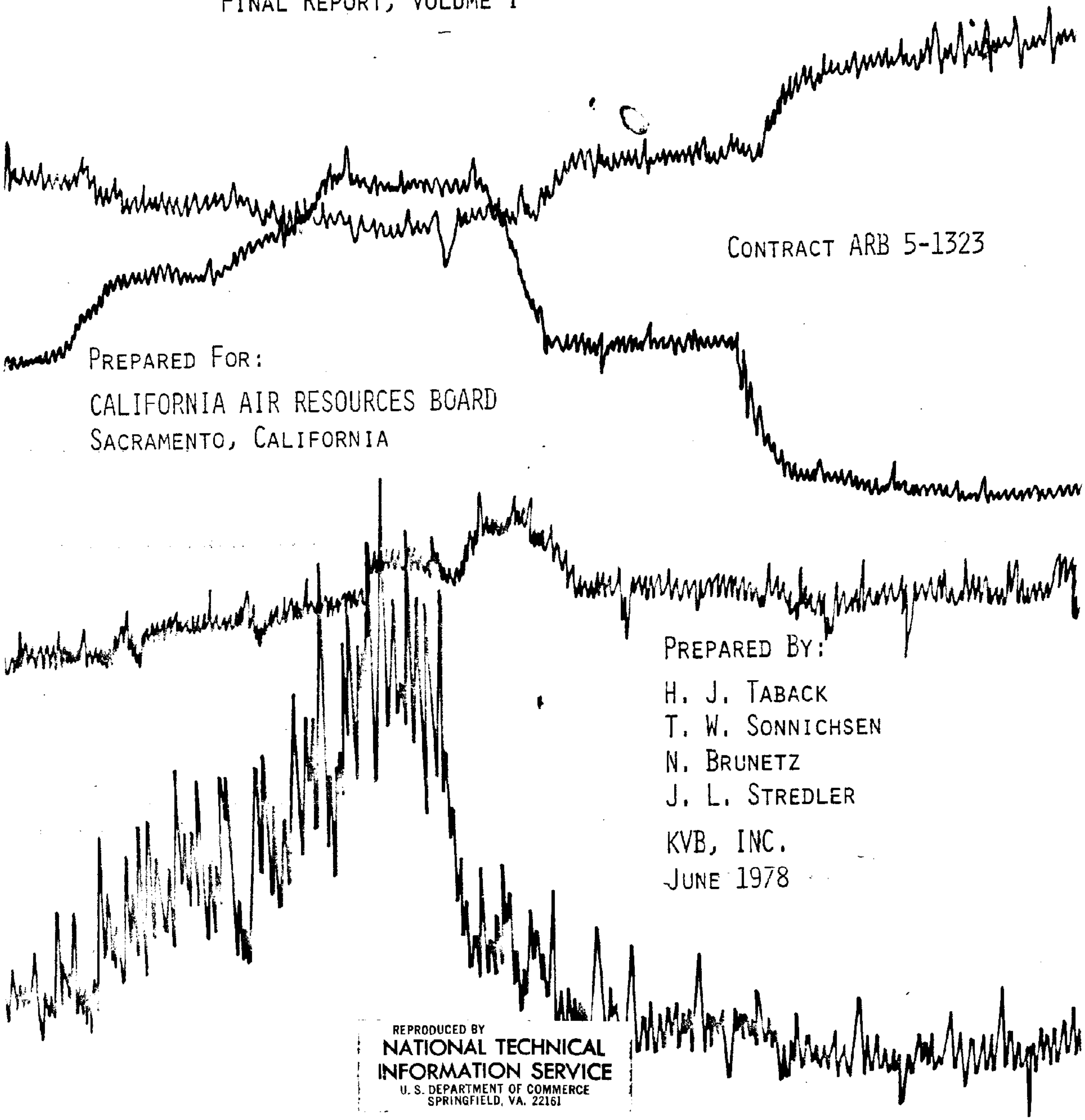
CONTROL OF HYDROCARBON EMISSIONS FROM STATIONARY SOURCES IN THE CALIFORNIA SOUTH COAST AIR BASIN

KVB 5804-714

FINAL REPORT, VOLUME I



CONTRACT ARB 5-1323

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72-101

PORT DOCUMENTATION PAGE

1. REPORT NO. ARB-R-5-1323-78-80

2.

3. Recipient's Accession No. PB283486

Title and Subtitle

ontrol of Hydrocarbon Emissions From Stationary Sources in the
alifornia South Coast Air Basin. Final Report, Volume I

5. Report Date June 1978

6.

Author(s)

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8. Performing Organization Rept. No. KVB 5804-714

Performing Organization Name and Address

VB, Inc.
7332 Irvine Blvd.
ustin, CA 92680

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) ARB 5-1323
(G)

Sponsoring Organization Name and Address

alifornia Air Resources Board
102 Q Street
. O. Box 2815
acramento, CA 95812

13. Type of Report & Period Covered Final

14.

Supplementary Notes

Reproduced from best available copy.

Abstract (Limit: 200 words)

n inventory of gaseous organic emissions from stationary sources was conducted in the
alifornia South Coast Air Basin. Based on a comprehensive field sampling and labor-
tory gas chromatograph - mass spectrograph analytical program, 140 unique speciated
mission profiles were developed to describe hydrocarbon emissions for various source
ategories. The profiles identified from one to thirty different organic species,
ncluding all species contributing more than one percent of the organic emissions from
ach source. The inventory was prepared in the EPA's Emission Inventory System format
nd all sources were located by Universal Transverse Mercator coordinates.

he inventory, which has a baseline of 1975-1976, shows total hydrocarbon emissions of
200 tons per day (tpd), of which one-half is methane. Point sources account for 350
pd and area sources account for 1850 tpd total hydrocarbon emissions.

he petroleum industry accounts for about 20 percent of the total emissions; 110 tpd
rom production, 120 tpd from refining, and 190 tpd from marketing. Solvent use accounts
or another 10 percent of the organic emissions.

n investigation of control techniques covers 60 industrial and commercial processes,
ith emphasis on efficiency and cost effectiveness.

. Document Analysis a. Descriptors

ir Pollution
ydrocarbon Emissions
ontrol Technology

b. Identifiers/Open-Ended Terms

tationary Source Emissions
ost-Effective Emission Reductions
outh Coast Air Basin

c. COSATI Field/Group

. Availability Statement

Release unlimited. Available from:
National Technical Information Service
5285 Port Royal Road, Springfield, VA 22161

19. Security Class (This Report)

20. Security Class (This Page)

22. Price A20 - A01

ANSI-Z39.18)

See Instructions on Reverse

OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

ABSTRACT

To provide detailed data for modeling the photochemical formation of atmospheric oxidants and information on which to base comprehensive control strategy, an inventory of gaseous organic emissions from stationary sources was conducted in the California South Coast Air Basin. Unlike most organic emissions inventories in the past, this one included the development of emission profiles, i.e., a breakdown of the individual organic species which contributed at least 1% of the total organic emissions from each source. Based on a comprehensive field sampling and laboratory GC-MS analytical program, as well as survey and literature data, 140 unique emission profiles were developed to describe hydrocarbon emissions for 740 SCC/SIC categories. The various profiles identified from one to thirty different species.

The inventory accounted for all known stationary source organic emissions including major and minor point sources, and area sources (oil production fields, architectural coatings, domestic solvent usage, etc.). The inventory was prepared in the EPA's Emission Inventory Subsystem (EIS) format. All sources were located by Universal Transverse Mercator (UTM) coordinates.

Also, a study of available control techniques for organic emission for various applications was performed. Control technique descriptions, application considerations and cost effectiveness data were compiled.

Finally, a prediction of emission trends based on expected growth and control strategies was made.

ACKNOWLEDGMENTS

KVB is pleased to acknowledge the participation of other organizations which contributed to the success of this program, as follows:

Abacus Programming Corporation, Santa Monica, CA
Inventory Software Design and Programming

Analytical Research Laboratories, Inc., Monrovia, CA
Analytical Chemistry Support in Test System Design and Sample Analysis

AeroVironment, Inc., Pasadena, CA
Ambient Testing and Plume Modeling

EcoScience Systems, Riverside, CA
Analytical Methods Critique and Data Quality Assessment

Western Oil and Gas Association, Los Angeles, CA
Voluntary Assistance and Guidance in Petroleum Production and Refining Aspects of the Program
(This acknowledgment does not imply an endorsement of this report by WOGA)

South Coast Air Quality Management District (El Monte), Ventura County APCD, and Santa Barbara County APCD
EIS Data Tapes, Preliminary Inventory Data and Valuable Consultation

The following individuals played key roles:

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SECTION 1.0

OVERVIEW

1.1 INTRODUCTION

Organic compounds emitted from stationary sources contribute to the formation of smog in the atmosphere. These compounds (often referred to as hydrocarbons) react photochemically with oxides of nitrogen, another pollutant, to form oxidants, a pollutant which irritates human tissue and causes damage to plant life. Organic pollutants also react with each other in the atmosphere to form long chain organic molecules which contribute to the atmospheric aerosol, another constituent of smog, which limits visibility. The ability of the various organic compounds to form oxidants or organic particulate matter varies with each specie of hydrocarbon and the measure of this ability is referred to as reactivity.

For some time scientists have been measuring the reactivity of organic compounds (with regard to both oxidant and aerosol formation) using smog chambers to simulate atmospheric conditions. Prior to this program, the actual hydrocarbon emissions from stationary sources had not been characterized by species. Only the total organic emissions or at best the methane/non-methane composition (also referred to respectively as "non-reactive" and "reactive" hydrocarbons) were available in existing inventories.

In order to develop an organic emission control strategy for the California South Coast Air Basin,* the ARB initiated this program to inventory organic compound emissions from stationary sources, investigate control technology and forecast emissions for the next ten years. The inventory would reveal which compounds are being emitted by various sources and where they are located. It would also specify the reactivity of those compounds according to a three-class scheme developed by the ARB. It was to account for all

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*The South Coast Air Basin for the purposes of this study includes part of Santa Barbara, Ventura, Los Angeles, Orange, Riverside, and San Bernardino Counties.

organic emissions from point, area, anthropogenic, and natural sources. Sources were to be categorized by application (the ARB-specified application categories) and by location. Each source was to be located geographically by Universal Transverse Mercator (UTM) coordinates, and the sources were to be grouped into ten-kilometer grid squares. Other portions of the study would reveal what could be done to reduce the objectionable species.

Later in the program, a requirement was added to present the inventory data in the Emission Inventory Subsystem, Permit and Registration (EIS/P&R) format. EIS/P&R (hereafter referred to as EIS -- a computerized data system) was developed by the EPA to be used by all local and state agencies for their own records as well as to provide data to a national data bank. Another added requirement was the reporting of emissions, specie by specie, for each one kilometer grid square in the Basin.

1.2 SUMMARY AND CONCLUSIONS

In order to accomplish these objectives, the first steps were to prepare a preliminary inventory of total organics (without specific species), to identify the major sources, and to determine the distribution of emissions among the various source types.

Next, a field test program was conducted to characterize emissions from sources selected on the basis of the preliminary inventory, emphasizing those source types comprising the greater amount of the emissions. Organic species contributing at least 1% of the total organic composition were identified using GC/MS analysis. Over 600 samples were collected and analyzed from various equipment in the following locations:

Adhesives Mfg. Plant
Aircraft Plant (2)
Appliance Plant (2)
Asphalt Plant
Auto Body Shop (2)
Automobile Plant (2)
Chemical Plant (2)
Dry Cleaning Plant
Equipment Mfg. (2)
Gas Compressor Plant
Gas Pumping Station
Gasoline Station
Landfill
Magnetic Tape Plant
Oil Field (2)
Oil Refinery (3)
Packaging Mfg. Plant
Printing Plant (2)
Roofing Kettle
Rubber Mfg.
Solvent Mfg. Plant
Steel Mill
Utility Boiler
Utility Gas Turbine

Equipment tested included:

Adhesive Spray Booth
API Separator (6)
Asphalt Paving
Basic Oxygen Furnace
Blast Furnace
Charcoal Adsorbers (4)
Chemical Mill
Chemical Process
Chemical Transfer
Coke Oven
Compressors (28)
Cooling Tower (2)
Degrease Tank (11)
Dip Tank
Dry Clean Tumbler
Drying Ovens (3)
Fiberglass Impregnation (2)
Filling Rack
Flow Coater (2)
Gravure Press (5)
Heater Treater
I.C. Engines (6)
Incinerator (10)
Lithograph (3)
Open Hearth Furnace
Paint Booth (32)
Precip. Outlets
Printed Circuit Board Proc.
Process Heater (3)
Pumps (200)
Rubber Process (3)
Sintering Plant
Sludge Incinerator
Storage Tank (5) (Species only)
Sumps (6)
Valves (24,000)
Vapor Recovery Tank to Car (3)
Vapor Recovery Truck to Tank
Well heads (5)

In addition to direct source sampling, one attempt was made to characterize emissions from a refinery, a complex point source, by collecting and analyzing air samples taken upwind and downwind of the refinery. Diffusion modeling techniques were used to predict emission factors from the refinery. The resulting emissions predicted by this indirect technique were lower than those determined by direct source methods by an order of magnitude. This was probably caused by vertical dispersion of the hydrocarbon emissions, which could not be adequately detected by fenceline measurements.

Test results were augmented by questionnaire responses and literature data to establish both emission factors and emission profiles (percent composition by weight). One hundred forty unique emission profiles for point and area sources were developed. These 140 profiles covered 740 different combinations of device category (SCC No.) and industry category (SIC No.). Where possible, emission factors, determined from field tests, were compared for validity with factors contained in AP-42, and those in the SCAQMD data base. No existing emission factors were found for oil production, IC engines, and landfills.

Coincident with this work, the South Coast Air Quality Management District (SCAQMD) (Los Angeles, Orange, Riverside, and San Bernardino Counties), and the Ventura and Santa Barbara County Air Pollution Control Districts (VAPCD and SBAPCD) were compiling new EIS files for their individual districts. These County EIS data files were provided to KVB, Inc. by the ARB, along with a breakdown of population data for the Basin in 1 Km grid squares.

The last step in the program was to generate a final inventory. The EIS data were the basis for this KVB final inventory. The emission factors used in the EIS files were reviewed by KVB and adjusted where necessary by applying correction factors determined from source tests to specific sources or to a group of sources identified with a certain Source Classification Code (SCC) number. The 140 emission profiles were also keyed to the sources. In addition, sources not contained in the EIS files, primarily area sources, were added to the data base.

The final inventory was delivered to the ARB under separate cover as computer printouts and magnetic tape files. The primary elements are as follows:

1. A Total Organic Emission Report by ARB Application Category
2. A Total Organic Emission Report by Ten-Km Grid Squares
3. An Emission Profile Listing

4. An Emission Summary Report for Each One Km Grid Square
5. An Individual Organic Specie Report by Application Category
6. A Point Source Emission File in EIS Format (Tape)
7. An Emission Profile File (Tape)
8. An Area Source File (Tape)
9. Miscellaneous Indexes, Listings and Files (Tapes) to Support the Items Above

The inventory which has a baseline of 1975-1976, shows total hydrocarbon emissions of 2200 ton/day of which one-half is methane. Point sources (major and minor) account for 350 ton/day and area sources account for 1850 ton/day total hydrocarbon emissions.

The petroleum industry accounts for 20% of the total emissions; 110 ton/day from production, 120 ton/day from refining and 190 ton/day from marketing. Solvent use accounts for another 10% of the organic emissions.

The largest source category is landfills, which account for over 40% of the total emissions, 930 tons/day, and are 99% methane, which is photochemically non-reactive. Natural terpene emissions from forest and scrub vegetation account for 15% of the total emissions, 300 ton/day. These emissions occur at the perimeter of the Basin and downwind of the central populated area, therefore, their contribution to smog formation in the metropolitan area is probably of much less significance than the anthropogenic emissions.

The primary organic species emitted are:

	Ton/Day (Avg.)
Methane	1100
Terpenes	300
Pentane	80
Butane	70
Hexane	60
Perchloroethylene	50
Ethane	50
Propane	40
Isopropyl Alcohol	30
Toluene	30

The emissions of compounds rated as Class 3, highest photochemical reactivity, account for 500 ton/day, of which 300 ton/day are natural terpenes. Other Class 3 emissions include:

	Ton/Day
Isopropyl Alcohol	30
Toluene	30
Ethylene	20
Ethyl Alcohol	20
Xylene	15
Pentene	10
Butyl Alcohol	6
Glycol Ether	6
Formaldehyde	6
Propylene	4

A breakdown of the sources of individual species emissions by 13 application categories (i.e., petroleum refinery, solvent use, combustion of fuel, etc.) is provided in Section 2.4.

In addition to the emission inventory, an investigation of control techniques for various application categories was performed. Control techniques described in this report include:

a. Activated carbon adsorption systems
b. Thermal and catalytic incinerators
c. Vapor condensation systems
d. Scrubbers (absorption systems)
e. Vapor space elimination (e.g., floating roof tanks)
f. Liquid/vapor exchange systems for fluid transfer
g. Enclosure (covering drains, sewers and separators)
h. Process and material changes (e.g., solvent substitutions, high solids coatings, etc.)
i. Improved maintenance.

Over 60 industrial and commercial processes are considered. For each process, applicable control techniques are identified. Finally, cost effectiveness data ($/unit weight of pollutant reduced) are developed for the techniques listed above.

With so many different processes and plant configurations involved, it is possible to determine most cost effective control technology only on a plant-by-plant basis. For the control of organic emissions from exhaust stacks, without a change in the basic process, activated carbon adsorbers and incinerators are the preferred add-on devices. For low hydrocarbon concentrations (around 100 ppm), carbon adsorption is more economical. For control of high concentrations (around 25% of the lower explosion limit, i.e., 12,000 ppm for hexane), carbon adsorption is both economical and can produce a profit if recovered solvents can be reused or sold. If the organic material cannot be reused, then for the high concentrations, incineration with primary heat recovery (using combustion gases to heat the incoming air/organic stream) is more economical than adsorption. Also, in general, it is more cost effective to control streams of high concentrations than of low concentrations. Between concentrations of 100 ppm and 10,000 ppm, the difference in cost effectiveness could be a factor of 10.

The conversion of architectural and industrial coatings to waterborne and solventless formulations should continue at the current rate over the next ten years. The pacing items are (1) necessary research to develop materials, (2) rate of facility obsolescence (i.e., replacing old facilities with ones incorporating provisions for low emission coatings), and (3) public resistance to change.

A ten-year forecast of organic emissions in the Basin indicates that the anthropogenic emissions will decline by 65% by 1986. Anthropogenic methane emissions will probably be reduced by 50% while non-methane emissions will be reduced by 70% since most control methods are less effective on methane than on non-methane emissions. A projection of natural emissions was beyond the program scope.

This report consists of four sections. Section 2.0 deals with the emission inventory describing the data sources and presents the detailed data used in its compilation. Various summary tables and plots are also presented. Section 3.0 deals with the field test program presenting sampling and analysis methodology, test results and an assessment of data quality. Section 4.0 is a summary of control technology state-of-the-art. Of major interest is Section 4.4 which provides cost effectiveness data for using control techniques. Finally, a prediction of future emission trends is presented in Section 5.0 based on expected industrial and population growth, control technology implementation, and control legislation.

1.3 RECOMMENDATIONS FOR FURTHER RESEARCH

1.3.1 Standard Procedures for Organic Emission Measurement

The measurement techniques employed on this program met the objectives of characterizing typical emissions. The techniques were of necessity universal in application, covering emissions of pure hydrocarbons as well as organic compounds containing oxygen, nitrogen, halogens, etc. If future control strategy involves placing a limitation on organic emissons, then some measurement standards must be established similar to those now specified in the Federal Register for NOx, SOx, particulates, H_2S, etc.

It was observed on this program that the collection and recovery of certain species was dependent on the techniques employed. Some materials used in sampling trains like plastic tubing are known to adsorb certain compounds. These are avoided in the KVB sampling train. Heating the collector to release the sample is effective on certain compounds but causes others to undergo a chemical change. Some types of GC columns are more effective than others for separating certain compounds. Also, a GC will have different responses to various compounds. Certain oxygenated compounds such as aldehydes and carboxylic acids essentially fail to respond while esters, ketones, alcohols, ethers, and alicyclics behave as pur hydrocarbons. While the GC used on this program was calibrated for varying responses for known compounds, it is possible that certain unexpected compounds may have gone undetected. On certain solvent sources such as automobile painting, there seems to be a surprising lack of oxygenated compounds.

Therefore it is recommended that a research program be conducted to define specific equipment and procedures for measuring the various classes of organic compounds. The program must include sufficient evaluation testing of the selected techniques to establish values of accuracy and precision.

The EPA is aware of this need and is sponsoring some work in this area. They have divided the organic emissions into three categories: (1) synthetic organic compounds, (2) oxygenated solvents, and (3) pure hydrocarbon compounds. Procedure work books are being prepared for Category (1). Category (3) has not been handled yet but is admittedly routine. They are without a good answer on Category (2) which is the situation in which KVB has also found itself. One aspect that EPA is not addressing is speciation. They are only interested in measuring methane, ethane, and total organics. For use in the Basin, specific compound identification would be desirable.

1.3.2 Investigation of Organic Solvent Emissions from Paint Spray Booths

Emissions from paint spray booths have been estimated based on paint usage times the fraction of solvent in the paint. Attempts at a material balance in measuring actual emissions indicate that the calculation method may produce higher results. Many oxygenated solvents are water miscible and their vapors may be absorbed by water curtains used in spray booths to collect overspray. These oxygenated solvent vapors may also be missed by GC analysis.

Another interesting observation made on this program is that the emissions from water-based paint operations in an automobile assembly plant are similar in tonnage and reactivity to those from a similar solvent-based painting operation.

Therefore it is recommended that a research program be conducted to characterize the release of organic emissions from new automobile painting operations comparing those using water-based and solvent-based paints.

1.3.3 Development of Measuring Techniques for Evaporative Emissions from Petroleum Sources

Separators, ponds, cellars, sewers, and cooling towers appear to be significant sources of hydrocarbon emissions. Attempts to characterize emissions from these sources on this program met with varied results. Consultation with other investigators in the field revealed similar frustrations. Future control strategy may require establishment and enforcement of maximum emission level from evaporative sources.

Therefore, it is recommended that research be conducted to develop reliable measurement techniques for evaporative sources of hydrocarbon emissions.

1.3.4 Gasoline Marketing Data

Because gasoline marketing is one of the large sources of hydrocarbon emissions in the Basin, the control of these emissions with vapor recovery systems is an important part of any air quality improvement strategy. To handle the control of such a large number of sources, a computerized system would be a great convenience. A source of computerized information regarding gasoline station location, throughput rate, hours of operation, etc. exists in a private company, Lundberg Surveys, North Hollywood, California, who update the data regularly and sell this information to oil companies as printed reports. While their computer tapes are jealously guarded with regard to other private industries, it is possible that a magnetic tape version of this report could be obtained for government purposes.

Therefore, it is recommended that the Lundberg Survey tapes be secured to support the control of gasoline station hydrocarbon emissions.

1.3.5 Development of an Organic Compound Flux Gage

Because of the difficulties encountered in measuring organic emissions from large evaporative sources such as storage tanks as well as separators, cooling towers, etc. as mentioned above, an instrument which could measure the flow of hydrocarbon vapors would be useful. Devices exist to measure concentrations of organic vapors in the form of sniffers. The proposed device would measure the vapor flow in weight per unit area per unit time. KVB began the development of such a device under WOGA sponsorship at a low funding level, but the project was later terminated because it appeared that it would require some extensive development just to evaluate the proposed concept. The KVB instrument was based on using two cryogenically cooled quartz crystals to collect and weigh the organic vapor. Whether or not the quartz crystal microbalance approach is feasible, some method of measuring flux should be investigated and, if possible, developed.

Therefore, it is recommended that a laboratory research program be conducted to investigate the feasibility of developing an organic vapor flux-measuring instrument. The program should include the development of a prototype unit capable of being evaluated in the field.

1.3.6 Oil Field and Off-Shore Platform Emissions

KVB estimated oil production emissions based on emission factors developed from field tests at two oil fields. These factors were applied on a per-well basis using the California Divison of Oil and Gas information on the number and location of oil wells. This was the best estimate that could be made within the program budget limitations. Previous inventories had ignored this significant area source.

A more thorough program would involve an inventory of oil field equipment throughout the Basin and further testing to support component emission factors. The API is currently sponsoring a program to develop oil production emission factors. However, most of their testing will be in oil fields and off-shore platforms on the Gulf of Mexico coast. An equipment inventory for the Basin will still be required. The APCDs have performed only a limited amount of inventory work on oil field emissions.

Therefore, it is recommended that further research be conducted to characterize oil field emissions. The program should include an inventory of equipment and testing as necessary to develop or confirm emission factors for the equipment identified.

1.3.7 Emissions from Stationary IC Engines

The KVB inventory identifies IC engines greater than 30 HP because they require permits and are in the EIS file. Smaller engines are used throughout the Basin and do not require permits. Each oil well at the Huntington Beach field has a 60-HP engine. There was not enough time to conduct an inventory of these small engines.

The organic emission factors in AP-42 were based on engines much larger than those normally found in the Basin. KVB's limited testing showed little agreement with the AP-42 values.

Therefore, it is recommended that an inventory be made of IC engines in the Basin and that selected testing be performed to develop emission factors. In addition to organic emissions, NOx should be measured to check emission factors which were questioned in KVB's NOx inventory report to the ARB.

The SCAQMD is currently engaged in an effort to locate these engines. Depending on their success, this may fulfill the inventory need. A program to develop emission factors would still be appropriate.

1.3.8 Refinery Maintenance

As discussed in Section 4.0, the cost/benefits of a special emission-control maintenance program in a refinery are debatable. KVB could only afford a few exploratory tests which revealed some potential for significant benefits to be achieved by such a program.

Therefore it is recommended that a special research program be conducted to determine what the cost/benefit ratio would be for a program in which a maintenance crew were dispatched on a continuing basis to detect and correct any leaks that exist. The program should determine optimum crew size, frequency of surveillance, and recommendations for equipment and techniques to be employed. The feasibility of such a program would be determined based on estimates of costs and emission reduction tonnage.

SECTION 2.0

INVENTORY

2.1 DATA SOURCES

The data used in this organic emission inventory were obtained from the following sources:

1. Various government agency files
2. Field testing
3. Questionnaires
4. Literature
5. Engineering analyses
6. Personal contacts with government and industry personnel.

All county enforcement agencies were in the process of a total recompilation of their permit files using the EPA's EIS/P&R* (Ref. 2-1) format (referred to as EIS hereafter) during the period of this inventory. The computerized permit file from Los Angeles County and the permit files from the other counties were used to obtain data for the preliminary inventory. It was planned that the final inventory would be compiled using the new EIS data base for the major point sources as soon as data entry was completed and checked for all counties in the inventory. The following key data were contained in the EIS data base:

1. Plant name, address, ID No., etc.
2. Standard Industrial Code (SIC)
3. Source Classification Codes (SCC)
4. UTM Coordinates
5. Stack Height
6. Pollutant Identification
7. Emission Factor
8. Throughput Rates

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*Emission Inventory Subsystems/Permit and Registration

9. Estimated emissions
10. Seasonal variations
11. Operating period (hr/day, day/week, week/yr)

For minor sources in LA County, the original permit file was used. Also a computer tape file of gasoline station locations in LA County was received from the SC AQMD. Both of these files had location coordinates on a one mile square grid basis. The ARB provided an algorithm for converting the one-mile grid to UTM coordinates (Ref. 2-2).

The ARB also provided a tape file of population by UTM coordinates which was used to distribute population related area source emissions.

Field test data were used to formulate emission profiles and to develop emission factors for new sources or check those factors on sources already characterized by the districts or the EPA in AP-42 (Ref. 2-3).

Questionnaires were received from approximately 100 industrial sources with comprehensive data on their solvent and fuel usage. Data received were used to develop emission profiles and to check values contained in the district files.

There was a great deal of activity in the area of organic emission assessment by other agencies and contractors. A list of those programs which provided valuable data for this inventory are summarized in Table 1. Excellent cooperation and data exchange were maintained with those contractors and agencies listed.

Other sources of information included personal contacts with various industry associations (dry cleaning, refinery, asphalt, printing, etc.) and government agencies (especially the ARB, California Division of Oil and Gas, EPA Office of Air Quality Planning and Standards in Durham, EPA Region 9, local air pollution districts and the Southern California Association of Governments, SCAG).

From data received from the above sources, comprehensive analyses were conducted to derive emission profiles in a form compatible with the inventory format. Analyses of test data from this and related programs listed in Table 2-1 were performed to create or evaluate existing emission factors.

TABLE 2-1. RELATED STUDIES ON ORGANIC COMPOUND EMISSIONS

Project Title	Scope	Sponsor*	Contractor	Status (as of Mid 1977)
Air Quality Impacts of Outer Continental Shelf Oil Development in the Santa Barbara Channel	Assess the impacts of OCS development on the environment	OPR	OPR Staff & ERT, Inc.	Final Report Draft issued March 1977
Fugitive Emissions from Oil Field Production Operations	Determine emission factors on a component basis for onshore and offshore facilities	API	Rockwell Air Monitoring Center	Work plan being developed
Assessment of the Environmental Effluents from Oil Refining	Determine validity of refinery emission factors currently used in AP-42	EPA	Radian, Inc.	Tests are currently being conducted in second refinery
Emissions from Ships and Shipping Operation including Transfer of Oil	Determine emissions from shipping operations in the SCAB	ARB	Scott Research Laboratory	Work plan being developed
Hydrocarbon Emissions from Floating Roof Petroleum Tanks	Determine validity of AP 2517	WOGA	Engineering Science, Inc.	Final Report released Jan. 1977
Hydrocarbon Emissions from Fixed Roof Tanks	Assess the validity of AP 2518	WOGA	Engineering Science, Inc.	Final Report released July, 1977
Hydrocarbon Emissions from Tanker Loading Operations	Determine HC emissions resulting from crude oil loading off Ventura and Santa Barbara counties	WOGA	Chevron Research, Inc.	Final Report originally scheduled for May 1977

TABLE 2-1 (Cont)

Project Title	Scope	Sponsor*	Contractor	Status (as of Mid 1977)
Floating Roof Tank Metallic Sealing Ring Emission Test Program	Determine effects of wind, ring quality, gap size and secondary seals on HC emissions	WOGA	Chicago Bridge and Iron	Final Report issued March 1977
Organic Compound Emissions From Natural Sources	Determine natural emission rates from forest vegetation	EPA	Washington State University	Final draft completed
Emission Factors from Burning Agricultural Wastes Collected in California	Determine emission factors from burning 31 field and orchard crops	ARB	UCR Statewide Air Pollution Research Center	Final Report, January 1977
ORGSOL Regulation Study Group Architectural Coatings Survey	Determine potential reduction of organic emission using H_2O borne paints	ARB	ARB Staff	Staff report issued June 1977
A Methodology for Reactive Organic Gas Emissions: Assessment of Pesticide Usage in California	Determine HC emissions from pesticide applications	ARB	ARB Staff	Report due August 1977
Gasoline Marketing Vapor Recovery System Development	Determine test procedures to assess the effectiveness of vapor recovery techniques applied to petroleum marketing	SDAPCD	SDAPCD	Test continuing

TABLE 2-1 (Cont)

Project Title	Scope	Sponsor*	Contractor	Status (as of Mid 1977)
Measurement of Atmospheric Organic Emission from Natural Sources	Determine HC emission factors from asphalt operations and landfills	EPA	Midwest Research Institute	Preliminary tests underway
Control of Volatile Organic Emissions for Existing Stationary Source	Preparation of documents for control of organic emissions	EPA	EPA Air Program Staff	Volume 1 issued November 1976. Future volumes to be released late 1977.

Abbreviation Code:

OPR - California Governor's Office of Planning and Research, Sacramento, Calif.

API - American Petroleum Institute, Washington, DC

EPA - U.S. Environmental Protection Agency, Research Triangle Park, North Carolina

ARB - Air Resources Board, Sacramento, Calif.

WOGA - Western Oil & Gas Association, Los Angeles, Calif.

SDAPCD - San Diego Air Pollution Control District, San Diego, Calif.

2.2 DATA MANAGEMENT

The data to be processed as part of the final organic emission included:

1. EIS data for major point sources for SCAQMD
2. Minor point source data from the SCAQMD (Metro Zone)
3. Gasoline station data for SCAQMD (Metro Zone)
4. EIS data for Ventura and Santa Barbara County (major and minor sources including gasoline stations)
5. Petroleum production field
6. Additional area data for sources such as forests, landfills, architectural coating, domestic solvent use, etc.
7. Emission profiles
8. Population distribution by one kilometer grid
9. Emission factor adjustments to EIS data

The available EIS data processing software was incorporated for processing the EIS data. In this system individual sources could be modified, added or deleted. KVB added a feature which also permitted the data to be modified by SCC number. For example, the emissions in the EIS data base from certain fixed roof tanks (identified by a specific SCC number) appeared to be too high based on recent test data. The emissions from those tanks were modified by one correction factor applied to all the emissions of that specific SCC number.

The profile data was organized with SCC number as the key. The specific organic specie emissions for any source were determined by factoring the total source emissions by the profile of specie weight percentages.

Area source emission rates were added to the EIS data file using the emission factor and inventories presented in Section 2.3.4. These sources, including natural emissions, architectural surface coatings, and gasoline marketing, constituted a large portion of the total emissions in the Basin. Since a standard format was not yet available for describing emissions not meeting the EIS point source criteria, KVB chose to develop an area source data base for this purpose based on general guidelines proposed by the ARB (Ref. 2-4). The format was designed to allow description of emissions by their one kilometer grid location and process (or activity).

Gasoline marketing data for this data base were acquired in three ways. In Los Angeles County, information concerning 10,000 stations in the Basin was computerized; however, individual station throughputs were missing. KVB chose to take the total sales for Los Angeles County and apportion the through-put by the total storage tank volume at each station. For Ventura County the gas station data were included in the EIS file. For consistency, KVB chose to take these EIS data and format them as the Los Angeles County data with the gas station locations and throughputs retained. KVB assigned new emission factors to the data. For the remaining counties the gas station emissions were apportioned by residential area based on the total county sales. These gas station data were formatted in the KVB area source format.

Since the EIS point source data base did not contain the organic emissions for minor point sources under permit in L.A. County (Metro Zone), these data were acquired from Metro Zone's permit files and formatted in the KVB area source format. Data on the emissions from minor point sources not under permit were also obtained and included in the KVB area source data base.

Finally the KVB area source data base contained data from all area sources identified by the KVB engineers. These emission sources included waste disposal, petroleum operations other than refining, domestic and agricultural sources, geogenic sources and natural emissions.

All point sources in the inventory were given an SCC number which was occasionally qualified by the SIC number. For area sources, process codes devised by the ARB Staff were used in lieu of SCC numbers. A file was created with all information relative to these SCC numbers (or process codes), the emission correction factors to be applied to all sources with the given SCC/SIC number; the profile key to identify the profile for this source type, the relevant ARB application category, and summer or winter differentials to be used to alter emissions seasonally if warranted by the source type. This SCC file was used as the major system link between sources and their profiles.

Within each ARB application category only unique profiles were identified. The profile records contained information concerning the method of determining the profile and estimated error. In addition, each profile contained the SAROAD code and percent by weight of each specie in the profile. Where the SAROAD coding was not comprehensive, KVB and their subcontractor, ARLI, added SAROAD codes in a logical manner. Since SAROAD codes were the only specie identifier in the profile data base, a separate tabular file was created to contain SAROAD codes, species name, molecular weights and ARB reactivity class.

From the data files used in this inventory, eight reports were produced. They included:

1. A <u>Total Organic Emission Report</u> containing:
   - a. Source information (county, APCD Point ID No., SSC No., SIC No.)
   - b. Total organic emissions, ton/year
   - c. Summer emissions, ton/day, broken down into weekday emissions and weekend emissions
   - d. Winter emissions, ton/day, broken down into weekday emissions and weekend emissions
   - e. Emission profile key which will relate to an emissions species breakdown in Item 2 below.

   These data were reported in two sorted orders:

   - a. According to the ARB application categories and including point and area sources (Report #1)
   - b. According to location in 10 Km UTM grid squares and including point and area sources (Report #2)

   A plant identification index (Report #3)

2. <u>An Emission Profile Listing</u> which lists each organic specie (by name and code no.) emitted by a particular source or source type, the reactivity class (according to the ARB's 3-class system) of that specie, and the percent by weight of the total emitted hydrocarbons that the specie contributes (Report #4).

3. An <u>Emission Summary</u> consisting of the following data for each 1 Km grid square in the Basin (Report #5):
    a. Total organic emissions, ton/year
    b. Individual specie emissions by code no., lb/year
    c. Emissions for each reactivity class: I, II, and III, ton/year
4. An <u>Individual Organic Specie Report</u> showing the emission of each specie broken down by ARB Application Categories (Report #6).
5. An SCC report listing the profile keys, application and emission correction factors for all SCC codes encountered in the source files reported in two sorted orders:
    a. By SCC code (Report #7)
    b. By profile key in order to reference all SCC codes attributed to a given profile (Report #8).

A more detailed description of these reports is presented in Section 2.4.1.

In addition to these reports which were delivered to ARB under separate cover as computer printouts, the following data files were prepared and submitted to ARB on IBM compatible magnetic tape:

1. An updated (for hydrocarbon emission) point source emission file in EIS format (File #1) (KVB Label No. 7077 and 7078)
2. An organic specie profile file (File #2) (Label No. 113)
3. An area source data file (File #3) (Label No. 111)
4. A chemical species description file (File #4) (Label No. 114)
5. An SCC description file (File #5) (Label No. 112)

2.3 ENGINEERING ANALYSIS

2.3.1 Point Source Emission Factors

There has been considerable interest in the development of emission factors that can be employed to estimate emissions from specific sources based upon a knowledge of the pertinent operating characteristics of the source. Such procedures are in common use throughout the country by local control agencies to estimate air pollution emission rates for point and area sources. One of the primary objectives of the ARB organic compound emission study was to critically evaluate the emission factors for organic compound emissions used by the SCAQMD and local APCD's and to develop new emission factors for sources not contained in the EIS data system that were applicable to the South Coast Air Basin. The following discussion outlines the methodology employed during the analysis for point sources. Emission factors for area sources have been separated into a separate section (Section 2.3.4) as they required a significantly different approach.

Point source emission factors for industrial point sources in the Basin were divided into three groups. The first group included the combustion of fuels and evaporative emissions from petroleum operations. In general, emission rates from these sources had been calculated by the local control agencies using emission factors and the appropriate information on fuel usage, petroleum product throughput, etc. This group, especially petroleum storage and transfer operation represented a large part of the total hydrocarbon emissions in the Basin and therefore was given primary emphasis in the analysis of point source emission factors.

The second group of sources included solvent evaporation. Emissions from these sources were generally not calculated by local control agencies using emission factors but rather were determined from solvent use questionnaires since the organic compound emissions were essentially predetermined by the solvent content of the materials employed. Therefore, correction to the EIS data base were made through updates of the solvent use inventory rather than corrections to emission factors. A discussion of the questionnaires used to update the EIS is contained in Section 2.3.3.

The third category included much less significant industrial point sources of organic compounds in the Basin such as metallurgical, mineral and food processing operations. For these sources, data contained in the EIS data base were left intact and no corrections were attempted.

A. Approach--

A comprehensive listing of point source emission factors was found in the EPA publication, "Compilation of Air Pollution Emission Factors" (Ref. 2-4), hereafter referred to as "AP-42." The SCAQMD had its own emission factors which had been employed in the process of estimating emission rates for industrial point sources contained in the EIS data file. To a certain extent, these emission factors were the same, because frequently SCAQMD data were used as the basis for the development of AP-42 emission factors. In other instances the emission factors differed because the SCAQMD sometimes based its emission factors on its own test data in preference to using AP-42 values.

A specific objective of this study was to examine the point source emission factors used by the SCAQMD and AP-42. This was done for three reasons. First, much of the data used to generate emission factors for specific source types such as petroleum operations and the combustion of fuels stem from studies conducted as far back as the 1950's. Considerable debate had been raised about their continued applicability in view of improved technology, sampling procedures, etc. Second, certain emission factors listed in AP-42 intended for use nationally may not necessarily represent conditions in the Basin. Finally, it was necessary to generate entirely new emission factors where none had existed previously.

Field tests were conducted to provide data to assist in emission factor evaluation and development. In addition, data from several related projects Table 2-1, specifically oriented to improving AP-42 emission factors have been incorporated into this analysis. In most cases, these studies had been directed at conditions within the Basin making them directly applicable to the current study.

Comparisons have been made between the emission factors used by the SCAQMD, those contained in AP-42 and those generated in this and related studies. Where KVB felt that available data disagreed with the SCAQMD emission factors, correction factors were applied to the emission rates listed in the EIS data system to update these emission estimates. The intent was to have the EIS data file, delivered to the ARB, reflect the best and most recent information available. This was a vital part of the improvements incorporated into the final KVB data base.

B. Results--

Emission factors selected for evaluation in this study are discussed in the following sections. Sources have been divided into four groups: (1) fuel combustion, (2) petroleum transfer and storage, (3) refinery fugitive emissions, and (4) petroleum production operations. A table for each of these source categories presents a general description of the source, appropriate SCC codes, units employed, emission factor listed in AP-42, those used by the local control agencies, and those resulting from recent investigations including field tests from this study. The "best" emission is also given along with the correction factor used to update the EIS data files. A complete discussion of each table is also presented.

1. Fuel combustion--It was appropriate to investigate the organic compound emission factors for the combustion of fuels used in the Basin. Emission factors used by the SCAQMD stem from data generated in the 1950's (Ref. 2-5) and were currently under revision during the study using more up-to-date test data.

AP-42 emission factors represented data accumulated over the last several years and generally had an emission factor rating of A. These emission factors, however, are still subject to revisions for specific sources.

Emission factors developed during the current program were themselves subject to error due to the broad nature of the test program and the limited number of samples that could be obtained for any one source type. Sources tested were selected so that the tests would be representative of that general sources type. A thorough evaluation of the test data was made to assure its accuracy. Table 2-2 presents a summary of the sources and emission factors for fuel combustion evaluated during this program.

Among the most important of the emission factors investigated was that from the combustion of residual oil in utility boilers. This represented one of the largest uses of fossil fuels in the Basin. The emission factor used by the SCAQMD was 2.6 times greater than that listed in AP-42. For this source type, the results of the KVB test program conducted on a utility boiler firing low sulfur residual oil tended to support the lower figure. Consequently, a correction factor was incorporated into the data management program.

Similarly, the SCAQMD emission factor for natural gas combustion in utility boilers was nine times that of AP-42. However, in this case, since the quantity of natural gas used by utilities has decreased dramatically in recent years, a decision was made to forego emissions testing of this source type. Since this represented a relatively insignificant source of organic compounds, the SCAQMD emission factor was not changed.

Refinery gas combustion, on the other hand, represented an important industrial source of organic compounds. In this case, good agreement between the three emission factor sources was obtained and no correction factor was necessary.

TABLE 2-2. ANALYSIS OF EMISSION FACTORS

Combustion of Fuels

Description	Applicable SCC Codes	Units	Emission Factors						Emission Factor Used in the Current Study	EIS* Correction Factor
			AP-42	SCAQMD	VAPCD	SBAPCD	Others	(Reference)		
Residual Oil Combustion Power Plants	1-01-004-XX	lb TOC/10^3 Gal.	1.0	2.6	1.0	1.0	0.7	(KVB)	1.0	0.40
Natural Gas Combustion Power Plants	1-01-006-XX	lb TOC/10^6 ft^3	1.0	8.8	1.0	1.0	-		8.8	1.00
Refinery Gas Combustion	3-06-001-02 3-06-001-04	lb TOC/10^6 ft^3	30.0	21.9	-	-	20.0	(KVB)	21.9	1.00
Natural Gas Industrial	1-02-006-XX	lb TOC/10^6 ft^3	3.0	7.0	3.0	3.0	30.0	(KVB)	7.0	1.00
CO Boiler	3-06-002-01	lb/10^3 Bbl Feed	200	1.6	-	-	1.13	(KVB)	1.6	1.00
Natural Gas IC Engines	2-02-002-02	lb TOC/10^6 ft^3	1400	-	1400	-	1850-11600	(KVB)	1400	NA

*EIS Correction Factor = Ratio of emission factor used in current study to the emission factor used by SCAQMD in their EIS file.

TOC = Total Organic Compounds

Industrial natural gas consumption also represents an extremely large energy use in the Basin. As shown in Table 2-2, the emission factor used by the SCAQMD was between the AP-42 and KVB emission factors so that again no correction factor appeared to be warranted.

Emissions from CO boilers treating exhaust gases downstream of an FCC unit were also evaluated. Since the SCAQMD used test results from these units rather than emission factors, the comparison between SCAQMD values and those obtained in this program has been made for a particular unit tested. Again, the SCAQMD value appeared to be reasonably close to that obtained during this study and no correction factor was necessary.

Natural gas combustion in IC engines represented another somewhat unique case. At the time of the study, sources of this type were not included in the EIS data file although a preliminary inventory of IC engines in the Basin had been made (Ref. 2-6). This inventory was incorporated into the area source data base for this study. A decision on an appropriate emission factor was somewhat difficult to make. Data presented in AP-42 represented emission factors of 800 hp units which are much larger than those typically found in the Basin. The results of the tests conducted by KVB on IC engines also resulted in large emission rates; however insufficient data were obtained to generalize an emission factor. The AP-42 value was used as it was somewhat conservative, although it was fully recognized that the emission rates from these sources may be higher.

2. Petroleum storage--Table 2-3 presents a comparison of the emission factors used to estimate organic compounds emitted from petroleum storage operations. Perhaps no other source has received so much recent investigation and is under so much controversy as those sources listed in this group. Responding to this controversy both the Western Oil and Gas Association (WOGA) and the California Air Resources Board have initiated field test programs (Refs. 2-7, 2-8, and 2-9) to investigate emission from petroleum storage operations. The results of the WOGA programs as well as the revised AP-42 emission factors (Ref. 2-10) are listed in Table 2-3.

TABLE 2-3. ANALYSIS OF EMISSION FACTORS PETROLEUM STORAGE

Description	Applicable SCC Codes	Units	Emission Factors -					(Reference)	Emission Factor Used in the Current Study	EIS Correction Factor *
			AP-42	SCAQMD	VAPCD	SBAPCD	Others			
Floating Roof Storage Tanks	4-03-002-XX	--	API Bulletin 2517	2517	2517	2517	50% of API 2517	(WOGA Report Ref. 2-7)	100% of API Bulletin 2517	1.00
Fixed Roof Storage	4-03-001-XX	--	API Bulletin 2518	2518	2518	2518	58% of API 2518	(WOGA Report Ref. 2-8)	60% of API Bulletin 2518	0.60

*EIS Correction Factor = Ratio of emission factor used in current study to the emission factor used by SCAQMD in their EIS file.

API Bulletins 2517 and 2518 are universally used to estimate emissions from floating roof and fixed storage tanks respectively. These formulas and their application to conditions in the Basin have resulted in two programs sponsored by WOGA.

Results of the first study on floating roof tanks (Ref. 2-7) are presented in Table 2-4. It has been widely published (Ref. 2-11) that the results of this program demonstrate that emission estimates using 2517 are twice those of actual test results. However, a statistical evaluation of the data does not seem to support any conclusions about the relationship of the API formula to actual test emissions. The correlation coefficient which relates the two sets of data in Table 2-4 was 0.489 and therefore not significant. Using Kendall's method of rank correlation yielded an even less significant correlation of 0.14. While a t-test on the API 2517 predictions versus the actual test results did tend to improve by factoring the API formulas by 0.60, it was felt that the floating roof data did not support any conclusions which attempted to relate the test results to the API predictions. When no correlations exist, attempts to state which set of data was more reliable could not be made. Therefore, it was considered inadvisable to use these data to make any estimate of a correction factor for API 2517. The final inventory used emission factors as calculated using API 2517.

TABLE 2-4. API 2517 CALCULATED VERSUS OBSERVED HYDROCARBON EMISSIONS

	Hydrocarbon Emission Rate (bbls/year)	
Tank	API 2517 Calculated	Observed
A	510	55
B	30	87
C	131	0
D	128	175
E	49	60
F	237	55
G	237	57
H	362	445
I	35	56
J	34	33
K	145	43
L	132	84
M	433	286

Data from the program on fixed roof tanks (Ref. 2-8), presented in Table 2-5, on the other hand, demonstrated that there was a correlation between the various sets of numbers. The correlation coefficient between the predicted and measured losses was calculated to be 0.749. This value was accepted as representative of a significant correlation suggesting that API Bulletin 2518 does predict the trends in emissions based on storage tank parameters. However, the API formula appeared to overestimate emissions.

In order to test the hypothesis that the emissions data calculated using the API formula represented the same data population as the actual measured emissions (i.e. the means of the differences of the pairs of data equal zero), the t-test was employed. For the API estimates versus the actual test results, the calculated value for t is 2.11 while the acceptance limit for t_o at 0.05% confidence and 20 degrees of freedom is 1.725. Therefore, the data did not seem to represent the same population.

To test the theory that the API formula was overestimating the fixed roof tank emissions, two numbers were chosen as factors for the API estimate. The actual ratio of the means of the two sets of data (0.58) was used as one factor and 0.60 was also tested. (The correlation coefficient was unaffected by changes in the estimated emissions factored by either 0.58 or 0.60.) Resulting t values were 0.631 and 0.119 for correction factors of 0.58 and 0.60, respectively, supporting the hypothesis that the corrected emission predictions from API 2518 were not significantly different from the test data. A correction factor of 0.60 was therefore applied to the EIS data base given in Table 2-3.

3. Refinery fugitive emissions--An analysis of the emission factors used to estimate fugitive emissions from valves and pumps in operation within petroleum refineries has been made. Emission estimates for both AP-42 and the SCAQMD generally stem from an extensive study conducted in 1958 of air pollution emissions from petroleum refining operations located in the Basin (Ref. 2-12). Considerable interest had been raised about the accuracy of these emission estimates in view of advances in technology in the form of better valve and pump packing materials and improved pump seal designs.

TABLE 2-5. MEASURED VERSUS API CALCULATED EMISSIONS FOR STANDING STORAGE FIXED-ROOF TANKS

Test No.	Measured Loss (bbls/yr)	API Calculated Breathing Loss (bbls/yr)
1	Negligible	17
2	< 1	51
3	Negligible	91
4	Negligible	10
5	1	101
6	Negligible	21
7	224	607
8	164	257
9	122	856
10	Negligible	44
11	< 1	26
12	6	74
13	240	167
14	3	17
15	84	138
16	339	490
17	1,086	783
18	Negligible	61
19	9	298
20	Negligible	2
21	20	38
TOTAL	2,400	4,149

Table 2-6 presents a summary of the analysis of the emission factors from fugitive sources within petroleum refineries. Since the SCAQMD did not use emission factors to estimate emission rates from these sources but rather used actual test data on specific sources only the emission factors listed in AP-42 (Ref. 2-10) are given. However, since both the SCAQMD and the emission estimates are based on the same data from Reference 2-12, a comparison of test data from the KVB study with AP-42 values was made to indicate if any corrections to the EIS data were necessary.

A specific objective of the KVB field test program, therefore, was to evaluate these emission factors listed in AP-42. Of course, a test program comparable to that described in Reference 2-12 was beyond the scope of this study. Therefore, a brief evaluation (as described in Section 3.0) was conducted with the aim of assessing the relative magnitude of these emission rates. The results of these tests are presented in Table 2-7. Given is a description of the device and the product carried, the total number of devices inspected, the number and class of leakers identified with the average leak rate measured (shown in parentheses) and the total emissions from each device. The corresponding emission factor on a per device basis is also given. These test results involve the inspection of approximately 18,000 valves and other fittings and 80 pumps.

Several conclusions were apparent from the results of the tests conducted on valves and fittings. As shown in Table 2-7, there was a substantial difference between the average emission rate for valves and that for metal connections in both gas and liquid service. Based on these results, emissions from metal connections such as flanges, unions, ties, etc. were assumed to be negligible. Note that there also was a significant difference between emissions for valves in gas service as opposed to those carrying liquid products.

A composite emission factor for valves was determined by applying an appropriate weighting factor to each of the gas and liquid emission factors. Previous inventories (Ref. 2-12) had reported that the ratio of valves in liquid service to those in gas service in refinery operations was approximately 3 to 1. Applying this ratio to the emission factors listed in Table 2-7 resulted in a composite emission factor of 0.15 lb/day·valve. Using these

TABLE 2-6. EMISSION FACTORS, REFINERY FUGITIVE EMISSIONS

Description	Applicable SCC Codes	Units	AP-42	Others	(Reference)	Emission Factor Used in the Current Study	EIS Correction Factor*
Valves	3-06-008-01	lb/day-valve	0.15	0.15	(KVB)	0.15	1
Pumps	3-06-008-03	lb/day-seal	3-5	4	(KVB)	3	1
Cooling Towers	3-06-007-01	lb/10^6 gal	6	12	(KVB)	6	1
FCC Units	(See Figure 2-2, CO Boiler)						

*EIS Correction Factor = Ratio of emission factor used in current study to the emission factor used by SCAQMD in their EIS file.

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TABLE 2-7. KVB FUGITIVE EMISSION DATA FOR PETROLEUM REFINING OPERATIONS*

Device Type	Product	Total Inventory No.	No. of Leakers Identified (Average Leak Rate, lb/day·leak)† Large	Medium	Small	Total Emissions (lb/day)	Emission Factor (lb/day·device)
Valves & Fittings							
Valves	Gas	1698	29(18)	23(3)	100(0.3)	620	0.4
Metal Connections	Gas	3100	0	1(3)	17(0.3)	8	0.003
Valves	Liquid	2774	2(18)	4(3)	32(0.02)	49	0.02
Metal Connections	Liquid	5661	1(18)	0	2(0.02)	18	0.003
Pump Seals							
Mechanical	< 26 RVP	93	3(7)	4(1)	17(0.01)	25	0.3
Mechanical	> 26 RVP	19	2(70)	0	8(0.06)	140	7
Packed	< 26 RVP	12	1(4)	0	5(0.06)	5	0.4
Packed	> 26 RVP	4	1(170)	0	0	170	40

* Based on test data from Source #7 only.

† See Table 3-48 for determination of average leak rate.

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results, the AP-42 emission factor of 0.15 lb/day·valve appeared to be reasonable and no correction factor was applied to the EIS data.

A similar analysis for pumps was conducted. As shown in Table 2-7, the product transferred and the type of seal both had a significant effect on emission rates. Tests conducted on pumps servicing liquid with a Reid Vapor Pressure (RVP) less than 26 had a relative low emission rate as compared with pumps carrying more volatile materials. Similarly, for pumps with high volatile materials, packed seals leaked at a rate five times that of mechanical seals. In general, these results were consistent with values reported in Reference 2-12.

A composite emission factor for pumps was difficult to determine since no inventory of pumps comparable to valves was available. Therefore a composite emission factor was developed using both the inventory data and emission factor presented in Table 2-7. The emission factor for mechanical and packed seals were 1.5 and 11 lb/seal·day respectively with a composite emission factor for all pumps of 3 lb/seal·day. This result compared favorably with the values listed in AP-42 and no correction factor was deemed necessary.

Additional field test data on emission rates from oil/water separators, cooling towers and compressor seals were obtained during this study. However, insufficient data from the field test conducted as part of this program were available to perform a creditable analysis of the emission factors.

4. Petroleum production fugitive emissions--(Although these sources have been considered as area sources and are included in Section 2.3.4, a discussion of the methodology used in determining emission factors from these sources was felt appropriate due to the similarity with previous analyses.)

Table 2-8 presents the emission factors developed by KVB to estimate fugitive emissions in petroleum production operations. These represent new data since emission factors from these sources had not appeared previously in AP-42 or in the EIS data base.

TABLE 2-8. EMISSION FACTORS, PETROLEUM PRODUCTION FUGITIVE EMISSIONS

Description	Applicable SCC Codes	Units	AP-42	County Agencies	Others	(Reference)	Emission Factor Used in the Current Study	EIS Correction * Factor
Valves	3-06-008-01	lb/day-valve	--	--	0.10	(KVB)	0.10	NA §
Separators	3-06-005-XX †	lb/day-ft^2	--	--	0.1	(KVB)	0.1	NA §
Compressor Seals	3-06-008-04	lb/day-unit	--	--	28	(KVB)	28	NA §
Well Heads	3-06-008-01 †	lb/well-day	--	--	0.05	(KVB)	0.05	NA §
Cellars	3-06-005-XX †	lb/well-day	--	--	2.0	(KVB)	2.0	NA §

*EIS Correction Factor = Ratio of emission factor used in current study to the emission factor used by SCAQMD in their EIS file.

†Best fit

§Data entered into EIS data base by KVB using listed Emission Factors

The emission factors for leaking valves and metal fittings were developed using the data in Table 2-9. The format for this table is similar to that used in Table 2-7. These data represent the results of the inspection of over 3000 possible leak sources.

As found in previous analysis for refinery operations, the emission rate from valves and fittings appeared to be highly dependent on both the type of device and the product involved. Again, (1) emission rates from metal fittings were much less than those from valves, and (2) valves in gas service had higher emission rates than those in liquid service. A composite emission factor developed using the emission rates and inventories presented in Table 2-9 was determined to be 0.10 lb/valve·day. This was comparable to that found for refining operations.

A similar procedure for fugitive emissions from compressor seals was used and the results are presented in Table 2-9. This represents data on only nine compressors (out of an estimated population of approximately 500) and therefore must have a lower level of confidence.

Another potential source of emissions was found to be the leakage from the stuffing box around the polish rod on the rod pumps used in production operations in the Basin. This was shown to be extremely small in comparison to other leak sources.

Techniques were also developed to estimate the evaporative loses from standing oil in pump cellars and oil/water separators. The emission factor presented in Table 2-8 for these sources represents composite data from eight cellars and seven separators evaluated during the current program.

TABLE 2- 9. FUGITIVE EMISSION FACTORS FOR PETROLEUM PRODUCTION OPERATIONS

Device Type	Product	Total Inventory	No. of Leakers Identified (Average Leak Rate, lb/day·leak)			Total Emissions (lb/day)	Emission Factor (lb/day·device)
			Large	Medium	Small		
Valves & Fittings							
Valve	Gas	910	15(13.0)	20(1.3)	42(0.2)	229	0.25
Metal Connections	Gas	372	3(13.0)	6(1.3)	20(0.2)	50	0.11
Valve	Crude	1,192	0	2(0.5)	4(0.05)	1	< 0.01
Metal Connections	Crude	339	0	0	3(0.05)	Neg.	Neg.
Compressor Seals	Gas	9 units	8(31.2)	5(0.5)	2(0.1)	280	28.0

2.3.2 Emission Profiles

A. Description--

A unique aspect of the current program was the development of emission profiles, the identification of the organic compound species represented by the total hydrocarbon emission rates currently given in emission measurements. Only one other study (Ref. 2-13) had previously attempted a breakdown into generic classes. That was done primarily for the purpose of dividing emissions into reactivity classes. The results of that previous study have been widely used in the Basin.

A primary objective of this program was to identify the organic compound emissions for each stationary source type in the Basin and develop a data management system capable of applying this information to the total hydrocarbon emissions in order to calculate the emissions of the individual organic compounds. Thus an emission profile was formulated for each Source Classification Code (SCC) emitting organic compound species in the Basin. Both point and area sources were included. In certain instances a further breakdown was made into individual industries identified by Standard Industrial Codes (SIC).

Another objective of this program was to predict future emission trends. Satisfying this objective required emission profiles based on SCC number rather than individual plant profiles based on individual plant characteristics. All plant devices identified by the same SCC and SIC number were given the same emission profile. Conversely, it was important that profiles be truly representative of the device in general. Additional advantages of developing aggregate profiles by SCC number were that: (1) estimations based on larger data samples were more statically reliable than single data samples, (2) the profiles were compatible with the EIS concept by describing devices by the SCC number system, and (3) the volume of profile data was reduced to a more manageable level.

The initial intent was to provide a profile for each SCC listed in the data base. In many instances, however, an individual profile was found to cover several SCC and SCC/SIC combinations. The profile data base was therefore formulated and indexed by a profile number. Separate profile numbers (with identical specie distributions) were given to specific SCC/SIC combinations to facilitate data management, specifically the segregation of emissions from devices with similar SCC codes in two different industry classes into the appropriate ARB Application Categories.

In each profile the organic species were identified by their appropriate SAROAD code, ARB reactivity classification (3 class) and molecular weight. Each profile was also "tagged" with other identifiers to assist those who may wish to use or evaluate these data. Associated with each emission profile was an estimate of its relative error. This "Error Estimate" was strictly subjective and has been included to give a relative level of confidence to the specific profile. No statistical significance have been or should be given to these error estimates.

Given in the Appendix is a listing of the emission profiles used in the current study. Two reports are used to relate the profiles to the devices in the inventory. The SCC report (sorted by SCC number and profile number) lists all devices in the inventory and gives the profile number of the profile that describes the emission breakdown for the particular device. The profile report lists the profiles by profile number.

A profile contains a subjective estimate of the probable error in the profile and also lists the SAROAD code, chemical name and percent contribution of each specie. The species are also summed by reactivity class. In all 270 profiles were identified as being unique by either the specie breakdown or application category.

Table 2-10 presents the emission profiles for some of the most significant source types in the Basin.

TABLE 2-10. EMISSION PROFILES

Chemical Name	Residual Oil Combustion	Refinery Gas Combustion	Fiberglass Mfg.	CO Boiler	Fugitive Emissions (Refinery)	Fugitive Emissions (Pet. Production)	Adhesives	Synthetic Dry Cleaning	Petroleum Solvent	Crude Oil Storage	Gasoline Marketing	Crude Tanker Loading	General Primer	General Enamel	General Flexographic	General Rotogravure	Architectural Surface Coating	Natural Forest	Landfills	Miscellaneous Petroleum Storage
	Profile (% Weight)																			
Methane	11.0	7.6		36.0	28.6	62.0				6.2		10.2			14.4				98.6	
Ethane		20.9			5.8	17.0	3.9			5.6		3.6			0.7				0.1	0.1
Ethylene																				0.2
Propane		18.9			11.5	11.1				17.6	1.8	23.4			0.2				0.1	1.0
Propylene		17.5			0.1															
Cyclopentane																			0.2	
N-Butane	14.0	23.1			18.3	4.4				27.1	19.8	26.5							0.2	1.4
Butene											1.8									
Iso-Butane		4.4			7.4	2.9				1.5	6.6	5.4			1.2				0.1	0.6
N-Pentane					7.7	0.7				14.6	10.6	7.3							0.1	1.4
Iso-Pentane					7.8	1.1				1.5	29.0	8.0								3.4
1-Pentene											6.2									
Hexane	5.0				3.4		59.0			7.9	2.5	5.6			0.7		20.7			8.9
Heptane					1.4					9.2	0.6	5.6								1.1
Octane					1.8					6.9	0.1	3.0								
Nonane					0.60							1.0								
Isomers of Hexane				13.0	1.6					0.3	8.9									0.9
Isomers of Heptane					0.8						2.0									1.0
N-Decane												0.3								0.1
Isomers of Octane					0.4				0.8		1.9									
Cyclohexane					0.1					0.1	2.1					10.0	20.7			
Undecane												0.1								
Isomers of Nonane					0.5				27.3		0.2									1.9
Isomers of Decane					0.3				69.3											4.9
Isomers of Undecane									2.6											0.2
C-7 Cyclo-paraffins					0.2					1.3	0.2									4.2
C-8 Cyclo-paraffins										0.5										
C-9 Cyclo-paraffins					0.1															
Terpenes																		100.0	0.1	
Mineral Spirits													41.0	67.6		51.0				

Continued

TABLE 2-10. (Continued).

	Profile (% Weight)																		
Chemical Name	Residual Oil Combustion	Refinery Gas Combustion	Fiberglass Mfg.	CC Boiler	Fugitive Emissions (Refinery)	Fugitive Emissions (Pet. Production)	Adhesives	Synthetic Dry Cleaning	Petroleum Solvent	Crude Oil Storage	Gasoline Marketing	Crude Tanker Loading	General Primer	General Enamel	General Flexographic	General Rotogravure	Architectural Surface Coating	Natural Forest	Landfills	Miscellaneous Petroleum Storage
Lactol Spirits															10.0					
Methyl Alcohol													1.0	0.7	3.6	6.0	3.9			
Ethyl Alcohol													0.8	0.5	2.4		0.6			2.6
Iso Propyl Alcohol													2.8	1.9	24.1	6.0	16.4			3.4
N-Butyl Alcohol													4.0	2.8		6.0	1.6			
Iso Butyl Alcohol																	0.6			2.6
Glycol Ether													11.5							
Propylene Glycol																	0.8			
Ethylene Glycol																	0.6			
Ethyl Acetate							4.1						0.9	0.3						4.4
Propyl Acetate															21.5					
N-Butyl Acetate													9.5	2.9		6.0	2.5			
Cellosolve Acetate																	1.3			
Isopropyl Acetate													0.8	0.3	9.5					
Isobutyl Acetate																	1.5			
Dimethyl Formamide																	0.5			
Isobutyl Iso-butyrate																	6.1			
Formaldehyde	42.0	7.6		51.0																0.4
Acetone	28.0						3.0						7.1	6.3	9.4		3.2			16.4
Methyl Ethyl Ketone													7.7	6.8	2.0		5.6			12.4
Methyl N-Butyl Ketone																	0.7			
Methyl Isobutyl Ketone													3.1	2.7			0.6			6.7
Ethylene Dichloride																				0.4
Perchloroethylene							30.0	100.0											0.3	5.1

Continued

TABLE 2-10. (Continued).

	Profile (% Weight)																			
Chemical Name	Residual Oil Combustion	Refinery Gas Combustion	Fiberglass Mfg.	CO Boiler	Fugitive Emissions (Refinery)	Fugitive Emissions (Pet. Production)	Adhesives	Synthetic Dry Cleaning	Petroleum Solvent	Crude Oil Storage	Gasoline Marketing	Crude Tanker Loading	General Primer	General Enamel	General Flexographic	General Rotogravure	Architectural Surface Coating	Natural Forest	Landfills	Miscellaneous Petroleum Storage
Naphtha													1.0							
Benzene					0.1					0.1	1.1				0.1					
Toluene					0.5						2.1		3.9	3.2	0.2		5.2		0.1	8.6
Ethylbenzene																6.0	4.3			
Tri-methyl-benzene											0.3									
Ethyltoluene											0.5									
Iso Diethyl-benzene																7.0				
Styrene			100.0																	
Xylenes					0.2						1.6		4.9	4.0			2.6		0.1	5.7
Dimethylethyl-benzene											0.1									
TOTAL %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

B. Methodology--

Two general approaches were used to formulate the emission profiles, one where only one data point was available to characterize many sources and another where multiple data points were available. In cases where a profile was available from only one source and that source was believed to be representative of all such source types in the Basin, then that particular source emission profile was used. An appropriate error estimate was given to reflect the relative confidence level of these data. It was anticipated early in the program that a significant number of source types would fall into this category due to the limited amount of field tests available. Therefore, test locations were carefully selected on the basis of the representative nature of their emissions to all other devices of that particular type. In this way, data from this source could be correctly applied to other non-tested sources. Test results are presented in Section 3.4. Similarly, questionnaires were submitted to and received from selected solvent users. Follow-ups were made to assure that the data from these large and representative sources were obtained.

Two examples of formulating profiles based on one data point from a selected source are the following. The first, concerned with the emission profile typical of residual oil fuel combustion, was obtained by (1) recognizing that 95% of all residual oil combustion in the Basin occurs in utility boilers, (2) selecting a boiler that was "typical" of such devices in the Basin and finally (3) conducting a test on this unit. Multiple samples were taken and the profile was based on an average composition.

The second example involved the use of data from questionnaires. One source in the Basin, according to the SCAQMD files, was responsible for 90% of the emissions from adhesive use. A questionnaire was mailed to this source and follow-up contacts were made to assure that information from this source was received. The questionnaire contained a comprehensive breakdown of the composition of the solvent composition and usage which formed the basis for the emission profile.

This approach of using one analysis to characterize a general source type also applied to profiles determined by inspection. For example, there were a few SCC's that specifically identify the solvent used in a coating operation or housed in a storage tank. In this case, a solvent identified by its SCC as toluene or xylene would be given an emission profile of 100% of that organic compound.

The second approach used was to develop emission profiles based on data from several sources within a particular source type. This involved (1) acquiring the data, (2) determining the relative magnitudes of each source compared to the total emissions from the source type, and (3) forming a composite profile by factoring the data from each source by an appropriate weighting factor. In this manner, emission profiles were developed for individual source types that in actuality represented the average emissions from sources of that category (SCC number).

An example of this approach was the formulation of a profile for "Miscellaneous Organic Storage" in the Basin. While SCC numbers had been assigned to storage tanks for gasoline, jet fuel, crude oil, various solvents, etc., the miscellaneous category covered all other petroleum products not listed. Table 2-11 presents a summary of the calculation procedures employed to determine this profile. Listed across the top are the various organic products identified and the fraction of the emissions from fixed roof tank storage for each based on information compiled from the SCAQMD file. Listed down the page are the various organic species that have been identified in the emissions from these products. The weight percentages of each specie associated with the product is listed in the appropriate column. The weight percentage for asphalt and Stoddard solvent were determined from KVB test data. The adhesive percentages came from questionnaire data. The remainder of the percentages were specified (e.g. 100% for acetone) or estimated based on contacts with industry (e.g. the breakdown of alcohols and ketone). The weight percent of each organic compound in the composite profile was determined by multiplying the weight percents by the appropriate fractions and are listed on the right hand side.

TABLE 2-11. COMPOSITE PROFILE FOR MISCELLANEOUS PETROLEUM STORAGE

(Fixed Roof Tanks)

Product Stored	Acetone	Adhesive	Alcohol	Asphalt	Perchloroethylene	Ethylene Dichloride	Formaldehyde	Ketone	Stoddard	Xylene	Others	Composite
Fraction of Emissions	0.163	0.022	0.084	0.078	0.051	0.004	0.004	0.191	0.071	0.057	0.275	
Organic Compounds												
Acetone	100.0	4.0										16.4
Perchloroethylene					100.0							5.1
Ethylene Dichloride						100.0						0.4
Formaldehyde							100.0					0.4
MEK								65.0				12.4
MIBK								35.0				6.7
Xylene										100.0		5.7
Toluene		5.6									31.0	8.6
Ethane				1.0								0.1
Ethylene				2.0								0.2
Propane				13.0								1.0
N-Butane				18.0								1.4
I-Butane				8.0								0.6
N-Pentane				18.0								1.4
I-Pentane											12.5	3.4
Hexane		84.6		2.0							25.0	8.9
I-Hexane				12.0								0.9
Heptane				14.0								1.1
I-Heptane				11.0								1.0
I-Octane				1.0					0.8			0.1
I-Nonane									27.3			1.9
I-Decane									69.4			4.9
I-Undecane									2.4			0.2
Ethyl Acetate		5.8									15.5	4.4
C-7 Cyclo-paraffins											15.5	4.2
Isopropyl Alcohol			40.0									3.4
Ethyl Alcohol			30.0									2.6
Isobutyl Alcohol			30.0									2.6

C. Key Profiles--

Due to the magnitude of the sources which they represent several emission profiles were recognized to have a significant impact on the results of the final inventory. These include gasoline vapors emitted from storage facilities and marketing operations, crude oil vapors released from production and refining storage tanks, fugitive emissions from petroleum refining operations, architectural surface coatings, automotive spray painting, land fills and natural forest emissions. Detailed discussions of the development of these profiles are included in the following sections.

1. Gasoline storage and marketing--For the purpose of the ARB hydrocarbon inventory, a general emission profile suitable for use for both gasoline storage and marketing operations was desired. Such a profile was difficult to develop for several reasons. First there was the problem of determining a "typical" gasoline blend. There were eight major brands and numerous independent brands of gasoline marketed in the Basin (Ref. 2-14). Each of these brands generally had three grades of gasoline including regular, premium and unleaded. In addition, there were seasonal variations in the properties of each of these grades as reported in Ref. 2-15. Therefore, a composite gasoline blend properly accounting for each of these factors would have involved the incorporation of scores of gasoline samples. Furthermore, obtaining a representative sample from each stock required careful sample preparation with minimum vapor losses prior to analysis. The analysis of gasoline liquid and vapor constituents represented perhaps the most complex of GC/MS analytical procedures due to the large number of organic constituents (greater than 100) that were present. It was apparent, therefore, that such determinations of vapor constituent were beyond the budget of this study.

Data for the gasoline vapor emission profile were obtained primarily from 1974 ARB studies of gasoline compositions in the Basin (Ref. 2-14 and 15). The objective of that study was to investigate differences in composition of gasolines (liquid) that would influence emissions to the atmosphere both from evaporative losses and engine exhaust. A blend of 55% leaded regular, 38% leaded premium and 7% unleaded was prepared. These three types of gasoline had each been blended from samples taken from large volume retailers of the eight major brands as shown below in Table 2-12.

TABLE 2-12. GASOLINE SALES: PERCENTAGE OF TOTAL FOR MAJOR CALIFORNIA BRANDS

ARCO	14.0
Exxon	12.1
Gulf	7.0
Mobil	10.1
Shell	14.4
Standard	20.0
Texaco	9.4
Union	13.0
Total	100.0

The composition of the liquid and the vapor at 70 °F were determined and are presented in Table 2-13 as the emission profiles used for this inventory.

In selecting and validating these data it was noted that the samples of gasoline blended and analyzed had been purchased in mid September 1974 (Ref. 2-14). This means that the blend should have been representative of the gasoline sold during 1975, the base year of the inventory. The validity of blending and measuring as compared with analyzing individual products and averaging the results was proved by the ARB (Ref. 2-15A) when they analyzed six samples individually and calculated an average composition which they compared with the analysis of a composite mixture of the six blends. The results agreed compound by compound within 5-15%.

In this same study the ARB (Ref. 2-14) presented their GC analyses results for the blends of leaded premium, leaded regular and unleaded. The results for the leaded premium and regular were compared with results published in 1968 by WOGA in a gasoline marketing emissions study (Ref. 2-16). The agreement in composition was found to be very close. To validate the unleaded gasoline composition a calculation was made of a gasoline vapor

TABLE 2-13. EMISSION PROFILE FOR THE COMPOSITE AVERAGE GASOLINE LIQUID AND VAPOR AT 70 °F IN THE SOUTH COAST AIR BASIN - 1975 (REF. 2-14 AND 2-15)

	Weight %	
Compound	Liquid (Spills)	Vapor (Evap. Loss)
Propane	0.1	1.8
Isobutane	0.5	6.6
Butane	2.2	19.8
Butenes	0.4	1.8
Isopentane	8.0	29.0
Pentane	4.2	10.6
Pentenes	2.5	6.2
2-methylpentane	5.9	6.3
3-methylpentane	3.0	2.6
Hexane	3.8	2.5
Methylcyclopentane	3.6	2.1
Benzene	2.4	1.1
2,3-dimethylpentane	3.3	1.2
3-methylhexane	2.4	0.8
2,2,4-trimethylpentane	3.5	1.1
Heptane	2.5	0.6
Methylcyclohexane	1.1	0.2
Dimethylhexane	1.7	0.3
Toluene	9.7	2.1
Iso-octane	3.6	0.5
Octane	1.3	0.1
Isononane	1.2	0.2
m & p-Xylene	9.9	1.2
o-Xylene	3.6	0.4
Nonane	0.6	--
Propylbenzene	0.3	--
3-ehtyltoluene	6.5	0.5
1,2,4-trimethylbenzene	3.8	0.3
1,2,3-trimethylbenzene	1.4	0.1
Dimethylethylbenzene	2.7	0.1
Butylbenzene	1.7	--
> C_{10}	2.2	--

composition based on the published composition of the unleaded gasoline liquid. This calculation involved the use of the laws of partial pressures and the gas law. The resulting vapor composition was compared with measurements of unleaded gasoline vapor made in early 1977 in San Diego during an investigation by KVB on gasoline marketing vapor recovery systems. Table 2-14 presents a comparison of the two compositions. The two are similar except that the ARB composition had approximately nine percent olefins and cycloparaffins which were not found in the San Diego test gasoline. It was suspected that the San Diego tests were conducted using straight-run gasoline. Straight-run gasoline means that the gasoline was merely fractionated from the crude oil and not formed by a cracking process which tends to form unsaturated and cyclic compounds. Since most gasoline in the Basin is a blend of the cracked and straight-run gasoline, it was felt that the use of the ARB composition was appropriate.

TABLE 2-14. COMPARISON OF UNLEADED GASOLINE VAPOR COMPOSITIONS
WEIGHT PERCENT

	Measured*	Calculated from Liquid†	
Propane	3.7	2.2	
N-Butane	26.1	31.3	
I-Butane	11.8	12.3	
N-Pentane	12.2	6.9	
I-Pentane	27.8	24.8	
N-Hexane	3.9	1.0	
I-Hexane	7.1	6.1	
I-Heptane	4.4	1.7	
I-Octane	1.5	0.7	
Other	1.5	13.0	(olefins, cycloparaffins and aromatics)
Total	100.0	100.0	

*Sample collected from automobile gas tank fill pipe during filling operation and analyzed by GC as described in Section 3.0

†Vapor composition calculated from liquid composition reported by ARB in Reference 2-14.

2. Crude oil storage--Approximately 45% of the crude oil refined in the Basin is produced locally. The balance comes from several sources including domestic and foregin suppliers. There exist significant differences therefore between the crude oils stored in production and refining in the Basin and that involved in marketing operations. The following discussion is therefore divided into the three general areas of production, marketing and refinery operations.

a. Production operations--Results from the current inventory show that the organic compound emissions from crude oil storage at petroleum production operation account for 35 tons per day or approximately 5% of all anthroprogenic sources. The emission profiles for the vapors released from these sources were developed using data from the field tests conducted on this program and the results of a recently completed study on fixed roof tank emissions sponsored by WOGA (Ref. 2-8).

A summary of the data used to determine this profile is included in Table 2-15. Since data from Reference 2-8 did not identify "normal" and "isomer" compounds, the organic compounds for these tests have been identified as "normal". The layout of this table is similar to previous tables with the identification of the crude oils across the top and the organic compounds listed vertically. The numbers in each column represent the weight percent of that specie in the associated crude oil vapors.

As seen in Table 2-15, there was a wide variation in the organic constituents of the crude oil vapors within the study area. The composite emission profile was developed using the weighting factor listed with each crude oil which represents roughly the fraction of the total crude oil produced within the Basin according to the California Division of Oil and Gas (Ref. 2-17).

b. Refining operations--A similar procedure was used to develop an emission profile for crude oil storage associated with refining operations. A summary of the data used to calculate a composite profile is included in Table 2-16. The crude oil stored in refineries showd a much larger variation in vapor compositions reflecting the diverse origins in the crude oil.

TABLE 2-15. CRUDE OIL STORAGE, PETROLEUM PRODUCTION OPERATIONS

	Production Field										
	† Huntington Beach	† Saticoy	§ Rosecrans	§ Wilmington	§ Seal Beach	§ Ventura	§ Santa Fe Springs	§ Brea Olinda	§ South Mountain	§ Ojai	Composite
Fraction of Production	0.13	0.01	0.10	0.45	0.05	0.12	0.02	0.08	0.05	0.01	1.0
Organic Compound (wt. %)											
Methane	3.0	7.1	1.0	10.8	2.0	1.2	5.3	1.4	7.9	0.2	6.2
Ethane	6.7	17.6	1.9	6.7	1.9	2.6	15.4	2.0	9.2	2.1	5.6
Propane	20.2	30.8	12.6	18.1	12.5	19.6	19.7	9.5	25.5	8.4	17.6
N-Butane	19.9	19.5	24.7	27.4	25.6	34.5	26.2	30.7	26.5	30.9	27.1
I-Butane	11.0	9.9									1.5
N-Pentane	8.0	5.1	19.3	13.1	30.7	14.7	13.0	23.5	10.5	25.6	14.6
I-Pentane	11.1	5.8									1.5
Hexane	5.0	2.1	12.9	6.8	12.3	9.4	5.8	11.3	5.8	11.3	7.9
I-Hexane	0.8										--
Heptane			17.2	9.3	9.2	10.7	6.2	13.7	7.5	11.8	9.2
Octane*			10.4	7.8	5.8	7.3	8.4	7.9	7.1	9.7	6.9
C-7 Cycloparaffins	9.9	0.6									1.3
C-8 Cycloparaffins	3.5										0.5
Benzene	1.0	0.1									0.1
Cyclohexane											--
3-Methyl Pentane		1.4									--
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* C_8 +

† Tests conducted during the current project

§ Ref. 2-8

Data in Table 2-16 represented vapors collected from both fixed and floating roof tanks. However, insufficient data were available to allow a differentiation between vapors emitted from each tank type. Regulations by the SCAQMD require storage of petroleum liquids with a vapor pressure greater than 1.5 psia in floating roof tanks. Therefore, it would seem reasonable to assume that differences between the vapor composition for crude oils above and below this limit would exist.

c. Crude oil storage and transfer operations--Table 2-17 presents the data employed to determine a composite emission profile for crude oil storage and transfer operations primarily at marine terminals. Significant variations in the crude oil vapors were observed between the various samples analyzed. The data shown were taken from the WOGA Fixed Roof Tank Study (Ref. 2-8).

3. Refinery fugitive emissions--A significant portion of the field test program involved the measurement and evaluation of fugitive emissions from leaking valves and pumps in refineries. This was done both to assess the accuracy of emission factors (discussed in Section 2.3.1) but also to develop emission profiles "typical" of refinery operations. Recognizing that such an undertaking was subject to numerous complications including variations among crude oils and resulting products, differences between various refineries and the extremely complex nature of refinery processes in general, an attempt was made to meet this objective.

As discussed in Section 2.3.1, tests were conducted to characterize the emission rate from valve and pumps within petroleum refineries. To complement these efforts, numerous samples of leaking vapors were collected and analyzed. These analyses were believed to be as representative of leaks in refinery processing as is reasonably possible. As in the previous analyses, the problem became one of apportioning the leaks from various product lines to form a composite leak emission profile "typical" of all leaks from valves within a refinery.

Figure 2-1 presents a schematic view of a simplified refining process. Basically three types of products result from crude processing: gases, low-viscosity liquids, and high-viscosity liquids.

TABLE 2-16. CRUDE OIL STORAGE, PETROLEUM REFINING OPERATIONS

Organic Compound (wt. %)	Crude Sources					
	Foreign*	Domestic*	Domestic*	Domestic*	Unknown†	Composite
Methane	5.3	9.0	0.1	2.7	26.8	8.8
Ethane	4.5	6.0	2.1		0.9	2.7
Propane	17.1	26.0	20.6	7.3	9.7	16.1
N-Butane	18.6	26.0	22.7	15.4	21.7	20.8
I-Butane	10.7	11.0	15.5	9.5		9.3
N-Pentane	15.0	8.0	8.0		19.4	10.1
I-Pentane	13.4	8.0	12.3	22.2		11.2
Hexane	7.3	3.0	0.2		12.8	4.7
I-Hexane	5.2	2.0	1.0	17.1		5.1
Heptane	0.9		0.2		8.7	2.0
I-Heptane	2.0	1.0	8.1	14.0		5.0
I-Octane			1.9			0.4
Benzene			4.3	7.9		2.4
Toluene			3.0	3.9		1.4
	100.0	100.0	100.0	100.0	100.0	100.0

* Tests conducted for the program

† Ref. 2-8

TABLE 2-17. CRUDE OIL STORAGE, PETROLEUM MARKETING OPERATIONS

Organic Compound (wt. %)	Crude Source			
	Foreign	Foreign	Domestic	Composite
Methane	6.0	0.4	1.5	2.6
Ethane	8.1	1.1	2.0	3.7
Propane	15.0	19.3	13.0	15.8
Butane	31.1	33.7	25.7	30.2
Pentane	12.8	22.7	20.1	18.5
Hexane	7.4	9.7	9.3	8.8
Heptane	8.8	8.5	15.0	10.8
Octane +	10.8	4.6	13.4	9.6
	100.0	100.0	100.0	100.0

Ref. 2-8

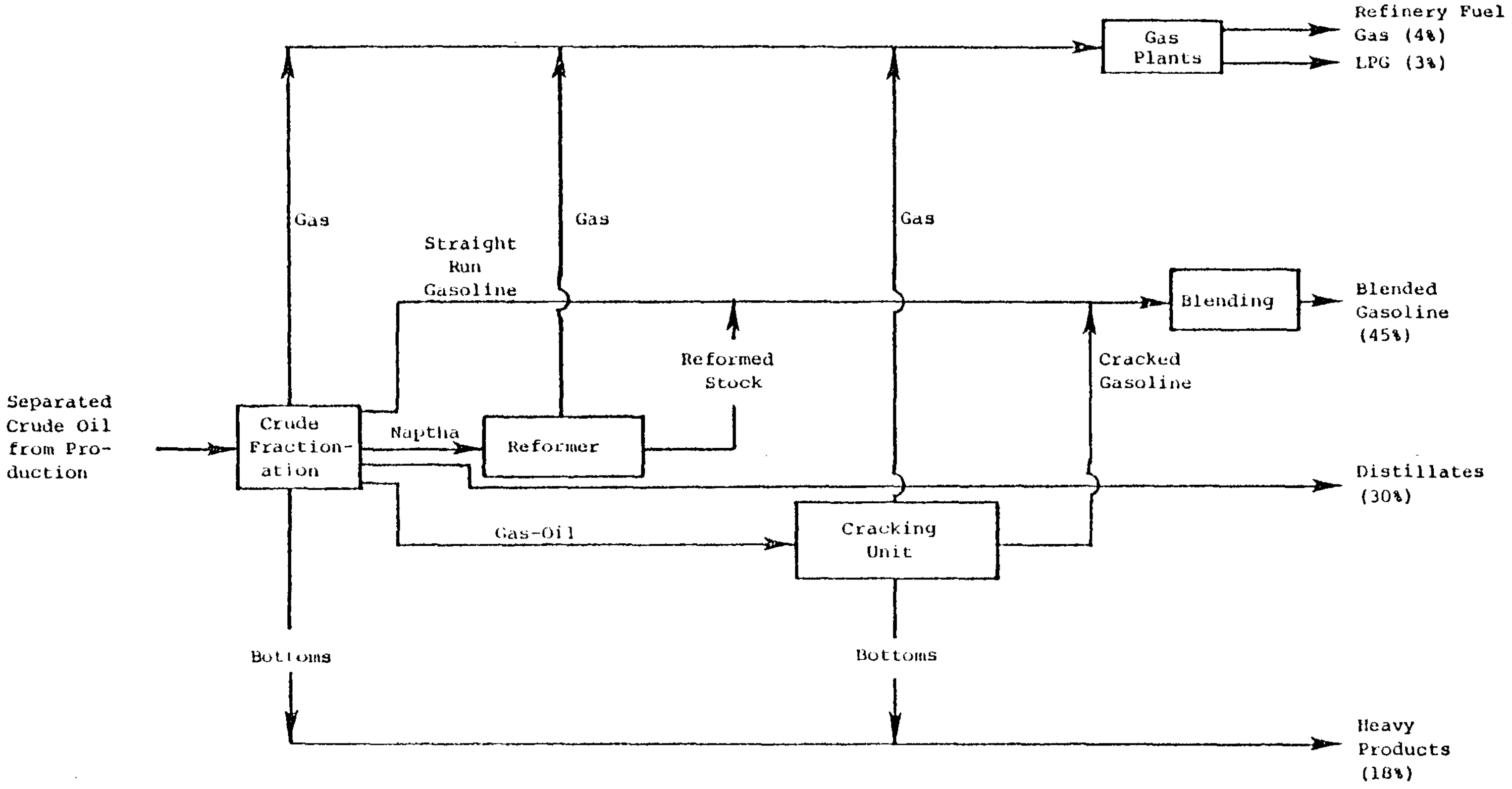

Figure 2-1. Refining process schematic.

The primary source of gaseous leaks was fuel gas lines. According to data issued by the SCAQMD, approximately 25% of the gas used in refineries is purchased natural gas. The balance is the refinery generated gas which varies from methane to butane.

Heavy liquids called "bottoms" were removed and used to form heavy fuel oils, coke and asphalt. For the purpose of this analysis and the subsequent analysis on fugitive emissions from pumps, it was assumed that the losses from product lines carrying heavy liquids were negligible. This assumption was verified by field tests conducted during this program and was thought to be due to either the leaks being self sealing or being so visible that maintenance is performed within a short time period.

The intermediate stream was composed of liquids that flow through various paths and ultimately ended up as gasoline and other petroleum distillates. There were interactions between these three product streams through the use of coking operations and vapor recovery which were intended to produce a higher fraction of gasoline and distillate products. Approximately 50% of the original crude oil (Ref. 2-18) that entered a refinery ultimately ended up as blended gasoline. As shown in Figure 2-1, this could have been through paths generating straight run gasoline, reformed stock or cracked gasoline to form the final gasoline products. Approximately 30% of the original crude became other distillate products.

a. Valves--As discussed in Section 2.3.1, the leak rate for valves in gaseous products was 0.424 lb/valve-day whereas the comparable leak rate for valves in liquid service was 0.022 lb/valve-day. Estimates (Ref. 2-13) of the total valves in gaseous and liquid service in refineries located in the Basin were 23.6% and 76.4% respectively. By applying these percentages to the associated leak rates it was determined that approximately 85% of leaks from valves result from those handling gaseous products.

Using the above information, a "typical" fugitive emission profile for valves was generated. Table 2-13 gives a summary of the calculation procedure. Listed are the analyzed emission profiles for leaks in various

TABLE 2-18. COMPOSITE PROFILE FOR REFINERY FUGITIVE EMISSIONS FROM VALVES

	Refinery Gas	Natural Gas	Straight Run Gasoline	Naphtha	Reformate Stock	Gas-Oil Stock	Cracked Gasoline	Distillate	Composite
Fraction of Emissions	0.64	0.21	0.015	0.015	0.015	0.03	0.03	0.045	
Organic Compounds (wt. percent)									
Methane	16.4	84.5				10.0		4.2	28.6
Ethane	5.1	11.0			0.9	3.8		1.0	5.8
Propane	15.9	3.6	0.2	0.6	13.9	3.3		5.3	11.5
Propylene		0.4							0.1
N-Butane	26.8	0.5	0.7	0.6	24.7	6.5	1.1	12.7	18.3
I-Butane	11.3		0.1					2.5	7.4
Butene							1.1		--
N-Pentane	9.4		1.3	1.3	21.5	7.4	19.7	11.0	7.7
I-Pentane	10.7			0.4		3.8	21.4	5.0	7.8
N-Hexane	2.8		3.2	6.2	19.3	11.8	15.4	9.0	3.4
I-Hexane	1.3		1.1	6.6		6.0	12.8	3.0	1.6
N-Heptane	0.1		1.4	1.8	10.0	8.3	14.9	8.6	1.4
I-Heptane	0.2		3.4			16.0		2.0	0.8
N-Octane			58.1	6.4	9.7	7.9		9.9	1.8
I-Octane			4.7	5.6			4.1	3.0	0.4
N-Nonane			2.8	8.3		4.4		6.5	0.6
I-Nonane			8.5	20.6			0.2	0.5	0.5
N-Decane						3.5		14.8*	0.8
I-Decane			2.6	16.6					0.3
C-7 Cycloparaffins			1.0	2.4			3.9		0.2
C-8 Cycloparaffins			0.2	0.6					--
C-9 Cycloparaffins			2.6	4.8			0.3		0.1
Toluene			3.2	6.2		7.3	3.0		0.5
Xylene			2.6	7.0			1.6		0.2
Benzene			1.4	2.5			0.5		0.1
Cyclohexane			0.9	1.5				1.0	0.1
	100	100	100	100	100	100	100	100	100

* C_{10},

product streams along with the estimated contribution from each to the total. For the purpose of this analysis it was assumed that the percentage of valves in liquid service are as follows:

Straight Run Gasoline	10%
Naphtha	10%
Reformate Stock	10%
Gas-Oil Stock	20%
Cracked Gasoline	20%
Distillate	25%

For this analysis, the distribution was not critical since the leaks from valves in liquid service constitute only 15% of the total emissions.

Because 85% of the emissions are from valves in gas service, the composition of the natural gas and refinery fuel gas had a very significant influence on the composite emission profile. A much more detailed analysis would have also incorporated leaks from other gaseous lines within the refinery however data on these internal gaseous stock transfer were not available.

b. Pumps--Tests were also conducted on 80 pumps to characterize emission rates from these fugitive sources. For the purposes of this analysis it has been assumed that leaks from pumps occur only from the liquid product lines as previously described. A summary of the calculation procedure is given in Table 2-19. As with valves, a much more complex analysis was possible; however, existing data are only sufficient to make a cursory estimate.

4. Architectural surface coatings--As described in Section 2.3.4, architectural surface coatings represented a significant source of organic compound emissions. These are comprised of the contribution of solvent from countless applications of surface coatings supplied by literally hundreds of paint manufacturers.

The approach used to establish a composite profile was to use the results of data generated by the AQMD and APCD's in the area. These agencies

TABLE 2-19. COMPOSITE PROFILE FOR REFINERY FUGITIVE EMISSIONS FROM PUMPS

	Straight Run Gasoline	Naphtha	Reformate Stock	Gas-Oil Stock	Cracked Gasoline	Distillate	Composite
Fraction of Emissions	0.10	0.10	0.10	0.20	0.20	0.30	
Organic Compounds (wt. percent)							
Methane				10.0		4.2	3.3
Ethane			0.9	3.8		1.0	1.2
Propane	0.2	0.6	13.9	3.3		5.3	3.7
N-Butane	0.7	0.6	24.7	6.5	1.1	12.7	7.9
I-Butane	0.1					2.5	0.8
Butene					1.1		0.2
N-Pentane	1.3	1.3	21.5	7.4	19.7	11.0	11.1
I-Pentane		0.4		3.8	21.4	5.0	6.6
N-Hexane	3.2	6.2	19.3	11.8	15.4	9.0	11.0
I-Hexane	1.1	6.6		6.0	12.8	3.0	5.5
N-Heptane	1.4	1.8	10.0	8.3	14.9	8.6	8.5
I-Heptane	3.4			16.0		2.0	4.1
N-Octane	58.1	6.4	9.7	7.9		9.9	12.0
I-Octane	4.7	5.6			4.1	3.0	2.8
N-Nonane	2.8	8.3		4.4		6.5	3.9
I-Nonane	8.5	20.6			0.2	0.5	3.1
N-Decane				3.5		14.8 *	5.1
I-Decane	2.6	16.6					1.9
C-7 Cycloparaffins	1.0	2.4			3.9		1.1
C-8 Cycloparaffins	0.2	0.6					0.1
C-9 Cycloparaffins	2.6	4.8			0.3		0.8
Toluene	3.2	6.2		7.3	3.0		3.0
Xylene	2.6	7.0			1.6		1.3
Benzene	1.4	2.5			0.5		0.5
Cyclohexane	0.9	1.5				1.0	0.5
	100	100	100	100	100	100	100

* C_{10}^{+}

had in their files all of the paint formulations and information on product sales within their jurisdiction. This information had been obtained directly from manufacturers and suppliers. Such an inventory was well beyond the scope of this study.

The most comprehensive architectural coating study was conducted by the San Diego APCD as described in the Appendix. The results of the SDAPCD study are summarized in Table 2-20. This table gives the total solvents that were contained in the architectural surface coatings marketed in San Diego County in 1974-75. This represented the most complete accounting of solvents used in this manner and was used to formulate the composite emission profiles for this inventory.

5. Automotive surface coatings--One of the largest sources of industrial solvent used in the Basin was surface coating operations associated with automotive assembly operations. Auto painting operations in the Basin include both water-based and oil-based formulations. An important aspect of the current test program was to document emissions from each of these sources to establish emission rates, compositions, and the effects of the water-based reformulation on possible control strategies.

Presented in Table 2-21 are the results of the test program conducted on the body priming and top coat operations for each of the coating types. The objective was to generate a composite emission profile representative of both water based and oil based coatings. Given also in Table 2-21 are the fractions of total emissions from each of the coating types. The composite emission profiles have been determined and are presented in Table 2-21.

6. Landfills--Table 2-22 presents the results of the samples of landfill gases collected during the current program. As expected, these gases were primarily methane with trace quantities of various other materials. Considering that there were approximately 1000 tons per day of total emissions from these sources (see Section 2.3.4) these trace quantities represented significant sources of each of the organic compounds to the atmosphere in excess of one ton per day.

TABLE 2-20. SOLVENTS USED IN ARCHITECTURAL COATINGS IN SAN DIEGO COUNTY (1974-75)

Solvent	lbs.	Solvent	lbs.
Acetone	324,315	Kerosene	554
Benzene	4,234	Methyl Amyl Ketone	681
iso-Butane	60	Methyl iso-Amyl Ketone	12,912
Butanol	158,340	Methyl Amyl Acetate	3,739
Butyl Acetate	257,417	Methyl Ethyl Ketone	571,769
iso-Butyl Acetate	130,443	Methyl n-Butyl Ketone	66,455
iso-Butyl Alcohol	60,985	Methyl iso-Butyl Ketone	59,043
Butyl Cellosolve	5,636	Methyl Heptyl Ketone	15,900
Butyl Cellosolve Acetate	25,881	Methylene Chloride	29,299
Butyl Lactate	129	Methanol	393,512
iso-Butyl iso-Butyrate	619,674	Monochlorobenzene	207
C_8+Aromatics	372,752	Monoethanolamine	2,870
Cellosolve Acetate	52,040	1 & 2 Nitro-propane	2,575
Cellosolve Solvent	75,212	Olefins	416
Cyclohexane	4,021	Paraffins & Naphthenes	4,169,717
Diacetone Alcohol	2,437	Pentoxone	3,876
Ortho-Dichlorobezene	1,309	n-Propanol	3,357
Diethylene Glycol	1,543	iso-Propanol	1,673,935
Dimethyl Formamide	51,529	n-Propyl Acetate	2,478
Dipentane	181	iso-Propyl Acetate	1,483
Ethanol	59,804	Propylene Carbonate	610
Ethyl Acetate	11,140	Propylene Glycol	74,462
Ethyl Amyl Ketone	663	Tetrahydrofuran	24
Ethyl Benzene	63,868	Triethanolamine	2,068
Ethylene Dichloride	1,144	Triethylene Glycol	1,323
Ethylene Glycol	62,513	Trichloroethylene	24
Hexane	303	Toluene	534,229
		Turpentine	6,088
		Xylene	269,177

TABLE 2-21. AUTOMOTIVE SPRAY BOOTH EMISSION PROFILE

	Type of Coating					
	Primer			Top Coat		
	Water-borne	Oil-borne	Composite	Water-borne	Oil-borne	Composite
Fraction of Emissions	0.3	0.7	1.0	0.1	0.9	1.0
Organic Compounds % wt						
Acetone	68.9		20.7	9.9		0.9
Benzene	22.2		6.6	16.0		1.6
Toluene	8.9		2.6	8.6		9.0
N-Heptane					0.4	0.4
I-Heptane					5.8	5.2
N-Octane		19.6	13.7		25.4	22.8
I-Octane		22.2	15.5		23.8	21.4
I-Nonane		37.1	26.0		16.4	14.8
Cyclohexane		2.2	1.5		7.4	6.7
C-7 Cycloparaffins		0	--		7.4	6.7
C-8 Cycloparaffins		8.0	5.6		10.9	9.8
C-9 Cycloparaffins		1.6	1.1		2.0	1.8
2 Methyl Pentane		8.7	6.1		0.5	0.5
3 Methyl Pentane		0.8	0.6			
Methane				39.6		3.9
Ethane				4.9		0.5
Ethyl Acetate				21.0		2.1

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TABLE 2-22. CLASS II LANDFILL SITE

	% by Wt.
Methane	98.6
Ethane	0.1
Propane	0.1
Cyclopentane	0.2
N-Butane	0.2
Iso-Butane	0.1
N-Pentane	0.1
Terpenes	0.1
Perchloroethylene	0.3
Toluene	0.1
Xylene	0.1
	100.0

7. Natural forest emissions--As discussed in Section 2.3.4, emissions from the natural interaction between forest vegetation and the atmosphere represented the largest source of organic compound emissions to the atmosphere, equaling approximately 1200 tons per day. These emissions had been identified by Rasmussen (Ref. 2-19) as consisting of terpenes. Specifically α pinene emissions had been associated with emissions from soft woods whereas hard wood tended to emit isoprene. However, since the identification and characterization of these emissions was far from complete a detailed profile development for the various forest types did not appear warranted. Therefore in this study, emissions from forest vegetation were identified simply as terpenes. Continued interest in those emission generated by additional verification of these emission rates and more complete identification of the organic compounds considered will no doubt result ultimately in a more detailed emission profile.

2.3.3 Solvent Use Questionnaires

Solvent use questionnaires were processed primarily to obtain information on the quantities and specific types of solvents used in the Basin during 1975 for use in developing emission profiles and factors. Other information on process equipment, control devices, future plans for modifications or expansion were also requested for checking the EIS data and forecasting emission trends.

KVB prepared the questionnaires using modified formats from Reference 2-20. Sections were specifically directed to the following solvent users:

- Degreasing Operations
- Dry Cleaning Operations
- Protective and Decorative Coatings
- Fabric and Rubberized Coatings
- Miscellaneous Coatings
- Ovens
- Printing Operations

Data were requested on an individual device basis using actual process records or best estimates from total plant consumption. Provisions for confidential or proprietary information were made. A copy of the organic solvent use questionnaire is presented in the Appendix.

Individual questionnaires were mailed to approximately 200 plants within the Basin with reported total organic compound emissions from solvent use in excess of 25 tons per year. Only the questionnaire forms that would pertain to the individual source operation were included. The response to these questionnaires was only 25% despite follow-up by telephone.

Of those returned, the quality and completeness of the information was excellent providing detailed information on solvent composition and operating parameters previously not available. Data were obtained from a wide cross section of industries which added depth to the data base. These data, along with updated solvent use patterns for those firms visited during the field test program have been incorporated into the final emission inventory.

2.3.4 Area Sources

An important aspect of the KVB organic compound inventory was the identification of sources of organic compound emissions not under permit and generally not included or adequately characterized in previous inventories. These sources were grouped as waste disposal, petroleum operations other than refining, domestic and agricultural sources, geogenic sources and natural emissions. Because these were diffuse sources not concentrated like industrial point sources, they are referred to as area sources. Emission factors for these sources were therefore based on land area, population, land use or other criteria characteristic of the area source.

Table 2-23 presents a summary of total hydrocarbon emission estimates from each of the area sources considered. Precise emission rates were difficult if not impossible to estimate due to the complex nature of each source type. A discussion of realistic limits to these values is presented in subsequent sections.

A second objective of the current project was to locate these area sources geographically in the Basin. To this end, information was secured from various governmental agencies on population distribution, land use, petroleum production operations, etc. Maps corresponding to the approximate location of each source were developed for each source. Area sources based on population were distributed on a per capita basis based on information received from the ARB.

The following sections present a discussion of the methodologies and references used in making these estimates. In general, the procedure involved the establishment of two factors, (1) an emission factor coupled with (2) an appropriate inventory. Using this procedure, improvements to either factor can be readily employed to improve future estimates.

It must be pointed out that the emission factors and inventories presented were developed for use in this study of the California South Coast Air Basin and are not necessarily appropriate or applicable to other study areas. Caution must be exercised in their application to other study areas.

A. Waste Disposal--

1. Agricultural burning--The organic compound emissions from the burning of agricultural wastes in California have been recognized for several years (Ref. 2-21). The ARB and the EPA have sponsored several on-going studies (Refs. 2-22, 2-23, 2-24) with the intent of developing emission factors for such operations.

TABLE 2-23. EMISSION ESTIMATES FOR AREA SOURCES (STATIONARY SOURCES ONLY)

	Tons/Day
Waste Disposal	
Agricultural Burning	2
Sanitary Landfills	900
Petroleum Operations	
Production Operations	70
Marine Terminals	3
Gasoline Marketing	80
Natural Gas Transmission	80
Domestic and Commercial Sources	
Architectural Surface Coatings	100
Solvent Use	30
Fuel Consumption	5
Agricultural	
Natural Emissions	15
Orchard Heaters	3
Animal Wastes	80
Pesticides	15
Geogenic Sources	
Natural Seeps	10
Forest Emissions	
Natural Emissions	300*
Forest Fires	40
Other Sources	
Dry Cleaning	25
Asphalt Paving Operations	1

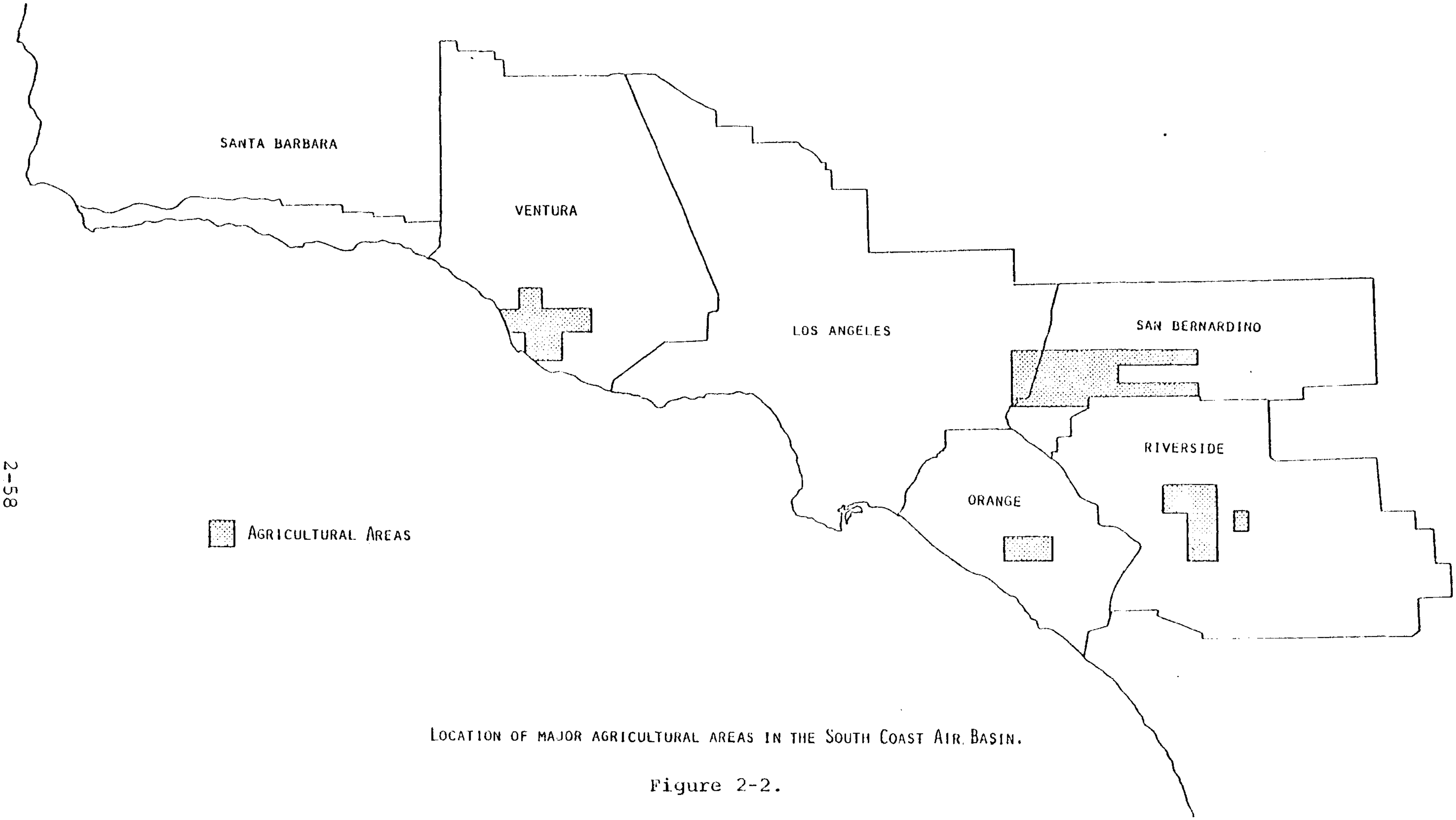
*An additional 200 tons/day is released above the inversion layers at altitudes above 3500 ft.

The ARB and local districts have also implemented regulations that severely restrict the open burning of waste materials. Existing regulations (Ref. 2-25) require burn permits to be issued by local government control agencies prior to the burning of farm wastes, burns conducted for range improvement, forest management, pest control or the improvement of wildlife or game habitats. Such burns can only be conducted during "permissive burn" days as determined by local meteorological conditions. Burn permits recorded the location and quantity of material to be burned.

Annual reports by the ARB were issued with estimates of the air pollution impact of these burns utilizing this inventory and the emission factors referred to above. It was estimated by the ARB that 550 tons of organic compound vapors were emitted in 1975 due to agricultural burning in the South Coast Air Basin. These emissions were distributed into the agricultural regions shown in Figure 2-2. The apportionment of these emissions were made based on the data on agricultural waste generation reported in the various county solid waste management plans and presented in Table 2-24.

2. Sanitary landfills--As shown in Table 2-25, over 15 million tons of liquid and solid wastes were disposed annually in the 45 major landfill sites distributed within the Basin as shown in Figure 2-3. Several studies (Refs. 2-26, 2-27) indicated that appreciable amounts of methane rich gas are generated due to the biological anerobic decomposition of these wastes. The production rate of this gas appeared to be highly dependent on the type, liquid content, soil composition and age of the particular site. These gases represent not only a potential source of useful energy but a large, currently uncontrolled source of organic compounds to the atmosphere.

No precise estimate of the emissions from landfill operations for the study area existed. Results from the above mentioned references and field tests during the current program were used to estimate the emissions from these sources. Three approaches were available. The first was to use the results from a recent study (Ref. 2-28) concerned with recovering these gases. Generally it was assumed that 3-6 cubic feet of methane gas are generated over the total period of decomposition for each pound of refuse.



LOCATION OF MAJOR AGRICULTURAL AREAS IN THE SOUTH COAST AIR BASIN.

Figure 2-2.

TABLE 2-24. AGRICULTURAL WASTE PRODUCTION IN THE SOUTH COAST AIR BASIN AND VENTURA COUNTY

	County				
Agricultural Wastes* (Tons/Year)	Ventura	Los Angeles	Orange	Riverside[†]	San Bernardino[†]
Fruit & Nut Crops	107,644	--	--	139,800	87,400
Field & Row Crops	30,900	60,000	112,000	765,000	9,800
Vegetable	481,800	--	--	--	--
Total	620,344	60,000	112,000	904,800	97,200

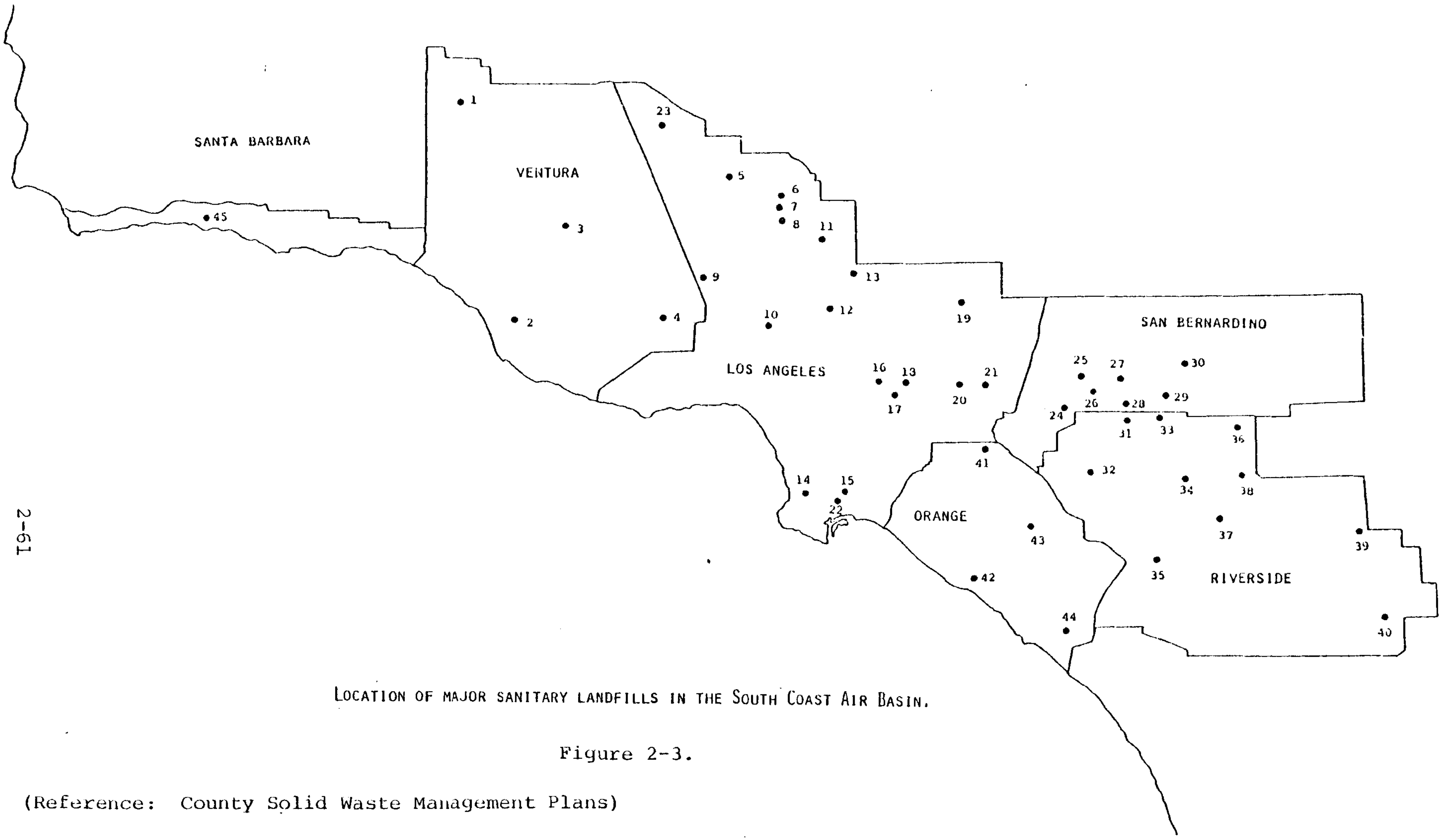
*Data from the county solid waste management plans.

[†] Totals only available for counties as a whole.

TABLE 2-25. EXISTING MAJOR CLASS I AND II SANITARY LANDFILL SITES IN THE SOUTH COAST AIR BASIN

(Reference - County Solid Waste Management Plans)

Quantity of Waste Received	Class	Reported Acreage	Tons/Year Liquid	Solid	Total
Ventura County, 1975					
1. Ozeha	II			- 1,086 -	1,086
2. Santa Clara	II	47		- 434,400 -	434,400
3. Toland Road	II	120		- 36,200 -	36,200
4. Simi	I	230		- 144,800 -	144,800
All Other Class II Sites		60		- 167,400 -	167,400
Total		457			783,886
Los Angeles County, 1974					
5. N. Valley Refuse Center	II	230	-	550,000	550,000
6. Bradley Avenue Dump	II	63	-	332,000	332,000
7. Penrose Pit	II	73	-	398,000	398,000
8. Hewitt Pit	II	117	-	436,000	436,000
9. Calabasas Land Fill	I	416	36,000	320,000	356,000
10. Mission Canyon Land Fill	II	1,491	-	1,394,000	1,394,000
11. Burbank City Land Fill	II	133	-	75,000	75,000
12. Toyon Canyon Land Fill	II	40	-	795,000	795,000
13. Scholl Canyon Land Fill	II	484	-	450,000	450,000
14. Palos Verdes Land Fill	I	295	280,000	1,300,000	1,580,000
15. Ascon	II	65	85,000	422,000	507,000
16. Operating Industries	II	190	177,000	589,000	766,000
17. City of Whittier Land Fill	II	117	-	107,000	107,000
18. Puente Hills Land Fill	II	1,214	17,000	1,165,000	1,182,000
19. Azusa Western	II	307	-	271,000	271,000
20. B.K.K. Land Fill	I	583	254,000	352,000	606,000
21. Spadra Land Fill	II	199	13,000	192,000	205,000
22. Harbor Dump	II	25	-	160,000	160,000
23. Chiquita Canyon Land Fill	II	40	-	33,000	33,000
All Other Minor Class II Sites		N.R.		56,050	56,050
Total		6,082	362,000	9,341,000	10,203,000
San Bernardino County, 1974					
24. Milliken	II	106	-	215,500	215,500
25. Cajon	II-2	106	1	- 117,500 -	117,500
26. Fontana	II	82	-	64,000	64,000
27. Heaps Peak	II	63	-	16,600	16,600
28. Colton	II	94	-	93,700	93,700
29. Yucaipa	II	560	-	34,600	34,600
30. Big Bear	II	70	-	11,600	11,600
Total		1,081			553,500
Riverside County, June 1975					
31. West Riverside	II-2	63	-	- 52,700 -	52,700
32. Corona	II-2	101		- 88,350 -	88,350
33. Highgrove	II-2	280	-	8,100	8,100
34. Mead Valley	II-2	240	-	8,100	8,100
35. Elsinore	II-2	44	-	12,400	12,400
36. Badlands	II-2	904	-	15,500	15,500
37. Double Butte	II-2	580	-	61,380	61,380
38. Lanb Canyon	II-2	788		- 48,050 -	48,050
39. Idyllwild	II-2	30	-	- 3,010 -	3,010
40. Anza	II-2	10	-	1,550	1,550
Total		3,040			299,140
Orange County, December 1975					
41. Olinda	II	235	-	758,000	758,000
42. Coyote Canyon	II	593	-	2,130,000	2,130,000
43. Santiago Canyon	II	160	-	374,000	374,000
44. Prina DeSchecha	II	945	-	478,000	478,000
Total		1,933		3,740,000	3,740,000
Santa Barbara, 1975					
45. Tajiguas	II	130	-	202,900	202,900
GRAND TOTAL		11,580			15,782,426



LOCATION OF MAJOR SANITARY LANDFILLS IN THE SOUTH COAST AIR BASIN.

Figure 2-3.

(Reference: County Solid Waste Management Plans)

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Assuming the lower figure, this represents a 13% conversion by weight of waste to generated organic vapors. For the 15 million tons of refuse deposited annually, this represented 2 million tons of methane gas or nearly 5500 tons per day, assuming that the decomposition period was one year.

The second approach used estimates of the rates of carbon escape over the "life" of the fill presented in a study by the California State Water Quality Control Board (Ref. 2-29). Using this study, it was found that

$$r = \frac{177}{3.75 + 1.95t}$$

where r = rate of carbon escape (lb/ton refuse·year)
t = age of refuse (years)

Note that carbon is released as both methane and carbon dioxide gas. To use this relation, a gross estimate of the total quantity and age of wastes presently "alive" in the Basin was needed. It was assumed for the purpose of this estimate that the quantity of materials disposed in landfills over the last 75 years was constant and therefore proportional to the total population with the Basin. A summary of the resulting computation using the above relation and the assumed age and quantity of refuse alive in the Basin is given in Table 2-26. As shown in Table 2-26, 90% of the carbon emission result from deposits made in the last 25 years. Assuming 15% by weight of the total carbon emitted is transformed to methane (Ref. 2-29), this would represent 340,000 tons per year or approximately 930 tons per day of methane emissions.

The third approach employed test data generated by KVB during the current test program. Utilizing techniques described in Section 3.0, it was estimated that 1500 lb/acre·yr of gas were evolved from landfills. This represented 240 tons/day from the 46 sites in the Basin. This however represents the results from only two tests on relatively small landfill surface areas of indeterminable composition and history.

TABLE 2-26. SUMMARY OF COMPUTATION OF TOTAL CARBON RELEASE FROM ACTIVE LANDFILL SITES DURING 1975*

Period	t (yr)	r (lb c/ton refuse)	% of 1975 Refuse (based on population)	Refuse Quantity for Period (10^6 tons)	Total Carbon Emissions in 1975 (10^6 lb)
1970-75	2.5	20.52	98	76.3	1566.49
1965-70	7.5	9.63	92	71.7	690.14
1960-65	12.5	6.29	83	64.7	406.68
1955-60	17.5	4.67	70	54.5	254.65
1950-55	22.5	3.72	55	42.8	159.38
1945-50	27.5	3.08	44	34.3	105.57
1940-45	32.5	2.64	35	27.3	71.98
1935-40	37.5	2.30	28	21.8	50.17
1930-35	42.5	2.04	23	17.9	36.55
1925-30	47.5	1.84	18	14.0	25.80
1920-25	52.5	1.67	13	10.1	16.91
1915-20	57.5	1.53	8	6.2	9.53
1910-15	62.5	1.41	4	3.1	4.39
1905-10	67.5	1.31	2	1.6	2.04
1900-05	72.5	1.22	1	0.8	0.95
Total				447.1	3401.23

*(Ref. 2-29)

For the final organic inventory, the second approach was selected because it appeared to have the most data to substantiate the emission factors. It was evident, however, that regardless of the approach used, the organic compound emissions from these sources were appreciable.

B. Petroleum Operations--

1. Production operations--As shown in Table 2-27, extensive petroleum production operations were underway in the Basin. Nearly 150 million barrels of crude oil and 116 billion cu.ft. of natural gas were produced in 1975 (Ref. 2-17). For this inventory only onshore production operations were considered. These production facilities were distributed throughout the study area as shown in Figure 2-4.

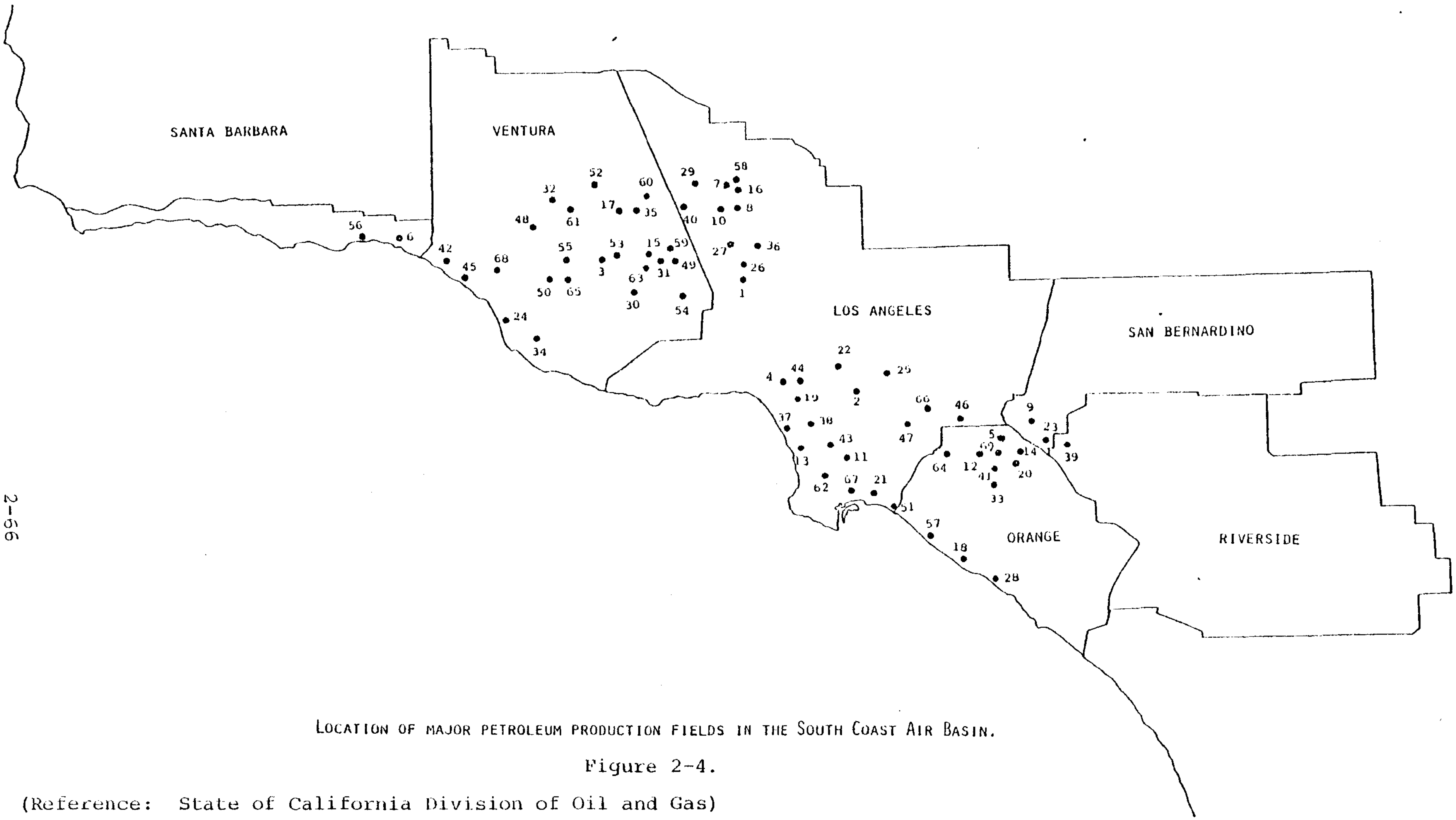
Prior to this ARB study, the magnitude and composition of organic compound emissions from production operations other than tank storage were essentially unknown. Tests were conducted at two locations recommended by the Western Oil and Gas Association as typical of such operations in the Basin. Since only brief test programs were possible during the current program, the emission factors developed should be considered as representative and useful for estimating purposes only. Discussion of the test procedures employed and the emission factors developed is included in Sections 2.3 and 3.0.

A summary of the emission factors and inventories used in the current study are given in Table 2-28. These inventories were made based on data from the California Department of Oil and Gas (Ref. 2-17), data from SCAQMD (Ref. 2-6) and numerous discussions with representatives of the major petroleum production companies operating in the Basin. It must be emphasized that these represented data for the study area only and should not be applied arbitrarily to any other situation. Confidence factors on a scale of A to E (A-high, E-poor) were also assigned to assist in the evaluation of these data.

TABLE 2-27. PETROLEUM PRODUCTION FIELDS IN THE SOUTH COAST AIR BASIN (1975)

(Reference: California Division of Oil and Gas)

		Average Number of Producing Wells	Oil Production 10^3 Bbl/yr	Gas Production 10^6 ft^3/yr
1.	Aliso Canyon	90	670	38,413
2.	Bandini	32	141	207
3.	Bardsdale	93	154	616
4.	Beverly Hills	179	5,141	7,168
5.	Brea-Olinda	736	3,185	4,136
6.	Carpenteria	61	1,452	1,730
7.	Casataic Hills	27	44	85
8.	Casataic Junction	27	473	1,806
9.	Chino-Sequel	8	5	-
10.	Delle Valley	33	99	1
11.	Dominques	132	1,035	503
12.	East Coyote	152	721	342
13.	El Segundo	6	37	19
14.	Esperanza	13	23	-
15.	Eureka	14	32	1
16.	Honor Ranch	15	140	328
17.	Hopper Canyon	9	96	109
18.	Huntington Beach	1,108	17,167	3,999
19.	Inglewood	441	3,580	1,788
20.	Kraemer	79	1,686	14
21.	Long Beach	623	2,594	1,562
22.	Los Angeles	46	52	858
23.	Mohala	34	143	47
24.	Montalvo	51	587	1,311
25.	Montebello	216	675	522
26.	Newhall	42	39	9
27.	Newhall-Potrero	80	444	7,699
28.	Newport	239	1,425	40
29.	Oak Canyon	19	185	293
30.	Oak Park	15	32	12
31.	Oakridge	20	207	81
32.	Ojai	138	1,127	1,814
33.	Olive	8	56	22
34.	Oxnard	92	368	281
35.	Piru	7	3	-
36.	Placentia	169	296	-
37.	Playa Del Rey	52	70	15
38.	Potrera	18	129	130
39.	Prado-Covona	13	69	32
40.	Ramona	101	179	384
41.	Richfield	257	1,666	138
42.	Rincon	311	2,919	3,729
43.	Rosecrans	115	503	589
44.	Salt Lake	57	1,019	761
45.	San Miquleto	62	1,794	882
46.	Sansinena	116	736	1,151
47.	Santa Fe Springs	216	709	688
48.	Santa Paula	17	10	2
49.	Santa Suzana	13	151	1,826
50.	Saticoy	33	200	150
51.	Seal Beach	173	1,205	355
52.	Sespi	182	1,085	1,380
53.	Shields	77	350	93
54.	Simi	39	42	17
55.	South Mountain	437	1,548	2,663
56.	Summerland Off Shore	22	259	1,328
57.	Sunset Beach	5	12	-
58.	Tapia	12	20	-
59.	Tapo	25	54	6
60.	Temescal	16	67	11
61.	Timber Canyon	25	90	260
62.	Torrence	388	2,859	1,421
63.	Torrey Canyon	41	207	2,659
64.	West Coyote	144	2,039	184
65.	West Mountain	23	50	77
66.	Whittier	208	693	669
67.	Wilmington	2,285	65,595	11,808
68.	Ventura	787	10,943	6,776
69.	Yorba Linda	486	3,726	11
	TOTALS	11,810	145,162	116,031



Location of major petroleum production fields in the South Coast Air Basin.

Figure 2-4.

(Reference: State of California Division of Oil and Gas)

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TABLE 2-28. PETROLEUM PRODUCTION EMISSION FACTORS AND INVENTORIES

Source	Units	Emission Factor	Inventory	Emission Estimate† (tons per day)	Confidence Level
Crude Oil Storage Tanks	--	*	1650 tanks	34	B
Process Drains	lb TOC/rod pump well-day	2.0	8000 rod pump wells	8	D
Oil/Water Separators	lb TOC/ft^2-day	0.1	184,000 ft^2	9	C
Fugitive Leaks from Valves	lb TOC/valve-day	0.10	150,000 valves	8	B
Pump Engine Exhausts	lb TOC/10^6 ft^3	1400	4250x10^6 ft^3/yr	8	C
Heaters and Boiler Exhausts	lb TOC/10^6 ft^3	30.0	5100x10^6 ft^3/yr	0	C
TOTAL				67	

* Emissions estimated by local control agenices using API 2518, adjusted to 60% of this using the analysis contained in Section 2.3.1.

† Emissions have been rounded to the nearest ton per day.

As shown in Table 2-28, petroleum production operations represented approximately 68 tons per day of which 50% were from storage tanks. The balance were primarily fugitive emissions from leaking valves and metal connections and evaporation from standing oil.

2. Marine terminals--As shown in Table 2-29, significant quantities of petroleum products were transferred through marine terminals in the Basin. These generally represented (1) crude oil loading off the Santa Barbara and Ventura coasts, (2) crude oil delivery to refineries in Los Angeles County and (3) refined product loaded at the Los Angeles and Long Beach Harbors and the El Segundo Marine Terminal as illustrated in Figure 2-5. A description of the various marine facilities within the study area can be found in Reference 2-30.

TABLE 2-29. MARINE TRANSFER OPERATIONS IN THE SOUTH COAST AIR BASIN

	Quantity (10^6 gal)	Emission Factor ($lb/10^3$ gal)	Emission Rate (Ton/Yr)
Loaded			
Fuel Oils	1304	0.0002	0.1
Gasolines	384	2.5	480.0
Distillates	881	0.005	2.2
Crude Oils	754	1.20	452.4
Lube Oils	29	< 0.001	0.0
Petrochemicals	57	0.56	16.0
			950.7
Unloaded			
Fuel Oil	951	--	--
Gasolines	627	-- (Not determined	--
Distillates	433	-- - mobile	--
Crude Oils	7724	-- sources)	--
Lube Oils	86	--	--
Petrochemicals	17	--	--

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Considerable interest was raised concerning the magnitude of these emissions. Several studies directly applicable to this program were initiated. These involved a WOGA/Chevron crude oil loading program in Santa Barbara and Ventura Counties (Ref. 2-31) and a SOHIO product transfer program in the Los Angeles/Long Beach Harbor area (Refs. 2-32, 2-33).

Emission factors for crude oil loading ranged from 0.5 to 2.0 lb/10^3 gal (Ref. 2-10) and appeared to be a function of the condition and cleanliness of the tanker prior to loading as well as the properties of the crude being loaded. For the purpose of this inventory, an emission factor of 1.2 lb/10^3 gal proposed by Laird (Ref. 2-34) and used by both the Santa Barbara and Ventura APCD's has been employed. Total organic compound emission rates based on this emission factor are presented in Table 2-29.

The loading of refined petroleum products had received much less recent investigation. Estimates of loading loses were made using a formula developed by API (Ref. 2-35):

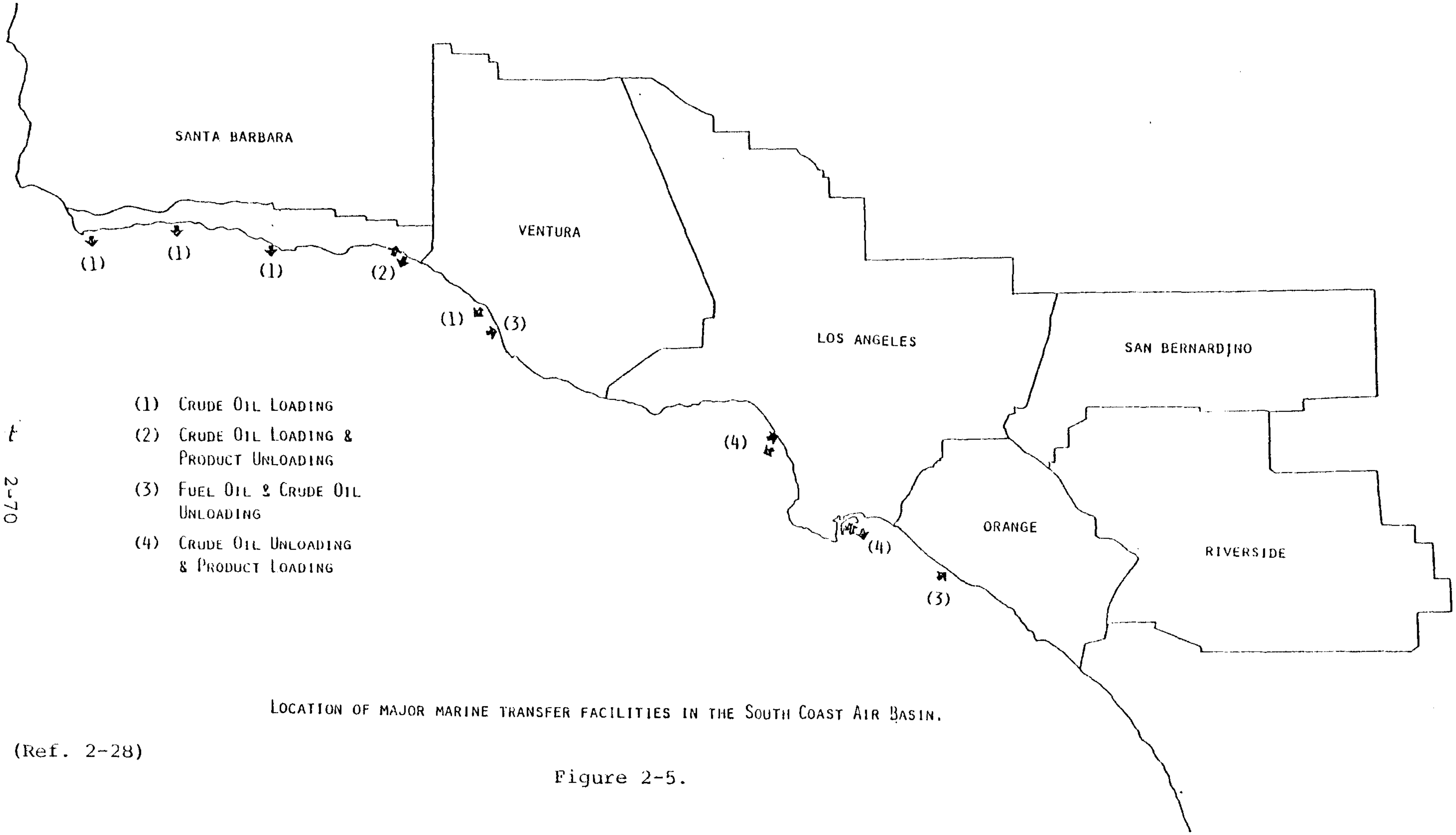
$$L = 0.3\ PW$$

where

L = loading loss lb/10^3 gal of load
P = true vapor pressure at storage temperature, psia
W = density of liquid at storage temperature, lb/gal

Inventories of the total product throughput in the harbors were obtained from the Corps of Engineers (Ref. 2-36). These inventories together with the above emission factor were employed to generate the emission rates given in Table 2-29.

Additional emissions resulting from what is generally termed "unloading losses" were considered and discarded. The great majority of these losses resulted from shipboard operations including bilging and venting which take place at sea as well as within the harbor area. Since these operations are small and more appropriately considered as "mobile sources," they are not included in the current inventory.



Location of major marine transfer facilities in the South Coast Air Basin.

(Ref. 2-28)

Figure 2-5.

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3. <u>Gasoline marketing</u>--Organic compound emissions from the transfer of gasoline to automobile tanks has been recognized as a major source of emissions to the atmosphere and has been studied extensively. Control measures were being implemented in counties in Southern California to reduce these emissions through vapor recovery techniques at both the tanker truck to storage tank transfer (Phase I) and the nozzle to vehicle tank transfer operations (Phase II). Phase I had been essentially completed within the Basin whereas Phase II operations had yet to be started at the time of this study. A description of both Phase I and II operations is presented in Section 4.0.

Emission factors have been recently revised (Ref. 2-10) to reflect additional test data on gasoline marketing operations and the effectiveness of these control measures. The emission factors used in this study (given in Table 2-30) represent not only information from Reference 2-10, but also discussions with representatives of the EPA and the San Diego County APCD, one of the most active of the local control agencies in assessing the validity of these emission rates and effectiveness of Phases I and II control measures. Note that the emission factor for submerged filling of underground tank (controlled) is 0.7 lb/10^3 gal. throughput which represents a 90% control efficiency, rather than the AP-42 (Ref. 2-3) value of 0.3 lb/10^3 gal. throughput which would represent a control efficiency of 95%. The 95% control efficiency is believed to be too high.

TABLE 2-30. GASOLINE MARKETING EMISSION FACTOR

Emission Source	lb/10^3 Gal Throughput
Submerged Filling of Underground Tank (Controlled)	0.7
Underground Tank Breathing	1.0
Vehicle Refueling Displacement Loss (Uncontrolled)	9.0
Vehicle Refueling Spillage Loss	0.7

These emission factors have been incorporated with an estimate of gasoline sales in the Basin generated for this program. Estimates by the California Board of Equalization (Ref. 2-37) indicated that 52% of the total gasoline sales in the state occurred in the six counties comprising the study area. This amount was corrected to account for the population of those counties which have areas outside the Basin. A summary of this calculation is presented in Table 2-31. This procedure resulted in an estimate of 5.3 billion gallons of gasoline sold annually in the Basin. Applying the appropriate emission factors from Table 2-30 resulted in an average daily emission rate of organic compounds from this source of 83 tons per day.

These emissions have been distributed by estimated sales and location of service stations as described in Section 2.2.2. Information on the sales from individual stations was available for Ventura and Santa Barbara Counties generated by surveys conducted by the local APCD's. Additional information on gasoline sales for specific service stations in Los Angeles County was available in Reference 2-39, however not in a form suitable for processing.

4. Natural gas distribution--The average daily consumption of natural gas by all sources in the South Coast Air Basin is in excess of 1.5 billion cubic feet. Although precise measurements are not available, the Southern California Gas Company (Ref. 2-40) estimated that of this total, 3.7 million cubic feet (0.25%) or 83 tons per day were lost to the atmosphere as fugitive emissions from valves, flanges and other metal connections as well as pipe failures or required maintenance works.

This estimate was made by SCGC by taking the difference between purchased gas that enters the system and the total sales volume from all users less internal SCGC usage. Of the remainder, 25% were assumed lost as fugitive emissions and the balance as metering inaccuracies.

These emissions have been distributed throughout the Basin on the basis of population. This generally reflects the location of transfer facilities and especially meters and their metal connections which have been shown to be the most prevalent source of fugitive emissions.

TABLE 2-31. COUNTY GASOLINE SALES

1976 Total State Sales - 10,756,387,557 Gallons of Gasoline*

County	% of Total State Sales*	Annual Sales gallons x 10^6	Total Population	Population in SCAB †	% of Population in SCAB	Total Sales in SCAB x 10^6 gal/yr
Los Angeles	34.25	3,684.063	6,963,604	6,884,933	98.87	3,642.284
Orange	7.64	821.788	1,722,042	1,722,042	100	821.788
Ventura	1.79	192.539	442,060	422,060	100	192.539
San Bernardino	3.92	421.650	701,220	578,409	82.49	347.803
Riverside	2.86	307.633	534,726	383,945	71.80	220.887
Santa Barbara	1.41	151.665	281,294	162,294	57.70	81.504
						5,312.805

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*Ref. 2-37.

†Ref. 2-38.

C. Domestic and Commercial Sources--

Over 10 million people reside in the Basin. Therefore sources of organic compound such as domestic fuel burning, solvent use, dry cleaning and surface coatings which may appear to be small for each individual, can collectively represent large sources of organic emissions. Emission factors were developed on this program on a per capita basis and were distributed by population.

1. Architectural surface coatings--Estimates of the total volume of coatings applied to the surface of stationary structure and marketed within the Basin was difficult to make due to the large number of manufacturers and suppliers involved. The most effective approach was to use marketing questionnaires. This proved to be very time consuming and costly operation without the legal authority to require responses by those questioned.

Surveys that were performed by the local control agencies in California showed that emissions of organic compounds from architectural surface coating applications were from 3.4 to 3.7 tons/1000 people/year (Ref. 2-41). The ARB estimated that 93 tons per day of emissions result from architectural coating within the Basin (Ref. 2-42) for annual emission factor of 3.3 tons per 1000 people. In the same study it was estimated that total emissions from architectural coating for the entire state amounted to 193.7 tons per day or an annual emission factor for the state of 3.3 tons per 1000 people consistent with the estimate for the South Coast Air Basin. Thus 3.3 tons/1000 people/year was used in this inventory resulting in total emissions within the study area of 97.6 tons per day.

2. Domestic solvent use--Numerous products used in residences, commercial establishments and industrial plants contain organic solvent materials. Such products included cleaning compounds, floor waxes, cosmetics, and health and beauty aids used in homes and commercial establishments (barber and beauty shops, shoe repair shops, etc.) and institutions (schools, hospitals, churches, etc.). The total contribution of solvent evaporation from these products had not heretofore been attempted. Due to the large potential for organic emissions, it was felt necessary to determine its magnitude.

Two approaches were used. The first consisted of obtaining information on product sales from a limited number of retail establishments in Orange County. These sales data were divided by the approximate consumer population for that establishment and an emission factor on a per capita basis was obtained.

The second approach used data from the Department of Commerce (Ref. 2-43) on the total value of these products manufactured nationally. A national use factor was then determined by dividing the total value by wholesale prices for each product. These wholesale prices were determined by KVB through a limited survey of local retail establishments and contacts with major manufacturing sales representatives. No itemized wholesale price information was available. A summary of the estimated national sales and solvent composition is presented in Table 2-32.

Both approaches yielded an annual emission factor for all products of approximately 1.1 tons per 1000 people. This corresponds to an emission rate of 31 tons of total organic vapors per day released within the Basin.

3. Domestic and commercial natural gas fuel consumption--Over 410 billion cubic feet of natural gas were consumed annually by domestic and commercial users within the study area (Refs. 2-40, 2-44). An emission factor of 8 lb per million cubic feet (Ref. 2-4) was used which corresponded to an emission rate of 4.5 tons per day and an annual emission factor of 0.16 tons per 1000 people.

D. Agricultural Sources--

1. Natural citrus emissions--Studies have shown that significant quantities of terpenes are emitted as part of the natural biological cycle of citrus trees. An emission factor of 0.06 tons per year per acre of citrus trees was proposed by Zimmerman (Ref. 2-45).

There were approximately 85,000 acres of citrus trees in the Basin which were distributed by specific type and county as shown in Table 2-33 (Ref. 2-46). Using this inventory and the emission factor it was estimated that 13.9 tons per day of organic compounds were emitted to the atmosphere each year by this source.

These emissions were distributed into approximate areas of major citrus growing activity as shown in Figure 2-6 based upon information obtained from Citrus Industry representatives (Ref. 2-47).

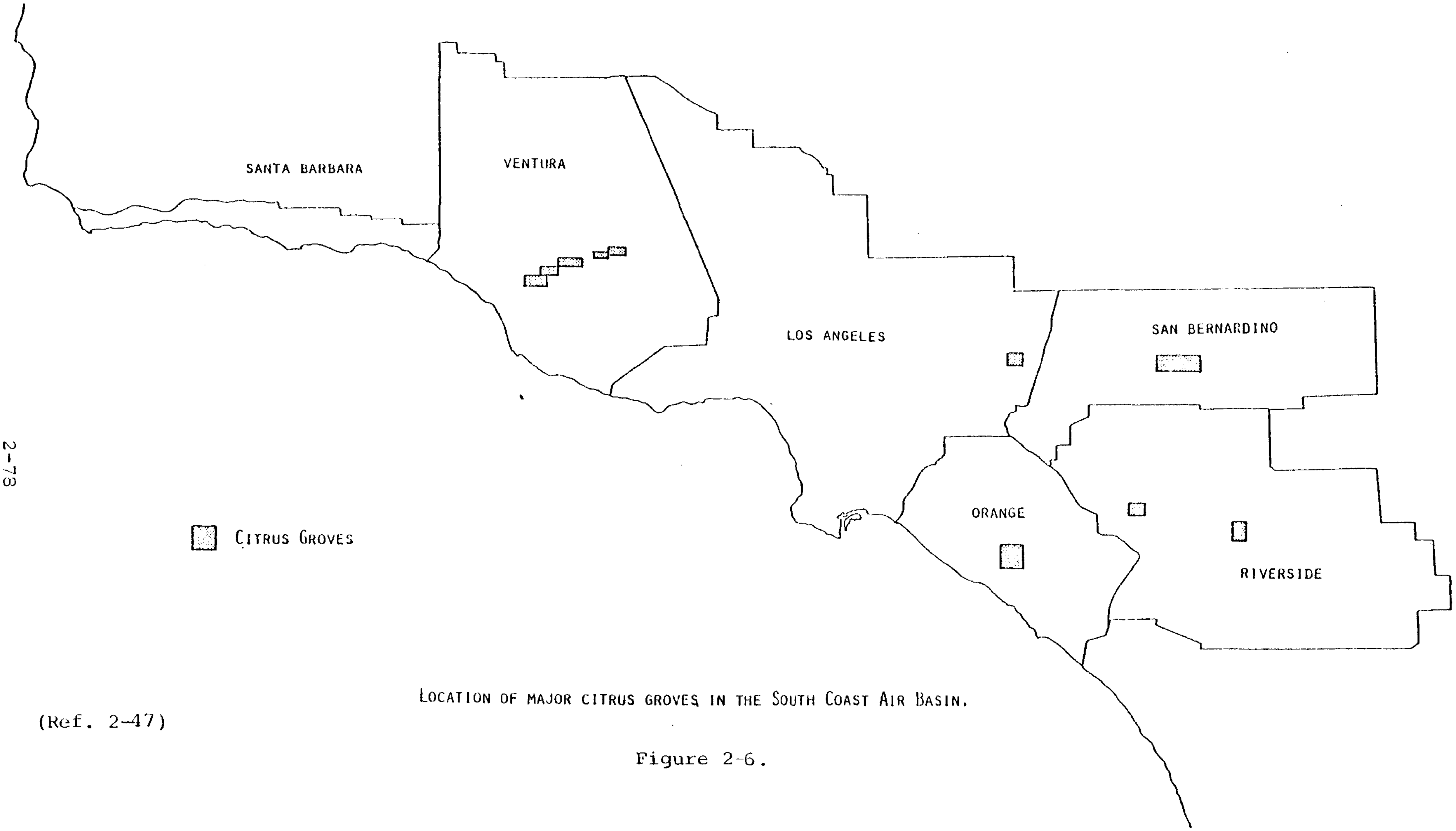
TABLE 2-32. NATIONAL DOMESTIC AND COMMERCIAL SOLVENT SALES
Based on Department of Commerce Data

Product	Estimated National Sales (10^6 lbs)	Solvents (wt. %)	Total Weight of Solvents (10^6 lbs)
Furniture Polish	53	40	21
Floor Polish	87	40	35
Shoe Polish	3	40	1
Metal Polish	8	40	3
Shaving Soap	56	5	3
After Shave	49	20	10
Perfumes, Toiletries & Cosmetics	17	39	7
Shampoo	152	10	15
Hair Tonics	5	5	0
Hair Spray	210	59	124
Hair Rinses	23	5	1
Mouthwash	119	14	17
Creams	74	30	22
Suntan Oil	9	50	5
Hand Lotion	51	20	10
Cleaning Lotions	23	60	14
Rubbing Alcohol	153	100	153
Deodorant	148	14	21
Nail Polish	1	50	1
Nail Polish Remover	8	90	7
TOTAL			469

TABLE 2-33. CITRUS GROVE ACREAGE (1975)

Citrus Crop	Ventura	Orange	Los Angeles	Riverside	San Bernardino
Grapefruit	838	431	14	2,500	1,532
Lemons	23,098	1,148	953	5,300	2,220
Navel Oranges	1,427	102	283	8,400	6,782
Valencia Oranges	15,879	10,754	201	8,400	4,277
TOTAL	41,242	12,435	1,451	24,600	14,811

Reference 2-43.



Location of major citrus groves in the South Coast Air Basin.

Figure 2-6.

(Ref. 2-47)

2. Orchard heaters--Orchard heaters were in common use in Ventura, San Bernardino and Riverside Counties to protect the citrus orchards from frost damage. It was estimated by the Ventura APCD (Ref. 2-48) that there were approximately 22 heaters per acre in citrus growth in that county.

Organic compound emissions resulted primarily from the evaporation of fuel oil and not as a result of the combustion process (Ref. 2-4). Therefore, even if the orchard heaters were used relatively infrequently, organic compound emissions were still present any time there was standing fuel exposed to the atmosphere. Emission estimates have been made in Reference 2-48A. The summer evaporation (March through November) averaged 2 gal./heater while the winter evaporation averaged 0.25 gal./heater, for a total of 2.25 gal./heater-year.

Emission estimates for the current program were based on published figures by the local control agencies. Total emissions from these sources were estimated to be 1200 tons per year.

3. Animal wastes--The existence of methane and other components in the gas generated by the biological decomposition of animal wastes had been extensively studied. These investigations had been aimed both at the potential for energy recovery (Ref. 2-49) as was the case with landfill gases and also to assess the harmful effects of these gases on livestock production in confined areas (Ref. 2-50).

Results from a recent study (Ref. 2-51) were employed to estimate the emission rates from these sources. A summary of the calculations is presented in Table 2-34. Inventories of the livestock population for each county were obtained from the County Agricultural Reports (Ref. 2-46). For these data, it was estimated that 77 tons per day of gases from animal wastes were generated in the agricultural areas shown in Figure 2-2.

TABLE 2-34. ORGANIC COMPOUND EMISSIONS FROM ANIMAL WASTES

	Total Inventory (10^3 Head)	Emission Factor (lb TOC/10^3 head·day)	Emissions (tons/day)
Cattle	147	440.5	32.4
Chickens	9992	7.0	35.0
Pigs	5	160.0	0.4
Horses	73	229.3	8.4
Sheep	87	33.2	1.4
Total			77.6

4. Pesticides--Application of pesticides for agricultural and domestic use have been included in previous inventories of hydrocarbon emissions conducted by the local control agencies. These inventories have generally been based on county reports in the State Pesticide Use Report (Ref. 2-51A).

This procedure has also been used in the study. It was learned that the data base for the State Pesticide Use Report had been computerized by the University of California-Davis (Ref. 2-51B). Arrangements were made with the University to have the data reported for each pesticide on a township basis (to allow geographic distribution) and for the Basin as a whole. It was estimated from these data that the total emissions of pesticides in the study area were 5000 tons per year of which approximately 40% was nonsynthetic and 60% synthetic organic materials.

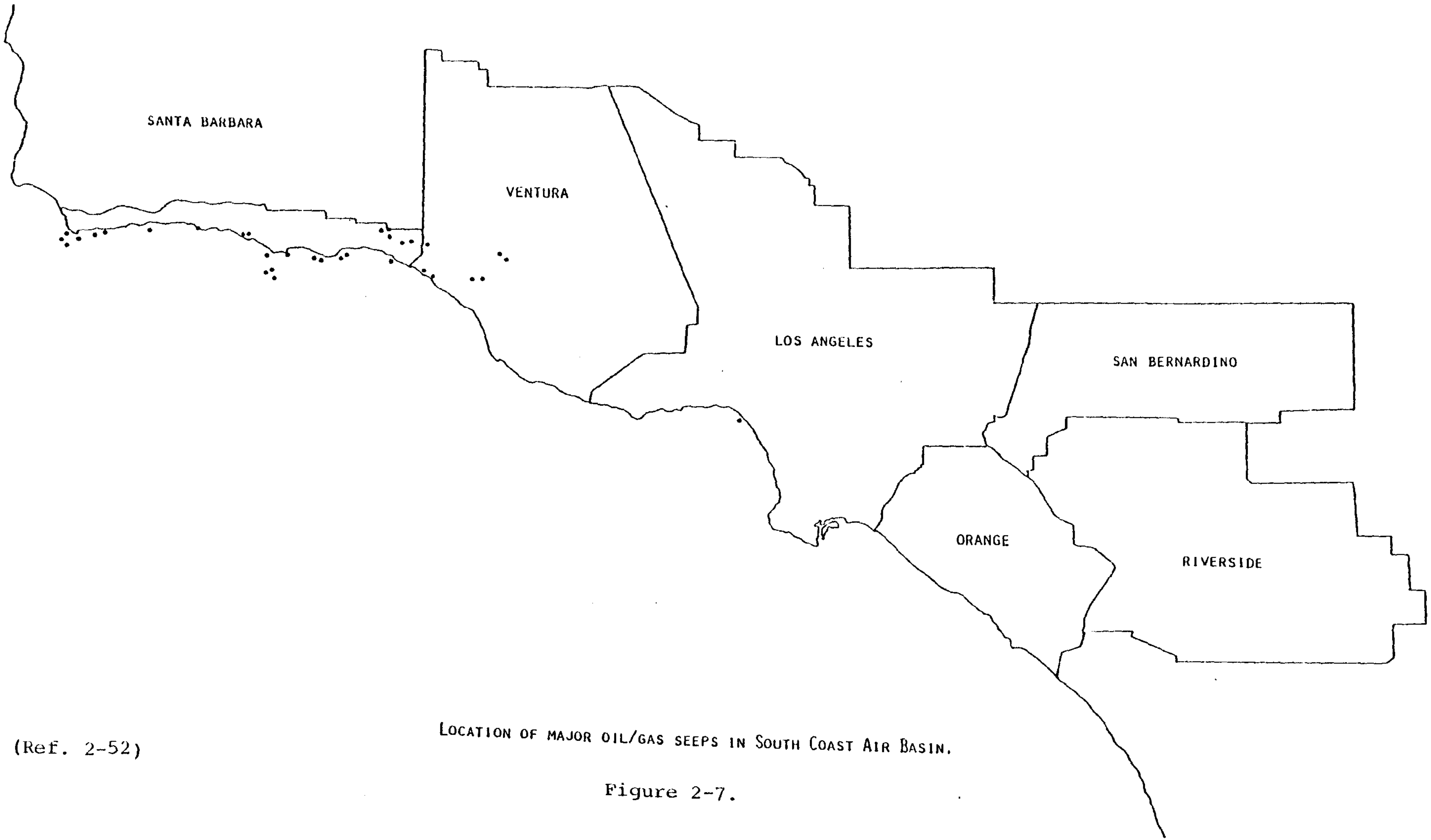
An estimate of the pesticide emissions due to domestic and commercial use has been made based on information from the Reference 2-51B for general pesticide use in the Basin. An emission factor of 9 tons/100,000 people·yr was developed from this data.

Recent more comprehensive examinations by CARB (Ref. 2-51C) have shown that the pesticide use reports under estimate the emissions from this source by factors of six and two for nonsynthetic and synthetic organic materials, respectively. Based on these estimates, the total emissions from these sources would be 17,000 tons per year. The quantification of these estimates was a complex problem as discussed in Reference 2-51B, and therefore the more conservative estimate, described above, was used in the inventory.

E. Geogenic Sources--

1. Natural seeps--Figure 2-7 (Ref. 2-52) shows the location of the major petroleum seeps within the study area. The presence of these seeps had created significant local pollution problems due to "petroleum odors" and evolution of heavy oil and tar.

Studies had been conducted to quantify the emission rates from two large offshore seeps in Santa Barbara County (Ref. 2-53). The largest of these was estimated to have organic compound emissions of approximately 6 tons per day. The California Division of Oil and Gas was in the process of mapping all existing oil seeps within the study area however no data on seepage or emission rates are expected (Ref. 2-54).



(Ref. 2-52)

Location of major oil/gas seeps in South Coast Air Basin.

Figure 2-7.

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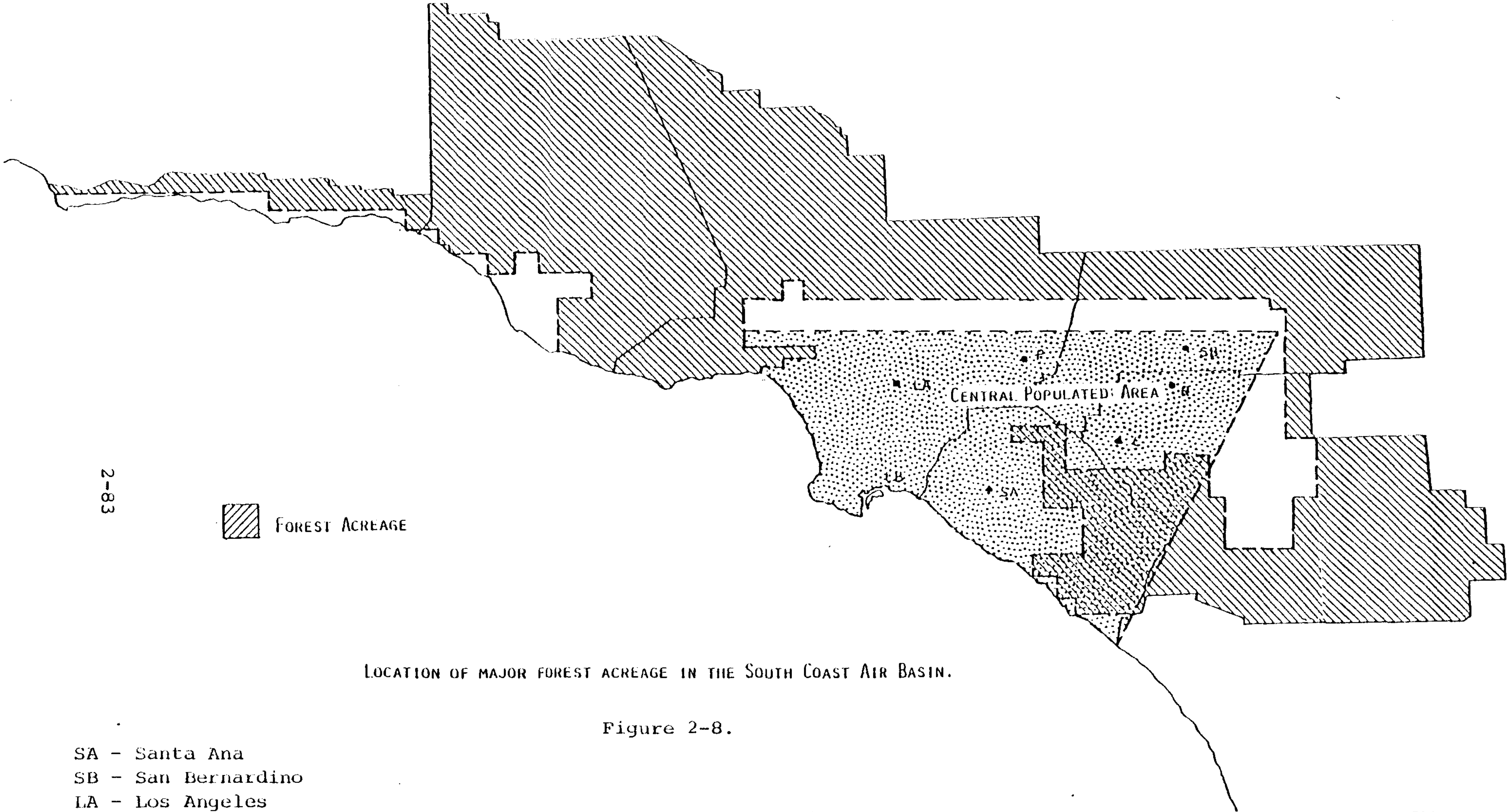
It was estimated by the Santa Barbara and Ventura County APCD's that the total emissions from these sources are approximately 4000 tons per year. These estimates were used for the final inventory.

F. Forest Emissions--

As illustrated in Figure 2-8, approximately 3.6 million acres of forest, located in the northern, eastern, and southern areas of the South Coast Air Basin, constitute nearly 2/3 of the total area. While the emissions from these forest areas may be significant, they probably have a lesser impact on the smog problem in the central population area shown on Figure 2-8 than the equivalent anthropogenic emissions because of their downwind location and the elevation at which they occur. Approximately 40% of the forest area lies above 3,500 ft elevation which is the normal maximum altitude of the inversion layer. While the forests are a source of natural terpenes and combustion products from forest fires, they also serve as a sink for the anthropogenic emissions generated in the Basin which cause damage to the plant life (Ref. 2-55). The forest areas referred to in this report comprise all of the open land in the Basin which are primarily of scrub forest type. Natural emissions from residential and commercial landscaping were ignored because preliminary measurements indicate that the emissions from this vegetation is one or two orders of magnitude lower than forest emissions for comparable acreage.

1. Natural emissions--Field investigations (Ref. 2-19 and 2-56) indicate that there are considerable α-pinene, β-pinene, and isoprene emissions from plant life found in the Southern California forests. The primary source of data on natural emission factors was Zimmerman, Washington State University (Ref. 2-56). Some of these data were unpublished at the time of this study. Information on the type and distribution of vegetation was obtained from the National Forest Service (Ref. 2-57).

The emission rate data provided by Zimmerman are presented in Table 2-35 along with the emission factors computed from these data. Table 2-36 presents a summary of the forest area by county and the type of vegetation found in each area. The National Forest Service provided data on the federal



Location of major forest acreage in the South Coast Air Basin.

Figure 2-8.

SA - Santa Ana
SB - San Bernardino
LA - Los Angeles
LB - Long Beach
P - Pomona
R - Riverside
C - Corona

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TABLE 2-35. FOREST NATURAL EMISSION RATES BASED ON LEAF BIOMASS

Forest Type (% Composition)	Active Emission Rate µg/g·hr	Dormant Emission Rate µg/g·hr	Leaf Biomass 10^5 kg/km^2	Annual Emission Factor ton/acre·yr
Hardwoods	-	-	-	0.02
(60%) Oak	4	0	3	-
(40%) Maple	1	0	3	-
Douglas Fir	1	0	11	0.02
Mixed Conifer	-	-	-	0.08
(60%) Ponderosa Pine	3	1.5	11	-
(40%) Douglas Fir	1	0	11	-
Pines	3	1.5	11	0.1
Pinjon Juniper	3	3	3	0.04
Brush	-	-	-	0.08
(85%) Sagebrush*	12	4	3	-
(10%) Scrub Oak	4	0	3	-
(5%) Juniper	3	3	3	-

(Ref. 2-56)

*Sagebrush equivalent to mesquite and chaparrel in emissions.

TABLE 2-36. FOREST AREA SUMMARY (10^3 ACRES)

	County						
Forest Type	Los Angeles	Ventura	Orange	Santa Barbara	San Bernardino	Riverside	Total
Hardwoods	161	370	59	27	48	6	671
Douglas Fir	195	146	2	8	20	1	372
Mixed Conifer	14	6	0	0	81	6	107
Pines	4	21	2	0	87	16	130
Pinjon Juniper	40	116	0	6	4	0	166
Brush	418	691	529	36	330	143	2,147
Total	832	1,350	592	77	570	172	3,593

Reference 2-55 and KVB estimates.

land and assisted KVB on estimating the location and vegetation for privately owned lands. It must be emphasized that both the emission factors, acreages and compositions are estimates and more specific information on the composition, emission rates, and acreage would improve the natural emission calculations used in this inventory.

It was apparent from the vegetation composition and the emission factors presented in these tables that the primary concern was with the category of "brush". In the Basin, the primary types of brush found are mesquite and chaparral. These are believed to have similar emission rates to sagebrush. The degree of uncertainty regarding this similarity is probably the same as the uncertainty in the basic emission rate levels for sagebrush itself.

Zimmerman, in support of a national emission assessment, generated emission rate and biomass data based on tests performed in the northwest and east coast areas of the U.S. For sagebrush, he reported emission rates of 17 μg/g·hr for both active and dormant periods with a leaf biomass of 3×10^5 kg/km^2. However, recent measurements of Southern California vegetation have shown emission rates that are lower, especially during the dormant period. In Southern California, there are two dormant periods which occur during the dry summer months of July, August, and September, and during the winter months of December, January, and February. Zimmerman measured emissions rates of 4 μg/g·hr for the dry dormant period which is usually the worst period for ambient air quality. Based on an assumption by Zimmerman that the sagebrush active emission factor for Southern California was lower than the 17 μg/g·hr found in areas of year-around precipitation, a value of 12 μg/g·hr was estimated for this study, making the average annual emission rate 8 μg/g·hr.

The leaf biomass estimate of 3×10^5 kg/km^2 for brush is on the low side of a world-wide inventory of leaf biomasses which (according to Ref. 2-56) vary only by a factor of eight from the most dense tropical jungle to a scrub desert like the Mojave in Southern California. Thus the leaf biomass value of 3×10^5 kg/km^2 shown in Table 2-35 could be as low as 2×10^5 kg/km^2, while the value of 11×10^5 kg/km^2 also found in the table for pine and fir forests could be as high as 16×10^5 kg/km^2.

Applying the emission factors presented in Table 2-35 to the inventory in Table 2-36 results in a total emission rate estimate of 600 tons/day. Considering that 40% of these emissions are released above the inversion layer, only 300 to 400 ton/day are emitted into the mixing layer. A value of 300 ton/day was used in Table 2-23.

The EPA intends to sponsor further emission rate measurements in an attempt to improve the emission factors for vegetation types found in Southern California (Ref. 2-58). These experiments should assist in further clarifying the extent of natural emissions in the Basin.

2. Forest fires--Forest fires consumed over 80,000 acres of National Forest and private lands in the South Coast Air Basin in 1975 (Ref. 2-59). These fires burned over 2 million tons of forest material. Studies (Ref. 2-23) had estimated that 14 pounds of organic compounds were released per ton of forest material consumed. Therefore it was estimated that there were approximately 13,700 tons of emission in 1975. Since these fires generally occurred during relatively short periods, they constituted a significant source of organic vapor emission to the atmosphere.

G. Other Area Sources--

1. Dry cleaning--For the purposes of this inventory, dry cleaning operation associated with residential customers were considered as an area source distributed on the basis of population. Those establishments previously listed in the EIS data base with total emissions less than 10 tons per year were removed from the EIS data file. This categorization was required due to the fact that these small dry cleaning establishments were identified in the EIS data base for Ventura and Los Angeles Counties only. For the remaining four counties, the EIS data base for these sources were incomplete. Large dry cleaning establishments (with emissions greater than 10 tons per year) that generally use Stoddard solvents were retained as part of the EIS data base.

An analysis of the Los Angeles County permit files conducted for the preliminary inventory resulted in a total emissions of 3800 tons per year for these small dry cleaning establishments, of which 90% were synthetic solvents (perchlorethylene) and 10% Stoddard solvents. This corresponded to an annual emission factor of 0.93 tons per 1000 people. Reports from the National Fabricare Institute (Ref. 2-60) listed the annual per capita consumption of perchloroethylene dry cleaning solvent in California as 1.75 to 2.0 pounds, or an annual emission factor of 0.9 tons per 1000 people, which showed excellent agreement. Total emissions from this source were therefore estimated to be 25.9 tons per day.

2. Asphalt paving--The Asphalt Institute reports that 24 million tons of road paving were laid in 1975 (Ref. 2-61). Data from the current program showed that approximately 1×10^{-6} pounds of total hydrocarbons were released per pound of asphalt concrete laid. The emissions in the South Coast Air Basin were therefore estimated to be approximately 0.1 tons per day.

2.4 INVENTORY RESULTS

The final organic emission inventory was produced in April 1978 using EIS data tapes received from the ARB. The tape from SCAQMD was produced in February 1978 and the tape from Ventura APCD was produced in December 1977. Placing a baseline date on the inventory is difficult. The EIS efforts at SCAQMD and VAPCD were initiated in 1975 but data processing, correcting and updating contined from that time until the tapes used on this inventory were finally produced. Considering the span time involved in incorporating new source data into the EIS system, the most appropriate time base to assign to the inventory is 1975-76.

An attempt to run a final inventory was made in August 1977 using the first EIS tapes produced by the SCAQMD and VAPCD. During the initial data validation step in the inventory processing, a large number of data records were found to be incomplete and in error with respect to data needed for this inventory. Error messages were provided to the two control districts, who completed or corrected the data entires. In April 1978, when the inventory was finally produced, only a negligible number of records were rejected for incomplete or inaccurate data. A check of the data records was made to attempt to locate any major point sources that had been omitted. None were found.

The area source data and emission profiles used in the inventory are discussed in the previous sections. In this section, the results of the inventory will be discussed.

2.4.1 Physical Description and Use Instructions

The inventory was delivered to the ARB in the form of three bound volumes of computer printouts plus four reels of computer tape as mentioned in Section 2.2. The following is a more detailed description of these reports to help facilitate their use.

A. Volume I--

Volume I of the printed reports contains a plant index, an inventory by application category and an inventory by 10 kilometer grid squares.

The plant index is aranged by counties and plant I.D. number. Five-hundred and thirty one plants are identified. For each plant, the following information is listed: County, Plant ID, Plant Name and Address and UTM Grid Coordinates. The other inventory reports identify the plants using the ID number. Therefore, the user must refer to the index to learn the plant name if he locates an entry in the inventory that he wishes to check. If the user wishes to look up a specific source, he must scan the index observing first the county (all plants are grouped by county [4200 is Los Angeles, 5440 is Orange, 6420 is Riverside, 6700 is San Bernardino and 8500 is Orange]), then the plant name. The plant names could not be sorted into correct alphabetical order because of a software problem on the EIS system. Fortunately, the Los Angeles County listing (by far the largest) is almost in alphabetical order. The first 228 entires are in alphatical order. The remaining 125 plants in LA County and those in the other counties will require individual scanning. Once the plant has been located in the index, the complete emission record can be found in the 10-Km grid file by noting the UTM coordinates and the Plant ID Number.

The Application Category Report contains the sources grouped by application categories (i.e., Petroleum Production, Petroleum Refining, Organic Solvent Use, Combustion of Fuel, etc.). The information listed for each line item record is: County, Plant ID, Point ID, SCC No., SIC No., Summer and and Winter Emissions (ton/day), each broken down into Weekday and Weekend emissions, Annual Emission (ton/year), Profile Key and UTM Coordinates. The Profile Key is a reference to Volume III which lists emission profiles, a breakdown of the chemical elements comprising the total hydrocarbon emissions. For small sources, the inventory may indicate 0.00 tons/day emissions. This means that the daily emission is less than 0.005 ton/day or 10 lb/day. These small sources were included because they are in a plant producing 25 ton/year or more. At the end of each application category listing, a summary is provided for Major, Minor and Area Sources. The Major sources are those listed. The Minor sources are point sources not listed because they have less than 25 ton/year emission and are not part of a plant with 25 ton/year emissions. Area sources are as discussed in Section 2.3.4.

The 10-Km Grid Report contains the same information as the Application Category Report but the sources are grouped by their location in UTM Coordinate grids. For each grid, the population and major city (if appropriate) is listed. After the point sources are listed for each grid, a summary of minor point and area source emissions is indicated by Application Category. (The printout only indicates "Area Sources" but the data include minor point sources.

B. Volume II--

Volume II of the inventory report contains the One-Kilometer-Grid, Emission Summary and an Individual Species Report.

The One-Kilometer Report lists for each set of UTM X and Y coordinates the total organic emission (ton/year), the total emission by reactivity class, I, II, III. (Refer to Table 3-32) and the emission of individual species (lb/year) by SAROAD Code. The code numbers listed are the last four digits of the SAROAD Code. In all cases the first number is "4" and therefore is not listed. The emissions are given in four digits (except for the last column "OTH"). In all cases the first three (two) digits are significant and the last digit indicates the decimal point location in places to the right of the left-hand side of the number (e.g., 0670 = .067, 5385 = 53,800).

The Individual Species Report lists each species in order of SAROAD Code and provides a listing of emissions broken down into Application Categories. One hundred and one species are included.

C. Volume III--

Volume III contains a SCC Description Report and the Emission Profiles. The SCC Description lists 739 source categories by SCC and SIC number, the emission profile key (which indicates the applicable profile), the ARB application category equivalent to that source, any emission factor correction (see Section 2.3.1). The last two columns are of no significance. The SCC Report is presented in two orders, the first by profile key and the other by SCC number.

The emission profiles contain the Profile Key, an estimate of error in the profile for any species, the reactivity class, SAROAD Code, chemical name, molecular weight and weight % for each species. Also included is a summary of the emissions for the three ARB emission reactivity classes.

2.4.2 Total Organic Emissions

The total organic emissions in the Basin plus Ventura County are 810,000 tons per year (2200 tons per day) of which 16% (350 ton/day) are from point sources. Over 5000 individual point sources are identified. A breakdown of these emissions according to application categories is presented in Table 2-37. Also presented in that table are the data from 1975 inventories conducted by KVB (the preliminary inventory on this program published in the Interim Report, November 1976) and a combined SCAQMD/Ventura APCD inventory for 1975 (Refs. 2-5, 4-48).

TABLE 2-37. COMPARISON OF EIS/KVB AND AQMD/VCAPCA EMISSION INVENTORIES

EMISSION TONS/YEAR

Application Cat.	Device Type	(No. of Major Sources)	EIS/KVB FILE				PRELIMINARY INVENTORY			AQMD/VCAPCA (1975)		
			Major Point	Minor Point	Area	Total	Point	Area	Total	Point	Area	Total
Petroleum Prod.		390	7900	970	30,000	39,000	12,400	--	12,400	7860[1]	14,600[2]	22,000
	Tanks				15,000		11,700	--		4700	14,700	19,300
	Other				15,000		700	--		3100	--	3,100
Petroleum Refining		1700	40,000	500	1900	42,000	30,000	--	30,000	15,600	--	15,600
	Tanks				--		21,900	--		3300	--	8,300
	Other				1,900		8,400	--		7300	--	7,300
Petroleum Mktg.		220	3700	200	64,000	68,000	22,000	57,000	79,000	14,000	33,000	47,000
	Tanks				--		9,500	--		11,700	--	11,600
	Gasoline Mktg.				30,000		12,400	57,000		1,180	33,000	34,000
	Mar. Loading				950		--	--		1,100	--	1,100
	NG Trans.				33,000		--	--		--	--	--
Solvent-Surface Coat		1600	31,000	5000	9000	45,000	39,000		39,000	45,000	--	45,000
- Dry Cleaning		80	2700	2100	9700	14,000	24,000	8,900	11,300	3,700	6,100	9,800
	Petroleum						2,400	--	2,400	3,700	--	3,700
	Synthetic						--	8,900		--	6,100	6,100
- Degreasing		310	9000	1100	2000	12,000	11,700	--	11,700	11,300	--	11,300
- Other		100	6400	150	200	6,800	9,100	--	9,100	13,000	--	13,000
	Printing						9,100		9,100	10,300	--	10,300
	Misc.						--		--	2,600	--	2,600
Chemical		30	1000	50	250	1,300	4,400	--	4,400	1,300	--	1,300
Metallurgical		45	950	50	50	1,050	--	--	--	200	--	200
Mineral		4	50	50	150	250	400	--	400	--	--	--
Waste Burning		5	0	0	550	550	--	--	--	--	140[1]	140[1]
Comb. of Fuel		480	5300	400	200	5,900	6,100	--	6,100	1,400	--	1,400
Food & Agriculture		10	200	150	50	400	--	40	40	300	--	300
Pesticides		0			5500		--	--	--	--	2,800	2,800
Misc. Inc.		90	3900	200	150	4,300	--	--	--	--	--	--

Continued

TABLE 2-37. Continued

EMISSION TONS/YEAR

			EIS/KVB FILE				PRELIMINARY INVENTORY			AQMD/VCAPCA (1975)		
			Major Point	Minor Point	Area	Total	Point	Area	Total	Point	Area	Total
Unclassified		90	3900	200	570,000	570,000	--	39,000	39,000	--	78,000	78,000
	Domestic Comb.				1,600		--	1,200	1,200	--	50[1]	50[1]
	Domestic Solvent				11,000		--	--	--	--	--	--
	Structure Fires				10,000		--	--	--	--	450[1]	450[1]
	Arch. Surf. Coat				33,000		--	38,000	38,000	--	77,000	77,000
	Forest Natural				124,000		--	--	--	--	--	--
	Forest Fires				13,700		--	--	--	--	--	--
	Animal Waste				28,000		--	--	--	--	--	--
	Landfills				340,000		--	--	--	--	--	--
	Seeps				4,000		--	--	--	--	--	--
	Citrus Trees				5,600		--	--	--	--	--	--
	Orchard Heaters				1,200		--	--	--	--	2,300	2,300
Total (tons/day)		5200	116,000	11,100	680,000	810,000	138,000	105,000	121,000	114,000	135,000	250,000
(tons/day)		Sources	(320)	(30)	(1,850)	(2,200)	(380)	(300)		(310)	(370)	(680)

(1) Ventura only

(2) SCAQMD only

The total emissions from the EIS/KVB inventory are greater than the respective totals of the other two inventories. However, the EIS/KVB inventory accounts for a greater number of source types than the other two inventories. The sources seem to be consistent. The major and minor point source emissions were calculated directly from the SCAQMD and VAPCD EIS data files. Adjustments were made to the emission factors of certain source types (see Section 2.3.1); but, essentially, the inventory results reflect the basic EIS inventory data. Since the EIS data base was built from the previous permit files used to compute the other two comparison inventories, it is encouraging to note the similarity in this area.

Seventy percent of the emissions are from area sources essentially unaccounted for in previous inventories. The largest of these are from landfills (which produce over 900 tons/day of 99% methane gas) and from trees and brush (which emit approximately 300 tons/day of terpenes.)

The refinery emissions in the EIS/KVB inventory are higher than those in the previous inventories. This is due exclusively to the EIS data. KVB made no adjustments in this area. Petroleum industry emissions account for over 50% of the point source emissions and 18% of the total emissions.

2.4.3 Emission by Species

A breakdown of the total organic emissions by species is presented in Table 3-38, which is arranged in order of SAROAD Code and includes the reactivity class designation for each compound. Table 2-38 is a summary of Table 2-39 which is an application category report for each of the species accounting for 1000 tons/year or greater.

Methane accounts for half of the total emissions and is considered relatively unreactive. The methane listing in Table 2-39 can be used to determine non-methane hydrocarbons from each application category as presented in Table 2-40.

2.4.4 Spatial Distribution

A map showing the spatial distribution of the emissions is shown in Figure 2-9. Table 2-41 identifies the grids with emissions of over 20 tons/day.

TABLE 2-38. SOUTH COAST AIR BASIN ORGANIC SPECIES INVENTORY EMISSIONS BY SPECIES

Chemical Name	SAROAD Code	React Class	Tons/Year
Methane	43201	1	415,000
Ethane	43202	1	17,000
Ethylene	43203	3	6,400
Propane	43204	2	14,000
Propylene	43205	3	1,600
Acetylene	43206	1	2,500
Cyclopentane	43210	2	700
N-Butane	43212	2	25,000
Butene	43213	3	900
I-Butane	43214	2	7,500
N-Pentane	43220	2	11,000
Pentene	43224	3	2,800
Hexane	43231	2	14,000
Heptane	43232	2	4,400
Octane	43233	2	3,500
I-Hexane	43236	2	6,700
I-Heptane	43237	2	2,100
I-Octane	43239	2	1,300
Cyclohexane	43240	2	8,600
I-Nonane	43242	2	1,100
I-Decane	43243	2	2,500
C-7 Cycloparaffin	43253	2	3,000
C-8 "	43254	2	400
Terpenes	43256	3	124,000
Mineral Spirits (C-4 to 8)	43263	2	10,000
I-Pentane	43268	2	17,000
Methyl Alcohol	43301	1	2,000
Ethyl Alcohol	43302	3	6,000
N-Propyl Alcohol	43303	3	500
I-Propyl Alcohol	43304	3	12,000
N-Butyl Alcohol	43305	3	2,000
I-Butyl Alcohol	43306	3	200
Cellosolves	43308 & 43309	3	300
Glycol Ether	43367	3	2,300
Glycol	43368	3	800
Propylene Glycol	43369	3	600
Ethylene Glycol	43370	3	200
Ethyl Acetate	43433	2	500
Propyl Acetate	43434	2	700
N-Butyl Acetate	43435	2	4,600
Cellosolve Acetate	43443	3	600
Isopropyl Acetate	43444	3	600
Isobutyl Acetate	43446	3	500
Dimethyl Formamide	43450	2	200
Isobutyl Isobutyrate	43451	2	2,000
Formaldehyde	43502	3	2,400
Acetone	43551	1	7,100
Methyl Ethyl Ketone	43552	2	8,100
Methyl N-Butyl Ketone	43559	2	200
Methyl-Isobutyl Ketone	43560	2	2,000
Ethylamine	43721	1	300
Trimethylamine	43740	1	300
Freon 11	43811	1	900
1.1.1-Trichloroethane	43815	1	2,600
Perchloroethylene	43817	1	20,000
Methylbromide	43819	1	500
1.1.2-Trichloroethane	43820	1	2,700
Naphtha	45101	2	1,700
Benzene	45201	1	3,400
Toluene	45202	3	12,000
Ethyl Benzene	45203	3	1,600
Isomers of Xylene	45222	3	5,200
Isomers of Ethyltoluene	45227	3	300
Isomers of Diethylbenzene	45229	3	200
Isomers of Trimethyl-benzene	45230	3	200
			810,000

TABLE 2-39. SPECIES BY APPLICATION CATEGORIES

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

   SAROAD CODE    CHEMICAL NAME      MOLEC. WEIGHT       REACTIVITY CLASS
     43201         METHANE               16.04                  1
                                                                %
          APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)       OF TOTAL

          PETROLEUM PRODUCTION          13770.02                    3.32
          PETROLEUM REFINING             3479.49                    0.84
          PETROLEUM MARKETING           28715.86                    6.92
          ORG SOL SURFACE COAT           2957.05                    0.71
          ORG SOL OTHER                   168.28                    0.04
          CHEMICAL                         16.63                    0.00
          METALLURGICAL                   547.89                    0.13
          MINERAL                          35.96                    0.01
          WASTE BURNING                    45.92                    0.01
          COMBUSTION OF FUELS            1494.59                    0.36
          FOOD AND AGRICULTURAL           147.85                    0.04
          UNCLASSIFIED                 359638.09                   86.67
          MISCELLANEOUS INDUSTR          3938.61                    0.95

                            TOTAL      414956.24                  100.00


KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

   SAROAD CODE    CHEMICAL NAME      MOLEC. WEIGHT       REACTIVITY CLASS
     43202         ETHANE                30.07                  1
                                                                %
          APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)       OF TOTAL

          PETROLEUM PRODUCTION           2662.80                   15.40
          PETROLEUM REFINING             1165.97                    6.75
          PETROLEUM MARKETING            3786.97                   21.91
          ORG SOL SURFACE COAT            222.46                    1.29
          ORG SOL OTHER                    19.73                    0.11
          CHEMICAL                          3.57                    0.02
          METALLURGICAL                    41.92                    0.24
          MINERAL                          10.01                    0.06
          WASTE BURNING                     0.80                    0.00
          COMBUSTION OF FUELS              81.50                    0.47
          UNCLASSIFIED                   9289.98                   53.74
          MISCELLANEOUS INDUSTR             0.20                    0.00

                            TOTAL       17285.91                   99.99


KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

   SAROAD CODE    CHEMICAL NAME      MOLEC. WEIGHT       REACTIVITY CLASS
     43203         ETHYLENE              28.05                  3
                                                                %
          APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)       OF TOTAL

          PETROLEUM PRODUCTION            681.01                   10.59
          PETROLEUM REFINING              100.40                    1.56
          PETROLEUM MARKETING              10.76                    0.17
          ORG SOL SURFACE COAT             88.92                    1.38
          ORG SOL OTHER                     1.57                    0.02
          CHEMICAL                        222.97                    3.47
          METALLURGICAL                   143.99                    2.24
          MINERAL                           4.65                    0.07
          WASTE BURNING                   108.08                    1.68
          COMBUSTION OF FUELS              19.02                    0.30
          FOOD AND AGRICULTURAL             2.03                    0.03
          UNCLASSIFIED                   5050.29                   78.50

                            TOTAL        6433.69                  100.01
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TABLE 2-39. (Continued).

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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43204       PROPANE                  44.09                   2
                                                                     %
        APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)         OF TOTAL

        PETROLEUM PRODUCTION           3962.49                      28.72
        PETROLEUM REFINING             4281.79                      31.03
        PETROLEUM MARKETING            2204.83                      15.98
        ORG SOL SURFACE COAT            136.06                       1.00
        ORG SOL OTHER                     6.58                       0.05
        CHEMICAL                          0.01                       0.00
        METALLURGICAL                    11.41                       0.08
        MINERAL                          14.67                       0.11
        WASTE BURNING                    10.70                       0.08
        COMBUSTION OF FUELS             176.08                       1.28
        FOOD AND AGRICULTURAL             0.20                       0.00
        UNCLASSIFIED                   2890.20                      20.95
        PESTICIDE USE                    98.61                       0.71
        MISCELLANEOUS INDUSTR             2.55                       0.02

                            TOTAL     13798.18                     100.01
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43205       PROPYLENE                42.08                   3
                                                                     %
        APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)         OF TOTAL

        PETROLEUM PRODUCTION             37.32                       2.33
        PETROLEUM REFINING              282.75                      17.64
        ORG SOL OTHER                    23.67                       1.48
        CHEMICAL                         92.90                       5.80
        METALLURGICAL                    10.55                       0.66
        MINERAL                           8.25                       0.51
        WASTE BURNING                    33.31                       2.08
        COMBUSTION OF FUELS              36.62                       2.28
        FOOD AND AGRICULTURAL             0.62                       0.04
        UNCLASSIFIED                   1053.85                      65.74
        MISCELLANEOUS INDUSTR            23.11                       1.44

                            TOTAL      1602.95                     100.00
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43206       ACETYLENE                26.04                   1
                                                                     %
        APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)         OF TOTAL

        PETROLEUM PRODUCTION            195.91                       7.99
        PETROLEUM REFINING                3.65                       0.15
        CHEMICAL                         10.32                       0.42
        METALLURGICAL                    10.03                       0.41
        WASTE BURNING                    11.75                       0.48
        COMBUSTION OF FUELS               0.85                       0.03
        FOOD AND AGRICULTURAL             0.20                       0.01
        UNCLASSIFIED                   2217.20                      90.39
        MISCELLANEOUS INDUSTR             2.94                       0.12

                            TOTAL      2452.85                     100.00
```

TABLE 2-39. (Continued).

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43212	N-BUTANE	58.12	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	5113.24	20.82
PETROLEUM REFINING	7464.08	30.39
PETROLEUM MARKETING	7070.71	28.79
ORG SOL SURFACE COAT	1040.33	4.24
ORG SOL OTHER	15.06	0.06
CHEMICAL	0.02	0.00
METALLURGICAL	12.78	0.05
MINERAL	25.52	0.10
WASTE BURNING	11.21	0.05
COMBUSTION OF FUELS	607.63	2.47
FOOD AND AGRICULTURAL	0.20	0.00
UNCLASSIFIED	2954.49	12.03
PESTICIDE USE	241.05	0.98
MISCELLANEOUS INDUSTR	1.37	0.01
TOTAL	24557.69	99.99

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43214	ISO-BUTANE	58.12	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	676.87	9.06
PETROLEUM REFINING	2968.55	39.75
PETROLEUM MARKETING	2521.57	33.77
ORG SOL SURFACE COAT	1.66	0.02
ORG SOL OTHER	11.15	0.15
CHEMICAL	0.01	0.00
MINERAL	25.35	0.34
WASTE BURNING	10.50	0.14
COMBUSTION OF FUELS	129.36	1.73
FOOD AND AGRICULTURAL	0.20	0.00
UNCLASSIFIED	1045.37	14.00
PESTICIDE USE	76.70	1.03
MISCELLANEOUS INDUSTR	0.20	0.00
TOTAL	7467.49	99.99

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43220	N-PENTANE	72.15	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	2692.53	25.55
PETROLEUM REFINING	3486.59	33.08
PETROLEUM MARKETING	3546.53	33.65
CHEMICAL	0.02	0.00
METALLURGICAL	8.52	0.08
MINERAL	15.28	0.15
WASTE BURNING	10.43	0.10
COMBUSTION OF FUELS	236.40	2.24
FOOD AND AGRICULTURAL	0.20	0.00
UNCLASSIFIED	361.93	3.43
PESTICIDE USE	175.31	1.66
MISCELLANEOUS INDUSTR	5.68	0.05
TOTAL	10539.42	99.99

TABLE 2-39. (Continued).

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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43224       1-PENTENE                70.13                    3
                                                                    %
          APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)        OF TOTAL

          PETROLEUM REFINING               739.79                   26.79
          PETROLEUM MARKETING             1960.43                   70.98
          ORG SOL OTHER                      5.14                    0.19
          MINERAL                            0.06                    0.00
          WASTE BURNING                     32.21                    1.17
          FOOD AND AGRICULTURAL              0.62                    0.02
          MISCELLANEOUS INDUSTR             23.50                    0.85

                             TOTAL        2761.75                  100.00
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43231        HEXANE                  86.17                    2
                                                                    %
          APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)        OF TOTAL

          PETROLEUM PRODUCTION            1648.37                   11.61
          PETROLEUM REFINING              1665.26                   11.73
          PETROLEUM MARKETING             1231.20                    8.67
          ORG SOL SURFACE COAT               0.72                    0.01
          ORG SOL OTHER                     15.99                    0.11
          CHEMICAL                          54.03                    0.38
          METALLURGICAL                     10.29                    0.07
          MINERAL                           19.06                    0.13
          WASTE BURNING                     75.90                    0.53
          COMBUSTION OF FUELS              332.52                    2.34
          FOOD AND AGRICULTURAL             26.58                    0.19
          UNCLASSIFIED                    8914.03                   62.79
          PESTICIDE USE                    202.70                    1.43

                             TOTAL       14196.65                   99.99
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43232        HEPTANE                100.20                    2
                                                                    %
          APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)        OF TOTAL

          PETROLEUM PRODUCTION            1411.83                   31.84
          PETROLEUM REFINING               513.22                   11.57
          PETROLEUM MARKETING              329.47                    7.43
          ORG SOL OTHER                      5.45                    0.12
          METALLURGICAL                     66.07                    1.49
          MINERAL                            3.11                    0.07
          WASTE BURNING                     75.88                    1.71
          COMBUSTION OF FUELS                8.62                    0.19
          FOOD AND AGRICULTURAL              1.45                    0.03
          UNCLASSIFIED                    2018.80                   45.53

                             TOTAL        4433.90                   99.98
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TABLE 2-39. (Continued).

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43233	OCTANE	114.23	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	1058.47	29.99
PETROLEUM REFINING	146.74	4.16
PETROLEUM MARKETING	91.22	2.58
ORG SOL SURFACE COAT	136.07	3.86
ORG SOL OTHER	0.86	0.02
METALLURGICAL	0.41	0.01
MINERAL	0.05	0.00
WASTE BURNING	75.33	2.13
FOOD AND AGRICULTURAL	1.44	0.04
UNCLASSIFIED	2018.80	57.20
TOTAL	3529.39	99.99

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43236	#ISOMERS OF HEXANE	86.17	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	910.74	12.19
PETROLEUM REFINING	2277.16	34.24
PETROLEUM MARKETING	2931.47	44.08
CHEMICAL	0.04	0.00
METALLURGICAL	1.42	0.02
MINERAL	19.76	0.30
WASTE BURNING	0.01	0.00
COMBUSTION OF FUELS	166.27	2.50
PESTICIDE USE	443.75	6.67
TOTAL	6650.62	100.00

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43237	#ISOMERS OF HEPTANE	100.20	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	3.71	0.18
PETROLEUM REFINING	1259.19	60.25
PETROLEUM MARKETING	734.39	35.14
ORG SOL OTHER	15.48	0.74
METALLURGICAL	0.01	0.00
MINERAL	2.41	0.12
COMBUSTION OF FUELS	74.69	3.57
TOTAL	2089.88	100.00

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43239	#ISOMERS OF OCTANE	114.23	2

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM PRODUCTION	12.16	0.90
PETROLEUM REFINING	410.44	30.41
PETROLEUM MARKETING	767.33	56.85
ORG SOL SURFACE COAT	6.91	0.51
ORG SOL DRY CLEANING	14.52	1.08
ORG SOL DEGREASING	1.33	0.10
ORG SOL OTHER	1.73	0.13
METALLURGICAL	0.01	0.00
MINERAL	0.37	0.03
COMBUSTION OF FUELS	135.01	10.00
TOTAL	1349.81	100.01

TABLE 2-39. (Continued)

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME        MOLEC. WEIGHT        REACTIVITY CLASS
     43240       #CYCLOHEXANE              84.16                     2
                                                                       %
               APPLICATION CATEGORY      EMISSIONS (TONS/YEAR)       OF TOTAL

               PETROLEUM PRODUCTION            0.17                    0.00
               PETROLEUM REFINING            309.67                    3.61
               PETROLEUM MARKETING           753.46                    8.79
               ORG SOL SURFACE COAT          227.15                    2.65
               ORG SOL OTHER                 312.78                    3.65
               CHEMICAL                       18.63                    0.22
               METALLURGICAL                   1.42                    0.02
               MINERAL                         0.01                    0.00
               WASTE BURNING                   0.01                    0.00
               COMBUSTION OF FUELS            16.90                    0.20
               FOOD AND AGRICULTURAL          38.19                    0.45
               UNCLASSIFIED                 6895.23                   80.42

                                 TOTAL      8573.62                  100.01
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME        MOLEC. WEIGHT        REACTIVITY CLASS
     43242       #ISOMERS OF NONANE        128.25                    2
                                                                       %
               APPLICATION CATEGORY      EMISSIONS (TONS/YEAR)       OF TOTAL

               PETROLEUM PRODUCTION            0.01                    0.00
               PETROLEUM REFINING            266.05                   23.59
               PETROLEUM MARKETING           123.84                   10.98
               ORG SOL SURFACE COAT          188.71                   16.74
               ORG SOL DRY CLEANING          495.53                   43.94
               ORG SOL DEGREASING             45.31                    4.02
               ORG SOL OTHER                   8.05                    0.71
               METALLURGICAL                   0.09                    0.01
               MINERAL                         0.05                    0.00

                                 TOTAL      1127.64                   99.99
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME        MOLEC. WEIGHT        REACTIVITY CLASS
     43243       #ISOMERS OF DECANE        142.28                    2
                                                                       %
               APPLICATION CATEGORY      EMISSIONS (TONS/YEAR)       OF TOTAL

               PETROLEUM REFINING            539.67                   21.51
               PETROLEUM MARKETING            94.20                    3.76
               ORG SOL SURFACE COAT          481.29                   19.19
               ORG SOL DRY CLEANING         1257.88                   50.14
               ORG SOL DEGREASING            115.01                    4.58
               ORG SOL OTHER                  20.53                    0.82

                                 TOTAL      2508.58                  100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME        MOLEC. WEIGHT        REACTIVITY CLASS
     43253       #C-7 CYCLOPARAFFINS        98.19                    2
                                                                       %
               APPLICATION CATEGORY      EMISSIONS (TONS/YEAR)       OF TOTAL

               PETROLEUM PRODUCTION         1816.23                   59.92
               PETROLEUM REFINING            142.37                    4.70
               PETROLEUM MARKETING            81.17                    2.68
               ORG SOL OTHER                 139.62                    4.61
               CHEMICAL                        0.08                    0.00
               METALLURGICAL                   0.01                    0.00
               MINERAL                         7.85                    0.26
               PESTICIDE USE                 843.67                   27.83

                                 TOTAL      3031.00                  100.00
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TABLE 2-39. (Continued).

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT       REACTIVITY CLASS
     43256       *TERPENES                136.24                  3
                                                                         %
             APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)          OF TOTAL

             UNCLASSIFIED                    205887.04                     100.00

                                   TOTAL     205887.04                     100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT       REACTIVITY CLASS
     43263       *MINERAL SPIRITS         114.00                  2
                                                                         %
             APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)          OF TOTAL

             ORG SOL SURFACE COAT              8410.35                      80.45
             ORG SOL OTHER                     1212.86                      11.60
             CHEMICAL                             9.71                       0.09
             PESTICIDE USE                      821.76                       7.86

                                   TOTAL      10454.68                     100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT       REACTIVITY CLASS
     43268       *ISOMERS OF PENTANE       72.15                  2
                                                                         %
             APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)          OF TOTAL

             PETROLEUM PRODUCTION               727.91                       4.35
             PETROLEUM REFINING                6005.69                      35.87
             PETROLEUM MARKETING               9477.45                      56.60
             CHEMICAL                             0.02                       0.00
             METALLURGICAL                       12.78                       0.08
             MINERAL                             12.10                       0.07
             WASTE BURNING                        0.09                       0.00
             COMBUSTION OF FUELS                310.07                       1.85
             UNCLASSIFIED                        29.22                       0.17
             PESTICIDE USE                      169.83                       1.01

                                   TOTAL      16745.16                     100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT       REACTIVITY CLASS
     43301        METHYL ALCOHOL           32.04                  1
                                                                         %
             APPLICATION CATEGORY          EMISSIONS (TONS/YEAR)          OF TOTAL

             PETROLEUM REFINING                  74.11                       3.73
             PETROLEUM MARKETING                 18.96                       0.95
             ORG SOL SURFACE COAT               363.47                      18.28
             ORG SOL OTHER                      169.65                       8.53
             CHEMICAL                            56.16                       2.83
             UNCLASSIFIED                      1299.10                      65.35
             MISCELLANEOUS INDUSTR                6.56                       0.33

                                   TOTAL       1988.01                     100.00
```

TABLE 2-39. (Continued).

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43302	ETHYL ALCOHOL	46.07	3

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM REFINING	116.49	1.95
PETROLEUM MARKETING	18.97	0.32
ORG SOL SURFACE COAT	324.18	5.43
ORG SOL OTHER	627.29	10.51
CHEMICAL	14.77	0.25
UNCLASSIFIED	4863.15	81.46
MISCELLANEOUS INDUSTR	5.27	0.09
TOTAL	5970.12	100.01

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43304	ISO-PROPYL ALCOHOL	60.09	3

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
PETROLEUM REFINING	131.41	1.06
PETROLEUM MARKETING	19.32	0.16
ORG SOL SURFACE COAT	1162.31	9.36
ORG SOL OTHER	750.43	6.05
CHEMICAL	27.23	0.22
UNCLASSIFIED	10303.82	83.00
MISCELLANEOUS INDUSTR	19.22	0.15
TOTAL	12413.74	100.00

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43305	N-BUTYL ALCOHOL	74.12	3

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
ORG SOL SURFACE COAT	1258.06	63.87
ORG SOL OTHER	144.41	7.33
CHEMICAL	6.67	0.34
UNCLASSIFIED	532.96	27.06
MISCELLANEOUS INDUSTR	27.54	1.40
TOTAL	1969.64	100.00

KVB - ORGANIC COMPOUNDS EMISSIONS REPORT - INDIVIDUAL SPECIES REPORT

SAROAD CODE	CHEMICAL NAME	MOLEC. WEIGHT	REACTIVITY CLASS
43367	*GLYCOL ETHER	62.07	3

APPLICATION CATEGORY	EMISSIONS (TONS/YEAR)	% OF TOTAL
ORG SOL SURFACE COAT	1374.64	59.50
ORG SOL OTHER	11.39	0.49
CHEMICAL	2.81	0.12
UNCLASSIFIED	921.58	39.89
TOTAL	2310.42	100.00

TABLE 2-39. (Continued).

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43435       N-BUTYL ACETATE          116.16                   2
                                                                    %
                 APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)        OF TOTAL

                 ORG SOL SURFACE COAT          3407.40                    74.48
                 ORG SOL OTHER                  188.92                     4.13
                 CHEMICAL                         1.22                     0.03
                 UNCLASSIFIED                   977.10                    21.36

                               TOTAL          4574.64                    100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43451       #ISOBUTYL ISOBUTYRATE    144.21                   2
                                                                    %
                 APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)        OF TOTAL

                 UNCLASSIFIED                  2031.93                   100.00

                               TOTAL          2031.93                    100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43502       FORMALDEHYDE              30.03                   3
                                                                    %
                 APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)        OF TOTAL

                 PETROLEUM PRODUCTION             0.02                     0.00
                 PETROLEUM REFINING             490.03                    20.20
                 PETROLEUM MARKETING             10.76                     0.44
                 ORG SOL OTHER                    9.41                     0.39
                 CHEMICAL                        17.55                     0.72
                 METALLURGICAL                   11.36                     0.47
                 MINERAL                          0.07                     0.00
                 WASTE BURNING                    0.25                     0.01
                 COMBUSTION OF FUELS           1787.34                    73.67
                 UNCLASSIFIED                    66.62                     2.75
                 MISCELLANEOUS INDUSTR           32.71                     1.35

                               TOTAL          2426.12                    100.00
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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
    43551       ACETONE                   58.08                   1
                                                                    %
                 APPLICATION CATEGORY        EMISSIONS (TONS/YEAR)        OF TOTAL

                 PETROLEUM REFINING             460.20                     6.48
                 PETROLEUM MARKETING             33.94                     0.48
                 ORG SOL SURFACE COAT          4352.21                    61.25
                 ORG SOL OTHER                  256.60                     3.61
                 CHEMICAL                         9.64                     0.14
                 MINERAL                          0.06                     0.00
                 WASTE BURNING                    2.81                     0.04
                 COMBUSTION OF FUELS            124.74                     1.76
                 UNCLASSIFIED                  1787.50                    25.16
                 MISCELLANEOUS INDUSTR           77.49                     1.09

                               TOTAL          7105.19                    100.01
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TABLE 2-39. (Continued).

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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43552      METHYL ETHYL KETONE       72.10                   2
                                                                        %
           APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)        OF TOTAL

           PETROLEUM REFINING              335.86                      4.14
           PETROLEUM MARKETING              33.92                      0.42
           ORG SOL SURFACE COAT           5762.77                     70.95
           ORG SOL OTHER                    34.35                      0.42
           CHEMICAL                          7.39                      0.09
           MINERAL                           5.56                      0.07
           UNCLASSIFIED                   1865.37                     22.97
           MISCELLANEOUS INDUSTR            77.08                      0.95

                               TOTAL      8122.30                    100.01
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43560      METHYL ISOBUTYL KETONE   100.16                   2
                                                                        %
           APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)        OF TOTAL

           PETROLEUM REFINING              177.33                      9.17
           PETROLEUM MARKETING              16.96                      0.88
           ORG SOL SURFACE COAT           1498.23                     77.44
           ORG SOL OTHER                     8.62                      0.45
           CHEMICAL                          2.94                      0.15
           UNCLASSIFIED                    199.86                     10.33
           MISCELLANEOUS INDUSTR            30.64                      1.58

                               TOTAL      1934.58                    100.00
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43814      1,1,1-TRICHLOROETHANE    133.42                   1
                                                                        %
           APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)        OF TOTAL

           ORG SOL DEGREASING             2594.58                    100.00

                               TOTAL      2594.58                    100.00
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KVB   -   ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
     43817      PERCHLOROETHYLENE        165.83                   1
                                                                        %
           APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)        OF TOTAL

           PETROLEUM REFINING              216.31                      1.09
           PETROLEUM MARKETING              33.89                      0.17
           ORG SOL SURFACE COAT            177.91                      0.90
           ORG SOL DRY CLEANING          12835.18                     64.77
           ORG SOL DEGREASING             5497.11                     27.74
           ORG SOL OTHER                     7.39                      0.04
           CHEMICAL                         27.46                      0.14
           UNCLASSIFIED                   1020.07                      5.15

                               TOTAL     19815.32                    100.00
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TABLE 2-39. (Continued).

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
   43820      1.1.2-TRICHLOROETHANE     131.66                   1
                                                                   %
          APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)     OF TOTAL

          ORG SOL DEGREASING              2737.39                 100.00

                               TOTAL      2737.39                 100.00

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
   45101        NAPTHA                  114.00                   2
                                                                   %
          APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)     OF TOTAL

          ORG SOL SURFACE COAT            1115.50                  65.25
          ORG SOL OTHER                      8.33                   0.49
          CHEMICAL                          82.07                   4.80
          WOOD PROCESSING                    4.00                   0.23
          UNCLASSIFIED                     499.65                  29.23

                               TOTAL      1709.55                 100.00

KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
   45201        BENZENE                  78.11                   1
                                                                   %
          APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)     OF TOTAL

          PETROLEUM PRODUCTION            1247.87                  36.94
          PETROLEUM REFINING               666.48                  19.73
          PETROLEUM MARKETING              382.24                  11.32
          ORG SOL SURFACE COAT              53.89                   1.60
          ORG SOL OTHER                     10.01                   0.30
          CHEMICAL                         103.43                   3.06
          METALLURGICAL                     90.31                   2.67
          MINERAL                           20.05                   0.59
          WASTE BURNING                      1.97                   0.06
          COMBUSTION OF FUELS              124.41                   3.68
          FOOD AND AGRICULTURAL              3.20                   0.09
          PESTICIDE USE                    673.84                  19.95

                               TOTAL      3377.70                  99.99

KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT  -  INDIVIDUAL SPECIES REPORT

 SAROAD CODE      CHEMICAL NAME       MOLEC. WEIGHT        REACTIVITY CLASS
   45202        TOLUENE                  92.13                   3
                                                                   %
          APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)     OF TOTAL

          PETROLEUM PRODUCTION             502.45                   4.29
          PETROLEUM REFINING               815.19                   6.96
          PETROLEUM MARKETING              833.69                   7.11
          ORG SOL SURFACE COAT            5788.21                  49.40
          ORG SOL OTHER                   1285.32                  10.97
          CHEMICAL                          49.43                   0.42
          METALLURGICAL                      8.06                   0.07
          MINERAL                            0.06                   0.00
          WASTE BURNING                      0.02                   0.00
          COMBUSTION OF FUELS               33.80                   0.29
          FOOD AND AGRICULTURAL             55.20                   0.47
          UNCLASSIFIED                    2072.16                  17.68
          PESTICIDE USE                    273.92                   2.34

                               TOTAL     11717.51                 100.00
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TABLE 2-39. (Continued).

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KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE     CHEMICAL NAME      MOLEC. WEIGHT       REACTIVITY CLASS
    45203       ETHYLBENZENE           106.16                   3
                                                                    %
           APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)        OF TOTAL

           ORG SOL OTHER                   137.61                      8.65
           CHEMICAL                          0.03                      0.00
           FOOD AND AGRICULTURAL            20.94                      1.32
           UNCLASSIFIED                   1432.34                     90.03

                             TOTAL        1590.92                    100.00


KVB  -  ORGANIC COMPOUNDS EMISSIONS REPORT   -   INDIVIDUAL SPECIES REPORT

  SAROAD CODE     CHEMICAL NAME      MOLEC. WEIGHT       REACTIVITY CLASS
    45222       *ISOMERS OF XYLENE     106.16                   3
                                                                    %
           APPLICATION CATEGORY         EMISSIONS (TONS/YEAR)        OF TOTAL

           PETROLEUM PRODUCTION              0.38                      0.01
           PETROLEUM REFINING              413.20                      7.92
           PETROLEUM MARKETING             745.67                     14.29
           ORG SOL SURFACE COAT           1933.91                     37.05
           ORG SOL OTHER                    16.55                      0.32
           CHEMICAL                         16.44                      0.32
           METALLURGICAL                     0.01                      0.00
           FOOD AND AGRICULTURAL            65.55                      1.26
           UNCLASSIFIED                   1206.09                     23.11
           PESTICIDE USE                   821.76                     15.74

                             TOTAL        5219.56                    100.02
```

TABLE 2-40. METHANE/NONMETHANE ORGANIC EMISSIONS

Application Category	Emissions Ton/Year Total Organic	 Methane	 Nonmethane	% of Total Nonmethane
Petroleum Production	39,000	14,000	25,000	6
Petroleum Refining	42,000	3,500	38,000	10
Petroleum Marketing	68,000	29,000	39,000	10
Solvent Use - Surface Coating	45,000	3,000	42,000	11
Solvent Use - Other	33,000	170	33,000	8
Chemical	1,300	17	1,300	< 1
Metallurigcal	1,000	500	500	< 1
Mineral	250	40	200	< 1
Waste Burning	550	50	500	< 1
Combustion of Fuel	5,900	1,500	4,400	1
Food & Agriculture	400	150	200	< 1
Unclassified (natural)	570,000	360,000	210,000	53
Misc. Industrial	4,300	3,900	400	< 1
Total	810,000	410,000	400,000	100
(Ton/Day)	(2,200)	(1,100)	(1,100)	

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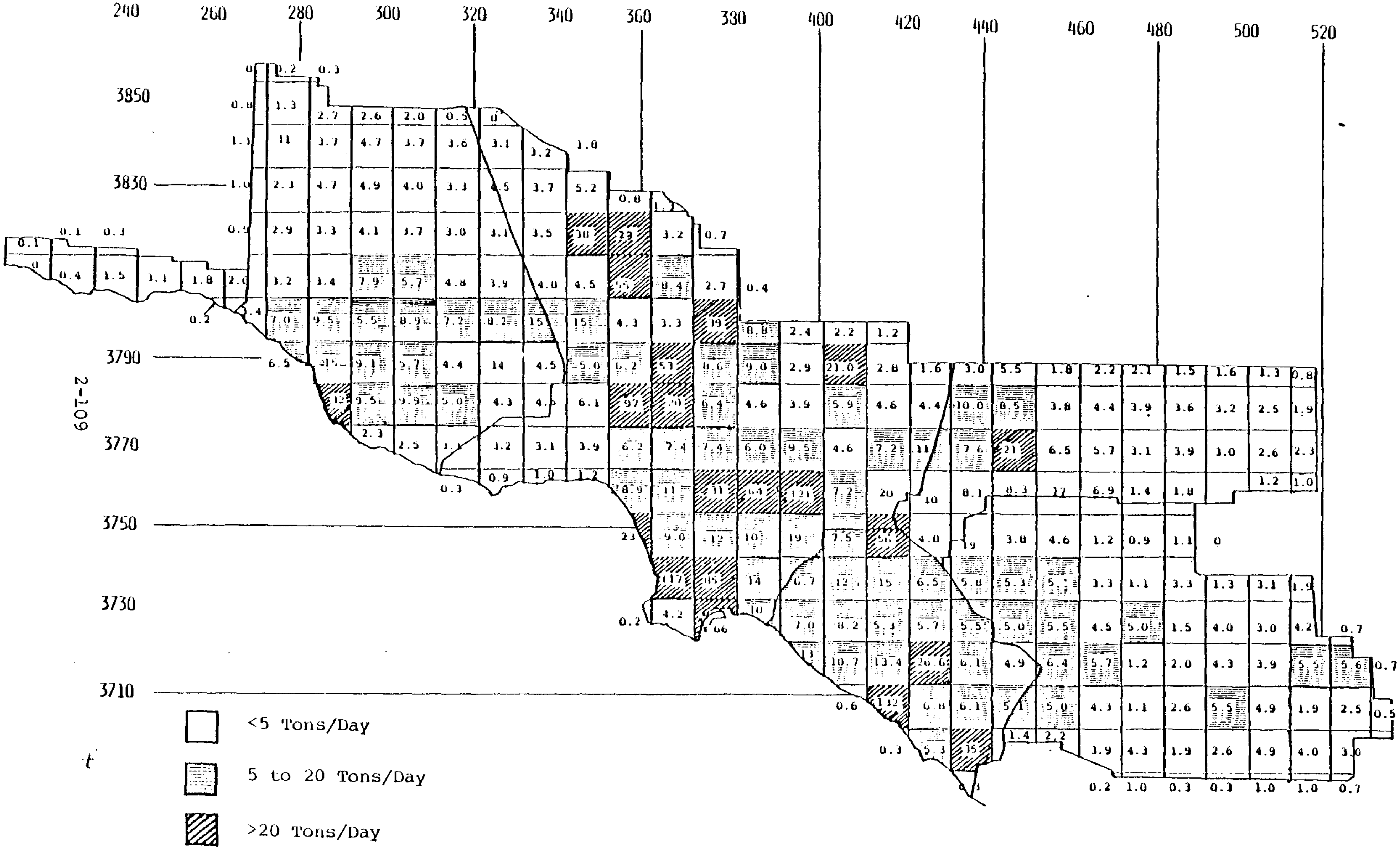

Figure 2-9. Spatial distribution of stationary source organic emissions (numbers in grid indicate emissions in tons/day).

TABLE 2-41. MAJOR 10-KM GRID EMITTERS

UTM Coord.		Nearest City	Emission Ton/Day	Principal Source Type
E/W	N/S			
290	3780	Oxnard	32	90% Landfill
350	3820	Castaic	38	Landfill
360	3820	Bouquet Cyn	23	Landfill
360	3810	Bouquet Cyn	55	Landfill
360	3780	Sepulveda	97	Landfill
360	3750	LA Intern A/P	23	278 Pt Sources
370	3790	Sunland	53	Landfill
370	3780	Burbank	20	177 Pt Sources
370	3740	Torrance	117	Landfill
380	3800	Ravenna	39	Landfill
380	3760	Downtown LA	31	330 Pt Sources
380	3740	Paramount	85	50% Pt and Area Sources 50% Landfill
380	3730	LA Harbor	66	55 Pt Sources and Oil Production
390	3760	Monterey Park	64	70% Landfill
400	3760	El Monte	121	Landfill
410	3790	Baldwin Park	21	Landfill
420	3750	Diamond Bar	56	Landfill
420	3710	N. Laguna	132	Landfill
430	3720	E. Irvine	27	Landfill
440	3700	S. Clemente	35	Landfill
450	3770	Fontana	21	50% Landfill 50% Pt Sources

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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.

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.

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.

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 C_1 - 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:

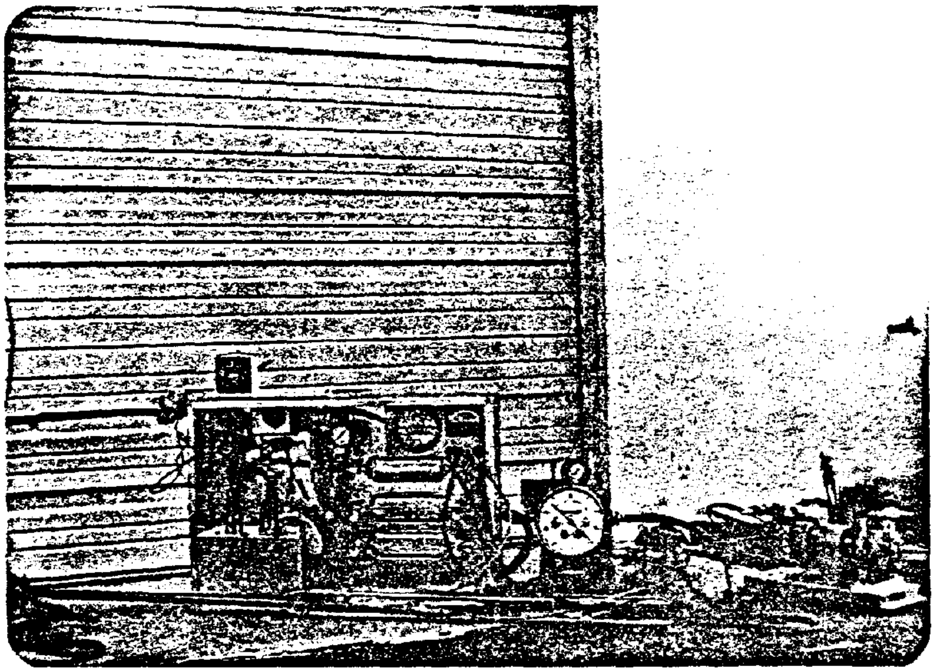
- all metal components were stainless steel
- seals were Viton or Teflon
- containers were borosilica glass
- flexible connections were latex rubber of minimal length.

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



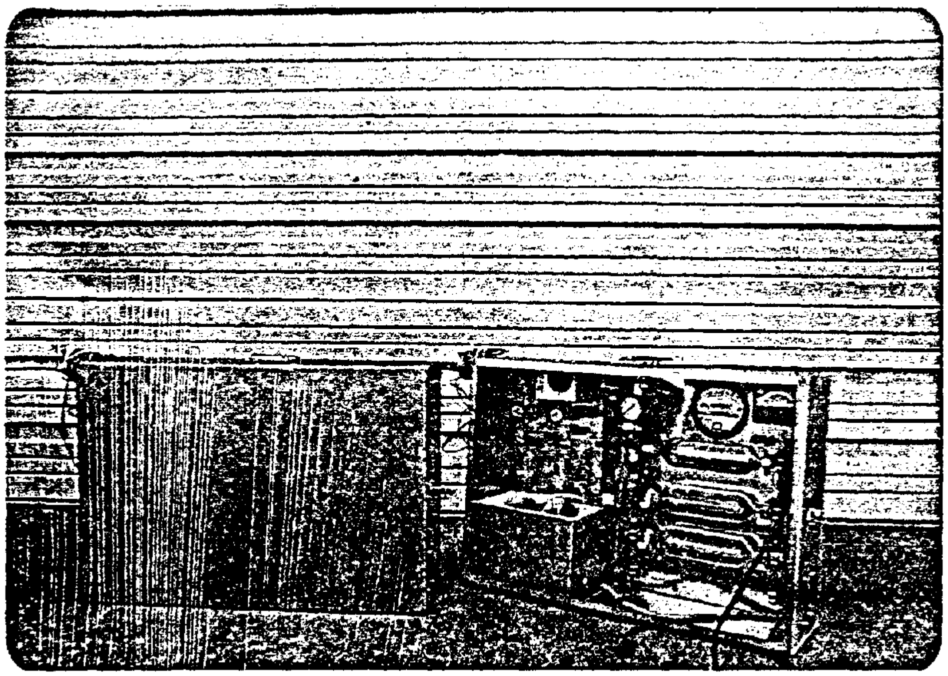


Figure 3-1. KVB hydrocarbon sampling trains.

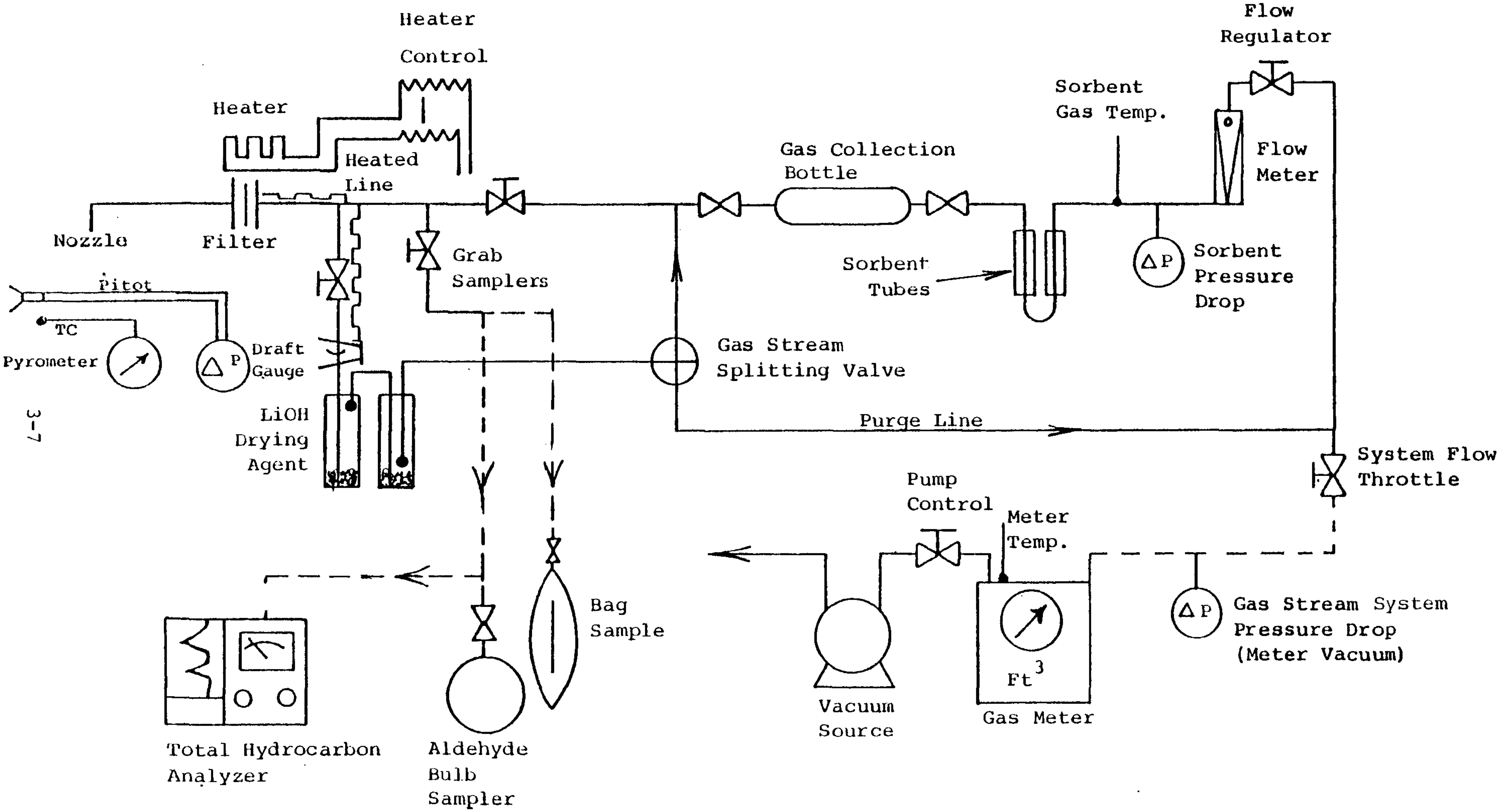


Figure 3-2. Complete organic sampling train as set up for a hot combustion source (> 180 °F) (Mode 1 in Table 3-5).

KVB 5804-714

- an Orsat analyzer for CO, CO_2, O_2, and N_2 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, NOx, SOx, 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 CO_2. In the sampling train it neutralized NOx and SOx 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 CS_2 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.

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_7H_{16}	100	11	--
n-C_8H_{18}	99	<1	--
n-C_9H_{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 (CS_2) was found to be an attractive solvent. Many of the other common solvents, such as methylene chloride (CH_2Cl_2), 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 CS_2 as well as in CH_2Cl_2. Carbosieve B showed poor recoveries with solvents. Testing was therefore primarily focused on solvent extraction of activated charcoal with CS_2 and XAD-2 resin extraction with CH_2Cl_2 (CS_2 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 CS_2 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/CS_2 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.

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_2Cl_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 (0)	1.64

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* FM: Fire Marshall

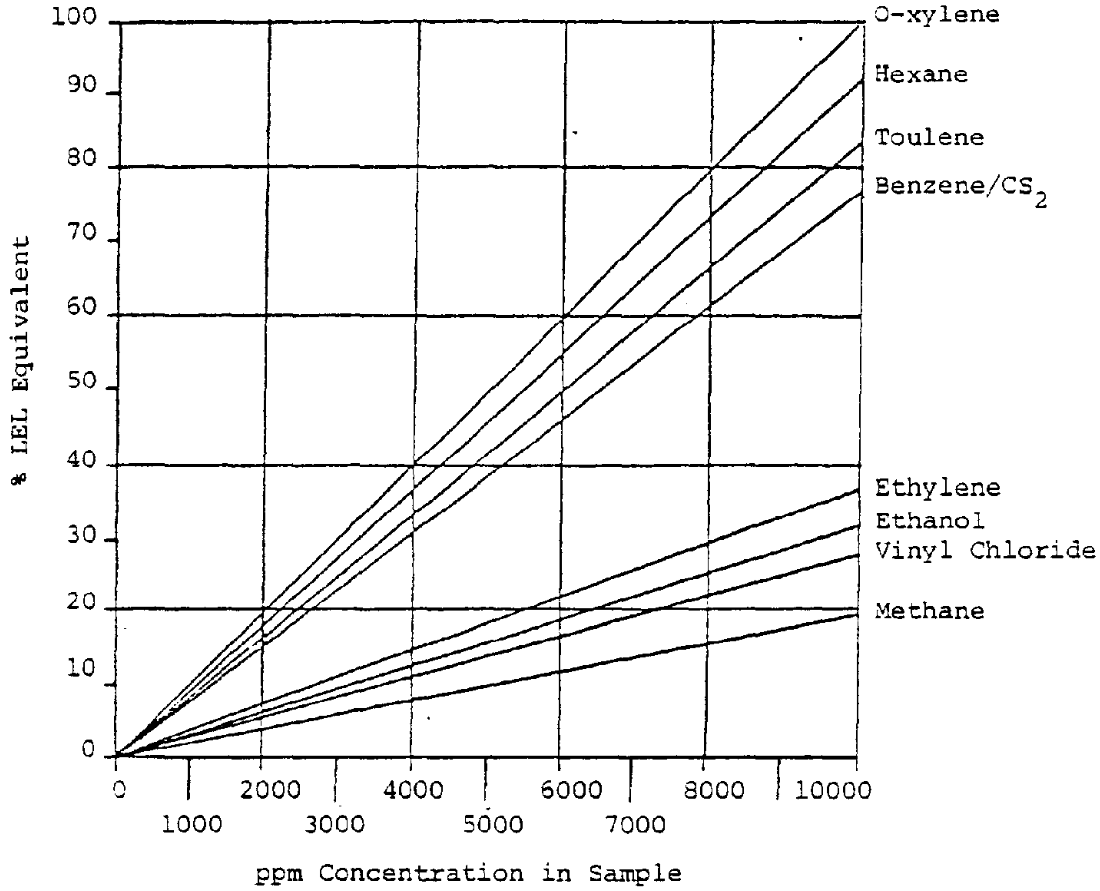

Figure 3-3. TLV sniffer: conversion curves showing relationship of ppm concentrations of various gases to percent LEL equivalents.

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	Heated	X	X	X	X	X	X	X										
	Unheated								X	X	X	X	X	X	X	X	X	X
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											
Aldehyde Bulbs		X	X	X	X	X	X	X		X	X							
Impinger, LiOH		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						X						X				X	X	
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			
Meter		X	X	X	X	X	X	X	X	X	X	X				X	X	
Gast Pump		X	X	X	X	X	X	X	X	X	X							
Pyrometer (Source T)		X	X	X	X	X	X											
Thermometer (Source T)								X	X	X	X	X	X	X	X		X	X
Psychrometer								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.

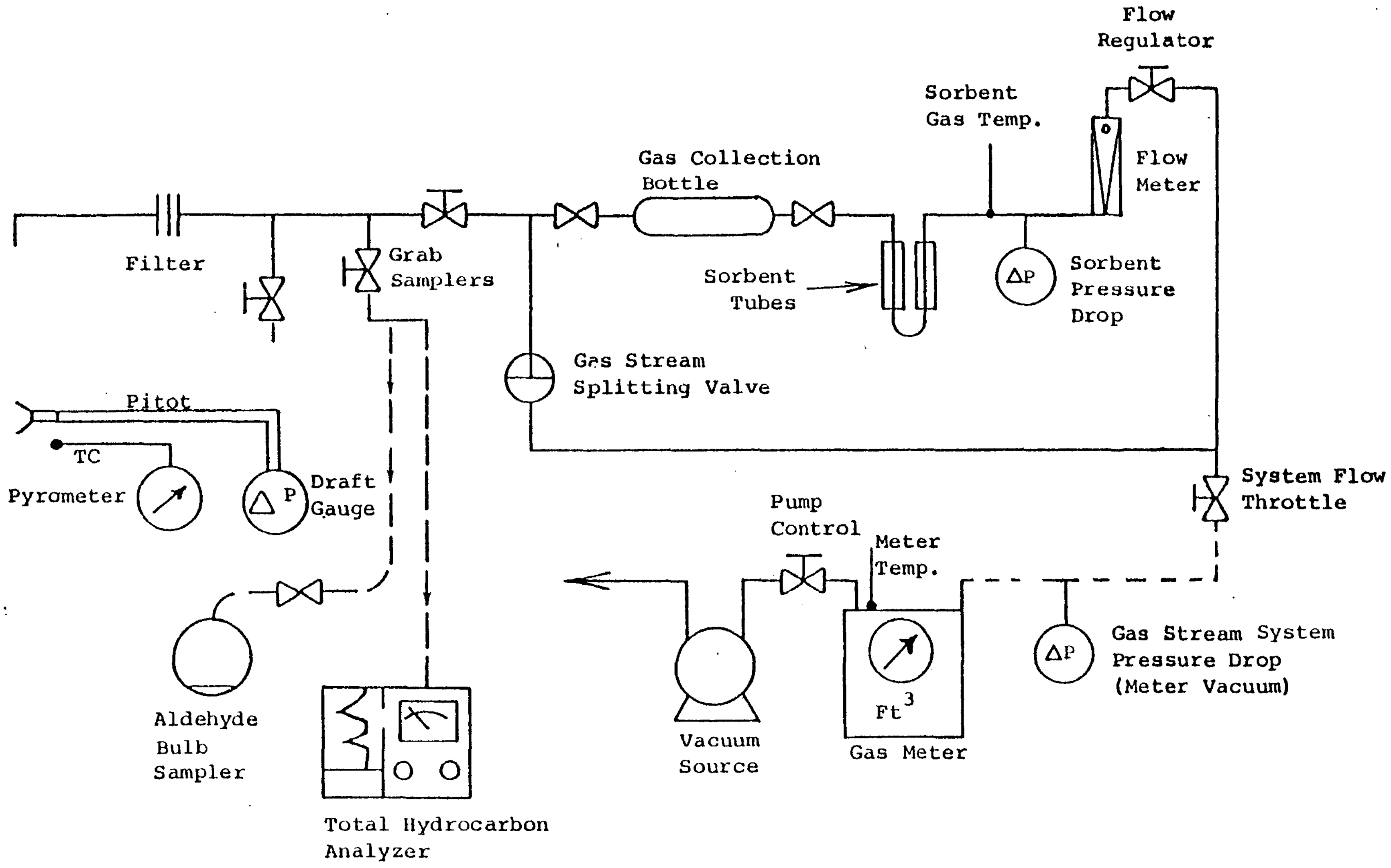

Figure 3-4. Organic sampling train configuration for continuous solvent process related sources of high complexity (Mode 2, Table 3-5).

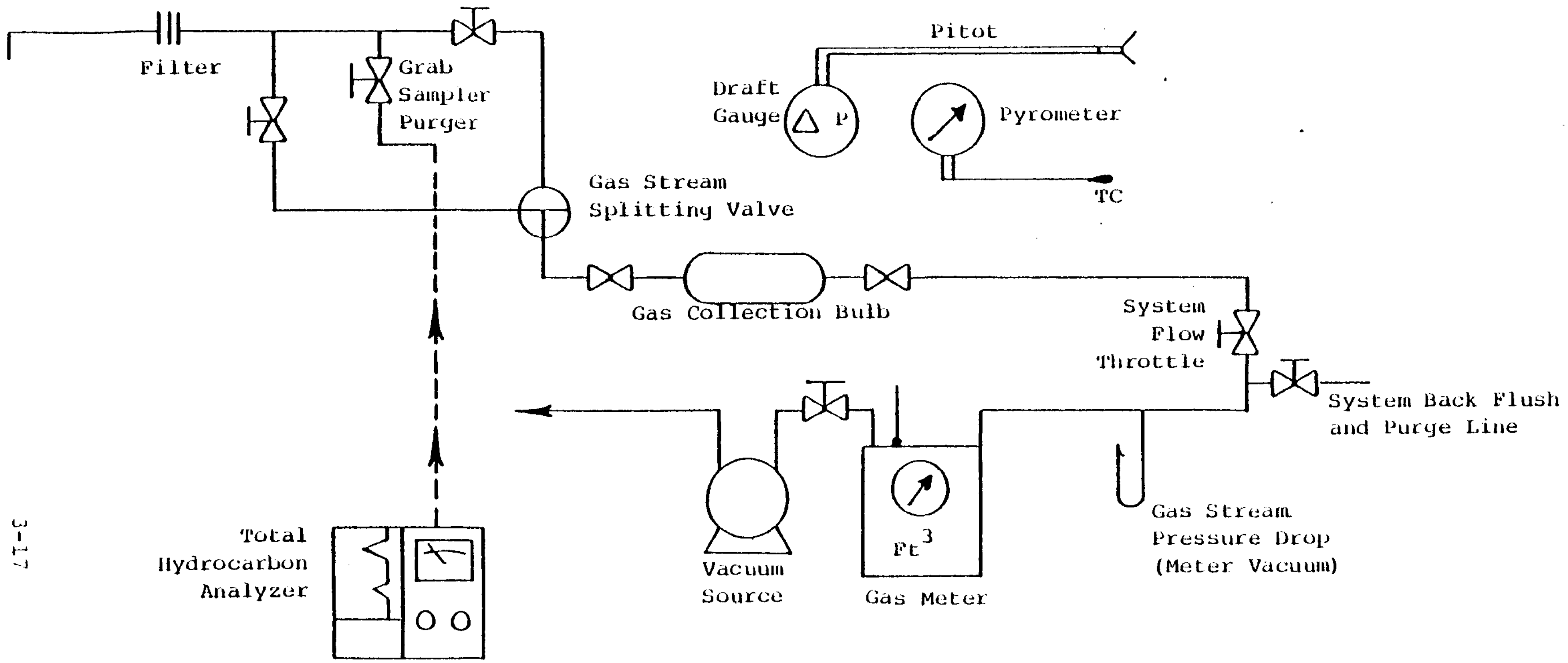

Figure 3-5. Organic sampling train configuration for solvent operations in batch operations (Mode 3, Table 3-5).

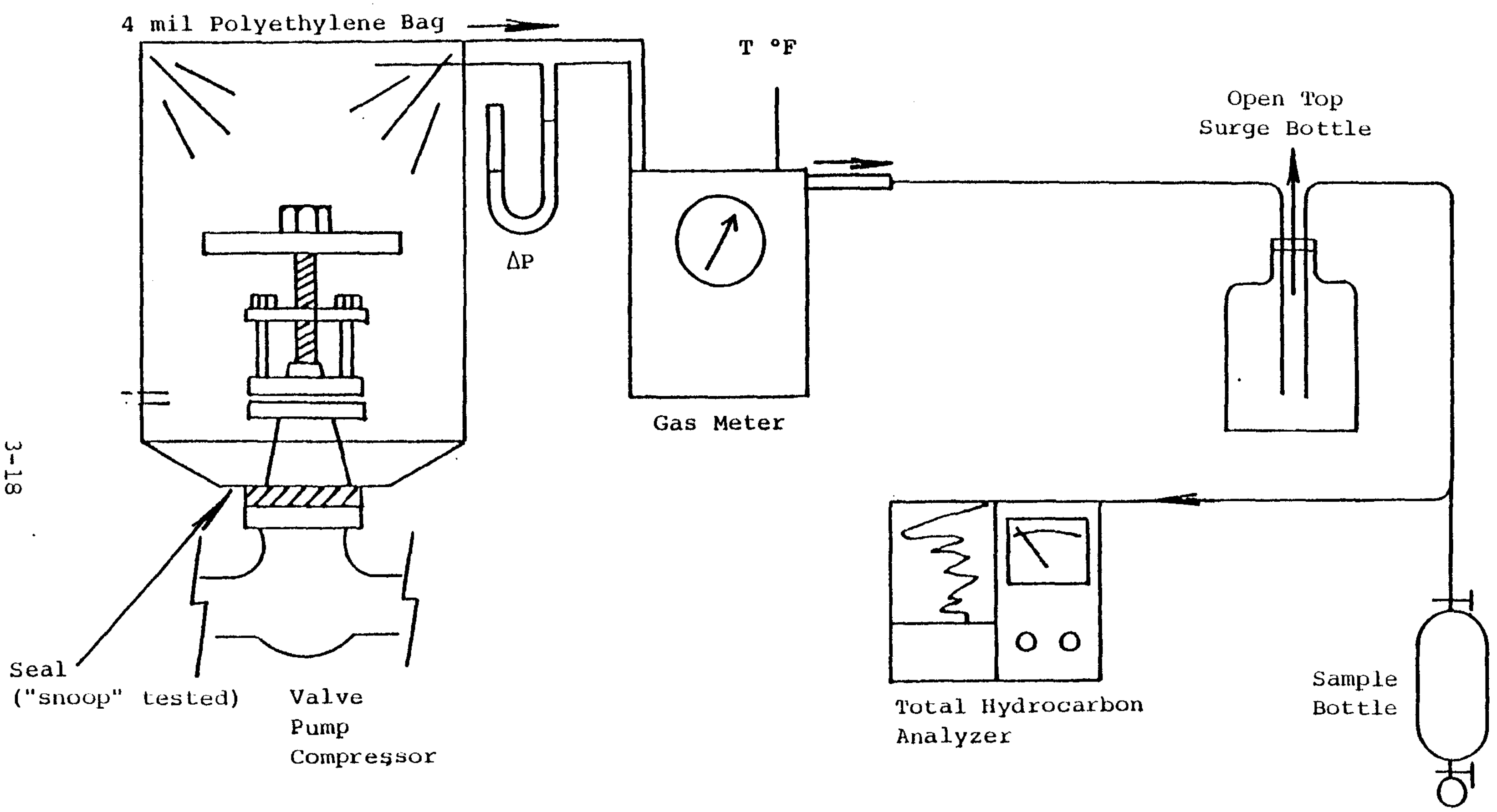

Figure 3-6. Leak rate and concentration measurement of ambient temperature fittings. High leak rates. (Mode 4, Table 3-5)

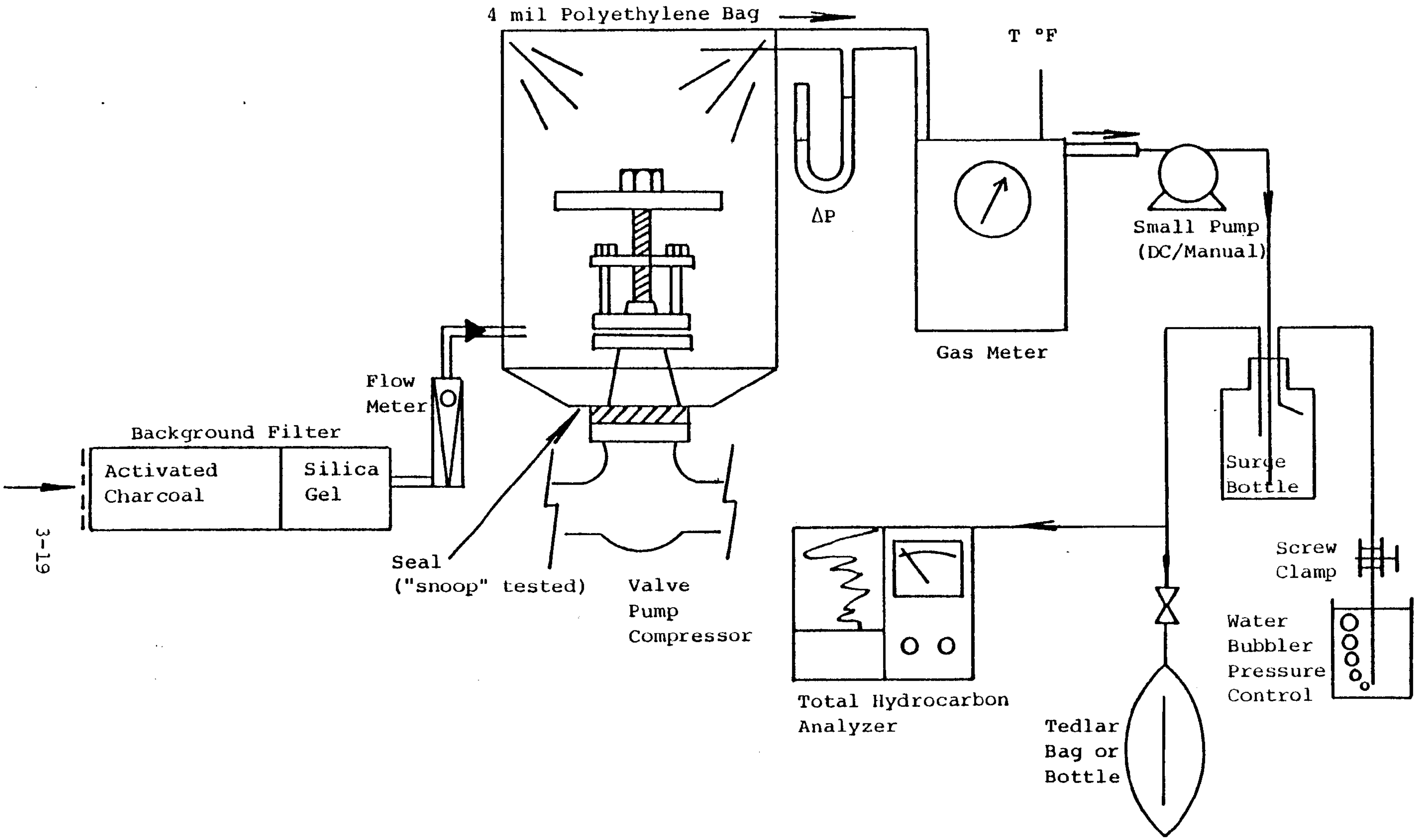

Figure 3-7. Leak rate by dilution sweep and sampling of ambient hydrocarbon fitting. Low leak rates. (Mode 4, Table 3-5)

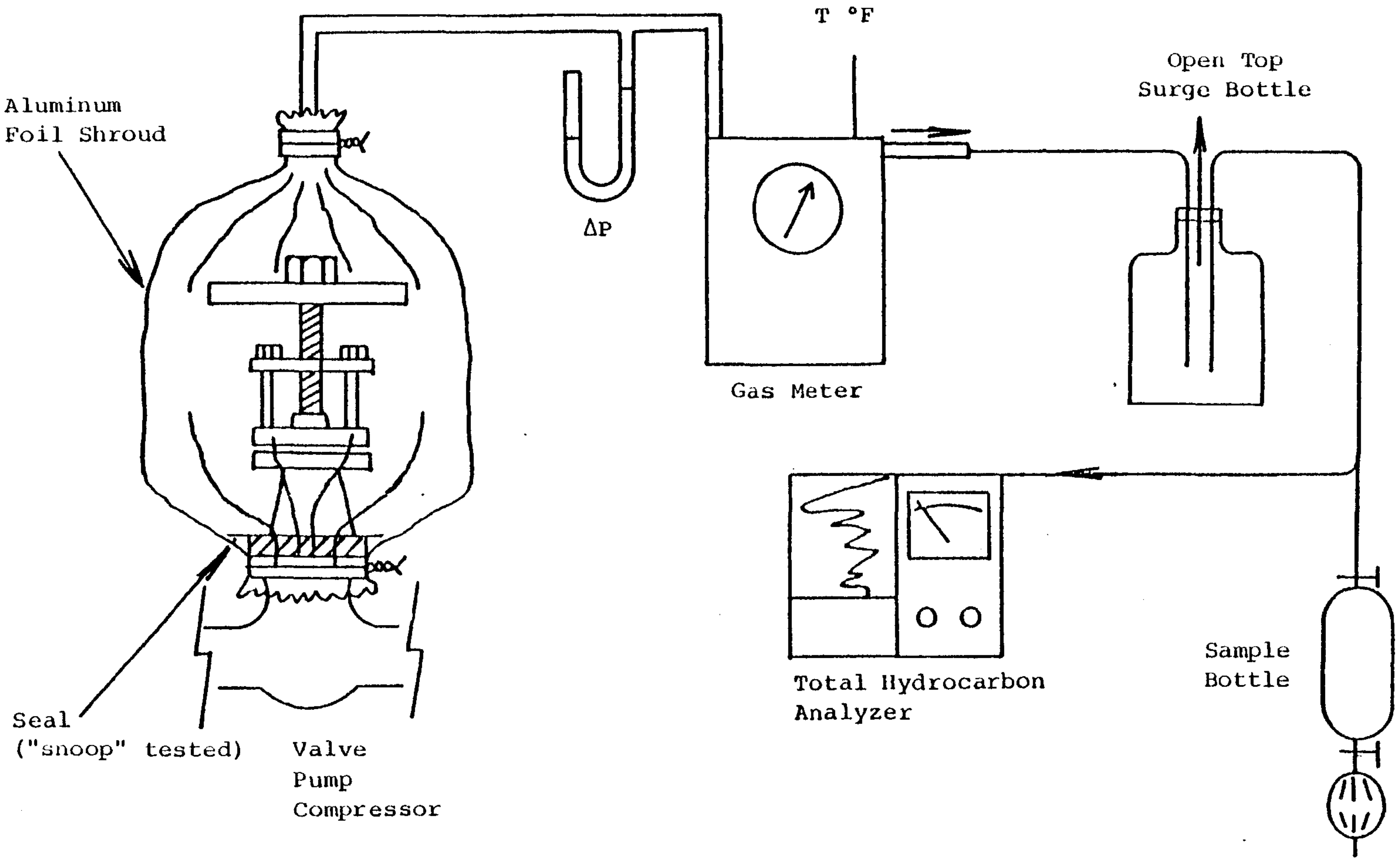

Figure 3-8. Leak rate measurement and concentration measurement of high temperature fitting.

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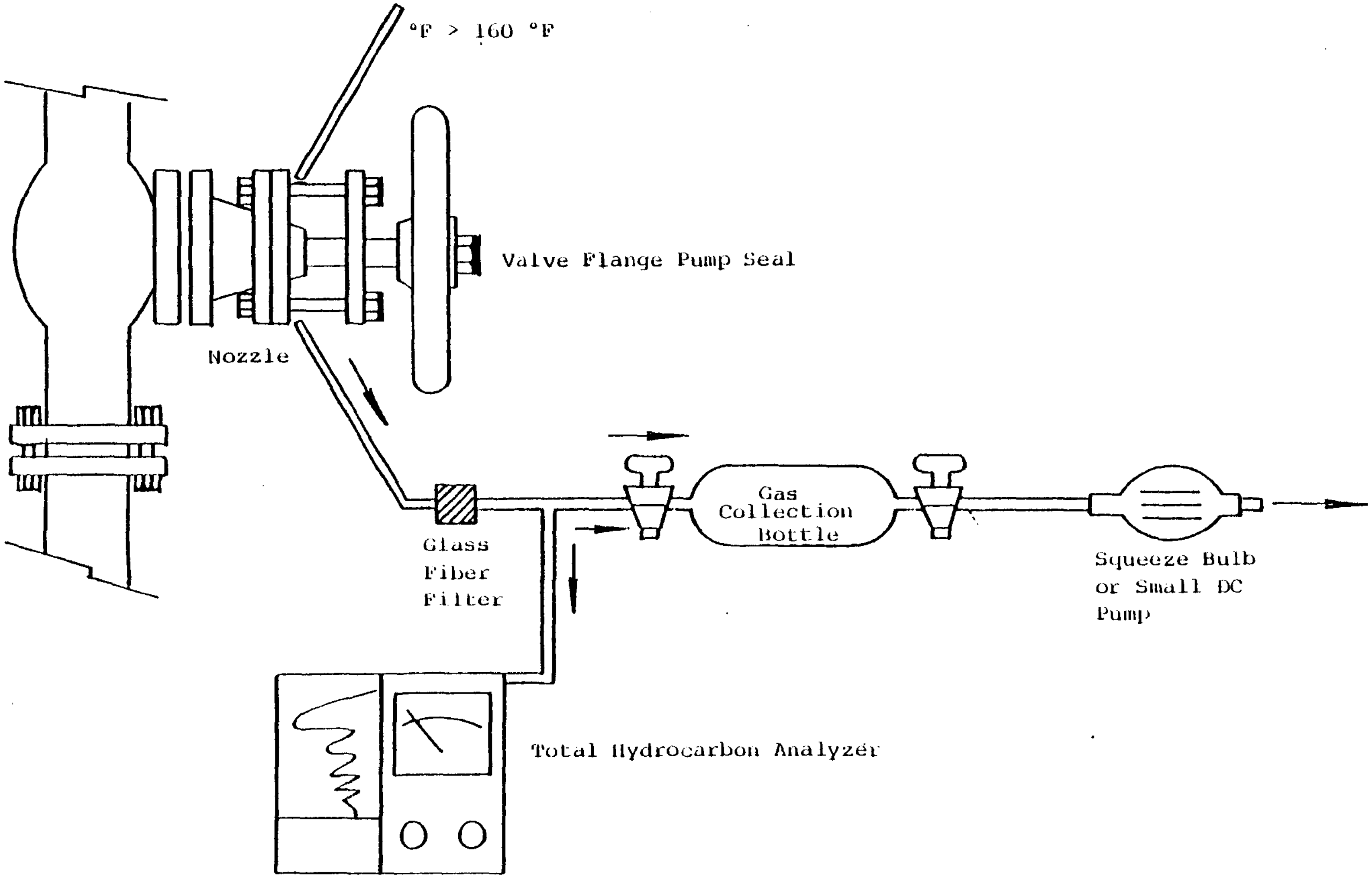

Figure 3-9. Hydrocarbon sampling from hot oil or solvent transfer (Mode 5, Table 3-5).

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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 andehydes, 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 ahdehydes, 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.

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:

$$HC = 1.36x10^{-5}\ ppm_{TLV} \times \frac{ft^3}{t}$$

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

$$1.36x10^{-5} ppm = \frac{1}{10^6} \times \frac{60\ min/hr}{379\ ft^3/lb\text{-}mole} \times 86\ \text{(Mwt. of Hexane)}$$

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

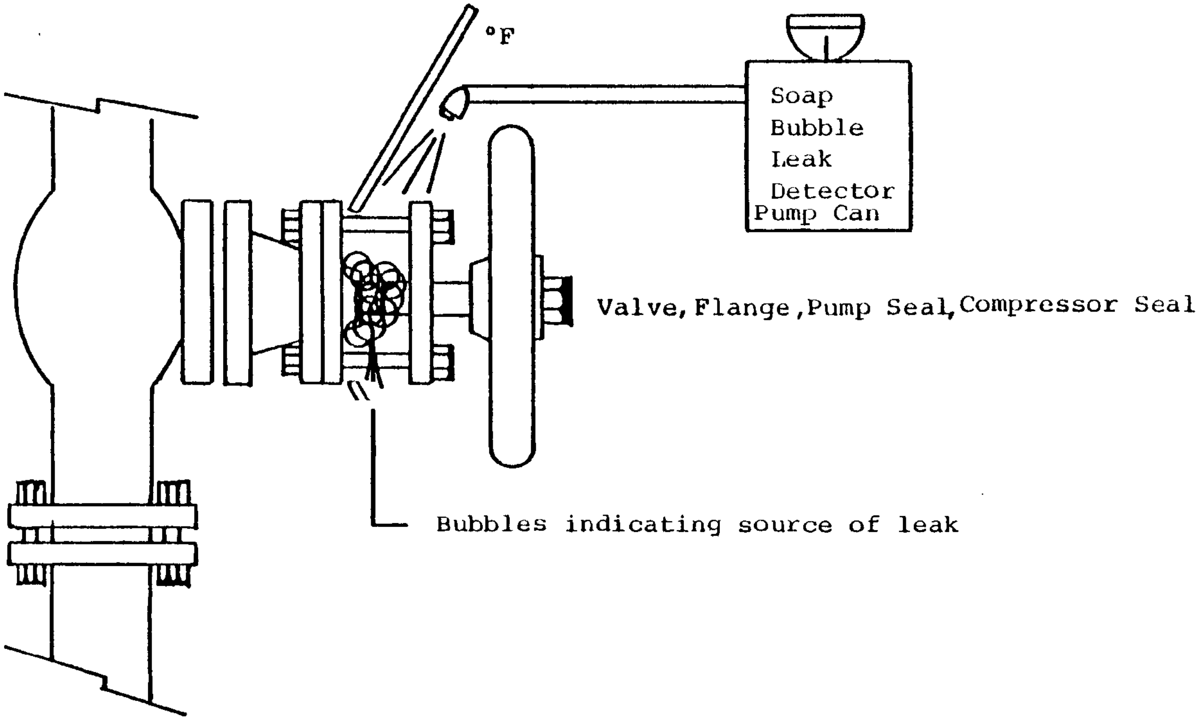

Figure 3-10. Soap bubble detection and temperature evaluation of hydrocarbon fittings.

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.

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 lease 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: H_2 - 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.

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 reagent prepared from rosanaline hydrochloride and sodium bisulfite. After a suitable development time, the adsorbance was read at 580 mμ 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 μg/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 μg 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., μg/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".

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% CO_2 (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. CO_2, Vol. %(Stack Cond.) (see page E) ________
22. O_2, Vol. % (Stack Cond.) (see page E) ________
23. CO, Vol. % (Stack Cond.) (see page E) ________
24. N_2, Vol. % (Stack Cond.) (see page E) ________

Tested by ________

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Sample Code ________ ________ ________

Test No. ________________ Tested By ______________________________

Date ________________ Page B-______________

SUMMARY: EMISSIONS TO ATMOSPHERE

Name of Firm ______________________________

Location of Plant ______________________________

Type of Operation ______________________________

____

Unit Tested ______________________________

Efficiency of Control Equipment, % ______________________________

Gas Flow Rate, SCFM ____________ Gas Temp. °F ____________ (see page D-1)

Test Method ______________________________

____

COMPOUNDS		ANALYZED		EMISSIONS		
Name	Mol. Wt.	ppm	µg	Gr./SCF	Lbs/Hour	Tons/year
				Total:		

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 ________________

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.	Sam-ple Pt.	THC Moni-tor ppm	Stack Temp °F	
	Reading Cu Ft. V_m	Vac. In.Hg P_m	Temp. °F T_m	Reading cc/min V_{S_x}	Vac. In.Hg P_S	Temp. °F T_S	Temp. °F T_i				
Net	Net	Av.	Av.	Net*	Av.	Av.	Av.		Av.		

*Net V_S Cu. Ft. = total cc x 3.531×10^{-5}

A. Material type sampled ______________________

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

C. Condensate Volume, ml ______________________

D. Condensate Vapor Volume, $0.0026 \times c \times (460 + T_m)/(29.9 - P_m)$, CF ________

E_1 Total Sampled Volume, Impingers = $V_m + D$, CF ______________________

E_2 Total Sampled Volume, Sorbent = $V_S + (D \times \frac{V_S}{V_m})$, CF ________

F_1 Sampled Volume in Impingers = $[E_1 \times 520 \times (29.9 - P_m)]/[29.9 \times (460 + T_m)]$, SCF ______________________

F_2 Sampled Volume in Sorbent Train = $[E_2 \times 520 \times (29.9 - P_S)]/[29.9 \times (460 + T_S)]$, SCF ______________________

Continued on page B

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 = $\sqrt{\frac{1.00}{J}}$ = ____________

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KVB

Sample Code

Firm and Unit

Test No.

Page F-

Sampling Station

Date

GAS VELOCITY DATA

Time Start Point	Vel.Head In. H_2O	Temp. °F	Vel. Ft/Sec.	Vel.Head In.H_2O	Temp. °F	Vel. Ft/Sec.	Vel.Head In.H_2O	Temp. °F	Vel. Ft/Sec.
Finish									

A. Average Velocity (Traverse) Ft/Sec

B. Av. Velocity (Ref. Point) Ft/Sec

C. Flue Factor A/B

D. Pitot Correction Factor

E. Gas Density Correction Factor

F. Corrected Vel., AxDxE, Ft/Sec

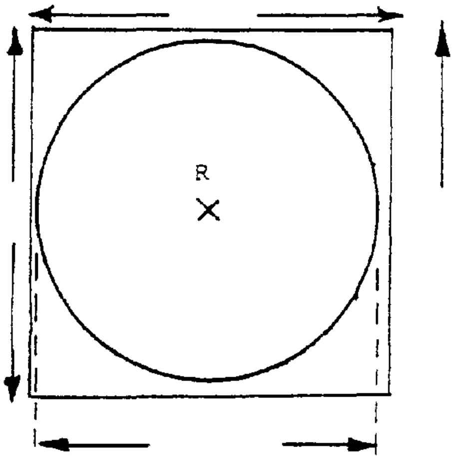
or BxCxDxE, Ft/Sec

G. Area of Flue, Sq. Ft.

H. Average Flue Temp., °F

I. Flow Rate, FxGx60, CFM

J. Flow Rate, 520 x I/(H+460), SCFM



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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, %						
________						

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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.

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

M = molecular weight

The reported hydrocarbon concentrations were calculated from the laboratory results as follows:

The hydrocarbon concentration provided by the laboratory was on a dry, CO_2-free basis. This was converted to actual moisture and CO_2 conditions at the source by the relation (page B of Table 3-7),

$$c_{HC} = (c_{HC})_d \frac{(100 - W.V. - CO_2)}{100}$$

where,

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

$(c_{HC})_d$ = concentration of hydrocarbons; dry, CO_2-free basis, from the analysis; parts per million by volume

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

CO_2 = 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,

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

where,

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

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

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

The $1.58\text{x}10^{-7}$ factor came from the following unit analysis:

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

$$M_{HC}\left(\frac{\text{lb}}{\text{hr}}\right) = c_{HC}\, Q\, (\text{M.W.})_{HC}\ [(1/10^6) \text{ x } (60/379) \text{ x } (\text{lb/hr})]$$

$$= 1.58\text{x}10^{-7}\ c_{HC}\, Q\, (\text{M.W.})_{HC}\quad (\text{lb/hr})$$

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.

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

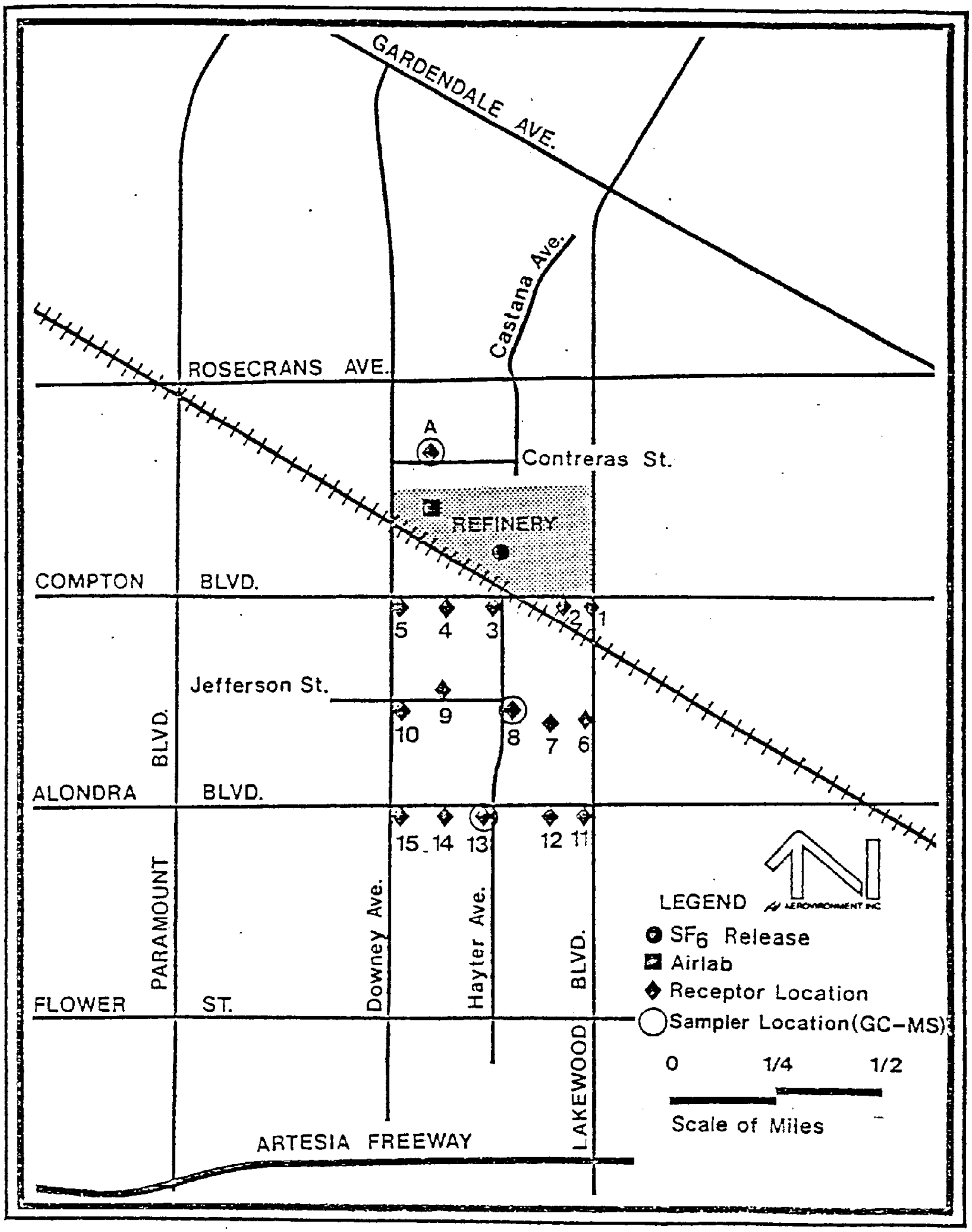

Figure 3-11. Schematic representation of test site for November 23, 1977.

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of 2.5 lb/hr. By knowing the SF_6 release rate and the receptor point concentrations, the source/receptor relationship were to be established by diffusion modelling. Both SF_6 and hydrocarbons were measured simultaneously so that the source/receptor relationship established for SF_6 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 SF_6. 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 SF_6, THC, CH_4 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.

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

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (^oC)	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	340	0.07	7.2	11	E	288,960	A	3.0	5.4	2.5	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	150	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	273,750	A	3.0	5.2	2.5	3.4
									1	3.7	6.5	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	3.8
									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	6.3
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	4.4
									1	8.2	6.6	2.8	OS
									2	12.0	5.9	2.8	6.3
									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

TABLE 3-8. Continued

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (^oC)	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	19.5	5.1	2.6	2.5
									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	13.5	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	4300	10.6	2.4	1.5
									4	13.5	5.9	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	500	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	13.5	4.9	2.9	2.2

TABLE 3-8. Continued

Date	Time	WS (m/sec)	WD (deg)	σ_w (m/sec)	σ_θ (deg)	Temp (^oC)	Stability	Q_{SF_6} (ug/sec)	Receptor	SF_6 (ppt)	THC (ppm)	CH_4 (ppm)	CO (ppm)
Run 11													
11/30/76	0530-0630	2.2	340	0.01	4	8	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	345	0.02	3	8	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	4.8	2.5	6.0

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 13													
12/1/76	0400-0500	2.0	315	0.01	6	8	F	295,650	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	9	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_θ (deg)	Temp (^oC)	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	330	0.09	7	13	F	286,220	A1	76.0	5.2	2.2	5.0
									A2	82.0	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	0900-100	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	18.5	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	7.3	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	6.3	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 SF_6 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 meterological 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 "SCAPCD" 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

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:

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

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

Q_1 = process areas and emulsion plant
Q_2 = asphalt plant
Q_3 = loading-unloading facilities
Q_4 = fixed roof storage tanks
Q_5 = 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

			KVB/ARB	
	SC APCD	AP-42	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

CH_4 emissions from the refinery. However, AV's ambient testing data showed little or no difference for the upwind and downwind CH_4 data. It is possible that under the very stable conditions most of the CH_4 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 ± 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."

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.

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.

	Certified	Analytical Results		
Compound	Contents	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.

	Certified	Analytical Results	
Compound	Contents	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	Analytical Results 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

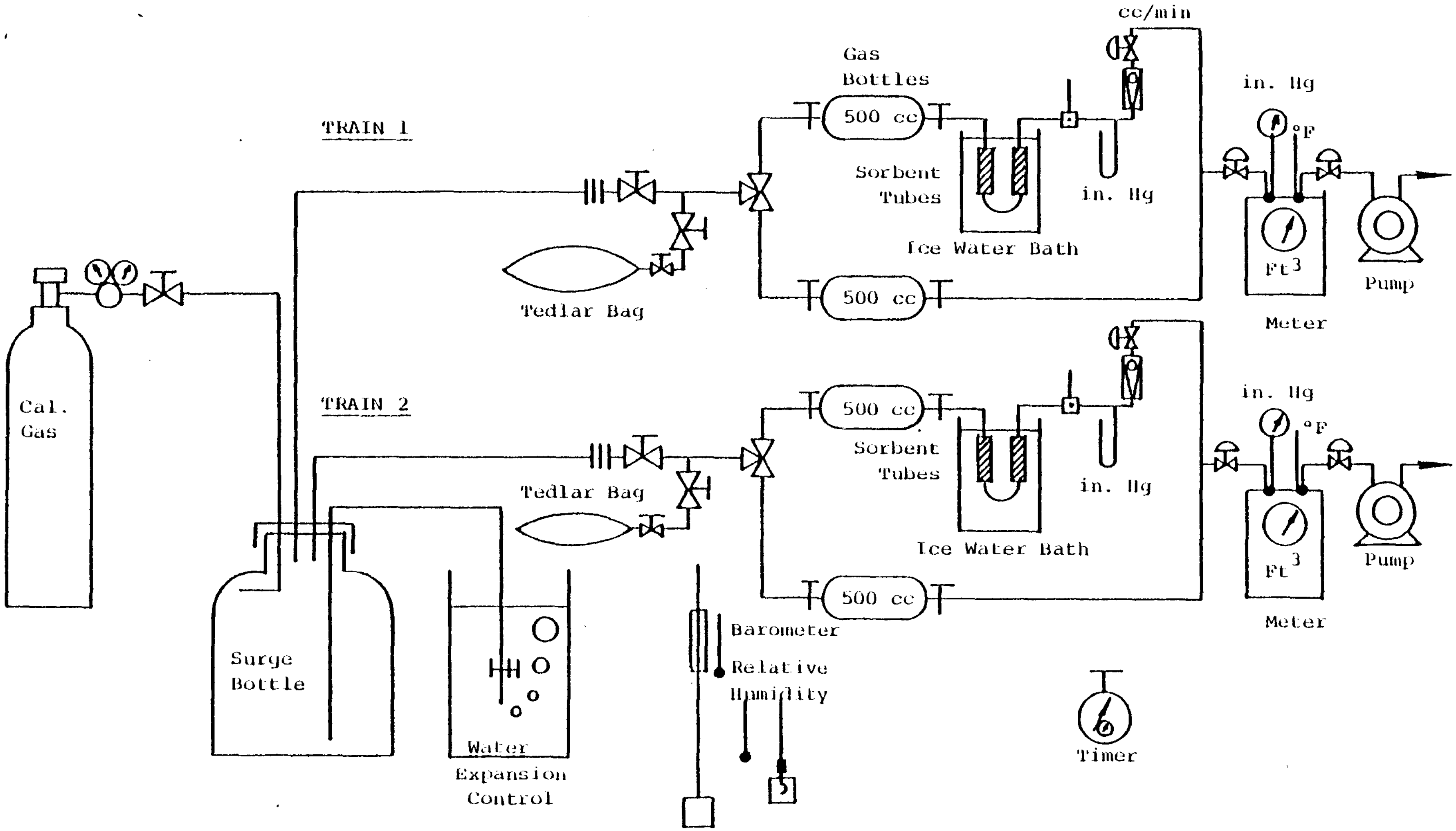

Figure 3-12. Sampling trains in QC test with calibration gas.

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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		
					Charcoal Tube			Charcoal Tube	
				Grab	Front	Back	Grab	Front	Back
Ethylene	51	50	46	33	0	0	29	0	0
Propane	53	47	47	37	14	0	32	12	8
Propene	53	57	48	30	14	0	27	10	9
1,3-Butadiene	51	3	33	8	25	0	8	24	(0.2)
n-Hexane	50	50	49	35	46	0	33	35	1
n-Heptane	51	46	49	36	43	0	36	44	0
Isooctane (2 Methyl Heptane)	50	43	45	34	43	0	32	45	0
Total Recovery	359	296	317	213	185		197	198	

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

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

*$MeCL_2$ 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.

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
Hexane	48	42	Recovery*	*	39	*	47
Methyl Alcohol	53	4	Less	*	<1	*	<1
Acetone	52	43	Than	*	25	*	28
Methyl Ethyl Ketone (2-Butanone)	51	45	ppm Level	*	39	*	47
Methyl Isobutyl Ketone	48	42		*	33	*	39
Total Recovery	252	176			136		161

*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 C_5 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, $< C_4$.

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 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	--

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	--

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	--

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	

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 spe cies. 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

	Train 1	Train 2
Bottle Sample	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
Charcoal Sample	(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

*CS_2 solvent masked the dichloromethane. Refer to bottle sample.

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

	Train 1 ppm	Train 2 ppm	Train 3 ppm
Bottle Sample			
Methane	3.1	3.1	2.9
Ethane	1.1	1.1	1.0
Charcoal Sample	(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

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

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

	Train 1 ppm	Train 2 ppm
Bottle Sample		
Methane	0.8	0.7
Charcoal Sample	0	0
Aldehydes	6.0	6.0

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

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

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 ($\frac{\text{Input - Output}}{\text{Input}}$ x 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.

TABLE 3-31. SUMMARY OF TEST RESULTS

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi- ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							CO_2 %	CO %	O_2 %	lb/hr	T/yr	lb/day	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	15.4	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	Total Organic Emissions lb/day	Species by % wt. of Total 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 #218	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	-	-	-	5.8×10^{-5}	2.5×10^{-4}	1.4×10^{-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	-	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
							CO$_2$ %	CO %	O$_2$ %	Total Organic Emission			Species by % wt. of Total			
										lb/hr	T/yr	lb/day	ARB Class 1	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	14.0	0.459	0.405	2.8 winter 1.1 summer	59	31	10	
Oil Field Well SD 81	10090	1-12-77	5-14		0.019	2	-	-	-	2.0×10^{-4}	8.7×10^{-4}	4.8×10^{-3}	20	80	-	
Oil Field Well #S-81E Wet Gas Valve	10091	1-12-77	5-15		0.108	2	-	-	-	3.2×10^{-4}	1.41×10^{-3}	7.7×10^{-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 Effi- ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							CO_2 %	CO %	O_2 %	lb/hr	T/yr	lb/day	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 S111	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, After-burner 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	-	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							CO_2 %	CO %	O_2 %	lb/hr	T/yr	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 Circu-lation 42600/GPM	0	-	-	-	0.72	3.14	17.28	-	100	-	
Oil Refinery FCC Gas Plant Sour H_2O Drain	10281	4-12-77	7-10		0.1 cc/min	0	-	-	-	6.8×10^{-6}	3×10^{-5}	1.6×10^{-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	-	-	-	6.7×10^{-3}	2.9×10^{-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	-	-	-	8.5×10^{-3}	3.7×10^{-2}	0.20	-	88	12	
Oil Refinery Pump Seal	10299	4-15-77	7-27		0.072	2	-	-	-	2.3×10^{-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	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							CO_2 %	CO %	O_2 %	lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	
Oil Refinery Pump Seal	10302	4-18-77	7-29		0.049	2	-	-	-	1.6×10^{-3}	7.2×10^{-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	-	-	-	5.4×10^{-4}	2.4×10^{-3}	1.3×10^{-2}	2	85	13	
Oil Refinery Pump Seal	10320	4-20-77	7-45		0.072	2	-	-	-	1.6×10^{-4}	6.9×10^{-4}	3.8×10^{-3}	2	85	13	

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			Species by % wt. of Total			
										lb/hr	T/yr	lb/day	ARB Class 1	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	-	-	-	$9.03x10^{-6}$	$3.97x10^{-5}$	$2.17x10^{-4}$	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	

TABLE 3-31(Continued).

							Orsat			Analytical Results						
										Total Organic Emissions			Species by % wt. of Total			
Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	CO_2 %	CO %	O_2 %	lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	Remarks
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 Cir. GPM 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		1.4×10^{-4}	-	-	-	-	0.026	0.11	0.79	-	~100	-	
Oil Refinery Tank 125002	10046	12-1-76	11-7		-	2	-	-	-	4.7	20.6	112.8 *	5	95	-	*API calc.
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	-	-	-				10	90	-	
Oil Refinery Tank 125002	10049	12-1-76	11-10		-	2	-	-	-	4.7	20.6	112.8	4	96	-	
Oil Refinery Vapor Recovery Pump	10051	12-1-76	11-12		0.083	0	-	-	-	0.006	0.026	0.144	5	48	47	
Oil Refinery API Separators	10053	12-1-76	11-13		Water Flow GPM 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	-	-	-	1.4×10^{-3}	0.006	0.034	-	100	-	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							CO_2 %	CO %	O_2 %	lb/hr	T/yr	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		-	-	-	1.32	5.8	31.7	-	100	-	
Oil Refinery Pump P-605	10058	12-2-76	11-18		7.1×10^{-3}	-	-	-	-	1.09	4.8	26.2	-	~100	-	
Oil Refinery Pump P-603	10059	12-2-76	11-19		1.4×10^{-3}	-	-	-	-	0.21	0.9	5.0	-	~100	-	
Oil Refinery Fuel Gas Valve	10060	12-2-76	11-20		0.123	0	-	-	-	0.216	0.945	5.18	17	83	-	
Oil Refinery Fuel Gas Valve	10061	12-2-76	11-21		0.049	0	-	-	-	2.2×10^{-3}	0.010	0.053	26	74	-	
Rubber Tire Mfg. #4 Tuber Solvents, Adhes.	10400	5-25-77	12-1		5066	1.7	-	-	-	51.55	160.8	1237.2	3	96	1	
Rubber Tire Mfg. #5 Tuber Cement	10401	5-25-77	12-2		5471	1.5	-	-	-	17.96	56.0	431.0	2	97	1	
Rubber Tire Mfg. #6 White Side-wall Tubers	10402	5-25-77	12-3		3654	1.6	-	-	-	62.16	32.3	248.6	8	92	-	
Rubber Tire Mfg. #69 Bead Dip Tank	10403	5-25-77	12-4		3739	1.4	-	-	-	49.26	30.8	236.4	1	99	-	
Auto Manuf. Solvent Based Paint Primer After-burner Inlet	10350	5-2-77	13-1		9484	2	-	-	-	21.20 (2 Burners)	30.75	195.3	95	-	5	
Solvent Based Paint Primer Afterburner Out	10351	5-2-77	13-2	98%	10756	8	2.6	0	15.2	0.486	0.705	4.70	23	-	77	
Solvent Based Paint Smoker Afterburner Inlet	10352	5-2-77	13-3		11264	4.55	0	0	19.0	3.899	5.654	37.70	61	32	7	
Solvent Based Paint Smoker Afterburner Outlet	10353	5-2-77	13-4	87%	11720	6.2	1.0	0.0	17.8	0.505	0.732	4.88	-	36	64	
Solvent Based Paint Primer Spray Booth	10354	5-3-77	13-5		44694	1.6	0	0	21	4.536	6.804	43.86	-	100	-	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi- ciency	Mass Flow Rate SCFM	Water %	Orsat CO$_2$ %	Orsat CO %	Orsat O$_2$ %	Analytical Results Total Organic Emissions lb/hr	Total Organic Emissions T/yr	Total Organic Emissions lb/day	Species by % wt. of Total ARB Class 1	ARB Class 2	ARB Class 3	Remarks
Solvent Based Paint Primer Spray Booth	10355	5-3-77	13-6		37799	1.6	-	-	-	6.991	10.137	67.60	-	100	-	
Solvent Based Paint Primer Spray Booth	10356	5-3-77	13-7		52978	1.5	-	-	-	5.481	7.948	53.00	-	100	-	
Solvent Based Paint Primer Spray Booth	10357	5-3-77	13-8		51529	1.5	-	-	-	2.161	3.134	20.90	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10358	5-4-77	13-9		12565	1.6	-	-	-	0.210	0.305	2.03	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10359	5-4-77	13-10		11550	1.6	-	-	-	0.179	0.260	1.73	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10360	5-4-77	13-11		70698	1.6	-	-	-	7.054	10.228	68.21	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10361	5-4-77	13-12		62140	1.6	-	-	-	2.728	3.955	26.38	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10362	5-4-77	13-13		39207	1.6	-	-	-	1.628	2.360	15.74	-	100	-	
Solvent Based Paint Topcoat Spray Booth	10363	5-4-77	13-14		40146	1.6	-	-	-	2.822	4.092	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	4.497	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	1.520	10.13	56	22	22	
Water-borne Paint Flowcoat Drip Holder	10366	5-5-77	13-17		3854	2	-	-	-	0.229	0.332	2.21	-	100	-	
Water-borne Paint Flowcoater Spray Booths (2)	10367	5-5-77	13-18		2590	2	-	-	-	0.120*	0.174	1.16	-	100	-	*Emissions are for both. 1 booth was tested, and the second booth was assumed to have same emissions.

TABLE 3-31 (Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							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.

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							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	0	20.01	4.7	20.59	112.8	-	71	29	
Metallurgical #6 Open Hearth Precip. Inlet	10031	11-23-76	16-1		32961	13.7	11.4	0.1	9.4	4.02	17.35	96.5	87	8	5	
Metallurgical #6 Open Hearth Precip. Outlet	10032	11-23-76	16-2	25% for HC	32961	13	10.2	0	10	3.02	13.05	72.5	54	42	4	
Metallurgical Coke Oven C	10033	11-23-77	16-3		40200	12	2.7	2.1	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	7.8	40.0	172.9	960	85	-	15	
Metallurgical Blast Furnace #4	10035	11-23-76	16-5		55000	13	14.1	0.2	4.0	0.7	2.82	16.8	100	-	-	
Metallurgical Sintering Plant	10036	11-23-76	16-6		152376	7.8	1.6	1.0	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	0.1	14.4	21.87	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	0	6.2	15.24	66.6	365.8	43	21	36	

TABLE 3-31(Continued).

							Orsat			Analytical Results			Species by % wt. of Total			
Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	CO_2 %	CO %	O_2 %	Total Organic Emissions lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	Remarks
Dry Cleaners* Tumble Dryer Stack	10247	3-30-77	19-1		1181	5.6	-	-	-	4.638	4.0	25.51	-	100	-	*Stod. 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	10126N	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	-	-	-	$6.5x10^{-6}$ $lb/hr/ft^2$		-	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 Effi- ciency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
							CO_2 %	CO %	O_2 %	Total Organic Emissions			Species by % wt. of Total			
										lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	
Oil Refinery Line Gas	10008	10-20-76	24-6										23	68	9	
Oil Refinery API Separator	10009	10-20-76	24-7		Water Flow 150 gpm	-	-	-	-	1.06	4.7	25.4	-	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	-	
Residential Furn. Outlet - Home Heater	10235	3-21-77	25-1		515					Not detectible						Natural Gas burner
Roofing Tar Roofing Kettle Fumes	10246	3-28-77	26-1		*	1.6	-	-	-	$1.9x10^{-3}$ per	$8.4x10^{-3}$ applied	$4.6x10^{-2}$ lb/ft^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	-	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	Orsat CO$_2$ %	Orsat CO %	Orsat O$_2$ %	Analytical Results: Total Organic Emissions lb/hr	Total Organic Emissions T/yr	Total Organic Emissions lb/day	Species by % wt. of Total: ARB Class 1	ARB Class 2	ARB Class 3	Remarks
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	-	

TABLE 3-31(Continued).

Process Name	KVB Test No.	Test Date	KVB Code	Control Efficiency	Mass Flow Rate SCFM	Water %	Orsat			Analytical Results						Remarks
										Total Organic Emissions			Species by % wt. of Total			
							CO_2 %	CO %	O_2 %	lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	
Oil Field Packing Gland/ Sucker Rod	10201	3-15-77	28-16		0.090	2	-	-	-	2.1×10^{-3}	3.9×10^{-3}	0.02	4	96	-	
Oil Field Well Cellar	10204	3-15-77	28-17							2.0×10^{-4}	9.0×10^{-4}	1.6×10^{-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 10.3	22.495 5.63	123.6 30.9	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	-	-	

TABLE 3-31(Continued).

										Analytical Results						
							Orsat			Total Organic Emissions			Species by % wt. of Total			
Process Name	KVB Test No.	Test Date	KVB Code	Control Effi-ciency	Mass Flow Rate SCFM	Water %	CO_2 %	CO %	O_2 %	lb/hr	T/yr	lb/day	ARB Class 1	ARB Class 2	ARB Class 3	Remarks
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
Benzeldehyde	2-Nitropropane	Branched alkyl Ketones
Acetone	C_3^+ Paraffins	Cellosolve acetate
Methanol	Cycloparaffins	Unsaturated Ketones
Tert-aklyl 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

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.

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

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

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

Name	ARB Class	Concentrations, ppm measured	Source Type
Fluoro-trichloromethane	1	10,000 - 100,000	Refrigerant fill line gas
Difluoro-dichloromethane	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-Trichloromethane (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 Dichloroethylene	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

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

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

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

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

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 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.

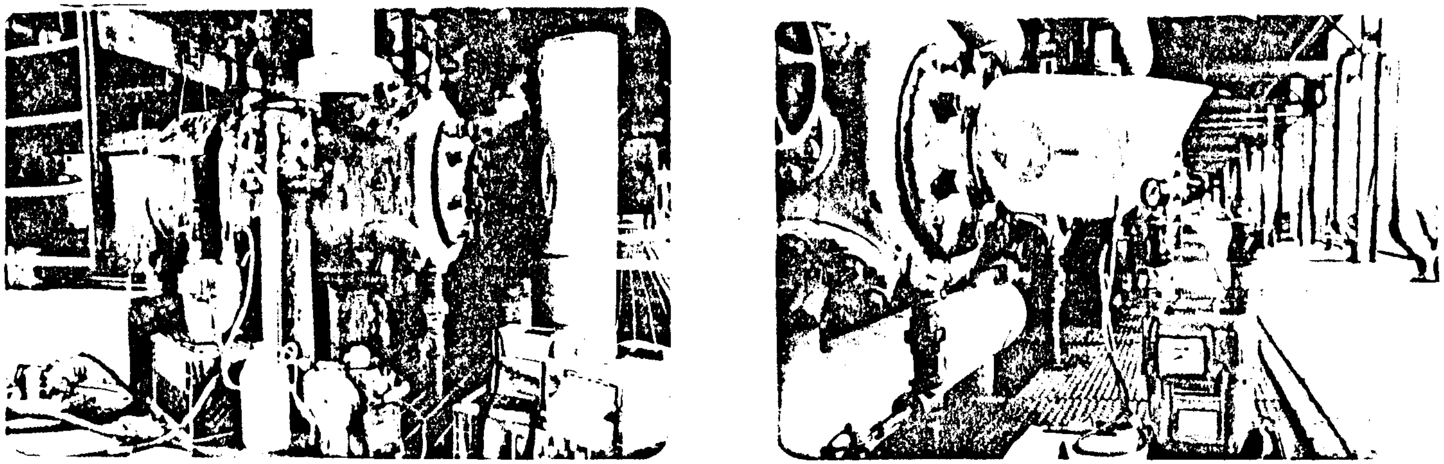
1. Test Results--

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.

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.

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

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

Device Type	Total Tested	Leakers Identified Small	Leakers Identified Medium	Leakers Identified 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

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

Product	Conditions Temperature (°F)	Conditions Pressure (psig)	Total Tested	Leakers Identified Small	Leakers Identified Medium	Leakers Identified 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

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

Device Type	Total Tested	Leakers Identified Small	Leakers Identified Medium	Leakers Identified 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

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

Device Type	Total Tested	Leakers Identified		
		Small	Medium	Large
Wet Gas Lines				
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
Crude Line Fittings	932	0	0	0

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

	Conditions			Leakers Identified		
Product	Temperature (°F)	Pressure (psig)	Total Tested	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

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 ft^3/min which for methane corresponds to a leak rate of 0.9 tons/year. The largest leak in the group was 0.29 ft^3/min corresponding to 3.1 ton/year of methane. Medium leaks ran between 0.006 and 0.08 ft^3/min with a minimum leak rate of 128 lb/year of methane. Small leaks ranged down to as small as 0.0002 ft^3/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

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

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

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.

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			

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.

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

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

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

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

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)
Large Leakers			
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	12	18 lb/day
7	Liquid	18	Large liquid valves 18 lb/day
Medium Leakers			
7	Gas	2	
7	Gas	6	Medium Gas Valves
7	Gas	2	3 lb/day
7	Liquid	2	
7	Liquid	3	Medium Liquid Valves
7	Liquid	5	3 lb/day
Small Leakers			
7	Gas	1.0	
7	Gas	0.2	
11	Gas	0.02	
7	Gas	0.02	Small Gas Valves
11	Gas	0.05	0.3 lb/day
7	Liquid	0.02	
7	Liquid	0.02	
7	Liquid	0.02	Small Liquid Valves
7	Liquid	0.0002	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 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:

TABLE 3-49. REFINERY EMISSIONS, PUMP SEALS

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

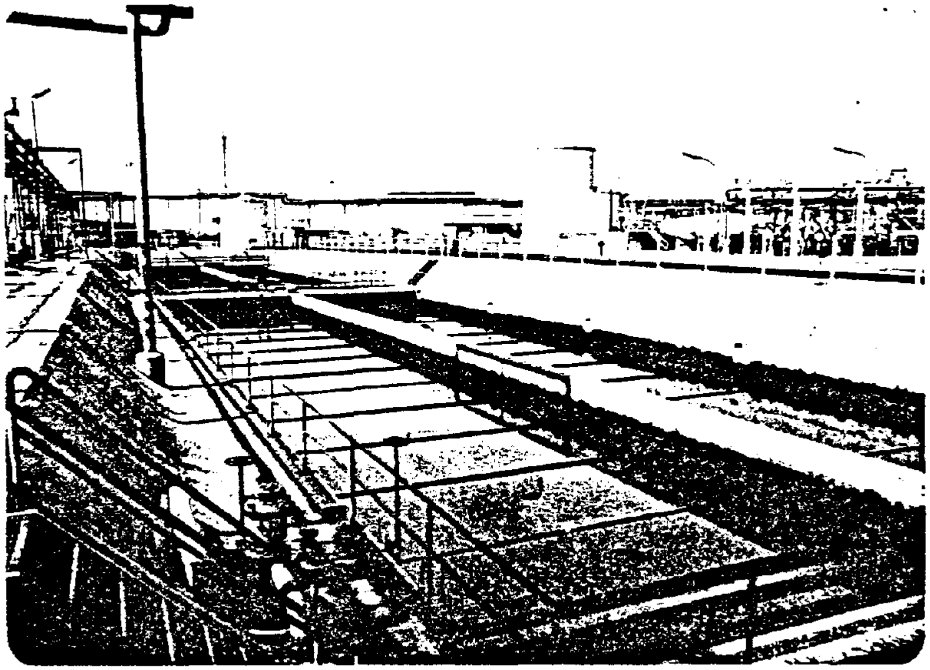

Figure 3-14. Oil/water separator tested.

Location Code	Evaporation Rate ($lb/hr \cdot ft^2$)
7	0.01
11	0.0002
24	0.004

The Code 7 separator in Figure 3-14 had a surface area of 14,000 ft^2. At the rate of 0.01 $lb/hr \cdot ft^2$ 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:

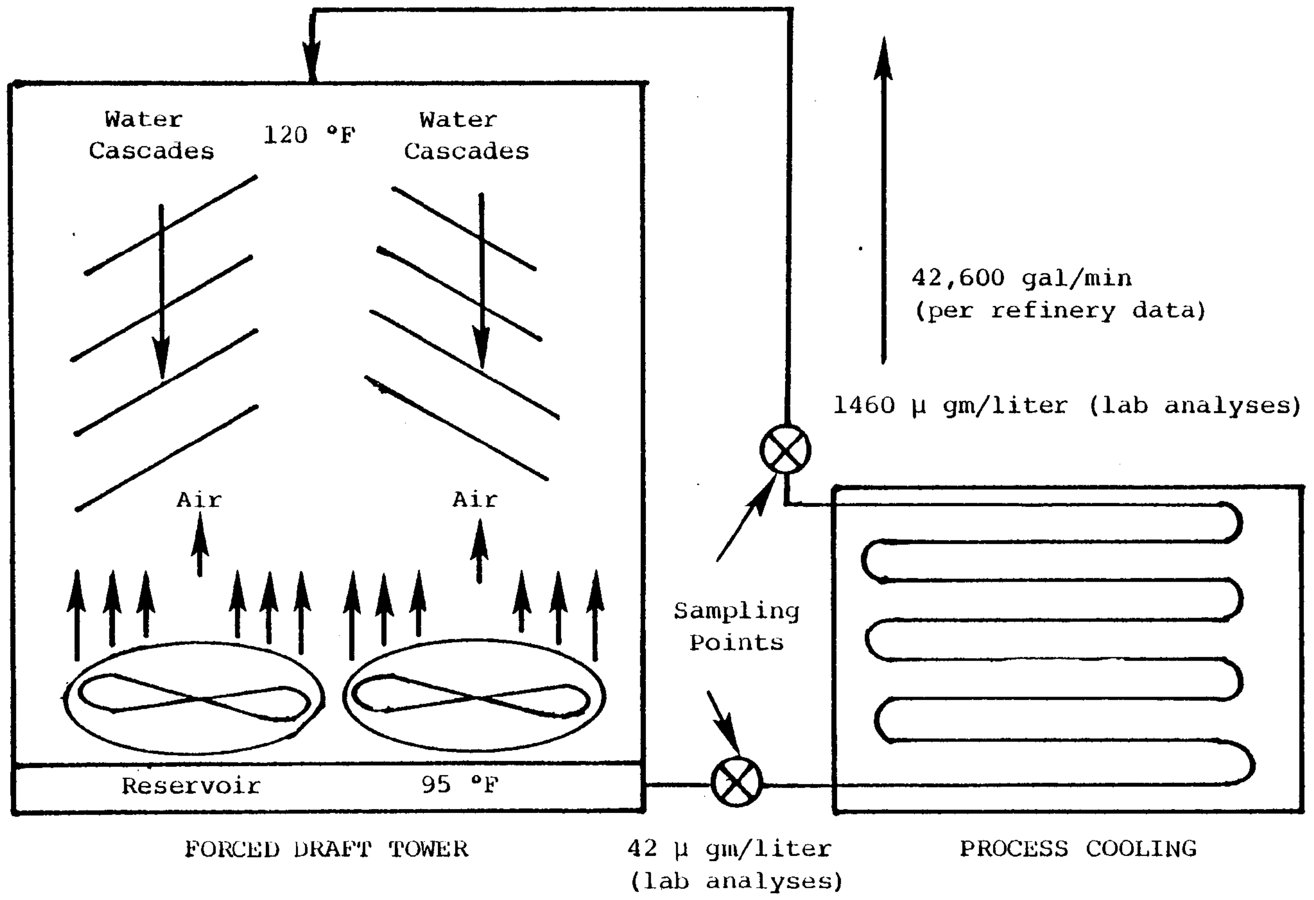

Figure 3-15. Forced-draft cooling tower schematic.

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

$$\text{Emission Rate} = 1418\ \frac{\mu\ \text{gm}}{\text{liter}} \times \frac{3.785\ \text{liter}}{\text{gal}} \times \frac{\text{gm}}{10^6\ \mu\ \text{gm}} \times \frac{\text{lb}}{454\ \text{gm}} \times \frac{42{,}600\ \text{gal}}{\text{min}} =$$

$$= 0.5\ \frac{\text{lb}}{\text{min}} \times \frac{60\ \text{min}}{\text{hr}} = 30\ \frac{\text{lb}}{\text{hr}} \times \frac{24\ \text{hr}}{\text{day}} = 700\ \frac{\text{lb}}{\text{day}} \times \frac{365\ \text{day}}{\text{yr}} \times \frac{\text{ton}}{2000\ \text{lb}} =$$

$$= 130\ \frac{\text{ton}}{\text{yr}}$$

To relate this to AP-42 the emissions must be put into lb/10^6 gal. Other emission factors are in lb/day/1000 GPM

0.5 lb/min x min/42,600 gal x 10^6 = <u>12 lb/10^6 gal</u>

700 lb/day ÷ 42,600 GPM/1000 = <u>16 lb/day/10^3 GPM</u>

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 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 lb/day/1000 GPM while a "more realistic average figure used by some refineries is 8 to 10 lb/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

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	6	
API 931*				
1957 Study	200	40		3 - 5
Best Estimate	400	70		8 - 10
KVB Tests	700	130	12	17

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

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*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. Applicance 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.

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	4	3	8	1
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.

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

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 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 consummed 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:

	%
ethyl acetate	18
n-butyl acetate	17
n-amyl acetate	11
C7-13 aliphatics	25
aromatics	28
isopropyl alcohol	1
	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.

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 x 13.5 = 5.4 lb.

Laboratory Paint Experiment	Field Measurement
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.

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.

3-2 Levache, B. and S. M. MacAskill, "Analysis of Organic Solvents Taken on Charcoal Samplers," Anal. Chem., 48, (1), 76-78, 1976.

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.

SECTION 4.0

HYDROCARBON EMISSION CONTROL TECHNOLOGY

The objective of this section is to report on the state-of-the-art of hydrocarbon emission control technology, and specifically to identify those control methods applicable to the sources in the Basin and the cost-effectiveness of these methods in each application. The information presented was intended to be used for organic emission control strategy along with the basic inventory presented in Section 2.0. In this regard, those source categories with the largest and most reactive emissions and the lowest control system cost effectiveness should be the primary candidates for emission reductions. Because the cost and performance efficiency of control equipment varies with the specific application, a great deal of engineering judgment was exercised in generalizing the cost effectiveness numbers. However, the "average" values were felt to be of sufficient accuracy to validate the relative cost effectiveness between the various methods and applications.

The installed costs used in this report, unless specified to the contrary, are the costs that an owner would pay to a contractor to install that piece of equipment including the equipment purchase price and the contractor's fees for designing, supervising, and installing the equipment. But these are not the total costs to the owner. In addition to these direct costs are such indirect costs as the engineering and management time necessary to recognize the problem; find alternative solutions; select equipment and contractor; supervise the construction and integration with the plant; company lost revenues for the time the plant is inoperative while the equipment is being installed; changes elsewhere in the plant due to the new control equipment; and the company's general and administrative expenses (bookkeeping, accounting, legal, etc.) associated with these expenditures. These indirect items can add 50% to 100% additional cost to the owner.

In the past year, the EPA has published a number of reports and guideline documents which contain extremely thorough treatments of the various aspects of organic emission control technology and its application to various industries and source types. Those documents, referenced in this section, were the basis for much of this discussion, and should be consulted for more detailed information.

A summary of the various control techniques and the sources to which they apply is shown in Table 4-1. This report section is based on this table. Control methods are discussed in Section 4.1, their application on the various sources listed in Table 4-1 are covered in Section 4.2, and cost effectiveness data are presented in Section 4.3.

TABLE 4-1. ORGANIC EMISSION CONTROL OPTIONS FOR VARIOUS PROCESSES

Control ➤ / Process	Carbon Adsorption	Thermal Incineration	Catalytic Incineration	Condensation	Absorption (Scrubbing)	Vapor Space Elimination (Floating Roof Tank)	Liquid/Vapor Exchange (Balance System)	Enclosure	Process and Material Changes	Improved Maintenance	Other	Remarks
1. **PETROLEUM OPERATIONS**												
Production												
Valves, Flanges, etc.									X	X		Plug valves freq'ly lubed
Pumps and Compressors									X	X		Mech. seals
Tanks (Prod. & Stor.)				X		X		X		X	X	Vapor Recovery, white paint
Waste Water Separators						X		X				Floating Covers
Well Vents (Tertiary Recov.)		X		X								
Boilers & Heaters										X	X	Combustion Optimization
IC Engines			X						X	X	X	4 cycle; Tuneups
Refining												
Valves, Flanges, etc.									X	X		Plug valves, lube frequently
Pumps and Compressors									X	X		Mech. seals
Waste Water Separators						X		X				Floating Covers
Vacuum jets				X								
Asphalt Air Blowing		X		X	X							
Boilers & Heaters										X	X	Combustion Optimization
Catalyst Regenerators		X										
Storage Tanks						X		X		X	X	Double seal, white paint
Transferring				X			X				X	Bottom filling
Blow Down	X	X		X								
Marketing												
Transferring												
Truck to Tank							X		X	X		Bottom filling
Tank to Car	X	X	X	X			X			X		Balance or vacuum system
Tank breathing				X							X	Stratified vent

NOTE: For each process, the X's indicate the candidate control devices to be considered. The final selection should be based on the most favorable economic factors.

TABLE 4-1 (Continued)

Control ➤ / Process ▼	Carbon Adsorp-tion	Thermal Incin-eration	Catalytic Incin-eration	Conden-sation	Absorption (Scrubbing)	Vapor Space Elimi-nation (Floating Roof Tank)	Liquid/Vapor Exchange (Balance System)	Enclo-sure	Process and Material Changes	Improved Mainten-ance	Other	Remarks
2. <u>ORGANIC SOLVENT OPERATIONS</u>												
<u>Metal Coating</u>												
Automotive	X	X	X						X			Water-borne paint
Cans	X	X	X						X			Low Solv. Coatings
Coil Coating	X	X	X						X			Low Solv. Coatings
Appliances	X	X	X						X			Low Solv. Coatings
Machinery	X	X	X						X			Low Solv. Coatings
Commercial Products	X	X	X						X			Low Solv. Coatings
Furniture	X	X	X						X			Low Solv. Coatings
<u>Paper & Film Coating</u>												
Adhesive tapes and Labels	X	X	X						X			Low Solv. Coatings
Decorated and Glazed Paper	X	X	X						X			Low Solv. Coatings
Photo Film & Paper	X	X	X						X			Low Solv. Coatings
Typewriter Ribbons	X	X	X						X			
Magnetic Tape	X	X	X						X			
<u>Fabric Coating</u>												
Dyeing	X	X	X						X			Water Sol. Dye
Scouring	X	X	X						X			Low Solv. Coating
Rubberizing	X	X	X						X			
Vinyl Coating	X	X	X						X			
Carpet Mfg.	X	X	X						X			
<u>Other</u>												
Printing	X	X	X						X			Water-borne Ink
Tire Mfg.	X	X	X									
Degreasing	X	X	X	X					X			Detergent
Pesticide Mfg.	X			X					X			Water vehicle
Dry Cleaning	X	X	X	X				X	X			Low Reactivity perchloro-ethylene
Architectural Coatings									X			Low Solv. Coatings
Wood Finishing	X	X	X	X					X			Low Solv. Coatings

NOTE: For each process, the X's indicate the candidate control devices to be considered. The final selection should be based on the most favorable economic factors.

TABLE 4-1 (Continued)

Control ➤ / Process	Carbon Adsorption	Thermal Incineration	Catalytic Incineration	Condensation	Absorption (Scrubbing)	Vapor Space Elimination (Floating Roof Tank)	Liquid/Vapor Exchange (Balance System)	Enclosure	Process and Material Changes	Improved Maintenance	Other	Remarks
3. <u>CHEMICAL MANUFACTURING</u>												
Solvent	X	X	X	X	X					X		
Resin	X	X	X	X						X		
Fibers and Plastics	X									X		
Paints, Varnishes and Inks	X	X	X	X								
Pharmaceuticals	X	X	X	X	X							
Cosmetics		X			X							
LPG's	X	X	X	X						X		
Carbon Black		X			X							
Misc. Industrial Chemicals	X	X	X	X	X					X		
4. <u>OTHER INDUSTRIAL PROCESSES</u>												
<u>Metallurgical</u>												
Coke Ovens		X			X							Primarily sulfur and particulate
Foundries		X										
Heat Treat Ovens					X			X		X	X	Combustion modif.
Blast Furnaces					X			X		X	X	
Open Hearth Furnaces					X			X		X	X	
<u>Mineral</u>												
Asphalt Paving					X				X			Water emulsion
Asphalt Roofing								X				Covered kettle
<u>Food</u>												
Processing	X	X	X	X								
Restaurants, etc	X	X	X	X								
Alcoholic Beverages	X	X	X		X							
Citrus Flavor Seal									X			
<u>Combustion of Fuel</u>												
Boilers										X	X	Combustion tuning
<u>Waste</u>												
Landfills		X						X				Waste heat boiler
Other		X						X				

NOTE: For each process, the X's indicate the candidate control devices to be considered. The final selection should be based on the most favorable economic factors.

4.1 CONTROL METHODS

Emissions of organic air pollutants can be reduced by (1) add-on control devices that either destroy the vapor or collect it for reuse or disposal, (2) covers or seals which prevent vapors from escaping, and (3) process or material changes that reduce or eliminate the use of organics.

The principal add-on control devices for the control of volatile organics are:

- Thermal and catalytic incinerators
- Activated carbon and other types of adsorbers
- Absorbers or liquid scrubbers
- Condensers that use refrigeration or compression.

Incineration is the technique most universally applied by industry, but it usually requires measurable supplemental fuel. Incineration, therefore, is most acceptable where the developed heat can offset other fuel or energy needs. Adsorption, absorption, and condensation techniques - although effective - are limited to exhaust streams with a much narrower range of process characteristics than is incineration.

Covers and seals include floating roof tanks for petroleum and petrochemical storage and covers for waste water separators to prevent evaporative losses from open pools.

Process and material changes are the most diverse options and are used primarily by the surface cleaning and coating industries. Among the available process and material changes are:

- New cleaning and degreasing techniques.
- New coating technologies--e.g. water-borne, high-solids, and powder coatings.
- Reduced ingestion of air into the gas stream requiring treatment.
- Inert gas curing techniques for coating.
- More efficient coating application methods.

Although these changes offer great promise, almost each one is unique. Consequently the number necessary to meet all product and process requirements is large. Development and conversion costs are sometimes very high. Process and material changes, therefore, can often be implemented only over much longer time periods than those required for installing add-on devices.

Several factors influence the effectiveness, cost and applicability of available control devices or techniques to a given source category. Quite often the characteristics of a particular process or exhaust gas stream dictate the use of certain control techniques. Many control methods are equivalent in reducing pollution but vary in cost. In the latter instances, it is assumed that the company will select the option that provides the most reduction for the fewest dollars over the expected lifetime of the device.

Other less obvious factors that are unique to the control of organic emissions influence the selection of a control option. For example, virtually all organics are derived from petroleum, and the increasing cost of crude oil provides considerable economic incentive to both reduce solvent consumption and maximize recovery for use. Other regulatory requirements also can preclude - or dictate - the use of certain options. Insurance and occupational safety requirements that specify maximum allowable organic concentrations for fire prevention and operator safety are examples of such regulatory requirements. Finally, long-term warranties or customer requirements can limit the scope of material or process changes.

4.1.1 Carbon Adsorption

Carbon adsorption uses a physical phenomenon to separate organic vapors from a gas stream and to concentrate these vapors to a more manageable form.

It is applicable to most organic-emitting industries (with a few solvents excepted) but the costs and difficulties will vary with the specific industry (Ref. 4-1).

The term "sorption" applies to two types of phenomena: (1) where vapor molecules are concentrated by adsorption on the surface, and (2) where vapors are concentrated by absorption of the vapor molecules into the mass of the sorbent. Adsorption is accomplished using four different types of materials: (1) chemically reactive adsorbents (2) polar adsorbents (3) molecular sieves, and (4) nonpolar adsorbents.

When adsorption is accompanied by chemical reaction, the process is termed "chemisorption," an exothermic process where molecules can only be one layer thick. It has been used for odorous sulfur compounds and some olefins but has little application at this time for organic solvent control.

When adsorption is not accompanied by chemical reaction, the process is termed physical adsorption. In general, polar adsorbents adsorb polar molecules (e.g., water) preferentially, while nonpolar adsorbents adsorb nonpolar molecules (e.g., hydrocarbon) preferentially. Physical adsorption is less selective then chemisorption, the process is reversible and vapor molecules can be adsorbed in more than one layer on the surface. Activated carbon is the only physical adsorbent presently in widespread use for organic vapor collection. It is a nonpolar adsorbent although it has some adsorptivity for water.

Activated carbon can be produced from a variety of carbonaceous materials, its characteristics depend on the raw material and the activation process. Carbon is activated by oxidation of portions of the carbon with steam or chemicals. The end-product of activation is a material with a fine, partially interconnected pore structure that has a very large surface area.

A. Adsorption--

The surface area of the activated carbon is the primary variable associated with carbon adsorption. The larger the available area, the larger the adsorption capacity of the carbon, other things being equal. A typical activated carbon may have a surface area of 1100 square meters per gram.

The capacity of carbon is often represented by "adsorption isotherms" such as Figure 4-1 showing the effect of increasing molecular weight of organics on carbon capacity. The isotherms level out as the micropores are filled. For pollution control situations, the range of interest is below a partial pressure of 10 mm of Hg. The effect of temperature on adsorption is shown by Figure 4-2.

For a fixed-bed carbon adsorber, the concentration profile in the bed changes with time as the capacity of the bed is approached. "Breakthrough" time is usually defined as the time when the outlet of the adsorber reaches a defined level (usually 1 percent of the inlet concentration). The bed should be regenerated after the breakthrough has occurred.

For exhaust streams containing multiple solvents, vapors of higher molecular weight (M.W.)* will displace vapors of lower M.W. As shown in Figure 4-3, adsorption will be as if each solvent was adsorbed independently in a bed when the vapors have very different M.W. As shown in Figure 4-4, there will be a co-adsorption when the vapors are close in M.W. In either case, the compound with the lowest M.W. will exit the adsorber bed first.

For more in-depth information on the theory of adsorption the reader should consult References 4-1 and 4-2.

B. Regeneration--

For concentrations greater than a few parts per million, carbon must be used many times for economic reasons. To desorb vapors and reuse the carbon, regeneration is necessary. Regeneration is accomplished by raising the temperature of the carbon, evacuating the bed, or both. Typical thermal regenerants are steam, hot air, and hot inert gas. The hotter the regenerant and the longer the regeneration, the more solvent will be desorbed from the bed. There is an economic optimum where adequate desorption occurs at reasonable energy cost. The residual solvent in the bed after regeneration is called the "heel" and "working capacity" the difference between full capacity and the heel.

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*Although molecular weight is used in this discussion, a more precise term is the liquid molar volume at normal boiling point usually denoted as V_m. M.W. is approximately proportional to V_m and is an easier property to perceive for the purposes of this discussion.

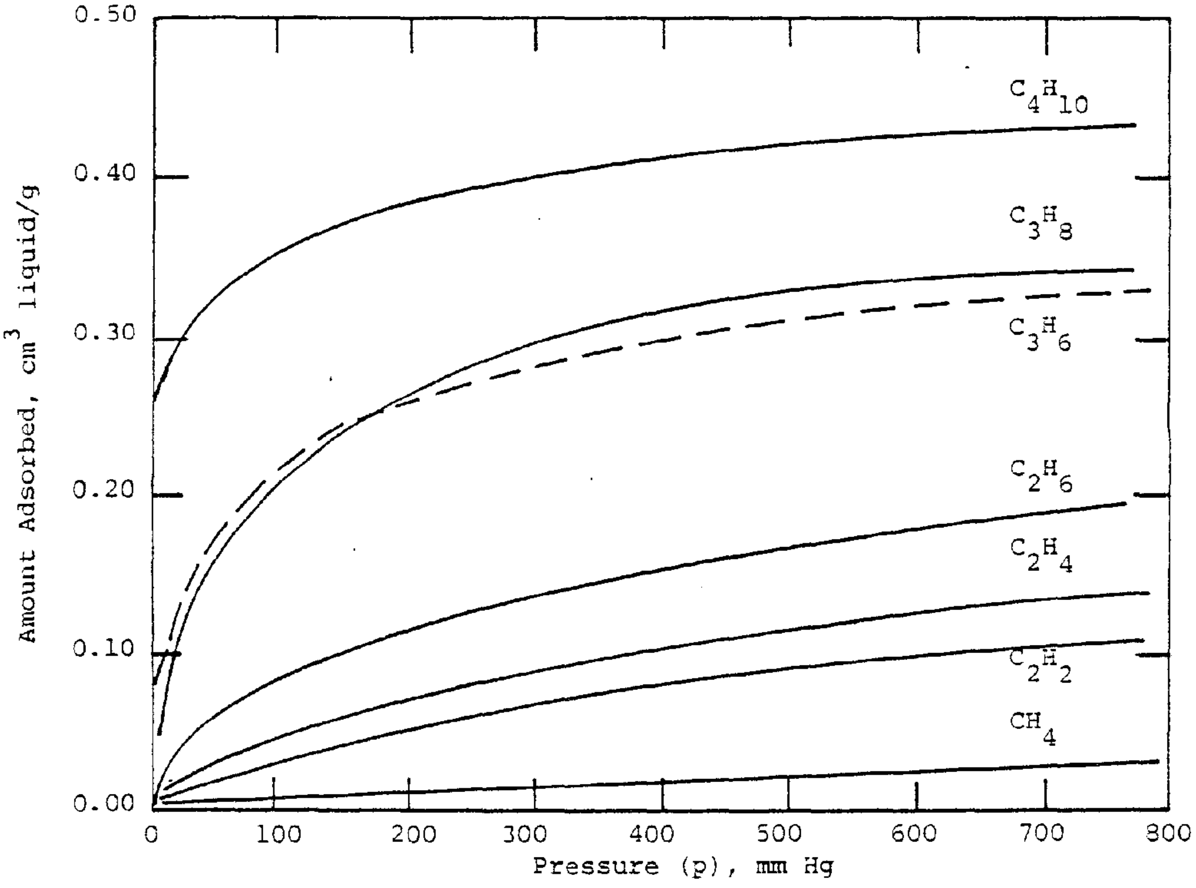

Figure 4-1. Adsorption isotherms of hydrocarbon vapors (amount adsorbed at pressure, p, on type Columbia L carbon at 100 °F, Ref. 4-1).

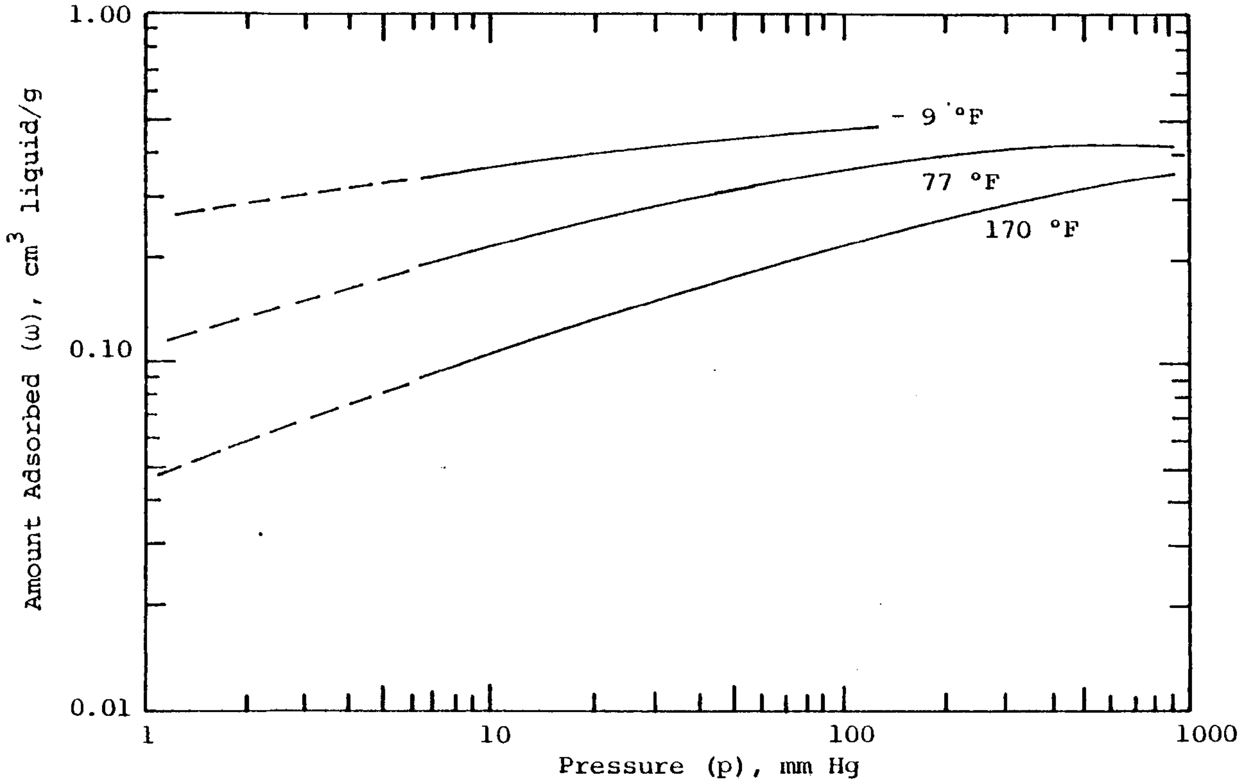

Figure 4-2. Adsorption isotherms of butane at three temperatures on Pittsburgh BPL type carbon (Ref. 4-1).

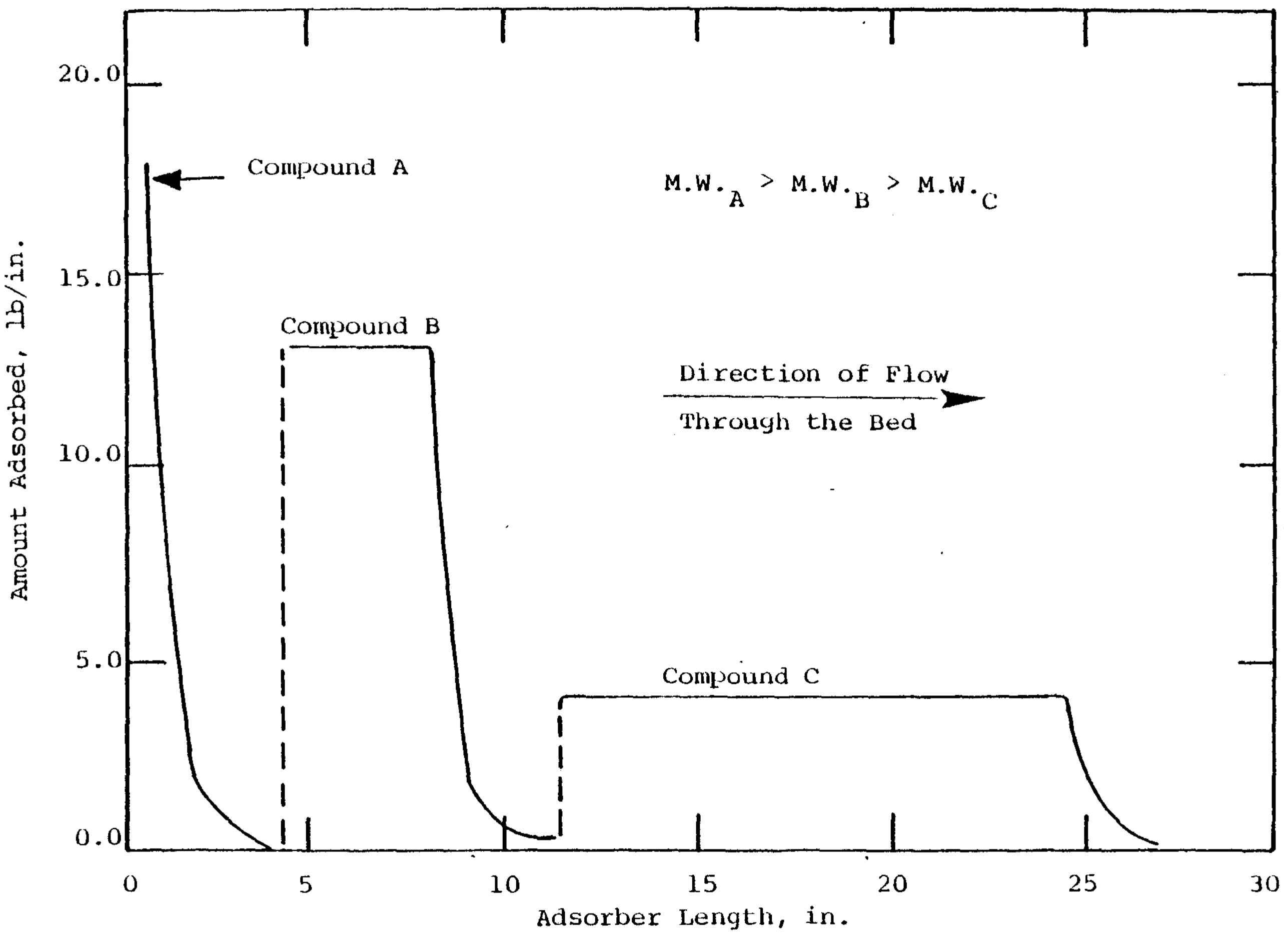

Figure 4-3. Adsorbed vapor profile in activated carbon bed after steady state is established but with no coadsorption (Ref. 4-1).

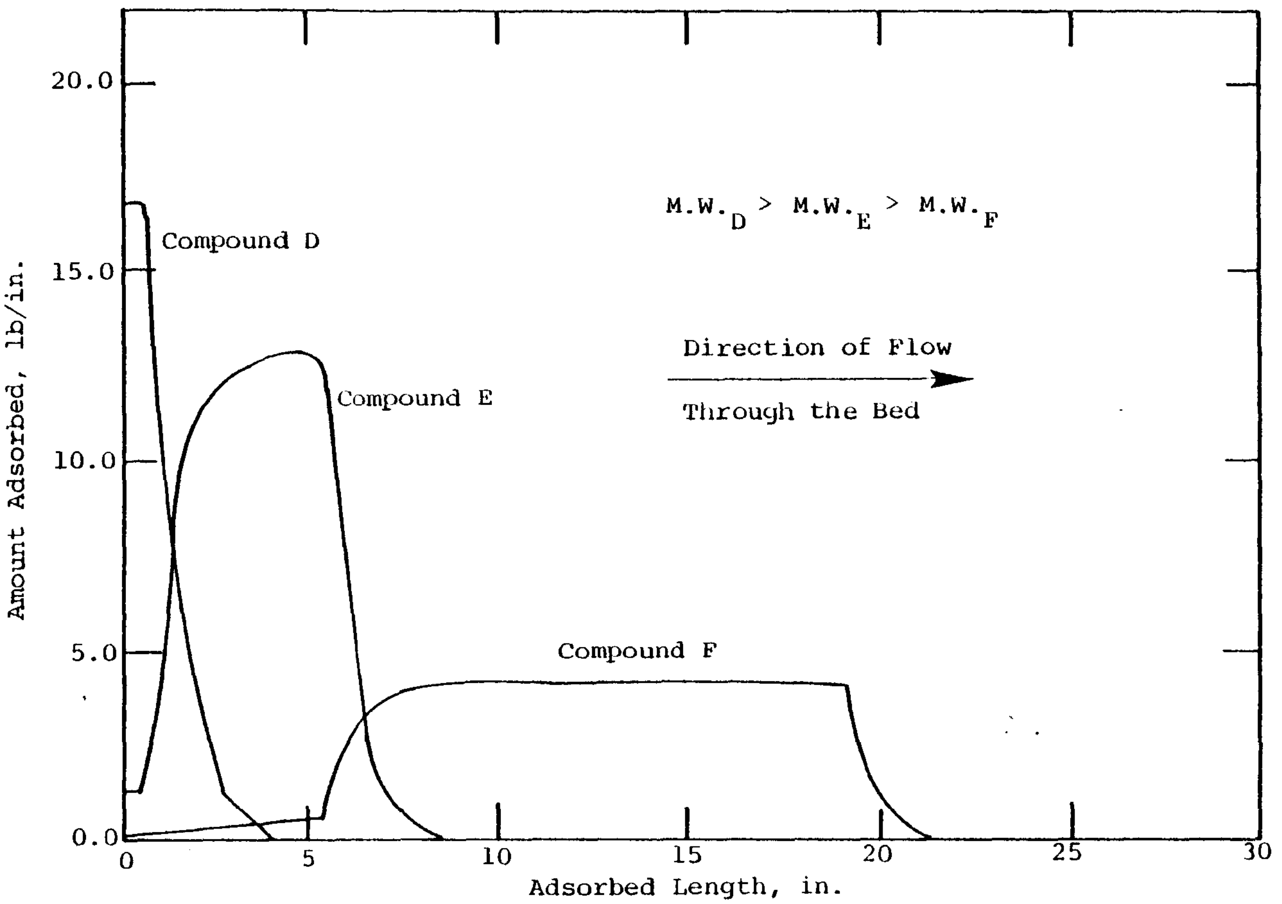

Figure 4-4. Adsorbed vapor profile in activated carbon bed after steady state is established with coadsorption (Ref. 4-1).

Regeneration is typically about 50% complete for each cycle under proper (or economic) operation. To optimize the frequency of regeneration, an automatic device that signals breakthrough may be useful if the size of the adsorber warrants.

1. Thermal Description--Steam is the most widely used regenerant. The bed is closed off from pollutant flow, and steam is introduced into the bed. The steam and the pollutant vapors are routed to a condenser after which they can usually be separated by gravity or distillation. Steam regeneration has the advantage of leaving the bed wet. By control of the degree of wetness in the bed, various degrees of gas cooling can be accomplished. In a variation of this scheme, steam and pollutant can be incinerated without condensation.

As inlet concentration decreases, the bed capacity is reduced. In order to achieve adequate working capacity for low concentrations, the heel must be minimized with consequent increased steam usage. Figures 4-5 and 4-6 show the amount of steam and heated air necessary to desorb two solvents at various initial concentrations. The two compounds (propanone and 4-methyl-2 pentanone) span the range of M.W. for which carbon adsorption is applicable. For concentrations less than 700 ppm, air or inert gas should be considered for regeneration, especially if (1) the adsorbed solvent has no value, (2) the material has appreciable miscibility with water, or (3) the solvent does not contain large amounts of halogen-, nitrogen-, or sulfur-containing compounds.

If a noncondensible gas is used for regeneration, the organics can be removed by condensation, adsorption, and/or incineration. Condensation of virtually all organics in a stream is possible if the stream is cooled to a low enough temperature. A more practical approach is to condense a portion of the vapor and to recycle the remainder back through the operating bed.

Secondary adsorption of the vapors in a smaller adsorber offers a possible method of recovering vapors from a dilute source. The primary adsorber is regenerated by heated inert gas, yielding a gas stream in which the vapor concentration is about 40 times as high as in the original stream. After cooling, this stream can then be passed through a secondary adsorber which is regenerated by steam and the organic material recovered. Reference 4-1 gives further details for this scheme.

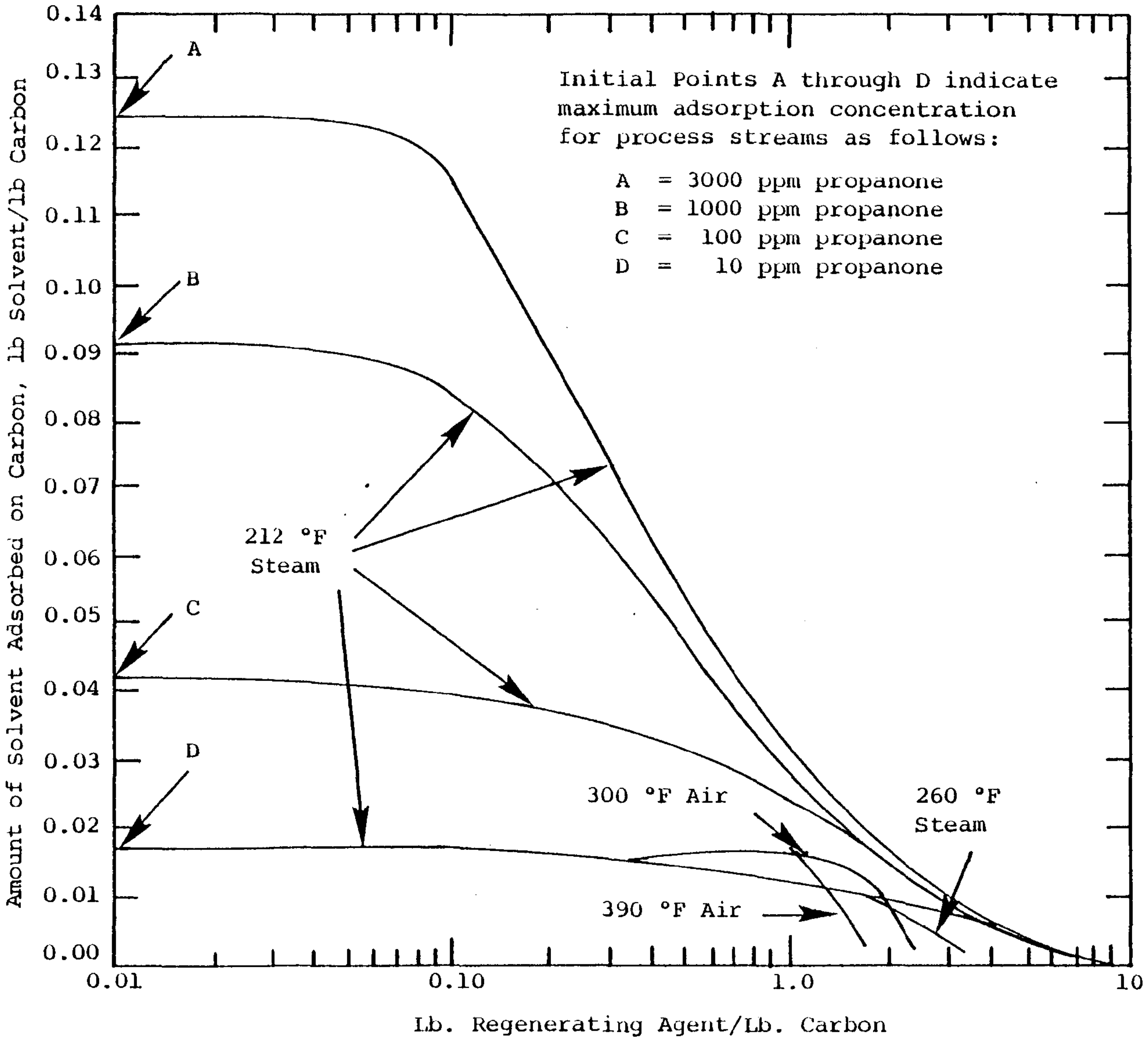

Figure 4-5. Amount of regenerating agent required to desorb BPL V type carbon equilibrated with propanone at varied initial concentrations (Ref. 4-1).

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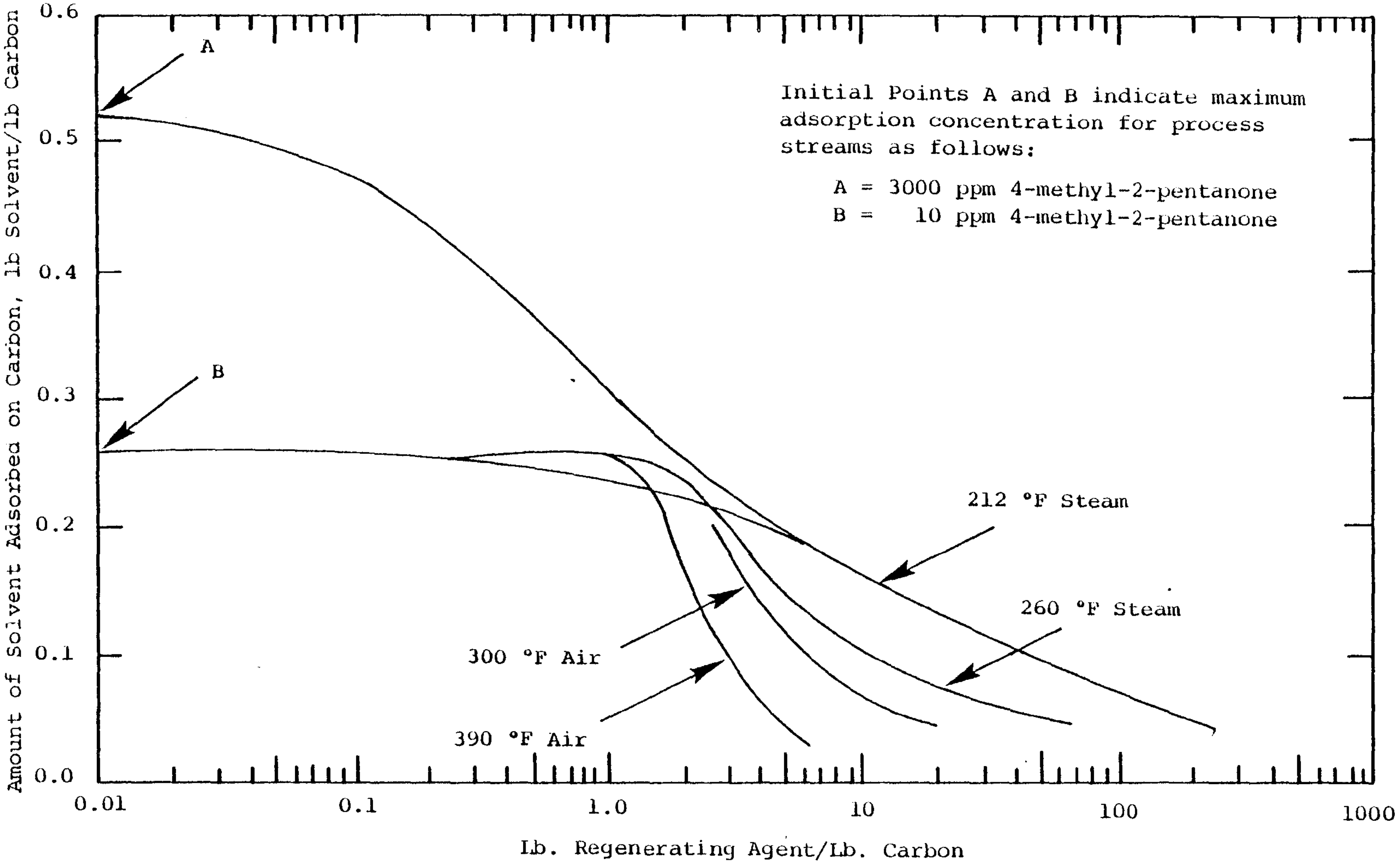
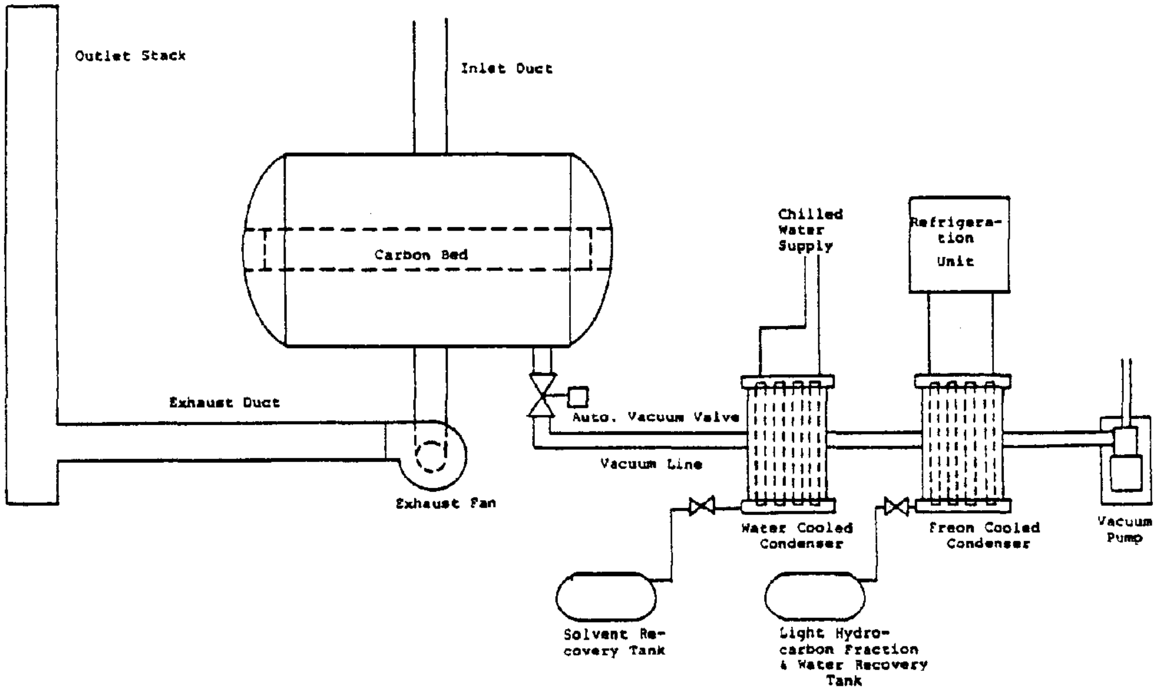


Figure 4-6. Amount of regenerating agent required to desorb GI type carbon with 4-methyl-2-pentanone by 10 and 3000 ppm process streams (Ref. 4-1).

2. Vacuum Desorption--By evacuating the carbon bed to absolute pressures of approximately 1 mm Hg, the boiling point of the adsorbed organic compound is reduced substantially. For example, C_{14} to C_{18} hydrocarbon oils have a boiling point of approximately 500 °F at one atmosphere which is reduced to 200 °F at 1 mm Hg. This lowered boiling point facilitates the breaking of the adsorption bond allowing it to take place at lower temperatures which saves energy. Another benefit is that carbon adsorption can be used to recover thermolabile materials which are unstable when heated. These materials would pyrolyze or rearrange chemically at higher temperatures.

Regeneration systems employing vacuum are heated with radiation/conduction heaters. A schematic of a typical process is shown below.



The tank to be regenerated is removed from the adsorbate stream by automatically closing the process vacuum valves at the top and bottom of the tank. Then, a smaller vacuum valve is automatically opened connecting the tank to a mechanical vacuum pump capable of producing a vacuum of 1 mm Hg in the tank. When the desired vacuum pressure is reached, heat is applied to the carbon bed through a series of cartridge heaters or, if economically practical, a recirculating heat transfer system. The simultaneous application of heat and vacuum strips the solvent from the carbon. The solvent is condensed in a water cooled chamber and then automatically flows into the condensate recovery tank to be returned to the process, or removed for disposal. The low-boiling hydrocarbons are trapped in a refrigerated condenser maintained at a temperature of about -40 °F. When the regeneration process is completed, the tank is once again returned on-stream.

C. Problem Areas with Carbon Adsorption--

Several problems are encountered in systems controlling the bake ovens which follow most surface coating operations. Thermal breakdown of the solvents and/or resins can generate a range of low M.W. compounds that cannot be adequately adsorbed. Examples are formaldehyde, methanol, and acetic acid. Polymerization reactions may produce tar-like products that will condense at the operating temperatures of carbon adsorbers and not be desorbed, causing fouling. These complications, if present, do not make carbon adsorption impossible for ovens, but they will necessitate precautions or lower carbon life.

Compounds such as acetone, methyl-ethyl ketone, and phenol, may cause problems because of high heat of adsorption. With proper design, however, problems can be avoided. The main requirement is the use of a wet bed and a controlled relative humidity in the inlet gases to provide a heat sink for the adsorbed vapors. Dimethyl formamide and nitropropanes are a more serious problem; carbon adsorption is probably not applicable where these solvents are used (Ref. 4-2).

1. Reuse of solvent--Unless a single solvent is used and breakdown is avoided, reuse of the solvent may not be feasible. Distillation is possible, but the complexity and cost are so variable that it is difficult to generalize. Reuse of mixed recovered solvents is unlikely if the source is one where many solvents are run on the same machine. In later cost studies it was assumed that if this type of mixed solvent is recovered, it had fuel value only.

2. Particulates--Particulate matter, if allowed to enter the carbon bed, can coat the carbon or plug the voids between carbon particles. Adsorbtivity is decreased and pressure drop increases. The net result is that the carbon must be replaced or cleaned more often. Siliconized coatings cause especially difficult problems.

A solution to a particulate problem is precleaning of the gas. Fabric collectors, mist eliminators, electrostatic precipitators, or scrubbers may be used. The particulate may be very small in particle size, viscous or tacky and hence difficult to remove. Mist eliminators may be used if the particulate is a liquid. If the condensed vapors harden at the operating temperature of the particulate collector, frequent cleaning may be necessary.

3. Temperature--Carbon capacity is greater at lower temperatures. Usually 100 °F is considered the maximum entry temperature. Cooling may be accomplished by direct water sprays or by cooling coils. If condensible gases are present, a spray cooler and mist eliminator should be placed ahead of the adsorber if possible.

4. Humidity--Although carbon preferentially adsorbs organic materials, water will compete with the organics for adsorption sites. To minimize this, relative humidity must be kept below about 50 percent. A minimum of 20 to 40 percent relative humidity should be maintained, however, especially if ketones are to be adsorbed. If gases are hot and wet, cooling followed by some reheat may be necessary. Water formed by fuel combustion must be considered.

5. Concentration--The range of concentrations for which carbon adsorption is applicable is limited. The increased operating cost of low concentrations has been discussed. There is also a potential problem with high concentrations. Adsorption is always an exothermic phenomenon; typically 200 to 300 Btu is generated per lb of solvent adsorbed. If sufficient air is not present to carry this off, the bed can overheat. This can result in poor adsorption and, in extreme cases, bed fires. For concentrations over 25 percent of the lower explosive limit (LEL),* heating of the bed must be considered in calculations. The problem can be minimized by leaving the bed wet with water.

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*The lower explosive limit of a substance is the lowest volume percent concentration of the vapor in air which can be ignited at 70 °F and normal atmospheric pressure.

D. Equipment Design and Operation--

Although there are a great variety of possible schemes for carbon adsorption, most applications are similar in design.

The face velocity is defined as the flow rate divided by cross sectional area of the bed. At high face velocities, the pressure drop increases and is the controlling factor in practical cases. Flow velocities for regenerable systems vary from 30 to 110 feet per minute. The sizes of necessary vessels are shown in Table 4-2 assuming a face velocity of 90 feet per minute. In evaluating the applicability of carbon adsorption to a source, floor or roof space must be considered.

TABLE 4-2. TYPICAL BED SIZES FOR CYLINDRICAL CARBON ADSORBERS

Flow rate, cfm	Bed Diameter, ft
1,000	4
3,000	7
10,000	12
30,000	21
60,000	30

The usual practice is to install at least two adsorbers and operate so that one is adsorbing while the other is regenerating. The largest vessel that can be factory assembled handles about 30,000 cfm. Thus for larger sources the designer has to choose between multiple packaged units and field assembled adsorbers. The largest adsorbers in the South Coast Air Basin are located at California Rotogravure Division of Alco Gravure Corp. They have four 30 ft diameter carbon canisters capable of 60,000 cfm each. At maximum capacity the system operates with three of the units adsorbing and one unit desorbing at all times.

The materials of construction depend on the source to be controlled. If carbon dioxide is present, carbonic acid may be formed. If halogenated compounds are formed, halogen acids may form. Formaldehydes can yield formic acid. Often a stainless or high nickel steel is required.

Bed depths vary with the organic vapor type, with the concentration of organic vapors and with the desired time between regenerations. The lower the M.W., the lower the capacity of the carbon. Higher concentrations increase the capacity of the carbon, but also increase the amount of organic vapor to be adsorbed per unit volume of gas. The net effect is that at higher concentrations, the bed must be deeper for a given vapor, face velocity, and time between regeneration. Bed depths typically range from 1-1/2 to 3 feet but can be less at low concentrations. Cycle times for regenerable systems usually run about 2 hours. Higher flow rates cause the adsorption zone to be longer. For the bed depth range of interest for regenerable systems, this length of 2 to 4 inches will not be significant in comparison with total bed depth.

For a system in which there are no compounds with high molecular weight ($> C_8$), and no polymer formers, or excessive particulates reaching the carbon, a carbon life of 5 to 10 years can be expected.

E. Control Efficiency--

Where carbon adsorption is applicable, 90 to 95 percent removal in the carbon adsorber is commonly attainable.

F. Adverse Environmental Effects of Carbon Adsorption--

If the organic solvents to be recovered are miscible with water, a potential water pollution problem exists. Ways to avoid this are to treat the water or to incinerate the desorbed vapor, together with the steam or air purge.

If incineration is used with solvents containing halogens, sulfur, or nitrogen compounds, acid gases, SOx and NOx will result.

4.1.2 Incineration

Incineration destroys organic emissions by oxidizing them to carbon dioxide and water vapor. Incineration is the most universally applicable control method for organics; given the proper conditions, any organic compound will oxidize. Oxidation proceeds more rapidly at higher temperatures and higher organic pollutant content. Catalysts are used on some systems to lower energy requirements. In the presence of a catalyst the oxidation reaction rate is increased permitting a reduction in the reaction temperature for a given degree of oxidation. Incinerators (also called afterburners) have been used for many years on a variety of sources ranging in size from less than 1000 scfm to greater than 40,000 scfm.

A. Design Considerations--

1. Use of existing process heaters for incineration--The use of existing boilers and process heaters for destruction of organic emissions provides for the possibility of pollution control at small capital cost and little or no fuel cost. The option is, however, severely limited in its application. Some of the requirements are:

- The heater must be operated whenever the pollution source is operated; it will be uncontrolled during process heater down time.
- The fuel rate to the burner cannot be allowed to fall below that required for effective combustion. On-off burner controls are not acceptable.
- Temperature and residence time in the heater firebox must be sufficient.
- For proper control, the volume of polluted exhaust gas must be much smaller than the burner air requirement and be located close to the process heater. For most plants doing surface coating, especially if surface coating is their main business, the combustion air requirement is smaller than the coater-related exhaust. In many diversified plants, the coating operation may be distant from heaters and boilers.
- Constituents of the coating-related exhaust must not damage the internals of the process heater.

Few boilers or heaters meet these conditions.

2. Use of add-on incinerators--In noncatalytic incinerators (sometimes called thermal or direct flame incinerators), a portion of the polluted gas may be passed through the burner(s) in which auxiliary fuel is fired. Gases exiting the burner(s) in excess of 2000 °F are blended with the bypassed gases and held at temperature until reaction is complete. The equilibrium temperature of mixed gases is critical for effective combustion of organic pollutants. A diagram of a typical arrangement is shown in Figure 4-7.

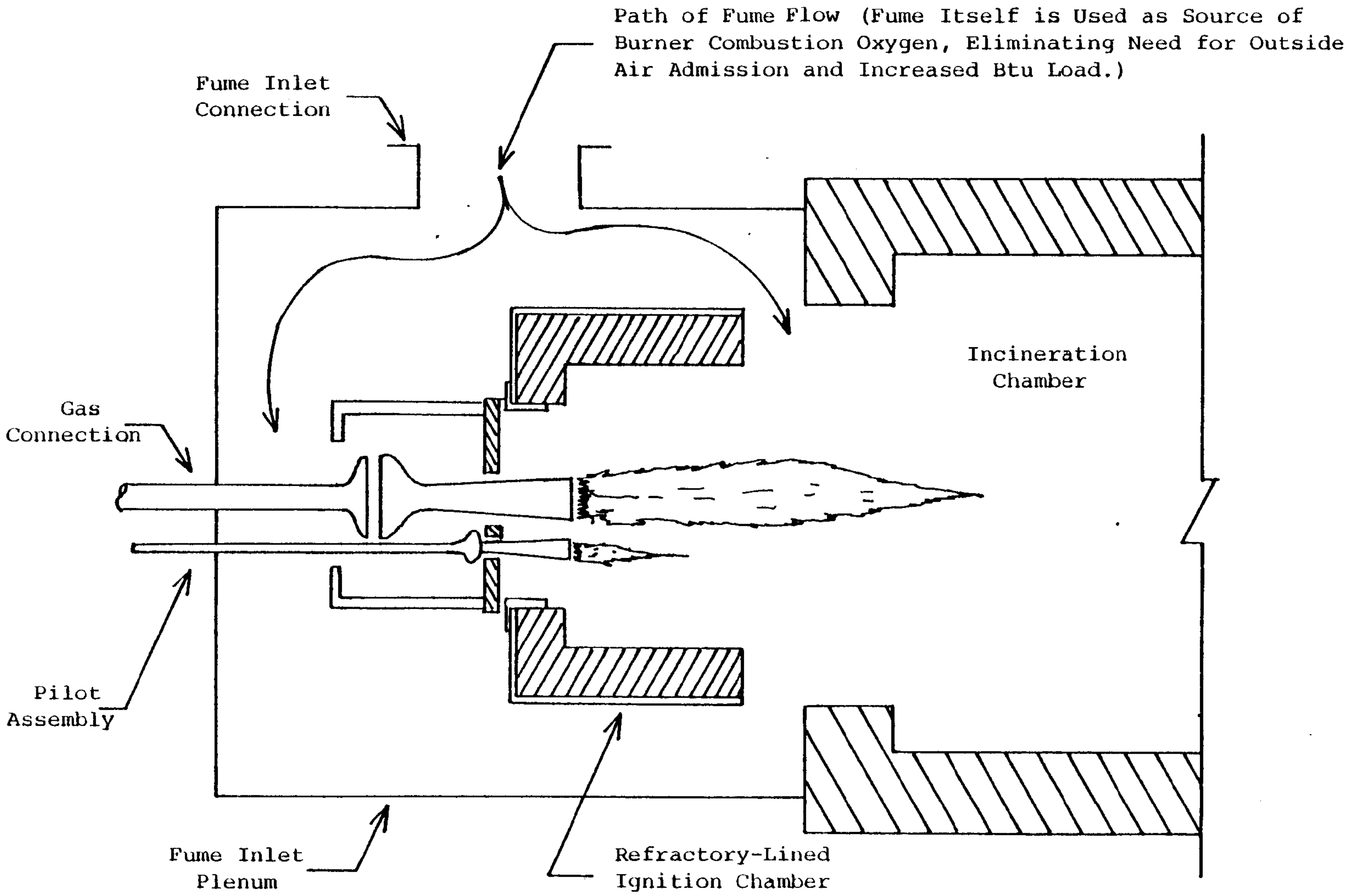

Figure 4-7. Typical burner and chamber arrangement used in direct-flame incinerator.

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The coupled effect of temperature and residence time is shown in Figure 4-8. Hydrocarbons will first oxidize to water, carbon monoxide and possibly carbon and partially oxidized organics. Complete oxidation converts CO and residuals to carbon dioxide and water. Figure 4-9 shows the effect of temperature on organic vapor oxidation and carbon monoxide oxidation.

A temperature of 1100 to 1250 °F at a residence time of 0.3 to 0.5 second (Ref. 4-3) is sufficient to achieve 90 percent oxidation of most organic vapors, but about 1400 to 1500 °F may be necessary to oxidize methane, cellosolve, and substituted aromatics such as toluene and xylene (Ref. 4-3).

3. Design--Incineration fuel requirements are determined by the concentration of the pollutants, the waste stream temperature and oxygen level, and the incineration temperature required. For most organic solvents, the heat of combustion level, and the incineration temperature required. For most organic solvents, the heat of combustion is about 0.5 Btu/scf for each percent of the LEL. This is enough to raise the waste stream temperature about 27.5 °F for each percent of the LEL (at 100 percent combustion). Thus, at 25 percent of the LEL, the temperature rise will be 620 °F for 90 percent conversion.

4. Fuel--Natural gas, LPG and distillate and residual oil are used to fuel incinerators. The use of natural gas or LPG results in lower maintenance costs; at present, natural gas also is the least expensive fuel. However, the dwindling natural gas supplies make it almost a necessity to provide newly installed incinerators with oil-burning capabilities.

In most cases where natural gas or LPG is not available, incinerators are fixed with distillate fuel oil; residual oil is seldom employed. Oil flames are more luminous and longer than gas flames, thus require longer fireboxes. Almost all fuel oils, even distillate, contain measurable sulfur compounds. Residual oils generally have greater sulfur and particulate contents and many have appreciable nitrogen fractions. Sulfur oxides, particulates and NOx in combustion products from fuel oil increase pollution emissions and cause corrosion and soot accumulation on incinerator working and heat transfer surfaces.

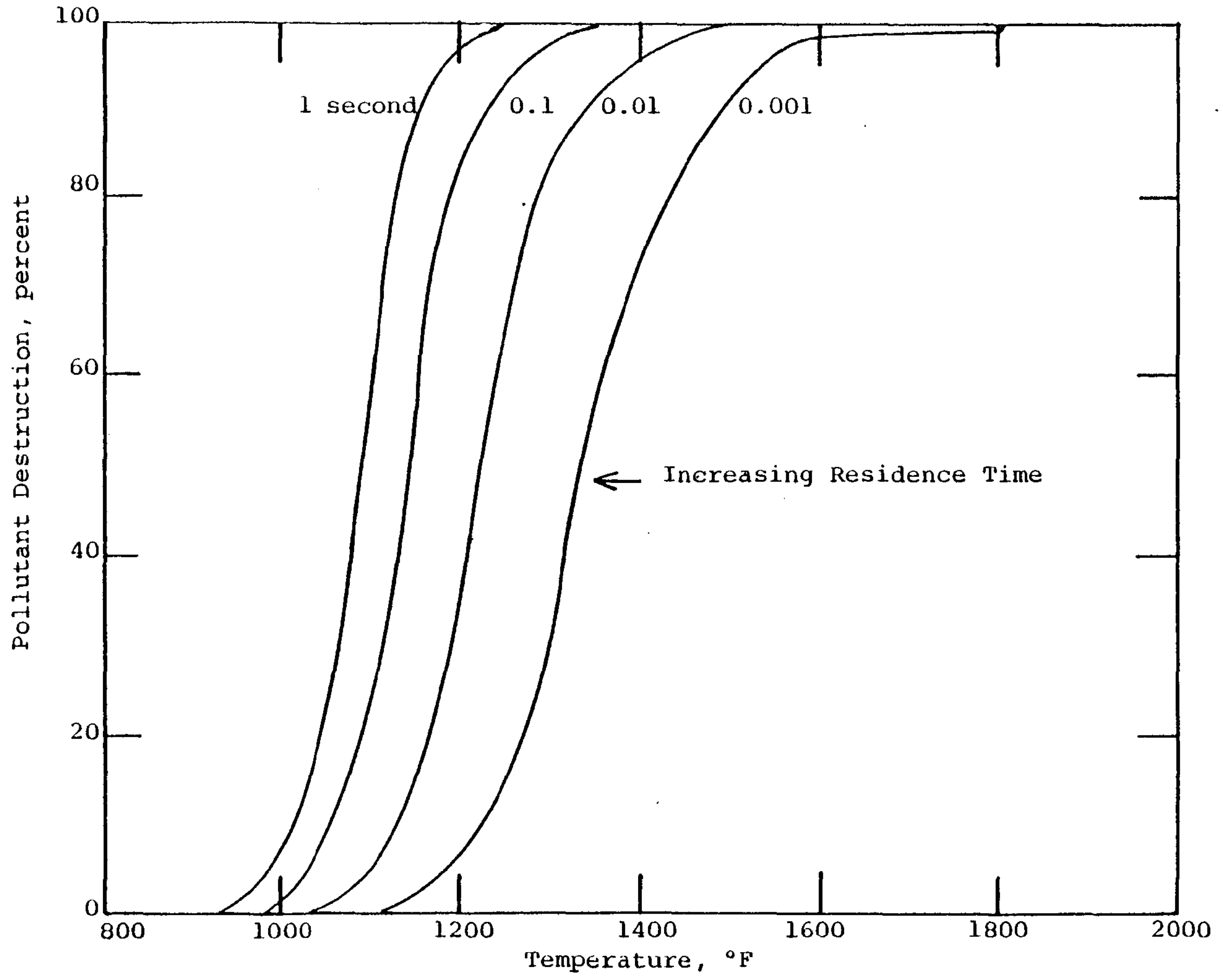

Figure 4-8. Coupled effects of temperature and time on rate of pollution oxidation (Ref. 4-1).

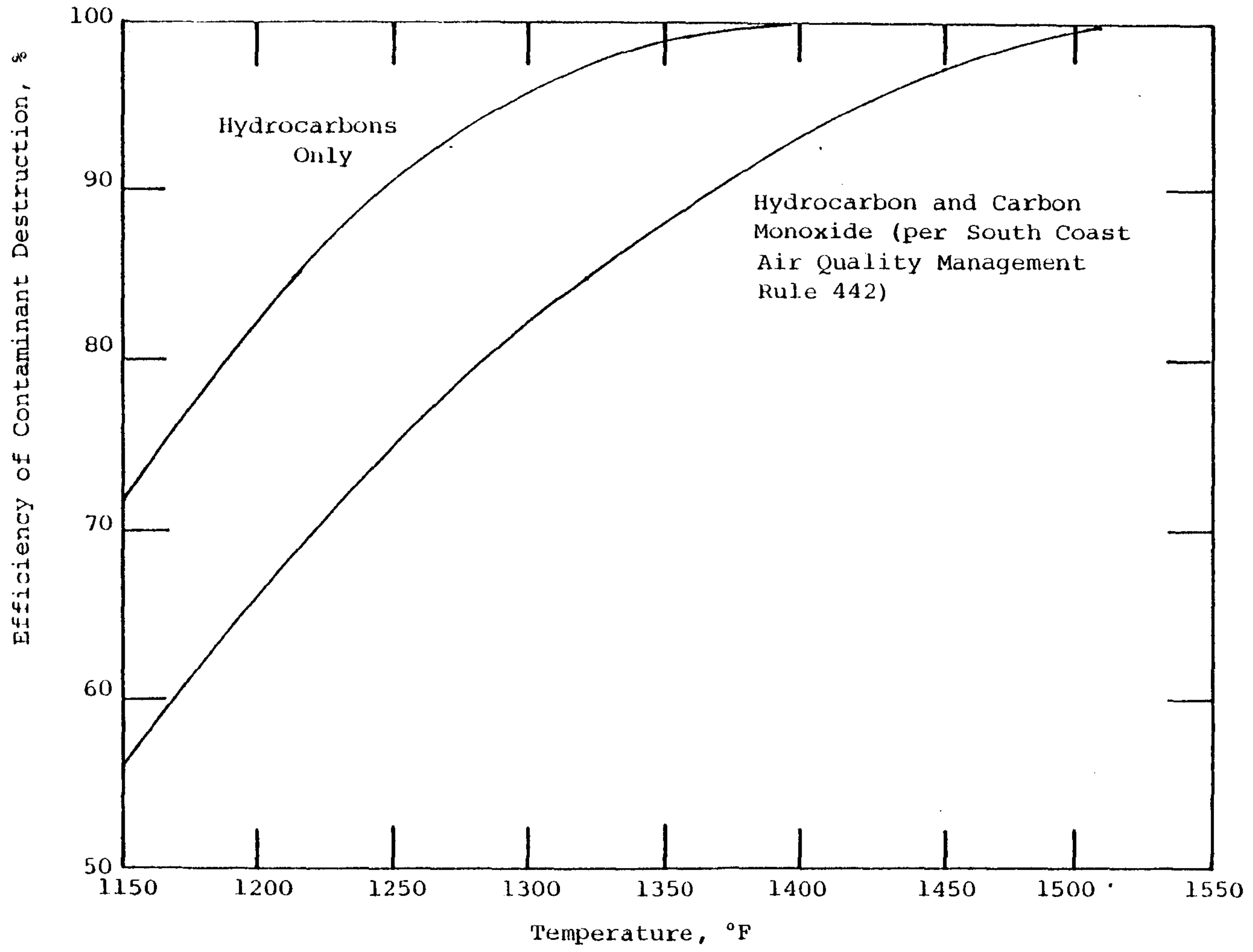

Figure 4-9. Typical effect of operating temperature on effectiveness of thermal afterburner for destruction of hydrocarbons and carbon monoxide (Ref. 4-1).

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5. Heat recovery--Heat recovery offers a way to reduce the energy consumption of incinerators. The simplest method is to use the hot cleaned gases exiting the incinerator to preheat the cooler incoming gases. Design is usually for 35 to 90 percent heat recovery efficiency.

The maximum usable efficiency is determined by the concentration of the organics in the gases, the temperature of the inlet gases, and the maximum temperature that the incinerator and heat exchangers can withstand.

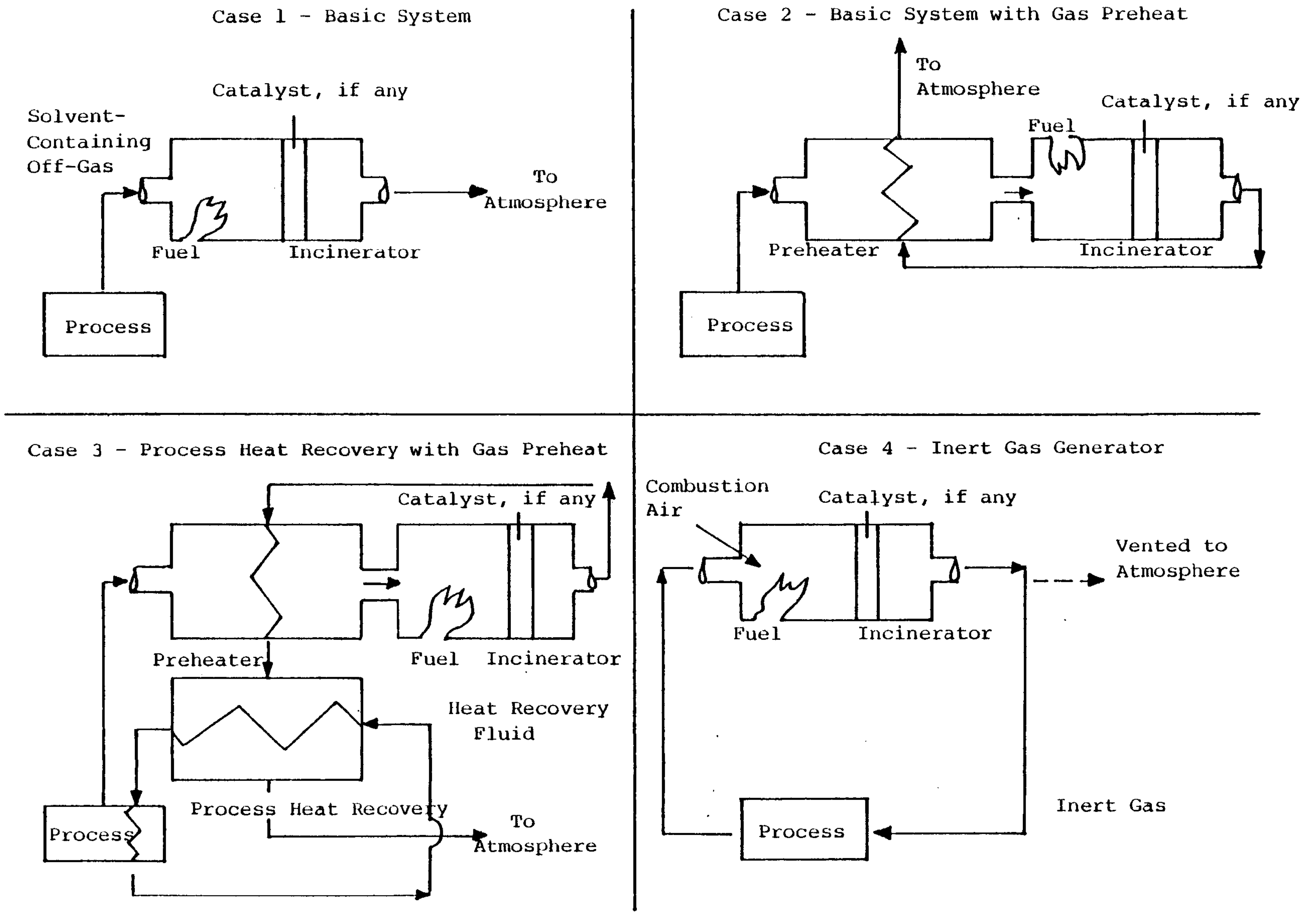
In a noncatalytic system with a primary heat exchanger, the preheat temperature should not exceed 680 °F, at 25 percent LEL, in order to limit incinerator exit temperatures to about 1450 °F for the protection of the heat exchanger. The auxiliary fuel would heat the stream about 150 °F and oxidation of the solvent would heat it about 620 °F for an exit temperature of 680 + 150 + 620 = 1450 °F. At 12 percent LEL the preheat temperature should not exceed 930 °F. Most burners have not been designed to tolerate temperatures above 1100°F.

There are several types of heat recovery equipment using different materials at various costs. The most common is the tube and shell heat exchanger. The higher temperature exhaust passes over tubes, which have lower temperature gas or liquid flowing through the tubes; thus increasing the temperature of that gas or liquid. Another method uses a rotating ceramic or metal wheel whose axis is along the wall between two tunnels. Hot exhaust flows through one tunnel and heats half of the wheel. Lower temperature air flows through the other tunnel and is heated as the wheel rotates. Another method uses several chambers containing inert ceramic materials with high heat retention capability. The hot gas (e.g. from the incinerator) passes through these beds and heats the ceramic material. The air flow is then reversed, and lower temperature gas passes through the heated beds; thus raising the temperature of that gas to near incineration temperature. Further details on various heat recovery methods and equipment can be obtained from the vendors of incinerators.

The use of incinerator exhaust to preheat incinerator inlet air is often referred to as "primary" heat recovery as illustrated in Case 2 of Figure 4-10. Since some systems have a maximum allowable inlet temperature for the incinerator, it may not be possible to recover all of the heat available in the incinerator exhaust. In such case, the inlet to the incinerator is controlled to minimize fuel requirements. Note that a noncatalytic incinerator always requires some fuel to initiate combustion.

"Secondary" heat recovery uses incinerator exhaust from the primary heat recovery stage (or from the incinerator directly if there is no primary heat recovery) to replace energy usage elsewhere in the plant. This energy can be used for process heat requirements or for plant heating. The amount of energy that a plant can recover and use depends on the individual circumstances at the plant. Usually recovery efficiency of 70 to 80 percent is achievable, making the net energy consumption of an incinerator minimal or even negative if gases are near or above 25 percent of the LEL. The use of primary and secondary heat recovery is illustrated in Case 3 of Figure 4-10. It should be noted that heat recovery reduces operating expenses for fuel at the expense of increased capital costs. Primary heat recovery systems are within the incinerator and require no long ducts. Secondary heat recovery may be difficult to install on an existing process because the sites where recovered energy may be used are often distant from the incinerator. In applying calculated values for recovered energy values in Case 3 to real plants, the cost of using recovered energy must be considered. If secondary heat recovery is used, often the plant cannot operate unless the control system is operating because it supplies heat required by the plant.

If the gases in an oven are inert, that is, contain little oxygen, explosions are not possible and high concentrations of organic solvent vapor can be handled safely. The oven exhaust can be blended with air and burned with minimal auxiliary fuel. The incinerator may be the source of inert gas for the oven. Cooling of the incinerator gas is necessary, removing energy that can be used elsewhere. Case 4 of Figure 4-10 illustrates this scheme. A modification of the scheme shown is the use of an external inert gas generator. This scheme can have a significant energy credit because the otherwise discarded organics are converted to useful energy. Because of the


Case 1 - Basic System

Case 2 - Basic System with Gas Preheat

Case 3 - Process Heat Recovery with Gas Preheat

Case 4 - Inert Gas Generator

Figure 4-10. Configurations for catalytic and noncatalytic incineration.

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specialized nature of Case 4, it may not be applicable to retrofits on existing ovens and costs for this case are not included in this study. Note that in this case the incinerator exhaust is in contact with the product. This limits the available fuel for this option to natural gas or propane. The use of this option would probably be impossible if any compounds containing appreciable sulfur or halogens are used.

To illustrate a specific case, Figure 4-11 outlines a source controlled by a noncatalytic incinerator. The source is assumed to operate 25 percent of the LEL and the incinerator has primary and secondary heat recovery. The primary heat exchanger raises the temperature to 700 °F, at 35 percent heat recovery efficiency. The heat of combustion of the organic vapors provides a 620 °F additional temperature rise at 90 percent combustion and the burner must supply only enough heat to raise the gases 80 °F to reach the design combustion temperature of 1400 °F. Combustion products pass through the primary heat exchanger--where they are cooled to 1025 °F--and enter a 35 percent efficient secondary heat exchanger. In the secondary heat exchanger, further energy is recovered for use in other areas. In this example, makeup air for the source is heated from ambient temperatures to source entrance temperatures (higher than oven exit temperatures).

The energy implications of this scheme can be seen by comparing the energy input of this controlled source with an uncontrolled source. In an uncontrolled source, fuel would be necessary to raise the temperature of the makeup air from 70 °F to 425 °F or 355 °F. For a controlled source, fuel would only need to raise the temperature 80 °F. Thus, the energy input would be reduced by over 80 percent by use of incineration simply because the organic vapors contribute heat when they burn.

In the above analysis, the assumptions made are important. If the organic vapors are more dilute, the temperature rise due to combustion will be less. Heat recovery can be more efficient than 35 percent, making up for all or some of this difference. Finally, the analysis assumes that the heat recovered in the secondary heat exchanger can be used in the plant. The heat can be used to produce steam, heat water, supply process heat or heat buildings. Obviously, a case-by-case analysis is necessary to ascertain how much recovered heat could be used.

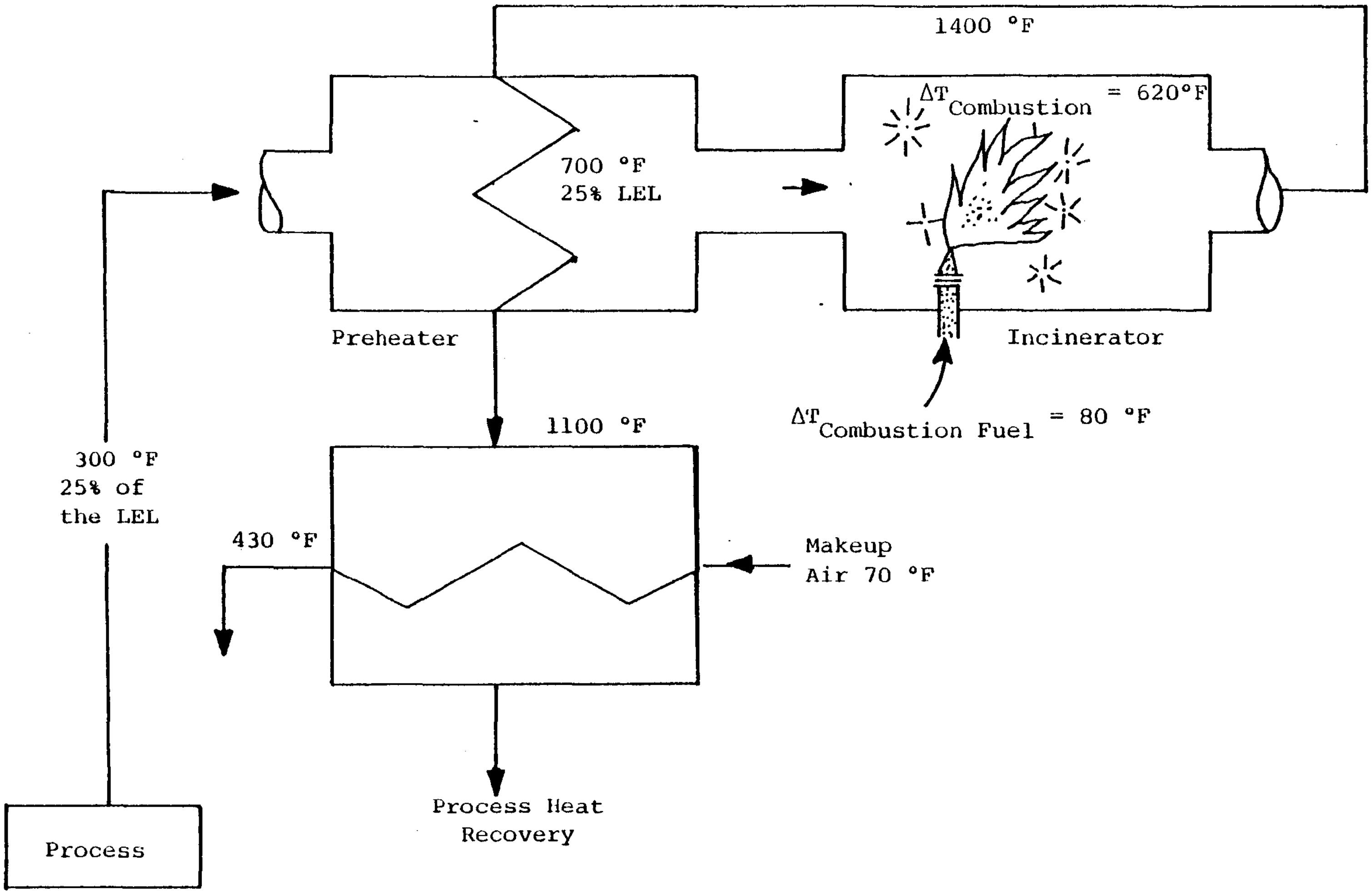

Figure 4-11. Example of incinerator on oven with primary and secondary heat recovery.

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6. Particulates--The level of particulate concentration found in surface coating operations should not pose any problems for noncatalytic volatile organic combustion. However, an incinerator designed for hydrocarbon removal usually will not have sufficient residence time to efficiently combust organic particulates.

7. Safety of preheat--(At 25 percent of the LEL), oxidation rates at temperatures below 1100°F are slow. Complete oxidation can take several seconds. Because the gases are in the heat exchanger for less than a second, preignition should not be a problem using heat recovery if temperatures are below approximately 1000 °F.

Some problems have occurred in the past with accumulations of condensed materials or particulates igniting in the heat recovery devices. If this occurs, the accumulations must be periodically removed from the heat transfer surfaces. The user should give careful consideration for his particular set of circumstances to potential safety problems. This is especially true if gases at a high percent of the LEL are preheated.

8. Adverse environmental effects--Sulfur-containing compounds will be converted to their oxides; halogen-containing compounds will be converted to acids. A portion of nitrogen-containing compounds will be converted to NOx and additional NOx will result from thermal fixation. If use of these compounds cannot be avoided, the benefit from incineration should be evaluated against the adverse effects and alternate methods of control should be thoroughly explored.

The concentration of oxides of nitrogen (NOx) is about 18 to 22 ppm for natural gas-fired noncatalytic incinerators and 40 to 50 ppm for oil-fired noncatalytic incinerators at a temperature of 1500 °F, assuming no nitrogen containing compounds are incinerated.

B. Special Design Considerations for Catalytic Incinerators--

A catalyst is a substance that speeds up the rate of chemical reaction at a given temperature without being permanently altered. The use of a catalyst in an incinerator reportedly enables satisfactory oxidation rates at temperatures in the range of 500 to 600 °F inlet and 750 to 1000 °F outlet. If heat recovery is not practiced, significant energy savings are possible by use of a catalyst. The fuel savings become less as primary and secondary heat recovery are added. Because of lower temperatures, materials of construction savings are possible for heat recovery and for the incinerator itself. A schematic of one possible configuration is shown in Figure 4-12.

Catalysts are specific in the types of reactions they promote. There are, however, oxidation catalysts available that will work on a wide range of organic solvents. The effect of temperature on conversion for solvent hydrocarbons is shown in Figure 4-13. Common catalysts are platinum or other metals on alumina pellet support or on a honeycomb support. All-metal catalysts can also be used.

The initial cost of the catalyst and its periodic replacement represents, respectively, increased capital and operating costs. The lifetime of the catalyst depends on the rate of catalyst deactivation.

1. Catalyst Deactivation--The effectiveness of a catalyst requires the accessability of "active sites" to reacting molecules. Every catalyst will begin to lose its effectiveness as soon as it is put into service. Compensation for this must be made by either overdesigning the amount of catalyst in the original charge or raising the temperature into the catalyst to maintain the required efficiency. At some time, however, activity decays to a point where the catalyst must be cleaned or replaced. Catalysts can be deactivated by normal aging, by use at excessively high temperature, by coating with particulates, or by poisoning. Catalyst lifetime of greater than 1 year is considered the minimum acceptable.

Catalyst material can be lost from the support by erosion, attrition, or vaporization. These processes increase with temperature. For metals on alumina, if the temperature is less than 1100 °F, life will be 3 to 5 years if no deactivation mechanisms are present. At 1250 to 1300 °F, this drops to 1 year. Even short-term exposure to 1400 to 1500 °F can result in near total loss of catalytic activity (Ref. 4-1).

The limited temperature range allowable for catalysts sets constraints on the system. As mentioned earlier, at 25 percent of the LEL and 90 percent combustion there will be about a 620 °F temperature rise as a result of organic combustion. Because an inlet temperature of 500 to 600 °F is necessary to initiate combustion, the catalyst bed exit temperature will be 1120 to 1220 °F at 25 percent of the LEL. This is the upper limit for good

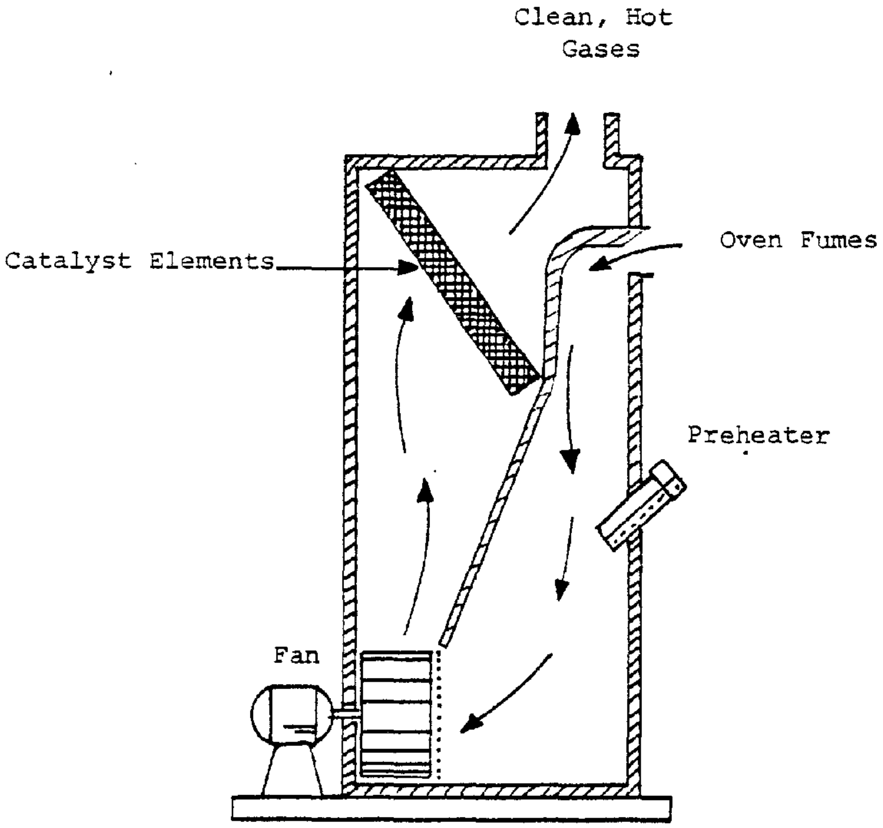

Figure 4-12. Schematic diagram of catalytic afterburner using torch-type preheat burner with flow of preheater waste stream through fan to promote mixing (Ref. 4-1).

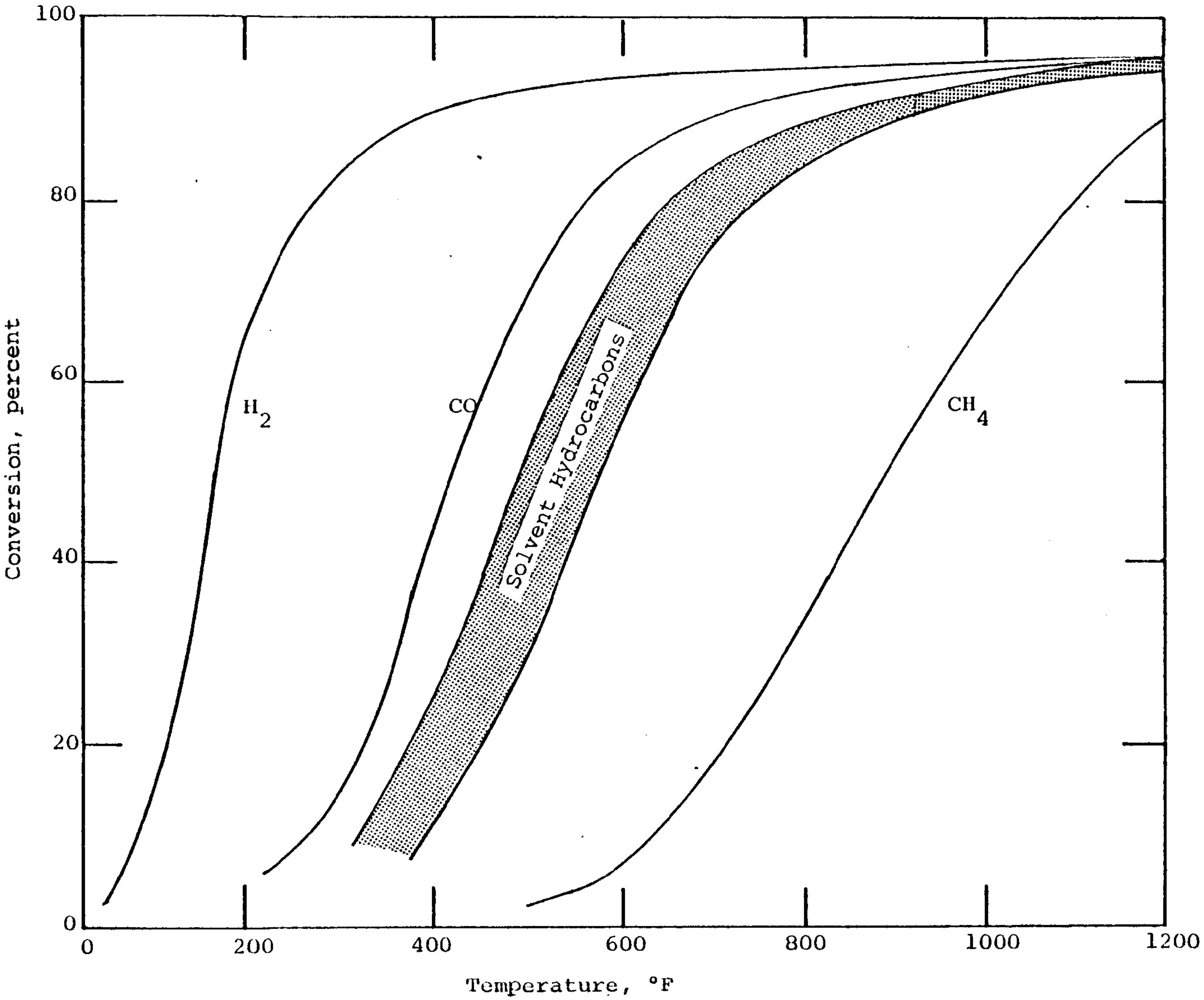

Figure 4-13. Effect of temperature on conversion for catalytic incineration (Ref. 4-1).

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catalyst life and thus concentrations of greater than 25 percent of the LEL cannot be incinerated in a catalytic incinerator without damage to the catalyst. Restrictions on heat recovery options are also mandated. These will be discussed later.

2. Coating with particulates--The buildup of condensed polymerized material or solid particulate can inhibit contact between the active sites of the catalyst and the gases to be controlled. Cleaning is the usual method for reactivation. Cleaning methods vary with the catalyst and instructions are usually given by the manufacturer.

3. Poisoning--Certain contaminants will chemically react or alloy with common catalysts and cause deactivation. A common list includes phosphorus, bismuth, arsenic, antimony, mercury, lead, zinc, and tin. The first five are considered fast acting; the last three are slow acting, especially below 1100 °F. Areas of care include avoiding the use of phosphate metal cleaning compounds and galvanized ductwork. Sulfur and halogens are also considered catalyst poisons, but their effect is reversible.

4. Fuel--Natural gas is the preferred fuel for catalytic incinerators because of its cleanliness. If properly designed and operated, a catalytic incinerator could possibly use distillate oil. However, much of the sulfur in the oil would probably be oxidized to SO_3 which would subsequently form sulfuric acid mist. This would necessitate corrosive resistant materials and would cause the emission of that very undesirable pollutant. Therefore, the use of fuel oil (even low sulfur) in a catalytic incinerator is not recommended.

The oxidation of methane in natural gas, as discussed previously, requires higher flame temperatures than some of the heavier fumes. A problem found in the South Coast Air Basin is that the total hydrocarbon level sometimes increased in passing through the catalytic incinerator. The heavier fumes were oxidized but the methane in the fuel gas was released at a concentration level greater than that of the original process input stream.

5. Heat Recovery--The amount of heat that can be transferred to the cooler gases is limited. The usual design is to have the exit temperature from the catalyst bed at about 1000 °F. If the gas is at 15 percent of the LEL, for example, the temperature rise across the bed would be about 375 °F, and the gas could only be preheated to about 625 °F. Secondary heat recovery

is limited by the ability to use the recovered energy. If a gas stream is already at combustion temperature, it is not useful to use "primary" heat recovery but "secondary" heat recovery may still be possible. Note that for catalytic incineration, no flame initiation is necessary and thus it is possible to have no fuel input.

As in noncatalytic systems, heat recovery equipment may need periodic cleaning if certain streams are to be processed.

4.1.3 Condensation

A. Application--

Any component of any vapor mixture can be condensed if brought to equilibrium at a low enough temperature. The temperature necessary to achieve a given solvent vapor concentration is dependent on the vapor pressures of the compounds.

When cooling a two-component vapor where one component can be considered noncondensible, for example, a solvent-air mixture, condensation will begin when a temperature is reached such that the vapor pressure of the volatile component is equal to its partial pressure. The point where condensation first occurs is called the dew point. As the vapor is cooled further, condensation continues such that the partial pressure stays equal to the vapor pressure. The less volatile a compound, that is, the higher the normal boiling point, the lower will be the amount that can remain vapor at a given temperature.

In cases where the solvent vapor concentration is high, for example, from the desorption cycle of a carbon adsorber, condensation is relatively easy. However, for sources where concentrations are typically below 25 percent of the LEL, condensation is very difficult. In some applications the concentration of the organic compound can be increased by compressing the process gas stream. Then condensation can take place at a higher temperature. Figure 4-14 shows the vapor pressure dependence on temperature for several compounds. Table 4-3 shows the temperature necessary to condense various amounts of compounds spanning the volatility range of compounds used for solvents.

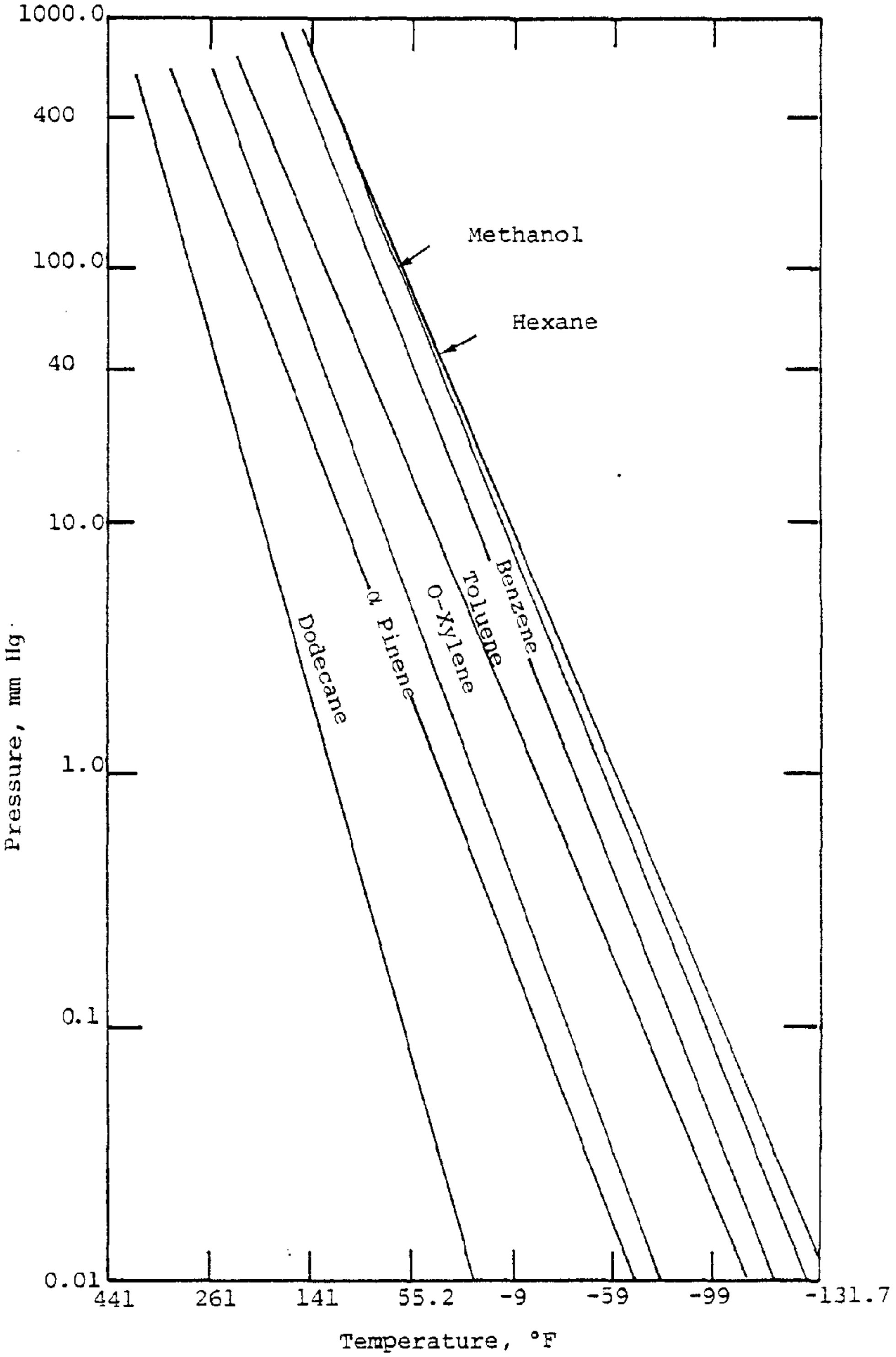

Figure 4-14. Vapor pressures of organic solvents versus temperature.

TABLE 4-3. PHYSICAL CONSTANTS AND CONDENSATION PROPERTIES OF SOME ORGANIC SOLVENTS

Compound	Normal Boiling Point, °F	LEL,* %	25% of LEL Concentration		90% Condensation from 25% of LEL		95% Condensation from 25% of LEL		90% Condensation from 200 ppm		95% Condensation from 50% Concentration	
			Partial Pressure, mm of Hg	Dew Point, °F	Partial Pressure, mm of Hg	† Temp., °F	Partial Pressure, mm of Hg	† Temp., °F	Partial Pressure, mm of Hg	† Temp., °F	Partial Pressure, mm of Hg	† Temp., °F
Dodecane	421	0.6	1.1	120	0.11	61	0.55	54.4	0.15	19	19	200
Pinene $C_{10}H_{16}$ (Terpentine)	300	0.7	1.3	53	0.13	16	0.065	-31.4	0.015	-60	19	130
O-xylene C_8H_{10}	280	1.0	1.9	26	0.19	-31	0.095	-36.5	0.015	-72	19	80
Toluene C_7H_8	211	1.4	2.7	5	0.27	-51	0.135	-54.3	0.015	-103	19	60
Benzene	175	1.4	2.5	-15	0.25	-69	0.125	-96.4	0.015	-114	19	30
Methanol C_2H_6O	147	6.0	11.4	2	1.14	-41	0.57	-68.7	0.015	-126	19	10
Hexane	155	1.2	2.3	-39	0.23	-93	0.115	-108	0.015	-129	19	0

*From Reference 4-1

†From Figure 4-14

Except for dodecane, which is not volatile enough to be a major component in an industrial solvent, all of the solvents require a low process temperature to condense 90% of the pollutant from a 25% LEL stream. This would be very uneconomical. However, as indicated by the last column in Table 4-3, if the concentration of the solvent is 50%, then the temperature to condense 95% of the material is in a practical range. Thus in applications like dry cleaning, degreasing and storage tank vapor recovery the condensation approach is practical. For surface coating, condensation is generally not applicable except in rare cases where high concentrations of relatively nonflammable materials are present.

The above calculations are for single condensable compound systems. The calculation methods for multiple condensable component systems are complex, particularly if there are significant departures from ideal behavior of the gases and liquids. As a simplification, the temperatures necessary for control by condensation can be roughly approximated by the weighted average of the temperatures necessary for condensation of a single condensable component system at concentrations equal to the total organic concentration.

Totally chlorinated and fluorinated compounds, for example, carbon tetrachloride and perchlorethylene, are nonflammable and may be handled safely in all concentrations for nonoccupied areas. Condensation may be practical if high concentrations of these solvents are present. In fact, condensation is widely used in drycleaning and vapor degreasing for perchloroethylene recovery, because the relatively high cost of chlorinated solvents makes recovery attractive. Totally chlorinated compounds, however, are not used extensively in the surface coating industry; therefore, condensation is rarely used as a control method in that industry. Other applications for condensation systems for organic vapor control are in the petroleum industry in various storage and transfer operations.

B. Equipment Design and Operation--

Many petroleum vapor recovery systems use refrigeration to condense and collect hydrocarbons. A typical installation in a gasoline bulk loading terminal is pictured in Figure 4-15 and shown schematically in Figure 4-16.

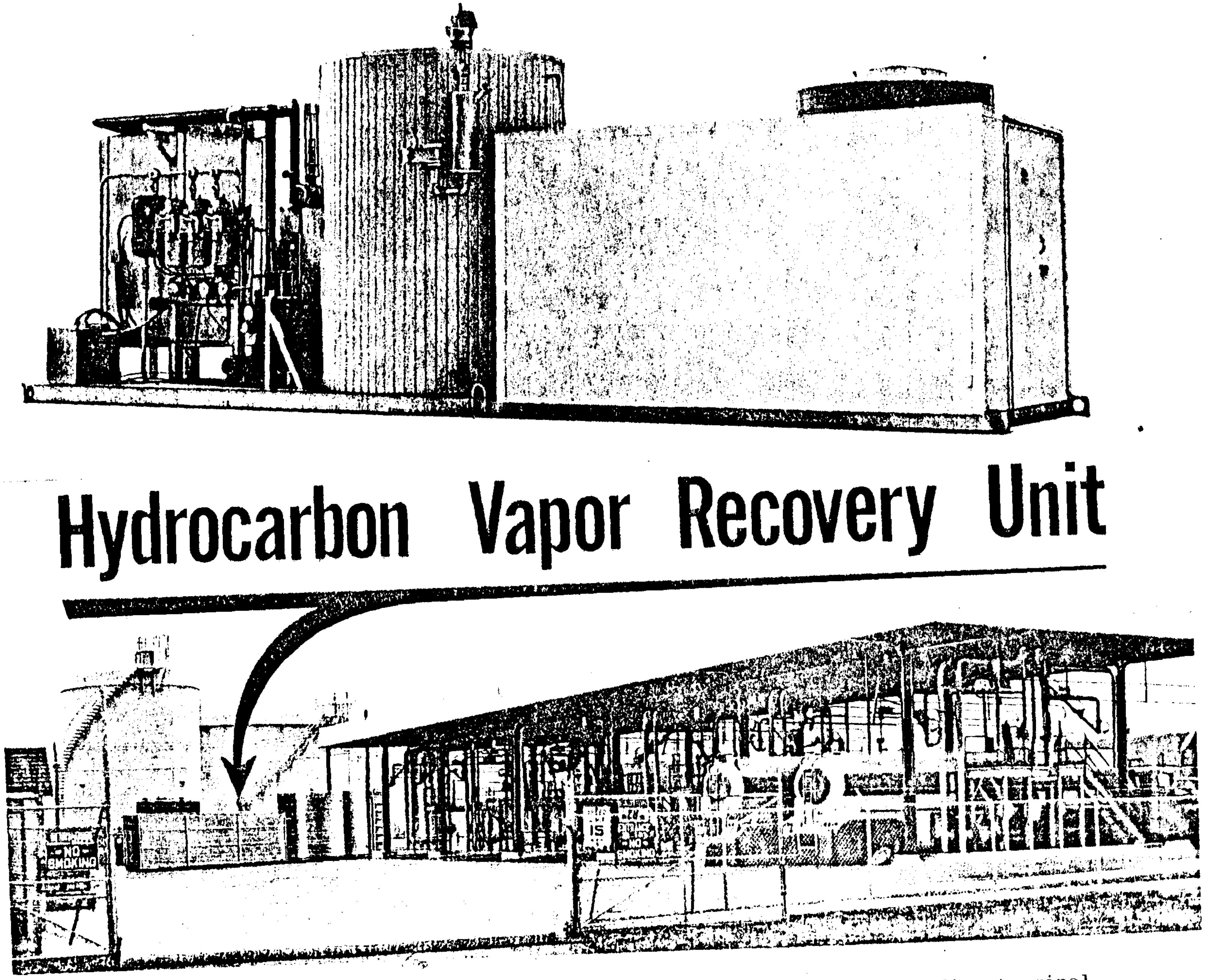

Figure 4-15. Condensation vapor recovery system in a gasoline bulk loading terminal.

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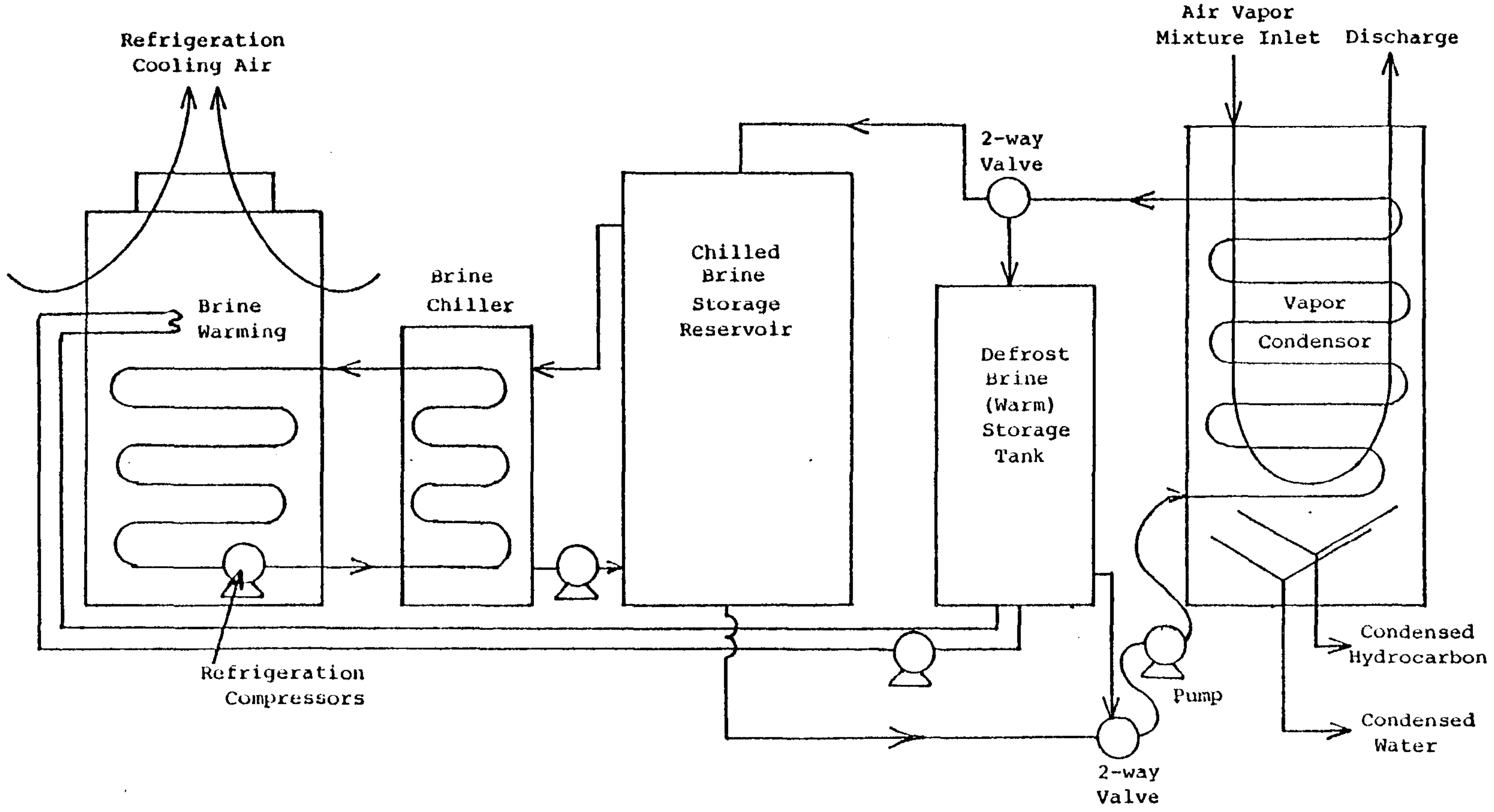

Figure 4-16. Schematic of condensation vapor recovery system.

This cascade refrigeration system follows conventional design producing temperature in the brine chiller of on the order of -90 °F to -100 °F. A cold brine pump circulates methylene chloride brine from the brine storage reservoir through the brine chiller to obtain the appropriate low temperature fluid (approximately -90 °F) for use in the vapor condenser.

In turn, the low temperature brine coolant is circulated through the finned tube sections of the vapor condenser. Hydrocarbon vapor and air mixture from the various bulk station filling points is passed over the finned tube sections of the vapor condenser. Entrained moisture in the entering vapor-air mixture condenses and collects as frost on the cold plate fins. Condensed liquid hydrocarbon is collected at the bottom of the vapor condenser.

At periodic intervals, defrosting of the finned surfaces is accomplished by circulation of warm brine stored in a separate reservoir. The temperature of the warm defrost brine is maintained by heat reclamation from the refrigeration equipment. Defrosting is completed in 10 to 30 minutes, depending upon the amount of frost collected on the finned coil.

A similar system is used in dry cleaning equipment. Heat vaporizes the solvent in the fabric and this vapor laden mixture is carried through refrigerant coils or through water. Solvent vapor is condensed, decanted from water and returned to the machine tank. The air is recirculated through the heater to the tumbling fabric. When the concentration of solvent vapor in the air stream from the drum drops below its dew point, and the solvent no longer can be condensed, a small amount of solvent will remain in the fabric being dried. At this point, the air is no longer recirculated to the heater but is exhausted to the atmosphere after one pass. This cools the fabric and deodorizes it by serving to evaporate and remove the final traces of solvent.

In solvent degreasers, refrigerated freeboard chillers can be added to control emissions. The freeboard is the distance from the surface of the solvent to the cover flange at the top of the unit (see Figure 4-17). The vapors created within a vapor degreaser are prevented from overflowing out of

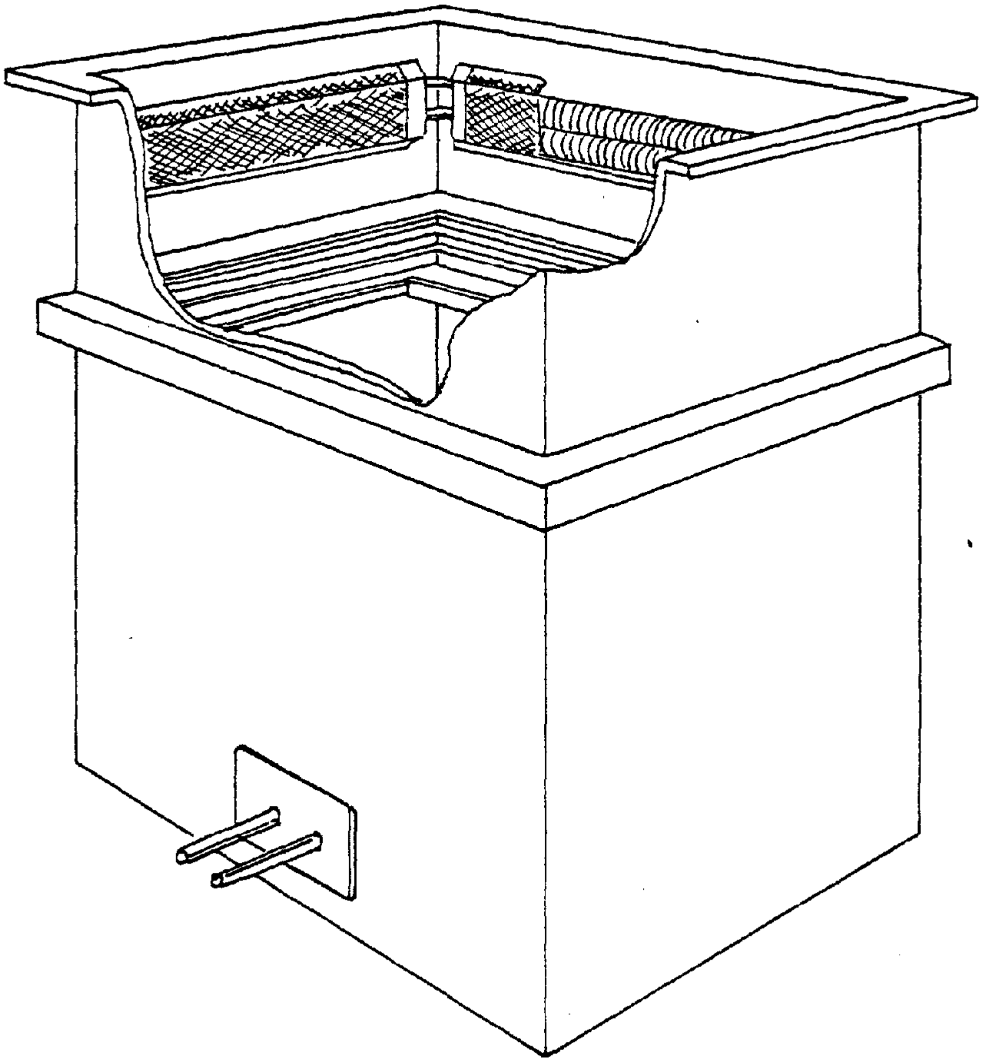

Figure 4-17. Refrigerated freeboard chiller.

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the equipment by means of condenser coils and a freeboard water jacket. Refrigerated freeboard chillers are an addition to this basic system. In appearance, they seem to be a second set of condenser coils located slightly above the primary condenser coils of the degreaser. Functionally, however, they achieve a different purpose. The primary condenser coils control the upper limit of the vapor zone, while the refrigerated freeboard chilling coils impede the diffusion of solvent vapors from the vapor zone into the work atmosphere. This is accomplished by chilling the air immediately above the vapor zone and creating a cold air blanket. The cold air blanket also reduces the mixing of air and solvent vapors by narrowing the air/vapor mixing zone, which results from a sharper temperature gradient. In addition, the chilling decreases the upward convection of warm solvent laden air.

4.1.4 Absorption (Scrubbing)

Absorption, as an air pollution control process, involves dissolving a soluble gas component in a relatively nonvolatile liquid. The absorption step is only the collection step. After the gas is dissolved, it must be recovered or reacted to an innocuous form.

Common absorbents for organic vapors are water, nonvolatile organics, and aqueous solutions (Ref. 4-4). Absorption is increased by lower temperatures, higher solubility of the gas, higher concentrations of the gas, higher liquid to gas ratios, lower concentrations of gas in the liquid, and greater contacting surface. Absorption has been widely used as a product recovery step in the petroleum and petrochemical industry where concentrations are typically very high. These products are generally recovered by heating to lower the solubility, or by distillation.

If a chemical oxidizer is present in the liquid stream, organics can be oxidized in the stream. This technique has been used to convert low concentrations of odorous compounds to less odorous forms. The expense of the oxidizing chemical, however, prevents its use where concentrations greater than a few parts per million are present.

The absorption-regeneration approach for organic solvents is severely limited by the low concentrations and consequent low solubilities of most organic gases in the absorbent. Exceptions are alcohols, ketones, amines, glycols, aldehydes, phenol, and organic acids. Gases may be regenerated by heating and reclaimed by condensation or destroyed by incineration.

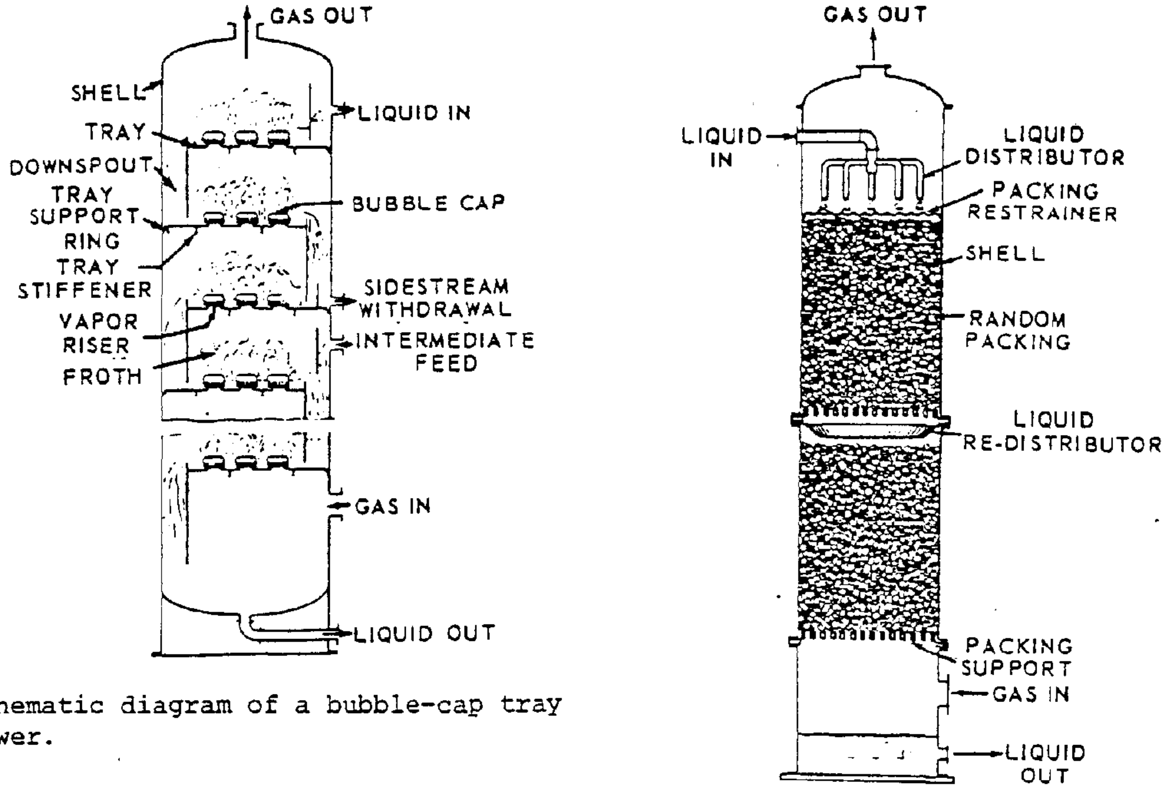
Direct contact with water may be used as a cooling method for removal of organic particulates or high boiling compounds to avoid opacity problems in the exhaust. It may also be used to preclean the air before a carbon absorber, but in most cases the materials do not go into solution to any appreciable extent. Figure 4-18 illustrates various types of scrubbers designed to provide thorough contact between the polluted gas stream and the water. If water is used for condensation in this way, water treatment may be necessary before discharge.

In summary, except for a few specialized cases involving water soluble compounds, absorption is not applicable to control of organic solvent emissions from surface coating except as a preliminary step for particulate and high-boiling compound removal.

4.1.5 Vapor Space Elimination

In storing or enclosing volatile organic liquid provisions must be made to control the escape of vapor due to temperature cycling or the change in liquid level. In a tank of fixed dimensions the organic vapors expand and contract with diurnal temperature changes and changes in the liquid contents. The pressure in the vapor space must be held constant within a few inches of water. Thus a fixed dimension tank must allow for vapor pressure compensation by venting organic vapor or intaking air as pressure or level changes occur.

The concept of a floating roof tank has developed over the years to eliminate the vapor space in storage tanks. The roof floats directly on the liquid in the tank moving up and down with changes in liquid level. At the periphery of the roof is a moving seal which rides against the tank wall. Compared to a fixed dimension or fixed roof tank, the emissions from a properly sealed floating roof tank is approximately 95% less (Refs. 4-5, 4-6).

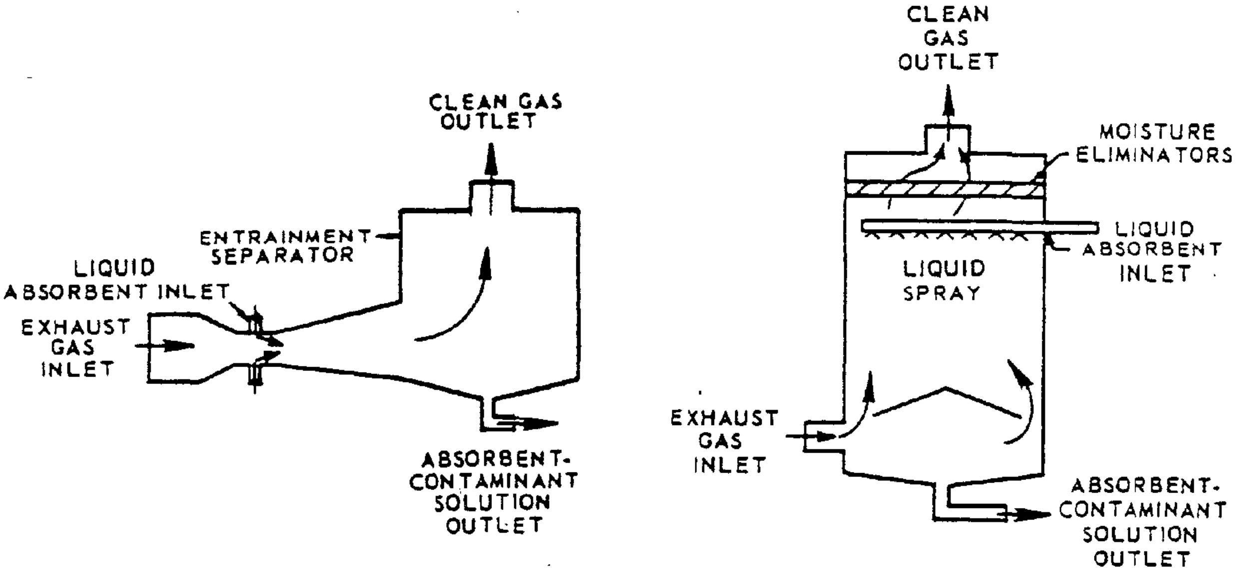


Schematic diagram of a bubble-cap tray tower.

(A)

Packed tower.

(B)



Venturi scrubber.

(C)

Spray tower.

(D)

Figure 4-18. Types of absorption systems.

While the floating roof concept is universally accepted as the proper method to store petroleum products, there has been an extensive amount of effort in the past year 1976-1977 to investigate the effects of the integrity of the roof-to-wall seal on the emissions from the floating roof tanks. In spite of work by the Western Oil and Gas Association (Ref. 4-7) and a joint effort by SOHIO and the Chicago Bridge and Iron Corp. (a tank manufacturer) (Ref. 4-8), the quantitative effects of the joint seal has not been rigorously measured. The API is currently undertaking a program to again attempt to measure actual tank emissions and to determine the effects of design and environmental parameters on the emission rate.

In the meantime the only "official" method of determining floating roof tank emissions is to use the calculation method of API Bulletin 2517 (Ref. 4-9). Although it is generally believed that this approach will not provide a accurate prediction of a given tank, it is felt to be as good a prediction as currently exists for the tanks in the field today. (Refer to further discussion in Section 2.0.)

The ARB has amended Rule 463, Storage of Organic Liquids, for the South Coast Air Quality Management District (SCAQMD) which requires floating roof tanks to have two seals with allowable gap requirements for the two seals specifically defined. Under these conditions some unofficial estimates of emissions are that they will be approximately 1/3 of those predicted by the equations in API 2517. SCAQMD's Rule 463 in its form at time of publishing this report is presented in the Appendix.

The concept of floating covers for waste water separators and other hydrocarbon pools can be used to reduce organic emissions. The problem is one of proper design to prevent the roof from sinking during adverse wind or precipitation conditions.

4.1.6 Liquid/Vapor Exchange (Balance System)

As organic liquid is transferred, the associated vapors are displaced by liquid. Instead of allowing these vapors to escape, they are ducted back to the transmitting vessel to complete a balanced system - hence the name, Balance System. As a tank truck is filled from a bulk loading tank the vapor from the truck is returned to the bulk tank. This is repeated as the tank truck fills the service station tank and again when an automobile's tank is filled. This is assuming that the equipment for balancing is available.

In the Basin most of the bulk terminals use the balance system. Very few service stations have installed systems yet. Bulk terminal systems have efficiencies ranging from 98-100%. Service station equipment has been demonstrated to have at least 90% efficiency*. However, the auto filling nozzles (specifically the nozzle to spout seal) are still in the development stage. The problem is to provide a reliable seal design that will stand up to the rugged handling of a self-service station.

Most automobile filling development activities are occurring in San Diego under the surveillance of the APCD. Several systems are being investigated: the balance system (Fig. 4-19); an augmented system in which a slight vacuum is created at the tank seal (Fig. 4-20); and the system in which the fumes are vacuum gathered for thermal incineration (Fig. 4-21), called the Hasselmann system. At the time of this writing, only the Hasselmann system has California ARB certification. It routes the vapors to a process unit where excess vapors are incinerated and provision is made to route liquids recovered back to the tank. A variation routes the vapors first through an underground storage tank, there via a vacuum pump to the process unit for incineration. The balance system is simple but it can be fouled by liquid gasoline blocking the return lines. If the nozzle seal is good and the tank overfills, the excess flows into the vent line. The second system uses an aspirator on the liquid fill line to create a slight vacuum on the vapor return line to assist in gathering the vapor at the vehicle tank interface. This should overcome any liquid blockage. That system (Fig. 4-20) also employs an enlarged vent pipe on

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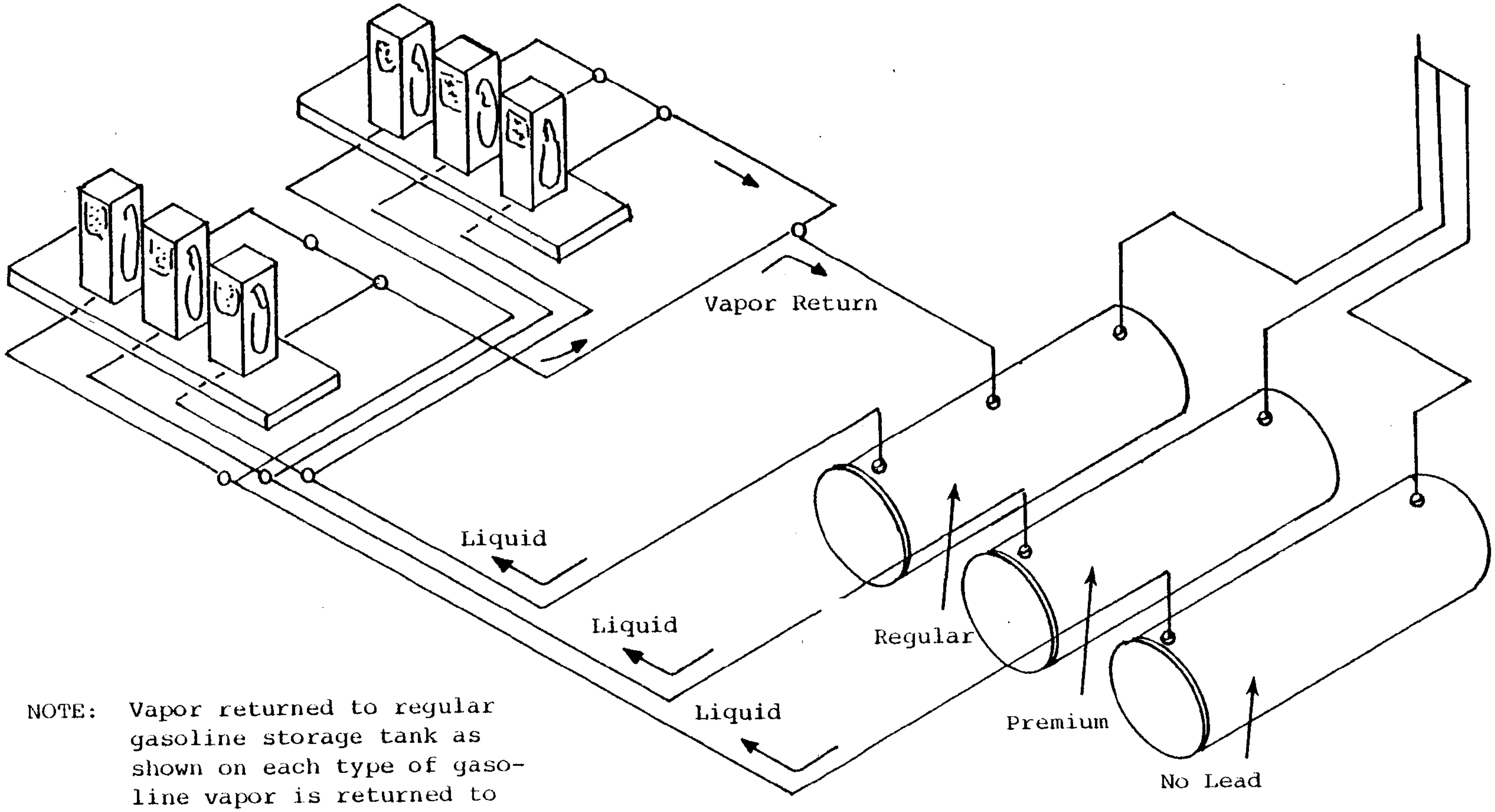
*The balance system (Fig. 4-19) is rated at 90% efficiency. The vacuum assisted systems (Figs. 4-20 and 4-41) have demonstrated 95% efficiency but they are not widely accepted.



NOTE: Vapor returned to regular gasoline storage tank as shown on each type of gasoline vapor is returned to its respective storage tank.

Figure 4-19. Diagram of a typical vapor balance system.

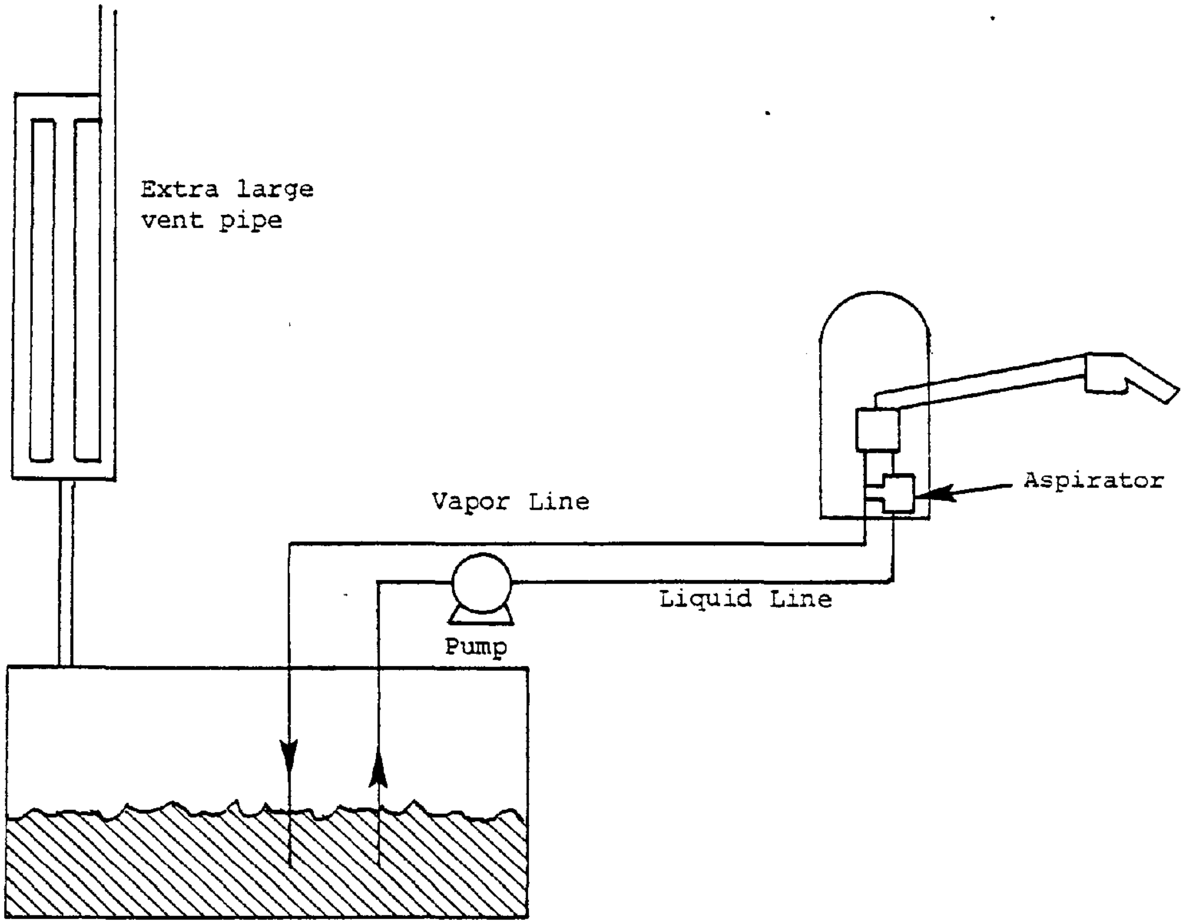


Figure 4-20. An augmented vapor recovery system for automobile refueling.

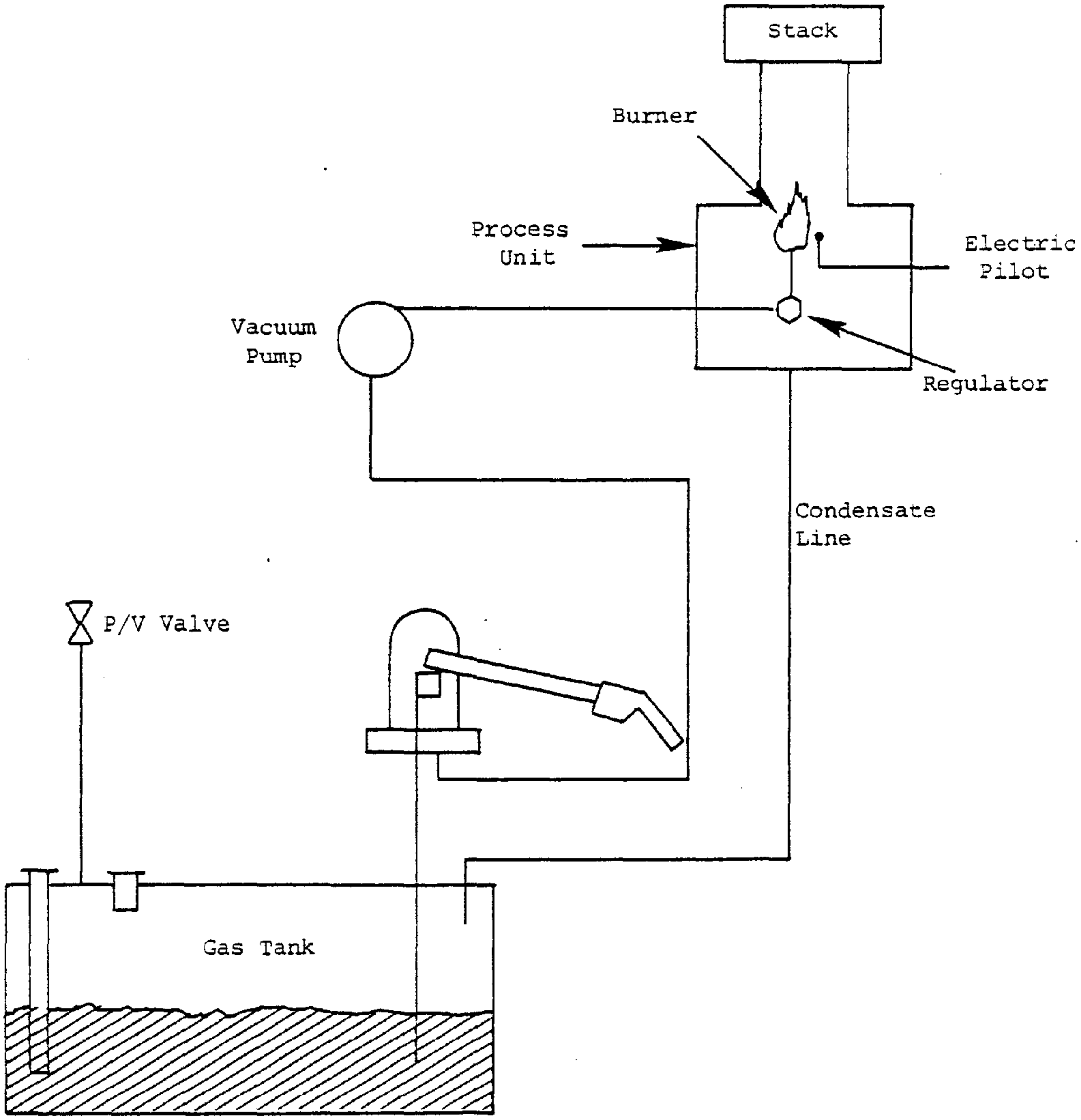


Figure 4-21. Hasselmann thermal oxidation system for control of automobile refueling vapors.

the underground tanks to contain the hydrocarbon gases (> C_3) in a stratified layer while air moves in and out slowly due to temperature cooling effects. The third system can be installed above ground. A vacuum pump pulls the vapors into a processing unit where condensation allows the return of the liquid to the storage tanks. The excess gases are then passed to the oxidation unit. The processing unit adds air to the hydrocarbon stream in a controlled amount to support combustion.

For a detailed treatment of the balance system and other systems of vapor recovery associated with petroleum marketing the reader should consult Reference 4-10.

4.1.7 Enclosure

In petroleum operations open pits, sewers and separators are still in use. As discussed in Section 2.0 these are significant sources of emissions depending on the temperature and vapor pressure of the source. Enclosing these open sources would reduce these fugitive emissions. Since an explosive mixture could be produced in this manner, care should be taken to adequately shield these enclosures from ignition sources. Vapor recovery devices or floating seals can reduce the explosion hazard.

Another version of enclosure is the variable vapor space tanks. These systems are primarily designed to limit breathing loss from fixed roof tanks. They are generally used for gasoline storage where tank throughput is low (less than 6 to 12 turnovers per year).

Usually a series of fixed roof tanks are connected to a variable vapor space tank by a series of manifolds. Vapors evolving from the products stored in the fixed roof tanks during periods of thermal expansion or reduced barometric pressure are temporarily stored in the variable vapor space tank. During periods when the vapors are contracting, such as at night, they are transferred back to the storage tanks. In this manner, normal breathing losses are effectively controlled. Filling losses are also controlled up to the point where the expelled vapor exceeds the capacity of the variable vapor space system. Figure 4-22 shows a tank designed to hold the vapors from another fixed roof tank.

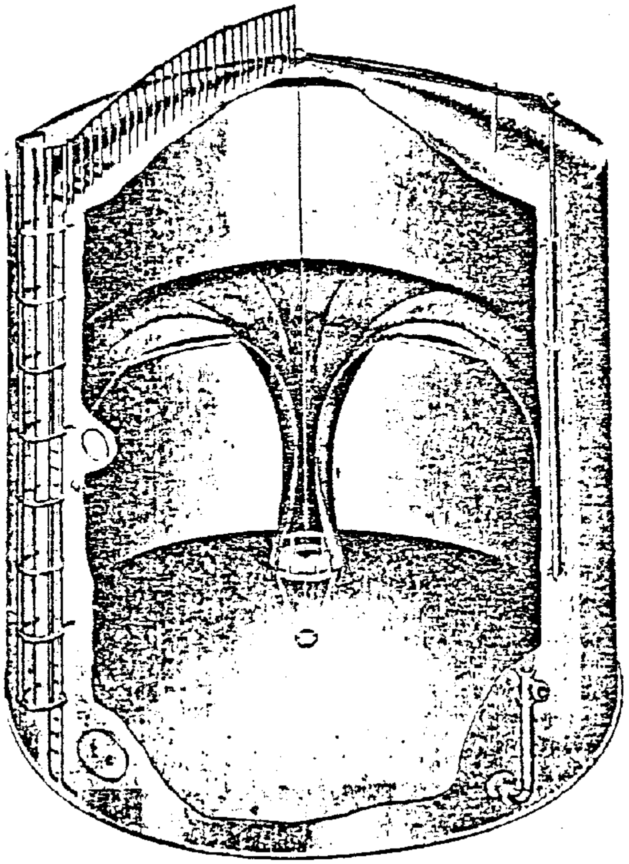


Figure 4-22. Separate variable vapor space tank (Ref. 4-11).

4.1.8 Process and Material Changes

A. Water-borne Coatings--

There is much confusion over the terminology of coatings containing water as part of their solvent content. Water-borne, water-reducible, water-based, water-thinnable, and latex are all used to describe these coatings. Strictly speaking, water-borne is the correct generic term for coatings containing water (Ref. 4-12). The base of a coating is the polymer or resin, but many use the term water-based interchangeably with water-borne.

There are three types of water-borne coatings: water-solutions, water-emulsions, and water-dispersions. Water-solution coatings feature very small particles dissolved in a mixture of water and a coupling solvent (Ref. 4-13). The water-soluble resins normally contain ionizable amine or carboxylic acid groups that solubilize the molecules (Ref. 4-12). These systems are more easily mixed and applied than other water-borne systems. However, resin properties that make the resin soluble can also cause water sensitivity after curing unless additions are made to eliminate this sensitivity.

Water-emulsions are high molecular weight particles suspended in water by some stabilizing, dispersing agent (Ref. 4-13). The resins, of which vinyls and acrylics are the most prominent, have very few functional groups and require emulsifying agents to maintain their form (Ref. 4-12). Emulsion coatings generally have the highest water resistance of the water-borne systems.

Water dispersion coatings are intermediate in particle size, in use of functional groups, and in water sensitivity.

1. Application techniques--Water-borne coatings may be applied using any of the methods used for organic solvent-borne coatings, that is, knife, blade, roller, dip, flow coat, and spray. The conductivity of water also enables use of electrophoresis to deposit a coating on conductive materials. By using a direct current potential in a bath and grounding the item to be coated, the item can act as an anode or cathode and be coated. Conversely, the conductivity makes electrostatic spray more difficult, although still feasible. Also, a new dip process is available in which the driving forces are chemical rather than electrical in nature (Refs. 4-2, 4-14, 4-15).

Water-borne spray coating solvent is typically 70 to 80 percent water and 20 to 30 percent organic solvent. The organic solvent is a necessary part of the coating that gives proper leveling and performance properties. Unlike organic solvent mixtures, water is only one compound with one evaporation rate and boiling point. The heat of vaporization is much higher than organic solvents and the rate of evaporation from a coating is very dependent on the relative humidity of the air surrounding the coating as well as the cosolvents used. Roller application followed immediately by curing has little humidity problem. When spray coating with water-borne coatings, humidity control is required. This increases energy consumption. This is an especially severe problem when spray booths are occupied.

2. Performance and appearance--Appearance of water-borne enamels can be as good as organic solvent-borne enamels if proper curing procedures are used. "Orange peel," that is, bumpiness of the surface, is greater for any enamel than for lacquer. The organic solvent portion of water-borne coatings minimizes this "orange peel" effect. Only a limited number of resins are available that allow the generation of high-gloss water-borne coatings. Water-borne coatings for aluminum are farthest advanced with tin-plate steel second. Coaters producing a wide variety of products and coaters who must warrant products for long periods of time in severe environments have the same problems with water-borne coatings as they do with other process changes.

3. Energy consumption--The energy required to remove the solvent is greater for a given amount of water than for the same amount of organic solvent. The heat of vaporization of water is about 1000 Btu/lb, about five times that of most organic solvents. The curing temperatures and time for water-borne coatings is greater than for organic solvent-borne coatings. It should be noted that the energy for heating the part itself often exceeds the energy to remove the solvent and cure the coating, particularly with large metal parts. Counterbalancing these higher energy items is a significant savings in oven air heating costs. Air recirculation is governed by

the necessity to maintain levels below 25 percent LEL (or somewhat greater with proper safety controls). Because of the lower solvent content per unit weight of solids, the volume of exhaust air can be safely reduced somewhat. In some cases, however, the coating quality can be adversely affected by too large a reduction, because of the drying properties of the coating. The net result is that the energy required to cure water-borne coatings is approximately equal to that for organic solvent-borne coatings for some applications but will be somewhat higher for most applications.

4. Safety--One of the major advantages of water-borne coatings is their non-flammability and low toxicity. Considerable savings in insurance costs can be realized in some cases.

B. High-solids Coatings--

The basic ingredient in an organic coating is the binder or resin. A resin is a film-forming organic polymer having glassy, plastic, or rubbery properties in the dried state. As applied the resins are liquids of controlled viscosity. On drying and curing (baking) the materials undergo polymerization and cross-linkage to form a solid film of the desired properties.

The materials for resins to be used in conventional solvent-borne coatings are "cooked" in resin kettles to yield liquids which have a high viscosity at ambient temperatures. To facilitate compounding with pigments the resins are dissolved in organic solvents which reduce the viscosity. To facilitate application more solvent may be added. After application, the solvent evaporates and the resins further polymerize to yield the solid film.

The viscosity of the coating as applied can be reduced by using low molecular weight monomers or "prepolymers," which are applied and then polymerized (cured) to the high molecular weight solid film. The amount of solvent required decreases with decreasing reactant molecular weight. However, as the molecular weight of the resin formers are reduced, the difficulty of controlling the polymerization reactions increases. The application and curing conditions must be precisely fitted to the reactant characteristics to yield a film of the desired properties.

Another method of reducing viscosity of high-solids coatings is by heating the coating material. As a rule of thumb an increase in temperature from 70 °F to 125 °F is equivalent to a 10 percent solvent reduction. However, heating can cause loss of solvent crucial to the application performance of high-solids coatings. Heating can also cause premature gelation of coatings, particularly on standing.

The solids content of a coating is expressed as the volume or weight of the final cured coating per volume or weight of the coating as applied. The term "high solids coatings" is usually reserved for low solvent coatings which are applied and cured by conventional means. Low molecular weight materials which are cured by radiation (ultraviolet, infrared, and electron beam) are classified separately. Radiation-cured coatings are discussed below.

High solids coatings were first defined by the Los Angeles County Air Pollution Control District in its Rule 66; coatings of 80 percent or more solids (by volume) were exempt from emission limitations.

1. Materials and processes--Most high solids resins fall into two categories, two component ambient temperature cured and single component heat converted. The most important types are as follows:

Two Component Ambient Cure	Single Component Heat Converted
Urethane	Epoxy
Acrylic-Urethane	Acrylic
Epoxy/amine	Polyester
	Alkyd

Many two component systems use a catalyst to increase the curing reactions. Although these chemical reactions can take place at room temperature, many plants use low-temperature ovens to cure two-component systems rapidly so that the coated product can be handled sooner. The oven temperatures required are much lower than for conventional ovens and the amount of solvent is lower. This will result in large energy savings. Most thermosetting high-solids coatings are based on epoxy or urethane resins. The most popular two-component coatings are based on polyurethane resins. Coatings properties compare favorably with those obtained from conventional based enamels. Toxicity of the isocyanates used for urethanes is a potential problem.

Fast-reacting two-component systems are usually applied with special spray guns that mix the two components at the spray nozzle. This equipment, more complicated than conventional spray equipment, is also more expensive. Some slower-reacting two-component coatings can be applied with conventional spray equipment.

High-solids coatings can be used in a variety of industrial coating processes. Two-component catalytically cured coatings are presently being air sprayed to coat small metal products. It might be possible to coat larger products such as automobiles with such systems. The coil coating industry is currently investigating the possibility of using high-solids coatings, especially two-component coatings (Ref. 4-16). The can industry is testing a roll-coat-applied high solids coating for can exteriors. Interiors of cans can possibly be coated with spray-applied high-solids coatings. Coatings of high viscosity can be applied with a knife coater, therefore, the paper and cloth industry may be able to apply high-solids coatings using existing knife coating equipment.

2. Advantages of high-solids coatings--In addition to reduction of solvent emissions high-solids coatings have other advantages:

- In most cases conventional application methods can be used. Therefore, conversion costs are low.
- In many cases, the energy required for curing is less than either conventional solvent coatings or water-borne coatings. However, in some cases higher curing temperatures are required and energy usage is greater than for conventional coatings.
- In some cases thick coatings can be applied, that mask surface defects (if desired), so that less surface preparation for a product is needed.

3. Disadvantages of high-solids coatings--The limitations of high-solids relate to the properties and availability of these coatings:

- Achieving the desired properties in the finished coating is difficult. In conventional coatings the necessary functional properties are created by polymer building in the resin kettle. Solvents are then added to optimize application and appearance. Most of the polymerization in high-solids coatings occurs after application and controlling the conditions so as to produce the desired properties is much more difficult.
- The availability of high-solids coatings is very limited. These coatings are just beginning to be converted from laboratory coatings to proven industrial finishing systems. Coating manufacturers report that efforts to produce coatings of 80 percent solids by volume have been unsuccessful. Coatings of 70 percent solids are still in the developmental stage. Only coatings in the 50 to 60 percent solids range appear to offer immediate prospects for expansion to widespread usage.
- Pot-life of two component systems is very short, leading to application difficulties.
- There is a health hazard associated with the isocyanates used in some two-component systems (urethanes).

4. Organic solvent emission reduction potential--In order to compare emissions for coatings of various formulations a common basis is necessary, such as a given volume or weight of cured solids. Table 4-4 makes such a comparison for organic solvent-borne coatings and water-borne coatings. The water-borne coating is assumed to have a volatile portion containing 80 percent water and 20 percent organic solvent. Such coatings are exempt from emission limitations by Rule 66 type regulations (Ref. 4-2). The last column shows the equivalent control device performance efficiency to achieve the same emission reductions.

C. Powder Coatings--

Powder coating involves the application of finely divided coating solids to a surface, followed by a melting of the coating solids into a continuous film. Very little solvent is used (less than one percent), and the process is thus almost pollution free. Several types of resins may be applied as a powder, but there are limitations on the type of objects that can be powder coated.

TABLE 4-4. COMPARISON OF EMISSIONS FROM ORGANIC SOLVENT-BORNE AND WATER-BORNE COATINGS

Basis: 1 gal. of solids weighing 11 lbs.

Organic Solvent-borne Coating		Organic Emissions*		Water-borne Coatings**		Organic Emissions		Percent Reduction
Percent Solids by Vol	Percent Solids by Wt.	gal.	lbs.	Percent Solids by Vol	Percent Solids by Wt.	gal.	lbs.	
12	20.5	7.3	42	10	13.3	1.8	11.9	72
20	29.7	4.0	26	15	19.6	1.1	7.4	72
30	41.7	2.3	15	20	26.2	0.8	5.3	65
40	52.7	1.5	9.9	25	31.4	0.6	4.0	60
50	62.5	1.0	6.6	30	36.9	0.5	3.1	53
60	72.0	0.67	4.3	35	42.7	0.37	2.4	44
70	79.7	0.43	2.8					
80	86.8	0.25	1.6					

*No control device.

**Volatile portion is assumed to be 80 percent water and 20 percent organic solvent.

1. Advantages of powder coating--In addition to the almost total elimination of organic solvent emissions, powder coating has several advantages over solvent-borne coating:

- Single coat application is possible with the fluidized bed technique for thickness up to 0.040 in. with one application versus several applications necessary for solvent-borne coatings.
- Material utilization can approach 100 percent if the powder can be collected and reused. This factor allows powder coating to be potentially the most economical coating material. The difficulty with the reuse of powder occurs if multiple colors are used. This will be discussed later.
- Safety aspects of powder coatings offer some advantages. Powders are low in toxicity and nonflammable in storage; however, virtually any organic powder suspended in air can be explosive.
- Maintenance is generally less because the powder can be vacuumed from any unbaked areas. Likewise the paint from any mistakes can simply be vacuumed off from unbaked items.
- Exhaust air volume is greatly reduced from that used for solvent-borne spray because application is generally either automatic or else done in a much smaller area. Spray booth air theoretically could be filtered and returned to the plant interior. Fan power is reduced as are space cooling or heating requirements.
- Water pollution problems are absent because dry particulate collection is possible.
- Natural gas usage can be theoretically decreased because little dilution air is required in ovens. However, higher bake temperatures are usually required, which may result in increased gas usage.

2. Disadvantages of powder coating--Some of the specific problems with different methods of application are discussed later. General problem areas include the following:

- Color change is a difficult problem for powder. The automobile and truck assembly industry has this problem in its extreme. Hence, color changes can occur as often as once a minute and with as little as 15 seconds to change colors between vehicles. Furthermore, more than a dozen colors are usually applied. For fluidized bed methods, considerable time would be necessary to switch colors because cleanout of the equipment would be necessary. A separate dip for each color would be necessary if color were changed more than once a day. For spray operations, the problem of changing colors can be solved by switching coating supply lines and purging the small amount of powder in the nozzle. This can, however, be a difficult mechanical problem. A remaining difficulty with color change is the problem of reusing overspray. If colors become mixed in the collection device, reuse of powder is impossible for any applications that change colors more than about once a day, unless the number of colors are few and it is feasible to use separate spray areas for each. Without the ability to reuse the oversprayed powder, powder coating loses one of its chief economic advantages--low materials loss.

- Color masking is more difficult for electrostatically applied powder coatings than for solvent-borne coatings. Fine detail, such as printing, is not possible and even two-tone automobiles present a problem, albeit a solvable one.
- Powder coating materials are discrete particles each of which must be the same color. Thus, there can be no user tinting or blending and all colors must be available from the manufacturer. For a coater that must match a given color, such as in a trademark, the necessary color may not be available. Color matching problems can occur when using recycled powder.
- The high curing temperature required for powder coatings mades them applicable only for metals and some plastics.
- A typical particle size for sprayed powder coating materials is generally greater than 15 micrometers (Ref. 4-18). Because 1 mil is about 25 micrometers, it is obvious that thin, uniform spray coatings are difficult to achieve at coating thickness of less than 2 to 3 mils. Fluidized bed coating materials are usually about 200 micrometers in diameter and thus are not applicable for thin coatings.

3. Application methods--The three general application methods for powder coatings are electrostatic spray, conventional fluidized bed, and electrostatic fluidized bed. For further details consult References 4-2 and 4-17.

D. Hot Melt Formulations--

Hot melt coatings are applied in a molten state. The molten resin film cools soon after being applied to the substrate. Because there is no solvent to evaporate, virtually 100 percent of the materials that are deposited remain as a solid part of the coating. Hot melt coatings are most often applied to paper, paperboard, cloth, and plastic.

When the hot melt coating has been applied and cooled, the film does not need further heat curing. Since the only heat required is that to melt the coating initially and to heat the coating applicator, a considerable energy savings can result compared to oven curing. Also, because an oven is not needed, less floor space is needed for the coating line. The line can be run faster with hot melts than with organic solvent-borne coatings. A chilled roll can be used to speed cooling, if necessary.

Hot melt coatings are applied at a variety of temperatures. Low melting point coatings are applied at temperatures as low as 150 to 210 °F. These are materials such as waxes or paraffin coatings that are soft and easy to scratch. To improve scratch resistance, higher melting resins are added. These are usually synthetic organic compounds. Hot melt blends with melting points in the range of 300 to 450 °F usually contain no paraffin, waxes, or other low melting point ingredients but rather are composed of film forming resins and plasticizers. The resultant films from such high melting point formulations show properties that are comparable to high grade solvent-borne coatings (Ref. 4-18).

Hot melt coatings must, of course, be applied at temperatures that are higher than the melting point of the coating. Because the substrate may be harmed by high temperatures, hot melt coatings with melting points above 400 °F cannot be used for some applications. However, some extrusion coatings are heated to 600 °F to achieve proper adhesion between the polymer and substrate (Ref. 4-19).

Hot melts may be applied in a variety of ways. Usually special heated coating equipment is required. Lower melting hot melts may be applied by heated rotogravure or roll coaters. Extrusion coaters are widely used also, especially with higher melting point materials.

Extrusion coatings are a large subclass of hot melt coatings. In this type of coating a screw extruder discharges a molten plastic sheet onto the substrate. Food containers such as milk cartons are often coated with extrusion coatings because the plastic film provides a good moisture barrier.

Ethylene/vinyl acetate copolymer, low and medium density polyethylenes are the resins most widely used for hot melt coatings. Polyethylene forms a strong film, mixes well with other resins and waxes, has good water resistance, has good flexibility at low temperatures, and is relatively low in cost. Other resins used include vinyls, cellulose esters, alkyl esters, maleic esters, and polystyrenes. All of these materials must have viscosities suitable for application and they must be chemically stable for long periods in the molten state.

Hot melts are applicable to the paper and fabric coating industry, although only for certain applications. Thus, hot melt coatings cannot be judged to be universally applicable in the paper and fabric coating industry at this time.

E. Electrostatic Spray Coating--

Electrostatic spray coating utilizes the attractive force between materials of opposite electrical charge as an aid in applying a uniform coating to various surfaces. The method reduces overspray and waste and thereby increases the coatings application efficiency over conventional spray coating processes. In the case of solvent- and water-borne coatings, this will in effect reduce the amount of coating solids and corresponding solvent carrier needed for a specific coating job. Electrostatic spray coating can be used to apply solvent-borne, water-borne, or powder coatings.

In typical electrostatic spray coating processes where relatively nonconductive solvent-based coatings are used, coating particles are charged up to 100,000 volts with an electrode (Ref. 4-20). The grounded object then attracts the negatively charged particles, which are captured to form a film. In instances where conductive coatings are used, water-borne coatings, for example, it is possible to use reverse polarity, that is, charging the object to be coated and grounding the spray equipment (Ref. 4-21).

Electrostatic spray coating is primarily applicable to metal surface coating. It is of particular value for complex shapes. Glass, plastics, paper and fabric have been successfully coated with this technique. Corners or extreme concave shapes on objects may escape coating due to the "Faraday cage" effect (Ref. 4-21). This phenomenon results from the repulsive electrical forces in corners or concave areas.

Electrostatic spray coating has the potential of reducing organic emissions since it can improve the efficiency of application of solids over ordinary spray. This results in less organic solvent emissions.

F. Electron Beam Curing--

The electron beam curing process uses high energy electrons to promote curing of electron beam-curable coatings. Electrons bombard a coating to produce free radicals throughout the coating. This initiates a crosslinking reaction that continues until the coating is cured. The entire process takes only a few milliseconds to complete (Ref. 4-22). Since most free radicals are terminated by oxygen, an inert atmosphere is desirable so that the surface of the coating will not be less highly crosslinked than the interior.

The energy requirements for electron beam curing are dependent on the size of the unit and the coating thickness but are typically lower than for thermal curing. There is an additional energy savings because of the instant startup and shutdown capability of the electron beam unit.

Electron beam curing units must be shielded properly to avoid radiation exposure. According to occupational Safety and Health Administration regulations, exposure should not exceed 5 millirems of radiation in 1 hour and 100 millirems in any 5 consecutive days (Ref. 4-23).

Some electron beam-curable coatings may contain monomers that are toxic. Caution should be taken when using such monomers.

There have been few, if any, tests performed to quantify organic vapors emitted during the curing process. It is generally assumed that some low molecular weight organic compounds are emitted during curing even though all the components are reactive. There also may be some ozone generated from the curing process itself (Ref. 4-24).

The use of electron beam curing is most effective on flat surfaces where the electron beam strikes the surface vertically. If the beam strikes the surface at an angle closer to the horizontal, the amount of absorbed energy can be too small and the coating will not cure properly.

Electron beam curing, unlike ultraviolet light curing, can cure thick and pigmented coatings because of the penetrating power of the electrons.

Because electron beam curing uses relatively new technology, the coatings necessary for the electron beam curing process are in the early stages of research and development. The use of electron beam curing is very limited at the present time.

G. Ultraviolet Curing--

In ultraviolet curing, ultraviolet light reacts with photosensitizers in the coating to initiate crosslinking to form a solid film. The basic components of an ultraviolet curable coating are: an ultraviolet-curable base polymer, diluent monomers, and ultraviolet photochemical initiators (Ref. 4-25).

The ultraviolet-curable polymers provide most of the desired coating properties. The diluent monomers decrease the viscosity of the polymers, increase the crosslinking density, and improve other features of the coating such as gloss, hardness, and curing speed. The photochemical initiators are unstable chemicals that form free radicals when bombarded by ultraviolet light to initiate the crosslinking process (Ref. 4-26).

The energy source used for ultraviolet curing is electrically produced ultraviolet light energy such as from mercury vapor lamps. The use of ultraviolet light for curing is most effective on flat surfaces where the light reaches the surface vertically. When the ultraviolet light strikes a surface at an angle closer to the horizontal, the amount of absorbed light can be too small for effective curing. Obviously, no curing will occur if an area is shielded from the light.

The actual performance and appearance of ultraviolet-curable coatings is not only dependent on the base polymers, diluent monomers, and photochemical initiators, but also on other agents such as pigments, fillers, and mar resistors added to the coating to provide the desired properties.

In certain industries, the use of ultraviolet light curing has been successful, although this success has been limited mostly to semitransparent coatings, such as inks. Ultraviolet cured polyester based coatings have made a significant penetration into the forest products industry as filler coatings for particle board. Most uses of ultraviolet coatings, however, are still in the research and development stage. Major problems are curing of thick coatings and coatings with pigmentation. The main difficulty with pigmentation is that the pigment particles absorb or reflect ultraviolet light, thus reducing the light energy available to cure the coatings in the deeper layers of the coating.

Because little if any flammable solvent is emitted, the amount of dilution air flow through ovens can be greatly reduced. There is a substantial decrease in energy usage compared with thermal curing. An ultraviolet curing unit may use only one-third the energy of a standard thermal oven (Ref. 4-27).

The ultraviolet curing equipment must be shielded properly to avoid exposure of the equipment operator. Exposure at short distances can cause severe burns to the skin and the eyes (Ref. 4-28).

Certain ultraviolet coating materials may produce skin and eye irritation. Others, such as those containing "the more volatile crylic monomers, are considered toxic and hazardous chemicals" (Ref. 4-28). The handling of ultraviolet-curable coatings requires care and caution.

There have been few, if any, emission tests performed to determine whether volatile organics are emitted during ultraviolet curing. Some low molecular weight organic compounds are probably emitted during the ultraviolet curing process even though all the components of the coating are reactive.

4.1.9 Improved Maintenance

The release of fugitive organic emission from leaks in process equipment and pipeline fittings as well as from spills and other equipment failure can be reduced by improved maintenance. In the field testing performed on this program at oil production fields and refineries it was found that more than 50% of the leaks found by the test crew could be stopped by a simple tightening of a valve packing nut or applying grease to seal a plug valve. Similarly, immediate attention given to liquid leaks developed in pumps or compressors can reduce the amount of evaporative loss.

Based on field test data taken during this program (see Section 3.0), an average leak rate of 0.15 lb HC/day was determined. Using the spray and sniff (soap bubbles and an explosimeter) technique developed by KVB for locating leaks, a single workman can locate and tighten the leaks in several hundred valves and fittings a day. Using the leak rate and assuming hypothetical workman efficiency and employee costs, KVB arrived at a figure which reflected possible savings. Those computations were submitted to Mr. J. H. Caldwell, Jr., Manager of Refinery Operations at the Carson plant of Atlantic Richfield Company for evaluation. His letter is included on the following pages.

According to the analysis set forth by Mr. Caldwell, it would seem that the cost of additional maintenance programs would exceed the economic gains. ARCO's present maintenance program coupled with the enforcement efforts of the SCAQMD represents what they believe to be the most cost effective approach.

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J. H. Caldwell, Jr.
Manager
Refinery Operations

August 4, 1977

Hal Taback
KVB Incorporated
17332 Irvine Boulevard
Tustin, California 92680

Subject: Fugitive Hydrocarbon Emissions - Valves and Fittings

Dear Mr. Taback:

As we indicated at our meeting of July 20, we have attempted to quantify the costs and benefits of a total monitoring and leak repair program for valves and fittings along the lines suggested by your draft report and the EPA draft document. At this time, our best guess is that a monthly survey of all valves and fittings in the refinery, including maintenance on leaks discovered, would cost approximately $1,500,000 per year in addition to our current maintenance budget. The value of the hydrocarbon product recovered by this maintenance expense would be only about $15,000 at a net cost of about $20,000/Ton of hydrocarbon emissions. Although this number may seem high, please recognize that there are over 1,000,000 valves and fittings in our refinery and a cost of about $0.10 each ($1.00 to $1.50/year) to survey and maintain these fittings is very reasonable.

These figures were arrived at in the following manner. A crude distillation unit with a rated capacity of 38,000 B/D was chosen for the experiment. This unit contains 3 fractionating towers, 8 other hydrocarbon pressure vessels, 2 fired heaters, 23 shell and tube heat exchangers and 22 hydrocarbon pumps. It's purpose is to fractionate incoming crude oil into the following streams: propane/butane, light gasoline, heavy gasoline (naphtha), kerosine, diesel and residuum. Normal operating and maintenance personnel were relieved of their normal duties and instructed to count <u>all</u> valves and fittings containing hydrocarbons, visually inspect for liquid leaks and soap test for vapor leaks and repair as many leaks as possible without shutting down the unit. No records were made other than the raw count of valves and fittings and time and materials spent on the job. For this unit, 65 man hours were spent for survey and repair and about $500 of materials were used. As shown on the attached table, 11,414 leak sources were identified and tested, 38 leaks were discovered of which 31 were repaired without a unit shutdown. All of the leaks were considered minor and most were barely detectable. Of the 7 leaks that could not be easily repaired, 6 were low vapor pressure liquid (4 flanges and 2 exchanger heads). One valve in propane service could not be repaired or replaced without a unit shutdown.

The basis for extrapolation of these results to the entire refinery is by the number of pumps. Many of the valves and fittings are directly associated with pumps and the number of manifolds, exchangers, etc. are related more nearly to pumps than other major equipment. Volumetric through-put is a very poor scaling factor as we have previously discussed. The crude distillation unit contains 1% of the hydrocarbon pumps in the refinery and is therefore assumed to contain 1% of the valves and fittings.

The basis for calculating emission reductions is a little more speculative. Obviously the only way to make a precise calculation is to assume "virgin territory" for a base line and run longitudinal studies with several surveys over an extended time period to determine the reoccurrence rate. The first such survey and at least some of the subsequent surveys would have to include bagging observed leaks to quantify emissions/leak. Even then, some arbitrary correction factor would have to be applied to relate an obviously experimental situation to the real world. In the absence of this data, the following was assumed:

1. "Large" leaks are identified and corrected as quickly as possible under present conditions for safety and economic reasons. This may not be true for all refineries in all locations but is reasonably accurate for major refineries under current standards. Our excellent safety record attests to this fact. Obviously there may be a difference of opinion as to what constitutes a "large" leak.

2. Most "medium" leaks and many "small" leaks are repaired in a timely fashion either because of safety and economic reasons or due to current weekly enforcement inspections by the SCAQMD. Full blown, total facility inspections are not likely to speed up this process and in fact may divert resources currently expended from repairing a few "large" leaks to many inconsequential ones.

3. Pre-turnaround inspections are currently conducted to identify the remaining minor leaks for repair during unit maintenance shutdowns when resources can be efficiently utilized. These turnarounds take place semi-annually to bi-annually depending on the type of process involved.

With this in mind, assuming 80% of the minor leaks discovered (0.3% of the valves and fittings surveyed) are repaired and stay repaired with a 50% reoccurrence rate multiplied by your factor for emissions per "small" leak (52 lb/day) gives about 100 tons/year emission reduction resulting from total monthly surveys in this plant. This result would only be valid for the first year of the program. Subsequent years would show diminishing returns since hopefully leaks would be repaired faster than they occur.

Finally, I cannot close without making a rather personal observation. Under normal circumstances my professional standards would not allow me to extrapolate limited data to the extent done above. However, I feel that in this case it is in the public's interest to give the fairest assessment possible in the limited time available. Both by corporate policy and personal commitment, I would not hesitate to recommend a program of the cost outlined if it meant a meaningful contribution to improvement in air quality in the Los Angeles Basin. Our current maintenance program coupled with the present enforcement efforts of the SCAQMD represents the most cost effective approach to reduction in fugitive emissions from valves and fittings. Nonproductive programs requiring large manpower expenditures only serve to divert precious resources from the real issue of supplying the energy requirements of society in an efficient, environmentally sound manner.

Very truly yours,

J. H. Caldwell Jr.

J. H. Caldwell, Jr.

JHC:pm

Attachment

SURVEY RESULTS

Fittings		Valves	Total
Bolted	Screwed	Stems, Bonnets	Leak Sources
3117	5465	2832	11414
7 leaks repaired	8 leaks repaired	16 valves repaired or replaced	31 leaks stopped
*6 leaks not repaired		1 valve yet to be repaired	7 leaks not stopped

* 2 exchanger heads leaking - unable to stop.

4 flanges leaking on vocss system - unable to take system out of service.

All leaks considered small - most barely detectable.

While KVB's tests at ARCO revealed leaks averaging 0.15 lb/valve/day, the major amount of the leakage (80%) occurred in the large leakers which Mr. Caldwell contends would have been eventually discovered.

4.2 APPLICATION

In the previous subsection, 4.1, the various control methods were reviewed in some detail. In this section, various industry devices and processes are discussed with regard to the types of control methods that are applicable. Table 4-1 summarizes the various devices and processes, and the applicable control technology.

4.2.1 Petroleum Operations

A. Production--

1. Valves, flanges, etc.--Fittings in oil fields are used in either gas or liquid service. Most leakage is found in the gas service pipelines. The most effective control was found to be improved maintenance. In the field tests by KVB on this program, a number of leaks were detected which could be stopped by simple tightening of valve packing nuts. This indicated that an improved maintenance program might be an effective measure. However, when the same approach was suggested for a refinery operation, it was refuted by refinery management as not being cost effective (see Section 4.1.9).

Although no data have been found to support this, it is the general consensus of the people in the petroleum business that plug valves are better than gate valves from a leakage standpoint. This would suggest that switching to plug valves would offer some advantage. Most plug valves rely on grease to seal them. KVB actually found proportionally more plug valves leaking than gate valves. However, the simple injection of grease into the valve always stopped the leak whereas on gate valves it was not always possible to stop a leak by merely tightening the packing nut. In some cases it was necessary to replace the entire packing.

If some data could be developed to establish which type of valves have the least leak rate, then the gradual switching to that type of valve should be initiated. Two programs are currently in progress in which petroleum valve leakage data will be obtained, an oil refinery emissions measurement program sponsored by EPA (Ref. 4-29) and a production field test program sponsored by API (Ref. 4-30). These results should be monitored in developing valve emission control techniques.

2. Pumps and compressors--The use of mechanical seals and a preventive maintenance program of testing and repairing will result in reduced emissions. The EPA and API studies mentioned above should provide further information as to the compressor and pump leakage rate and the difference between packed and mechanical seals.

3. Tanks, storage and production--Crude oil processing involves heating and compression for water, oil and gas separation. Production and storage vessels are usually of the fixed or cone roof type. The most effective emission control system is the vapor recovery units used to retain as much of the gaseous product as possible. A typical installation is shown in Figure 4-23.

A battery of cone (fixed) roof storage tanks are connected by a series of gas manifolds to a gas holder (usually a low pressure diaphragm type design).

Provision is made for removing excess gas from the gas holder with a compressor. To make up for this lost gas a blanket gas is allowed to flow into the vapor space of the cone roof tanks during periods of vapor contraction (due to cooling or barometric pressure changes) or during periods of liquid withdrawal. The blanket gas usually consists of natural gas and its purpose is to maintain a non-explosive mixture in the vapor space of the cone roof tanks. The natural gas vapors recovered from the gas holder represent a high grade combustible fuel gas. This gas may or may not be processed through various stages of refinement such as cooling to condense low volatile liquids separating them from the gas stream as shown in Figure 4-23. The fuel gas can be used as an energy source for the various gas-fired devices in the production field.

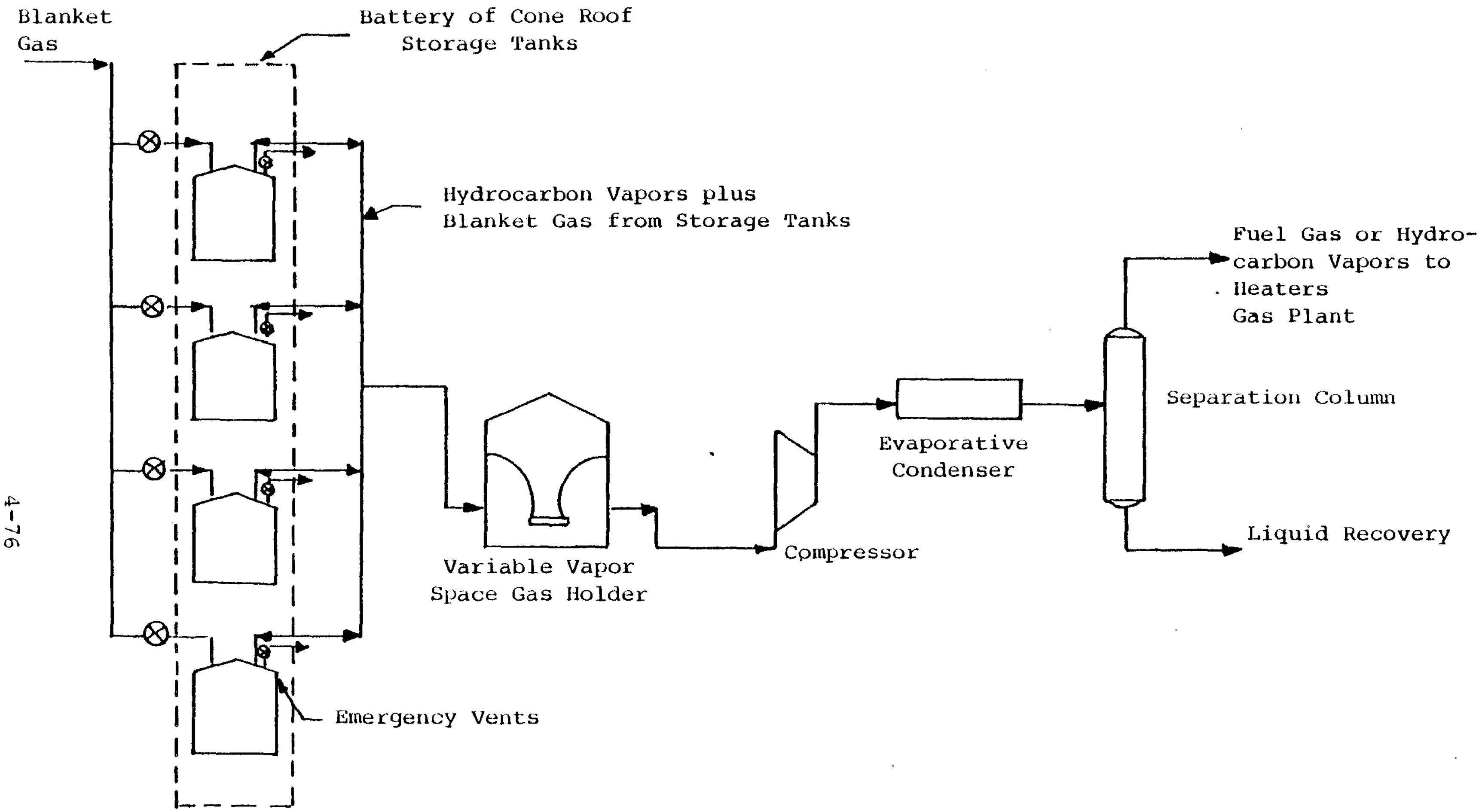

Figure 4-23. Simplified schematic of a typical vapor recovery system (Ref. 4-6).

Where no vapor recovery system is used, painting the tanks white will minimize breathing losses. H_2S gas sometimes present in crude oil was found to have corrosive effects on tank sample port covers. Leaks in these covers can result in significant loss since the gas blanket is at a slight positive pressure to prevent air intrusion. Therefore maintenance is required to insure tight cover fit.

4. Waste water separators--Most oil fields process waste water from their heater treaters and water knockout tanks in open pools, skimming off the oil in various stages. In the final stage a vacuum truck periodically removes the oil layer. This has been an acceptable practice under current rules because it was felt that the Reid vapor pressure was below 0.5 psi. KVB tests conducted as part of this program suggest that a significant amount of H/C emissions may be evolved from the surface of the pool. Solid or floating covers will reduce these emissions by up to 95%.

5. Well vents--In certain oil fields in the Basin, steam is injected into oil wells to stimulate the recovery of crude oil. This form of tertiary oil recovery along with another method, referred to as in-situ burning or fire flooding, causes gaseous hydrocarbons to be emitted from well vents. Fire flooding involves pumping air underground to burn some of the oil to heat the remaining oil and lower its viscosity. The emissions contain hydrocarbons and some odorous compounds like H_2S and mercaptans. The hydrocarbon emissions are in relatively high concentration, 2-3,000 ppm, and the odorous compounds are in low concentration, a few ppm or less. The control devices applied are water cooled finned condensors and charcoal-absorbers to collect the H_2S and mercaptans.

6. Boiler and heater--Boilers are used to create the steam to be injected into the ground. Process heaters are used to separate crude oil from the associated water. Both of these devices emit low concentrations of hydrocarbons. The best way to minimize these emissions is to keep the device well maintained and to use optimum burner designs which will have good atomization and mixing.

7. IC engines--Natural gas fired piston engines are often used to drive oil well pumps. Two stroke engines emit a substantial amount of gaseous H/C's because part of the fuel never burns. On a two stroke engine intake and exhaust occur on the same stroke so that some of the fuel as scavanged with the exhaust products. The best control approach is to replace the two stroke engines with four stroke engines and to keep the engines well tuned.

B. Refining--

Valves and flanges--

Compressors and pumps--

Waste water separators--

Boilers and heaters--

The approach for these items in a refinery is identical for the respective devices in an oil field as presented above.

1. Vacuum jets--These vacuum ejectors are used on vacuum distillation towers. With the exception of the stripping steam the ejected stream is all hydrocarbon which may be condensed by a water cooler and vented to the refinery fuel gas. Condensible products are collected and processed further.

2. Asphalt air blowing--Asphalt is normally obtained from select crude oils by means of vacuum distillation or solvent extraction. To make it suitable for paving, roofing, or pipe coating, asphalt is sometimes reacted with air. Air-blowing is mainly a dehydrogenation process. Oxygen in the air combines with hydrogen in the oil molecules to form water vapor. The progressive loss of hydrogen results in polymerization or condensation of the asphalt to the desired consistency.

Blowing is usually carried out in batches, starting with the asphalt at a temperature of 300 °F to 400 °F. Little additional heat is needed since the reaction becomes exothermic.

Effluents from the asphalt air-blowing stills include oxygen, nitrogen, water vapor, sulfur compounds, and hydrocarbons in the forms of gases, odors, and aerosols. Discharge of these odors and airborne oil particles can be disagreeable.

Control of emissions from asphalt air-blowing stills has been accomplished by scrubbing and incineration, singly or in combination. Most installations use the combination. For scrubbing alone to be effective, a very high water-to-gas ratio of about 100 gallons per 1,000 standard cubic feet per minute is necessary.

Where removal of most of the potential air pollutants is not feasible by scrubbing alone, the noncondensibles must be incinerated. Essential to effective incineration is direct-flame contact with the effluents, a minimum retention time of 0.3 second in the combustion zone, and maintenance of a minimum combustion chamber temperature of 1,200 °F. Other desirable features include turbulent mixing of vapors in the combustion chamber, and adequate instrumentation. Primary condensation of steam and water vapor allows use of smaller incinerators and results in fuel savings. Some of the heat released by incineration of the waste gases may be recovered by using it to generate steam (Ref. 4-4).

3. Catalyst regenerators--Petroleum fractions are cracked to produce compounds of lower molecular weight. Catalysts in the form of powders or beads are utilized. The catalyst particles become coated with carbon and high-molecular-weight compounds. These materials must be burned off the catalyst in order to maintain its activity. The catalyst continuously circulates from the reactor chamber to the regenerator chamber. In the regenerator, a controlled amount of air is admitted to burn off the coatings. This causes the formation of CO and hydrocarbons. These emissions can be controlled by incineration using a waste heat boiler. These boilers are commonly referred to as CO boilers (Ref. 4-4).

4. Storage tanks--In a refinery both fixed roof and floating roof tanks are employed. In the Basin the storage of organic liquids is controlled by SCAQMD Rule 463 which, if the Reid vapor pressure is greater than 0.5 psi, requires the use of floating roof tank with double seals or fixed roof tanks with variable vapor space or vapor recovery. If the RVP is lower than 0.5 psi, then the liquid may be stored in a fixed roof tank without control.

5. Transferring--Movement of hydrocarbons throughout a refinery from vessel to vessel can produce working losses. To minimize these losses the vapors created and displaced must be minimized or handled to prevent their

escape. Floating roof tanks, variable vapor spaces and vapor recovery systems can be employed. In filling tankers and tank trucks, bottom filling procedures minimize the escaping hydrocarbons. Liquid/vapor exchange is also used to reduce emissions as well as for vehicle safety. Reference 4-10 has a thorough treatment of these methods.

6. Blow downs--Refinery units are periodically shut down and emptied for internal inspection and maintenance. The process of unit shutdown, repair or inspection, and start-up is termed a unit turnaround. The purging of the contents of a vessel to provide a safe interior atmosphere for workmen is termed a vessel blowdown. In a typical process unit turnaround the liquid contents are pumped from the vessel to some available storage facility. The vessel is then depressurized, flushed with water, steam, or nitrogen and ventilated. Depending on the refinery configuration, the vapor content of the vessel may be vented to the fuel gas system, flare, or if released directly to the atmosphere, it is through a blowdown stack which is usually remotely located to ensure that combustible mixtures will not be released within the refinery.

The emission factor for refinery blowdown is 856 kilograms per 1000 cubic meters ($kg/10^3 m^3$) of refinery throughput (Ref. 4-31). This factor is based on a one-year (1956) record of refinery turnarounds in Los Angeles County. In this one-year period, eight refineries reported 382 turnarounds with blowdown; 56 percent of these resulted in emission to the atmosphere, while 44 percent resulted in no emissions (Ref. 4-32).

C. Marketing - Transferring--

In gasoline marketing the product is transferred from the bulk station to the local service station and then to the automobile. Vapor control can be maintained by the balance system of vapor liquid exchange. The losses are further reduced by using the procedure of bottom filling the tank trucks and service station tanks to minimize the amount of aerosol in the vapor being transferred. In terms of control strategies to reduce hydrocarbon emissions in the Basin, the implementation of auto refueling vapor recovery systems should have the most significant benefit. This is discussed further in Section 5.0.

4.2.2 Organic Solvent Operations

With few exceptions organic solvent operations have the choice of four candidate emission control systems; charcoal adsorption, thermal incineration, catalytic incineration, or process and material changes. The choice must be made after a detailed study of the particular constraints on a given installation. However in this section a few pertinent observations regarding the peculiarities of certain operations will be presented.

A. Metal Coating--

Automotive--The automobile assembly industry is most adaptable to incineration and adsorption. Both thermal and catalytic incineration are in use in the two assembly plants in the Basin. Because of the color changes required on the assembly line certain of the low solvent coatings are not applicable. But water-borne paint has proved to be feasible and is now being used as a top coat by GM in their plants in Los Angeles. The switchover has been expensive. An estimate of costs associated with switching an entire assembly plant to using water-borne paint (electrophoretic primer and spray-applied top coat) is between \$30 and \$50 million capital cost depending on whether booths and ovens are replaced or retrofitted, and \$6 million per year operating costs (Ref. 4-33). The equipment and process modifications necessary to implement a complete water-borne paint system are as follows (Refs. 4-33 and 4-10):

1. Special primer facilities--The electrophoretic primer requires better precleaning and a de-ionized water bath before priming. It requires a large tank with extensive controls on temperature, pH, solids, and voltage. A final rinse usually with de-ionized water is also required.

2. Lengthening of ovens--Water-borne coatings require a longer flash tunnel prior to drying. Temperatures must also be raised more slowly and brought to higher levels in order to evaporate the water slowly enough to avoid pitting the coating. This necessitates longer ovens, which in turn may force some existing equipment to be moved to other locations at considerable cost.

3. Cleanliness requirements--Water-borne coatings do not "touch dry" as quickly as solvent-borne coatings. Thus, they are much more susceptible to dirt pickup. This necessitates filtration of incoming air. Overhead conveyors may also be inadequate because of potential for dropped dirt.

4. Humidity and temperature requirements--Because the major solvent being evaporated is water, proper temperature and humidity conditioning of the air is vital. If the humidity is too high or the temperature too low, the coating will sag on vertical surfaces. Conversely, if the humidity is too low or the temperature too high, the water will evaporate too rapidly and the coating will "orange peel" or pit. Each coating must be formulated for a narrow humidity range, but formulations for different humidities are possible.

Water can be removed from incoming air by chemical or mechanical means. The chemical means involves use of a hygroscopic solution; the mechanical means involves use of a refrigeration cycle. The proper choice depends on both the climate and the availability of energy at the plant. The chemical choice involves more complexity, but less energy consumption than the mechanical method. Steam availability favors the chemical choice.

5. Shutdown problems--Because of the potential for rusting and dirt pickup, vehicles coated with water-borne coatings cannot be left wet overnight or during shift changes. The assembly line must have facilities for carrying painted vehicles through the following oven after shutdowns. Accommodations must also be made for storage of these vehicles until the process resumes. These requirements necessitate special ovens, surge storage areas, and independent conveyor chains for each of the dip tables and spray booths with resultant controls and costs.

6. Clean-up problems--Unlike organic solvent-borne coating, water-borne coating overspray does not dry in the air before being drawn through the particulate collector. This results in an increased clean-up problem for water-borne coatings with attendant increased clean-up labor costs. The fans also become coated with over-spray and require frequent cleaning.

7. Sludge handling problems--Water-borne coatings do not harden in the water of the water-wash particulate collectors on the spray booth. Sludge handling is thus more difficult for water-borne systems.

8. Corrosion problems--The black iron pipes commonly used to pump solvent-borne coatings from central mixing areas to the spray booth are not suitable for water-borne coatings and must be replaced with a non-corrosive. The lifetime of steel spray booths may also be lessened where water-borne coatings are used.

9. Maintenance requirements--Maintenance requirements are increased by the new air conditioning and humidity control systems required.

Can coating (Ref. 4-33)--Can coating includes: the roller coating of one or both sides of metal sheets to be used for can bodies or ends, the side seam spray coating of three-piece cans, the interior body spray coating and side seam spray coating of three-piece beer and beverage cans, the exterior roller coating and the interior body spray coating of two-piece cans, and the sealing compound coating of can ends. The fabricated cans are used as containers for products ranging from beverages to tennis balls.

Lacquers or other coatings for the interior base coat are used in the three-piece cans to provide a protective lining between the can metal and product, especially for food products. It is important that the interior lacquer does not react with the product to alter the product taste, odor, or appearance. All interior coatings for cans that will contain edible products must be approved by the Food and Drug Administration (Refs. 4-34, 4-35).

Some common resins used in can coating lacquers are butadienes, phenolics, epoxies and vinyls that range from 30 to 40 percent solids content by weight and organosols that range from 52 to 66 percent solids content by weight (Refs. 4-34, 4-35).

The exterior base coat is usually a white coating used to provide adhesion and background for the lithographs or printing operation. Some of the coating resins used are polyesters, alkyds, and acrylics at approximately 55 to 65 percent solids content by weight.

The solvents most often used in the interior and exterior base coats, the over varnish, and the primer are mineral spirits, xylol, toluol, diacetone alcohol, methyl iso-butyl ketone, methyl ethyl ketone, isophorone Solvesso 150 (TM), Cellosolve (TM), ethanol, cyclohexanone, Butyl Cellosolve (TM), Cellosolve acetate (TM), n-butanol, isopropanol, butyl carbinol, propylene oxide, mesityl oxide, aliphatic petroleum hydrocarbons, di-iso-butyl ketone, di methyl formamide, and I-nitropropane.

A new coating formulation for the cans not only has to satisfy the can manufacturers but also must be approved by the customer. Customer approval of a new coating formulation may take a minimum of 6 to 9 months. Federal Food and Drug Administration approval for a new coating to be used for edible products may take as long as 4 years.

Incineration is a proven retrofit control system that can control organic solvent emissions from can coating facilities. Although incineration without heat recovery is a considerable energy user, installation of primary and secondary heat recovery systems significantly reduce the incremental consumption of energy. Incineration is the most economical retrofit control option when combined with heat recovery.

Water-borne, high-solids, powder and ultraviolet curable coatings can reduce organic solvent emissions with the same efficiency as incineration and may use less energy than solvent-borne coatings. Conversion to water-borne, high-solids, powder and ultraviolet curable coatings has been successful on some can coating formulations; however, many coatings are still in the development stages or are undergoing tests by both the Food and Drug Administration and the customers. The ability to convert to water-borne, high-solids, powder and ultraviolet curable coatings as a control option will vary from plant to plant depending on the type of product for which the cans are being coated or manufactured.

A carbon adsorption unit retrofitted on a sheet or can coating facility can reduce organic solvent emissions even though additional measures are needed in some cases to clean the process gas stream prior to adsorption. Because different mixtures of solvents are used, there is little market value for the solvent. The solvent can be recovered and used as fuel for the boiler to generate steam for the regeneration of the carbon bed; however, the recovered solvent may not be enough for the required boiler if concentrations are low. The cost of removing each ton of organic emissions using carbon adsorption without any credit for recovered solvent is greater than incineration but will approach the cost of incineration without heat recovery if the recovered solvent can be used as fuel.

The cost of controlling each ton of organic emissions from the can coating industry using water-borne, high solids, powder or ultraviolet curable coating is difficult to determine because of the variable factors of the manufacturing process.

It would be costly to retrofit add-on control devices to reduce organic emissions from the three-piece can side seam spray coaters, the beer and beverage can interior spray coaters and ovens, and the can end sealing compound coaters and ovens because 75-100 percent of the organic solvent vapors are emitted within the plant and not from the oven. Conversion to water-borne, high solids or powder coatings is the best control option for those systems. Moreover, conversion to water-borne, high solids, powder or ultraviolet-curable coatings for the two-piece can coating lines and the sheet coating lines would be the best and most economical control options if such coatings have been developed to replace original organic solvent-borne coatings. Otherwise, incinceration with heat recovery or carbon adsorption with solvent recovery for fuel purposes is recommended.

Coil coating--Coil coating is defined as the coating of any flat metal sheet or strip that comes in rolls or coils (Ref. 4-36). The metal is typically roll coated on one or both sides on a continuous production line basis. The metal may also be printed or embossed. The coated metal is slit and fabricated by drawing, stamping, roll-forming, or other shaping operations into finished products to be used for cans, appliances, roof decks, shelving, industrial and residential siding, cameras, culvert stock, cars, gutters, and many other items. The metals coated in the coil coating industry include various types of aluminum alloys; steel; plate steel; steel alloys; and some zinc, brass, and copper.

Some plants may use as many as 900 different coatings each containing four to ten different solvents, and some use as much as 40,000 gallons of coatings per month. Coatings and approximate percentage of volatiles in these coatings most often used in the coil coating industry are shown in Table 4-5.

TABLE 4-5. COATINGS USED IN COIL COATING (Refs. 4-37, 4-38, 4-39)

Coatings	Volatiles, percent
Acrylics	40-45
Adhesives	75-80
Alkyds	35-40
Epoxies	45-50
Fluorocarbons	55-60
Lumar (TM)	55-60
Organosols	10-15
Phenolics	45-50
Plastisols	10-50
Polyesters	45-50
Silicones	35-40
Vinyls	60-70
Zincromet (TM)	--
Dacromet (TM)	--

The solvents most often used in the coil coating industry include xylol, toluene, methyl ethyl ketone, Cellosolve acetate (TM), butanol, diacetone alcohol, Cellosolve (TM), butyl Cellosolve (TM), Solvesso 150 (TM), isophorone, butyl carbitol, mineral spirits, ethanol, 2-nitropropane, tetrahydrofuran, Panasolve (TM), and methyl iso-butyl ketone.

Coil coating line configurations differ from one another. On some lines, the metal is uncoiled at one end of the line and recoiled at the opposite end. On other coil coating lines, called "wrap around" lines, the metal is uncoiled and recoiled at about the same point on the line. Some coil coating lines have a single coater and one curing or baking oven; other coil coating lines, called "tandem" lines, have several successive coaters each followed by an oven so that several different coatings may be applied in a single pass. Figure 4-24 is a schematic of a "tandem" coil coating line.

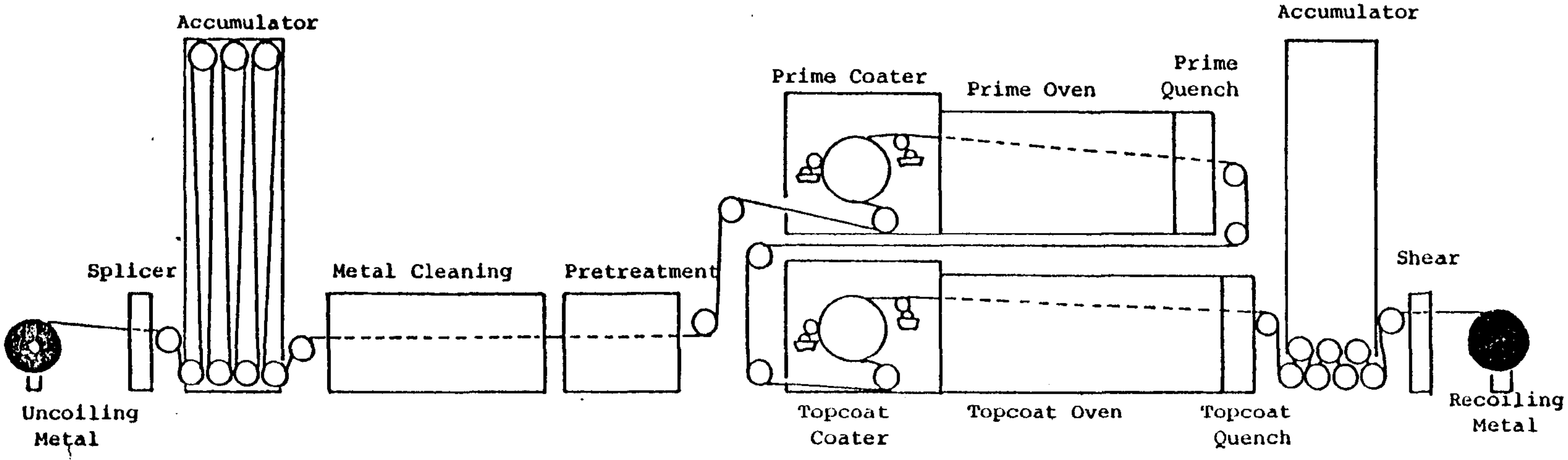

Figure 4-24. Diagram of coil coating line.

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The use of carbon adsorption is limited because the high oven discharge temperatures necessitate a large amount of cooling upstream of the adsorber. Also polymerization and cracking of organics form condensable products that can foul or poison the adsorbent, necessitating pretreatment. (Pretreatment by water scrubbing may produce a potential water pollution problem.) Moreover, some products will still foul the carbon bed, even with scrubbing or filtering, resulting in an inefficient collection of organic vapors. There would be little market value for recovered solvents because of the mixtures of solvents used.

Incineration and conversion to water-borne or high-solids coatings have been determined to be the most reasonable control options for reducing organic emissions from coil coating lines because of the typically high curing temperatures and the various mixtures of organic solvents found in the coatings used by the coil coating industry. Incineration and water-borne coatings have been successfully applied to existing coil coating lines. Over 90 percent reduction of organic emissions is achievable with incineration and 80-95 percent reduction is achievable with water-borne coatings, depending on the processes solvent-borne coatings used.

There are limitations on these control options. Some coatings used in the industry can poison an incinerator catalyst. There is a lack of water-borne and high-solids coatings equivalent to solvent-borne coatings for some metal uses, especially where resistance to corrosion or wear is critical or to withstand certain forming operations. Incineration, especially noncatalytic, may increase the use of natural gas or other fuels if there are no nearby facilities where recovered energy can be used. Carbon adsorption may be applicable to certain coil coaters who use uniform coating formulations and operate low temperature ovens. If carbon adsorption is considered, it is advisable to analyze the gaseous and condensable organics in the gas stream coming out of the ovens.

There does not appear to be a single best control system for the entire coil coating industry; therefore, each plant must be considered separately in selecting the best system applicable to that plant's situation (Ref. 4-37).

Appliances and other commercial products--These items are smaller and more uniform in size and color. Unlike automotive coating, long runs of the same color can be made. This makes the use of solventless coatings very attractive. As the size of some of the companies producing these products is small, developing a new coating could involve indeterminate risk, whereas the selection and installation of an adsorption or incineration system involves a more clearly assessible cost and performance.

Machinery--These products range from stationary machine shop equipment to automatic processing and assembly devices to large earth moving equipment. The coating requirements are more for service and less for aesthetic quality. The relative cost of coating for this type of product is less than most commercial products because of the normally high basic cost. Powder coatings and other low solvent coating with high durability would be excellent candidates for this application.

B. Paper and Film Coatings--

1. Adhesive tapes and tables--Paper is coated for a variety of decorative and functional purposes, using water-borne, organic solvent-borne, and solventless extrusion materials. Because the organic solvent-borne coating process is a source of hydrocarbon emissions, it is an air pollution concern. Among products that are coated using organic solvents are: adhesive tapes; adhesive labels; fancy paper, coated, and glazed paper; book covers; office copier paper (zinc oxide coated); carbon paper; typewriter ribbons; and photographic films.

In organic solvent paper coating, resins are dissolved in an organic solvent or solvent mixture and this solution is applied to a web (continuous roll) of paper. When the coated web is dried, the organic solvent evaporates and the coating cures. Use of an organic solvent has several advantages: it allows organic resins to be made soluble, its components can be changed to affect drying rate, and it creates coatings that show superior water resistance and better mechanical properties than some other coatings. In addition, a large variety of finishes can be obtained with solvent coatings (Ref. 4-39).

The ingredients usually used in organic solvent-borne paper coatings may be divided into the following classes: film-forming materials, plasticizers, pigments, and solvents. Dozens of organic solvents are used for paper coating. The major ones are: toluene, methyl ethyl ketone, isopropyl alcohol, methanol, acetone, and ethanol.

Although a single solvent is frequently used, often a solvent mixture is necessary to allow the drying rate to be controlled. Too rapid drying results in bubbles and an "orange peel" effect in the coating; whereas, too slow drying can require excessive oven lengths. Variations in the composition of the solvent mixture affect the solvency power of the mix.

The main classes of film formers used in paper coating are cellulose derivatives and vinyl resins. The most commonly used cellulose derivative is nitrocellulose. The most commonly used vinyl resin is the copolymer of vinyl chloride and vinyl acetate.

Nitrocellulose has been used for paper coating since the 1920's for decorative paper and book covers and other items. It is relatively easy to formulate and handle and dries quickly, allowing lower oven temperatures to be used than for vinyl coatings.

The vinyl copolymers have superior toughness, flexibility, and abrasion resistance compared with nitrocellulose. They also show good resistance to acids, alkyds, alcohols, and greases, and are nonflammable. Vinyl coatings tend to retain solvent, however, so that comparatively high temperatures are needed for drying. In general, nitrocellulose is most applicable to the decorative paper field, whereas vinyl copolymers are used for function papers (Ref. 4-39).

Plasticizers are often added to the coating to improve its flexibility. Some of the many common plasticizers are dioctyl phthalate, tricresyl phosphate, and castor oil. Each type resin has an optimum plasticizer concentration. As plasticizer concentration increases, the coating becomes more flexible until it begins to be soft and tacky.

In the production of pressure sensitive tapes and labels, adhesives and silicone release agents are applied with organic solvents. The adhesive layer on a tape or label is usually based on one of the following organic solvent-borne resins: natural rubber, synthetic rubber, acrylic, and silicone.

Because of their low cost, natural and synthetic rubber compounds are the main film formers used for adhesives in pressure sensitive tapes and labels, although acrylic and silicone adhesives offer performance advantages for certain applications.

The paper to which adhesive labels are attached must be treated with a release agent so that the adhesive tag may be removed. This release agent is usually a silicone coating that is applied with solvents. Silicone and other types of release agents are applied with organic solvents to the backside of pressure sensitive tapes so that tapes can be unwound.

Figure 4-25 shows a typical paper coating line. Components of a coating line include an unwind device, a coating applicator (knife, reverse roll, or gravure), an oven, various tension and chill rolls, and a rewind device. The unwind, rewind, and tension rolls display various degrees of complexity depending on the design of the line. The coating applicator and the oven are the main areas of organic emission in the paper coating facility.

Most solvent emissions from paper coating come from the dryer or oven. Ovens range from 20 to 200 feet in length and may be divided into two to five temperature zones. The first zone, where the coated paper enters the oven, is usually a low temperature (∿ 110 °F) area. Solvent emissions are highest in this zone. Other zones have progressively higher temperatures that cure the coating after most of the solvent has evaporated. The typical curing temperature is 250 °F, although in some ovens temperatures of 400 °F are reached. This is generally the maximum because higher temperatures can damage the paper. The oven zones may be exhausted independently to the atmosphere or exhausted into a common header, with the total effluent sent to some type of air pollution control device. The average exhaust temperature is about 200 °F.

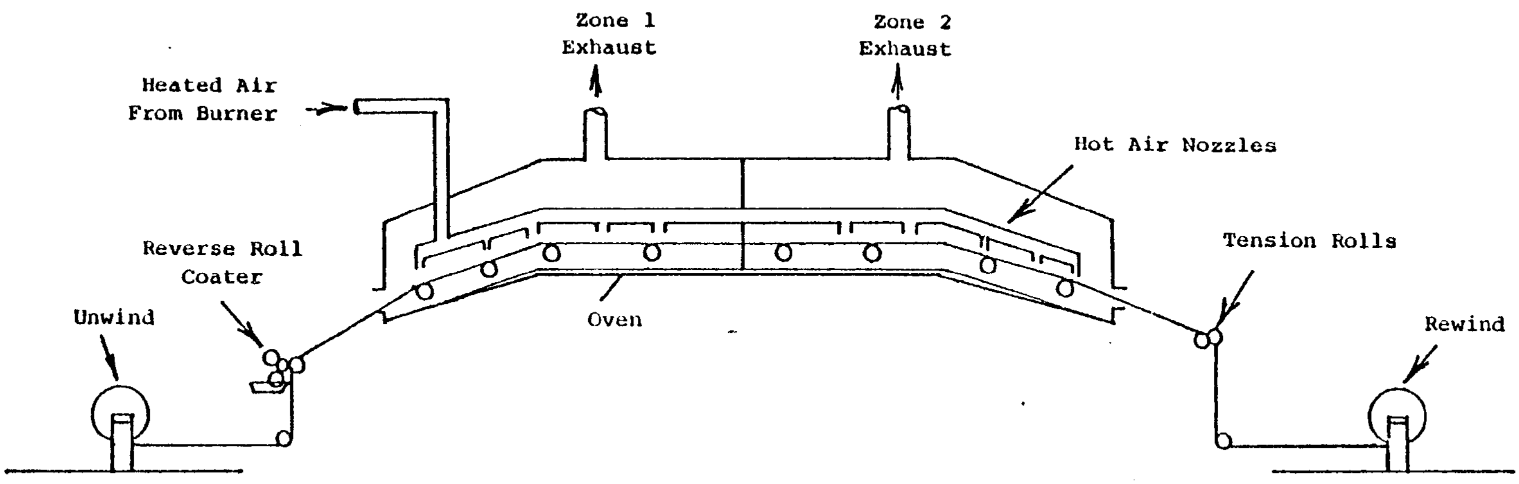

Figure 4-25. Diagram of typical paper coating line.

Most paper coaters try to maintain air flow through their ovens so the solvent concentration will be 25 percent of the LEL, although many ovens are actually run at much lower solvent concentrations. As energy shortages intensify, coaters are becoming aware that such low solvent concentrations require the heating of unnecessarily large amounts of intake air for their ovens.

Insurance and safety requirements permit even higher solvent concentrations than 25 percent LEL in some instances. The Handbook of Industrial Loss Prevention notes that flammable vapor concentrations up to 50 percent of the LEL may be tolerated if approved continuous vapor concentration indicators controllers are used (Ref. 4-40). The controller must sound an alarm when concentrations reach 50 percent, and shut the oven down automatically when concentrations reach 60 percent of the LEL.

Part of the solvent remains in the finished product after it has cured in the oven. For example, certain types of pressure-sensitive tapes have 150 to 2,000 ppm by weight of solvent in the adhesive mass on the finished tape. One coater has claimed that 3 to 10 percent of his solvent remains in the product.

The manufacture of photographic film exhibits special solvent control problems. Four or more layers of coatings may be applied to a photographic film, using equipment and coating techniques similar to those used for other paper coatings. Because the coatings on the photographic film later undergo chemical reactions, the composition and quality of the coatings must be tightly controlled. Because of the nature of these coatings, certain control options may not be possible. For example, it may be impossible to recover solvents in a carbon adsorption unit and then reuse these solvents in new photographic coatings since the reclaimed solvents may contain enough impurities to contaminate the film.

The two well proven add-on control devices for controlling organic solvent emissions from paper coating lines are incinerators and carbon adsorbers. Both of these control devices have been retrofitted onto a number of paper coating lines and are being operated successfully.

The only constraint to the use of incinerators is the possible shortage of natural gas. However, in many cases the combination of afterburner and oven will use no more fuel than the oven alone if proper heat recovery is used. Incinerators can be altered to operate on No. 2 fuel oil if new natural gas is not available. If recovered solvent has no value, incineration with heat recovery is more economical than carbon adsorption.

The major drawback to the use of carbon adsorption is that in some cases solvent mixtures may not be economically recoverable in usable form. If the recovered solvent can be used as fuel, then carbon adsorption compares favorably in operating cost with an incinerator. If the solvent can be recovered as usable solvent, use of carbon adsorption represents an economic advantage to the paper coater.

It is more difficult to estimate costs for low solvent coatings, because the cost will vary depending on the type of coating used. For some applications, the use of low organic solvent coatings will cost less in dollars per pound of coatings solids applied than will conventional organic solvent coatings when some type of add-on control device is used.

Low solvent coatings have been well developed for some applications, but considerable development is needed in other areas. The main incentive paper coaters will have to develop new low solvent coatings will be strict requirements for add-on control devices if conventional organic solvent coatings are used.

An estimate of solvent emission reduction using low solvent coatings is presented in Table 4-6.

C. Fabric Coating--

Fabric coating involves the coating of a textile substrate with a knife or roller spreader to impart properties that are not initially present, such as strength, stability, water or acid repellancy or appearance (Ref. 4-41).

TABLE 4-6. ACHIEVABLE SOLVENT REDUCTIONS USING LOW SOLVENT COATINGS IN PAPER COATING INDUSTRY (REF. 4-33)

Type of Low Solvent Coating	Reduction Achievable, %*
Water-borne coatings	80-99
Plastisols	95-99
Extrusion coatings	99+
Hot melts	99+
Pressure sensitive adhesives	
Hot melt	99
Water-borne	80-99
Prepolymer	99
Silicone release agents	
Water-borne emulsions	80-99
100 percent nonvolatile coatings	99+

*Based on comparison with a conventional coating containing 35 percent solids by volume and 65 percent organic solvent by volume.

The fabric coating industry is a diverse industry, concentrated in the East with a few plants in the South Coast Air Basin. The industry consists mainly of small to moderate sized plants each of which specialize in a limited product line.

Substrates (textile materials used for coating purposes) can be either natural or man-made. Although polyvinyl chloride (PVC) sheets are not technically fabrics, coating of these sheets is covered in this section.

Coatings used include latexes, acrylics, polyurethanes, and natural and synthetic rubbers.

It is estimated that between 85 and 96 percent of the solvent emissions from fabric coating are from the drying process (Refs. 4-42, 4-43). Estimated and reported solvent concentration levels from drying operations range between 0.05 and 0.4 percent by volume (Refs. 4-42, 4-43). Typically, drying ovens are designed to process fabric on a continuous basis operating with a web or conveyor feed system. Ovens can be enclosed or semienclosed and may exhaust from a few thousand cubic feet per minute to tens of thousands of cubic feet per minute of air (Ref. 4-44).

Drying ovens in older plants are often only semienclosed and operate with low solvent concentrations. Calculated and reported solvent levels in the exhaust streams are between 5 percent and 12 percent of the LEL. Newer installations, however, are reported to be operating at exhaust solvent concentrations up to 40 percent of the LEL (Refs. 4-42, 4-43).

Reductions of 90 percent of contained emissions are achievable using catalytic or noncatalytic incineration. Because of the so-called fugitive emissions, the overall reduction in plant emissions is less than 90 percent.

Carbon adsorption can remove over 90 percent of the organic vapors from the gases that pass through it. Overall plant reductions will be less percent due to losses during handling. Experience has shown that in facilities using activated carbon, the greatest losses of solvent occur in handling.

Organic emissions can be reduced by 80 to 100 percent by the use of low organic solvent coatings such as high-solids or water-borne. The actual reduction depends on the previous coating and the organic solvent to solids ratio of the new coating.

Carbon adsorption and incineration are most applicable to those sources that cannot use low polluting coatings. Carbon adsorption is most economical for sources that use a single solvent or solvent mixture for all uses. The large capital investment requirement, however, may impose major problems for some companies.

Incineration with primary and secondary heat recovery is most applicable at those sources that use a large variety of solvents and cannot reuse them.

The most desirable strategy is probably the conversion to low polluting coatings but this is limited by the lack of such coatings for some uses.

D. Other Solvent Operations--

1. Printing--There are four main types of printing operations: letterpress, lithographic, flexographic and gravure.

Letterpress, the oldest printing process, is defined as printing from raised type. The process is based on the simple stamping principle and produces a high quality of print on almost any type of paper or board. There are essentially three types of letterpresses in commercial use; platen, flat-bed, and web rotary. Platen presses can print a variety of jobs, from a simple one-color to multicolor. The flat-bed press is widely used in printing catalogs, books, and booklets. The web rotary press consists of two cylinders, one for the plate and the other for impression. This equipment is capable of very high speeds and is used for publications, packaging and commercial printing.

Lithographic printing is based on the principal of oil and water immiscibility. The level printing surface is prepared chemically resulting in the image area accepting oleophilic ink and the nonprinting area accepting water. Lithography has many advantages. Plate making is simple, fewer mechanical operations are required and it is economical for short runs.

Flexographic printing is a special form of relief printing. A flexible typographic rubber plate is mounted on a cylinder and is used to transfer the lacquer-type ink. This type of operation allows printing on hard surfaces, such as plastic films, calendered papers and metallic foils. Equipment for flexographic printing is divided into two classes; stack presses and common-impression equipment. In stack presses each color has its own unit consisting of fountain, roller, plate cylinder and impression cylinder. In common-impression, one large cylinder is used for several printing units, and is particularly useful for the decoration or plastic films.

Gravure printing utilizes a recessed surface for transferring the lacquer-type ink. It is the only process in which the ink film does not contact a flexible synthetic roller. Gravure ink is instant drying and the polymers must be preformed to be useful. The resins must be tack free and have excellent solvent release properties. Unlike other printing processes, the pressure is not transmitted through the ink film; instead it is only on the cylinder plate, impression roller, and substrate.

Certain types of inks are used with certain methods. Table 4-7 indicates the range of percent solvent content in inks for two drying methods versus the four printing processes.

TABLE 4-7. PERCENTAGE OF INK SOLVENT CONTENT FOR TWO DRYING METHODS VERSUS FOUR PRINTING PROCESSES

Drying Method	Letterpress	Flexographic	Lithographic	Gravure
Evaporation	--	(40-75%)*	--	40-75%
Heat set	-10%	(0-30%)†	-16%	--

*Solvent-base ink
†Water-base ink

The flexographic and gravure process account for approximately one-third of all inks used. They mainly use solvent-based inks containing 40 to 75 percent solvent, which is then evaporated on drying. Water-borne inks are also coming into use in the flexographic process. Some of these water-borne inks also contain solvent (0-30 percent) for faster drying. The screen process uses oil and lacquer-type inks which contain 0 to 60 percent solvents. However, this class accounts for less than 6 percent of the national total solvent used for inks. Letterpress and lithographic inks, which account for about one-third of the total inks used, are oil-based and emit some solvents when heat-set letterpress or heat-set web offset is used.

Where available, the use of water-borne ink is the most economical emission control technique. However, because water-borne inks are not sufficiently versatile in color and substrate compatibility, most large presses in the Basin depend on carbon adsorption and incineration. The largest gravure printing plant in the Basin has installed a 180,000 CFM carbon adsorption system which has an efficiency of over 95% and the solvent is 100% recoverable. The condensed water from the steam desorption system is separated from the solvent so efficiently that it is reused as boiler feed water.

2. Rubber Manufacturing (Ref. 4-4)--The most important operations in the manufacture of rubber are as follows: (1) physical treatment of raw rubber to prepare it for addition of compounding ingredients; (2) incorporation of various substances, especially fillers; (3) pretreatment of mix to make it satisfactory for preparing the final product; (4) forming the final product; and (5) vulcanization or curing the molded article.

The compounding ingredients added to rubber are as follows: (1) plasticizers or softeners, (2) vulcanizing agents, (3) accelerators, (4) activators and retarders, (5) antioxidants, (6) fillers, and (7) miscellaneous ingredients such as pigments, rubber substitutes, odorants, abrasives, stiffeners, and blowing agents.

The first step in this process is plasticization which can be done in several ways. Mechanical plasticization is accomplished on a mixing mill or internal mixer which rolls the rubber and makes it soft and plastic. Heat plasticization is accomplished by heating in ovens for about 24 hours at 300 ° to 400 °F. Chemical plasticization is accomplished by adding peptizing agents on the mills and is more rapid and economical than other means under certain conditions. Typical peptizing agents are naphthyl mercaptan, xylyl mercaptan, zinc salt of pentachlorothiophenol and dithio-bis-benzanilide.

Typical antioxidants that create hydrocarbon and organic pollutants are aromatic amines, aldehyde-amine condensation products, derivatives of secondary napthylamines, aromatic diamine derivatives, and ketone-amine condensation products.

To vulcanize or cure the molded article, the material is held at elevated temperatures of 200 ° to 300 °F from a few seconds to several hours. This is the operation during which many of the plasticizers, accelerators, and other organics are volatilized and driven off as air pollutants. One of the major problems associated with rubber production is odor.

The principal methods used to control air pollutants from rubber manufacture are; reformulation, condensation, adsorption, absorption, and incineration. Many of the rubber manufacturers have been recovering solvents for economic reasons. In one case, a rubber company installed an activated-carbon adsorption system and found that with a 65 percent recovery figure for a base, the system could save them up to $39,000 in the first full 12 months of operation (Ref. 4-45).

In reformulation, use of nonreactive solvents in place of reactive ones would alleviate hydrocarbons and odor problems.

Direct-flame incineration has proved to be very successful in controlling both hydrocarbons and odors. In one rubber processing plant, tests of a direct-flame incineration system showed that for a total system flow of 31,000 pounds per hour, and an incineration temperature of 1,120 °F, total hydrocarbons were reduced from 1,305 to 207 ppm by weight with an efficiency of 84 percent (Ref. 4-46) (calculations based on reduction of total hydrocarbons in pounds per hour). With allowance for the contribution of fuel oil, as established during the blank run, the efficiency of process contamination removal became 89 percent. This was stated to be closer to the overall efficiency expected if the incinerator were fired with natural gas.

In a similar run at an incineration temperature of 1,190 °F, total hydrocarbons were reduced from 1,155 to 89 ppm by weight for an efficiency of 92 percent. Allowing for fuel oil contribution would increase this efficiency to 97 percent.

Catalytic-type combustion has been investigated thoroughly for removing pollutants from rubber plants. In some cases, however, it has been found that temperatures only 100 °F below those required for direct-flame incineration were required, and thus increased costs of catalyst-type operations would not be justified. In other tests (Ref. 4-46), this type of combustion was abandoned because of (1) the danger of poisoning of the catalyst and (2) the impairment of its effectiveness as the catalyst became coated with carbonaceous deposits.

3. Degreasing--Metal parts must be thoroughly cleaned of all grease and oil before they can be plated, painted, or further processed.

If solvent is used for cleaning and it is maintained by heat input at its atmospheric boiling point in the process equipment, and if this equipment is designed to control and minimize solvent losses to the air, then the cleaning process is called "vapor degreasing."

If the solvent used for cleaning is at or near room temperature and if the equipment used is not designed to control solvent losses, then such a process is referred to as "solvent cleaning" or "cold solvent cleaning." The solvents used in these processes may be halogenated, non-haolologenated or mixture of them.

In other words, vapor degreasing is a specific type of cleaning process designed to use only halogenated solvents, which are essentially nonflammable and have a relatively high vapor density. Complete descriptions of "solvent cleaning" and "vapor degreasing" are presented in the chapter on metal cleaning in the Metals Handbook (Ref. 4-47).

A typical degreaser is pictured in Figure 4-18. The methods that can reduce emissions are (1) improved covers, (2) high freeboard with water cooled walls, (3) refrigerated chillers, (4) carbon adsorption and process change. Incineration is generally impractical because chlorinated solvents are usually used which form highly toxic fumes when burned.

Efficient covers are the most effective means of containing the vapor. Automatic covers open when a work piece is to be inserted and withdrawn. Horizontally acting doors cause the least disturbances of the vapor. A high freeboard with cooled walls help retain the heavier than air vapors inside the cover. A refrigerated chiller around the upper part of the freeboard condenses fumes that would curl over the upper edge. A hood, fan and charcoal adsorption system will also capture vapors that escape. Finally, the substitution of steam, detergent or other nonorganic cleaning methods where the work permits will eliminate nearly all vapor emissions.

4. <u>Pesticide manufacture (and use)</u>--A pesticide is a compound or mixture of compounds intended for preventing, destroying, or repelling or mitigating any insects, rodents, nematodes, fungi, or weeds or any other forms of life declared to be pests; and any compound or mixture of compounds intended for use as a plant regulator, defoliant, or desiccant.

Pesticides are rarely used in their pure form, but usually are first combined with other materials into what is called a formulation. The common formulations are powders or dusts, wettable or soluble powders, emulsifiable concentrates, granules, and aerosols. In addition to the active ingredient, each pesticide formulation may contain one or more of the following: a carrier or diluent, a solvent, an emulsifier, a spreading and sticking agent, or others. Each of these additives are usually inert as far as the pesticide action is concerned but provide a mechanism for even distribution of the pesticide. There are about 500 active ingredients and about 50,000-60,000 different formulations on the market today (Ref. 4-48).

Any or all of the constituents of a pesticide formulation can be a volatile organic compound including the active ingredient itself. Some typical active ingredients are listed in Table 4-8. Typically 90-90% of the applied formulations are volatile. Depending on the active ingredient and the application the carrier can be organic or water.

The control of organic air pollutants from pesticides can be performed by minimizing the use of solvent or petroleum borne formulation and substituting, where possible, water-borne or dry formulations. The other method is to use more efficient application techniques to reduce the amount of over spray necessary to obtain the desired coverage. In the latter case electrostatic spraying has been shown to reduce the amount of pesticide required by as much as 80% (Ref. 4-49). Personnel contact with the pesticide is also reduced.

5. <u>Dry cleaning</u>--Clothing and other textiles may be cleaned by treating them with organic solvents. This treatment process involves agitating the clothing in a solvent bath, rinsing with clean solvent, and drying with warm air.

TABLE 4-8. SOME VOLATILE ORGANIC PESTICIDES (Ref. 4-50)

Aromatic Petroleum Solvents (liquids)

Butoxyl polypropylene glycol (liquid)

2,4-D Butoxyethanol (liquid)

Chlordane ($C_{10}H_6Cl_8$) (liquid)

Chlorobenzene (liquid)

Chlorobenzilate (liquid)

Chloropicrin (liquid)

2,4-D Isopropyl Ether (liquid)

2,4-D Propylene Glycolbuty Ether (liquid)

Dalapan (Sodium Salt) CH_3CCl_2COOH (liquid)

DBCP Dibromochloropropane (liquid)

D-D Mixture (a mixture of 1,2-Dichloropropane (l) and 1,3-Dichloropropene (l) and related C_3 compounds)

DDVP (Dichlorvos) 2,2-Dichlorovinyl-0, 0-di-Methyl Phosphate (liquid)

DEF S, S, S-Tributyl Phosophorotrithioate (liquid)

Demeton (Systox) 0,0-Diethyl 0-2-ethylthio ethyl phosphorothioates

Diazinon (colorless liquid)

2,2-Dichloropropionic Acid (liquid)

DNBP 2,4-Dinitro-6-sec butylphenol (brown liquid)

2,4-DP Butoxylthanol (liquid)

Ethylene Dibromide (liquid)

Fenthion (Baytex) yellow tan liquid

Malathion (liquid)

Metaldehyde (sublimable) (white crystals)

Mineral Oil (liquid)

Omite-R (viscous liquid)

Parathion (yellow liquid)

Petroleum Distillates (liquid)

Petroleum Distillates, Aromatic (liquids)

Petroleum Hydrocarbons (liquids)

Petroleum Oil, unclassified (Stoddard solvent and diesel oil)

Phorate (Thimet) (clear liquid)

Phosdim-R (yellow to orange liquid)

Phosphamidon (oily liquid)

Phosphamidon, other related (oily liquid)

Pine Oil (liquid)

Piperonyl Butoxide (liquid)

Pyrethrins (I and II) (viscous liquid)

Telone-R (Dichloropropene) (liquid)

Xylene (liquid)

Xylene Range Aromatic Solvent (liquid)

There are basically two types of dry-cleaning installations: those using petroleum solvents (Stoddard), and those using chlorinated synthetic solvents (perchloroethylene). The Stoddard solvent in use in the South Coast Basin is about 48% paraffin, 44% naphthenes and 8% aromatics. Compared to perchloroethylene the Stoddard solvent is less expensive by a factor of ten, less corrosive to the cleaning equipment, less toxic, but more hazardous from a fire safety standpoint and more reactive from a photochemical smog standpoint. Perchloroethylene is used exclusively in the neighborhood cleaning plants while Stoddard solvent is used in some larger industrial cleaning plants.

In a petroleum-solvent dry-cleaning plant, the equipment generally consists of a washer, centrifuge (extractor), tumbler, filter, and often a batch still. The centrifuge is used to recover solvent by spinning it from the clothes. The clothes then enter a tumbler where they are dried with warm air. The tumbler is usually vented through a lint trap to the atmosphere in this type of plant.

In synthetic solvent plants, the washer and extractor are a single unit. The tumbler operates as a closed system, having a condenser for vapor recovery. The tumbler is vented to the atmosphere or to a carbon adsorber only during a short deodorizing period.

Both adsorption and condensation systems may be used to control solvent emissions from dry-cleaning plants using synthetic solvents. Solvent recovery systems are not only commercially available as part of a synthetic solvent cleaning plant, but they are also economically attractive. The primary control element is a water-cooled condenser, which is an integral part of the closed cycle in the tumbler or drying system. Up to 95 percent of the solvent that is evaporated from the clothing can be recovered here. About half of the remaining solvent can then be recovered in an activated-carbon adsorber, giving an overall control efficiency of 97-98 percent.

There are no commercially available control units for solvent recovery in petroleum-solvent plants because it is not economical to recover the vapors. The vaporized solvent is not condensible at the temperatures employed, and thus the whole solvent recovery burden would fall on an adsorption system, necessitating equipment up to 20 times larger than that used in a comparable synthetic solvent plant.

Another way of controlling solvent emissions from petroleum plants is through direct-fired afterburners. Estimates show that a saving in capital cost could be achieved, but an increase in operating costs would also be incurred compared to carbon adsorbers. Afterburners are not suitable for synthetic chlorinated hydrocarbons because of the danger of producing hydrogen chloride, phosgene, or other toxic gases.

A complete treatment of emission reduction from the dry cleaning industry is contained in Ref. 4-64.

6. Architectural coatings--Architectural coating consist of those paints, varnishes, stains, sealers, etc. used on the exterior or interior surfaces of buildings, homes, civil engineering structurals, etc. These are the coating to which add on controls do not normally apply.

This is currently the area of greatest application of water-borne paints. Besides lower emissions water-borne paints offer easier application and cleanup and equivalent or superior durability. Except for aerosols, clear coatings and metal paints the water-borne paints are growing in popularity. A survey by the ARB indicated that 60% of the architectural paint sold in the state was water-borne.

The control methods for architectural coatings are to continue to persuade the professionals and non-professionals to substitute water-borne paint for solvent based paint; and to use, when possible, other solventless coatings as colored stucco, epoxy, and other low solvent coatings, prefinished panels, etc.

7. Wood finishing--Wood finishes involve varnishes, shellac, stain, wax, and plastic coatings. Water-borne and low solvent coatings are the primary method of solvent emission control in this area. However, certain pigments and high gloss finishes can only be accommodated with the solvent based formulations. In this case add-on devices like charcoal adsorbers as well as thermal and catalytic incinerators can be used to control air pollution emissions.

4.2.3 Chemical Manufacturing

Manufacturers of synthetic organic chemicals such as elastomers, dyes, flavors, perfumes, plastics, resins, plasticizers, pigments, paints, varnishes, rubber processing chemicals, pharmaceuticals, and miscellaneous solvents have the problems of controlling emissions of hydrocarbons from raw materials and from products made from these materials.

Of the thousands of chemical manufacturing processes, each has unique control problems. The types of chemical conversions utilized in these processes are classified below.

Alkylation is the union of an olefin with an aromatic or paraffinic hydrocarbon. Ethyl benzene is produced by alkylating benzene with ethylene, and naphthalene, by dealkylation of a petroleum fraction.

In amination, an amino compound is formed by using ammonia (or a substituted ammonia) as the agent. Other amines are made by reducing a nitro compound. Ethanolamines, for example, are obtained when ethylene oxide is bubbled through an ammonia solution.

Hydrogenation, the addition of hydrogen, is used to manufacture a broad range of products. For example, methanol is made by reacting CO with hydrogen.

Dehydrogenation, the removal of hydrogen, produces unsaturated compounds. Benzene is made by dehydrogenation of substituted cyclohexanes.

Dehydration, the removal of water, produces ethers from alcohols. Hydration, the addition of water, produces ethyl alcohol from ethylene.

In esterification, an alcohol reacts with an organic acid to form an ester. Ethyl alcohol reacts with acetic acid to form ethyl acetate, an important solvent.

Halogenation and dehalogenation are the addition or removal of a halogen. Methyl chloride is made by chlorination of methane. Chlorine, bromine, iodine, and fluorine are the halogenation agents.

Oxidation, the addition of oxygen, is one of the most valuable conversion processes. Ethylene oxide is made by oxidation of ethylene. The cheapest oxidizing agent is air, but pure oxygen has advantages in many applications.

Nitration introduces nitrogen into hydrocarbons. Nitrobenzene is an important product of nitration.

Polymerization is the reaction of simple molecules to form more complex polymers. For example, ethylene is polymerized to polyethylene.

The raw materials and the products are potential sources of emissions in any chemical conversion operation. Chemical reactions for production of a desired product usually result in several by-products. Although the formation of by-products is minimized by adjusting the conversion conditions, the quantities formed must be either recovered for use or be properly disposed of as wastes. Waste disposal is a primary problem, complicated by the fact that wastes may be highly toxic. Thus air-cleaning methods that merely transfer the emissions to streams or other waters are not satisfactory.

The major sources of emissions to the air are streams of waste gases, vapors from distillation columns, and leakage from feed and product transport lines. Many chemical plants generate their own steam for use in refining and for supplying power; therefore, emissions characteristic of power plants are an inherent part of the total. The manufacture or regeneration of catalysts usually result in nonhydrocarbon emissions.

Often, control of emissions by the chemical industry is based on economic incentives. In other words, condensers are used to recover vapors containing usable reactants, and wastes are burned to recover heat value. This is not possible for all processes, however. For example, catalytic oxidations are seldom, if ever, free of odor. Large quantites of air are pumped through the reaction system to provide the oxygen necessary for the conversion. Low concentrations of the main reactants are carried into the air. Existing methods for recovery of these low concentrations are often unattractive economically, in the sense that the recovered material does not pay for the cost of recovery.

Recently, however, new developments in recovery methods using automated jet compressors (Ref. 4-51) have begun to reduce the economic burden of recovery or disposal.

A. Halogenates--

Organic emissions containing a halogen (primarily chlorine) are a special problem, because the halogen atoms are not combustible. Accordingly, incineration of chlorine-containing organic compounds can produce HCl, elemental chlorine, or other chlorinated compounds.

The problem is to design an incineration system that will first produce the hydrogen halide gas and then absorb it. Experimentation has shown that if the hydrogen-to-halogen ratio is high enough, approximately 5 to 1, essentially all of the halogen in the products of combustion will be in the form of the hydrogen halide (Ref. 4-4).

To maintain this ratio for substances like ethylene or propylene dichloride, some hydrocarbon fuel must be added to the combustion system to supply hydrogen. A technique developed to do this for organic chlorides recovers up to 99 percent of the hydrogen chloride as 18° Baumé acid from gas streams containing as little as 3 percent hydrogen chloride (Ref. 4-52).

In this recovery system, the waste is incinerated in a vortex-type burner and immediately quenched in a graphite- or carbon-lined tower; the resulting vapors are processed through a series of impervious, graphite, tubular cascade absorbers, which are designed to produce 18° Baumé acid, with up to 100 ppm of hydrogen chloride in the vent gas. If additional treatment is required, another scrubbing station is provided to produce very weak hydrochloric acid to be used as make-up liquor in the main absorption equipment. The remaining vapors usually contain fewer than 50 ppm hydrogen chloride. This recovery system, depending on the disposal rate, can produce a positive return on investment.

B. Coal Gases--

Catalytic vapor incinerators can eliminate essentially all hydrocarbons contained in a relatively cool waste gas stream. The heart of the system is a catalyst that makes it possible to burn ethylene that is present in concentrations too low to support normal incineration. The treated stream does not contain catalyst poisons.

C. Varnishes (Paints, etc.)--

The vapors emitted from varnish cookers possess penetrating and disagreeable odors and other irritating characteristics. These vapors consist of (1) low-melting-temperature constituents of natural gums, synthetic acids, and resins, some of which are purposely driven off for process reasons; (2) thermal decomposition and oxidation products volatilized during bodying of oils; and (3) volatile thinners, which distill off during thinning of hot varnish.

Total emissions to the atmosphere depend on the composition of the batch, rate of temperature application, maximum temperature of the process, method of adding solvents and driers, amount of stirring employed, extent of air-blowing, length of cooking time, and amount of pollution of other process control equipment employed. Typical losses from various cooking processes are as follows:

1. Total loss from oleoresinous varnish cooks average 3 to 6 percent, with some losses as high as 10 to 12 percent.
2. Losses from alkyd resin cooks range from 4 to 6 percent.
3. Cooking and blowing of oils produce losses of 1 to 3 percent.
4. Heat polymerization of acrylic resins produces losses of less than 1 percent unless the reaction gets out of control.

The most effective means of controlling emissions from varnish-making operations has been combustion (Ref. 4-4). Vapor disposal by combustion has several advantages over other control methods because it requires a minimum of equipment, assures complete vapor elimination from the atmosphere, and consumes very little fuel in correctly designed furnaces. Incineration, of these hot combustible vapors calls, however, for special devices to protect against flame propagation in the opposite direction of the flow of vapors between the kettle and the incinerating furnace. In some systems, a series of water jets or a water scrubber are interposed between the varnish kettle and the furnace. In another system, the vapors are passed first through a water-cooled condenser and then to a combustion hearth. In still another, the varnish vapors are assisted from the kettle by means of a steam nozzle. The mixture of steam and vapor is condensed. The reduced pressure, which results from the vapor condensation pulls the vapors from the kettle. The noncondensibles are then burned.

In designing condensers to control emissions from varnish-making operations, the standard design factors such as the type(s) of compounds and their physical properties, such as temperature, volume, concentration, vapor pressure, and specific heat must be considered. In addition, in many of these processes noncondensible substances must be removed by other means. Many of the lower-boiling-point noncondensible hydrocarbons are very inflammable, and provision must be made to remove the risk of flashes. For example, to remove copal vapors, a satisfactory condensation unit should include the following:

1. A condenser to remove most of the vapors, followed by scrubbing and combustion, charcoal adsorption, or a ventilating stack to remove the traces.
2. Means for vapor withdrawal.
3. Provision for cooling and collecting a large volume of distillate.
4. Corrosion-resistant materials of construction.
5. Precaution against flashes.
6. Provision for overflow between cooking kettle and first condenser.
7. Recirculation of cooling water to reduce quantities required.
8. Separate unit for each kettle if possible.

Both surface-type and direct-contact-type condensers have been employed in this industry.

Several different types of scrubbers have been used by the varnish industry. These include (1) a countercurrent device in which the vapors enter at the bottom against a descending water stream and leave through the top, (2) a parallel-current water scrubber succeeded by smaller countercurrent scrubbers, (3) water jet scrubbers, and a (4) scrubber with spinning discs located on a revolving vertical spindle.

D. Pharmaceuticals--

Pharmaceuticals encompass a broad spectrum of materials, ranging from purified anesthetic-grade ethers and other anesthetics to the extraction and purification of cod-liver oil. "Biological" odors are conventionally controlled by incineration. Solvents may be recovered by adsorption. Usually there is no provision for recovery of the adsorbed materials. Frequently, the use of packaged replaceable adsorption units is feasible.

4.2.4 Other Industrial Processes

A. Metallurgical--

Metallurgical processes are some of the largest sources of pollution in the Basin. However, compared to carbon monoxide, particulate and sulfur emissions these sources emit small amounts of hydrocarbons. These sources include coke ovens, blast furnaces, steel making furnaces, remelting processes as in a foundry or reheating processes as in forming or heat treating. Hydrocarbons are emitted from stacks as exhaust gas from fuel combustion and as fugitive emissions from openings or leaks in material processing retorts. References 4-53, 4-54, 4-44, 4-2, and 4-55 contain descriptions of these processes and details of emission sources and control measures. Reference 4-54 is a comprehensive report by the ARB staff on a steel mill in the Basin. Table 4-9 summarizes the emissions from that plant and shows the relatively small amount of organic gases emitted. However, since 25 tons/yr constitute a major source in this study, the 865 tons/year listed does make this plant a significant hydrocarbon source.

TABLE 4-9. AMOUNT OF POLLUTANTS GENERATED BY KAISER STEEL AT FONTANA, CALIFORNIA (REF. 4-54)

	Organic Gases, Total	Tons/Year NOx	SO_2	CO	Particulate
Kaiser emissions	865	8,107	13,636	78,267	2,475
Percent of Kaiser's contribution to all pollutants emitted into atmosphere from all stationary sources in the SCAQMD	0.37%	5.6%	10.0%	69.3%	8.2%

KVB's measurements of stack emissions (refer to the Appendix) account for 75% of the organic gases shown in the table. The remainder could well be fugitive emissions from leaks that escape directly into the air. Actually, the hydrocarbons emitted from the stacks are most likely caused by internal leakage from the coke ovens into the combustion gas stream near the end of the gas pass. The combustion gases apparently are no longer hot enough to react all of the leaking coke oven gases. In KVB's tests of two different coke oven exhaust stacks 200 and 700 ppm of methane were found respectively. CO levels were 1 and 2% respectively. These hydrocarbon and CO values are very high, indicating incomplete combustion. But since the O_2 levels in these gases were 7 and 15% respectively, which is very excessive, the possibility of incomplete combustion is not reasonable. One possible explanation is that methane is leaking into the exhaust gases through the metal and ceramic heat transfer wall at a point where the combustion gases have cooled down sufficiently that some of the methane does not have time to oxidize.

Methods for controlling hydrocarbon emissions from coke ovens and metal manufacturing processes are essentially the same as those for controlling particulate and sulfur emissions, i.e., seal up the leaks or enclose the processes in a vapor collector and remove the pollutants. After the vapor collected has been scrubbed for sulfur and particulate removal, the remaining gases can be adsorbed on charcoal to increase the concentration and recycled into the fuel gas supply. Other hydrocarbon emissions from combustion of fuel associated with these metallurgical processes should be very low in hydrocarbon concentration (of the order of 1 to 10 ppm). If combustion processes are found where emissions are greater than this level, the best approach is to improve burner design, recirculation patterns, air/fuel ratio to bring the emissions to acceptable levels. In some cases, where oil coated scrap material is charge into a furnace for instance, the hydrocarbon content of the exhaust gas becomes high enough to require a secondary incineration process.

B. Mineral--

Most of the mineral processes are primarily particulate emitters and have little hydrocarbon emissions. Asphalt is often used for paving or roofing applications. Freshly applied asphalt concrete does emit some hydrocarbon emissions. KVB measured an emission factor of 10^{-6} lb hydrocarbon per lb of asphalt hot mix paving material (including aggregate). Midwest Research (Ref. 4-56) recently measured a weight loss rate for the list melt asphalt (without aggregate) of $4x10^{-3}$ lb hydrocarbon loss/lb asphalt. Assuming the asphalt is 5% of the paving mixture (5-10% is the normal range) this emission factor would become $2x10^{-4}$ lb hydrocarbon/lb of paving material or 200 times greater than KVB's measurement. Since both emissions are small, this variation could be well within the experimental error. Reference 4-57 contains emission data from the preparation of hot mix which indicates that these emissions are of the order of 10^{-9} lb hydrocarbon/lb asphalt paving material, negligible compared to the emission from the paving operations. Based on a geometric average of the MRI and KVB data (i.e., 10^{-5} lb/lb) a mile of asphalt paving, 60 ft wide and 3 inches thick would emit 300 lb plus or minus a factor of ten.

Although these emissions are low in rate they were found to be high olefinic species which are most reactive in smog formation.

The best control option is to substitute Portland cement type concrete for the asphalt type. This doubles the installed cost but saves some of this extra cost in maintenance and repair. When cutback asphalt is used (i.e. asphalt mixed with a petroleum thinner) the emissions can be 10 to 100 times higher according to MRI (Ref. 4-56). Where cutback asphalt has been used the emission can be reduced by as much as 95% by substituting water emulsified asphalt. The water emulsified asphalt has good fluidity but emissions as low or lower than the basic uncut asphalt.

Roofing operations also use asphalt, the type that has been oxidized by air blowing as discussed above under oil refining. This type of asphalt is uncut and the practice is to use heat to melt and apply the material to the roof. In this operation the principal emissions come from the roofing kettles. The control methods involve the use of enclosed kettles in which the solid asphalt "keg" is inserted into the kettle through quick opening/closing doors. Liquid asphalt is tapped off into buckets that are quickly applied to the roof where the material cools rapidly minimizing the emissions. Some emissions escape through door seals and other leaks in the kettles. Any system for evacuating the vapors from inside the kettle have been rejected because of the possible of drawing air into the kettle causing an explosive mixture.

C. Food Processing--

Food sources of hydrocarbons include operations such as the cooking, frying, broiling, baking, and roasting of vegetables, fruits, nuts, meat, fish, and fowl. These operations may involve food processing for commercial or domestic consumption, restaurant food preparation, or fermentation processes. Emissions range from light hydrocarbons from fermentation to medium from baking and roasting of vegetable products to heavy hydrocarbons from meat cooking. The disposition or concentration of inedible parts of meat and fish cause objectionable odorous emissions in the form of trimethylamine. Alcohols, esters and aldehydes constitute a large part of these emissions which are highly reactive from a photochemical smog standpoint.

The universal method for controlling these emissions is incineration which is usually an effective measure for odor control. Often, however, the medium to heavy emissions tend to condense and form organic particulates that can be filtered out of the gas stream mechanically. Condensation can be promoted by use of cold surface contact and direct water scrubbing. For low concentration streams where malodorous pollutants are concerned, charcoal adsorption can be employed with the desorbed products concentration and burned.

D. Combustion of Fuel--

The combustion of fuels may result in the emission of hydrocarbons and other organic material if combustion is not complete. When properly operated and designed, however, stationary fuel combustion equipment is not a large source of organic emissions, and control equipment is not required.

Fuels are burned in a wide variety of equipment ranging from small hand-fired coal furnaces to large oil, gas, and coal-fired steam-electric generating plants. Due to variations in combustion efficiency and type of fuel, hydrocarbon emissions will depend on the particular type of combustion device. Table 4-10 presents some typical hydrocarbon emissions for various types of fuels and furnace sizes. Considerable variation in these emissions can occur, however, depending on the operation of an individual unit.

TABLE 4-10. TYPICAL HYDROCARBON EMISSIONS FROM STATIONARY FUEL COMBUSTION SOURCES (lb/10^9 Btu)

	Size Range		
Fuel	Steam-Electric	Industrial	Domestic and Commercial
Oil	5	10	20
Gas	0.01	0.1	0.5

Hydrocarbon emissions from fuel combustion can be reduced or eliminated by essentially three techniques: improved operating practices, improved equipment design, and fuel substitution.

Good operating practice is the most practical technique for reducing hydrocarbon emissions from existing stationary combustion sources. Even the best equipment will perform poorly if improperly applied, installed, operated, or maintained and emit hydrocarbons, smoke, and other pollutants. Hydrocarbon emissions are directly related to the three common combustion parameters of time, temperature, and turbulence. A high degree of fuel and air turbulence will greatly reduce hydrocarbon emissions, increase combustion efficiency, and reduce fuel consumption. Flue gas monitoring systems such as oxygen and smoke recorders are helpful in indicating the operation of the furnace and are useful in keeping emissions at a minimum.

In the Basin very little waste disposal is performed by burning because the best control for this process is to substitute sanitary landfills as discussed in the next section.

E. Waste--

The primary waste disposal technique in the Basin is sanitary landfills. Collected waste is dumped into natural or excavated cavities and mixed and covered with earth. The decay process which takes place causes copious quantities of light hydrocarbons (primarily methane) to be emitted.

Until the recent awareness of an energy shortage these emissions were ignored except where a specific problem (odors, etc.) was generated by encroachment of residential areas on landfill sites. In this event a control method of collecting the generated gases was instituted. To collect the gas a network of perforated PVC pipe was buried in the landfill. The pipes were connected to a vacuum pump through which the gas was discharged to atmosphere or incinerator. Recently, with energy conservation incentives there has been an effort made to use the collected gases to augment the fuel supply in utility or industrial boilers.

4.3 COST EFFECTIVENESS

Cost effectiveness has been defined as the total cost associated with the reduction of one ton of pollution. There are many factors effecting the investment and annual cost of gaseous organic control systems such as the:

a. Gas stream volumetric flow rate
b. Gas stream temperature
c. Organic specie concentration in the gas stream
d. Specific organic compounds contained in the stream
e. Present degree of control
f. Facility modifications required
g. Energy consumption
h. Operating and maintenance labor
i. Waste heat applications
j. Usefulness of recovered materials.
k. Available space and structural requirements

With so many factors involved, it is only possible to present costs that represent some typical situations and which might apply to an industry average but not necessarily for a specific plant. For any real applications, a more specific look at these cost elements should be made in determining the optimum system. KVB has attempted to assemble cost data from the literature and from equipment manufacturers to provide the ARB with an indication of the cost impact of any control strategy that they may consider. As discussed in Section 4.1, the total cost for any control scheme includes the installed costs plus operating costs, as well as the indirect costs which can add 50% to 100% to the direct costs.

4.3.1 Carbon Adsorption

The cost effectiveness study presented was based on an extensive effort by the EPA Emission Standards and Engineering Division in Durham, NC as presented in Reference 4-2. The study considered both investment and operating cost and included all of the typical facility modification costs associated with an add-on system. Operating costs were adjusted for solvent recovery.

The basic assumptions used in developing this cost were as follows:

a. Exhaust gases contain benzene and hexane (50/50 weight percent) mixture in air

b. Exhaust gas temperatures of 70, 170, and 375 °F

c. Hydrocarbon concentrations of 100 ppm, 15 percent of the lower explosion limit (LEL) and 25 percent of the LEL

d. Exhaust gas flow rates of 1,000, 10,000, 50,000 scfm

e. Fuel costs of $1.50/million Btu*

f. Electricity at $0.03/kW-hr

g. Activated carbon at $0.68/lb

h. Water at $0.04/thousand gallons

i. Steam at $2/thousand lb

j. 5-year life of activated carbon

k. Adsorber operating at 100 °F

l. Market value (December 1975) of benzene = $0.85/gallon; market value (December 1975) of hexane = $0.465/gallon.

m. Normal retrofit situation

n. Direct labor assessed at 0.5 hr/shift x 730 shifts/yr x $8/hour = $2920/yr

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*September 1977 fuel costs in the Basin were $1.85/million BTU per Southern California Gas Company.

o. Annual maintenance, taxes, insurance, building overhead, depreciation, and interest on borrowed money taken at 25 percent of capital investment

p. Operating time = 5840 hr/yr.

In addition the recovered solvent was valued at three levels:

a. no value

b. fuel value - $1.50/MMBtu ($0.20/gal)

c. market value - see above list

The assumed solvent concentration levels of 15 and 25% of LEL is based on typical fire safety standards which specify 25% of LEL as a maximum safe concentration level for normal operations. In some areas plants can operate up to 50%. Some typical solvents and their LEL are as follows:

Solvent	LEL, ppm
Acetone	25,000
Benzene	14,000
Carbon Disulfide	12,000
Dichloroethylene	62,000
Ethyl Alcohol	35,000
Ethylene Glycol	32,000
Gasoline	13,000
Hexane	12,000
Methyl Alcohol	67,000
Methyl Butyl Ketone	14,000
Methyl Ethyl Ketone	18,000
Tolulene	13,000
Turpentine	8,000

No provisions were made for any distillation or water treatment equipment. If a plant emits water soluble organics in the exhaust, the cost would be considerably higher. The estimates did not include any particulate removal equipment. Finally, it was assumed that the solvents to be collected were of the middle range with regard to adsorptivity. Compounds which are difficult to adsorb (light compounds) or desorb (heavy compounds) can add considerably to both installation and operating costs.

Capital costs for adsorption systems designed to recover the solvent are presented in Figure 4-26.

Annual control costs for adsorbers are presented in Figures 4-27 through 4-29. For figures that give total annual cost, cost effectiveness information is also presented, that is, the cost per ton of hydrocarbon removed. Cost effectiveness information is a useful criterion when trying to devise air pollution control strategies to reduce the total amount of a pollutant emitted at a minimum cost. In this study annual depreciation was viewed as a cost, not as a credit, against taxable income. Thus the analysis was simplified and the resulting effect may be a slightly higher annual control cost. The curves indicate the importance of the value of the recovered solvents.

KVB obtained some case history data to check these curves as follows:

Case 1 - A Magnetic Tape Manufacturer

A 10,000 scfm, three-canister, activated carbon system with steam regeneration and distillation for solvent recovery was installed to collect methyl isobutyl ketone (MIBK) vapors which were originally emitted at a rate of 500 lb/hr or 3000 ppm (22% LEL) at that flow rate. The system recovered 450 lb/hr of MIBK at a cost of $10/hr excluding equipment depreciation, taxes, insurance, building overhead, etc. and the price of the recovered solvent.

A comparison of the reported cost parameters with the parameters predicted by the cost curves presented is as follows:

Parameter	Reported Actual (Ref. 4-58)	Predicted by Study
Installed Cost, $	250,000	270,000
Annual Cost, $ (no credit for recovered solvent)	110,000*	100,000
Annual Wt. of Solvent Recovered, tons	1,300	--
Cost Effectiveness, $/ton	85	125

*Include 25% of Installed Cost for depreciation, taxes, insurance, overhead, etc. the same as used in the study.

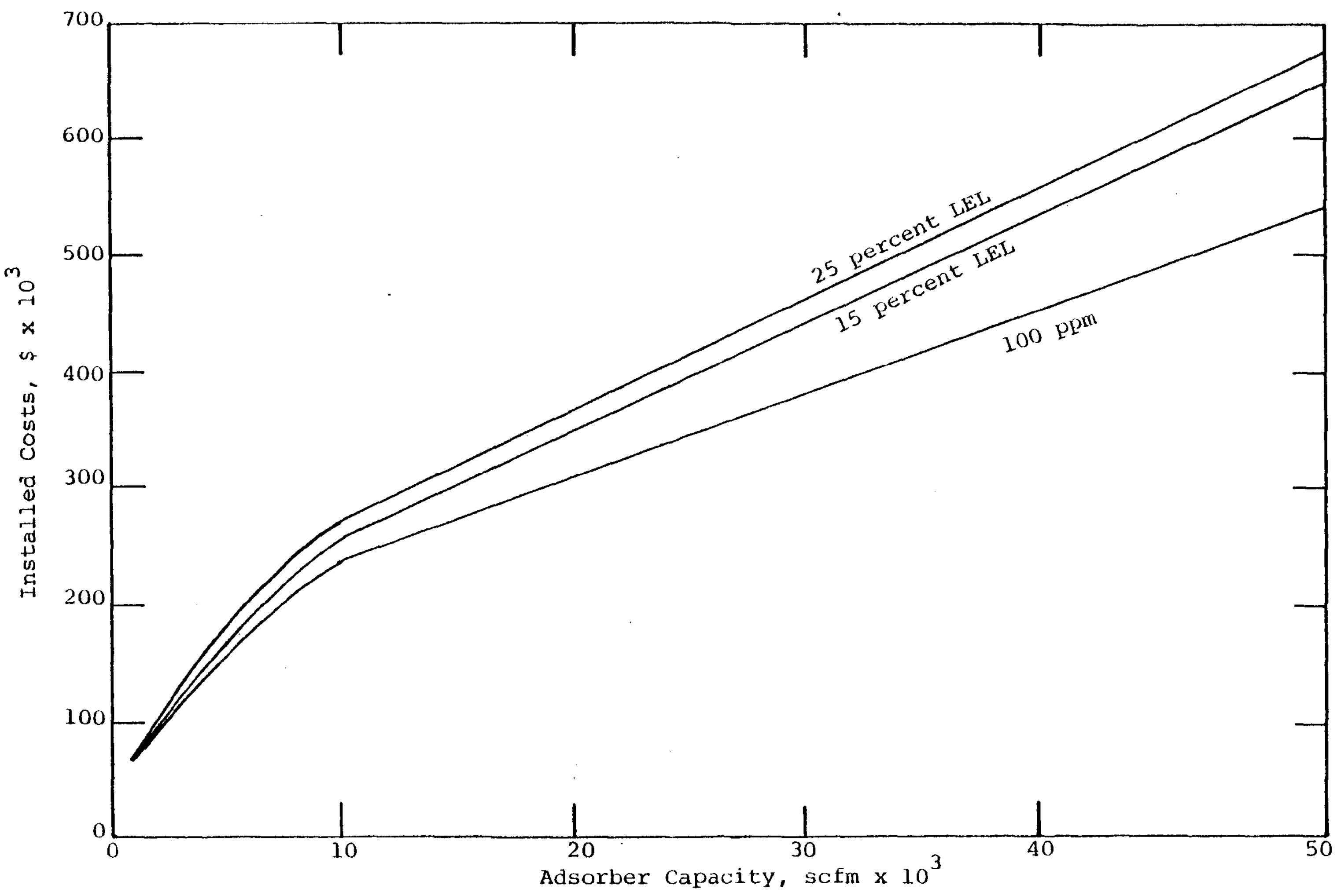

Figure 4-26. Estimated installed adsorption system cost (Ref. 4-2) (1976 prices).

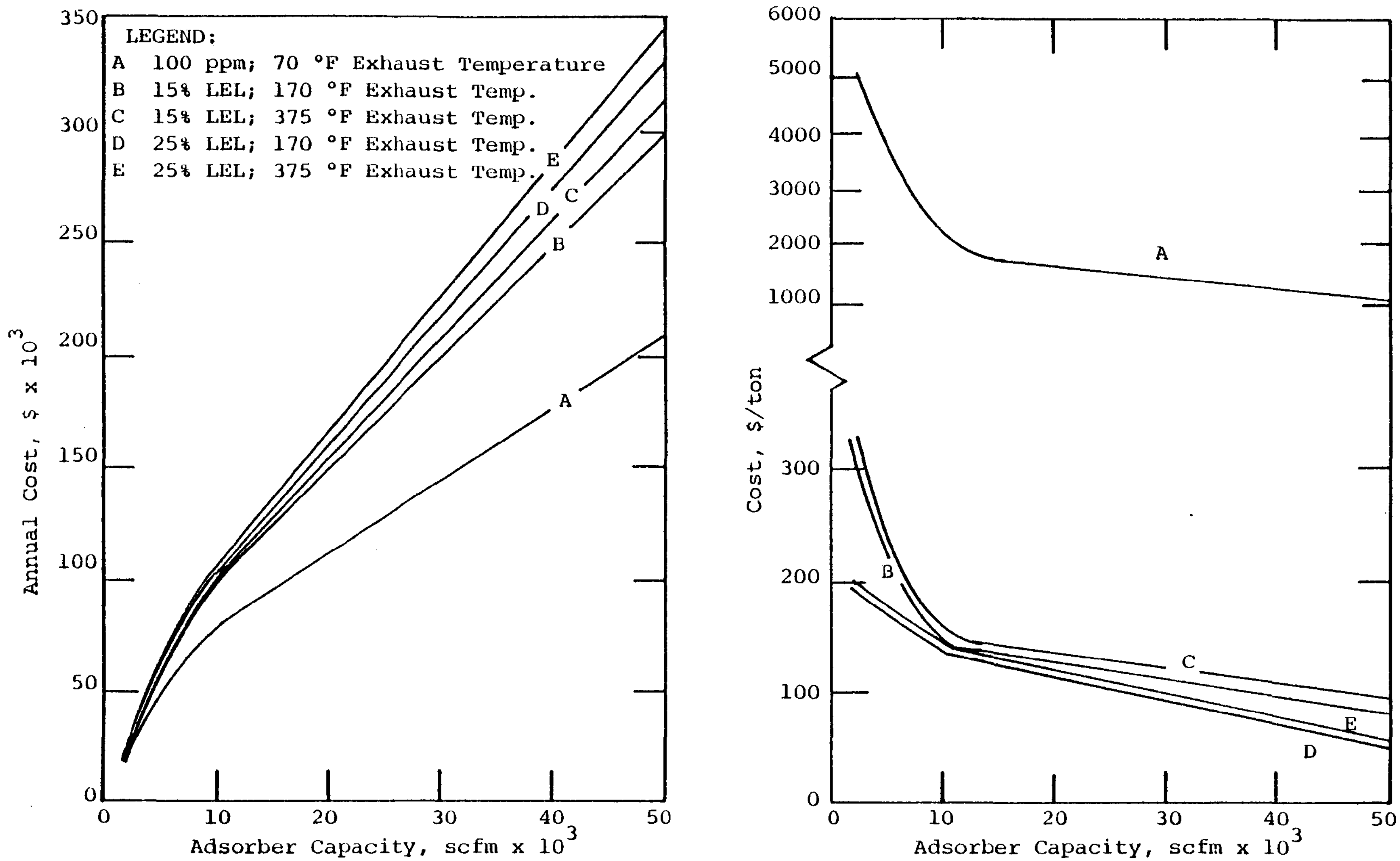

Figure 4-27. Annual cost and cost-effectiveness of carbon adsorption systems (1976 prices) (no credit given for recovered solvents) (Ref. 4-2).

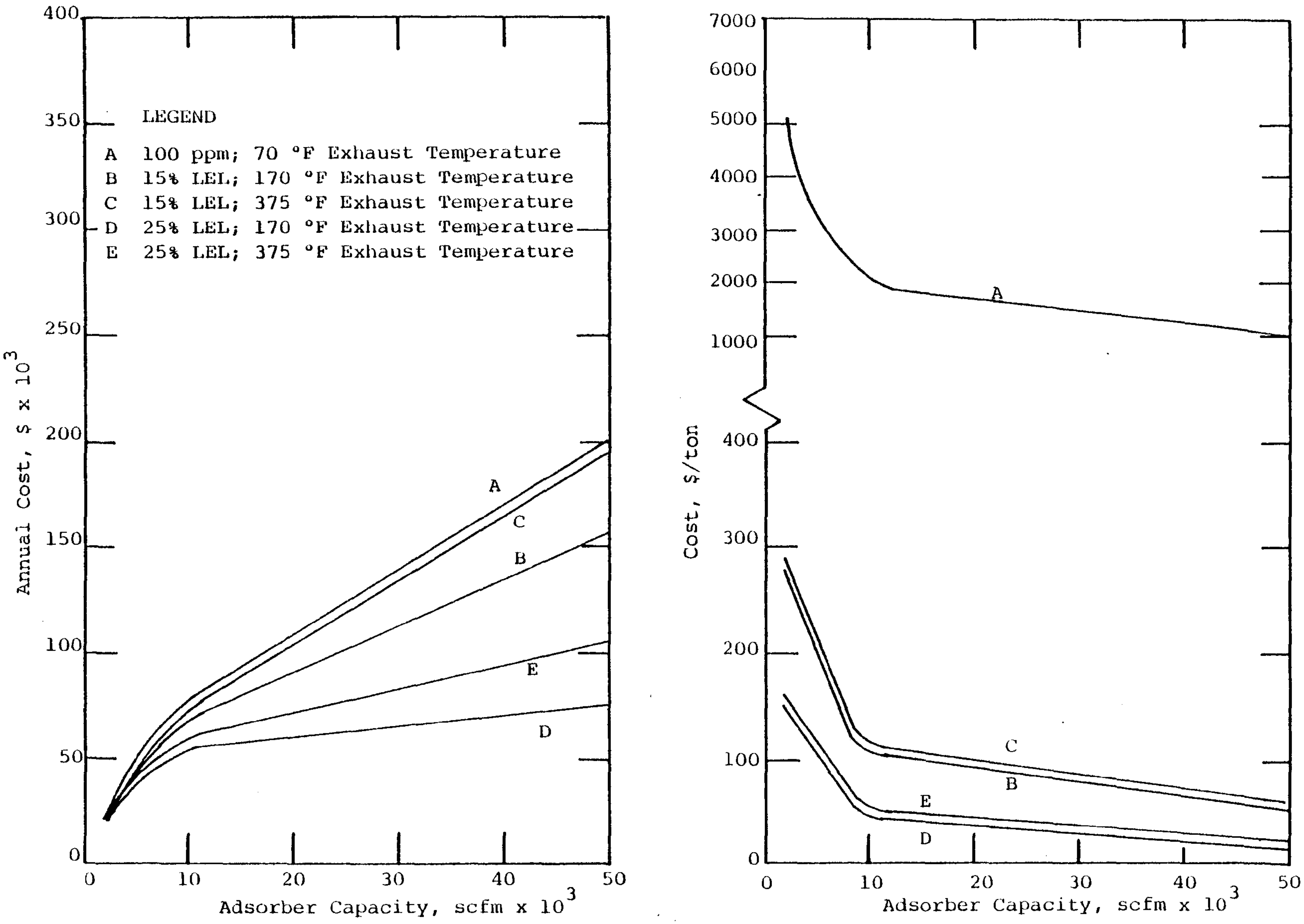

Figure 4-28. Annual cost and cost-effectiveness of carbon adsorption systems (recovered solvent credited at fuel value) (Ref. 4-2)

NOTE: Fuel price used was \$1.50/MMBtu compared to \$1.85/MMBtu which is the September 1977 fuel price in the Basin.

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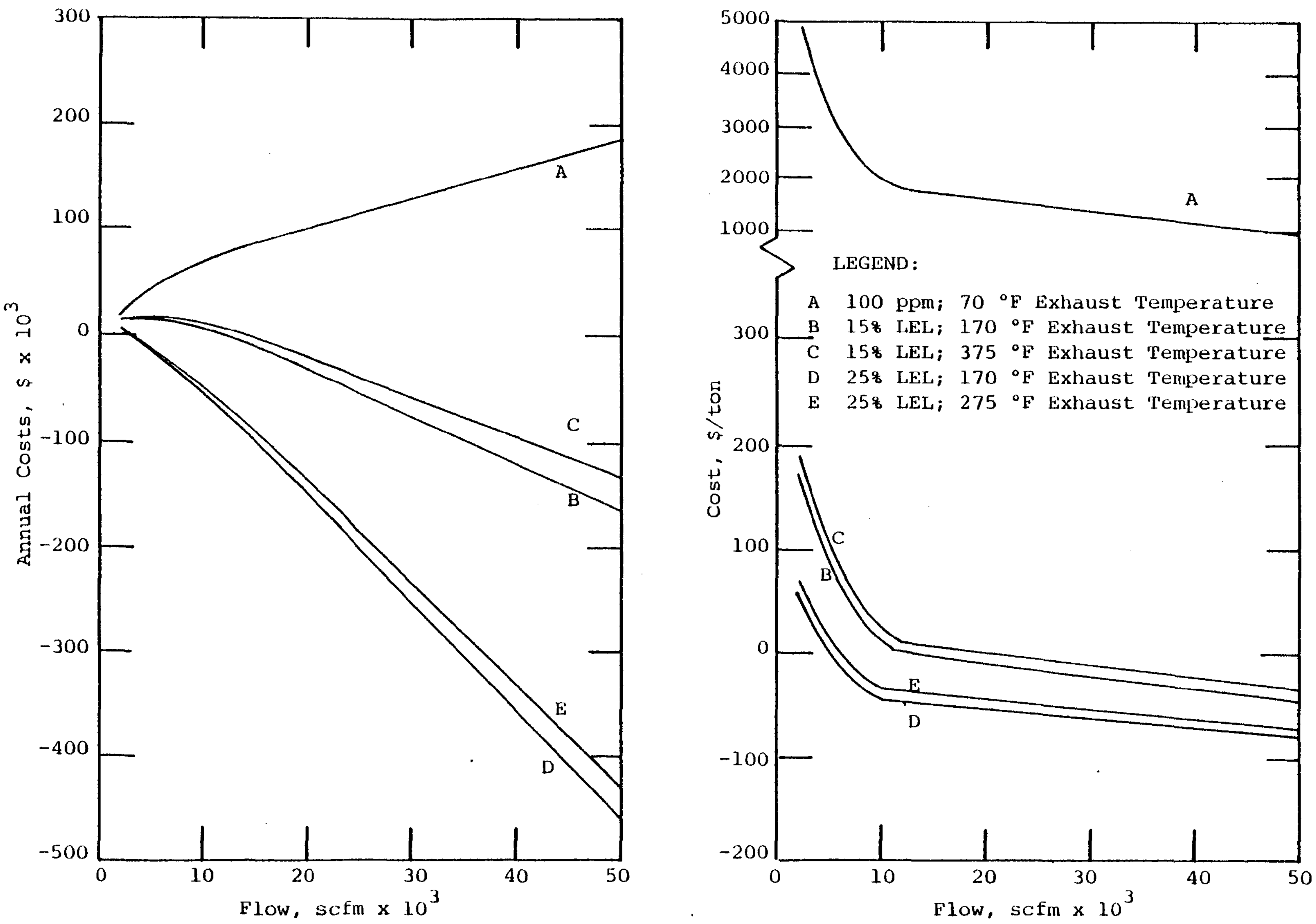

Figure 4-29. Annual cost and cost-effectiveness of carbon adsorption systems (recovered solvent credited at market chemical value) (1976 prices) (Ref. 4-2).

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The MIBK was valued at $2.50/gal. which means that the 1300 tons of solvent recovered was worth approximately $800,000, over three times the original investment.

Case 2 - A Pharmaceutical Company

A 10,000 scfm, three-canister, activated carbon system with distillation for solvent recovery was installed to collect acetone vapors which were emitted at a rate of 500 lb/hr or 5000 ppm (20% LEL) at that flow rate. The system recovered 450 lb/hr of acetone at cost of $10/hr excluding equipment depreciation, taxes, etc. and the price of the recovered solvent. The comparison of reported cost and those predicted by the study are:

Parameter	Reported Actual (Ref. 4-58)	Predicted by Study
Installed Cost, $	250,000	270,000
Annual Cost, $ (no credit for recovered solvent)	120,000*	100,000
Annual Weight of Solvent Recovered, tons	1,300	--
Cost Effectiveness, $/ton	90	125

*Includes 25% of Installed Cost

The acetone was valued at $1.25/gal which means that the 1300 tons recovered was worth approximately $500,000 or twice the original investment.

Case 3 - A Gravure Printing Plant

This plant has an 180,000 scfm, four-canister, activated carbon system with a solvent recovery system. The solvent concentration is 1000 to 3000 (10-25% LEL) ppm of a blend of aliphatic and aromatic (< 20%) hydrocarbons. The installed cost of this system was reported as $5 million compared to a predicted $3.5 million extrapolated from Figure 4-26. The operating costs were not disclosed, however, a payback period of 12 to 15 years was estimated. This would reflect an approximate operation cost of from $100 to $200/ton of pollutant compared to $10 to $50/ton from Figure 4-29.

Case 4 - An Automotive Spray Paint Booth

100 ppm hexane - 90% removal - 5840 hrs of operation/year

Parameter	Reported Actual (Ref. 4-33)	Predicted by Study
Solvent Concentration	100 ppm	100 ppm
Flow Rate, SCFM	248,000	248,000
Wt Recovered, tons	870	---
Installed Cost, %	2,700,000	2,200,000
Annual Cost, $ (no credit for solvent)	1,000,000	900,000
Cost Effectiveness, $/ton	1150	Beyond Extrapolation

Case 5 - An Automotive Spray Booth

Parameter	Reported Actual (Ref. 4-64)	Predicted by Study
Solvent Concentration	100 ppm	100 ppm
Flow Rate, SCFM	1,815,000	1,815,000
Installed Cost, $	19,600,000	15,000,000
Annual Cost, $	7,300,000	2,700,000
Cost Effectiveness, $/ton	1150	Beyond Extrapolation

4.3.2 Incineration (Thermal and Catalytic)

The cost effectiveness data presented in this section are taken from a 1976 EPA study, Reference 4-2. For additional cost data, especially on automobile painting incinerators, consult Reference 4-33. Incineration can be an economical control alternative if heat recovery techniques can be utilized. To illustrate the importance of heat recovery, three cases were investigated:

- No heat recovery
- 25 percent primary heat recovery
- 35 percent primary heat recovery and 55 percent secondary heat recovery of the remaining 65 percent.

For each case, cost estimates were made for three inlet flow rates (5,000, 15,000, and 30,000 scfm), two inlet stream temperatures (70 and 300 °F), and three stream concentrations (0, 15, and 25 percent of the LEL*). Other assumptions used in developing the estimates are as follows:

a. Noncatalytic incinerators designed for both oil and natural gas operation
b. Catalytic incinerators designed for natural gas and propane operation
c. Catalytic incinerators capable of 800 °F operation below 6 percent LEL; 1200 °F design capability for operation from 6 percent to 25 percent LEL
d. 3-year catalyst life
e. Costs based on outdoor location
f. Rooftop installation requiring structural steel
g. Fuel cost of $1.50/million Btu**(gross). Correction factors were provided to determine operating costs at higher fuel prices
h. Electricity at $0.03 kW-hr
i. Depreciation and interest was taken as 16 percent of capital investment. Annual maintenance was assumed to be 5 percent of capital cost, taxes and insurance, 2 percent, and building overhead, 2 percent
j. Direct labor assessed at 0.5 hr/shift x 730 shifts/yr x $8.00/hr = $2920/yr direct labor expense
k. Operating time: 2 shifts/day x 8 hr/shift x 365 days/yr = 5840 hr/yr. Correction factors are provided to determine annual cost at different operating times

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*See Section 4.3.1 for Lower Explosion Limit (LEL) values.

**Actual fuel cost (gas) in the Basin in September 1977 was $1.85/million Btu.

l. The noncatalytic incinerator utilized was based on:

   - 1500 °F capability
   - 0.5-second residence time
   - Nozzle mix burner capable of No. 2 through No. 6 oil firing
   - Forced mixing of the burner products of combustion using a slotted cylinder mixing arrangement. This cylinder allows the burner flame to establish itself before radial entry of the effluent through slots in the far end of the cylinder
   - A portion of the effluent to be incinerated is ducted to the burner to serve as combustion air. This allows the burner to act as a raw gas burner, thus saving fuel over conventional nozzle mix burners. This design can only be used, however, when the O_2 content of the oven exhaust is 17 percent by volume or above

m. The catalytic afterburner was costed for two design points, 800 and 1200 °F; the higher temperature design required for LEL levels exceeding 6 percent. (At 600 °F into the catalyst and a 6 percent LEL, the outlet temperature of the catalyst is approximately 800 °F; at a 25 percent LEL condition and a minimum initiation temperature of 500 °F, the catalyst reaches an outlet temperature of around 1200 °F.)

Based upon the results of the cost estimates, cost curves were developed (Figures 4-30 through 4-44). Because of the unique plant facility characteristics, actual control costs for some plants can be substantially higher than estimates given here. To adjust for the differences between the $1.50/MMBtu used in the study and the current fuel price of $1.85/MMBtu or to adjust for different operating times, refer to Figures 4-45 and 4-48.

A. Installed Cost of Incinerators--

Figures 4-30, 4-35, and 4-40 give the installed cost for incinerators designed for (1) no heat recovery, (2) primary heat recovery, and (3) primary and secondary heat recovery. The costs were intended to represent typical retrofit situations. However, further investigation has revealed that the costs are more representative of the minimum retrofit situation, essentially the same as installation during the construction of a new plant. The installed cost in more typical retrofit situations will be 1.5 to 2 times the values shown in Figures 4-30, 4-35, and 4-40. In very difficult cases, the cost can be 3 to 5 times that shown in the figures.

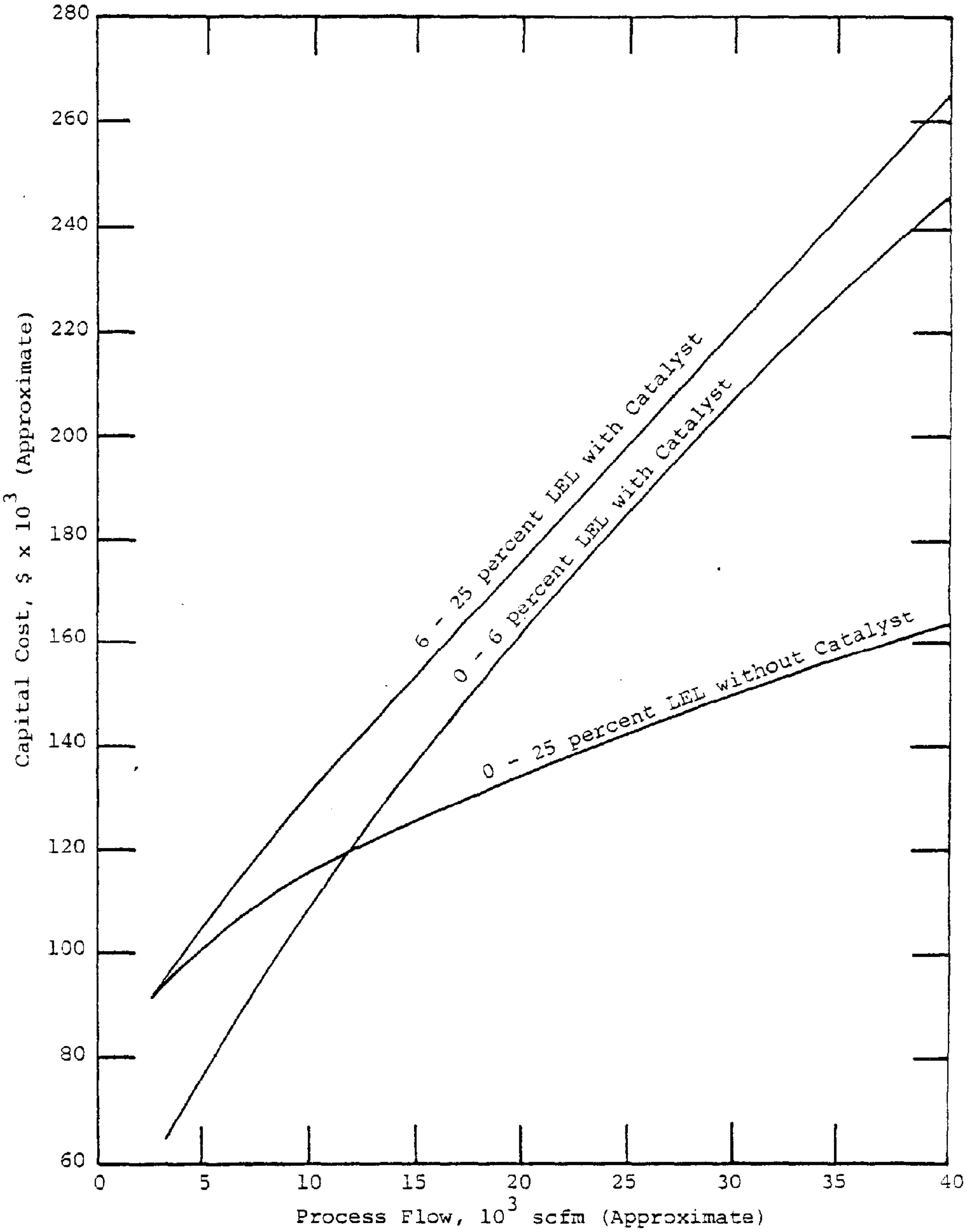

Figure 4-30. Capital cost for direct flame and catalytic afterburners without heat recovery (70 - 300 °F process gas inlet) Case 1 (1976 prices) (Ref. 4-2).

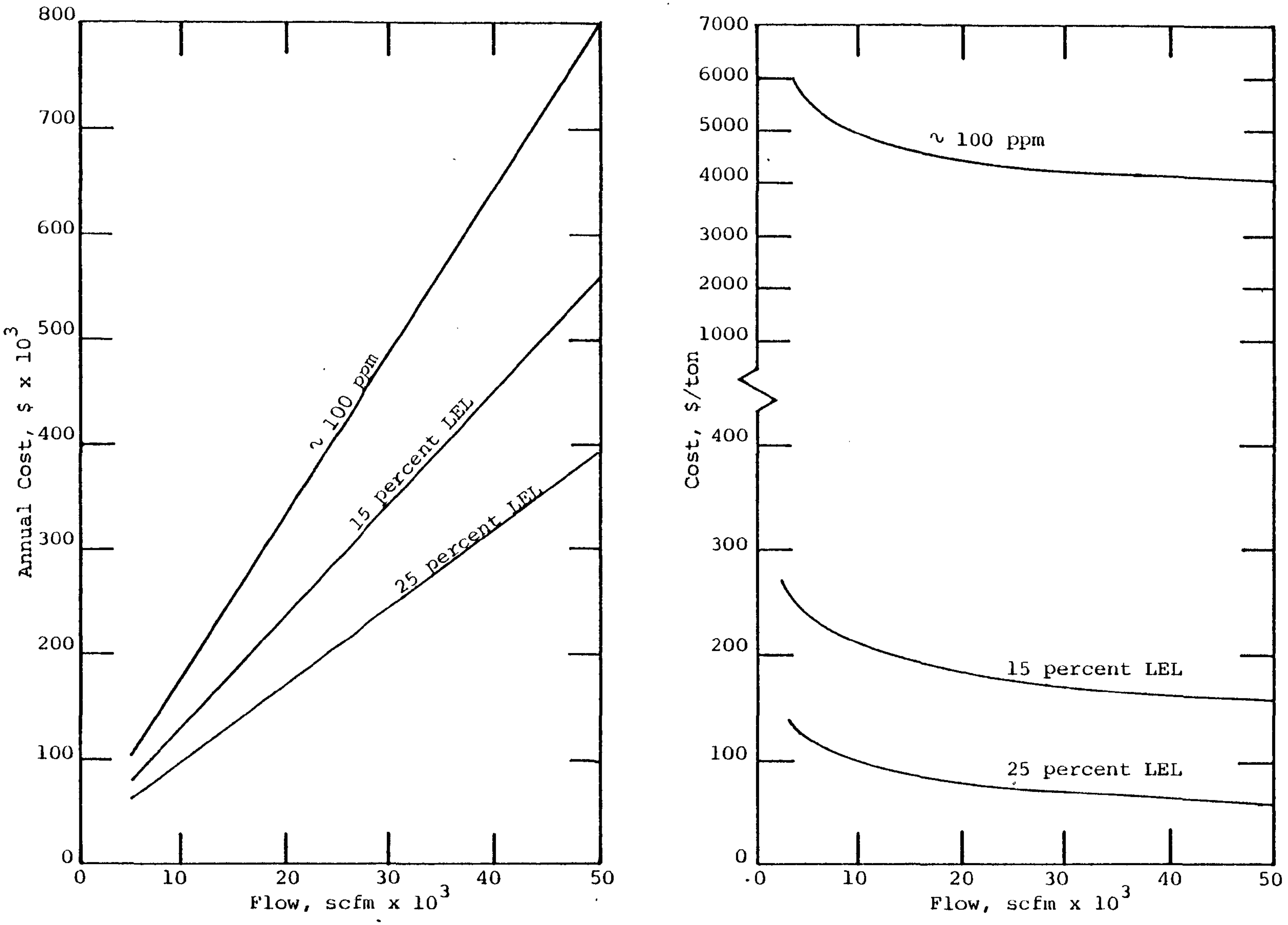

Figure 4-31. Annual cost and cost-effectiveness of direct flame incinerators (1976 prices) (no heat recovery, process temperature = 70 °F) Case 1 (Ref. 4-2).

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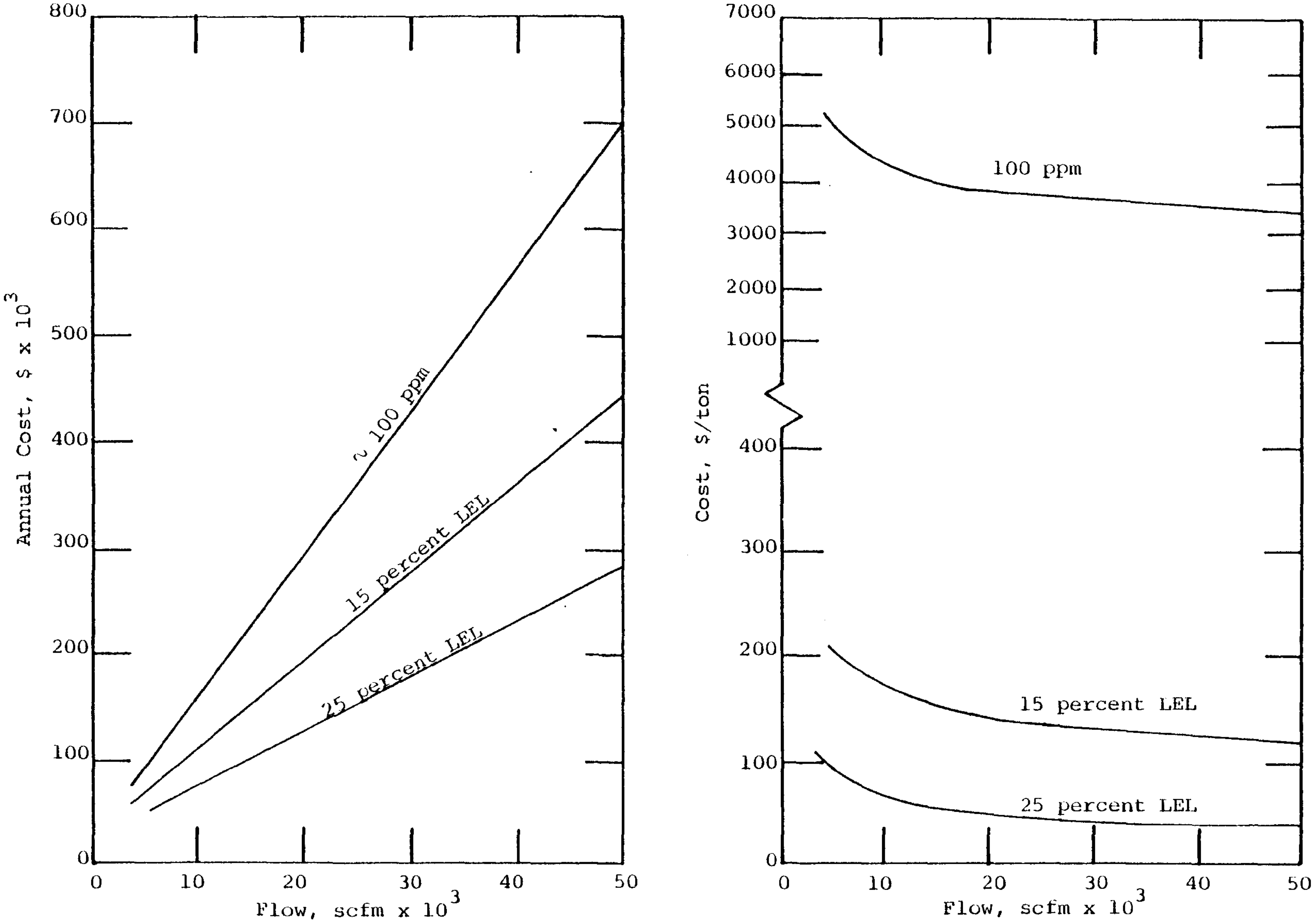

Figure 4-32. Annual cost and cost-effectiveness of direct flame incinerators (1976 prices) (no heat recovery - process temperature = 300 °F) Case 1 (Ref. 4-2).

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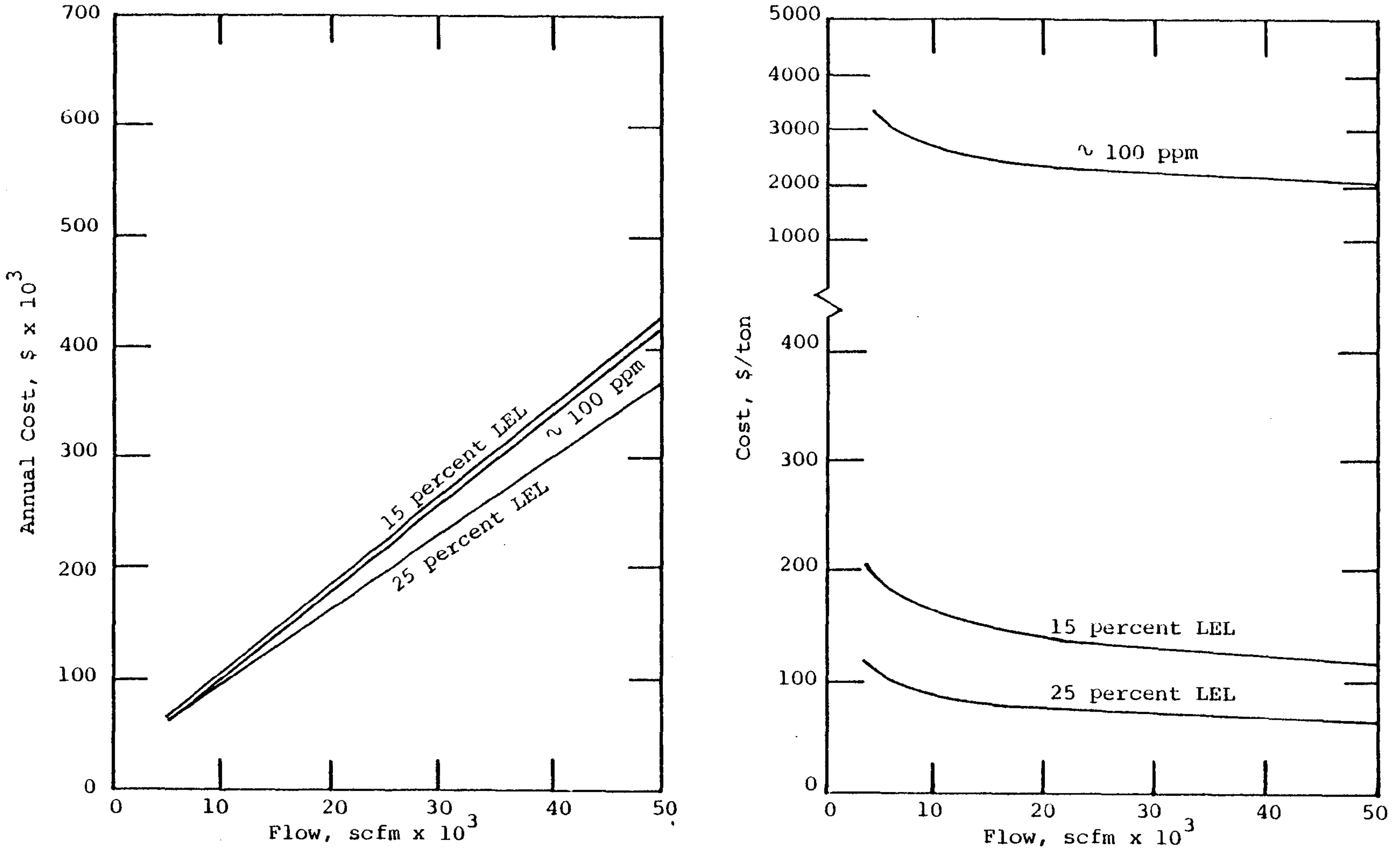

Figure 4-33. Annual cost and cost-effectiveness of catalytic incinerators (1976 prices) (no heat recovery - process temperature = 70 °F) Case 1 (Ref. 4-2).

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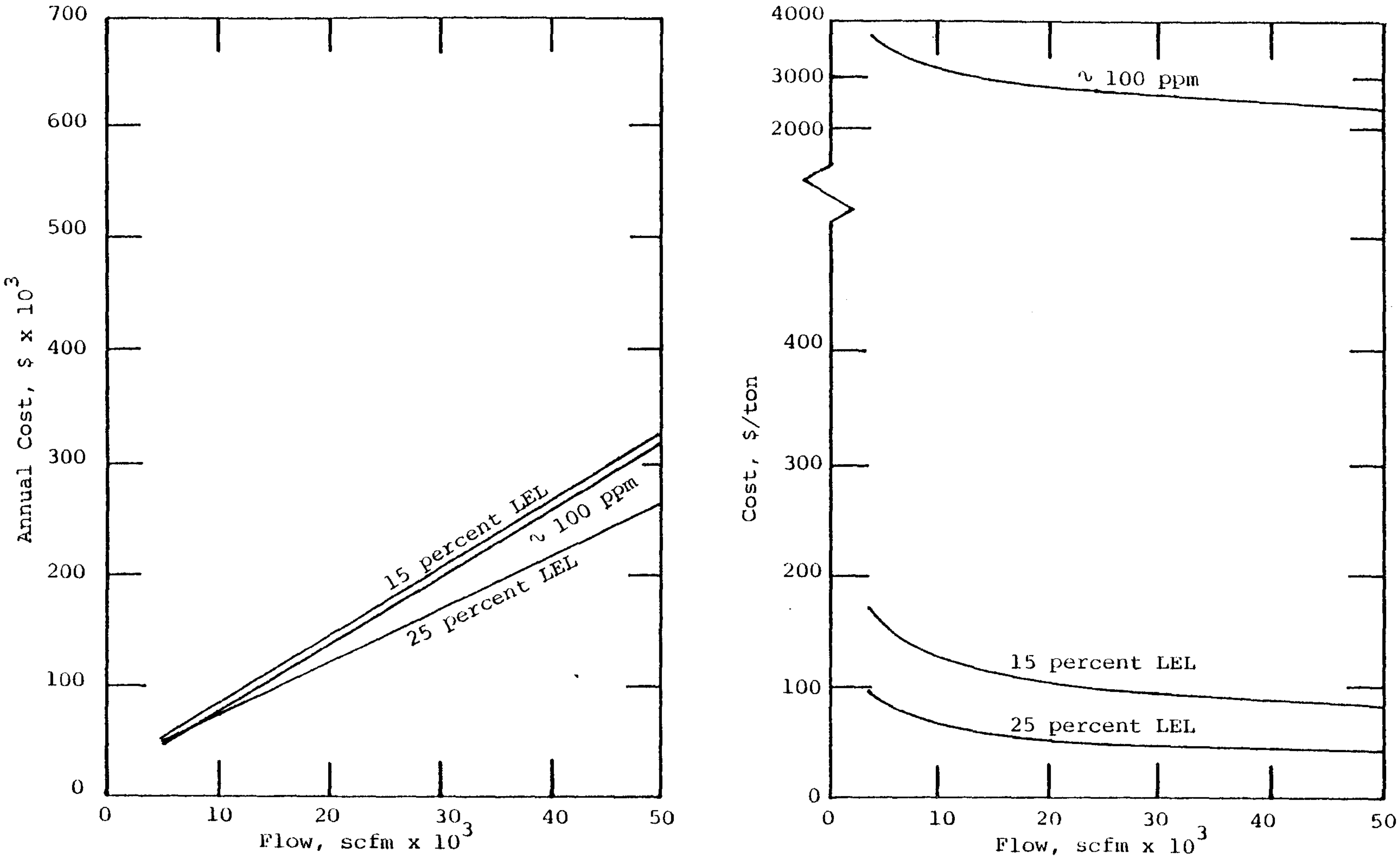

Figure 4-34. Annual cost and cost-effectiveness of catalytic incinerators (1976 prices). (no heat recovery - process temperature = 300 °F) Case 1 (Ref. 4-2).

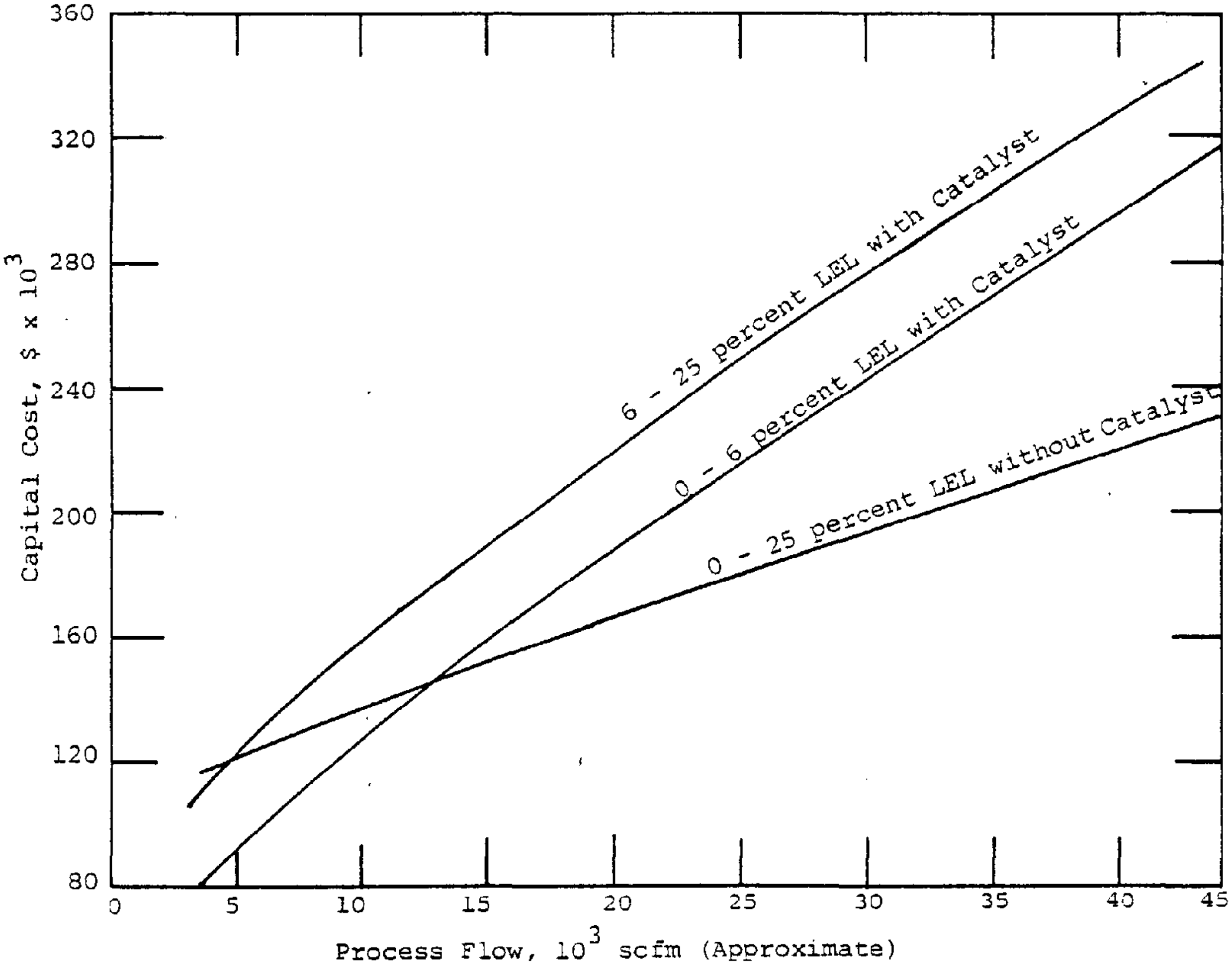

Figure 4-35. Capital cost for direct flame and catalytic afterburners with primary heat recovery (70 - 300 °F process gas inlet) (1976 prices) Case 2 (Ref. 4-2).

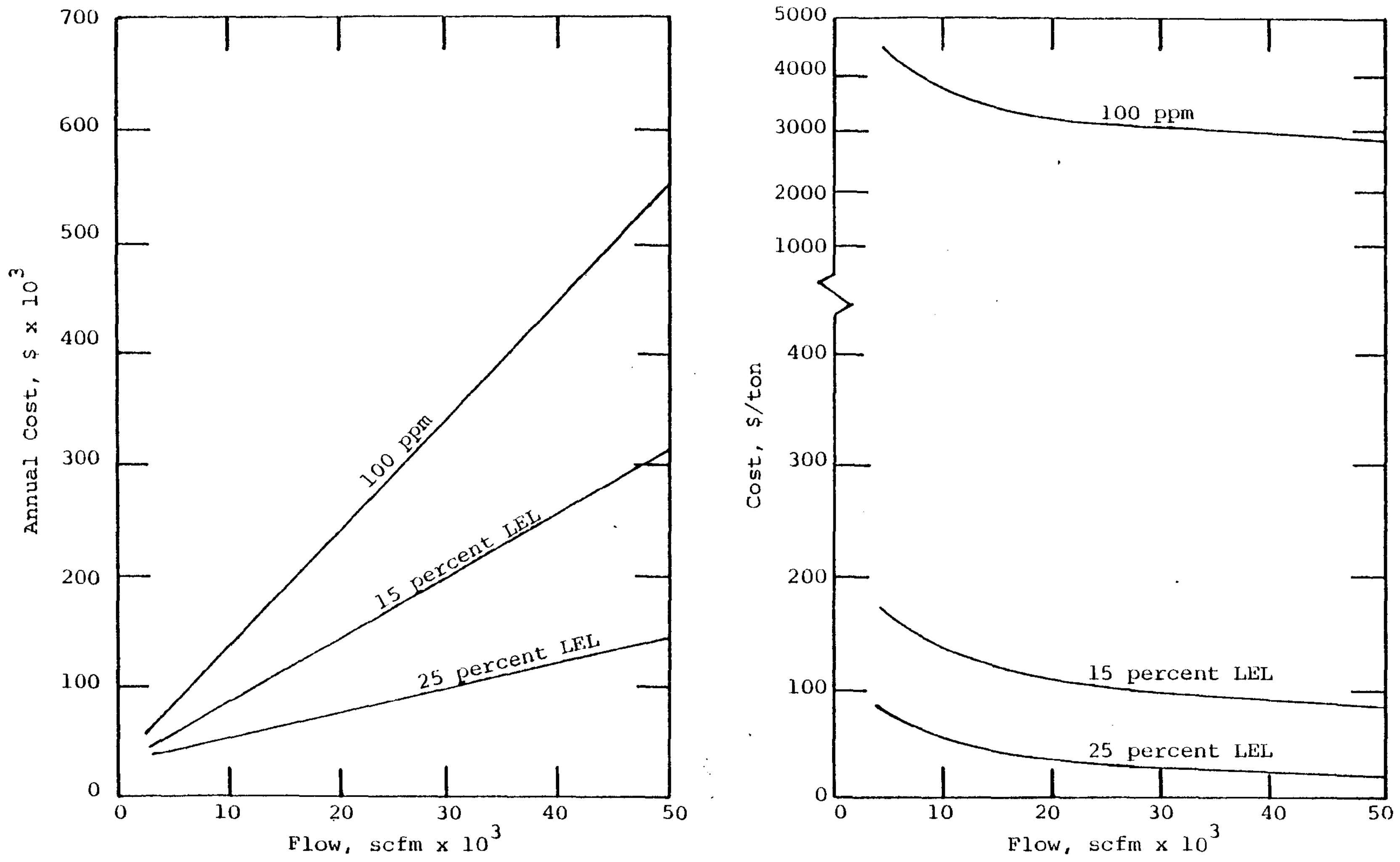

Figure 4-36. Annual cost and cost-effectiveness of direct flame incinerators (primary heat recovery - process temperature = 70 °F) Case 2 (1976 prices) (Ref. 4-2).

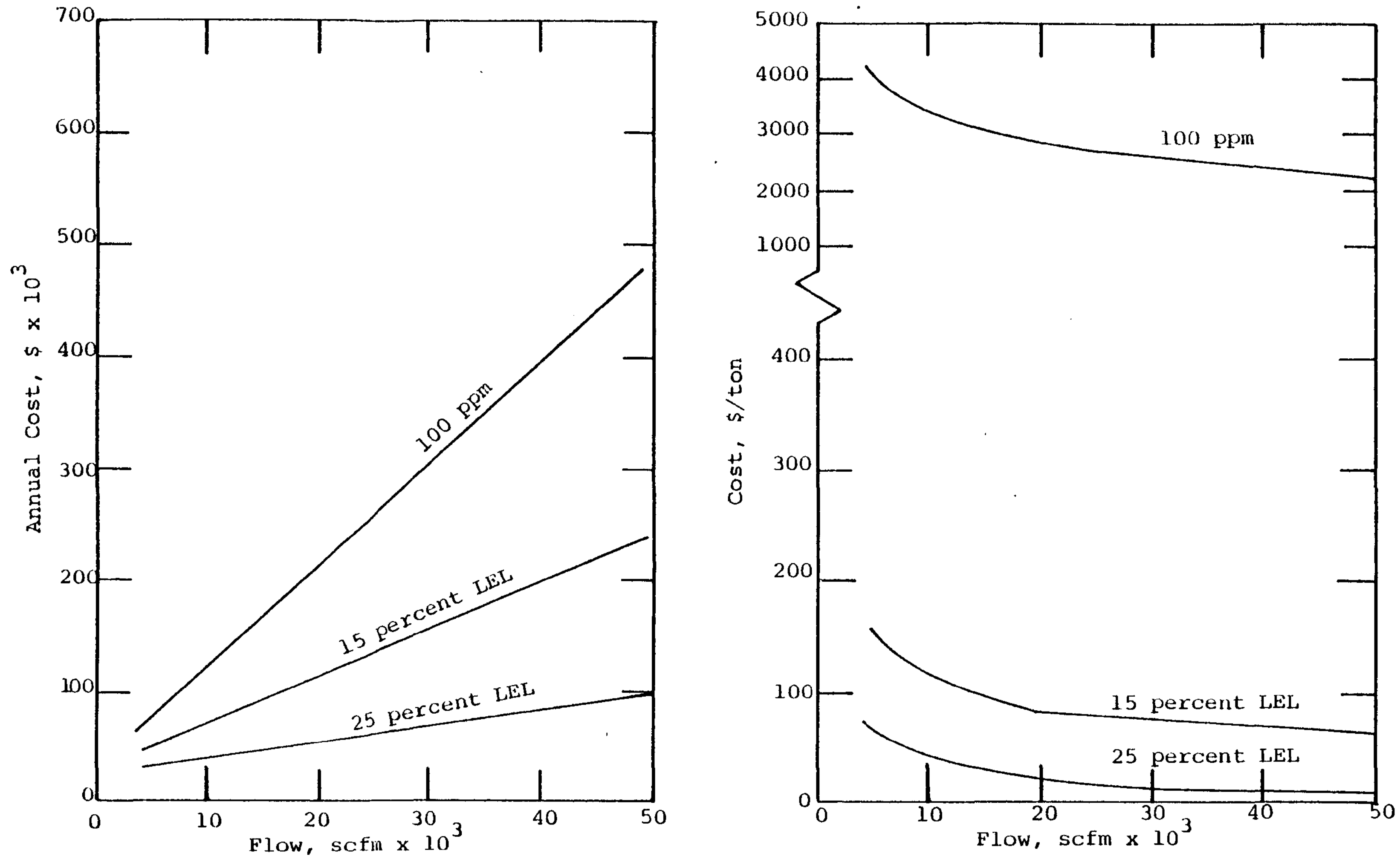

Figure 4-37. Annual cost and cost-effectiveness of direct flame incinerators (primary heat recovery - process temperature = 300 °F) Case 2 (1976 prices) (Ref. 4-2).

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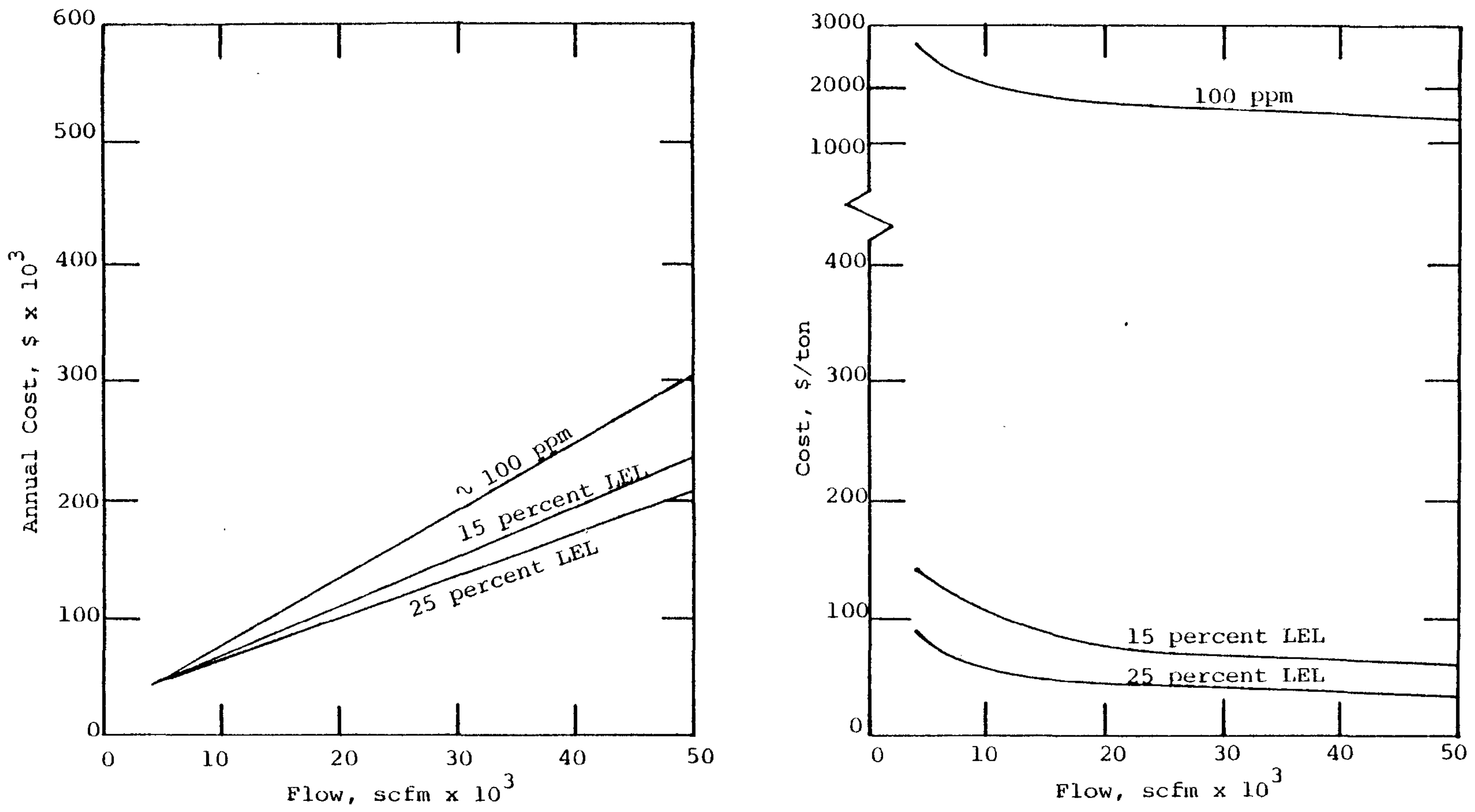

Figure 4-38. Annual cost and cost-effectiveness of catalytic incinerators (primary heat recovery - process temperature = 300 °F) Case 2 (1976 prices) (Ref. 4-2).

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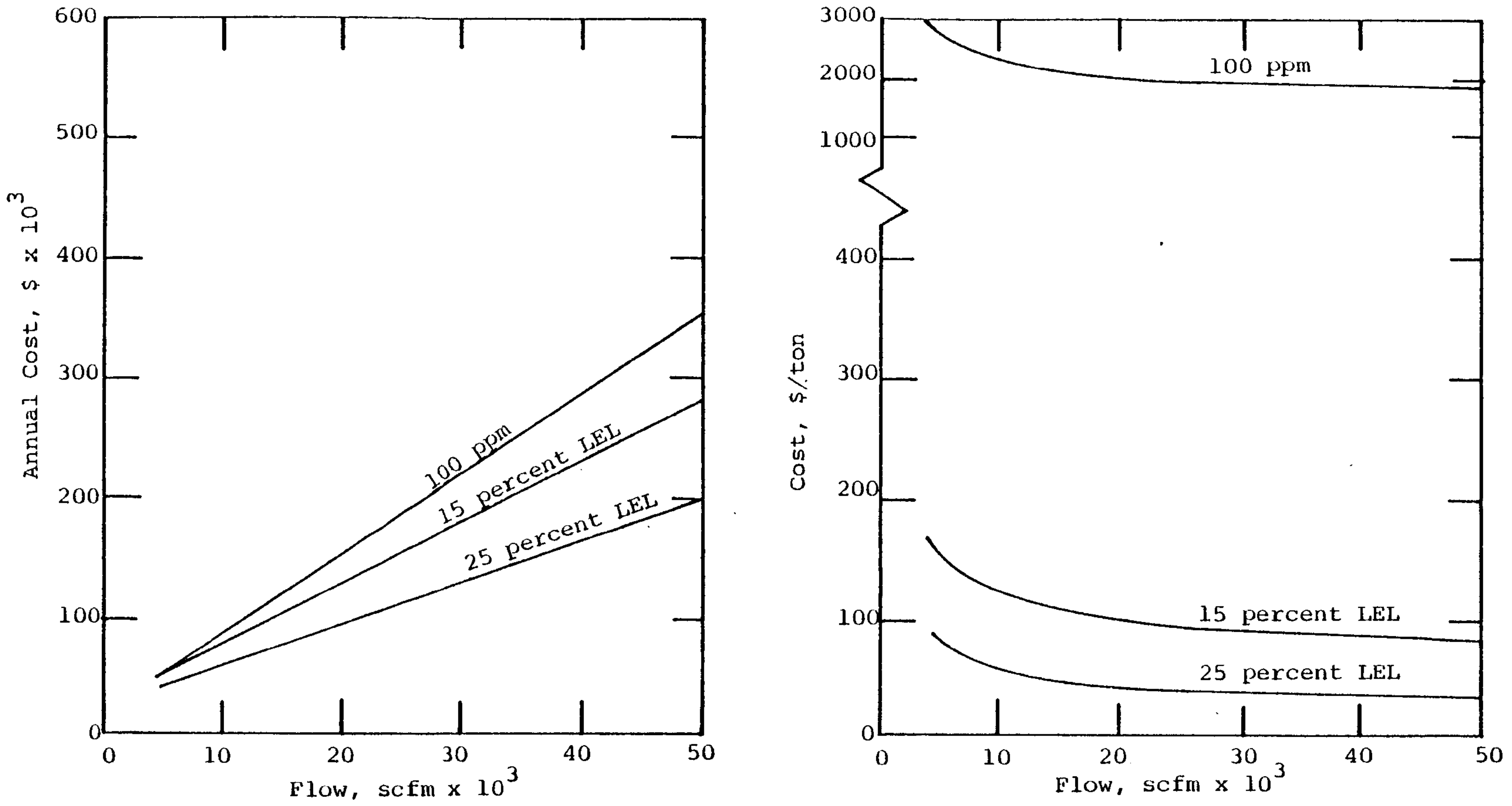

Figure 4-39. Annual cost and cost effectiveness of catalytic incinerators (primary heat recovery - process temperature = 70 °F) Case 2 (1976 prices) (Ref. 4-2).

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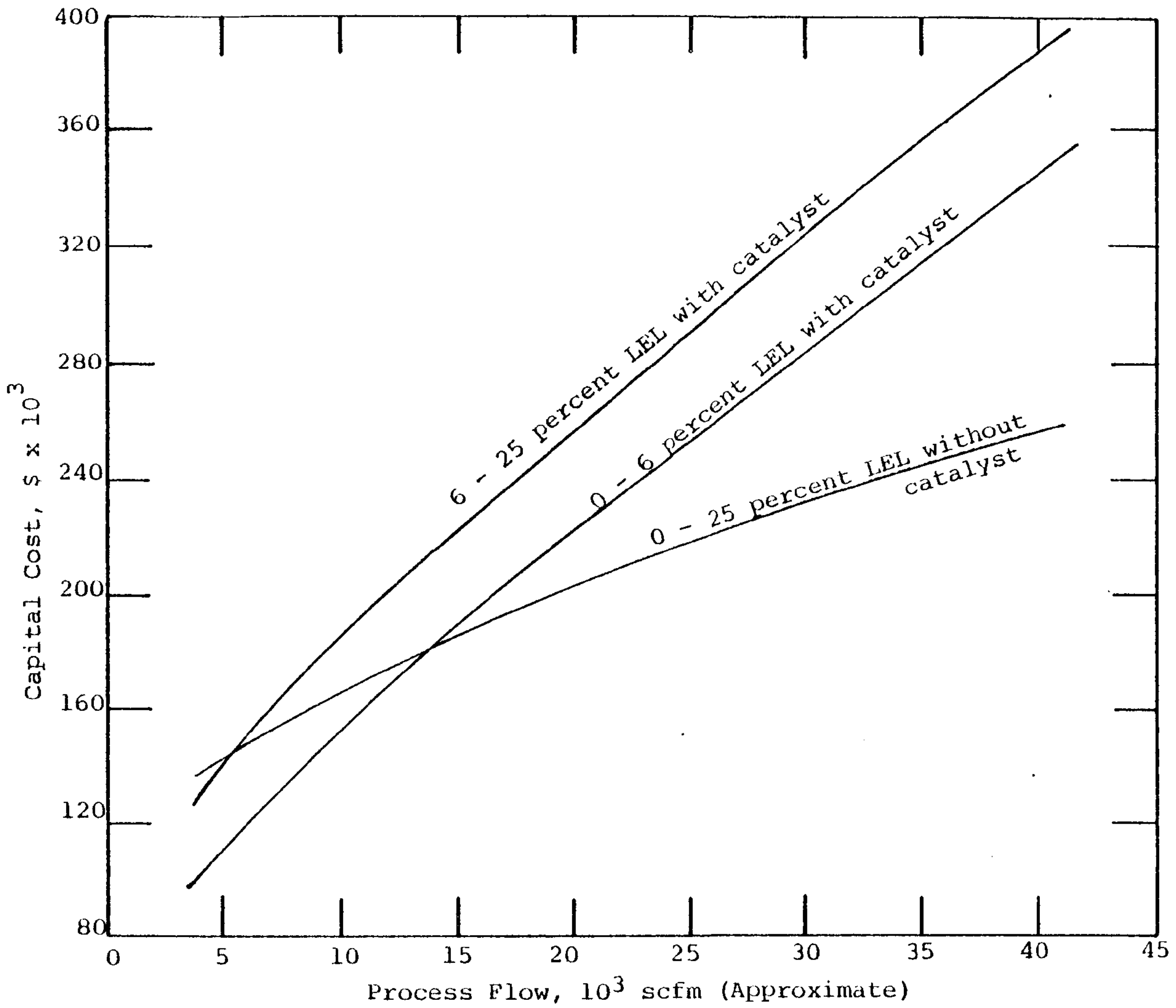

Figure 4-40. Capital cost for direct flame and catalytic afterburners with primary and secondary heat recovery (70 - 300 °F process gas inlet) Case 3 (1976 prices) (Ref. 4-2).

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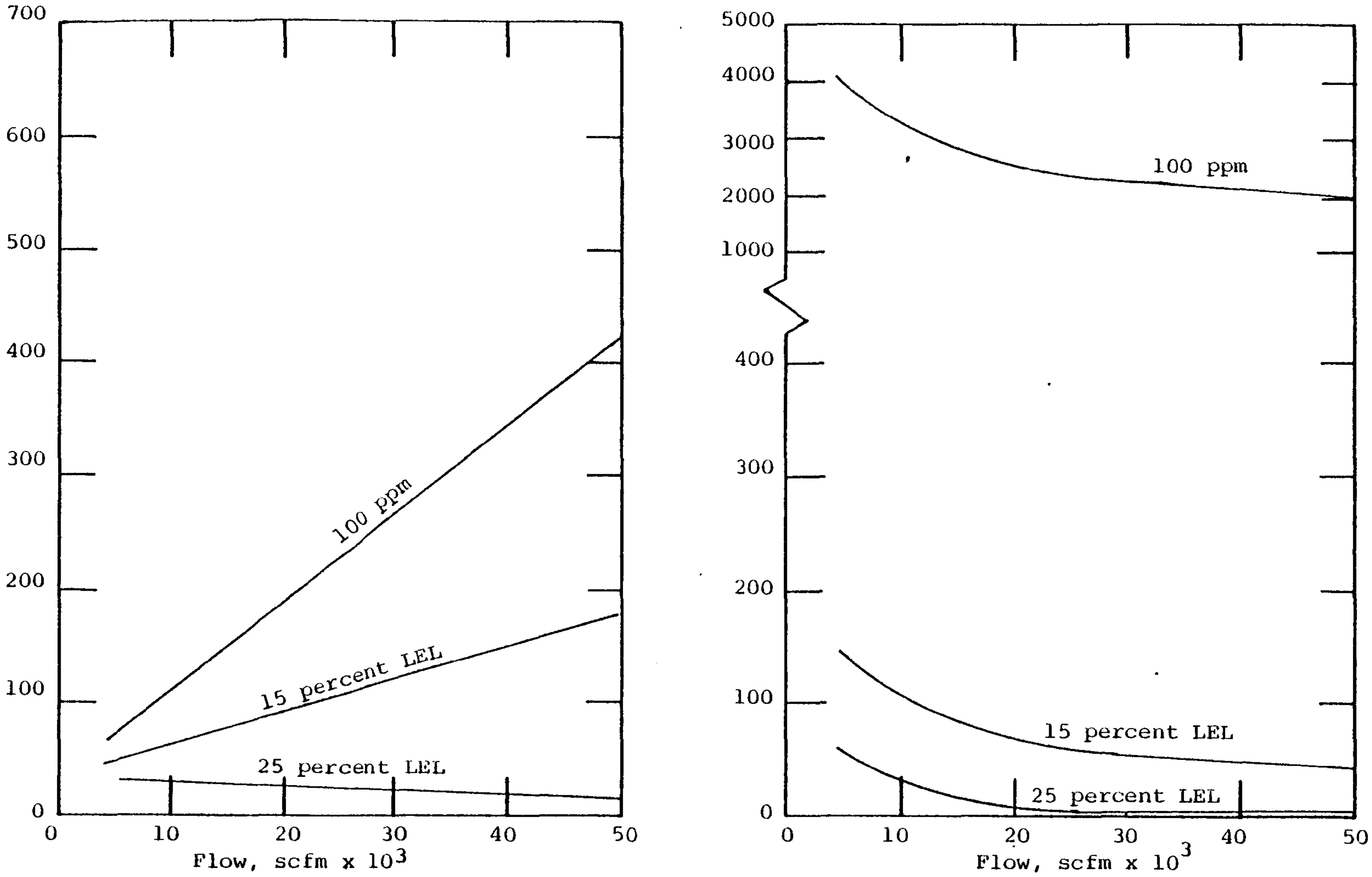

Figure 4-41. Annual cost and cost-effectiveness of direct flame incinerators (primary and secondary heat recovery - process temperature = 70 °F) Case 3 (1976 prices) (Ref. 4-2).

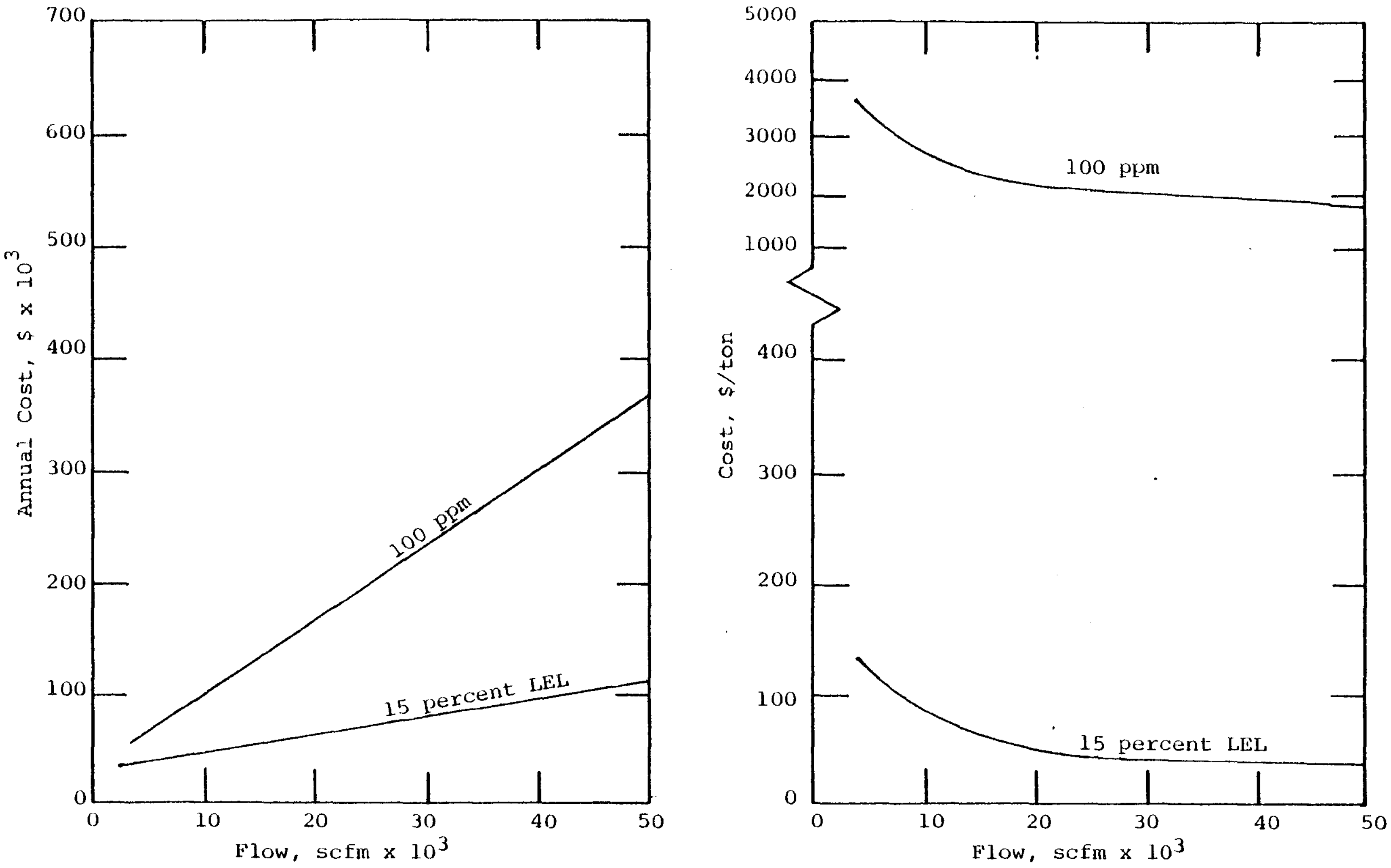

Figure 4-42. Annual cost and cost-effectiveness of direct flame incinerators (primary and secondary heat recovery - process temperature = 300 °F) Case 3 (1976 prices) (Ref. 4-2).

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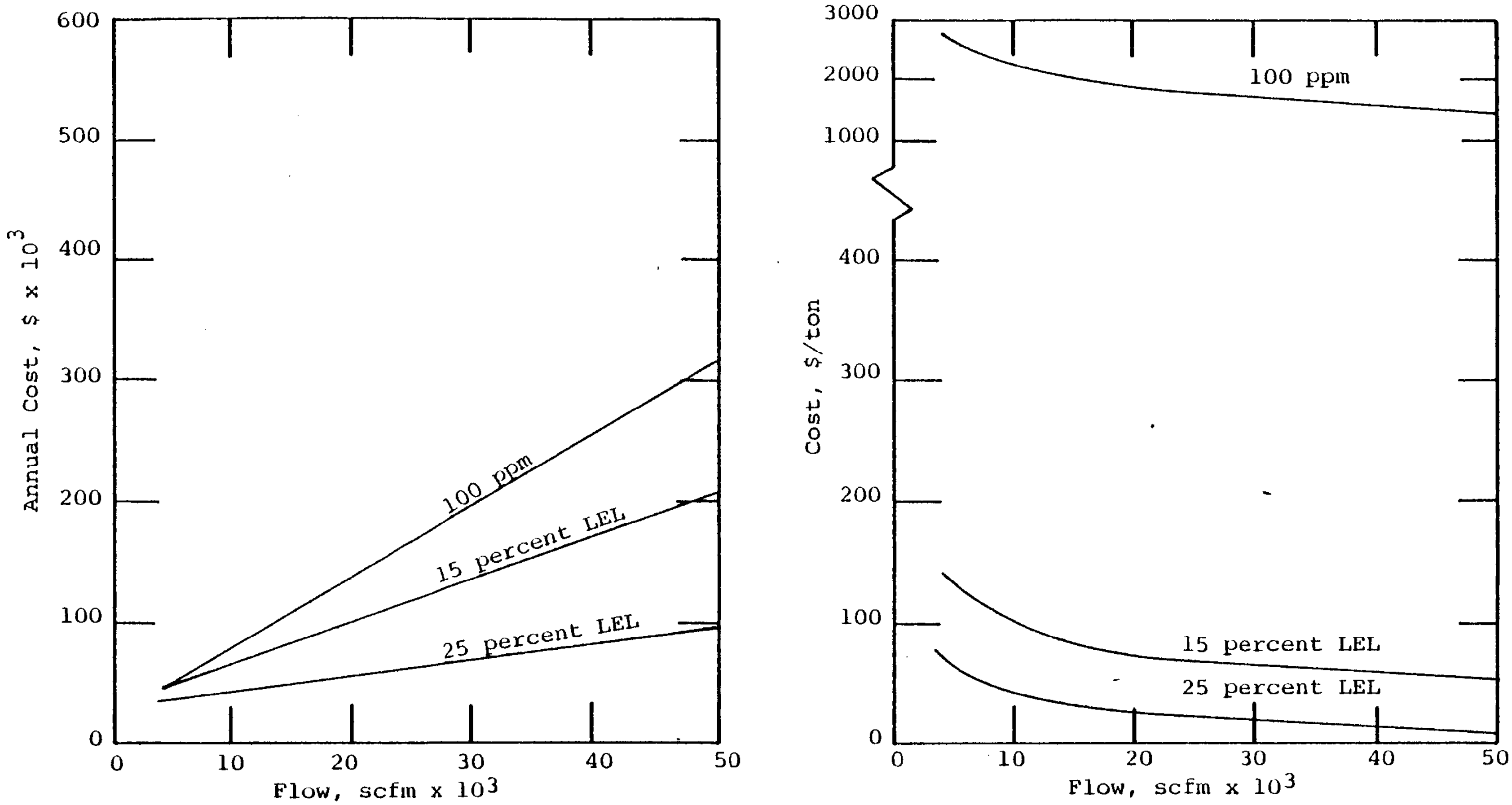

Figure 4-43. Annual cost and cost-effectiveness of catalytic incinerators (primary and secondary heat recovery - process temperature = 70 °F) Case 3 (1976 prices) (Ref. 4-2).

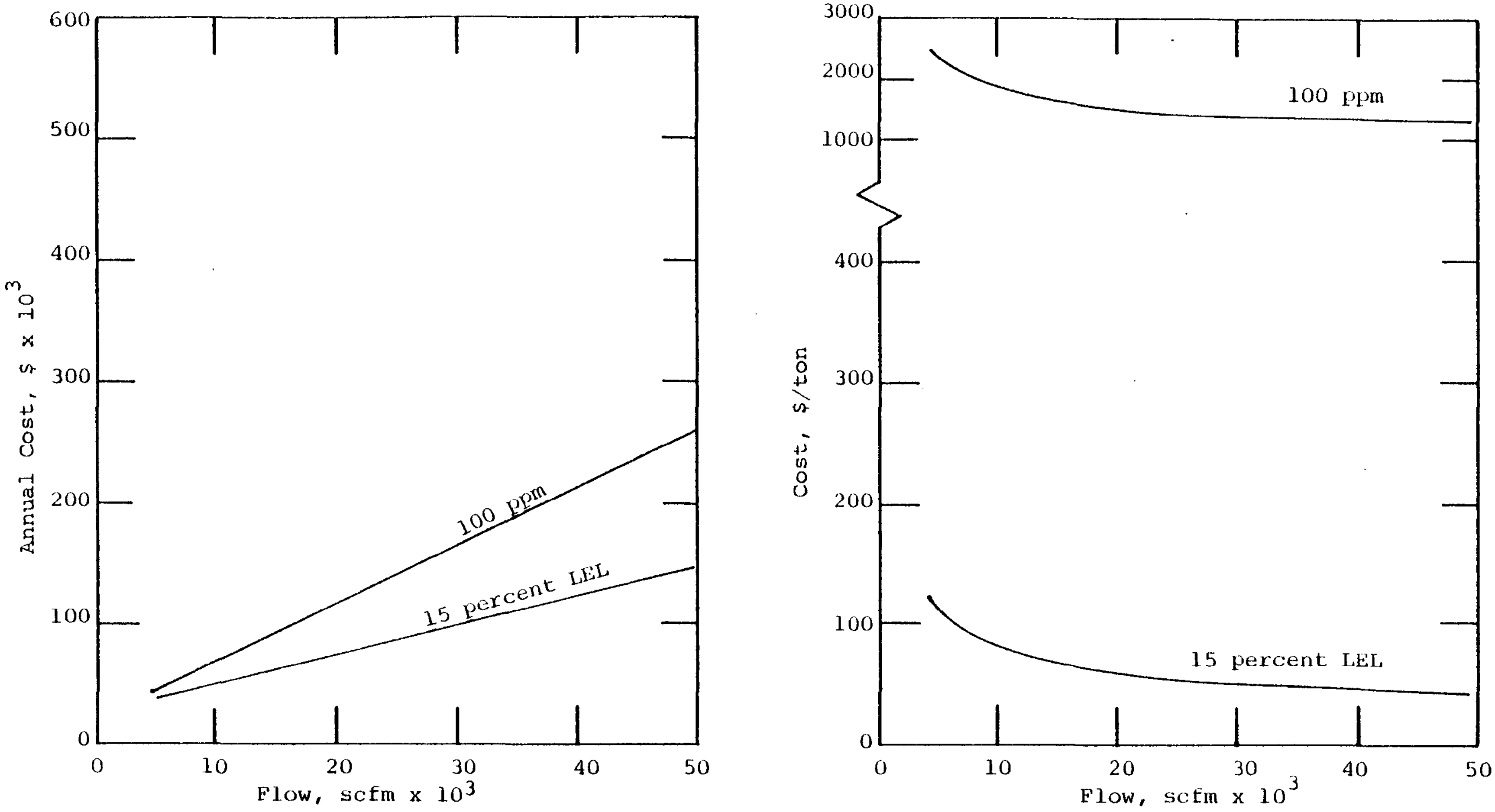

Figure 4-44. Annual cost and cost-effectiveness of catalytic incinerators (primary and secondary heat recovery - process temperature = 300 °F) Case 3 (1976 prices) (Ref. 4-2).

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The average installed cost of incinerators with primary heat recovery is roughly 25 to 30 percent greater than incinerators without heat recovery. Incinerators with primary and secondary heat recovery have roughly 50 to 60 percent higher installed costs than incinerators without heat recovery.

B. Annual Control Cost of Incinerators--

Annual control cost curves are given in Figures 4-31 through 4-34, Figures 4-36 through 4-39, and Figures 4-41 through 4-44 for the three heat recovery cases investigated. The costs obtained from these figures include a fuel cost of \$1.50/million Btu and operating time of 5840 hr/yr. If fuel cost and/or operating time for a specific installation differ from these values, the annual costs obtained from these figures can be adjusted by correction factors obtained from Figures 4-45 through 4-48. The annual costs read from the figures are multiplied by the correction factor(s). The cost effectiveness can be corrected by the following equation:

$$CE_c = CE_i \times F_f \times F_h \times \frac{5840}{\text{actual hours operated}}$$

where:

CE_c = corrected cost effectiveness

CE_i = cost effectiveness read from the appropriate figure

F_f = correction factor for fuel cost

F_h = correction factor for hours operated

The costs given in annual cost figures include depreciation and interest for the capital investment at a minimum retrofit cost situation. In cases where retrofit difficulties cause the installed cost to be increased substantially, an appropriate multiplying factor (retrofit difficulty factor) can be used to obtain the increased capital cost. The increase in annual cost, for a given retrofit difficulty factor, will be a varying amount for the different cases of vapor concentration, initial temperature, and heat recovery. The increase in the annual cost for the different cases is given in Tables 4-11 and 4-12. The annual cost is first read from the applicable figure, then is increased by the percentage given in Tables 4-11 and 4-12 under the appropriate difficulty factor.

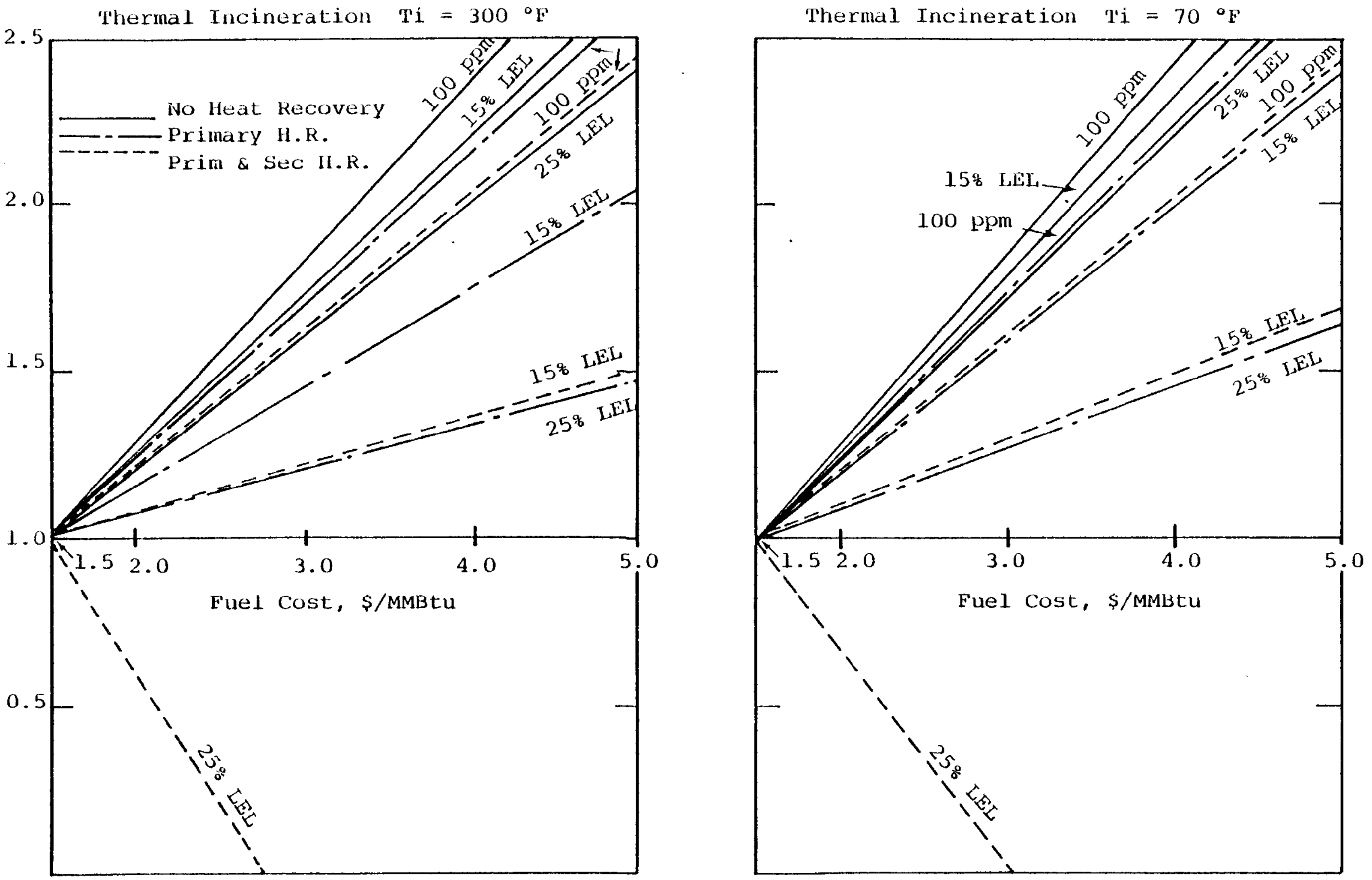

Figure 4-45. Factors to correct annual cost of thermal incineration for varying fuel cost (Ref. 4-2). Baseline cost $1.50/MMBtu.

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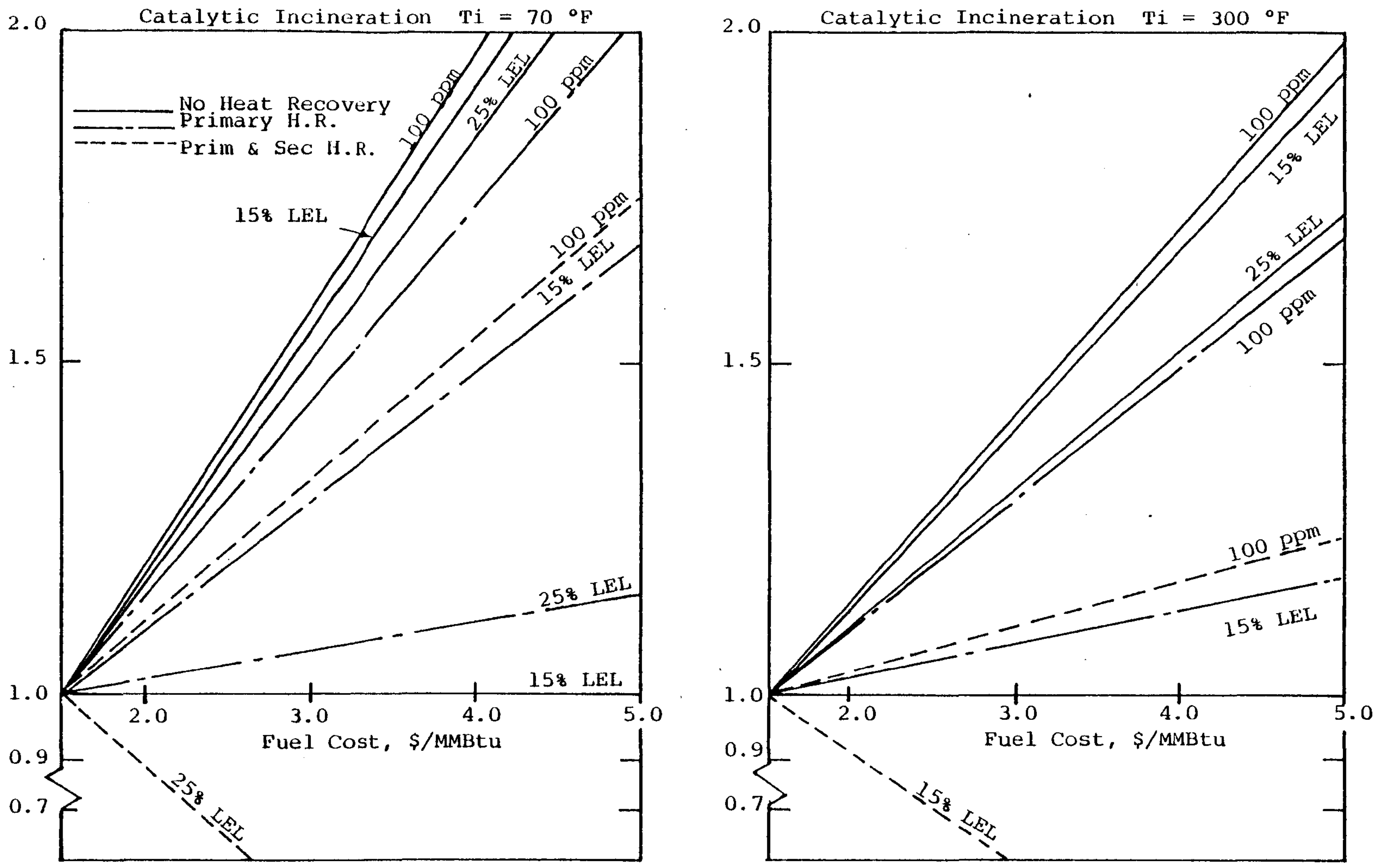

Figure 4-46. Factors to correct annual cost of catalytic incineration for varying fuel cost (Ref. 4-2). Baseline cost $1.50/MMBtu.

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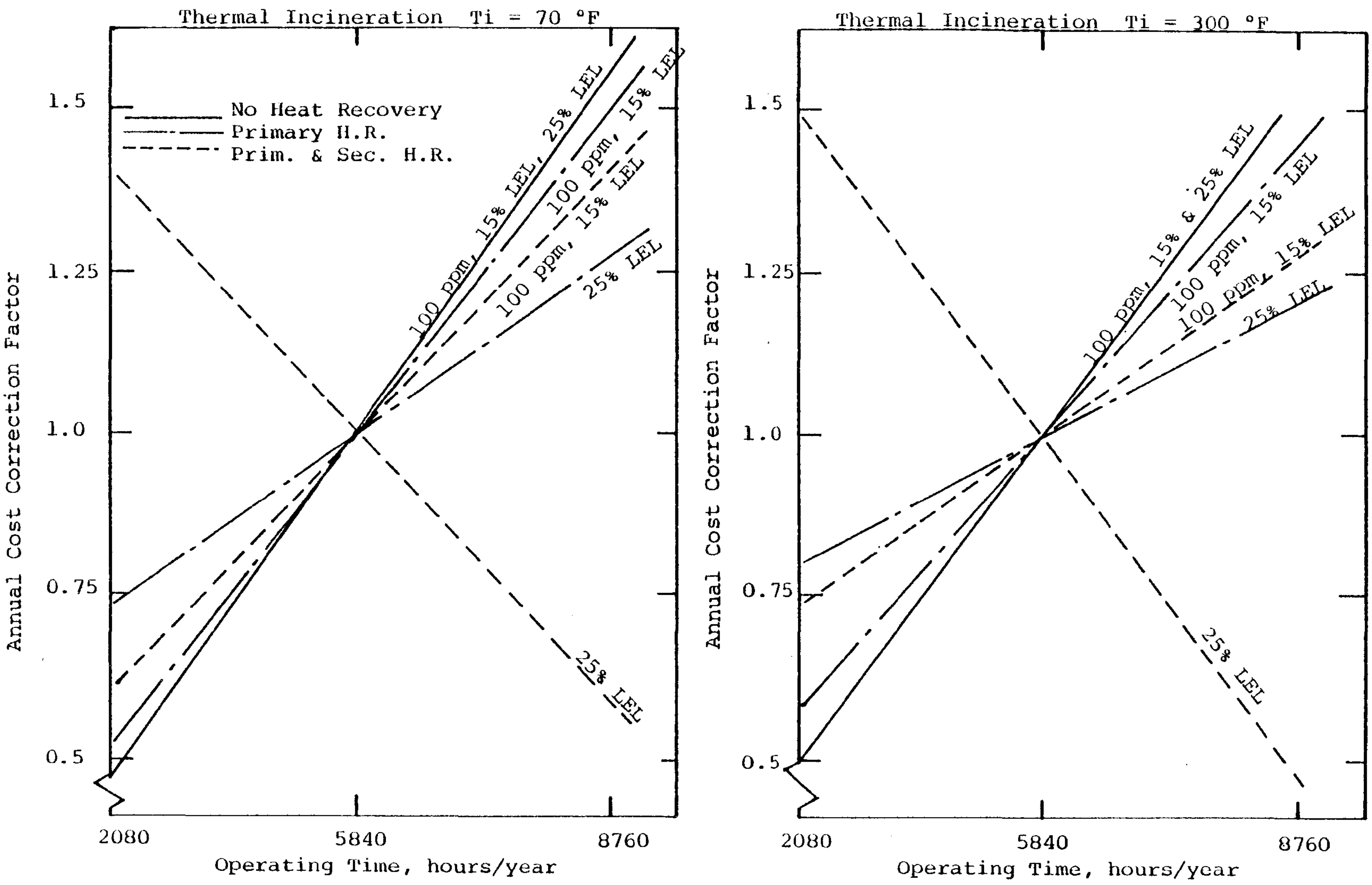

Figure 4-47. Factors to correct annual cost of thermal incineration for varying operating time (Ref. 4-2). Baseline operating time - 5840 hrs/yr.

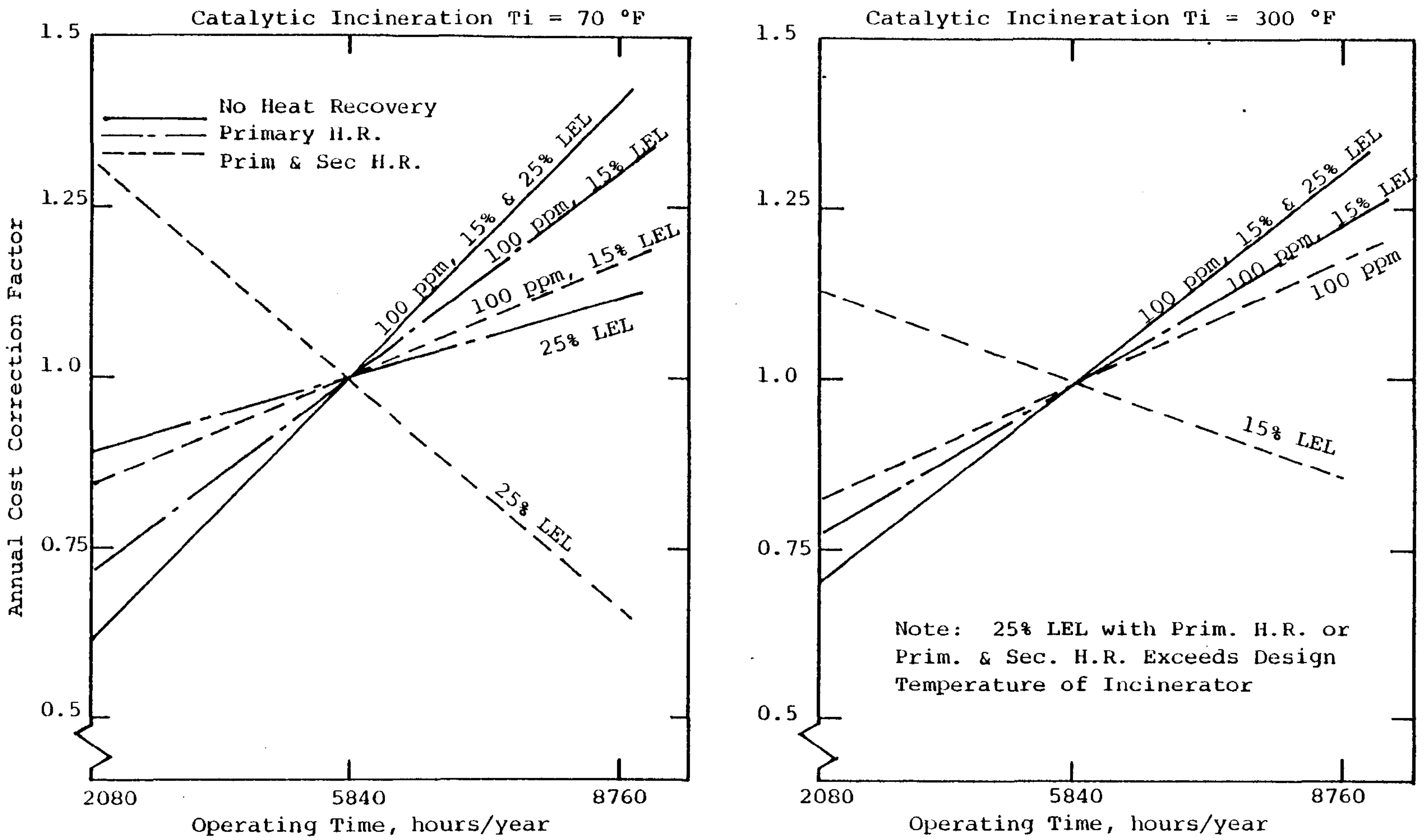

Figure 4-48. Factors to correct annual cost of catalytic incineration for varying operating time (Ref. 4-2). Baseline operating time - 5840 hrs/yr.

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TABLE 4-11. INCREASE IN ANNUAL COST OF DIRECT FLAME INCINERATORS DUE TO RETROFIT DIFFICULTY FACTORS (Ref. 4-2)

Vapor Concentration	Process Temperature	Heat Recovery	Percent Increase in Annual Cost At Retrofit Difficulty Factor: 1.5	2	3
100 ppm	70 °	None	2	5	9
15 percent LEL	70 °	None	4	7	14
25 percent LEL	70 °	None	5	10	20
100 ppm	300 °	None	3	6	11
15 percent LEL	300 °	None	4	8	16
25 percent LEL	300 °	None	7	15	30
100 ppm	70 °	Primary	4	9	18
15 percent LEL	70 °	Primary	8	16	32
25 percent LEL	70 °	Primary	17	33	66
100 ppm	300 °	Primary	5	10	20
15 percent LEL	300 °	Primary	10	20	40
25 percent LEL	300 °	Primary	20	40	80
100 ppm	70 °	Pri. & Sec.	8	16	32
15 percent LEL	70 °	Pri. & Sec.	16	32	64
25 percent LEL	70 °	Pri. & Sec.	80	160	320
100 ppm	300 °	Pri. & Sec.	10	20	40
15 percent LEL	300 °	Pri. & Sec.	25	50	100

TABLE 4-12. INCREASE IN ANNUAL COST OF CATALYTIC INCINERATORS DUE TO RETROFIT DIFFICULTY FACTORS (Ref. 4-2)

Vapor Concentration	Process Temperature	Heat Recovery	Percent Increase in Annual Cost At Retrofit Difficulty Factor: 1.5	2	3
100 ppm	70 °	None	6	13	25
15 percent LEL	70 °	None	6	13	26
25 percent LEL	70 °	None	8	15	30
100 ppm	300 °	None	8	16	33
15 percent LEL	300 °	None	9	17	34
25 percent LEL	300 °	None	11	22	43
100 ppm	70 °	Primary	6	13	25
15 percent LEL	70 °	Primary	11	22	45
25 percent LEL	70 °	Primary	22	44	88
100 ppm	300 °	Primary	10	20	40
15 percent LEL	300 °	Primary	15	30	60
25 percent LEL	300 °	Primary	16	33	65
100 ppm	70 °	Pri. & Sec.	12	24	48
15 percent LEL	70 °	Pri. & Sec.	18	36	72
25 percent LEL	70 °	Pri. & Sec.	36	72	144
100 ppm	300 °	Pri. & Sec.	14	28	56
15 percent LEL	300 °	Pri. & Sec.	25	50	100

C. Case Histories--

To check the data developed by EPA, KVB investigated several incinerator installations as follows:

Case 1 - A Metal Lithographic Sheet Coating

Parameter	Actual Case (Ref. 4-59)	Predicted by Study
Pollutant	Toluol 19	
Flow Capacity, scfm	6,000	6,000
Type Equipment	Direct Flame	Direct Flame
Concentration, ppm	2,500 (20% LEL)	20% LEL
H/C Flow, lb/hr	215	
Heat Recovery, 2 stage	31%/80%	35%/65%
Process Temperature, °F	300	300
Installed Cost, $	152,000	150,000
Annual Cost, $	65,000	40,000

Case 2 - An Antibiotic Spray Drying System

Parameter	Actual Case (Ref. 4-59)	Predicted by Study
Equipment Type	Direct Flame	Direct Flame
Pollutant	Soy & Corn Oil	
Flow Capacity, scfm	23,000	23,000
Heat Recovery, 2 stage	65%/43%	35%/65%
Installed Costs, $	240,000	210,000
Annual Cost, $	150,000	180,000

Case 3 - A Carbon Bake Oven

Parameter	Actual Case (Ref. 4-59)	Predicted by Study
Equipment Type	Direct Flame	Direct Flame
Pollutant	H/C & Particulate	
Flow Capacity, scfm	22,000	22,000
Heat Recovery, 2 stage	65%/62%	35%/65%
Installed Cost, $	235,000	200,000
Annual Cost, $	150,000	N/A

Case 4 - A Meat Rendering Plant

Parameter	Actual Case	Predicted by Study
Equipment Type	Direct Flame	Direct Flame
Pollutant	Odor	
Flow Capacity, scfm	6,800	6,800
Heat Recovery	2 stage	2 stage
Installed Cost, $	47,000	140,000
Annual Cost, $	14,000	50,000

Case 5 - A Rubber Processing Device

Parameter	Actual Case	Predicted by Study
Equipment Type	Direct Flame	Direct Flame
Pollutant	Mineral Oil	
Flow Capacity, scfm	4,000	4,000
Heat Recovery	2 stage	2 stage
Installed Cost, $	30,000	11,000
Annual Cost, $	11,000	40,000

4.3.3 Condensation

Condensation is used for recovery of organic vapor in various industries. The most frequent application is in the gasoline marketing field especially at bulk terminals where nearly saturated gasoline vapors are collected, condensed, and returned to liquid stage. Radian (Ref. 4-60) reviewed the various vapor recovery systems including costs using a 250,000 gal/day bulk terminal as a basis for comparison. Three systems were compared as follows:

1. Compression/Refrigeration/Adsorption (CPA)
   (The vapor is condensed by raising the pressure, cooling and spraying with liquid product)
2. Compression/Refrigeration/Condensation (CRC)
   (The vapor is condensed by pressure and cooling alone)
3. Refrigeration (R)
   (The vapor is condensed by a chiller alone)

A comparison of the three systems is presented in Table 4-13. The costs presented in this table have been escalated for inflationary trends from 1974 to 1976 over the costs presented in Reference 4-60. Escalation was according to the labor and equipment rates present in Chemical Engineering, May 9, 1977 (16% for equipment and labor).

In a vapor degreaser, chillers are used to reduce vapor emissions. EPA (Ref. 4-61) reports the following costs for refrigerated chillers:

	New Units	Retrofit
Installed Cost, 10^3 $	2.7 - 5.0	4.0 - 7.5
Net Annual Cost, $	(1066) to (24)	(646) to 204
Ton/year Saved	1 to 5	1 to 5
Cost Effectiveness, $/ton	(200)	(100)

This shows that both for new and retrofit applications the refrigerated chillers will pay for themselves in two to three years.

4.3.4 Absorption (Scrubbing)

Scrubbers are used primarily to remove SO_2 and particulates of all types - sulfates, nitrates and organics. In a few cases they may be used to control gaseous organic emissions particularly where the pollutant is water soluble. "Lean oil" has also been used as an absorbent in a scrubber to collect organic vapor such as gasoline. The "lean oil" absorption vapor recovery system is based on the absorption of gasoline vapors into lean gasoline stripped of light ends. Gasoline vapors are displaced through a packed absorber column where they are absorbed by cascading lean gasoline (also termed "sponge oil") at atmospheric temperature and pressure. Cleaned air is vented from the top of the absorber column. The enriched gasoline is returned to storage. Lean gasoline for the absorber is generated by heating gasoline from the storage tanks and evaporating off the light ends. The separated light ends are compreseed, condensed, and returned to storage, and the lean gasoline is stored separately for use in the absorption column.

TABLE 4-13. COST COMPARISON FOR VARIOUS CONDENSATION VAPOR RECOVERY SYSTEM FOR A 250,000 GAL/DAY BULK GASOLINE TERMINAL (Ref. 4-60)

System	SCFM	Installed Cost 10^3\$	Annual[†] Cost 10^3\$	Recovery Efficiency %	Tons Recovered/yr from 65/35(V) Gasoline/Air Ratio[§]	Cost Effectiveness \$/ton
CRA*	150	120-200	36-60	90-97	4,000	9-15
CRC*	150	100-145	30-45	90-96	4,000	8-11
R*	370	85-95	20-25	93-99	9,700	2-3

*CRA - Compression/Refrigeration/Adsorption

CRC - Compression/Refrigeration/Condensation

R - Refrigeration

[†] Annual Cost includes 25% of Installed Cost for depreciation, taxes, insurance, facilities overhead, etc.

[§] 0.23 lb/ft^3 (gasoline vapor) x scfm x 0.65 x 60 min/hr x 5840 hr/yr x ton/2000/lb = tons/yr

The reader is directed to the McIlvane Scrubber Manual (Ref. 4-62) for comprehensive cost data. The cost of a scrubber as with most add on systems depends on the volumetric flow rate and the properties of the exhaust stream. For an example, according to McIlvane (Ch. XI, Figure 8.2) scrubbers on an asphalt batching plant and animal rendering plant require the least amount of auxiliary equipment. The installed price for this type of scrubber at a flow of 50,000 ACFM would be approximately $70,000. A basic oxygen furnace closed hood system is among the most complex systems and a 50,000 ACFM scrubber would cost approximately $4 million. Thus it can be seen that the installed cost can run from $1 to $100 per CFM.

4.3.5 Vapor Space Elimination

A. Floating Roof Tanks--

The most common application of vapor space elimination is the use of floating roof tanks to replace fixed roof tanks. The EPA published some comparative costs for floating vs. fixed roof tanks and some cost effectiveness data for retrofitting fixed roof tanks to floating roofs (Ref. 4-63). These data are presented in Tables 4-14 and 4-15. The costs have been escalated by 20% to allow for the difference between prices in 1974 when Reference 4-63 was published to the present. Note that the storage of gasoline in floating-roof tanks rather than fixed-roof tanks, results in a slight savings, while the storage of the less volatile jet naphtha in floating-roof tanks rather than fixed roof tanks, results in a slight cost.

TABLE 4-14. INVESTMENTS - FLOATING ROOF VS. FIXED ROOF TANKS (Ref. 4-63)

Tank Size		Cost to Retrofit Fixed Roof to:		Δ Cost for New Construction Floating Roof Type vs. Fixed Roof		
Diameter in feet	Normal Capacity bbl*	Covered Floating Roof	Internal Floating Cover	External Pontoon Floating Roof	Covered Floating Roof	Internal Floating Cover
20	1,100	--	$3,400	--	--	$3,400
40	9,000	$20,000	$7,800	--	NA	$8,000
60	22,000	$31,000	$14,000	+$24,000	+$20,000	+$14,000
90	54,000	$50,000	$26,000	+$30,000	+28,000	+$29,000
110	80,000	$64,000	$48,000	+$32,000	+$40,000	--

*42 gals/bbl

TABLE 4-15. CONTROL COSTS FOR RETROFITTING FIXED ROOF TANKS (Ref. 4-63) TO COVERED FLOATING ROOFS

Product	Gasoline			Jet Naphtha		
Tank Size (10^3 bbls)	1.1	22	80	1.1	50	80
Investment Floating vs. Fixed (10^3 \$)	3.4	31	64	3.4	31	64
Annualized Cost* (10^3 \$)	(0.2)	(2.3)	(18)	0.4	2.9	3.4
Cost per gallon thruput ¢/gal	(0.04)	(0.04)	(0.04)	0.06	0.02	0.01

*Savings represented by parentheses

Recently, the ARB passed a new regulation for the South Coast Air Quality Management District (Rule 463) requiring double seals on floating roof tanks storing organic liquid with a true vapor pressure of 1.5 psi or greater. The installed cost of retrofitting existing tanks with a double seal which would comply with this rule has been estimated at $30 to $55 per linear foot of tank seal (Ref. 4-8). Since most storage tanks are field erected the additional cost for a double seal on a new tank would only be slightly less than the retrofit cost and probably within the range of $30 to $55 per foot indicated above.

B. Floating Covers on Oil/Water Separators--

The EPA (Ref. 4-65) based on their contacts with oil companies, provided an estimate of $\$8/ft^2$ for covering a new API separator with a floating roof and $13/ft for a retrofit. For a 5000 ft^2 forebay and waste water separator, the estimated costs were as follows:

Floating Cover	Capital Cost	Annual Cost*	Cost Effectiveness†
New	$40,000	$12,000	$140/ton
Existing	$65,000	$20,000	$230/ton

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*Includes 10% of capital used for operation and maintenance plus 10% interest for 10-year life.

†Based on an emission factor of 0.1 $lb/day/ft^3$ and a 95% control efficiency.

4.3.6 Liquid/Vapor Exchange

The primary use of liquid/vapor exchange emission control is for the transfer of petroleum and solvent products especially in gasoline marketing which is a major source of hydrocarbon emissions. In 1974 the EPA issued a study of control methods for gasoline marketing operations (Refs. 4-60 and 4-63). The following liquid/vapor exchange systems were proposed:

Tank Truck Delivery - Balance System

Per Service Station Delivering 25,000 gal/month of gasoline

	Recycled Vapor to Tank Truck	Vapor Recovery at Bulk Terminal	Total
Installed Cost, $	1,200	800**	2,000
Annual Cost,* $/yr	220	150	370
Emission Red., #/yr	1,900	1,700	3,600
Cost Effectiveness, $/ton	230	170	400
Cost per Gallon, $	0.001	0.0005	0.0015

*Includes 10% of Installed cost for amortization, etc.

**Bulk terminal cost indicated reflects proportioned amount per service station.

All costs escalated 15% from 1974 values in Ref. 4-63.

Automobile Filling - Balance System

25,000 gal/month Stations (Ref. 4-65)

Installed Cost - Retrofit, $	9,000
Installed Cost - New, $	3,000
Annual Cost (Retro)*, $	1,500
Emission Reduction, lb/yr	1,600
Cost Effectiveness, $/ton	1,875
Cost per Gallon, $	0.005

*Includes 10% of Installed cost for depreciation, etc.

From these data it can be seen that while the cost effectiveness $/ton is relatively high the actual price per gallon is minor.

4.3.7 Enclosure

The installed cost for 90-ft dia., 50,000 bbls, variable-vapor-space tanks are as follows:

Lifter Roof 5' dia.	$140,000
Lifter Roof 10' dia.	$170,000
Flexible	$180,000

These costs are based on values in Reference 4-60 escalated from 1961 to 1977 prices. Based on recent costs of $160,000 for a 50,000 bbl fixed roof tank in the same publication the escalation of the tabulated numbers seems reasonable. Based on AP-42 a 50,000 bbl, fixed roof tank would have breathing losses of 90 ton/yr of gasoline vapor. If 95% were recovered by addition of a variable vapor space tank at an annual cost of $17,000 (10% of the total tank price) the cost effectiveness would be $200/ton. The recovered vapor would be worth approximately $100/ton so the net cost effectiveness would be approximately $100/ton. In comparing this with the results in Table 4-16 it appears that the variable vapor space tank may be less cost effective than the floating roof tank. However, in view of the additional cost associated with the SCAQMD Rule 463 (double seal FRT) the variable vapor space tank may be reconsidered for storage applications.

The cost of covering drains as separators is difficult to estimate and no values could be found in the literature. Recently KVB investigated a technique for reducing emissions from refinery sewer systems. It was noted that vapors were emitted from the sewer opening where drainage pipes from various items of equipment discharged their leakage into the sewer. The emissions from the sewer opening were measured as a function of the wind blowing over the opening. It was noted that the emissions increased significantly with wind velocity and it was felt that a jet pumping action was produced by the wind.

4.3.8 Process and Material Charges

A. Automotive--

1. Electrophoretic dip premixing (Ref. 4-33)--The installed cost of an electrophoretic system for a typical vehicle assembly plant would be about $8 million. Costs will vary considerably depending on what building alteration and relocation of existing equipment is necessary. Table 4-16 gives increased operating costs for electrophoretic primer, based on electricity of $0.03/kWhr, interest and depreciation at 12 percent of capital costs, and operation for 4000 hours per year.

2. Low solvent primer and top coat (Ref. 4-33)--The achievable reduction depends on both the old coating and its replacement. For example, the 50 volume percent coating achieves an 86 percent reduction if it replaces a lacquer with 12 volume percent solids, but only a 53 percent reduction if it replaces an enamel with 32 volume percent solids. Obviously, even further reductions can be achieved if an add-on control device is also installed.

Typical capital costs for this option are difficult to assess because they depend completely on the specific plant situation. It is estimated that a change from lacquer to enamel would require a capital cost (including engineering) of $1,000,000. (General Motors claimed that it would be higher.) Based on a rule of thumb 12 percent of capital investment, annualized operating costs could be as high as $120,000 per year although this would be affected by the lower manpower required to apply enamels and the increased manpower which would be needed to repair damaged coatings.

3. Water-borne top coats--The cost of converting to water-borne top coats for an existing plant will vary. A major variable will be the age of the existing coating equipment. If near retirement, it may be better to build entirely new spray booths and ovens. This was done at one of two automobile plants in the Basin which converted to water-borne coatings. If the coating equipment is still relatively modern, however, retrofitting will entail lengthening of ovens and modification of spray booths and conveyors. This was the approach taken at the other automobile plant in the Basin using water-borne top coats.

TABLE 4-16. INCREASED ANNUAL OPERATING COST FOR ELECTROPHORETIC DIP PRIMERS COMPARED TO SOLVENT-BORNE PRIMER (REF. 4-33)

Utilities:		
Electricity	\$0.03/kWhr x 4000 hrs/yr x 1400 kW	168,000
Direct labor:		
Savings of	8 hrs/shift x 500 shift/yr 3 workers/shift \$15/hr	-180,000*
Interest and depreciation	12 percent x (1,000,000 to 8,000,000)[†§]	120,000 to 960,000

Total increased operating cost --- 108,000 to 948,000 \$/yr

*There is a net credit for labor cost for electrophoretic dip coating. The calculation is for the difference between one operator versus four in a conventional spray booth applying organic solvent-borne primer.

[†] Assuming 20 year life, 10 percent interest.

[§] The range of values is for different ages of the existing prime line. The lower value represents the increased total installed cost of an electrophoretic dip line over an organic solvent-borne prime line for a plant with an old prime line ready for replacement. The higher value represents the total installed cost for a plant with a new solvent-borne prime line.

Capital costs for a switch to water-borne top coats employing all new spray booths and ovens was estimated at $10 million while for a plant where the booths and ovens were retrofitted, the capital costs would be about half that amount.

Incremental operating costs include increased electrical requirements and increased maintenance labor. Coating material costs are approximately the same. Higher oven temperature causes an increase in natural gas usage. Annualized operating costs for the model are given in Table 4-17.

TABLE 4-17. INCREASED ANNUAL OPERATING COST ESTIMATE FOR WATER-BORNE TOP COATS OVER ORGANIC SOLVENT-BORNE TOP COATS (Ref. 4-33)

Utilities: Electricity	$0.03/kWhr x 4000 hrs/yr x 5000 kW	$600,000
Direct labor:	20 additional hrs/shift x 500 shifts/yr $15/hr	$150,000
Maintenance Building overhead Taxes and insurance Interest and depreciation*	21 percent x capital costs = 0.21 x $20,000,000	$4,200,000
Total increased operating cost		$4,950,000/yr

*Assuming a 20 year life and 10 percent interest charge

B. Paper Coating - Low Solvent Coatings--

Costs will vary for low solvent systems depending on the type of low solvent coating and the particular end use. The low solvent coatings will be economical once the technology has been established, but there can be large costs involved in initially developing the coatings, purchasing new application equipment and learning to use the new systems.

Cost comparisons between various low solvent coatings are not as easy to make as are cost comparisons between various types of add-on control systems. However, a detailed cost comparison has been made between various types of silicone application systems. This comparison is shown in Table 4-18. The cost of learning to apply water-borne systems to paper could be very large.

TABLE 4-18. CAPITAL COST OF SILICONE COATING SYSTEMS IN PAPER COATING INDUSTRY

Coating systems	Net Cost $/lb of Silicone Solids on Paper
Solvent (with solvent recovery)	8.20
Solvent (with solvent incineration)	7.38
Solventless (heat cure)	7.11
Solvent (with no recovery)	6.69
Water emulsion system	5.28

The emulsion system is the lowest in cost, but the 100 percent solventless (pre-polymer) process may prove to be the most practical system in the long run. It may be difficult for paper coaters that are familiar with organic solvent-borne systems to switch to a water-borne system because of wrinkling of the paper and other application problems.

Additional costs will be associated with switching to 100 percent nonvolatile (pre-polymer) coatings. Most organic solvent-borne silicone release coatings are currently applied by gravure or reverse roller. None of these are suitable for solventless coatings. Solventless coatings must be applied with 3-roll or 4-roll offset gravure presses. These cost from $25,000 to $200,000 per coating line. A cost of $100,000 would be about average. Because of these costs, availability of capital can be an impediment to the adoption of solventless silicone coatings.

4.3.9 Maintenance

The cost effectiveness is impossible to generalize. As discussed in Section 4.1.9, it is debatable as to whether a special leak control program in a refinery would be cost effective. (The leak control program would be beyond the scope of normal maintenance.) A study more comprehensive than afforded by this program would be required to completely assess this prospect.

The EPA (Ref. 4-65) provided some interesting cost data which could contribute to a study of overall costs of reducing fugitive emissions from refineries. Their information came from equipment manufacturers and oil companies, and are based on 1976 prices:

A. Pump Seals--

1. Mechanical seals (cost per pump)

Extra cost for mechanical seals on new pumps (shaft size 1" to 3")	\$200 to \$1200
Retrofit cost for mechanical seals on used pumps (shaft size 1" to 3")	\$2000 to \$3000
Annual cost to replace seals every two years (shaft size 1" to 3")	\$500 to \$1200

2. Dual mechanical seals (cost per pump)

Extra cost for new pumps (shaft size 1" to 3")	\$800 to \$3000
Retrofit cost (shaft size 1" to 3")	\$3000 to \$3500
Annual cost to replace seals every two years (shaft size 1" to 3")	\$1300 to \$2700

The costs vary with the shaft size over the range indicated.

B. Compressor Seals--

1. Centrifugal--Centrifugal compressors may be equipped with oil seals which collect hydrocarbon emissions. The oil is processed by a system which reclaims the product collected in the oil. The 1976 costs for an oil seal system on a compressor between 1500 and 10,000 HP, based on the EPA data from industry, is as follows:

New compressor cost including oil system	$700,000
Retrofit cost	$150,000
Annual cost	$ 45,000

2. Reciprocating compressors--Reciprocating compressors may be equipped with labyrinth type mechanical seals. An estimate of costs for a double labyrinth seal compressors in the size range of 50 to 1500 HP is as follows:

New compressor	$50,000 to $500,000
Extra cost for double labyrinth seal	$1,000 to $8,000
Retrofit cost	$25,000 to $250,000 (up to cost of new unit)
Annual cost	$7,000 to $80,000

These and other miscellaneous refinery costs should be published by the EPA in a report entitled "Control of Hydrocarbon Emissions from Miscellaneous Refinery Sources."

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SECTION 5.0

ANTHROPOGENIC EMISSION FORECAST

With the inventory results presented in Section 2.4 as a baseline, a ten-year forecast was made of the stationary source anthropogenic emissions. The forecast was based on the industry growth projections prepared by the ARB (Ref. 5-1) and some unpublished projections provided by SCAG (Ref. 5-2). Table 5-1 summarizes the projection calculations. The 1975-76 emissions come from Table 2-40. The industrial growth factor was based on the projections in the above references. A weighted average of the various county growth factors was determined. Weighting was distributed according to the point source emissions, which emphasize emissions in LA County. The general industrial growth is 3%/year. Combustion of fuel was projected at a lower rate because of natural gas curtailment and because of the anticipated requirements for adding sulfur dioxide scrubbers on oil-fired units. Probably no additional utility boilers will be built in the Basin and the numbers of new industrial boilers will be few. Also since the population in the Basin is projected to increase 10 to 15% (mostly in counties other than LA), there will be some increase in domestic fuel consumption.

The projections of emission reductions due to controls was based on the impetus provided by the Clean Air Act as amended in 1977. This requires each state and air quality control region to implement a plan to achieve the national ambient air quality standards for oxidant by 1987.

An estimated 80 to 85% reduction for petroleum sources is based on recent ARB/AQMC/APCD efforts to control pipeline and storage tank leakage. Improved valve maintenance and retrofit double seals on floating roof tanks is predicted.

Combustion of fuels offers little potential for organic emission reductions. In most instances, the organic emission concentration is of the order of 1 to 10 ppm. There are no practical methods to reduce emissions at this level. Only in the case of poorly maintained combustion devices, some significant improvement may be made. Some of these maintenance improvements, which will be made, account for the 5% reduction estimate. The surface coating reduction of 75% is attributed to improved controls on industrial operations, the changing to water-borne paints, etc. However, recognition is given to the continued use of solvent based paints for repainting operations as well as for numerous specialized commercial and domestic painting applications.

The dry cleaning reduction of 40% may seem low; although exhaust emission can be controlled to better than 99%, many of the emissions are fugitive. Solvent, which adheres to the cleaned clothes, eventually evaporates.

The reduction of methane emission can be accomplished by preventing leaks (of all types.) Other control techniques like adsorption or incineration are not very effective for abating methane emissions. Therefore, the 50% reduction of methane emissions was assumed for petroleum sources due to improved maintenance practices reducing leaks.

The projected emissions are a simple calculation of baseline emissions X (1 + projected growth) X (1 - control efficiency). The results are tabulated in Table 5-1. Figure 5-1 shows a plot and summary of the emissions projected for the next ten years. The percent reductions at the end of the ten years are summarized on the figure.

TABLE 5-1. STATIONARY SOURCES IN THE SOUTH COAST AIR BASIN
ANTHROPOGENIC EMISSIONS PROJECTION
1976-1986

Application Categories	1975-76 Emissions, Ton/Day Nonmethane	1975-76 Emissions, Ton/Day Methane	Projected Industry Growth By 1986 %	Aver. Control Efficiency by 1986 % Reduction Nonmethane	Aver. Control Efficiency by 1986 % Reduction Methane	Projected Emissions Ton/Day Nonmethane	Projected Emissions Ton/Day Methane
Petroleum Production	56	38	6	85	50	11	20
Petroleum Refining	107	8	20	85	50	19	5
Petroleum Marketing	110	80	0	80	50	22	40
Surface Coating	115	8	30	75	25	38	8
Dry Cleaning	38	0	0	40	--	22	0
Degreasing	33	0	30	80	--	8	0
Other	18	1	30	90	--	2	1
Chemical	4	0	50	85	--	1	0
Metallurgical	1	1	15	50	--	1	1
Mineral	1	0	10	90	--	0	0
Waste Burning	0	1	0	40	--	0	1
Combustion of Fuel	12	4	6	5	--	12	4
Food & Agriculture	1	0.4	15	80	--	0	0
Pesticide	15	0.4	10	50	--	8	0
Misc. Industrial	1	11	30	90	--	0	1
	510	150				150	80

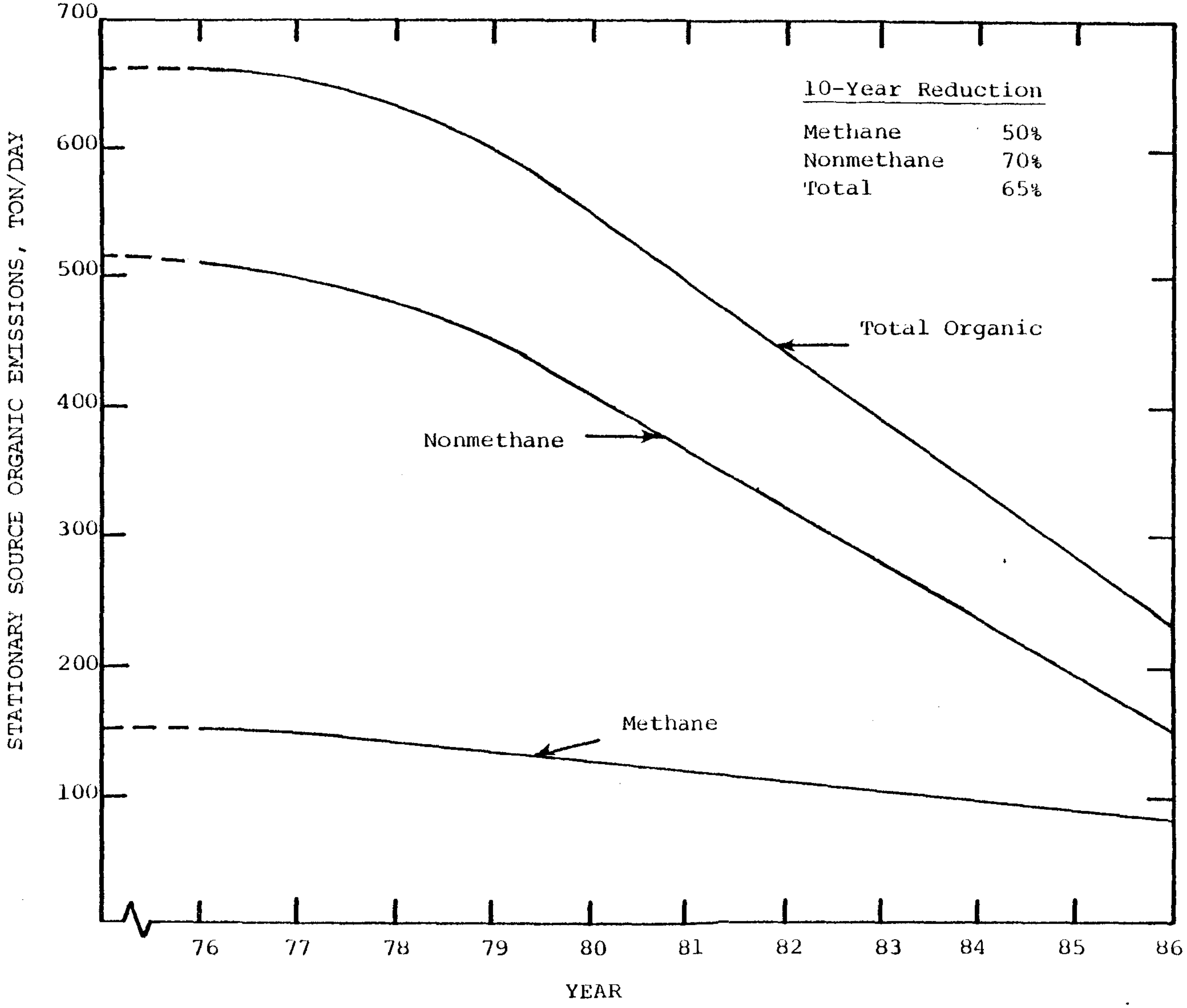

Figure 5-1. Anthropogenic stationary source organic emissions projection, 1976-1986.

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SECTION 6.0

ABBREVIATION LIST

ACFM	- Actual Cubic Feet per Minute
AP-42	- Emission Factor Publication (see Reference 2.3)
APCD	- Air Pollution Control District
API	- American Petroleum Institute
AQCR	- Air Quality Control Region
ARB	- California Air Resources Board
ARCO	- Atlantic Richfield Corporation
ARLI	- Analytical Research Laboratories, Inc. of Monrovia, CA
AV	- AeroVironment, Inc. of Pasadena, CA (consultants)
AVQUAL	- Designation given to a plume dispersion model
C2, C3, etc.	- General hydrocarbon formula (aliphatic) indicating number of carbon atoms in the molecule
CARB	- California Air Resources Board (usually just ARB)
CEC	- Consolidated Electrodynamics Corp.
EIS/P&R	- Emission Inventory Subsystem/Permit and Registration
EPA	- Environmental Protection Agency
ESS	- Eco Science System, Riverside, CA (consultants)
FCC	- Fluidized-bed Catalytic Cracker, refining equipment
FID	- Flame Ionization Detector
FM	- Fire Marshall (as in FM approved)
GC	- Gas Chromatograph
GC/FID	- Gas Chromatograph with a Flame Ionization Detector
GC/MS	- Gas Chromatography/Mass Spectrometry
GM	- General Motors
HC	- Hydrocarbon
HP	- Horsepower
IBM	- International Business Machines
IC	- Internal Combustion
ID	- Identification
LA	- Los Angeles
LEL	- Lower Explosion Limit
M.E.K.	- Methyl Ethyl Ketone
MIBK	- Methyl Isobutyl Ketone
MMBtu	- Million British Thermal Units
M.W.	- Molecular Weight
Mwt	- Molecular Weight
NBS	- National Bureau of Standards
NC	- No (emission) Control

Continued

ABBREVIATION LIST (continued)

OPR	- California Governor's Office of Planning and Research
PD	- Positive Displacement
ppm	- Parts per Million
P/V	- Pressure/Volume
PVC	- Polyvinyl Chloride
QC	- Quality Control
RETA	- Ryckman, Edgerley, Tomlinson & Associates, Consultants in St. Louis, MO
RVP	- Reid Vapor Pressure
SAROAD	- Storage and Retrieval of Aerometric Data (A Coding System for Aerometric Data)
SBAPCD	- Santa Barbara Air Pollution Control District
SCAB	- South Coast Air Basin (often just Basin)
SCAG	- Southern California Association of Governments
SCAPCD	- Southern California Air Pollution Control District (predecessor to SCAQMD)
SCAQMD	- South Coast Air Quality Maintenance District
SCC	- Source Classification Code
SDAPCD	- San Diego Air Pollution Control District
SIC	- Standard Industrial Code
SKC	- SKC, West Fullerton, CA (Chemical Equipment Supplies)
SOHIO	- Standard Oil of Ohio
TLV	- Total Level; Designation for Bacharach Total Hydrocarbon Sniffer
TOC	- Total Organic Content
UCR	- University of California at Riverside
UTM	- Universal Transverse Mercator
UV/VIS	- Ultraviolet, Visual Range
VAPCD	- Ventura Air Polltuion Control District
VW	- Volkswagen
WOGA	- Western Oil and Gas Association
XAD-2	- Designation for a sorbent material, i.e., chromasorb XAD-2