

SECTION 3.0

FIELD TESTING

The field tests conducted on this program provided a realistic assessment of the organic emissions from stationary sources in the Basin. From the outset the experimental plans and procedures were coordinated with numerous government and industry associations to benefit from the advice of other researchers, avoid duplication, identify representative sources and insure high data quality. In that standard measurement procedures for organic emissions are as yet unestablished, KVB felt it important to obtain a consensus of those active in the field in developing those plans and procedures. ARB, EPA, SCAQMD and WOGA were the agencies most involved in this coordination.

The following sections present the experimental methods employed, an evaluation of data quality by an independent consulting firm, and a discussion of test results.

3.1 APPROACH

The number of stationary sources of organic emissions in the Basin is huge. The objective of the test program was to provide as much information as possible to characterize the organic emissions from these sources. An initial goal of 600 to 800 samples was established.

The EPA has categorized pollution sources using a system of Source Classification Codes (SCC). The sources in the Basin account for approximately 350 SCC numbers. For each of these an emission factor and an emission profile was required. In many cases emission factor data were available. Very little data were available on which to base emission profiles. Therefore, the major emphasis was given to obtaining emission profile data with emission flow rates taken whenever possible as a routine part of the test.

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From the preliminary inventory it was determined that petroleum production, refining and marketing accounted for 50% of the emissions in the Basin and solvent usage accounted for 40%. Major plants were identified in each source types such as refineries, oil fields, printing, automobile, and rubber plants. Special sources like a steel mill, landfill, chemical plant, etc. were also listed.

Industry was found to be cautious and concerned about this testing. They often requested a full technical briefing. The petroleum industry used WOGA as an agent to monitor and control their participation. As a result of this concern a great deal of engineering time was required to gain entry to plants for testing. Even after tests were completed, there were return visits to review data. In the case of WOGA, formal presentations of plans and results were made for each site tested. On one oil field test, WOGA engaged a consultant to take samples along with KVB for comparative analyses. (Good agreement was obtained which added to the credibility of the program data as indicated in Section 3.3.)

To minimize the amount of coordination work, KVB took the approach of testing as many different types of sources as possible at each plant visited consistent with the total number of tests budgeted for that source or device type.

The test crew consisted of two engineers and two technicians. On major tests all four worked together. These major tests required from two to ten working days at each plant. In order to complete sampling of all devices on the SCC listing, occasionally the crew divided into two-man teams to collect two or four samples on a special device or process that could not be obtained during a major test.

As an attempt to characterize the fugitive emissions from a refinery KVB engaged AeroVironment Inc. (AV) to measure upwind and downwind and predict the refinery emissions by diffusion modelling. At the same time KVB was in the refinery measuring the source emissions. This test is summarized in Section 3.4 and a complete report is included in the Appendix.

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All GC/MS analyses of the field samples were conducted at Analytical Research Laboratories Inc. (ARLI) who also measured aldehydes and total organic content. A two man level of effort in the laboratory supported the field operation and was the limiting element in the analytical sequence. KVB performed some total organic measurements using an FID, and AV also performed sample analysis on a Beckman 6500 GC. However, all speciation for emission profile purposes were performed by ARLI.

In all, 618 field samples were taken by KVB and analyzed at ARLI or KVB. Approximately 50 samples were taken by AV and analyzed at ARLI or AV. In addition, approximately 50 GC/MS runs were conducted by ARLI in developing the program methodology and evaluating the data quality.

A summary of the plants and device types tested was presented in Section 1.0.

3.2 METHODOLOGY

Sampling and analysis methodology described in this section was developed during the Phase I period of the program. The objectives were to develop techniques and equipment as necessary to (1) determine the hydrocarbon emission rate from both ducted and fugitive sources, (2) collect and preserve representative samples of these emissions and (3) analyze the samples for their organic chemical composition. The general approach to emission rate determination was to either measure the emission rate or to determine it by calculations from process data or by experiment. From sources with stacks, emissions were determined by pitot traverse. Various techniques were used on fugitive emission sources. Where information was available on the amount of organic material lost from a process, this was used to determine emissions. Where the emissions were due to leaks or spills or other types of fugitive emissions, attempt was made to either measure or estimate those emissions. In some instances, special experiments were conducted to obtain estimates of emission rates. An example of the type of experiments that were conducted is the determination of the amount of solvent which was emitted from an architectural coating as it was drying or curing. KVB's tests indicated that as much as 30 to 40 percent of the solvent is permanently retained in the paint after it is cured. Other experiments included emissions from open ponds, asphalt paving, auto gas tank filling, and domestic solvents.

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For analytical purposes, samples of emission gases were collected in the following type of containers:

- . tubes filled with activated charcoal
- . borosilicate glass bottles
- . Tedlar bags
- . glass bulb containing 1% sodium bisulphite solution (aldehyde determinations).

The charcoal sorbent tubes were used to collect aliphatic organic compounds with boiling points above that of n-pentane and all other compounds from C₁ - up. The gas collection bottles and bags were used to collect aliphatic compounds with boiling points below that of n-pentane. On most major sources, a combination of sorbent tubes and either bags or bottles were used. Bags or bottles were used for the entire compound range when utilized for grab sampling.

All samples were analyzed using gas chromatography (GC) and mass spectrometry (MS) techniques on a tandem GC/MS apparatus. The bottle or bag grab samples were introduced directly into the apparatus while the samples collected on charcoal were first extracted with carbon disulfide. Because of the survey nature of the program only those GC peaks which contributed at least 1% of the total hydrocarbons were identified unless a substance of special importance was suspected to exist in the sample.

Presented in the following sections are a detailed description of the field test and laboratory equipment, some explanation for their selection, the results of test runs using this equipment, and a detailed description of test procedures and data reduction techniques followed during the program.

3.2.1 Sampling

A. Equipment Description--

1. Sampling train--KVB designed and built two identical portable sampling units that could:

- . measure stack gas temperature and velocity
- . filter out particulates larger than 2 microns
- . collect samples in sorbent tubes, glass or polybags.

Figure 3-1 illustrates the assembled sampling trains. Materials of construction were as follows:

- . all metal components were stainless steel
- . seals were Viton or Teflon
- . containers were borosilica glass
- . flexible connections were latex rubber of minimal length.

The general flow diagram, Figure 3-2, illustrates all components of the assembly which are available to be switched into several sampling modes to conform to requirements dictated by the source to be tested. The components are:

- . a sample nozzle
- . a filter holder with 2.5 micron pore size glass fiber filter
- . a filter and line heater and thermostatic control
- . an impinger train containing LiOH crystals
- . a borosilicate (Pyrex) gas collection bottle
- . a sorbent tube train with thermometer and vacuum gauge
- . a Brooks flowmeter with needle valve flow control
- . various interior and exterior valves and connectors as indicated in Figure 3-2
- . a meter connection to PD gas meter
- . a pressure gauge and pyrometer for use with a pitot tube.

The above system was unitized within a portable aluminum closure. Its interior arrangement permitted significant freedom of directional orientation for rigging convenience. In addition to the packaged sampling unit, the following additional test equipment was used:

- . two pitot tubes for velocity measurements
- . two thermocouples for stack temperature measurements
- . three dry gas meters
- . additional glass sorbent tubes containing charcoal sorbent
- . two Gast vacuum pumps
- . six Spectrex diaphragm pumps
- . two squeeze bulb type hand pumps

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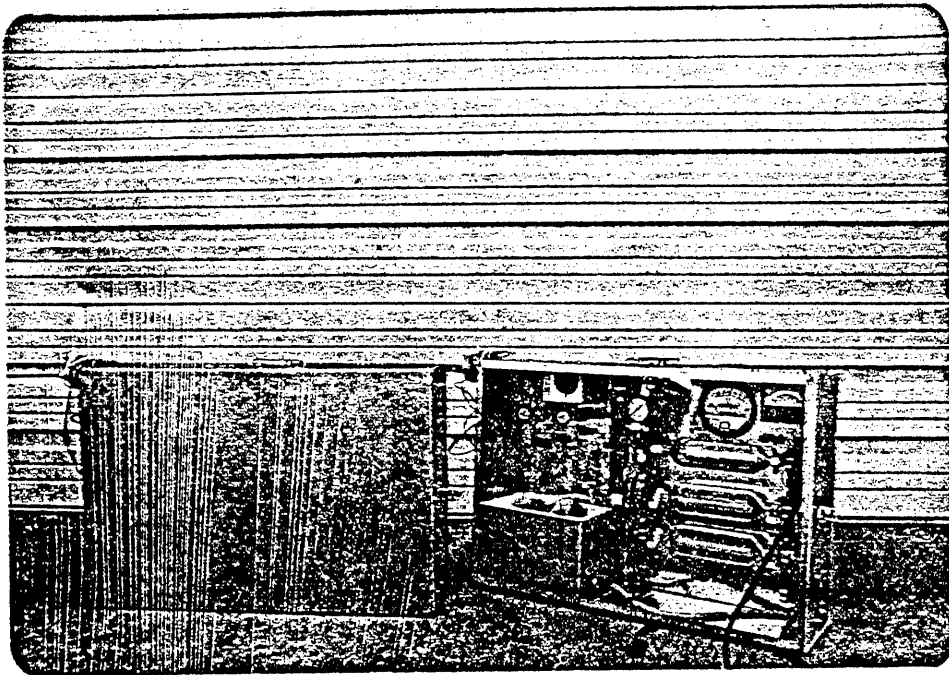
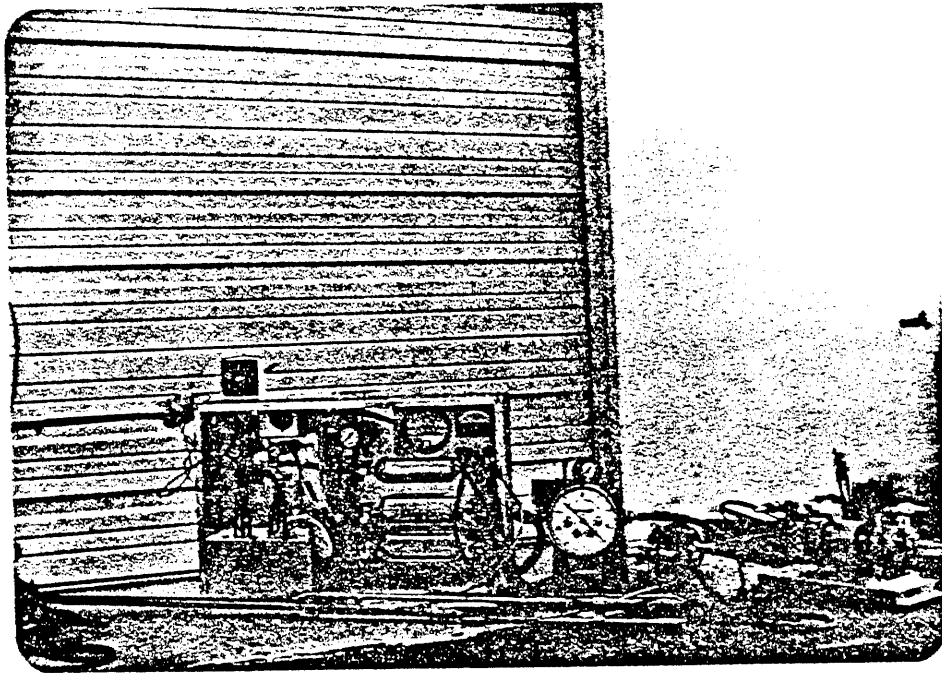


Figure 3-1. KVB hydrocarbon sampling trains.

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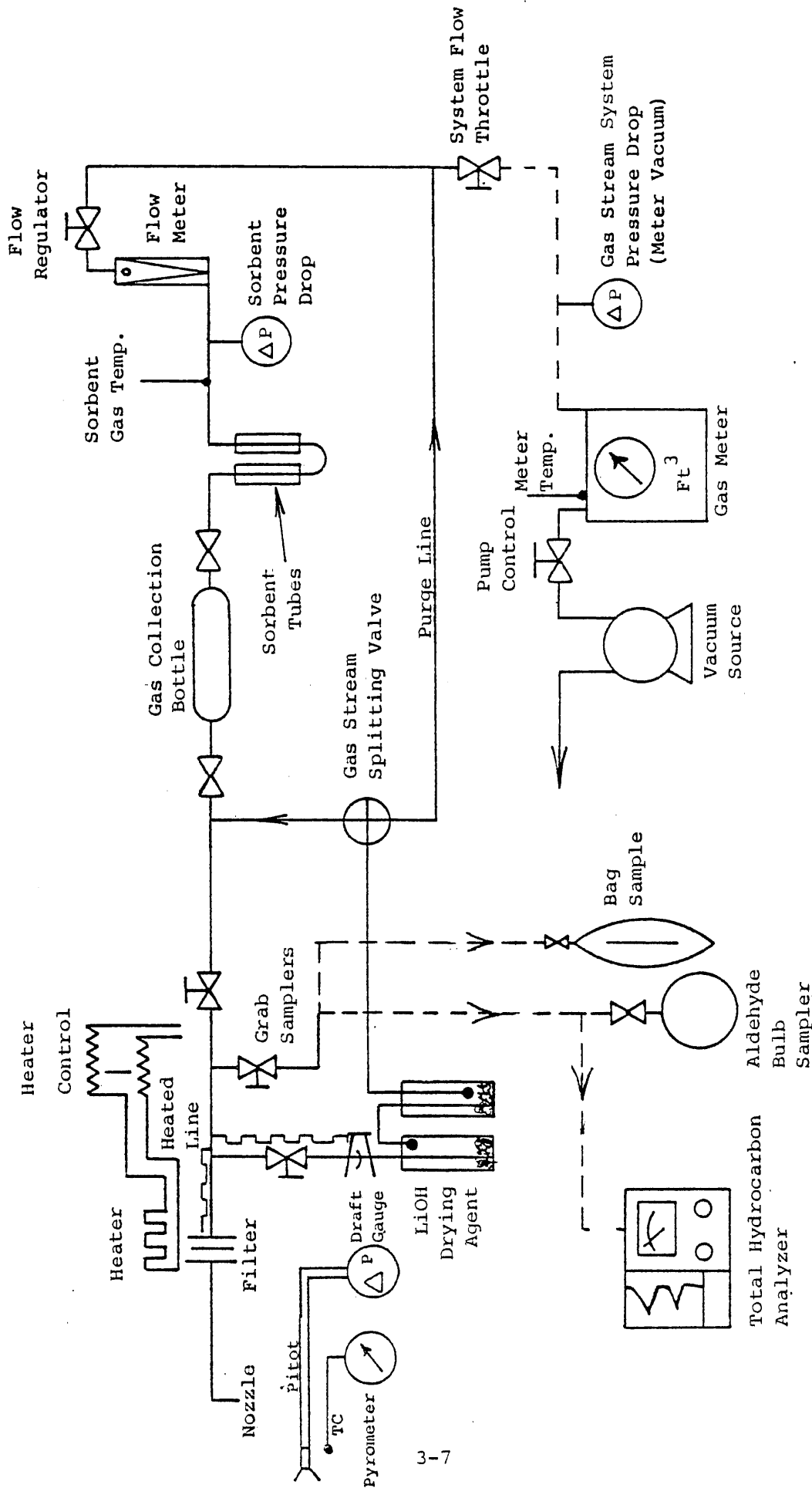


Figure 3-2. Complete organic sampling train as set up for a hot combustion source (> 180 °F) (Mode 1 in Table 3-5).

- . an Orsat analyzer for CO, CO₂, O₂, and N₂ determination
- . a Draeger gas detector with detector tubes
- . a TLV sniffer with recorder (a total hydrocarbon tester with 0-10,000, 0-1,000, and 0-100 ppm range)
- . an anemometer
- . thermometers of various ranges
- . liquid sampling equipment, graduated cylinders, and funnels
- . rigging tools
- . two VW micro buses as support vehicles for equipment transportation.

Typical test setup and configurations are discussed later under sampling methods.

2. Sampling Train Selection--

a. LiOH Impinger--The lithium hydroxide in the dry impinger train was selected for use based on experience gained on the Apollo space capsule. Initially an ice water impinger was considered for moisture, NO_x, SO_x, and CO removal. The problem with this approach was that it was felt that the alcohols and some other oxygenates would be highly water soluble and would not be easily separated for analysis. (The impinger solution was analyzed for hydrocarbons.) LiOH was used in the Apollo life support system to adsorb primarily CO₂. In the sampling train it neutralized NO_x and SO_x which would react with the hydrocarbons and adsorbed most of the condensed moisture. Furthermore according to Apollo data the LiOH does not adsorb hydrocarbons. A CS₂ extraction and a hydrocarbon analysis were made on the impinger contents and no hydrocarbons were found.

The probe, filter, line and valves leading to the impinger were maintained at less than 220 °F. Some light condensation was found downstream of the impingers in the collection bottles and sorbent tubes but this did not interfere with the hydrocarbon determinations. The water content of the exhaust gases was determined using a separate water knockout train, or aquasorb.

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b. Sorbent--The suitability of several different types of sorbent materials was investigated. The materials tested included: Tenax GC, Carbosieve B, activated charcoal, and XAD-2 resin. The criteria observed in the selection of the sorbent included quantitative retention and recoverability of every analyte possible. These qualities were dimensionalized by measurement of breakthrough volumes and recovery efficiencies. Table 3-1 presents the breakthrough volumes of the sorbents (25 °C) for hexane and benzene. These analytes were considered to represent about the upper limit of materials that can be analyzed in gas grab samples. Carbosieve B and activated charcoal showed particularly high retention capacities.

Another important parameter in sorbent selection is the analyte recovery efficiency. Elevated temperature, thermal stripping (with a purge gas or in vacuo) or adsorbed components on Tenax, Carbosieve B and XAD-2 was considered but later rejected because the entire sample must be committed in a single determination. Recovery efficiencies using the thermal/purge-gas techniques also showed high molecular weight discrimination (see Table 3-2).

TABLE 3-1. RETENTION EFFICIENCIES OF VARIOUS SORBENTS

	Breakthrough Volumes,* l/g sorbent	
	Benzene	Hexane
Carbosieve B	47	65
Tenax GC	3	1.4
XAD-2 Resin	12	20
Activated Charcoal	30	43

*Measured as the volume of gas/grams of sorbent in cartridge to give a 0.1% FID response to gas stream containing 50 ppm of test component.

TABLE 3-2. RECOVERY EFFICIENCY OF PURGE-THERMAL STRIPPING OF SELECTED ANALYTES

	TENAX % Recovery	Carbosieve B % Recovery	XAD-2 % Recovery
Benzene	105	--	--
n-C ₇ H ₁₆	100	11	--
n-C ₈ H ₁₈	99	<1	--
n-C ₉ H ₂₀	94	<1	--
n-C ₁₀ H ₂₂	72	<1	62
n-C ₁₁ H ₂₄	67	<1	60
n-C ₁₂ H ₂₆	67	<1	--
n-C ₁₃ H ₂₈	58	<1	--
n-C ₁₄ H ₃₀	56	<1	--
n-C ₁₅ H ₃₂	61	<1	--
n-C ₁₆ H ₃₄	46	<1	--

Solvent stripping for analyte elution preparatory to chromatographic analysis was investigated. Carbon disulfide (CS₂) was found to be an attractive solvent. Many of the other common solvents, such as methylene chloride (CH₂Cl₂), chloroform, hexane, benzene, etc., tended to swamp the chromatogram, obliterating any signals of components that have boiling points even decades higher.

Unfortunately, it was found that Tenax GC is soluble in CS₂ as well as in CH₂Cl₂. Carbosieve B showed poor recoveries with solvents. Testing was therefore primarily focused on solvent extraction of activated charcoal with CS₂ and XAD-2 resin extraction with CH₂Cl₂ (CS₂ also dissolved XAD-2). Table 3-3 presents the results. Mueller and Miller (Ref. 3-1) reported similar efficiencies for halogenated and oxygenated hydrocarbons using charcoal adsorption followed by CS₂ elution. Based on the data they presented and the precedent set by the National Institute for Occupational Safety and Health (NIOSH) in the selection and published (Refs. 3-2 to 3-4) characterization of the charcoal/CS₂ analysis scheme, the use of coconut-derived activated charcoal as supplied by Mine Safety Appliances or SKC, Inc. was selected as the material of choice for source sampling.

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TABLE 3-3. SORBENT RECOVERY EFFICIENCIES FOR NORMAL ALKANES USING SOLVENT ELUTION TECHNIQUES

n-Alkane	Activated Charcoal/CS ₂	Carbosieve B/CS ₂	XAD-2 Resin/CH ₂ Cl ₂
n-C ₆	97	<1.0	Solvent Masked
n-C ₇	98	<1.0	Solvent Masked
n-C ₈	92	<1.0	Solvent Masked
n-C ₉	87	<1.0	Solvent Masked
n-C ₁₀	90	<1.0	100+
n-C ₁₁	90	<1.0	97
n-C ₁₂	90	<1.0	--
n-C ₁₃	100+	<1.0	--
n-C ₁₄	76	<1.0	--

3. TLV Sniffer--The Bacharach TLV sniffer was selected for use on this program to (1) provide a preliminary estimate of total hydrocarbon emissions, (2) provide an indication of variations in hydrocarbon concentrations in the exhaust gas due to process changes and (3) assist in the quantifying of fugitive emissions. It also served as indicator check on the results attained by GC/MS analysis of fuel samples. This device was selected because compared to other total hydrocarbon measuring devices it was smaller, lighter in weight, fast responding and less expensive. The price was under \$1000. Other devices of total H/C measuring capabilities cost \$3000 or more. These other instruments are more versatile and possibly more accurate. However, the Bacharach is explosion-proof (FM approved) whereas some of the more expensive units were not.

The TLV sniffer is an improved version of a lower-explosive-limit (LEL) detector of combustible organics with an improved sensor and an accuracy greater than the conventional LEL type instruments. It detects hydrocarbon emissions and quantitatively records them in ppm as hexane; however, this read-out can be converted to any specific hydrocarbon or LEL readings. Because it is FM* approved, it can be used in refineries or other locations where potential explosive mixtures exists. It incorporates a contact mass sensor with resistance to catalytic poisonings, an explosion proof potentiometric recorder output, automatic voltage regulation, meter display, sampling pump and a rechargeable battery power source. The system uses the heat of combustion of the gas-in-air mixture as hydrocarbon sensing. A relative response curve supplied with the instrument permits quantitative measurement of some individual gas species.

Table 3-4 illustrates the conversion factors for converting meter readings of hexane to other gases.

Figure 3-3 illustrates the conversion factors of ppm readings to LEL equivalents.

TABLE 3-4. MULTIPLYING FACTORS FOR CONVERTING ppm METER READINGS OF HEXANE-CALIBRATED INSTRUMENTS TO ppm CONCENTRATIONS OF OTHER GASES ON TLV SNIFFER

Gas Detected	Factor	Gas Detected	Factor
Acetone	1.50	Methane	1.58
Acetylene	1.78	Methanol	3.71
Benzene	1.02	Methyl Acrylate	3.37
1,3 Butadiene	1.52	Methyl Chloride	3.81
Butyl Acetate	2.08	Methyl Chloroform	4.44
Carbon Disulfide	5.92	Pentane	1.04
Cyclo Hexane	1.02	Perchlorethylene	13.66
Ethyl Acetate	2.22	Propane	1.14
Ethylene Oxide	2.05	Styrene	2.25
Heptane	1.05	Toluene	1.03
Hexane	1.00	Trichloroethylene	6.40
Hydrogen	1.45	Vinyl Chloride	2.24
M.E.K.	1.60	Xylene (O)	1.64

* FM: Fire Marshall

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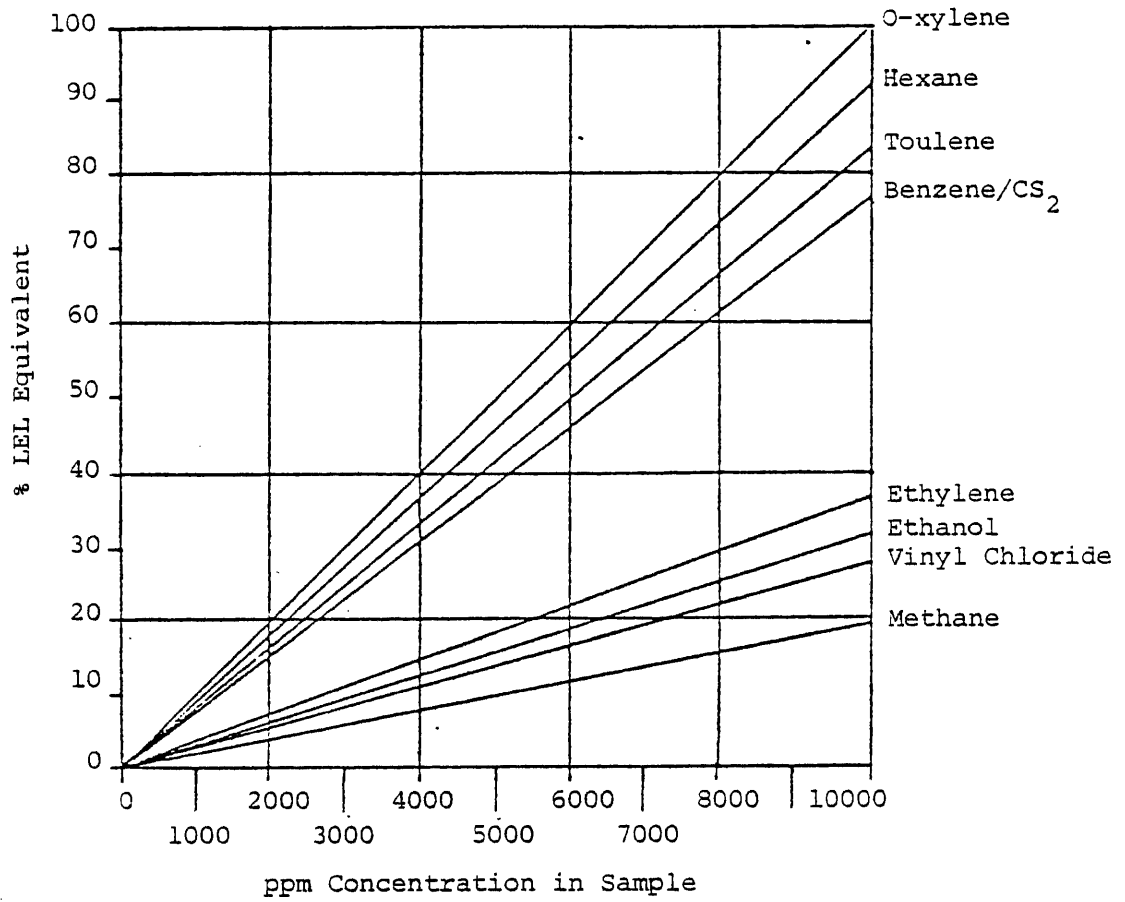


Figure 3-3. TLV sniffer: conversion curves showing relationship of ppm concentrations of various gases to percent LEL equivalents.

B. Sampling Method--

After permission for testing had been received from plant management, plant visits and on-site inspections of the source were made. The following preparatory information was obtained:

- . plant size and location
- . process parameters: type, temperature, process mass flow
- . plant safety requirements
- . sampling facility and accessibility.

This information was used by KVB's field test engineers to prepare equipment and recording forms and analytical support. A definite test date was scheduled in coordination with the management of the plant or source to be tested.

1. Train selection--The specific sampling train configuration to be used on a particular source depended on the following factors:

- . the classes of organic compounds expected in the emissions
- . the temperature of the emissions
- . the water content of the emissions
- . the type of emission flow (i.e., ducted or fugitive).

Table 3-5 indicates the sampling equipment used for 17 different source types. For each ducted source the universal sampling train presented earlier in Section 3.2.1.A was adapted as indicated in Table 3-5 by the "mode" numbers one through five. Figures 3-2, 3-4, and 3-5 show the first three of these different adaption modes. Modes four and five involve the measurement of fugitive emissions. Figures 3-6 through 3-9 illustrate the sampling setups for a typical fugitive source, in this case a petroleum transfer line valve. In Figures 3-6 and 3-7 the setups for a cold valve are shown for two different leak rates while in Figures 3-8 and 3-9 the setups for a hot valve ($T > 160$ °F) are shown.

TABLE 3-5. TEST AND SAMPLING TRAIN CONFIGURATIONS BY SOURCE TYPES

Sampling Train Components	SOURCE TYPE																
	Refinery Combustion	Fuel Combustion	Waste Disposal and Burning	Coking Operation	Catalytic Burners	Metal (Smelting) Production	Heat Treated Surface Coating	Air Dried Surface Coating	Printing Operations	Rubber, Adhesive Production	Hydrocarbon Storage	Degreasing, Stripping	Paint Shops	Dry Cleaning	Oil Field Production	Oil, Solvent Transfer, Cold	Oil, Solvent Transfer, Hot
Filter and Lines	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Heated																	
Unheated																	
Draeger Gas Indicator	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Total Hydrocarbon Instr.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Orsat Analyzer	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Aldehyde Bulbs	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Impinger, LiOH	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Sorbent Tubes *	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Gas Collection Bottle *	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Bags, Metered Flow																	
Bags, Rapid Fill	X		X									X					
Minimum Sample Nos.	5	4	5	4	2x5	4	3	2	3	3	3	2	1	1	1	2	1
Velocity Measurement	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Meter	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Gas Pump	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Pyrometer (Source T)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Thermometer (Source T)							X	X	X	X	X	X	X	X	X	X	X
Psychrometer							X	X	X	X	X	X	X	X	X	X	X
Hand or Small Pump											X	X	X	X	X	X	X
Mode	1	1	1	1	1	1	2	2	2	2	2	3	3	3	4	4	5
Type No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

* Either or both.

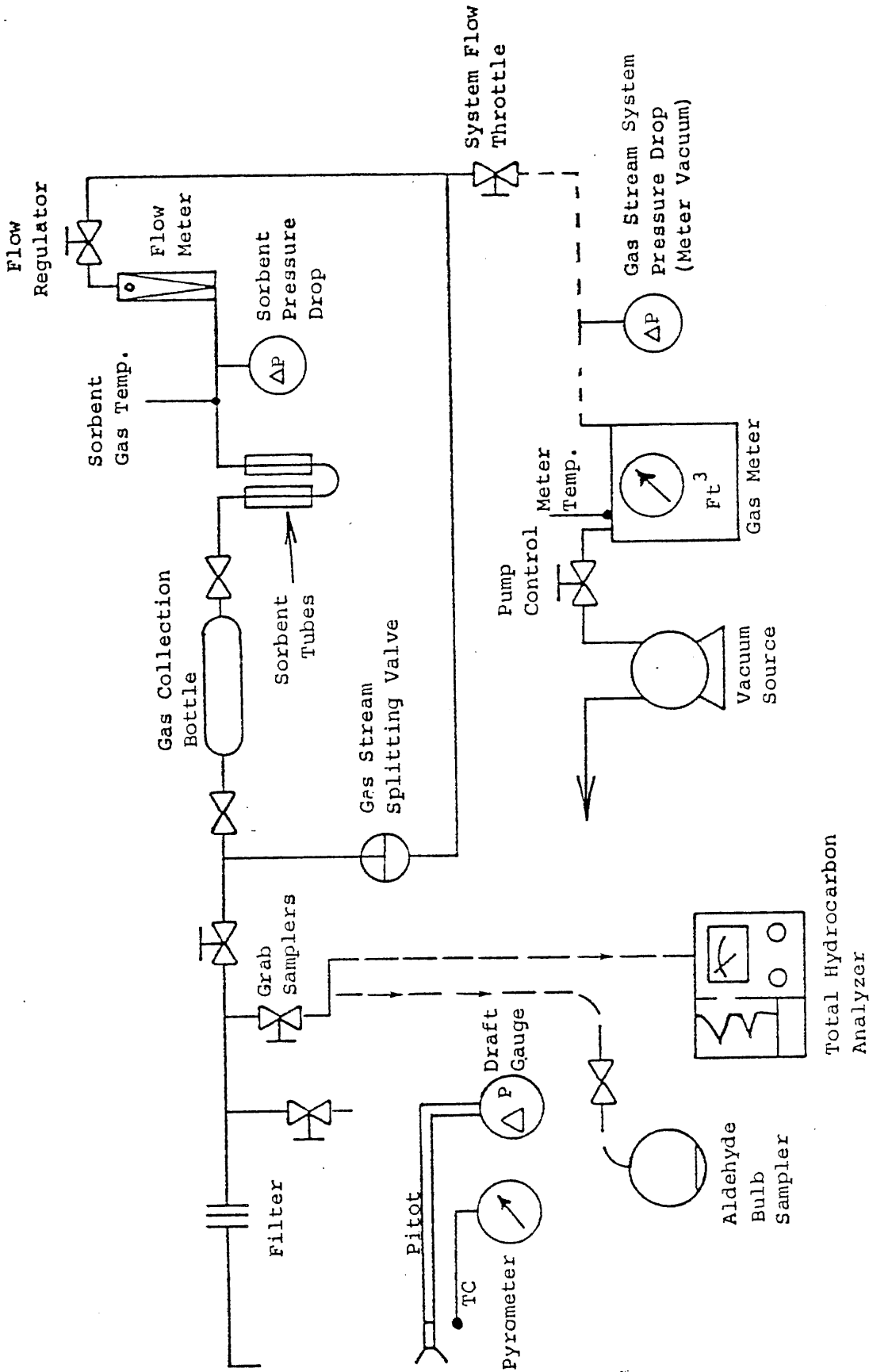
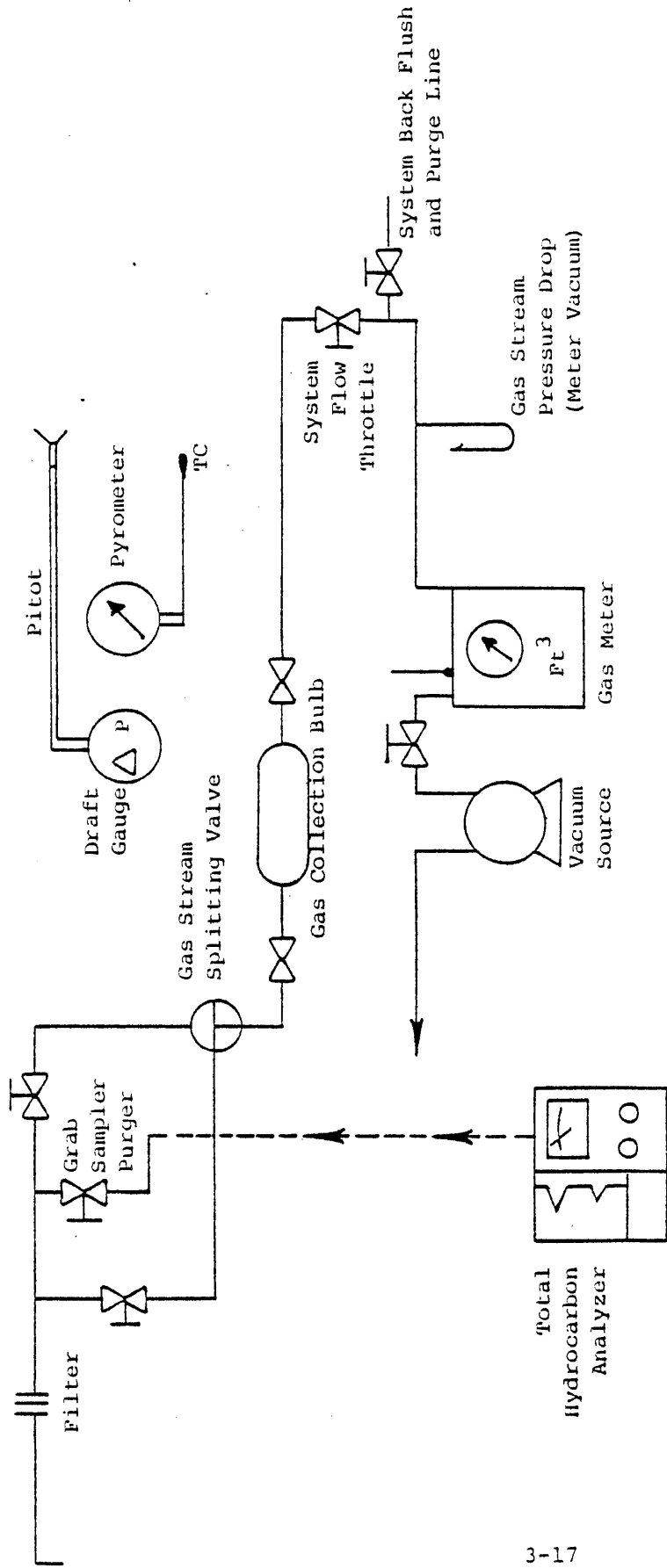


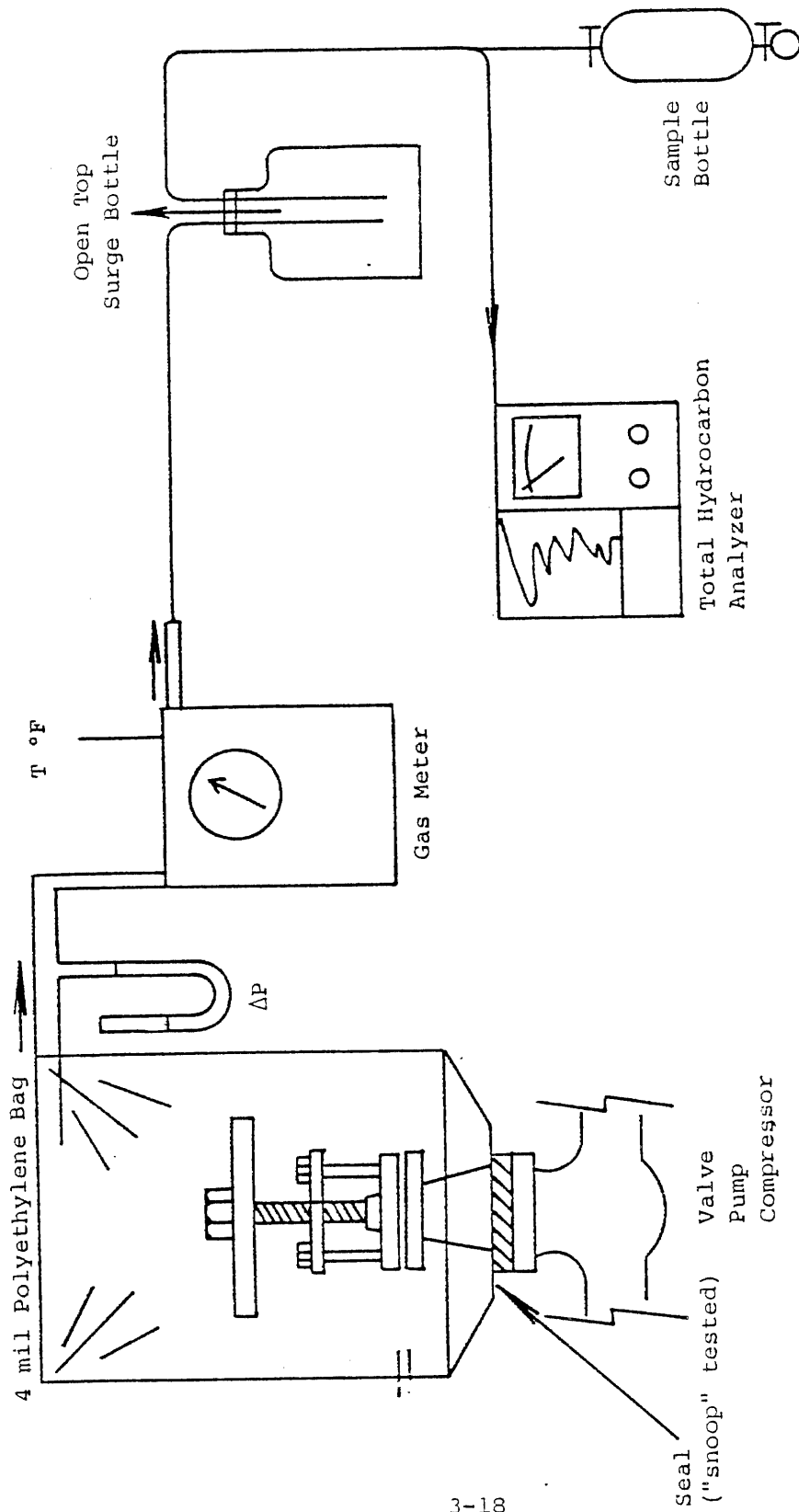
Figure 3-4. Organic sampling train configuration for continuous solvent process related sources of high complexity (Mode 2, Table 3-5).

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Figure 3-5. Organic sampling train configuration for solvent operations in batch operations (Mode 3, Table 3-5).



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Figure 3-6. Leak rate and concentration measurement of ambient temperature fittings. High leak rates. (Mode 4, Table 3-5)

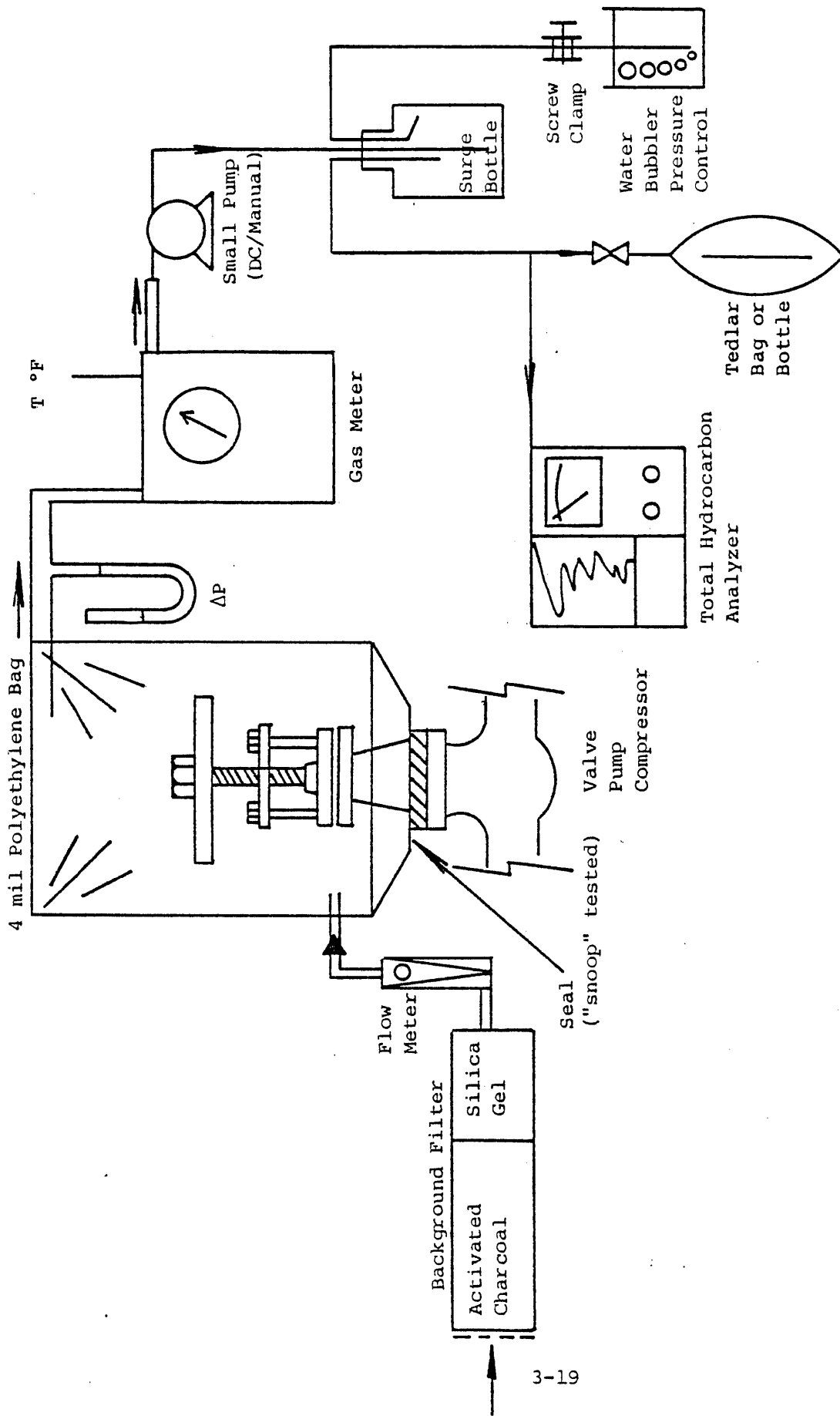


Figure 3-7. Leak rate by dilution sweep and sampling of ambient hydrocarbon fitting. Low leak rates. (Mode 4, Table 3-5)

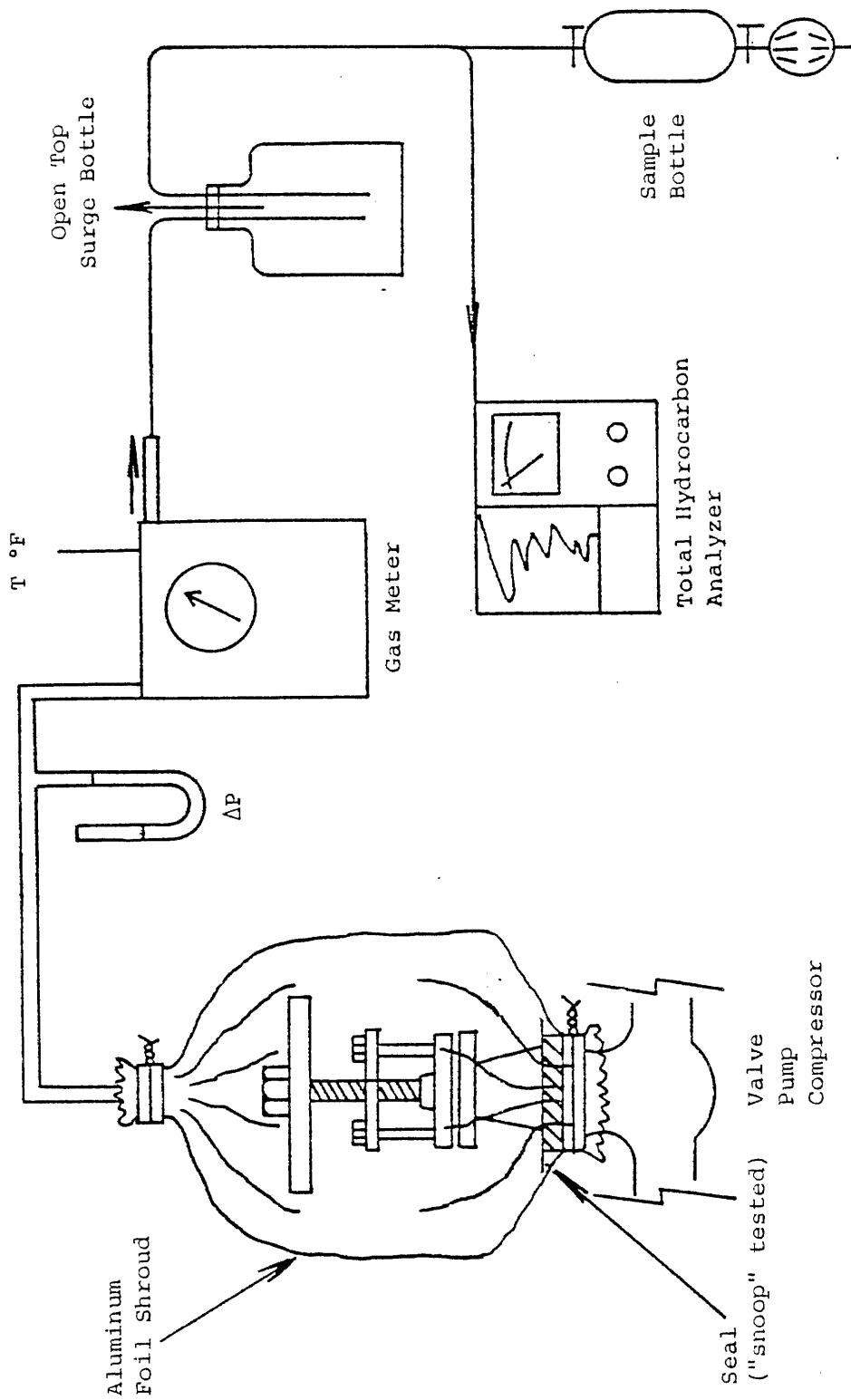


Figure 3-8. Leak rate measurement and concentration measurement of high temperature fitting.

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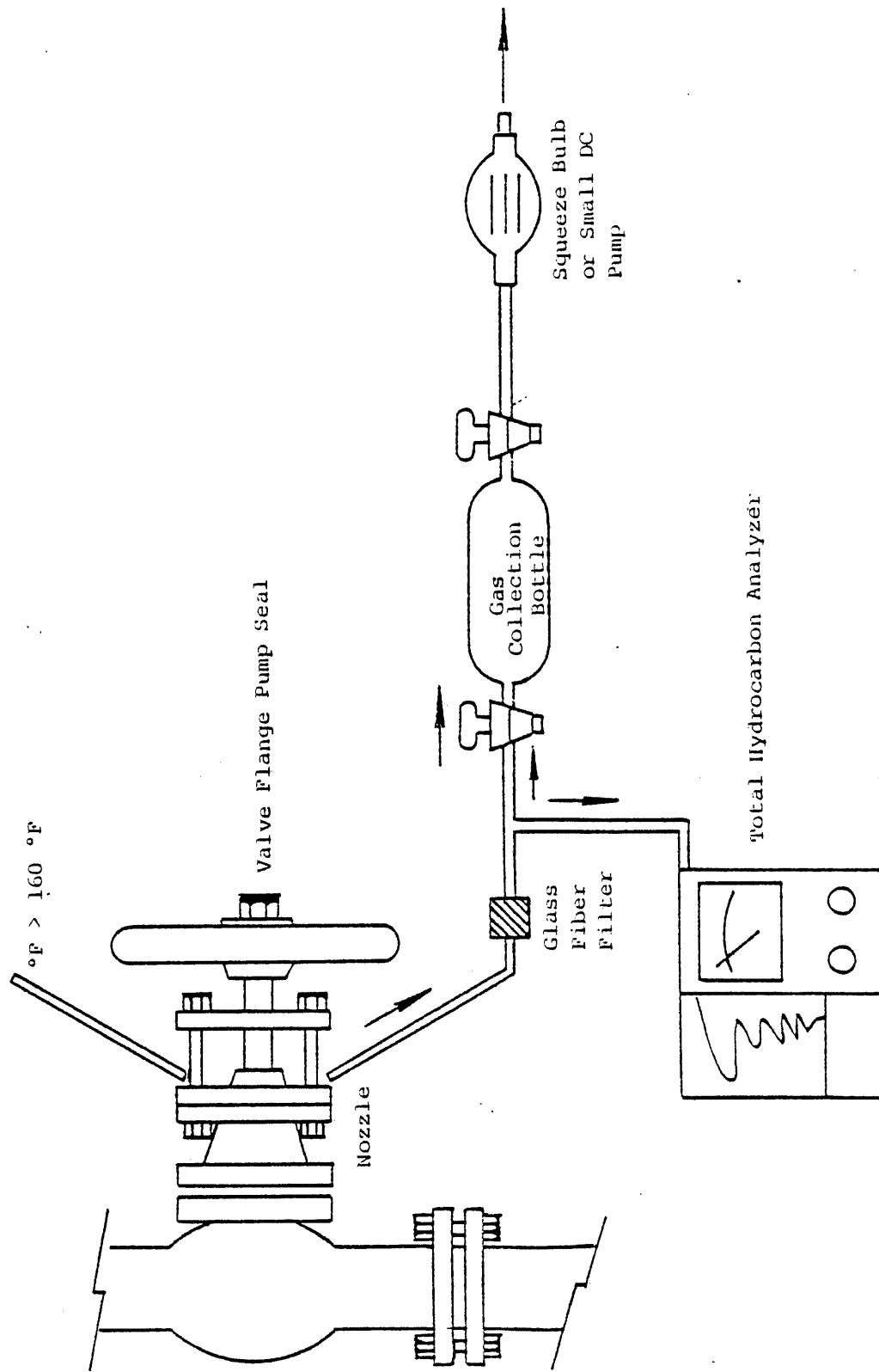


Figure 3-9. Hydrocarbon sampling from hot oil or solvent transfer (Mode 5, Table 3-5).

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Figure 3-2 illustrates the train setup for high temperature combustion source sampling. The train filters out particulates at stack temperature, collects aldehydes, collects moisture, NOx, SOx and CO on LiOH in two impingers, and collects hydrocarbons by entrapment in a bottle and by adsorption in sorbent tubes.

Figure 3-4 illustrates the sample train as used sampling high and low temperature sources with insignificant water vapor content. The train filters out particles, collects aldehydes, and collects hydrocarbons by entrapment and by adsorption. It records fluctuation in total hydrocarbon emissions using the TLV sniffer.

Figure 3-5 shows the configuration used in sampling cold solvent sources such as dry cleaning, degreasing and painting processes. The train filters particulates, monitors total hydrocarbon emissions fluctuations, and entraps hydrocarbons in gas collection bottles.

Figures 3-6 and 3-7 illustrate sampling setup for testing fugitive emission sources. The rate of emission is measured, total hydrocarbon concentrations monitored, and gaseous emissions are collected for analysis. In Figure 3-6 the H/C leak rate is so great that the vapors fill the tent and drive the gas meter. In Figure 3-7 a pump is used to draw purified air through the tent to pick up the emitted H/C vapors.

Figures 3-8 and 3-9 illustrate test setup for sampling a high temperature fugitive emission source. In Figure 3-8 aluminum foil is substituted for polyfilm and rates are measured as Figure 3-6 or 3-7. When the foil cannot be used the setup in Figure 3-9 is used. The temperature of the source is measured, a grab sample is obtained in a gas collection bottle, and the concentration of total hydrocarbons is measured. The leak rate is obtained by applying engineering judgments.

2. Ducted sources--Exhaust gas volumetric flow rate was determined by measurements using EPA Method #1 described in the Federal Register. These measurements were checked by material balance calculations if sufficient source information was available. Before testing, approximation of the gaseous hydrocarbon concentrations was made utilizing a Draeger gas detector with specific indicator tubes, or the TLV sniffer or both.

The ducted sources were sampled at an accessible point closest to the point of average gas velocity. An attempt was made to maintain an isokinetic sampling rate. Sampling time was adjusted according to hydrocarbon concentration to avoid breakthrough on the sorbent tube.

The test data and process data were recorded throughout the test. At the end of the test period the impingers were sealed, labeled and delivered to the laboratory. The sorbent tubes were removed from the train by disconnecting the flexible tubings from them, sealed with polyethylene end caps, labeled, identified and placed into a shipping container. The gas collection bulbs, bottles and bags were closed, labeled, identified and shipped to the laboratory for analysis.

Wherever possible, a small sample of the process feed and that of the product were obtained for analytical determinations, such as evaporation rate and vapor pressure. These data were used to obtain a material balance.

The TLV sniffer was used to indicate expected or unexpected process fluctuations.

3. Fugitive sources--The measurement of emission rates for non-ducted or fugitive emissions required ingenuity on the part of the test crew. As mentioned earlier, frequently these emissions were estimated or calculated on process data such as solvent make-up rates or on experimental data such as evaporation rates or emission factors for petroleum storage tanks. In certain cases, it was desirable to make selected measurements in order to estimate total emission rates. The most useful techniques for detecting and measuring leak rates involve the use of bubbling soap solutions and tenting with polyfilm sheeting. KVB used this approach in refineries, chemical plants, etc. where leakage losses could not be readily detected from the process flow rates.

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The approach used was to usually check all of the accessible hydrocarbon-transfer fittings (valves, flanges, etc.) for signs of leakage (stains, etc.). Next the fittings were checked with soap solution, Figure 3-10. Fittings showing leakage with soap solution were categorized as to their estimated leakage rate: low, medium, or high. Depending on the time available and the number of "leakers", a selected, representative number of leakers were tented and their emissions measured.

The test setup for measuring leakage rates is shown in Figure 3-7. The small Spectrex pump pulls a low rate of air through the polyfilm envelope. The air drawn into the envelope is filtered to remove background hydrocarbon where necessary and is metered with a rotameter as shown. The outlet air and hydrocarbon mixture is metered and delivered to the TLV analyzer where the total hydrocarbon level is measured continuously. When a steady state has been reached, the TLV analyzer reads a constant ppm level. Readings are taken for several minutes. Then a Tedlar bag of the emissions is taken. The total hydrocarbon leak rate is determined by the following calculations:

$$HC = 1.36 \times 10^{-5} \text{ ppm}_{TLV} \times \frac{\text{ft}^3}{t}$$

where

HC = hydrocarbon leak rate, lb/hr

ppm_{TLV} = parts per million total hydrocarbon concentration detected on TLV as hexane

ft^3 = meter reading on gas meter corrected to 60 °F and 29.9 in. Hg, in cu. ft.

t = time in minutes ft^3 was measured

$$1.36 \times 10^{-5} \text{ ppm} = \frac{1}{10^6} \times \frac{60 \text{ min/hr}}{379 \text{ ft}^3/\text{lb-mole}} \times 86 \text{ (Mwt. of Hexane)}$$

This calculation was checked with the data from the Tedlar bag. The volume of emissions collected in the bag and the filling time of the bag was measured and recorded. The total hydrocarbon content of the bag was determined by GC analysis in the laboratory as well as the specie breakdown and average molecular weight. From this information the total hydrocarbon emission rate

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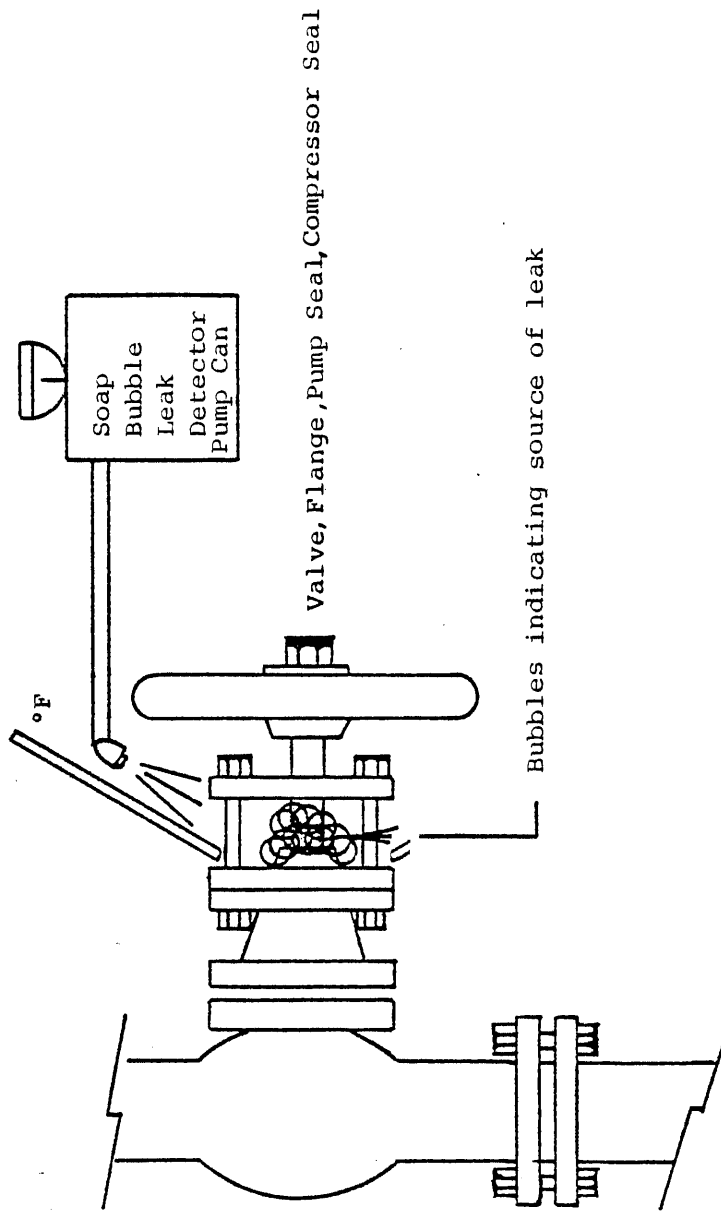


Figure 3-10. Soap bubble detection and temperature evaluation of hydrocarbon fittings.

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was determined to check the results determined by the TLV. The percent composition determined by GC analysis was used to apportion the total hydrocarbon emission rate among the various species.

Based on these measured leakage rates, the leakage rates for other fittings were estimated on the basis of observing their performance during the soap-solution test. KVB also applied the use of the TLV sniffer to determine relative total hydrocarbon emissions from these types of fittings. This proved to be successful and it became particularly valuable for use on hot fittings and on pump seals.

3.2.2 Analysis

The primary analytical chemistry work on this program was performed by Analytical Research Laboratories Inc. (ARLI), Monrovia, CA. Their final report is presented in the appendix. ARLI assisted KVB in the design of the sampling train, the selection of a sorbent and the design of a quality control system. Portions of their work were reported in Section 3.2.1 (sorbent section). This section is a summary of the equipment and methods used in analyzing field samples.

Samples received from the field included: 500 ml or 250 ml glass bottles, Tedlar bags, glass tubes containing charcoal sorbent and 100 ml flasks containing 1% sodium bisulfite solution. The bottles, bags and sorbent were analyzed for all organic species while the liquid in the flask was only analyzed for aldehydes.

Most of the gaseous samples in the bottles and bags were analyzed within 2-3 days following receipt, except for a small number that were processed as long as two weeks later. Several tests were made with synthetic samples to evaluate storage effects on the contents of capped charcoal sampling tubes. Recoveries did not change, within experimental error, between 24 hours and 30 days. Therefore, the charcoal samples could stand for longer periods without fear of losses, and were not usually analyzed until after the gas samples in the same sets had been analyzed. The charcoal eluates were usually run within an hour after the carbon disulfide was added to extract the sample components.

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Initial analysis of all samples was conducted using a gas chromatograph (GC). Lower boiling component identifications were based on retention times established by repeated analyses of standards. If there were questions as to the positive identity of a GC peak,* the sample was rerun using GC/MS methods for the identification. This approach was often necessary because a number of chromatographic peaks contained at least two and sometimes three components. The mass spectra also provided a basis for determining ratios of the components in the GC peak being examined. These data were then used in making quantitative measurements of the contents of chromatographically unresolved but computer-integratable peaks. All peaks which contributed at least one volume percent of the total organic vapor were identified and quantified. A sample report of a sample analysis is presented in Table 3-6.

A Beckman Model GC-55 equipped with a precision temperature-programmed, column oven and a flame ionization detector (FID) was used for most of the GC work performed on the program. The column was 1/8" O.D. by 6 ft. long stainless steel tubing containing a stationary phase of 100-200 mesh Poropak Q. Using the analytical conditions described below, this column furnished good resolution of the lowest boiling materials encountered while still eluting with good results the higher boiling hydrocarbons representing the top of the range of interest.

Analyses were performed using helium as the carrier gas at a flow rate of 30 cc/min. Detector gas flows were: H₂ - 40 cc/min; air - 300 cc/min. The following conditions were used for GC analyses: 6 min. at 40 °C followed by temperature programming at 10 °C/min to 190 °C and holding at 190 °C for approximately one hour.

The GC column effluent of the Beckman GC-55 gas chromatography was split into two streams. One stream was directed to the FID of the GC, the other to a heated transfer line which carried the stream to a Finigan Jet Separator and into the mass spectrometer. The separator provided a twenty fold concentration of the material of interest in the gas stream.

*Conventional gas chromatograph data are recorded on a strip chart with a recording pen which moves literally in proportion to the concentration of the gas being emitted from the GC column. The resultant image on the chart is a peak-shaped trace whose area is proportional to the quantity of the gas present. Thus the term peak is used to refer to an indication of a component of the gas mixture being analyzed.

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TABLE 3-6. GC ANALYSIS REPORT

TYPICAL COMPONENT ANALYSIS
I/C ENGINE EXHAUST

SAMPLE NUMBER: BOTTLE 10130 A

ARB CODE	EPA NUMBER	CHEMICAL NAME	MOL.WT	UG/L	%WT	PPM	%VOL
1	43201	METHANE	16	2860.	74.8	4350.	87.2
1	43202	ETHANE	30	378.	10.0	307.	6.2
3	43203	ETHYLENE	28	35.	1.2	4.9	1.1
2	43204	PROPANE	44	370.	9.8	205.	4.2
2	43212	N-BUTANE	58	101.	2.7	42.3	0.9
2	43214	ISO-BUTANE	58	58.	1.5	24.4	0.5
TOTALS				3770.	100.	4930.	100.

TOTAL PPM FROM GC AS HEXANE 1070.
TOTAL PPM FROM TOC AS HEXANE 1010.

2 COMPOUNDS OF ARB CLASS I
3 COMPOUNDS OF ARB CLASS II
1 COMPOUNDS OF ARB CLASS III

The mass spectrometer used on this program was a Consolidated Electrodynamics Corporation (CEC) Model 21-104. This was a 180 degree magnetic sector instrument having an electron impact ion source and an electron multiplier detector system which permitted modernately high-speed mass scanning.

Multiple MS scans were taken when a GC signal was observed on the strip chart recorder. Multiple scan studies indicated that approximately 2 seconds were required for the maxima to be observed by the MS. Multiple scans were required to insure representative ion pair formation.

Mass spectra were interpreted manually using such reference works as:

- . "Compilation of Mass Spectral Data," Cornu, A. and R. Massot, Heyden & Son, Ltd., London, England, 1966.
- . "Index of Mass Spectral Data," AMD II, Americal Society for Testing and Materials, Philadelphia, 1969.
- . "Eight Peak Index of Mass Spectra," Atomic Weapons Research Establishment, Aldermaston, England, 1970.
- . "Atlas of Mass Spectra Data," Stenhagen, E., et al., Interscience, New York, NY, 1969.
- . "API Project 44 Selected Mass Spectra Data," Thermodynamics Research Center, Texas A&M University.

When an unknown peak could not be positively identified by this means, the spectrum was compared with the mass spectra of some 27,000 different compounds in the library of the Cyphernetics Corp. Mass Spectral Search System. This computerized search system was directly accessible on a time-shared basis. It was successfully used to verify assignments made during the earlier work on this program.

A spectrophotometric method similar to that specified by the NIOSH was used for the determination of aldehydes. The total volume of liquid in the aldehyde sample flasks was measured, and an aliquot taken for the determination. The sample was allowed to react with a modified Schiff's

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reagent prepared from rosanaline hydrochloride and sodium bisulfite. After a suitable development time, the adsorbance was read at 580 m μ against a reagent blank on a UV-vis spectrophotometer. Concentration was read from a calibration curve. The same determination was performed on a sample of the sodium bisulfite used for collecting/stabilizing the aldehydes and a 1 μ g/ml formaldehyde standard. Results were calculated and reported as total micrograms of formaldehyde equivalent in the sample. The minimum amounts of aldehydes that could be detected by this method were typically 1-3 μ g total (as formaldehyde).

3.2.3 Data Reduction

In the field, the total volumetric emissions from a source were measured. The laboratory analysis provided composition data in the form of weight of individual specie per unit volume (i.e., μ g/ml). The calculations required to convert these data to weight/unit time of the individual species were performed using the test data and calculation sheets shown in Table 3-7. For each test the completed Page B, "Summary: Emissions to Atmosphere" is enclosed in the Appendix.

The volumetric measurements of ducted sources were made using EPA Method 1 as described in the Federal Register, Volume 36, Number 159, August 17, 1971. Standard conditions used in all calculations were 60 °F and 29.95 in. of mercury pressure. Gas density correction factors were based on Chapter 3 of the "Source Testing Manual" published by the Air Pollution Control District of Los Angeles County, 1972 (now SCAQMD Metro Division). Page E of the KVB data forms (Table 3-7) shows the step-by-step computation for deriving the gas correction factors for volumetric source analysis using moisture content and Orsat data.

Combustion source flow rates were measured by Method 1 and checked using Orsat analysis and combustion calculations based on fuel analysis and process data pertaining to the source tested. The method used is described in detail in Section 5.4 of the "Source Testing Manual".

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TABLE 3-7. TEST DATA AND CALCULATION SHEETS
(Nine Sheets)

KVB

Sample Codes _____

Test No. _____

Page A-

SUMMARY OF RESULTS

Date _____

1. Name of Firm (see page C) _____
2. Plant Location (see page C) _____
3. Basic Equipment (see page B) _____
4. Control Equipment(see page B) _____
5. Equipment Tested (see page B) _____
6. Process Weight Per Hour (see page C) _____
 Test: (see page C) _____
7. Sampling Station (see page D-1 & G) _____
8. Av. Gas Velocity, FPS (see page F) _____
9. Gas Temperature, °F (see page F&D-1) _____
10. Gas Flow Rate, SCFM (see page F) _____
11. Material Sampled(see page D-1 & G) _____
12. Time of Test-Begin (see page D-1) _____
13. Time of Test-End (see page D-1) _____
14. Net Sampling Time, Min. (see page D-1) _____
15. Conc., Gr./SCF (see pgs. B,D-2 & G) _____
16. Conc., Gr/SCF at 12% CO₂ (see pgs.-B,D-2 & G) _____
17. Conc., Volume ppm (see pages B,D-2 & G) _____
18. Pounds/Hour (see pages B,D-2 & G) _____
19. Collection Efficiency, % (see page B) _____
20. Water Vapor, Vol. % (see page E) _____
21. CO₂, Vol. % (Stack Cond.) (see page E) _____
22. O₂, Vol. % (Stack Cond.) (see page E) _____
23. CO, Vol. % (Stack Cond.) (see page E) _____
24. N₂, Vol. % (Stack Cond.) (see page E) _____

Tested by _____

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KVB

Sample Code _____

Tested by: _____

Date _____

Page C _____

STATEMENT OF PROCESS WEIGHT OR VOLUME

Firm Name _____

Address _____

DATA ON OPERATING CYCLE TIME:

Start of Operation, Time _____

End of Operation, Time _____

Elapsed Time, Minutes _____

Idle Time During Cycle, Min. _____

Net Time of Cycle, Minutes _____

DATA ON MATERIAL CHARGED TO PROCESS DURING OPERATING CYCLE:

Material	_____	Weight	_____	lbs, gal
Material	_____	or	_____	lbs, gal
Material	_____	Volume	_____	lbs, gal
Material	_____		_____	lbs, gal
Material	_____		_____	lbs, gal
Material	_____		_____	lbs, gal
Material	_____		_____	lbs, gal

Total: _____

Signature _____

Title _____

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KVB

Sample Code _____

Firm and Unit _____

Test No. _____

Page D-1

Sampling Station _____ Date _____

SAMPLING TRAIN DATA AND CALCULATIONS

Time	Gas Meter			Flow Meter			Imping.	Sample Pt.	THC Moni- tor pom	Stack Temp °F
	Reading	Vac.	Temp.	Reading	Vac.	Temp.	Temp.			
	Cu Ft. V _m	In. Hg P _m	°F T _m	cc/min V _s	In. Hg P _s	°F T _s	°F T _i			
Net	Net	Av.	Av.	Net*	Av.	Av.	Av.		Av.	

*Net V_s Cu.-Ft. = total cc x 3.531 x 10⁻⁵

A. Material type sampled _____

B. Source Flow Rate SCFM (line J of page F) _____

C. Condensate Volume, ml _____

D. Condensate Vapor Volume, 0.0026 x c x (460 + T_m) / (29.9 - P_m), CF _____

E₁ Total Sampled Volume, Impingers = V_m + D, CF _____

E₂ Total Sampled Volume, Sorbent = V_s + (D x $\frac{V_s}{V_m}$), CF _____

F₁ Sampled Volume in Impingers = [E₁ x 520 x (29.9 - P_m)] / [29.9 x (460 + T_{m})], SCF _____}

F₂ Sampled Volume in Sorbent Train = [E₂ x 520 x (29.9 - P_s)] / [29.9 x (460 + T_{s})], SCF _____}

Continued on page B

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KVB

Sample Code _____

Firm Name and Unit _____

Test No. _____ Page D-2 _____

Sampling Station _____ Date _____

SPOT MONITORING DATA BY DRAEGER OR TLV SNIFFER

INSTRUMENT USED	FUNCTIONAL DATA	COMPOUND NAME	CONCENTRATION		
			ppm	Grs/SCF	Lbs/Hour

KVB

Sample Code _____

Firm and Unit _____

Test No. _____

Page E- _____

Sampling Station _____

Date _____

WATER VAPOR AND GAS DENSITY CALCULATIONS

Percent Water Vapor in Gases

- A. Gas Pressure at Meter, In. Hg (Absolute) _____
- B. Vapor Pressure of Water at Impinger Temp., In. Hg _____
- C. Volume of Metered Gas, Cu. Ft. _____
- D. Volume of Water Vapor Metered, BXC/A, Cu. Ft. _____
- E. Volume of Water Vapor Condensed, Cu. Ft.* _____
- F. Total Volume of Water Vapor in Gas Sample, D+E, Cu. Ft. _____
- G. Total Volume of Gas Sample, C+E, Cu. Ft. _____
- H. % Water Vapor in Sampled Gas, 100 x F/G _____

* See D on sampling train data sheet, page D-1

Gas Density Correction Factor

Component	Volume Percent X Moisture Collection	X Mol. Wt. =	Weight Per Mole Wet Basis
Water		1.0	18.0
CarbonDioxide	Dry Basis		44.0
CarbonMonoxide	Dry Basis		28.0
Oxygen	Dry Basis		32.0
Nitrogen + Inerts	Dry Basis		28.2
Average Molecular Weight			

J. Density of Gas Referred to Air = $\frac{\text{Av. Mol. Wt.}}{28.95} =$ _____

K. Gas Density Correction Factor = $\sqrt{\frac{1.00}{J}} =$ _____

KVB

Sample Code _____

Firm and Unit _____

st No. _____

Page G- _____

Date _____

GRAB AND BAG SAMPLE RESULTS HYDROCARBONS, ALDEHYDES

SAMPLE STATION	Sample Type and Sampling Time	Components	ppm Dry Basis	ppm Stack Conditions	Grains/SCF Stack Conditions	LBS/HR Loss
Location _____ _____						
Temp., °F _____						
Humidity, % _____						
Location _____ _____						
Temp., °F _____						
Humidity, % _____						
Location _____ _____						
Temp., °F _____						
Humidity, % _____						

CONVERSION FACTORS AND CONSTANTS

Unless otherwise noted, all conversion factors and constants are at standard conditions of 60°F temperature and 14.7 psia pressure.

<u>TO CONVERT FROM</u>	<u>TO</u>	<u>MULTIPLY BY</u>	
grains/cubic foot	parts per million (by volume)	$5.416 \times 10^4 / \underline{M}$	
	per cent by volume	$5.416 / \underline{M}$	
	milligrams/cubic meter	2289	
	milligrams/cubic foot	64.8	
	milligrams/liter	2.29	
	pounds/1000 pounds air	1.87	
	pounds/cubic foot	1.429×10^{-4}	
	parts per million (by volume)	grains/cubic foot	$1.846 \times 10^{-5} \underline{M}$
		per cent by volume	10^{-4}
		milligrams/cubic meter	$4.23 \times 10^{-2} \underline{M}$
milligrams/cubic foot		$1.196 \times 10^{-3} \underline{M}$	
per cent by volume	milligrams/liter	$4.23 \times 10^{-5} \underline{M}$	
	parts per million (by volume)	10^4	
	grains/cubic foot	0.1846 <u>M</u>	
milligrams/cubic meter	milligrams/liter	0.423 <u>M</u>	
	milligrams/cubic foot	11.96 <u>M</u>	
	grains/cubic foot	4.37×10^{-4}	
milligrams/cubic foot	parts per million (by volume)	$23.7 / \underline{M}$	
	milligrams/cubic foot	0.0283	
	grains/cubic foot	0.01543	
milligrams/liter	parts per million (by volume)	$836 / \underline{M}$	
	milligrams/liter	0.0353	
	grains/cubic foot	0.437	
cubic feet	parts per million (by volume)	$2.37 \times 10^4 / \underline{M}$	
	milligrams/cubic foot	28.32	
	liters	28.32	
liters	cubic feet	0.03531	
grams	grains	15.43	
grains	milligrams	64.8	
pounds	grains	7000	

M = molecular weight
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The reported hydrocarbon concentrations were calculated from the laboratory results as follows:

The hydrocarbon concentration provided by the laboratory was on a dry, CO₂-free basis. This was converted to actual moisture and CO₂ conditions at the source by the relation (page B of Table 3-7),

$$c_{\text{HC}} = (c_{\text{HC}})_d \frac{(100 - \text{W.V.} - \text{CO}_2)}{100}$$

where,

c_{HC} = concentration of hydrocarbons at source (actual) conditions, parts per million by volume

$(c_{\text{HC}})_d$ = concentration of hydrocarbons; dry, CO₂-free basis, from the analysis; parts per million by volume

W.V. = water vapor in source gases, percent by volume

CO₂ = carbon dioxide in source gases, stack conditions, percent by volume

The water vapor concentration was measured during the source test using an ice water impinger or Aquasorb tube. The carbon dioxide concentration was obtained from Orsat analysis (dry basis), converting to stack conditions by multiplying by the factor (1-M.W./100).

The reported emission rate of hydrocarbons was calculated by the general relation,

$$M_{\text{HC}} = 1.58 \times 10^{-7} c_{\text{HC}} Q (\text{M.W.})_{\text{HC}}$$

where,

M_{HC} = emission rate of hydrocarbons, pounds per hour

Q = stack gas flow rate, standard cubic feet per minute (SCFM)

$(\text{M.W.})_{\text{HC}}$ = molecular weight of hydrocarbon

The 1.58×10^{-7} factor came from the following unit analysis:

$$M_{\text{HC}} \left(\frac{\text{lb}}{\text{hr}} \right) = c_{\text{HC}} (\text{ppm}) \times \left(\frac{\text{ppm}}{10^6} \right) \times Q \left(\frac{\text{ft}^3}{\text{MW}} \right) \left(\frac{60 \text{ min}}{\text{hr}} \right) \times (\text{M.W.})_{\text{HC}} \left(\frac{\text{lb}}{\text{mole}} \right) \left(\frac{1 \text{ mole}}{379 \text{ ft}^3} \right)$$

$$\begin{aligned} M_{\text{HC}} \left(\frac{\text{lb}}{\text{hr}} \right) &= c_{\text{HC}} Q (\text{M.W.})_{\text{HC}} [(1/10^6) \times (60/379) \times (\text{lb/hr})] \\ &= 1.58 \times 10^{-7} c_{\text{HC}} Q (\text{M.W.})_{\text{HC}} (\text{lb/hr}) \end{aligned}$$

The conversion factors used in the test series are summarized on Page H of Table 3-7.

3.2.4 Ambient Tests - Douglas Refinery

The emissions from a refinery were characterized by measuring the organic compound concentrations upwind and downwind and using plume dispersion modelling techniques to calculate a source emission rate. Because refinery emissions are primarily of the fugitive type (i.e., from leaks, spills, and open ponds rather than from stacks), characterizing these emissions requires tens or even hundreds of thousands of individual measurements. At best, this program could only test some representative sources (i.e., valves, flanges, pumps, etc.) and then extrapolate these measurements for an estimate of the entire refinery. If this complex source could be treated as a single point source by defining a plume of emissions, it seemed possible that the source emissions could be defined by the concentration changes in the plume. The process of predicting downwind air pollution impacts of potential new plants had developed to an acceptable science. There the source emissions are defined and the downwind concentrations are calculated. The approach taken on this program was the reverse. The downwind concentrations were measured, and the emissions were calculated.

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KVB engaged AeroVironment, Inc. (AV) to perform the ambient testing and modelling while the KVB engineers simultaneously determined the refinery emissions using discrete source accounting techniques involving source sampling, equipment inventorying and emission calculations on an item by item basis.

AV's final report of this experiment is presented in the Appendix. This section presents a summary of that report.

A. Site Selection--

After a thorough survey of all of the refineries in the Basin, AV selected the Douglas Refinery in Paramount, CA as the test site for the following reasons:

- . Location - the refinery was located in an area largely residential and commercial - several miles from any other major source of hydrocarbons
- . Meteorology - in the early morning hours when traffic interference is least the wind was found to be stable with a light (5 mph) and uniform wind
- . Size - this was one of the smaller refineries in the Basin and thus the problems of plume monitoring were minimized.

Agreement with this selection was received from ARB and WOGA although it was realized that the Douglas refinery is a specialized refinery that has only a few of the processes found in other refineries in the Basin. For the first attempt at this type of test, it was conceded by all that this site was an acceptable choice.

B. Test Approach--

Four test runs were conducted over an eight day period at the end of November 1976. A system of receptors was arranged as shown on the map in Figure 3-11. A source of sulfur hexafluoride (SF_6) was installed at a central location in the refinery (Figure 3-11). SF_6 was released at a rate

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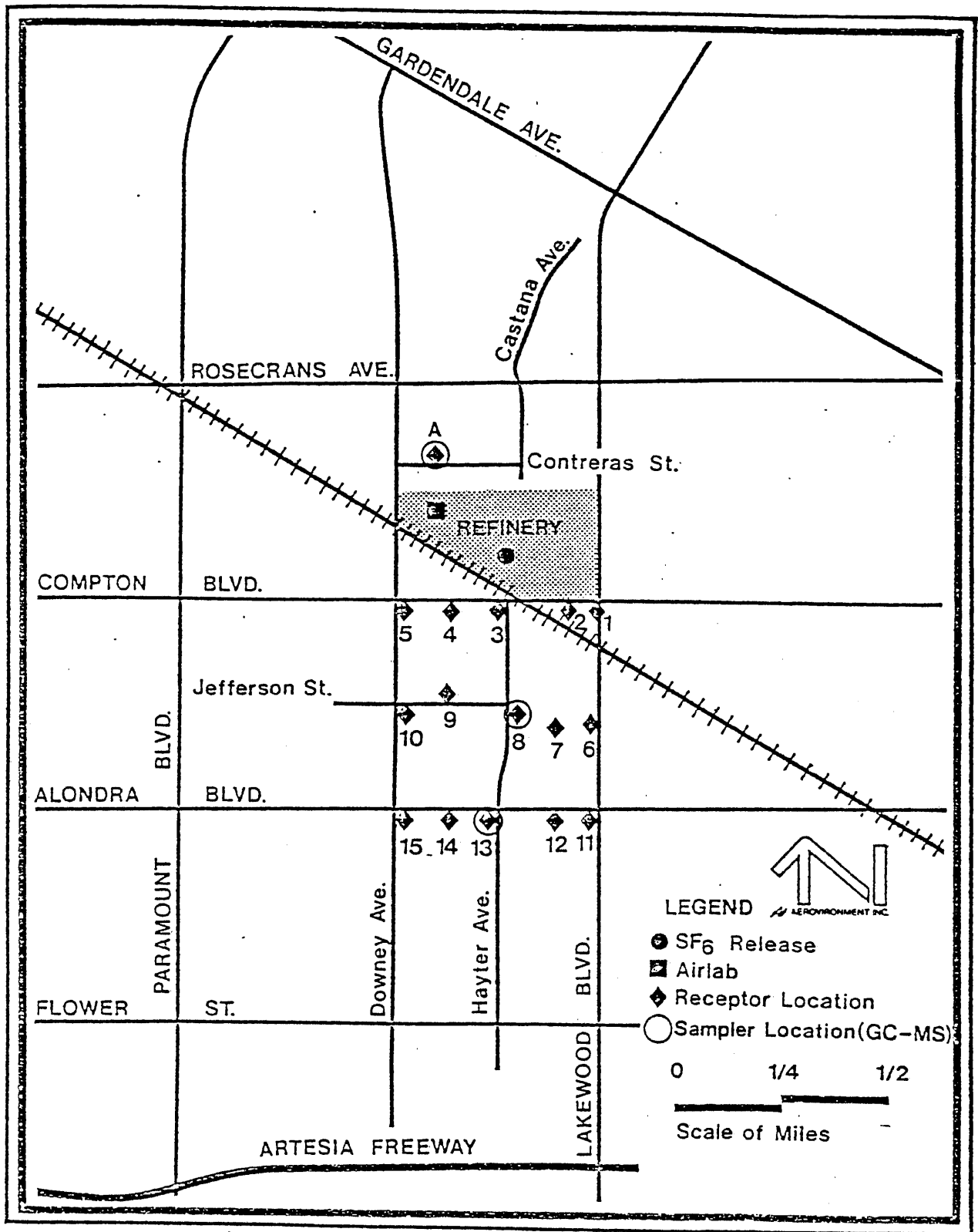


Figure 3-11. Schematic representation of test site for November 23, 1977.

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of 2.5 lb/hr. By knowing the SF₆ release rate and the receptor point concentrations, the source/receptor relationship were to be established by diffusion modelling. Both SF₆ and hydrocarbons were measured simultaneously so that the source/receptor relationship established for SF₆ at that time would also be applicable to hydrocarbons.

At each receptor location the air was sampled for four hours (3:30 to 7:30 a.m.) replacing collection bags at the end of each hour. The bag contents were analyzed on site (at the AV mobile lab) for methane, non-methane hydrocarbons, CO and SF₆. The bags were then delivered to ARLI for GC/MS speciation of organic contents.

C. Meteorology--

On three of the four test days the atmosphere was calm. Wind was generally from the north with a speed of 3-7 mph, a typical drainage flow in that area. Occasional wind shifts were experienced. On one run the conditions were too calm and both upwind and downwind receptors recorded about the same concentrations. Wind direction was recorded continuously at the AV mobile laboratory. Helium-filled balloons were released to check the uniformity of wind direction at higher elevations.

D. Test Results--

Table 3-8 is a summary of the test results. A run number was assigned for each hour. Runs 5-8 which correspond to the November 24 test runs were not tabulated because of the calm conditions mentioned above. The receptor location designation is consistent with that given in Figure 3-11. The reader is referred to the appendix for further details on receptor location which were varied slightly on each of the test days.

The contribution of the refinery plume to a specific receptor point was the difference between that receptor point and the point upwind. This was true for SF₆, THC, CH₄ and CO provided that no interference was present. These net results were used for diffusion modelling. A magnification factor of 1.36 was used in the AV hydrocarbon measurements to correlate with ARLI data as discussed in the AV reports.

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TABLE 3-8. SUMMARY OF TEST RESULTS
(Six Sheets)

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_n (deg)	Temp (°C)	Stability	Q SF ₆ (ug/sec)	Receptor	SF ₆ (ppt)	THC (ppm)	CH ₄ (ppm)	CO (ppm)
Run 1													
11/23/76	0330-0430	1.6	360	0.07	7.2	11	E	283,960	A	3.0	5.4	2.3	3.8
									1	6.4	6.6	2.5	4.0
									2	3.0	6.7	2.5	3.8
									3	1525	7.3	2.5	3.7
									4	116	7.9	2.5	3.7
									5	9.6	6.0	2.5	4.0
									6	-	6.0	2.5	3.5
									7	6.0	5.6	2.5	3.7
									8	-	6.3	2.5	3.6
									9	130	5.8	2.5	3.8
									10	420	5.4	2.5	3.9
									11	3.0	6.9	2.5	4.0
									12	3.0	6.0	2.5	3.8
									13	-	7.1	2.5	3.9
									14	13.0	6.1	2.5	3.8
									15	21.0	7.6	2.5	3.8
Run 2													
11/23/76	0430-0530	1.1	345	0.05	7.8	11	E	273,730	A	3.0	5.2	2.5	3.4
									1	3.7	6.3	2.6	4.0
									2	-	5.8	2.6	3.6
									3	738	6.0	2.6	3.4
									4	49	6.6	2.7	4.2
									5	6.4	5.4	2.6	3.9
									6	-	5.9	2.6	3.4
									7	3.0	5.3	2.6	3.4
									8	9.2	5.9	2.6	3.4
									9	5.4	5.2	2.5	3.5
									10	11.0	6.0	2.5	3.4
									11	6.4	6.0	2.6	4.0
									12	6.4	5.6	2.7	4.2
									13	14.0	5.8	2.7	3.6
									14	10.0	5.2	2.7	4.0
									15	8.2	6.5	2.7	4.2

TABLE 3-8. Continued

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (°C)	Stability	Q SF ₆ (ug/sec)	Receptor	SF ₆ (ppt)	THC (ppm)	CH ₄ (ppm)	CO (ppm)
Run 3													
11/23/76	0530-0630	0.9	340	0.06	7.4	10	E	276,790	A	5.4	5.2	2.7	3.3
									1	4.7	6.0	2.8	5.4
									2	-	-	-	-
									3	-	-	-	-
									4	6.6	6.5	2.8	4.5
									5	6.0	5.4	2.7	5.1
									6	11.0	5.1	2.8	3.8
									7	10.0	5.8	2.7	3.5
									8	25.0	5.9	2.7	3.8
									9	5.0	5.3	2.8	3.7
									10	4.7	5.2	2.7	4.3
									11	32.0	6.5	2.7	5.5
									12	36.1	5.9	2.8	5.2
									13	30.0	6.1	2.8	5.5
									14	14.0	5.9	2.8	6.4
									15	11.5	6.5	2.8	6.1
Run 4													
11/23/76	0630-0730	1.1	340	0.05	6.5	10	E	267,060	A	6.8	5.2	2.8	4.0
									1	8.2	6.6	2.8	OS
									2	12.0	5.9	2.8	6.1
									3	32.0	6.0	2.8	5.1
									4	120	6.7	2.8	6.7
									5	144	6.4	2.8	OS
									6	10.0	5.9	2.8	4.6
									7	9.2	5.6	2.8	4.4
									8	11.0	5.9	2.8	4.3
									9	18.5	5.8	2.8	5.7
									10	36.1	5.7	2.8	5.5
									11	17.5	6.7	2.8	OS
									12	15.5	5.9	2.8	6.4
									13	14.0	6.0	2.8	6.2
									14	-	-	-	-
									15	59.0	7.1	2.8	OS

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TABLE 3-8. Continued

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (°C)	Stability	Q_{SF_6} (ug/sec)	Receptor	SF ₆ (ppt)	THC (ppm)	CH ₄ (ppm)	CO (ppm)
Run 9													
11/30/76	0330-0430	2.5	335	0.02	4	9	F	299,604	A	19.3	5.1	2.6	2.3
									1	26.0	6.0	2.6	2.8
									2	22.5	6.1	2.5	2.2
									3	4300	9.4	2.6	2.3
									4	13.5	9.2	3.2	2.5
									5	16.5	5.5	3.0	3.3
									6	-	6.0	2.6	2.3
									7	20.5	5.5	2.5	2.1
									8	460	7.0	3.0	2.8
									9	-	5.2	3.0	3.1
									10	17.5	5.9	3.1	5.2
									11	37.0	5.4	2.8	3.2
									12	740	6.0	2.6	2.5
									13	1010	6.5	2.8	2.5
									14	16.5	5.3	2.9	2.9
									15	17.5	6.0	3.0	2.6
Run 10													
11/30/76	0430-0530	2.0	330	0.01	5	8	F	299,604	A	13.3	4.7	2.7	2.3
									1	16.0	5.3	2.5	2.2
									2	17.5	5.7	2.4	1.5
									3	4800	10.6	2.4	1.5
									4	13.5	5.4	3.1	2.0
									5	13.0	4.6	2.7	2.9
									6	13.0	6.0	2.7	1.8
									7	24.0	5.3	2.4	1.6
									8	-	-	-	-
									9	13.0	4.6	2.8	2.7
									10	11.8	5.0	2.8	2.1
									11	130	5.7	2.6	2.8
									12	300	6.3	2.7	2.3
									13	22.5	5.1	2.7	2.1
									14	11.5	4.6	2.8	2.7
									15	13.3	4.9	2.9	2.2

TABLE 3-8. Continued

Date	Time	WS (m/sec)	WT (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (°C)	Stability	Q_{SF_6} (ug/sec)	Receptor	SF ₆ (ppt)	TIC (ppm)	CH ₄ (ppm)	CO (ppm)
Run 11													
11/30/76	0530-0630	2.2	360	0.01		3	F	299,604	A	5.6	4.7	2.6	4.1
									1	9.8	6.4	2.4	5.0
									2	5.6	5.5	2.3	1.9
									3	4700	7.6	2.4	2.4
									4	10.5	10.0	3.1	2.7
									5	6.3	4.8	2.6	6.6
									6	7.7	5.6	2.7	4.5
									7	7.0	4.9	2.5	2.3
									8	455	7.9	2.4	1.1
									9	6.3	4.7	2.6	4.8
									10	9.0	4.5	2.6	2.0
									11	62.0	5.3	2.6	2.7
									12	1200	6.1	2.4	1.8
									13	425	6.1	2.6	2.5
									14	-	-	-	-
									15	9.4	4.6	2.6	3.1
Run 12													
11/30/76	0630-0730	2.9	365	0.02		3	F	299,604	A	9.0	5.1	2.5	OS
									1	7.0	5.9	2.5	OS
									2	25.0	6.3	2.3	5.6
									3	2100	9.7	2.4	5.1
									4	23.0	OS	2.4	4.8
									5	12.0	6.3	2.8	OS
									6	5.6	5.3	2.4	7.3
									7	9.0	5.2	2.3	4.9
									8	2800	5.7	2.3	2.9
									9	37.0	6.0	2.7	OS
									10	9.0	4.7	2.6	5.0
									11	9.0	4.7	2.4	6.0
									12	820	6.0	2.3	5.2
									13	1175	6.0	2.3	4.3
									14	155	6.0	2.6	OS
									15	29.0	4.5	2.5	6.0

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TABLE 3-8. Continued

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (°C)	Stability (F)	Q_{SF_6} (ug/sec)	Receptor	SF ₆ (ppt)	FHC (ppm)	CH ₄ (ppm)	CO (ppm)
Run 13													
12/1/76	0400-0500	2.0	315	0.01		S	F	295,630	A1	4.8	5.2	2.9	2.5
									A2	3.4	5.3	3.0	2.5
									1	4.8	7.8	3.2	2.7
									2	3.0	5.4	3.0	2.3
									3	4.2	5.4	2.8	2.7
									4	48.0	7.4	2.9	2.5
									5	-	-	-	-
									6	460	6.6	2.8	2.1
									7	1300	6.1	2.9	2.3
									8	100	6.1	2.9	2.3
									9	464	5.9	2.9	2.2
									10	13.0	5.3	2.9	2.3
									11	4.8	5.4	3.3	2.3
									12	125	6.1	2.8	2.3
									13	30.5	5.4	2.9	2.9
									14	42.5	5.2	2.8	2.4
									15	4.8	5.3	2.8	2.5
Run 14													
12/1/76	0500-0600	2.2	335	0.01		4	F	293,217	A1	4.2	5.0	2.9	3.1
									A2	4.2	5.0	3.0	3.6
									1	5.4	5.8	3.1	3.2
									2	2.6	6.5	3.1	1.8
									3	6.6	5.1	2.8	3.8
									4	2.6	6.0	3.3	2.5
									5	2.6	5.7	2.8	2.5
									6	2.6	6.3	2.6	2.0
									7	1550	6.3	2.7	2.3
									8	17.0	6.5	3.0	2.3
									9	315	6.0	2.8	1.8
									10	-	-	-	-
									11	22.5	5.5	3.1	2.3
									12	200	6.2	2.8	2.4
									13	245	5.1	2.8	2.4
									14	1025	5.3	2.8	4.1
									15	6.0	5.0	2.8	3.2

TABLE 3-8. Continued

Date	Time	\overline{WS} (m/sec)	\overline{WD} (deg)	σ_w (m/sec)	σ_n (deg)	Temp (°C)	Stability	Q_{SF_6} (ug/sec)	Receptor	SF_6 (ppt)	THC (ppm)	CH_4 (ppm)	CO (ppm)
Run 15													
12/1/76	0800-0900	1.6	310	0.09	7	13	F	286,220	A1	76.0	5.2	2.2	5.0
									A2	32.0	6.0	2.3	5.5
									1	-	7.3	2.3	4.1
									2	200	7.8	2.4	5.2
									3	1100	6.7	2.4	7.4
									4	34.5	5.4	2.2	4.9
									5	96.0	6.4	2.3	5.5
									6	150	6.5	2.2	4.7
									7	1400	7.2	2.3	5.3
									8	71	6.0	2.4	6.0
									9	450	6.4	2.3	6.1
									10	480	6.7	2.3	4.4
									11	-	OS	2.3	5.0
									12	-	6.9	2.3	5.3
									13	480	6.0	2.3	5.1
									14	500	5.2	2.3	4.1
									15	498	6.8	2.3	5.9
Run 16													
12/1/76	0900-1000	1.8	325	0.11	8	17	F	282,875	A1	28.0	6.1	2.4	6.0
									A2	32.0	5.2	2.4	6.0
									1	2.6	5.9	2.1	4.7
									2	9.8	7.3	2.4	5.6
									3	7.8	6.8	2.5	6.9
									4	10.5	5.9	2.2	4.7
									5	7.8	6.5	2.2	5.0
									6	13.5	5.8	2.2	4.8
									7	205	6.4	2.3	5.5
									8	15.0	6.0	2.2	5.3
									9	76.0	6.2	2.3	4.9
									10	140	7.3	2.4	5.5
									11	7.8	8.2	2.5	5.5
									12	44.0	7.4	2.1	4.9
									13	29.0	6.0	2.3	5.1
									14	13.5	5.2	2.4	5.5
									15	96.0	6.8	2.4	5.1

- = missing data
 OS = over-scale
 \overline{WS} = mean wind speed
 \overline{WD} = mean wind direction
 Q_{SF_6} = SF_6 release rate

E. Diffusion Model--

The AVQUAL diffusion model, in conjunction with local measurements of ambient test conditions, was used to predict concentrations downstream of the refinery. Subsequently, AV attempted to validate or "calibrate" its diffusion model using the test data presented above. Because of apparent meteorological changes in the refinery which were not detected at the mobile laboratory site, substantial differences existed between the SF₆ concentrations predicted by the model and those actually measured. Variations were attributed to large structures (tanks, towers, etc.) and high-temperature processes in the refineries which caused increases in vertical wind velocity of up to two orders of magnitude. To use the AVQUAL diffusion model, calibration data were developed for selected runs. These are shown in Table 3-9. In the table, a_v is the vertical dispersion speed and λ is the ratio of vertical to horizontal dispersion speed. The difference in the latter two parameters between "measured" and "calibrated" should be noted.

F. Emission Prediction--

After calibrating the AVQUAL the refinery was divided into five zones. Using receptor concentrations and calibrated meteorological data the source concentrations were calculated. The predicted emissions in lb/hr are shown in Table 3-10. The KVB calculated emissions are shown in Table 3-11. For comparison the "Total" emission column in Table 3-10 should be compared for the "Total" row in Table 3-11. Specifically the average prediction of 26 lb/hr should be compared to KVB's predicted nighttime emission of 134 lb/hr. The "SCAFCD" values indicated were the emission rates listed in the SCAPCD permit file as of mid 1976. The "AP-42" values were computed using the equipment inventory taken by KVB and emission factors for that equipment. The "KVB/ARB" column reflects KVB best predictions using emission factors reflecting test data taken at the Douglas refinery. The nighttime emissions are lower because the fixed roof storage tanks are inhaling at night and do not emit.

A possible cause of the discrepancy between the AV prediction and the KVB source testing results was the vertical diffusion of the hydrocarbon gas, especially the lighter ends so that the fenseline monitors did not receive a representative concentration. Source testing data clearly indicated

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TABLE 3-9. COMPARISON OF MEASURED AND CALIBRATED METEOROLOGICAL DATA

Run No.	Mean Wind Speed (m/sec)	Mean Wind Direction (deg)		a_v (m/sec)		λ	
		Measured	Calibrated	Measured*	Calibrated	Measured**	Calibrated
1	1.6	340	360	0.07	4.4	0.35	10
9	2.5	335	355	0.02	2.5	0.11	3.5
10	2.0	330	350	0.01	1.8	0.06	3.0
11	2.2	340	355	0.01	2.5	0.07	5.5
15	1.6	330	355	0.09	2.5	0.46	5.0

* assuming $a_v = \sigma_w$

** calculated as follows:

$$\lambda = \frac{a_v}{a} = \frac{\sigma_w}{(\bar{\mu}_\theta)(\sigma_\theta)}$$

where σ_θ in radian

TABLE 3-10. HYDROCARBON EMISSION PREDICTIONS FOR VARIOUS SOURCE CATEGORIES OF THE DOUGLAS REFINERY IN LB/HR

Run No.	Q ₁	Q ₂	Q ₃	Q ₄	Q ₅	Total
1	8	0	0	0	39	47
9	14	0	0	0	10	24
10	12	0	0	3	0	15
11	18	0	0	1	0	19
15	23	0	0	0	0	23
Avg.	15	0	0	1	10	26

- Q₁ = process areas and emulsion plant
- Q₂ = asphalt plant
- Q₃ = loading-unloading facilities
- Q₄ = fixed roof storage tanks
- Q₅ = floating roof storage tanks

TABLE 3-11. COMPARISON OF KVB'S PRELIMINARY HYDROCARBON EMISSIONS SOURCE TESTING RESULTS WITH THE RESULTS CALCULATED BY USING THE SCAPCD AND AP-42 DATA FOR THE DOUGLAS REFINERY IN LB/HR

	SC APCD	AP-42	KVB/ARB	
			24 Hr. Av.	Night
Stack Emissions	11	26	13	13
Fugitive Emissions	84	123	54	54
Tank Storage and Transfer	90	95	95	67
TOTAL	185	244	162	134

CH₄ emissions from the refinery. However, AV's ambient testing data showed little or no difference for the upwind and downwind CH₄ data. It is possible that under the very stable conditions most of the CH₄ emitted would diffuse upward, and thus is not detectable in the ground level. Heavier hydrocarbons (in relation to air) under the same stable atmospheric conditions would tend to diffuse downward. However, the various thermal processes in the refinery cause substantial updrafts which could cause upward movement of hydrocarbon gases heavier than air.

G. Conclusions--

Despite some indication that with further work the AV diffusion model might be able to predict refinery emissions with ambient sampling data (i.e., high wind velocity and additional receptor stations above ground level), KVB did not feel that the results of these tests warranted the further use of the method. Originally, it was planned to use this method on two sources if the refinery results turned out to be satisfactory.

3.3 QUALITY CONTROL

A comprehensive quality control program was conducted as an integral part of the overall organic-emission field tests. The program featured:

1. Calibration of field test instruments with ASTM methods and NBS standards
2. Frequent response-factor calibration of laboratory instruments
3. Interlaboratory checks for accuracy
4. Concurrent samples taken from the same source with separate but identical trains for precision checks
5. Separate total organic content analysis to backup the GC analysis
6. Unannounced "blanks" of zero gas, calibration gas, etc.
7. An independent QC consulting team.

From the outset KVB engaged the services of three experts in the field of organic analysis, Drs. James N. Pitts, Jr., Daniel Grosjean and Barbara Finlaysen-Pitts working as a team from EcoScience Systems Inc. (ESS). This team participated in the initial evaluation of the sampling equipment and analytical methodology and defined a quality program with the above mentioned features. The special QC tests (duplicates, blanks, round robins, etc.) accounted for approximately 10% of the test budget and afforded an excellent assessment of measurement error which was as follows:

1. The total hydrocarbon emissions were good to within $\pm 25\%$.
2. Values for the emissions of individual hydrocarbons, however, were less certain than that for total hydrocarbons.
3. The sum of the errors in sampling and analyses for individual alkanes probably was in the range of 25-50%.
4. The concentrations of oxygenates, aromatics and halogenates must be considered lower limits only with the possible error being a factor of three or more.

In addition to the above numerical assessment ESS concluded, "In summary then, the most feasible and reliable field sampling and laboratory analytical techniques were employed in this program to yield accurate source emissions data. The latter can be confidently applied to the development of a hydrocarbon emission inventory for stationary sources in the SCAB with 'state-of-the-art' accuracy and precision."

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The ESS report is presented in the Appendix. Their report contains not only a discussion of selected data which lead to the above numerical error assessment but copies of comparative test data calibration data report forms documenting blank sample analyses results, etc.

Presented below are some selected data which illustrate the basis of the conclusions reached by ESS.

3.3.1 Round Robin and Sample Recovery Tests

Before beginning the field tests an analytical program was conducted to establish assurance in sampling and analysis for stationary pollution source studies. This included an evaluation of field sampling equipment, laboratory gas sampling, instrument variability, standardization of gas chromatographic analysis columns, accuracy and precision of data. To test these parameters, four calibration gases were procured in "K" bottles from Precision Gas Products, Inc. including selected (1) aliphatic hydrocarbons, (2) aromatic hydrocarbons, (3) oxygenated organics and (4) halogenated organic compounds. Concentrations were specified and controlled by the KVB program manager who retained certifications until analyses were performed.

Upon receipt of the four "K" bottles, three sets of samples were prepared in 250 ml gas collection bottles by KVB and delivered to ARLI, the SCAPCD laboratory in Los Angeles and the ARB laboratory in El Monte. (Only the aliphatic and aromatic samples were sent to the ARB.) The results of these analyses are presented in Tables 3-12 through 3-15. Added to each standard as a control compound was hexane selected because of its unreactive nature and low adsorptivity.

Two of the sampling trains shown in Figure 3-1 were used to collect samples of the four calibration gases using the setup shown in Figure 3-12. Results of the analyses of these samples are compared to other analyses of these calibration gases using various handling and analysis methods are presented in Tables 3-16 through 3-19 and discussed below.

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TABLE 3-12. QUALITY ASSURANCE ALIPHATIC STANDARD

All data are reported in ppm in nitrogen.

Compound	Certified Contents*	Analytical Results		
		ARLI	SCAPCD	CARB
Ethylene	51	50	21	D [§]
Propane	53	47	27	32
Propylene	53	57	32	30
1,3-Butadiene	51	3 [#]	28 ⁺	28
Isobutane	NR	NR [‡]	NR	0.4
Hexane	50	50	30	40
Heptane	51	46	24	D
Isooctane	50	43	26	D

*Analytical information prepared by Precision Gas Products Co.

⁺ Identified as 1-butene

[§]D = Identified but not quantified (insufficient sample)

[#]The ARLI recovery of butadiene was significantly below the certified composition. This was apparently caused during thermal desorption treatment of the sample bottle and transfer equipment. SCAPCD and CARB labs are believed not to have heated the sample bottles.

[‡]NR = not reported

TABLE 3-13. QUALITY ASSURANCE AROMATIC STANDARD

All data reported in ppm in nitrogen.

Compound	Certified Contents	Analytical Results		
		ARLI	SCAPCD	CARB
Benzene	52	50	15	34
Toluene	48	46	11	34
Ethylbenzene	49	51	5	20
Chlorobenzene	50	51	3	NR
Hexane	49	50	20	35
Xylene	NR	NR	3	D

NR = Not reported D = detected but not quantified

TABLE 3-14. QUALITY ASSURANCE HALOGENATED HYDROCARBON STANDARD

All data reported in ppm in nitrogen.

Compound	Certified Contents	Analytical Results	
		ARLI	SCAPCD
Freon 113	48	47	22
Hexane	50	50	5
Methyl Chloride	55	48	NR
1,1,1 Trichloroethane (Methyl chloroform)	50	46	37
Chloroform	49	46	49

NR - Not reported

TABLE 3-15. QUALITY ASSURANCE OXYGENATED ORGANICS STANDARD

All data reported in ppm in nitrogen.

Compound	Certified Contents	Analytical Results	
		ARLI	SCAPCD
Methanol	53	4	NR
Acetone	52	43	7
Isopropanol	NR	NR	9
Methyl Ethyl Ketone (2-Butanone)	51	45	2
Methyl Isobutyl Ketone	48	42*	20
Hexane	48	50	37

* Identified as 2-hexenone

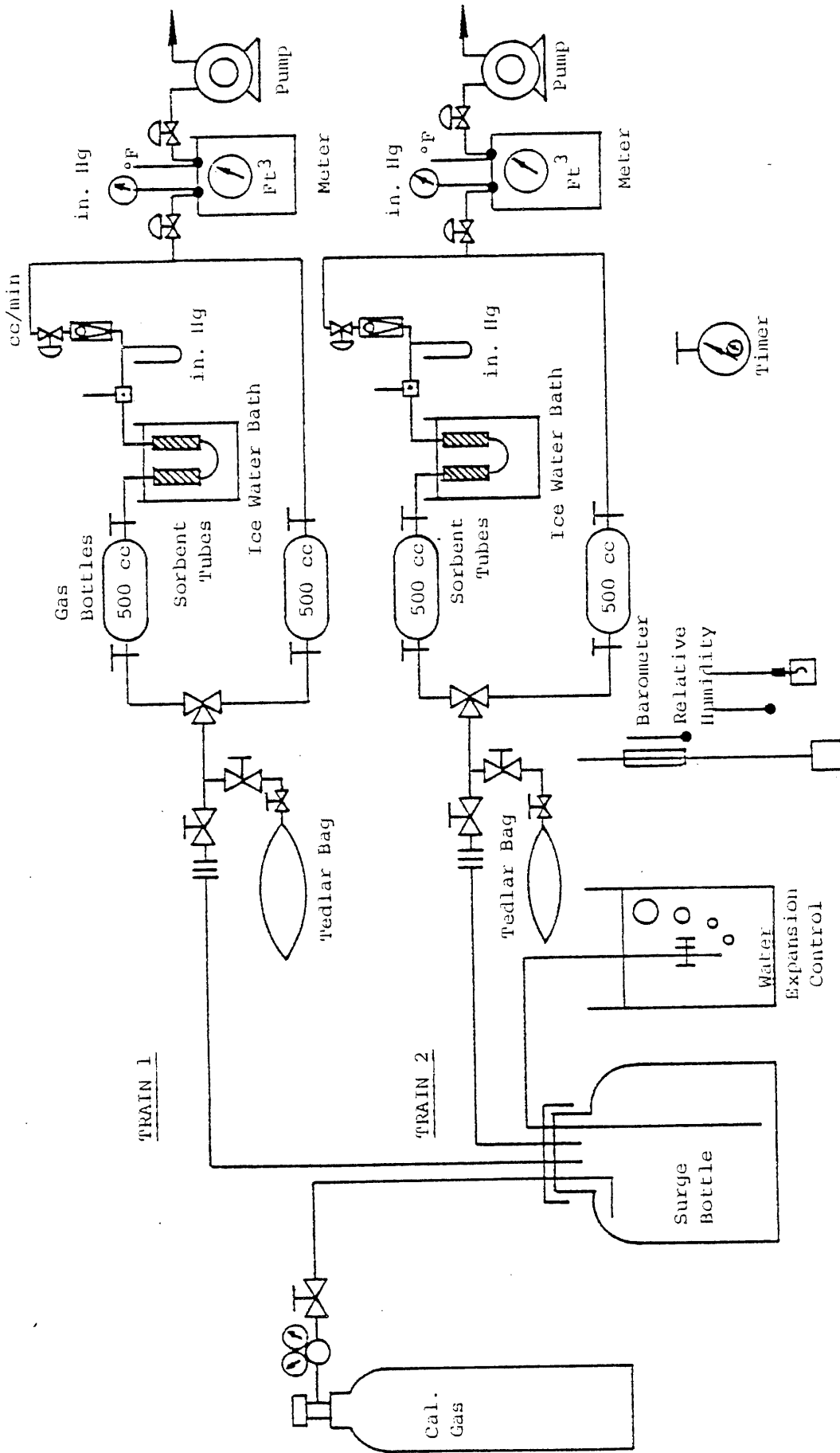


Figure 3-12. Sampling trains in QC test with calibration gas.

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TABLE 3-16. RECOVERY STUDIES USING THE ALIPHATIC STANDARD

Analysis by Gas Chromatography - Porapak Q Column Temperature Programmed
Reported as ppm of Component in Nitrogen

Compound	Case 1	Case 2	Case 3	Case 4		Case 5	
	51	50	46	Grab	Charcoal Tube	Grab	Charcoal Tube
				Front	Back	Front	Back
Ethylene	51	50	46	33	0	29	0
Propane	53	47	47	37	14	32	12
Propene	53	57	48	30	14	27	10
1,3-Butadiene	51	3	33	8	25	8	24
n-Hexane	50	50	49	35	46	33	35
n-Heptane	51	46	49	36	43	36	44
Isooctane							
(2 Methyl Heptane)	<u>50</u>	<u>43</u>	<u>45</u>	<u>34</u>	<u>43</u>	<u>32</u>	<u>45</u>
Total Recovery	359	296	317	213	185	197	198

3
0
1

- Case 1. Certified contents - gravimetrically prepared.
- Case 2. Glass-Teflon grab sample, GC analyzed on receipt; sample bottle and transfer lines heated during sampling and analysis.
- Case 3. Glass-Teflon grab sample - sampled and analyzed without heating during transfer process.
- Case 4. Glass-Teflon grab sample and activated carbon sorption tube using field sampling train - first test. 27.7 liters of standard gas sampled.
- Case 5. Same sampling conditions as for Case 4 - second test. 32 liters of standard gas sampled.

TABLE 3-17. RECOVERY STUDIES USING THE AROMATIC STANDARD
 Analysis by Gas Chromatography - Porapac Q Column Temperature Programmed
 Reported as ppm of Component in Nitrogen

Compound	Case 1		Case 2		Case 3		Case 4		Case 5	
	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube
n-Hexane	49	50	40	43	43	45 ± 2	44	45 ± 3	44	45 ± 3
Benzene	52	50	43	47	47	45 ± 2	47	46 ± 4	47	46 ± 4
Toluene	48	46	26	28	28	45 ± 1	23	47 ± 3	23	47 ± 3
Ethylbenzene	49	51	23	25	25	46 ± 1	20	49 ± 3	20	49 ± 3
Chlorobenzene	50	51	45	48	48	37 ± 1	46	39 ± 3	46	39 ± 3
Total Recovery	248	248	177	191	191	218 ± 2	180	226 ± 3	180	226 ± 3

61
62

- Case 1. Certified contents - gravimetrically prepared.
- Case 2. Glass-Teflon grab sample, GC analyzed on receipt; sample bottle and transfer lines heated during sampling and analysis.
- Case 3. Glass-Teflon grab sample - sampled and analyzed without heating during transfer process.
- Case 4. Glass-Teflon grab sample and activated carbon sorption tube using field sampling train - first test. 30 liters of standard gas sampled.
- Case 5. Same sampling conditions as for Case 4 - second test. 28 liters of standard gas sampled.

TABLE 3-18. RECOVERY STUDIES USING THE HALOCARBON STANDARD

Analyzed by Gas Chromatography - Porapak Q Column Temperature Programmed
Reported as ppm of Component in Nitrogen

Compound	Case 1		Case 2		Case 3		Case 4		Case 5
	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube	Charcoal Tube
Hexane	50	50	44	33	40	38	49	3	49 + 3
Methylene chloride	55	48	<0.1*	<0.1	<0.1	<0.1	50	3	50 + 3
Chloroform	49	46	15	28	19	31	33	1	33 + 1
Methylchloroform (1,1,1-Trichloroethane)	50	46	<1	30	<1	34	41	2	41 + 2
Freon 113 (1,1,2-Trichloro - 2,2,1-Trifluoroethane)	48	47	37	21	34	28	33	3	33 + 3
Total Recovery	252	237	112	131	206	3			

*MeCL₂ masked by solvent.

Case 1. Certified contents - gravimetrically prepared.

Case 2. Glass-Teflon grab sample analyzed on receipt of standard sample bottle and transfer lines heated during sampling and analysis.

Case 3. Glass-Teflon grab sample and activated carbon sorption tube using field sampling train - first test. 24 liters of standard gas sampled.

Case 4. Same as Case 3, second test. 28 liters of standard gas sampled.

Case 5. Glass-Teflon grab sample analyzed approximately 45 days after sample receipt. Heated transfer lines and heated grab sample during analyses.

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TABLE 3-19. RECOVERY STUDIES USING OXYGENATED ORGANICS STANDARD
 Analysis by Gas Chromatography - Porapak Q Column Temperature Programmed
 Reported as ppm of Component in Nitrogen

Compound	Case 1		Case 2		Case 3		Case 4		Case 5	
	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube	Grab	Charcoal Tube
Hexane	48	42	Recovery*	39	*	39	*	47	*	47
Methyl Alcohol	53	4	Less Than	<1	*	<1	*	<1	*	<1
Acetone	52	43	ppm Level	25	*	25	*	28	*	28
Methyl Ethyl Ketone (2-Butanone)	51	45		39	*	39	*	47	*	47
Methyl Isobutyl Ketone	<u>48</u>	<u>42</u>		<u>33</u>	*	<u>33</u>	*	<u>39</u>	*	<u>39</u>
Total Recovery	252	176		136		136		161		161

3 1 4

*The oxygenated material could not be displaced from the sampling container without heating because of adsorption or moisture and absorption.

- Case 1. Certified contents - gravimetrically prepared.
- Case 2. Glass-Teflon grab sample analyzed by GC on receipt of standard mixture. All transfer lines and sampling system heated.
- Case 3. Same as Case 2 without heating.
- Case 4. Glass-Teflon grab sample and activated carbon sorption tube using field sampling train - first test. 28 liters of standard gas sampled.
- Case 5. Same as Case 4, second test. 23.8 liters of standard gas sampled.

Recovery studies using the aliphatic hydrocarbon standard indicated some limitations in sampling or analysis. For example, when the collection train was used as shown in Case 5 of Table 3-16, 32 liters of gas at the selected flow rate of 3 liter/minute showed a breakthrough of low molecular weight hydrocarbons on charcoal. This, of course, did not affect sample collection because the intended use of the adsorbents were for compounds boiling above 80 °F. Low values reported for butadiene seemed to indicate polymerization or decomposition. The analytical data for Case 2 showed a recovery of only 3 ppm when the sampling container was heated to approximately 120 °F during transfer to the chromatograph. Case 3 of the gas sample was transferred to the GC loop without heating (33 ppm of butadiene was recovered). Because ARLI and the other referee laboratories found approximately 30 ppm of butadiene in all tests, it can be assumed that the gas phase of the Precision Gas Standard contains only this amount. Either wall adsorption or catalytic polymerization within the "K" bottle could explain the difference between the analyzed and gravimetrically prepared material. The accuracy observed for sorbent collected hydrocarbons above C₅ was within experimental error. It was also indicated that heating of the glass grab sample containers to 100 °F would maximize recovery of the lower hydrocarbons, < C₄.

Table 3-17 shows the data obtained on the aromatic hydrocarbon gas standard sample. These data showed that accuracy could be achieved within the limitations of analytical repeatability. Warming the grab sample bottle of toluene and ethylbenzene appear to improve the yield. Unexplained retention of chlorobenzene on the charcoal was observed although 80% recoveries of higher molecular weight compounds are considered acceptable by most laboratories and government agencies. No corrections were made for hydrocarbon sampling to actual and projected stack emissions.

Table 3-18 reflects the analytical studies made on halocarbon gas mixtures. These data are not consistent with the accuracy and reproducibility of the hydrocarbon data. It would appear that for the higher molecular weight halogenated materials, between 20 and 30% losses occurred simply on

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standing in the metal "K" bottle. Case 5 of Table 3-18 illustrates this condition. The loss of methylene chloride in grab sampling appeared to be real although in ARLI's previous experience with analyzing for traces of methylene chloride there had been no problem. Methylene chloride elutes with carbon disulfide from a Porapak Q column. Therefore, no accurate measure of concentration could be made. The reported value of < 0.1 ppm appeared to be a small shoulder on the solvent peak and was probably an impurity in one or both of the compounds.

Table 3-19 presents the results obtained for oxygenated organic materials. If it can be assumed that the amount of methyl alcohol found in the "K" bottle by analysis, restandardization, and reanalysis (as was actually performed in the laboratory) were correct, the recoveries were within 20%. Methyl ethyl ketone elutes with hexane from the Porapak Q column. However, from other recovery data, standards and grab samples of the Precision Gas mixture, and response factors applied to the measured area, the calculated concentration reported under Case 4 and 5 agree within the experimental limits.

The oxygenated materials were strongly adsorbed on the glass bottle walls. This was apparent in the data present for the grab-train samples of Case 4 and 5 as well as the ambient grab sample of Case 3. All field grab samples that were expected to contain oxygenated materials were warmed and the transfer lines maintained at an elevated temperature injection into the GC.

3.3.2 Interlaboratory Field Sample Analysis

During the test of the Huntington Beach oil field emissions WOGA used a consulting firm, RETA, to monitor KVB's procedures. RETA collected duplicate samples of gas in grab bottles which were analyzed by the Union Oil Research Laboratory in Brea, CA. A comparison of the KVB-ARLI results with those of RETA-Union are shown in Tables 3-20 through 3-25.

TABLE 3-20. COMPARISON OF RESULTS OF KVB-ARLI AND RETA-UNION OIL LABORATORIES TESTS ON LEAKY VALVES

Compound	KVB Sample #10062	
	KVB-ARLI Gas Bottle ppm	RETA Union Oil Gas Bottle ppm
Methane	523,000	455,000
Ethane	38,000	27,000
Propane	20,700	13,000
Cyclopentane	88	00
n-Butane	4,890	2,900
i-Butane	3,980	2,500
n-Pentane	778	400
i-Pentane	1,270	700
Methylcyclopentane	476	--
Isomers of hexane	370	500
C-7 Cycloparaffins	450	--
C-8 Cycloparaffins	54	--
Benzene	17	--

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TABLE 3-21. COMPARISON OF RESULTS OF KVB-ARLI AND RETA-UNION OIL LABORATORIES TESTS ON LEAKY VALVES

Compound	KVB Sample #10105A KVB-ARLI Gas Bottle ppm	RETA-Union Oil Gas Bottle ppm
Methane	816,000	710,300
Ethane	28,700	35,700
Propane	29,600	36,200
Cyclopentane	674	--
n-Butane	14,700	19,000
i-Butane	8,010	10,200
n-Pentane	4,350	6,500
i-Pentane	5,890	8,400
Hexane	3,020	--
Isomers of Hexane	1,950	20,400
Cyclohexane	321	--
C-7 Cycloparaffins	2,010	--
C-8 Cycloparaffins	166	--

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TABLE 3-22. COMPARISON OF RESULTS OF KVB-ARLI AND RETA-UNION OIL LABORATORIES TESTS ON LEAKY VALVES

Compound	KVB Sample #10063A KVB-ARLI Gas Bottle ppm	RETA-Union Oil Gas Bottle ppm
Methane	16,300	15,000
Ethane	2,050	800
Propane	300	100
n-Butane	36	--
i-Butane	23	--
n-Pentane	12	--
i-Pentane	8	100
Hexane	47	100

TABLE 3-23. COMPARISON OF RESULTS OF KVB-ARLI AND RETA-UNION OIL LABORATORIES TESTS ON LEAKY VALVES

Compound	KVB Sample #10072A KVB-ARLI Gas Bottle ppm	RETA-Union Oil Gas Bottle ppm
Methane	13,900	15,200
Ethane	786	1,000
Propane	438	600
n-Butane	128	100
i-Butane	87	100
n-Pentane	23	--
i-Pentane	33	--

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TABLE 3-24. COMPARISON OF RESULTS OF KVB-ARLI AND RETA-UNION OIL LABORATORIES TESTS ON LEAKY VALVES

Compound	KVB Sample #10090 KVB-ARLI Gas Bottle ppm	RETA-Union Oil Gas Bottle ppm
Methane	688	1000
Ethane	42	
Propane	29	
Cyclopentane	4	
n-Butane	20	
i-Butane	14	
n-Pentane	32	
i-Pentane	16	
Methylcyclopentane	39	
Isomers of hexane	25	800
C-7 Cycloparaffins	102	
C-8 Cycloparaffins	71	
C-9 Cycloparaffins	10	
Benzene	11	

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TABLE 3-25. COMPARISON OF RESULTS OF KVB-ARLI AND RETA-UNION OIL LABORATORIES TESTS ON LEAKY VALVES

Compound	KVB Sample #10094B KVB-ARLI Gas Bottle ppm	RETA-Union Oil Gas Bottle ppm
Methane	6280	8300
Ethane	356	300
Propane	112	
Cyclopentane	1	
n-Butane	52	
i-Butane	15	
n-Pentane	27	
i-Pentane	12	
Hexane	119	
Heptane	1	
Isomers of Hexane	14	
Isomers of Heptane	4	
Benzene	3	

Although these samples were taken sequentially rather than simultaneously, the results in these tables show good agreement for total hydrocarbons as well as for the two major components methane and ethane. For example deviations from the mean methane concentration ranged from -28% to +10% the average deviation being 13%. The agreement was consistent over a range of concentrations from under 700 to over 800,000 ppm. The greatest discrepancies percentagewise were in the low concentration species. This latter phenomenon was generally observed throughout the QC program.

3.3.3 Redundant Field Samples

On selected sources two or three independent trains were inserted into the source for simultaneous sampling. The analyses of the samples were performed without informing the laboratory of identical nature of the sources. The results of some of these tests are presented in Tables 3-26 through 3-30.

Table 3-30 presents the results of two train configurations, one with the LiOH agent in the impinger and one without. Note that for that stack the results were unchange with or without the use of LiOH which was used in every combustion source test.

TABLE 3-26. REDUNDANT TESTS AT A PRINTED CIRCUIT BOARD
PHOTOETCH OPERATION

	<u>Train 1</u>	<u>Train 2</u>
<u>Bottle Sample</u>	ppm	ppm
Methane	0	98
Ethane	0	39
Propane	66	72
I-Butane	40	51
Methanol	4200	4500
Dichloromethane	23000	25000
1.1.1 Trichloromethane	47	38
<u>Charcoal Sample</u>	(0.59 SCF)	(0.71 SCF)
Methanol	59	17
Dichloromethane	*	*
1.1.1 Trichloromethane	18	10
Benzene	2	1.1
Toluene	0.6	1.4

*CS₂ solvent masked the dichloromethane. Refer to bottle sample.

TABLE 3-27. REDUNDANT TESTS AT AN AUTOMOTIVE ASSEMBLY PLANT

	<u>Train 1</u> <u>ppm</u>	<u>Train 2</u> <u>ppm</u>	<u>Train 3</u> <u>ppm</u>
<u>Bottle Sample</u>			
Methane	3.1	3.1	2.9
Ethane	1.1	1.1	1.0
<u>Charcoal Sample</u>			
	(0.70 SCF)	(0.57 SCF)	(0.46 SCF)
Heptane	1.5	0.9	0.8

TABLE 3-28. REDUNDANT TESTS AT A UTILITY BOILER

	<u>Train 1</u> <u>ppm</u>	<u>Train 2</u> <u>ppm</u>
<u>Bottle Sample</u>		
Methane	0	1.4
N-Butane	0.5	0
<u>Charcoal Sample</u>		
Hexane	0.1	0
Acetone	0.2	1.8
Aldehyde	2.2	2.2

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TABLE 3-29. REDUNDANT TESTS ON A GAS TURBINE EXHAUST

	<u>Train 1</u> <u>ppm</u>	<u>Train 2</u> <u>ppm</u>
<u>Bottle Sample</u>		
Methane	0.8	0.7
<u>Charcoal Sample</u>	0	0
<u>Aldehydes</u>	6.0	6.0

TABLE 3-30. REDUNDANT TESTS ON A REFINERY CO BOILER

	<u>Train 1</u> <u>With LiOH</u> <u>ppm</u>	<u>Train 2</u> <u>With LiOH</u> <u>ppm</u>
<u>Bottle Sample</u>		
Methane	2.2	2.3
<u>Charcoal Sample</u>		
Hexane	0.2	0.2
<u>Aldehydes</u>	2.1	2.1
	<u>Train 3</u> <u>Without LiOH</u> <u>ppm</u>	<u>Train 4</u> <u>Without LiOH</u> <u>ppm</u>
<u>Charcoal Sample</u>		
Hexane	0.2	0.2
<u>Aldehydes</u>	2.1	2.1

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3.4 TEST RESULTS

3.4.1 Summary

The key results of all field tests are summarized in Table 3-31. The process name is a brief description of the process or device tested with an indication whether or not a control device was involved. The KVB Test No. was the control number used to identify samples and results between the field, laboratory and office. The KVB Code was assigned to identify the plant and test site. Except for Douglas Oil Co. the specific test sites will not be identified. Because of the unique series of ambient tests run at Douglas (Section 3.2.4) it was necessary to reveal this source to better appreciate the test accomplishment. Where a control device was tested the measured control efficiency ($\frac{\text{Input} - \text{Output}}{\text{Input}} \times 100$, percent) is indicated. The total hydrocarbon emissions are based on KVB measurements (lb/hr) extrapolated using information provided by the source or the AQMD on operational data (hr/day, days/wk, whk/yr). In the columns headed "Species by % wt of Total" is a breakdown of the total organic emission by the three reactivity classes defined by the ARB as shown in Table 3-32. A detailed breakdown of organic compounds for each of these tests is presented in the Appendix.

Care must be taken in using the quantitative data in Table 3-31 and the Appendix as typical of the process. While KVB attempted to test these devices under average or typically representative conditions, it must be realized that most of the processes tested were time dependent and many varied from product to product in the same plant. KVB's tests were of a survey nature. Actual sampling time was under twenty minutes.

The data are most valuable as an indication of the type of compounds being emitted and some assessment of how much to the extent of judging the validity of other available emissions data. As discussed in Section 2.0 KVB used these data to check the emission factors in AP 42 and those used by the SCAQMD in preparing their emissions inventory.

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TABLE 3-31. SUMMARY OF TEST RESULTS

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat		Total Organic Emissions			Analytical Results			Remarks	
							CO ₂	CO	O ₂	lb/hr	T/Yr	lb/day	Species by % wt. of Total ARB			
													ARB Class 1	ARB Class 2		ARB Class 3
Printing Press #3 Press	10018	11-9-76	1-1		2000	0	-	-	2.11	6.6	38	51	47	2		
Printing Press #4 Press	10019	11-9-76	1-2		4702	0	-	-	8.38	26.4	151	62	38	< 1		
Printing Press #5 Press South & North Combined	10020 10022	11-9-76 11-9-76	1-3/4		7845 3581 11426	0	-	-	189	596	4538	3	96	1		
Printing Press #3 Oven, L-2 Laminator	10021	11-9-76	1-5		1048	0	-	-	2.39	5.3	30.1	22	69	9		
Rotogravure Press Charcoal Sorbent Outlet	10500	6-9-77	2-1	96.4	83924	2.5	-	-	40.7	127	975	30	48	22		
Rotogravure Press Peripheral Fans	10501	6-9-77	2-2		46250*	-	-	-	52.7	164	1264	3	69	28	*One stack measured, extrapolated to seven stacks	
Rotogravure Press Inlet to Charcoal Beds	10502	6-9-77	2-3		83924	2.0	-	-	1124	3506	26973	4	63	33		
Chemical Plant Phth. Anhyd. Incin. Outlet	10132	2-9-77	3-1		27796	8.1	3.0	0	22.5*	98.5	540	93	4	3	*Atypical operation resulting from burner decay	
Chemical Plant Sump Entry Accum.	10134	2-9-77	3-2		63.0	7.5	-	-	0.018	0.078	0.43	-	100	-		
Chemical Plant Leaky Elbow-Pumpline	10135	2-10-77	3-3		0.081	0	-	-	0.10031	0.4394	2.41	98	1	1		
Chemical Plant Fluorocarbon Filling Rack	10136A	2-10-77	3-4		0.009	2.1	-	-	0.0387	0.170	0.9288	89	11	-		

TABLE 3-31 (Continued)

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Analytical Results				Remarks	
							CO ₂	CO	O ₂	Total Organic Emissions lb/hr	Total Organic Emissions T/yr	ARB Class 1	ARB Class 2		ARB Class 3
Electrostatic Paint Sp. & Oven Afterburner-Inlet	10120	1-27-77	4-1		823	4.4	0	0	19.6	4	14.64	96	45	5	50
Paint Sp. & Oven Afterburner-Outlet	10121	1-27-77	4-2	94%	4569	3.52	1.0	0.4	18.2	0.223	0.834	5.35	49	6	45
Paint Sp. & Oven Stack Vent	10122	1/27/77	4-3	96%	2156	3.52	-	-	-	0.152	0.569	3.65	35	49	16
Oil Field Wet Gas Valve From Traps - SE	10062	1-10-77	5-1		0.043	0	-	-	-	0.08	0.4	1.92	87	13	-
Oil Field Level Controller	10063	1-10-77	5-2		0.056	0	-	-	-	0.003	0.013	0.072	93	7	-
Oil Field Fuel Gas Line #21B	10064	1-10-77	5-3		0.020	0	-	-	-	0.012	0.050	0.288	86	14	-
Oil Field Dry Gas Line #11 Valve	10065	1-10-77	5-4		0.18	0	-	-	-	0.104	0.454	2.50	86	14	-
Oil Field Dry Gas Line #9 Valve	10066	1-10-77	5-5		<0.001	0	-	-	-	5.8x10 ⁻⁵	2.5x10 ⁻⁴	1.4x10 ⁻³	86	14	-
Oil Field Dry Gas Line #152 Valve	10068A	1-10-77	5-6		0.253	0	-	-	-	0.145	0.64	3.46	86	14	-
Oil Field Heater Treater (Pilot) Left	10069	1-10-77	5-7		3.0 assumed	5.8	0.9	0	18.1	0.008	0.03	0.19	7	41	52
Oil Field Dry Gas Line Valve #6	10070	1-10-77	5-8		0.221	2	-	-	-	0.01	<0.1	0.04	-	100	-
Oil Field Dry Gas Line Valve #11	10071	1-10-77	5-9		0.4	2	-	-	-	0.003	0.01	0.013	86	14	-

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Orsat			Total Organic Emission lb/hr	Total Organic Emission T/yr	ARB Class 1	Soccies by % WT. of Total ARB Class			Remarks
							CO ₂ %	CO %	O ₂ %				ARB Class 2	ARB Class 3		
Oil Field #3 Crude Oil Line #37 Valve	10072	1-10-77	5-10		0.56	0	-	-	0.026	0.11	0.624	87	13	-		
Oil Field Crude Line #18 Valve	10075	1-11-77	5-11		0.1	0	-	-	0.15	0.66	3.6	11	89	-		
Oil Field Hot Water Tank	10080	1-11-77	5-12		-	2	-	-	1.93	8.45	46.3	8	91	1		
Oil Field Heater Treater (Firing) Left	10089	1-11-77	5-13		2606	7.5	4.5	0	0.459	0.405	2.8	59	31	10		
Oil Field Well SD 81	10090	1-12-77	5-14		0.019	2	-	-	2.0x10 ⁻⁴	8.7x10 ⁻⁴	4.8x10 ⁻³	20	80	-		
Oil Field Well #S-81E Wet Gas Valve	10091	1-12-77	5-15		0.108	2	-	-	3.2x10 ⁻⁴	1.41x10 ⁻³	7.7x10 ⁻³	50	50	-		
Oil Field Well SD81 Union #62	10092	1-12-77	5-16		0.082	0	-	-	0.05	0.2	1.2	89	11	-		
Oil Field Well #S-81E Wet Gas Valve	10093	1-12-77	5-17		0.27	2	-	-	0.004	0.02	0.096	87	13	-		
Oil Field Crude Oil Line #26 Valve	10094	1-12-77	5-18		0.483	2	-	-	0.0101	0.0447	0.2424	89	11	-		
Oil Field Well 72A Casing Valve	10098	1-13-77	5-19		0.514	2	-	-	0.02	0.09	0.48	58	42	-		
Oil Field Well SB 72B	10099	1-13-77	5-20		0.342	2	-	-	0.001	0.004	0.024	50	50	-		
Oil Field Well 72A Sump Area	10100	1-13-77	5-21		-	2	-	-	0.007	0.031	0.168	38	46	16		
Oil Field Elbow #57 Well S-72B	10102	1-13-77	5-22		0.17	0	-	-	0.003	0.013	0.072	86	14	-		

TABLE 3-31 (Continued)

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Total Organic Emissions lb/hr	T/Yr lb/day	Analytical Results			Remarks			
							CO ₂	CO	O ₂			ARB Class 1	ARB Class 2	ARB Class 3		Species by % wt. of Total		
																ARB Class 1	ARB Class 2	ARB Class 3
Oil Field Compressor #33 Shaft	10103	1-14-77	5-23		0.490	2	-	-	-	0.22	1.0	5.3	97	3	-			
Oil Field, Valve	10104	1-14-77	5-24		0.106	0	-	-	-	0.061	0.265	1.5	86	14	-			
Oil Field Compressor #26 1st Stage	10105	1-14-77	5-25		0.114	0	-	-	-	0.32	1.42	7.68	78	22	-			
Oil Field Compressor #26 Piston Seal	10106	1-14-77	5-26		0.042	0	-	-	-	0.13	0.55	3.12	78	22	-			
Oil Field Valve #12	10107	1-14-77	5-27		0.120	0	-	-	-	0.01	0.1	0.24	0	100	-			
Oil Field Well SB 72B	10249	3-31-77	5-28		29.8	17.9	10.4	1.1	1.0	0.145	0.7	3.48	96	1	3			
Oil Field Well S72	10250	3-31-77	5-29		55.9	20.0	9.2	2.5	0.3	1.22	5.3	29.3	96	1	3			
Oil Field Well S11	10251	3-31-77	5-30		38.6	18.1	9.7	0	2.7	0.111	0.4	2.7	96	1	3			
Oil Field Well SB72-B	10096	1-13-77	5-31		26.1	19.8	10.2	0.2	0.8	0.1183	0.516	2.8	96	1	3			
Litho Printing Press #3 Catalyst Outlet	10254	4-4-77	6-1	Neg.	8512	6.5	2.4	0	15.6	83.9	174.5	956	87	13	-			
Litho Printing Press #3 Catalyst Inlet	10255	4-4-77	6-2	-	8512	6.2	0.2	0	18.6	3.05	6.4	34.8	76	7	17			
Litho Printing Press #9 Afterburner Inlet	10256	4-4-77	6-3		3926	2.1	0	0	21	0.56	0.09	0.48	72	21	7			
Litho Printing Press #9, Afterburner Outlet	10257	4-4-77	6-4	64%	3926	5.8	1.2	0	17.8	0.2	0.04	0.17	13	-	87			
Oil Refinery CO Boiler	10272 10276	4-11-77	7-1/5		189870	13.1	13.8	0	1.1	2.28	9.9	54.7	36	13	51			
Oil Refinery FCC Pump	10277	4-12-77	7-6							0.07	0.31	1.68	-	100	-			

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Analytical			Results			Remarks
							CO ₂	CO	O ₂	Total Organic Emissions lb/hr	T/VF	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	
Oil Refinery FCC #9 Cooling Tower	10279-10280	4-11-77	7-8/9		Water Circulation 42600/GPM	0	-	-	-	0.72	0.14	17.28	-	100	-	
Oil Refinery FCC Gas Plant Sour H ₂ O Drain	10281	4-12-77	7-10		0.1 cc/min	0	-	-	-	6.8x10 ⁻⁶	3x10 ⁻⁵	1.6x10 ⁻⁴	1	99	-	
Oil Refinery FCC Gas Plant Leaky Valve	10282	4-12-77	7-11		0.291	0	-	-	-	1.64	7.2	1.92	29	28	43	
Oil Refinery Valve Seal	10284	4-13-77	7-12		0.0034	0	-	-	-	0.05	0.2	1.2	5	83	12	
Oil Refinery Valve Seal	10285	4-13-77	7-13		0.0143	0	-	-	-	0.22	0.90	5.3	5	83	12	
Oil Refinery Valve Seal	10286	4-13-77	7-14		0.085	0	-	-	-	0.57	2.5	13.7	-	28	72	
Oil Refinery Valve Seal	10287	4-14-77	7-15		0.001	0	-	-	-	6.7x10 ⁻³	2.9x10 ⁻²	0.16	-	28	72	
Oil Refinery Valve Seal	10288	4-14-77	7-16		0.120	0	-	-	-	0.77	3.4	18.5	8	50	42	
Oil Refinery Valve Seal	10289	4-14-77	7-17		0.013	0	-	-	-	0.085	0.371	2.04	8	51	41	
Oil Refinery Valve Seal	10290	4-14-77	7-18		0.097	0	-	-	-	0.31	1.4	7.4	68	26	6	
Oil Refinery Valve Seal	10291	4-14-77	7-19		<0.001	0	-	-	-	0.01	<0.1	0.24	-	100	-	
Oil Refinery #9 API Separator	10292-10297	4-14-77	7-20/25		3000 gpm	0	-	-	-	15.42	6.75	370	-	100	-	
Oil Refinery Pump Seal	10298	4-14-77	7-26		0.059	2	-	-	-	8.5x10 ⁻³	3.7x10 ⁻²	0.20	-	88	12	
Oil Refinery Pump Seal	10299	4-15-77	7-27		0.072	2	-	-	-	2.3x10 ⁻³	0.01	0.127	1	93	6	
Oil Refinery Tower (Pump Seal)	10300	4-15-77	7-28		0.078	0	-	-	-	0.53	2.3	12.7	-	21	79	

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TABLE 3-31 (Continued).

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Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Analytical Results			Remarks			
							CO ₂	CO	O ₂	Total Organic Emissions T/YF	lb/hr	lb/day		ARB Class	ARB Class	ARB Class
Oil Refinery Pump Seal	10302	4-18-77	7-29		0.049	2	-	-	-	1.6x10 ⁻³	7.2x10 ⁻³	0.038	-	54	46	
Oil Refinery Pump Seal	10303	4-18-77	7-30		0.095	2	-	-	-	0.20	0.9	4.8	15	20	65	
Oil Refinery Pump Seal	10304	4-18-77	7-31		1.150	0	-	-	-	6.87	30.2	164.9	20	22	58	
Oil Refinery Valve	10305	4-18-77	7-32		0.039	0	-	-	-	0.27	1.18	6.5	-	100	-	
Oil Refinery Valve	10306	4-18-77	7-33		0.098	0	-	-	-	0.64	2.8	15.4	14	15	71	
Oil Refinery Valve	10307	4-18-77	7-34		0.0125	0	-	-	-	0.071	0.311	1.704	14	15	71	
Oil Refinery Valve	10308	4-18-77	7-35		0.183	0	-	-	-	1.05	4.6	25.2	13	15	72	
Oil Refinery Valve	10309	4-19-77	7-36		0.022	0	-	-	-	0.09	0.4	2.16	100	-	-	
Oil Refinery Valve	10310	4-19-77	7-37		0.044	0	-	-	-	0.19	0.8	4.56	100	-	-	
Oil Refinery Valve	10311	4-19-77	7-38		0.0064	0	-	-	-	0.04	0.2	0.96	-	100	-	
Oil Refinery Heater #21	10314	4-19-77	7-39		22489	19	10.8	0	1.6	1.43	6.3	34.3	29	46	25	
Oil Refinery Heater #22	10315	4-19-77	7-40		13752	17.3	11.6	0	1.0	0.34	1.5	8.16	-	85	15	
Oil Refinery Diesel Pump Seal	10316	4-20-77	7-41		liquid	0	-	-	-	0.05	0.22	1.2	-	100	-	
Oil Refinery Valve Pump	10317	4-20-77	7-42		0.042	0	-	-	-	0.20	0.9	4.8	1	99	-	
Oil Refinery Pump, Kerosene	10318	4-20-77	7-43		liquid	0	-	-	-	0.16	0.72	3.84	-	100	-	
Oil Refinery Pump Seal	10319	4-20-77	7-44		0.042	2	-	-	-	5.4x10 ⁻⁴	2.4x10 ⁻³	1.3x10 ⁻²	2	85	13	
Oil Refinery Pump Seal	10320	4-20-77	7-45		0.072	2	-	-	-	1.6x10 ⁻⁴	6.9x10 ⁻⁴	3.8x10 ⁻³	2	85	13	

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TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Total Organic Emissions lb/hr	Analytical Results			Remarks	
							CO ₂	CO	O ₂		ARB Class 1	Total Organic Emissions T/yr	ARB Class 2		ARB Class 3
Oil Refinery Pump Seal	10321	4-21-77	7-46		liquid	0	-	-	-	0.18	0.79	4.3	-	100	-
Oil Refinery Pump Seal	10322	4-21-77	7-47		0.107	2	-	-	-	9.03x10 ⁻⁶	1.97x10 ⁻⁵	2.17x10 ⁻⁴	12	85	3
Oil Refinery Valve	10323	4-21-77	7-48		0.076	2	-	-	-	9.9x10 ⁻⁶	4.3x10 ⁻⁵	2.4x10 ⁻⁴	5	83	12
Oil Refinery Valve	10324	4-21-77	7-49		0.061	2	-	-	-	7x10 ⁻⁴	3x10 ⁻³	1.7x10 ⁻²	2	92	6
Oil Refinery Heater #21	10326	4-22-77	7-50			0	-	-	-	9.6x10 ⁻³	4.2x10 ⁻²	0.23	100	-	-
Mag. Tape Mfg. Act. Carb. Abs. Outlet	10236	3-22-77	8-1	99%	7203	3.9	-	-	-	0.353	1.101	6.0	-	-	100
Mag. Tape Mfg. Act. Carb. Abs. Inlet	10237	3-22-77	8-2		7613	2	-	-	-	181.5	566.3	3086	-	-	100
Paint Spray Booth	10239	3-23-77	9-1		8782	2	-	-	-	8.19	15.07	93.6	71	22	7
Small Degreaser	10241	3-23-77	9-2		430	2	-	-	-	0.347	0.319	2.776	100	-	-
Spray Booth	10242	3-23-77	9-3		4073	2	-	-	-	14.79	27.214	168.9	33	59	8
Spray Booth	10243	3-23-77	9-4		5361	2	-	-	-	22.30	52.18	382.2	51	29	20
Large Degreaser	10244	3-24-77	9-5		902	2	-	-	-	14.857	24.514	169.67	100	-	-
Adhesive Spray Booth	10245	3-24-77	9-6		3261	2	-	-	-	1.960	3.606	22.38	91	9	-
Gas Turbine	10258 10259	4-8-77	10-1/ 2		-	5.6	2.6	0	16	4.5	0.18	6.93	7	-	93

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Orsat			Total Organic lb/hr	T/Yr lb/day	Species by % WT. of Total ARB			Remarks	
							CO ₂ %	CO %	O ₂ %			ARB Class 1	ARB Class 2	ARB Class 3		
																CO ₂ %
Oil Refinery Reformer Heater #305	10040	11-29-76	11-1		4375	15.8	7.9	0	6.1	0.280	1.23	6.72	-	93	7	
Oil Refinery Naphtha Heater 101	10041	11-29-76	11-2		3472	14.5	8.7	0	5.6	0.095	0.42	2.28	14	41	45	
Oil Refinery Reformer Cooling Tower	10042	11-29-76	11-3		Water CIE. 2500	-	-	-	-	6.0	26.0	144	-	100	-	
Oil Refinery Scot Incinerator	10043	11-29-76	11-4		2836	15	3.1	0	10.9	0.557	2.44	13.37	-	98	2	
Oil Refinery Pump Valve P-315	10044	11-30-76	11-5		0.071	0	-	-	-	0.200	0.876	4.8	1	99	-	
Oil Refinery Pump P-305	10045	11-30-76	11-6		1.4x10 ⁻⁴	-	-	-	-	0.026	0.11	0.79	-	~100	-	*API calc.
Oil Refinery Tank 125002	10046	12-1-76	11-7		-	2	-	-	-	4.7	20.6	112.8*	5	95	-	
Oil Refinery Tank 80003	10047	12-1-76	11-8		-	2	-	-	-	2.4	10.5	57.6	15	85	-	
Oil Refinery Tank 50003	10048	12-1-76	11-9		-	2	-	-	-	4.7	20.6	112.0	4	96	-	
Oil Refinery Tank 125002	10049	12-1-76	11-10		-	2	-	-	-	0.006	0.026	0.144	5	48	47	
Oil Refinery Vapor Recovery Pump	10051	12-1-76	11-12		0.083	0	-	-	-	0.04	0.18	0.96	-	100	-	
Oil Refinery API Separators	10053	12-1-76	11-13		Water Flow 150	-	-	-	-	0.04	0.18	0.96	-	100	-	
Oil Refinery Asphalt Heater #602	10054	12-1-76	11-14		5462	13	6.8	0.1	8.1	1.271	5.57	30.5	-	53	47	
Oil Refinery Crude Heater #801	10055	12-1-76	11-15		4695	13.1	9.1	-	6.0	0.078	0.34	1.87	-	37	63	
Oil Refinery Tank 1012 Blower	10056	12-2-76	11-16		1.540	15.1	-	-	-	1.4x10 ⁻³	0.006	0.034	-	100	-	

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TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Oxstat		Analytical Results			Species by % wt. of Total ARB			Remarks
							CO %	CO ₂ %	Total Organic Emissions lb/hr	T/YE lb/day	ARB Class 1	ARB Class 2	ARB Class 3		
Oil Refinery Crude Cooling Tower	10057	12-2-76	11-17		Water Circ: 2500 GPM	-	-	-	5.8	31.7	-	100	-	-	
Oil Refinery Pump P-605	10058	12-2-76	11-18		7.1x10 ⁻³	-	-	-	4.8	26.2	-	100	-	-	
Oil Refinery Pump P-603	10059	12-2-76	11-19		1.4x10 ⁻³	-	-	-	0.9	5.0	-	100	-	-	
Oil Refinery Fuel Gas Valve	10060	12-2-76	11-20		0.123	0	-	-	0.945	5.18	17	83	-	-	
Oil Refinery Fuel Gas Valve	10061	12-2-76	11-21		0.049	0	-	-	2.2x10 ⁻³	0.053	26	74	-	-	
Rubber Tire Mfg. #4 Tubers Solvents, Adhes.	10400	5-25-77	12-1		5066	1.7	-	-	160.8	1237.2	3	96	1	-	
Rubber Tire Mfg. #5 Tubers Cement	10401	5-25-77	12-2		5471	1.5	-	-	56.0	431.0	2	97	1	-	
Rubber Tire Mfg. #6 White Side-wall Tubers	10402	5-25-77	12-3		3654	1.6	-	-	32.3	248.6	8	92	-	-	
Rubber Tire Mfg. #69 Bead Dip Tank	10403	5-25-77	12-4		3739	1.4	-	-	30.8	236.4	1	99	-	-	
Auto Manuf. Solvent Based Paint Primer Afterburner Inlet	10350	5-2-77	13-1		9484	2	-	-	30.75 (2 Burners)	195.3	95	-	5	-	
Solvent Based Paint Primer Afterburner Out	10351	5-2-77	13-2	98%	10756	8	2.6	0	0.705	4.70	23	-	77	-	
Solvent Based Paint Smoker Afterburner Inlet	10352	5-2-77	13-3		11264	4.55	0	0	5.654	37.70	61	32	7	-	
Solvent Based Paint Smoker Afterburner Outlet	10353	5-2-77	13-4	97%	11720	6.2	1.0	0.0	0.732	4.88	-	36	64	-	
Solvent Based Paint Primer Spray Booth	10354	5-3-77	13-5		44694	1.6	0	0	6.804	43.86	-	100	-	-	

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Total Organic Emissions T/Yr	lb/day	Species by % wt. of Total ARB			Remarks
							CO ₂	CO	O ₂			ARB Class 1	ARB Class 2	ARB Class 3	
Solvent Based Paint Primer Spray Booth	10355	5-3-77	13-6		37759	1.6	-	-	-	6.991	67.60	-	100	-	
Solvent Based Paint Primer Spray Booth	10356	5-3-77	13-7		52978	1.5	-	-	-	5.481	53.00	-	100	-	
Solvent Based Paint Primer Spray Booth	10357	5-3-77	13-8		51529	1.5	-	-	-	2.161	20.90	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10358	5-4-77	13-9		12565	1.6	-	-	-	0.210	2.03	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10359	5-4-77	13-10		11550	1.6	-	-	-	0.179	1.73	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10360	5-4-77	13-11		70698	1.6	-	-	-	7.054	68.21	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10361	5-4-77	13-12		62140	1.6	-	-	-	2.728	26.38	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10362	5-4-77	13-13		39207	1.6	-	-	-	1.628	15.74	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10363	5-4-77	13-14		40146	1.6	-	-	-	2.822	27.29	-	100	-	
Solvent Based Paint Topcoat Catalytic Afterburner Outlet	10364	5-3-77	13-15		9633	3.86	0	0	19.3	2.998	28.99	32	61	7	
Solvent Based Paint Topcoat Catalytic Afterburner Inlet	10365	5-3-77	13-16	65%	9319	4.55	1	0	18	1.048	10.13	56	22	22	
Water-borne Paint Flowcoat Drip holder	10366	5-5-77	13-17		3854	2	-	-	-	0.229	2.21	-	100	-	*Emissions are for both. 1 booth was tested, and the second booth was assumed to have same emissions.
Water-borne Paint Flowcoat Spray Booths (2)	10367	5-5-77	13-18		2590	2	-	-	-	0.120*	1.16	-	100	-	

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Orsat			Total Organic Emissions			Analytical Results			Remarks
							CO ₂ %	CO %	O ₂ %	lb/hr	T/Yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	
Water-borne Paint Flowcoat After-burner Inlet	10368	5-5-77	13-19		6298	4.55	-	-	19	0.916	1.328	8.86	-	100	-	
Water-borne Paint Flowcoat After-burner Outlet	10369	5-5-77	13-20	84%	5941	8.31	2.1	0	15.2	0.143	0.207	1.38	23	10	67	
Water-borne Paint #1 Primer Spray Booth 13 stacks	10150-10155	2-15-77	14-1/6		185130	2	-	-	-	6.148	11.804	98.37	91	-	9	
Water-borne Paint #1 Primer Oven	10156	2-14-77	14-7		29800	5	-	-	-	0.83	1.51	13.28	88	-	12	
Water-borne Paint #2 Top Coat Spray Booth	10157-10161	2-14-77	14-8/11		193339	2	-	-	-	19.270*	36.998	308.3	81	19	-	*Emissions based on air flow rate for 5 stacks extrapolated to 12 stacks
Water-borne Paint #2 Top Coat Spray Stack	10162	2-14-77	14-12		37137	5	-	-	-	2.26	4.34	36.16	96	4	-	
Water-borne Paint Elpo Incinerator Inlet	10163	2-15-77	14-13		13137	0.029	-	0.002	0.195	5.87	11.27	93.92	4	-	96	
Water-borne Paint Elpo Incinerator Outlet	10164	2-15-77	14-14	88%	12516	3.34	1.4	-	18.2	0.699	1.35	16.78	18	30	52	
Water-borne Paint #1 Top Coat Spray Booth	10165	2-15-77	14-15		15484	0	-	-	-	0.81	21.77	12.96	72	21	9	
Water-borne Paint #2 Top Coat Spray Booth	10166	2-16-77	14-16		19120	2	-	-	-	1.998	3.837	31.97	77	23	-	Triplicate parallel tests, data base for KVB Test #10157 - 10161 above.
Water-borne Paint #2 Topcoat Spray Booth	10167	2-16-77	14-17		19120	2	-	-	-	1.822	3.498	29.15	85	15	-	Triplicate parallel tests, data base for KVB Test #10157 - 10161 above.
Water-borne Paint #2 Topcoat Spray Booth	10168	2-16-77	14-18		19120	2	-	-	-	1.817	3.489	29.07	80	20	-	Triplicate parallel tests, data base for KVB Test #10157 - 10161 above.

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TABLE 3-31 (Continued)

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Total Organic Emissions			Species by % wt. of Total ARB Class			Remarks
							CO ₂	CO	O ₂	lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	
Water-borne Paint Vinyl Adhes. Spray Booth	10169	2-16-77	14-19		10038	0	-	-	-	0.50	0.96	8	46	40	14	
Water-borne Paint Vinyl Adhes. Dry Oven	10170	2-16-77	14-20		17359	0	-	-	-	3.70	7.10	59.2	72	25	3	
Water-borne Paint Lacquer Spray Booth	10171	2-17-77	14-21		73937	0	-	-	-	6.41	12.31	102.56	21	49	30	
Auto Paint Spray Booth	10001	9-22-76	15-1		7047	4.7	0	20.01	4.7	20.59	112.8	-	71	8	29	
Metallurgical #6 Open Hearth Precip. Inlet	10031	11-23-76	16-1		32961	13.7	11.4	9.4	4.02	17.35	96.5	87	42	5		
Metallurgical #6 Open Hearth Precip. Outlet	10032	11-23-76	16-2	25% for HC	32961	13	10.2	10	3.02	13.05	72.5	54	-	4		
Metallurgical Coke Oven C	10033	11-23-77	16-3		40200	12	2.7	15.3	88.3	381.4	2119.2	88	-	12		
Metallurgical Coke Oven D	10034	11-23-76	16-4		31164	4.2	14.4	7.8	40.0	172.9	960	85	-	15		
Metallurgical Blast Furnace #4	10035	11-23-76	16-5		55000	13	14.1	4.0	0.7	2.82	16.8	100	-	-		
Metallurgical Sintering Plant	10036	11-23-76	16-6		152376	7.8	1.6	18.4	15.0	65.8	360	91	-	9		
Metallurgical Basic Oxygen Furnace Outlet	10037	11-23-76	16-7		240836	8	-	-	6.42	27.76	154.1	60	40	-		
Gas Plant, Valve	10129	2-7-77	17-1		0.039	0	-	-	0.072	0.315	1.728	96	4	-		
Gas Plant IC Engine	10130	2-7-77	17-2		1679	7.3	3.2	14.4	21.07	95.79	524.88	86	12	2		
Power Plant Oil Fired Steam Boiler	10252 10253	4-1-77	18-1/ 2		646927	9.4	10.8	6.2	15.24	66.6	365.8	43	21	36		

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	CO ₂	Orsat CO	O ₂	Total Organic Emissions lb/hr	T/yr	Analytical Results			Remarks	
												ARB Class 1	ARB Class 2	ARB Class 3		
Dry Cleaners* Tumble Dryer Stack	10247	3-30-77	19-1		1181	5.6	-	-	-	4.638	4.0	25.51	-	100	-	*Std. Solvent type
Degreaser Vapor Degreaser	10124	2-1-77	20-1		3082	2	-	-	-	6.5	6.8	52	100	-	-	
Degreaser Metal Treating	10125	2-1-77	20-2		3283	2	-	-	-	13.9	14.5	111.2	86	14	-	
Degreaser Flowcoater Oven	10126	2-1-77	20-3		2966	2	-	-	-	50.0	52.0	400	99	1	-	
Degreaser**	10126S	2-1-77	20-3		2260											**Concentrations for both ovens (assumed equal)
Sewage Plant Sludge Incinerator	10174	2-23-77	21-1		1230	6.9	8.5	-	9.5	0.248	1.09	5.95	90	10	-	
Sewage Plant Sludge Centrifuge	10175	2-23-77	21-2		1728	5.9	-	-	-	4.111	18.006	98.67	100	-	-	
Sewage Plant IC Engine	10178	3-1-77	21-3		279	7.95	12.6	2.1	3.6	1.370	6.001	32.88	93	3	4	
Metallurgical Primer Coat Dryer	20021	3-1-77	22-1		3725	2	-	-	-	5.162	9.034	49.6	1	95	4	
Metallurgical Flow Coater	20022	3-1-77	22-2		2976	2	-	-	-	23.816	41.678	228.6	-	99	1	
Paving Asphalt (black-top) Evap.	10234	3-17-77	23-1		*	1.6	-	-	-	6.5x10 ⁻⁶	-	-	30	66	4	*Flow rates estimated
Oil Refinery FCC CO Boiler Unit	10003	10-19-76	24-1		32657	9.33	14.6	0	1.9	22.536	98.708	540.86	-	88	12	
Oil Refinery Tank	10004	10-20-76	24-2										7	90	3	
Oil Refinery Tank	10005	10-20-76	24-3										11	85	4	
Oil Refinery Pump P-6 Flash Stream	10006	10-20-76	24-4							0.013	0.06	0.312	5	89	6	
Oil Refinery Tank	10007	10-20-76	24-6										-	94	6	

TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat		Total Organic Emissions lb/hr	Analytical Results			Remarks		
							CO ₂	CO		ARB Class 1	ARB Class 2	ARB Class 3		Total Organic Emissions lb/day	ARB Class 1
Oil Refinery Line Gas	10008	10-20-76	24-6						1.06	4.7	25.4	23	68	9	
Oil Refinery API Separator	10009	10-20-76	24-7		Water Flow 150 gpm	-	-	-				-	100	-	
Oil Refinery FCC Pump Leak	10010	10-20-76	24-8									11	81	8	
Oil Refinery FCC Charge Pump	10011	10-20-77	24-9		2.1x10 ⁻²	-	-	-	0.0011	0.005	0.026	-	100	-	Natural Gas burner
Residential Furn. Outlet - Home Heater	10235	3-21-77	25-1		515				Not detectible						
Roofing Tar Roofing Kettle Fumes	10246	3-28-77	26-1			1.6	-	-	1.9x10 ⁻³	8.4x10 ⁻³	4.6x10 ⁻²	30	60	10	*Estimated rate of application
Gasoline Fill Vapor Recovery	20001	11-8-76	27-1												*No flow rates available
Gasoline Fill Vapor Recovery	20002	11-8-76	27-2										100	-	*No flow rates available
Gasoline Fill Vapor Recovery	20003	11-8-76	27-3												
Gasoline Fill Vapor Recovery	20004	11-15-76	27-4										100	-	
Gasoline Fill Vapor Recovery	20005	11-15-76	27-5										100	-	
Gasoline Fill Vapor Recovery	20006	11-15-76	27-6									1	99	-	
Gasoline Fill Vapor Recovery	20007	11-15-76	27-7									1	99	-	
Gasoline Fill Vapor Recovery	20008	11-15-76	27-8									1	99	-	

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TABLE 3-31 (Continued)

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Analytical Results			Remarks		
							CO ₂	CO	O ₂	Total Organic Emissions T/yr	Total Organic Emissions lb/day	ARB Class 1		ARB Class 2	ARB Class 3
Oil Field Compressor Seal	10184	3-14-77	28-1		0.334	0	-	-	-	1.287	5.64	30.89	42	58	-
Oil Field Compressor Valve	10185	3-14-77	28-2		0.001	0	-	-	-	0.004	0.02	0.096	42	58	-
Oil Field Compressor Valve	10186	3-14-77	28-3		0.450	0	-	-	-	1.484	6.50	35.62	50	50	-
Oil Field Compressor Valve	10187	3-14-77	28-4		0.369	0	-	-	-	1.419	6.21	34.06	42	58	-
Oil Field Tank Vapor Recovery	10189	3-14-77	28-5		0.227	0	-	-	-	1.279	5.60	30.7	32	68	-
Oil Field Tank Vapor Recovery	10190	3-14-77	28-6		0.125	0	-	-	-	0.604	2.65	14.50	43	57	-
Oil Field Tank Vapor Recovery	10191	3-14-77	28-7		0.056	0	-	-	-	0.066	0.29	1.58	83	17	-
Oil Field Gas Shut Off	10192	3-14-77	28-8		0.075	0	-	-	-	0.217	0.951	5.21	67	33	-
Oil Field SSP #17 Valve	10193	3-14-77	28-9		0.289	0	-	-	-	0.836	3.66	20.1	68	32	-
Oil Field Tank Farm Drainage Ditch	10194	3-14-77	28-10		-	-	-	-	-	218.1	955.2	5232	-	100	-
Oil Field Edwards Tank Vapor Recovery	10195	3-15-77	28-11		0.151	0	-	-	-	0.964	4.22	23.1	25	75	-
Oil Field API Separator Evaporation	10196	3-15-77	28-12		-	-	-	-	-	6.907	30.252	165.8	-	100	-
Oil Field API Separator Evaporation	10197	3-15-77	28-13		-	-	-	-	-	13.669	59.868	328.1	-	100	-
Oil Field Valve	10199	3-15-77	28-14		0.126	0	-	-	-	0.365	1.60	8.76	67	33	-
Oil Field Wellhead Drippings	10200	3-15-77	28-15		-	-	-	-	-	0.032	0.140	0.77	-	100	-

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water	Orsat			Total Organic Emissions lb/hr	Total Organic Emissions T/Yr	lb/day	Species by % wt. of Total ARB			Remarks
							CO ₂	CO	O ₂				ARB Class 1	ARB Class 2	ARB Class 3	
Oil Field Packing Gland/Sucker Rod	10201	3-15-77	28-16		0.090	2	-	-	-	2.1x10 ⁻³	3.9x10 ⁻³	0.02	4	96	-	
Oil Field Well Cellar	10204	3-15-77	28-17							2.0x10 ⁻⁴	9.0x10 ⁻⁴	1.6x10 ⁻³	-	100	-	
Oil Field Average Well Emissions	10200 10201 10204	3-15-77								1.166*	4.923	28.0	-	100	-	*Average emissions for one well extrapolated to 34 producing wells
Oil Field Tank Farm - Valve	10202	3-15-77	28-18		0.037	0	-	-	-	0.107	0.469	2.57	67	33	-	
Oil Field Wash Tank Vent	10203	3-15-77	28-19		0.114	0	-	-	-	0.134	0.613	3.22	80	20	-	
Oil Field Gas Drive Casing	10206	3-15-77	28-20		0.096	0	-	-	-	0.279	1.22	6.70	67	33	-	
Oil Field Valve Leak	10207	3-15-77	28-21		0.065	0	-	-	-	0.082	0.359	1.97	81	19	-	
Oil Field Valve Leak	10230	3-16-77	28-22		0.114	1	-	-	-	0.337	1.48	1.48	47	53	-	
Landfill	10179	3-2-77	29-1		41.2	1.9	33	0	19	18.413	40.352	220.96	98	2	-	
Adhesives Impregnator Drying Oven	10180	3-8-77	30-1		100% Cap. 10749 25% Cap.	2.1	0	0	20	41.2	22.495	123.6	1	99	-	
Adhesives Fiberglass Impregnator	10182	3-8-77	30-2		4782 100% Cap.	2.2	-	-	20	1.80	1.00	5.40	-	100	-	
Adhesives Fiberglass Impregnator	10182	3-8-77	30-2		4782 25% Cap.	2.2	-	-	20	0.45	0.25	1.35	-	100	-	
Solvents PC Board Process	10110	1-25-77	31-1		1195	2	-	-	-	9.14	19.10	105.1	100	-	-	
Solvents #4 Stripper	10111	1-25-77	31-2		9170	2	-	-	-	45.12	94.30	518.9	100	-	-	

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TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Orsat			Total Organic Emissions			Analytical Results			Remarks
							CO ₂ %	CO %	O ₂ %	lb/hr	T/Yr	lb/day	ARB Class 1	Species by % wt. of Total		
														ARB Class 2	ARB Class 3	
Solvents #2 Stripper	10113	1-25-77	31-3		531	1.8	-	-	-	61.99	129.5	712.9	99	1	-	
Solvents #2 Stripper	10114	1-25-77	31-4		531	1.8	-	-	-	48.30	100.97	555.5	99	1	-	
Solvents Roof Ambient Background	10116	1-25-77	31-5			2	-	-	-	7.8	16.5	89.7	100	-	-	
Solvents #1 Screen Oven	10117	1-25-77	31-6		439	2	-	-	-	1.13	2.36	13.0	100	-	-	
Cleaners Dry Clean Tumbler	10002	9-29-76	32-1		136	4.6	0	0	20	3.78	2.83	22.7	100	-	-	

TABLE 3-32. ARB REACTIVITY CLASSIFICATION
OF ORGANIC COMPOUNDS

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C ₁ -C ₂ Paraffins	Mono-tert-alkyl-benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic Ketones	All Olefinic hydrocarbons (including partially halogenated)
Benzene	Alkyl acetates	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	Branched alkyl Ketones
Acetone	C ₃ ⁺ Paraffins	Cellosolve acetate
Methanol	Cycloparaffins	Unsaturated Ketones
Tert-alkyl alcohols	n-alkyl Ketones	Primary and secondary C ₂ ⁺ alcohols
Phenyl acetate	N-methyl pyrrolidone	Diacetone alcohol
Methyl benzoate	N,N-dimethyl acetamide	Ethers
Ethyl Amines	Alkyl Phenols*	Cellosolves
Dimethyl formamide	Methyl phthalates**	Glycols*
Perhalogenated hydrocarbons		C ₂ ⁺ Alkyl phthalates**
Partially halogenated paraffins		Other Esters**
Phthalic Anhydride**		Alcohol Amines**
Phthalic Acids**		C ₃ ⁺ Organic acids + di acid**
Acetonitrile*		C ₃ ⁺ di acid anhydrides**
Acetic Acid		Formin** (Hexa methylene-tetramine)
Aromatic Amines		Terpenic hydrocarbons
Hydroxyl Amines		Olefin oxides**
Naphthalene*		
Chlorobenzenes*		
Nitrogenzenes*		
Phenol		

*Reactivity data are either non-existent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable

** Reactivity data are uncertain

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Table 3-33 is a breakdown of the organic species detected during the program with its reactivity class, the concentration levels found and a list of the sources that emitted that compound.

3.4.2 Discussion

The following are some observations on the test results for various categories of devices tested during the program. The code number indicated on the tables below refer to Table 3-31.

A. Printing (Codes 1, 2, and 6)--

Three types of printing processes were tested: flexographic, rotogravure and lithographic. The flexographic process had no controls and was emitting less than a hundred tons propyl acetate (Class 2) per year. The rotogravure plant had one of the largest charcoal adsorbers (120,000 SCFM capacity) in the Basin which was new and working very well (over 96% efficiency). Even with controls the plant was found to emit over 200 tons/year of aliphatic (80%) and aromatics (20%). More than half of this came from ventilation fans located in the roof of the building (peripheral fans) used to remove fugitive emissions. They were not controlled because of their low concentration.

The lithograph plant had two afterburners, one catalytic and one thermal (non-catalytic). The non-catalytic unit performed well. The 64% efficiency was probably caused by the low inlet concentration at the time of testing. The catalytic unit was operating poorly with a negative efficiency of 27%. The natural gas used in the afterburner was not reacting efficiently in the catalytic burner. As a result, over 100 tons per year of low reactivity methane and ethane were being released each year. One ton per year of olefins found in the inlet to the catalytic burner was completely destroyed, so the unit had significant benefit. KVB found this combustion inefficiency on several catalytic afterburners. KVB was advised by the operators and SCAQMD field test personnel that there is a universal problem in this area.

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TABLE 3-33A. TEST RESULTS BY SPECIES, ALCOHOLS

Name	ARB Class	Concentrations, ppm measured	Source Type
Methyl Alcohol	1	1 - 100	Appliance enamel, Flexograph ink, Landfill, Printed circuit stripper
Ethyl Alcohol	3	0.1 - 10	Appliance enamel, Flexograph ink
Isopropyl Alcohol	3	0.1 - 1.0	Lithograph ink inlet to control only (thermo burner)
n Butyl Alcohol	3	1 - 10	Appliance enamel
Isobutyl Alcohol	3	0.1 - 1.0	Appliance enamel

TABLE 3-33B. TEST RESULTS BY SPECIES, KETONES

Name	ARB Class	Concentrations, ppm measured	Source Type
Acetone	1	0.1 - 100	Adhesives, Appliance enamel, Flexograph ink; Landfill gas, Plastics coatings, Power plant combustion, Sewage gas, Water based paint
Methyl Ethyl Ketone	2	1 - 100	Appliance enamel, Plastics coatings
Methyl Isobutyl Ketone	2	1 - 10,000	Magnetic tape coating

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TABLE 3-33C. TEST RESULTS BY SPECIES, THIO COMPOUNDS

Name	ARB Class	Concentrations, ppm measured	Source Type
Thiols, Ethylmercaptan Butyl mercaptan	3	10 - 100	Refinery sour water
Thiophenes	3	100 - 1,000	Refinery sour water

TABLE 3-33D. TEST RESULTS BY SPECIES, ESTERS (ACETATES)

Name	ARB Class	Concentrations, ppm measured	Source Type
Ethyl Acetate	2	0.1 - 10	Adhesives, Landfill gas, Water based paint
n Propyl Acetate	2	10 - 100	Flexograph ink
Isopropyl Acetate	2	0.1 - 100	Flexograph ink
n Butyl Acetate	2	10 - 100	Appliance enamel

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TABLE 3-33E. TEST RESULTS BY SPECIES, HALO-COMPOUNDS

Name	ARB Class	Concentrations, ppm measured	Source Type
Fluoro-trichloro-methane	1	10,000 - 100,000	Refrigerant fill line gas
Difluoro-dichloro-methane	1	100,000 - 1,000,000	Refrigerant fill line gas
Methylene Chloride (dichloromethane)	1	1 - 10,000	Landfill gas, Lithograph ink, Printed circuit stripper solvent, Rubber masking paint
1,1,1-Trichloro-methane (methylchloroform)	1	1 - 1,000	Metal degreaser fluid, Printed circuit stripper
Vinyl Chloride	3	0.1 - 1.0	Landfill gas
Methyl Chloride	1	1 - 10	Printed circuit, Process Plant Background
1,2 Dichloro-ethylene	3	1 - 10	Landfill gas
Perchloroethylene (tetrachloroethylene)	1	0.1 - 1,000	Adhesive, Appliance enamel, Landfill gas, Metal degreaser fluid, Rubber masking plant
Trimethylfluorosilane	1	0.1 - 10	Steel furnace gases

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TABLE 3-33F. TEST RESULTS BY SPECIES, AROMATICS

Name	ARB Class	Concentrations, ppm measured	Source Type
Benzene	1	1 - 10 10 - 100 100 - 1,000 1,000 - 10,000	Appliance enamel paint; Automotive water based paint; Coke oven gas; Crude oil, heavy API°, gas; Crude oil, light API°, gas; Dip enamel paint; Flexograph ink; Gasoline; Lacquer paint, automotive; Landfill gas; Natural gas combustion; Oil field gas drier; Oil field sump; Paving asphalt; Refinery process gas; Refinery pump seal leak; Refinery sour water; Refinery stock for blending; Roofing tar; Rotogravure ink; Rubber solvent; Stripper solvent for printed circuits; Vinyl adhesive
Toluene	3	1 - 10 10 - 100 100 - 1,000 1,000 - 10,000	Appliance enamel paint, Automotive water based paint, Automotive lacquer paint, Dip enamel paint, Flexograph ink, Gasoline, Landfill gas, Natural gas pilot light combustion, Process gas combustion, Refinery blending stock, Refinery process gas, Refinery pump leak, Refinery sour water, Roofing tar, Rotogravure ink
Xylenes	3	1 - 10 10 - 100 100 - 1,000	Appliance enamel paint, Chemical blending process, Dip enamel paint, Flexograph ink, Gasoline, Landfill gas, Refinery blend stock, Refinery pump leak, Rotogravure ink
Ethylbenzene	3	1 - 10	Appliance enamel paint

TABLE 3-33G. TEST RESULTS BY SPECIES, ALDEHYDES

Name	ARB Class	Concentrations, ppm measured	Source Type
Formaldehyde	3	1 - 100	Combustion Sources: Appliance enamel oven afterburner, Gas combustion, Gas turbine, Lithograph ink afterburner, Natural gas IC engine, Pilot burner gas, Power plant boiler oil, Refinery CO boiler, Refinery process heater, Sewage-sludge gas burning IC engine, Solvent based automotive paint oven afterburner-catalytic afterburner, Water based automotive paint afterburner, Water based automotive base coat spray booth, Water based automotive base coat fume incinerator

TABLE 3-33H. TEST RESULTS BY SPECIES, OLEFIN OXIDE

Name	ARB Class	Concentrations, ppm measured	Source Type
1,4 Dioxane (Diethylene dioxide)	3	0.1 - 1.0	Vapor degreaser solvent

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TABLE 3-33I. TEST RESULTS BY SPECIES, ACETYLENES

Name	ARB Class	Concentrations, ppm measured	Source Type
Acetylene	1	1 - 10	Steel processing coke ovens, sintering plant

TABLE 3-33J. TEST RESULTS BY SPECIES, CYCLOPARAFFINS

Name	ARB Class	Concentrations, ppm measured	Source Type
Cycloparaffins	2	1 - 100*	Appliance enamel paint; Automotive solvent based paint, primer, top coat; Crude oil, light API°, heavy API°, wet and dry gases; Dip enamel paint; Gasoline; Landfill gas; Paving asphalt; Refinery blend stock; Roofing tar; Rubber adhesive; Rubber solvent; Rotogravure ink

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TABLE 3-33K. TEST RESULTS BY SPECIES, OLEFINS

Name	ARB Class	Concentrations, ppm measured	Source Type
Ethylene	3	1 ppm to 100%	Appliance enamel paint; Automotive paint, solvent based primer oven, afterburner; Automotive paint, solvent based top coat oven, catalytic afterburner; Automotive paint, water based primer oven; Coke oven gas; Gasoline; Lithograph ink catalytic afterburner; Natural gas; Paving asphalt; Refinery process gas; Roofing tar; Sewage sludge gas, IC engines
Propylene Butene Pentene, etc.	3	1 ppm to 100%	Appliance enamel paint; Automotive solvent based primer paint; Coke oven gas; Crude oil, heavy API°, wet and dry gas; Flexograph ink oven; Gasoline; Landfill gas; Paving asphalt; Refinery blend stock, process gas, process gas heater; Sewage gas; Sintering plant, Steel mill
Terpenes	3	10 - 100	Landfill gas

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TABLE 3-33L. TEST RESULTS BY SPECIES, PARAFFINS

Name	ARB Class	Concentrations, ppm measured	Source Type
Methane	1	1 ppm to 100%	Adhesives; Appliance enamel; Asphalt processing; Automotive solvent based primer paint oven and afterburner, top coat oven catalytic afterburner; Automotive water based basecoat paint, top coat paint and oven; Coke oven gas; Crude oil, light API°, heavy API°, wet gas, dry gas; Degreaser, Flexograph ink oven; Gas turbine, Gasoline; Landfill gas; Lithograph ink catalytic afterburner, thermo afterburner; Natural gas; Paving asphalt; Power plants; Refinery fugitives, process gas, process heaters, CO boiler; Roofing tar; Rotogravure ink; Sewage Gas; Stripping solvent for printed circuits
Ethane Propane C ₁ - C ₃	2		
C ₄ and higher and their isomers	2	1 ppm to 100%	Adhesive, vinyl; Appliance enamel paint; Automotive solvent based paint, primer, topcoat, catalytic afterburner, thermo afterburner; Automotive water based paints, undercoat, topcoat, ovens, afterburner incinerator; Automotive lacquer paint; Cleaning solvent, Stoddard; Crude oil, light API°, heavy API°, wet gas, dry gas; Degreaser; Flexograph ink oven; Gasoline; Landfill gas; Lithograph afterburners; Paving asphalt; Refinery blend stock, process gas, process heater; Rotogravure ink, Roofing tar; Rubber adhesive; Rubber solvent; Stripper solvent for printed circuit board

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B. Chemical Plant (Code 3)--

The emissions from this plant are low. However, when KVB tested the pthalic anhydride afterburner, the burner was corroded and functioning improperly. After replacing the burner the plant personnel had the unit retested and reported that the methane emissions had been nearly eliminated.

C. Electrostatic Spray Booth and Oven (Code 4)--

In this process appliances were electrostatically coated with solvent based paint in an oven heated by the exhaust gases from the oven incinerator. The painting operation was automated. The incinerator itself was 94% efficient but since half of the gas was recirculated the actual emissions to atmosphere were further reduced to a factor of 96%.

D. Oil Field (Codes 5 and 28)--

Based on three fugitive emission tests on two oil production fields, KVB estimated the oil field emissions for the entire Basin. With the advice of the WOGA Production Subcommittee, KVB selected the fields tested to be representative of two different types of operations found in the Basin. The field in Huntington Beach produced a heavy (API°14) crude using IC engine-powered rod pumps. Periodic steam injection was used to improve production. The field in Saticoy produced a light (API°34) crude using both electric-powered rod pumps and gas-lift techniques. In the latter technique compressed natural gas is injected into the well to raise the crude to the surface. Characteristic of most oil fields in the Basin, both of these fields had a tank farm for oil/water separation and gas compression equipment.

Leaks in fittings and seals, evaporative loses from open vessels, and exhaust gases from IC engines and process heaters were the sources of emissions. A technique of spraying fittings with soap solution was used successfully to locate and roughly quantify leaks. Over 3500 fittings were tested in this manner. Every accessible fitting in a given location was

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systematically sprayed and logged indicating the fitting type (valve, flange, etc.), line size, product in the line, pressure and temperature of the product, and the size of leak detected (none, small, medium or large). If a leak was detected; it was tagged "small," "medium" or "large" depending on the judgement of the engineer or technician performing the test.

Measuring the leak rates and sampling the escaping organic gases was conducted using the tenting technique described in Section 3.2 and shown in Figure 3-13. Most of the "large" leakers were tested for leak rate. Some of the "medium" leakers and a few of the small leakers were measured to "calibrate" the visual appearance which was the primary method of quantifying the smaller leaks.

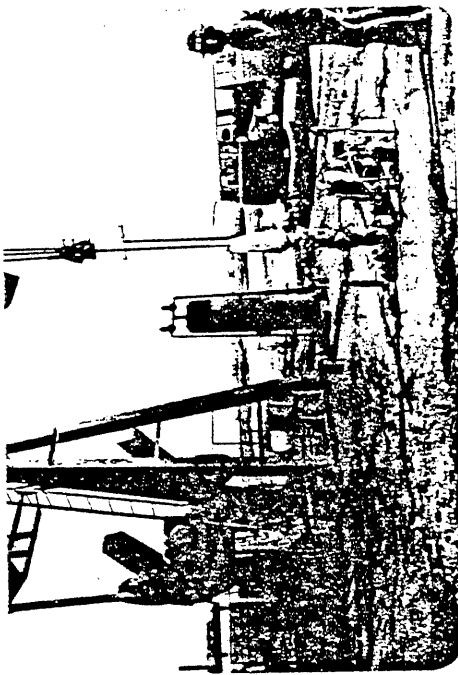
Emissions from open vessels like waste water separators or oil well cellars were estimated by collecting samples of the material in the vessel and performing evaporation tests in the laboratory.

1. Test Results--

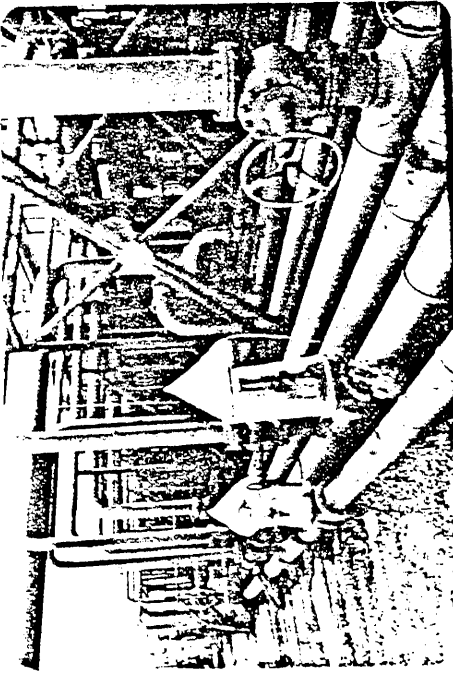
Tables 3-34 and 3-35 show the results of testing seven wells at each field. At the Saticoy field only the gas-lift wells were tested since the rod-pump well were used exclusively at the Huntington Beach field. The tables show how many fittings of each type were tested and how many leaks of what size (small, medium or large) were found. Table 3-36 summarizes the leaks by the type of product in the pipe line and the temperature and pressure of those products. The dry gas lines were found to have the greatest leakage. Dry gas was used at the Huntington Beach field to fuel the IC engines (30-40 psig) and at the Saticoy field to effect the gas lift operation (900 psig). The wet gas and crude oil were products from the wells being transported to the tank farms.

Tables 3-37 and 3-38 present leak test results for the respective tank farms. Table 3-39 combines the tank farm data and summarizes the data by the material in the pipeline. As for the oil wells the leaks in the tank farm area were found primarily in the gas lines. A few small or medium leaks were found in the crude lines at Huntington Beach but none were found at Saticoy despite a concentrated effort in which nearly 1000 fittings were sprayed with soap solution.

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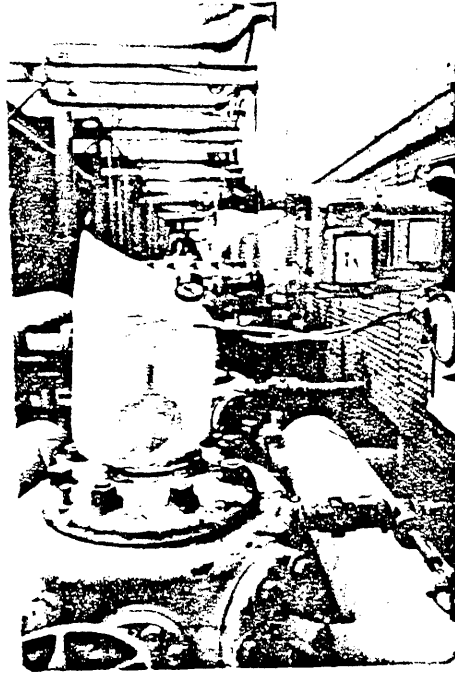
a. Well head leaks



b. Valve leaks



c. Compressor seal leaks



d. Compressor fitting leaks

Figure 3-13. Measuring fugitive emissions from petroleum production operations.

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TABLE 3-34. HUNTINGTON BEACH OIL FIELD, LEAK TEST RESULTS
7 ROD-PUMP WELLS

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Flanges	61	0	0	0
Valves - gate	98	11	2	2
butterfly	7	0	0	0
plug/ball	85	1	0	0
relief	7	0	0	0
Threaded Connections				
- ells	159	5	0	0
tees	94	1	0	0
unions	78	1	2	1
couplings	24	0	0	0
swages	53	0	0	0
bushings	13	0	0	0
others	68	0	1	0
Total	747	19	5	3

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TABLE 3-35. SATICOY OIL FIELD, LEAK TEST RESULTS
7 GAS LIFT WELLS

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Valves - gate	35	10	5	0
Threaded Connections				
- ells	36	1	0	0
tees	15	0	0	0
couplings	42	10	1	1
others	29			
Control valves	7	0	0	1
Total	164	21	6	2

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TABLE 3-36. OIL WELL LEAKS, SUMMARY BY PIPELINE CONDITIONS

Product	Conditions		Total Tested	Leakers Identified		
	Temperature (°F)	Pressure (psig)		Small	Medium	Large
Wet Gas	90	80 - 110	255	2	0	1
Dry Gas	70	30 - 40	130	16	5	2
	70	900 (gas lift)	164	21	6	2
Crude	90	80 - 110	362	1	0	0
Total			911	40	11	5

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TABLE 3-37. HUNTINGTON BEACH OIL FIELD, LEAK TEST RESULTS
TANK FARM

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Flanges	181	0	0	0
Valves - gate	243	16	11	5
butterfly	113	0	0	0
plug/ball	44	1	0	1
relief	8	0	0	0
Threaded Connections				
- ells	103	0	0	0
tees	49	0	1	0
unions	19	1	0	1
couplings	27	1	0	0
bushings	12	1	0	0
others	29	2	0	0
Total	828	22	12	7

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TABLE 3-38. SATICOY OIL FIELD, LEAK TEST RESULTS
TANK FARM

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
<u>Wet Gas Lines</u>				
Flanges	95	0	0	0
Valves - gate	122	7	4	2
plug/ball	49	0	0	1
relief	10	0	0	0
Threaded Connection				
- ells	48	0	0	0
tees	18	0	1	0
others	12	0	0	4
Control Valves	8	0	0	4
Total	362	7	5	11
<u>Crude Line Fittings</u>	932	0	0	0

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TABLE 3-39. OIL FIELD TANK FARM LEAKS, SUMMARIZED BY PIPELINE CONDITIONS

Product	Conditions		Total Tested	Leakers Identified		
	Temperature (°F)	Pressure (psig)		Small	Medium	Large
Wet Gas	Amb.	10 - 45	436	8	5	8
Dry Gas	Amb.	55	312	15	10	10
Crude	Amb. - 180	20 - 65	1169	6	2	0
Waste Water	Amb. - 180	20 - 40	32	0	0	0
Dump Line	Amb.	Amb.	173	0	0	0
Total			2122	29	17	18

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The gas and compressor plant results are summarized in Tables 3-40 and 3-41 respectively.

To quantify the leak rates designated small, medium and large, the actual leakage was measured on 21 fittings as shown in Table 3-42. Large leaks were found to be greater than $0.08 \text{ ft}^3/\text{min}$ which for methane corresponds to a leak rate of 0.9 tons/year. The largest leak in the group was $0.29 \text{ ft}^3/\text{min}$ corresponding to 3.1 ton/year of methane. Medium leaks ran between 0.006 and $0.08 \text{ ft}^3/\text{min}$ with a minimum leak rate of 128 lb/year of methane. Small leaks ranged down to as small as $0.0002 \text{ ft}^3/\text{min}$ or 4 lb/year of methane. This established the overwhelming importance of the large leakers on the total emissions and validated the visual technique for estimating small and medium leak rates.

The fugitive emission data reported above were used to compute emission factors and emission profiles for petroleum production operations as discussed in Section 2.3.

At the Saticoy field a special study of the effects of routine maintenance was made. Forty-three leaking fittings, primarily valves, were tightened by oil field personnel in an attempt to stop the leaks. No seal replacement or other major overhauling was attempted. The results are in Table 3-43. More than 50% of the leakers were stopped by a simple tightening of the packing nut.

TABLE 3-40. HUNTINGTON BEACH OIL FIELD, LEAK TEST RESULTS
GAS PLANT (4 OF 6 COMPRESSORS IN SERVICE)

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Compressor Valves	40	1	4	1
Covers	160	1	1	4
Wet Gas Valves	29	0	3	3
Wet Gas Flanges	70	1	0	0
Total	299	3	8	8

TABLE 3-41. SATICOY OIL FIELD, LEAK TEST RESULTS
COMPRESSOR PLANT (1 OF 2 COMPRESSORS IN SERVICE)

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Compressor Valves	12	0	0	3
Covers	6	0	0	0
Wet Gas Valves and Flanges	60	5	1	0
Dry Gas Valves and Flanges	93	3	2	0
Dry Gas Control Valves	3	0	0	3
Total	174	8	3	6

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TABLE 3-42. OIL FIELD LEAK RATE DATA, MEASURED

Fluid	Leak Rate (ft ³ /min)	Designation (soap spray)
Wet gas	0.17	Large
Dry gas	0.08	Large
Wet gas	0.29	Large
Wet gas	0.11	Large
Wet gas	0.12	Large
Dry gas	0.18	Large
Dry gas	0.26	Large
Dry gas	0.02	Medium
Wet gas	0.04	Medium
Dry gas	0.06	Medium
Dry gas	0.009	Medium
Crude	0.007	Medium
Crude	0.009	Medium
Wet gas	0.006	Medium
Wet gas	0.04	Medium
Dry gas	0.0009	Small
Crude	0.0005	Small
Dry gas	0.0009	Small
Crude	0.002	Small
Wet gas	0.004	Small
Crude	0.0005	Small

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TABLE 3-43. SATICOY FIELDS, EFFECT OF VALVE TIGHTENING

	Number Identified	Stopped	Reduced	No Effect
Gate valves				
Small leakers	16	14	0	2
Medium leakers	5	2	1	2
Large leakers	5	1	0	4
Other valves & connections				
Small leakers	5	5	0	0
Medium leakers	3	2	0	1
Large leakers	1	0	0	1
Control valves	8	0	0	8
Total	43	24	1	18

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E. Refinery Emissions (Codes 7, 11, and 24)--

The objectives of the refinery tests on this program were to (1) obtain emission profile data (% composition), (2) check emission factors in AP-42 and (3) evaluate ambient testing as a means of characterizing refinery emissions. The ambient tests were discussed in Section 3.2.4. The fugitive emission rates from eight major refineries were measured in the late 50's by the LA APCD in a joint Federal, State and District project. These test results were the basis for most emission factors in AP-42. It was felt that the testing permitted by the ARB program budget would be sufficient to validate the AP-42 emission factors or determine that current maintenance practices and sealing technology had caused a reduction in emission factors. Also by sampling and analyzing the emissions from typical refinery processes an emission profile for various refinery processes was obtained.

One major refinery (Code 7) was tested primarily for device type emission factors. The small Douglas Oil refinery (Code 11) was tested for ambient test evaluation as discussed in Section 3.2.4. Another small independent refinery (Code 24) was used for some preliminary testing to checkout test procedures.

The effort included stack tests on process heaters and FCC units plus fugitive emission tests on valves, fittings, pumps, compressors, cooling towers and oil/water separation pools. As discussed in Section 3.2.1, fugitive emissions from process hardware were determined by spraying the components with soap solution and characterizing the leak rates by the rate of bubble formation. By measuring a number of small, medium and large leaks a characteristic leak rate was determined for each of these leak sizes. Emissions from cooling towers and pools were estimated by determining organic evaporation rates from samples taken from these sources.

The samples taken from refineries for laboratory analysis are summarized in Table 3-31. A breakdown of organic compounds for each emission sample listing in Table 3-31 is presented in the Appendix. The refinery fugitive emission measurements are summarized in Table 3-44 and discussed below. The emission factors used in the emission inventory are discussed in Section 2.3.1.

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TABLE 3-44. OIL REFINERY FUGITIVE EMISSION SUMMARY

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Valves	5765	157	62	33
Flanges	11821	38	20	7
Pumps	115	30	4	7
Compressors	5	1	0	0
Separators	3			
Cooling Towers	3			

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1. Refinery Valves and Flanges--

A breakdown of valve and flange test results is presented in Table 3-45. The number of flanges tested was approximately twice the number of valves since most installations of valves in pipelines involve two flanges. In spraying fittings with soap solution all of the accessible valves and flanges in a process area were inventoried and tested. The valve type breakdown shown was based on the testing at the Code 7 refinery while those listed as unclassified were measured at the Code 11 refinery. In testing at the Code 11 refinery the objective was to correlate the emission estimate using ambient techniques (Section 3.2.4) with those using direct measurement. The emphasis was to assess emissions by process unit and the valve types were not identified. The Code 11 breakdown by process unit is presented below.

A surprising result in Table 3-45 was the proportionately larger number of leaks of all types found in the plug valves. Plug valves were believed to represent "improved technology" over gate valves. However, plug valves require periodic lubrication to prevent leaks. In nearly every case of a leaking plug valve, the leak could be stopped by application of sealing grease. The fact that these leaks were found was an indication that the refineries were in a normal maintenance condition when the tests were conducted.

A breakdown of valve and flange emissions by pipeline size and fluid content is presented in Table 3-46. Ethane and propane lines contained gaseous product while all of the other products were liquids.

Table 3-47 presents a breakdown of the emissions from the Code 11 refinery by processing units. For each component at each unit the number of components tested is indicated along with the percentage of those components that were tested in that unit. For example, on Crude Unit #2 80% of the valves were tested. The 20% of the valves not tested were not readily accessible without special apparatus.

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TABLE 3-45. REFINERY EMISSION SUMMARY, LEAKING VALVES BY VALVE TYPE

Valve Type	Number Tested	Leaks Measured	Leakers Identified		
			Small	Medium	Large
Plug	1320	15	76	21	24
Gate	3077	5	47	6	4
Control	75	2	9	0	3
Unclassified	1293	3	25	35	2
Total	5765	25	157	62	33
Flanges	11821	0	38	20	7

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TABLE 3-46. REFINERY EMISSION SUMMARY (CODE 7)
VALVE AND FLANGE LEAKS BY SIZE AND FLUID SERVICE

	Valves less than 2 in.	Valves 2 in. and Greater	Fittings & Flanges Less than 2 in.	Fittings & Flanges 2 in. and Greater
Propane	928	596	1180	1583
Small	56	39	13	3
Medium	10	12	0	0
Large	8	16	0	0
Light Gasoline	137	88	146	249
Small	0	0	0	0
Medium	0	0	0	0
Large	0	1	0	0
Gasoline	538	358	551	1007
Small	5	13	1	0
Medium	1	0	0	0
Large	1	0	1	0
Naphtha	56	60	230	176
Small	3	1	0	0
Medium	0	0	0	0
Large	0	0	0	0
Gas Oil	227	352	4	1004
Small	0	1	0	1
Medium	0	0	0	0
Large	0	0	0	0
Fuel Oil	327	220	765	655
Small	4	1	0	0
Medium	2	0	0	0
Large	0	0	0	0
Crude	96	126	367	357
Small	0	4	0	0
Medium	0	1	0	0
Large	0	0	0	0
Residual Oil	62	29	70	80
Small	0	0	0	0
Medium	0	0	0	0
Large	0	0	0	0
Ethane	52	56	73	152
Small	1	4	1	0
Medium	1	0	1	0
Large	0	5	0	0
Freon	37	30	37	75
Small	0	0	0	0
Medium	0	0	0	0
Large	0	0	0	0
Sour Water	47	50	--	--
Small	0	0	0	0
Medium	0	0	0	0
Large	0	0	0	0

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TABLE 3-47. CODE 11 REFINERY EMISSIONS, VALVE, FLANGE AND PUMP INVENTORY

No. Tested (% of Total)	Reformer Unit	Naphtha Unit	Crude Unit #2
<u>Valves</u>	500 (100%)	318 (100%)	475 (80%)
Large leaks	0	0	2
Medium leaks	26	0	9
Small leaks	13	5	7
<u>Flanges</u>	852 (70%)	889 (70%)	1,319 (80%)
Large leaks	0	0	0
Medium leaks	13	0	7
Small leaks	7	0	11
<u>Pumps</u>	12 (100%)	7 (100%)	30 (100%)
Large leaks	0	0	1
Medium leaks	1	0	0
Small leaks	1	0	2

Table 3-48 summarizes the leak rate measurements and calibration of visual leak rating. The leak rates were measured by tenting techniques. The "large," "medium", "small" designations were assigned in the field prior to measuring leak rate. Thus a "large" gas line leak ranged from 7 to 38 lb/day with an average of 18 lb/day.

The computation of emission factors for refinery valves is presented in Table 2-7. For valves in gas service the leak rate per valve is 0.4 lb/day and for liquid service is 0.003 lb/day. To compare this to AP-42 which makes no distinction between gas and liquid service refer to Table 2-7. The total emissions for gas and liquid service is $620 + 49 = 669$ lb/day divided by the total valves $(1698 + 2774) 4472$ $(669/4472)$ equals 0.15 lb/day/valve which is identical to the value given in AP-42. Therefore, it was concluded that no correction factor needed to be applied to the data in the SCAQMD EIS file for the purposes of the emission inventory.

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TABLE 3-48. REFINERY EMISSION SUMMARY, VALVE LEAK RATE MEASUREMENTS

Location Code	Fluid	Leak Rate lb/day	Average Leak Rate (calibration of visual leak rating)
<u>Large Leakers</u>			
7	Gas	25	
7	Gas	7	
7	Gas	19	
7	Gas	13	
7	Gas	14	
7	Gas	15	
7	Gas	38	
11	Gas	22	Large Gas Valves
11	Gas	<u>12</u>	18 lb/day
7	Liquid	<u>18</u>	Large liquid valves 18 lb/day
<u>Medium Leakers</u>			
7	Gas	2	
7	Gas	6	Medium Gas Valves
7	Gas	<u>2</u>	3 lb/day
7	Liquid	2	
7	Liquid	3	Medium Liquid Valves
7	Liquid	<u>5</u>	3 lb/day
<u>Small Leakers</u>			
7	Gas	1.0	
7	Gas	0.2	
11	Gas	0.02	
7	Gas	0.02	Small Gas Valves
11	Gas	<u>0.05</u>	0.3 lb/day
7	Liquid	0.02	
7	Liquid	0.02	
7	Liquid	0.02	Small Liquid Valves
7	Liquid	<u>0.0002</u>	0.02 lb/day

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2. Refinery Pumps--

Refinery pump test results are shown in Tables 3-49 and 3-50. While Table 3-49 indicates that mechanical seals and packed seals have the same proportionate number of leakers (approximately 50%). Table 3-50 shows that mechanical seals have generally lower leak rates and especially for gas service. Referring back to Table 2-7 where the emission factors were calculated the mechanical and packed seals showed nearly the same emission factor for liquid service (< 26 RVP) while for gas service the mechanical seal emission factor was one-sixth that for the packed seal. The leak rate data for the Location Code 11 refinery (Table 3-50) agree with those for Code 7 amazingly well. During testing the type seals and fluid RVP were not recorded at Code 11. Later it was established that all their pump seals were mechanical and generally the fluid RVP was below 26 psi. These assumptions were made in developing emission factors.

Based on the above data an overall pump emission factor was calculated (refer to Table 2-7). Total emissions = 25 + 140 + 5 + 170 = 340 lb/day divided by seal tested (93 + 19 + 12 + 4 = 128) $340/128 = 3 \text{ lb/day/seal}$. or 0.5 tons/year/seal.

3. Refinery Compressors--

Only five refinery compressors were located and tested. One tiny leak of 0.0003 lb/day was located. For emission factor data on compressors refer to the petroleum production data, e.g., Table 2-8.

4. Refinery Separators--

Open separators were found at all three refineries visited. The largest separator found is shown in Figure 3-14. Samples were taken from pools in each refinery. The sampled oil was taken to the KVB laboratory where the oil was separated from the water and the oil was placed in a dish for evaporation tests at the recorded pool temperatures. The measured evaporation rates were:

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TABLE 3-49. REFINERY EMISSIONS, PUMP SEALS

Seal Type	Reid Vapor Pressure psi	No. Tested	Leakers Identified		
			Small	Medium	Large
Mechanical (Code 7)	> 26	19	8	0	2
	< 26	<u>44</u>	<u>14</u>	<u>3</u>	<u>2</u>
	Total	63	22	3	4
Packed (Code 7)	> 26	4	0	0	1
	< 26	<u>12</u>	<u>5</u>	<u>0</u>	<u>1</u>
	Total	16	5	0	2
Unclassified (Code 11)		49	3	1	1

TABLE 3-50. REFINERY EMISSION SUMMARY, PUMP SEAL LEAK RATE MEASUREMENTS

	Reid Vapor Pressure psi	Seal Type	Measured Leak Rate lb/day	Average Leak Rate, lb/day (Calibrations of Visual Leak Rating)
LOCATION CODE 7				
<u>Large Leakers</u>				
	< 26	Mechanical	10	} 7
	< 26	Mechanical	4	
	< 26	Packed	4	4
	> 26	Mechanical	5	} 70
	> 26	Mechanical	130	
	> 26	Packed	170	170
<u>Medium Leakers</u>				
	< 26	Mechanical	2	} 1
	< 26	Mechanical	1	
	< 26	Mechanical	0.002	
<u>Small Leakers</u>				
	< 26	Mechanical	0.05	} 0.01
	< 26	Mechanical	0.01	
	< 26	Mechanical	0.002	
	< 26	Mechanical	0.002	
	< 26	Mechanical	0.005	
	< 26	Packed	0.2	} 0.06
	< 26	Packed	0.05	
	< 26	Packed	0.0005	
	< 26	Packed	0.0005	
	> 26	Mechanical	0.07	} 0.04
	> 26	Mechanical	0.007	
LOCATION CODE 11				
<u>Large Leakers</u>				
	< 26	Mechanical	24	} 7
	< 26	Mechanical	5	
	< 26	Mechanical	2	
	< 26	Mechanical	2	
<u>Medium Leakers</u>				
	< 26	Mechanical	1	1

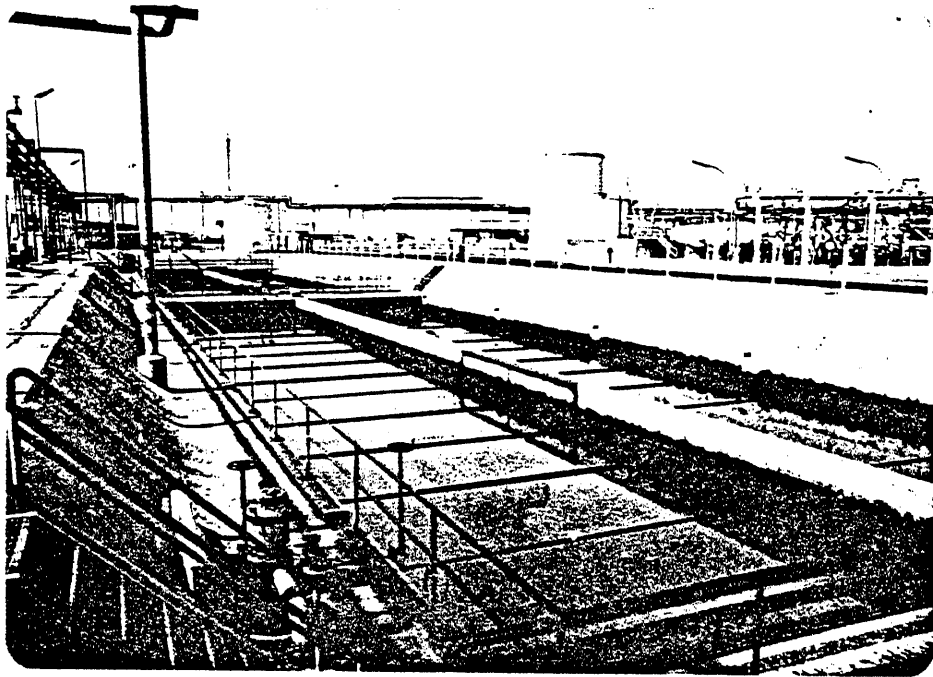


Figure 3-14. Oil/water separator tested.

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<u>Location Code</u>	<u>Evaporation Rate (lb/hr·ft²)</u>
7	0.01
11	0.0002
24	0.004

The Code 7 separator in Figure 3-14 had a surface area of 14,000 ft². At the rate of 0.01 lb/hr·ft² the emissions from that separator would be 140 lb/hr. The operators of the refinery estimated that the water flow through the separator was 3000 gal/min. or 180,000 gal/hr. At these rates the emission factor for the separator would be 140/180 or 1 lb/1000 gal. The AP-42 emission factor for process drains, uncontrolled is 5 lb/1000 gal waste water. If the KVB measurement were correct the emission from that separator would be 600 tons/year. SCAQMD rates this separator at 1.5 ton/yr in their permit file. More work is needed in this area.

5. Refinery Cooling Towers--

Of the three cooling towers tested valid data were obtained on only one. The unit tested is illustrated in Figure 3-15. It was a large tower serving an FCC unit, the gas plant for that FCC and a reformer unit. The water circulation was 42,500 gal/min. Cooling water circulated through the various processes and returned to the tower where the water was evaporatively cooled by forced air circulation. Leaking fittings in the pipelines of the process unit, being cooled by the circulated water, caused hydrocarbon to be picked up by the water. On passing through the cooling tower the hydrocarbons vaporize and escape to the atmosphere.

Water samples were taken at the inlet and outlet of the tower as shown and analyzed (xylene extraction and GC analysis) on organic content. The organic content was identified as 100% isopentane with concentrations indicated on the schematic. The emissions were determined to be the difference in organic concentration times the flow rate as follows:

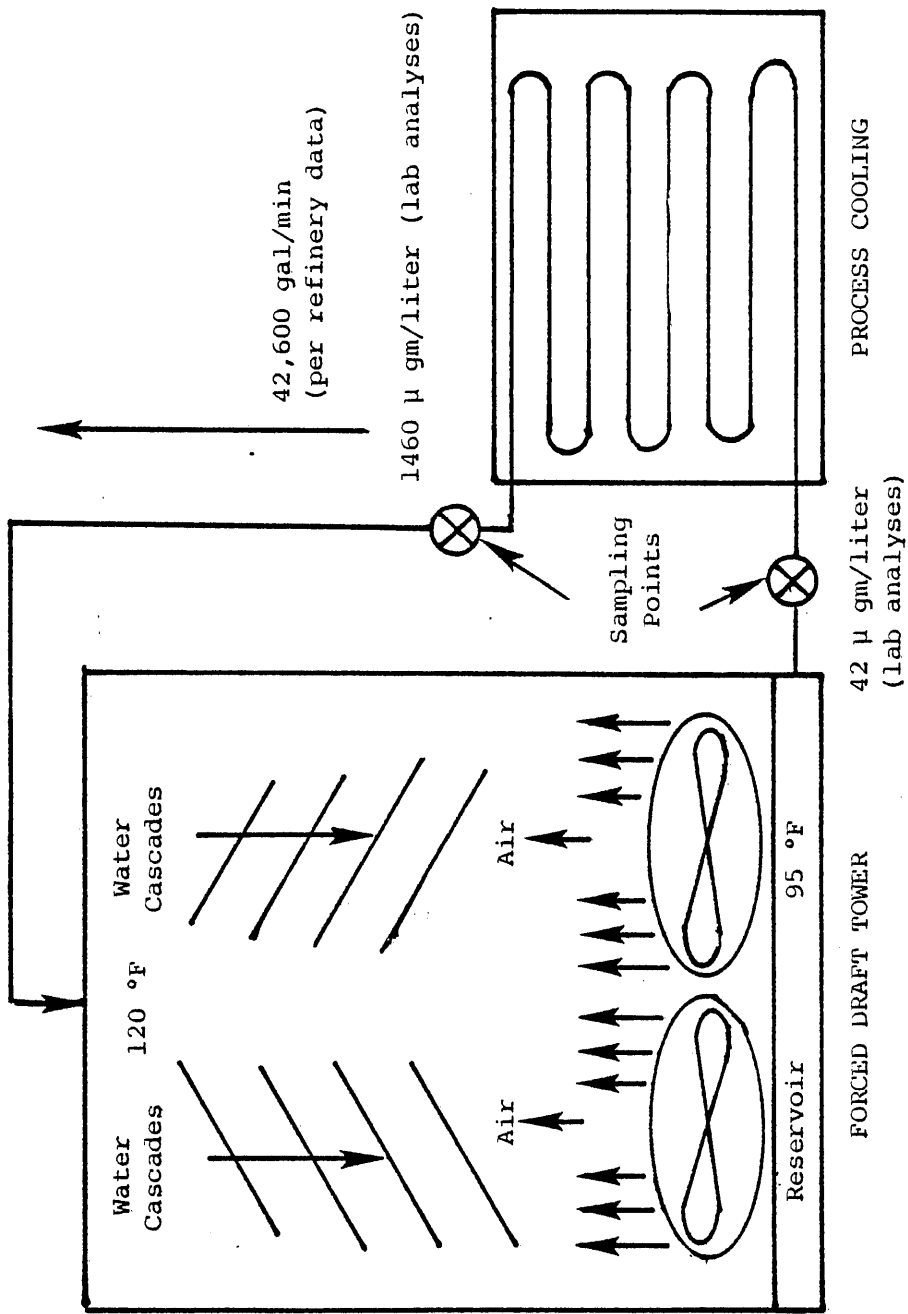


Figure 3-15. Forced-draft cooling tower schematic.

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Change in concentration = 1460 - 42 = 1418 μ gm/liter

$$\begin{aligned} \text{Emission Rate} &= 1418 \frac{\mu \text{ gm}}{\text{liter}} \times \frac{3.785 \text{ liter}}{\text{gal}} \times \frac{\text{gm}}{10^6 \mu \text{ gm}} \times \frac{\text{lb}}{454 \text{ gm}} \times \frac{42,600 \text{ gal}}{\text{min}} = \\ &= 0.5 \frac{\text{lb}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} = 30 \frac{\text{lb}}{\text{hr}} \times \frac{24 \text{ hr}}{\text{day}} = 700 \frac{\text{lb}}{\text{day}} \times \frac{365 \text{ day}}{\text{yr}} \times \frac{\text{ton}}{2000 \text{ lb}} = \\ &= 130 \frac{\text{ton}}{\text{yr}} \end{aligned}$$

To relate this to AP-42 the emissions must be put into $\text{lb}/10^6$ gal.

Other emission factors are in $\text{lb}/\text{day}/1000$ GPM

$$0.5 \text{ lb}/\text{min} \times \text{min}/42,600 \text{ gal} \times 10^6 = \underline{12 \text{ lb}/10^6 \text{ gal}}$$

$$700 \text{ lb}/\text{day} \div 42,600 \text{ GPM}/1000 = \underline{16 \text{ lb}/\text{day}/10^3 \text{ GPM}}$$

A comparison of these results with results calculated from published emission factors is shown in Table 3-51. EPA publication AP-42 lists an emission factor of $6 \text{ lb}/10^6$ gal of cooling water. The API document, referenced on the table, discusses the emissions and indicates that a 1957 study (probably the Los Angeles joint project) specified an emission factor of 3 to 5.3 $\text{lb}/\text{day}/1000$ GPM while a "more realistic average figure used by some refineries is 8 to 10 $\text{lb}/\text{day}/1000$ GPM." From these emissions factors an emission rate was calculated based on the 43,000 GPM water circulation rate. These emissions are shown in Table 3-51 compared to the KVB measured emissions from with emission factors were calculated as indicated in the table.

The higher emission factor determined by the KVB test can be explained by the fact that the hydrocarbon emitted by this particular cooling tower was isopentane, a fairly volatile material. Since the AP-42 and the API "best estimate" agree, KVB feels that the AP-42 emission factor is still a reasonable value for an average cooling tower.

F. Magnetic Tape Manufacturing (Code 8)--

The outstanding feature of the tape manufacturing plant was the charcoal adsorption unit (also discussed in Section 4) which had an efficiency in excess of 99%. Measurements showed that only 0.2% of the photochemically-reactive MIBK used in the process escaped to atmosphere. MIBK is recovered

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TABLE 3-51. COOLING TOWER EMISSIONS AND EMISSION FACTORS
43,000 GPM Water Flow

Data Source	Emission Rates		Emission Factors	
	lb/day	ton/yr	lb/10 ⁶ gal	lb/day/1000 GPM
AP-42	400	70	<u>6</u>	<u>6</u>
API 931*				
1957 Study	200	40		<u>3 - 5</u>
Best Estimate	400	70		<u>8 - 10</u>
KVB Tests	<u>700</u>	<u>130</u>	12	<u>17</u>

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Note: Underlined figures were given and other figures were calculated.

*API Publication 931, Manual on Disposal of Refinery Wastes, Volume on Atmospheric Emissions, Chap. 7, Pages 7 - 12, Hydrocarbon Emissions, API Refining Dept., Washington, D.C., February 1976.

from the charcoal adsorber. The reclaimed solvent is reused at great savings to the company, who reportedly pay off the adsorber in just a few months of operation.

G. Appliicance Manufacturing - Air Conditioners (Code 9)--

This plant had five stacks emitting organics from the following processes:

- a. degrease tanks (2)
- b. paint spray booths (2)
- c. adhesive spray booth.

This plant employed solvent substitution as their primary control technique. No incinerators or adsorbers were used. The two degrease tanks emitted 25 tons/year of low reactivity perchloroethylene. One painting operation employing electrostatic spraying emitted 15 tons/year of organics-vapor composed of 71% perchloroethylene, 22% saturated aliphatics and 7% reactive aromatics. The other paint spray booth emitted 27 tons/year composed of 33% perchloroethylene, 56% saturated aliphatic compounds, 9% reactive aromatics and 2% butyl alcohol. The adhesive spray booth emitted 4 ton/year of primarily perchloroethylene.

H. Combustion of Fuel (Codes 10 and 18)--

A utility boiler burning residual oil and a utility gas turbent burning gas were tested. As was expected the organic concentrations in the exhaust gases were low, 5 ppm for the boiler and 7 ppm for the turbine. Analyses of these emissions confirmed that they were primarily oxygenates. The boiler emissions were 36% aldehydes and 31% acetone. The remaining third was saturated aliphatics, mostly methane and butane. The turbine emitted 93% aldehydes and 7% methane. The low concentration of organics in these large combustion devices is attributed to the relatively long residence time of the combustion gases which have ample time to completely combust. The asphaltines in the residual oil which fail to react form particulate matter which will be measured as part of a later ARB study.

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I. Rubber Tire Manufacturing (Code 12)--

The ducted emissions from one tire manufacturing plant were sampled for organic content. Little information on the manufacturing processes were released by the plant except for the operating schedule and that the process at the time of measurement was typical. No control devices (incinerators, adsorbers, etc.) were employed.

Emissions from all four stacks were similar as follows:

Emissions, ton/year	160	60	30	30
Composition, %				
Straight and Isoparaffins	31	14	58	3
Cycloparaffins	65	83	34	96
Aromatics	<u>4</u>	<u>3</u>	<u>8</u>	<u>1</u>
Total	100	100	100	100

The data obtained were considered excellent for the purpose of obtaining an emission profile. Emission rate data from the SCAQMD files were used for the inventory.

J. Automobile Assembly (Codes 13 and 14)--

Two automobile assembly plants were tested, one using solvent based paint (Code 13) and one using water based paint (Code 14).

The solvent based process consisted of a phosphate treatment, a primer coat, and two top coats. The water based process consisted of an electrostatic dip coat, a light primer coat and two top coats. The primer and top coats were sprayed in large booths with water curtains to capture overspray. The plant using solvent based paint use electrostatic applications to minimize overspray. The water based process had no incinerators while the solvent based process used incinerators on the ovens but not on the booths.

Table 3-52 is a comparison of emissions from similar operations in each process. (Additional data are contained in Table 3-31 and the Appendix however the data in Table 3-52 are representative of the measured emissions.) Both processes ran at nearly the same rate, approximately 55 cars per hour although the water based plant operated approximately 25% more total hours in the year as indicated.

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TABLE 3-52. AUTOMOBILE ASSEMBLY PLANT EMISSION SUMMARY
WATER BASE COMPARED TO SOLVENT BASE PAINT

Device	Emissions					
	Water Based (Code 14)			Solvent Based (Code 13)		
	Rate** ton/yr	Composition	KVB Code	Rate*** ton/yr	Composition	KVB Code
Primer Spray Booth	12 (NC) *	70/30 acetone/benzene	14/1-6	28 (NC)	C8 & 9 aliphatics	13/5-8
Primer Oven	2 (NC)	40/30/25 methane/acetone/aromatics	14/7	1 (31) *	70/25 aldehydes/methane (inlet 95% natural gas)	13/1-2
Primer "Smoker" Oven		Not Required		1 (6)	65/35 aldehydes/C3-4 paraffins	13/3-4
Top Coat Booth	37 (NC)	75/5/20 methane/ethane/heptane	14/8-11	21 (NC)	C6 to 9 paraffins	13/9-14
Top Coat Oven	4 (NC)	55/5/40 methane/butane/benzene	14/12	1.5 (4.5)	55/15/25/5 methane/aldehyde/C2 to 6 paraffins/ethylene	13/15-16
Vinyl Top Adhes.	7 (NC)	40/25/15/17/3 perchloroethylene/acetone/ ethyl acetate/Cl to 4 paraffins/toluene	14/20		Not available but probably similar	

* (NC) = no control device. Number in parenthesis, e.g. 1(31), means rate of organics to inlet of control device in tons/year.

**3840 hr/yr

***3000 hr/yr

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The total measured emissions were similar varying more or less at each process. The emissions from the solvent based paint are mostly mineral spirits, i.e., C2 to 9 paraffins including some cycloparaffins; aldehydes from the combustion products of the incinerators and methane from the oven heaters and incinerator burners. A small amount of ethylene was detected from the top coat catalytic afterburner which also had a relatively low efficiency of 65% because of the large amount of methane that was emitted. Excessive methane emissions seem to be characteristic of the catalytic incinerators.

The water based paint contained low-reactivity methane and acetone, some aromatics and some light paraffins. The vinyl top cement produced perchloroethylene, ethyl acetate, light paraffin; and some toluene vapors. It was understood that these emissions were similar in each plant so they were only measured at one.

The methane at the water based plant was probably due to the heating/air conditioning system in the booths and ovens which recirculates some of the heated air in the air conditioning (dehumidification) system. The methane comes from the oven heaters and was measured as a principal emission in the ovens and booths.

The absence of more oxygenated compounds causes some speculations. Both water and solvent based paints usually have compounds such as acetates, alcohols, ketones, glycols, ethers, etc. Possible explanations are that (1) these compounds, which are water soluble, may be absorbed by the water curtain or (2) the GC/FID system used in this program was incapable of detecting them.

Company engineers at the automobile plants had similar suspicions regarding water absorption. They felt, however, that the water, which is recirculated, would reach equilibrium in time.

As discussed in Sections 3.2.2 and 3.3 the detection of oxygenated compounds was marginal in the system selected for the program. The system was designed for its universal detection ability. The FID sensor on the GC was relatively insensitive to certain oxygenates. When detected a

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response factor could be determined. However it is possible that some compounds were not detected. Only a limited amount of program funds could be devoted to this response definition. Therefore it is possible that some of the compounds may not have been detected. Note, however, that acetone and ethyl acetate were detected so that the system was not totally insensitive.

Because of the proprietary paint formulae and the uncertainty of solvent retention in the cured paint, it was difficult to conduct material balances which would account for solvent emissions. However, it did seem incorrect to assume that 100% of the solvent in the paint consumed escaped in the form of atmospheric emissions.

K. Automobile Repainting (Code 15)--

A commercial automobile paint spray booth was tested. Complete disclosure was made of manufacturer's specification for paints and solvents including those compounds used for thinning and catalyzing. The emissions covered a broad spectrum including:

	<u>%</u>
ethyl acetate	18
n-butyl acetate	17
n-amyl acetate	11
C7-13 aliphatics	25
aromatics	28
isopropyl alcohol	<u>1</u>
	100

No water curtain or other controls were used except for a coarse metal mesh filter for particulate control. On this test a material balance was run by experiment. Coupons were coated with paint and weighed periodically up to 24 hours after painting. The weight loss corresponded to 4.3 lb in 20 minutes and 5.4 lb in 24 hours. The spray booth sampling time was 30 minutes during the painting operation. During that time the measured emissions were 4.7 lb.

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The paint sprayed was determined by weighing the paint in the gun before and after spraying. The paint sprayed was 13.5 lb. Manufacturers data indicated that 60% of the paint would remain as a coating and 40% would evaporate. $0.4 \times 13.5 = 5.4$ lb.

<u>Laboratory Paint Experiment</u>	<u>Field Measurement</u>
20 min. Equiv. Solvent Loss - 4.3 lb	4.7 lb - Measured Emissions
24 min. Equiv. Solvent Loss - 5.4 lb	5.4 lb - Manufacturers specified solvent weight loss

Since the particular being painted during the test was a small foreign sedan, the emission factor for automobile repainting is estimated at from five to ten lb. of total hydrocarbon per car depending on the car size.

L. Steel Manufacturing (Code 16)--

Emissions were measured in

- . an open hearth
- . two coke oven batteries
- . a blast furnace
- . a steel sintering plant
- . a basic oxygen furnace.

The results are presented in Table 3-31 and the Appendix. The emissions were high. The coke oven appeared to be a significant source of ethylene, propylene and benzene. An unusual compound, trimethylfluorosilane, was found in the emissions of the open hearth, blast and basic oxygen furnaces where its presence was attributed to fluorine compounds in the scrap metal.

While organic emission controls were not used, it was observed that the open hearth precipitator reduced hydrocarbon emissions by 25%.

M. Roofing Kettle--

A sample of emissions from a roofing kettle at 390 °F was taken and found to contain a mixture of 20 compounds each comprising more than 1%. The detailed composition is in the Appendix and Table 3-31 summarized the emissions by reactivity class.

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REFERENCES FOR SECTION 3.0

- 3-1 Mueller, F. X. and J. A. Miller, "Determination of Organic Vapors in Industrial Atmospheres," Amer. Lab., 49-61, May 1964.
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- 3-3 Nelson, G. O., et al., "Respiratory Cartridge Efficiency Statistics; VII. Effect of Relative Humidity and Temperature," Amer. Ind. Hyg. Assoc. J., 37, (5), 280-288, 1976.
- 3-4 Parkes, D. G., et al., "A Simple Gas Chromatographic Method for the Analysis of Trace Organics in Ambient Air," Amer. Ind. Hyg. Assoc. J., 37, (3), 165-173, 1976.

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