewing the QAPjP and comparing it with the EPA guidance documents, viewing the videotape by E.J. Richards titled "VOC Fugitive Emissions Procedures and Equipment," preparing an audit checklist and an audit notebook, and reviewing the use of audit equipment with Robert Murdoch of RTI.

2.1.2 Oxygen Monitor

2.1.2.1 Calibration--

The Baker Teledyne oxygen analyzer was used by the Radian teams in the field at each of the four refineries. The analyzer is a small, portable oxygen monitor which measures the percent oxygen on three scales: a low scale (0-5%), a medium scale (0-10%), and a high scale (0-25%). All three scales were used when measuring oxygen concentration in the field. The oxygen analyzer was used to verify the point of equilibrium using the "blow-through" tenting technique. This technique involved flowing ultra-high purity nitrogen gas (N₂) through the tent until the oxygen concentration equilibrated below 5%. At this point, Radian technicians proceeded to screen with the OVA and collect a canister sample.

During the audit trip to ARCO and Pacific Oil Refineries, the oxygen monitor was calibrated using ambient air (20.9% oxygen) and then checked for linearity using a 5% oxygen calibration standard. At ARCO, this calibration procedure indicated a variation from 5.25 to 5.6% oxygen. Calibration data from Pacific revealed a larger variation ranging from 5.4% to 7.0% oxygen.

During calibration, efforts were made to recheck fittings, shorten connections, and evacuate and refill the 5% oxygen calibration bag to achieve the 5% oxygen reading. RTI recommended flushing the 5% oxygen calibration bag at least twice due to the potential air in-leakage which increases the percent oxygen in the bag. RTI also suggested that cylinder regulators be purged two to three times when filling calibration gas bags. It was suggested that acceptance criterion for the 5% oxygen check be tightened to between 4 and 6% oxygen, or within $\pm 20\%$ of the calibration concentration value.

In response to the variation in the 5% oxygen check, Radian called for a change in the oxygen analyzer calibration procedure. Upon returning for the second audit trip to Chevron and Ultramar Oil Refineries, auditors found that a new calibration procedure had been implemented. This new procedure called for calibrating the analyzer with the 5.0% oxygen calibration standard and using the ambient oxygen concentration (20.9% O₂) as a calibration check. At Chevron, the changed procedure resulted in ambient oxygen concentrations that were 1.3 to 2.3% low. Ambient oxygen concentrations were found to be 0.6 to 1.6% low at Ultramar. Since, for this study, important oxygen measurements occur at the low end of the scale, better data will be measured and recorded as a result of the change in procedure. It was observed that the Tedlar bags used to contain the calibration gases, the zero air, the QC check standard, and the oxygen calibration standard were being purged at least once prior to filling. Some were being purged twice and three times. It was again recommended that the bag purging protocol be standardized, and that the 5% oxygen bag be purged at least twice since Tedlar bags are permeable to oxygen.

2.1.3 Organic Vapor Analyzer (OVA)

2.1.3.1 Daily Checkout--

The TSA also involved observation of the daily checkout procedures performed on the OVA. During the refinery visits, auditors observed operators checking the hydrogen supply and the battery status prior to turning on the OVA amplifier. This was in accordance with the Century OVA Model 108 Instruction Book 3433 and E. J. Richard's videotape, "VOC Fugitive Emissions Procedures and Equipment." A 5-minute warm-up period was required for the amplifier before the electronic linearity of the instrument was checked. This practice was observed at each of the four refineries. Also, the videotape suggested leak checks of the sample gas handling system such as the probe fitting, sample line, and sample line fitting. A probe filter check and probe cleaning were also recommended prior to OVA calibration. The probe filter collects deposits of organic residue over time and should be cleaned on a daily basis. No leak or probe filter checks were observed during the first audit at the ARCO and Pacific Refineries. Implementation of these leak and probe filter checks were observed in the second audit at Chevron and Ultramar, however. Operators also initiated checking the gas sample flow rate into the OVA prior to the second audit.

2.1.3.2 Calibration--

Another objective of the TSA was to observe calibration of the OVA. Prior to OVA calibration, auditors observed Tedlar bags being filled with calibration gas standards consisting of a zero air standard; normal methane concentrations of 10, 100, 1000, and 10,000 ppm; and a 2.5 or 3.5 percent methane in air standard for calibration of the dilution probe. The 1000-ppm midrange methane standard was designated as the QC calibration check. The QC check was performed after each field sample to determine the need for OVA recalibration. If the OVA screened outside $\pm 20\%$ of 1000 ppm methane concentration for the QC check, the OVA was recalibrated. Auditors noted that the Tedlar bags containing the calibration gases, the zero air, and the QC check standard needed to be purged at least once prior to

filling. No standardized purging of the bags was observed during the first audit. During the second audit, bags were purged two and three times. Auditors recommended that the bag purging protocol be standardized and suggested that the gas cylinder regulators should be flushed two to three times before calibration bags were filled.

The multipoint calibration consisted of measuring the concentration of each of the bagged standards after electronic calibration had been done. Operators then recorded the indicated concentration of each standard along with the date and time in the logbook.

In case of poor calibration results (e.g., $r^2 < 0.995$), operators would run the 100-ppm methane standard and adjust the OVA using the calibration adjust knob on the face of the sidepack assembly to read 100 ppm. The operators would then close off the hydrogen supply valve to extinguish the flame and adjust the gas select control to OVA full-scale reading. Operators also flushed and refilled the Tedlar bag with the particular calibration standard. This is the proper calibration procedure according to Foxboro's Century® OVA 108 Portable Organic Vapor Analyzer Instruction Book.

Radian technicians at all refineries evaluated the linearity of the OVA calibration curve by fitting the OVA responses to a linear regression equation to determine whether the correlation coefficient, r , was greater than or equal to 0.995. Calibration gas concentration was the independent (x) variable, and the OVA response was the dependent (y) variable. An observation was made by RTI that results would be dominated by the higher level points in the correlation due to unequal spacing between the calibration gas concentrations, resulting in misleadingly high values for the correlation coefficient. Auditors suggested use of a logarithmic transform of both the x and y variables prior to the linear regression in order to equally space the data points. At the second audit, however, it was observed that this log-log transformation was not being done.

2.1.3.3 Dilution Probe Checks--

The dilution probe was calibrated using a 2.5 or 3.5 percent methane standard and a lower 1000-ppm methane standard at ARCO and Pacific. At Chevron and Ultramar, a third calibration standard, approximately 10,000 ppm methane, was used in the dilution probe calibration procedure. According to the QAPjP, the objective was to set the dilution ratio at 10:1 to permit screening of leaks up to 100,000 ppm. Although 10:1 was the target, the dilution factors obtained with the dilution probe varied significantly between calibration gases at different calibration concentrations. This variability was seen at all four refineries. Further discussion of this variability, with example data, may be found in Section 2.2.2 below.

Auditors felt that Radian should investigate the origin of this variability and make any necessary equipment modifications to correct the problem. Auditors suggested that a target goal of agreement such as $\pm 20\%$ be established between the dilution ratios obtained from the different standards. The uncertainty in the dilution factor directly affects the hydrocarbon concentration, which is calculated as OVA readout times dilution factor. This error should be taken into consideration when making critical measurements with the probe.

2.1.3.4 OVA Flow Rate--

It was observed during the first audit that the gas flow rate into the OVA probe tip was not measured and recorded. A sample flow rate indicator was located on the front of the sidepack assembly, but this indicator was not calibrated in physical units. Auditors recommended that sample flow rate at the inlet of the OVA probe be measured with an external device and recorded during calibration and before and after each battery charge.

By the second audit trip to Chevron and Ultramar, Radian operators had implemented the measuring and recording of OVA flow rates. The flow rates were recorded in the logbook once at the beginning and once at the end of the day. A comparison between start and end flow rates appeared to indicate a decreasing

trend. This was possibly attributable to a battery losing its charge over a day's use. Example flow rates of a new battery can be seen on 12/15/92. The flow rate increased by the end of the day from 785 mL/min to 790 mL/min. These measurements might provide valuable indicators of a low battery and might provide an explanation for the instrument losing its calibration over the course of the day. The most important use for this information, however, may be in comparing measurements made at different flow rates, as when different makes and models of analyzers are used.

2.1.4 Tenting and Sampling

2.1.4.1 Tenting Procedures--

One objective of the TSA was to review and observe tenting procedures in the field. Auditors observed tenting procedures at each of the four refineries and found them consistent. Tenting technique varied somewhat between technician teams. The technicians at ARCO and Ultramar, Jeff Davis and Joe Colin, were very meticulous in constructing the tent around a component. One problem common to all Radian technicians was the difficulty in obtaining an air-tight seal. This was due to the variable structures and locations of the components being tented. The technicians performed tenting procedures well, however, given the adverse locations and angles of some of the components.

Prior to tenting, auditors observed technicians screening the component to verify the leak previously tagged by refinery personnel. If data for a leaking component of this type and leak rate were required by the sampling matrix, identification information was recorded on a tenting data entry form. This information included sample, plant, instrument, and component identification. Component sub-category, component services, and ambient temperature were also recorded on the form. Pieces of Mylar plastic were cut to fit around the component. Two sample ports were cut into the Mylar and fitted with Swagelok® fittings. One port was for the attachment of the nitrogen gas line from the gas cylinder. This port was angled so that the nitrogen gas line was positioned to

directly interface with the leak and allow proper mixing of the two streams. The second port allowed measurement of oxygen, temperature, and collection of samples from the tent. The surface of the component was wiped clean with a dry cloth prior to wrapping the Mylar around the component. At ARCO and Ultramar, Jeff Davis and Joe Colin applied duct tape to the component directly before wrapping it with Mylar to get a better seal. Duct tape was applied over the top of the Mylar and used to seal the seams forming the tent. Great effort was given to ensure that the tent was completely sealed from the outside air prior to sampling.

It was also noted out in the field that pieces of Mylar were reused throughout tenting at all four refineries. This was of minor concern due to possible negligible carry-over from tent to tent. Technicians at ARCO and Ultramar wiped the surfaces of the used Mylar pieces prior to tenting.

2.1.4.2 Sampling Procedures--

QA support to the project also involved observation of the sampling procedures. Sampling procedures were consistent at each site; however, there were a few modifications made in the sampling technique after the first audit trip to the ARCO and Pacific Refineries. The following discussion details the auditors' observations and what modifications were implemented.

First the nitrogen flow rate was established and recorded on the tenting data entry form before the nitrogen gas line was connected to the port in the tent. The nitrogen stream was positioned to allow proper mixing with the leak. The nitrogen flow rate was measured using a Mini-Buck flow calibrator manufactured by A.P. Buck, Inc. Initial temperature in the tent was measured and recorded using an Omega hand-held thermocouple. Oxygen concentration in the tent was measured next in sequence by a Teledyne oxygen analyzer. The analyzer was used to monitor when the oxygen concentration inside the tent fell below 5%. This was a critical measurement in determining when to take a sample. If the oxygen concentration did not decrease below 5 percent, duct tape was used to reinforce

the tent seals until the oxygen concentration was reduced. At Chevron, the oxygen concentration was monitored to very low concentrations, approximately 0.2 to 0.4 percent oxygen, and a reading was measured every other minute for three minutes to get an average oxygen concentration. At other sites, oxygen was allowed to fall below 5%; then the oxygen instrument was disconnected.

The leak was then screened using the OVA Model 108 with a dilution probe to get a reading for the total hydrocarbon concentration within the tent at equilibrium. The dilution probe was always required while screening tent samples because the high concentration of nitrogen from the blow-through gas extinguishes the OVA burner flame. Sample collection involved first flushing the "TEE" joint used to monitor the pressure during canister fill by including the vacuum gauge in the train during the oxygen measurement. The pump in the oxygen analyzer draws the sample through, flushing the gauge. Flushing of the TEE joint was not performed at ARCO, but was included in the sampling protocol at Chevron, Pacific, and Ultramar. The canister used to collect the sample was a polished, stainless-steel Summa® canister. The canister was initially at -29 inches vacuum Hg and was filled to -10 inches Hg and the fill time was recorded. The canister was assigned an identification number and packed for shipment to Air Toxics, Ltd., to be sent the following day. The tent was disassembled and the component was screened with the OVA for the final screening value which was recorded. A QC check (1000-ppm methane in air) was screened by the OVA after each tent. If the screening value was outside $\pm 20\%$, the OVA was recalibrated prior to the tenting of the next component.

During the January audit at Chevron and Ultramar, it was observed that Swagelok® fittings were used in the connections to the oxygen analyzer and also to the Mini-Buck. This provided an improvement in the fit of the connectors to the instruments. Also during the screening, the OVA probe tip was inserted into a piece of Tygon connected to a pressure gauge. The pressure gauge was then connected to the tent using a Swagelok® connector. Previously, the OVA probe tip had been inserted directly into a section of Tygon tubing which connected to the

tent Swaglok®. This modification in sampling procedure was made to avoid leakage to the OVA.

2.1.5 Review of Field Documentation

Auditors obtained photocopies of data records and logbooks kept by Radian technicians for the dates that the auditors were on-site at each refinery. The information obtained included a daily log, OVA calibration data, oxygen meter calibration data, a master log, and tenting data entry forms for the components tented during RTI's audits.

The daily log was reviewed and found to provide adequate information concerning the day's events. Unexpected changes in procedure or mechanical difficulties with equipment were recorded in the log. Logbook entries were made on a daily basis. Auditors observed that field operators were not identified on a daily basis. This daily identification was suggested in the preliminary audit report.

Calibrations of the OVA were logged according to the date and time the procedures were performed. The multipoint calibration involved calibration standards at 0, 100, 1000, and 10,000 ppm methane in air. The dilution probe was calibrated at two concentrations at ARCO and Pacific, a low range and a high range standard. A midrange standard was included and recorded at Chevron and Ultramar. The correlation coefficient, r^2 , was calculated using linear regression and logged daily. Auditors suggested that a leak check of the OVA and measurement of OVA flow rate be included in the logbook prior to the second audit. This suggestion was implemented at both Chevron and Pacific Oil Refineries.

Oxygen calibration information was also properly documented. The master log included the following information: sample identification, tag number, type of component, component size, screen value, tent total hydrocarbon concentration, nitrogen flow into the tent, canister identification, phase of component process

stream, and any observations made by the technicians. This information was also recorded on a daily basis.

The tenting data entry forms were used in the field to record information during tenting operations. These forms contained the same information listed in the master logs as well as other tenting data parameters. The tenting data parameters included initial and final screening values, nitrogen flow rates, tent temperatures, oxygen concentrations, total hydrocarbon concentrations, and sample collection information, as well as the times for each. Auditors identified the need for a section on the form for recording the QC calibration check results with the 1000-ppm midrange methane standard. Radian operators usually added these measurements at the bottom of the form in the margin.

2.2 PERFORMANCE AUDITS

2.2.1 Oxygen Challenge

The PEAs of the oxygen analyzers consisted of challenging Radian's oxygen analyzers with a 5% oxygen in nitrogen audit gas from RTI. This challenge was performed at each refinery after the oxygen analyzer was calibrated. The PEA was carried out by first measuring the flow rate into the oxygen analyzer. A sufficient flow rate was established from RTI's 5.0% oxygen in nitrogen audit gas cylinder and plumbed to the oxygen analyzer. The analyzer response was then measured and recorded.

At ARCO and Pacific, two readings were measured and averaged to give a mean oxygen analyzer response. The summary of the oxygen analyzer audit results can be seen in Table 2-1. Prior to the challenge, the oxygen analyzers at ARCO and Pacific were calibrated using ambient air (20.9%) and checked with 5% oxygen. According to the historical calibration data from the notebooks, the analyzers consistently read higher than the 5% oxygen standard used by Radian. The responses ranged from 5.3% to as high as 7.0% oxygen. Upon challenging the analyzers with RTI's audit gas, the responses were found to be accurate, reading

TABLE 2-1. SUMMARY OF OXYGEN ANALYZER AUDIT RESULTS

Date and Location	Instrument, Manufacturer, Model, and Serial Number	Audit Gas	Audit Gas Concentration (%)	Radian's Mean O ₂ Analyzer Response (%)	Standard Deviation	Number of Readings	Precision (%RSD)	% Bias
12/4/92 ARCO Oil Refinery Carson, CA	Baker Teledyne Portable O ₂ Analyzer S/N 131087	O ₂ in N ₂	5.0	5.0	0	2	0	0
12/7/92 Pacific Oil Refinery Hercules, CA	Baker Teledyne Portable O ₂ Analyzer S/N 128109	O ₂ in N ₂	5.0	5.0	0	2	0	0
1/5/93 Chevron Oil Refinery Richmond, CA	Baker Teledyne Portable O ₂ Analyzer S/N 128109	O ₂ in N ₂	5.0	4.7	0.025	3	0.54	-6.0
1/7/93 Ultramar Oil Refinery Wilmington, CA	Baker Teledyne Portable O ₂ Analyzer S/N 131087	O ₂ in N ₂	5.0	5.1	0.029	4	0.57	+2.0

exactly 5.0% oxygen. These results indicated that the Tedlar bags used to contain the 5.0% oxygen calibration gas may have been permeable to outside air, causing higher calibration responses. The results of this PEA lend support to RTI's recommendation to purge and refill the 5.0% oxygen calibration bag at least twice to rid the bag of any excess oxygen.

At Chevron, a -6.0% bias was seen in the PEA results with a mean oxygen analyzer response of 4.7%. At Ultramar, four readings were measured and recorded, resulting in a mean oxygen analyzer response of 5.1%. Radian's calibration data for the oxygen analyzers at Chevron and Ultramar showed great improvement due to the implementation of purging the calibration gas bags, calibrating the analyzer with 5% O₂, and checking with ambient as of 1/4/93.

2.2.2 OVA Challenge

The results of the OVA challenge are presented in Table 2-2. The PEA was conducted by challenging the OVA with three audit gas concentrations: 1094 ppm and 9034 ppm methane in air and 7850 ppm methane/ethane in nitrogen. The methane in air audit gases were screened both with and without the dilution probe. The methane/ethane in nitrogen audit gas was screened with the dilution probe only, because if screened without the dilution probe, the lack of oxygen would extinguish the OVA burner flame. During the first audit of the ARCO and Pacific Refineries, two readings were taken for each audit concentration to calculate a mean OVA response. The number of readings was increased to three and four at Chevron and Ultramar, respectively.

Audit results from the ARCO Refinery were well within the specified QA objective of $\pm 20\%$ for the accuracy of the OVA, with the exception of the OVA response to the 7850 methane/ethane ppm audit gas. This OVA response resulted in a negative bias of 60.7% with a standard deviation from the mean OVA response of 91.0. During this audit, it was observed by auditors that the OVA connectors and probes were leaking, which may have contributed to the significant variation between OVA readings. Problems establishing the 10:1 dilution ratio

TABLE 2-2. SUMMARY OF OVA CHALLENGE RESULTS

Date and Location	Instrument Manufacturer, Model, and Serial Number	Audit Gas	Audit Gas Concentration (ppm)	Mean OVA Response (ppm)	Standard Deviation	Number of Readings	Relative Standard Deviation (%)	% Bias
12/4/92 ARCO Oil Refinery Carson CA	OVA Model 108 S/N 20143 Smith and Benson, Inc.	CH ₄ in Air	9034	9860* 9290	605 336	2 2	6.1 3.6	+9.1 +2.8
		CH ₄ in Air	1094	1123* 1069	139 0	2 2	12.3 0	+2.6 -2.3
		C ₂ H ₆ /CH ₄ in N ₂	7850	3082*	91	2	3.0	-60.7
12/7/92 Pacific Oil Refinery Hercules CA	OVA Model 108 S/N 2254 Smith and Benson, Inc.	CH ₄ in Air	9034	9920* off scale	71 -	2	0.71 -	+9.8 -
		CH ₄ in Air	1094	1657* 1771	57 35	2 2	3.4 2.0	+51.5 +61.9
		C ₂ H ₆ /CH ₄ in N ₂	7850	9222	353	2	3.8	+17.5

* Denotes screening measurement with dilution probe (OVA reading times dilution factor). (continued)

TABLE 2-2. (continued)

Date and Location	Instrument Manufacturer, Model, and Serial Number	Audit Gas	Audit Gas Concentration (ppm)	Mean OVA Response (ppm)	Standard Deviation	Number of Readings	Relative Standard Deviation (%)	% Bias
1/5/93 Chevron Oil Refinery Richmond CA	OVA Model 108 S/N 2254 Smith and Benson, Inc.	CH ₄ in Air	9034	9909* 8602	57 464	3 3	0.6 5.4	+9.7 -4.8
		CH ₄ in Air	1094	1270* 1029	38 21	3 3	3.0 2.0	+16.1 -5.9
		C ₂ H ₆ /CH ₄ in N ₂	7850	10861*	616	3	5.7	+38.4
1/7/93 Ultramar Oil Refinery Wilmington CA	OVA Model 108 S/N A21664** Smith and Benson, Inc.	CH ₄ in Air	9034	8993* 7548	1213 276	3 3	13.5 3.6	-0.5 -16.4
		CH ₄ in Air	1094	792* 910	5 14	3 3	0.6 1.5	-27.6 -16.8
		C ₂ H ₆ /CH ₄ in N ₂	7850	7496*	136	3	1.8	-4.5
1/8/93	OVA Model 108 S/N 20143** Smith and Benson, Inc.	CH ₄ in Air	1094	1041* 1115	14 47	4 4	1.3 4.2	-4.8 +1.9

* Denotes screening measurement with dilution probe (OVA reading times dilution factor).

** Radian's repaired OVA (S/N 20143) used on 1/8/93. Ultramar Oil Refinery OVA (S/N A21664) used on 1/7/93.

while calibrating the dilution probe also contributed to the large negative bias obtained while screening the 7850-ppm audit gas with the dilution probe attached to the OVA. This problem in conjunction with air-in-leakage from the OVA connectors and probe may have diluted the gas from the original audit concentration of 7850 ppm to the mean OVA response of 3082 ppm.

It should be noted that this result was not reported to the operators nor in the preliminary audit memorandum because RTI wished to confirm the concentration units that had been provided for the methane/ethane mixture. The auditors later received clarification from the RTI analyst that the units were in parts per million "as carbon," and thus should be compatible with the calibration which had been performed using methane. PEAs conducted with this calibration cylinder at other refineries gave results consistent with the value of 7850 ppmC.

OVA serial number 20143 used at ARCO was also used at the Ultramar Refinery. On the day of the audit, however, this OVA had to be sent for repairs due to instrument malfunction during calibration. A substitute OVA, serial number A21664, owned by the Ultramar Refinery, was used during the first day of the audit, 1/7/93. The results of the challenge to this OVA varied from a -0.5% bias with the dilution probe to a -16.4% bias without the dilution probe for the 9034-ppm audit gas concentration. The most significant error in data was measured when screening the 1094-ppm audit concentration with the dilution probe. The mean OVA response was 792, ppm resulting in a negative bias of 27.6%. These data did not meet the specified QAPjP criteria range of $\pm 20\%$. Standard deviations were very large (1213 and 276) for the OVA responses to the audit concentration 9034 ppm, particularly when using the dilution probe. Overall, Ultramar's OVA responses screened lower than the reference gas concentrations. Auditors observed that leak checks of the OVA had been implemented as standard procedure during calibration during this audit. This points to the dilution probe as the source of variability in OVA readings.

On 1/8/93, Radian's original OVA, serial number 20143, was repaired and returned. Auditors challenged the required OVA with only one audit gas, 1094

ppm methane in air, due to a time constraint. The standard deviation of the mean OVA response with the dilution probe was significantly smaller compared to that indicated at ARCO for the same audit conditions. As at ARCO, this OVA performed satisfactorily with a smaller bias for the 1094 ppm audit.

OVA serial number 2254 was used at the two Northern California refineries, Pacific and Chevron. At Pacific, the OVA performed unsatisfactorily with bias results as large as +51.5 with the dilution probe and +61.9 without the dilution probe for the 1094 ppm audit concentration. The OVA screened as high as 1657 ppm with and 1771 ppm without the dilution probe. During the first audit with this instrument at the Pacific Refinery, significant leaks were found in the OVA. These leaks had been corrected by the second audit at Chevron.

At Chevron, the largest variability was observed while screening the 7850-ppm audit gas concentration. The mean OVA response was 10,861 ppm with a standard deviation of 616 and a positive bias of 38.4 using the dilution probe. Use of the dilution probe resulted in an overall increase in the OVA response from the three audit concentrations. Again, these results point to the dilution probe as a point of concern.

A comparison of dilution factors obtained by Radian and RTI during the OVA challenge is presented in Table 2-3. The relative percent difference (RPD) between the two dilution factors is also shown in the far right column. Radian's dilution factors were obtained by screening methane concentrations in air of 100, 10,000, 25,000 or 35,000 ppm with the dilution probe during the calibration of the OVA. RTI's dilution factors were calculated by dividing the audit gas concentration by the average of the OVA responses, with the dilution probe installed, for that particular audit concentration. Overall, Table 2-3 supports RTI's conclusion that the dilution probe introduces bias into the OVA responses.

2.2.3 Flow Rate Audit

Auditors challenged the Mini-Buck calibrator at each refinery using an NIST-traceable Teledyne Hastings bubble flowmeter. The results of the flow rate

TABLE 2-3. COMPARISON OF RTI'S AND RADIAN'S DILUTION FACTORS

Refinery	Audit Gas	RTI (Avg.) Readings	Dilution Factors		
			RTI	Radian	RPD (%)*
ARCO	9034.0	1150.0	7.8	9.0	14.3
	1094.0	128.5	8.5	9.0	5.7
	7850.0	357.5	22.0	9.0	83.9
Pacific	9034.0	995.0	9.1	10.0	9.4
	1094.0	166.0	6.6	10.0	41.0
	7850.0	925.0	8.5	10.0	16.2
Chevron	9034.0	1003.0	9.0	9.8	8.5
	1094.0	155.0	7.1	8.0	11.9
	7850.0	1100.0	7.1	9.8	32.0
Ultramar	9034.0	660.0	13.7	13.0	5.2
	1094.0	91.0	12.0	8.0	40.0
	7850.0	550.0	14.3	13.0	9.5

* RPD = Relative Percent Difference = $\frac{|Radian - RTI|}{RTI} \times 100$

audit are presented in Table 2-4. A zero air gas cylinder was set up and used as the flow source and plumbed to the Mini-Buck calibrator with Teflon tubing. The Hastings bubble flowmeter monitored gas flow rate by measuring the time for a change in bubble height between two fixed points. A bubble rise from the point at the cylinder bottom to the midway point is equivalent to a volume of 500 cm³. In turn, a bubble rise from the bottom point to the top point equals a volume of 1000 cm³. Auditors could use either volume when performing the audit. The bubble rise was timed beginning when the bubble crossed the bottom mark until it reached either the 500-cm³ or 1000-cm³ mark with a stopwatch. At Pacific, however, the timing was done using a wrist watch with a sweep secondhand, due to a stopwatch malfunction.

At ARCO, two mean bubble flow rates, a low and a high flow rate, were chosen to challenge the Mini-Buck calibrator. Two readings were recorded for each range using the Mini-Buck and the bubble meter and then averaged to get a mean flow rate for each instrument. The challenge performed at the Pacific Refinery included a midrange flow rate as well as a higher and a lower range rate. Each rate was measured four times using the Mini-Buck and the bubble flowmeter to get an average flow rate. The standard deviation among the readings is less precise due to use of a wrist watch with a sweep secondhand to time the flow rate instead of a stopwatch. The results of the Chevron and Ultramar flow rate audits were satisfactory with small negative percent biases of -2.8 and -2.6, respectively.

In general, the flow rate audit results were satisfactory. RTI personnel did find some confusion on the part of Radian technicians as to the operation of the Mini-Buck calibrator. Upon questioning various technicians, different responses were given as to how readings were measured and recorded. For example, when pressing the button to initiate measurement, did this action clear the monitor each time for a new reading or did it average this reading and the previous one? With the exception of this confusion, the Mini-Buck calibrator appeared to give adequate and satisfactory data.

TABLE 2-4. SUMMARY OF FLOW RATE AUDIT RESULTS

Date and Location	Instrument Manufacturer, Model, and Serial Number	RTI's Hastings Bubble Flowmeter Reading (mL/min)	Radian's Mean Mini-Buck Flowmeter Reading (mL/min)	Standard Deviation	Number of Readings	Precision (%RSD)	% Bias
12/4/92 ARCO Oil Refinery Carson, CA	Mini-Buck Calibrator AP Buck, Inc. S/N M-2312 Model M-5	1276.4	1256.0	2.8	2	0.2	-1.60
		3193.9	3142.0	5.7	2	0.2	-1.60
12/7/92 Pacific Oil Refinery Hercules, CA	Mini-Buck Calibrator AP Buck, Inc. S/N M-4570B Model M-5	1119.2	1081.0	4.3*	4	0.4*	-3.40
		2462.1	2406.3	17.2*	4	0.7*	-2.30
		4325.9	4234.5	51.5*	4	1.2*	-2.10
1/4/93 Chevron Oil Refinery Richmond, CA	Mini-Buck Calibrator AP Buck, Inc. S/N M-4570B Model M-5	892.2	911.5	2.9	4	0.3	+2.20
		1006.1	1005.8	4.0	4	0.4	-0.03
		1587.5	1555.5	1.3	4	0.1	-2.80
1/7/93 Ultramar Oil Refinery Wilmington, CA	Mini-Buck Calibrator AP Buck, Inc. S/N M-2312 Model M-5	1040.0	1024.0	4.2	4	0.4	-1.50
		1853.6	1805.8	8.8	4	0.5	-2.60
		2566.2	2533.0	6.9	3	0.3	-1.30

* Due to a stopwatch malfunction, timing was done using a wrist watch with a sweep secondhand. Reported standard deviation may be inflated due to poorer measurement precision.

2.2.4 Laboratory Analyses

Data from samples P081, U148, C085, A049, and A095 were requested and delivered to RTI for review in April 1993. The laboratory narrative explained the calibration, an initial five-point curve with continuing calibration checks with each set of samples. The narrative also explained the reporting units. Total hydrocarbons (THCs) are reported by ATL in units of ppmv "as propane." For intercomparison with the certified values and RTI's analytical values, it was necessary to convert units.

Data summaries from ATL indicated use of laboratory duplicates and method spikes with analytical batches. Chain-of-custody sheets were provided. Continuing calibration checks and laboratory blanks were also provided.

2.3 AUDIT OF DATA QUALITY (ADQ)

2.3.1 Field Data

The final set of field data sheets and logbook copies were received on 3/30/93 from Radian. These included field logbooks from all five plants. Portions of these data are reproduced in Appendix D.

2.3.2 Laboratory Data

Copies of raw laboratory data were received on 3/22/93 from Air Toxics, Ltd., through Radian and EPA. Specific samples were selected for examination because of the expense of compiling extra information. The specific sample data selected were P081, U148, C085, A049, and A095. Other supporting data including field data sheets had been received earlier. Because of the termination of speciation studies during December, the TO-14 data were not subjected to an exhaustive audit; however, all compounds present in the multi-component QA audit cylinders were identified correctly.

THCs and methane results were evaluated primarily through the results on the multi-component audit cylinders. These results are shown in Table 2-5,

reported in units of ppm "as propane" for THC and "as methane" for methane. Perhaps the most significant result with respect to sampling errors was comparing the QA samples in which the audit gas flowed through the tented volume to the results when the audit gas was connected directly to the canister. The certified values (Scott) were as follows:

high level: 693.6 ppmv "as propane"

low level: 169.0 ppmv "as methane".

The corresponding analysis data reported by ATL were:

Through Tent

High Level Sample	ppmv "as propane"	Low Level Sample	ppmv "as methane"
A028	450	A026	150
C085	760	C087	200
C086	670	P042	200
P044	730	U151	170
U153	690	U152	180
Mean	660	Mean	180
Standard Deviation	122	Standard Deviation	21

Directly Filled

High Level Sample	ppmv "as propane"	Low Level Sample	ppmv "as methane"
A034	490	A031	160
C089	590	A032	97
U149	720	C088	170
		P046	240
		U148	190
Mean	600	Mean	171
Standard Deviation	115	Standard Deviation	52

TABLE 2-5. SUMMARY OF INTERLABORATORY AND QA ANALYSIS DATA

Sample Number		Type of Sample ³	ATL Results		RTI Results		Certified Value	
ATL	RTI		THC ¹	Methane ¹	THC ¹	Methane ¹	THC ¹	Methane ¹
A026	A027	Audit Gas - through tent	150	15	170	--	168.7	0
A028	A029	Audit Gas - through tent	450	<2.9	600	--	693.7	0
A031	A030	Audit Gas - direct	160	15	170	--	168.7	0
A032	A030 ²	Audit Gas - direct (field duplicate)	97	4.2	170	--	168.7	0
A034	A033	Audit Gas - direct	490	<2.9	660	--	693.7	0
A048	A049	Duplicate - leaker	30	<1.9	16	--	--	--
A049	A049 ²	Reanalysis by ATL	37	<2.8	16	--	--	--
A095	A096	Duplicate - leaker	660	280	353	--	--	--
A107	A109	Duplicate - leaker	950	<2.0	1150	--	--	--
A108	A109 ²	Duplicate - leaker (field duplicate)	960	<2.0	1150	--	--	--
A118	A119	Duplicate - leaker	1700	3.4	2000	--	--	--
A130	A131	Duplicate - leaker	140	<2.0	160	--	--	--
C070	C071	Duplicate - leaker	<0.09	<1.8	<1	--	--	--
C085	--	Audit Gas - through tent	760	<1.8	--	--	693.7	0

(continued)

TABLE 2-5. (continued)

Sample Number		Type of Sample ³	ATL Results		RTI Results		Certified Value	
ATL	RTI		THC ¹	Methane ¹	THC ¹	Methane ¹	THC ¹	Methane ¹
C086	--	Audit Gas - through tent	670	<1.8	--	--	693.7	0
C087	--	Audit Gas - through tent	200	15	--	--	168.7	0
C088	--	Audit Gas - direct	170	17	--	--	168.7	0
C089	--	Audit Gas - direct	590	<1.8	--	--	693.7	0
C096	C097	Duplicate - leaker	18000	<1.8	14500	--	--	--
P033	P034	Duplicate - leaker	190	<1.8	224	--	--	--
P034	P034 ²	Reanalysis by ATL	200	11/14	224	--	--	--
P034	P034 ²	Reanalysis by ATL (lab duplicate)	200	--	224	--	--	--
P042	P043	Audit Gas - through tent	200	5.3	155	--	168.7	0
P043	P043 ²	Reanalysis by ATL	180	--	155	--	168.7	0
P044	P045	Audit Gas - through tent	730	4.8	640	--	693.7	0
P045	P045 ²	Reanalysis by ATL	700	--	640	--	693.7	0
P046	P047	Audit Gas - direct	240	5.3	180	--	168.7	0
P047	P047 ²	Reanalysis by ATL	200	--	180	--	168.7	0

(continued)

TABLE 2-5. (continued)

Sample Number		Type of Sample ³	ATL Results		RTI Results		Certified Value	
ATL	RTI		THC ¹	Methane ¹	THC ¹	Methane ¹	THC ¹	Methane ¹
P047	P047 ²	Reanalysis by ATL (lab duplicate)	200	--	180	--	168.7	0
P054	P055	Duplicate - leaker	610	<1.9	430	--	--	--
P055	P055 ²	Reanalysis by ATL	530	--	430	--	--	--
P067	P068	Duplicate - leaker	910	730	990	--	--	--
P068	P068 ²	Reanalysis by ATL	990	--	990	--	--	--
P081	P082	Duplicate - leaker	2200	5600	2440	1820	--	--
P097	P098	Duplicate - leaker	25	22	16	6.7	--	--
P100	P101	Duplicate - leaker	140000	1800	136000	9.4	--	--
U082	U084	Duplicate - leaker	370	<1.9	450	--	--	--
U083	U084 ²	Duplicate - leaker (field duplicate)	400	<2.0	450	--	--	--
U084	U084 ²	Reanalysis by ATL	370	--	450	--	--	--
U098	U099	Duplicate - leaker	100	23	27.8	--	--	--
U099	U099 ²	Reanalysis by ATL	35	25	27.8	--	--	--
U111	U113	Duplicate - leaker	160	<2.0	145	--	--	--

(continued)

TABLE 2-5. (continued)

Sample Number		Type of Sample ³	ATL Results		RTI Results		Certified Value	
ATL	RTI		THC ¹	Methane ¹	THC ¹	Methane ¹	THC ¹	Methane ¹
U112	U113 ²	Duplicate - leaker (field duplicate)	150	<2.0	145	--	--	--
U113	U113 ²	Reanalysis by ATL	170	--	145	--	--	--
U125	U126	Duplicate - leaker	290	<2.0	363	--	--	--
U126	U126 ²	Reanalysis by ATL	460	--	363	--	--	--
U148	--	Audit Gas - direct	190	15	--	--	168.7	0
U149	--	Audit Gas - direct	720	<2.0	--	--	693.7	0
U150	--	Blank	<0.095	<1.9	--	--	--	--
U151	--	Audit Gas - through tent	170	14	--	--	168.7	0
U152	--	Audit Gas - through tent (field duplicate)	180	16	--	--	168.7	0
U153	--	Audit Gas - through tent	690	<1.9	--	--	693.7	0

¹ Units: THC reported as ppmv as propane; methane as ppmv as methane.

² These samples were only analyzed once by RTI, but correspond to two different ATL analyses.

³ "Reanalysis by ATL" indicates that sample was sent first to RTI for analysis, then returned to ATL for their analysis.

"Duplicate - leaker" indicates two field samples were taken from the same bag, and are sent to RTI, one to ATL.

"(field duplicate)" indicates two field samples were sent to ATL in separate containers.

"(lab duplicate)" indicates ATL performed duplicate analysis on the same field sample.

Comparison of the average results obtained by ATL for the PEA samples either through the bag or directly into the canister revealed ~~no statistically~~ significant difference. There was also no statistically significant difference between either set of data and the certified concentrations.

A low level of methane, 4 to 17 ppmv, was consistently reported by ATL for the low level standard. Since methane was not contained in this standard, the origin of the artifact is unknown. The cylinder contained isooctane, toluene, and cumene.

2.4 REVIEW OF WSPA DATA SET AND WSPA/RADIAN FINAL REPORT

The WSPA/Radian Draft Final Report was expected to be available by mid-August, 1993 for review as part of this QA report. It was not available by the end of August, and thus only the spreadsheet data set provided by Radian in May was included in the data audit. The data set provided by Radian was received on 5/12/93, and consists of a tabular summary of all samples analyzed, including QC and audit samples. The tabulation hides the identity of the individual plants where the data were taken, but the encoding was provided to RTI by Radian. Data were spot-checked against other data sources including those original logbooks and data forms shown in the Appendices. Transcription errors rates appeared to be low based on this review. The results are shown in a number of different systems of reporting units, however, and users of the data should be careful to use the applicable set. Perhaps most confusing is the use of units such as ppmv "as propane," ppmv "as methane," and ppmv "as carbon." Conversion from these units to mass rate units for emission factor reporting requires using the molecular weight for the correct calibration gas.

3.0 FINDINGS AND CORRECTIVE ACTIONS TAKEN

3.1 OVA SCREENING MEASUREMENTS

3.1.1 OVA Leakage and Maintenance Concerns

The probes and connectors for the OVA Model 108 used at both plants were found to be leaking. Leakage will change the overall dilution of the pollutant as well as the flow characteristics at the inlet. This could potentially result in erroneous screening values. Leak checks were not routinely conducted prior to the first audit. It was recommended that frequent leak checks be conducted as described in the video tape, "VOC Fugitive Emissions Procedures and Equipment," by E.J. Richards. This recommendation was communicated to the Radian field staff at the time of the audit. Satisfactory leak checks were being performed during the second audit. The effect of leaks on OVA screening data is not clear. Depending on whether the leakage was more during calibration or more during screening, the measurement could be either high or low; however, the use of the field check gas, a bag of 1000-ppm calibration gas, indicates that results were fairly consistent in spite of possible leaks.

3.1.2 Calibration Bag Purge Problem

During the first audit it was observed that the bags used by Radian to transfer audit gas from the pressurized gas cylinders for use in auditing the OVA and oxygen meter were not being thoroughly flushed. Any in-leak of air since the last use could lead to contamination of the contents. The result of this practice may have been seen in the oxygen calibrations, particularly in the Pacific Refinery results. There it was observed that when the oxygen meter was set at 21% ambient oxygen, a check using Radian's 5% oxygen cylinder routinely read high. At the second audit, Radian personnel were purging and refilling the bags once or twice, which seemed to improve the oxygen readings somewhat.

3.1.3 Change of Oxygen Meter Calibration Point

In a related change initiated by Radian, the oxygen meter adjustment point was changed from 21% (ambient air) to 5% (cylinder gas). The rationale for this change was that all critical measurements would be made below 5%, and therefore it was more important that the instrument be calibrated at this value. Air was used as a secondary check.

Because this is a change in procedure in which a possible source of bias was removed, RTI considered what impact it might have on data interpretation. The primary use for the oxygen data is for the correction of the tented component concentration back to 0% oxygen to compensate for in-leakage of air. It was determined that a 1% error in oxygen level (e.g., 6% instead of 5% O₂) would result in a 5% error in the hydrocarbon measurement (e.g., 105 ppm instead of 100 ppm). This is a relatively small component of the total errors of measurement, and should have only minor impact on results.

3.1.4 OVA Flow Rate Variability Measurement

At the first audit it was seen that gas flow rates into the probe inlet of the OVA were not being measured and recorded. When measured directly using either the Mini-Buck calibrator or the Hastings bubble flowmeter, the actual flows into the OVA probe appeared to be a factor of 2 or 3 lower than indicated by the OVA's built-in flow indicator. It was later determined this indicator was intended by the manufacturer only as an indication that flow was present.

The effect of sample flow rate on OVA response is a matter of debate. The impact of sample flow rate on individual samples will vary depending on the nature of the source; i.e., whether it is diffuse or concentrated. A diffuse source will be less sensitive to variations in sample flow rate than a point source. It was recommended that sample flow rate at the inlet of the OVA probe be measured and recorded during calibration and before and after each battery change. These data should be added to the data base for evaluation of equipment performance.

This was reported by RTI as an urgent recommendation, and was implemented by Radian starting in January 1993.

3.1.5 OVA Dilution Probe Problems

During the first audit it was seen that dilution factors obtained with the OVA dilution probe varied significantly between calibration gases at two different concentrations. This was observed at both plants. For example, at the Pacific Refinery on 12/8/92, the 1000-ppm calibration standard gave a dilution factor of 10:1, whereas the 35,000-ppm standard gave a dilution factor of 18.4:1. Based on limited observations during the two audits, inconsistent dilution factors appeared to be correlated with the probe leakage noted in section 3.1.1.

Uncertainty in the true dilution factor will directly impact the hydrocarbon concentration, which is calculated as OVA readout times the dilution factor. In the case of very high leakers (>10,000 ppm), where the dilution probe must be used to obtain the screening value, this is a critical measurement for development of the emission rate model.

The following recommendations were made regarding field operations:

- The OVA probe assembly should be free of leaks.
- Radian should investigate the origin of this variability and make any necessary procedural or equipment modifications to control it.
- Operators should be instructed to make sure that the dilution ratios obtained with different standards agree within a target goal, such as $\pm 20\%$. Corrective measures should be taken if the goal is not achieved.

The following additional suggestions for further investigation were also made:

- Leak-checking should be implemented immediately because RTI suspected that the dilution factor discrepancies may be related to probe leaks.

- Operation of the dilution probe should be investigated. Modified procedures should be in place by January.

All of the above recommendations and suggestions were being implemented at the time of the January audit. The dilution probe assembly had been slightly modified, and leak checks were a routine part of daily operations.

3.1.6 Project Data not Comparable to Data Taken with Probe Tip Standoff

During the second on-site audit, it was learned that it was common practice elsewhere to use a small standoff or spacer to prevent the OVA probe tip from touching the equipment being screened. Since use of a standoff was not part of Radian's procedure, the emission rate correlations may not be applicable to data taken with a standoff. Before data taken with and without the standoff can be compared, or the same correlation equations used, an intercomparison study should be conducted. It is recommended that Radian include a statement to this effect in its final report and wherever the correlation equations are reproduced.

3.2 TENTING AND SAMPLING

3.2.1 TEE Purging

During the December audit of the Southern California plant, it was noted that there was air in the TEE joint used to monitor pressure while the canister was being filled. The volume of the joint is small relative to the total canister volume, so dilution of the sample by air will probably make only a slightly low bias if the joint contains only ambient air. If a high concentration of hydrocarbon is present in the joint from a previous sample, however, carryover could result. It was recommended that the joint be cleared of gas prior to using it to fill a canister.

Radian developed a procedure of pulling air through the joint using the oxygen meter pump immediately prior to attaching it to the canister. They also

were concerned with carryover contamination from previous use with high leakers, and have also implemented a nitrogen flush for better removal of contamination.

3.2.2 Completeness of Tent Purging

With satisfactory taping of the Mylar tent material and sufficient blow through nitrogen flow, it should be possible to reduce oxygen in the tent to trace levels. Because of the difficulty of tenting some of the complex equipment and sealing all possible leaks, however, oxygen levels from 1 to 5 percent were frequently encountered. It was also noted that some of the Radian operators would proceed to take a canister sample as soon as the oxygen level went below about 3 percent, not waiting to see it stabilize at the lowest possible level. When the first set of QA data was returned for analysis, RTI employed the oxygen correction equation in Table 6-1 of the Radian QAPjP. It was found that the oxygen correction changed the VOC concentration in the right direction, but tended to overestimate the correction needed. Because of the relatively small contribution to total variability of the oxygen correction, however, this is not considered to be a major qualification on the data.

In summary, RTI's recommendations follow:

- Operators should attempt to stabilize the oxygen reading at a low level before taking the canister sample.
- During data analysis, the effect of the oxygen correction should be explored. Ideally, the magnitude of the correction should have an insignificant impact on the final correlation results.

3.2.3 Purge Gas Flow Rate Variability

Purified nitrogen is used to flush the tented volume. The flow rate must be known accurately because at equilibrium the concentration within the tent is a function of the leak rate and the nitrogen flow rate. The approximate flow rate is set using a rotameter and is measured more precisely using the Buck flow meter. The Buck meter was audited by RTI and found to be accurate and reproducible.

The rotameter, which was used only for indication, was not audited. Measurements of nitrogen flow taken before and after tenting indicated that stability of flow rate was good (see section 4.2.1.2).

3.3 LABORATORY PERFORMANCE - THC METHODS

3.3.1 Performance Evaluation Audit and Interlaboratory Comparisons

There were two methods used by the external auditors to assess the laboratory performance in terms of accuracy and precision: 1) performance evaluation audit samples made by an external supplier and 2) an interlaboratory comparison between Air Toxics, Limited (ATL) and RTI. Radian also had ATL analyze duplicates as part of WSPA's overall QC program.

The PEA gases were prepared by Scott Specialty Gases and analyzed by RTI. These standards are believed to be accurate within 5% of the certified value and stable over the timeframe of the project as verified by reanalysis by RTI at the conclusion of the field audits. RTI's independent analyses of samples, including both PEA samples and unknowns, should not be considered to be superior in accuracy to ATL's analyses, but provide another benchmark for estimating analytical error.

3.3.2 Audit of Data Quality

The audit of data quality consisted of reviewing the following:

- Laboratory raw data from ATL, including chromatograms, dilution data, and calibration. See Appendix E.
- Comparison of samples analyzed by both ATL and RTI, including both PEA standards and unknown samples from the same location by Radian.
- Examination of the Interim Final Report, a spreadsheet of Radian's data set for the program.

3.3.2.1 Laboratory Raw Data from Air Toxics Limited--

Data from samples P081, U148, C085, A049, and A095 were requested and reviewed by RTI. Findings included the following:

- The initial five point calibration curve for propane indicates curvature, even though the value for r-square is reported as 1.00 in the graph. See Appendix E.
- Chromatograms occasionally showed a rising baseline indicative of contamination. This was usually noted by the operator. Baseline correction assured that only well-defined peaks were counted.
- A095 had a Radian chain-of-custody sheet marked as "COC not signed as relinquished by the client." This was apparently an oversight on the part of the technicians sending the canister to ATL.

3.3.2.2 Interlaboratory Comparison--

A wide variety of different sample concentrations were used with the comparison of ATL's laboratory results and those of RTI. Table 2-5 provides a summary of interlaboratory results. Several instances of large differences, both high and low, were seen. Other analyses agreed well.

Several of the reported ATL analyses were done in duplicate, either at about the same time or after an interval of time. For example, samples A048 and A049 were field duplicates of a low level leaker. Sample A048 was analyzed by ATL. Sample A049 was analyzed first by RTI and later by ATL. The two ATL analyses for THC gave 30 and 37 ppm for samples A048 and A049, respectively. The RTI analysis for sample A049 gave a result of 16 ppm.

In another case, sample U098, one of two laboratory duplicates done by ATL, was close to the RTI value for a duplicate, while the other was high by a factor of about 3.

It is recommended that all of ATL's QC duplicate data be summarized and examined for Radian's final report.

3.4 LABORATORY PERFORMANCE - SPECIATION ANALYSES

Laboratory speciation analysis was discontinued in December 1992 because of poor comparability between the liquid samples and the canister (gas) samples. RTI QA samples sent to ATL as blind canisters were analyzed prior to discontinuation of the TO-3 and TO-14 speciation analyses. All compounds present in these samples were correctly identified by the laboratory.

4.0 DATA USABILITY

Data usability is defined as suitability of data for its intended purpose. For the critical measurements, this will be discussed in terms of accuracy and precision.

4.1 OVA SCREENING MEASUREMENTS

4.1.1 Accuracy

As shown in Table 2-2, the performance of the OVA was measured using certified methane in air standard gases from Scott Specialty Gases and a methane-ethane mixture in nitrogen from RTI which is certified under the program. Early in the audit proceedings, it was suspected that using the dilution probe induced variability into the OVA screening measurements. Table 4-1 compares the bias present in the OVA measurements using the dilution probe versus those made not using the probe. The data appear to indicate that bias increases by using the dilution probe. From the table, it may be seen that bias increases for six of the eight measurements when the dilution probe was used, although the direction of the bias was not predictable. Therefore those screening measurements performed below 10,000 ppmv without the dilution probe should be considered more accurate than those performed with the probe.

The statistics from the earlier audit at Arco and Pacific may also be reflective of leaking OVA instruments. From Table 4-1, it may be seen that bias whether with or without the dilution probe was, in general, higher at the first two refineries audited than at the second two refineries, where leak-checking procedures were in place. For nine measurements at the earlier audits, the standard deviation from the mean of the calculated bias was +35, while for 12 measurements at the later audits, it was +17. Average bias for the earlier audits was +10.2%, and at the later audits, -1.3%. Bias had, in general, decreased in the

TABLE 4-1. BIAS VERSUS CONCENTRATION WITH AND WITHOUT DILUTION PROBE

Date	Refinery	OVA Model 108 Serial Number	Methane in Air 1094 ppmv		Methane in Air 9034 ppmv		Methane/Ethane in Nitrogen 7850 ppmv	
			without probe	with probe	without probe	with probe	without probe	with probe
12/4/92	ARCO	20143	-2.3	+2.6	+2.8	+9.1	--	-60.7
12/7/92	Pacific	2254	+61.9	+51.5	--	+9.8	--	+17.5
1/5/93	Chevron	2254	-5.9	+16.1	-4.8	+9.7	--	+38.4
1/7/93	Ultramar ¹	A21664	-16.8	-27.6	-16.4	-0.5	--	-4.5
1/8/93	Ultramar ²	20143	+1.9	-4.8	--	--	--	--

1 Ultramar Refinery OVA Model 108, S/N A21664.

2 Radian OVA Model 108, S/N 20143.

second audits due presumably to the reduction of leaks. Figures 4-1 and 4-2 illustrate this point. Figure 4-1 shows dilution factors at ARCO and Pacific taken prior to the recommendation regarding leak-checking. Figure 4-2 shows the same information for the Chevron and Ultramar sites after leak-checking had been in practice. Clearly, there is less scatter with leak-checking than without. In both figures, dilution factors taken during a single calibration are connected.

The dilution probe must be used at concentrations above 10,000 ppmv since these values are out of the range of the OVA Model 108 instrument. The reliability of calculation of dilution factors for concentrations in this range is indicated in Table 4-2. Dilution factors differed depending upon the concentration of the calibration or audit gas. Factors calculated at concentrations of 1000 ppmv were always smaller than those calculated at 10,000 ppmv. Both Radian and the auditors observed this trend. Dilutions greater than 10,000 ppmv were measured only by Radian and these appeared to be probe-dependent. The probe in use in the refineries of northern California gave large dilution factors while the probe in use at the southern California refineries tended to peak at 10,000 ppmv (where the dilution was set at 10) and to become smaller at either higher or lower concentrations. This dependence of the dilution upon concentration and upon the particular probe in use renders all OVA screening measurements above 10,000 ppmv suspect.

The bias induced into the screening measurements because the OVAs' response factors were not determined for the actual organic species encountered is not known. Because the target analytes of the project as listed in the QA plan (total non-methane hydrocarbons, benzene, ethyl benzene, n-hexane, isopropyl benzene, propylene, toluene, 2,2,4-trimethyl pentane, and the xylenes) are expected to respond to an FID at approximately the same intensity as methane, the auditors believe that the lack of specific response factors is not a significant source of error compared to other sources and will not affect the usability of the data for this project.

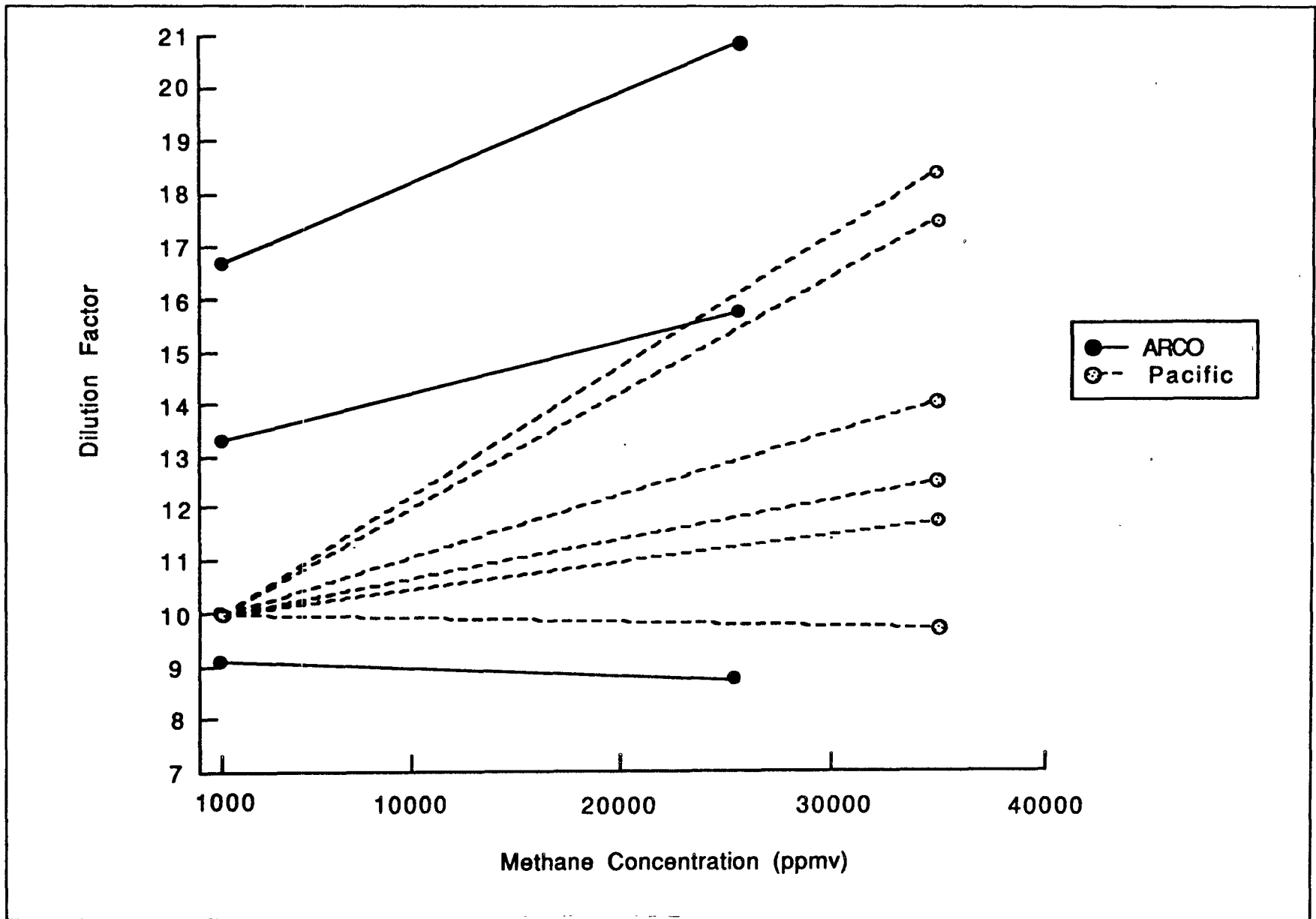


Figure 4-1. Concentration vs. dilution factors.

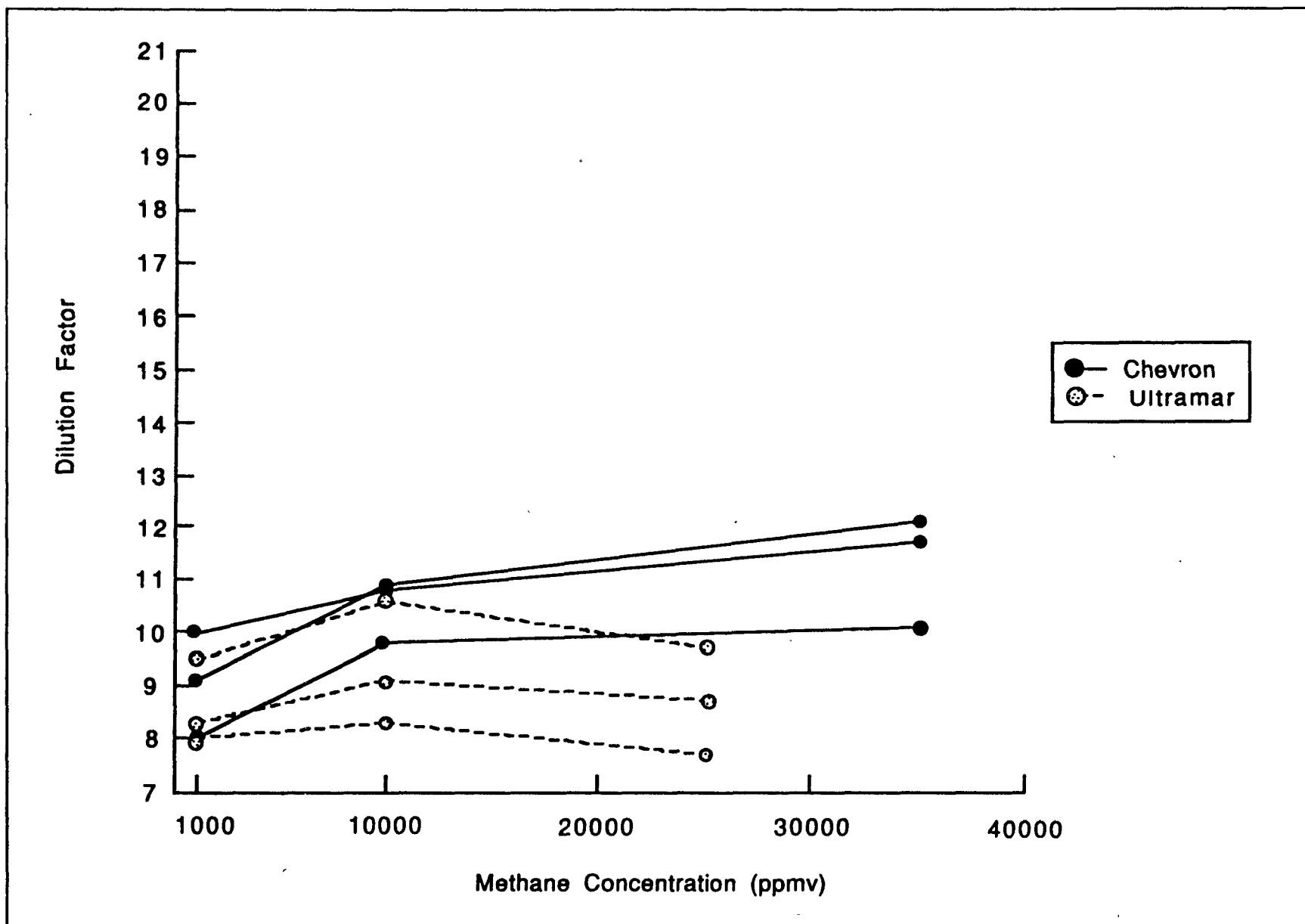


Figure 4-2. Concentration vs. dilution factors.

TABLE 4-2. RADIAN DILUTION FACTORS

Date	Refinery	OVA Model 108 Serial Number	Methane in Air Concentration (ppmv)			
			1000	10,000	25,100	35,000
12/3/92	ARCO ¹	20143	13.3		15.7	
12/4/92			16.7		20.9	
12/4/92			9.1		8.7	
12/7/92	Pacific ²	2254 (20162)	10			12.5
12/7/92			10			9.7
12/7/92			10			14
12/7/92			10			11.7
12/8/92			10			18.4
12/8/92			10			17.5
1/4/93	Chevron ²	2254	9.1	10.9		12.1
1/4/93			10.0	10.8		11.7
1/5/93			8.0	9.8		10.0
1/4/93	Ultramar ¹	20143	8.0	8.3	7.7	
1/5/93			8.3	9.1	8.7	
1/8/93			9.5	10.6	9.7	

1 ARCO and Ultramar are located in the Los Angeles area and were serviced by the same Radian crew and equipment.

2 Pacific and Chevron are located in the San Francisco area.

3 These dilution factors were measured after repositioning a leaky probe.

The bias induced by leaking OVA instruments early in the project may have been significant for some of the screening measurements before the first audit. As an illustration of the effect of air leakage, consider the following example. On day 2 of the audit at the ARCO Refinery, the project personnel were finding dilution factors of 15 and 21 for the 1000 ppmv and the 25,100 ppmv standards, respectively. The previous day, the factors had been 13 and 16. Prior to that time the factors had usually fallen in a range of 8-12 for the low dilution factor and 9-18 for the high dilution factor. On this day it was discovered that the probe was not fully seated and secured in the probe holding device of the OVA. After reinserting and tightening down the probe, the dilution factors reverted to 9 for both low and high concentrations. That the dilution factor could change from 21 to 9, a 233% difference, by correcting leakage illustrates the magnitude of the error that may have occurred during early screening measurements for this project. Early screening data should therefore be carefully examined for usability.

4.1.2 Precision

The OVA Model 108 instrument was carefully calibrated daily using five certified calibration standards. The calibration standards bracketed the screening measurements between 0 and 10,000 ppmv. All calibrations were tested for linearity by performing a regression and determining that the correlation coefficient was not less than 0.995. All calibrations met this test. The data from screening measurements in the range of 0 to 10,000 ppmv therefore should be reasonably precise and comparable on a day-to-day basis as determined from the auditors' examination of the daily calibration logs.

An examination of calibration data above 10,000 ppmv using the dilution probe shows that screening measurements above this value are expected to be more variable. This variability results not just from the error induced because of the dilution probe, but also the error induced because of leaking fittings. The use of the dilution probe appeared to magnify any problem due to leakage. This variability will affect the usability of the data.

Radian also very carefully checked calibration of the OVA instrument while in the field. Personnel carried a 1000-ppmv bag of methane with them during bagging (tenting) operations, and checked the calibration of the OVA after each bagging episode. If the measurement fell below 20% of the original measurement taken during the multipoint calibration, the instrument was returned to the shop to undergo a new complete multipoint calibration before further screening was performed. By this method, Radian personnel prevented the instrument from falling out of calibration by more than 20% during screening and bagging operations. The major factor affecting calibration was the OVA flow rate. As the battery providing power for the gas pump discharged, the OVA flow rate decreased, affecting calibration. Use of the check standard alerted field personnel to the battery status and prevented loss of calibration from becoming a factor in data usability.

4.2 MASS EMISSION MEASUREMENTS

4.2.1 Tenting and Sampling

4.2.1.1 Accuracy--

One condition that affected the accuracy of the tenting operations was whether steady-state conditions had been achieved before a test sample was withdrawn from the tent. The QAPjP and test plan attempted to ensure equilibrium by requiring that the oxygen level fall below the 5% level from the 21% level of ambient air. In practice, levels far below 5% were easily achieved within 5 minutes of initiating nitrogen flow through the tent. The field data sheets show a variety of oxygen readings both before and after sampling (see Table 4-3). This variation can be attributed to several causes. Some of the operators took readings until the oxygen levels fell below 5%, then proceeded with sampling. Others waited until the oxygen concentration stabilized at a low value before recording the first reading. Of the 25 bagging episodes observed by the auditors, oxygen concentrations fell to 0.6% or below before being recorded during

TABLE 4-3. OXYGEN TENT CONCENTRATIONS

Date	Sample	Before Sampling	After Sampling	Time Elapsed (min)
12/3/92	A019	4.4	0.3	12
12/3/92	A020	3.5	1.1	4
12/3/92	A021	0.3	0.15	6
12/3/92	A022	1.9	0.2	6
12/3/92	A023/A024	2.4	1.7	7
12/3/92	A025	0.2	0.2	5
12/3/92*	A026/A027	0.3	0.2	9
12/3/92*	A028/A029	0.15	0.1	8
12/7/92	P033/P034	1.4	0.2/0.4	9
12/7/92	P036	0.2	0.2	9
12/7/92	P037	0.2	0.2	10
12/7/92	P038	3.5	3.5	7
12/7/92	P039	0.2	0.2	6
12/8/92	P040	2.6	0.5	17
12/8/92	P041	2.5	4.0	10
12/8/92*	P042/P043	1.5	3.0	10
12/8/92*	P044/P045	2.0	3.5	9
1/4/93	C082	0.3	0.3	13
1/4/93	C083	0.2	0.2	10
1/4/93	C084	0.2	0.2	27
1/4/93*	C085/C086	0.2	0.2	33
1/5/93*	C087	0.3	0.6	12
1/7/93	U150	0.6	0.2	8
1/7/93*	U151/U152	2.4	0.2	13
1/7/93*	U153	1.6	0.2	8

* These were QA samples supplied by RTI.

13 of the episodes. Twelve of the initial oxygen measurements ranged from 1.4 to 4.4%. Final oxygen measurements were taken in a range from 5 minutes to 33 minutes later, with most readings being taken in the 7-to-13-minute range. At that time, oxygen levels had fallen to 0.6% or below for 19 of the 25 tenting episodes. The other six finished in an oxygen range of 1.1 to 3.5%. It is obvious from these figures that equilibrium had not been fully established for the tents whose oxygen concentrations continued to fall, and that leaks may have been a concern for the six episodes in which the oxygen never fell below 1%.

Through the use of QA samples, the auditors had an opportunity to observe the effect at equilibrium. Two QA samples were collected at ARCO and analyzed by RTI's laboratory. The oxygen concentration was never above 0.3% at any time during the collection of these samples. RTI's analyses showed less than 5% bias relative to Scott's certified analyses. QA samples were also collected at the Pacific Refinery. During these sampling episodes the oxygen concentration rose for both. Sample P043 began at 1.5% oxygen and climbed to 3.0% in the 10 minutes during which the sample was collected. P045 began at 2.0% oxygen and climbed to 3.5% during the 9 minutes between readings. Analysis of these samples showed a negative bias of less than 10%. When mathematically corrected for oxygen concentration, the bias became positive, but still less than 10%. Therefore, it appears to matter little to the usability of the data that often the oxygen was not fully depleted at the time sampling was initiated as long as it was below the 5% level. If necessary, the concentrations can be corrected to reflect the dilution indicated by the final oxygen reading.

4.2.1.2 Precision--

Another condition which may have affected the concentration of the collected samples was the stability of the flow of nitrogen through the tents. Flow rates varied from less than 1 L/min for small bags to more than 8 L/min for large bags. The flow rate was measured before the outlet of the nitrogen tank was attached to the tent, and again after the outlet was removed from the tent. Of the

17 sampling episodes observed by the auditors in which nitrogen flowed through the tent, 16 pairs of flows recorded by the operator were replicated within 5% of the beginning flow rate (see Table 4-4). The 17th episode was missing an observation because of an operational problem. From this observation, it appears that stability of nitrogen flow rate during sampling is not a large factor in the variability of results.

There has been some concern on this project that the different flow rates of the nitrogen through the bags might contribute to the variability of results. In principle, different nitrogen flow rates will not significantly contribute to variability of results provided that they exceed the intake flow of the OVA or the intake flow into the sampling canisters. Flow measurements at the OVA inlet were initiated after the first audit and ranged from about 0.8 to 1.0 L/min. The auditors observed the 1-L canisters were filled during time spans of 85 seconds to 180 seconds, indicating intake flow rates into the canisters of about 0.7 L/min or less. Therefore intake flows into the OVAs or into the canisters are not expected to affect data usability on this project. Radian has undertaken a study of the effects of N₂ flow rate, but this information was not available.

4.2.2 THC and Methane Analysis

Based on results of the PEAs sent to ATL, the sampling and analysis procedures are expected to contribute a relatively small percentage of the total error, which are likely to be dominated by intrinsic errors in the screening measurement method.

4.3 SPECIATION ANALYSES

The intercomparison between gas-phase and liquid-phase samples submitted for speciation was halted by WSPA and Radian approximately midway into the program. The laboratory correctly identified all six of the unknown compounds using Method TO-14, and no further comment can be made regarding the quality or usability of these data based on the QA information generated by this program.

TABLE 4-4. NITROGEN FLOW RATES

Date	Sample	Before Sampling (mL/min)	After Sampling (mL/min)	Time Elapsed (min)	% Change
12/3/92	A019	4001	3899	22	-2.5
12/3/92	A020	3896	3826	16	-1.8
12/3/92	A021	858	842	11	-1.9
12/3/92	A022	1878	1852	12	-1.4
12/3/92	A023/A024	1900	1891	14	-0.5
12/3/92	A025	1940	1959	9	+0.7
12/3/92	A026/A027 ¹	1955	1989	17	+1.7
12/3/92	A028/A029 ¹	2014	2025	22	+0.5
12/7/92	P033/P034	4670	4828	58	+3.4
12/7/92	P036	4309	4359	26	+1.2
12/7/92	P037	1463 ²	4095	14	--
12/7/92	P038	8658	8658	29	0
12/7/92	P039	1839	1835	9	-0.2
12/8/92	P040	2466	2494	20	+1.1
12/8/92	P041	2263	2236	21	-1.2
12/8/92	P042/P043 ¹	2232	2308	14	+3.4
12/8/92	P044/P045 ¹	2217	2241	15	+1.1
1/4/93	C082	1894	1886	25	-0.4
1/4/93	C083	2113	2110	19	-0.1
1/4/93	C084	1882	1805	45	-4.1
1/4/93	C085/C086 ¹	1678	1354	46	-19.3
1/5/93	C087 ¹	3424	3600	27	+5.1
1/7/93	U150	1578	1558	14	-1.3
1/7/93	U151/U152 ¹	1361	1486	17	+9.2
1/7/93	U153 ¹	1240	1156	14	-6.8

- 1 These were the pre-mixed QA samples supplied by RTI. Flow rates for these samples did not affect canister concentration.
- 2 This value is believed to be a recording error.

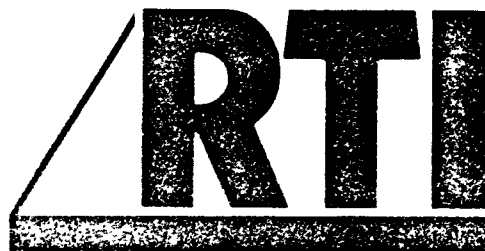
5.0 BACKGROUND INFORMATION

In preparing for the audits, background information was obtained from the following documents:

- Radian Corporation, Inc. Quality Assurance Project Plan and Test Plan for the WSPA/API Refinery Fugitive Emissions Study, Phase III. Prepared for Western States Petroleum Association, September 24, 1992.
- Richards, E. J. "VOC Fugitive Emissions Procedures and Equipment" (video).
- Instruction Book 3433 Century® OVA 108 Portable Organic Vapor Analyzer. The Foxboro Company.
- Method T03: Method for the Determination of Volatile Organic Compounds in Ambient Air Using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection.
- Method T014: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis.
- ASTM Method D3416: Standard Test Method for Total Hydrocarbons, Methane, and Carbon Monoxide in the Atmosphere (Gas Chromatographic Method).
- Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. 40 CFR, Pt. 60, App. A.
- U.S. Environmental Protection Agency. "Updated Equipment Leaks Protocol Document." September 30, 1992 (draft) (includes Appendix describing development of average emission factors).
- "Suggested Guidelines for a QA/QC Protocol."
- Method 21: Determination of Volatile Organic Compound Leaks. 40 CFR, Pt. 60, App. A (7/1/91 Edition).

APPENDIX A

REVIEW OF RADIAN QAPjP



RESEARCH TRIANGLE INSTITUTE

RTI 5500-042/01/01F

December 11, 1992

REVIEW COMMENTS ON RADIAN CORPORATION'S
QUALITY ASSURANCE PROJECT AND TEST PLAN
FOR
WSPA/API REFINERY FUGITIVE EMISSIONS STUDY, PHASE III

Prepared for:
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Review of QAPjP and Test Plan

WSPA/API REFINERY FUGITIVE EMISSIONS STUDY, PHASE III

Part 1

The following comments are offered in the interest of improving the quality of the data on this project.

<u>Sect., Paragraph, Page</u>	<u>Comments</u>
3.0, 3, 3-1	The discussion of accuracy is incomplete. It is unclear how accuracy is to be assessed for EPA Method 18, ASTM D 3146, and EPA Methods TO3 and TO14. Specific check standards, NIST standards, or spikes have not been described.
Table 4-1, p. 4-2	Under the new Hazardous Organic NESHA (HON) rules, the analyzer response factor must be less than 3, not less than 10 as stated.
4.1, 7, 4-3	Possible causes for poor OVA instrument performance have not been included.
4.2, 2, 4-3	The procedure for measuring oxygen concentration inside the bag has not been described.
4.2, 3, 4-5	The maximum holding time of the samples has not been defined. The time allowed from collection to analysis has not been defined.
4.2, 5, 4-5	The mass of the liquid may be better measured by collection in a weighed graduated cylinder, then weighing the filled container at the end of the collection time. By this method, opportunity for error is reduced. The suggested procedure requires volume, density, and time measurements: three opportunities for error.

Sect., Paragraph, Page

Comments

4.2, 7, 4-7

Duplicates are mentioned for precision assessment, but no spikes for accuracy assessment. Except for the bagging accuracy check (Table 4-3, step 1), there is no mention of an accuracy check of the field gas collection and subsequent laboratory analysis activities. Spikes or independent performance evaluation samples injected into a bagged non-leaking component would correct this omission.

Table 4-4, p. 4-9

The equations to be tested and the sets of data to be correlated have not been included.

4.2, 12, 4-10

The term "default zero" is introduced without explanation. Calculation of the initial default zero has not been explained.

4.2, 16, 4-10

Adding 15 nonzero, nonpegged component sources to 10 zero sources and 10 pegged sources adds to 35, not 45. Multiplying by the 9 categories of page 4-7 gives 315 samples plus blanks and duplicates to be collected. Because Radian proposes to collect a total of 525 samples, there should be plenty of opportunity to spike samples, to collect duplicates, and to provide QA samples for independent analysis. The QA samples that will be collected have not been described.

4.3, 1, 4-11

OVA measurement criteria by which a bag will be declared a default zero bag have not been described.

4.3, 7, 4-15

Laboratory duplicates are mentioned, but laboratory spikes are not. The procedure to evaluate accuracy in the laboratory has not been described.

4.4, 2, 4-16

It has not been explained whether or not nalgene bottles have been determined to adequately contain hydrocarbon compounds.

Sect., Paragraph, Page

Comments

4.4, 4, 4-16

This section refers to "preparing a gas sample of the liquid sample." It has not been explained how this will be performed. It has also not been explained if all compounds of the liquid process stream will be accounted for, and in the proportions as found in the process stream.

5.1, 3, 5-1

The OVAs will be calibrated with methane. The GCs will be calibrated with propane (section 4.3, paragraph 2, p. 4-13). Calibration with propane is contrary to the stated method ASTM D 3416 which calls for methane calibration. The output will be ppbv (section 4.3, paragraph 3, p. 4-13). If different standards are used, outputs will not be directly comparable.

Table 6-1, p. 6-3

The discussion on the dilution correction factor for the hydrocarbon leak into the tent (1 - tent O₂%/21%) makes certain assumptions. The factor as given assumes that there is essentially no concentration of the hydrocarbon in the tent at the time nitrogen flow is started.

In the case of a heavily leaking component, however, the initial concentration of the hydrocarbon, C₀, at the time the nitrogen flow is started, (t=t₀), could be significant.

If C₀ is significant, the concentration of the hydrocarbon at equilibrium (C_E) is as follows:

$$C_E = (C_t - C_0) / (1 - \text{tent O}_2\%/21\%) + C_0$$

where C_t is the concentration of the hydrocarbon at time, t.

As C₀ → 0, the correction reduces to that given in Table 6-1.

Sect., Paragraph, Page

Comments

	<p>The protocol for determining when equilibrium has occurred for heavy leakers, therefore, should include some discussion of the leveling out of the C_i before it can be decided that equilibrium has been established. For very small leakers, C_0 will not be a factor.</p>
6.1.2, 4, 6-2	<p>If the hydrocarbon stream contains oxygenated compounds, there will be significant problems in using Method TO3 for analysis due to often incomplete desorption from the cryogenic trap. Performance evaluation samples containing oxygenated compounds will be needed.</p>
6.1.2, 12, 6-6	<p>It has not been explained how accuracy estimates will be calculated.</p>
6.1.3, 1, 6-6	<p>Considering how the liquids are to be analyzed, the question of whether the concentration of compound fractions in the bulk stream is the measured entity should be addressed.</p>
6.2.3, 1, 6-9	<p>It is not explained how accuracy is measured and calculated.</p>
Table 7-2, p. 7-3	<p>Under accuracy, "laboratory and trip spikes" are mentioned, but it is not described how many of these there are and what kind will there be.</p>
7.3, 2, 7-4	<p>The laboratory QC check standards should be distinguished from calibration standards. Also the spikes mentioned in Table 7-2 should be part of this discussion.</p>

Part 2

The purpose of the QAPjP and Test Plan is to enable the reader to clearly understand the project. If the writer acted upon the following comments, this document would be clearer and more understandable.

<u>Sect., Paragraph, Page</u>	<u>Comments</u>
3.0, 2, 3-1	"Twenty-five bagging duplicates will be taken in the field." Since a bagging duplicate is not described until section 4.2, paragraph 7, a reference here to that section would be helpful.
Table 4-1, p. 4-2	A leak definition value should be discussed here. The concentration that will be defined as a leak is not discussed in the text until section 6.1.2, paragraph 9, p. 6-5.
Table 4-3, p. 4-6	<p>Step 1. The accuracy test is not described until section 7. A reference to section 7 would be helpful here.</p> <p>Step 5. It is not clear if the N₂ flow is measured before it enters the tent or at the tent exit. Perhaps both should be measured for added assurance.</p> <p>Step 6. If the N₂ flow is measured as suggested, steps 5 and 6 should be reversed.</p> <p>Step 7. It is not clear how O₂ concentration in the tent is measured.</p> <p>Step 8. "There is no collection at this point--just measurement with the OVA." This statement should be rewritten.</p> <p>Step 9. The reader does not know how bag temperature is to be measured (a thermocouple) until section 5.4. A reference to this section would be useful here.</p>

Sect., Paragraph, Page

Comments

	Step 10. A more correct statement would be, "Collect canister sample, and send to laboratory for analysis."
	Step 11. This step would be a repeat of step 5.
	Step 15. This step should refer to the <u>process</u> stream.
4.2, 6, 4-7	Nine categories of leaking components are listed. The QAPjP assumes there are 10 in subsequent calculations (see page 4-10).
Table 4-4, p. 4-9	Some changes in the table, "Draft Bagging Matrix," would make the design of the bagging experiment clearer.
	It should be stated that each column represents one step in a plan to collect enough data to prove or disprove correlation equations.
	The equations to be tested should be given, or a reference where the equations may be found should be stated.
	The sets of data to be correlated should be stated. (Some of this discussion occurs later in section 6.1.2, paragraphs 7 and 8, page 6-5.)
4.2, 14, 4-10	The term "current U.S. EPA-published equation" is introduced without explanation or reference. If the equation is published, a reference should be given.
4.3, 2, 4-13	Beginning with this paragraph, the types of analysis are discussed. A table or list of the samples and what analyses they are to undergo would clarify the analysis scheme.
4.3, 5, 4-15	Method TO14 is not in Appendix A.
4.4, 1, 4-16	The reference to Table 4-4 is incorrect. It should be Table 4-5.

Sect., Paragraph, Page

Comments

6.1.2, 9, 6-5

To show the relationship between "default zero emission factor", "default zero emission rate", and "default zero screening value", an example would be illustrative.

6.1.2, 11, 6-6

"Inaccessible components will be assigned screening values determined from the distribution of screening values of a sample of inaccessible components." If the components are inaccessible, screening values are not available, by definition.

The meaning of "uncontrolled components" is unclear in this paragraph.

Part 3

Comparison of the Sampling and Data Reduction Procedures in Three Documents

The following three documents were compared to identify differences in sampling and data reduction procedures:

1. Radian Corporation's Quality Assurance and Test Plan for WSPA/API Refinery Fugitive Emissions Study, Phase III
2. Suggested Guidelines for a QA/QC Protocol to Determine Volatile Organic Compound Emission Rates from Equipment Components (QA/QC Guidelines for Screening and Bagging)
3. Protocols for Emission Estimates of Equipment Leaks of VOC and VHAP, OAQPS, October 1992 (draft).

Sampling Differences

1. Sample Containers

For this study, Radian will be collecting the bagging samples in polished summa canisters. Document 2 lists no collection containers and document 3 lists Mylar, Teflon, and Tedlar bags as suitable containers.

2. Recording of Field Data

Documents 2 and 3 give standard forms for data collection. The Radian document does not.

3. Response Factors

Radian will determine the response factors for the OVA, but does not indicate that they will measure the response factors for individual organic compounds. Document 2 calls for response factors to be measured in the laboratory. Document 3 lists response factors in Appendix C.

4. Calibration of the OVA

Radian will calibrate the OVA with 5 calibration standards in a range of 0 to 10,000 ppm of methane in air. Documents 2 and 3 call for 4 standards from 0 to 1000 ppm of an "organic" in air.

5. Frequency of Zero and Span Checks

Radian will perform these checks "daily." The protocols of documents 2 and 3 call for checks twice a day.

6. Total Measurement Accuracy for Evaluation of Combined Sampling and Analysis

Radian will conduct one accuracy bagging check per site. Acceptance criteria will be $\pm 50\%$. The protocols of documents 2 and 3 call for accuracy checks in which a leak rate is calculated. The criterion for acceptance is within $\pm 20\%$ of the true value.

7. Blind Standards for Analytical Accuracy

The Radian QAPjP and Test Plan does not mention blind standards. Documents 2 and 3 both call for blind standards as a means of assessing analytical accuracy. They call for a frequency of twice weekly with an acceptance criterion of within $\pm 25\%$ of the true value.

8. Purge Gas Analysis

Radian does not mention analyzing the purge gas, but the protocols specify this analysis.

9. OVA Flameout

There is a protocol for restarting the OVA after a flameout in the protocol documents. Radian does not mention it.

10. QC Procedures for Bagging

A table of QC procedures for bagging is listed in the protocol documents. Radian does not list these procedures and does not mention the following procedures listed by the protocols:

a. A background bag is collected with every bagged equipment sample bag. Radian is planning to collect three "blanks" per 97 equipment component bagged samples.

b. Specific directions are given for where the dilution gas is to be directed (directly onto the leak interface). Radian does not specify the location of the dilution gas line.

Data Reduction Procedure Differences

1. Calculating Emission Rates

In RTI's evaluation, the equations included in Table 6-1 of Radian's QAPjP will provide acceptable data although they differ from those equations pertaining to measurements made on a volume or mole-fraction basis (in Table 4-2 and Appendix B of document 3). The emission rate equation differences follow:

a. "MW" in Radian's equation refers to the molecular weight of the diluent stream, whereas "MW" in the protocol equation refers to the cumulative molecular weights of the VOC gases in the stream. Radian's assumption of an MW of approximately 28 for purge gas in the equation is satisfactory because the presence of small amounts of hydrocarbon, oxygen, and any other trace gas will not change the average molecular weight a significant amount.

b. "GC" in Radian's equation refers to the concentration of the VOCs in the stream in ppm by weight, whereas "GC" in the protocol equation refers to the concentration of the VOCs in the stream by volume. If FID response is reported in ppmw, a manner which takes into account the mass of the calibration gas being used, instead of ppmv which may not take the calibration gas into account, there is less likelihood of error from one instrument to the next when different calibration gases are used.

c. Radian's equation adds another factor, RF. This takes into account the response factor of the leaking VOC relative to the response factor of the calibration gas.

2. Appendix B

The mass emission rate equation of Appendix B of document 3 is different from the mass emission rate equation of the Radian QAPjP as described above under the topic, "Calculating Emission Rates."

Radian intends to reduce the data by preparing log-log plots of emission rates versus screening values, and develop correlation equations from these plots. This is the same procedure as discussed in detail in Appendix B.

Radian intends to calculate the default zero emission factor as the mean from a log normal distribution. The procedure is presented in greater detail in Appendix B which includes a scale bias correction factor.

Radian intends to use discreet screening values for emission factor development of components leaking in excess of 100,000 ppmv (pegged values), but does not specify the method. Appendix B uses averages to substitute for the pegged screening readings.

APPENDIX B

TECHNICAL SYSTEMS AUDITS:

ARCO REFINERY: 12/3-4/92

PACIFIC REFINERY: 12/7-8/93

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: ARCO Refinery, Carson, CA

Date 12/4/92

Controller: Mini-Buck Calibrator

S/N: M-2312, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	<u>1000</u>	<u>0.790</u>	<u>1270.7</u>	<u>1254.0</u>
2	<u>1000</u>	<u>0.780</u>	<u>1282.1</u>	<u>1258.0</u>
3	<u> </u>	<u> </u>	<u> </u>	<u> </u>
4	<u> </u>	<u> </u>	<u> </u>	<u> </u>
			Mean: <u>1276.4</u>	Mean: <u>1256.0</u>
			Std. Dev.: <u>8.0</u>	Std. Dev.: <u>2.8</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: ARCO Refinery, Carson, CA

Date 12/4/92

Controller: Mini-Buck Calibrator

S/N: M-2312, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	1000	0.310	3208.2	3138.0
2	1000	0.310	3179.6	3146.0
3				
4				
			Mean: <u>3193.9</u>	Mean: <u>3142.0</u>
			Std. Dev.: <u>20.2</u>	Std. Dev.: <u>5.7</u>

AUDIT CHECKLIST

Location: ARCO Refinery
 Carson, CA
 Organization Audited: Radian Corporation
 Dates of Audit: 12/3-4/92
 RTI Auditors: J. Flanagan, L. Pearce
 Audited's Personnel: J. Davis 12/3-4/92
 J. Colin 12/3/92
 Other Personnel: Miriam Lev-On, ARCO 12/3/92

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
A. OVA CALIBRATION, CHECKOUT, AND MAINTENANCE				
Are initial instrument checks performed prior to OVA use such as the following:				
A. Enough hydrogen for day's work?	✓			
B. Battery charged?	✓			
C. Flame arrestor in place?	✓			
D. Amplifier warmed up at least ten minutes?	✓			
E. Amplifier electronic linearity checked in both high and low concentration regions?	✓			
F. Leaks checked of the sample gas handling system such as probe fitting, sample line, and sample line fitting?		✓		Not routinely checked
G. Checked for prefilter and probe cleanliness?	✓			
H. Is the gas sample flow rate checked? If so, how?		✓		Not routinely measured

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument calibrated daily prior to sampling? After sampling?	✓	✓		
Is the probe tip covered with teflon tubing?	*			Tygon Tubing is used
How often are multipoint linearity checks performed?			✓	Daily
Are the Tedlar bags purged with calibration gas 2 or 3 times before filling?		✓		O ₂ calibration reads slightly high.
Are the regulators on the calibration gas cylinders purged before use?				No opportunity to observe.
Do the linear and measuring ranges include the leak definition value?	*			Measurement/calibration range includes leak definition values for study.
Are instrument accuracy checks performed? How frequently? What reference standards are used?	*			Other than calibration standards, there are no independent gas standards. Instrument drift is checked before each measurement using one calibration gas level.
Are precision checks performed prior to testing on a daily basis?		*		Only calibration standards are used.
B. SCREENING MEASUREMENTS				
Are the instrument response factors for each of the VOCs to be measured less than 3? Record, if available. How was response factor derived? (which compound?)				Unable to verify. Response factors are not being determined by field personnel.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument response time equal to or less than 30 seconds? When is the response time checked?	*			Response to calibration gases appeared to be very rapid (< 5 sec).
How is the calibration precision determined?				Linear correlation coefficient, R, must be < 0.995.
Is the calibration precision equal to or less than 10 percent of the calibration gas value?		*		Because R is calculated on a linear rather than a log-log scale, relative error at lower concentration levels can exceed $\pm 10\%$, even if R is acceptable.
Is the instrument intrinsically safe?	✓			
Are duplicate screening measurements taken? How many?	✓			Before and after bagging.
How often are drift and blank checks performed?				Before each leaking component is checked.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
<p>Observe the operator screen at least 3 different types of components: valve, flange, Note proper technique in following areas:</p> <ul style="list-style-type: none"> - Identifying the area where leaks should be screened ✓ - Proper distance of probe from component ____ (how far) * - Proper angle of probe with leaking source (diagram) * - Time sufficient to take a stable reading ____ (how long) ✓ - Reading replicated? How long between readings? ____ Any difference in location or angle between readings? Describe. 				<p>Probe placed as close as possible to equipment.</p> <p>Angle usually 90° from surface, except when constrained by equipment.</p> <p>Readings are made at 90° intervals around valve insertions. Highest concentration is set as "north." Readings replicated before and after tenting.</p>
C. BAGGING				
Sketch the bagging accuracy check set up.				
Are duplicate bagging measurements routinely taken? How many? What frequency?	✓			One sample in 20 is duplicated for ATL.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Are ambient and internal bag temperatures recorded for each bagged component?	✓			
Describe bagging accuracy: What is the concentration of the accuracy standard? Which component was chosen as the "dummy"? What is the induced leak rate?				Radian performs an initial "accuracy" check at each new site. Water valve is used for dummy. Data not available for this check.
When is the nitrogen flow rate measured for bagged components?				Before and after bagging.
How is the oxygen concentration inside the bag measured? What criteria are used to verify that the nitrogen purging is complete and effective?				Portable O ₂ meter. O ₂ measurement < 5%. Usually < 1%.
What is the time from collection of samples to analysis? - Holding time until shipped - Holding time in laboratory (if known)				Holding for shipment seldom more than 3 days. Check with laboratory
Is the OVA used to establish purge gas equilibrium?	✓			Yes. Using dilution probe to supply oxygen value is recorded.
Are there any obvious opportunities for leakage from or into the bag?	✓			Very difficult to get a perfect seal with a stiff MYLAR and duct tape.
Is the N ₂ flow rate sufficient to maintain positive pressure on the bag, even while sample is being withdrawn?	*			Usually; however, operator did not know the OVA flow rate.
Are sample lines to the canister purged before filling?	✓			

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the tee purged before filling the canister?		✓		
Is canister pressure monitored? Flow rate?	✓	✓		Flow is controlled by controlling the rate of pressure rise.
Is canister hookup (valves, unions, fittings, tubing, etc.) checked for leaks prior to sampling?		✓		Difficult to test under vacuum.

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Pacific Refinery, Hercules, CA Date 12/7/92

Controller: Mini-Buck Calibrator

S/N: M-4570B, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	1000	0.870	1149.4	1075.0
2	1000	0.900	1111.1	1083.0
3	1000	0.900	1111.1	1085.0
4	1000	0.910	1098.9	1081.0
			Mean: <u>1117.6</u>	Mean: <u>1081.0</u>
			Std. Dev.: <u>21.9</u>	Std. Dev.: <u>4.3</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Pacific Refinery, Hercules, CA Date 12/7/92

Controller: Mini-Buck Calibrator

S/N: M-4570B, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	1000	0.400	2500.0	2432.0
2	1000	0.405	2469.1	2396.0
3	1000	0.420	2380.9	2398.0
4	1000	0.403	2481.4	2399.0
			Mean: <u>2457.8</u>	Mean: <u>2406.2</u>
			Std. Dev.: <u>52.8</u>	Std. Dev.: <u>17.2</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Pacific Refinery, Hercules, CA Date 12/7/92

Controller: Mini-Buck Calibrator

S/N: M-4570B, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	1000	0.230	4347.8	4290.0
2	1000	0.225	4444.4	4169.0
3	1000	0.230	4347.8	4256.0
4	1000	0.230	4347.8	4223.0
			Mean: <u>4371.9</u>	Mean: <u>4234.5</u>
			Std. Dev.: <u>48.3</u>	Std. Dev.: <u>51.5</u>

AUDIT CHECKLIST

Location: Pacific Refinery
Hercules, CA
Organization Audited: Radian Corporation
Dates of Audit: 12/7-8/92
RTI Auditors: J. Flanagan, L. Pearce
Audited's Personnel: R. Ricks12/7/92
D. Ranham12/7-8/92
Other Personnel: R.Hughes12/8/92

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
A. OVA CALIBRATION, CHECKOUT, AND MAINTENANCE				
Are initial instrument checks performed prior to OVA use such as the following:				
A. Enough hydrogen for day's work?	✓			
B. Battery charged?	✓			
C. Flame arrestor in place?	✓			
D. Amplifier warmed up at least ten minutes?	✓			
E. Amplifier electronic linearity checked in both high and low concentration regions?	✓			
F. Leaks checked of the sample gas handling system such as probe fitting, sample line, and sample line fitting?		✓		Not routinely checked
G. Checked for prefilter and probe cleanliness?		✓		
H. Is the gas sample flow rate checked? If so, how?		✓		Not routinely measured

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument calibrated daily prior to sampling? After sampling?	✓	✓		
Is the probe tip covered with teflon tubing?	*			Tygon Tubing is used
How often are multipoint linearity checks performed?			✓	Daily
Are the Tedlar bags purged with calibration gas 2 or 3 times before filling?		✓		O ₂ calibration gas reads high.
Are the regulators on the calibration gas cylinders purged before use?		✓		
Do the linear and measuring ranges include the leak definition value?	*			Measurement/calibration range includes leak definition values for study.
Are instrument accuracy checks performed? How frequently? What reference standards are used?	✓			1000 ppm QC check is performed prior to each measurement for instrument drift. Only calibration gas standards are used.
Are precision checks performed prior to testing on a daily basis?		*		Only calibration standards are used.
B. SCREENING MEASUREMENTS				
Are the instrument response factors for each of the VOCs to be measured less than 3? Record, if available. How was response factor derived? (which compound?)			✓	Response factors are not being determined by field personnel.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument response time equal to or less than 30 seconds? When is the response time checked?	✓	✓		LL takes ~ 10 sec to respond. For HL, needle responds slowly. No response time checked.
How is the calibration precision determined?				Linear correlation coefficient, R, must be < 0.995.
Is the calibration precision equal to or less than 10 percent of the calibration gas value?		✓		Because R is calculated on a linear rather than a log-log scale, relative error at lower concentration levels can exceed $\pm 10\%$, even if R is acceptable.
Is the instrument intrinsically safe?	✓			
Are duplicate screening measurements taken? How many?	✓			Before and after bagging.
How often are drift and blank checks performed?				Before each leaking component is checked.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
<p>Observe the operator screen at least 3 different types of components: valve, flange, Note proper technique in following areas:</p> <ul style="list-style-type: none"> - Identifying the area where leaks should be screened ✓ - Proper distance of probe from component ____ (how far) ✓ - Proper angle of probe with leaking source (diagram) * - Time sufficient to take a stable reading ____ (how long) ✓ - Reading replicated? How long between readings? ____ ✓ - Any difference in location or angle between readings? Describe. ✓ 				<p>Probe placed as close as possible to equipment. Angle usually 90° from surface, except when constrained by equipment. ~ 10 sec LL. Longer for HL. Readings are taken before and after tenting. Readings are made at 90° intervals around valve insertions. Highest concentration is set as "north."</p>
C. BAGGING				
Sketch the bagging accuracy check set up.				
<p>Are duplicate bagging measurements routinely taken? How many? What frequency?</p>	✓			<p>One sample in 20 is duplicated for ATL.</p>

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Are ambient and internal bag temperatures recorded for each bagged component?	✓			
Describe bagging accuracy: What is the concentration of the accuracy standard? Which component was chosen as the "dummy"? What is the induced leak rate?				Radian performs an initial "accuracy" check at each new site. Water valve is used for dummy. Data not available for this check.
When is the nitrogen flow rate measured for bagged components?			✓	Before and after bagging.
How is the oxygen concentration inside the bag measured? What criteria are used to verify that the nitrogen purging is complete and effective?			✓	Portable O ₂ analyzer. O ₂ measurement < 5%. Usually < 1%.
What is the time from collection of samples to analysis? - Holding time until shipped - Holding time in laboratory (if known)			✓	One week. Longest st site is 2 days. Check with laboratory
Is the OVA used to establish purge gas equilibrium?	✓			Yes. Checked alternately with O ₂ meter. Operator watches for stability.
Are there any obvious opportunities for leakage from or into the bag?	✓			Very difficult to get a perfect seal with a stiff MYLAR tenting material.
Is the N ₂ flow rate sufficient to maintain positive pressure on the bag, even while sample is being withdrawn?	*			Usually; however, operator did not know the OVA flow rate.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Are sample lines to the canister purged before filling?	✓			
Is the tee purged before filling the canister?		✓		
Is canister pressure monitored? Flow rate?	✓	✓		Flow is controlled by controlling the rate of pressure rise from -29 in Hg to -10 in Hg.
Is canister hookup (valves, unions, fittings, tubing, etc.) checked for leaks prior to sampling?		✓		

PRELIMINARY REPORT ON THE SITE VISIT AND TECHNICAL SYSTEMS
AUDIT CONDUCTED AT ARCO AND PACIFIC REFINERIES

RTI Project No.: 5500-042

From: James B. Flanagan (919/541-6417) FAX: (919/541-7215)
Lori L. Pearce (919/541-7182)

Date: December 14, 1992

1. a) Finding: The probes and connectors for the OVA Model 108 used at both plants were found to be leaking.
- b) Effect on Data: Leakage will change the overall dilution of the pollutant as well as the flow characteristics at the inlet. This can result in erroneously low screening values. All data taken to date are suspect because leak checks were not routinely conducted.
- c) Recommendation: It is recommended that frequent leak checks be conducted as described in the video tape, "VOC Fugitive Emissions Procedures and Equipment," by E.J. Richards.
- d) Urgency of Implementation: This recommendation was communicated to the Radian field staff at the time of the audit. This is a critical recommendation that should be implemented immediately.
2. a) Finding: At both plants the gas flow rates into the probe inlet of the OVA Model 108 were not being measured and recorded. When measured directly, the actual flows into the OVA probe were a factor of 2 or 3 lower than indicated by the built-in flow indicator.

- b) Effect on Data: The effect of sample flow rate on OVA response is a matter of debate. The impact of sample flow rate on individual samples will vary depending on the nature of the source; i.e., whether it is diffuse or concentrated. A diffuse source will be less sensitive to variations in sample flow rate than a point source.
 - c) Recommendation: It is recommended that sample flow rate at the inlet of the OVA probe be measured and recorded during calibration and before and after each battery change. These data should be added to the data base for evaluation as part of the emission rate model.
 - d) Urgency of Implementation: This recommendation should be communicated to Radian for implementation as soon as possible.
3. a) Finding: Dilution factors obtained with the OVA dilution probe varied significantly between calibration gases at two different concentrations. This was observed at both plants. For example, at the Pacific refinery on 12/18/92, the 1000-ppm calibration standard gave a dilution factor of 10:1, whereas the 35,000-ppm standard gave a dilution factor of 18.4:1. Based on limited observations during the two audits, inconsistent dilution factors appeared to be correlated with the probe leakage observed in Finding 1.
- b) Effect on Data: Uncertainty in the true dilution factor will directly impact the hydrocarbon concentration, which is calculated as OVA readout times the dilution factor. In the case of very high leakers (>10,000 ppm), where the dilution probe must be used to obtain the screening value, this is a critical measurement for development of the emission rate model.
 - c) Recommendation:
 - (1) Ensure that the OVA probe assembly is free of leaks (see Finding 1).
 - (2) Radian should investigate the origin of this variability and make any necessary procedural or equipment modifications to control it.

- (3) Field operators should be instructed to make sure that the dilution ratios obtained with the two different standards agree within a target goal, such as $\pm 20\%$. Corrective measures should be taken if the goal is not achieved.
- d) Urgency of Implementation:
 - (1) Leak-checking should be implemented immediately.
 - (2) Operation of the dilution probe should be investigated. Modified procedures should be in place by January.
 - (3) Field operators should try to minimize the observed discrepancy, if possible, by checking for leaks, etc. This should be started as soon as possible.
- 4. a) Finding: O₂ Calibration checks at the Pacific plant often read higher than the 5% standard gas level. Calibration gas bags used for the OVA and O₂ analyzer were not thoroughly purged prior to refilling at the Pacific plant. Tedlar bags are filled from standard cylinders prior to calibration. The operator squeezes the old gas from the bag and refills it only once. Oxygen calibration checks at the 5% level read as high as 7% at the Pacific plant. Checks at the ARCO plant for the 5% O₂ standard did not exceed 5.3%.
- b) Effect on Data: This error could mask a true malfunction of the instrument. Effect on OVA calibration is unknown.
- c) Recommendation:
 - (1) Calibration bags should be purged more effectively by repeatedly emptying and refilling the bag with standard gas. This is particularly important after long periods between bagging (e.g., weekends or delays due to bad weather).
 - (2) Field personnel should not accept an O₂ calibration check unless the reading is between 4 and 6% on the 5% gas.
- d) Urgency of Implementation: These recommendations should be implemented as soon as possible.

5.
 - a) Finding: Radian technicians at both plants are currently evaluating the multipoint OVA calibrations by fitting the OVA results to a linear regression equation and determining whether the correlation coefficient, r , is high enough (> 0.995). Calibration gas concentration is the independent (x) variable, and the OVA response is the dependent (y) variable. Calibration gases are in a geometric series of 10, 100, 1,000, and 10,000 ppm. This spacing is unequal and results in the correlation being dominated by the higher-level points. Use of a logarithmic transform of both the x and y variables prior to the linear regression would make the points more equally spaced.
 - b) Effect on Data: Using the linear scale rather than a log-log scale for evaluating linearity of the calibration curve causes a loss of information about the lower concentration points. Misleadingly high values for the correlation coefficient, r , can result. This can result in failing to detect noisy or nonlinear calibrations.
 - c) Recommendation: The linear regression/correlation should be done with log-transformed concentration values.
 - d) Urgency of Implementation: This procedure should be implemented as soon as possible.
6.
 - a) Finding: There was air in the "TEE" joint used to monitor pressure while the canister is being filled. This was observed only at the ARCO plant. Radian alerted operators to purge the joint on 12/4/92, consequently, the operators at the Pacific refinery were using a revised procedure when audited on 12/7 and 12/8/92.
 - b) Effect on Data: The volume of the joint is small relative to the total canister volume, so dilution of the sample by air will probably make only a slightly low bias if the joint contains only ambient air. If a high concentration of hydrocarbon is present in the joint from a previous sample, however, carryover could result.
 - c) Recommendation: The joint should be cleared of gas prior to using it to fill a canister. This can be done in two alternative ways:
 - (1) Evacuate the joint to a high vacuum prior to opening the canister valve, OR

- (2) Flush the joint with gas directly from the bag before the canister valve is opened. NOTE: This may require use of a pump to pull the bag gas through the joint, because there may not be sufficient pressure in the bag to force gas through the joint.
 - d) Urgency of Implementation: Radian has already (as of 12/4/92) told the operators to flush the TEE joint prior to sampling by connecting the joint to the bag and opening the valve on the joint before connecting it to the canister. Because a pump is not used, however, this procedure may not be effective due to insufficient bag pressure to force gas through the joint. A modified procedure should be investigated and implemented by January.
7. a) Finding: The OVA used at Pacific appeared to be in poor condition.
- (1) There were leaks in the connector between the probe and the OVA due to a missing Swagelok ferrule. It was found that the field personnel at the Pacific refinery did not have Swagelok hardware of the correct size to repair the OVA.
 - (2) Ambient hydrocarbon measurements with the Radian instrument were consistently <1 ppm, while two OVAs from the Bay Area AQMD which were on-site on 12/8/92 read about 2 ppm.
- b) Effect on Data:
- (1) See Finding 1 for the effect of leaks on OVA response.
 - (2) Screening data below 10 ppm may be biased low due to the low response observed at ambient levels.
- c) Recommendations:
- (1) Field crews at both sites should be provided with necessary supplies to repair OVA leaks. These supplies should include spare Swagelok hardware of the appropriate size for the instrument.
 - (2) The instrument used at Pacific should be checked and serviced if necessary to improve low-end accuracy.
- d) Urgency of Implementation: These recommendations should be followed prior to the next sampling session in January.

Minor Findings and Recommendations

1. Operator names should be recorded daily in the logbook.
2. All operators should view E.J. Richards' videotape, "VOC Fugitive Emissions Procedures and Equipment." This videotape is available from Kirk Foster in the Air Pollution Training Institute of OAQPS.

APPENDIX C

TECHNICAL SYSTEMS AUDITS:

CHEVRON REFINERY: 1/4-5/93

ULTRAMAR REFINERY: 1/7-8/93

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Chevron Refinery, Richmond, CA Date 1/4/93

Controller: Mini-Buck Calibrator

S/N: M-4570B, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	500	0.3083	1621.8	1557.0
2	500	0.3105	1610.3	1555.0
3	500	0.3163	1580.8	1554.0
4	500	0.3253	1537.0	1556.0
			Mean: <u>1587.5</u>	Mean: <u>1555.5</u>
			Std. Dev.: <u>37.8</u>	Std. Dev.: <u>1.3</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Chevron Refinery, Richmond, CA Date 1/4/93

Controller: Mini-Buck Calibrator

S/N: M-4570B, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	500	0.4923	1015.6	1001.0
2	500	0.5027	994.6	1004.0
3	500	0.4960	1008.1	1009.0
4	500	0.4970	1006.0	1009.0
			Mean: <u>1006.1</u>	Mean: <u>1005.7</u>
			Std. Dev.: <u>8.7</u>	Std. Dev.: <u>3.9</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Chevron Refinery, Richmond, CA Date 1/4/93

Controller: Mini-Buck Calibrator
S/N: M-4570B, Model M-5
Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter
S/N: 793, Model HBM-1A
Manufacturer: Teledyne

Gas: Zero Air
Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	500	0.5700	877.2	910.4
2	500	0.5605	892.1	915.8
3	500	0.5530	904.2	910.0
4	500	0.5583	895.6	909.7
			Mean: <u>892.3</u>	Mean: <u>911.5</u>
			Std. Dev.: <u>11.3</u>	Std. Dev.: <u>2.9</u>

AUDIT CHECKLIST

Location: Chevron Refinery
 Richmond, CA
 Organization Audited: Radian Corporation
 Dates of Audit: 1/4-5/93
 RTI Auditors: S. Wasson, L. Pearce
 Audited's Personnel: R. Ricks1/4-5/93
 K. Worl1/4-5/93

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
A. OVA CALIBRATION, CHECKOUT, AND MAINTENANCE				
Are initial instrument checks performed prior to OVA use such as the following:				
A. Enough hydrogen for day's work?	✓			
B. Battery charged?	✓			
C. Flame arrestor in place?	✓			
D. Amplifier warmed up at least ten minutes?	✓			
E. Amplifier electronic linearity checked in both high and low concentration regions?	✓			
F. Leaks checked of the sample gas handling system such as probe fitting, sample line, and sample line fitting?	✓			
G. Checked for prefilter and probe cleanliness?	✓			
H. Is the gas sample flow rate checked? If so, how?	✓			Mini-buck

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument calibrated daily prior to sampling? After sampling?	✓			
Is the probe tip covered with teflon tubing?	✓			
How often are multipoint linearity checks performed?				Daily and after battery changes.
Are the Tedlar bags purged with calibration gas 2 or 3 times before filling?	✓			
Are the regulators on the calibration gas cylinders purged before use?	✓			
Do the linear and measuring ranges include the leak definition value?				What is the leak definition value?
Are instrument accuracy checks performed? How frequently? What reference standards are used?				1000 ppm 35,000 ppm with dilution probe.
Are precision checks performed prior to testing on a daily basis?				Blanks, linear regression and switch button.
B. SCREENING MEASUREMENTS				
Are the instrument response factors for each of the VOCs to be measured less than 3? Record, if available. How was response factor derived? (which compound?)				Methane calibration if nitrogen or chal. - we could do response factor

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument response time equal to or less than 30 seconds? When is the response time checked?	✓			During daily checks.
How is the calibration precision determined?				Linear regression
Is the calibration precision equal to or less than 10 percent of the calibration gas value?				
Is the instrument intrinsically safe?	✓			
Are duplicate screening measurements taken? How many?				Before and after bagging.
How often are drift and blank checks performed?				After every canister - drift > 20%, redone. every 20th sample - duplicate bagging and analytical

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Describe bagging accuracy: What is the concentration of the accuracy standard? Which component was chosen as the "dummy"? What is the induced leak rate?				We did not check theirs - our own - water valve induced flow = 3.4 L/min.
When is the nitrogen flow rate measured for bagged components?				Before and after
How is the oxygen concentration inside the bag measured? What criteria are used to verify that the nitrogen purging is complete and effective?				Oxygen analyzer << 5% usually < .5%.
What is the time from collection of samples to analysis? - Holding time until shipped - Holding time in laboratory (if known)				Collection to analysis - two weeks.
Is the OVA used to establish purge gas equilibrium?	✓			Yes - screening taken.
Are there any obvious opportunities for leakage from or into the bag?		✓		Bags were tight.
Is the N ₂ flow rate sufficient to maintain positive pressure on the bag, even while sample is being withdrawn?				Always - N ₂ flow rate exceeds flow rate of OVA.
Are sample lines to the canister purged before filling?	✓			Yes, also gauge pulled through the vacuum, by O ₂ meter.
Is the tee purged before filling the canister?	✓			Yes

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is canister pressure monitored? Flow rate?	✓			Slow - flow - 2 minutes to fill canister.
Is canister hookup (valves, unions, fittings, tubing, etc.) checked for leaks prior to sampling?		✓		Not necessary if positive pressure from N ₂ - with proper flow rates.

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Ultramar Refinery, Wilmington, CA Date 1/7/93

Controller: Mini-Buck Calibrator

S/N: M-2312, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	500	0.2660	1879.7	1812.0
2	500	0.2702	1850.5	1813.0
3	500	0.2732	1830.2	1794.0
4				1804.0
			Mean: <u>1853.5</u>	Mean: <u>1805.7</u>
			Std. Dev.: <u>24.9</u>	Std. Dev.: <u>8.8</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Ultramar Refinery, Wilmington, CA Date 1/7/93

Controller: Mini-Buck Calibrator
S/N: M-2312, Model M-5
Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter
S/N: 793, Model HBM-1A
Manufacturer: Teledyne

Gas: Zero Air
Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	1000	0.3843	2602.1	2541.0
2	1000	0.3900	2564.1	2529.0
3	1000	0.3948	2534.9	2529.0
4				
			Mean: <u>2566.4</u>	Mean: <u>2533.0</u>
			Std. Dev.: <u>34.7</u>	Std. Dev.: <u>6.9</u>

Flow Rate Audit

Have operator establish a standard flow rate using his equipment. Measure the flow using the bubble meter kit.

Location: Ultramar Refinery, Wilmington, CA Date 1/7/93

Controller: Mini-Buck Calibrator

S/N: M-2312, Model M-5

Manufacturer: AP Buck, Inc.

RTI Reference: Hastings Bubble Flow Meter

S/N: 793, Model HBM-1A

Manufacturer: Teledyne

Gas: Zero Air

Flow Measure Under Vacuum or Pressure: Vacuum

	ΔV (mL)	Δt (min)	Bubble Flow Rate (mL/min)	Mini-Buck Flow Rate (mL/min)
1	500	0.4765	1049.3	1029.0
2	500	0.4777	1046.7	1025.0
3	500	0.4817	1038.0	1019.0
4	500	0.4865	1027.7	1023.0
5	500	0.4817	1038.0	
			Mean: <u>1040.0</u>	Mean: <u>1024.0</u>
			Std. Dev.: <u>8.5</u>	Std. Dev.: <u>4.2</u>

AUDIT CHECKLIST

Location: Ultramar Refinery
 Wilmington, CA
 Organization Audited: Radian Corporation
 Dates of Audit: 1/7-8/93
 RTI Auditors: S. Wasson, L. Pearce
 Audited's Personnel: J. Davis 12/7/92
 J. Colin 12/7-8/92

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
A. OVA CALIBRATION, CHECKOUT, AND MAINTENANCE				
Are initial instrument checks performed prior to OVA use such as the following:				
A. Enough hydrogen for day's work?	✓			1540 psi.
B. Battery charged?	✓			
C. Flame arrestor in place?	✓			
D. Amplifier warmed up at least ten minutes?				J.D. says 5 minutes warm-up
E. Amplifier electronic linearity checked in both high and low concentration regions?	✓			OK 10 and 10,000
F. Leaks checked of the sample gas handling system such as probe fitting, sample line, and sample line fitting?	✓			Routinely checked during calibration. logged.
G. Checked for prefilter and probe cleanliness?	✓			OK
H. Is the gas sample flow rate checked? If so, how?	✓			

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument calibrated daily prior to sampling? After sampling?	✓			Calibration on 100 ppm (do twice). Zero <1, 10→11.5, 1000→900, 9520→2900 also QC gas in field after every bag within 20% of 900
Is the probe tip covered with teflon tubing?	✓			
How often are multipoint linearity checks performed?	✓			Daily and fails QC test change
Are the Tedlar bags purged with calibration gas 2 or 3 times before filling?	✓			Once.
Are the regulators on the calibration gas cylinders purged before use?	✓			Did not see, says purge.
Do the linear and measuring ranges include the leak definition value?			✓	NA to this study.
Are instrument accuracy checks performed? How frequently? What reference standards are used?				1000 midrange check standard after every bagging.
Are precision checks performed prior to testing on a daily basis?				
B. SCREENING MEASUREMENTS				
Are the instrument response factors for each of the VOCs to be measured less than 3? Record, if available. How was response factor derived? (which compound?)			✓	Measure relative to methane.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is the instrument response time equal to or less than 30 seconds? When is the response time checked?	✓			
How is the calibration precision determined?				Constant rechecking of 1000 ppm bag.
Is the calibration precision equal to or less than 10 percent of the calibration gas value?				
Is the instrument intrinsically safe?	✓			
Are duplicate screening measurements taken? How many?	✓			Every 20.
How often are drift and blank checks performed?				After bagging - before every measurement. ambient

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
<p>Observe the operator screen at least 3 different types of components: valve, flange, Note proper technique in following areas:</p> <ul style="list-style-type: none"> - Identifying the area where leaks should be screened ✓ - Proper distance of probe from component ____ (how far) - Proper angle of probe with leaking source (diagram) - Time sufficient to take a stable reading ____ (how long) - Reading replicated? How long between readings? ____ Any difference in location or angle between readings? Describe. 				<p>Gate valves only. OK</p> <p>Probe is touching component (Tedlar extension). Directly on.</p> <p>Several minutes.</p> <p>Before and after bagging.</p>
C. BAGGING				
Sketch the bagging accuracy check set up.				
Are duplicate bagging measurements routinely taken? How many? What frequency?				Every 20
Are ambient and internal bag temperatures recorded for each bagged component?	✓			

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Describe bagging accuracy: What is the concentration of the accuracy standard? Which component was chosen as the "dummy"? What is the induced leak rate?			✓	Once per refinery. 9520 Water valve Flow rate established depends on bag size.
When is the nitrogen flow rate measured for bagged components?	✓			Before and after bagging.
How is the oxygen concentration inside the bag measured? What criteria are used to verify that the nitrogen purging is complete and effective?				O ₂ meter drags and drops; fluctuates - more later. < 5% O ₂
What is the time from collection of samples to analysis? - Holding time until shipped - Holding time in laboratory (if known)				Two weeks. Send out that night or next day.
Is the OVA used to establish purge gas equilibrium?	✓			Before and after sample collection.
Are there any obvious opportunities for leakage from or into the bag?		✓		No leakage observed.
Is the N ₂ flow rate sufficient to maintain positive pressure on the bag, even while sample is being withdrawn?				1 to 6 L per minute smaller 1 L larger 5-6 L
Are sample lines to the canister purged before filling?	✓			
Is the tee purged before filling the canister?	✓			Pulled through gauge by O ₂ meter and OVA.

AUDIT QUESTIONS	RESPONSE			NOTES
	Y	N	N/A	
Is canister pressure monitored? Flow rate?	✓	✓		Flow rate is not measured but canister is filled very slowly. 1½ to 3 minutes usual time.
Is canister hookup (valves, unions, fittings, tubing, etc.) checked for leaks prior to sampling?		✓		These fittings are tight as evidenced by O ₂ drop.

**Preliminary Report on the Site Visit and Technical Systems Audit
Conducted at Chevron and Ultramar Refineries**

RTI Project No.: 5500-42

From: Shirley J. Wasson (919/541-7417) Fax: (919/541-7215)
Lori L. Pearce (919/541-7182)

Date: January 13, 1993

INTRODUCTION

The Chevron refinery in Richmond, CA, was visited on January 4 and 5, 1993. Radian personnel Ron Ricks and Kim Worl were present. The Ultramar refinery in Wilmington, CA, was visited on January 7 and 8, 1993. Radian personnel Jeff Davis and Joe Colin were present.

MAJOR FINDINGS

1. **Finding:** The dilution probe continues to be a probable source of error. This observation arises from the variability with which the performance audits were measured with and without the dilution probe, and the variability with which dilution factors were measured by Radian and audit personnel. Several specific problems were identified: (1) variation in measured dilution factors with different gas concentrations; (2) variation in dilution factors dependent on the source, even with gases of the same concentration; (3) high background readings with the dilution probe in place (e.g., 50 ppm ambient background with dilution probe versus 5 ppm without the probe).

Effect on Data: The dilution probe is used for readings in two parts of the process: (1) screening leaks above the 10,000 ppm upper limit of the OVA; and (2) verifying that the blow-through gas has stabilized at a constant value before a canister sample is taken. Since screening measurements below 10,000 ppm are made without a dilution probe, the correlation equations for leaks below 10,000 ppm should not be affected. Screening values for leaks above 10,000 ppm, for which a dilution probe is required, **however, will be affected**. Measurement of the blow-through gas is not used in developing the correlation equations. Since these measurements are not

quantitatively accurate, they should not be used for any purpose other than verifying that the component enclosure has been completely purged.

Recommendation: There should be a study of the design of the dilution probe to determine the source of the problems and the impact on data acquired with the probe. In particular, the role of back pressure in slowing the pump on the OVA and thereby affecting calibration should be examined. Further, the charcoal trap, used to remove hydrocarbons from the dilution air stream, should be examined for contamination and to determine how often it should be replaced.

Need for Implementation: The dilution probe has been scrutinized and modified already for this project, but the screening results above 10,000 ppm will continue to have uncorrectable errors until the dilution probe problems are solved. This is a significant continuing concern because higher leakers, although rare, may contribute significantly to total emissions for a facility.

2. Finding: There are two methods in widespread use for taking the screening measurements. The method used by Radian for this project, in accord with Method 21, takes a reading with the probe tip as close as possible to the leak source, the tip being extended with Tygon tubing of the same diameter as the metal probe so that there is effectively zero distance between the component being screened and the OVA probe tip. Another method, reportedly in widespread use, uses a metal clip on the probe tip as a spacer. This permits a free flow of dilution air to enter the probe. Data taken with the two methods may not be comparable, and correlation equations developed in this program are applicable only to screening data taken without the spacer.

Effect on Data: Correlation equations arising from data collected this way versus data collected using a metal clip which keeps the probe some distance away from the component surface will be different.

Recommendation: Radian's final report should clearly point out this qualification to the correlation equations.

Need for Implementation: Screening data collected even 1/4 inch away from the surface of leaking components will not be relevant to these correlation equations because the reading can be as much as several orders of magnitude lower than data collected with the probe tip touching the component. This is a critical qualification to these data.

MINOR FINDINGS

3. **Finding:** Radian performs field QC calibration checks for the OVA, but there is no place on the field data sheet for the measurement to be recorded. These checks are done using the same 1000 ppm gas that is used for calibration. The check is considered acceptable if the value read on the OVA is within 20% of the calibration value (i.e., typically between 800 and 1200 ppm). During the audit at the Chevron plant, Radian's Northern California field personnel added these measurements at the bottom margin of the field data sheets. However, the Southern California team recorded the calibration check results on only one of the three field sheets filled out at Ultramar on 1/7/93.

Effect on Data: There will be no effect on any individual screening measurement unless field personnel inadvertently forget to perform the check when the instrument is losing its calibration due to a low battery or other problem. This could increase the frequency of outliers in the data base and reduce the overall precision and accuracy of the results.

Recommendation: A line should be added to the Bagging Data Entry Form so that operators will be reminded to perform and record the calibration check.

Need for Implementation: This suggestion should be implemented immediately.

4. **Finding:** The word "bagging" has two definitions in this study. Documents from the EPA define bagging as collecting a sample in a Mylar or other suitable bag. Radian defines bagging as surrounding a component with Mylar, passing nitrogen through the bag, and collecting the vapors in a suitable container. (In this study, the containers are polished summa canisters.) EPA refers to the action just described as "tenting".

Effect on Data: When "bagging" refers to two very different operations in pertinent documents pertaining to this study, it leads to confusion.

Recommendation: In the final report on this project, Radian should conform their terminology to that of EPA.

Need for Implementation: Implementing this suggestion would eliminate some confusion for the reader of the literature pertaining to this study.

RESPONSE TO PREVIOUS FINDINGS

Radian has implemented many of the suggestions RTI made in the preliminary report from the earlier audits of this project (ARCO and Pacific refineries, 12/15/92). The specific suggestions made in that report were reviewed during the January audits with the following results:

1. As recommended, the probes and connectors for the OVA Model 108 field screening instrument are being leak-checked as a routine part of the daily calibration procedure. The leak checks were being recorded by Radian personnel in the project daily logs.

2. The gas flow rates into the probe inlet of the OVA Model 108 are now being measured and recorded. These measurements have been valuable indicators of low battery and provide explanation for the instrument losing its calibration during the course of the day.

3. Dilution factors continue to be variable. This is an instrumental problem rather than a procedural problem, but Radian must document the magnitude of the error and qualify any critical measurements taken with the dilution probe.

4. The finding that oxygen calibration checks often read higher than the 5% standard gas level prompted a change in procedure. Until the January audit, the oxygen meters were calibrated on ambient air (20.9% oxygen) and checked on 5% oxygen. The oxygen is now being calibrated on 5% oxygen and checked on ambient air. The revised procedure combined with effective purging discussed in the next paragraph will result in more accurate data since the important oxygen measurements are occurring at the low end of the scale nearest the 5% calibration point.

The Tedlar bags used to contain the calibration gases, the zero air, the QC check standard, and the oxygen calibration standard are now being purged at least once prior to filling as recommended by RTI. Some were being purged twice and three times, however, depending on the operator's preference. It is recommended that the bag-purging protocol be standardized. The 5% oxygen bag should be purged at least twice since Tedlar bags are permeable to oxygen. Bags used for the methane/air standards should be purged once between uses at the same concentration level.

5. Radian is continuing to use linear regression with untransformed data rather than log-transformed data recommended in the previous report. As stated previously, this practice can mask calibration errors and nonlinearity at the low end of the OVA's range.

6. The "TEE" joint used to monitor the pressure during canister fill is now being routinely purged prior to sample collection by including the gauge in the train during the oxygen measurement. The pump from the oxygen meter pulls sample gas through the "TEE" to assure thorough purging. This should effectively address the original concern.

7. All OVAs examined were in good repair and were not leaking. The OVA in use at the Ultramar refinery had been performing well up until the day the auditors arrived. It failed its initial checkout on that day due to an instrument malfunction. It was sent out for repair before being used for any further field measurements.

APPENDIX D

EXAMPLES OF RAW DATA FROM FIELD SAMPLING

- **Bagging Data Entry Forms**
- **Sample Acquisition Pages from Logbook**
- **Daily OVA Calibrations from Logbook**
- **Daily Oxygen Calibrations from Logbook**

TITLE MASTER Log - Pacific Refinery & Chevron

Project No. _____

Book No. 2782i

RADIAN
CORPORATION

From Page No. _____	Sample No.	Comp ID	Comp Type	Service	Can ID	HHC Base Cont.	N ₂ Flow	Comments
14/11	P073	FA-3-P205A-5	8" Gate Valve	LL	12386	465	4153	Assoc w/ P077L
	P074	FA-2-FV123-5	3" Gate V.	LL	11436	1700	4385	
	P075L	FA1-FV218A-6	Plug Conn 1"	LL	—	—	—	Liq Assoc w/ P070 (Can 11434)
	P076L	FA1-F218B-3	4" Gate Valve	LL	—	—	—	Liq Assoc w/ P069 (Can 11440)
	P077L	FA3-P205A-8	8" Gate Valve	LL	—	—	—	Liq Assoc w/ P073 (Can 12386)
	P078	NA	NA	NA	11446	NA	NA	Blank
RICHMOND CHEVRON: Cont From Page 53								
14/16	C073	104-1025	Pump	HL	11828	350	4030	
	C074	—	—	—	12030	—	—	Blank
	C075	104-109	V6a 4"	HL	12381	105	4530	
	C076	104-0106	V G 3/4"	HL	11629	140	1750	
	C077	104-0119	V6a 4"	LL	11900	1650	4815	
	C078	104-0468	V G 2"	HL	12391	60	2620	Default Zero
	C079	104-2021	Pump 4"	HL	11832	3300	4518	P-103A - Pump C.
	C080	on P103A	OEL 3/4"	HL	11895	650	1335	
	C081	—	—	—	05371	—	—	Blank
	C082	953-430	V Ball 3/4"	Gas	11900	1866	1890	
	C083	956-0435	V Ball 3/4"	Gas	12381	34	2112	default zero
dp 1/5	C084	956-0425	V Ball 3/4"	Gas	12033	~15	1844	default zero
	C085	956-0425	V Ball 3/4"	Gas	11832	320	1516	RTI audit gas through bag
	C086	956-0425	V Ball 3/4"	Gas	12391	320	1516	RTI audit gas through bag
	C087	NA	V G 2 1/2"	—	11896	128	3512	RTI audit gas through bag
1/5/13	C088	NA	NA	—	12373	—	—	RTI audit gas direct
	C089	NA	NA	—	11439	—	—	RTI audit gas direct
	C090	121-1353	V G 3"	Gas	12370	17580	6714	
	C091	121-1344	V G 3"	Gas	11443	3000	6190	
	C092	121P	Pump	LL	12037	700,000		55 on steel ball on rotameter 103
1/6/93	C093	P775	Pump	LL	12384	208	2288	
	C094	P773	Pump	LL	12286	274	2240	
	C095	121-1043	V G 8"	LL	11822	45,000	7690	
	C096	121-0493	V G 2"	GL	11821	22,500	4968	N ₂ flow test #1
1/22/93	C097	121-0493	V G 2"	GL	RTI #12	22,500	4968	RTI duplicate - N ₂ test 1
	C098	121-0493	V G 2"	GL	12354	39,000	2934	N ₂ test 1
	C099	121-0493	V G 2"	GL	11824	8,400	10356	N ₂ test 1
	C100	121-0493	V G 2"	GL	11428	3,450	24,396	N ₂ test 1

Witnessed & Understood by me, _____

Date _____

Invented by _____

Date _____

Recorded by _____

To Page No. 61

TITLE CNA CALIBRATION S/N 20162 PACIFIC

Project No. 27821 **RADIAN**
Book No. 27821

From Page No. <u>198</u> 1.99 3 3.99 Dilution Probe									
DATE	ZERO AIR	9.5 mm	9.5 mm	1000 mm	0.99999 mm	1000 mm	3.5% mm	DL mm	TIME
11/30	3	14	100	800	8500	110	3000	1.3	1.330
12/1	1.5	10	100	1000	11000	120	3600	8.3/9.1	1010
12/1	<1	9.8	100	1200	21000	200	7000	5/5	1250 replaced battery
12/1	<1	8	70	1000	11000	200	8000	5/4.4	1307 replaced battery
12/2	<1	8.8	100	1000	11000	100	2800	10/12.5	0730
12/2	<1	8	110	1200	12000	1000	2500	10/14	
12/2	<1	8	100	1000	10000	100	2800	10/12.5	
12/3	<1	9.5	100	1000	11000	100	2800	10/12.5	0730
12/3	<1	8.5	100						0800
12/3	<1	8	90	1000	10000	100	3500	10/10	0800
12/3	<1	9	100	1200	12000	100	2500	10/14	1013 replaced battery
12/3	<1	8	80	1000	10000	100	3000	10/11.7	1105 GC > 20%
12/3	<1	9	100	1200	12000	100	3200	10/14.9	1306
12/4	<1	8	100	1000	10000	100	3000	10/11.7	
12/4	<1	8	100	1000	10000	100	3000	10/11.7	
12/7	<1	7	100	1000	10000	100	2800	10/12.5	1007
12/7	<1	7	90	1000	10000	100	3600	10/14.7	1045 due to instr drift
12/7	<1	8	100	1000	10000	100	2500	10/14	1400 instr drift
12/7	<1	8	95	1000	10000	100	3000	10/11.7	1440 replaced battery
12/8	<1	11	100						0720 replaced electronics pcb
12/8	<1	10	100	1000	8000	100	1900	10/18.4	830
12/8	<1	9	100	1000	9000	100	2000		1000 GC DRIFT
12/9	<1	9.5	2	1000	10000	100	1800	10/14.6	702 N/A Pump = 1170
12/9	<1	9.5	100	1000	10000	100	1800	10/14.6	0817
12/9	<1	8	100	1000	9000	100	1850		1240
12/9	<1	9.5	100	1000	10000	100	1850		N/A Pump = 1003 mL
12/10	<1	9.5	99	1000	9800	100	1600	10/12.9	0754 N/A Pump = 114
12/11	<1	9.2	95	1000	9600	100	3500	10/10	0750 N/A Pump = 114

ed & Understood by me, _____ Date _____

From Page No. _____

DATE	AMBIENT O ₂ CONC.	5% O ₂ READING	
11/2/92	21.5	5.3 RDR 5.7	
11-3-92	20.8	5.6	
11-4-92	18.5	5.2	Fully charged - maybe overcharged
11-5-92	19.0	5.0	TIME
11-6-92	19.0	5.2	0710
11-9-92	19.5	5.0	645
11-10-92	20	5.0	645
11-11-92	20.2	5.2	745
11-12-92	17	5.2	730
11-13	17	5.0	720
11-18	17	5.0	710
11-19	19.5	5.0	705
12-15	21	6	735
1-4-93	18.7	5.0	1043
1-5-93	19.7	5.0	0753
1-8-93	20.0	5.0	0817
1-22-93	(below) 20.4 (above) 19.5	6.0	0741
1-27-93	19.5	5.0	0754
1-28-93	19.5	5.0	0732
	cont. p 32		

To Page No. _____

Witnessed & Understood by me,

Date

Invented by

Date

Recorded by

Bagging Data Entry Form

Sample ID: <u>693-430</u>	Liquid Sample ID: <u>—</u>
Plant ID: <u>Chevron</u>	Date: <u>1-4-93</u>
Unit ID: <u>VG0</u>	Bagging Team: <u>RDK/KMW</u>
Instrument ID: <u>2254</u>	Stream ID: <u>Fuel gas</u>
Component ID: <u>953-430</u>	Component Type (valve, pump, etc.): <u>Valve</u>
Component Sub-Category (gate, globe, etc.): <u>ball</u>	Valve Actuation (manual, control): <u>manual control RDK</u>
Component Service (HL, LL, gas): <u>gas</u>	Component Size (in.): <u>3"</u>
Ambient Temperature (°F): <u>53</u>	Windspeed (mph): <u>~2 mph</u>
Barometric Pressure (Hg): <u>30.15</u>	Background (ppm): <u>1.6</u>
Stream Pressure (psia):	Stream Temperature (°F):
Unit Age:	Seal Age:
Stream Hydrocarbon Content (%):	Seal Packing Type:
I&M Screening Value (ppm):	I&M Screening Date:

Time	Bagging Data Parameter	Value
1245	Initial Screening Value (ppm)	3800
1321	Initial Nitrogen Flow Rate (ml/min)	1894
1324	Initial Bag Temperature (°F)	81
1327	Bag O ₂ Concentration at Equilibrium (ppm) <u>0.3%</u>	0.3%
1331	Bag THC Concentration at Equilibrium (ppm) <u>200 x 9.1</u>	1820
1335	SAMPLE COLLECTION STARTED <u>can # 11900</u>	<u>1335 RDK</u>
1337	SAMPLE COLLECTION ENDED	—
1342	Final Bag O ₂ Concentration (%)	0.3
1343	Final Bag THC Concentration (ppm) <u>210 x 9.1</u>	<u>1911 RDK</u>
1345	Final Bag Temperature (°F)	81
1346	Final Nitrogen Flow Rate (ml/min)	1286
1352	Final Screening Value (ppm)	4000

Interim Data								
Time	OVA	O ₂	Time	OVA	O ₂	Time	OVA	O ₂

(Q.C. = 950
950

APPENDIX E

EXAMPLE OF RAW DATA FROM LABORATORY ANALYSIS FOR ADQ

- Multi-point Calibration
- Data for P081


Response to
RTI AUDIT OF DATA QUALITY
Memo of 3/30/93

Cross Reference for Raw Data

Field SampleID	Lab Work Order ID	Page #
P081	9302025 A and B	3 - 28
U148	9301041 A and B	29- 49
C085	9301014 A and B	50 - 67
A049	9301022 A and B	68- 91
A095	9301117 A and B	92-100

The raw data requested on 3/30/93 is provided in this deliverable organized by lab work order ID. A copy of the final lab report, raw data for associated daily lab QC and raw sample data appears under each work order.

Reviewed By


Linda L. Freeman/Director
AIR TOXICS LIMITED

DATE: 4/5/93

LABORATORY NARRATIVE

Calibration equations and constants used to convert area counts to concentration units and original calibration data

Both Method 18-THC and Methane-D3416 approaches involved an original five point calibration at the start of the project to as a measure of instrument linearity. Calibration tables and regression curves are provided at the front of the deliverable. A daily CCC was analyzed with every set of samples and referenced to the original five point. The original five point regression was used to calculate sample results.

Explanation of final reporting units and an example calculation.

Calibration is performed using certified gas standards containing target species in units of ppmv. The sample concentration is calculated taking into account the canister dilution factor (due to pressurization) and the calculated amount (ppmv) derived under linear regression from the calibration curves. Method 18 and ASTM D3416 are calibrated using simple ESTD multilevel calibration. The absolute response (amount/area) is used for linear regression.

$$\text{Reported Amount (ppmv)} = \text{Analysis Amount (ppmv)} \times \text{Dil. Factor}$$

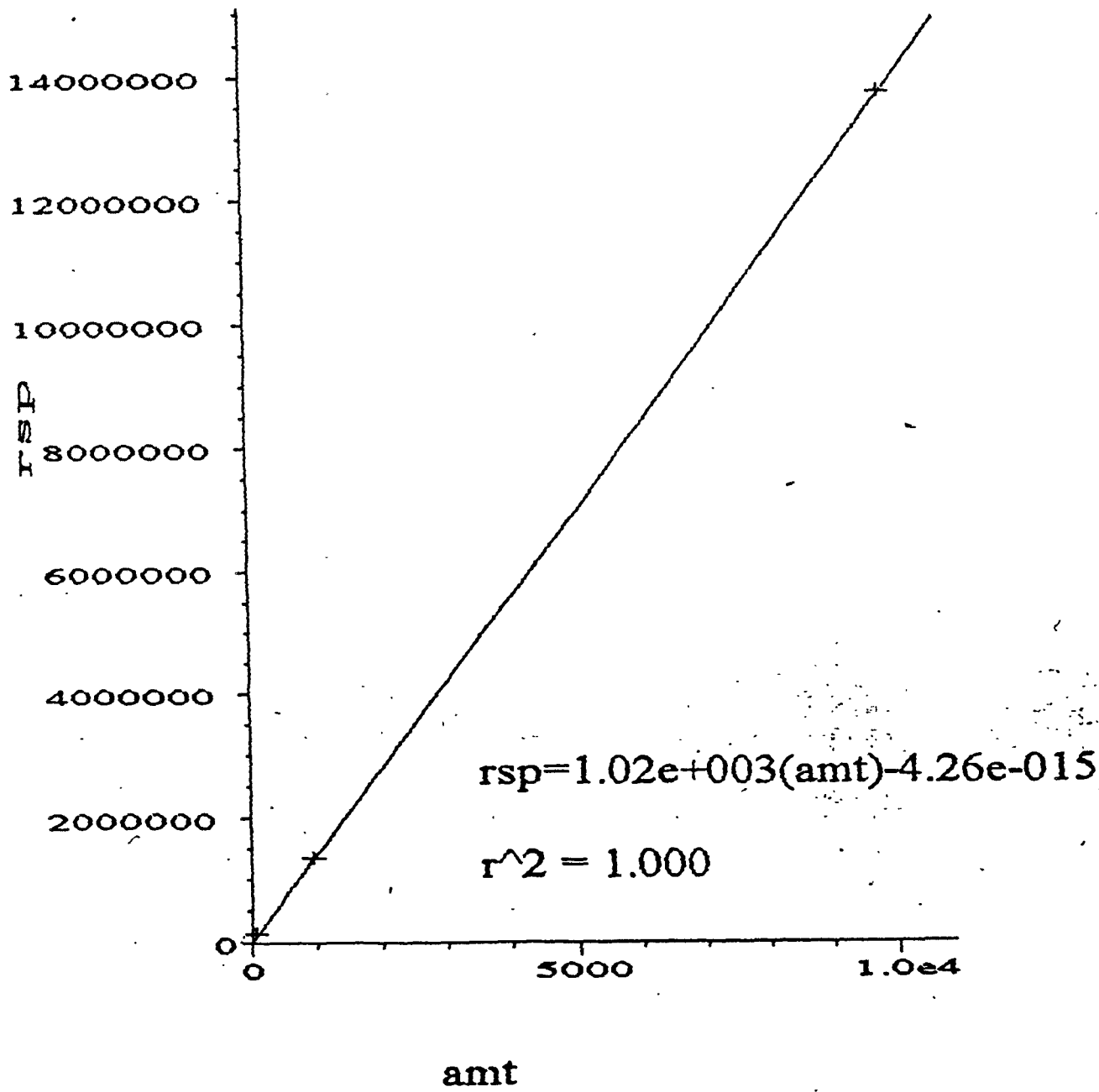
A table of canister dilution factors appears at the end of this deliverable along with copies of laboratory analysis logbook pages.

Calibration Table

000001

Pk#	RT	Lvl	ppmv	Amt/Area	Ref Istd I#	Name
1	5.372	1	9.72	6.9866e-004	1	Methane
		2	49.5	6.3173e-004		
		3	99.0	7.1688e-004		
		4	987.0	7.35e-004		
		5	9900.0	7.2036e-004		
2	12.502	1	11.4	1.811e-004	1	Propane
		2	995.0	1.674e-004		
		3	9960.0	2.133e-004		

Methane

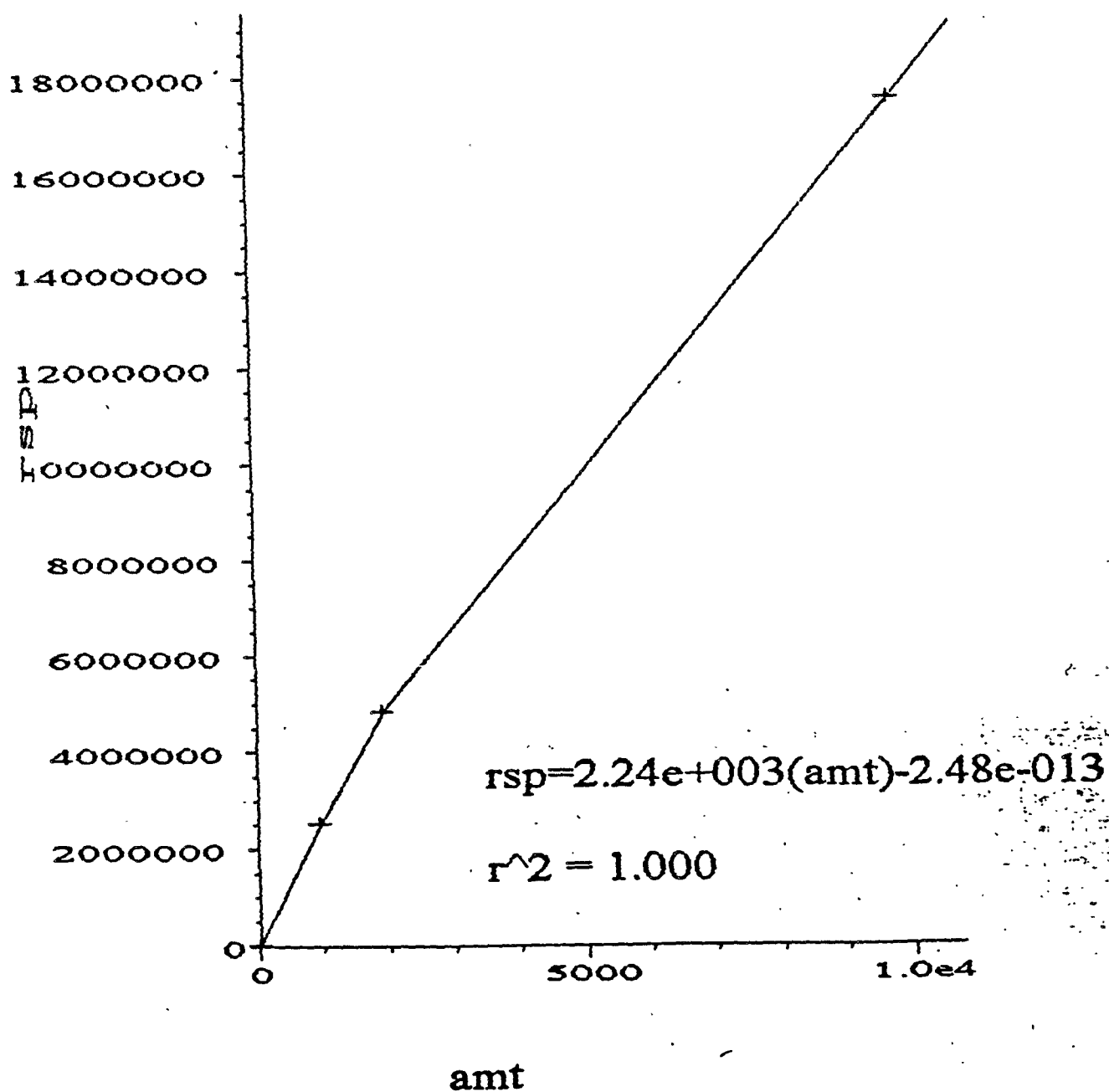


Calibration Table

Pk#	RT	Lvl	PPMV	Amt/Area	Ref Istd I#	Name
1	0.210	1	1.14	4.458e-004	1	THC-PROPANE
		2	11.4	5.454e-004		
		3	980.0	3.904e-004		
		4	1960.0	4.073e-004		
		5	9800.0	5.571e-004		

000002

THC-PROPANE



@ AIR TOXICS LTD.**000003**

AN ENVIRONMENTAL ANALYTICAL LABORATORY

WORK ORDER #: 9302025**Work Order Summary**

CLIENT: Ms. Randi Beuttler
Radian Corporation
10389 Old Placerville Rd.
Sacramento, CA 95827

BILL TO: Subcontracts Payable
Radian Corporation
P.O. Box 201088
Austin, TX 78720-1088

PHONE: 362-5332
FAX: 362-2318
DATE RECEIVED: 2/4/93
DATE COMPLETED: 2/18/93

INVOICE # 0286
P.O. # S00202034
PROJECT # 209-081-04-01
AMOUNT\$: \$540.00

<u>FRACTION #</u>	<u>NAME</u>	<u>TEST</u>	<u>RECEIPT VAC./PRES.</u>	<u>PRICE</u>
01A/B	P081	Meth.18/ASTM D 3416	9.0 "Hg	\$50.00
01A/B DUP	P081 Duplicate	Meth.18/ASTM D 3416	8.0 "Hg	NC
02A/B	P080	Meth.18/ASTM D 3416	8.0 "Hg	\$50.00
03A/B	P079	Meth.18/ASTM D 3416	8.0 "Hg	\$50.00
04A/B	P083	Meth.18/ASTM D 3416	8.0 "Hg	\$50.00
05A/B	P084	Meth.18/ASTM D 3416	8.0 "Hg	\$50.00
06A/B	P085	Meth.18/ASTM D 3416	8.5 "Hg	\$50.00
07A/B	P086	Meth.18/ASTM D 3416	8.5 "Hg	\$50.00
08A/B	P087	Meth.18/ASTM D 3416	4.0 "Hg	\$50.00
09A/B	P088	Meth.18/ASTM D 3416	9.0 "Hg	\$50.00
10A/B	Method Spike	Meth.18/ASTM D 3416	NA	NC
11A/B	Lab Blank	Meth.18/ASTM D 3416	NA	NC

Misc Charges 1 Liter SUMMA Canister Preparation (9) @ \$10.00 each. \$90.00

CERTIFIED BY:

Janet L. Tison
Laboratory Director

DATE:

2/18/93

11325 SUNRISE GOLD CIRCLE, SUITE E • RANCHO CORDOVA, CA 95742
(916) 638-9892 • FAX (916) 638-9917

AIR TOXICS LTD.

THC by EPA Method 18 GC/FID
Methane by ASTM D 3416 GC/TCD/FID

Field Sample I.D.	Lab Sample I.D.	File Name	Sample Date	Analyzed For	Dilution Factor	MDL (ppmv)	Amount (ppmv)
P081	9302025-01A	2020531	2/1/93	THC-Meth. 18	1.9	0.095	2200
	9302025-01B	3020503		Methane-D 3416	1.9	1.9	5600
P081 Duplicate	9302025-01A DUP	2020532	2/1/93	THC-Meth. 18	1.9	0.095	2200
	9302025-01B DUP	3020504		Methane-D 3416	1.9	1.9	5700
P080	9302025-02A	2020533	2/1/93	THC-Meth. 18	1.8	0.090	7800
	9302025-02B	3020506		Methane-D 3416	1.8	1.8	18000
P079	9302025-03A	2020535	2/1/93	THC-Meth. 18	180	9.0	130000
	9302025-03B	3020507		Methane-D 3416	1.8	1.8	240000
P083	9302025-04A	2020529	2/2/93	THC-Meth. 18	1.8	0.090	3.5
	9302025-04B	3020508		Methane-D 3416	1.8	1.8	Not Detected
P084	9302025-05A	2020530	2/2/93	THC-Meth. 18	1.8	0.090	1.9
	9302025-05B	3020509		Methane-D 3416	1.8	1.8	Not Detected
P085	9302025-06A	2020527	2/2/93	THC-Meth. 18	1.9	0.095	310
	9302025-06B	3020510		Methane-D 3416	1.9	1.9	620
P086	9302025-07A	2020526	2/2/93	THC-Meth. 18	1.9	0.095	43
	9302025-07B	3020511		Methane-D 3416	1.8	1.9	96
P087	9302025-08A	2020528	2/2/93	THC-Meth. 18	1.6	0.080	48
	9302025-08B	3020512		Methane-D 3416	1.6	1.6	110
P088	9302025-09A	2020511	2/2/93	THC-Meth. 18	1.9	0.095	540
	9302025-09B	3020505		Methane-D 3416	1.9	1.9	Not Detected
Lab Blank	9302025-11A	2020503	NA	THC-Meth. 18	1.0	0.050	Not Detected
	9302025-11B	3020502		Methane-D 3416	1.0	1.0	Not Detected
Spiked Samples						% Recovery	
Method Spike	9302025-10A	2020501	NA	THC-Meth. 18	1.0	0.050	108
	9302025-10B	3020501		Methane-D 3416	1.0	1.0	102

Method 18 Analysis Date: 2/5/93
ASTM D 3416 Analysis Date: 2/5/93

Container Type: 1 Liter SUMMA Canister

Comments: Total Hydrocarbons (THC) referenced to Propane (MW=44)
NA=Not Applicable

000004

RADIAN
CORPORATION10389 Old Placerville Road
Sacramento CA 95827

000005

CHAIN OF CUSTODY RECORD

FIELD SECTION

CLIENT NAME Pacific Refining - WSPA PROJECT ADDRESS _____
Number Street City ZipSAMPLED BY NFD/KMW Radian CONTAINERS OBTAINED FROM Air Toxics
Name (PRINT) OrganizationPRESERVATIVE USED None STORAGE TEMPERATURE ☒ Ambient ☐ 4° C ☐ -10° C Other _____☐ HAZARDOUS ☒ NON-HAZARDOUS SPECIAL HANDLING INSTRUCTIONS _____

FIELD REMARKS _____

COLLECTOR'S SAMPLE NO.	DATE	COMP.	GRAB	TYPE (cell, H ₂ O)	FIELD DATA	STATION LOCATION (grid, depth, etc.)	NO. OF CON- TAINERS	ANALYSIS REQUIRED				REMARKS
								Asm	3% E/F	1/2		
PO81	2/1/93	X		nc	~ -10 "H"	>100,000 ppm	1	X	X			Can # 11299 + Dep
PO80	"	X		VOC	~ -10 "H"	>100,000 ppm	1	X	X			12386
PO79	"	X		VOC	~ -10 "H"	>100,000 ppm	1	X	X			12030
PO83	2/2/93	X		VOC	~ -10 "H"	<1 ppm	1	X	X			11446
PO84	2/2	X		VOC	~ -10 "H"	<1 ppm	1	X	X			11442
PO85	2/2	X		VOC	~ -10 "H"	~ 2800 ppm	1	X	X			10973
PO86	2/2	X		nc	~ -10 "H"	~ 264 ppm	1	X	X			0537/ 8.5"
PO87	2/2	X		VOC	~ -5.5 "H"	~ 146 ppm	1	X	X			12362
PO88	2/2	X		VOC	~ -9.9 "H"	~ 335 ppm	1	X	X			12713 9"

Nicole Haw Radian 2/2/93 1752 Remain Prot 2/4/93 9:00
 Released by Organization Date/Time Received by Organization Date/Time
Fed-X 4601940114

Released by Organization Date/Time Received by Organization Date/Time

Released by Organization Date/Time Received by Organization Date/Time

LABORATORY SECTION

TEMPERATURE RECEIVED _____ FEDX AIRBILL# _____ HAND DELIVERED _____

ANALYSIS RECORD

TYPE OF ANALYSIS	PERFORMED BY (Signed)	DATE OF ANALYSIS	RECORDED (LAB BOOK NO.)	COMMENTS

Original (Page 1)

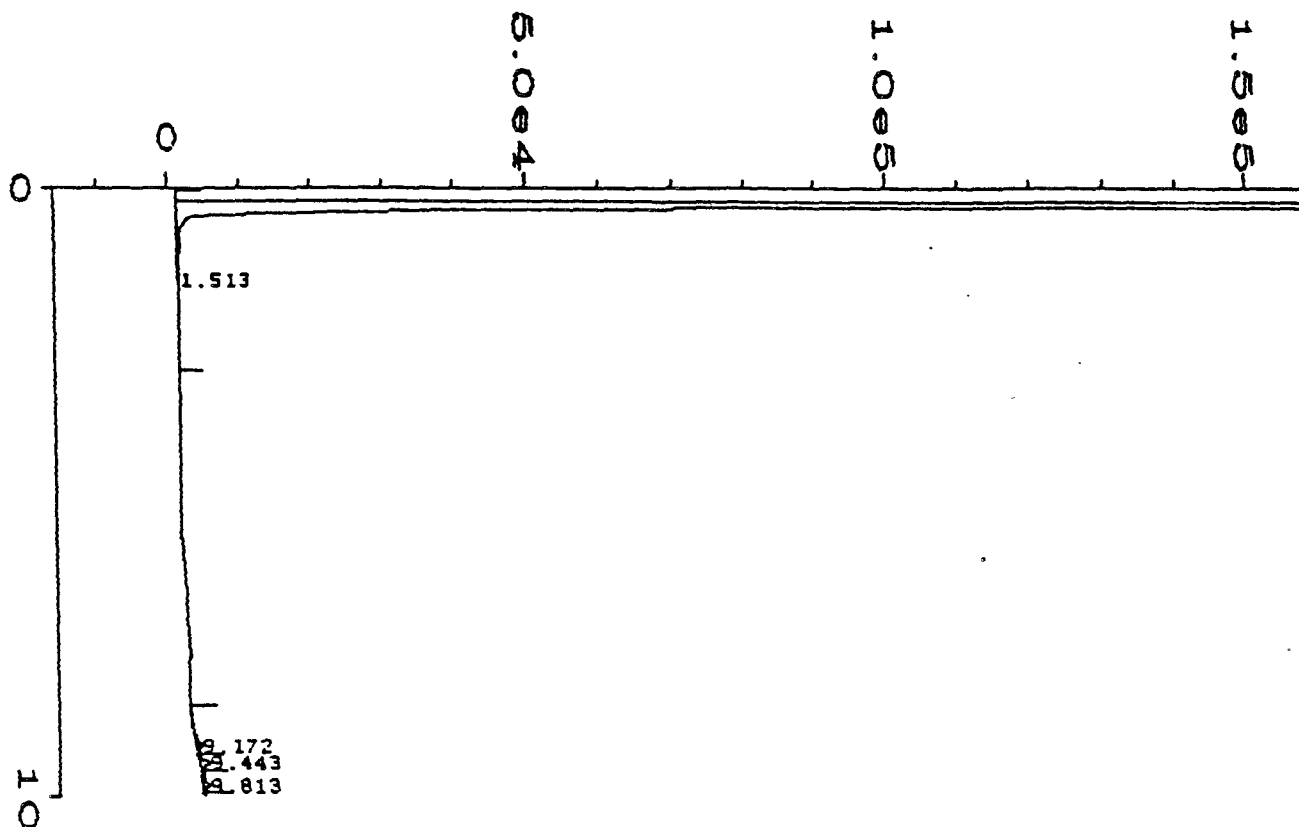
Laboratory (Page 2)

Samples (Page 3)

REVIEWED BY *a* 2/10/93
C. G. G. G.

P081

000006



External Standard Report

Data File Name	: C:\HPCHEM\1\DATA\2-05FEB\2020531A.D	Page Number	: 1
Operator	: CP	Vial Number	:
Instrument	: GC-2	Injection Number	:
Sample Name	: 9302025-01A	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA0106.MT-
Acquired on	: 05 Feb 93 05:28 PM	Analysis Method	: WSPA0106.MT-
Report Created on:	05 Feb 93 05:38 PM	Sample Amount	: 0
Last Recalib on	: 18 SEP 92 01:06 PM	ISTD Amount	:
Multiplier	: 1.91		
Sample Info	: WSPA CAN# 11299 9" Hg -> 5 PSI		

000007

2/17/93
CP

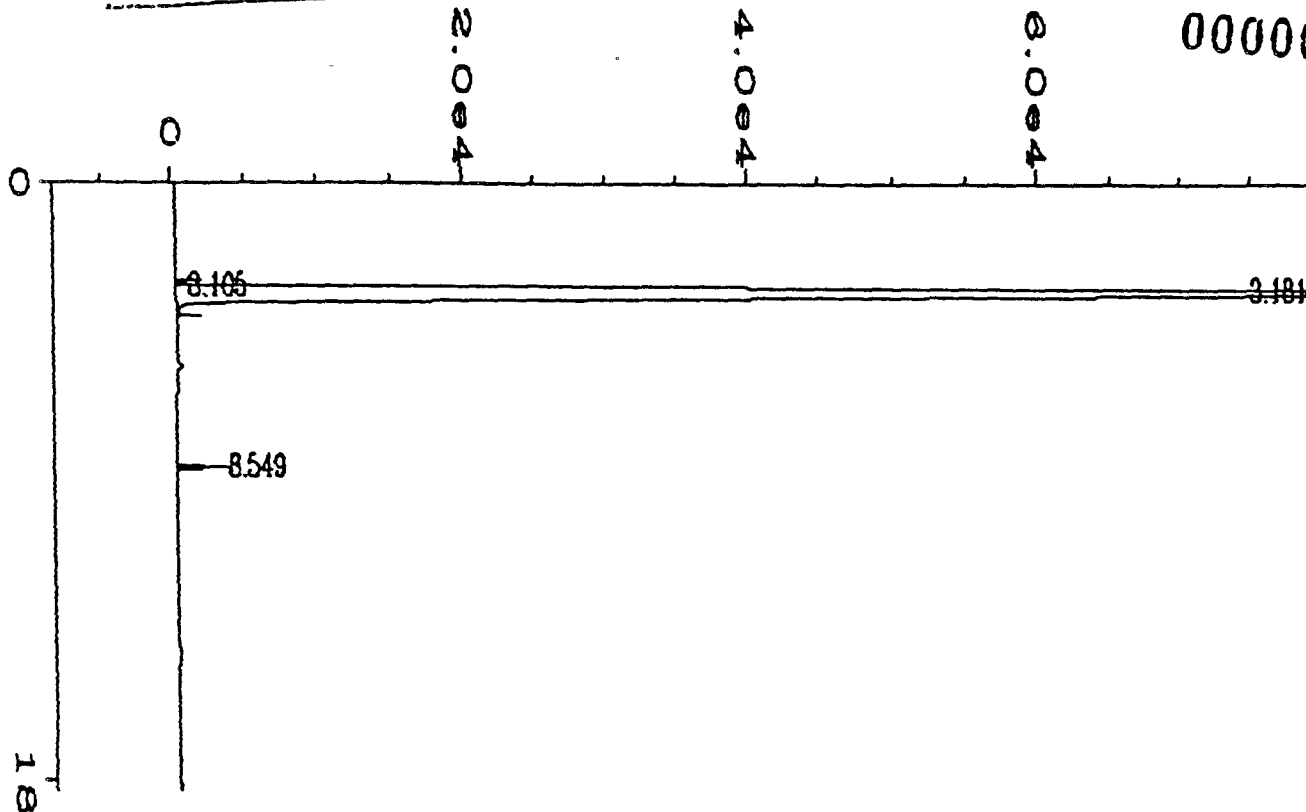
Sig. 1 in C:\HPCHEM\1\DATA\2-05FEB\2020531A.D

Ret Time	Area	Type	Width	Ref#	PPMV	Name
1.513	2983216	BB +	0.000	1	<u>2256.393</u>	THC-PROPANE
9.172	546	BV	0.040		8.489	* uncalibrated *
9.443	10147	PV	0.106		9.893	* uncalibrated *
9.813	9552	VV	0.133		8.560	* uncalibrated *

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P081

DATE 2/10/93
 0.000008



External Standard Report

Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020503A.D	Page Number	: 1
Operator	: AEP	Vial Number	: 2
Instrument	: GC-3	Injection Number	:
Sample Name	: 9302025-01A	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA_TCD.MTH
Acquired on	: 05 Feb 93 10:16 AM	Analysis Method	: WSPA_TCD.MTH
Report Created on	: 05 Feb 93 10:35 AM	Sample Amount	: 0
Last Recalib on	: 22 SEP 92 03:23 PM	ISTD Amount	:
Multiplier	: 1.91		
Sample Info	: WSPA CAN# 11299 9" Hg -> 5 PSI		

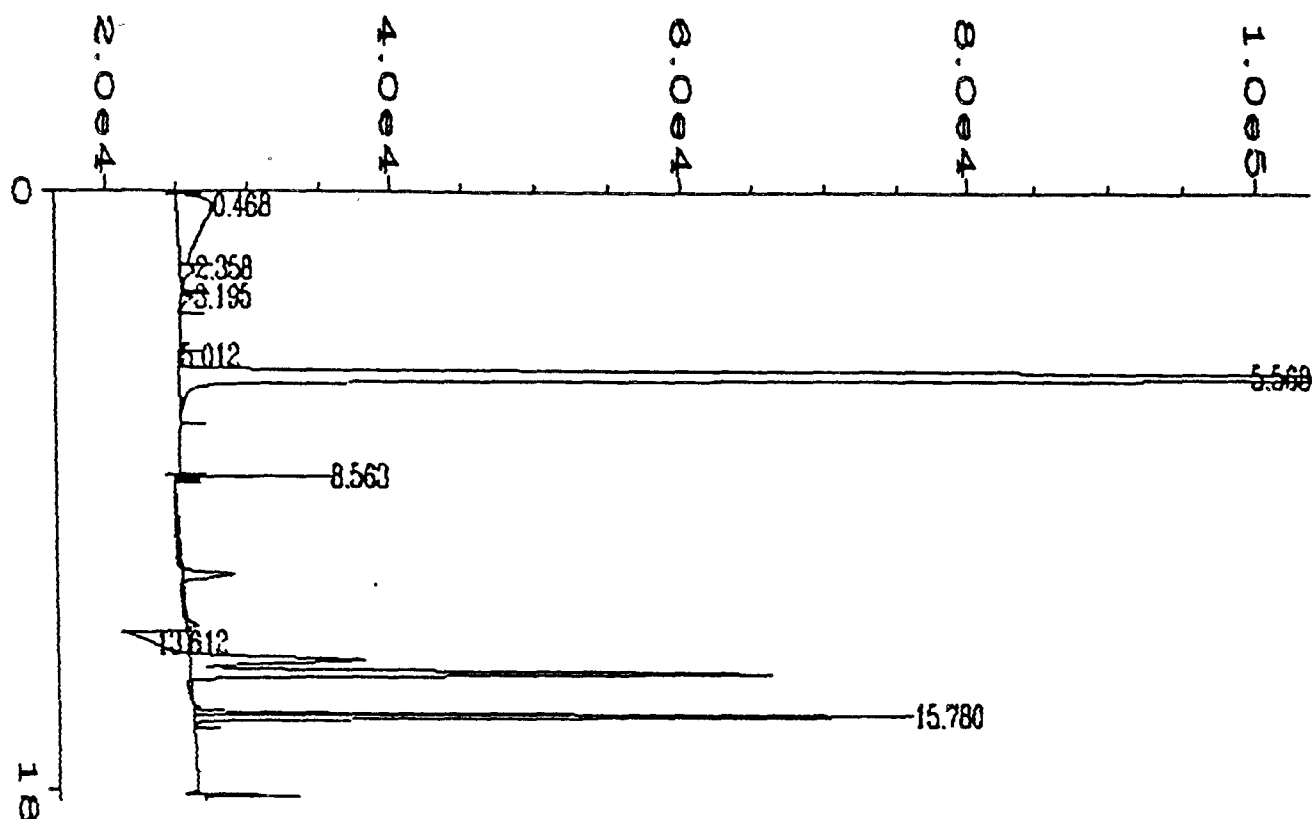
5.046 * not found * 1

Not all calibrated peaks were found

000009

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000010



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External Standard Report

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Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020503B.D	Page Number	: 1
Operator	: AEP	Vial Number	: 2
Instrument	: GC-3	Injection Number	:
Sample Name	: 9302025-01A	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA_TCD.MT-
Acquired on	: 05 Feb 93 10:16 AM	Analysis Method	: WSPA_FID.MT-
Report Created on:	: 05 Feb 93 10:35 AM	Sample Amount	: 0
Last Recalib on	: 22 SEP 92 02:13 PM	ISTD Amount	:
Multiplier	: 1.91		
Sample Info	: WSPA CAN# 11299 9" Hg -> 5 PSI		

Sig. 2 in C:\HPCHEM\2\DATA\3-05FEB\3020503B.D

Ret Time Area Type Width Ref# pmv

Name

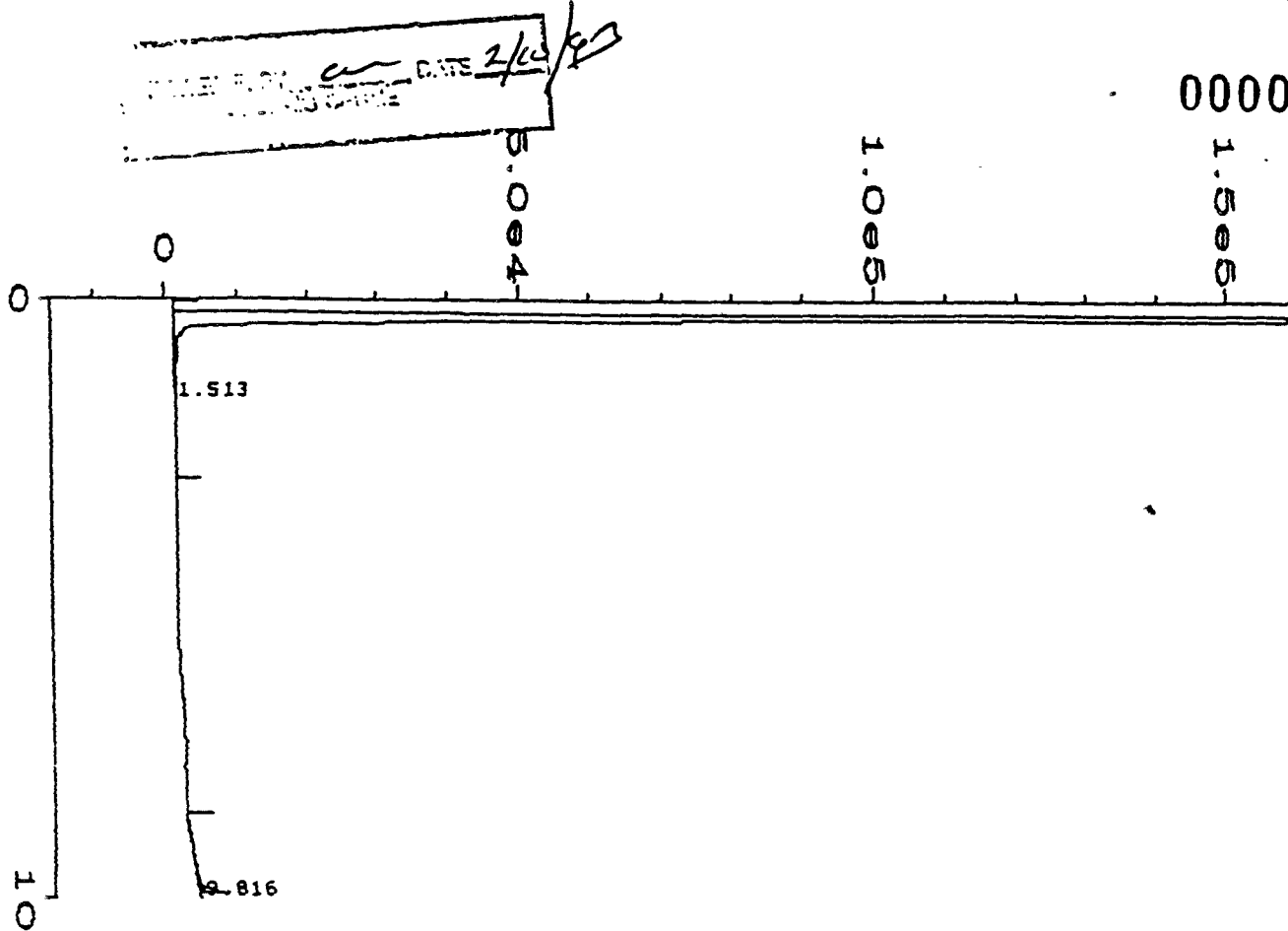
5.568	4086276 PB	0.165	1	5626.600	Methane	2/1/93
13.612	556460 BV +	0.000	1	17.509	Propane	CP
0.468	181826 BV	0.907		347288.2	* uncalibrated *	
2.358	19642 VB	0.269		37517.08	* uncalibrated *	

ata File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020503B.D	000011
perator	: AEP	Page Number : 2
nstrument	: GC-3	Vial Number : 2
ample Name	: 9302025-01A	Injection Number :
un Time Bar Code:		Sequence Line :
quired on	: 05 Feb 93 10:16 AM	Instrument Method: WSPA_TCD.M
eport Created on:	: 05 Feb 93 10:35 AM	Analysis Method : WSPA_FID.M
ast Recalib on	: 22 SEP 92 02:13 PM	Sample Amount : 0
ultiplier	: 1.91	ISTD Amount :

3.195	8485 BB	0.129	16207.03	* uncalibrated *
5.012	1779 BV	0.184	3397.451	* uncalibrated *
8.563	10098 BB S	0.035	19286.69	* uncalibrated *
15.780	304372 VV	0.104	581349.8	* uncalibrated *

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P084 Dup



000012

External Standard Report

Data File Name	: C:\HPCHEM\1\DATA\2-05FEB\2020532A.D	Page Number	: 1
Operator	: CP	Vial Number	:
Instrument	: GC-2	Injection Number	:
Sample Name	: 9302025-01BDUP	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA0106.MT
Acquired on	: 05 Feb 93 05:45 PM	Analysis Method	: WSPA0106.MT
Report Created on:	05 Feb 93 05:55 PM	Sample Amount	: 0
Last Recalib on	: 18 SEP 92 01:06 PM	ISTD Amount	:
Multiplier	: 1.91		
Sample Info	: WSPA CAN# 11299 9" Hg -> 5 PSI		

000013

2/9/93
CP

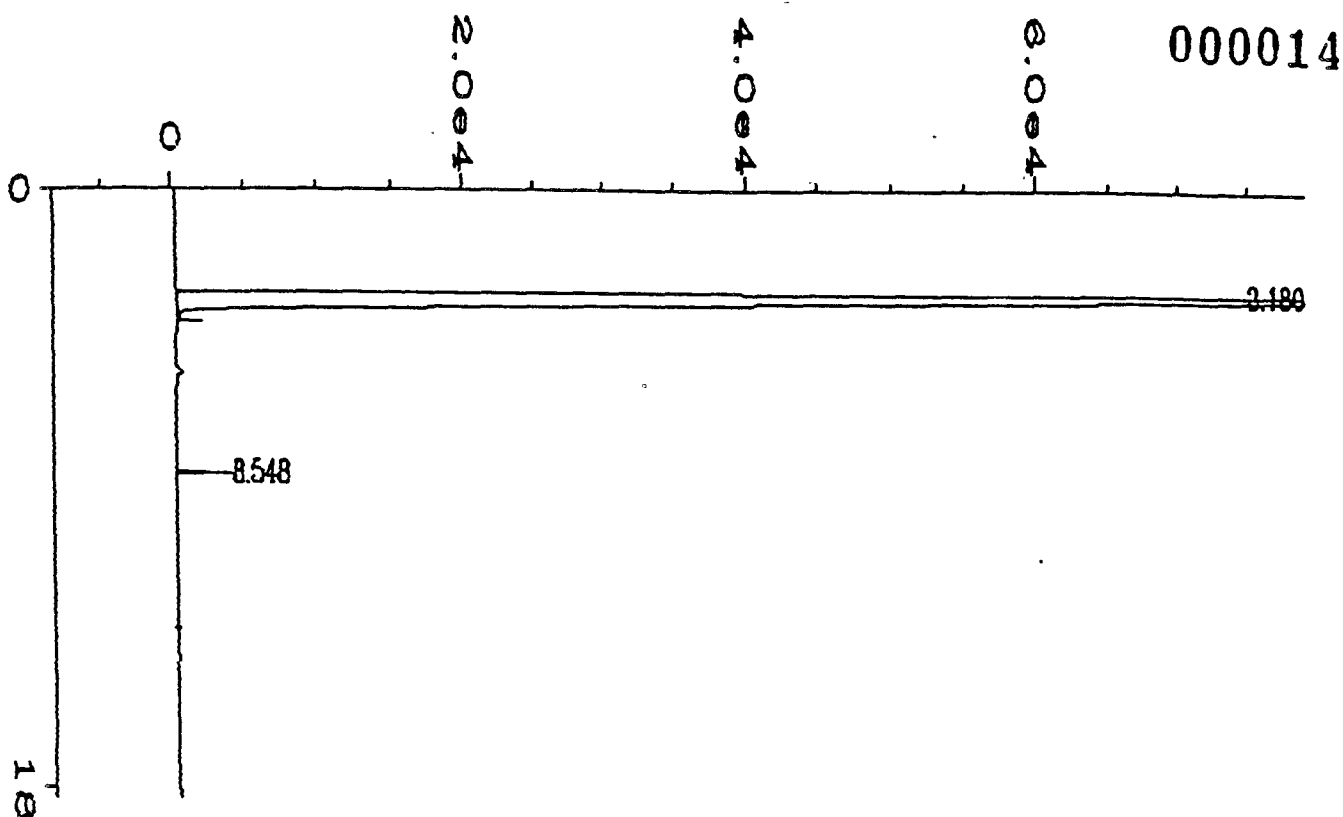
Sig. 1 in C:\HPCHEM\1\DATA\2-05FEB\2020532A.D

Ret Time	Area	Type	Width	Ref#	PPMV	Name
1.513	2954807	BB +	0.000	1	<u>2233.292</u>	THC-PROPANE
9.816	5014	BV	0.093		4.424	* uncalibrated *

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DATE 2/9/93

P081 Dup



External Standard Report

Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020504A.D	Page Number	: 1
Operator	: AEP	Vial Number	: 2
Instrument	: GC-3	Injection Number	:
Sample Name	: 9302025-01B	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA_TCD.MTH
Acquired on	: 05 Feb 93 10:43 AM	Analysis Method	: WSPA_TCD.MTH
Report Created on:	: 05 Feb 93 11:02 AM	Sample Amount	: 0
Last Recalib on	: 22 SEP 92 03:23 PM	ISTD Amount	:
Multiplier	: 1.91		
Sample Info	: WSPA CAN# 11299 9" Hg -> 5 PSI		
	DUPLICATE SAMPLE		

5.046 * not found *

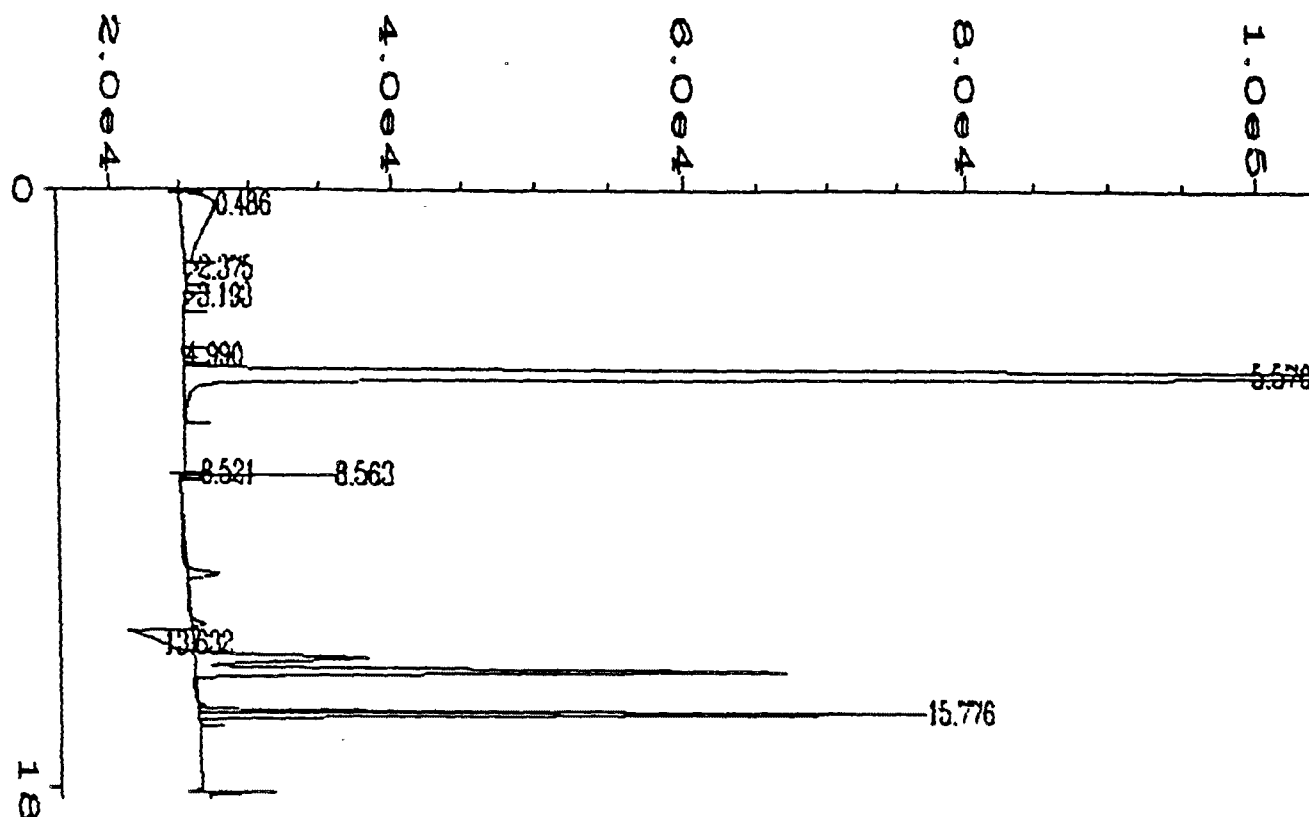
1

ot all calibrated peaks were found

000015

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000016



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External Standard Report

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Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020504B.D	Page Number	: 1
Operator	: AEP	Vial Number	: 2
Instrument	: GC-3	Injection Number	:
Sample Name	: 9302025-01B	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA_TCD.MT-
Acquired on	: 05 Feb 93 10:43 AM	Analysis Method	: WSPA_FID.MT-
Report Created on:	: 05 Feb 93 11:02 AM	Sample Amount	: 0
Last Recalib on	: 22 SEP 92 02:13 PM	ISTD Amount	:
Multiplier	: 1.91		
Sample Info	: WSPA CAN# 11299 9" Hg -> 5 PSI		
	DUPLICATE SAMPLE		

5.570	4169749 BB	0.165	1	<u>5741.439</u> Methane	2/9/93
13.632	549663 BV +	0.000	1	17.295 Propane	CP
0.486	179720 BV	0.883		343265.3 * uncalibrated *	
2.375	18245 VV	0.255		34848.46 * uncalibrated *	

Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\30205048.D		000017
Operator	: AEP	Page Number	: 2
Instrument	: GC-3	Vial Number	: 2
Sample Name	: 9302025-018	Injection Number	:
Run Time Bar Code:		Sequence Line	:
Acquired on	: 05 Feb 93 10:43 AM	Instrument Method	: WSPA_TCD.M
Report Created on	: 05 Feb 93 11:02 AM	Analysis Method	: WSPA_FID.M
Last Recalib on	: 22 SEP 92 02:13 PM	Sample Amount	: 0
Multiplier	: 1.91	ISTD Amount	:

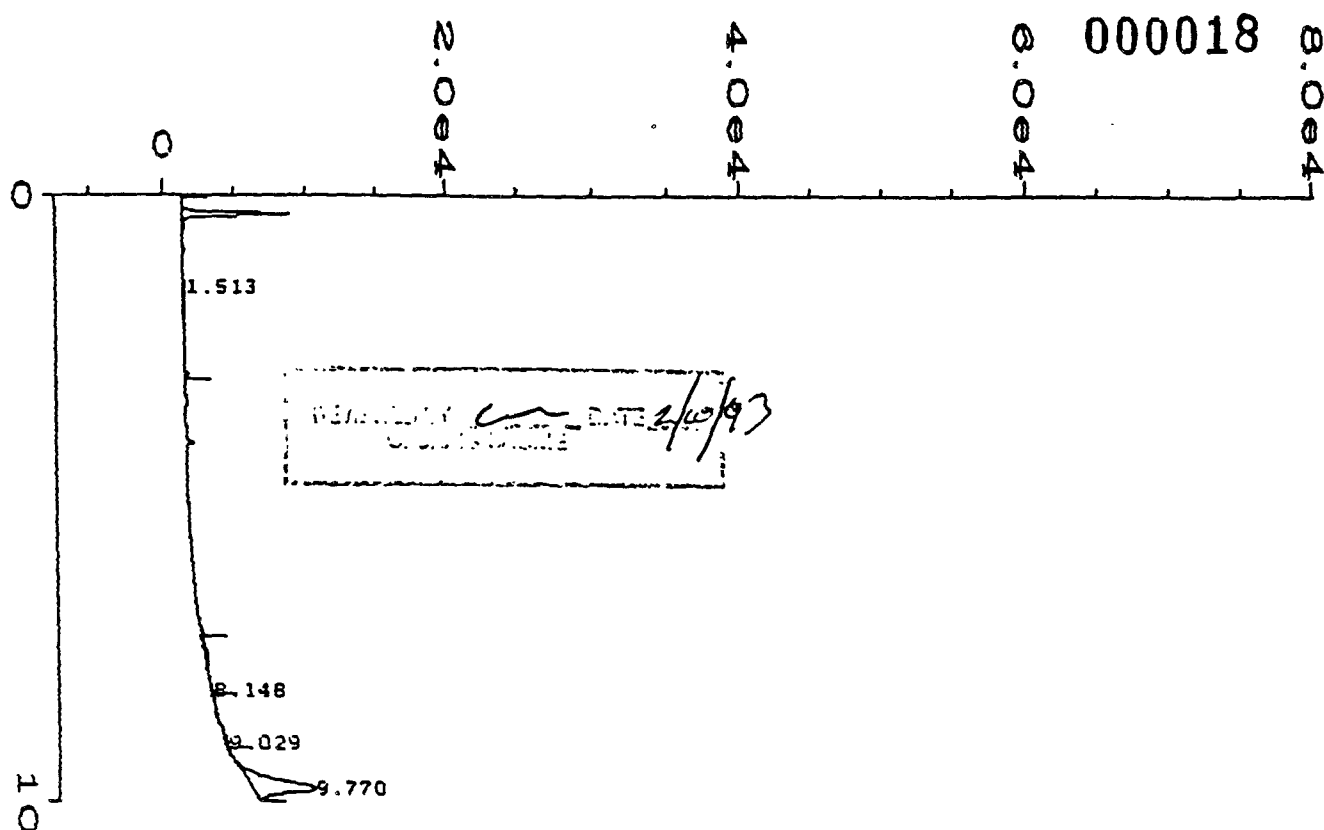
3.193	9535 BV	0.136	18211.07 * uncalibrated *
4.990	1403 BB	0.151	2680.681 * uncalibrated *
8.521	741 BH S	0.012	1415.045 * uncalibrated *
8.563	8688 HB S	0.013	16594.57 * uncalibrated *
15.776	315018 VV	0.249	601685.2 * uncalibrated *

=====

4.990 * not found *
13.602 * not found *

1
1

Methane
Propane



External Standard Report

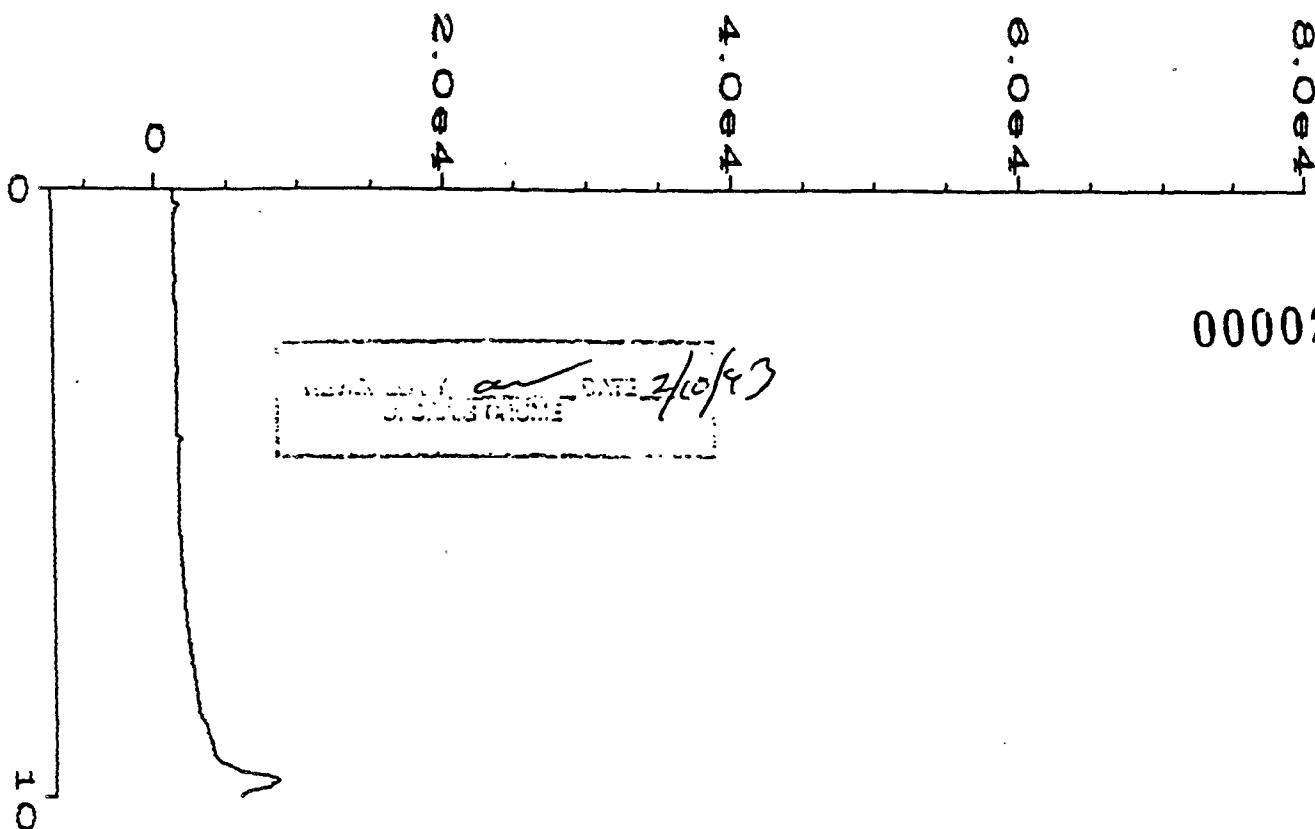
Data File Name	: C:\HPCHEM\1\DATA\2-05FEB\2020501.D	Page Number	: 1
Operator	: AEP	Vial Number	:
Instrument	: GC-2	Injection Number	:
Sample Name	: #42-81	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA0106.MT
Acquired on	: 05 Feb 93 08:48 AM	Analysis Method	: WSPA0106.MT
Report Created on	: 05 Feb 93 08:58 AM	Sample Amount	: 0
Last Recalib on	: 18 SEP 92 01:06 PM	ISTD Amount	:
Multiplier	: 1		
Sample Info	: PROPANE STD (11.4 PPMV)		

000019

Sig. 1 in C:\HPCHEM\1\DATA\2-05FEB\2020501.D

Ret Time	Area	Type	Width	Ref#	PPMV	Name
1.513	23191	BB +	0.000	1	12.291	THC-PROPANE (12.29/11.4) m/z = 107%
8.148	3249	PV	0.629		1.524	* uncalibrated *
9.029	2118	PV	0.137		0.994	* uncalibrated *
9.770	66181	PBA	0.225		31.052	* uncalibrated *

===== ACP 2/5/4 =====



000020

External Standard Report

Data File Name	: C:\HFCHEM\1\DATA\2-05FEB\2020503.D	Page Number	: 1
Operator	: AEP	Vial Number	:
Instrument	: GC-2	Injection Number	:
Sample Name	: LAB BLANK	Sequence Line	:
Run Time Bar Code:		Instrument Method:	WSPA0106.MT-
Acquired on	: 05 Feb 93 09:27 AM	Analysis Method	: WSPA0106.MT
Report Created on:	05 Feb 93 09:37 AM	Sample Amount	: 0
Last Recalib on	: 18 SEP 92 01:06 PM	ISTD Amount	:
Multiplier	: 1		
Sample Info	:		

Fig. 1 in C:\HPCHEM\1\DATA\2-05FEB\2020503.D

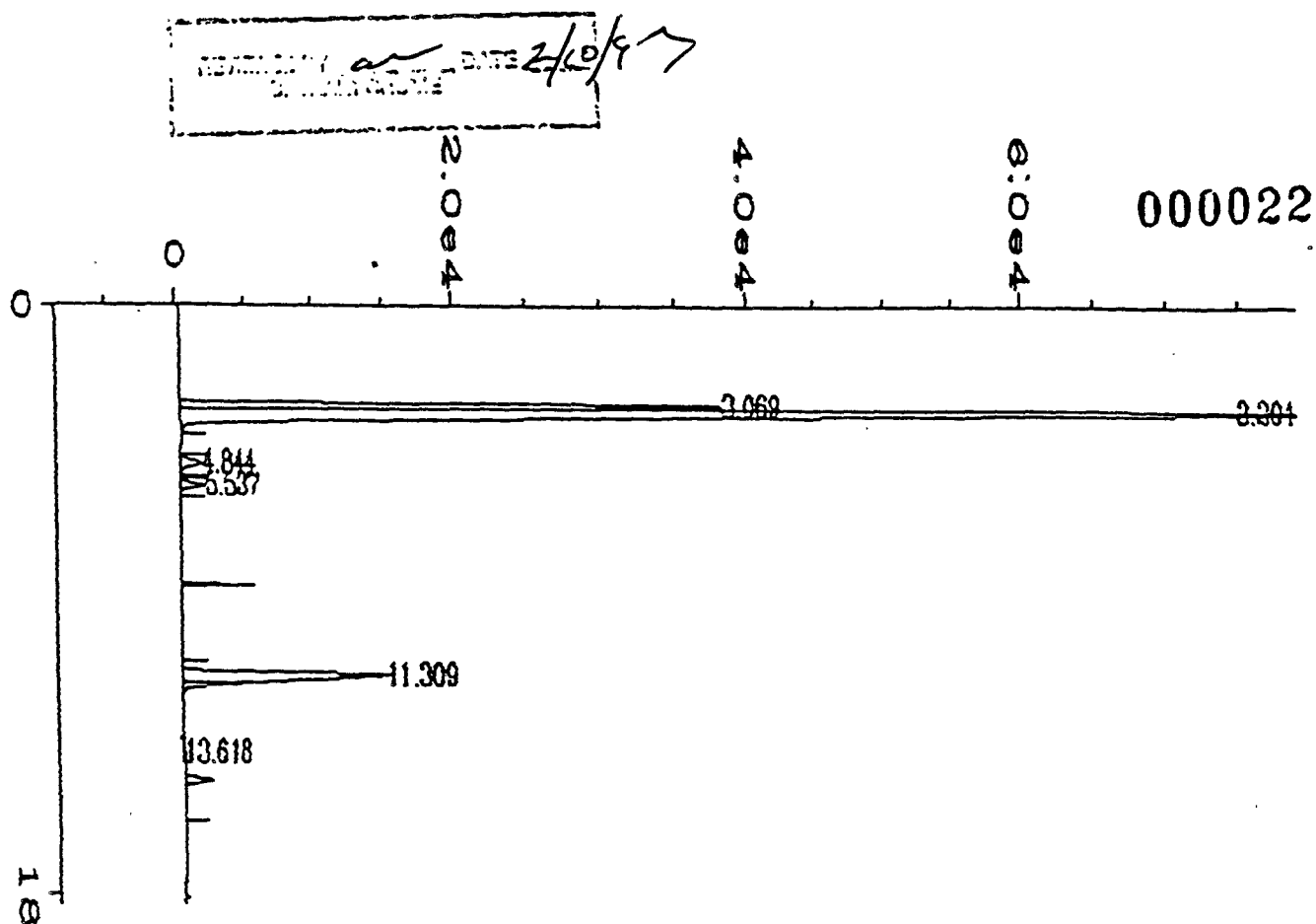
2/5/93
CP

Ret Time	Area	Type	Width	Ref#	PPMV	Name
0.210	* not found *			1	(ND)	THC-PROPANE

Not all calibrated peaks were found

000021

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External Standard Report

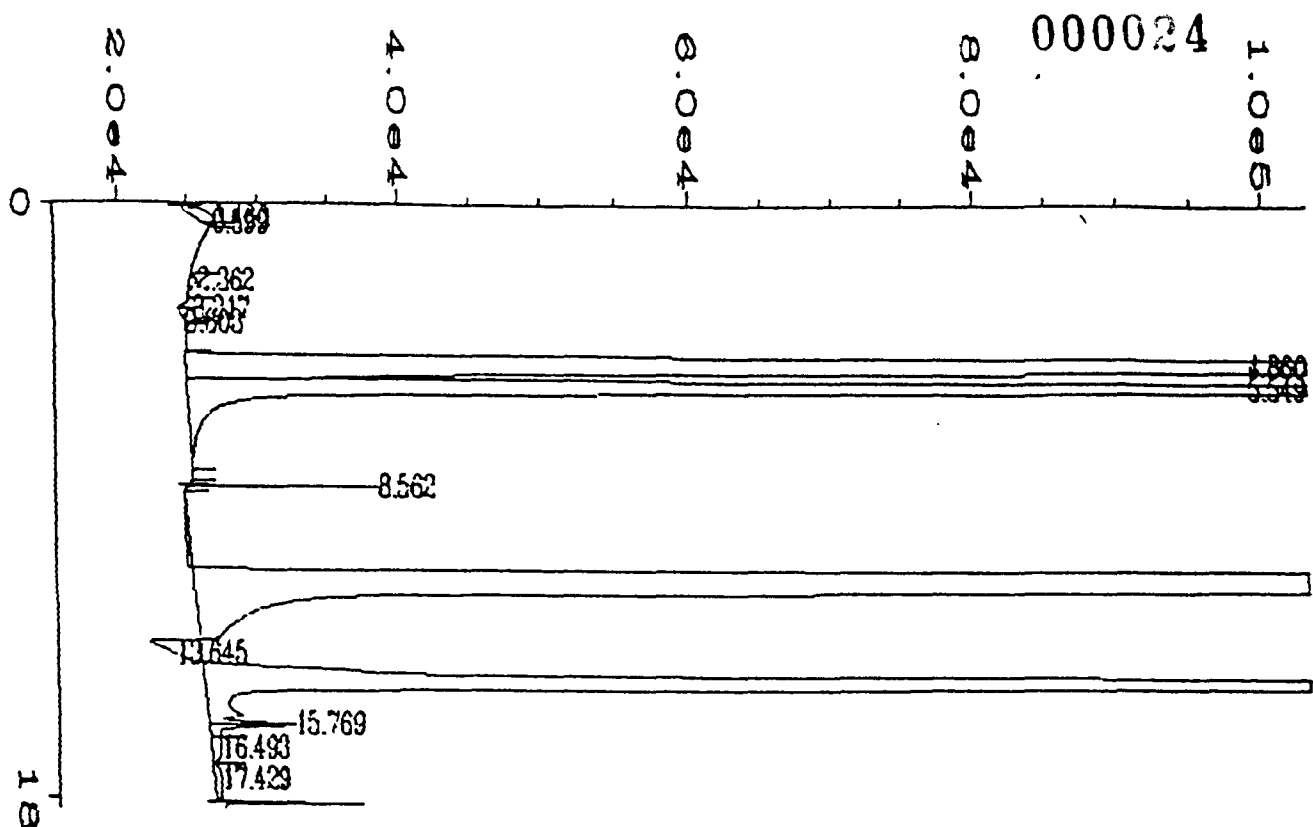
Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020501A.D	Page Number	: 1
Operator	: AEP	Vial Number	: 2
Instrument	: GC-3	Injection Number	:
Sample Name	: 9106-156-1	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA_TCD.MT
Acquired on	: 05 Feb 93 08:55 AM	Analysis Method	: WSPA_TCD.MT
Report Created on	: 05 Feb 93 09:13 AM	Sample Amount	: 0
Last Recalib on	: 22 SEP 92 03:23 PM	ISTD Amount	:
Multiplier	: 1		
Sample Info	: SCOTT ATM GAS STD		

5.046 * not found *

1

not all calibrated peaks were found

000023



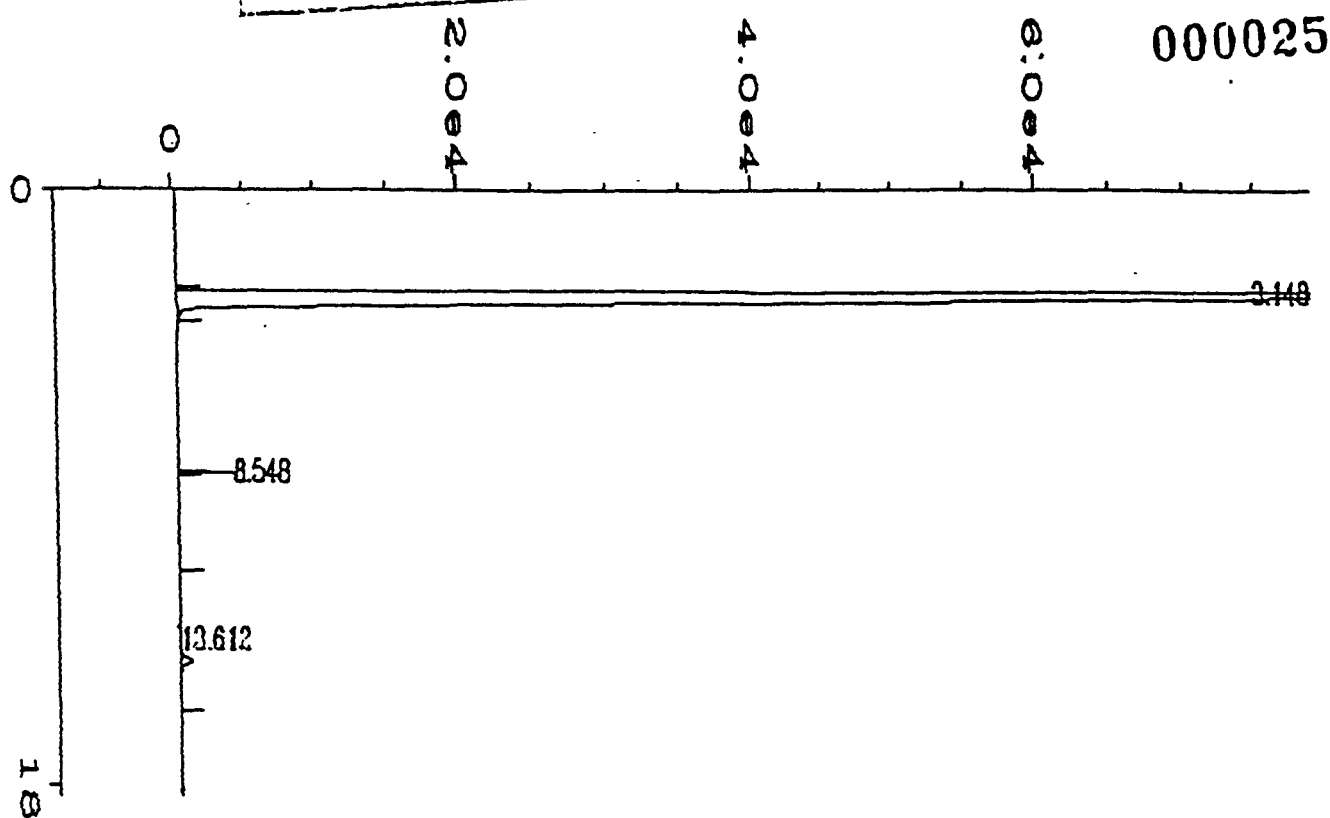
External Standard Report

Data File Name : C:\HPCHEM\2\DATA\3-05FEB\3020501B.D
 Operator : AEF Page Number : 1
 Instrument : GC-3 Vial Number : 2
 Sample Name : 9106-156-1 Injection Number :
 Run Time Bar Code: Sequence Line :
 Acquired on : 05 Feb 93 08:55 AM Instrument Method: WSPA_TCD.MT
 Report Created on: 05 Feb 93 09:18 AM Analysis Method : WSPA_FID.MT
 Last Recalib on : 22 SEP 92 02:13 PM Sample Amount : 0
 Multiplier : 1 ISTD Amount :

Sig. 2 in C:\HPCHEM\2\DATA\3-05FEB\3020501B.D

Ret Time Area Type Width Ref# ppmv Name

 5.549 1.40462E+007 VB 0.165 1 10119.90 Methane 19900 = 102%
 13.645 1.84991E+008 BV + 0.000 1 39808.23 Propane
 0.460 29366 BV 0.319 29366.36 * uncalibrated *
 0.599 3018 VB 0.085 3017.657 * uncalibrated *
 2.362 9745 BV 0.229 9745.093 * uncalibrated *
 3.217 10825 PV 0.151 10825.22 * uncalibrated *
 3.603 104 VB 0.033 104.462 * uncalibrated *
 4.860 1.39101E+007 BV 0.228 1.4E+007 * uncalibrated *
 8.562 13848 BV S 0.035 13848.04 * uncalibrated *
 15.769 35447 VV 0.098 35447.45 * uncalibrated *
 16.493 30152 VV 0.606 30151.93 * uncalibrated *
 17.429 26914 VV 0.818 26913.90 * uncalibrated *



External Standard Report

Data File Name	: C:\HPCHEM\2\DATA\3-05FEB\3020502A.D	Page Number	: 1
Operator	: AEP	Vial Number	: 2
Instrument	: GC-3	Injection Number	:
Sample Name	: LAB BLANK	Sequence Line	:
Run Time Bar Code:		Instrument Method	: WSPA_TCD.MT
Acquired on	: 05 Feb 93 09:50 AM	Analysis Method	: WSPA_TCD.MT
Report Created on	: 05 Feb 93 10:08 AM	Sample Amount	: 0
Last Recalib on	: 22 SEP 92 03:23 PM	ISTD Amount	:
Multiplier	: 1		
Sample Info	:		

5.046 * not found *

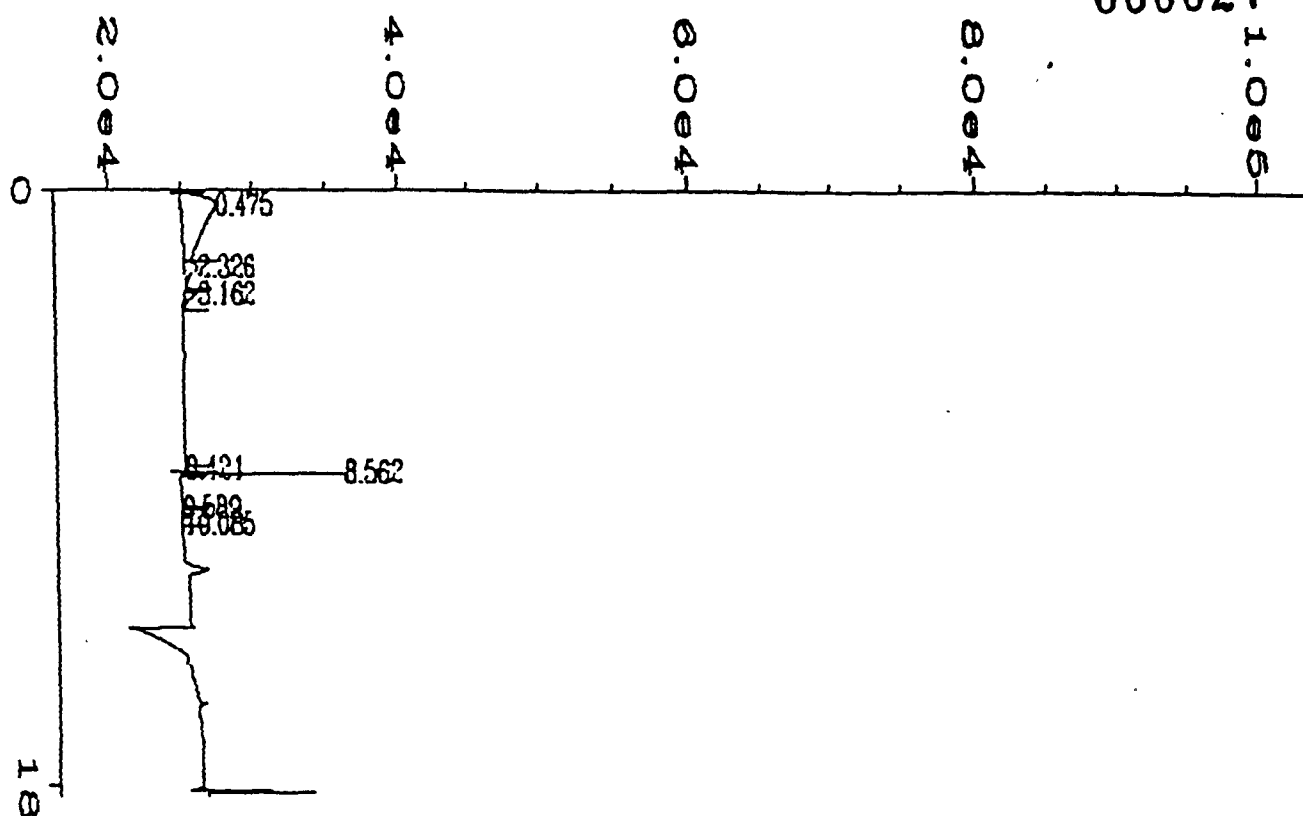
1

Not all calibrated peaks were found

000026

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000027



External Standard Report

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Data File Name      : C:\HPCHEM\2\DATA\3-05FEB\3020502B.D
Operator           : AEP
Instrument          : GC-3
Sample Name        : LAB BLANK
Run Time Bar Code  :
Acquired on        : 05 Feb 93 09:50 AM
Report Created on  : 05 Feb 93 10:09 AM
Last Recalib on    : 22 SEP 92 02:13 PM
Multiplier         : 1
Sample Info        :
Page Number        : 1
Vial Number        : 2
Injection Number    :
Sequence Line      :
Instrument Method   : WSPA_TCD.MT
Analysis Method     : WSPA_FID.MT
Sample Amount       : 0
ISTD Amount        :
  
```

12.602 * not found *
0.475 172632 BV 0.972
2.326 19085 VB 0.262

1

(N)
Propane
172632.2 * uncalibrated *
19084.57 * uncalibrated *

2/9/93
CP

Data File Name : C:\HPCHEM\2\DATA\3-05FEB\30205028.D

Operator : AEP

Page Number

: 2

Instrument : GC-3

Vial Number

: 000028

Sample Name : LAB BLANK

Injection Number :

Run Time Bar Code:

Sequence Line :

Acquired on : 05 Feb 93 09:50 AM

Instrument Method: WSPA_TCD.M

Report Created on: 05 Feb 93 10:09 AM

Analysis Method : WSPA_FID.M

Last Recalib on : 22 SEP 92 02:13 PM

Sample Amount : 0

Multiplier : 1

ISTD Amount :

3.162 10173 BV 0.142
8.421 431 BH S 0.829
8.562 9788 BV T 0.023
9.589 22 BV T 0.022
10.085 72 PV T 0.078

10172.83 * uncalibrated *
431.202 * uncalibrated *
9787.976 * uncalibrated *
21.932 * uncalibrated *
71.667 * uncalibrated *

Not all calibrated peaks were found

=====

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-454/R-93-033		2.	3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Independent Quality Assurance Of Refinery Fugitive Testing by Western States Petroleum Association - Final Audit Report		5. REPORT DATE September 1993		
		6. PERFORMING ORGANIZATION CODE		
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.		
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT NO.		
		11. CONTRACT/GRANT NO.		
12. SPONSORING AGENCY NAME AND ADDRESS Office of Air Quality Planning and Standards Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED		
		14. SPONSORING AGENCY CODE		
15. SUPPLEMENTARY NOTES				
16. ABSTRACT This report provides detailed results of field and laboratory performance audits for the Western States Petroleum Association - sponsored fugitives testing conducted December 1992 and January 1993 in four California refineries.				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Refinery Fugitive Emissions				
18. DISTRIBUTION STATEMENT Unclassified		19. SECURITY CLASS (This Report)		21. NO. OF PAGES 170
		20. SECURITY CLASS (This page)		22. PRICE