

Final Report

on

Development of Species Profiles for Selected Organic Emission Sources

Volume I : Oil Field Fugitive Emissions

Prepared by

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California Polytechnic State University

Prepared for California Air Resources Board

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## **ABSTRACT**

This project involved the characterization of fugitive emissions from three source categories. Category 1 sources comprised emissions from California oil production facilities. Site selection criteria were developed, and resulted in the generation of a prioritized list of locations where emissions from light, medium and heavy crude petroleum operations would be sampled. At each site, samples from wellhead, pipeline, processing and storage systems were obtained. Specific components for sampling were pre-screened for positive hydrocarbon emissions using a portable hydrocarbon analyzer. The sampling methodology involved collection of 38 samples in evacuated stainless steel canisters. Detailed emission species profiles were determined by gas chromatography, with flame ionization detection. Peak identification was based on retention times, as well as separate gas chromatographic runs using a mass selective detector.

Category 2 and 3 sources included exhaust from utility and heavy-duty engines. The selection of 20 samples, based on estimates of engine populations in California, was described. The design and fabrication of a portable exhaust dilution system was discussed. Diluted exhaust from selected engines was sampled simultaneously for hydrocarbons and aldehydes. Diesel engines were additionally sampled for higher hydrocarbons. Hydrocarbon species were collected into evacuated stainless steel canisters. Aldehydes were absorbed into midget impingers containing DNPH/acetonitrile. High molecular weight hydrocarbons from Diesel exhaust were adsorbed in sorbent tubes filled with XAD-2 resin. Hydrocarbons were speciated by gas chromatographic techniques, as with Category 1 sources. Analysis of DNPH-aldehyde derivatives was performed using high performance liquid chromatography. Extracts from the XAD-2 resin were analyzed by gas chromatography, using a mass selective detector.

## DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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## SUMMARY

In accordance with the Request for Proposal issued by the California Air Resources Board, this project involved the characterization of hydrocarbon and aldehyde emissions from a variety of sources. This report deals with Task 1 of that project, the development of a plan for sampling and analysis, as well as the Task 2 implementation of the approved sampling plan. Sources to be sampled were divided into three categories:

Category 1 - Oil Production Fugitive Emissions

Category 2 - Utility Engine Exhaust

Category 3 - Farm and Heavy-Duty Engine Exhaust

### CATEGORY 1 SOURCES

As originally proposed, 38 samples from this category were to be collected and analyzed. The numerous components in an oil production field were segregated into "systems". These systems were classified as wellhead, pipeline, processing and storage. Each of these systems is progressively farther from the well than the preceding system. A sampling matrix was developed, consisting of various systems in fields producing light, medium and heavy crude oil. Samples from two secondary sumps were collected from a flux chamber in SUMMA electropolished, evacuated stainless steel canisters. Storage tank headspace samples were collected in evacuated steel canisters. Samples from other systems were obtained by isolating the selected component(s) with a Teflon shroud, and collecting the shroud effluent in evacuated steel canisters. Additional samples from several sources were taken by direct connection of the evacuated canisters to pipe fittings in the distribution lines, using Teflon tubing. Analysis for desired hydrocarbon constituents were performed using a variety of validated chromatographic methods.

### CATEGORY 2 AND 3 SOURCES

Using estimates of engine populations in California, a ranking of these sources was developed. Classification was based on engine type, rather than equipment type. A total of 12 samples from Category 2, and 8 samples from Category 3 was recommended for sampling. Sampling for these sources involved dilution of the engine exhaust in a portable mini-tunnel. Hydrocarbons were collected in evacuated stainless steel canisters, while aldehydes were derivatized in DNPH/acetonitrile fileed midget impingers.. High molecular weight hydrocarbons were adsorbed in XAD-2 sorbent tubes. Hydrocarbon analysis were performed using gas chromatographic methods. Aldehyde derivatives were analyzed using high performance liquid chromatography. Extracts from XAD resin were analyzed by GC-MS. Details on this portion of the study are reported separately, in Volume II of this report.

## Final Report, Task 1

### I. Introduction

The general objective of this project was "to develop improved hydrocarbon species profiles for oil production equipment, and exhaust from utility and heavy-duty equipment". (ARB RFP, Feb. 1988). These species profiles, when multiplied by the appropriate emission rate factors, will yield detailed information on the mass emission rates for specific compounds. This report is divided into two volumes. The first volume deals with Category 1 sources (Oil Field Fugitive Emissions). The second volume discusses all aspects of Category 2 and 3 sources (Engine Tests). To address the various technical aspects of the project, a team of researchers was assembled. Team personnel, and their primary responsibilities, are shown in Figure 1.

### II. Category 1 Sources

#### A. Site Selection Criteria

Efforts in this category were aimed at extracting hydrocarbon profiles from a variety of fugitive emission sources associated with petroleum production operations (Figure 2). There are several classification methods by which California oil production facilities may be grouped. The first of these methods involves classification by type of oil produced. Table 1 illustrates how the American Petroleum Institute (API) gravity may be used to divide crude oil production into light, medium and heavy categories. API gravity is inversely related to the specific gravity of the oil, as shown in Figure 3. Examination of the distribution of oil fields in California (Figure 4) reveals another potential classification scheme. There are three regions in which oil fields appear to cluster: the Salinas Valley (Coastal), the San Joaquin Valley, and the Los Angeles Basin. Figure 5 contains information on the size of the major oil fields in California. It was certainly desirable to have the major fields be included in this study. Thus, the Ventura, Elk Hills and Wilmington fields were targeted for further investigation. While there may be variations in API gravity within a given field, an estimate of the average composition of various fields was developed (Table 2). Moving to a list of major oil producers in California (Table 3), contacts were initiated with personnel from Shell, Chevron, Bechtel, Texaco, Union Oil, and THUMS Long Beach Company. Details of key personnel contacted will be found in Appendix A. Discussions with these people helped clarify the nature and API gravity produced in a large number of lease fields. Combining the information on crude oil type with location produced a sampling matrix, shown in Table 4. The ARB-approved work plan allowed for sampling and analysis of 38 Category 1 Sources. The use of budgeted funds to collect all samples in duplicate did not appear to be an efficient method of quality assurance. Instead, we collected replicates from a single component in a test field. Results from the analyses of these samples provided an estimate of uncertainty in the entire sampling/analysis chain.

**Figure 1 - Personnel**

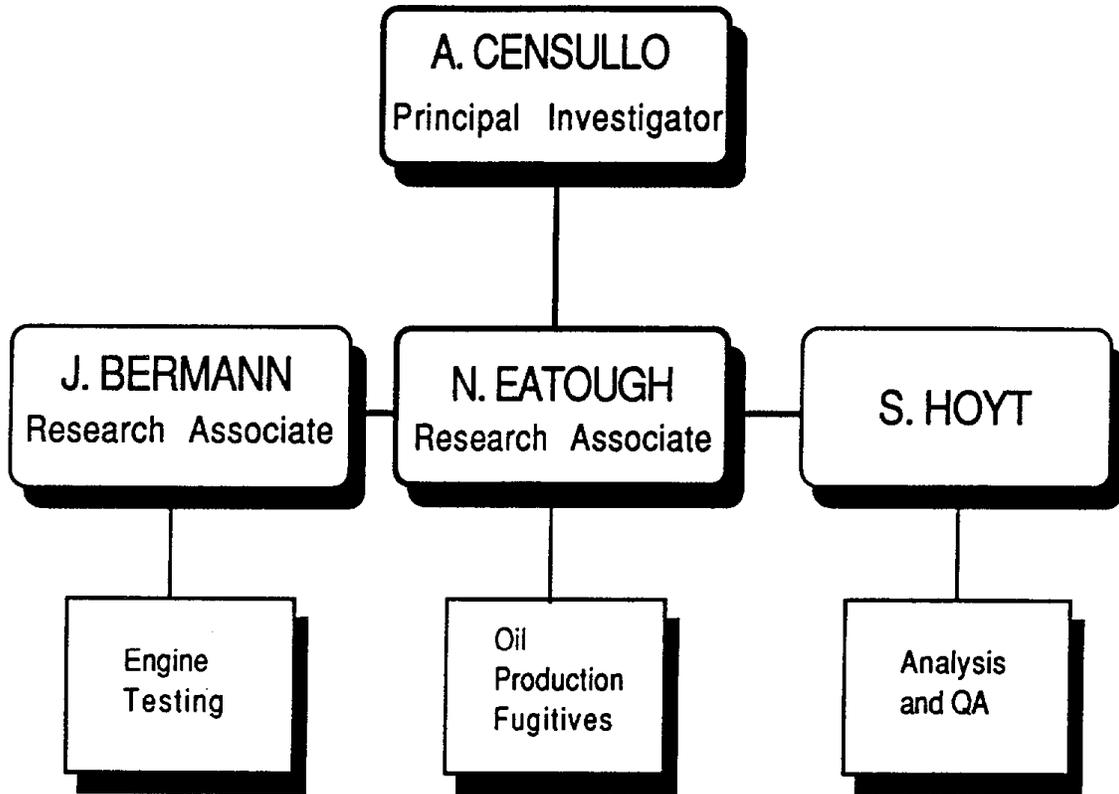


Figure 2 - Category 1 Sources

- Tanks
- Pipeline valves / fittings from  $\left\{ \begin{array}{l} \text{light} \\ \text{medium} \\ \text{heavy} \end{array} \right\}$  crude
- Sumps and pits

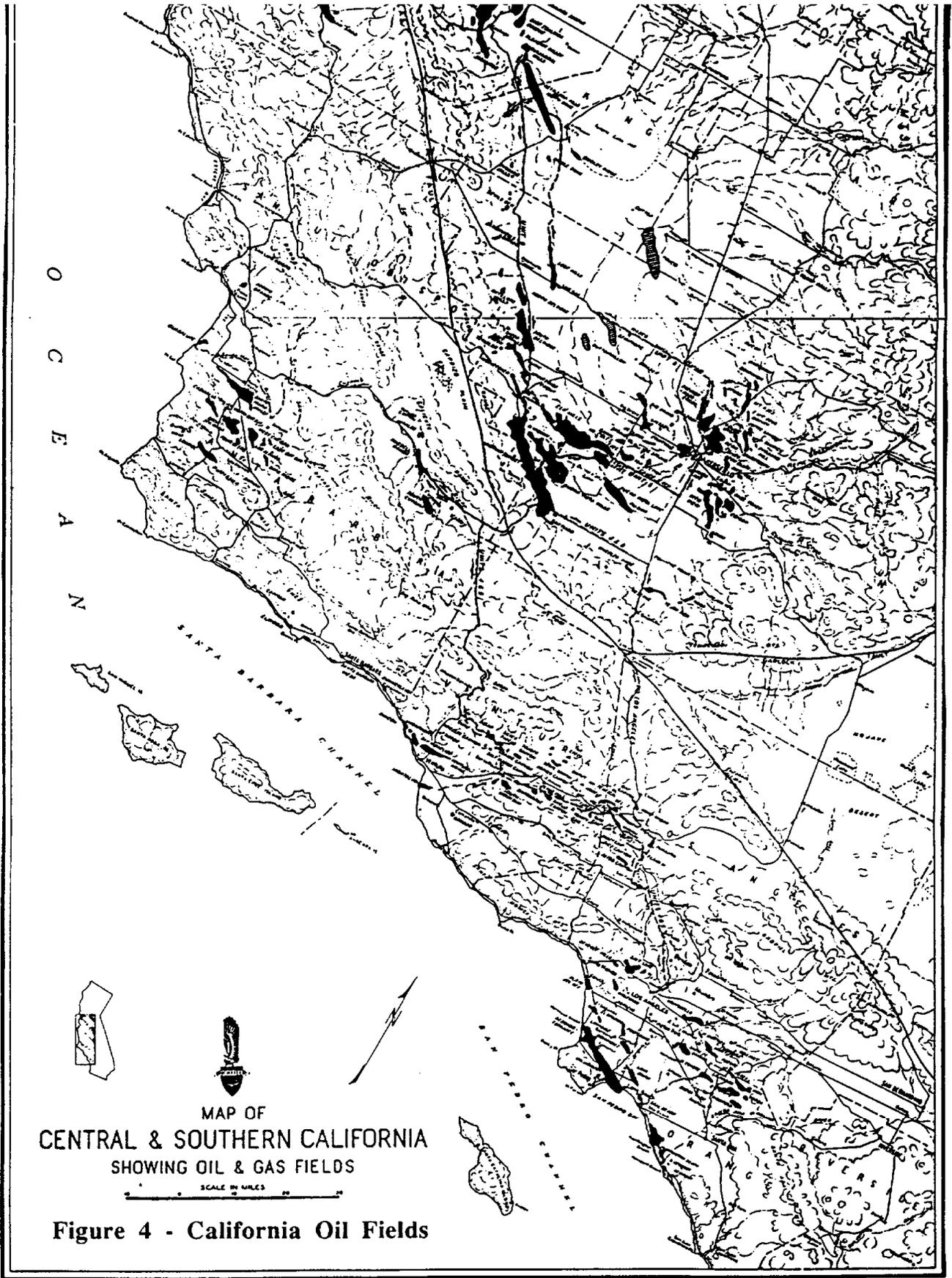
Table 1 - - API GRAVITY OF SELECTED FIELDS

0.85 ' from bottom FIELD	BASIN	API <sup>0</sup>
Cat Canyon	Coastal	4
Midway-Sunset (shallow)	San Joaquin	12
San Ardo	Coastal	12
Kern River	San Joaquin	13
McKittrick Main Area	San Joaquin	15
Santa Maria Valley	Coastal	16
Torrance	LA	16
Wilmington (shallow)	LA	18
Whitter	LA	18
Richfield	LA	22
Coyote East	LA	22
Montebello	LA	22
Huntington Beach	LA	24
Belridge South	San Joaquin	25
Elk Hills	San Joaquin	25
Inglewood	LA	26
Midway-Sunset (deep)	San Joaquin	26
Long Beach	LA	27
Coyote West	LA	28
Coalinga Nose	San Joaquin	32
Dominguez Hills	LA	32
Rosecrans	LA	32
Wilmington (deep)	LA	32
Santa Fe Springs	LA	33
Montebello (deep)	LA	36
Kettleman Hills	San Joaquin	38
Coles Levee	San Joaquin	40
Rio Bravo	San Joaquin	40
Paloma	San Joaquin	50

Figure 3 - API Gravity

$$^{\circ}\text{API} = \frac{141.5}{\text{specific gravity}} - 131.5$$

$^{\circ}\text{API}$	specific gravity	Example
10	1.000	water
20	0.934	heavy crude
30	0.876	light crude



MAP OF  
CENTRAL & SOUTHERN CALIFORNIA  
SHOWING OIL & GAS FIELDS

SCALE IN MILES

Figure 4 - California Oil Fields

Figure 5 -

Figure 5 - Size of Major Oil Fields

**CALIFORNIA'S GIANT OIL FIELDS**

(Fields with ultimate recovery of 100 million barrels or more)

FIELD	YEAR DISCOVERED	CUMULATIVE PRODUCTION (Mbbbl)	ESTIMATED RESERVES (12/31/87) (Mbbbl)	1987 PRODUCTION (Mbbbl)	1987 PRODUCTION (Mbbbl)	PRODUCING WELLS (1987)
1. Wilmington	1932	2,261,472	526,686	32,109	32,109	2,055
2. Midway-Sunset	1894	1,821,712	430,645	57,761	57,761	9,875
3. Kern River	1899	1,158,042	789,674	45,667	45,667	7,220
4. Huntington Beach	1920	1,060,187	77,874	6,058	6,058	998
5. Long Beach	1921	907,115	20,313	2,589	2,589	415
6. Ventura	1918	887,658	103,763	1,378	1,378	670
7. Elk Hills	1917	854,146	638,889	40,572	40,572	1,217
8. Coalinga	1890	743,996	162,399	10,384	10,384	2,343
9. Buena Vista	1909	645,722	38,938	1,515	1,515	1,035
10. Belridge, South	1911	616,000	491,942	63,562	63,562	6,161
11. Santa Fe Springs	1919	612,295	4,299	1,020	1,020	166
12. Coalinga, East, Intension	1938	457,432	1,183	1,183	1,183	57
13. Sycamore North Dome	1947	403,692	126,333	4,843	4,843	610
14. Sycamore	1947	403,692	126,333	4,843	4,843	610
15. Area-Ollinda	1880	381,801	56,800	2,320	2,320	746
16. Irjewood	1924	343,066	57,048	3,078	3,078	398
17. Cat Canyon	1908	285,509	49,409	2,940	2,940	412
18. Dominguez	1856	241,000	1,150	1,150	1,150	57
19. Hillier	1856	241,000	1,150	1,150	1,150	57
20. Mount Paso	1926	256,653	85,465	3,880	3,880	1,067
21. Coyote, West	1909	249,705	8,217	830	830	126
22. Cuyana, South	1949	217,567	7,476	519	519	105
23. Torrance	1922	210,358	37,204	1,481	1,481	366
24. Dos Cuadras Offshore	1948	207,294	93,465	2,880	2,880	1,067
25. Seal Beach	1924	202,242	14,394	7,094	7,094	500
26. Santa Maria Valley	1934	196,302	42,140	1,902	1,902	185
27. Cyritic	1909	191,434	38,454	6,988	6,988	1,144
28. McTebeillo	1917	181,197	10,807	516	516	164
29. Richfield	1919	180,369	28,971	1,612	1,612	227
30. Lost Hills	1910	172,551	67,292	5,293	5,293	1,795
31. Kern Front	1912	171,574	57,369	1,703	1,703	953
32. Orcutt	1901	164,968	11,154	976	976	148
33. Coles Levee, North	1938	159,800	3,194	464	464	86
34. Rincon	1927	147,625	17,110	1,364	1,364	244
35. South Mountain	1916	145,214	17,821	1,741	1,741	371
36. Edison	1926	132,861	28,117	1,538	1,538	836
37. Kern Hills	1906	128,710	4,420	2,733	2,733	121
38. Rio Bravo	1937	115,899	1,474	1,833	1,833	70
39. Fruitvale	1928	114,932	14,283	670	670	346
40. Greeley	1936	112,476	2,001	256	256	35
41. Coyote, East	1909	108,076	13,753	625	625	129
42. Elwood	1928	105,276	2,408	385	385	7
43. Round Mountain	1927	94,010	5,756	261	261	243
44. San Higinelto	1921	85,208	6,789	1,842	1,842	119
45. Caspiteria Offshore (total)	1966	85,411	31,379	2,666	2,666	119
46. Belridge, North	1912	82,485	45,458	2,420	2,420	550
47. Bordo Offshore	1869	79,378	122,522	9,587	9,587	21
48. Poso Creek	1820	75,005	25,691	836	836	692
49. Yotlum	1874	74,721	33,750	7,946	7,946	73
50. Beta Offshore	1916	33,704	180,568	6,650	6,650	61

NOTE: If future reserve estimates are revised upwards, Yorba Linda field may be included on the list. The cumulative production for this field is 83,163 Mbbbl, and estimated reserve is 11,618 Mbbbl.

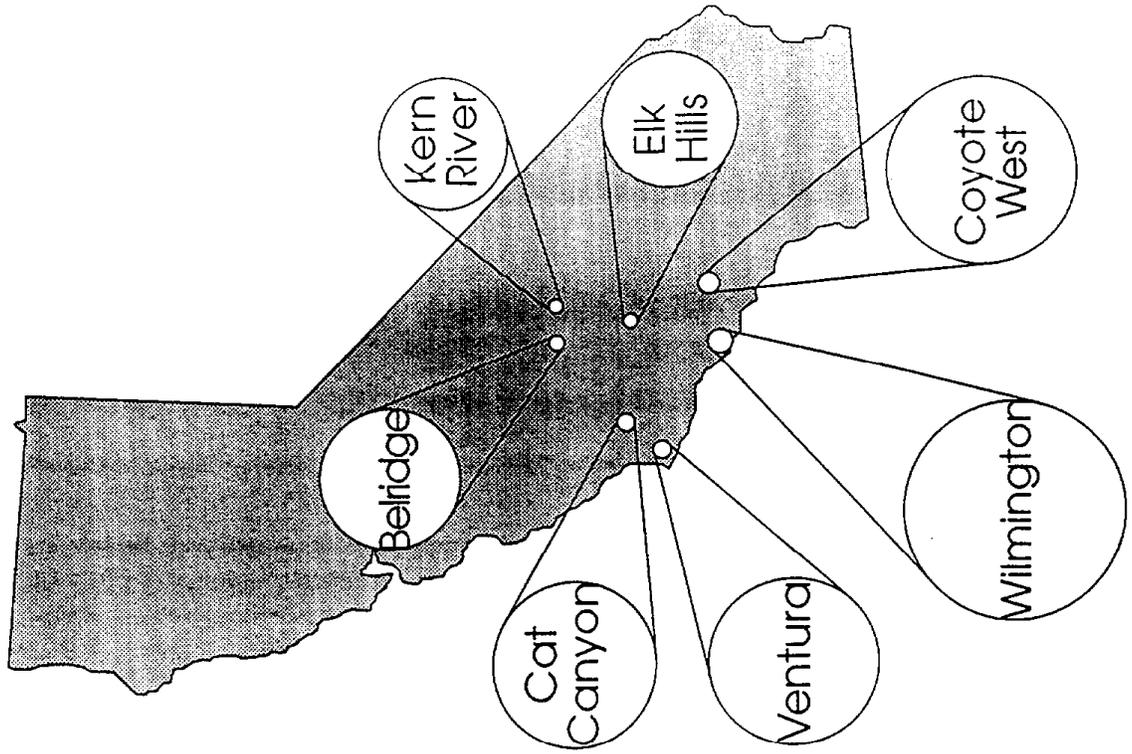


Table 2 -

## THIRTY LARGEST OIL PRODUCERS IN CALIFORNIA - 1987\*

PRODUCER	OIL PRODUCTION (Mbb1)
1. Shell Western E. & P. Inc. (1)+	85,902
2. Texaco, Inc. (2)	48,492
3. Bechtel Petroleum Operations Inc. (4) a/	40,654
4. Chevron U.S.A. Inc. (3)	40,057
5. Mobil Oil Corporation (6)	22,127
6. THUMS Long Beach Company (5)	20,953
7. Santa Fe Energy Company (9)	16,320
8. Tenneco Oil Company (8)	16,177
9. Union Oil Company of California (7)	15,835
10. Sun Oil Company (10)	10,732
11. ARCO Oil and Gas Company (11)	6,980
12. Celeron Oil and Gas Company (15)	4,716
13. Union Pacific Resources Company (14) b/	2,994
14. Exxon Corporation (16)	2,731
15. Berry Petroleum Company (NA) c/	2,517
16. Conoco, Inc. (17)	2,275
17. M. H. Whittier Corporation (18)	2,259
18. Long Beach Oil Development Company (19)	1,844
19. McFarland Energy Inc. (22)	1,023
20. Cities Service Oil Company (21)	881
21. Tannehill Oil Company (NA)	805
22. Mission Resources (20)	726
23. Occidental Petroleum Corporation (25)	672
24. Powerline Oil Company (Operator for the City of Long Beach) (24)	670
25. West Newport Oil Company (26)	661
26. Mobil Exploration & Production, North America, Inc. (27)	638
27. Petro-Lewis Corporation (13)	506
28. Signal Hill Petroleum (30)	440
29. Chase Production Company (NA)	416
30. Barto/Signal Petroleum Inc. (NA)	403

\* Does not include federal OCS figures. Also, total production from unitized operations is credited to the unit operators and not allocated to the other unit participants; therefore, production figures are overstated for unit operators and understated for other unit participants.

+ Numbers in parentheses indicate last years rankings.

a/ Production shown for Bechtel Petroleum Operations Inc. includes Chevron U.S.A. Inc's portion of Elk Hills production, which was 8,841 Mbb1., and is not included in Chevron's total.

b/ Formerly listed as Champlin Petroleum Company.

c/ Includes figures formerly reported separately under Berry & Ewing, Berry Holding Co., Berry Ventures, Sig Ten Oil Co., Ethel D. Co., and Berry Oil Co.

Table 3 - Sampling Matrix for Oil Production Facilities

<u>Site</u>	<u># of samples</u>	<u>Operator</u>	<u>Basin</u>	<u>Oil type</u>	<u>Preferred, alternate</u>
1. Santa Maria	4	Union Oil	Coastal	Heavy	preferred
2. Ventura	4	Chevron	Coastal	Heavy	preferred
3. San Ardo	4	Texaco	Coastal	Heavy, sour	alternate
4. Coyote West	6	Chevron	LA	Medium	preferred
5. Wilmington	6	THUMS	LA	Heavy	preferred
6. Elk Hills	8	Bechtel (DOE)	San Joaquin	Light	preferred
7. Bellridge	8	Shell	San Joaquin	Light	preferred
8. Kern River	8	Texaco	San Joaquin	Medium	alternate

## B. Component Selection Criteria

Once suitable sites had been identified, selection of the mix of components to sample became the next consideration. Using previous related studies (Figure 6) as a starting point, an inventory of possible components was generated (Figure 17). The distribution of various components is shown in Figure 8. Reported incidence of leaks for these components is shown in Table 5. A Rockwell study categorized components into 9 types, and 51 styles (Figure 9). It became apparent that the 38 budgeted samples could not be selected on a component basis. An alternative approach is to consider the numerous components arranged into systems of varying complexity and function. Within each system, the nature of fugitive emissions from various components will be identical (or at least very similar). For example, the composition of fugitive emissions from a leaking gate valve at the wellhead will be the same as the emissions leaking from a flange a few inches away. Consider the same valve/flange combination at a storage tank. The emissions will now reflect the composition of the tank's contents. Systems to be sampled include wellhead, pipeline, processing and storage. Discussions with ARB at the 2/9/89 meeting confirmed that this approach should yield data compatible with the project's goal. At each site identified in the previous section, components from each system would be sampled, up to the amount of samples allotted per site. This process allowed for more efficient use of the limited number of samples budgeted for analysis than would be possible in a component-driven sample selection process. Table 6 represents a summary of all oil field samples collected.

## C. Sampling Methodology

The general steps involved in sampling fugitive emissions are outlined in Figure 10. Facility maps, and piping and instrumentation drawings will provide an estimate of where the maximum density of components to be sampled are located. Previous studies have indicated that usually these drawings are either not available or not current enough to be useful. Consequently, we performed final component selection on-site, using a rapid screening method to identify potential components. Oil field personnel at each site provided assistance in locating sampling sites meeting our selection criteria. Each selected component was tested using a Gastech Analyzer to verify the presence of hydrocarbons. The component would then be sampled, subject to conforming to the desired systems and sample numbers at the site. Sample characteristics, including temperature, size, estimated leak rate (from soap leak test), and condition were recorded. At least 3 photographs were taken of each component sampled. These showed the component in isolation, its location in a system, and the sampling device used. Appendix B shows some selected sampling setups.

### 1. Sampling Fittings

While there is no "standard" method for sampling components of varying sizes and shapes for fugitive emissions, past studies have isolated the desired component, using a "shroud" of inert sheeting. An example of such a sampling system is shown in Figure 11. If the component has a leak rate in excess of 1 liter/minute, the emission will purge and inflate the shroud in a reasonably short period of time. This "direct" approach will not work for small leaks. An "indirect" method for sampling small leaks involves capturing the emission with a stream of dilution air. Previous studies have used ambient air for dilution. This required an independent analysis of ambient air for each component sampled. The proposed sampling system to be used in this study is illustrated in Figure 12. The component shrouds were fabricated from Teflon (FEP) bags. A quantity of 12" x 12" and 24" x 36" bags were prepared, as illustrated in Figure 13. A cylinder of ultra-zero air (<0.1 ppm hydrocarbons) was used for the source of dilution. A size 3 cylinder holding 30 cubic feet at 2000 PSI, and weighing less than 30 pounds was

**Figure 6 - Previous Oil Production Fugitive Emission Studies**

- 1. RADIAN CORP (EPA) , 1978**
- 2. EMSI (ROCKWELL) , 1979**
- 3. KVB (ARB) , 1980**
- 4. ERT (WOGA) , 1983**
- 5. EMSI (MIN. MGMT. CORP) , 1988**

## Figure 7 - Oil Production Components

### Oil Production Equipment

#### I. Tanks

##### A. Storage

- Fixed roof
- Floating roof
- Internal floating cover
- Variable space

##### B. Surge

##### C. Flotation

##### D. Vapor recovery

##### E. Wash

#### II. Pipeline Valves and Flanges

##### A. Valves

- Gate
- Ball
- Plug
- Globe
- Needle
- Check
- Butterfly
- Relief

##### B. Flanges

- Raised face
- Flat face
- API ring
- Access

#### III. Sumps and Pits

##### A. Cleanout sumps

##### B. Produced water sumps

##### C. Sucker rod pits

##### D. Well cellars

Figure 8 - COMPONENT DISTRIBUTION

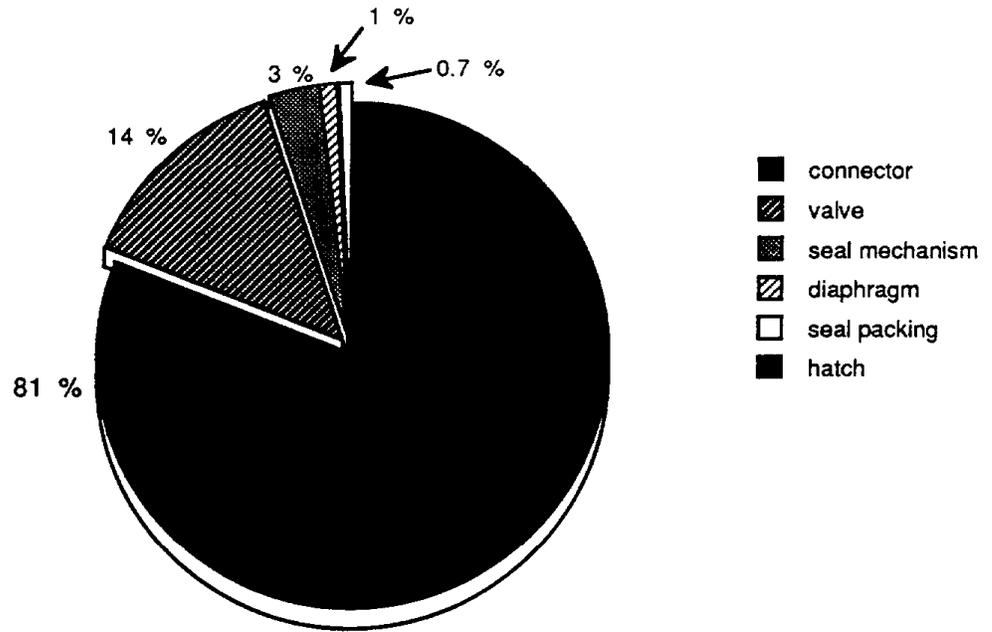


Table 4 - INCIDENCE OF LEAKS

(From 1979 EMSI Study)

	Number of Components Tested	Percent Leaking
Valves	9427	6.4
Flanges	54,694	2.8
Tank Hatches	170	2.4
Seals	474	30.6
Pits	26	100

Figure 9 - Detailed Component Categories

<u>Component Types</u>			<u>Systems</u>
1	VL	Valve	1 Well head
2	CN	Connection	2 Pipelines
3	SG	Sight Glass	3 Processing
4	MT	Meter	4 Storage
5	HA	Hatch	
6	SP	Seal Packing	
7	DI	Diaphragm	
8	SM	Sealing Mechanism	
9	PP	Sump, Pile, Pit, Etc.	

Component Styles

1- 1	VL	GATE	Gate	5- 1	HA	FLFF	Flanged
1- 2	VL	MULT	Multi-Directional	5- 2	HA	FLGA	Flat, Soft Gasket
1- 3	VL	BALL	Ball	5- 3	HA	THIF	Thief
1- 4	VL	PLUG	Plug	6- 1	SP	RERO	Reciprocating Rod
1- 5	VL	GLBE	Globe	6- 2	SP	ROSH	Rotating Shaft
1- 6	VL	NDLE	Needle	6- 3	SP	MESL	Mechanical Seal
1- 7	VL	CHCK	Check	6- 4	SP	WLHD	Wellhead, Stuffing Box
1- 8	VL	BTFY	Butterfly	7- 1	DI	VLOP	Valve Operator
1- 9	VL	RELF	Relief	7- 2	DI	DPRS	Differential Pressure Sensing
1-10	VL	CHOK	Choke				
1-11	VL	BEAN	Bean Choke				
2- 1	CN	FLFF	Raised or Flat Face Flange	8- 1	SM	GATE	Gate
2- 2	CN	FLRI	Ring Flange	8- 2	SM	MULT	Multi-Directional
2- 3	CN	FLBO	Flanged Bonnet	8- 3	SM	BALL	Ball
2- 4	CN	THRD	Threaded	8- 4	SM	PLUG	Plug
2- 5	CN	GRVD	Grooved	8- 5	SM	GLBE	Globe
2- 6	CN	FRIC	Friction	8- 6	SM	NDLE	Needle
2- 7	CN	GASK	Gasket	8- 7	SM	CHCK	Check
2- 8	CN	UNIN	Union	8- 8	SM	BTFY	Butterfly
2- 9	CN	LAND	Landing Flange	8- 9	SM	RELF	Relief
2-10	CN	TUBE	Tubing	8-10	SM	CHOK	Choke
2-11	CN	ORIN	O-Ring	8-11	SM	BEAN	Bean
2-12	CN	FLGA	Flat, Soft Gasket	9- 1	PP	OPSU	Open Sump (Produced Water)
3- 1	SG	GLSS	Glass Type	9- 2	PP	CLSU	Closed Sump
4- 1	MT	FLOW	Flow	9- 3	PP	WLCL	Well Cellar
4- 2	MT	TURB	Turbine Type Flow	9- 4	PP	COSU	Clean-out Sump
				9- 5	PP	OPTK	Open Roofed Tank

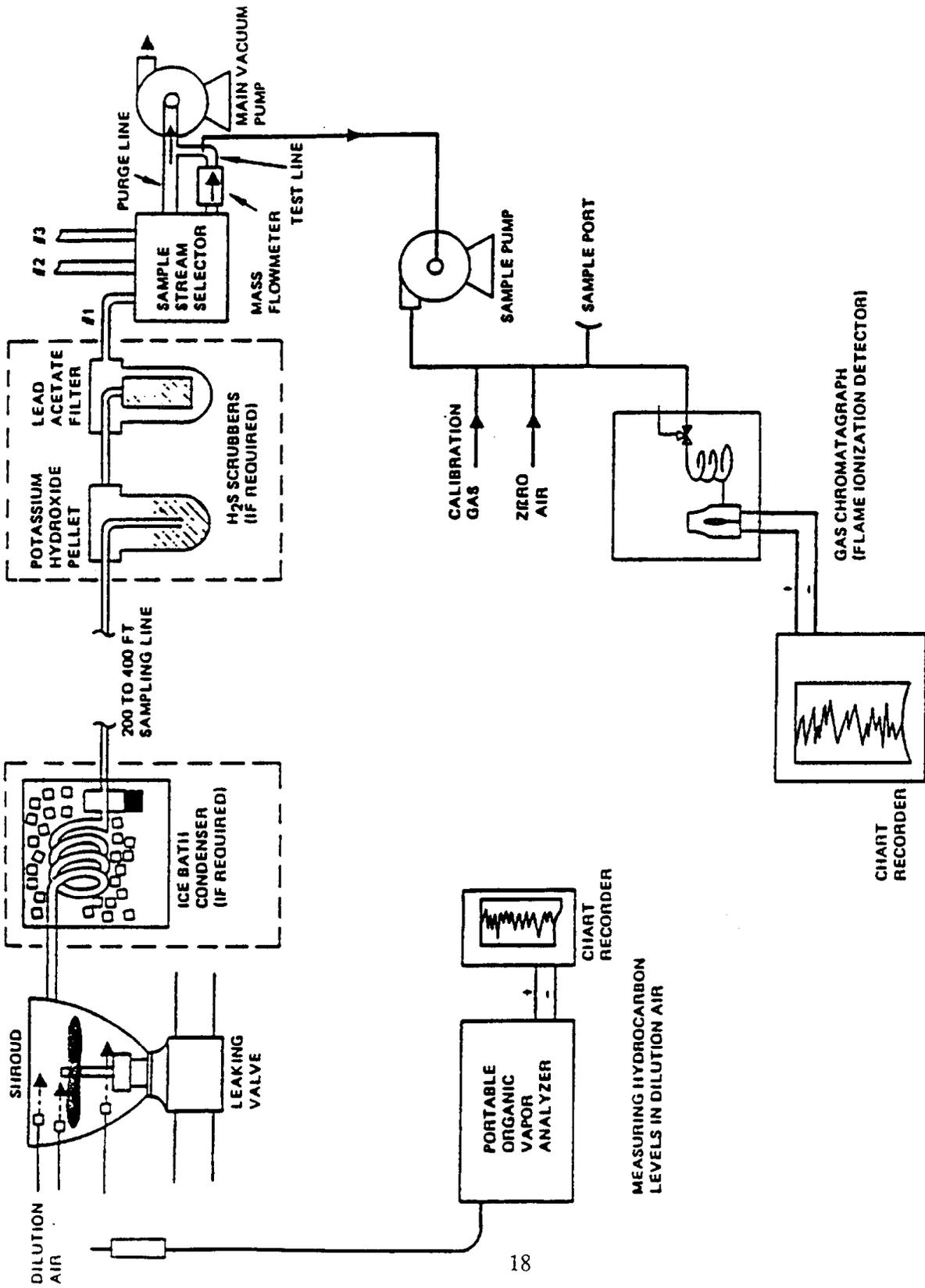
Table 5- Oil Field Sampling Sites

sample #	API <sup>o</sup>	location	method	comments
<b>Kern River</b>				
OF-1	13.5	gage tank (AWT143)	headspace	roof hatch
OF-2	13.5	well 406	bag valve	
OF-3	13.5	well 406	bag valve	duplicate of OF 2
OF-4	13.5	shipping tank #40	headspace	roof hatch
OF-5	13.5	surge tank	headspace	roof hatch
OF-6	13.5	well 271	bag valve	well duplicate
<b>Elk Hills</b>				
OF-10	23	tank 11105	bag sampling port	headspace
OF-11	23	compressor FR1364	canister direct	vapor recovery: NPT connection
OF-12	23	separator 11044		
OF-13	36	tank 11470	same as OF-10	Stevens zone
OF-14	36	separator 14255		
OF-15	36	tank 14217	bag sampling port	headspace
OF-16	22	tank 53579	bag 2" port	steamflood operation
OF-17	22	test separator	bag meter valve	steamflood produced gas
<b>Belridge</b>				
OF-20	33	tank LOTS 201	canister direct	20 well composite vapor
OF-21	33	well 548G-34	bag valve	casing gas
OF-22	26	tank LOTS 209	canister direct	1/4 NPT gauge port
OF-23	21	well 551-A33	gas valve	casing gas
OF-24	28	tank LOHF	canister direct	20 LOTS composite
OF-25	13	tank DEHY #27	canister direct	heavy field composite
OF-26	13	tank HOTS 113	bag valve port	50 well heavy composite
OF-27	13	tank HOTS 192	bag valve port	50 well heavy composite
<b>Cat Canyon</b>				
OF-40	14	well 53	bag valve	casing gas
OF-41	14	well 53	bag valve	tubing gas
OF-42	14	vapor recovery	bag valve	composite of all tanks
OF-43	14	sump, inlet end	flux chamber	
OF-44	14	sump, outlet end	flux chamber	
<b>Ventura</b>				
OF-50	29	tank	bag valve	100 well composite
OF-51	29	well L-131	bag valve	casing gas
OF-52	29	vapor recovery	canister direct	field composite
OF-53	29	vapor recovery	canister direct	shipping tank
<b>Wilmington</b>				
OF-60	18	Pier J sump	flux chamber	
OF-61	18	tank TK 003	headspace	roof hatch
OF-62	18	FWKO tank #3	canister direct	
OF-63	18	well J-341	bag valve	casing gas
<b>West Coyote</b>				
OF-70	28	AWT tank 105	bag valve	
OF-71	28	work tank #1	headspace	roof vent
OF-72	28	stock tank	bag port	manometer port
OF-73	28	vapor recovery	bag valve	field vapor recovery

**Figure 10 - FUGITIVE EMISSIONS SAMPLING PLAN**

- **STUDY FACILITY MAPS / DRAWINGS**
- **INVENTORY AND "SOAP TEST" COMPONENTS**
- **CHECK LEAKERS WITH OVA**
- **SAMPLE LEAKERS PER COMPONENT MIX**
- **DOCUMENT SAMPLED COMPONENTS**

Figure 11 - Literature Sampling System



**Figure 12 - SCHEMATIC REPRESENTATION OF SAMPLING FOR VALVES AND FLANGES**

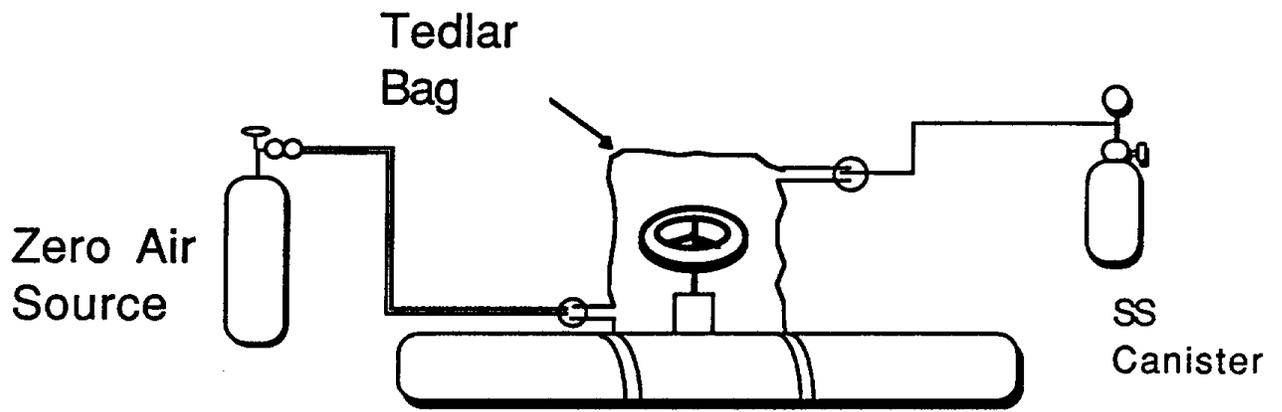
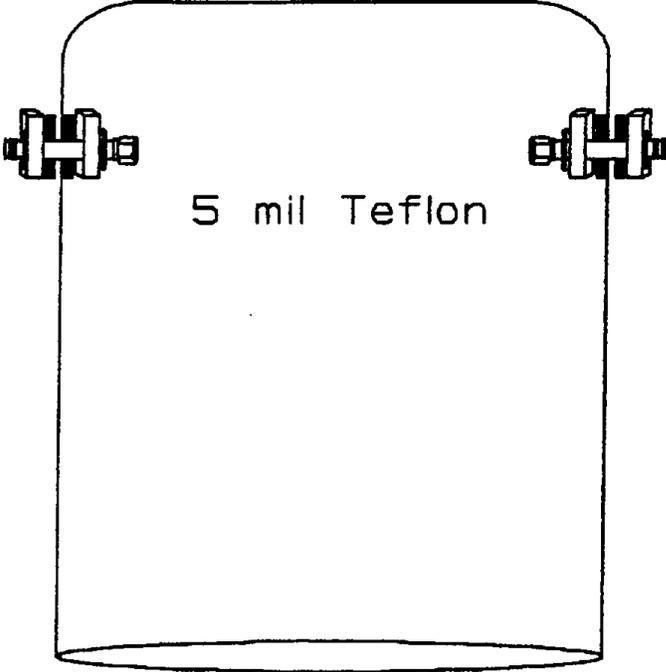
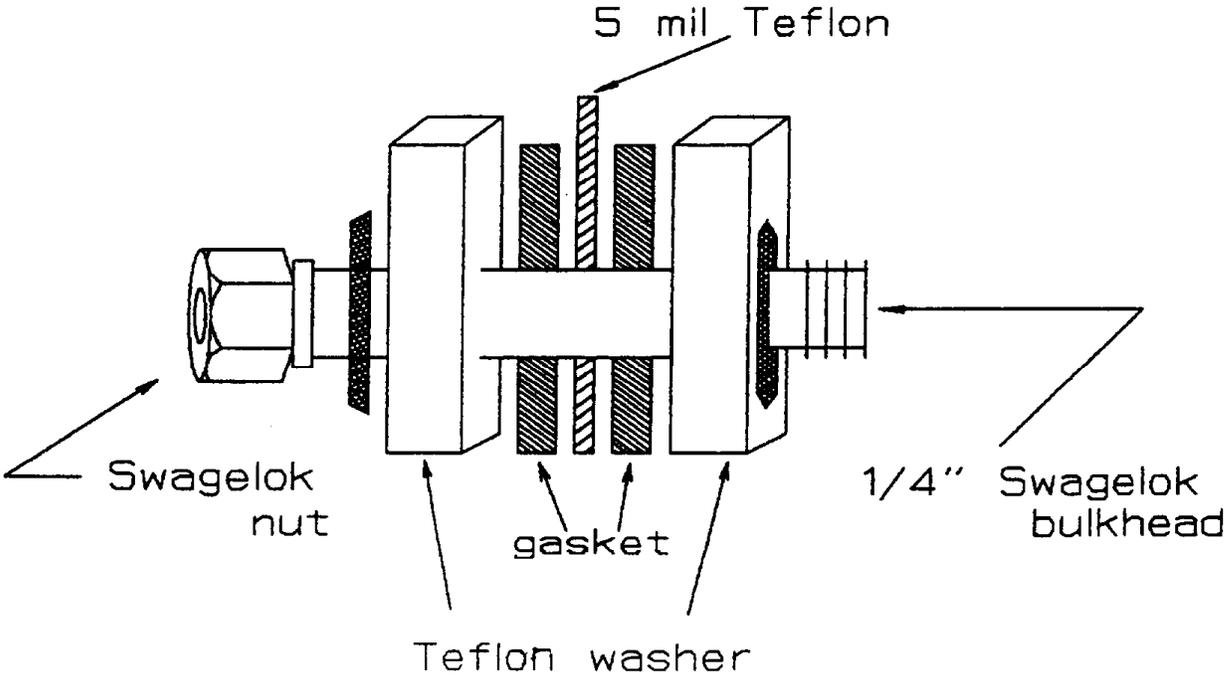


Figure 13 - Teflon Bag Construction

# TEFLON SAMPLING BAG



## FITTING DETAIL



brought to each oil field site. A manual control valve attached to the cylinder ensured contamination-free and reliable delivery of the zero air. In using this scheme, resources need not be spent on determining ambient concentrations in dilution air. Once the shroud has been filled with emissions, sampling from the shroud into an evacuated, SUMMA electropolished stainless steel canister (Figure 14) may be started. The long-term stability of hydrocarbons in these containers has been well-established<sup>1</sup>. Since no sampling pumps are needed in the field, contamination or degradation of the collected samples is virtually impossible. Pre- and post-sampling canister pressure checks were performed in the field, using a portable vacuum/pressure gauge. These pressures were verified at the analytical laboratory. In practice, purging of sampled components (indirect emission sampling) proved to be unnecessary, due to the large "leak rates" of components selected for sampling. Consistent with the objectives of the program, representative vapor samples were obtained at selected points in the overall process. While the exact method of sampling fugitive emissions depended on the source, several general methods were employed. In some instances, existing pipe fittings were connected to the evacuated stainless steel canisters by 0.25 inch diameter Teflon tubing equipped with stainless steel Swagelok fittings. Sampling flowrate could be controlled by the needle valve on the canister. For cases in which no suitable pipe fittings were available, pipe ends equipped with shutoff valves were often located. In these cases, the exposed pipe end was surrounded with a Teflon bag, secured with a large rubber band. The sampling bag was then purged and inflated with source emissions. This "buffer" volume was sampled into an evacuated canister connected to the bag by a length of 0.25 inch Teflon tubing. These approaches worked well for sources which were above atmospheric pressure. Samples ranging in pressure from 50 PSI to a few inches of water were successfully sampled by these methods. Sampling was normally continued until canister pressure, monitored by an attached pressure/vacuum gauge, reached atmospheric pressure.

## 2. Sampling for Sumps and Pits

In order to obtain samples of fugitive emissions from sumps and pits, some sort of emission isolation (flux) chamber is required. The U.S. EPA<sup>2</sup> and California ARB<sup>3</sup> have validated designs used for emission rate measurements. For the sump samples, an ARB sump sampler used in previous studies was modified. The existing acrylic flux box was removed. A new flux chamber, fabricated from a 14" diameter stainless steel hemisphere, was prepared, as shown in Figure 15. A latching valve was incorporated into the design to allow sampling to be initiated remotely. The sampling canister was located on the sump sampler to minimize the potential for contamination or losses in the sampling line. A circuit to produce pulses of the proper characteristics to operate the latching valve was constructed (See Figure 16). The circuit was powered by two 9 volt transistor batteries. These batteries provided several hundred activation cycles during testing without appreciable loss of working voltage. Pulses were approximately 50 milliseconds in duration. An umbilical was necessary to convey air and latching voltage pulses to the sampler. Three 1/4" Teflon lines, and one four conductor shielded cable were bundled together with nylon cable ties. One Teflon line was used with a zero air source to control the pneumatic pistons which ultimately raised and lowered the attached flux chamber. A second Teflon line provided the ultra-zero sweep air to the flux chamber. The third Teflon line returned the flux chamber purge gas to shore for testing. The total length of the umbilical was 50 feet. The aluminum pontoons of the ARB sampler were moved apart several inches to allow for the mounting of the new flux chamber. The assembled device was tested for buoyancy on an irrigation pond at Cal Poly. The final configuration proved to be stable and buoyant.

Figure 14 - Stainless Steel Canister Design

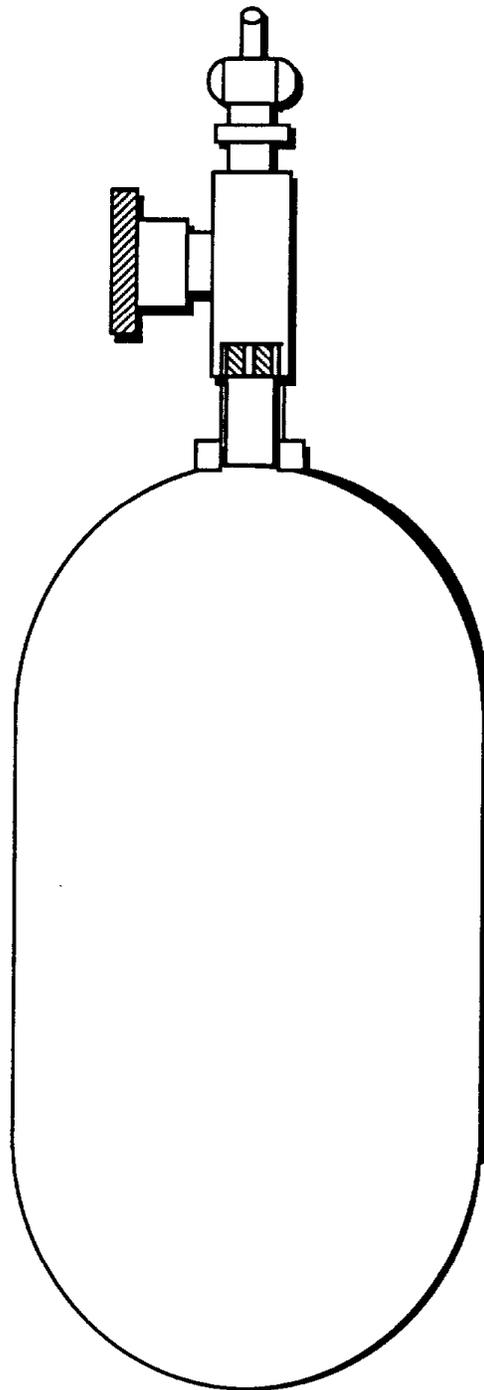


Figure 15- Flux Chamber Design

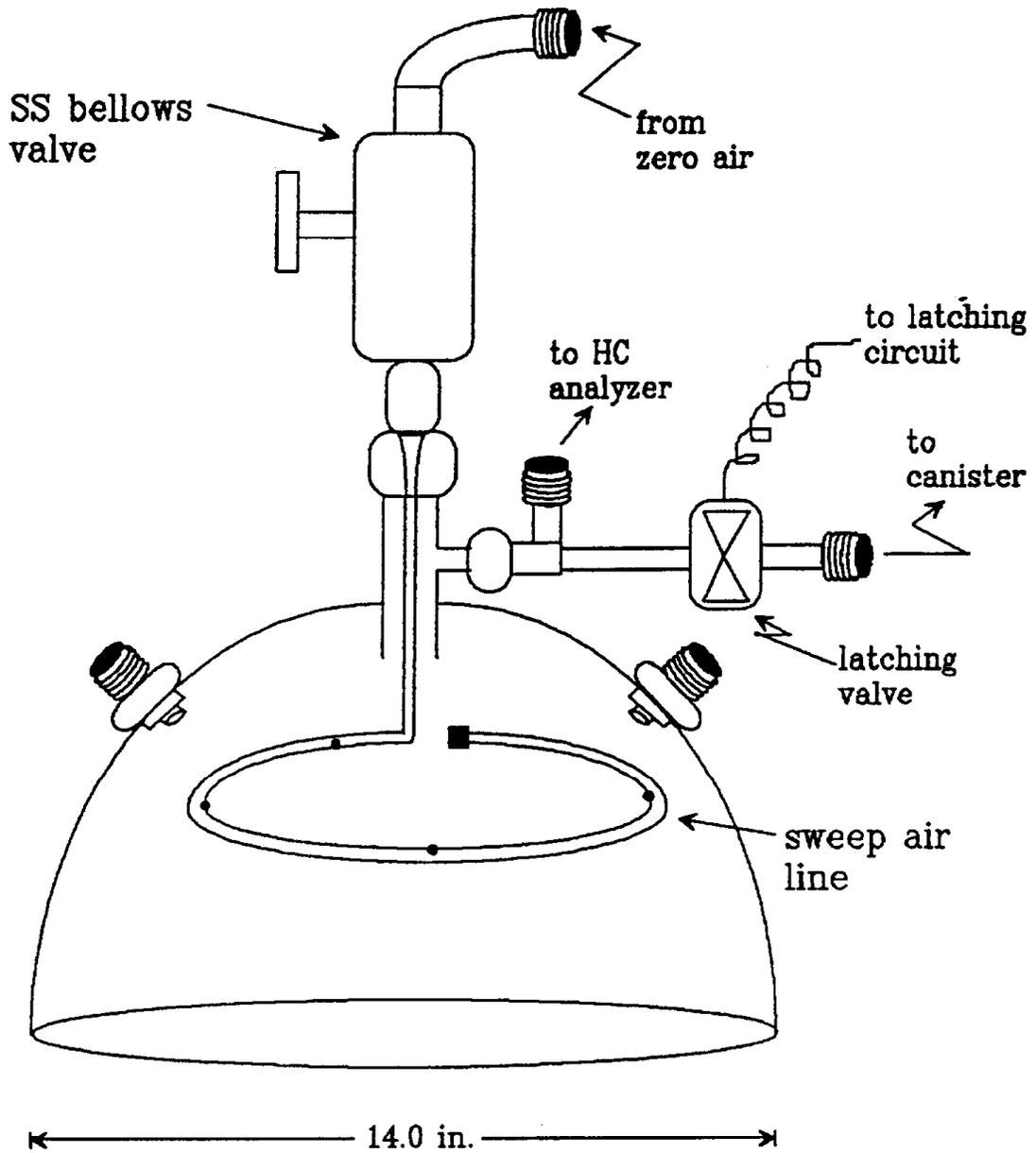
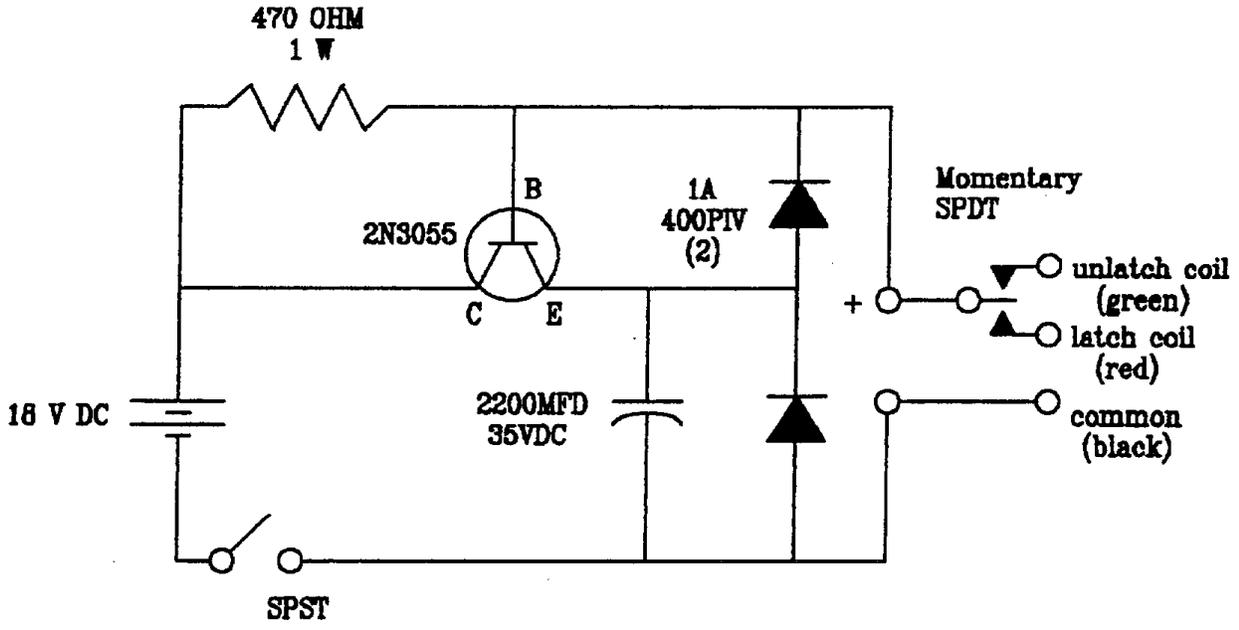
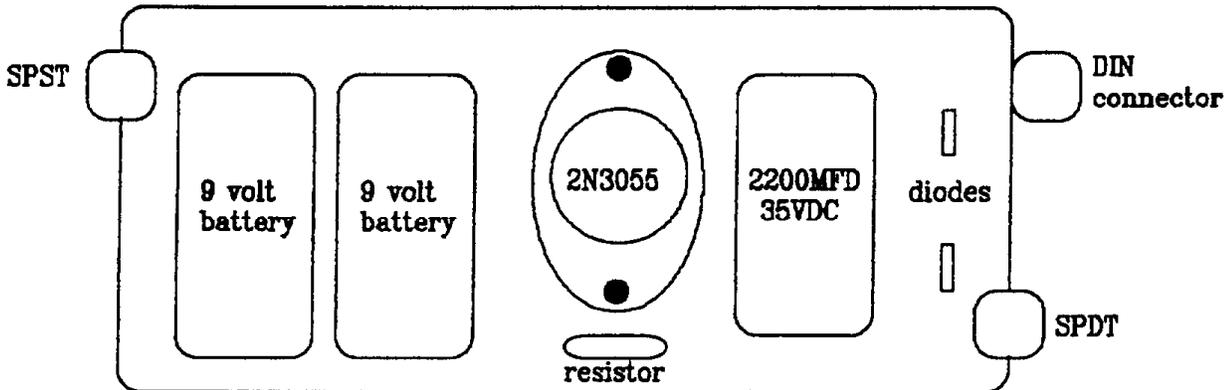


Figure 16 VALVE LATCHING CIRCUIT

schematic



component placement



Sampling was conducted at a flow rate of 5 liters/minute, following the suggested EPA protocol. Chamber volume was roughly 15 liters, so the residence time at this flowrate was on the order of 3 minutes. According to the adopted protocol, sampling would begin after 4 chamber volumes had been purged (12 minutes). At the end of 12 minutes, a sample was pulled into an evacuated stainless steel canister, via the latching valve. In order to prevent the canister from drawing air at a greater rate than was provided (5 liter/minute), some method of flow control was required. Although the sampling canisters used were fitted with bellows valves, it proved impossible to reliably control flow by partially opening the valves. A limiting orifice was fabricated from an 18 gauge hypodermic needle. See Figure 17 for construction details. The canister metal bellows valve was kept in the fully open position at all times. The latching valve enabled/disabled flow, while the limiting orifice controlled the flow rate into the canister. This simple approach worked reliably in field tests. The canister thus equipped would fill in roughly 90 seconds, for an average flow rate of  $3.2 \text{ liters}/1.5 \text{ min} = 2.1 \text{ liters}/\text{min}$ .

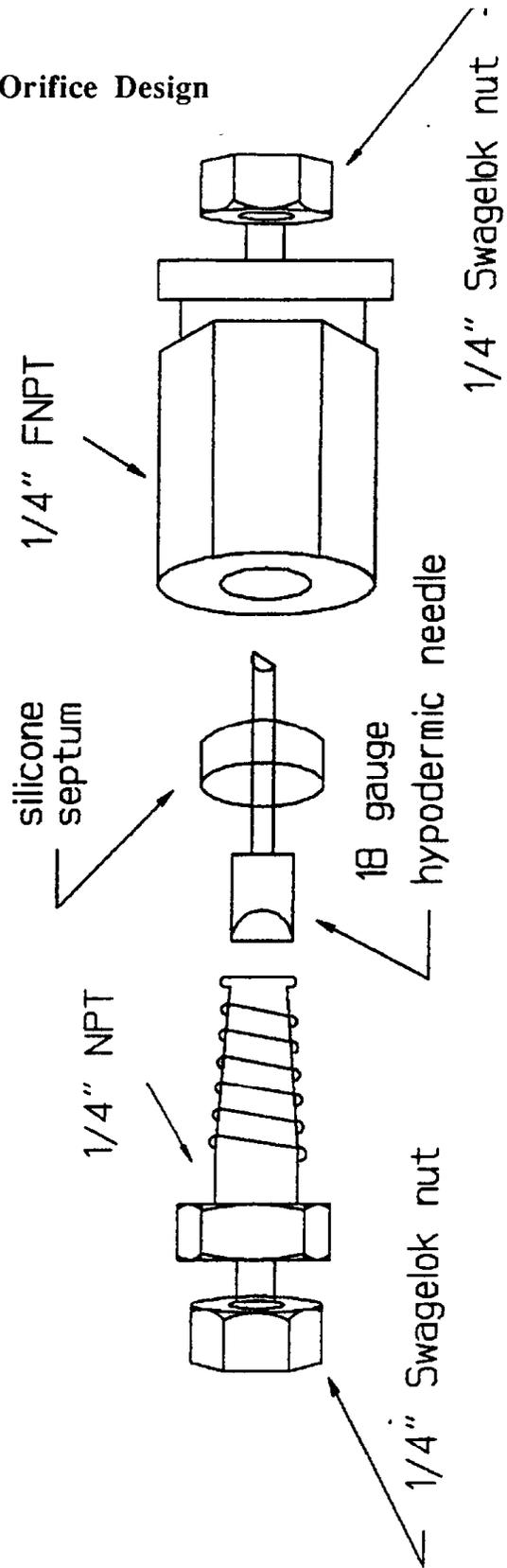
Prior to use in the field, a test to explore possible pressure buildup inside the chamber at the anticipated flowrate was undertaken. The flux chamber was suspended in a basin of water, so that the lower lip was immersed about one inch below the liquid surface. Pressure inside the chamber was measured with a Magnehelic gauge while 5 liters/minute of sweep air was admitted to the chamber. The Magnehelic gauge indicated a differential pressure of less than 0.2 inches of water, which was deemed satisfactory. This sampling system utilized the same zero air source and stainless steel canisters as used for sampling fittings (vide supra). Samples presented to the laboratory for analysis thus had identical sample handling procedures, regardless of whether the samples were taken from shrouds, sumps/pits or storage tanks (vide infra). Since secondary sumps comprise approximately 99% of total sump areas, and since most secondary sumps have areas in excess of 1000 square feet, secondary sumps larger than 1000 square feet were used to satisfy sampling requirements for sumps. Previous work<sup>3</sup> involving the characterization of hydrocarbon emissions from sumps failed to show a clear dependence of emission rate or composition on location within a sump. Consequently, we proposed testing each sump at a single location. If accessibility permitted, a spot near the center of the sump was selected. The composition at the center of the sump is more likely to be representative of the average sump area than locations near a sump inlet or outlet. At each location, a sketch and photograph(s) were produced. Pertinent information about the sump, including temperature, oil depth, and size will be recorded on a data sheet prior to sampling. Detailed protocols for sampling these components will be found in Appendix C. The use of sumps in California petroleum fields has been declining dramatically in recent years. Consequently, only two sumps were sampled in this study.

### 3. Sampling from Storage Tanks

Storage tanks have long been recognized as potentially large sources of fugitive emissions. Consequently, extensive work on storage tank design has produced alternatives which attempt to reduce the quantity of fugitive emissions. Some of these schemes such as the floating roof, produce systems in which accurate sampling for fugitive emissions is quite difficult. Since this project is more concerned with emission composition than emission rate measurements, a conceptually simple approach to collecting accurate samples from tanks was discussed with ARB. Regardless of tank design, if it leaks at all, it will leak the headspace of the tank. Thus, sampling the headspace inside the tank should provide all the information needed for this study. Conversations with personnel (Hagist and Rutledge, Appendix A) in petroleum operations confirmed that access hatches are located on top of storage tanks, and are readily accessible for

# CRITICAL ORIFICE CONSTRUCTION

Figure 17 - Critical Orifice Design



sampling headspace. At the 2/9/89 meeting, the Board approved of headspace sampling for storage tanks. Most of the tanks sampled in this study were equipped with access hatches on the roof. If the tank headspace were at atmospheric pressure, its contents were sampled into an evacuated canister by means of a short 0.25 inch diameter stainless steel probe inserted through the access hatch. In several cases, the tanks were maintained above atmospheric pressure by the vapor recovery system. Opening the roof hatch on tanks so equipped would require venting appreciable amounts of vapor to the atmosphere. In these cases, a sampling port external to the tank was located. The pipe end was bagged, and the emissions were sampled from this bag, as described earlier.

Detailed protocols for sampling fugitive emissions from oil production facilities may be found in Appendix C.

#### D. Quality Assurance

Quality assurance (QA) activities for Category 1 sources may be divided into three categories:

1. Pre-field sampling QA
2. Field sampling QA
3. Analytical QA

Pre-field activities included a complete checkout of all sampling system components. Data on the analysis of gas cylinders to be used were compiled. Data forms, sample labels and containers were located and prepared. To verify proper operation of the sump sampler, the flux chamber was placed on top of a clean sheet of Teflon, and zero air was allowed to flow through the system. This purge air was collected and analyzed, to verify the absence of background contamination. Prior to sample collection, all sample lines were thoroughly flushed with zero air. Adherence to the written protocols found in Appendix C enhanced the overall reliability and reproducibility of data obtained. Quality assurance activities pertaining to analyses are described in Appendix D.

#### E. Analytical Methodologies

A variety of analytical techniques were needed to quantitate the hydrocarbon species present in the oil field samples. This section summarizes the analytical methodologies used by the Project Subcontractor, Environmental Analytical Service, Inc. (EAS). Details and standard operating procedures for the methods of analysis will be found in Appendix D.

Methane was analyzed using a molecular sieve 5A column, operated isothermally at 50 °C. Light hydrocarbons were separated using a ten foot column packed with phenylisocyanate on 80/100 mesh Durapak. Samples with high hydrocarbon content were analyzed on a 30 foot column containing 23 % SP-1700 on 80/100 mesh Chromosorb PAW. Heavy hydrocarbons were analyzed using a 100 meter fused silica capillary column.

Comparison of the light (packed column) and heavy hydrocarbon (capillary column) runs could be made using a number of peaks in the C2 to C4 range. The heavy stationary phase loading of the 100 meter capillary column allowed for the separation of the lighter hydrocarbons. In this project, values for the light hydrocarbons (from C2 on) obtained from the capillary column run were used for all calculations shown in the Results section of the report. Values obtained from the analyses of light hydrocarbons on the two columns (packed and capillary) were generally comparable (within 10% of each other). In many instances, the capillary column allowed for the identification of peaks which were listed as "OTHER" by the packed column method. It became operationally simpler to utilize data from the capillary run to quantitate all hydrocarbon species (other than

methane), and this procedure obviously eliminated the effect of compounding and propagating analysis errors from two different analytical methods.

## F. Oil Field Sampling

### 1. Kern River field

A site visit was planned to finalize sampling methodologies and location. The trip was conducted on May 12, 1989. Censullo and Eatough toured the facility with Tim Stoner of Texaco. Plans were made for sampling on July 10. The average API gravity of this field is 13.5°. Recovery method in this field is primarily steamflood. Six samples were taken, as outlined below.

<b>Kern River</b>				air temp	source temp
OF-1	gage tank (AWT143)	headspace	roof hatch	33° C	72° C
OF-2	well 406	bag valve		35° C	100° C
OF-3	well 406	bag valve	duplicate of OF 2	35° C	100° C
OF-4	shipping tank #40	headspace	roof hatch	35° C	69° C
OF-5	surge tank	headspace	roof hatch	35° C	36° C
OF-6	well 271	bag valve	well duplicate	36° C	100° C

### 2. Elk Hills field

Sampling at this site was conducted on July 17, 1989. Two producing zones were sampled. The SOZ zone has an API gravity of 22-25°; the deeper Stevens zone contains oil in the range of 30-35° API. The waterflood method is used for recovery in most of the field. A small scale steamflood project was also operating at that time. Seven samples were taken, as outlined below.

<b>Elk Hills</b>				air temp	source temp
OF-10	tank 11105	bag sampling port	headspace	29° C	29° C
OF-11	compressor FR1364	canister direct	vapor recovery: NPT connection	33° C	33° C
OF-12	separator 11044			30° C	30° C
OF-13	tank 11470	same as OF-10	Stevens zone	36° C	36° C
OF-14	separator 14255			36° C	44° C
OF-15	tank 14217	bag sampling port	headspace	35° C	35° C
OF-16	tank 53579	bag 2" sampling port	steamflood operation	33° C	33° C
OF-17	test separator	bag meter valve	steamflood produced gas	33° C	46° C

### 3. Belridge Field

Sampling was performed on July 24, 1989. Light, medium and heavy crude is produced in this field. Eight samples originating from light crude of 33° API gravity, a medium crude of 26-28° and a heavy crude of 13° gravity were taken. A portion of recovery is by waterflood, with the balance being primary production. Samples taken are described in the following table.

Belridge				air temp	source temp
OF-20	tank LOTS 201	canister direct	20 well composite vapor	34° C	34° C
OF-21	well 548G-34	bag valve	casing gas	33° C	39° C
OF-22	tank LOTS 209	canister direct	1/4 NPT gauge port	37° C	37° C
OF-23	well 551-A33	gas valve	casing gas	35° C	37° C
OF-24	tank LOHF	canister direct	20 LOTS composite	35° C	35° C
OF-25	tank DEHY #27	canister direct	heavy field composite	36° C	36° C
OF-26	tank HOTS 113	bag valve port	50 well heavy composite	37° C	110° C
OF-27	tank HOTS 192	bag valve port	50 well heavy composite	39° C	71° C

### 4. Cat Canyon Field

A pre-sampling visit was arranged for July 21, 1989. Sampling plans were discussed with Union Oil personnel, and facilities were toured. A sump was identified for testing. The sampling date was set for August 8. The field produces heavy crude, with an average API gravity of 14°. A total of 5 samples were obtained, as outlined below. Dr. Robert Grant (ARB) was present for this sampling episode.

Cat Canyon				air temp	source temp
OF-40	well 53	bag valve	casing gas	28° C	28° C
OF-41	well 53	bag valve	tubing gas	22° C	22° C
OF-42	vapor recovery	bag valve	composite of all tanks	27° C	27° C
OF-43	sump, inlet end	flux chamber		30° C	39° C
OF-44	sump, outlet end	flux chamber		32° C	43° C

### 5. Ventura Field

Texaco's Ventura Avenue Field was sampled on August 11, 1989. The field produces 28-30° gravity oil, by waterflood recovery. Four samples were obtained, as outlined below.

Ventura				air temp	source temp
OF-50	tank	bag valve	100 well composite	25° C	40° C
OF-51	well L-131	bag valve	casing gas	22° C	27° C
OF-52	vapor recovery	canister direct	field composite	27° C	41° C
OF-53	vapor recovery	canister direct	shipping tank	30° C	35° C

## 6. Wilmington Field

Sampling was conducted at THUMS Pier J location on August 28, 1989. A secondary sump was sampled here, using the flux chamber described earlier. The pontoon system was not used. A 4' x 8' section of the sump covering was removed, and the flux chamber was lowered to the surface with a rope. Four samples were obtained at this location, as shown below. Average field gravity was 17.5° API.

Wilmington				air temp	source temp
OF-60	Pier J sump	flux chamber		18° C	34° C
OF-61	tank TK 003	headspace	roof hatch	24° C	37° C
OF-62	FWKO tank #3	canister direct		23° C	26° C
OF-63	well J-341	bag valve	casing gas	24° C	26° C

## 7. West Coyote Field

Sampling was conducted on August 28, 1989. This field produces crude oil in the 26-30° gravity range. Waterflood is the method of recovery. No heat treating is performed at this facility. Four samples were obtained, as shown below.

West Coyote				air temp	source temp
OF-70	AWT tank 105	bag valve		30° C	32° C
OF-71	work tank #1	headspace	roof vent	34° C	40° C
OF-72	stock tank	bag port	manometer port	34° C	34° C
OF-73	vapor recovery	bag valve	field vapor recovery	31° C	32° C

## 8. Other

The Union Oil HS&P facility supporting Platform Irene production was visited on May 19, 1989. This facility was recently built, and contains state-of-the-art emission controls. No readily accessible sampling points were available. This facility was not sampled.

On June 2, 1989, the San Ardo field was visited. A facility tour was conducted, and revealed very high H<sub>2</sub>S concentrations (in excess of 10,000 PPM) at most sampling locations. The operators (Texaco) indicated that self-contained breathing apparatus (SCBA) would be required for sampling. This site was omitted from further consideration. The Cat Canyon field satisfied the Coastal Crude sampling requirements.

## G. Format For Results

The analytical results are reported in a format illustrated by Table 6. The concentrations of all integrated peaks in the original sample were initially converted to mg/m<sup>3</sup>. These concentrations were summed with the methane concentration (expressed in mg/m<sup>3</sup>) and results were converted to a percentage of this total (expressed as % by mass). For most samples, the high resolution capillary column provided as many as several hundred resolvable peaks, as shown in Figure 18. Not all of these peaks could be positively identified. To aid in interpretation, each chromatogram was divided into regions bounded by a normal hydrocarbon., as shown in Figure 19. This

classification scheme results in assigning all unknown peaks as  $C_n$  if they appear between normal  $C_n$  and  $C_{n+1}$  hydrocarbons. By this method,  $C_5$  hydrocarbons are defined as having retention times between n-pentane and n-hexane. Another way of looking at this classification is based on the Kovats Retention Index (KRI). A compound listed as "OTHER  $C_n$ " will have a KRI between  $100*n$  and  $100*(n+1)$ . Those chromatographic peaks which could not be positively identified were placed in a carbon number category by this method. **It is important to note that these are operational definitions, and do not represent the actual number of carbon atoms in a given component.** Branching of a hydrocarbon tends to make it more volatile than its straight-chain homolog. Thus, unidentified branched hydrocarbons with n carbons will usually be assigned to the  $C_{n-1}$  carbon range.

Table 6- Format for Oil Field Results

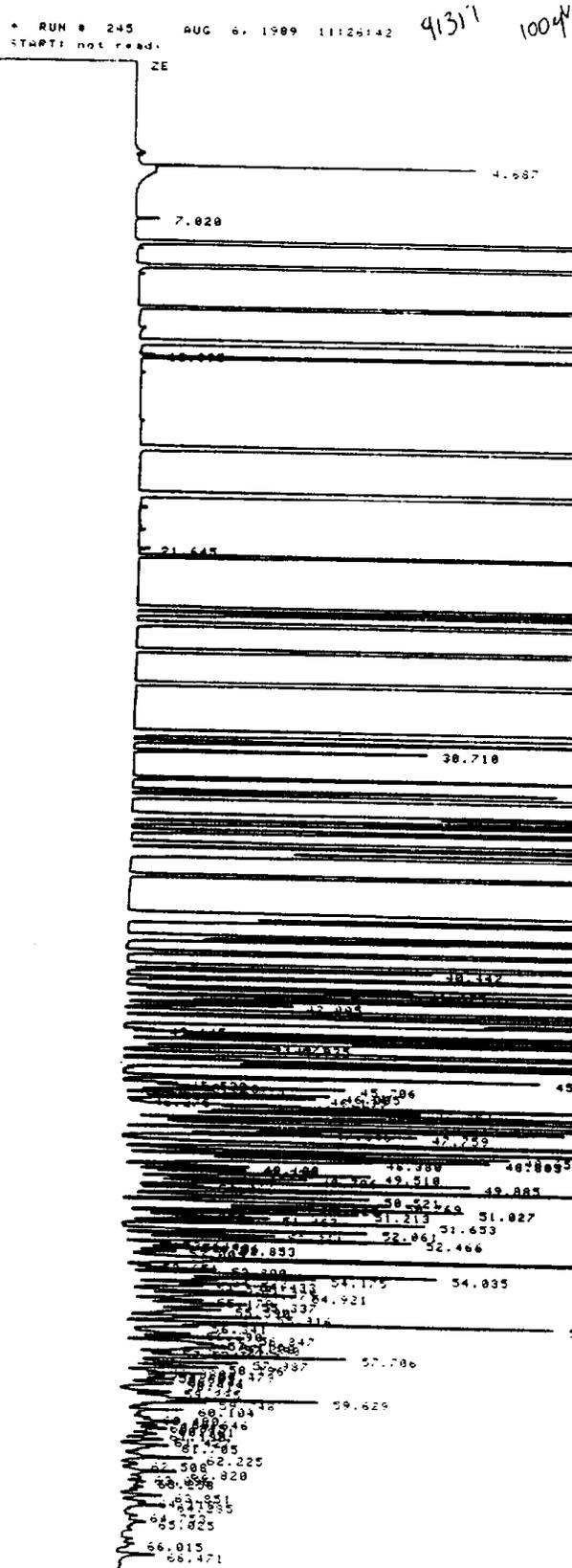
## Hydrocarbon Species by % Mass

	OF-63
Methane	9.3724
Ethane	8.6278
Propane	3.7709
i-Butane	7.6645
n-Butane	14.2861
2,2-dimethylpropane	0.1059
i-Pentane	8.6462
n-Pentane	5.4645
2,2-Dimethylbutane	0.1539
Cyclopentane	0.5612
2,3-Dimethylbutane	0.0000
2-Methylpentane	2.6425
3-Methylpentane	1.9294
n-Hexane	1.9154
Methylcyclopentane	3.1383
2,4-Dimethylpentane	0.1542
Benzene	0.5559
Cyclohexane	0.0316
2-Methylhexane	0.5707
2,3-Dimethylpentane	0.5102
3-Methylhexane	0.8294
n-Heptane	1.0401
Methylcyclohexane	2.0397
2,4-Dimethylhexane	0.1030
2,3,4-Trimethylpentane	0.0523
Toluene	0.1805
2,3-Dimethylhexane	0.0840
2-Methylheptane	0.6672
3-Ethylhexane	0.3136
n-Octane	0.6727
Ethylbenzene	0.5052
p-Xylene	0.0000
m-Xylene	0.5832
o-Xylene	0.2485
n-Nonane	0.3525
i-Propylbenzene	0.0516
n-Propylbenzene	0.1527
3-Ethyltoluene	0.1630
1,3,5-Trimethylbenzene	0.1066
2-Ethyltoluene	0.0694
t-butylbenzene	0.0000
1,2,4-Trimethylbenzene	0.2217
i-butylbenzene	0.0500
s-butylbenzene	0.0608
n-Decane	0.0000
1,2,3-Trimethylbenzene	0.1393
1,3-Diethylbenzene	0.0486
1,4-Diethylbenzene	0.0457
n-butylbenzene	0.0000
1,2-diethylbenzene	0.0000
n-undecane	0.0000
Other C4	0.0000
Other C5	0.9634
Other C6	5.6426
Other C7	5.4870
Other C8	5.4826
Other C9	2.7415
Other C10	0.6598
Other C11	0.1404

## H. Results

Hydrocarbon speciation information is arranged by oil field. Tables 7 through 13 contain results for all samples listed in Table 6. Additionally, these data were organized into a LOTUS 1-2-3 database. The format of the database is actually the transpose of the results shown in Tables 7-13. Compound names are column headings (fields), and sample numbers are rows (records). A portion of the database is shown in Table 14. A copy of the database, named OF\_SUMRY.WK1, was copied to a 3.5 inch floppy disk, and sent to ARB along with this report.

# Figure 18- Representative Chromatogram



# Figure 19 - Hydrocarbon Classification by Carbon Number

TIMETABLE STOP

Error storing signal to M:SIGNAL .BNC  
ATTEMPTED WRITE PAST END OF FILE

RUN# 176 JUL 18. 1989 08:53:33

AREA#	RT	AREA	TYPE	WIDTH	AREA#	
	9.387	528	VP	.053	.15155	
	12.054	648	OV	.097	.10454	
	21.567	1875	VV	.048	.53817	
	24.438	1826	PV	.057	.38884	
	33.467	1040	BP	.060	.29050	
	38.035	1261	BP	.063	.36194	
	38.882	581	PV	.069	.16676	
	39.416	3179	BP	.069	.91244	
	40.010	628	VV	.075	.18025	
	40.211	887	VV	.069	.23163	
	42.100	559	PV	.098	.16845	
	42.295	2904	VV	.068	.83351	
	42.540	890	VV	.067	.25545	
	43.860	828	BP	.067	.23765	
	44.304	5823	PV	.067	1.67133	n-octane
	45.019	2530	VV	.069	.72617	
	45.301	873	VV	.098	.25057	
	45.470	1953	VV	.079	.56055	
	45.668	925	VV	.078	.26550	
	46.408	917	VV	.115	.26320	
	46.593	863	VV	.079	.24770	
	46.834	1303	VV	.074	.37399	
	47.081	1937	VV	.080	.55596	
	47.296	1757	VV	.082	.50438	
	47.516	1286	VP	.081	.36911	
	47.864	585	BH	.075	.16791	
	48.212	5338	HH	.088	1.58884	ETHYL
	48.408	832	HH	.107	.23888	
	49.082	1594	HH	.090	.45751	
	49.194	1239	HH	.090	.35562	
	49.557	2624	HH	.095	.75315	
	49.820	534	HH	.096	.15327	
	49.984	2571	HH	.107	.73793	
	50.245	2003	HH	.115	.57491	
	50.505	2042	HH	.137	.58610	
	50.680	1626	HH	.081	.48105	
	50.926	5369	HH	.143	1.54102	
	51.103	664	HH	.071	.19058	11192
	51.206	1056	HH	.127	.53371	
	51.731	2255	HH	.081	.64724	
	51.815	3703	HH	.088	1.06284	
	52.005	1612	HH	.112	.46268	
	52.239	6078	HH	.104	1.74452	
	52.637	1438	HH	.099	.41274	
	53.009	2926	HH	.103	.83983	
	53.118	4369	HH	.138	1.25480	
	53.405	813	HH	.087	.23335	
	53.526	2925	HH	.114	.83954	
	53.741	7882	HH	.131	2.26231	
	54.022	5077	HH	.094	1.45721	
	54.186	3848	HH	.104	1.18446	
	54.208	2504	HH	.092	.71870	
	54.525	2335	HH	.102	.67020	
	54.640	1800	HH	.110	.53960	
	54.958	3235	HH	.168	.92852	
	55.111	2215	HH	.116	.63575	

Handwritten annotations: C7, C8, C9, ETHYL, 11192, and circled values in the AREA column.