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Proceedings:
Symposium on Atmospheric Emissions from Petroleum Refineries (November 1979, Austin, TX)

Interagency Energy/Environment R&D Program Report

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EPA REVIEW NOTICE

Proceedings: Symposium on Atmospheric Emissions from Petroleum Refineries (November 1979, Austin, TX)

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ABSTRACT

The proceedings are a compilation of papers, formal discussions, and question and answer sessions from the EPA-sponsored Symposium on Atmospheric Emissions from Petroleum Refineries, November 5-6, 1979, in Austin, Texas. The symposium focused on results of the petroleum refining environmental assessment program conducted by Radian Corporation under the sponsorship and direction of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC. The 4-year program cost $2.5 million and included extensive sampling of atmospheric emissions in 13 oil refineries throughout the U.S. Papers were presented by Radian and EPA on emissions measurement, quality control, and analysis and application of results. Emphasis was on fugitive emissions. Formal discussions of each paper were provided: discussors included petroleum industry representatives, environmental consultants, and state environmental regulatory personnel. Each paper and formal discussion was followed by a question and answer session between the audience and the presenter.

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WELCOME

Dr. Donald M. Carlton

President, Radian Corporation

Austin, Texas

I appreciate this opportunity to visit with you for a few minutes this morning. Anyone who shows up at 8:30 on Monday morning to talk about fugitive emissions has to be very dedicated. So it is a pleasure to see so many people.

The term fugitive emissions and the whole topic means a lot of things to a lot of different people. I would like to give you a little Radian history on fugitive emissions, because I think it might set the stage for why we are here this morning.

At Radian Corporation, fugitive emissions began as a topic of some interest in the early 70s. We received a contract from EPA and CEQ to investigate the environmental impact associated with siting petroleum refineries. In particular, refineries sited in coastal areas. The ground rules were to make use of existing information. We were fortunate being able to find quite a bit of information in the literature about refinery technology.

Then we came to the issue of fugitive emissions, and we found two sources of information about fugitive emissions. One was some work that Bernie Steigerwald and others did in Los Angeles in the late 50s. The other was unaccounted for data furnished by API. Those were fairly tenuous grounds for the basis of fugitive emission projections, but nevertheless, that is all we had. We reported that if you believed that kind of information, fugitive emissions were a first class problem. We reported that you should be careful with these numbers and that we felt like they did not mean a whole lot. But, as those kind of things typically happen, there is sometimes a matter of interpretation. All of a sudden, we found that the name Radian Corporation was the subject of much criticism among oil companies and petrochemical processors for awhile.

But, as I am sure each of you know this is indeed an important topic and has tended to be an emotional topic, because after that particular report we found ourselves testifying in several hearings on refinery technology, about the need for addressing the issue of fugitive

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emission's experimentally. The EPA and API, of course, were well aware of the problem. They got their heads together, and fortunately, all of that conversation led to where we are today.

We hope, as a result of these two-day discussions, that we will be able to come away with a far better understanding of the issue of fugitive emissions and hopefully "incumber the topic with data" as someone said. So, I am hopeful, as I am sure you are, that we will get fugitive emissions on a much firmer ground.

So, it is my pleasure to welcome you here today. I certainly hope we all have a good two days and want you to know that if there is anything that we can do to make you stay more informative, more enjoyable, please be sure to let us know.

Glad to have you.

OPENING COMMENTS

Dr. Donald D. Rosebrook

Senior Program Manager, Radian Corporation

Austin, Texas

I would like to acknowledge the support of the EPA for providing
the funding for this symposium. I would like to thank in advance those
people who have so graciously given of their time to be reviewers of these
papers.

We have had previous symposia on emissions from petroleum refining.
In those cases we have generally invited industry participation, participa-
tion from other government agencies and from other consulting firms. In
this case our object is to report completely on the results of the EPA
study conducted by Radian. In order to give it a more general form, our
format was to invite reviews from eminently qualified people in the
industry and from among our competition. We hope that this meeting will
serve a good purpose for all of you who have attended.

We started the work which we are going to report upon almost four
years ago, and first went into the field almost three years ago. We have
had a great deal of cooperation from all parties involved, and we would
also like to acknowledge that; especially the refiners who were so gracious
as hosts in this study. And we thank them for their participation and their
desire to understand what we were doing and to help us do it. And it is,
in a very large measure, their assistance which has made this study possible.

We have visited thirteen refineries to provide the data which
you are going to hear today. In addition to that we have had contributions
from other refineries, where the work was done under contract to the
refiners, and Radian and the EPA considered the data to be of sufficient
importance to use those pieces which were appropriate in preparing the
results of this study.

We started with three objectives. We think that by in large we
have met the requirements of those three objectives. The first of those
and that which is probably the most publicized was to determine emission
factors for fugitive emissions from refining activities. The second was
to evaluate the available control technology for not only fugitive emissions,
but other refining activities which could have atmospheric hydrocarbon

emissions. The third objective was to determine precisely what was the composition of those emissions and to determine whether or not materials, which were being emitted, posed some type of a human health hazard.

The presentations which you will hear today and tomorrow will address these questions, and will show that we have met the objectives of the study.

We would like to start today's presentations with a description of the methodology that was used and we will proceed to the methodology used in evaluating the data, then show you the data. We will proceed to talk about control technology and the other factors which this meeting will address.

METHODOLOGY – SAMPLING AND ANALYSIS OF ATMOSPHERIC EMISSIONS FROM PETROLEUM REFINERIES

C. D. Smith
Radian Corporation
Austin, Texas

ABSTRACT

This paper contains a description of the sampling and analytical methodologies used to sample fugitive emissions and emissions from point sources in petroleum refineries. Emphasis is placed on fugitive emissions.

RESUME

Calvin D. Smith is a Senior Scientist in the Technical Division at Radian Corporation. His formal training at Clemson University and the University of Georgia was in physical-organic chemistry. He has worked in industry as Operations Manager of Story Chemical Corporation and as Manager of Pilot Plants at Velsicol Chemical Corporation. At Radian Mr. Smith was Field Supervisor for Refinery Sampling Program.

C. D. Smith

METHODOLOGY - SAMPLING AND ANALYSIS OF ATMOSPHERIC
EMISSIONS FROM PETROLEUM REFINERIES

SECTION 1

INTRODUCTION

The purpose of this paper is to describe the sampling and analytical methodology used while sampling for atmospheric emissions at petroleum refineries. Those methods that are commonly accepted as routine methods will receive less emphasis than newer techniques.

Three areas of sampling took place.

- Stack effluents.

- Wastewater and cooling tower emissions.

- Fugitive emissions from process unit sources.

These will be discussed in the following sections.

SECTION 2

FIELD SAMPLING

FUGITIVE EMISSIONS FROM PROCESS SOURCES

Baggable sources have been defined as those sources that can be completely enclosed and sealed in a manner sufficient to prevent any loss of material to the atmosphere from inside the enclosure or "bag." These sources represent the majority of the potential sources selected for testing at each refinery. They include valves, flanges, pump seals, compressor seals, drains and relief devices.

Baggable Source Selection – Important Variables

Variables thought to affect the fugitive emissions from baggable sources were classified into choice and correlating parameters. The variables were further defined according to availability and usefulness. Availability was determined from the degree of difficulty expected when obtaining the necessary data in the field. Some information, such as pressure or temperature, is readily available. Other facts, such as age of valve packing, might be unavailable.

The final usefulness of a variable in the computation of the fugitive emissions from a refinery was also considered. Some important variables were not categorized for sampling because of their lack of ultimate usefulness. For example, using the age of some equipment as a parameter may not be very useful. Most refiners do not know the age of valve packing or flange gaskets, for example.

Prioritizing variables according to these criteria allowed the most significant ones to be determined for each baggable source. Decisions were then made concerning which categories should be used to define the types and numbers of fugitive sources to be sampled.

Site-Specific Sampling Plan

Structured flexibility formed the tone of the sampling plan. The structure assured that all needed measurement and analysis requirements were efficiently covered. Flexibility was maintained within a procedural framework to apply what was learned toward subsequent sampling and analysis.

The sampling plan structure consisted of outlining detailed procedures before sampling began. This included:

- Identification of process units to be sampled.

- Number and type of fittings within units.

- Specifying choice and correlating variables (choice variables specify sampling categories, while correlating variables are others we wished to record because they might be important).

- Developing forms for recording screening, sampling, variables, and analysis results.

Each site specific sampling plan reflected modifications due to what had been learned at previous refineries.

Baggable Source Selection - Field Selection

The initial steps of the selection process were carried out prior to the start of field sampling. These steps included the selection of individual process units to be sampled, and the development of a format for the selection of individual sources.

The primary goals of the preselection process were to obtain:

- A statistically unbiased set of fittings, selected in a random manner.

- A wide range of correlating parameters or process conditions for each set of selected fittings.

The selection of individual baggable sources was done using piping and instrumentation diagrams or process flow diagrams supplied by the refiner. Baggable sources included valves, flanges, pumps, compressors, drains, and pressure relief devices. The approixmate number of sources selected at each refinery was:

Valves	250 – 300
Flanges	100 – 750
Pumps	100 – 127
Compressors	10 – 20
Drains	20 – 40
Relief Devices	20 – 40

Selecting fittings from the process flow diagrams gave two important benefits. First, this method eliminated any bias which might have resulted had these fittings been selected in the field. That is, fittings which could

be determined to be leaking by observation were not selected preferentially over nonleaking fittings or vice versa. Second, a wide variation in process conditions was desired. Using basic knowledge of the process operation, it was possible to distribute the allotted fittings such that a wide range in the values of variables thought to affect the emissions rate was obtained.

The variables chosen for each type of fitting consisted of the characteristics of the fluid within the fitting and the physical character-istics of the fitting itself. Choice parameters were defined as variables that might directly affect fugitive emissions and were used in selecting the source distribution. The choice parameters used for each fitting type at the first nine refineries are listed in Table 1.

Valve Selection

The selection method used in the field is detailed below for valves.

The most difficult choice parameter to select was the valve size. In most cases, a complete range of valve sizes was not present in an individual process unit. However, since many of the same process units were chosen in several refineries, an exact distribution within each individual unit was not considered essential.

In general, all of the different hydrocarbon streams within the process unit were incorporated into the valve selection process. When there was more than one valve for each process stream (as was most always the case), valves were selected to give a variety of temperature/pressure combinations for each process stream.

The selection of valves within each process unit was based on a format of the type illustrated in Figure 1. In general, the number of valves allotted to each final grouping was based roughly on the proportion of valves in the process unit corresponding to that grouping. For example, a larger fraction of the valves would be assigned to the gas/vapor groups in a gas processing unit than in a lube oil processing unit.

Screening

In order to minimize the number of sources which were bagged, a preliminary screening was carried out to determine the need for sampling. Those sources which were found to be leaking significant amounts of material were sampled. When it was determined that the leaks were absent or insignifi-cant, sampling was not done. All the choice and correlating variables were recorded, however, for those sources that were screened but not sampled as well as for those sampled. The values were recorded on formatted data sheets. An example of these data sheets is shown in Figure 2.

TABLE 1.   RANGE OF CHOICE VARIABLES FOR SCREENED BAGGABLE SOURCES

Baggable Source	Choice Variable	Variable Ranges for Screened Sources
Valves	Pressure	-10 - 3000 psig
	Temperature	-190 - 925°F
	Fluid State	Gas, Liquid, 2-phase
	Service	In-line, Open-ended
	Function	Block, Throttling, Control
	Size	0.5 - .36 inches
Flanges	Pressure	-14 - 3000 psig
	Temperature	-30 - 950°F
	Fluid State	Gas, Liquid, 2-phase
	Service	Pipe, Exchanger, Vessel, Orifice
	Size	1 - 54 inches
Pump Seals	Pressure	0 - 3090 psig
	Temperature	0 - 800°F
	Capacity	0 - 100;000 gpm
	Shaft Motion	Centrifugal, Reciprocating
	Seal Type	Mechanical Seal, packed seal
	Liquid RVP	Complete range
Compressor Seals	Pressure	0 - 3000 psig
	Temperature	40 - 300°F
	Shaft Motion	Centrifugal, reciprocating
	Seal Type	Packed, labyrinth, mechanical
	Lubrication Method	Hydrocarbon lubricant
	Capacity	0.06 - 66.0 MMSCFD
Drains	Service	Active, Wash-up
Relief Valves	Pressure	0 - 1350 psig
	Temperature	40 - 1100°F
	Fluid	Gas, Liquid

Organization of Choice Variables	Typical Number of Allotted Valves

Selected Process Unit —— In Line Valves

Gas/Vapor Service

Control Valves

Size

4"	1
4-8"	2
8"	1

Block Valves

Size

4"	2
4-8"	4
8"	2

Liquid Service

Control Valves

Size

4"	3
4-8"	3
8"	3

Block Valves

Size 4"	7
4-8"	7
8"	7

Open Ended Valves — Drain Valves	1
Sample Valves	1
	44
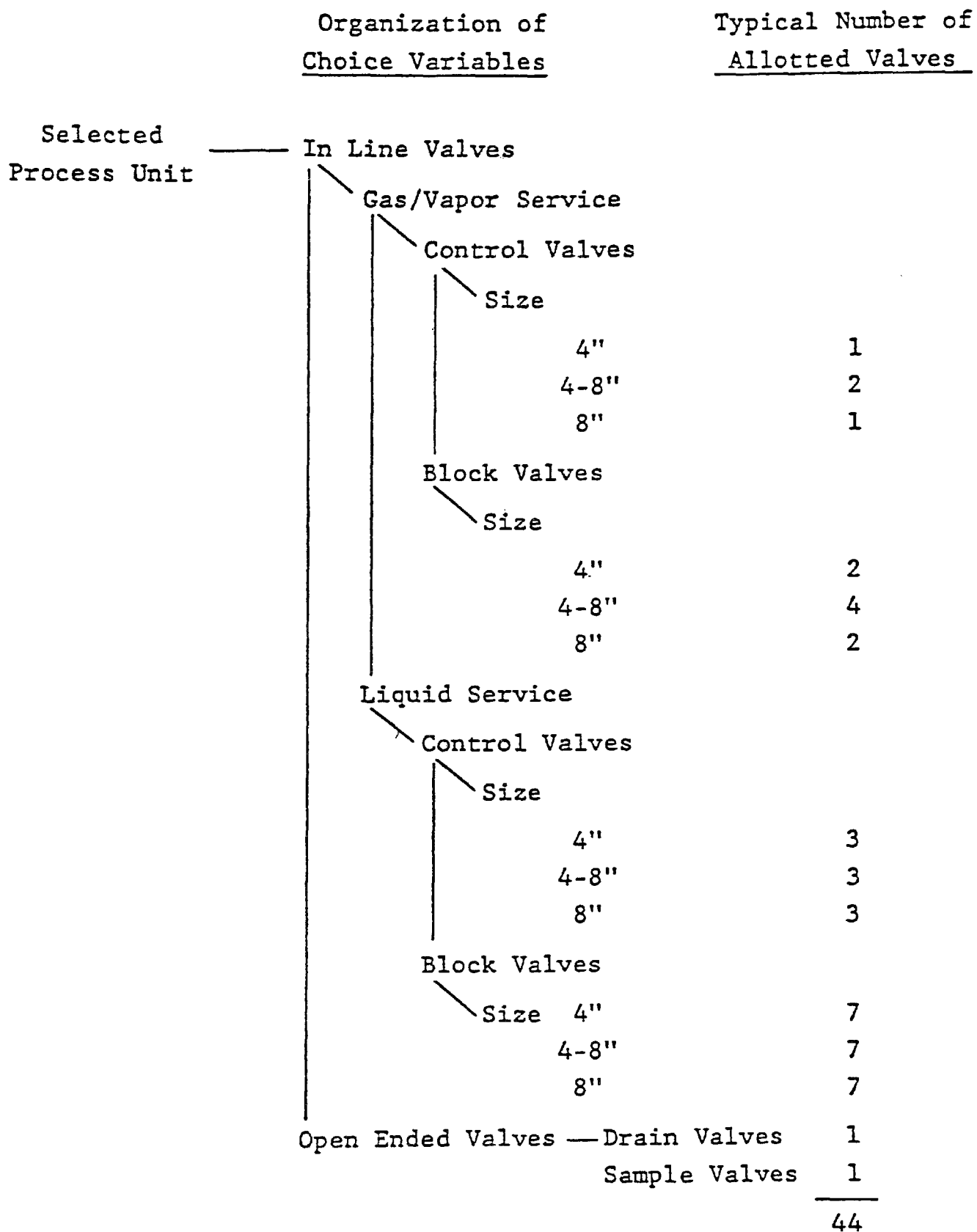
Figure 1. Typical Valve Selection Format

1. Radian ID# [_____]
        1 2 3 4 5 6 7 8

2. Unit _____

3. Refinery ID# _____

VARIABLES:

4. Pressure, psig [_____]
           9 10 11 12

5. Temperature, °F [_____]
           13 14 15 16

6. Gas or liquid (G, L) [__]
                  17

7. Line size, in _____ [__]
                18 19

8. Type
WE – weld
TH – threaded
FF – flat face
RF – raised face
FH – floating head tube sheet
[__]
20 21

9. Special service
A – air cooler
O – orifice plate
V – vessel/extn.
[__]
22

10. Age, yrs [__]
           23 24

11. Mts. of const.
ST – steel
OT – other
_____ [__]
25 26

12. Manufacturer _____ [__]
           27 28

13. Gasket mtl _____ [__]
           29 30

14. Vibration
N – none
S – slight
M – moderate
H – heavy
[__]
31

PROCESS FLUID DESCRIPTION:

15. Name [_____] _____
      32 33 34 35 36 37 38 39 40 41

SCREENING DATA:

16. Date of screening [_____]
                42 43 44 45 46 47

17. Screening team [__] ____/____
               48 49

18. Liquid leak (Y, N) [__]
                  50

19. TLV readings _____

20. Max TLV [_____]
        51 52 53 54 55 56

Remarks:

Figure 2. Data Sheet – Flange

Screening Techniques

There are several techniques that have historically been used to screen potential sources in the baggable classification for leaks. These include visual observation of vapor leaks, visual observation of liquid leaks or buildup of residue, and spraying with soap solution. These methods are commonly used in refineries as a means of identifying those equipment items in need of maintenance, repair, or replacement. All these methods are qualitative, however. A leak detected by any of these methods will be relatively significant and would be bagged and sampled.

Many, if not the majority, of potential baggable emission sources have skin temperatures above 100°C. Above this temperature, the technique of spraying soap solution is unusable since it vaporizes on the hot source. Any bubbles created by leaking vapors are indistinguishable from those created by the vaporizing solution.

In Radian's experience in screening these sources, significant leakage has been measured where none of the visual methods indicated a leak. For this reason, a more quantitative estimate of leak rate was required to adequately screen the selected sources and identify those that require bagging.

Instrumentation

A Bacharach Instrument Company J-W Model TLV Sniffer has been found to be useful for the screening of baggable sources. This instrument utilizes a catalytic combustion detector to measure low concentrations of flammable vapors. It can detect hydrocarbon concentrations as low as 1.0 ppm. Three concentration scales; 0 - 100 ppm, 0 - 1000 ppm, and 0 - 10,000 ppm, are built into this instrument. A dilution probe was used when the TLV readings exceeded 10,000 ppm which allowed readings of up to 100,000 ppm. The instrument meter displays the result as ppm hexane by volume. It is battery operated, self-contained, compact and portable. The instrument performance has been very satisfactory.

A second instrument used to screen for hydrocarbon emissions was the Century Instrument Company Organic Vapor Analyzer (Model OVA-108). This instrument utilized a flame ionization detector to measure hydrocarbon concentrations.

The role of the OVA was limited to obtaining original screening values only. When leaking sources were identified, they were rescreened with the TLV Sniffer when the sources were sampled.

Dilution Probe

The probe can also function as a dilution probe. This extends the range of the TLV from 10,000 ppm to 100,000 ppm. To operate the dilution

probe, the black rubber washer is pulled back to expose the dilution air intake holes. In this mode, the meter will read a concentration which is approximately one-tenth of the actual concentration.

This dilution factor can be verified by reading the high-range (x100) gas standard with the meter zeroed on the midrange (x10) scale. The dilution factor is calculated as follows:

$$\text{Dilution factor} = \frac{\text{ppmv, calibration gas}}{\text{ppmv, meter reading}} \approx 10$$

All subsequent screening results are multiplied by the dilution factor obtained here. However, if the calculated dilution factor falls between 9 and 11, it is sufficient to use a factor of 10. This simplifies the screening process considerably.

Screening Procedures

The procedure used for screening with the devices was quite simple. The sample probe was held as close as possible to the suspected leak source. This reduced the effect of the wind and increased the reproducibility of the readings. The screening procedure differed slightly for each baggable source type as discussed below.

Valves--Most of the valves that were selected for screening were either gate, globe, or control valves. Hydrocarbon leaks from these valves occur at the stem and/or the packing gland, as indicated in Figure 3. Some plug valves were also selected. Hydrocarbon leaks from this type of valve can occur at the plug square or under the malleable gland.

Both the stem and the packing gland of selected valves were screened. The probe locations used included the four compass points around the seal, relative to the valve casing. Thus, a total of eight such readings were taken for each valve. In addition, two more readings (one for the stem and one for the glands) were obtained at a distance of 5 cm from the leak source. The probe was rotated in a circular path around the leak source and the maximum reading was recorded.

Flanges--Flanges were screened by placing the TLV Sniffer probe at two-inch intervals around the perimeter of the flange. After locating the maximum leak point, three additional readings were taken at the remaining compass points, relative to the location of the maximum leak point.

Pump and Compressor Seals--Pump seals were screened in a manner similar to that used for screening valves. Leakage occurs around the rotating shaft at the

Gate, globe, and
control valves are
screened at these
two locations. Four
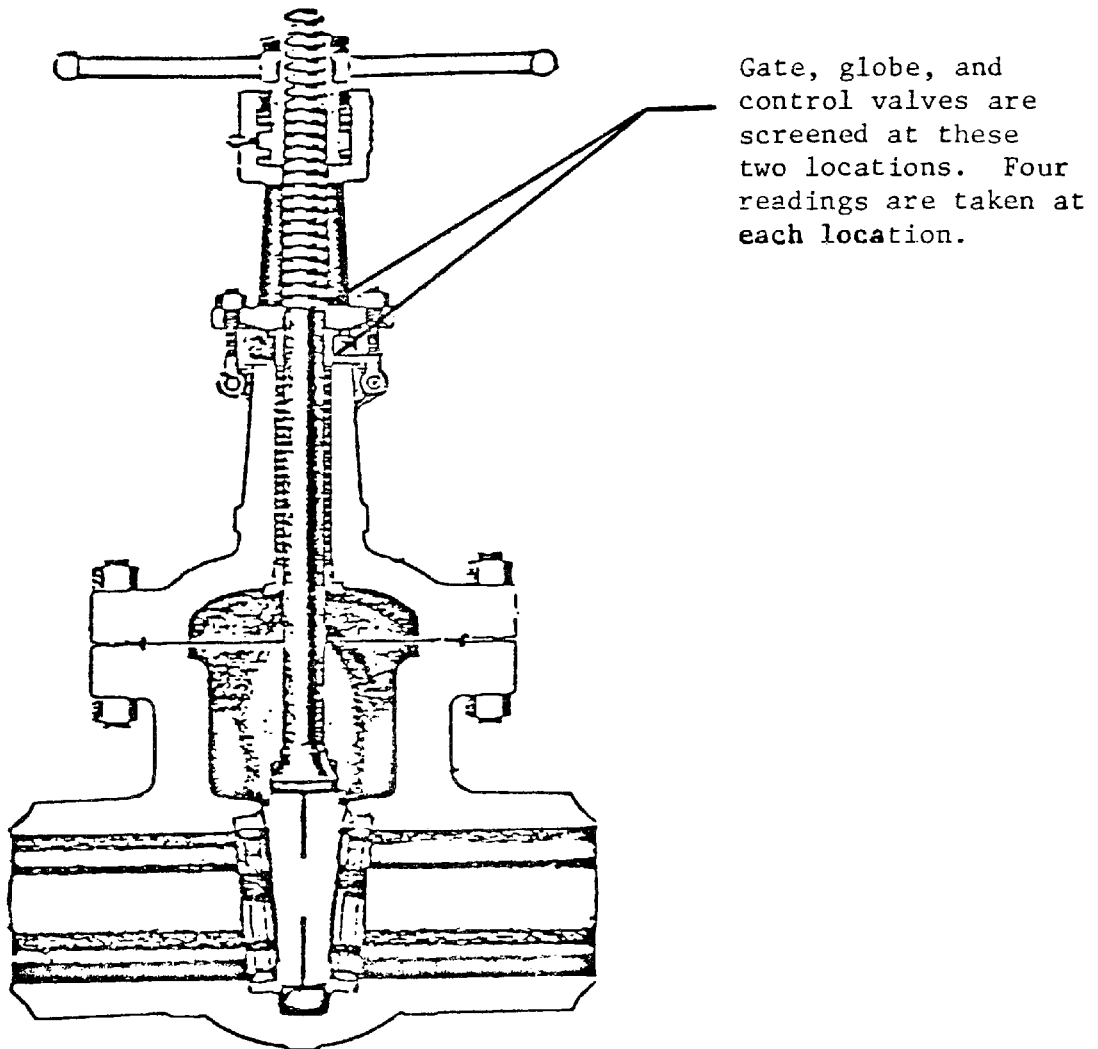readings are taken at
each location.

Figure 3. Gate Valve

point where it enters the pump housing. The Bacharach TLV Sniffer probe was placed as close as possible to the potential leak point around the shaft at the pump housing. Prior to this, the instrument was zeroed at ambient conditions. Four readings were taken at points 90° apart around the shaft. Also, the maximum readings, taken at a distance of 5 cm, was recorded. The probe was left at each point for a minimum of 5 seconds. The detection of hydrocarbon at a concentration of 200 ppm at any of the four points resulted in the pump being bagged and sampled.

Large pumps or pumps in severe services may have two seals, an inboard seal and an outboard seal. In these cases, each seal was screened separately.

The screening procedure for compressors depended on the accessibility of the seal area. If the seal area was accessible, the screening procedure was identical to that for pumps. After zeroing at ambient conditions, the TLV Sniffer probe was placed at four locations 90° apart around the shaft and right at the point where the shaft enters the compressor housing. A hydrocarbon concentration of 200 ppm or more at any point indicated the need for bagging and sampling of the seal.

In many cases the seal area was enclosed and hydrocarbons leaking from the seal were vented to the atmosphere or to a vapor recovery system. When compressors vented to the atmosphere were encountered, they were screened and sampled, if necessary, at the point where the vent pipe discharged to the air. The TLV probe was positioned at a point located just inside the end of the vent.

Compressors often have more than one seal. Each seal was individually screened and, if necessary, bagged and sampled.

Pressure-Relief Devices--Only those pressure-relief devices that are vented to the atmosphere were screened. Those devices that are vented to blowdown and flare systems can only leak to the atmosphere at the connecting flanges, and these leak sources are considered to be flanges.

The relief valves were screened using the Bacharach TLV Sniffer. After zeroing the instrument at ambient conditions, the probe was placed at two-inch intervals around the perimeter of the vent (horn) just at the exit. The probe was also placed at the center of the vent opening at a level with the vent exit.

When the top of the horn was inaccessible, a screening value was obtained at the weep hole, located near the bottom of the horn. The probe was left at each location for a minimum of 5 seconds. If a hydrocarbon concentration of 20 ppm was detected during this 5-second period, the probe was left in place for at least an additional 5 seconds. The maximum TLV readings during the 10-second period were recorded. If any readings exceeded 200 ppm, the relief device was to be sampled and bagged.

Common Operating Problems - TLV--There are several situations which may arise that could cause difficulty in obtaining proper results. Some of the more common problems are discussed below.

On some TLV Sniffers, the zeros for each of the three concentration ranges may not coincide. If this is the case, the magnitude of the difference should be determined and screening values adjusted accordingly. For example, assume that the meter has been zeroed on the (x1) scale and a reading of 500 ppm is obtained when the meter is switched to the (x100) scale. In this case, 500 should be subtracted from all readings taken on the (x100) scale. Small differences from one scale to the next, however, may be neglected.

In some cases, it may be difficult to determine whether a meter response is due to high ambient air hydrocarbons or a source leak, particularly when the ambient reading is highly variable. This problem is commonly experienced in compressor houses or other enclosed areas. One method to determine if the source is leaking is to place the probe at the leak source and then remove it from the leak source. This operation is repeated at regular intervals. If the movement of the needle corresponds to the placement and removal of the probe (keeping in mind the two-second time lag), the source is probably leaking. The screening value is then determined by subtracting the ambient reading from the measured screening result. A variety of such situations may be encountered and a judgment on the part of the operator may be required to obtain a representative reading.

Occasionally, a source may be encountered which has a highly variable leak rate. The design of the TLV Sniffer tends to damp these variations somewhat; however, some oscillation in the reading may still occur. In general the maximum sustained reading or the maximum repeatable reading should be recorded. Again, a judgement on the part of the operator may be required to obtain a representative reading.

One further screening difficulty may arise when screening sources contain heavier hydrocarbon streams, particularly on hot sources. When these valves are screened, some of the vapor tends to condense on the interval probe-sample hose surfaces. The response of the meter is considerably slower for these sources relative to that seen when screening lighter hydrocarbons. And, the meter may require more time to return to zero. When screening this type of source, the meter should be allowed to stabilize before recording the result. The meter should be allowed to return to about 20 percent of the recorded value before moving to the next screening point. Prior to screening the next source, sufficient time should be allowed for the meter to stabilize or return to zero. Often the meter will not return completely to zero and a considerable adjustment may be required.

Under no circumstances should the end of the probe be placed in contact with liquid. If liquid is drawn through the sample hose, it will damage the catalytic element. A liquid trap, connected between the TLV

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Sniffer and the sample hose, was used. This gave some protection against damage to the element.

Sampling Train

The method preferred for sampling leaks from baggable sources is the dilution or flow-through method. The sampling train that was used in this method is shown in Figure 4. The train was contained on a portable cart, which could be easily pushed around the unit from source to source.

An alternate method, "blow-through," was used when very high or very low air flow rates were required.

The vacuum pump was a 4.8 CFM Teflon-ring piston-type equipped with a 3/4 horsepower air-driven motor. Low pressure air ($\sim$ 100 psig) is available at or near most refinery process units.

The dry gas meter was a Rockwell Model 1755 Test Gas Meter with a Number 83 Test Index.

The leak source is shown as a valve in the figure. However, the same sampling train was used for all baggable source sampling with a flow-through technique. The size and shape of the leak source enclosure (tent) was changed and adjusted to fit each particular source shape and operating condition.

When the sampling train is operating, the vacuum pump is able to maintain a maximum flow rate of approximately 2 1/2 cubic feet per minute.

Sample bags were used to collect gas samples and transport them to the mobile laboratory for analyses. Several types of bags were tested by Radian in the laboratory and in the field. Most of them, including Calibrated Instrument Company's five-layer "snout" bags, were found to adsorb hydrocarbons, making them unsuitable for use. Bags of 2 mil Mylar and Tedlar plastic were constructed, and were found to be very satisfactory. A drawing of a typical sample bag is shown in Figure 5.

A cold trap was placed in the system to condense water and heavy hydrocarbons, thus preventing condensation in down-stream lines and equipment. The cold trap was simply a 500 ml flask in an ice bath and was placed as close as possible to the tent. This ice bath was found to be very effective in preventing condensation in the remainder of the sampling train and in the gas sample bag. Any organic condensate that collected in the cold trap was measured and recorded for later use in calculating total leak rates. The use of such a cold trap is critical; without it, order of magnitude errors are possible and, in some cases, probable.
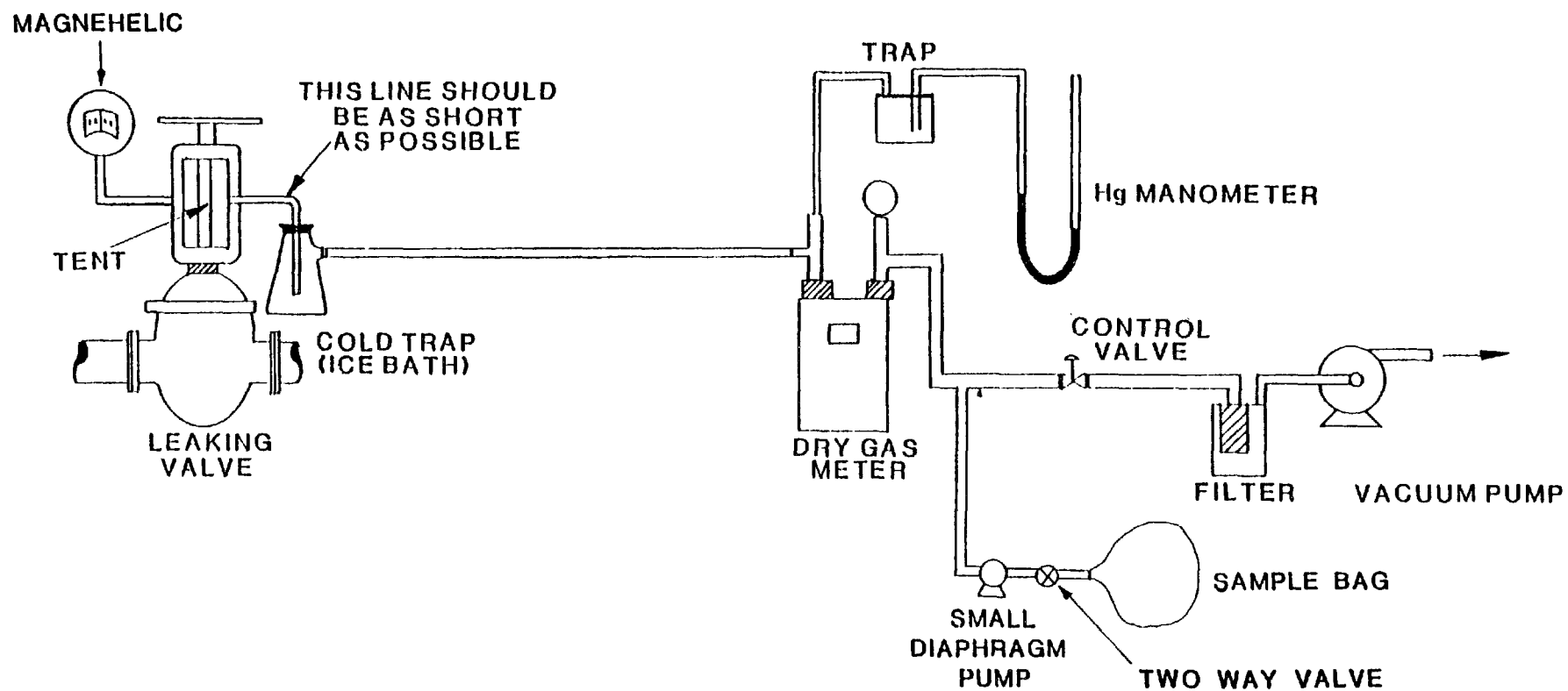
Figure 4. Sampling Train for Baggable Sources of Hydrocarbon
Emmissions Using a Diaphragm Sampling Pump
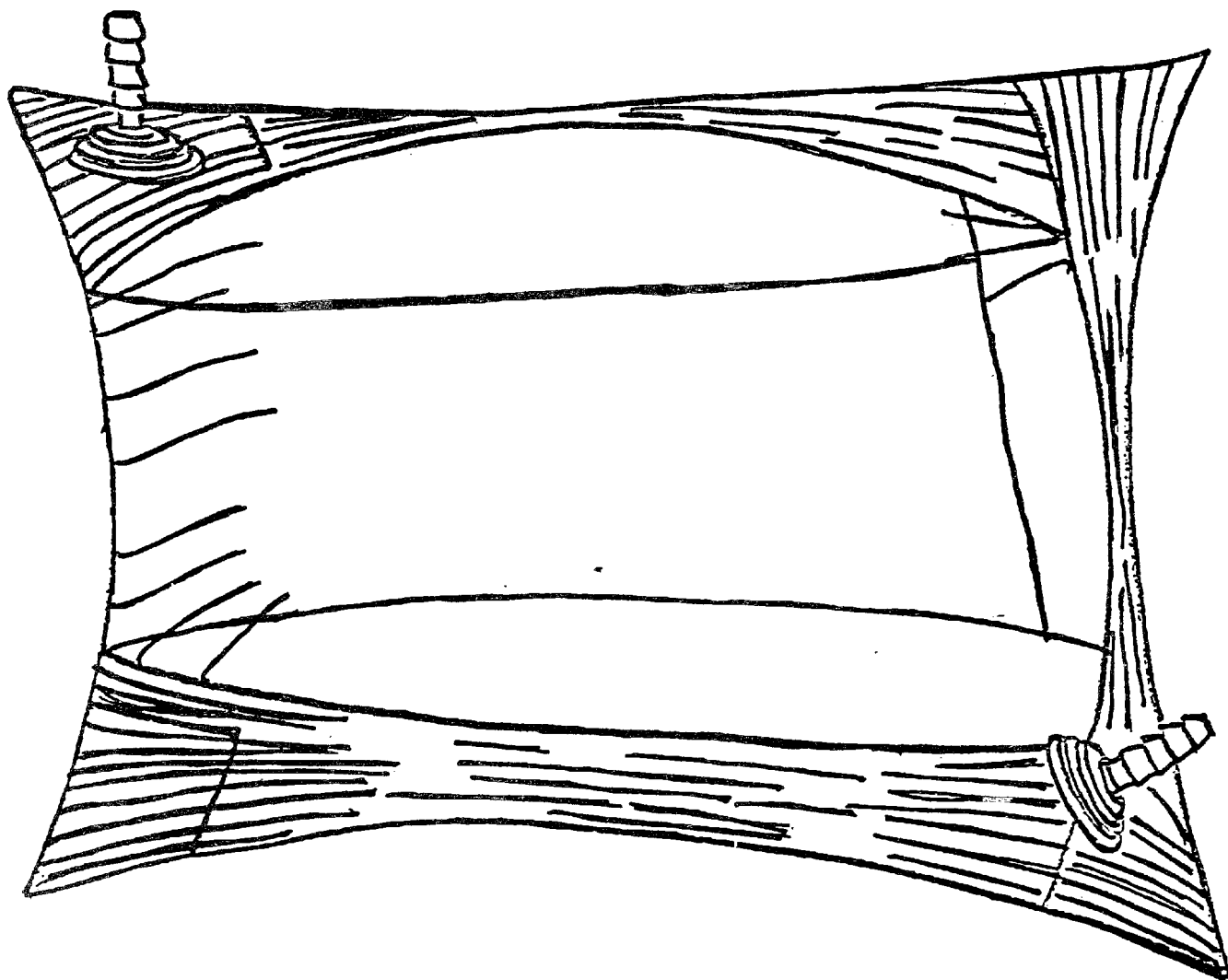
Figure 5. Mylar Plastic Sample Bag

C. D. Smith

"Tent" Construction

An enclosure or "tent" of Mylar plastic (polyethylene terephthalate) is formed around the leak source. The thickness of the Mylar can range from 1.5 – 15 mil depending on the type of source being bagged. Radian has found that Mylar is well suited to this function as it does not absorb significant amounts of hydrocarbons, it is very tough, and it has a high melting point (250°C). A typical tent is shown in Figure 6.

The enclosures were kept as small as practical. This had several beneficial effects:

- The time required to reach equilibrium was kept to a minimum.

- The time required to construct the enclosure was minimized.

- A more effective seal resulted from the reduced seal area.

- Condensation of heavy hydrocarbons inside the enclosures was minimized or prevented due to reduced residence time and decreased surface area available for heat transfer.

In a typical sampling operation, the tent was constructed around the leak source and connected by means of a bulkhead fitting and Teflon hose to the sample train.

A separate line was connected from the tent to a magnehelic. This allowed continuous monitoring of the pressure.

Sampling – Total Leak

The cold trap was connected to the tent and immersed in an ice bath. Then the vacuum pump was started and the timing of the run was simultaneously initiated. The time, pressure and temperature at the dry gas meter, and dry gas meter reading was recorded. These data were recorded at 2 – 10 minute intervals. Equilibrium was normally reached within 5 minutes or less. Sampling was not started until equilibrium had been established throughout the system.

The TLV Sniffer was placed in the sample train at the exit of the vacuum pump. The instrument was used to monitor the gas stream in order to assure that equilibrium had been established.

To sample the gas stream, an evacuated Mylar sample bag, which had been previously completely flushed with air for an extended period at the

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Surgical Tubing
Pressure Top

Silver Duct Tape——Bag—Seal

Line Seal

Mylar Bagging

Flexible Plastic
Mesh Reinforcing
Material Beneath
Bag

Outlet to
Pump

Figure 6. Tent Construction Around the Seal Area of a Vertical
Pump

mobile laboratory, was attached to the diaphragm pump exhaust. The bag was first completely flushed with sample gas. Then a sample was transferred into the bag.

At the same time that this sample was being withdrawn, an ambient air sample was taken near the tent. This air sample was taken with a large plastic syringe and transferred to a Mylar sample bag. The gas sample and ambient air sample were taken to the mobile laboratory for analysis. T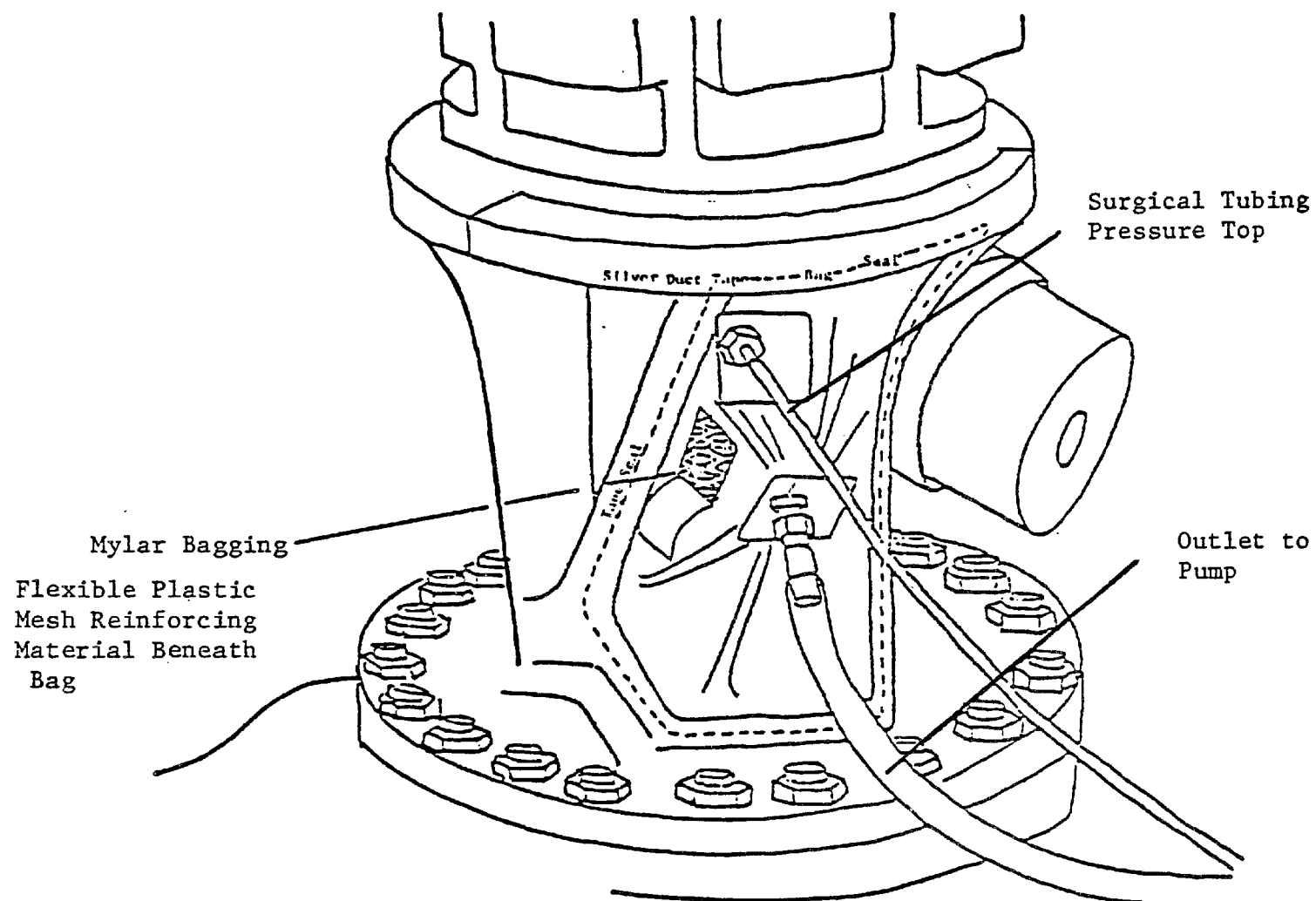he vacuum pump was then stopped and a final set of readings recorded. The cold trap was removed from the ice bath, sealed, and sent to the laboratory for analysis. The tent was then removed from the source, and the train moved to the next sampling point.

The "Blow-Through" Method – a schematic diagram of the sampling train used with the "blow-through" method of measuring hydrocarbon emission rates is shown in Figure 7.

In this method, plant air is used as the source of diluent air to the enclosure around the leaking source. Plant air is first passed through an activated carbon canister to remove contaminants. The air then passes through a dry gas meter and into the enclosure. The air is exhausted from the enclosure through a line connected to the opposite side of the tent. A fraction of the exit air is continually drawn through an air driven vacuum (sampling) pump. When equilibrium has been established, this fraction of the air stream is collected in a plastic bag. The contents are then analyzed for methane and total nonmethane hydrocarbon using gas chromatographs equipped with flame ionization detectors.

The hydrocarbon emission rates can be calculated from the inlet air flow rate and the hydrocarbon concentration in the outlet air. The "blow-through" method can be used when very low or very high flow rates of air are required.

Speciation Selection and Sampling

During the sampling for total hydrocarbon emissions a minimum number of samples was taken for complete characterization. It is from these that the effects of refinery size and location on the characteristics of emissions were determined. For this reason it was important that a wide variety of process units be included in the overall speciation-sample gathering task.

The number of samples projected to be taken from each source was based upon the likelihood of that source containing hazardous organic materials. It was felt that this is the most efficient and accurate way to obtain a comprehensive picture of potentially hazardous components in refinery streams.

It was believed that this sampling scheme would provide a complete description of the potentially hazardous compounds emitted from refining operations. Essentially all streams selected were included for at least duplicate analysis.
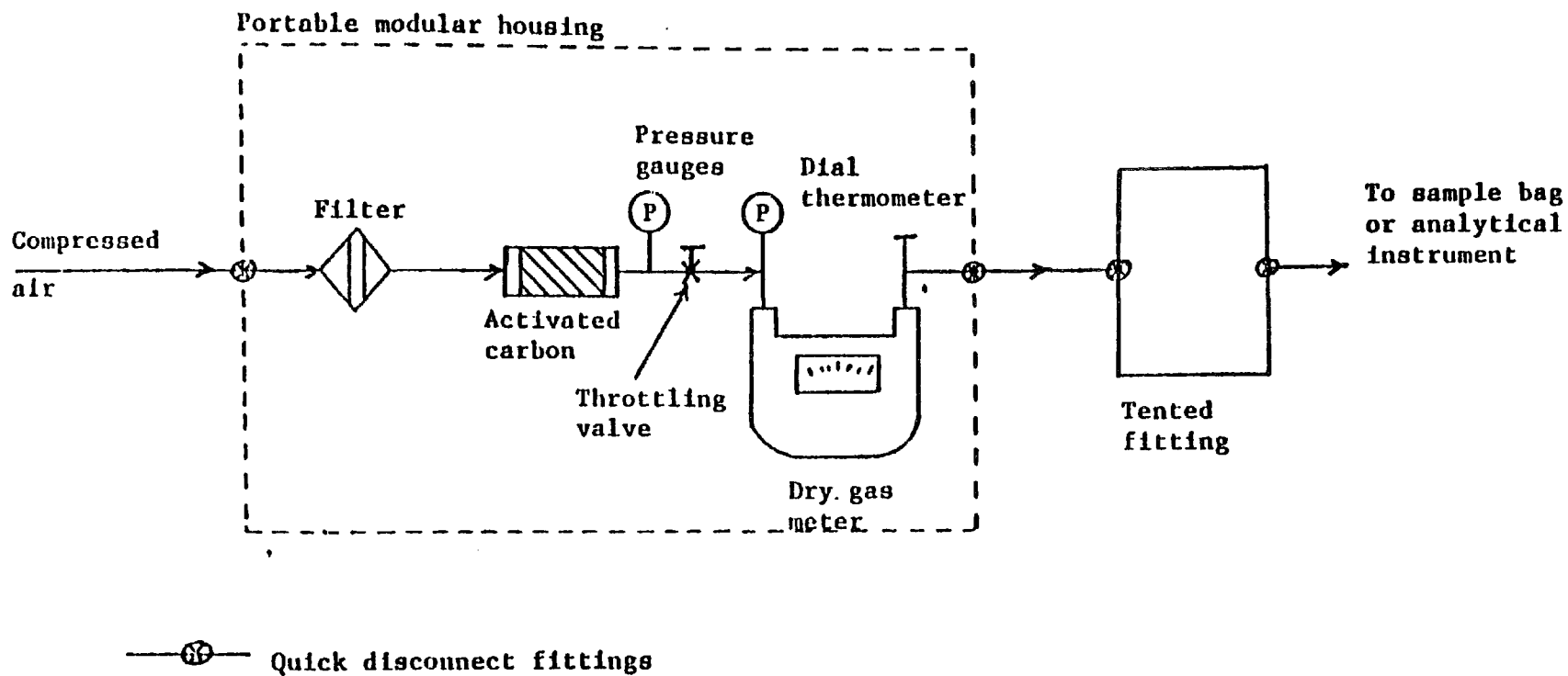
Figure 7.   Schematic Diagram of the Apparatus for the Blow-Through
Sampling Technique

Vapor/Liquid Compositions of Fugitive Emissions

The relationship between the composition of a vapor leak and the composition of the stream from which it came was investigated by taking both liquid and vapor speciation samples wherever possible. (This was not always possible because not every stream selected for speciation sampling contained vapor-leaking sources.)

Vapor samples for speciation analyses were taken by means of adsorption on a porous polymer. Extraction with an organic solvent releases the adsorbed material for analysis. The effect of this technique is removal and concentration of materials in the hydrocarbon/air mixture.

Liquid samples taken as speciation samples were drawn directly from sample lines or ports. In some cases, it was necessary to pass hot liquid through a cooling coil in an ice bath as it came out of the line. In this manner, vaporization of the more volatile constituents was prevented.

Sorbents

For broad boiling range speciation a combination of sorbent techniques is advisable. For volatile organics from acetone to naphthalene, Tenax can be used as a sorbent and thermally desorbed. Benzenes, toluenes and xylenes are the compounds in the volatility range that would be expected as fugitives with known adverse environmental effects. Charcoal tubes are also efficient in the trapping of very volatile emissions, such as vinyl chloride, which are of interest from a health effects standpoint, but not expected as fugitives from the refining process. To provide a volatility continuum, charcoal tubes should be used in the fugitive sampling procedure and the extracts analyzed for any compounds of interest in the 120°C to 150°C boiling range. For the high molecular weight fugitives XAD-2 is recommended as an adsorbent. Heterocyclic nitrogen and sulfur compounds and polynuclear aromatic emissions are trapped with the XAD-2 sampling module. Each sorbent system is outlined in the following sections.

Collection of Leaking Vapor for Species Identification

Samples of the leaking vapor were collected on Tenax adsorbent, XAD-2 resin, and charcoal. The air containing hydrocarbons from the enclosed leaking valve was passed through tubes containing the various adsorbents. Both the "draw-through" and the "blow-through" methods were used for this purpose. Sampling trains are shown in Figures 8 and 9 and Table 2 shows sampling conditions for the three types.

Collection of Bulk Liquid Samples

Samples of various representative liquid streams were collected from sampling points along the reprocessing lines. All samples were taken
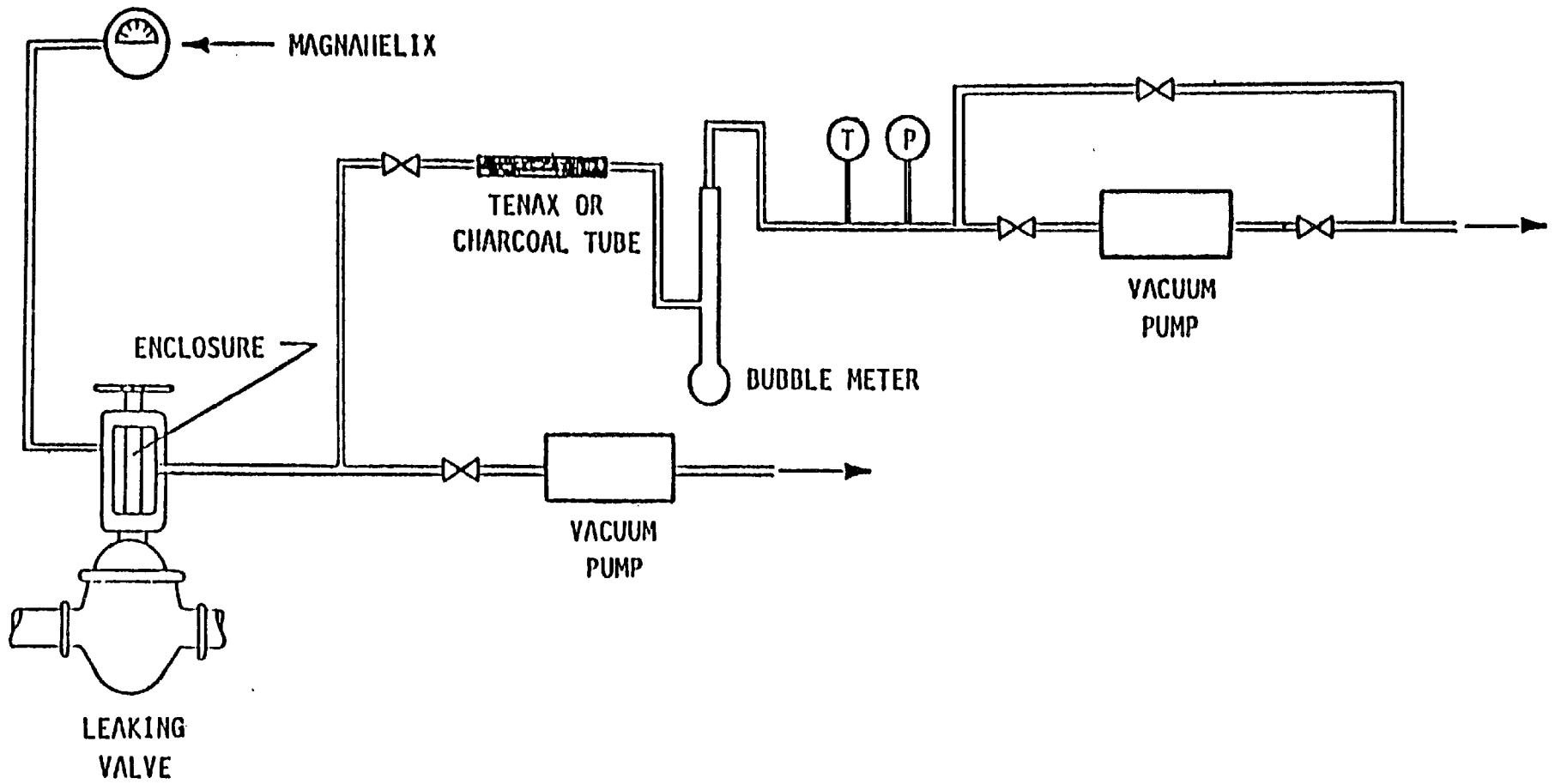
Figure 8.   Typical Sampling Train for Taking Gas Samples on
Tenax Resin and Charcoal Using the Flow-Through
Method
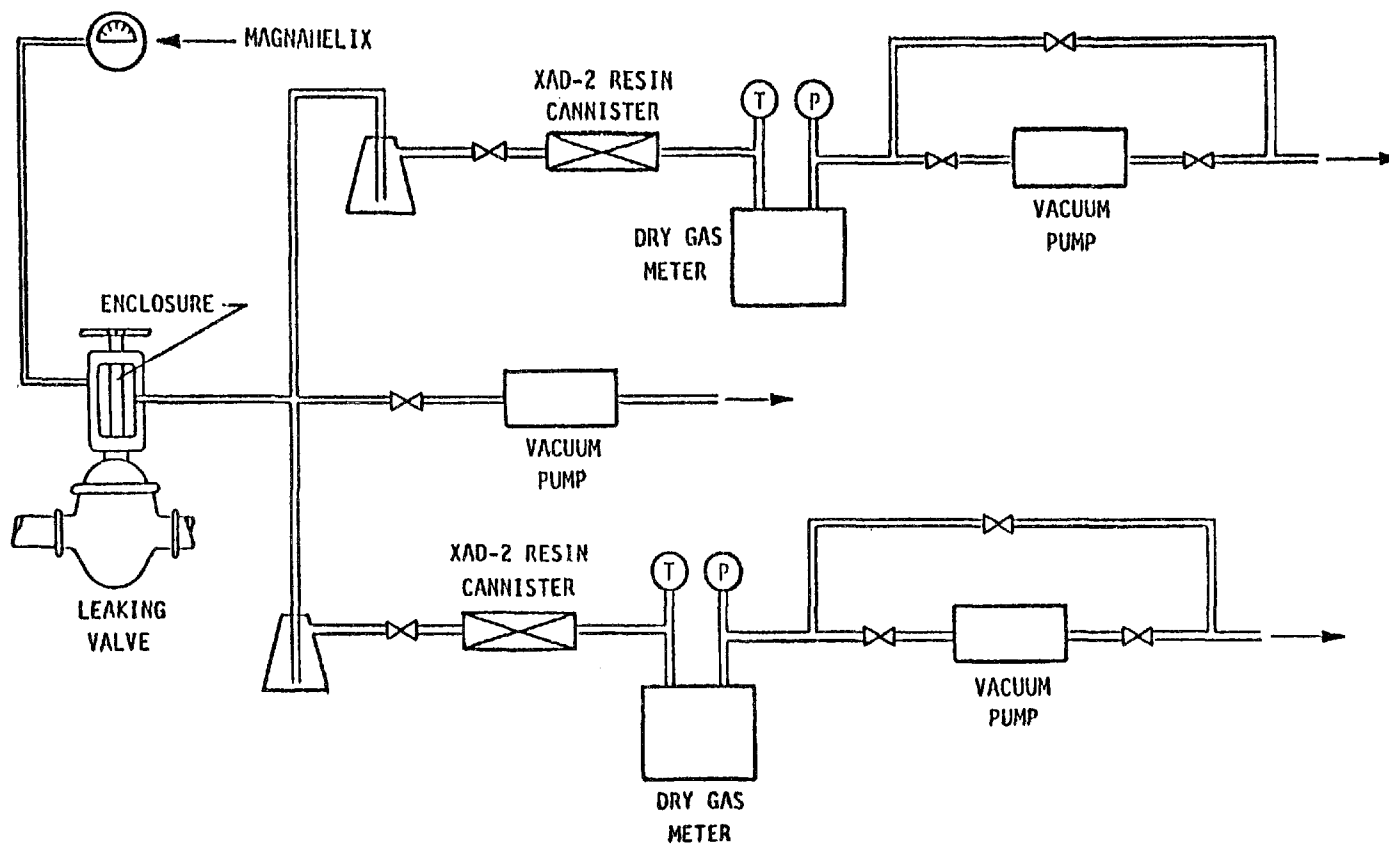
Figure 9. Typical Sampling Train for Taking Gas Samples on XAD-2 Resin Using the Flow-Through Method

TABLE 2. NOMINAL OPERATING CONDITIONS FOR SAMPLING WITH ADSORBENTS

Sorbent	Detection Limit	Method	Recommended Ranges			Inlet Concentration
			Volume	Flow	Mass	
TENAX	∿1 PPB	GC/MS	1-2 L	10-25 ml/min	50-100 ng minimum	
Charcoal*	∿500 PPB	GC/MS	5-10 L	20-50 ml/min	2-15 mg	200-500 vPPM
	∿50 PPM	GC				
XAD-2	∿50-100 PPB	GC/MS	300-600 L	5-10 1/min	3-4 G maximum	100-1000 vPPM

in Pyrex sample bottles, tightly sealed with Teflon-lined screw caps, and refrigerated until analyzed.

WASTEWATER AND COOLING TOWERS

There are a number of potential hydrocarbon emission sources in a refinery that are not amenable to sampling with bags or enclosures. These sources include operations that are broad in area, intermittent in operation, and/or very complex in their functioning.

Nonbaggable sources include drainage and wastewater systems, cooling towers, barometric condensers, removal of coke from delayed cokers, sampling operations, blind changing, and maintenance turnarounds. Some of these sources can only be sampled using very elaborate and complex sampling procedures and equipment. Nonbaggable sources that were sampled are the wastewater system and cooling towers.

Nonbaggable Sampling Philosophy

The sampled nonbaggable systems were the wastewater processing units and the cooling towers. The approach to sampling nonbaggable systems was to use a mass balance around the particular unit. The difference between the hydrocarbon into the system (liquid influent) and hydrocarbon out (liquid effluent) is equal to fugitive emissions to the atmosphere.

The key elements to this approach are collection of representative samples of liquid streams into and out of a particular unit and accurate measurement of flow rates through the system.

Oil-Water Separators

Oil-water separation is normally the first process that the wastewater encounters as it enters the wastewater treatment section of a refinery. Oil-water separation can be accomplished in a surge tank, API separator, or corrugated-plate interceptor. The API separator is the most widely used of these three types of separators. The sampling methods described below for API separators can be applied to the other two types of units, also.

The inlet liquid to the separator consists of a mixture of hydrocarbon and water. The principal problem encountered in sampling is the procurement of truly representative samples of two-phase streams. Samples of each phase were obtained from the separator inlet line, or from the separator at a point as close as possible to the oil-water inlet.

Three streams normally exit from an API separator. These are the oil that is skimmed from the surface of the liquid in the separator, the water, and sludge that is pumped from the bottom of the separator. The sludge was not considered in the sampling program, because it is not a significant source of emissions to the air at this point.

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The oil that is skimmed from the surface of the separator is normally pumped to a slop-oil tank. Oil samples were preferably taken at the outlet of this pump to insure a reasonably representative sample. Other sampling points were the skim pipe itself, the line from the separator to the slop tank, and the slop tank itself.

In the separator the water flows under a barrier weir and then over another weir to a basin from which it is pumped or allowed to flow by gravity to the next processing area in the wastewater treatment. Water samples were taken at the overflow weir. Samples were obtained at several points along the weir, and were composited to form one sample. Factors which determined the particular sampling point for a given separator included accessibility, residence time in the basin, and presence of sample taps in the pump discharge line.

The average oil outlet rate can be determined from level readings on the slop-oil tank over given periods of time. The average outlet oil rate was used to estimate the residence time in the API separator. The thickness of the oil layer in the separator, and the dimensions of the area containing the oil layer also are required in estimating the oil residence time.

Samples were taken of each stream of each separator several times a day for several days. Daily samples from each sample point were composited before analysis. The oil and water samples from the inlet and outlet of the API separator were collected in glass bottles. These bottles were completely filled and kept tightly capped to prevent the escape of volatile hydrocarbons.

Dissolved-Air Flotation Units

If dissolved-air flotation (DAF) units are used in a refinery wastewater treating system, they usually process water from the oil-water separators. Air is dissolved or sparged into the water, and the air bubbles attach themselves to colloidal oil droplets, causing them to rise to the surface, where the oil-air emulsion is removed.

Some DAF units are partially enclosed and others are completely open to the atmosphere. The hydrocarbon material balance method is the preferred technique for determining hydrocarbon emissions from open units, and may also be used for partially enclosed units.

Only one stream containing a significant amount of hydrocarbons enters the DAF unit. This is the water phase from the oil-water separator. There is normally little free oil in this water. Ambient air, which may contain low background concentrations of hydrocarbons is also injected or sparged into the water. Three streams leave the DAF unit. These are the water, the air-oil emulsion and air. All these streams contain some hydrocarbons.

When applying the material balance method to DAF units, samples of inlet water were taken. These were normally the same as the outlet water samples from the API separator, and the same analysis sufficed for both separator and DAF hydrocarbon material balances.

In order to close the material balance sufficiently to calculate hydrocarbon emissions, samples of the outlet water stream and the air-oil emulsion must also be taken. The outlet water sample was taken at the over-flow weir. The emulsion samples were judged to be negligible contributors to air emissions.

The water samples were collected several times each day for several days. The daily samples from each point were composited for analysis.

Cooling Towers

The preferred method for determining hydrocarbon emissions from cooling towers is the hydrocarbon material balance. Water enters the cooling towers from two sources: make-up water and the hot water from process exchange. Water leaves as vapor from the top of the cooling tower, as cooled water returning to process exchange, and as blowdown. A water material balance shows that the outlet rate to the process must equal the inlet water rate from the process, since the make-up water rate is controlled to exactly balance blowdown plus evaporation.

Thus, if the hydrocarbon content of the incoming hot water and the return cooled water are known, the evaporative hydrocarbon emissions can be determined.

Samples of inlet and outlet cooling water were collected daily from each selected tower over a period of several days. In order to diminish the effect of hydrocarbon concentration fluctuations, the outlet sample was taken from the water flowing downward through the tower at a location just above the level of the cooling tower basin. The inlet samples were taken from one of the many small sampling valves which are normally present and branch off the large cooling water return risers. Many of these are continually flushed into the tower basin.

The samples were kept in sealed bottles under refrigeration until they were analyzed.

SAMPLING STACK EFFLUENTS

Stacks or vents which can be identified as emission points for hydrocarbons and other criteria pollutants are classified as process sources. The general strategy regarding the sampling of point source emission included sampling the total hydrocarbon emissions, obtaining samples for speciation analysis and sampling for other criteria pollutants.

Measurements made in the base case were: EPA Reference Methods No. 1, 2, 3, and 4 on all stacks; methane and nonmethane hydrocarbons on all stacks; particulate and vapor collection for organic characterization on one stack; and, sulfur gases on the sulfur recovery and/or tail-gas treating stack.

Stack sampling procedures are a combination of: EPA approved methods for criteria pollutants (SO_2, SO_3, and particulates); EPA Level 1 screening procedures (SO_2, COS, CS, H_2S, NO, NO_x, "organic vapor"); Texas Air Control Board methodology; and, Radian-devised methods (HCN, NH_3, THC). The procedures were selected with several criteria in mind:

- Accepted or proved methodology.

- Accurate, reproducible Measurements.

- Commercially available equipment.

- Freedom from interference.

- Cost-effective trade-off between sampling and analysis.

- Shortest feasible sampling time.

Figures 10 through 12 depict the sampling trains used.

Stack Sampling Methods

The characterization of refinery stack emission involved sampling and analysis for the following species:

particulates	total hydrocarbons
SO_x	fixed gas
trace organic species	sulfur species
total aldehydes	nitrogen species

Particulates

Particulate samples were collected from each stack according to the procedures described in the EPA Reference Method 5 using a Lear Sigeler, Inc. stack sampling train. Sampling was performed isokinetically along two perpendicular traverses of each stack. Duplicate sample runs were made on each stack insofar as possible. Stacks were sampled that did not meet EPA requirements. In those cases the number of traverse points was taken that was felt to be useful.
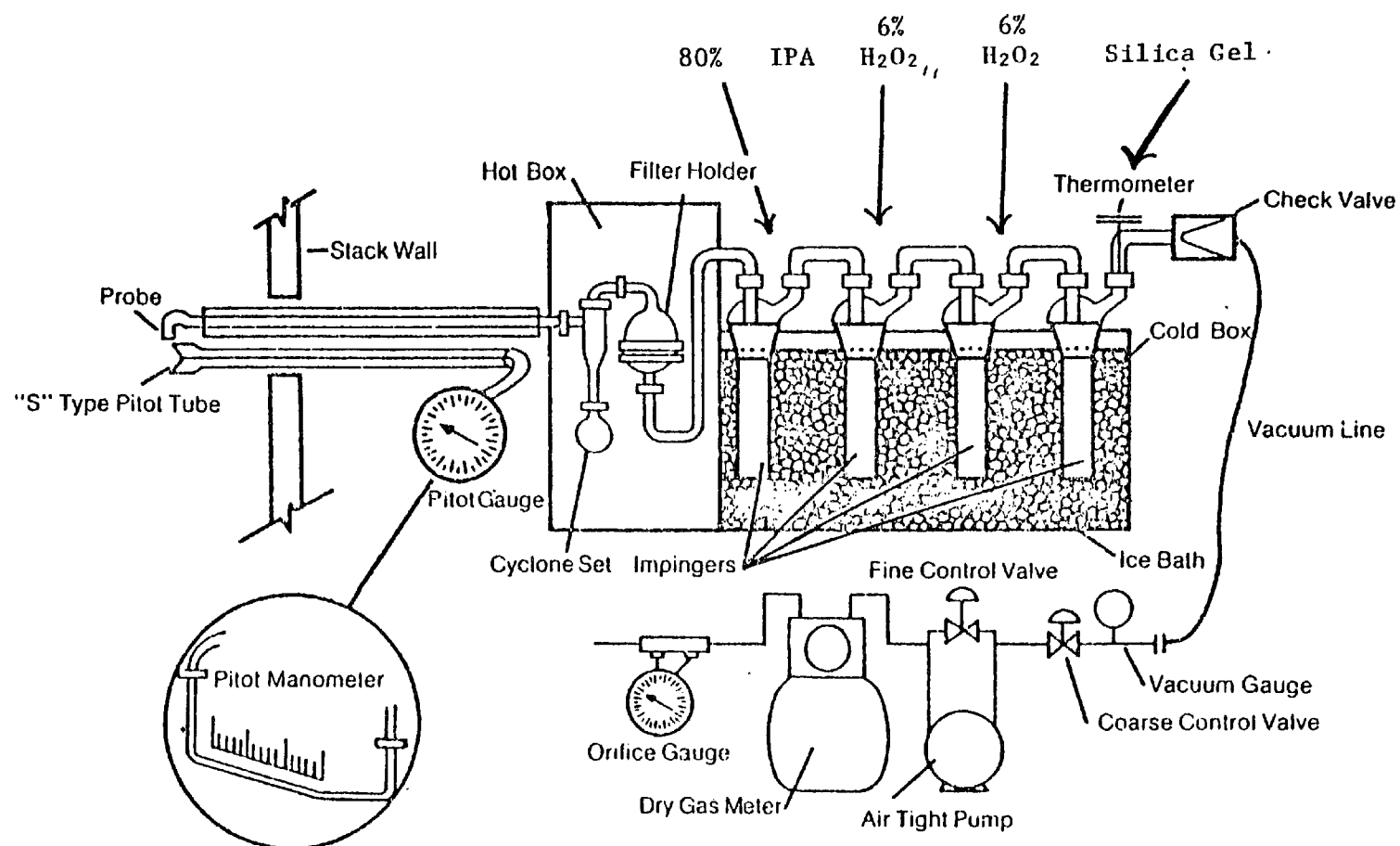
Source: Lear Siegler, Inc., PM 100 - Operation & Maintenance Manual.

Figure 10. Method 5 Train for SO_2 and Particulates

Teflon/Glass Fiber Filter

Gas Sample

Ice Bath

Water

1% NaHSO$_3$

Gas Vent

Rotometer/Flow Controller

Vacuum Pump
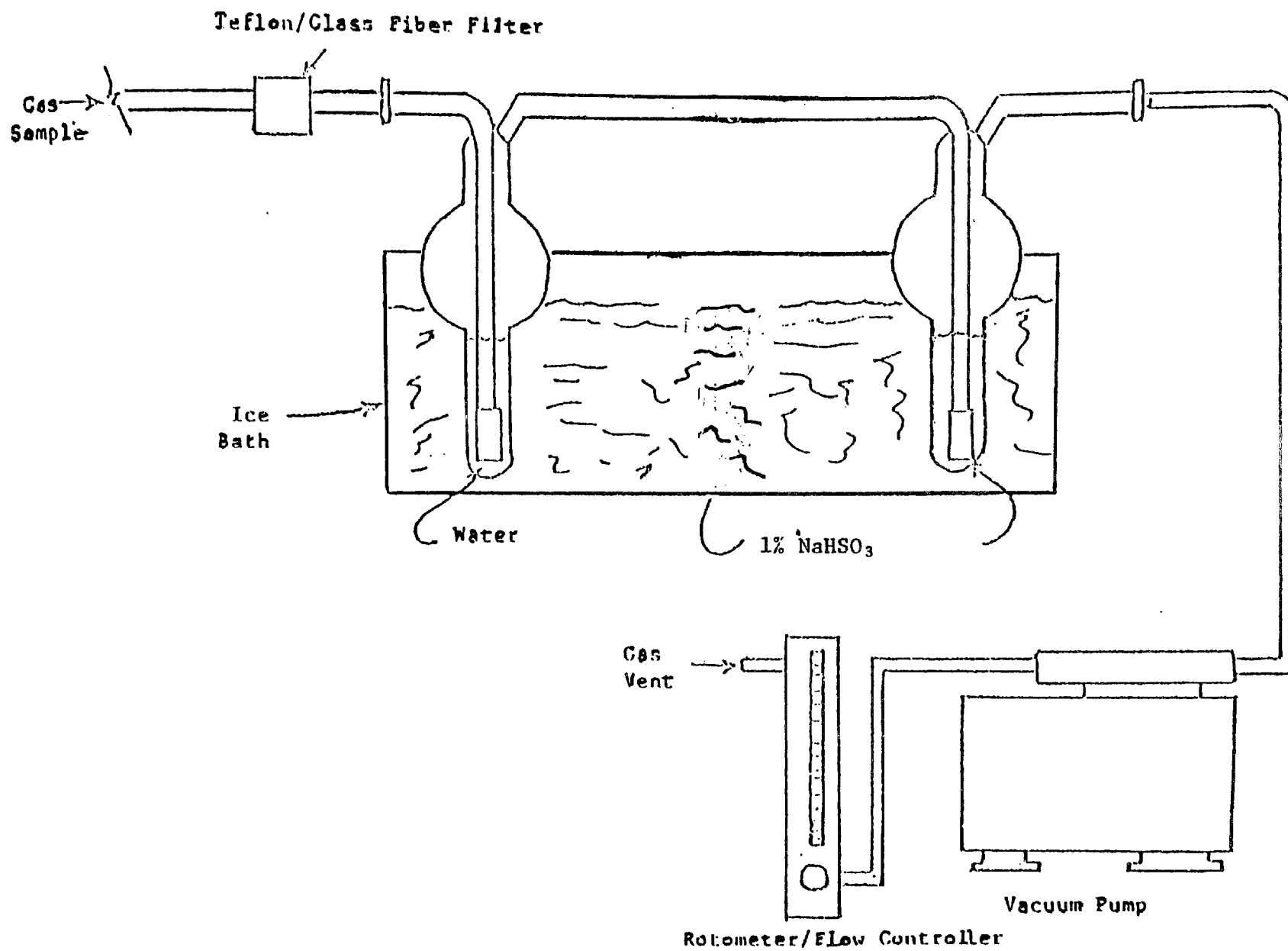
Figure 11. Aldehyde Impinger Train

Gas Sample

Stainless Steel
Probe

Teflon/Glass
Fiber Filter

Perma Pure Drier

Heated Teflon
Sample Line

Humid
Air

Dry
Air

Teflon-Lined
Vacuum Sample
Pump

Rotometer/
Flow Controller

Tellar Bag
(Total Hydrocarbons)

Glass Bomb (NO_x)

Glass Bomb
(Sulfur Species)

Scotchpak Bag
(Fixed Gases)

Impingers
(HCN, NH_3)
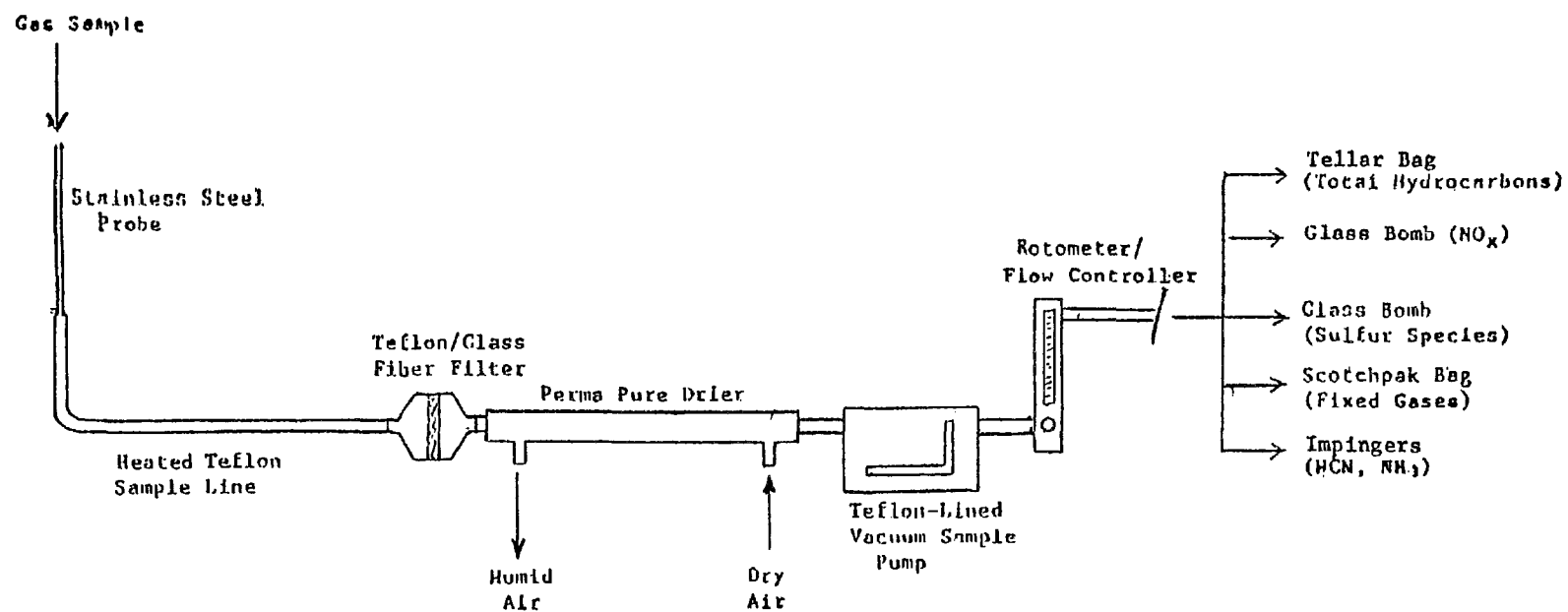
Figure 12.   Grab Sample Collection and Preparation System

SO_x

Oxides of sulfur (SO_3 and SO_2) were collected according to EPA Reference Method 8. This was done during each particulate collection run by passing the filtered sample gases through an impinger train consisting of an 80 percent isopropanol impinger for SO_3 followed by two 6 percent aqueous hydrogen peroxide impingers for SO_2 and a silica gel impinger. The total mass of water collected in this train was used to determine the moisture content of the stack gas.

Aldehydes

The aldehyde train (Figure 11) used in sampling stacks consisted of two ice-cooled impingers, each containing 10 ml of a 1.0 percent aqueous sodium bisulfate solution. Approximately 12 liters of stack gas were drawn through each impinger train at a rate of 200 ml per minute. A stainless steel probe was inserted into the stack to a point of average velocity, and the gas was transferred to the impinger train by a small vacuum sampling pump through a heated Teflon sample line equipped with a Teflon particulate filter. Radian has found that the use of a heated transfer line is very important to prevent moisture condensation and subsequent loss of sample by absorption and dissolution.

HCN and NH_3

Hydrogen cyanide was collected using the Method 5 stack sampling equipment by passing the filtered sample gases through three impingers containing 2.0 N sodium hydroxide. Ammonia was collected similarly using three impingers containing 0.1 N sulfuric acid. In each case sampling was conducted over thirty-minute periods and resulted in approximately 10 SCF of gas for each sample.

Grab Samples

The remaining four categories of species are all collected by grab sampling techniques (Figure 12). From Radian's experience in sampling for these species in refinery stack gases, it has been found that collecting and transporting the sample in a way that preserves its integrity is a nontrivial task. All of the following factors have been found to contribute to the nonrepresentativeness and/or degradation of the sample:

- Sampling equipment construction.

- condensation of moisture in the sample line and vessel.

- Particulate removal.

- Sample vessel construction.

- Time lag between sampling and analysis.

Radian has developed a sampling and operating procedure which eliminates the negative aspects of all five of the above factors. A stainless steel probe is inserted into the stack to the point of average velocity, and the sample gas is drawn out through a heated Teflon sampling line. The construction of the sample line is important to prevent moisture condensation and reaction of the reactive species with any non-inert surfaces. The sample then passes through a heated Teflon glass/fiber filter to remove particulates followed by a permeation drying system to remove moisture. The Perma-Pure Products, Inc.® multi-tube drier has been found to be effective in removing moisture down to 100 ppm while causing only a 1 - 3 percent loss of the desired species. Without this sample drying technique, condensation of moisture inside the sample vessels and the resulting reaction, absorption or dissolution of reactive species has resulted in poor analyses and complete loss of sample. Movement of the sample through the system is accomplished by a miniature Thomas vacuum pump equipped with Teflon heads and diaphragm. The outlet stream from the pump is directed to the several bags and bombs used to transport the samples to the field laboratory for analysis. Sampling and analysis procedures allow no more than 15 minutes elapsed time between sample catch and start of analysis. If the sample was not analyzed within that time, a new sample was obtained.

Hydrocarbons—Samples for methane and nonmethane hydrocarbons analysis were collected in 4 liter Tedlar sample bags. Bags made of aluminized polyethylene have been tried, but substantial sample loss through absorption or reaction was observed. The Tedlar bags were flushed with zero grade air prior to use.

Fixed Gases—Samples for fixed gases (CO_2, N_2, H_2, O_2, CO) analysis were collected in aluminized Scotchpak sample bags. These species are quite unreactive and are not prone to absorb onto the bag walls significantly.

Gaseous Sulfur Species—The sulfur species, CS_2, H_2S, COS, and SO_2, proved to be the most difficult to collect and transport. The two major problems of reaction/dissolution with condensed moisture and reaction/absorption on the surfaces of the sample vessel were eliminated by using the sample system described in Figure 12.

NO_x (A)—Samples for NO_x were collected in evacuated 2 liter flasks to which had been added 25 ml of a potassium dichromate-aqueous sulfuric acid solution. The temperature and pressure of the gas were recorded.

NO_x (B)—Samples for NO_x were collected in evacuated 2 liter flasks to which had been added 15 ml of chromotropic acid solution. The temperature and pressure of the gas were recorded.

Flue Gas and Particulate Sampling--Samples for trace organics speciation
were collected from the selected stack using a modified Aerotherm Source
Assessment Sampling System (SASS) (see Figure 13). A 1154 SCF sample of
stack gas was drawn from a point of average velocity in the stack. The
particulates were removed on a filter, and the gas was then cooled and
passed through a sorbent canister (Figure 13a) filled with XAD-2 resin to
trap any nonvolatile organic compounds. The particulates, the condensate
that resulted from cooling the gas, and the XAD-2 resin were collected and
returned to Austin for extraction and analysis.

The organic concentrator for the SASS train is a canister filled
with XAD-2 resin. It replaces the canister that comes with the SASS train.
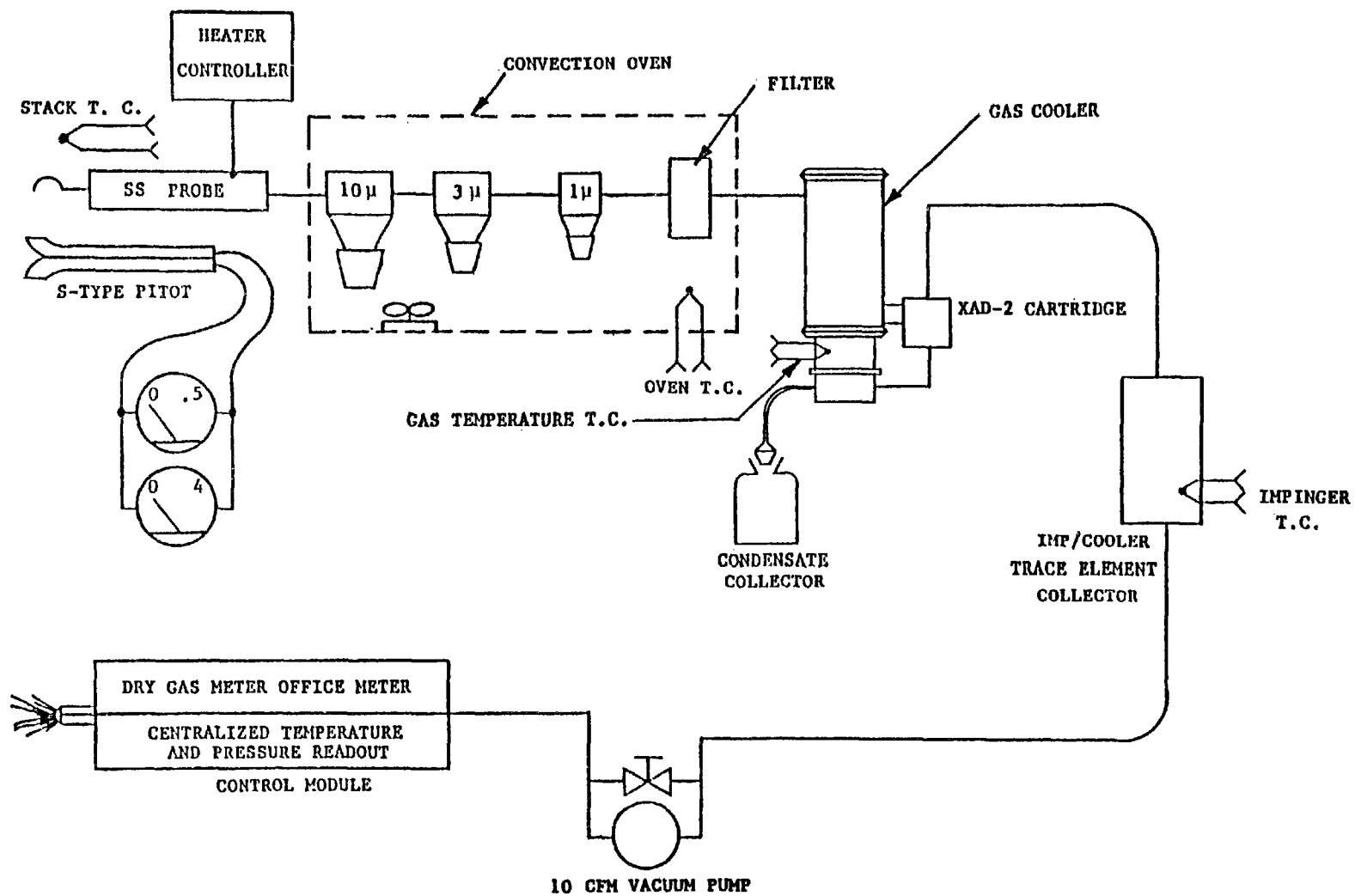
Figure 13. Source Assessment Sampling System

3-WAY SOLENOID VALVE

TO COOLING BATH

FROM COOLING BATH

HOT GAS
FROM OVEN

LIQUID PASSAGE
GAS PASSAGE

COOLING FLUID
RESERVOIR

GAS COOLER

IMMERSION
HEATER

COOL GAS
TO IMPINGER

LIQUID PUMP

XAD-2 CARTRIDGE

TEMPERATURE
CONTROLLER

CONDENSATE
RESERVOIR
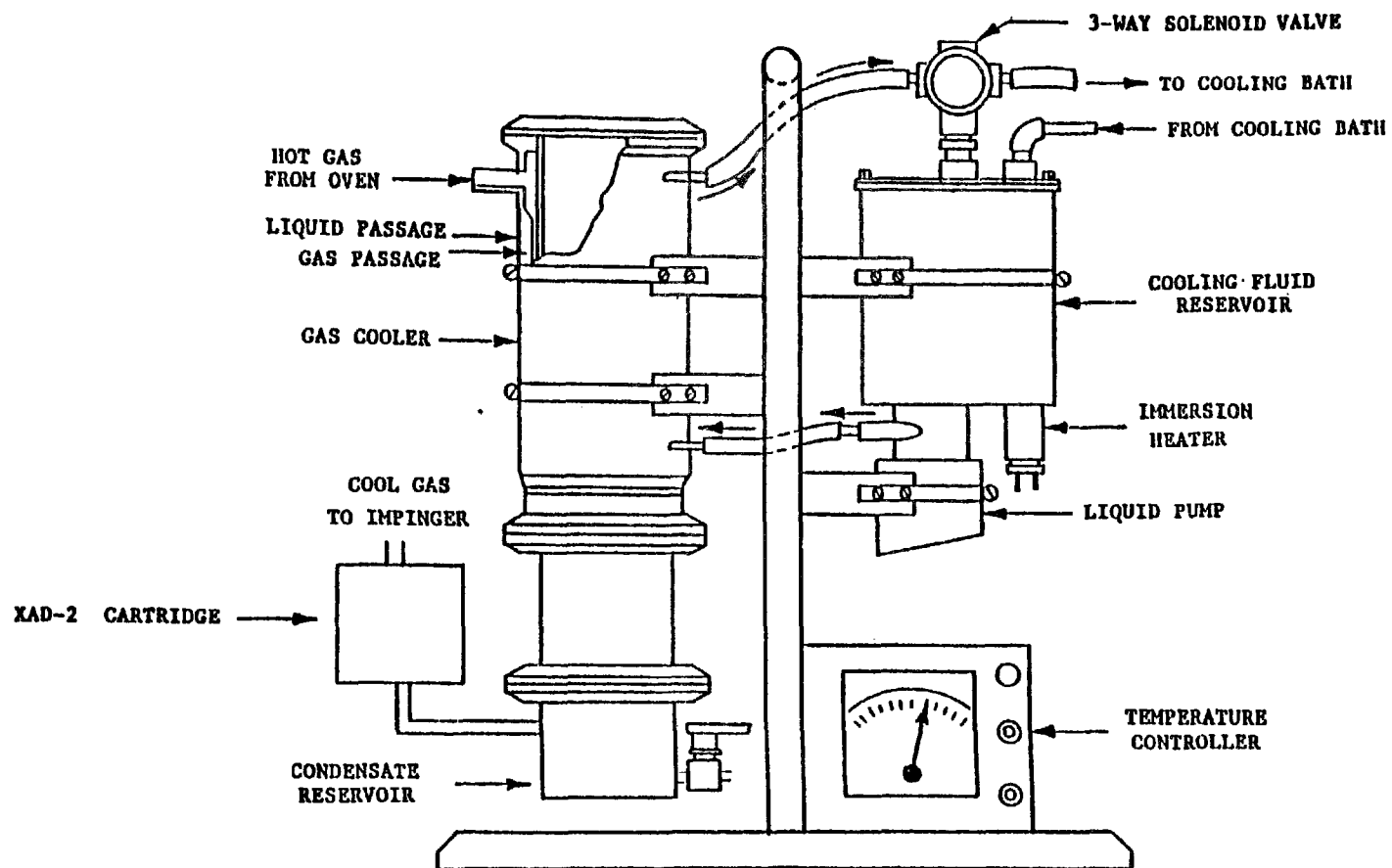
Figure 13a. XAD-2 Sorbent Trap Module

SECTION 3

FIELD ANALYSIS

MOBILE LABORATORY

Radian dedicated a mobile laboratory to the sampling in refineries. The laboratory is housed in an 8' × 26' van trailer and has the capability of supporting a wide variety of sampling and analytical procedures. The forward area is equipped with counter space and utilities to support the wide variety of analytical instruments contained in the trailer.

The remainder of the laboratory is equipped with standard wet-chemistry benches and extensive equipment storage space. A fume hood, with externally mounted explosion-proof blowers, has been provided for containment of hazardous experiments and exhaust of vapors. All external components of the air-conditioning system are explosion proof. Electrical, water, and drainage utilities needed to operate the laboratory are obtained on-site, and external connections are provided to interface with the required services.

FUGITIVE EMISSIONS ANALYSES FROM PROCESS SOURCES

Total Hydrocarbon Content (Methane/Nonmethane)

The analysis for methane and nonmethane hydrocarbon content of fugitive emission gas samples was accomplished using a specially designed Total Hydrocarbon Analyzer (THC) Model 301C made for Radian by Byron Instruments. The instrument is made to accept samples by:

- Sampling from a bag.

- Syringe injection.

- Unattended, continuous in-line sampling.

Analysis of baggable samples of gas was accomplished by pumping gas out of the Mylar sampling bag into a gas sample loop using an integral pump in the THC analyzer. The instrument operates automatically after being connected to the bag. The results of the first run were discarded to avoid contamination occurring from sample retained from the previous analysis or ambient air entering the system during sample changing. Two additional runs are made and the results recorded by a strip-chart recorder.

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The instrument has several ranges for both methane and nonmethane hydrocarbons. The full-scale direct readout ranges from 0 – 2 to 0 – 20,000 ppm by weight. When these ranges were exceeded, a portion of the sample was diluted with zero grade air until it could be analyzed on one of the above ranges. Then the dilution factor was used to calculate the original concentration.

The THC uses a flame ionization detector for measurement of hydro-carbon concentration and, thus, produces a linear readout over the entire range of the instrument. Hydrocarbon-free air is used for the carrier gas.

Quantitative Analysis

The chromatograph gives a voltage output which changes with time. The simplest device for handling this is the strip chart recorder, which produces a sheet of paper with an inked line on it.

The easiest thing to measure is the maximum amount by which the peak departs from the baseline, i.e., peak height. The advantages of this means of quantitation are speed and ease. It is, however, subject to many sources of error. Anything which alters the peak shape will create problems.

Area under the curve does not depend on shape. So long as the same amount of material is injected, even if the column overloads, the same area will be obtained. Operator technique variation, assuming the same amount injected, has essentially no effect on the area figure. Electronic integration is the best approach for measuring area.

Radian used a gas chromatographic instrument that resolves hydro-carbon mixtures into two peaks. Methane is separated from all other hydro-carbons and passed through the FID and then all other hydrocarbons are passed through the FID simultaneously.

To quantitatively measure methane the following procedure is used.

A known volume of sample of known parts per million by weight (ppmw) of methane in air was injected into the analyzer. The peak height was measured. For a single component peak height is an adequate measure of response. A plot of peak height versus ppmw then allows any peak height of an unknown sample to be directly translated into ppmw. The equation of the line shown in Figure 14 is:

peak height = (slope) (ppmw) + intercept

intercept = 0, no material, no response

slope = $\dfrac{\text{peak height of standard material}}{\text{ppmw of standard material}}$

Peak Height

ppmw
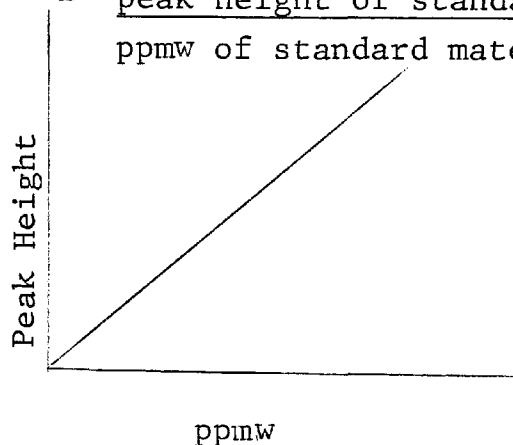
Figure 14

The instrument was calibrated with the standard of known methane so that the slope was identical from day to day or shift to shift.

To quantitatively measure the nonmethane hydrocarbons a similar procedure was used. A standard of propane of known ppmw in air was used daily to calculate and keep constant the slope of a line similar to that of Figure 15.

Area Under
Nonmethane
Hydrocarbon
Peak

ppmw Hydrocarbon

Figure 15

43
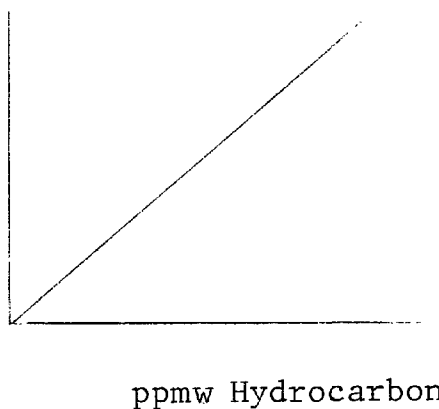
Standardization of the THC was accomplished through a separate gas sampling loop without disconnecting the instrument from the sample being analyzed. The instrument was standardized every time it was turned on or once per laboratory shift, whichever was more frequent. The standard contained 100 ppm methane and 100 ppm propane on a molar basis. Repeated tests against other standards have demonstrated the linearity of the response of the instrument.

Calculations

The hydrocarbon emission or leak rate from each sampled source was calculated as a sum of the methane emission rate, the nonmethane gas emission rate, and the organic condensate rate, i.e.,

$$E_T = E_M + E_{NM} + E_L$$

where

E_T = total hydrocarbon emission rate, lb/hr.

E_M = methane emission rate, lb/hr.

E_L = condensed organic liquid rate, lb/hr.

E_{NM} = nonmethane hydrocarbon emission rate, lb/hr.

The emission rates of methane and nonmethane hydrocarbons may be calculated from the following equation:

$$E_H = K \frac{QPM_A}{T} (C_s - C_a)_H \qquad T = 460° + °F$$

where

E_H = hydrocarbon emission rate, methane and/or nonmethane, lb/hr.

K = 2.74 × 10^{-5}, a factor incorporating conversion factors and standard temperature and pressure.

Q = flow rate of gas through the sample train, actual cubic feet/minute.

P = sampling system pressure at the dry gas meter, psia.

M_A = molecular weight of the air/hydrocarbon mixture, effectively the molecular weight of air.

C_s = concentration of methane/nonmethane hydrocarbon in the gas sample from the sampling train, ppm by weight.

C_a = concentration of methane/nonmethane hydrocarbon in the ambient air, ppm by weight.

$(C_s - C_a)_H$ = methane and/or nonmethane concentration difference between gas and ambient air, ppm by weight.

T = sampling system temperature at the dry gas meter, °R.

The organic condensate rate, E_L, was calculated from the following equation:

$$E_L = \frac{0.115\ V}{t}$$

where

E_L = organic condensate rate, pounds/hour.

V = volume of condensate collected, ml.

t = time over which the sample was collected, min.

This calculation assumes an average density of 0.75 gr/cc for the organic condensate. The condensate was measured, and this weight was used to calculate the condensate rate. The data sheet containing the appropriate information is shown in Figure 16.

Organic Species Characterization

The measurement of organic species was accomplished by a combination of experimental methods employing gas chromatography and mass spectrometry (GC/MS), as described in the following subsections.

Samples were collected and analyzed for characterization of the following:

- Point source emissions such as CO boiler regenerator flue gas.

- Fugitive emissions from valves, pumps, etc.

- Effluent streams from wastewater treatment processes.

1. Radian ID# [ ] 1 2 3 4 5 6 7 8

2. Type of sample [ ] 9 10
   - 1S - magnesia sample
   - 1Q - magnesia quality control
   - 1A - blank sample (tested)
   - 1C - blank quality control

3. Sampling date [ ] 11 12 13 14 15 16

4. Sampling team [ ] 17 18

5. Cart ID# [ ] 19

6. Time _____

7. N.B.# _____

8. Pages _____

9. Flowrate, cfm [ ] 20 21 22 23

10. Temp, °F [ ] 24 25 26

11. Bar. press., in. Hg [ ] 27 28 29 30 31

12. ΔP, in. Hg [ ] 32 33 34 35 36

13. DGM correction factor [ ] 37 38 39 40 41

14. Meter # _____

15. Total vol. condensate, ml [ ] 42 43 44 45 46

16. Vol. org. condensate, ml [ ] 47 48 49 50 51

17. Coll. time, min [ ] 52 53 54 55

18. Specific gravity of organic condensate [ ] 56 57 58

ANALYSIS DATA:

	Methane	Nonmethane
Ambient air (1)	_____	(1) _____
(2)	_____	(2) _____
19. Avg.	[ ] 59 60 61 62 63	20. [ ] 64 65 66 67 68
Sample (1)	_____	(1) _____
(2)	_____	(2) _____
21. Avg.	[ ] 69 70 71 72 73	22. [ ] 74 75 76 77 78 79

ALTERNATE ANALYSIS METHOD:

	Methane	Nonmethane
	(1) _____	(1) _____
	(2) _____	(2) _____
19.	[ ] 59 60 61 62 63	20. [ ] 64 65 66 67 68
	(1) _____	(1) _____
	(2) _____	(2) _____
21. Avg.	[ ] 69 70 71 72 73	22. [ ] 74 75 76 77 78 79

CALCULATED LEAK RATES (lb/hr):

Methane	Nonmethane		Total
	Vapor	Condensate	
_____	_____	_____	_____

RESCREENING DATA: Screening Team _____

Radian ID# [ ] 1 2 3 4 5 6 7 8

Rescreening Date [ ] 9 10 11 12 13 14

Screening Team [ ] 15 16

Screening Concentration, ppm

All sources, Valve Stem [ ] 17 18 19 20 21 22 [ ] 23 24 25 26 27 28 [ ] 29 30 31 32 33 34 [ ] 35 36 37 38 39 40

5 CM Reading _____

Valve Packing Gland [ ] 41 42 43 44 45 46 [ ] 47 48 49 50 51 52 [ ] 53 54 55 56 57 58 [ ] 59 60 61 62 63 64

5 CM Reading _____

REMARKS:

Figure 16.   Data Sheet - Baggables and Tented Liquid Leaks

Qualitative Analysis

Instrumentation--Analyses for organic species were performed in Radian's GC/MS laboratory. The instrumentation used is summarized in Table 3.

Extraction--Depending on the sample type and emission source, different analytical procedures were employed to adequately measure the organic species. Table 4 lists the sample type received and the analytical procedures employed for each sample. Each of these procedures will be described in the following subsections.

Preliminary Sample Treatment--The analysis of trace organic species by GC/MS required preliminary sample treatment. These preliminary steps and their purposes were:

- Isolation, to remove the organic species or interest.

- Separation, to divide the isolated organic species into groups of similar chemical or physical properties.

- Enrichment, to increase the concentration of the organic species.

Each of the samples collected during this work required some or all of these steps as described below.

Isolation of the Organic Species--Removal of the organic species was performed by two techniques, solvent extraction and thermal desorption. The thermal desorption of volatile species from Tenax tubes is an integral part of the analysis and, as such, will be discussed later.

The determination of trace organic species required special precautions in the sample preparation. Only high-purity distilled-in-glass solvents (Burdick and Jackson) were employed. All laboratory glassware was cleaned with chromic acid before use. Immediately prior to use, the glassware was rinsed with an organic solvent to remove any traces of organic material. Only teflon, glass or stainless steel labware contacted the sample. Aqueous reagents were presaturated with solvent before use.

Isolation of the organic species from the XAD-2 resin and particulate samples was performed by a 24-hour Soxhlet extraction with diethyl ether. Diethyl ether was preferred because:

- It has been demonstrated that ether is a superior solvent for removal of polynuclear aromatics and other species from XAD-2 resin.

TABLE 3.   MASS SPECTROMETERS - RADIAN

INSTRUMENT	NO.	TYPE	MAXIMUM RESOLUTION	IONIZATION MODES	SAMPLE INLETS	GC/MS INTERFACE	SIM	DATA SYSTEM	OTHER FEATURES
Hewlett Packard (5982)	1	Quadrapole	Unit	EI, CI	GC, Probe	Glass jet or membrane or direct	Yes	Hewlett Packard (5933)	Capillary GC, Subambient GC, Purge and Trap VOA Analysis
Hewlett Packard (5985)	1	Quadrapole	Unit	EI, CI	GC, Probe	Glass jet or direct	Yes	Hewlett Packard (ZIMX-E)	Capillary GC, Subambient GC, Purge and Trap VOA Analysis
	1							Hewlett Packard (5934 A)	Disc - Tape Interface digital tape unit, zeta plotter, acoustical telephone coupler

TABLE 4. SUMMARY OF SAMPLE TYPES AND ANALYSIS PROCEDURES

SAMPLE TYPE	SAMPLE COMPOSITION	EMISSION SOURCE	ANALYTICAL PROCEDURE
Process Liquid	Organic Liquid	Fugitive	Pentane Dilution [1]
Tenax	Sorbed organic vapor	Fugitive	Thermal Desorption
XAD-2 Resin	Sorbed organic vapor	Point	ABN
Particulate	Particulate	Point	ABN
Effluent Water	Aqueous	Point	Ether extraction
Charcoal	Sorbed organic vapor	Fugitive	CS_2 extraction

Note: 1) Some samples also fractionated on silica gel.

- Any water associated with the resin is removed by the ether.

Aqueous samples were manually extracted with diethyl ether in a separatory funnel.

Thus, at the conclusion of this phase of analysis, the organic species in each sample had been transferred to a different matrix. The process liquids were ready for analysis. The effluent water sample still required concentration as described later. The XAD-2 resin and particulate sample extracts were further separated as described in the following section.

The ABN Separation/Derivitization Scheme--The acid-base-neutral (ABN) separation strategy was developed by Radian Corporation for the analysis of complex environmental samples. The ABN approach is illustrated schematically in Figure 17. The strategy is based on a series of liquid-liquid extractions that separate a sample into three principal fractions:

A - organic acids whose salts partition into water at high pH.

B - organic bases whose salts partition into water at low pH.

N - neutral hydrophobic compounds.

These principal fractions are then further subdivided to yield a total of seven fractions which are analyzed by GC/MS.

The ABN extraction procedure was employed to characterize the semi-volatile organic species in the XAD-2 resin and particulate samples. This separation scheme was chosen on the bases that (1) the distribution of compounds throughout the procedure can be predicted with reasonable accuracy, (2) the procedures do not involve elevated temperatures and (3) the number of fractions presented for analysis is minimal.

The purpose of the separation scheme was to effect a sufficient division of organic components so that those compounds of primary interest could be identified and quantitated. This scheme was not intended to be the ultimate in separations, and it was not intended that every compound collected in a particular sample would be isolated and identified.

The complete ABN separation scheme is described in the subsections below.

Separation of Neutral, Acidic, and Basic Species--The ether extract of the XAD-2 resin, in particular, was extracted with three 100 ml portions of 5 percent HCl in a separatory funnel. The combined acidic and neutral extract was then separated as described later. The pH of the aqueous phase was adjusted to a pH of 11 with NaOH pellets and then extracted with three
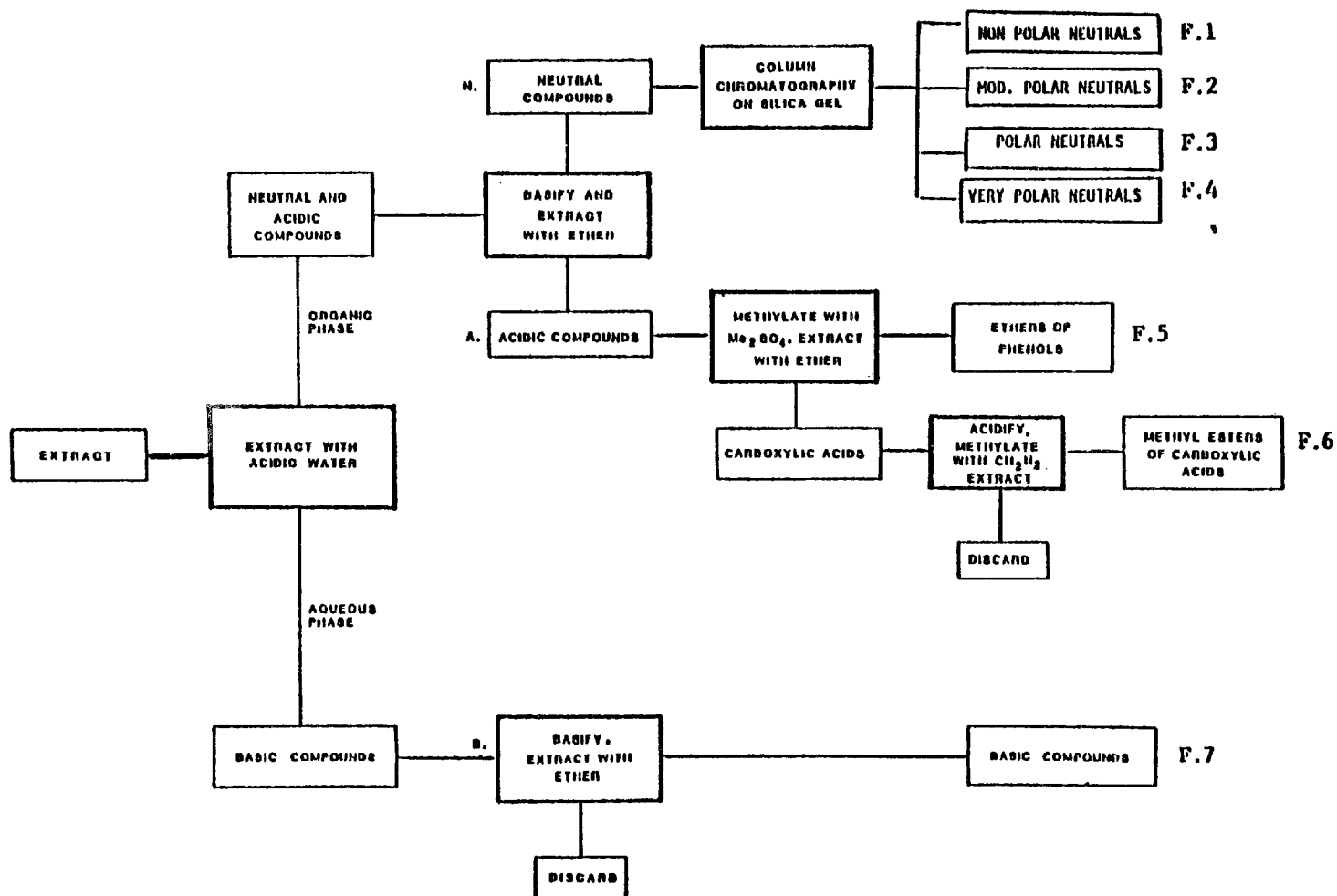
Figure 17. ABN Scheme

100 ml portions of ether. This ether extract containing basic species was then concentrated.

The acidic/neutral extract was extracted with three 100 ml portions of 5 percent NaOH. The remaining neutral extract was separated while the basic aqueous extract was extracted and derivatized.

Separation of Neutral Compounds—The ether extract containing the neutral species was dried by passing it through a column of sodium sulfate and then concentrated to 1 ml. Hexane (10 ml) was then added and the sample was reconcentrated to 5 ml to remove the ether.

Silica gel (E Merck, grade 60, 70 – 230 mesh) was fully activated by placing it in an oven at 180°C for four hours. A small plug of glass wool was placed in the tip of a 1 cm × 100 cm column and the silica gel was transferred while still hot to a depth of 70 cm. A 1 cm bed of sand was placed on top of the packed silica gel and 100 ml of dry n-hexane was added to the column. The hexane was eluted using enough nitrogen pressure to give a flow rate of about 5 ml per minute. The flow was stopped when the solvent level reached the top of the bed and the quantity of hexane eluted was measured. The void volume of the column was calculated according to the following equation:

$$[V = (ml\ hexane\ added) - (ml\ hexane\ measured)].$$

The hexane concentrate containing the neutral compounds was then transferred to the silica gel column and the receiver was rinsed with a small volume of hexane which was added to the column. The reservoir was filled with hexane. As the solvent level dropped, a total of 5 column volumes was added. When the solvent reaches the bed, five column volumes of the next solvent are added after the receiver is rinsed with small portions of this solvent. In a similar manner, five column volumes of each succeeding solvent combinations were added to give a total of four fractions.

The solvents and desired order were:

- F-1, Non-polar neutrals, eluted with hexane.

- F-2, Moderately polar neutrals, eluted with 1:1 hexane: methylene chloride.

- F-3, Polar neutrals, eluted with 99:1 methylene chloride: methanol.

- F-4, Very polar neutrals, eluted with methanol.

Each fraction was collected and then concentrated.

<u>Separation and Derivatization of Acidic Compounds</u>--The alkaline
extract containing the acidic compounds was methylated in two steps to con-
vert phenols into methyl ethers using dimethyl sulfate and carboxylic acids
into methyl esters diazomethane to yield fractions F-5 and F-6 as described
below.

The alkaline extract was placed in a 250 ml round bottom flask and
10 ml of 50 percent NaOH was added. The flask was heated to 90°C after which
time 10 ml of dimethyl sulfate was added dropwise over a period of ten
minutes. After the addition of dimethyl sulfate, the mixture was stirred
for one hour. After the excess dimethyl sulfate was destroyed by addition
of 5 ml of 50 percent NaOH, the mixture was cooled to room temperature. The
aqueous mixture was then extracted in a continuous extractor for 24 hours
with ethyl ether. The ether extract containing the ethers of phenols was
concentrated to 1 ml.

After extracting the phenol ethers, the alkaline solution was
acidified with 6N HCl to a pH $\leq$ 2. This acidic solution was extracted in a
continuous extractor for 24 hours with ethyl ether. The ethereal extract
was concentrated to about 1 to 2 ml and then transferred to an open hypo-vial.
About 1 ml of a diazomethane solution prepared as described below was added
to the extract concentrate. After swirling the mixture, more diazomethane
was added until a yellow color persisted. The mixture was allowed to sit
for 15 minutes with occasional swirling. The excess diazomethane was then
removed by evaporation on top of a steam bath. The solution containing
methyl esters of carboxylic acids was concentrated.

Diazomethane was prepared in a special distillation apparatus that
has Clear-Seal joints in place of ground glass joints to prevent possible
explosions (Adrich cat. #210-0250). The preparative procedure which follows
was supplied with this kit. Twenty-five ml of 95 percent ethanol is added
to a solution of KOH in water (5g in 8 ml) contained in a 100 ml distilling
flask fitted with a dropping funnel and a condenser. The condenser is
connected to two receiving flasks in series, the second containing 20 to 30
ml of ethyl ether. Both receivers are cooled to 0°C.

The flask containing the KOH solution is heated in a water bath
to 65°C and a solution of 21.5g (0.1 mole) of Diazald in about 200 ml of
ethyl ether is added through the dropping funnel in about 25 minutes. When
the dropping funnel is empty, another 40 ml of ether is added and the dis-
tillation is continued until the distilling ether is colorless. This
distillate contains about 3 grams of diazomethane.

<u>Concentration of Sample Extract</u>--Each of the sample extracts
generated in this separation scheme were concentrated before analysis.
Radian employed both macro and micro Kuderna-Danish (K-D) concentrators for
this purpose. Typically, an extract was concentrated to 5 - 10 ml in a
large K-D and then further concentrated to 1 ml in a micro K-D. An internal
standard, d_{10}-anthracene was then added to each extract at a known level,

typically 200 ppm. All sample concentrates were stored in crimp-top vials with Teflon-lined seals.

Identification of Individual Components--Each extract generated as described previously was analyzed by combined gas chromatography/mass spectrometry (GC/MS) utilizing either a Hewlett Packard Model 5982 or a Hewlett Packard Model 5985 GC/MS computer system. Both capillary and packed column gas chromatography were employed as described in the following subsections.

Identification of the chromatographic peaks was achieved by analysis of the individual mass spectra. Interpretation of mass spectra was performed by three approaches:

- Manual interpretation of an unknown mass spectrum.

- Comparison of the unknown mass spectrum against the mass spectrum generated from the analysis of a previously analyzed standard.

- Computer search of the unknown mass spectrum against libraries containing reference spectra.

In addition, another technique was utilized to identify selected organic species at trace levels. This technique, termed selected ion current profile (SICP) searches, is based on the appearance of key ions within a narrow retention time window. This technique was utilized to search for certain compounds, especially polynuclear aromatic hydrocarbons, in the extracts. Identification of the suspected compounds was confirmed by examination of their mass spectra.

Analysis of ABN Sample Extracts--Each extract from the ABN separation scheme was analyzed on a six-foot chromatographic column containing one percent SP-2250 on 80/100 Supelcoport. Typically, 2μℓ of each sample extract was injected onto the column.

The GC conditions were as follows: After an initial hold at 50°C for four minutes, the column was temperature programmed to 260°C at 8°C per minute. The organic species which eluted from the gas chromatograph were transferred to the ion source of the mass spectrometer by means of a glass jet separator. The mass spectrometer was scanned continuously from m/e 50 to m/e 350 with a cycle time of three seconds.

Analysis of Process Liquids--The process liquids were analyzed by capillary GC/MS employing a special large bore 60M SP-2100 WOOT capillary column. The chromatographic and mass spectrometer conditions were the same as the ABN analysis with 1μℓ of each sample injected.

Analysis of Tenax Tubes--Volatile species were determined by thermally desorbing the organics sorbed onto the Tenax tubes into the GC/MS system. A Tekmar Liquid Sample Concentrator was employed for this purpose. The

sample was desorbed by rapidly heating the Tenax trap to 180°C and passing a helium flow over the sorbent. The sorbent tube effluent was connected directly to the head of a cold (– 40°C) gas chromatographic column. A 9-foot column packed with Carbopack C (80/100 mesh) coated with 0.2 percent Carbowax 1500, preceded by a one-foot section packed with Chromosorb W coated with 3 percent Carbowax 1500 was employed for this analysis. Quantitative analysis was achieved by injecting 50 ng of d_8-toluene in methanol onto the cold chromatographic column.

The mass spectrometer was operated in the repetitive scanning mode, scanning continuously from m/e 45 to m/e 300. Electron impact (70 eV) ionization was also employed for this work. After the thermal desorption was completed, the gas chromatograph was rapidly heated to 60°C. The temperature was held at 60°C for four minutes and then temperature programmed to 170°C at 4°C per minute. The temperature was held at 170°C until all of the volatile species had eluted.

Semi-Quantitative Analysis

Semi-quantitative analysis of the identified compounds was achieved by measurement of the area under the selected ion current profile for each compound. For a given compound, the area under the most abundant ion was calculated using the data system. The computed area was then compared against the area found from the most abundant ion of the appropriate internal standard, d_{10}-anthracene or d_8-toluene. The concentration of the species is then calculated using the following equation:

$$C = \frac{A_c \times C_a}{A_a \times R}$$

where C is the concentration of the component. A_c is the integrated area of the characteristic ion from the selected ion current profile, R is the response factor for this component relative to the internal standard, A_a is the integrated area of the characteristic ion for the internal standard and C_a is the concentration of the internal standard in the sample.

Radian determined response factors for many compounds relative to d_{10}-anthracene and d_8-toluene. Where the response factor was not known, a value of 1.0 was employed.

Electron impact (70 eV) ionization was employed exclusively for analyses. The mass spectral information obtained was stored on a magnetic disc for future interpretation and reference.

C. D. Smith

Wastewater and Cooling Tower Analyses

Oil

The oil layer samples are assayed by placing 2 ml of oil into an open container. The sample is stirred for 8 hours which allows the volatile material in the sample to evaporate. The volatiles content is represented by the change in the sample weight over the test period.

Calculation of volatile organics in an oil sample can be accomplished with the equation below:

$$VO = \frac{\Delta w}{w_i}$$

where

VO = weight fraction of volatiles in sample.

Δw = initial sample weight – final sample weight.

w_i = initial sample weight.

The emission rate of volatile hydrocarbons from oil can be calculated using the following equation:

$$ER_{oil} = \frac{G(VO_i - VO_o)}{1 - VO_i}$$

where

ER_{oil} = emission rate of hydrocarbon, lb/hr.

G = flow of weathered oil, lb/hr.

VO_i = weight fraction of volatiles in inlet oil.

VO_o = weight fraction of volatiles in outlet oil.

Water

Wastewater samples are analyzed for the amount of purgeable organics. The basis for the analysis is that only the volatile components in the wastewater collection and treatment systems will be lost as fugitive emissions. These volatile compounds comprise the bulk of the purgeable organics in the liquid.

The purgeable organics are swept out of the water into a Teflon sampling bag. At the conclusion of the purging cycle, the contents of the Teflon bag are analyzed on the Total Hydrocarbon Analyzer as previously described. The equipment for this analysis is organized as shown in Figure 18. The bag is a standard Teflon sampling bag. The purge gas for the Bellar unit is zero grade nitrogen with a flow rate of approximately 30 ml/min. The flow rate is controlled with two needle valves but will vary slightly from sample to sample and must be measured each time using a bubble meter on the downstream side of the Bellar apparatus. Purging is continued for approximately 30 minutes. The Bellar apparatus requires thorough cleaning between samples. The Teflon bag must be thoroughly flushed with zero grade nitrogen between each sample and a blank sample is analyzed for total hydrocarbons at the end of the flushing cycle.

The volatile hydrocarbon content of the water can be calculated from the following equation:

$$VO = (FR)(time)(ppmw)(P_{purge\ gas})$$

where

VO = volatile organics, grams.

FR = purge flow rate, ml/min.

time = time of purge, min.

ppmw = concentration of total hydrocarbon in bag, parts per million by weight.

$P_{purge\ gas}$ = density of purge gas, g/ml.

The emission rate of volatile hydrocarbons can then be calculated with the following equation:

$$ER_{water} = \frac{500(f_w)(VO_i - VO_o)}{V_s}$$

where

ER_{water} = emission rate of hydrocarbon, lb/hr.

f_w = flow rate of water through system, gal/min.

VO_i = volatile organics in the inlet water stream, grams.

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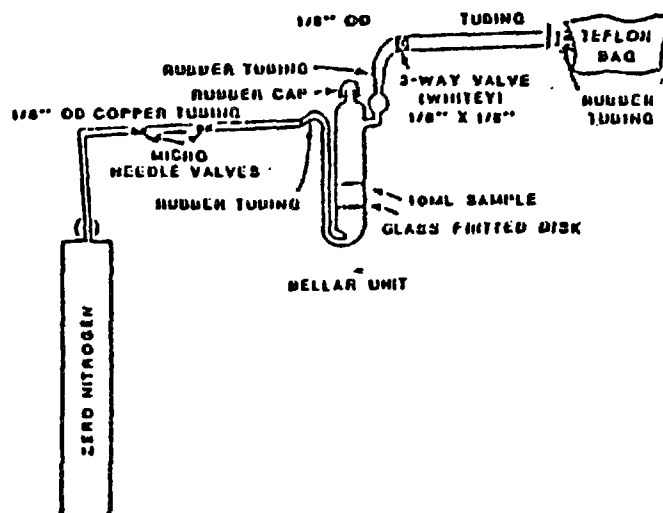
Figure 18. Wastewater and Cooling Tower Samples Purge Apparatus

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VO_o = volatile organics in the outlet water stream, grams.

V_s = volume of sample, ml.

Total Organic Carbon

Total organic carbon assays were accomplished with a Dohrmann DC52D TOC Analyzer. This instrument oxidizes organics to carbon dioxide and then reduces the carbon dioxide to methane. The methane is measured with a flame ionization detector.

The instrument is zeroed using a "zero carbon water standard" especially prepared for this analysis by Radian. The water is deionized, filtered and distilled from potassium permanganate under helium with a high reflux. This has proven to be superior to commercial standards. The standard for the analysis is 180 ppm carbon in water available from Dohrmann.

Several replications of each sample were required because the size of the portion of the sample actually analyzed is so small (30 $\mu\ell$) that it is difficult to obtain a representative portion.

Stack Gas Analyses

Particulate Determination

The total weight of the particulates was determined from the combined weight of material collected on the filter, on the exposed surfaces preceeding the filter in the EPA Method 5 sampling train, and in the first impinger. Procedures described in EPA Reference Method 5 were used, and a gain loading value was determined based on the total volume of stack gas sampled.

Sulfur Oxides (SO_x)

Separate analyses for SO_3 and SO_2 were performed on the impinger samples collected during each EPA Method 5 train operation. Aliquots of the isopropanol (SO_3) and the two 6 percent H_2O_2(SO_2) impingers were titrated with barium perchlorate to a Thorin indicator and point as specified in the EPA Reference Method 8. The amount of sulfate found was used to determine the amounts of SO_3 and SO_2 originally collected from the volume of stack gas sampled.

Determination of Nitrogen Oxides – Phenoldisulfonic Acid Method

Nitrogen oxides (NO and/or NO_2, or collectively, NO_x) in stack gas are determined as nitrate (NO_3) colorimetrically. NO_x is collected in a

glass flow-through type bomb and converted to nitrate ion by reaction with
aqueous hydrogen peroxide which is injected immediately following collection
of the sample. A yellow color is developed at a later time by the addition
of reagents. The color intensity developed is a function of the concentra-
tion of the nitrate. The intensity is measured using a spectrophotometer
capable of operating at 410 nM.

Referee Method for Low Concentrations of Nitrate:
Spectrophotometric Using Chromotropic Acid

In this method a 2-ml nitrate sample is mixed with masking reagents
and chromotropic acid indicator in a sulfuric acid medium.

$$2NO_3^- + \qquad \underset{\text{OH}}{\overset{\text{OH}}{\text{(naphthalene with OH, OH, SO}_3\text{H, SO}_3\text{H)}}} \quad \xrightarrow{\ \text{H}_2\text{SO}_4\ \text{medium}\ } \quad \text{Yellow Color, Max.}\ \text{Absorbance} = 410\ \text{nM}$$
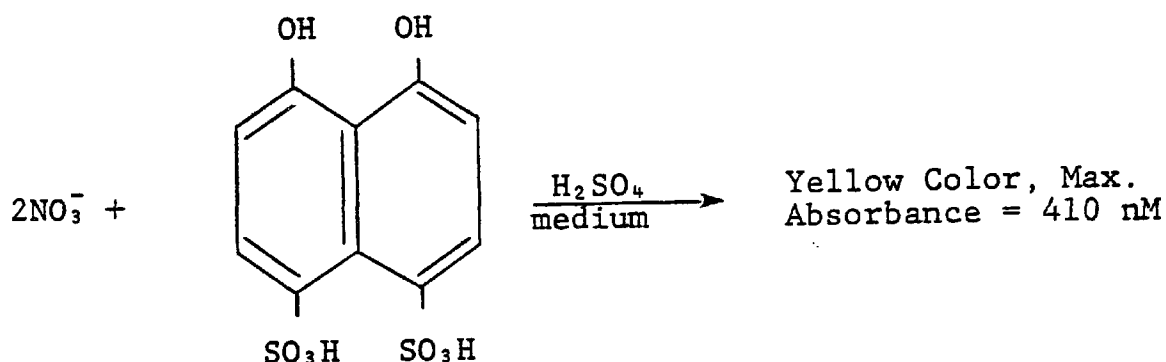
The absorbance of the yellow reaction product is measured in a 1-cm cell at
410 nM. The nitrate concentration is calculated by comparing the absorbance
to that of a known nitrate standard.

Aldehydes

The 1 percent solution bisulfite impinger solutions were analyzed
using an iodine-starch titration. Samples were collected, diluted to 50 ml
and treated with 10 ml of bisulfite and 1 ml starch indicator. Any excess
bisulfite was then destroyed with an excess of 0.1 N iodine. The excess
iodine was then destroyed with a few drops of sodium thiosulfate. The
thiosulfate was then titrated to a faint blue endpoint. Addition of 25 ml
of carbonate buffer solution released the complexed bisulfite which was
titrated to a final endpoint with 0.01 N iodine.

This procedure measures total aldehydes as formaldehyde. One ml
of 0.01 N iodine is equivalent to 0.15 mg of formaldehyde. By accurately
measuring the amount of titrant used in the final titration only, the total
mg of aldehyde may be calculated.

Ammonia

Ammonia in the gas stream is collected by bubbling the gas through impingers containing sulfuric acid at a pH < 2. Ammonia is determined by a distillation-titration method in which the sample is buffered to pH of 9.5 by using sodium hydroxide and a sodium tetraborate buffer. The sample is then placed in a distillation flask with the ammonia being driven off and bubbled through an indicating boric acid scrubbing solution. This scrubbing solution changes color upon reaction with the ammonia. The amount of ammonia present is quantified by a titration technique utilizing a standard sulfuric acid solution to titrate back to the indicator's original color.

Hydrogen Cyanide

Cyanide in the gas stream is collected by bubbling the gas through impingers containing sodium hydroxide at pH < 12. The resulting impinger solutions are tested for the presence of oxidizing agents, which if found are removed by the addition of ascorbic acid. The solutions are also tested for the presence of sulfide, which if found is precipitated using lead nitrate and filtered off. An aliquot of sample is then placed in a cyanide distillation apparatus and an air purge is applied with a vacuum. The sample is acidified using sulfuric acid with the resultant off-gases being collected in a bubbler containing a solution of sodium hydroxide. This distillation is used to separate CN^- from other cyano compounds. The concentration of CN^- in the scrubber solution is then determined by colorimetric determination using pyridine-barbituric acid, which forms an intense blue color with free cyanide. The absorbance is then read and concentrations determined against standards. These concentrations are calculated as hydrogen cyanide.

REVIEW

by

R. M. Roberts
KVB, A Research-Cottrell Company
Tustin, California

on

METHODOLOGY – SAMPLING AND ANALYSIS OF ATMOSPHERIC

EMISSIONS FROM PETROLEUM REFINERIES

RESUME

Richard M. Roberts is a Principal Engineer in the Research & Analyses Division at KVB. His academic background comprises a B.S. degree in Chemistry from U.C.L.A. at Aerojet-General Corp., he moved from analytical chemistry to specialized instrumentation development and thence to bench and engineering studies involving various processes keyed to pollution control or energy conservation. Prior to his recent affiliation with KVB, Mr. Roberts was vice president of Analytical Research Laboratories, Inc., in charge of government contract operations.

REVIEW

by

R. M. Roberts
KVB, A Research-Cottrell Company
Tustin, California

on

METHODOLOGY - SAMPLING AND ANALYSIS OF ATMOSPHERIC
EMISSIONS FROM PETROLEUM REFINERIES

OVERVIEW

Perhaps unlike other papers given at this symposium, it is almost inappropriate for a reviewer to comment on the present one in generalized terms. Mr. Smith has described very specific methodology, such that the commentator has no alternative but to deal in the same coin—specifics.

Because of this, and the possibility that some of these specifics may have been misunderstood, the reviewer met with Calvin Smith before the symposium. This resulted in several clarifications of what were indeed reviewer's misconceptions. The editing, if any, of the preprinted symposium proceedings may not incorporate all of these clarifications, however. These misunderstood subjects are therefore still addressed here, assuming that other readers may stumble on the same topics. In such cases, the clarifications provided by Mr. Smith have been provided.

The reviewer's knowledge base of the present work was limited to the paper considered here and that presented by D. D. Rosebrook at the last annual APCA meeting. It is, nonetheless, clear from these publications that one of the key products of the study was the development of nomographs for estimating mass losses from valves and flanges using TLV readouts.

We hope to apply this very powerful tool at an early date at a large west coast refinery. We would, however, first prescreen a large population of valves and flanges using the old soap technique, then quantify all the leakers found using the TLV sniffer. As is suggested in some of the following comments, this "broad brush" approach is statistically safe and may, perhaps, be actually less laborious than systematically preselecting a small count of representative fittings.

SPECIFIC COMMENTS

Statistical Base

It is hoped that the population of valves and flanges selected for testing (see p. 8, Smith report) can be supported by statistical arguments. It would seem, given the expectable incidence of leakers, that the field sizes may be too small, inviting skewing in the findings. For example, at one refinery, we tested 3,100 gas service and 4,700 liquid service flanges and located only 17 leakers in the former and 2 leakers in the latter category. Considering that Radian recommends an upper test population of less than one-tenth that, the number of leakers found could be only one or two. In contrast, the populations of pumps, compressors, drains, and relief devices specified appears quite adequate.

A point of clarification regarding valve and flange populations involves Figure 3 (p. 15). The failure there to identify the bonnet flange as a potential valve leakage point results from Radian's practice of including that seal as part of the flange population rather than considering it as part of a valve.

Sampling Trains

Flow Through Method

Explanation of the mode of operation of the sampling train principally used (Figure 4, p. 19) omitted a key factor. No vent is shown. Mr. Smith pointed out that the tent is affixed to the top of the valve with intentional gaps being produced in the taping. The tent itself is sometimes punctured to allow inflow of purge air.

A problem with this arrangement is that one is bleeding refinery air into the bag and that air may be of questionable and spatially variable quality. This is corrected for by taking a background sample, the total hydrocarbon content of which is input to the leakage formula.

We would suggest that if an intentional vent, fitted with sections of activated charcoal and silica gel, is used, you will obviate the need for making the background correction. This means, of course, that the sealing of the tent must be tight since the envelope is being operated at a slight negative pressure. Thus the sealing as shown in Figure 6 (p. 22) could invite leakage, since oily surfaces might be involved.

An incidental comment here addresses compressor testing. Mr. Smith advised that only the seals on these devices are tested. Our experience has shown that cap nuts, particularly the end one, also leak occasionally and should be checked.

Blow-Through Technique

Mr. Smith acknowledged the problems with this technique, which consequently resulted in its very minor usage on the program. The principal problem is that, in using a compressed air carrier, any leakage from the tent could result in erroneous data. Flow is measured upstream of the potential leak sites (in the tent). Also, since such tent leaks may not involve completely mixed gas, outflow composition may not truly represent that which would result from the fully confined mixing of the air carrier and the hydrocarbons escaping from the valve or fitting.

It is assumed that the flow-through method was actually used in lieu of the blow-through method. This would be appropriate for the slow leaking components. In the case of high leakers, however, volumetric loss is usually enough to drive the train without use of pump or carrier. The fitting is tightly bagged and the sample line run out to a gas meter, analyzer, and any collection device required.

Stack Grab Samples

Management of moisture in flue gas grab samples has always been a serious problem. A technique for circumventing this is shown in Figure 12 (p. 35). Calvin Smith acknowledged that the system proved to be less than successful.

Our experience has shown that use of the Perma Pure Drier in any train in which compositional analyses are conducted should be cautiously approached. The device is definitely not permselective for water. Hydrocarbon species of interest also permeate the membrance and are lost to the measurement.

Oil-Water Separators

The methodology described for estimating hydrocarbon releases from oil-water separators apparently did not furnish acceptable results. The IERL has now contracted with Engineering-Sciences to develop a more acceptable approach. The virtual source technique is being investigated there. It is hoped that this controversial technique will prove successful.

Water Cooling Towers

The discussion of in/out hydrocarbon change in water cooling towers (p. 56) introduces a disturbing feature. Emissions are based on the difference in hydrocarbons measured in the purgeable organic fraction present in the pre- and post-cooled streams. Problems were encountered when total organic carbon measurements were attempted.

Working with the purgeable fraction is technically all right, if the system is faithfully measured the same way each time. The bellar Lichtenberg procedure was intended only for compounds that are quantitatively

recovered by the method. These are then specifically analyzed, usually by GC/MS. When total hydrocarbon readouts are used, as described here, you also involve unresolved components that are higher boiling and which are not quantitatively recovered. His fractional recovery effect for materials of intermediate volatility will vary with test conditions. Thus, unless the transfer process is not carefully reproduced, unreliable data can result.

There is also the obvious question of the effect of measuring only a fraction of substances that are also fractionally lost during the cooling process. That is, if half of intermediate boiler "Z" emits to the air while passing through the cooling effects and only half is measured during analyses of the in/out water samples, then the analysis would account for only one quarter of "Z" being emitted to the air.

C. D. Smith

QUESTIONS AND ANSWERS

Q. James J. Morgester/California Air Resources Board - I was interested in how you handled hot valves.

A. - In the case of hot valves we used a little different technique for constructing the enclosure around it. We generally had asbestos tape and aluminum foil which actually made the seal at the valve. A standard hose clamp is enough to seal the aluminum foil on the asbestos tape. I should like to point out that you do not need a very tight seal with this vacuum technique for sampling leaks. As a matter of fact, sometimes with duct tape and Mylar, the seals were made too tight. In that case, you must punch a small hole into the Mylar to reduce the vacuum inside that enclosure.

Q. James J. Morgester/California Air Resources Board - Thank you! Do you have an estimate of the total number of valves that you actually did bag and what percentage of those were hot valves?

A. - I am not certain but I would say that the percentage of the valves that we actually bagged that were hot was probably 3 or 4 percent.

Q. James J. Morgester/California Air Resources Board - How did you limit your sampling?

A. - You will get this information in detail in the succeeding papers. As I remember, with our arbitrary 200 ppm cut-off on the screening value, we, in general, had designated something like 20 percent (± 5%), at any given refinery of the valves to be bagged. And for the first four refineries, or so, we bagged everyone of those. As the data base grew we realized two things. We were not able to bag everyone that we wanted to because of time constraints, but additionally we realized that we had enough data so that we could now bag a statistical sampling of those valves and flanges. So we did reduce the number that we sampled that were above 200 ppm after about the fifth or sixth refinery. For instance, it seems to me like we bagged something like one out of 40 below 200 ppm as part of the quality control program, and at low screening values (between 200 and 5,000 ppm), we would bag something like 50 percent. We never reduced the number that we bagged in the high leak rate ranges, because they were the ones that were going to have a pronounced influence on the emission factors, so we bagged every one above a certain screening value.

C. D. Smith

Q. James J. Morgester/California Air Resources Board - I noticed you calibrated your lab device with propane and your field device with hexane, was that simply an artifact that showed up or was there a reason for that?

A. - Well, there was a reason for it, I'm not sure how good it was. The fact is that you can obtain NBS standard of propane but you cannot get an NBS standard of hexane in that concentration range. We wanted to calibrate the total hydrocarbon analyzer with the same material that we had an NBS standard for. For the TLV, as you know, its not nearly as critical that you have that instrument calibrated exactly, because the readings that you get from that instrument are quite variable. We had certified standards of hexane from manufacturers, but they were not traceable to an NBS standard, whereas on the analyses of the bag samples we did want them traceable to an NBS standard.

Q. James J. Morgester/California Air Resources Board - If we developed, however, some kind of a regulation or standard that uses the field screening devices, which is the direction we are all going, does Radian recommend that standard be set up on hexane standard or propane standard?

A. - I don't know what Radian recommends. I think we and several others are in the process of formulating what that should be.

Q. James Stone/Louisiana Air Control Commission - I have several questions. One of them is what type of refineries did you visit? I've seen that generally refineries fall into two types. There is a major refinery that would have its own crude oil supply available to it and it would have its own internal engineering standards that it would adhere to and it would be one type. Then, the other type would be usually a bit smaller. They would usually get their crude from the spot market and a lot of times they are running almost on a shoe string and so their maintenance procedures are quite a bit different from what the major refineries usually are. Did you make any attempt to include or exclude different types?

A. - In the design we tried to get something that was representative of the refinery industry. So we went to refineries in four geographical locations. We had them broken down into old and new refineries, the cut-off being an old refinery was older than 20 years, or contained any unit that was over 20 years old. We went to large refineries and small refineries. The cut-off there being any refinery that processed less than 50,000 barrels of crude per day was a small refinery. Anything more than that was a large refinery. We went to refineries that were primarily producing gasoline, refineries that produced lubricating oils, and refineries that had mixes of everything. So, we think we have a pretty representative sample of all the different types of refineries.

Q. James Stone/Louisiana Air Control Commission - Second question is what about heat exchangers? When I've gone through refineries there have been many of these that are leaking. They are a large source of fugitive emissions, but it is a very difficult one to control or characterize.

A. - I believe that some of the flanges, in our data base, are in fact the flanges on heat exchangers.

Q. James Stone/Louisiana Air Control Commission - Looking at your sample train it appears to me that you could adjust the amount of hydrocarbon measured to any convenient number by the way you handle the apparatus.

A. - I didn't understand that.

Q. James Stone/Louisiana Air Control Commission - O.K., if you have a small leak and you sample at a slow rate, then you've got a large number, and if you have a large leak you sample at a fast rate, you've got a small number.

A. - Yes, there is some adjustment of the concentration at equilibrium in that sampling train, but that doesn't adjust the emission rate.

Q. James Stone/Louisiana Air Control Commission - I think your sampling system is very subject to being biased by the way you run it. What you are measuring is not independent of the operator, it is very much determined by the way the operator handles the equipment.

A. - By adjusting the flow through the sampling train all you do is introduce more or less dilution air. The amount of hydrocarbon that is leaking out of the valve is constant. You are varying the concentration, in that sampling train, by diluting it with more or less ambient air, depending on how fast you run the vacuum pump.

Q. James Stone/Louisiana Air Control Commission - But usually you don't measure how much ambient air is leaking into it. You just punch a hold. That is no way to measure.

A. - No! The hydrocarbon leak from the valve plus the ambient air, that total flow rate through the system, is measured by a dry gas meter on the sampling train. So, we do measure the amount of air that is coming through that enclosure.

Q. Paul Harrison/Engineering-Science - Why did you use the TLV Sniffer for the correlations instead of the OVA?

A. - We used the TLV because it was the first one that we encountered that was a reasonable device. It only weighs 2 to 3 pounds. It is pretty compact. It is battery operated, and it is pretty sensitive. You can read on those scales that I showed you between 0 - 100 ppm, or 0 - 1,000 ppm, or 0 - 10,000 ppm, or 0 - 100,000 ppm. That is pretty flexible in terms of the concentrations. The reason we went to the OVA is because some people in the EPA, decided that instrument gave a much faster response time than the TLV did, and consequently you could measure the screening values at valves a little bit faster. In addition, it has a flame ionization detector, which most people tend to think is a better, more reliable, detector for

measuring hydrocarbons. Also, response factors for hydrocarbons are generally centered around one (1), relative to each other, with a flame ionization detector, whereas with thermal conductivity cells sometimes they are not. With other kinds of detectors the response factors are normally so tightly grouped.

We started with the TLV early into the program and when the EPA began evaluating an OVA then we decided that we should probably do that too.

Q. Paul Harrison/Engineering-Science - What was your experience with each, I realize some of the reasons why one is better than the other, from what I have heard, but what did you think of it in the field?

A. - As far as actually being able to carry it around and operate it, I would say that the only differences between the OVA and the TLV are: the OVA is a little heavier, and if you are the guy that has to lug it up a tower, then you are a little bit more reluctant to do that; it does recover faster from a source that is leaking at a higher rate. If you screen a source that leaks at a 100,000 ppm with the TLV, it may be two or three minutes before it has come back to baseline. So, in fact, the OVA does have a faster response in terms of return to baseline. My basic problem with OVA is that it has a fairly peculiar-type flame ionization detector. Even though on most flame ionization detectors all hydrocarbons, and generally they are referenced to heptane, have response factors of one ± 5 or 6 percent, on the OVA that is not the case. Those response factors vary considerably and the "magic" of FID I think is a little misleading there.

Q. Paul Harrison/Engineering-Science - What was the smallest refinery you hit?

A. - I think it was something like 8,000 barrels a day.

Q. Paul Harrison/Engineering-Science - Was it fully integrated?

A. - No.

Q. Paul Harrison/Engineering-Science - I should comment that we have seen things like Scotts Bluff in Nebraska where they are fully integrated at that size, so there are a few that try to be fully integrated. They look like toys.

Why don't you use the more readily available methane standards? From the operational point of view, it is much easier to get in pressurized cylinders. I can use either one, but it seems to me that methane is much more available.

A. - I suppose that it is just as easy to choose methane or hexane. We were, however, relating the emission rates to hexane, as was done in previous studies,

so we chose to calibrate the TLV with hexane. It was just as arbitrary, or a little less arbitrary actually, for the total hydrocarbon analyser. As I said the reason we chose propane to calibrate it was because we could trace it to a NBS standard. And the other thing, that always tempers it, is that with methane, not very many people are concerned about the amount of methane that is being emitted, so why relate everything to methane? Those are arbitrary decisions, but I think that is probably the kind of thinking that went into it.

COMMENT/Donald D. Rosebrook/Radian Corporation - If I may, I would like to call for a short discussion from someone here in the audience. As you are aware, it was brought out somewhat by Calvin and much more broadly by Mike, that we did not feel any confidence at all, in the numbers that we generated for fugitive emissions from wastewater systems, and you should be aware that the EPA has undertaken another study to measure those fugitive emissions. I would imagine that study has, within the last month or so, gotten underway. That contract, as I understand it, is placed with Engineering-Science. There are some representatives here today of Engineering-Science and of EPA. I would like to make a general request that they give us a short summary as to their approach, and how they intend to conduct these measurements. Is there someone here who is willing to address that question?

COMMENT/Bruce A. Tichenor/USEPA-IERL/RTP - I am the project officer on the study that Don just mentioned. The contract was let a month ago. It is going to extend for 16 months, and that 16 months means that is until the final report is due.

Basically, all we are talking about is a three-phase program. The first phase is scheduled for about three months and is essentially the development of the experimental methodology. The second phase will also extend about three months, and these numbers may be off a month or so, but I don't think so. That will be the verification of that methodology in the field at operating petroleum refineries and we are going to look at two petroleum refineries to do this. What we are talking about is not relying specifically on one method, but always having an alternative method so there will be some way to verify that the data we do get are reasonable. And the third phase will be the data collection phase, which will be very similar to the Radian program that will be discussed in the next two days, and is going out into the field looking at operating wastewater systems, and gathering emission data from them. The range of sampling methods that are being looked at include: upwind, downwind dispersions; use of tracers; the possible enclosing of the systems for some of the smaller systems; and, the possibility of looking at laboratory models of the systems. We are going to look at approximately ten petroleum refineries, and we will hopefully get the same cooperation from the industry we got with the Radian program. That is it in a nutshell, but like I said if any of you are interested in more details feel free to contact me, Paul, or anyone else from Engineering-Science. I am sure we can provide you that information.

C. D. Smith

COMMENT/Donald D. Rosebrook/Radian Corporation - Thank you! Are there any further questions for either Mike or Calvin or any further commentary from the conferees?

Q. Joseph Zabago/Mobil Oil - What did you do about bonnet flanges?

A. - We considered the bonnet flange a flange.

Q. Thomas Goff/Kern County Air Pollution Control District - I was wondering if the baggable sources selected off the P&I diagram, which I understand is about 20 percent of those selected that were actually bagged and tested, turned out to be the ones at ground level?

A. - We could not tell, on the piping and instrumentation diagrams which ones were above grade and which ones were not. Then of course, the screening value dictated which ones were sampled and which ones were not sampled. If one above grade leaked, we sampled it. If you will remember the slides showing the sampling train, you saw the coil of black hose, the Teflon lined hose. We had enough hose to sample at levels of around 120 to 150 feet. As a matter of fact, we used that to sample relief valves.

Q. P. L. Scupholme/BP - Environmental Control Center/ENGLAND - Can I first of all say how impressive I've found your presentation. My colleagues in Europe hope we can use some of the data at European refineries in the years to come. My question though is probably simple, hopefully not irrelevant. What effect do you think weather conditions may have on these emissions, either ambient temperature or wind speed?

A. - I have no data that allows me to say one way or the other. I have no idea.

COMMENT/Donald D. Rosebrook/Radian Corporation - We can say one thing. We can tell you a little bit about what weather conditions do to the sample team and therefore some of the variability of the data. I think you will see later in some of these presentations, where there is some significant variability, there apparently is some small bias introduced from one refinery where the weather was rotten. If you count sleet, snow and high wind and cold rain at about 30°F, rotten weather, that is what it was.

Q. (To Roberts) William Benusa/Gulf R & D Company - You commented on the sampling technique using the Bellar system as probably not being very adequate. Did you have a recommendation as to a better system for getting hydrocarbons from your cooling towers or wastewater treatment systems?

A. (By Roberts) - We are thinking about writing a proposal on that very subject now. I'm afraid I can't comment on the approach that we would recommend, but I think there is a better way. It involves, in essence, the same type of methodology that Calvin described, looking at hydrocarbons in and out. It is just a matter of the measurement of these moieties.

Q. William Benusa/Gulf R & D Company - When you sampled, say valves with liquid leaks, under the screening procedure what kind of a judgment do you make as to the placement of the probe?

A. - You'll find very quickly that you don't put the probe in the liquid or you've destroyed that reading. In general, if the valve stem is coming out like this, the liquid is going to be dripping down there, so you obviously don't put the probe right in the liquid, but still you choose four cardinal points. You just rotate them so that you don't have the probe in the liquid. It obviously is going to bias the reading, but then if you have a liquid leak it is going to be a highly leaking valve anyway.

QUALITY ASSURANCE AND DEVELOPMENT OF
STATISTICAL MODELS

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ABSTRACT

This paper discusses the primary quality assurance and statistical analysis procedures used in Radian's fugitive emissions sampling program. Quality control data from the screening and sampling of baggable sources is analyzed and a critical evaluation of the statistical models used to estimate emission factors is presented.

RESUME

Lloyd Provost is the Quality Assurance Director for Radian Corporation. He received his B.S. degree from the University of Tennessee in Statistics and his M.S. degree from the University of Florida in Applied Statistics. He worked for the U.S. Department of Agriculture as a mathematical statistician for seven years prior to joining Radian in 1977. His duties at Radian include overseeing quality assurance programs for all of Radian's contract work, coordinating the development and execution of specific quality control programs, and coordination of data analyses for specific projects. Mr. Provost is a member of the American Statistical Association, ASTM Committee E11 on Statistical Methods, ANSI Z-1 Committee on Quality Assurance and the American Society for Quality Control (ASQC).

L. P. Provost

QUALITY ASSURANCE AND DEVELOPMENT OF
STATISTICAL MODELS

SECTION 1

INTRODUCTION

This paper presents and discusses the most significant quality
control efforts in Radian's Refinery Fugitive Emissions Sampling program.
The complete QA/QC procedures and data are described in Appendix C to the
final report, "Quality Assurance and Statistical Analysis of Emissions Data."

This paper presents the results in three major areas of the QA
program:

- Quality control for hydrocarbon screening devices.

- Quality control for hydrocarbon measurements from baggable sources.

- Statistical procedures for analyzing the emissions data.

L. P. Provost

SECTION 2

QUALITY CONTROL FOR HYDROCARBON SCREENING DEVICES

The screening of sources during this field sampling program was accomplished with sensitive portable hydrocarbon detectors. The principal device used in this study was the J. W. Bacharach Instrument Co. "TLV Sniffer." The Century Instrument Company Organic Vapor Analyzer (Model OVA-108) was used for some screening, but these values were not included in the primary correlation calculations. The instruments were calibrated daily with standard mixtures of hexane in air. The OVA-108 and TLV Sniffer give direct readings of hydrocarbon concentrations in ppm by volume.

When screening, the probe of the hydrocarbon detector was normally placed as close as possible to the potentially leaking source. The maximum reading obtained on the source was used as the screening value. For evaluation purposes, some readings were also obtained five centimeters from the source for all source types.

SCREENING DEVICE CALIBRATION CHECKS

The TLV and OVA instruments were calibrated each day they were used. Standards of 500-525 ppmv and 2000 ppmv hexane in air were used to get a two point calibration each day. Before a recalibration was made each day, the values obtained from the instrument were recorded. This served two purposes:

● Check for instrument damage or malfunction,

● Document the stability of the daily calibration.

The results of these calibration checks at selected refineries visited are shown in Figure 1 for the lower standard. The data for the high standard were similar. Three different TLV instruments were used at these refineries. Table 1 gives a statistical summary of these data. None of the devices gives any indication of a consistent bias (or drift) at either the high or low level. The maximum percent differences found were always less than 20 percent of the known concentration.

Based on this data, it is concluded that the daily calibration of the screening devices at two levels using standard gases was adequate for obtaining consistent, unbiased readings.

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Symbol is code for device:

```
1   TLV    7C7C04
2   TLV    7C7C16
3   TLV    7ESB55
```

```
        620 +
        615 +                                                                                    1
        610 +
        605 +
  T     600 +                    1   TLV    7C7C04
  L     595 +                    2   TLV    7C7C16
  V     590 +                    3   TLV    7ESB55                                           1
        585 +
  R     580 +
  E     575 +
  A     570 +
  D     565 +
  I     560 +                          3                              3
  N     555 +                                            3
  G     550 +
        545 +
  O     540 +            3              2        1                  1           1
  N     535 +                                                 3
        530 +        3       2       2  1          3   3
  L     525 +--------------1---------2---1-----------------1-----------------1-----------------------
  O     520 +                              2              3  1  3        1              3
  W     515 +        2                     3                             3   1
        510 +        3                     1                             3
  S     505 +        3                     1           1
  T     500 +    1       2        1                                              3
  D     495 +                                                                    3
        490 +            1
        485 +
        480 +        1       1                                                        1
        475 +
        470 +                                               3
        465 +
        460 +
        455 +                                                                    1
        450 +    2           3                                                  1
            +---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---+---
             1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16  17  18  19  20  21  22
```

TEST

NOTE: 3 OBS HIDDEN

Figure 1.   Calibration Checks for TLV Sniffer – Low Standard

TABLE 1.   STATISTICAL SUMMARY OF CALIBRATION CHECKS

	Number of Checks	Average Difference (ppm)	Average Percent Difference	Minimum Percent Difference	Maximum Percent Difference	Standard Deviation of % Difference	95% Confidence Interval for Average Percent Difference
Instrument 1							
Low Standard (525 ppm)	21	– 4.4	–0.8	–12.3	19.5	7.3	(–4.1 , 2.5)
High Standard (2023 ppm)	21	–28.0	–1.4	–11.0	3.8	4.1	(–3.3 , .5)
Instrument 2							
Low Standard	8	–16.9	–3.2	– 6.1	3.8	5.4	(–7.7 , 1.3)
High Standard	8	– 4.8	–0.2	–14.3	2.9	2.9	(–4.7 , 4.3)
Instrument 3							
Low Standard	20	– 5.3	–1.0	–14.3	7.9	5.2	(–3.4 , 1.4)
High Standard	20	–19.8	–1.0	–11.0	8.7	4.1	(–2.0 , 0.9)

Percent difference = (Measured – Standard) x 100/Standard

REPEATABILITY AND REPRODUCIBILITY OF SCREENING DEVICES

The repeatability of the screening process was investigated by performing repeated screenings on the same source by the same operators. Both the TLV sniffer and the OVA-108 instruments were used to screen at the sources and 5 cm from the source. The absolute value of the percent difference between the duplicate readings is plotted against the mean of the duplicate readings in Figures 2 and 3 for maximum reading using a TLV and OVA, respectively. Most percent differences at the source are less than 75 percent for the TLV and below 40 percent for the OVA. The percent differences for the TLV at 5 cm tend to be higher, indicating that the method is not as repeatable as screening directly at the source.

Quality control studies were run on the TLV sniffer to determine the reproducibility of the measurement method. Between one and five sources at selected refineries were selected with screening values between 200 and 10,000 ppm. Each day that screening was done, at least one team would screen each of the sources. Duplicate readings were sometimes performed on each device, both at the source and 5 cm from the source. Figure 4 illustrates typical results obtained from the repeated screenings using the TLV sniffer at the source. Within a day, the screening results from each team were generally close. A visual comparison of duplicate readings by the same team can also be seen. The magnitude of the concentrations at 5 cm is less than at the source. The magnitude of the difference between operators is larger, in one case, and about the same in the other case.

A variance component analysis was run on both TLV sniffer and OVA-108 data from the reproducibility and repeatability studies on selected devices. The results of this analysis for each device are given in Table 2. The pooled standard deviation for all TLV repeat readings at the source (all devices) is 0.50 $\ln$ (screening value), yielding a 90 percent repeatability of 117 percent.

The effect of different operators can also be observed in this analysis. Pooling the data from pumps and valves, the standard deviation is 56 percent. Ninety percent reproducibility is then equal to 130 percent. The pooled standard deviation for all OVA (at the source) repeat readings is 30.5 percent producing a repeatability of 85 percent. Note that the repeatability of the OVA instrument appears better than that of the TLV, but that there is less data available to evaluate the OVA.

A similar variance component analysis was done on the 5 cm TLV readings. The pooled standard deviation for repeat readings was 0.79 $\ln$ (screening value) and the pooled 90 percent repeatability is 184 percent. This high repeatability figure again shows the 5 cm method to be more variable than screening at the source. Reproducibility was also calculated by pooling the variance from both TLV sniffers to describe the operator effect. The standard deviation is 1.06 and the percent reproducibility is 246 percent, again much higher than that for screening at the source.
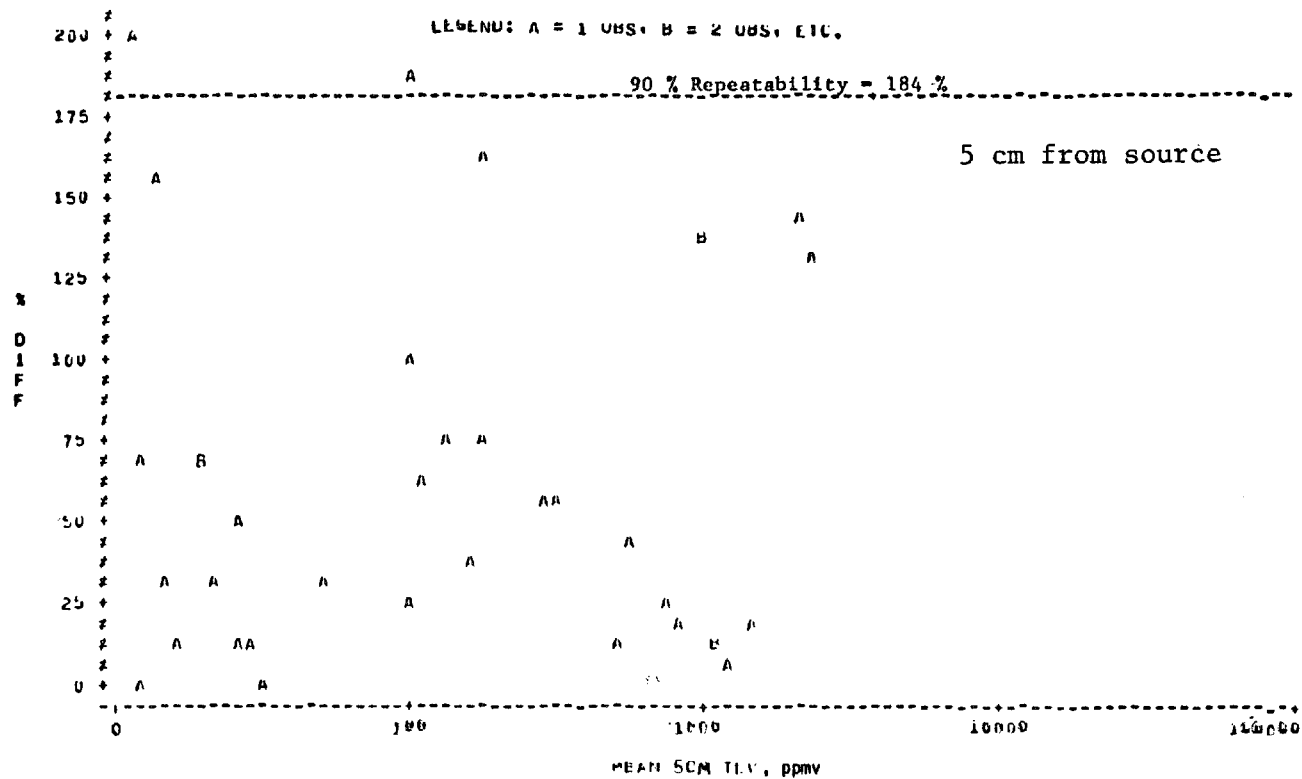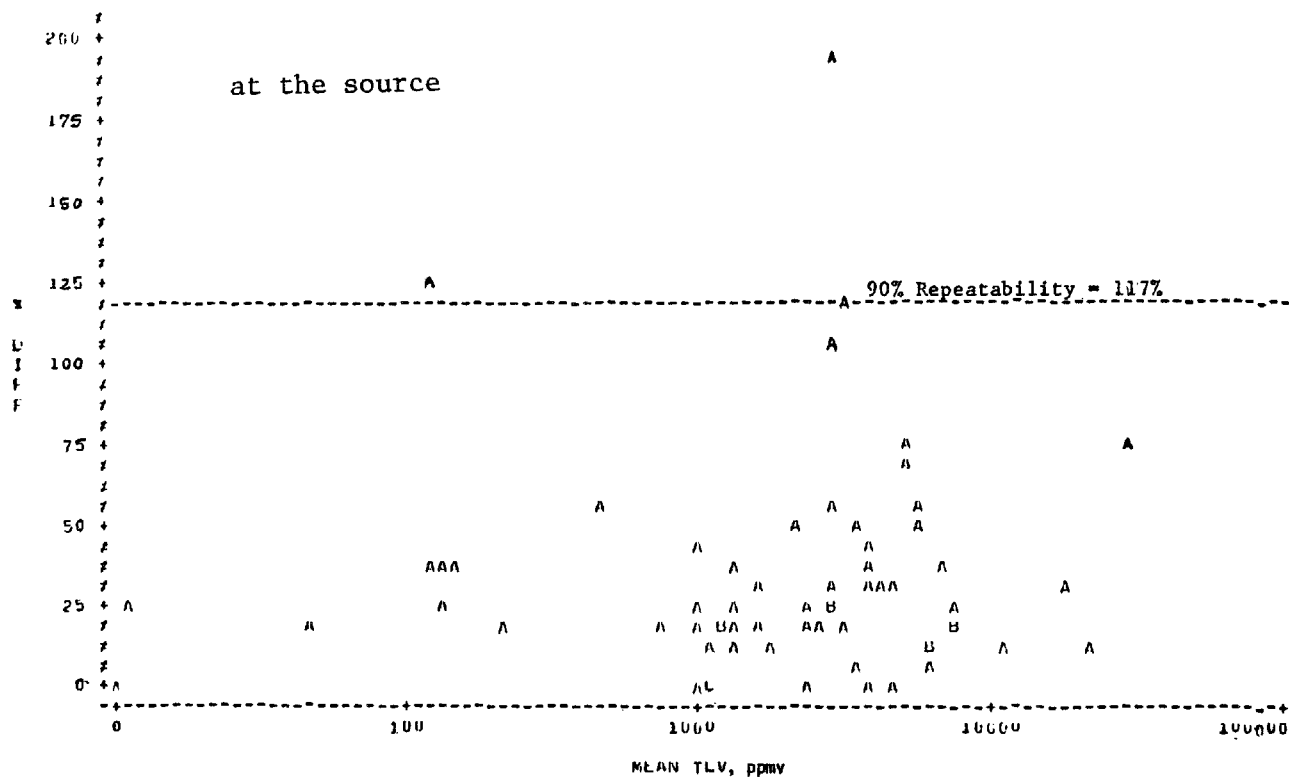
Figure 2. Percent Difference Between Duplicate TLV Readings
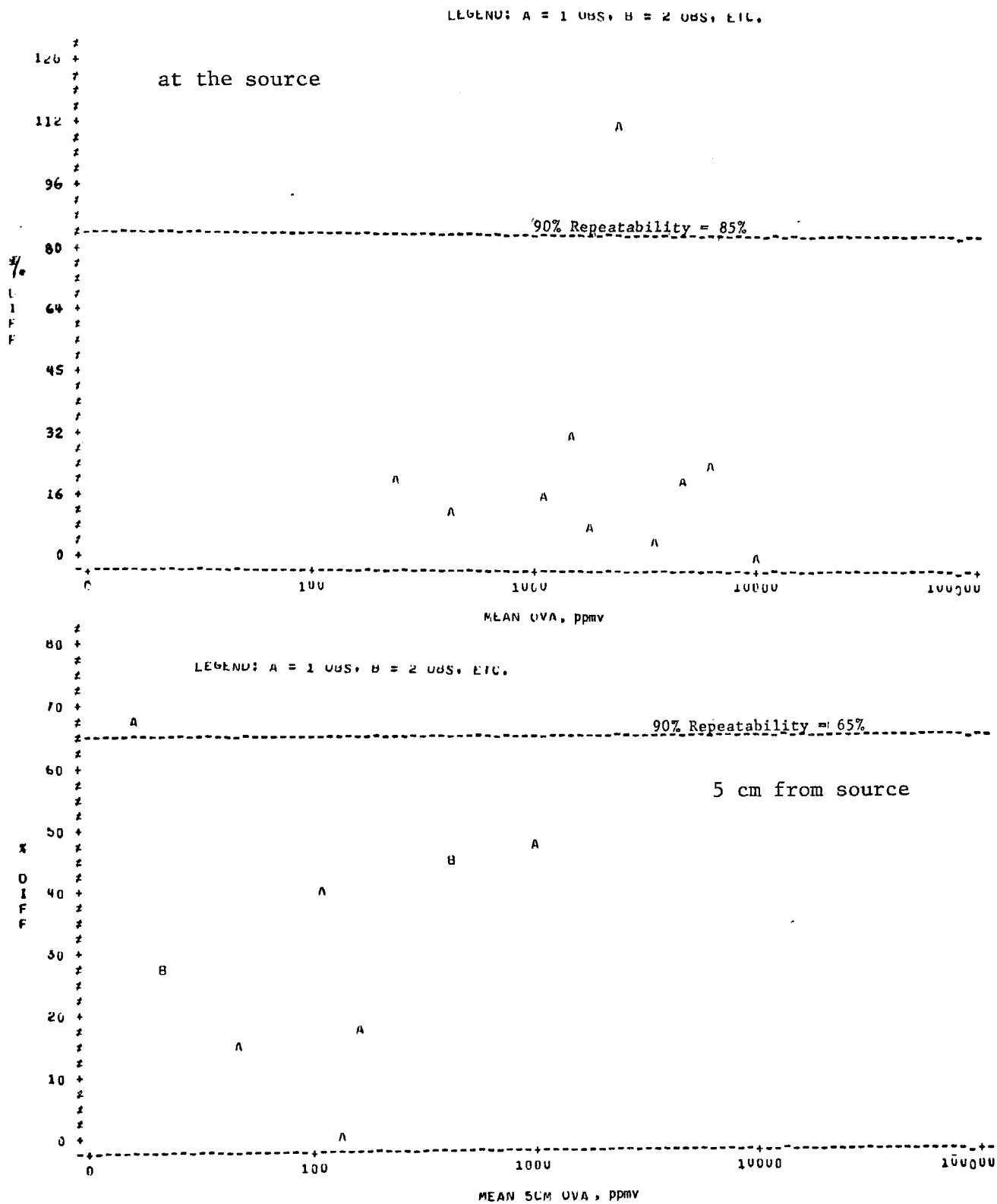
Figure 3. Percent Difference Between Duplicate OVA Readings
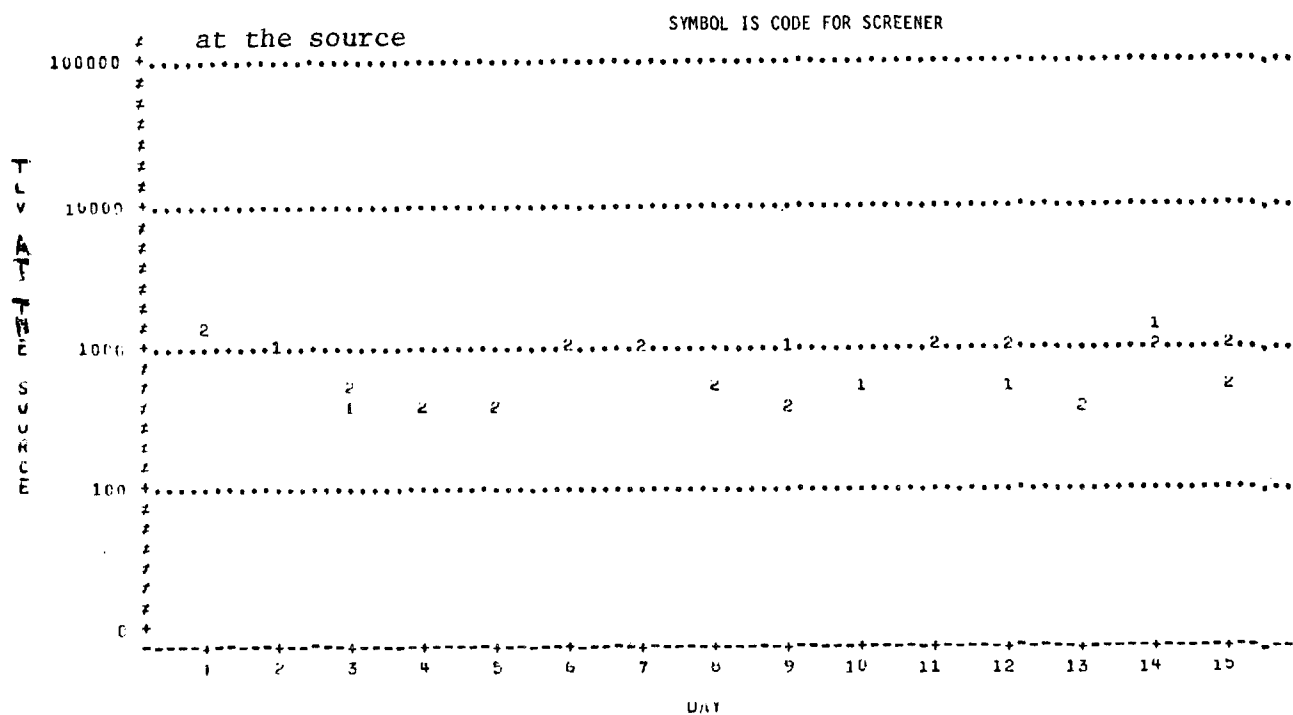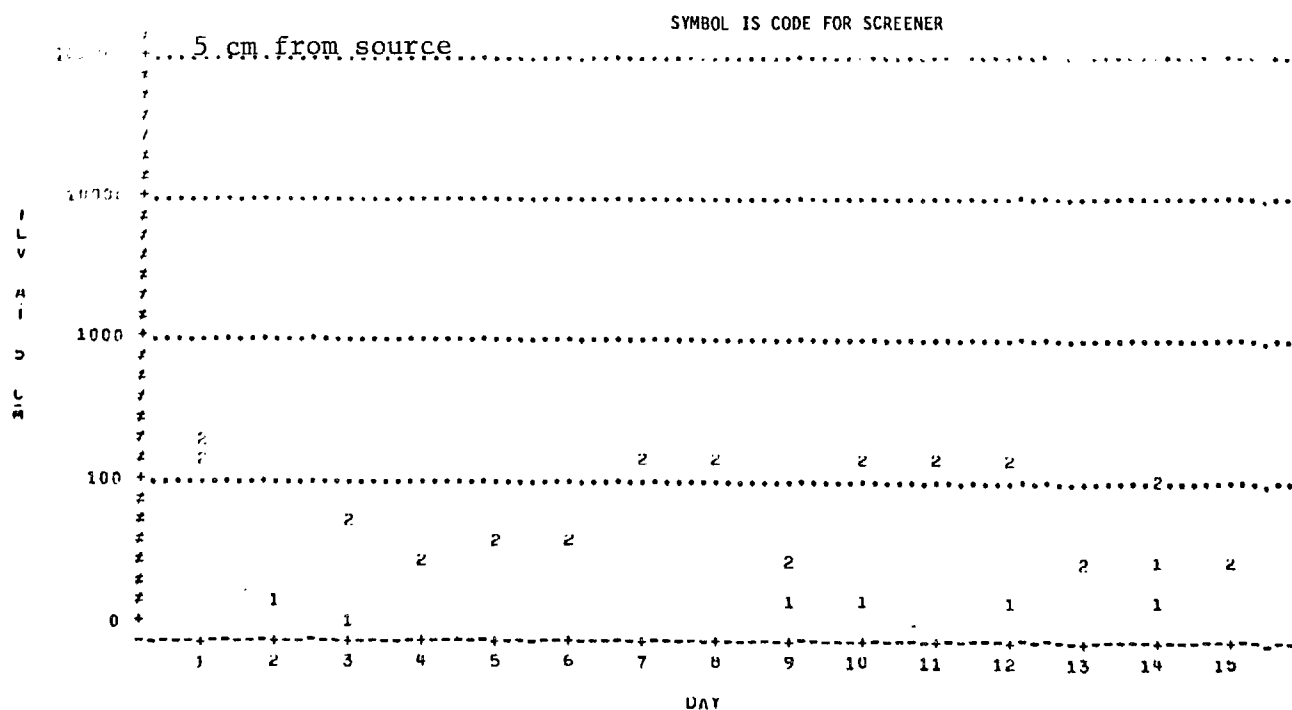
Figure 4. TLV Quality Control - Daily Readings - Refinery F, Pump Seal 92

TABLE 2. VARIANCE COMPONENTS FOR SCREENING MEASUREMENTS AT THE SOURCE

(for OVA)

Valves ℓn (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	23	2.342	100
INDIVIDUAL VALVES	2	1.799	76.8
DAY	15	0.401	17.1
REPEAT	6	0.141	6.1

90% Repeatability = 87%

Pump Seals - ℓn (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	15	0.908	100
INDIVIDUAL PUMPS	1	0.359	39.5
DAY	10	0.528	58.2
REPEAT	4	0.021	2.3

90% Repeatability = 36%

(for TLV)

Valves - ℓn (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	155	2.847	100
INDIVIDUAL VALVES	5	1.384	48.6
DAY	70	1.134	39.8
OPERATOR	39	0.060	2.1 ·
REPEAT	41	0.269	9.5

90% Repeatability = 121%

90% Reproducibility = 134%

Pump Seals - ℓn (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	46	0.427	100
INDIVIDUAL PUMPS	1	-0.008	0.0
DAY	27	0.192	44.9
OPERATOR	10	0.068	15.9
REPEAT	8	0.167	39.2

90% Repeatability = 95%

90% Reproducibility - 113%

The OVA-108 screening device data from 5 cm was also checked for repeatability. The pooled standard deviation for repeated readings is 0.28 $\ln$ (screening value) and the percent repeatability is 65 percent. The repeatability for the 5 cm OVA readings is slightly better than that for OVA screened at the source (72 percent) but the difference is not statistically significant.

TLV READINGS VS LEAK RATE

Screening values were obtained during the field sampling program when the source was first located and rescreening values were obtained nearer to the time that the source was actually sampled. Correlations and nomographs have been developed to relate the maximum TLV with leak rates. These will be reported in another paper at this conference. A number of summary statistics were evaluated before selecting the maximum reading. Table 3 reports simple correlations between leak rates and selected screening statistics (including individual readings) for valves. The maximum at the source was selected because of its high correlations and simple determination.

TLV READINGS COMPARED TO "SOAP SCREENING"

At one refinery, a short test was made to compare screening of sources using a soap solution with screening using a TLV sniffer. Following the usual screening technique on selected sources, the maximum TLV value was obtained. Then the source was sprayed with either a "snoop" soap solution (relatively thin) or a relatively thick solution made from Ivory liquid soap. Then the "action" or "description" of the soap solution was recorded.

This data is plotted in Figure 5. As can be seen, the soap solution formed bubbles for all screening values greater than 1000 ppm except for the vertical sources and one other valve.

CONCLUSIONS

(1) Daily two point calibration of the screening devices is adequate to obtain unbiased readings. Calibration will almost always be less than 10%.

(2) Readings from both the TLV and OVA devices are quite variable. Differences by the same operator at the same time can be up to 100% for readings at the source and 200% for 5 cm readings. Reproducibility (different operators, different instrument) can be up to 200% at the source and 300% at 5 cm. For valves and pump seals, these variations are small relative to the order of magnitude differences between days and between devices.

(3) The maximum screening value, which is easily determined, correlates with leak rate as well as other possible statistics.

TABLE 3. CORRELATIONS OF SCREENING VARIABLES AND NONMETHANE LEAK RATES
(lb/hr) - VALVES (All Correlations Based on Log of Variable)

VARIABLE	(2) MAX SC	(3) MAX RSC	(4) AVG RSC	(5) 5-CM	(6) N. STM	(7) N. CL
1. Nonmethane Leak	.628(584)	.715(260)	.739(260)	.685(246)	.703(251)	.511(195)
2. Maximum Screening Value	–	.745	.748	.593	.677	.434
3. Maximum Rescreening Value		–	.978	.804	.858	.633
4. Average Rescreening Value			–	.837	.890	.693
5. Avg of Maximum 5-CM Reading				–	.733	.722
6. North Stem Reading					–	.545
7. North Gland Reading						–

Tabled values are r (m)

r = simple correlation coefficient = $\dfrac{\Sigma(X1 - \bar{X})(Y1 - \bar{Y})}{\sqrt{\Sigma(X1 - \bar{X})^2 \ \Sigma(Y1 - \bar{Y})^2}}$ = where X and Y are the paired variables

m = number of pairs of data observations used in computing correlation coefficient
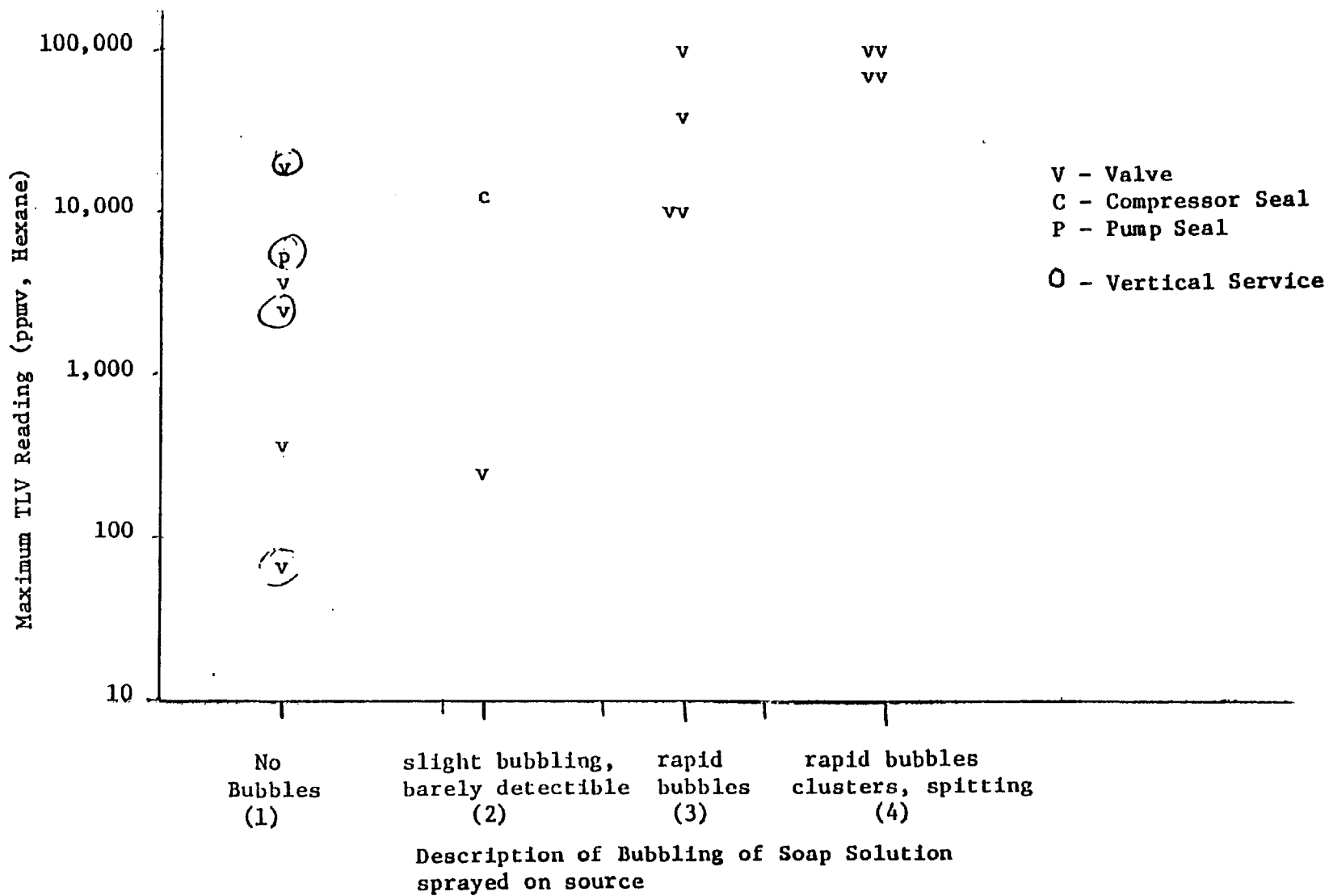
Figure 5. Relationship of TLV Reading and Bubbling From Soap Solution

    (4) When comparing "soap bubble" screening to the TLV, a general positive correlation is apparent, except for devices in vertical service.

SECTION 3

QUALITY CONTROL FOR HYDROCARBON MEASUREMENTS
FROM BAGGABLE SOURCES

This section describes the quality control procedures implemented
during the analysis of samples for methane and nomethane hydrocarbon from
process valves, pump seals, compressor seals, flanges, relief valves, and
drains. A significant amount of the total quality assurance effort went into
this area because the sampling procedure had not been previously validated
under field conditions and because of the extreme variability of leak rates
found from these sources. The quality control procedures discussed here
include laboratory blind standards analysis, repeatability of the total hydro-
carbon (THC) analysis, recovery studies of the sampling train, and repro-
ducibility of the sampling/analysis from a given source.

LABORATORY STANDARD ANALYSIS

Regularly scheduled analyses of blind standards were used to
evaluate the THC daily calibration as well as the stability of the calibra-
tion. The quality assurance protocol required at least one blind standard
to be analyzed each week. The following standard gases were used for these
checks:

Propane (NBS)	16.3 ppmv –	722 ppmv
Hexane	525 ppmv –	8393 ppmv
Methane	103 ppmv –	433 ppmv
C_1 – C_6 Hydrocarbons	100 ppmv	

Most of the propane standards were NBS standards of propane in air.

Figure 6 shows the percent difference versus the measured concen-
tration where percent differences is computed as:

% difference = (Known–Measured) × 100/Known.

The differences ranged from – 88 ppm to + 66 ppm with an average
difference of – 2.5 ppmv and a standard deviation of 22.5 ppm. A 95% con-
fidence interval for the mean difference is – 2.5 ± 6.6 ppm or – 9.1 to
4.1 ppm.
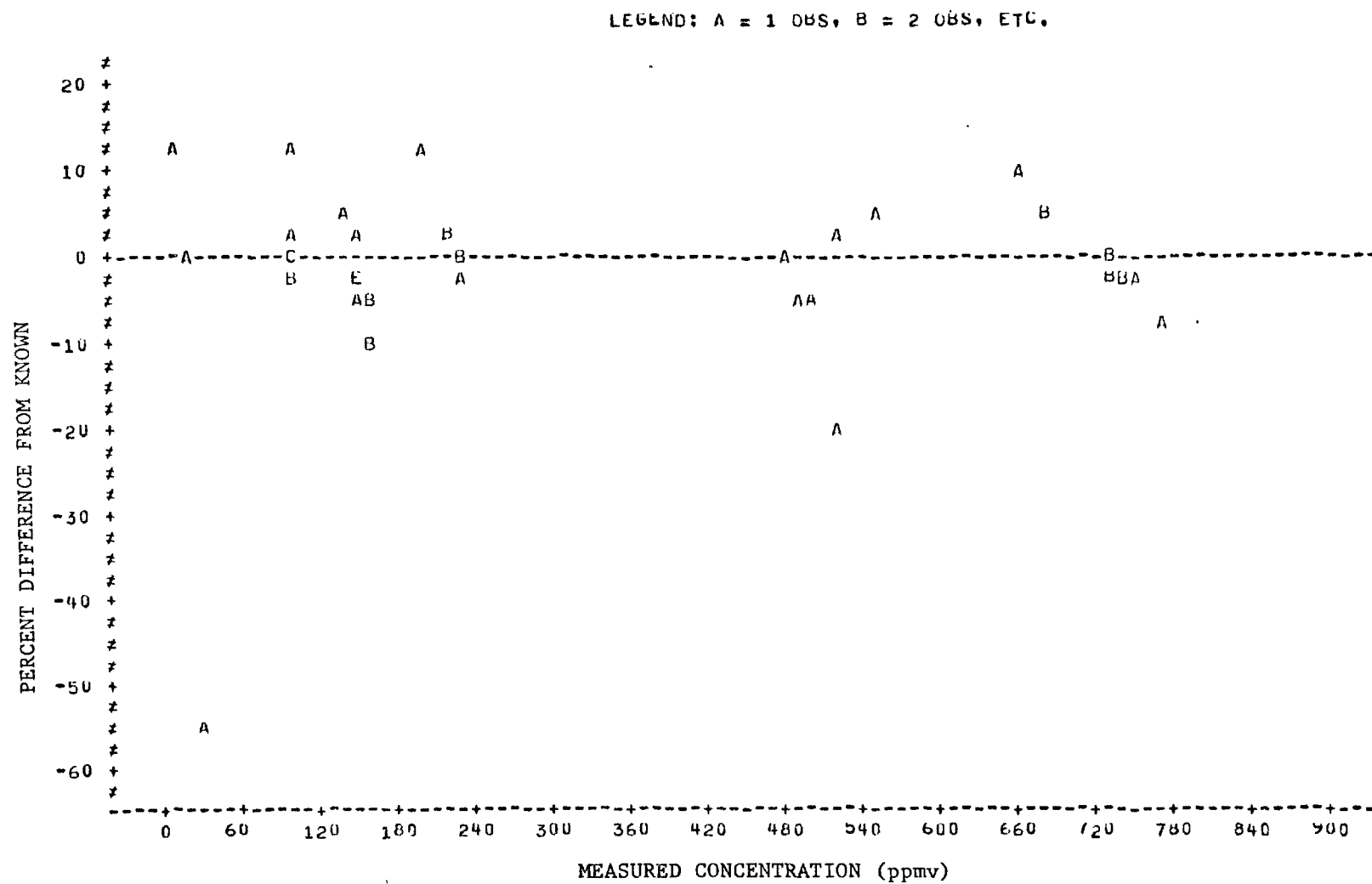
Figure 6. Hydrocarbon Blind Standards Analysis Percent Differences

The percent differences ranged from - 54.6% to 12.9% with an average difference of - 1.65% and standard deviation of 9.9%. This gives a 95% confidence interval for the mean difference of - 1.65 ± 3.0% or - 4.7% to 1.4%.

REPLICATE THC ANALYSES

The analysis for methane and nomenthane hydrocarbon content of fugitive emission gas samples was accomplished using a specially designed Total Hydrocarbon Analyzer (THC) Model 301C made for Radian by Byron Instruments. For each sample, two runs were made with the results recorded by a strip-chart recorder.

To document the precision of this analysis, a stratified random sample of pairs of runs were selected at each refinery and statistically analyzed. The percent difference for each pair was calculated using:

$$\% \text{ difference} = \frac{(\text{1st analyses} - \text{2nd analysis})}{\text{average of two analyses}}$$

Figure 7 shows a plot of these percent differences obtained at each refinery. As can be seen, most differences were within the target limits of ± 7%. The 7% target limit was based on Radian laboratory studies prior to using the THC in the field.

The standard deviation was computed for each pair of readings. These standard deviations are shown graphically in Figure 8. The following statistics summarize the duplicate THC analyses.

# of replicate pairs:	130
pooled standard deviation:	2.44%
repeatability - maximum difference expected between two readings 95% of time:	6.2%
95% confidence interval for mean reading based on single analysis:	± 4.8%
95% confidence interval for mean reading based on the average of two analyses:	± 3.4%

Since the average of the two readings was used in computing leaking for all sources, the ± 3.4% interval best describes the precision of the THC analysis.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
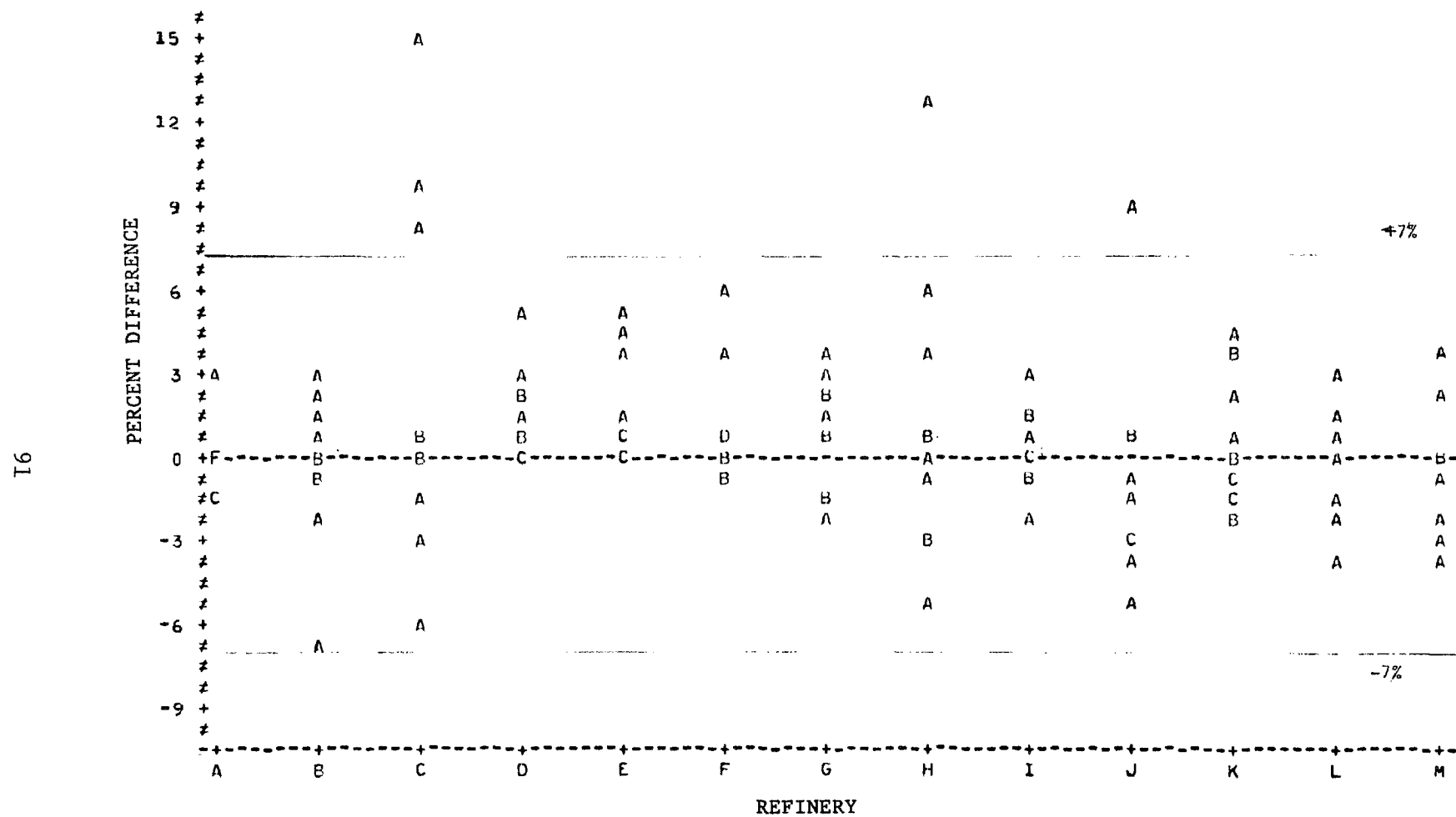
Figure 7. Percent Difference in Replicate THC Analysis for Each Refinery

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
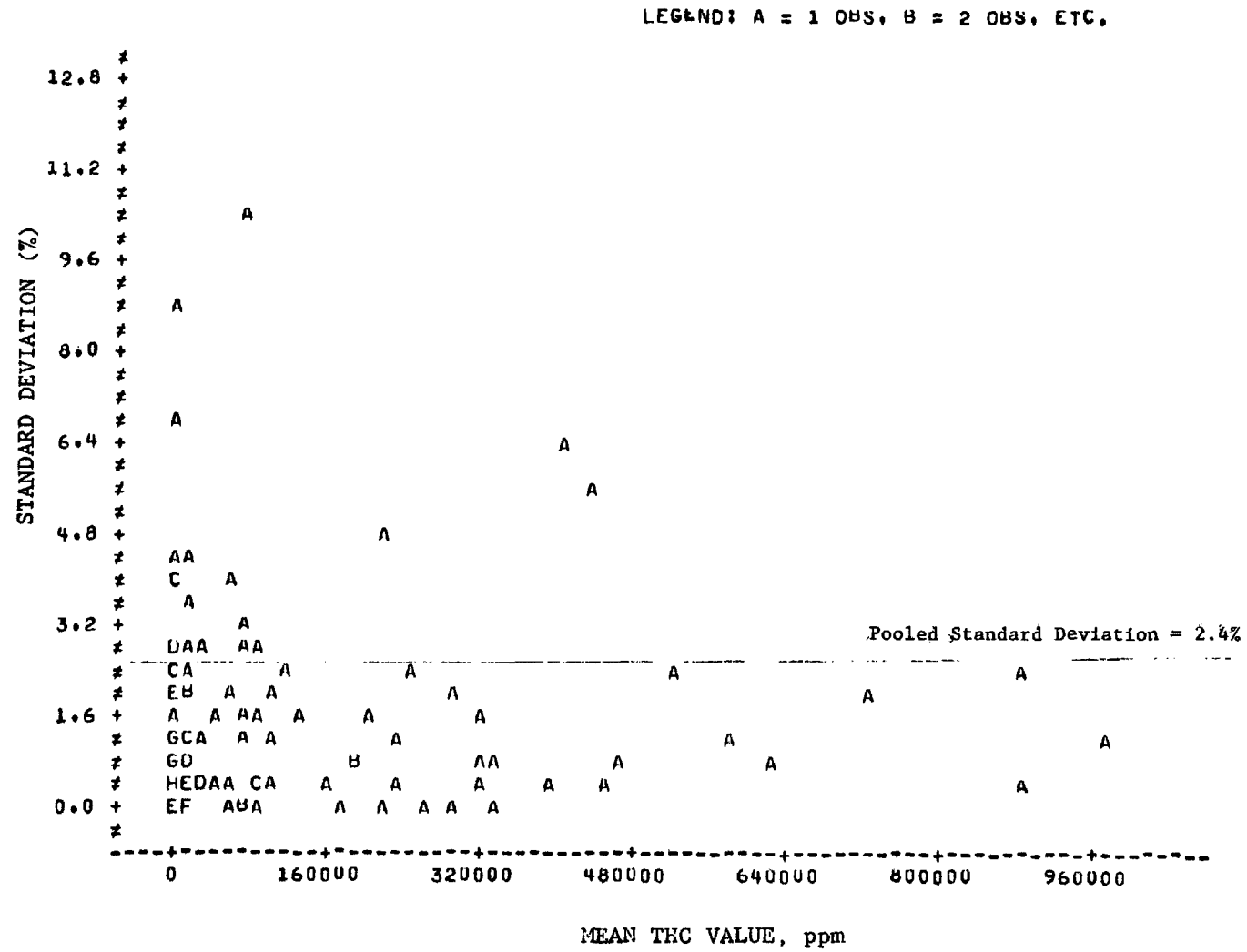
Figure 8. Standard Deviation for Replicate THC Analysis Versus THC Level

SAMPLING AND ANALYSIS OF STANDARDS - RECOVERY STUDIES

To evaluate the overall accuracy of the baggable sampling and analysis technique, a procedure was devised to generate "known" leak rates. Standards of propane and propylene were used as the emissions source, and the leak rate was varied by altering the flow of these standards into the sampling cart. The use of flow meters to measure the rate of gas induced into the system introduced an additional source of variation into the sampling/analysis system. Extensive calibration procedures were followed to insure that no systematic error was introduced by using the flow meters. Samples of the induced leak were collected in bags using the usual procedure and set for THC analysis as a "blind standard."

Sixty-three recovery checks were made at the nine refineries visited beginning with Refinery "E". In addition, six similar checks were made of the sampling train by Research Triangle Institute (RTI) during an EPA audit at Refinery "E". Eleven recovery checks were made at the Radian laboratory between the visit to Refineries "I" and "J". The induced leak rates ranged from 0.007 to 2.93 lbs/hr. Figure 9 shows the percent recovery for each induced leak rate plotted versus the induced leak rate with the plotted symbol representing the refinery at which the check was made.

Figure 10 shows a schematic plot of the recoveries obtained at each refinery in the order in which they were visited. A high recovery value of 235% obtained at Refinery "J" could not be explained for physical reasons. The value was eliminated from further statistical analysis after it was rejected using Dixon's statistical outlier test. Some differences in average recovery rates are evident from these plots.

Table 4 contains a statistical summary of the recoveries at each refinery and overall. The results from the RTI audit are also given in the table. The 95% confidence intervals for the average recovery included 100% for all refineries except "F" and "G", with the upper limit for "G" at 98.5%. At Refinery "F" a new technique for pumping air through the sampling train was instituted. A check of the system after reviewing the accuracy checks showed that a low bias would be introduced by the way the pump was fitted. Therefore it was concluded that the leak rate data from Refinery "F" could be about 15% low. When the accuracy checks from Refinery "F" are removed, the remaining checks average 98.7% recovery with a 95% confidence interval of 95% to 103%. It was therefore concluded that there was no significant source of bias in the sampling/analysis system except for leak rate data from Refinery "F". Adjustments based on the amount of data obtained at Refinery "F" and the estimated 15% bias were made to calculate emission factors and their confidence intervals.

REPEATED SAMPLES FROM INDIVIDUAL SOURCES

A significant effort was extended throughout the field sampling program to evaluate the repeatability of the sampling/analysis procedures for

SYMBOL IS CODE FOR REFINERY
(R represents checks made at Radian)

PERCENT RECOVERY

250 +

Not used in
further analysis   J

225 +

200 +

175 +   K

150 +   I

125 +   K   G
         I K E
         JI K   100% Recovery
    K   R   J-K   R
100 +--------------------J--K-L--EE----------------H----ER----J-K------R--------------GG---------------------------
         M   I I   E H
                   I   R   GH   F K   G F   G   F   F G
                     E   H   G
75 +   I E   G   G
                                                                              F
                 E   G

50 +

    0.00   0.01   0.10   1.00   10.00

INDUCED LEAK RATE (16/hr)
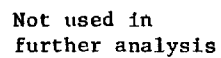
Figure 9. Recovery Studies – Percent Recovery Versus Induced Leak Rate
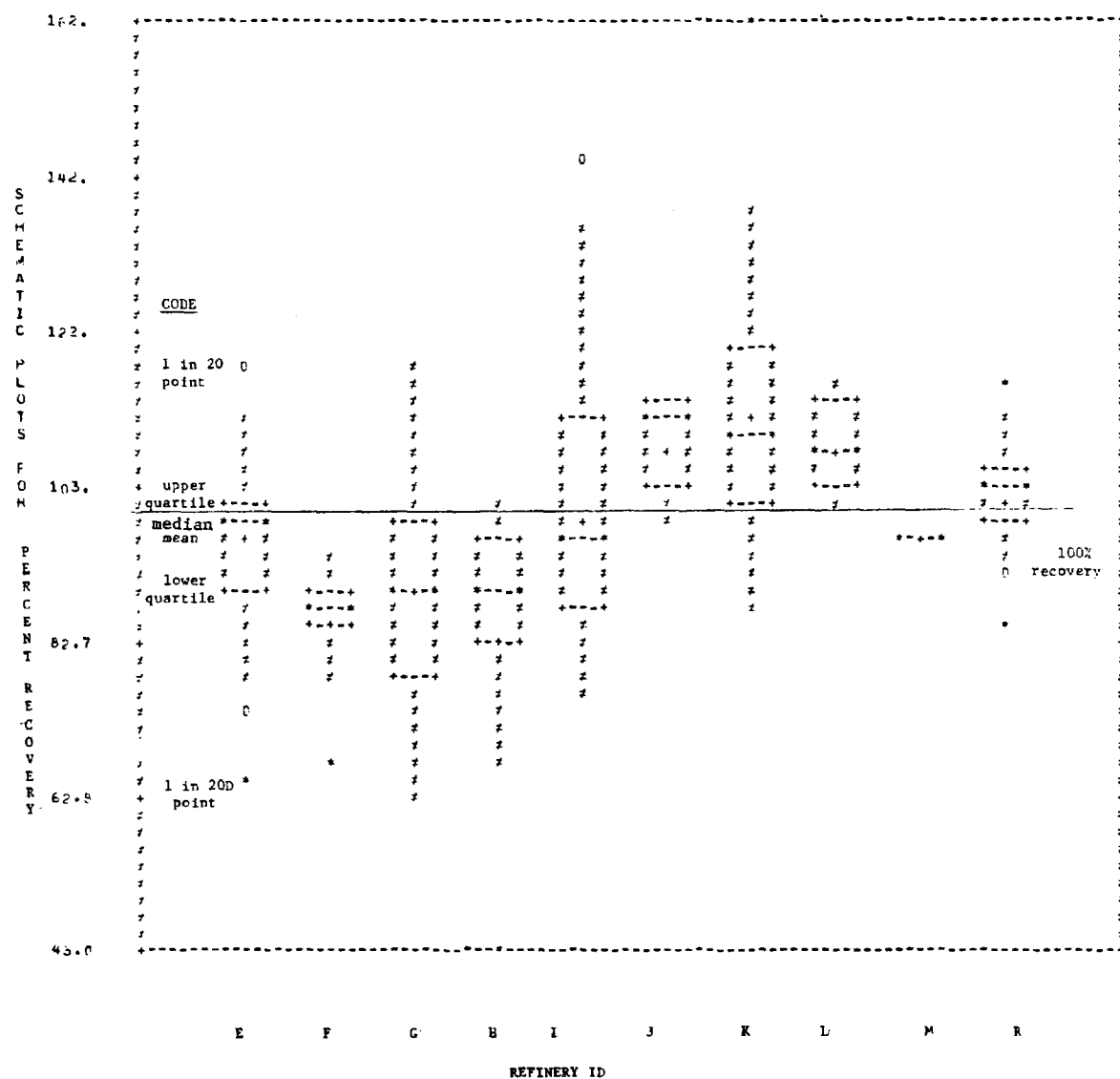
Figure 10. Sample Train Recovery Studies – Refinery Fugitive Emissions

TABLE 4.   STATISTICAL SUMMARY OF RECOVERY STUDIES

L. P. Provost

REFINERY	NUMBER OF RECOVERY CHECKS	AVERAGE RECOVERY (%)	STANDARD DEVIATION OF RECOVERY (%)	RANGE OF RECOVERIES (%) MINIMUM	MAXIMUM	95% CONFIDENCE INTERVAL FOR AVERAGE RECOVERY (%)
E	12	95.3	15.5	64.4	118.8	(85.5 , 105.1)
F	7	85.7	8.5	66.9	92.8	(77.4 , 93.0)
G	11	89.0	14.2	63.5	117.6	(79.5 , 98.0)
·H	5	82.4	22.5	44.0	100.0	(54.5 , 110.3)
I	9	99.2	22.0	76.0	145.0	(82.3 , 116.1)
J	5	107.4	7.1	97.4	113.6	(98.6 , 116.2)
K	9	112.3	21.2	88.0	161.3	(96.0 , 128.6)
L	4	107.4	7.0	100.7	115.3	(96.2 , 118.6)
M	1	96.5	--	--	--	-- --
Radian	11	100.7	7.5	85.6	114.8	(95.7 , 105.7)
TOTAL	74	97.4	17.2	44.0	161.3	(93.5 , 101.3)
TOTAL WITHOUT F	67	98.7	17.3	44.0	161.3	(94.5 , 102.9)
RTI AUDIT DURING REFINERY E	6	92.6	12.3	78.5	112.2	(79.7 , 105.5)

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baggable sources. Repeated samplings were done to determine the variability in the leak rate due to the sampling procedure, sampling teams, inherent changes in the leak rate over time, and level of leak rate. The number of quality control samples was as follows:

Source Type	Number of Sources Sampled	Number of Sources with QC Samples	Percent of Sources with QC Samples	Total Number of QC Samples
Valves	627	65	10.4	137
Pump Seals	382	62	16.2	133
Compressor Seals	124	40	32.3	66
Flanges	62	7	11.3	12
Relief Valves	52	16	30.7	30
Drains	49	14	28.6	33
TOTAL	1296	204	15.7%	411

Approximately 16% of the sources sampled had one or more quality control sample with an average of about two quality control samples for each source with QC.

Control charts were provided for recording the intra- and inter-team differences at each refinery as soon as the analyses were completed. An example of the charts for one refinery are shown in Figure 11. Figures 12, 13, and 14 show the percent differences for each QC check grouped by refineries for valves, pump seals, and drains. Figure 15 shows these same percent differences plotted versus the average leak rate of the samples for valves. Control limits of ± 70% are included on these plots. A maximum 70% difference between samples was the original goal for the baggables sampling and analysis procedure. As can be seen, a significant number of checks were outside these limits. Leak rates from drains were especially nonrepeatable. A frequency distribution of the percent differences for valves shown in Figure 16.

Figure 17 shows the standard deviation of leak rates for each valve versus the average leak rate of the original and quality control samples. Since the standard deviation is obviously related to the concentration level, percent standard deviations were computed. The percent standard deviations are plotted versus the mean leak rate in Figure 18. The percent standard deviation appears fairly constant for all levels with a slightly larger percent difference for leak rates less than 0.01 lbs/hr.
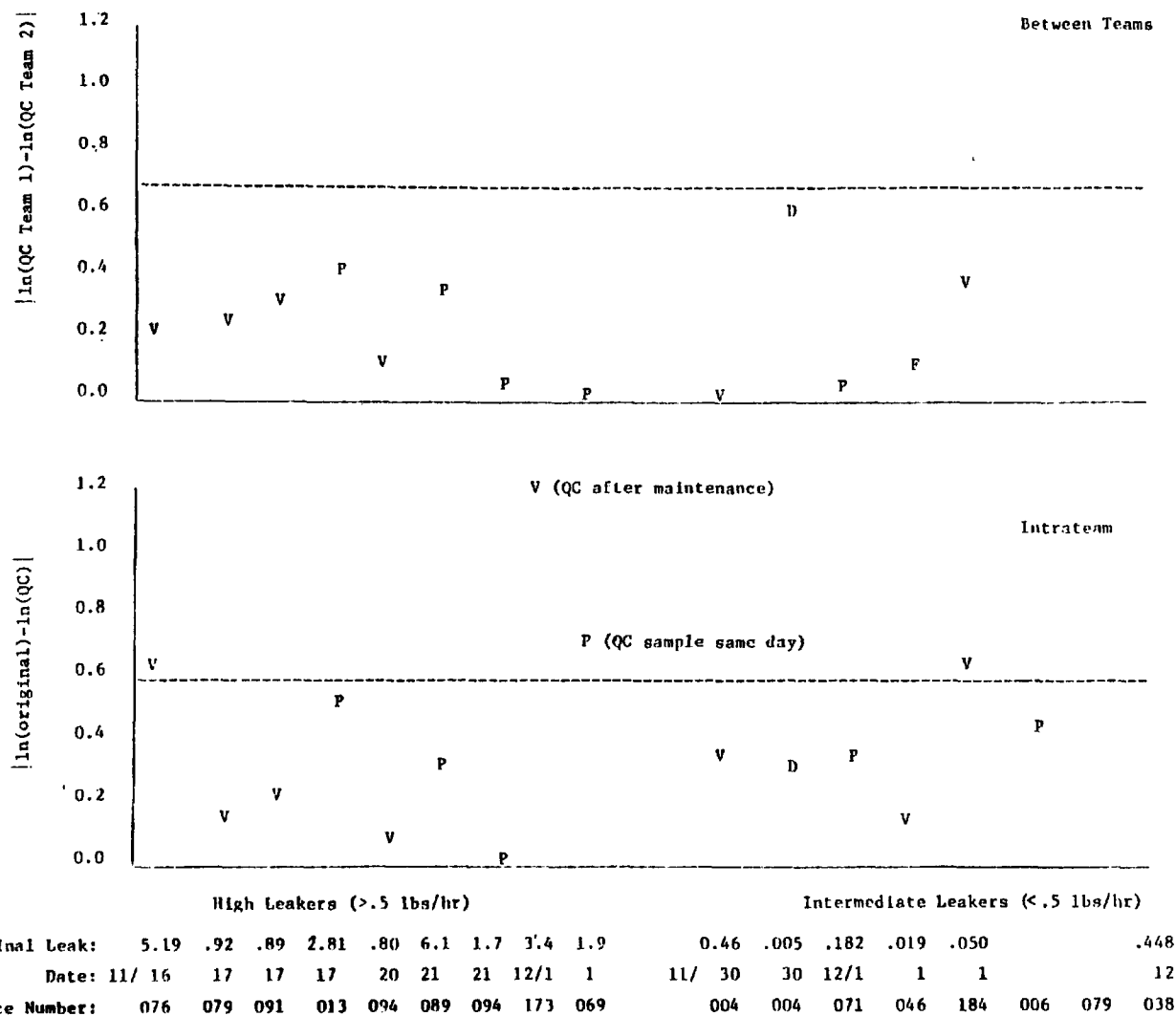
Figure 11. Example Quality Control Charts for Repeat Samples

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
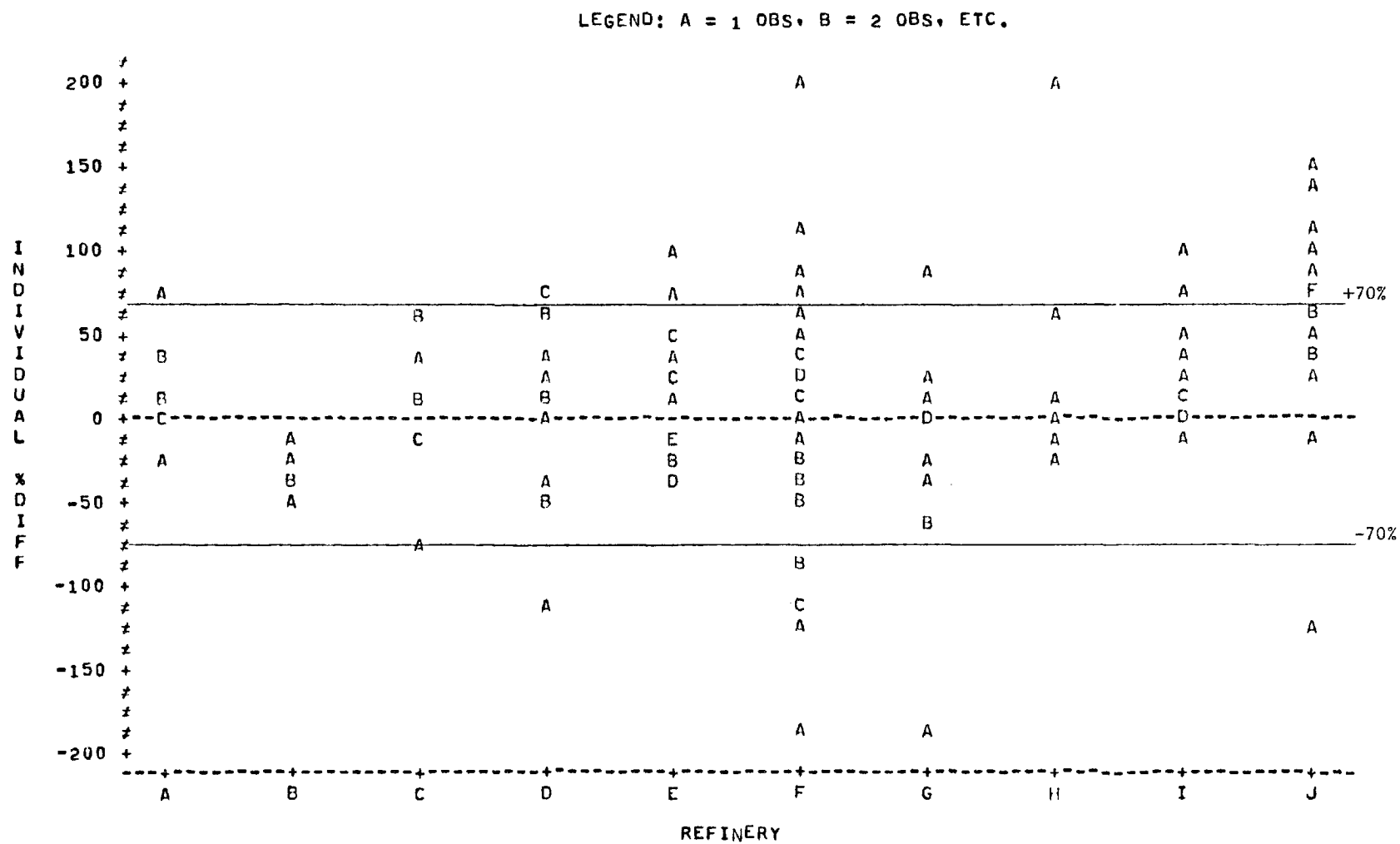
Figure 12. Percent Difference Between Repeat Samples by Refinery - Valves

LEGEND: A = 1 OBS, B = 2 OBS, ETC,

```
      #
200 + #
      #
      #          A                                      A            B
      #
150 + #          A                                      A
      #
      #          A                                      B            A
    # #          A                                      B            A
100 + #                                                 A
I     #                                                 C            A
N   # #                                  B                           A            +70%
D     #                                  A                           B
I     #
V  50 + #        B                       A              A            A                         A
I     #                       A          A                     D     A            A            A
D   # #          B                       C              D            A            A            B
U     #          A                       B              A            D            A      B
A   0 +--D----------------------------A---------A-----------B---------A------------------D-----------A----
L   # #          D            B                  B             A                    C                 B
    # #          A                       B                           A            A      B
%   # #                                                 B            B
D -50 + #        C            A          A              A            A
I     #                                                 C            C            B
F   # #                                                 C                                       A      A  -70%
F     #                                                 A            A
  -100 + #                                              C
      #
    # #          B                                      A
    # #          D
 -150 + #        C
      #
    # #          A
      #
    # #                       B
 -200 + #
      -----+-----------+-----------+-----------+-----------+-----------+-----------+-----------+-----+--
           A           B           C           D           E           F           G           H           I

                                              REFINERY
```
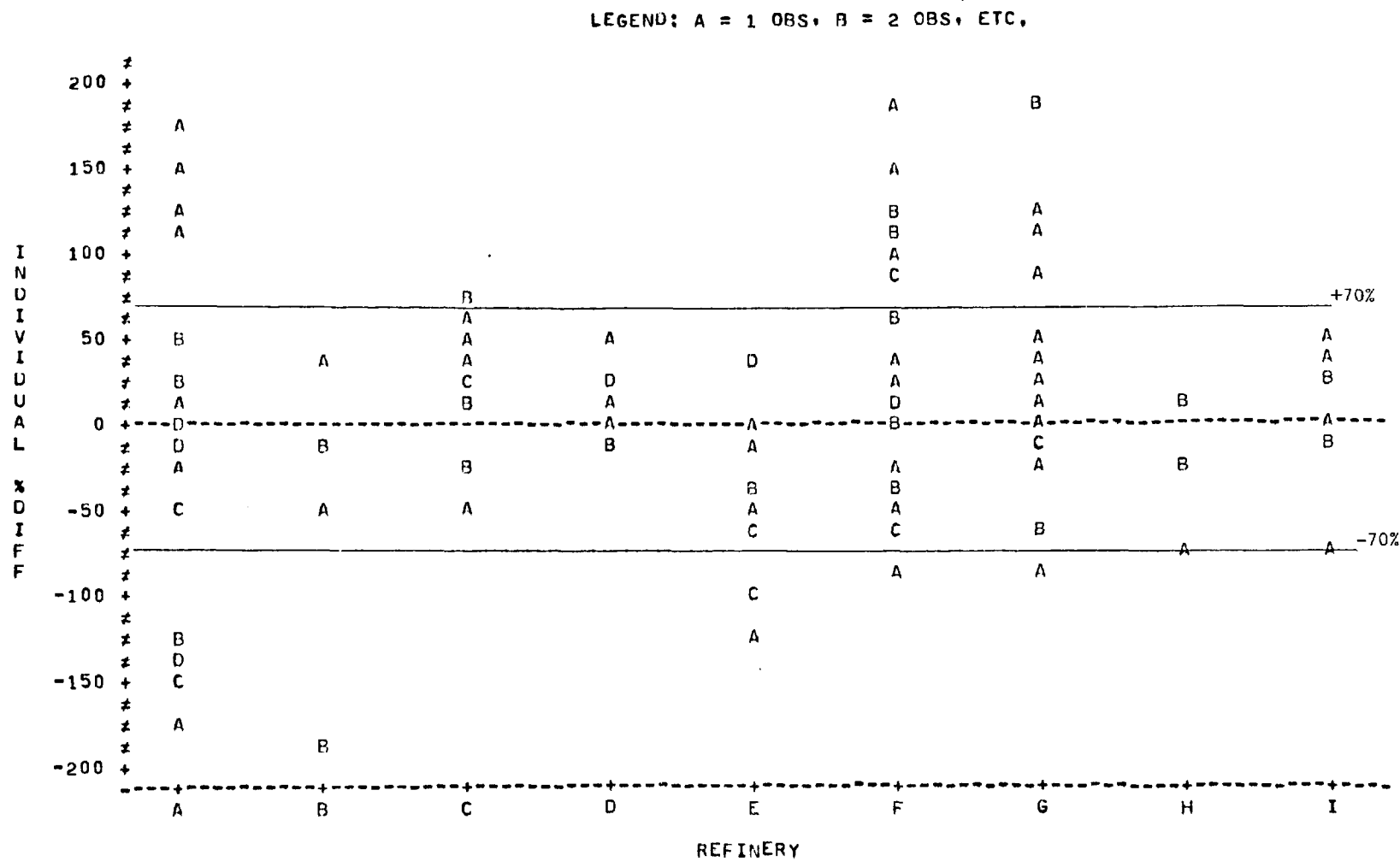
Figure 13.   Percent Difference Between Repeat Samples by Refinery – Pump Seals

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
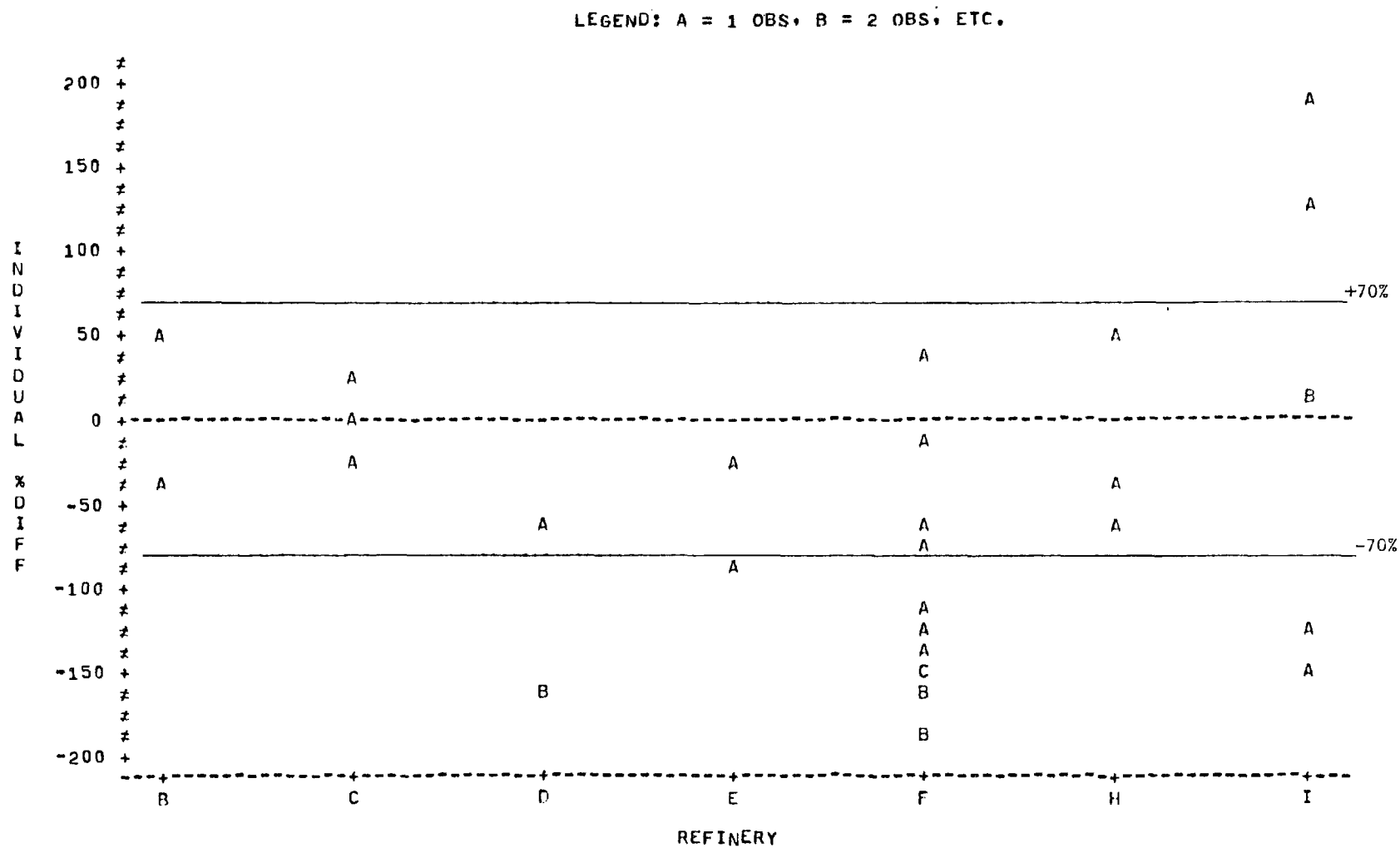
Figure 14. Percent Difference for Repeat Samples by Refinery – Drains

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

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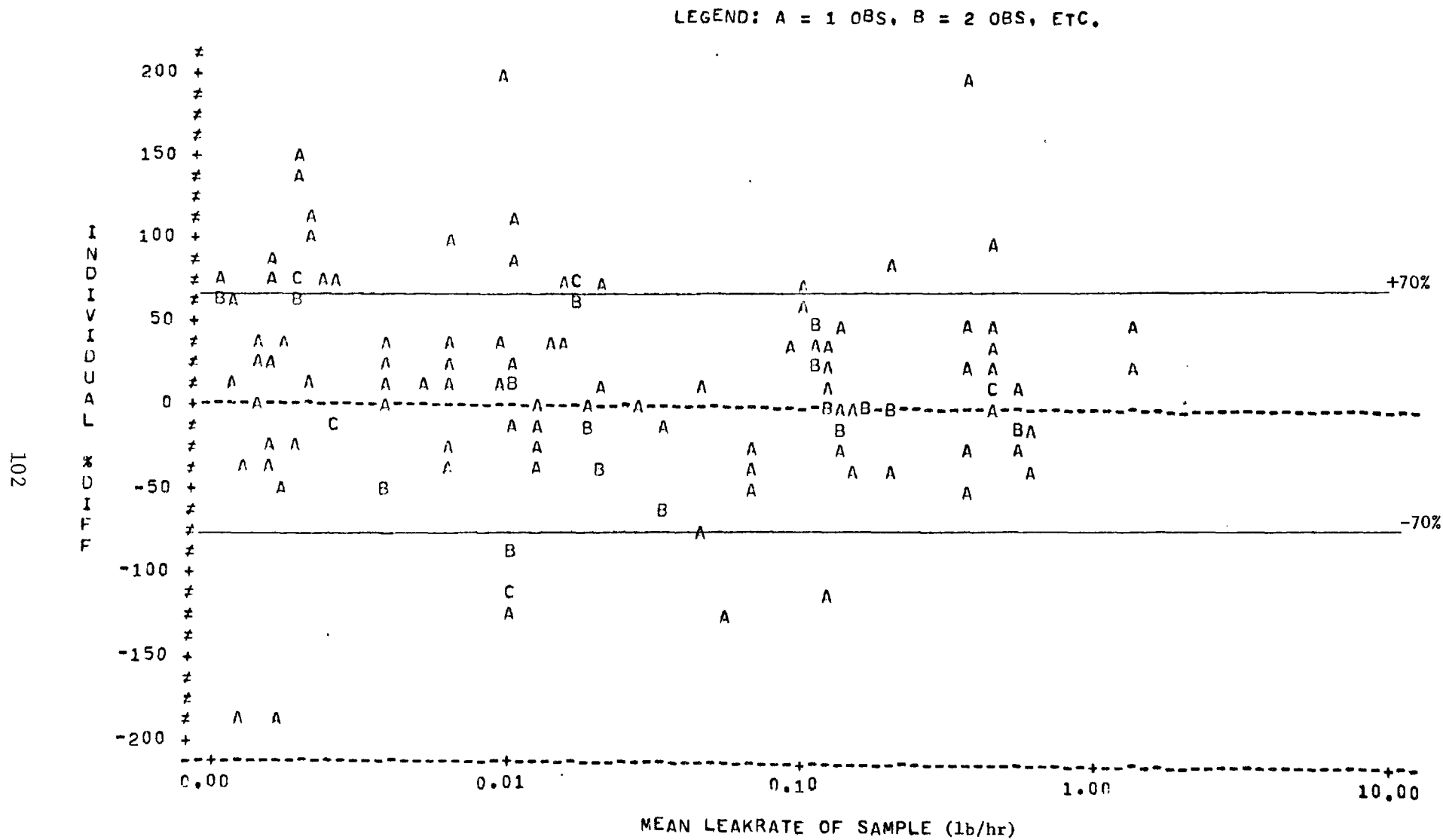
Figure 15. Percent Difference for Repeat Samples Versus Mean Leak Rate – Valves

FREQUENCY

```
       ≠                                                  *****
       ≠                                       *****      *****
       ≠                                       *****      *****
   40  +                                       *****      *****
       ≠                                       *****      *****
       ≠                                       *****      *****
       ≠                                       *****      *****
       ≠                                       *****      *****
   30  +                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                                       *****      *****      *****
   20  +                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                                       *****      *****      *****
   10  +                                       *****      *****      *****
       ≠                                       *****      *****      *****
       ≠                  *****      *****      *****      *****      *****      *****
       ≠                  *****      *****      *****      *****      *****      *****
       ≠        *****      *****      *****      *****      *****      *****      *****      *****
       ------------------------------------------------------------------------------------
              -175       -125       -75        -25         25         75        125        175
```

PERCENT DIFFERENCE MIDPOINT
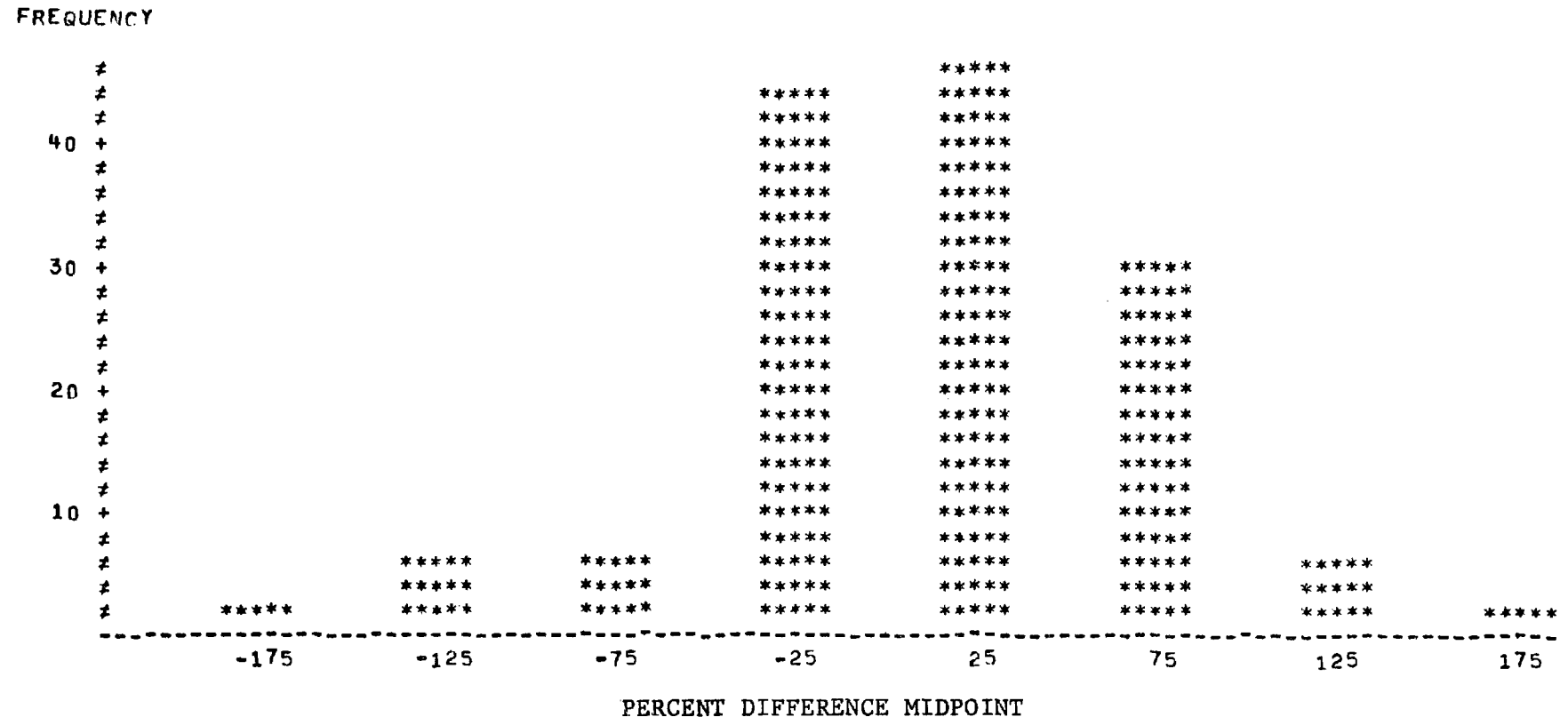
Figure 16. Frequency Bar Chart for Percent Differences Between Samples – Valves

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
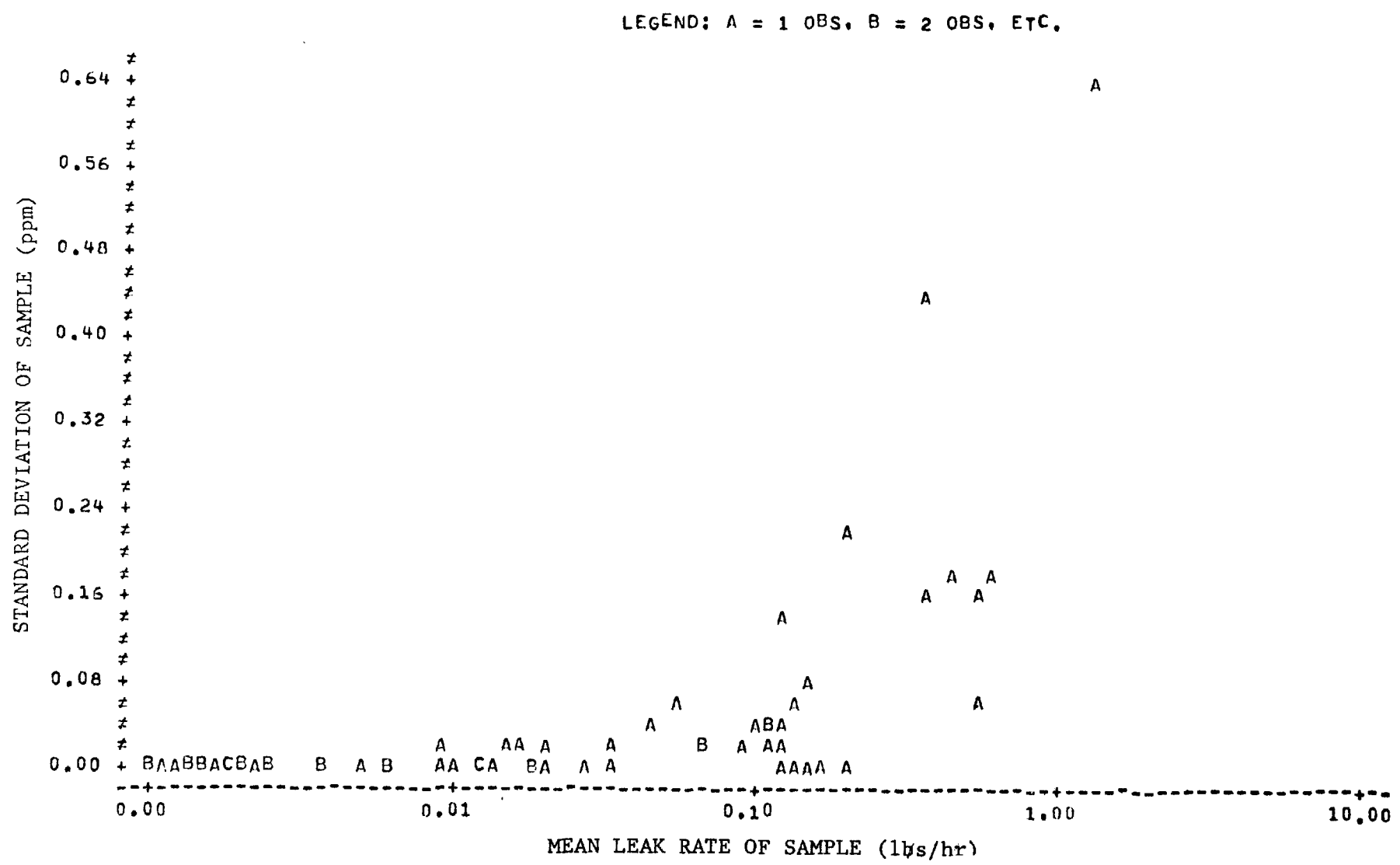
Figure 17. Standard Deviation of Repeat Samples Versus Mean Leak Rate – Valves

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Figure 18.   Percent Standard Deviation Between Samples Versus Mean Leak Rate – Valves

Table 5 summarizes the statistical analysis of the repeat QC samples. The variability for drains is significantly higher than the other sources while the variability for relief valves is significantly less. Problems when sampling drains were noted by the field sampling crew. The other sources have a standard deviation averaging about 40% or a confidence limit based on a single test of ± 80%.

This standard deviation of 40% is composed of variation due to analysis, sampling train components, sampling team effect, and inherent variability in the leak rate. In previous sections, the standard deviation for the THC analysis was shown to be about 2.4% and the standard deviation for sampling and analysis of standard gases was shown to be about 17%. No significant differences between sampling teams or sampling carts were found, therefore a significant portion of the variability in the leak rate quality control samples is probably due to short term changes in the leak rate from a given source.

VARIANCE COMPONENT ANALYSIS

The variability when measuring the leak rate from a single source can be put in proper perspective for this program by comparing this observed variation from sampling/analysis of a given source with the total variability of the leak rate data from all sources. Statistical analyses of variance techniques can be used to separate the total variability of the measured leak rate into its various components.

Table 6 summarizes the estimation of variance components for the six baggable source types. The variation of the logarithm of the leak rate is broken down into four components of variation:

- refineries

- units within a refinery

- individual sources within a unit

- sampling/analysis, short-term leak variations.

The estimation technique assumes all the components are random, i.e., a random selection of refineries, of units within a refinery, of sources within a unit, and of samples from a particular source. The degrees of freedom in the table is the number of independent pieces of data available for estimating the component of variation.

As can be seen from Table 6, the largest percentage of the variation in the log leak rate is due to individual sources, except for compressor seals. The variation due to differences between refineries is negligible for all sources except relief valves. The percentage variation due to the sampling and analysis procedures ranges from 3.8% for relief valves to 21.4% for drains. This component for valves is 5.7%. Therefore, the standard

TABLE 5.   SUMMARY OF BAGGABLE LEAK RATE QUALITY CONTROL SAMPLE

Source Type	Number Of Sources With QC	Total QC Samples	Average % Difference[1]	Standard Deviation of Sampling Analysis[2]	95% Reproducibility of Sampling/Analysis[3]	90% Confidence Interval about a Sample Test Result[4]
Valves	65	137	37.8	36.6	101.4%	± 71.7%
Pump Seals	62	133	44.7	41.9	116.2%	± 82.2%
Compressor Seals	40	66	39.5	38.1	105.6%	± 74.4%
Flanges	7	12	40.0	39.1	108.2%	± 76.6%
Relief Valves	16	30	18.5	19.5	54.0%	± 38.2%
Drains	14	33	71.1	59.1	163.7%	±115.8%
Overall	204	411	41.9	40.7	112.8%	± 79.8%

[1]Average % difference - average of pooled percent differences for each source with QC sample.

Where: % diff = [original - QC leak]/(average of original and QC leak).

[2]Standard deviation of sampling/analysis - estimated standard deviation of the sampling and analyses procedures for non-methane hydrocarbons. Estimated from the pool individual percent differences for each QC sample.

[3]95% reproducibility of sampling/analysis - quantity that will be exceeded only about 5% of the time by the difference of two test results on a given source under similar process conditions. The quantity is equal to 2.77 x standard deviation.

[4]90% confidence interval - When taken about a single test result, 95% of these intervals would be expected to include the "actual" leak rate (without bias considerations); the quantity is equal to 1.96 x standard deviation.

TABLE 6.   VARIANCE COMPONENT ANALYSIS - BAGGABLE SOURCES - LN (Leak Rate)

SOURCE OF VARIATION	df*	VALVES variance component	percent of variation	df*	PUMP SEALS variance component	percent of variation	df*	FLANGES variance component	percent of variation
Refineries	8	-0.174	0.0	8	-0.064	0.0	7	-0.141	0.0
Unit/Refinery	43	0.881	14.2	43	0.666	12.0	16	0.973	0.0
Sources/Unit	573	4.952	80.1	326	4.350	78.2	38	4.591	92.1
Sampling-Analysis	116	0.351	5.7	137	0.544	9.8	12	0.396	7.9
TOTAL	740	6.184	100%	514	5.560	100%	73	4.987	100%

SOURCE OF VARIATION	df*	COMPRESSOR SEALS variance component	percent of variation	df*	RELIEF VALVES variance component	percent of variation	df*	DRAINS variance component	percent of variation
Refineries	12	-0.207	0.0	8	0.840	12.7	8	-0.224	0.0
Unit/Refinery	24	3.907	59.0	9	0.822	12.5	23	2.354	37.0
Source/Unit	140	1.927	29.1	40	4.685	71.0	17	2.648	41.6
Sampling-Analysis	76	0.792	11.9	31	0.250	3.8	34	1.360	21.4
TOTAL	252	6.626	100%	88	6.598	100%	82	6.362	100%

* df = degrees of freedom

deviation of 40% shown above is not large when compared to the total variability of the leak rate in the data base where leak rates span seven orders of magnitude. Since the emphasis on this program is on overall estimates rather than estimates of individual leak rates, the variability of the sampling and analysis process is certainly acceptable for the program objectives.

CONCLUSIONS

(1) Laboratory standards analysis indicated no overall biases in the THC analysis.

(2) Replicate THC analysis had percent differences less than 7% most of the time. The analytical leak rate as developed in this study can be assumed to be within ± 3.4% of the concentration in the sample bag.

(3) After removing the data from one refinery, the standard leaks collected in the sampling train and analyzed on the THC had an average recovery of 98.7 ± 4.3% of the induced leak. The standard deviation of the recoveries was found to be 17% indicating that a sample estimate would be within ± 34% of the actual leak rate most of the time.

(4) Repeated samples from individual sources were quite variable. About 16% of the sources sampled in the study were resampled for quality control purposes. Overall, a repeat sample could be expected to differ by as much as 113% of the original leak rate. The overall standard deviation between samples was about 41%. This is higher than the 17% standard deviation for repeated sampling of standards. The difference is assumed attributable to inherent short term variations in the actual leak rate.

(5) A variance component analysis showed that most of the variation in leak rates measured in the study can be attributed to differences between sources. The sampling/analytical variance accounted for less than 10% for all sources except compressor seals (12%) and drains (21%). Differences in leak rates between refineries were negligible except for relief valves.

SECTION 4

STATISTICAL PROCEDURES FOR ANALYZING

EMISSIONS DATA

A number of statistical analysis procedures were used in analyzing the emissions data from this program. The discussions in the previous sections have shown that individual hydrocarbon measurements were not very precise (precision was usually greater than ± 50%) and that variability of leak rates from different sources spanned several orders of magnitude. This extreme variability made the use of properly selected statistical models and techniques very important in extrapolating the data selected from this program to the population of fugitive emissions.

The estimation of emission factors was one important objective of this program. Because of the high degree of skewness in the distribution of nonmethane leak rates from baggable sources, conventional statistics were inadequate for efficient estimation of emission factors and their variances. In addition to the skewness, a large percentage of the sources studied were considered "nonleaking." These sources affect the emission factor and therefore had to be considered in developing estimates for these factors. Another statistical problem which had to be addressed in developing the emission factors was the estimation of leak rates for sources which screened greater than or equal to 200 ppmv but were not sampled for economic reasons.

The population to which the data from this study can be extrapolated is the total number of sources from all United States refineries. For this analysis, it is assumed that a random selection was made for refineries, units within a refinery, and sources within a specific choice variable category within a unit. The "true value," e.g., of an emission factor, is an abstract concept. Essentially, this "true value" is that number which would be obtained if at a given point in time all sources of a particular type in the population could be sampled, analyzed and averaged.

ESTIMATING EMISSIONS FOR NONSAMPLED SOURCES

Due to time and equipment constraints, it was not always possible to sample all sources that screened greater than 200 ppmv. At the fifth refinery, a sampling strategy was developed to reduce the sampling workload. All sources screening greater than 10,000 ppmv were sampled, but only one-fourth of the valves and pumps with screening values between 200 and 10,000 ppmv were sampled. In order not to bias the distribution of leaking sources,

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it was necessary to develop estimated values for all sources screening
greater than 200 ppmv and not sampled. The number of sources sampled and
estimated for each source type is shown in the following table:

Baggable Source Type	Total Sources Sampled or Screened > 200 ppmv	Sources Sampled	Sources to Be Estimated
Valves	627	474	153
Pump Seals	382	281	101
Compressor Seals			
Hydrocarbon Service	102	83	19
Hydrogen Service	69	60	9
Flanges	62	43	19
Drains	49	28	21
Relief Valves	58	31	27

Least-squares regression analyses were done for each device type,
regressing the logarithm of the nonmethane leak rate on the logarithm of
the maximum screening reading. Both the original screening value and
rescreening values (taken closer to the time of sampling for leak rate) were
evaluated and a "best" equation was selected for each device as summarized
in Table 7.

Using the equations in Table 7 , predicted log-nonmethane leak rates
were computed for each source not sampled with a screening value greater than
or equal to 200 ppmv. Leak rates (lb/hr) were then computed using

$$\text{leak rate} = \exp_{10}[\log \text{ leak} + z \text{ (standard error of estimate)}],$$

the number of sources estimated, where z is a random number from a standard-
normal distribution. The use of the random number is an attempt to yield a
predicted distribution of leak rates which would approximate the distribution
if all sources were sampled. No bias correction factor is needed in con-
verting from the log to linear scale since the mean leak rate is not being
predicted. The predicted leak rates were used in further analyses and
development of emission factors.

Because the true leak rate/screening relationship is unknown, there
is a potential bias introduced when these predicted leak rates are used in
developing emission factors. The potential bias is proportional to the

TABLE 7. PREDICTION EQUATIONS FOR NONMETHANE LEAK RATES
BASED ON MAXIMUM TLV SCREENING OR RESCREENING VALUES

SOURCE TYPE	LEAST - SQUARES EQUATION	NUMBER OF DATA PAIRS	CORRELATION COEFFICIENT (r)	STANDARD ERROR OF ESTIMATE
Valves	LOG(NMLK)= -5.41 + 0.88 LOG(MXTLV-RS)	177	0.78	0.736
Pump Seals	LOG(NMLK)= -4.64 + 0.89 LOG(MXTLV-RS)	171	0.68	0.820
Compressor Seals:				
Hydrocarbon Service	LOG(NMLK)= -4.77 + 0.92 LOG(MXTLV-RS)	48	0.58	0.791
Hydrogen Service	LOG(NMLK)= -3.66 + 0.44 LOG(MXTLV- S)	44	0.36	0.884
Flanges	LOG(NMLK)= -5.11 + 0.84 LOG(MXTLV- S)	47	0.74	0.535
Drains	LOG(NMLK)= -5.02 + 1.16 LOG(MXTLV- S)	60	0.72	0.807
Relief Valves	LOG(NMLK)= -4.47 + 0.87 LOG(MXTLV-RS)	53	0.78	0.637

NMLK - Nonmethane leak rate (lb/hr)
MXTLV- S - Maximum value - original screening (ppmv)
MXTLV-RS - Maximum value - rescreening (ppmv)
LOG - Logarithm, base 10

standard error of the estimates adjusted for number of data pairs used to develop the equation and the impact of the bias on emission factors depends on the percent of sources leaking. The potential bias for each source type estimated was approximated and found to be less than 6% for all source types except compressors (14% potential bias for compressors in hydrocarbon service). The potential biases were taken into consideration in developing confidence intervals for emission factors.

STATISTICAL DISTRIBUTION MODELS FOR LEAK RATES

A lognormal distribution was used to model the distribution of leaking sources. This distribution has the property that when the original data are transformed by taking natural logarithms, the transformed data will follow a normal distribution. The lognormal distribution is often appropriate when the standard error of an individual value is proportional to the magnitude of the value. The form of the lognormal distribution is as follows:

$$
f(x) = \begin{cases} \dfrac{\exp\left[-\dfrac{(\ln x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} & \text{for } 0 > x > \infty \\[20pt] 0 & \text{for } x \le 0 \end{cases}
$$

$$
\text{Mean} = \exp\left[\mu + \frac{\sigma^2}{2}\right]
$$

$$
\text{Variance} = \exp[2\mu + 2\sigma^2] - \exp[2\mu + \sigma^2]
$$

In order to develop estimates for emission factors, the nonleaking sources (leak rate assumed equal to zero) also had to be modeled. A mixed distribution, specifically a lognormal distribution with a discrete probability mass at zero, was used for this purpose. Letting ρ equal the fraction of nonleaking sources in the population, this mixed-lognormal distribution has the following form:

$$
f(x) = \begin{cases} \dfrac{(1-\rho)\exp\left[-\dfrac{(\ln x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} & \text{for } 0 < x < \infty \\[20pt] \rho & \text{for } x = 0 \\[10pt] 0 & \text{for } x < 0 \end{cases}
$$

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$$\text{Mean} = (1 - \rho) \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = (1 - \rho) \left[\exp(2\mu + \sigma^2)\right] \left[\exp(\sigma^2) - (1 - \rho)\right]$$

Efficient estimates of the mean and variance of the population model by this mixed distribution have been developed [Finney (1941), Aitchison (1955)]. These estimates are as follows:

The best, unbiased estimator of the population mean emission rate is

$$m = \left\{\left(1 - \frac{r}{n}\right) \exp\left[(\bar{x})\right] g\left(\frac{s^2}{2}\right)\right\}$$

and the best, unbiased estimator of the population variance of the emission rates is

$$v = \left(1 - \frac{r}{n}\right) \exp(2\bar{x}) \left[g(2s^2) - \left(1 - \frac{r}{n-1}\right) g\left(\frac{n-r-2}{n-r-1} s^2\right)\right]$$

where

n = number of sources screened

r = number of sources screened < 200 ppm or with measured leak < 10^{-5} lbs/hr

m = n - r = number of "leaking" sources

g(t) = infinite series

$$= 1 + \frac{(m-1)t}{m} + \frac{(m-1)^3 t^2}{m^2 2! (m+1)} + \frac{(m-1)^5 t^3}{m^3 3! (m+1)(m+3)} \cdots$$

$\bar{x}$ = average of the logarithm of leaking sources

$$= \sum_{1}^{n-r} \ell n \text{ (nonmethane leaks)}/(n - r)$$

s^2 = variance of the logarithm of leaking sources

$$= \sum_{1}^{n-r} [\ell n \text{ (nonmethane leaks)} - \bar{x}]^2/(n - r - 1).$$

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The mean and variance formulas hold whenever there is more than one leaking source $(n - r > 1)$. When only one leaking source is identified, the following estimates are appropriate:

$$\text{mean} = \frac{x_1}{n} \text{ and variance} = \frac{x_1^2}{n} \text{ ,}$$

where x is the single measured leak. If no leaks are found $(r = n)$, then the best estimate for both the mean and variance is zero.

This estimator for the mean was used for all emission factors developed in this program. Finney (1941) showed that this estimator of the mean is more than twice as efficient as the arithmetic average for data distributed similarly to the leak rates from baggable sources.

Since data distributed lognormally can be transformed to a normal distribution by taking natural logarithms of the data, the distribution assumption for the leaking sources can be tested by examining distributions of the log leak rates. Histograms displaying these distributions were constructed for all important source type and process stream classifications. The data for most sources appeared to adequately approximate a normal distribution. Figure 19 shows the leak rate histogram for valves in light liquid and two-phase streams. The compressor seal data from hydrocarbon service and the heavy stream data for pump seals both appeared skewed to the left. Compressor seals with sampled leak rates less than 10^{-3} were considered as negligible (zero) to minimize this skewness.

To statistically test the assumption of a normal distribution for the log-leak rates, skewness and kurtosis statistics were computed for each data group and tested for departures from their expected values of zero in a normal distribution. Table 8 summarizes these statistics. Only three of the twelve cases indicate significant lack of normality, confirming the conclusions from the histograms.

The other assumption made in using the mixed-lognormal model was that the sources with screening values less than 200 ppmv (calibrated to hexane) had insignificant leak rates which could be assumed equal to zero. A number of sources with TLV's less than 200 were sampled during the program in order to evaluate this assumption. Table 9 summarizes the leak rate data for these sources. A "worst-case" impact of this zero-emission assumption on emission factor estimates can be evaluated by comparing the median value times the percent of sources screening < 200 ppmv that were used in computing the emission factor. Table 10 summarizes this comparison.

Only for flanges does the zero assumption appear to have a potential impact on the emission factor estimate. For flanges, the median leak rate for the 5 sources screening < 200 ppmv was approximately equal to the emission factor. Setting all sources that were considered zero to 0.00054 lbs/hr would almost double the emission factor. This potential bias was

FREQUENCY

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  ------------------------------------------------------------------------------------------
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```

MIDPOINT OF LN OF NON METHANE LEAK RATE
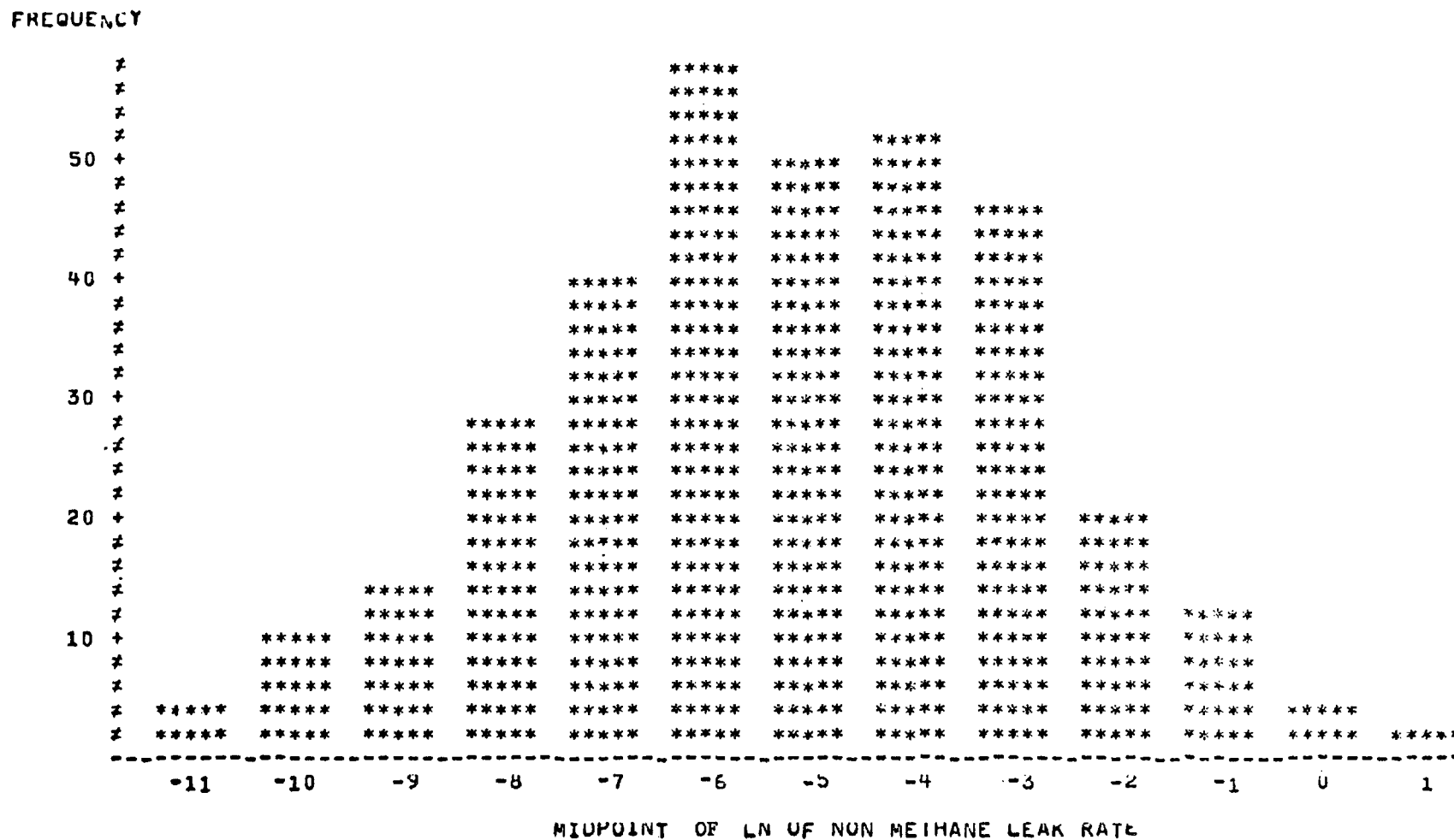
Figure 19. Histogram of LN of nonmethane Leak Rate Valves
Light Liquids/Two-Phase Streams

TABLE 8.   SKEWNESS AND KURTOSIS STATISTICS

Source Type/ Stream Group	Number of Leaking Sources	Skewness	Kurtosis
Valves			
Gas/Vapor Streams	154	0.19	-0.33
Light Liquids/Two-Phase	330	-0.16	-0.18
Heavy Liquids	32	0.28	-0.88
Hydrogen Streams	59	-0.18	-1.09*
Open-ended Valves	30	-0.01	-0.98
Pump Seals			
Light Liquids	296	0.03	-0.36
Heavy Liquids	66	-0.77*	0.06
Compressor Seals			
Hydrocarbon Service	102	-0.99*	1.16*
Hydrocarbon Service	69	-0.29	0.69
Flanges	62	0.39	0.20
Drains	49	-0.04	-0.47
Relief Valves	57	-0.05	-0.21

* probability <.05 given a normal distribution.

TABLE 9.   LEAK RATES FOR SOURCES SCREENING LESS THAN 200 PPM.

Source Type	# Sampled <200ppmv	MAX TLV (ppmv) Minimum	Maximum	Leak Rates (lb/hr) Minimum	Median	Maximum	% of Total Sources Screened <200
Compressor Seals	3	0	140	0.00086	0.00416	0.1058	23.5
Drains	5	0	120	0.00056	0.00197	0.1078	81.8
Flanges	5	0	110	0.00007	0.00056	0.0047	96.9
Pump Seals	12	8	180	0.00006	0.00137	0.0052	51.5
Relief Valves	8	40	180	0.00037	0.00132	0.0765	60.8
Valves	30	0	190	0.00001	0.00042	0.0383	67.2

TABLE 10.   IMPACT OF "ZERO LEAK RATE" ASSUMPTION ON EMISSION FACTOR

Source	Approximate Emission Factor Estimate (lb/hr)	Median Leak Rate Times Percent of Sources < 200 (lb/hr)	Median Times % of Sources <200 Expressed as Percent of Emission Factor
Compressor Seals	0.8	0.00098	0.1
Drains	0.07	0.00161	2.3
Flanges	0.00058	0.00054	92.8
Pump Seals	0.17	0.00071	0.4
Relief Valves	0.19	0.00080	0.4
Valves	0.023	0.00029	1.2

accounted for in developing confidence intervals for the emission factor estimate for flanges.

CONFIDENCE INTERVALS FOR PERCENT SOURCES LEAKING AND FOR EMISSION FACTORS

Confidence intervals for the percent of leaking sources were computed using the Binomial Distribution. The Binomial is used to model data when a random sample is selected and each item is classified into one of two categories (leaking or nonleaking here). Exact confidence limits (level $1 - \alpha$) for the estimate of percent leaking can be obtained by iteration solving for P_ℓ in

$$\sum_{i=k}^{n} \binom{n}{i} P_\ell^i (1 - P_\ell)^{n-1} = \frac{\alpha}{2} \quad \text{for the lower limit and for } P_u \text{ in}$$

$$\sum_{i=0}^{k} \binom{n}{i} P_u^i (1 - P_u)^{n-i} = \frac{\alpha}{2} \quad \text{for the upper limit}$$

where

n = number of sources screened

k = number of leaking sources

Tables of these solutions, available for most cases, were used to develop 95% confidence intervals for reporting and for computing 97.5% confidence intervals which were used in developing confidence intervals for emission factors. 97.5% was selected so that 95% confidence intervals for emission factors would result when the estimated percent leaking was combined with the estimated mean leak rate ($0.975 \times 0.975 \simeq 0.95$).

Patterson (1966) described how confidence intervals for the mean from a lognormal distribution can be computed using estimators developed by Finney (1941). 97.5% confidence intervals were computed for the average, $\bar{y}$, of the transformed data, $y = \ell n$ (leak), using

$$C_\ell = \text{lower limit} = \bar{y} - 2.24 \, [s^2/(n - r)]^{1/2}$$

and

$$C_u = \text{upper limit} = \bar{y} + 2.24 \ [s^2/(n-r)]^{1/2}$$

where

s^2 = the variance of the transformed data

$n - r$ = the number of leaking sources.

Then, following Patterson's arguments, confidence intervals for the mean leak rate can be computed using:

$$C_{\ell}^{\tilde{}} = \text{lower limit} = \exp \ [C_{\ell}] \ g(s^2/2)$$

and

$$C_u^{\tilde{}} = \text{upper limit} = \exp[C_u] \ g(s^2/2)$$

where

g(t) = the series given above

To obtain 95% confidence limits for the emission factors, the confidence limits for the percent leaking and for the mean leak rate were combined as follows:

lower 95% limit for emission factor = $P_{\ell} \ (C_{\ell}^{\tilde{}})$

upper 95% limit for emission factor = $P_u \ (C_u^{\tilde{}})$

These confidence intervals are conservative in the sense that 95% is a lower bound for the confidence coefficient for the intervals. The confidence intervals should be interpreted as follows:

When we state that the true emission factor falls within the limits computed as described above, we expect to be correct at least 95% of the time.

These confidence intervals consider random sampling variation and random test error, with no adjustments for potential bias in the sampling and analytical methods. The potential sources for bias have been discussed in previous sections.

(1) recoveries from sampling

(2) analytical inaccuracies

(3) biases in estimating leak rates from nonsampled sources

(4) bias in assuming sources screening < 200 could be considered as zero leak rates.

Each of these potential biases was evaluated during the quality assurance activities as previously discussed.

The potential systematic errors were considered independent so the net effect of combining all types of systematic errors was used in adjusting the emission factors and confidence limits. The following table summarizes these net systematic adjustments made to emission factors and confidence intervals:

Source Type	Total Systematic Adjustments (%)		
	Lower Confidence Limit	Upper Confidence Limit	Emission Factor Estimate
Valves	− 0.6	+ 2.7	+ 1.8
Pump Seals	− 0.9	+ 4.7	+ 2.0
Flanges	+ 0.4	+ 93.6	+ 0.7
Compressor Seals:			
Hydrocarbon	− 13.8	+ 12.1	+ 0.3
Hydrogen	− 2.9	+ 1.9	+ 0.3
Relief Valves	− 4.6	+ 6.5	+ 1.4
Drains	− 2.1	+ 5.6	+ 2.1

DEVELOPMENT OF NOMOGRAPHS

Nomographs were developed as part of the statistical analyses for this project to predict the mean leak rate from screening values. An example of these nomographs is given in Figure 20. A statistical analysis of covariance was done to determine if different equations were required for the various source types and stream groupings. Although the equations were developed on a logarithmic scale, the nomographs are shown on an arithmetic scale for ease in reading and interpolation. Predicting the arithmetic mean leak rate for a given screening value is similar to predicting the mean from a lognormal distribution as previously discussed. The mean value for a given screening value on the nomograph was computed as follows:

$$\text{mean} = \exp_{10}[B_0 + B_1 \log_{10}(\text{screening})] \; g(SE^2 \; \ell n / 2)$$

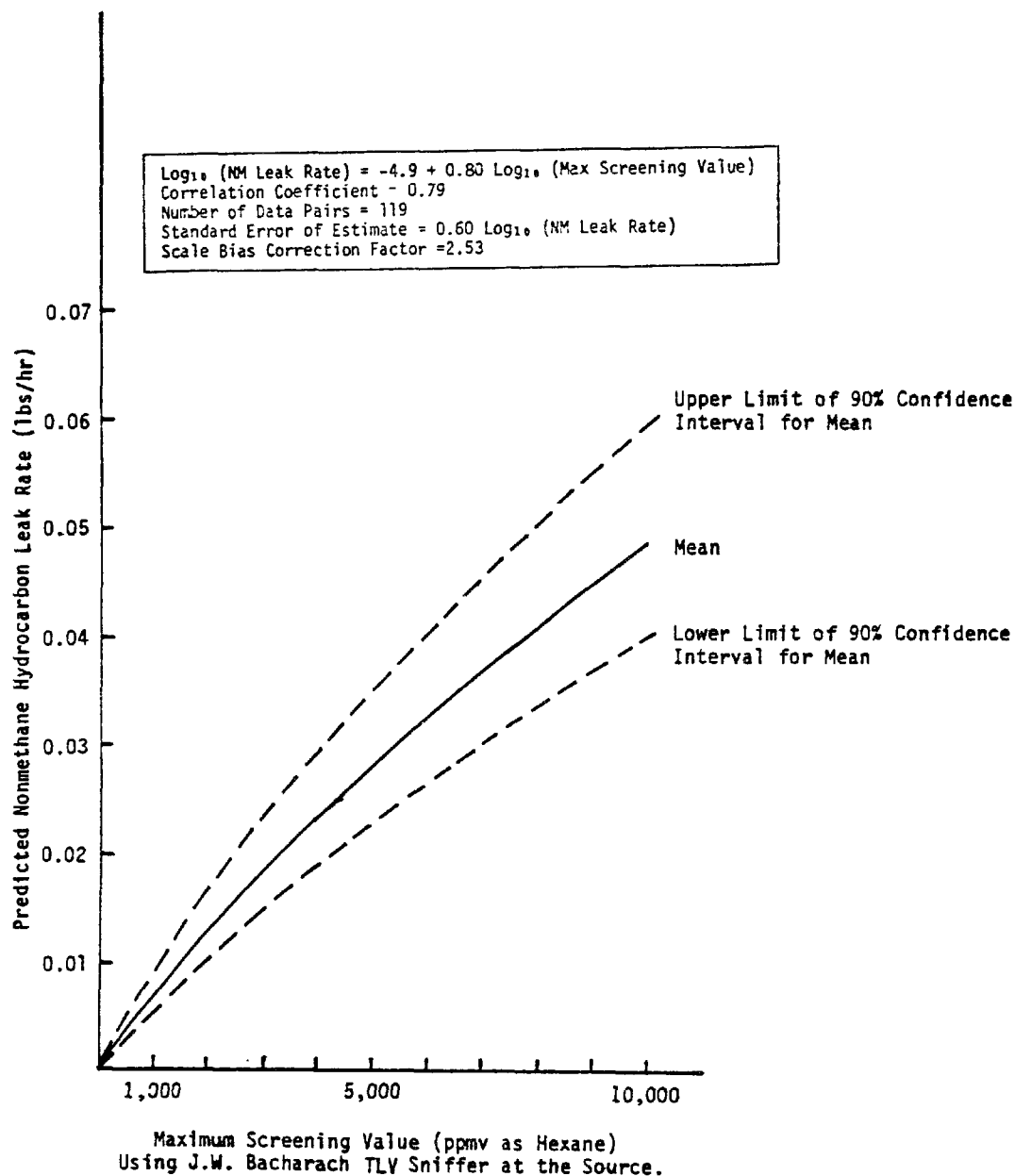$$= (10)^{B_0}(\text{screening value})^{B_1} \; (\text{scale bias correction factor})$$

Figure 20. Nomograph For Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves, Light Liquid/Two-Phase Streams (Part I: Screening Values from 0 - 10,000 ppm)

where

B_0 = log regression intercept

B_1 = log regression slope

$SE_{\ell n}$ = standard error of estimate in natural log scale

$g(t)$ = series previously described

Ninety percent confidence intervals for the predicted mean leak rate for a given screening value were computed in a similar manner to the confidence intervals for the mean leak rate as previously described.

CONCLUSIONS

(1) The leak rate measurements for baggable sources obtained in this program required special statistical analysis procedures because the high degree of skewness in the leak rate.

(2) Procedures were developed to predict leak rates for non-sampled sources. Potential biases in using these estimates were evaluated.

(3) A mixed lognormal distribution with a discrete probability mass at zero was used to model the leak rate data. The model was shown to adequately fit the data in most cases. Emission factor estimates based on this model are known to give much more efficient estimates than arithmetic averages.

(4) Confidence intervals were developed for estimates of percent leaking and for emission factor estimates. These confidence intervals account for random variations and potential biases from the sampling, analysis, and estimation procedures.

(5) Nomographs were developed to give unbiased estimates of the expected leak rate for a selected screening value.

L. P. Provost

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REVIEW

by

Kenneth Baker
Greene & Associates, Inc.
Dallas, Texas

on

QUALITY ASSURANCE AND DEVELOPMENT OF
STATISTICAL MODELS

RESUME

Kenneth Baker is a consultant for Greene & Associates, Inc., a firm of registered professional consulting engineers dedicated to serving all sectors of the energy and chemical industries. Mr. Baker received his B.S. and M.S. degrees in Chemical Engineering from Texas Technological College in Lubbock, Texas. Prior to joining Greene & Associates, Inc. in 1975 he spent three years with the U.S. Environmental Protection Agency and seven years with Celanese Chemical Company. While with the EPA he worked as a project officer on research and development efforts dealing with petroleum refineries and petrochemical processes. With Celanese he worked on feasibility studies, process developments at pilot and semi-works scale and commercial units. Mr. Baker now provides expertise in feasibility studies and economic evaluations, project management, and investigations, expert testimony and representation of petroleum refining, natural gas processing and chemical industries. He has worked for major and independent oil companies, gas processing companies, banks, Government regulatory agencies, petrochemical companies and various law firms. He is a member of the American Institute of Chemical Engineers, the American Association of Cost Engineers and the American Society for Testing and Materials.

REVIEW

by

Kenneth Baker
Greene & Associates, Inc.
Dallas, Texas

on

QUALITY ASSURANCE AND DEVELOPMENT OF
STATISTICAL MODELS

In 1883, Lord Kelvin wrote "When you can measure what you are speaking about and express it in numbers you know something about it. . . When you cannot express it in numbers, your knowledge is of meagre and unsatisfactory kind: you have scarcely advanced to the stage of science."

Lord Kelvin's quotation certainly applies when one is concerned with quality assurance and quality control. For knowledge of the refinery fugitive emissions to be satisfactory we must speak and express it in numbers. Mr. Provost in his paper has presented the procedures used in three major areas of Radian's quality assurance program. It is obvious that quality assurance and quality control has been a major concern for this sampling project from the very first. It has involved a commitment by all of the people, all of the time who have been associated with this project. Quality control and quality assurance cannot be a one-man or step-child type of effort for a testing program of this magnitude.

Knowledge of how the testing results are to be used and the accuracy required must be understood. Then, plans must be made to get sufficient test data to meet the requirements to assure that the end results are useful. But it must be emphasized that quality control does not stop there. It continues throughout the project--data acquisition, testing results, analysis and reporting. A breakdown at any point will reduce the credibility of the results.

I would like to now quote a man with a vastly different background than Lord Kelvin. Stanley Marcus in his book Quest for the Best says: "I learned to differentiate not between good and bad but between better and best, and to pursue the best, regardless of cost or effort. The difference in cost to achieve the best may be negligible but overcoming the inertia of

the status quo and the willingness of most people to settle for less than perfection always takes greater effort." Because the rates measured by these tests will probably be used for years in evaluating existing and potential new refineries, the best must be pursued. Industry, EPA and Radian must practice what Mr. Marcus learned.

A quality assurance program should test for the properties of a good experiment. It should test for:

1. systematic error
2. precision
3. range of validity
4. simplicity
5. calculation of the uncertainties

The testing should be free from systematic error. Although this statement seems totally obvious and compelling, it is sometimes flagrantly violated, knowingly or not. As an example, suppose that tests were made to compare the emission rates resulting from two valves. Although the test equipment may be quite sophisticated, there are only two valves to be tested. Through Valve A is flowing propane and through a second valve flows butane. Regardless of laboratory techniques and precisions of measurement, the comparison of emission rates in the valves is handicapped by the systematic error incorporated in the comparison of the valves for the comparison is also a comparison of the materials flowing through them. Needless to say, such systematic errors should be avoided if possible. The primary technique which is used to eliminate systematic errors is that of randomization. Radian has tried to do this at each of the refineries and for the types of sources sampled.

Secondly, the need for precision may be clearly perceived; however, it is not so obvious how it is to be achieved. The variance in precision of many tests and their differences is dependent on the inherent variability of the source being tested and the number of tests and the design or sequence of the testing. While the tester can do nothing about the first factor, he can exercise considerable control to achieve the needed precision through the second and third factors.

The third property of a good experiment is the range of validity. The basic idea of the testing should encompass a sufficiently wide range of values, so that reasonable inferences about the emission rates from refineries may be drawn from the testing. With the emission rates measured in different refineries ranging over several orders of magnitude, an adequate range of validity has been covered.

It should be noted that in incorporating a wide range of emission rates into the testing tends to decrease the precision of the testing.

The fourth requirement of a good test is that it is simple. It does not mean that it is naive or stupid. On the other hand, it behooves one to keep the test as simple and as uncomplicated as possible so as to minimize the potential points for variation.

Finally, the testing program should be planned so that the uncertainties of the results can be calculated. Back to what Lord Kelvin said... "express it in numbers...". As noted above, precision depends on the variability of the test. This variability can be classified into two areas:

1. the random or chance portion, which is uncontrollable and is the sum of all the causes of chance that are involved, and

2. the assignable causes, that is, the differences between testing equipment, the differences between workers, the differences among the sources being tested, and the differences in these above three factors over a period of time.

Differences in the above relationships one to another will also change the quality of the testing results. As described in Mr. Provost's paper, Radian has considered each of these areas.

In the first part of his paper on the quality control of hydrocarbons screening devices, Mr. Provost evaluated the Bacharach "TLV Sniffer" and the Century Model OVA-108 used for screening the refinery sources that would ultimately be tested. It was important that these screening instruments be properly calibrated, their results be reproducible and that a correlation be developed between screening value and the emission leak rate, because it is not practical to sample all possible sources in each or any refinery. However, a sufficient number of sources could be screened. The existence of a good correlation between maximum screening value and the measured emission rate is a very important result. Without such a correlation many more detailed samples would have been required.

In the section on quality control for hydrocarbon measurements from baggable sources, Radian covered the five points of a good test. They reviewed the analytical instrument, the total hydrocarbon analysis instrument used; they measured the variation due to different operating teams; the differences in sources sampled: valves, flanges, pumps, etc. Additionally, they considered the variation and interrelationship of these variables over time.

It is reported that a repeat sample could be expected to differ by as much as 113 percent of the original leak rate and the overall standard deviation between samples was 41 percent. While these numbers may initially appear high when considered relative to the total amounts being emitted from a single source and the inherent short-term variation in the leak rate, the differences do not negate the usefulness of the results.

In the last part of Mr. Provost's paper the statistical procedures were discussed. As noted for the first part of his paper, the correlation between screening values and leak rates was an important development. The use of these correlations and other estimates to predict leak rates created the potential for biases. The potential biases in using the correlations and estimates to predict leak rates was a point of concern. Statistics have been used to determine confidence intervals for the estimates.

Nomographs of the type presented in Mr. Provost's paper and those for the other equipment types studied will certainly be used for years to come.

I have been favorably impressed with the results of this project. However, when one uses the generalizing words such as some, several, good, bad, etc. because they "read or sound" better, we do not demonstrate satisfactory knowledge of our subject. However, each of us can understand exactly the difference in numbers.

I would like to suggest that as often as possible we practice what Lord Kelvin and Mr. Marcus said "...express it in numbers . . . and . . . differentiate . . . and pursue the best." These are things we must strive for in quality control efforts.

Thank you.

Lloyd P. Provost

QUESTIONS AND ANSWERS

Q. James Stone/Louisiana Air Control Commission – I have two questions. One, when you measure relief valves and drains, what were they actually measuring? And, the other one is, did you concentrate the refineries in one part of the country or did you grab them from all over the place?

A. (By Rosebrook) – The data came from three refineries in California, one in the State of Washington, one in Texas, one in Oklahoma, one in Louisiana, one in Illinois, one in Indiana, one in Pennsylvania, one in Delaware, one in Kansas, and one in New Jersey. Relief valves were bagged just as valves and pumps were. We put a tent around them, pulled the sample and took that to the lab and measured the hydrocarbon.

Q. James Stone/Louisiana Air Control Commission – Were you only measuring the ones that were not hooked up to a flare-header?

A. (By Rosebrook) – Yes!

Q. James Stone/Louisiana Air Control Commission – On drains, were you just dropping a probe down in the drain and measuring?

A. (By Rosebrook) – No, in drains, when we screened them, we screened around the lip of the drain. When we measured them and this is reflected in the problems with that data, we bagged them, pulled a slow air flow across the top of the drain, and tried not to induce flow back from the drain up into the bags through our air movement. Obviously, we believe that we were not able to achieve that as well as we achieved a lot of other things.

Q. S. M. D'Orsie/Exxon Company-USA – In the next paper there is a table that I think provides some summary statistics, and you present a 95 percent confidence interval around emission factors. I just want to make sure that I understand how this ties with the work that you just presented. And what I am thinking is that, all your exercises here, in terms of determining the statistical reliability of the data were used to determine these final confidence intervals. Is that a correct statement?

A. – The rest of the speakers will be reporting a lot of different emission factors and hopefully, almost all the time, they will have a confidence interval associated with that. A confidence interval is what we feel is good measurement of how well we have estimated the emission factor. We called it 95 percent because we felt that it was approximately in that area, and it does consider random variations as well as the corrections we made

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for potential sources of bias. So, in answer to your question, yes the methodology I just went through, was used to produce both the emission factors and the confidence intervals you'll see in the rest of the papers.

Q. S. M. D'Orsie/Exxon Company-USA - So, in your data handling then, when we talk about the goodness of the data, what conceptualizing in terms of confidence intervals, rather than more simplistic definitions such as plus or minus 100 percent, has been done.

A. - Two different things, I think. We talked about the goodness of the data, individual measurements of pounds per hour baggings, and actual hydrocarbon measurements. I used simple statistics, plus or minus, for individual readings, and in one case, an average of two readings.

For emission factors, it is a very complicated statistic, and it required a little more complicated expression, but the interpretation is the same thing, just like an individual piece of data might be plus or minus 70 percent, the confidence intervals presented, represent plus or minus how good that emission factor is estimated. Just as 70 percent tells how well an individual piece of data is estimated.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - I noticed in the earlier presentation you showed your screening tool, how did you maintain the 5 cm probe distance? I didn't see any kind of device on it.

A. (By Rosebrook) - Since there is no device attached to it, normally, and since that was a study done to accommodate some results requested by another part of EPA, we merely attach a wire or guide to set it at the desired distance. I'd like to point out that we have also done this in the State of California where their requirement is 1 cm. We then attached a small Teflon pointer, or whatever you care to call it, so that you maintain the 1 cm distance.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - Were you changing back and forth when you were doing both measurements at the same time? Where you do the probe on the source and then you take it back and put the 5 cm thing on it and do it right then or how were you flipping back and forth? We have trouble doing that.

A. (By Rosebrook) - Yes!

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - The other question we have is from our OSHA people. They say 1 cm is the same as on the source because you don't plug the probe. You just mentioned that California says that 1 cm is on the source. What is right in this business?

A. (By Rosebrook) - I have a comment and then Mr. Morgester has a comment. Why don't you speak first Jim?

COMMENT/James J. Morgester/California Air Resources Board – Let me just give you a little background on where the 1 cm came from. There wasn't anything magical about it. The original regulation required measurement right on the source and 1 cm was simply picked because when you use the FID, if you put it right on the source, it puts the flame out. A gentleman here says it is put out at 1 cm too.

COMMENT/Rosebrook – It is a problem that we don't have with the TLV and it allowed us, in our estimation, to be more reproducible. We were not affected by the weather, to the same extent.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. – Which way is EPA going to pursue, do you know that?

A. (By Rosebrook) – Which way is EPA going to pursue? On the source? Yes.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. – Can you use the OVA then, based on the previous comment? As the flame goes out the thing probably doesn't work.

A. (By Rosebrook) – Well, as the flame goes out you know you've got a leak. You've got quite a leak. The flame goes out because basically you overwhelm it and you can't support combustion. It doesn't got out merely by the act of putting it there. You've got to find a good size leak.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. – What number do you put down on your sheet?

COMMENT/John Sawyer/ACCUREX Corporation – I had quite a bit of experience with the OVA, and if the flame does go out it will readily relight when you pull away from the source. You also have a 10 to 1 dilution probe which you can put on, and if it puts it out at 100,000 ppm, then you've got a pretty serious leak.

COMMENT/Rosebrook – We have also done some work with double-dilution probes so that we can measure, theoretically up to a million ppm.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. – I would like to see it standardized, so that we all do it the same, I guess that is my main distress.

A. (By Rosebrook) – I don't have much control over that!

Q. Paul Harrison/Engineering-Science – I think the compromise is if you want to use English units use 2-1/2 cm, if you want to use cgs then 2 cm. If you have a pinhole leak and you put the OVA, or any sampler on that leak, two things happen. One, is that after awhile you get a 100 percent of the leak plus whatever air it can suck in, and two, you have problems of the grease around the seal. There are logistical problems, and just field problems about using at the source. It is very easy to develop a nomograph

for any reasonable distance up to 5 cm. And, as you pointed out there is about an order of magnitude difference between 1 cm and 5 cm. The 1 to 2-1/2 cm distance also eliminates most wind effects except under pretty high wind conditions and turbulent conditions if you simply go for the highest value, which of course is typically downwind of the leak. I don't really feel there is much difference between 1 cm and 2-1/2 cm except setting a universal standard. I would not recommend, and the State of California originally said at the source, right on the leak, and of course they had the logistical problems and had to pull back to 1 cm, which is perfectly alright. But it really doesn't make that much difference except in the level that you set for your survey. Originally we started out at 5 cm and the original guideline documents for EPA was 5 cm, because most of the data that was available at that time was 5 cm.

COMMENT/Rosebrook - Bruce (Tichenor), do you still have a comment?

COMMENT/Bruce A. Tichenor/US-EPA-IERL-RTP - I am speaking for ORD, not OAQPS. I agree with some of the comments that were made. It really doesn't make much difference. There are two factors, I think. One is you say "at the source" and you are at the source, and there is no confusion. You say a centimeter and you have the thing tilted one way or another, you have a problem. The second is that the data that Lloyd showed does show that the variability of the individual readings are less at the source then they are from some distance from the source. The other thing is that when we talk about these screening values of 200 or 1,000 or 10,000, again those are not regulatory requirements at this point, at least not for what I am talking about. For the purpose of this program 200 was simply selected as a break-point to enable us to go and get the data. I am not answering the question as to what is best. From my point, from an R&D standpoint I think "at the source" is best because I think they have less problems. Now whether that's going to translate itself into a regulatory requirement, I don't know.

Q. R. C. Weber/US-EPA-IERL-Cincinnati - Calvin commented a little bit about the difficulty with sampling "at the source" since that is the way it was primarily done in the refinery program; was there a significant problem of plugging of the probe or whatever?

A. (By Smith) - Well, of course not every valve is the cleanest piece of equipment in the world, so certainly there is a film of oil or grease on some of the valves. Part of the equipment that our engineers carried in the unit when they were screening these sources was a package of pipe cleaners to clean out the probe, because occasionally you do get material inside the probe from just simply touching the valve. After they back away from the valve, of course the instrument goes back to whatever the ambient reading is. Sometimes if you have very heavy hydrocarbon streams, and use the TLV, that material will coat the inside of the probe and the detector will take some time to come back to an ambient reading. When you get the tip of the probe or the inside of the probe contaminated you can tell very quickly because the ambient reading will be a lot higher than what you would expect, and at that point you just simply take a pipe cleaner and clean it out.

Q. Cynthia M. Harvey/PEDCo Environmental, Inc. - What you have talked about is the statistical approach that has been used once you gathered your data. What I'm interested in is what statistical approach did you use to get your sample and are you sure that you have a representative sample of the valves, flanges, etc.?

A. - The first speaker went into that briefly, I think it is probably covered more in detail in Calvin's paper, but if not, there have been a number of previous presentations. I know Don Rosebrook has made two or three and Bob Wetherold has made one at other conferences which described the detailed experimental design used on this program. Just real briefly, we started off with a factorial approach. We named what we call choice variables, variables that we thought could affect the leak rate, like temperature, unit, pressure, gas lines, liquid lines, types of equipment, valves, pumps and so forth and came up with a factorial representation of those and then picked a number in each cell and from there we handed it to an engineer. He picked them on a P&ID at random before he went out into the unit. The intent was to minimize any bias from looking at the unit. It was a kind of modified fractional/fractorial with extensive quality control on the back end to document the precision of the measurements.

RESULTS OF MEASUREMENT AND CHARACTERIZATION
OF ATMOSPHERIC EMISSIONS FROM
PETROLEUM REFINERIES

by

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ABSTRACT

The results of the sampling and analytical efforts in the measurement of fugitive emissions from point and area sources in petroleum refineries are summarized. Nomographs useful in the prediction of emissions are presented as are the statistically determined emission factors for each source category.

RESUME

Dr. Frank G. Mesich is an Assistant Vice President of Radian Corporation in the Office of Research and Engineering. He is also General Manager of Radian's Northern Virginia facility. His educational background includes a bachelor's degree in chemistry from the Colorado College and a Doctorate in Physical Chemistry from Iowa State University. His industrial experience includes seven years of process development and improvement with Celanese Corporation. With Radian he has directed a wide variety of environmentally related programs and served as Program Manager for the initial phases of the refinery fugitive emission work.

F. G. Mesich

RESULTS OF MEASUREMENT AND CHARACTERIZATION

OF ATMOSPHERIC EMISSIONS FROM

PETROLEUM REFINERIES

Previous papers have generally described the overall program conducted by Radian Corporation for the Environmental Protection Agency to perform an "Assessment of Environmental Emissions From Oil Refining." The program required extensive sampling of both controlled (stack emissions) and uncontrolled (fugitive) emissions. With strong industry cooperation sampling was conducted at thirteen (13) refineries geographically spread across the continental United States. This paper summarizes the results of the fugitive emission sampling and presents the emission factors derived from a statistical analysis of the data. The complete results will be the subject of a final report to EPA which is nearing completion.

DESCRIPTION OF EMISSION SOURCES

The fugitive emissions associated with petroleum refining operations present two very different sampling problems. From a sampling standpoint the sources of emissions or leaks within the refinery battery limits may be classed into (1) those which emit from a localized area or point source, termed "baggable" sources and (2) those which are emitted from a diffuse area such as wastewater treatment. Tankage leaks are the subject of many other studies and were not included in this program.

Baggable sources, which can be enclosed for accurate sampling, included valves of all types, flanges, compressor and pump seals, and plant drains. The other, less tractable, sources include cooling towers, oil/water separators and other components of the wastewater treament systems. The bulk of this discussion will center around the baggable sources where the preponderance of data exist.

RESULTS OF THE SAMPLING OF BAGGABLE SOURCES

As was discussed in detail in a previous paper, two fundamental measurements of non-methane hydrocarbons were made for each source: rapid screening using a hand held hydrocarbon detector in the immediate vicinity of a suspected leak and a precise measurement of leak rate by enclosing the source.

Based on the average emission results of this program the baggable sources can be grouped into twelve (12) categories listed in Table 1. It

TABLE 1.   CATEGORIES OF BAGGABLE SOURCES

Category	Source Description	Number of Sources Screened
1	Valves, Gas/Vapor Streams	563
2	Valves, Light Liquid/Two-Phase Streams	913
3	Valves, Heavy Liquid Streams	485
4	Valves, Predominantly Hydrogen Streams	135
5	Open-ended Valves (all streams)	129
6	Pump Seals, Light Liquid Streams	470
7	Pump Seals, Heavy Liquid Streams	292
8	Compressor Seals, Hydrocarbon Service	142
9	Compressor Seals, Hydrogen Service	83
10	Flanges (all streams)	2094
11	Drains (all streams)	257
12	Relief Valves (venting to atmosphere)	148

should be noted that several subcategories are defined based on the service for which the equipment is used. Our results show that stream composition, particularly vapor pressure, has a significant effect on the leak rate or emission factor. Table 2 summarizes the emissions factors determined from the analysis of all of the program data. Twelve emission factors are given representing the twelve categories. Confidence intervals are shown for both the percentage of leaking sources and for the estimated emission factors. Thus, the table provides an estimate at the 95 percent confidence level for predicting both average emissions and occurrence of leaks.

A "leaking" source in this study was defined as any source with measured emissions greater than 10^{-5} lbs/hr or any source not sampled with a screening value greater than 200 ppmv (TLV calibrated to hexane). Several important conclusions can be drawn from the data in Table 2. Stream service has a large measurable effect on the frequency and size of non-methane hydrocarbon leaks. For the valve category, which includes block, gate, and control valves, the average emission per valve ranges from 0.0005 lb/hr for valves in heavy liquid service to 0.059 lb/hr for those in vapor service. Pumps show a similar trend. Relief valves show both the highest occurrence rate and mass emissions on a per valve basis of any of the valves. The highest per source emission is for compressor seals while the lowest is for flanges.

The primary use of these data is in the prediction of emission levels from either existing or contemplated refineries. It must be remembered that these emission factor estimates are based on data from thirteen (13) refineries and only form the basis for an estimate of any single refinery. The confidence limits describe how well the average emission factors (on a national level) are estimated.

Tables 3 and 4 summarize the information collected during sampling as a function of the process unit studied for valves and pump seals. Similar tables for the other source types will be available in the final report. The data within each process unit are a composite of all data collected for that unit. Within these unit processes, the unit emission factors should be used with caution owing to some deviations from completely random process selection. More sources processing vapor materials were sampled than in heavy liquid service in order to increase the accuracy of the individual valve emission factors. The overall emission factors in Table 1 are not subject to the same biases and may be used within the stated confidence limits.

During the planning and conduct of this program, heavy attention was given to determining any correlations which exist between leak rates and process or equipment variables. These will be addressed in detail in another of this series of papers.

As a conclusion to the discussion of emission factors, consider their application to a hypothetical refinery. The analyses of the emissions rate data show that hydrocarbon emissions from valves, pump seals, and compressor seals are functions of the service or process stream properties. To

TABLE 2. SUMMARY STATISTICS AND ESTIMATED VAPOR EMISSION FACTORS
FOR NONMETHANE HYDROCARBONS FROM BAGGABLE SOURCES

Source Type	Number Screened	Number Leaking	Percent Leaking	95% Confidence Interval for Percent Leaking	Emission Factor Estimate (lb/hr/source)	95% Confidence Interval for Emission Factor (lb/hr/source)
Valves						
Gas Vapor Streams	563	154	27.4	(24, 31)	0.059	(0.030, 0.110)
Light Liquid/Two-Phase	913	330	36.1	(33, 39)	0.024	(0.017, 0.036)
Heavy Liquid	485	32	6.6	(4, 9)	0.0005	(0.0002, 0.0015)
Hydrogen	135	59	43.7	(35, 52)	0.018	(0.007, 0.045)
Open-Ended Valves	129	30	23.3	(16, 31)	0.005	(0.0016, 0.016)
Pumps						
Light Liquid Streams	470	296	63.0	(59, 67)	0.25	(0.16, 0.37)
Heavy Liquid Streams	292	66	22.6	(18, 27)	0.046	(0.019, 0.11)
Drains	257	49	19.1	(14, 24)	0.070	(0.023, 0.20)
Flanges	2094	62	3.0	(2, 4)	0.00056	(0.0002, 0.0025)
Relief Valves	148	58	39.2	(31, 47)	0.19	(0.070, 0.49)
Compressors						
Hydrocarbon Service	142	102	71.8	(64, 79)	1.4	(0.66, 2.9)
Hydrogen Service	83	69	83.1	(75, 91)	0.11	(0.05, 0.23)

TABLE 3. SUMMARY OF EMISSIONS DATA BY PROCESS UNIT - VALVES

Unit Code	Unit Identification	Number Screened	Number Leaking	Percent Leaking	95% Confidence Interval for Percent Leaking	Nonmethane Hydrocarbons	
						Estimated Emission Factor (lb/hr/source)	95% Confidence Interval for Emission Factor (lb/hr/source)
15	Atmospheric Distillation	278	62	22.3	(17, 27)	0.0023	(0.001, 0.005)
13	Fuel Gas/Light Ends Processing	460	158	34.3	(30, 39)	0.046	(0.026, 0.084)
22	Catalytic Cracking	190	49	25.8	(20, 33)	0.047	(0.015, 0.14)
1	Catalytic Reforming	153	86	56.2	(46, 67)	0.029	(0.015, 0.059)
27	Alkylation	227	85	37.4	(31, 44)	0.031	(0.015, 0.065)
17	Vacuum Distillation	57	0	0.0	(0, 6)	neg	(neg, 0.009)
2,4,8	Catalytic Hydrotreating/ Refining	285	69	24.2	(19, 29)	0.0051	(0.002, 0.012)
33	Aromatics Extraction	45	15	33.3	(20, 49)	0.0053	(0.001, 0.03)
23	Delayed Coking	86	9	10.5	(5, 19)	0.0019	(0.001, 0.02)
32, 34,35	Dewaxing, Treating	289	44	15.2	(11, 19)	0.011	(0.003, 0.04)
18	Sulfur Recovery	10	0	0.0	(0, 31)	*	*
5	Hydrocracking	83	27	32.5	(23, 44)	0.057	(0.01, 0.30)
11	Hydrogen Production	49	9	18.4	(9, 32)	0.0013	(neg, 0.02)
36	Hydrodealkylation	36	14	38.9	(23, 57)	0.013	(0.001, 0.09)
	Other	11	0	0.0	(0, 28)	*	*

* Insufficient data

TABLE 4. SUMMARY OF EMISSIONS DATA BY PROCESS UNIT - PUMP SEALS

Unit Code	Unit Identification	Number Screened	Number Leaking	Percent Leaking	95% Confidence Interval for Percent Leaking	Nonmethane Hydrocarbons	
						Estimated Emission Factor (lb/hr/source)	95% Confidence Interval for Emission Factor (lb/hr/source)
15	Atmospheric Distillation	149	65	43.6	(36, 52)	0.022	(0.001, 0.023)
13	Fuel Gas/Light Ends Processing	156	83	53.2	(45, 61)	0.19	(0.09, 0.40)
22	Catalytic Cracking	77	31	40.3	(29, 52)	0.081	(0.02, 0.29)
1	Catalytic Reforming	41	32	78.0	(62, 89)	0.18	(0.06, 0.51)
27	Alkylation	76	60	78.9	(68, 87)	1.3	(0.51, 3.5)
17	Vacuum Distillation	25	3	12.0	(3, 31)	*	*
2,4,8	Catalytic Hydrotreating/Refining	61	23	37.7	(26, 51)	0.033	(0.01, 0.13)
33	Aromatics Extraction	43	25	58.1	(42, 73)	0.20	(0.05, 0.73)
23	Delayed Coking	37	10	27.0	(14, 44)	0.020	(0.002, 0.15)
32, 34,35	Dewaxing, Treating	65	26	40.0	(26, 56)	0.056	(0.02, 0.20)
5	Hydrocracking	40	20	50.0	(34, 66)	0.053	(0.01, 0.20)
11	Hydrogen Production	7	0	0.0	(0, 41)	*	*
36	Hydrodealkylation	5	4	80.0	(28, 99)	*	*
	Other	5	0	0.0	(0, 52)	*	*

* Insufficient data

estimate the total hydrocarbon emissions from a refinery or unit process, the populations of the various potential sources must be known. To aid in these calculations, two other tasks were accomplished during this program--counting the number of fittings and other sources in a number of selected refinery units and making an estimate of the relative number of each source type associated with various process stream types.

SOURCE COUNTS

Individual sources were physically counted in several process units at five refineries. The sources counted included valves, flanges, pumps, compressors, drains, and relief valves (venting to atmosphere). The counts include only those sources in hydrocarbon service.

The visual source counts were used as a basis for estimating the total source populations in some of the major types of refinery process units. These estimated source populations are presented in Table 5. Sources were not counted in some types of process units including vaccuum distribution, aromatics extraction, delayed coking, hydrodealkylation, and sulfur recovery units. The number of sources in these units were estimated from source counts obtained in other types of units. The distribution of source counts by process stream classification are presented in detail in the final report.

FUGITIVE HYDROCARBON EMISSIONS FROM A HYPOTHETICAL REFINERY

An estimate was made of the total fugitive hydrocarbon emissions from six source types in a hypothetical refinery. The Texas Gulf Coast Cluster Model Refinery, developed by Arthur D. Little, Inc.,[2] was used for this purpose. The major process units are shown in Table 6. These process units were developed from the block flow diagram of the ADL Gulf Coast Model Refinery. Two atmospheric distillation units, two reformers, and a hydrogen plant are included in the list of process units. The capacities of each unit are also shown in Table 6.

An estimate of the total number of each source type and their total hydrocarbon emissions are given in Table 7. Where applicable, the number of sources and the total emissions from sources in the various stream services are also presented.

It should be emphasized that this example is intended only to be illustrative of the use of the emission factor data and serves to show some of the factors which must be known before making such an estimate.

DISTRIBUTION OF LEAKS

In addition to the derivation of emission factors, a number of other uses may be made of the data developed during this program. For example, the distribution of leaks within a source category gives insight

TABLE 5. ESTIMATED NUMBER OF INDIVIDUAL EMISSION SOURCES[2] IN FIFTEEN
SPECIFIC REFINERY PROCESS UNITS

Process Unit	Estimated Number of Sources Within Battery Limits of Process Units					
	Valves	Flanges	Pumps[3]	Compressors[4]	Drains	Relief Valves
Atmospheric Distillation	890	3540	31	1	69	6
Vacuum Distillation[1]	500	2000	16	0[1]	35	6
Fuel Gas/Light Ends Processing	180	760	3	2	11	6
Catalytic Hydroprocessing	650	2600	10	3	24	6
Catalytic Cracking	1310	5200	30	3	65	6
Hydrocracking	930	3760	22	3	58	6
Catalytic Reforming	690	2760	14	3	49	6
Aromatics Extraction[1]	600	2400	18[1]	0[1]	41	6
Alkylation	680	2280	11	0	41	6
Delayed Coking[1]	300	1240	9[1]	0[1]	28	6
Fluid Coking	300	1240	9	4	28	6
Hydroealkylation[1]	690	3760	14[1]	3[1]	58	6
Treating/Dewaxing	600	2290	18	1	44	6
Hydrogen Production	180	640	5	3	17	4
Sulfur Recovery[1]	200	800	6[1]	0[1]	20	4

[1] Sources were not counted in process units of this type. The number of sources was estimated.
[2] Only those sources in hydrocarbon (or organic compound) service.
[3] Number of pump seals = 1.4 x number of pumps.
[4] Number of compressor seals = 2.0 x number of compressors.

TABLE 6. MAJOR PROCESS UNITS IN HYPOTHETICAL REFINERY

ADL – Texas Gulf Cluster Model: 330,000 BPCD

Refinery Process Unit	Capacity, BPCD
Atmospheric Distillation #1	200,000
Atmospheric Distillation #2	131,000
Vacuum Distillation	134,000
Light Ends/Gas Processing	12,000
HDU: Reformer Feed	57,000
HDU: Light Gas Oil	11,000
HDU: Heavy Gas Oil	15,000
HDU: Light Cycle Oil	15,000
HDU: Vacuum Gas Oil	17,000
HDU: Coker Naphtha	3,000
Hydrocracker	15,000
FCCU	93,000
Catalytic Reformer: #1	41,000
Catalytic Reformer: #2	30,000
Aromatics Extraction	16,000
Alkylation	18,000
Coker	17,000
Hydrogen Plant	----

TABLE 7.   HYPOTHETICAL REFINERY: HYDROCARBON EMISSIONS[1]

Process Unit	Number of Valves in Units				Valve Emissions, lb/hr				Relief Valves		Flanges	
	Gas Service	Lt. Liq. Service	Hvy. Liq. Service	Total	Gas Service	Lt. Liq. Service	Hvy. Liq. Service	Total	Total R.V.	Emissions, lb/hr	Total Flanges	Emissions, lb/hr
Atmospheric Distillation: No. 1	90	280	520	890	5.31	6.72	0.26	12.29	6	1.14	3,560	1.99
Atmospheric Distillation: No. 2	90	280	520	890	5.31	6.72	0.26	12.29	6	1.14	3,560	1.99
Vacuum Distillation	50	50	400	500	2.95	1.20	0.20	4.35	6	1.14	2,000	1.12
Light Ends/Gas Processing	90	80	20	190	5.31	1.92	0.01	7.24	6	1.14	760	0.43
HDS: Reformer Feed	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Light Gas Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Heavy Gas Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Light Cycle Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Vacuum Gas Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Coker Naphtha	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
FCCU	380	410	510	1,300	22.42	9.84	0.26	32.52	6	1.14·	5,200	2.91
Hydrocracking	250*	380	310	940	11.68	9.12	0.16	20.96	6	1.14	3,760	2.11
Catalytic Reformer No. 1	260*	390	40	690	12.14	9.36	0.02	21.52	6	1.14	2,760	1.55
Catalytic Reformer No. 2	260*	390	40	690	12.14	9.36	0.02	21.52	6	1.14	2,760	1.55
Aromatics Extraction	60	500	40	600	3.54	12.00	0.02	15.56	6	1.14	2,400	1.34
Alkylation	230	340	0	570	13.57	8.16	0.00	21.73	6	1.14	2,280	1.28
Coking	30	60	220	310	1.77	1.44	0.11	3.32	6	1.14	1,240	0.69
Hydrogen Production	80*	80	20	180	3.74	1.92	0.01	5.67	4	0.76	640	0.36
	3,910	4,500	3,240	11,650	195.16	108.00	1.63	304.79	106	20.14	46,520	26.08

*Thirty percent of these valves are assumed to be in service in streams containing more than 50% hydrogen.

TABLE 7. (Continued)

Process Unit	Number of Pump Seals			Pump Seal Emissions, lb/hr			Compressor		Drains	
	Lt. Liq. Service	Hvy. Liq. Service	Total	Lt. Liq. Service	Hvy. Liq. Service	Total	Total Seals	Emissions, lb/hr	Total Drains	Emissions, lb/hr
Atmospheric Distillation: No. 1	15	28	43	3.75	1.29	5.04	2	2.80	69	4.83
Atmospheric Distillation: No. 2	15	28	43	3.75	1.29	5.04	2	2.80	69	4.83
Vacuum Distillation	2	19	21	0.50	0.87	1.37	–	--	35	2.45
Light Ends/Gas Processing	4	0	4	1.00	0.00	1.00	4	5.20	11	0.77
HDS: Reformer Feed	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Light Gas Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Heavy Gas Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Light Cycle Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Vacuum Gas Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Coker Naphtha	9	5	14	2.25	0.23	2.48	6	0.66	22.	1.54
FCCU	18	24	42	4.50	1.10	5.60	6	8.40	65	4.55
Hydrocracking	17	14	31	4.25	0.64	4.89	6	0.66	58	4.06
Catalytic Reformer No. 1	18	2	20	4.50	0.09	4.59	6	0.66	49	3.43
Catalytic Reformer No. 2	18	2	20	4.50	0.09	4.59	6	0.66	49	3.43
Aromatics Extraction	15	2	17	3.75	0.09	3.84	0	--	41	2.87
Alkylation	15	0	15	3.75	0.00	3.75	0	--	41	2.87
Coking	3	10	13	0.75	0.46	1.21	0	--	28	1.96
	194	159	353	48.50	7.30	55.80	68	25.14	647	45.29

[1]Emissions from within the battery limits of the respective process units.

into the question of approaches to leak detection and control. Table 8 shows
the distribution of non-methane hydrocarbon leaks for each of the baggable
source categories. Typical histograms developed from the same data illustrate
leak distribution within the source categories and are shown in Figures 1,
2, and 3.

These data demonstrate that the bulk of emissions from the fugitive
sources result from a small fraction of the sources. For example, 93 percent
of the total measured leaks from valves in gas service are emitted from only
4.4 percent of the valves. With flanges, 89 percent of the leakage results
from less than 1 percent of the total number of figures. With pumps in light
liquid services, 20 percent of the pumps account for 95 percent of the mass
of the leaks.

While it is encouraging that the majority of the hydrocarbon emis-
sions are coming from only a small fraction of the possible leaking sources,
in order to repair the leaks one must first find them. This program ran into
the same situation when identifying sources for bagging. To be useful, a
technique for screening potential leak sources must be rapid, convenient,
and enable an estimate of the magnitude of the leak.

SCREENING DATA

The screening of sources during this program was accomplished with
sensitive portable hydrocarbon detectors. The principal device used in this
study was the J. W. Bacharach Instrument Co. "TLV Sniffer." The Century
Instrument Co. Organic Vapor Analyzer (Model OVA-108) was used for some
screening, but these readings were not included in the correlations which
follow. The instruments were calibrated with standard mixtures of hexane
in air. The OVA-108 and TLV Sniffer give direct readings of hydrocarbon
concentrations in ppm by volume. In this report, the terms "screening
values" and "TLV screening values" refer to the maximum hydrocarbon concen-
tration detected at selected baggable sources.

Screening values were obtained when the source was first located,
and rescreening values were taken at the time each source was sampled. The
rescreening values were taken at the time each source was sampled. The
rescreening values were generally more highly correlated with leak rates
than are the original screening results. For example, the correlation
coefficient for the original screening values and non-methane hydrocarbon
leak rates of all valves is 0.63. A correlation coefficient of 0.72 is
obtained for the maximum rescreening values and non-methane hydrocarbon
leak rates of valves.

The final report of this study will contain detailed descriptions
of the least-squares linear regression equations developed for predicting
leak rates from unsampled sources in the data base. For potential predic-
tion purposes outside this data base, a statistical analysis of covariance
was done to determine whether different linear equations are required for

TABLE 8. DISTRIBUTION OF NONMETHANE LEAK RATES FROM
SAMPLED SOURCES

Leak Range (lb/hr)	Leaking Sources Within Range			Total Leakage Within Range	
	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
Valves, Gas/Vapor Streams = 563 Screened					
>1.0	7	4.6	1.2	17.7654	70.0
0.1 - 1.0	18	11.7	3.2	5.9187	23.3
0.01 - .1	43	27.9	7.6	1.4867	5.9
0.001 - 0.01	49	31.8	8.7	0.2052	0.8
0.00001 - 0.001	37	24.0	6.6	0.0133	0.1
	154	100%	20.3%	25.3893	100%
Valves, Light Liquid/Two-Phase Streams = 913 Screened					
>1.0	1	0.3	0.1	2.2297	14.4
0.1 - 1.0	31	9.4	3.4	9.3351	60.3
0.01 - .1	105	31.8	11.5	3.3877	21.9
0.001 - 0.01	121	36.7	13.3	0.5028	3.2
0.00001 - 0.001	72	21.8	7.8	0.0266	0.2
	330	100%	36.1%	15.4819	100%
Valves, Heavy Liquid Streams = 485 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	0	0.0	0.0	0.0	0.0
0.01 - .1	5	15.6	1.0	0.1773	74.1
0.001 - 0.01	13	40.6	2.7	0.0569	23.8
0.00001 - 0.001	14	43.8	2.9	0.0051	2.1
	32	100%	6.6%	0.2393	100%

Continued

TABLE 8. (Continued)

Leak Range (lb/hr)	Leaking Sources Within Range			Total Leakage Within Range	
	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
Valves, Predominantly Hydrogen Streams = 135 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	3	5.1	2.2	0.3789	34.2
0.01 - .1	19	32.2	14.1	0.6691	60.5
0.001 - 0.01	18	30.5	13.3	0.0532	4.8
0.00001 - 0.001	19	32.2	14.1	0.0059	0.5
	59	100%	43.7%	1.1071	100%
Open-Ended Valves, All Streams = 129 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	1	3.3	0.8	0.1242	23.3
0.01 - .1	9	30.0	7.0	0.3475	65.3
0.001 - 0.01	12	40.0	9.3	0.0576	10.8
0.00001 - 0.001	8	26.7	6.2	0.0033	0.6
	30	100%	23.3%	0.5326	100%
Flanges = 2094 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	4	6.4	0.19	0.8655	63.2
0.01 - .1	12	19.4	0.57	0.4117	30.1
0.001 - 0.01	28	45.2	1.33	0.0820	6.0
0.00001 - 0.001	18	29.0	0.86	0.0096	0.7
	62	100%	2.95%	1.3688	100%

TABLE 8. (Continued)

Leak Range (lb/hr)	Leaking Sources Within Range			Total Leakage Within Range	
	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
Pump Seals, Light Liquid Streams = 470 Screened					
>1.0	19	6.4	4.0	63.1913	70.6
0.1 - 1.0	73	24.7	15.5	22.0347	24.6
0.01 - .1	107	36.1	22.7	3.9430	4.4
0.001 - 0.01	77	26.0	16.4	0.3274	0.4
0.00001 - 0.001	20	6.8	4.3	0.0086	0.0
	296	100%	62.9%	89.5051	100%
Pump Seals, Heavy Liquid Streams = 292 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	16	24.2	5.5	4.3189	73.2
0.01 - .1	28	42.4	9.6	1.5089	25.6
0.001 - 0.01	17	25.8	5.8	0.0699	1.2
0.00001 - 0.001	5	7.6	1.7	0.00178	0.0
	66	100%	22.6%	5.8995	100%
Drains = 257 Screened					
>1.0	4	8.2	1.6	7.3958	61.6
0.1 - 1.0	12	24.5	4.7	3.9615	33.0
0.01 - .1	17	34.7	6.6	0.5939	4.9
0.001 - 0.01	13	26.5	5.1	0.0630	0.5
0.00001 - 0.001	3	6.1	1.1	0.0013	0.0
	49	100%	19.1%	12.0155	100%

TABLE 8. (Continued)

Leak Range (lb/hr)	Leaking Sources Within Range			Total Leakage Within Range	
	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
Relief Valves = 148 Screened					
>1.0	5	8.6	3.4	15.5383	76.0
0.1 - 1.0	15	25.9	10.1	3.9313	19.2
0.01 - .1	22	37.9	14.7	0.9121	4.5
0.001 - 0.01	12	20.7	8.1	0.0580	0.3
0.00001 - 0.001	4	6.9	2.7	0.0022	0.0
	58	100%	39.0 %	20.4419	100%
Compressor Seals, Hydrocarbon Service = 142 Screened					
>1.0	23	21.9	16.2	67.9440	74.3
0.1 - 1.0	48	45.7	33.8	22.2482	24.3
0.01 - .1	24	22.9	16.9	1.3014	1.4
0.001 - 0.01	7	6.6	4.9	0.0224	0.0
0.00001 - 0.001	3	2.9	2.1	0.0013	0.0
	105	100%	73.9 %	91.5172	100%
Compressor Seals, Hydrogen Service = 83 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	14	20.3	16.9	3.3954	75.6
0.01 - .1	22	31.9	26.5	1.0105	22.5
0.001 - 0.01	21	30.4	25.3	0.0794	1.8
0.00001 - 0.001	12	17.4	14.5	0.0064	0.1
	69	100%	83.2	4.4917	100%
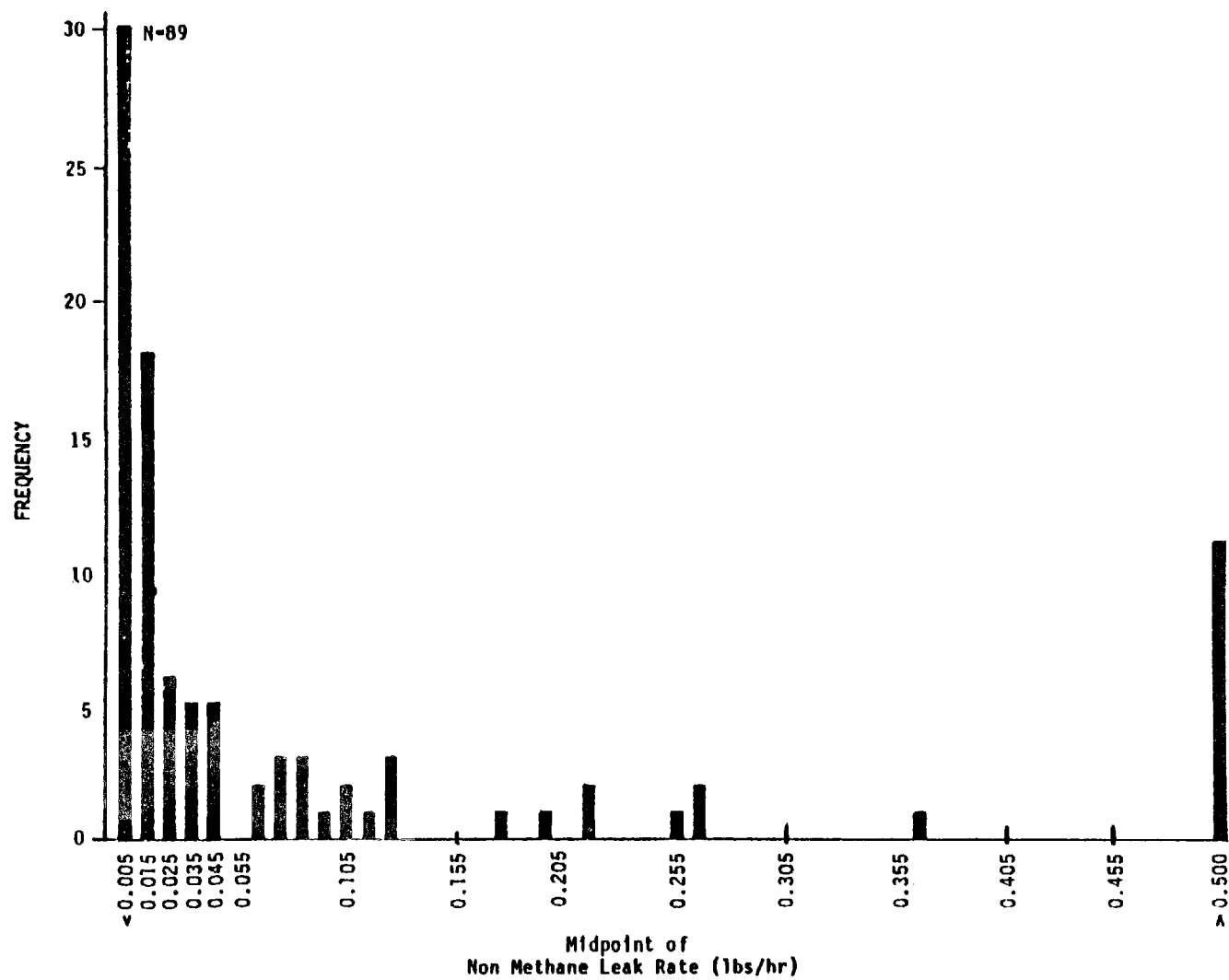
Figure 1. Distribution of Leak Rates for
Valves - Gas Vapor Streams
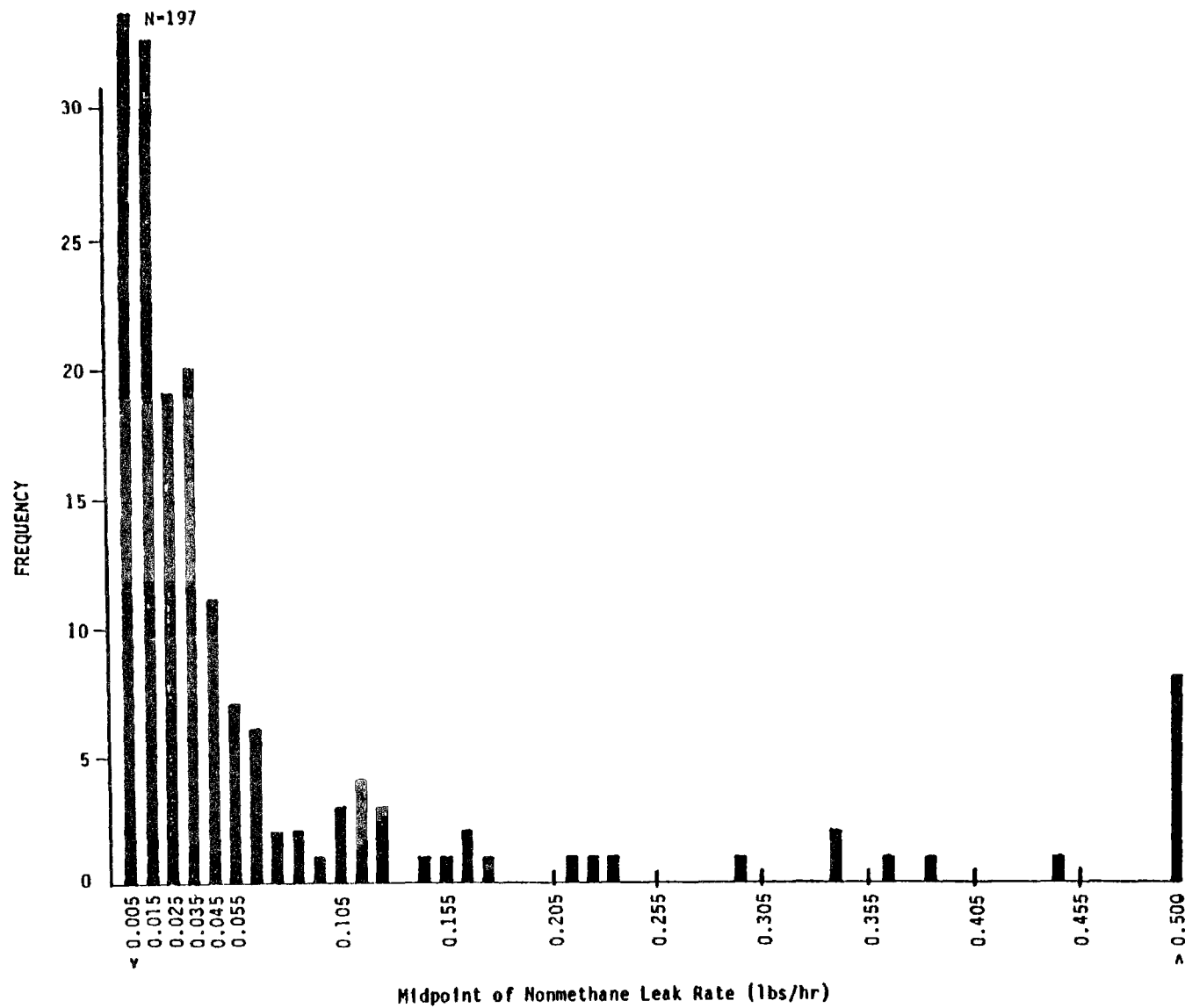
Figure 2. Distribution of Leak Rates for Valves - Light
Liquid/Two-Phase Streams
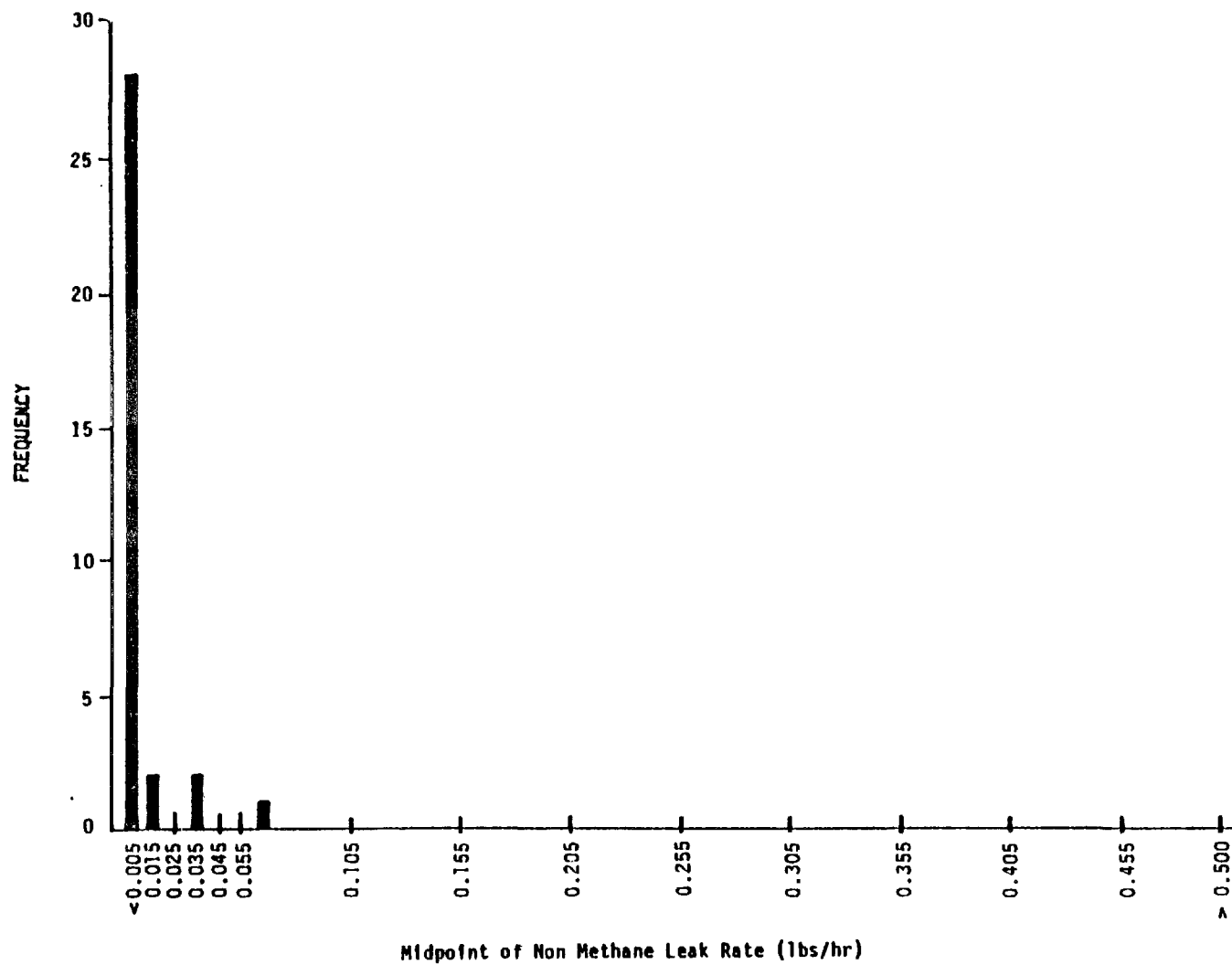
Figure 3.   Distribution of Leak Rates of
Valves – Heavy Liquid Streams.

each baggable source and stream type. It was found that the source and stream types could be grouped such that seven (7) equations were adequate for predicting leak rates from screened sources. The seven groups are as follows:

o Pumps in light liquid/two-phase streams, compressors, and relief valves in gas/vapor streams

o Valves and compressor seals in hydrogen service

o Valves in gas/vapor streams

o Valves in light liquid/two-phase streams

o Flanges

o Drains

o Pump seals in heavy liquid streams.

The equations for flanges, drains, and pump seals in heavy liquid streams were developed from the original maximum screening values. This is because small sample sizes (less than 20) would have been available in each of the three (3) cases if the rescreening values had been used. No equation was developed for valves in heavy liquid streams; a sample size of less than 20 was available with either the maximum screening or maximum rescreening values.

Typical data used to develop these equations are shown in Figures 4 through 6.

The resulting equations were used to develop nomographs which relate the predicted leak rate to the screening values for the various source and stream types. Examples of these nomographs are shown in Figures 7 through 12.

Each nomograph gives the predicted mean leak rate as a function of the maximum TLV Sniffer screening readings taken directly at the source of the leak. Although the equations were developed on a logarithmic scale, the nomographs are shown on a arithmetic scale for ease in reading and interpolation.

The 90 percent confidence intervals shown on the nomographs are for the mean leak rate and should not be confused with confidence intervals for individual leak rates for given screening values. Figures 13 and 14 graphically compare the confidence intervals for individual leak rates with the confidence interval for the mean leak rate for valves (light liquid/two-phase streams).
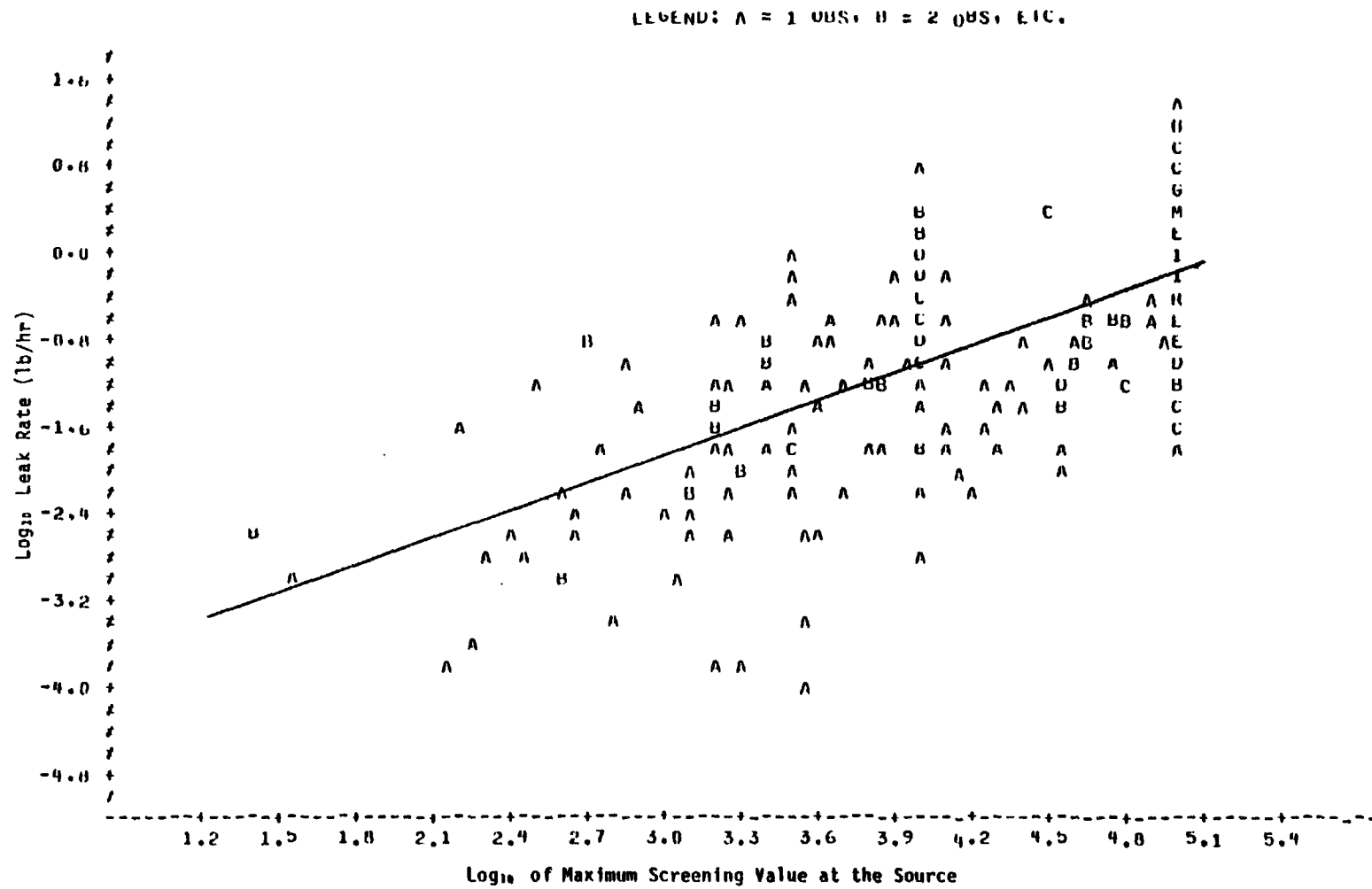
Figure 4. Leak Rate/Screening Relationship - Pump Seals (Light Liquid/
Two-Phase Streams), Compressor Seals and Relief Valves (Gas/
Vapor Streams).

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Log₁₀ Leak Rate (lb/hr)
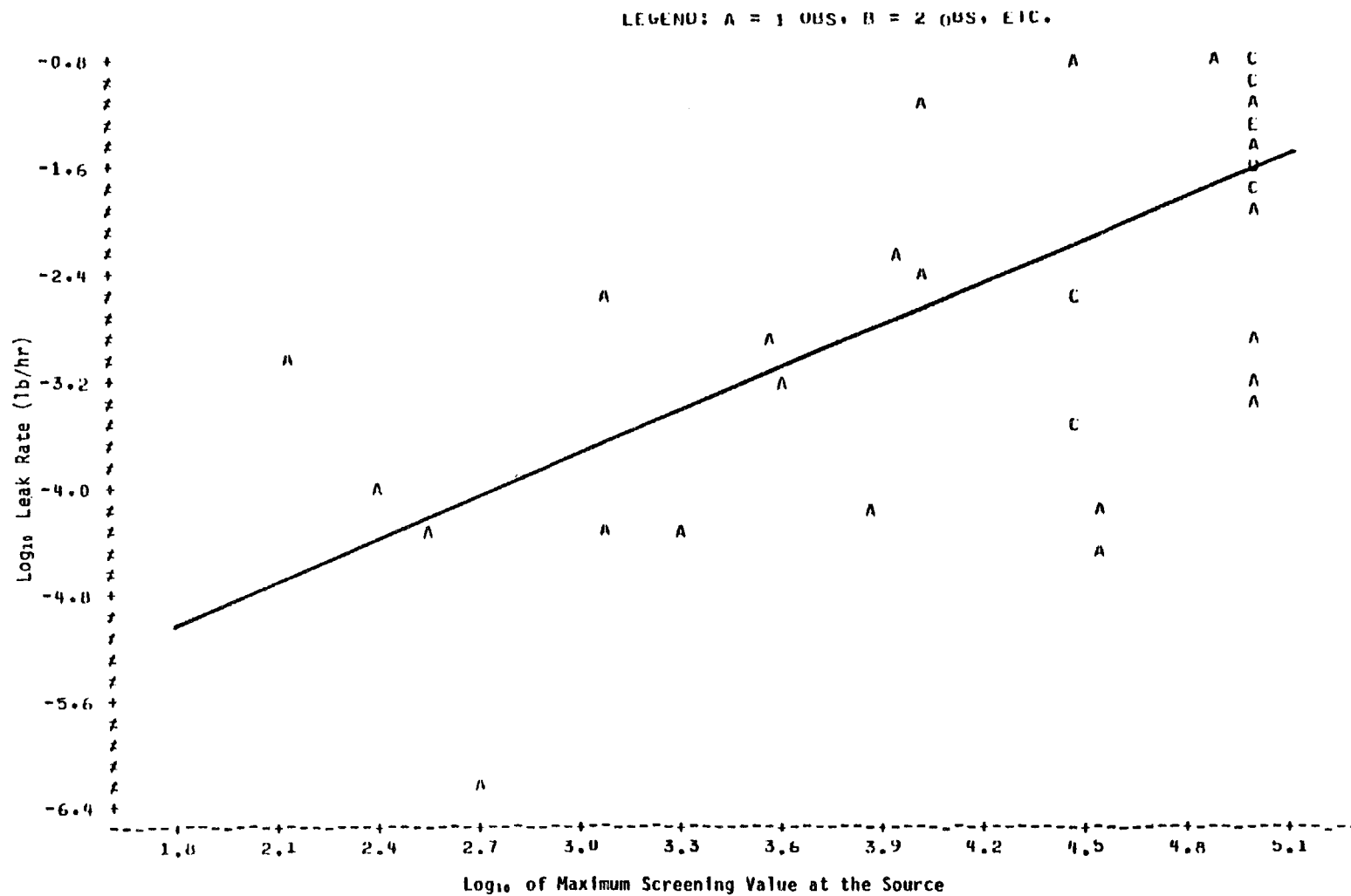
Log₁₀ of Maximum Screening Value at the Source

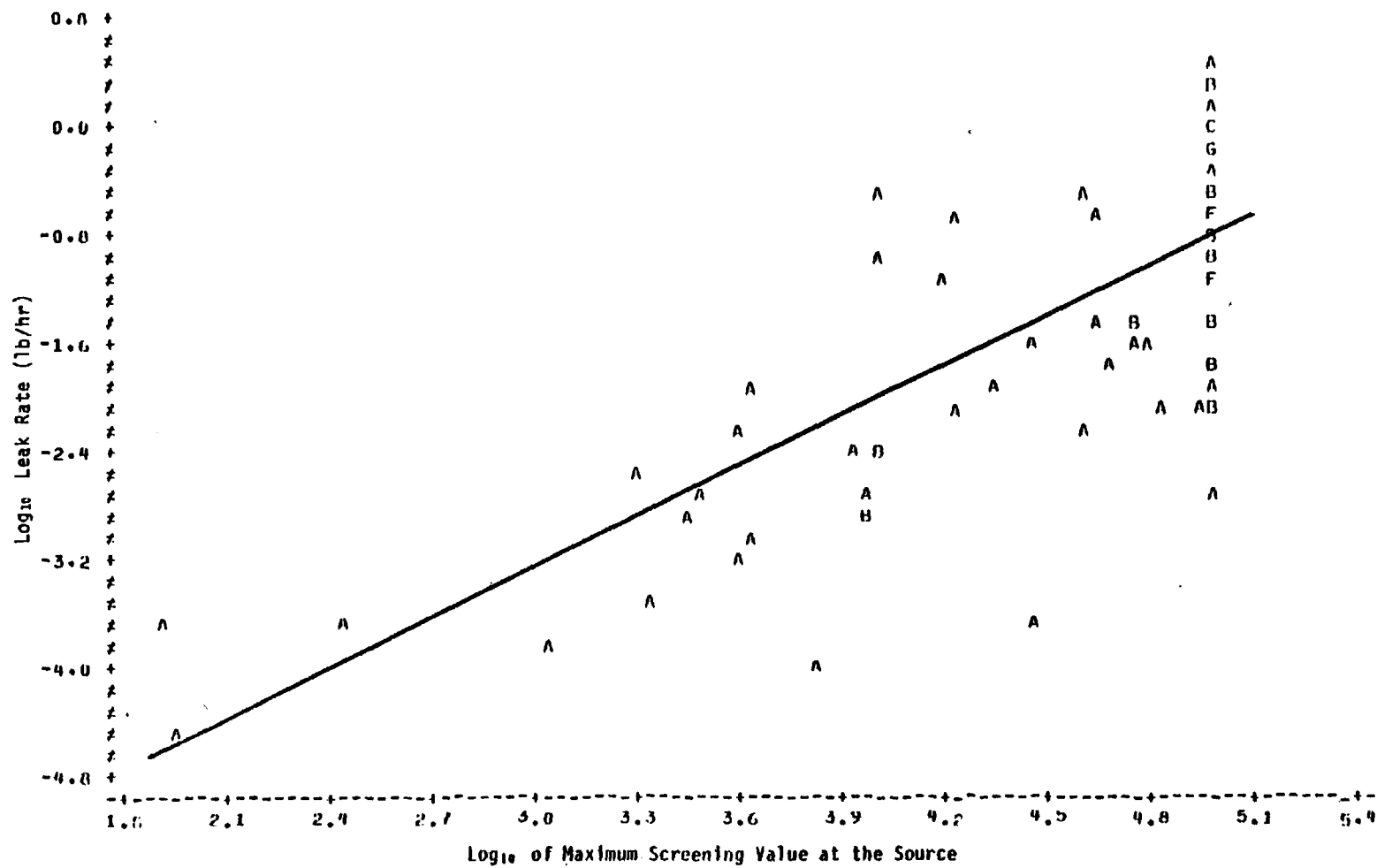Figure 5. Leak Rate/Screening Relationship - Valves and
Compressor Seals, Hydrogen Streams.

Figure 6. Leak Rate/Screening Relationship - Valves,
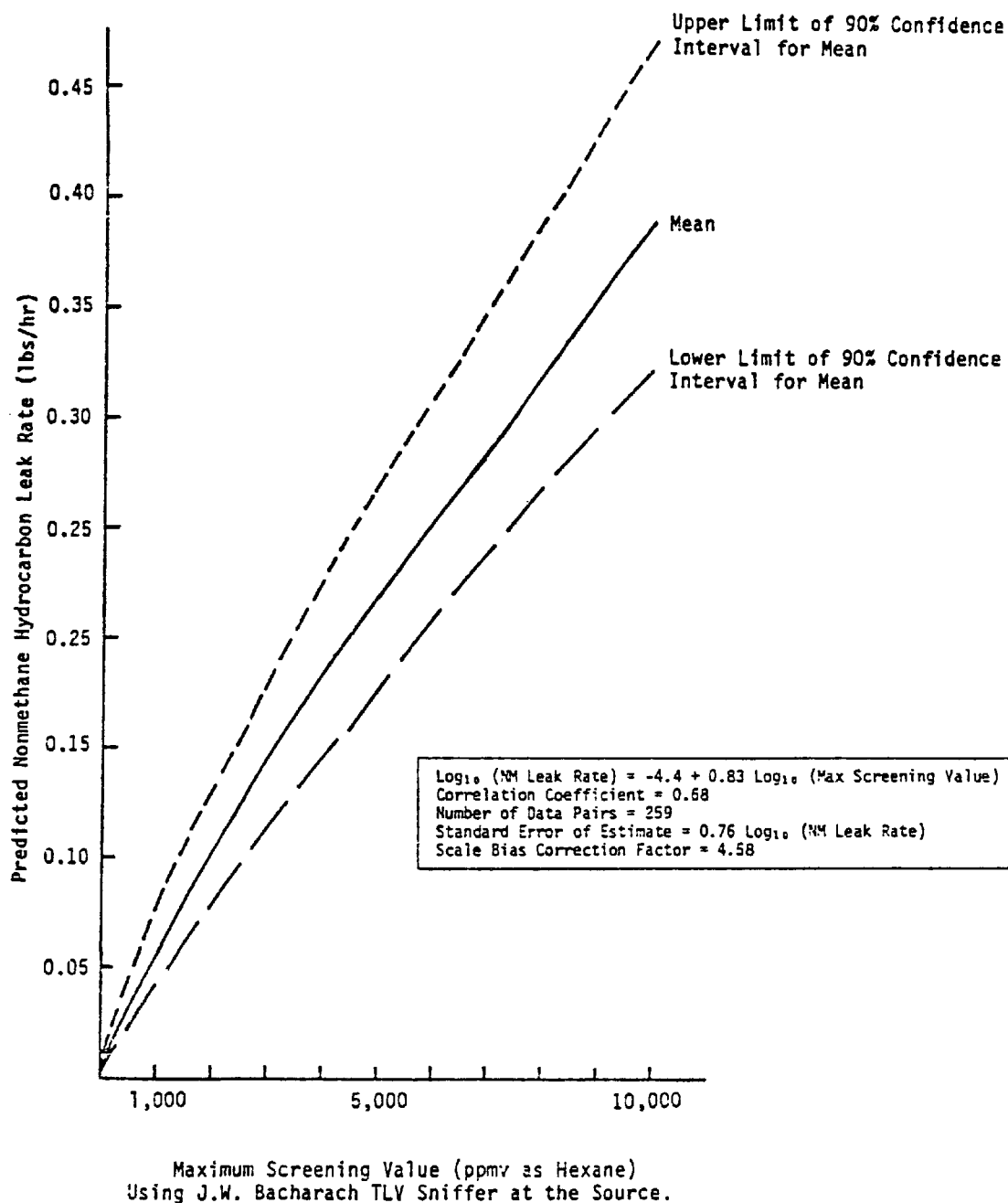Gas/Vapor Streams.

Figure 7. Nomograph for Predicting Total Hydrocarbon Leak Rates From Maximum Screening Values – Pumps (Light Liquids), Compressors, Relief Valves (Gas/Vapor Streams) (Part I: Screening Values from 0-10,000 ppm).
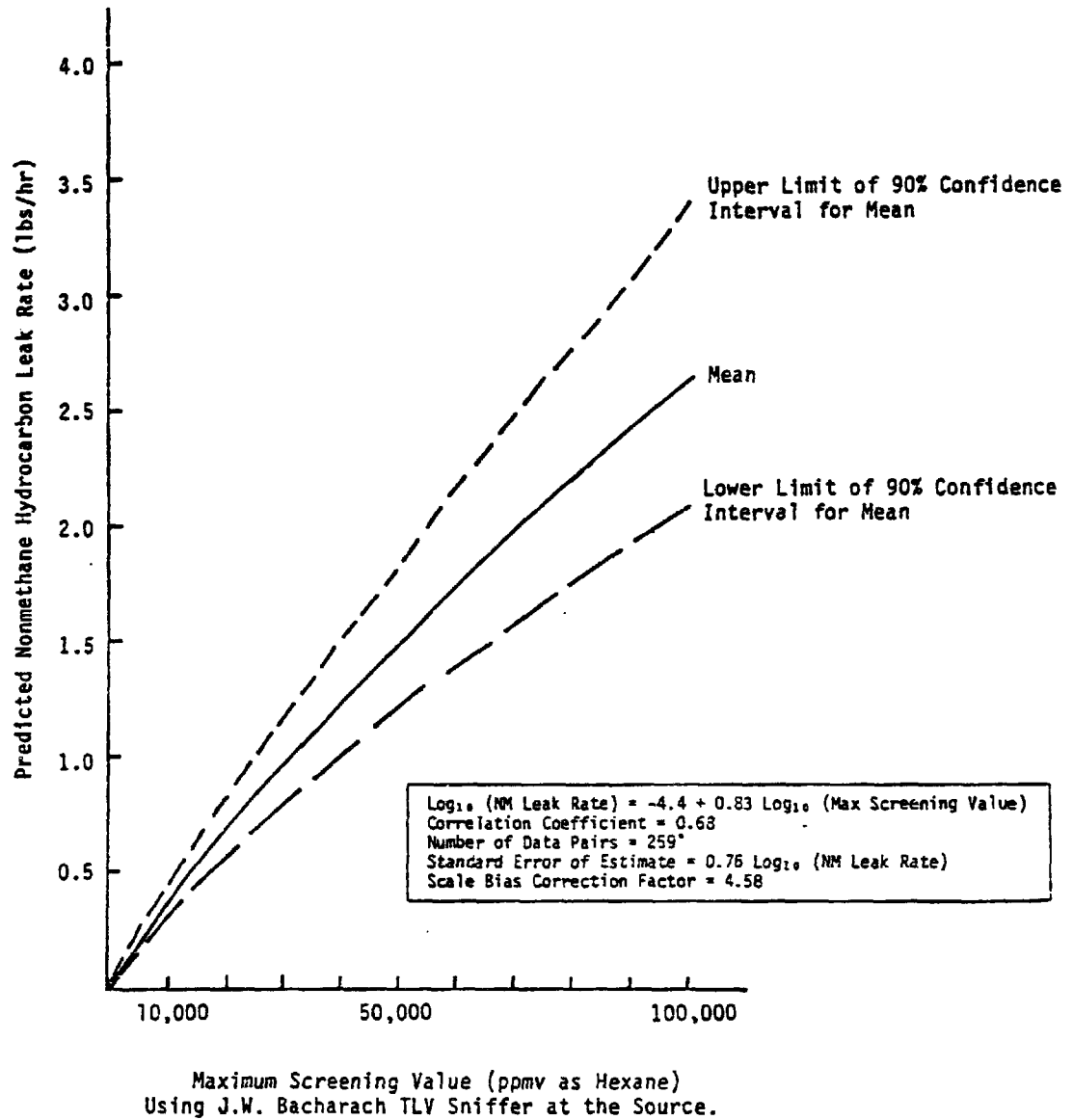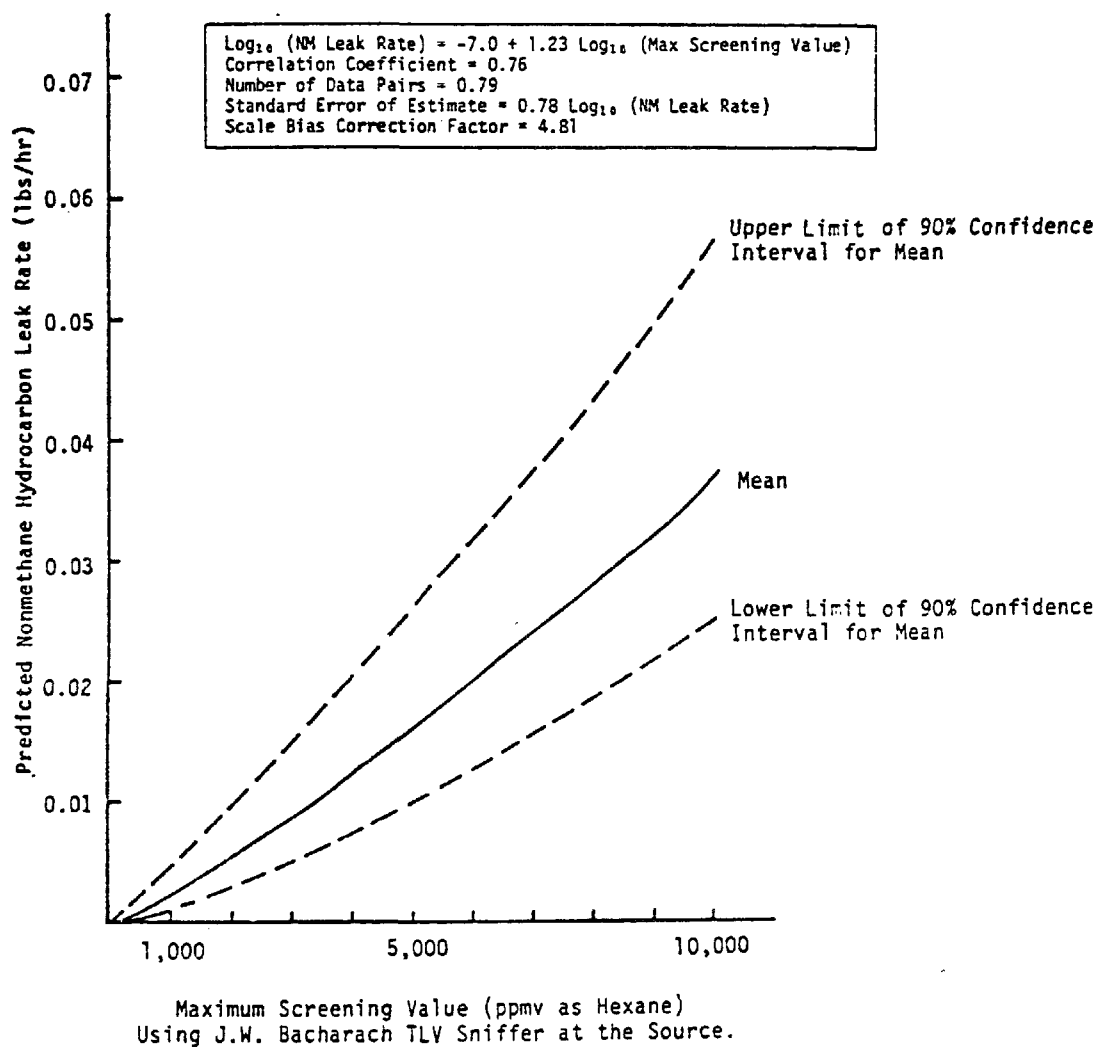
Figure 8. Nomograph for Predicting Total Hydrocarbon Leak
Rates from Maximum Screening Values - Pumps (Light
Liquids), Compressors, Relief Valves (Gas/Vapor
Streams) (Part II: Screening Values from
0-100,000 ppm).

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Figure 9. Nomograph for Predicting Total Nonmethane
Hydrocarbon Leak Rates from Maximum Screening
Values - Valves, Gas/Vapor Streams (Part I:
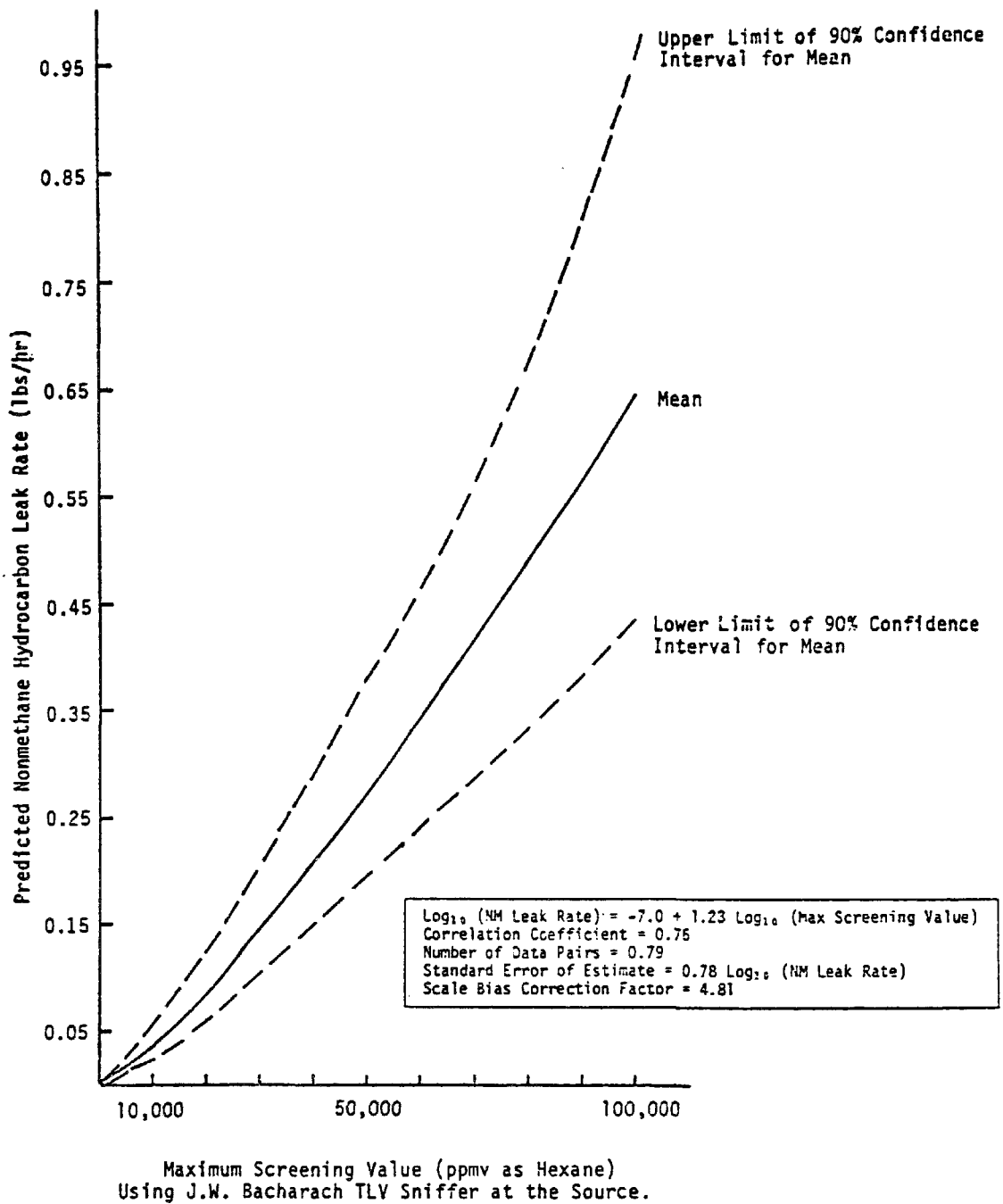Screening Values from 0-10,000 ppm).

Figure 10. Nomograph for Predicting Total Nonmethane
Hydrocarbon Leak Rates from Maximum Screening
Values – Valves, Gas/Vapor Streams (Part II:
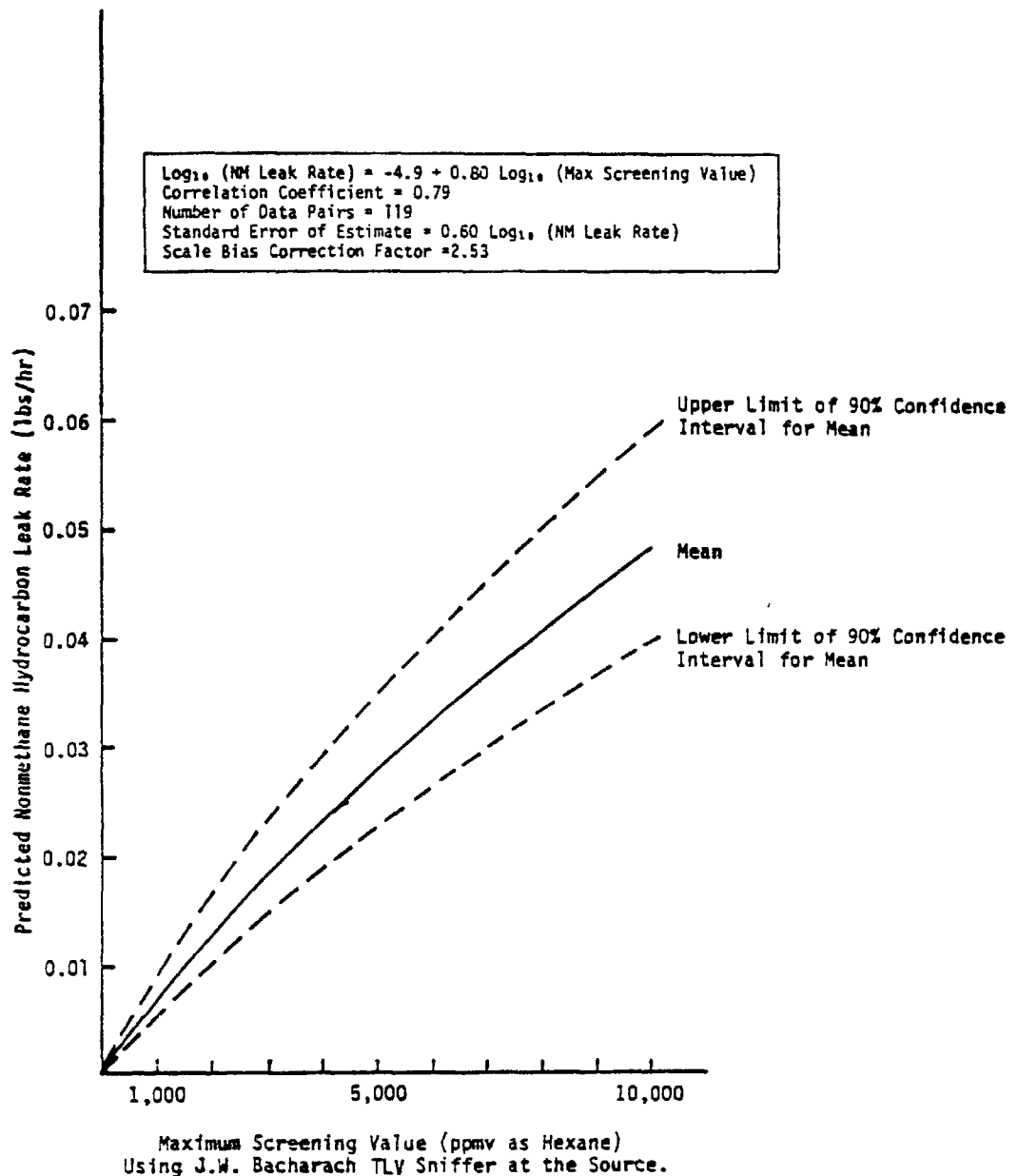Screening Values from 0-100,000 ppm).

Figure 11. Nomograph for Predicting Total Nonmethane
Hydrocarbon Leak Rates from Maximum Screening
Values - Valves, Light Liquid/Two-Phase Streams
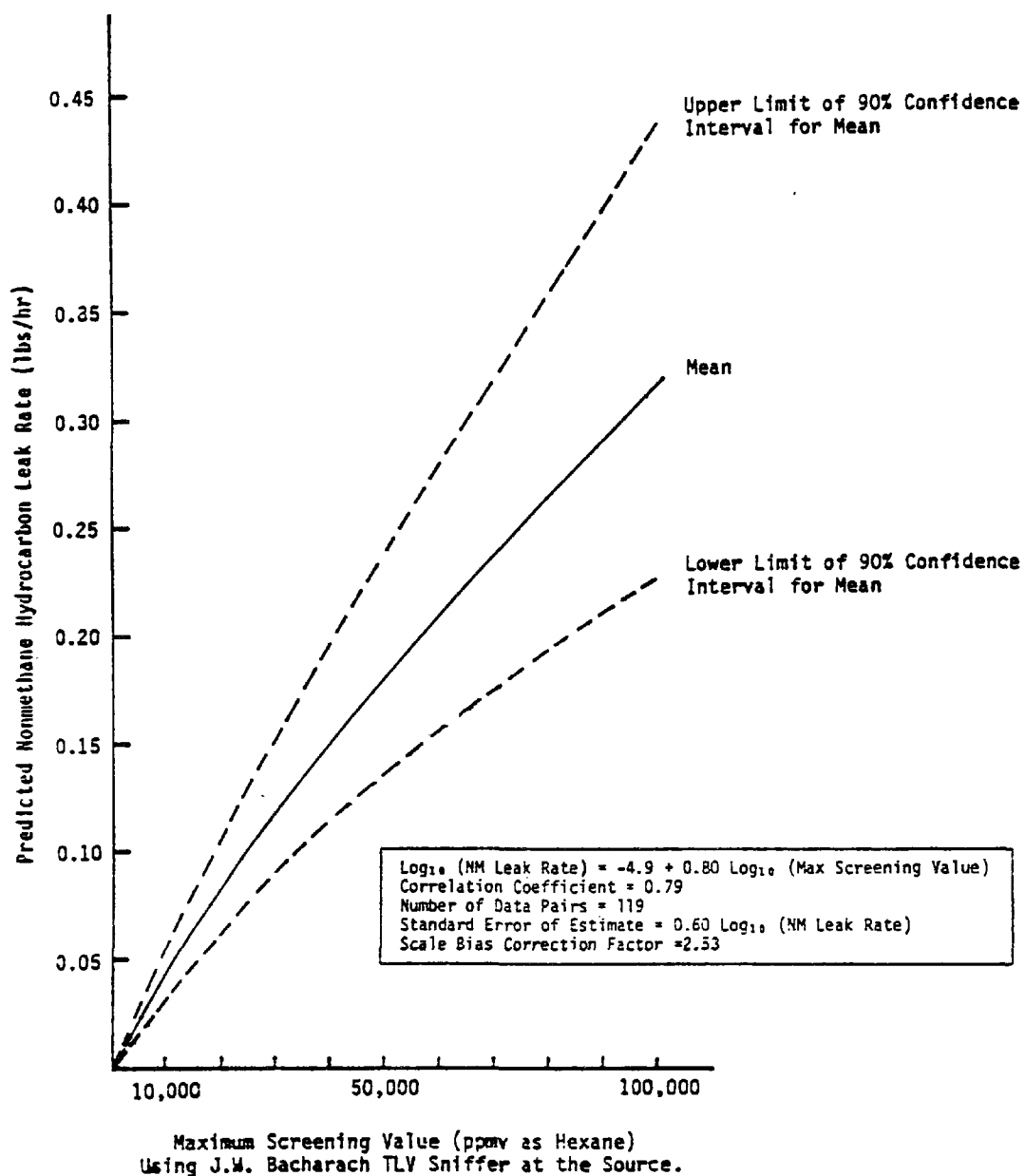(Part I: Screening Values from 0-10,000 ppm).

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Figure 12: Nomograph for Predicting Total Nonmethane
Hydrocarbon Leak Rates from Maximum Screening
Values - Valves, Light Liquid/Two-Phase Streams
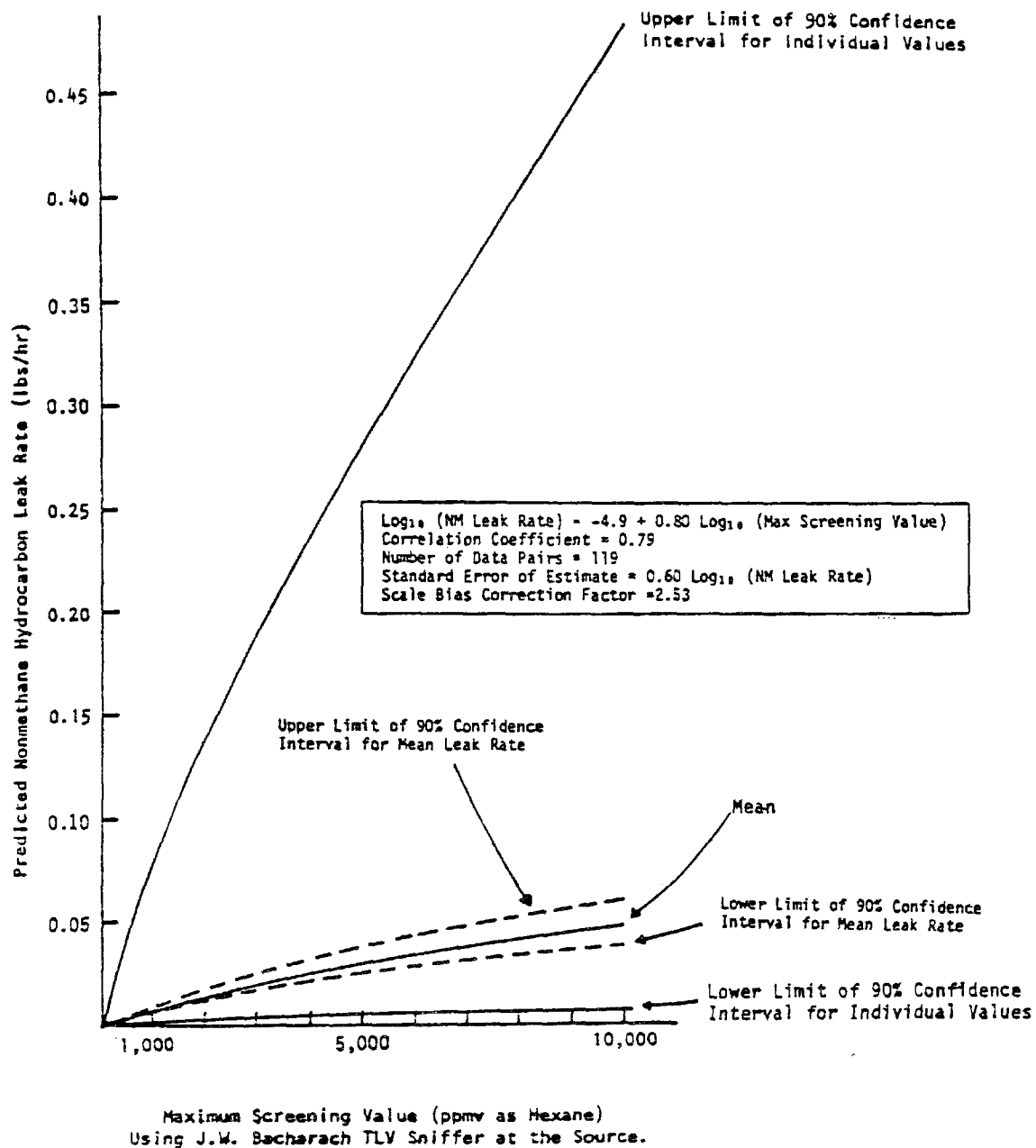(Part II: Screening Values from 0-100,000 ppm).

Figure 13. Nomograph for Predicting Total Nonmethane
Hydrocarbon Leak Rates from Maximum Screening
Values - Valves, Light Liquid/Two-Phase Streams
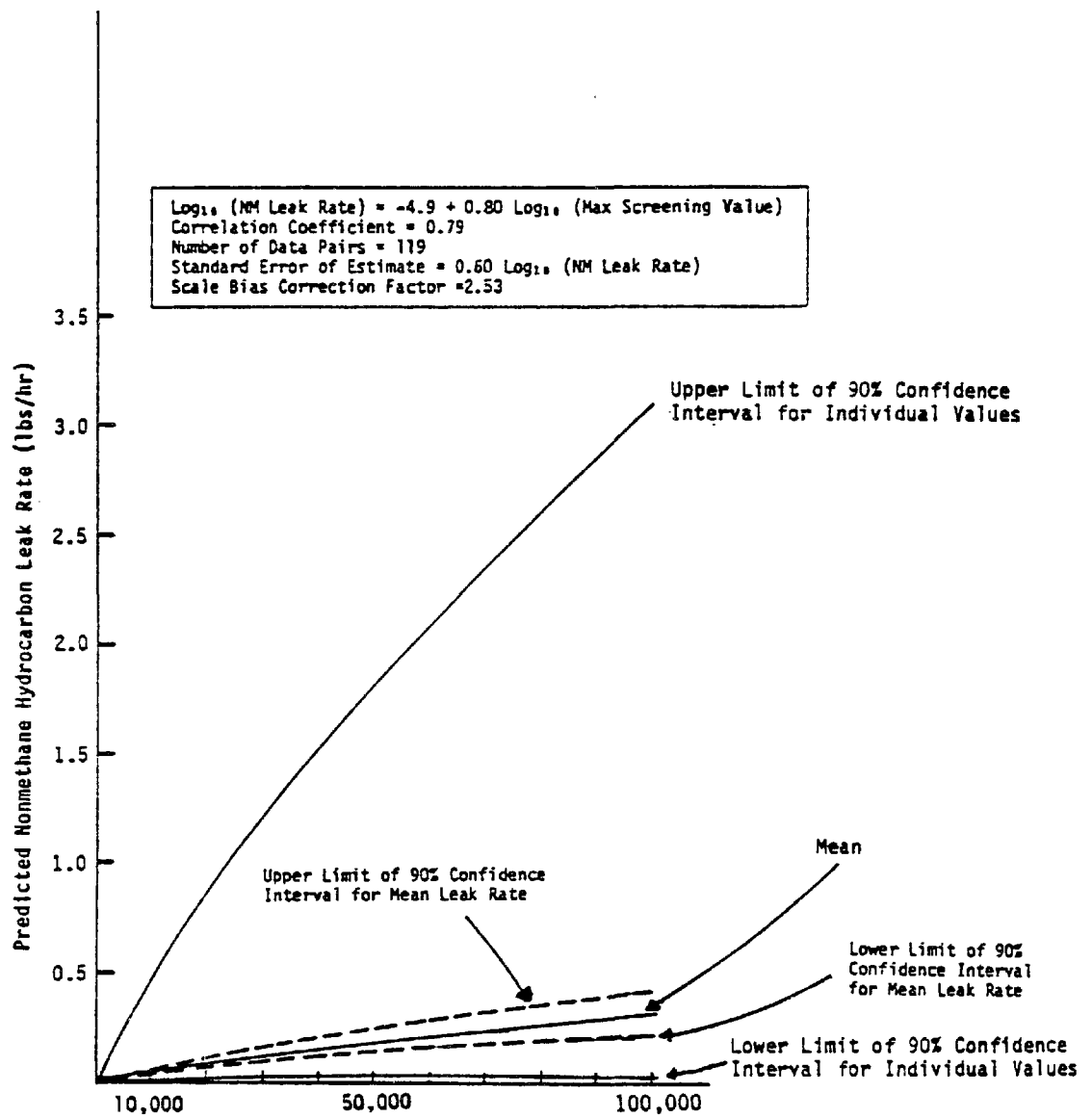(Part I: Screening Values from 0-10,000 ppm).

Figure 14. Nomograph for Predicting Total Nonmethane
Hydrocarbon Leak Rates from Maximum Screening
Values – Valves, Light Liquid/Two-Phase Streams
(Part II: Screening Values from 0-100,000 ppm).

From the results of this study, nomographs have also been prepared relating hydrocarbon concentration at the source (screening value) to the percentage of each source type expected to have screening values above any selected value. Other nomographs have been prepared relating screening values to the percentage of total mass emissions which can be expected from sources with screening values greater than any given value.

These nomographs for the valves, flanges, and pump seals (with appropriate stream groups) are presented in Figures 15 through 21. The "B" figures relate the percent of total mass emissions for a given source category to screening values; the "A" figures relate the percent of sources to screening values. The screening values in these nomographs are the hydrocarbon concentrations obtained at the source (0 cm) with a Bacharach TLV Sniffer calibrated with hexane.

Confidence intervals are included on each of these nomographs. The confidence intervals for both types of nomographs indicate how well the cumulative function has been estimated from the data collected in this program.

The 95 percent confidence intervals for the cumulative percent of sources can be interpreted as ranges of values which contain the actual percent from the population of sources studied. Note that these intervals apply to the entire population of sources (i.e., a composite of all United States refineries), and are not necessarily applicable to a finite number of sources at any particular refinery. Because of the nature of the function, the confidence intervals will be approximately valid any time a random sample of greater than 100 sources is being considered.

The 90 percent confidence intervals for the cumulative percent of total emissions function can be interpreted as ranges of values which contain the actual percent of total emissions function for the entire population of sources. Again, these intervals describe how well the function has been estimated for the entire population and are not directly applicable to a particular refinery situation with a finite number of sources. The variation of the function for a particular sample of sources is a complex function of the number of sources.

The nomographs must be carefully evaluated when comparing these estimates to actual measured emissions (samples sources). As discussed earlier, the correlation between screening values and actual leak rates is imperfect. Because of this, values obtained from the nomographs for percent of total emissions caused by a specific percent of total sources may not exactly match similar values for measured leak rates. Table 8 gave the distribution of total emissions as a function of measured leak rates. In most cases, the nomographs will indicate a higher percentage than in Table 8 of sources being responsible for a given percentage of total emissions. In this sense, if actual leak rates could be measured, the
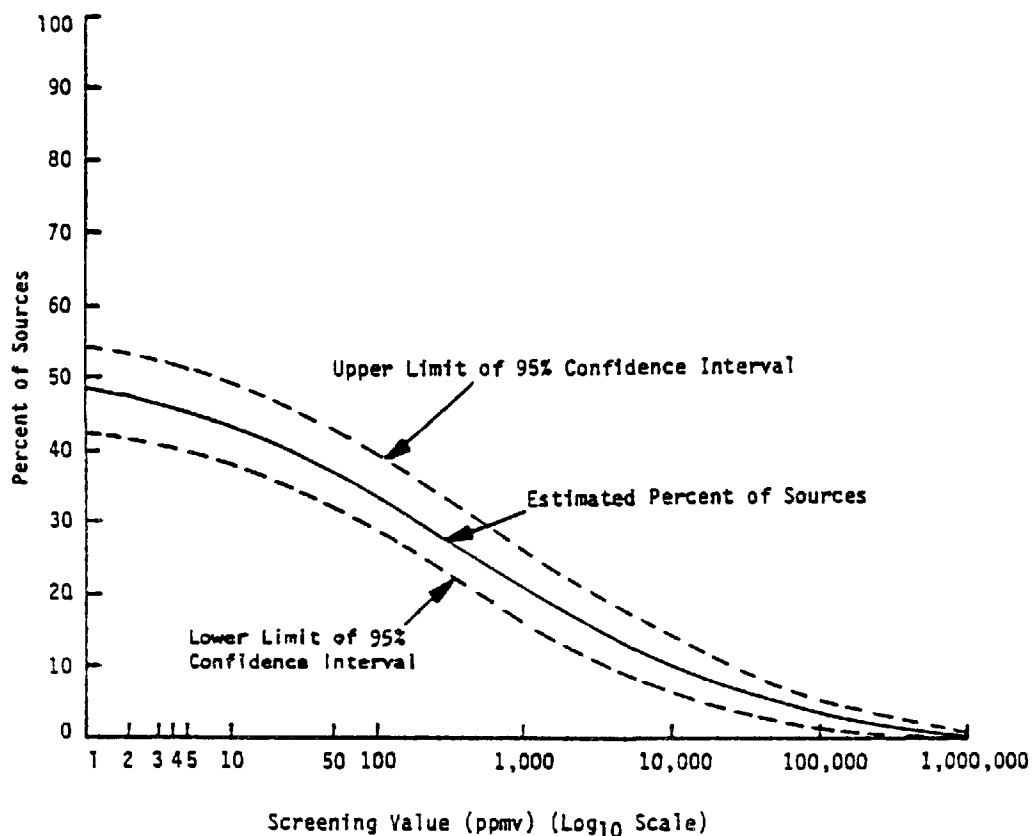
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Percent of Sources - indicates the percent of sources with screening
values greater than the selected value.

Figure 15A. Cumulative Distribution of Sources and
Total Emissions by Screening Values for
Valves - Gas/Vapor Streams.

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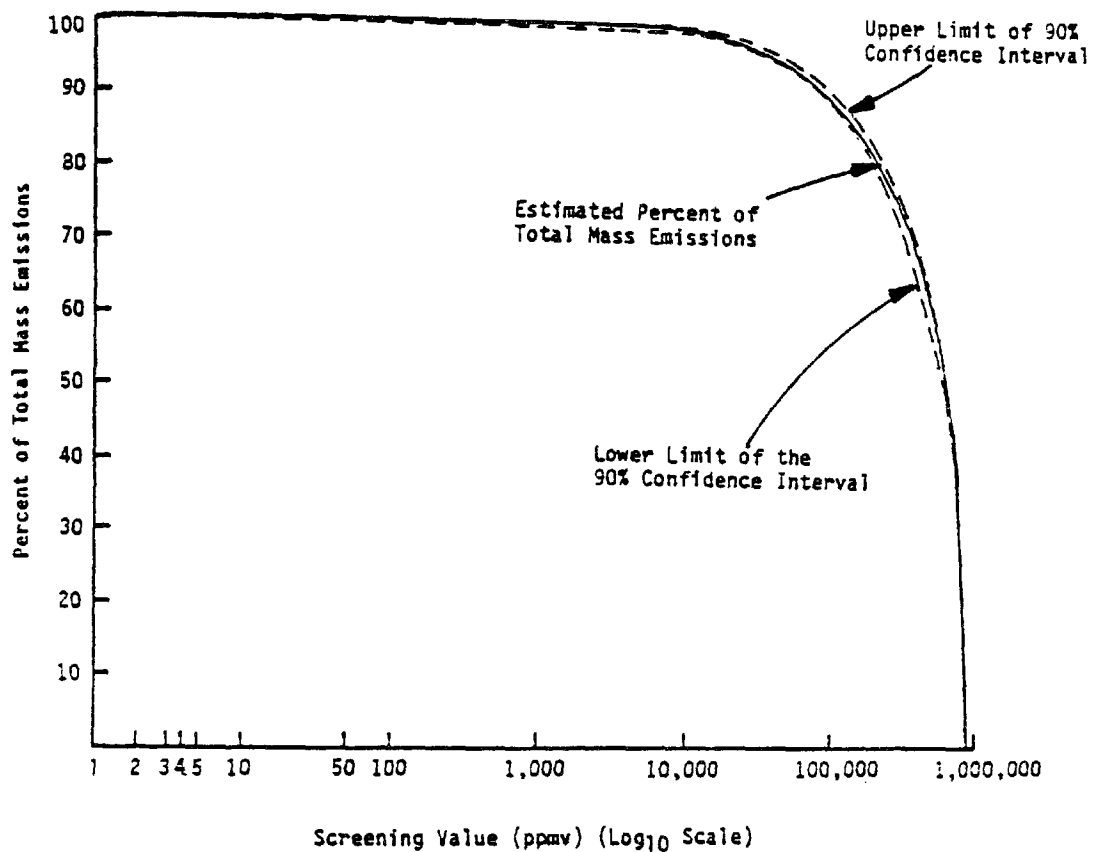
Figure 15B.   Cumulative Distribution of Source and Total
              Emissions by Screening Values for Valves -
              Gas/Vapor Stream.

Screening Value (ppmv) (Log₁₀ Scale)

Percent of Sources - indicates the percent of sources with screening
values greater than the selected value.

Figure 16A. Cumulative Distribution of Source and
Total Emissions by Screening Values for
Valves - Light Liquid/Two-Phase Streams.

Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.
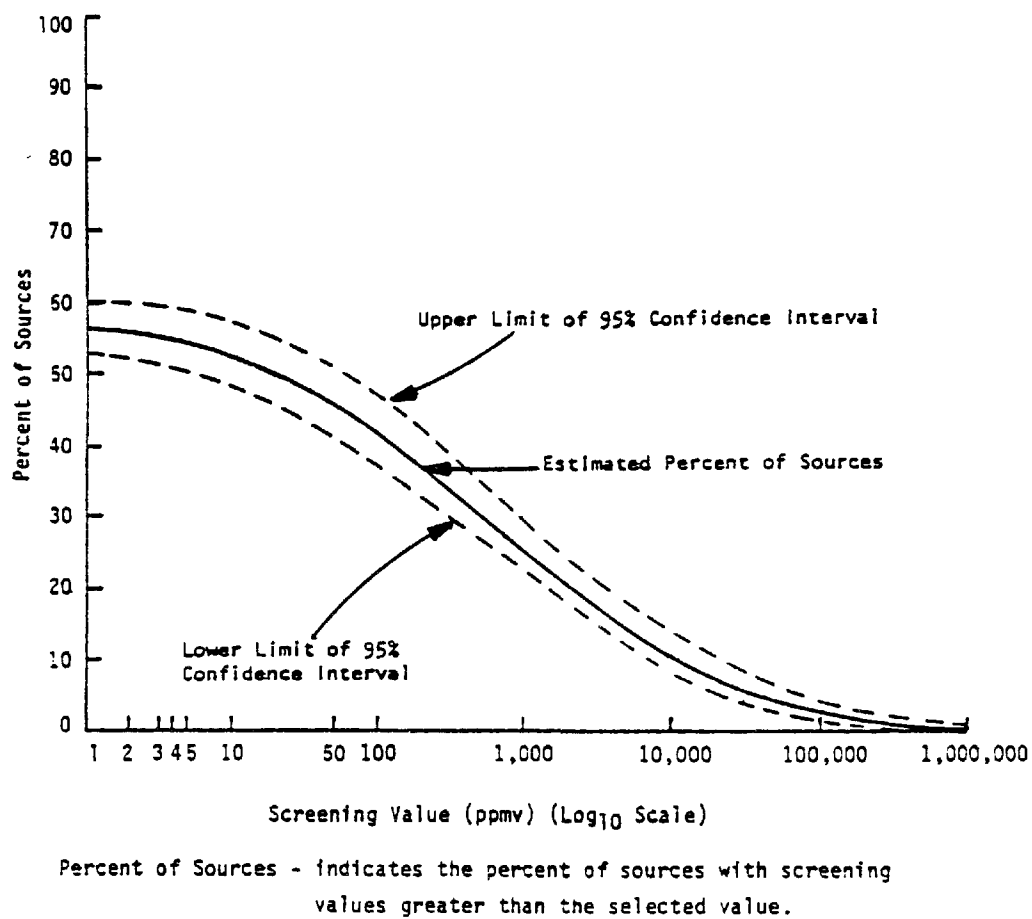
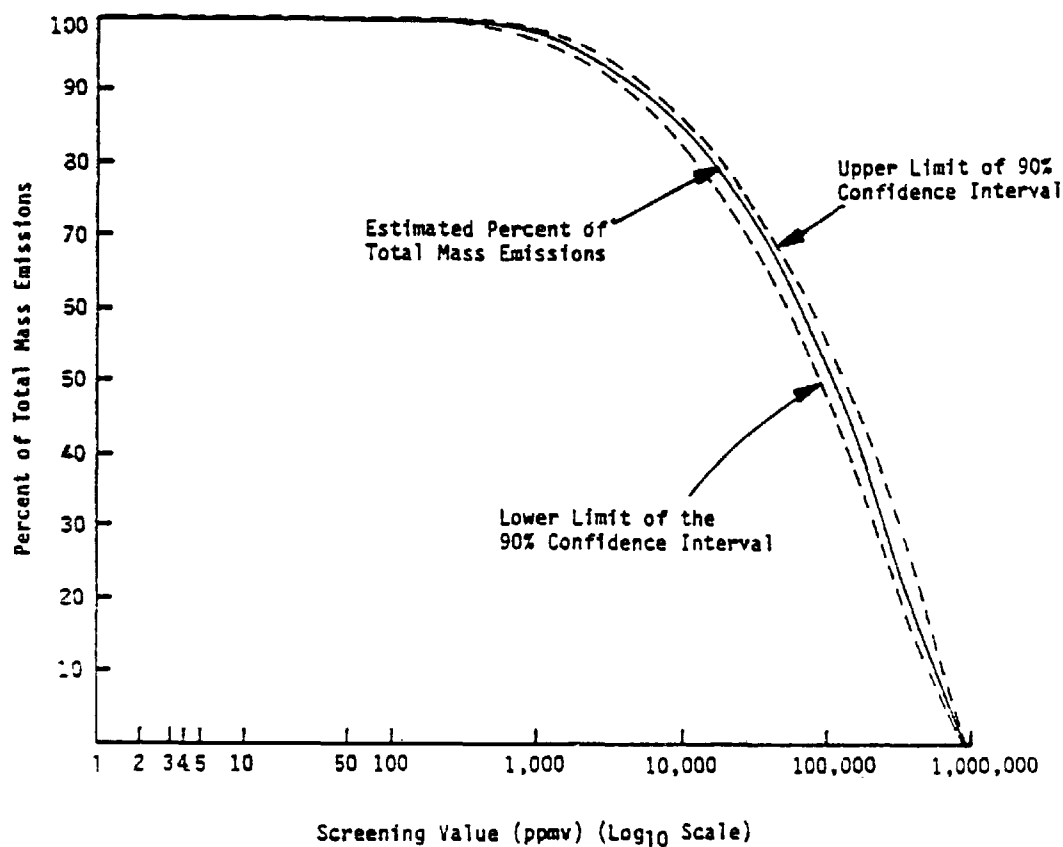Figure 16B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves - Light Liquid/Two-Phase Streams.

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Figure 17A. Cumulative Distribution of Sources and
Total Emissions by Screening Values for
Valves - Heavy Liquids Stream.

Figure 17B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves – Heavy Liquid Streams.

Figure 18A. Cumulative Distribution of Sources and
Total Emissions by Screening Values for
Valves - Hydrogen Service.
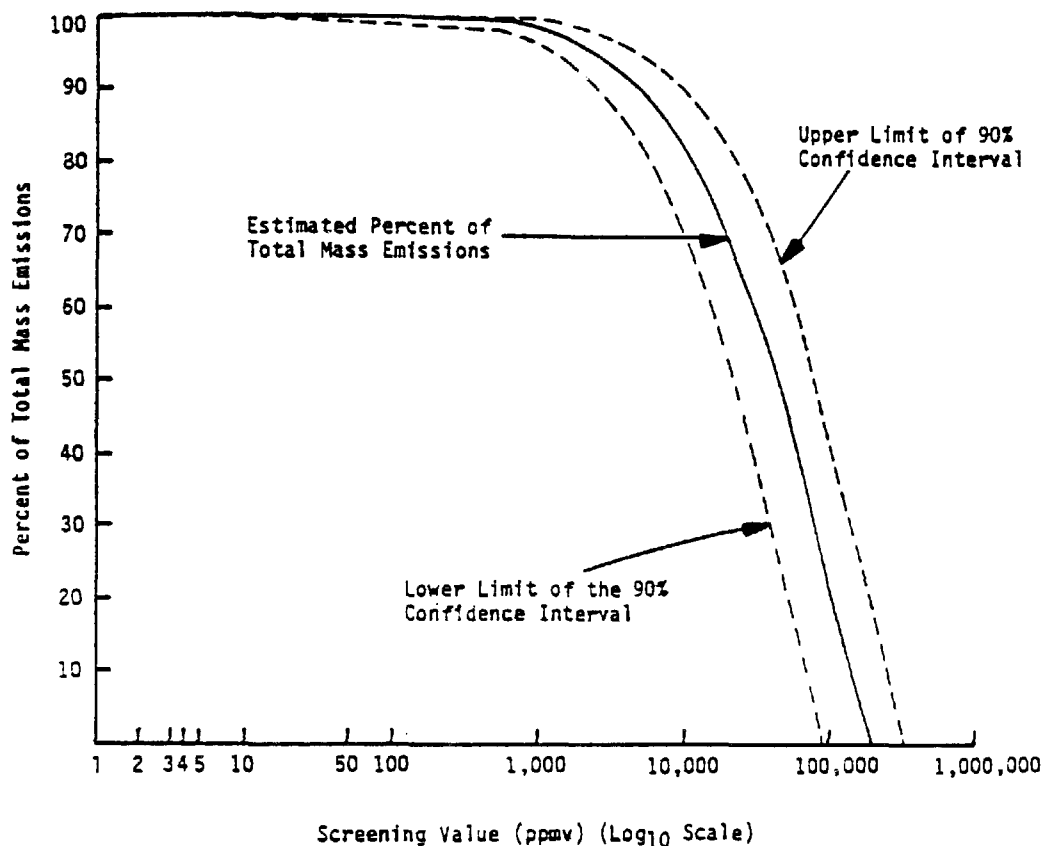
Figure 18B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves — Hydrogen Service.
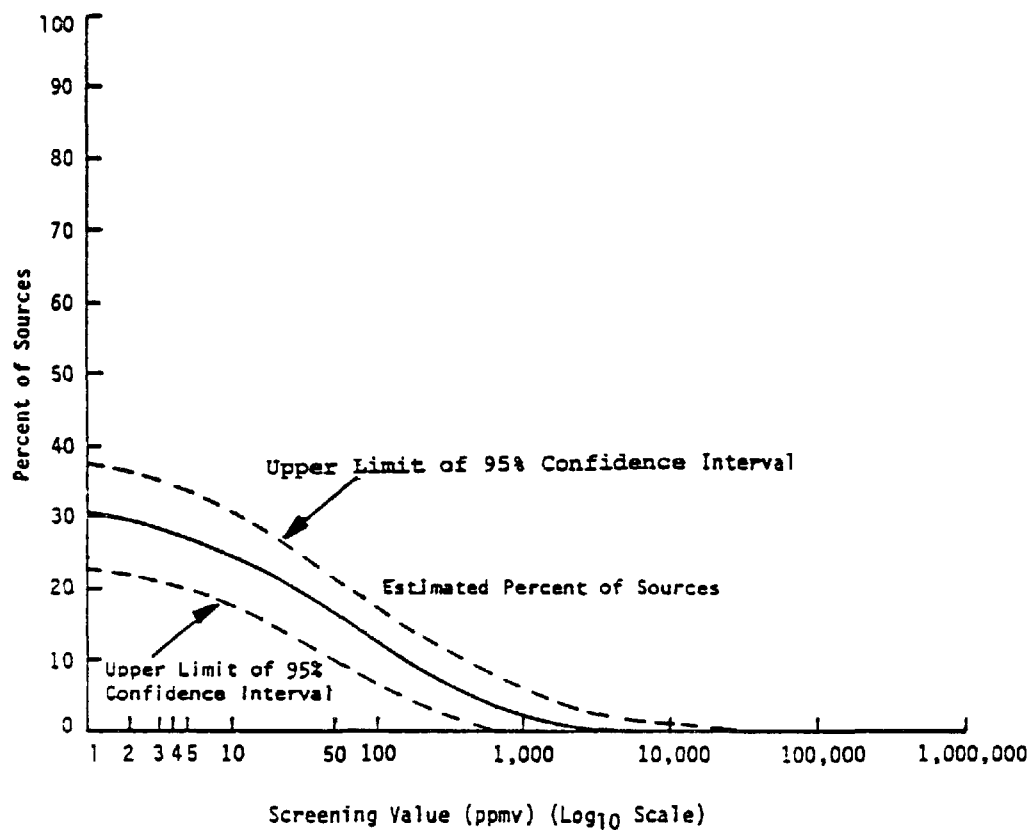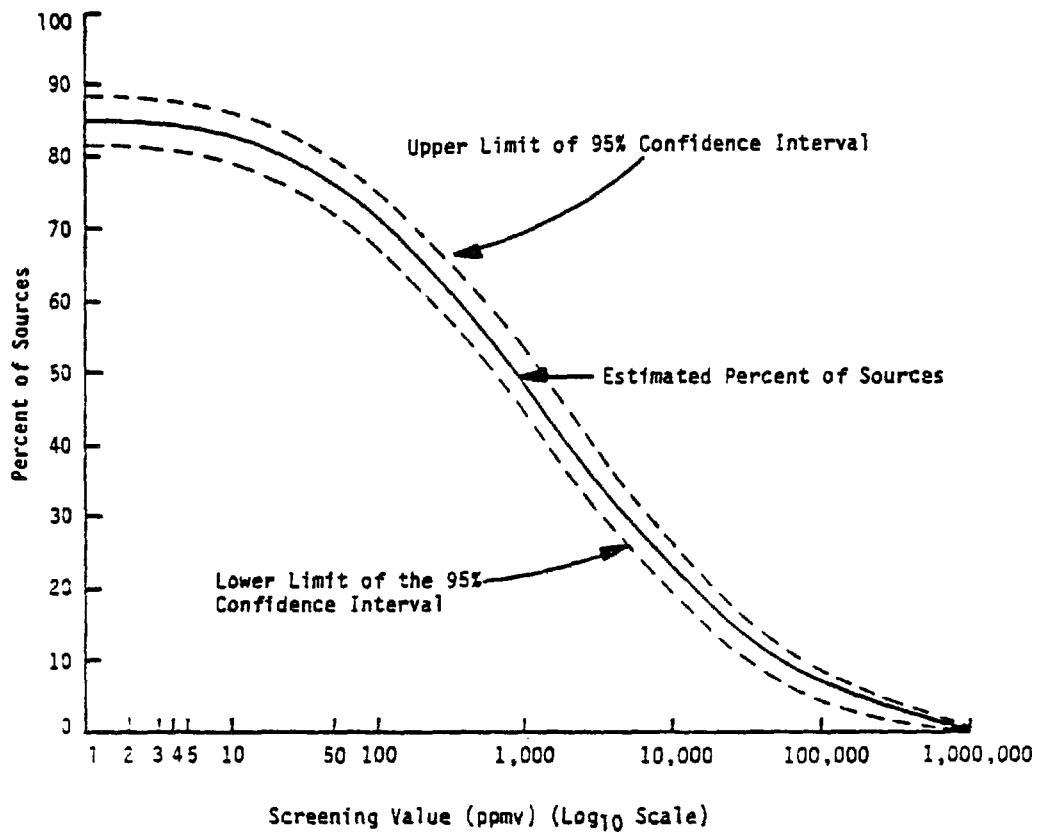
Figure 19A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Pump Seals - Light Liquid/Two-Phase Streams.

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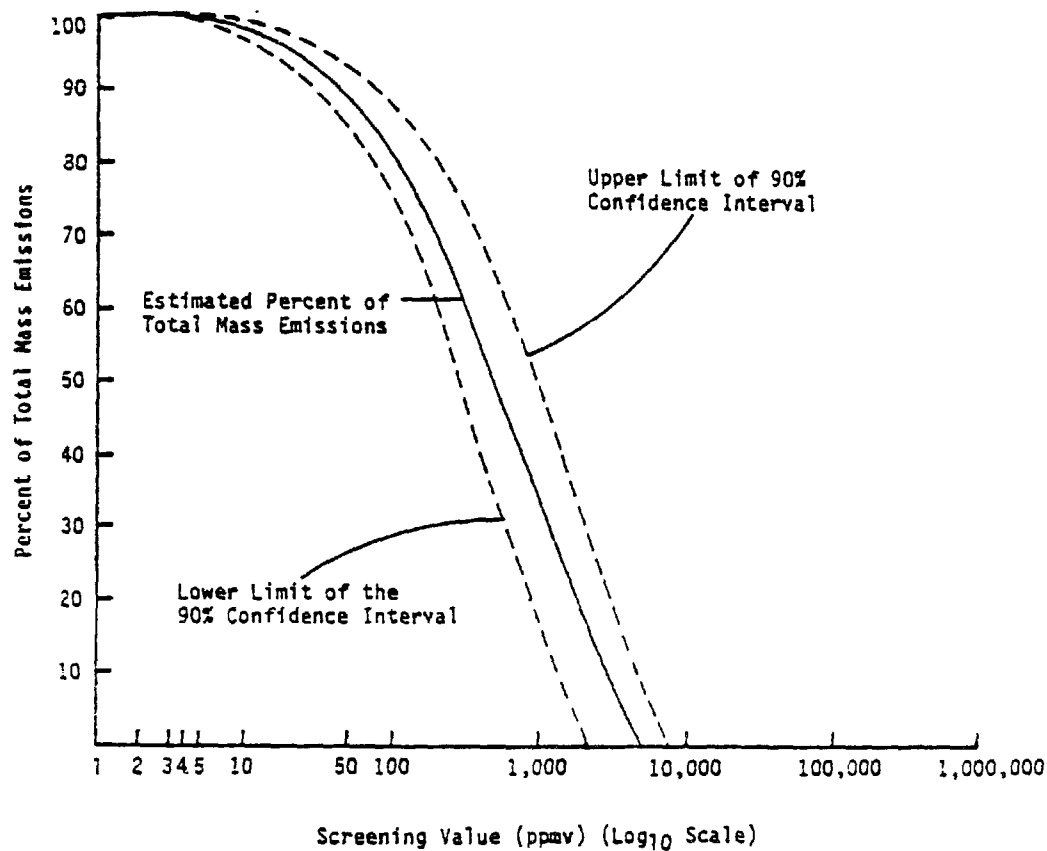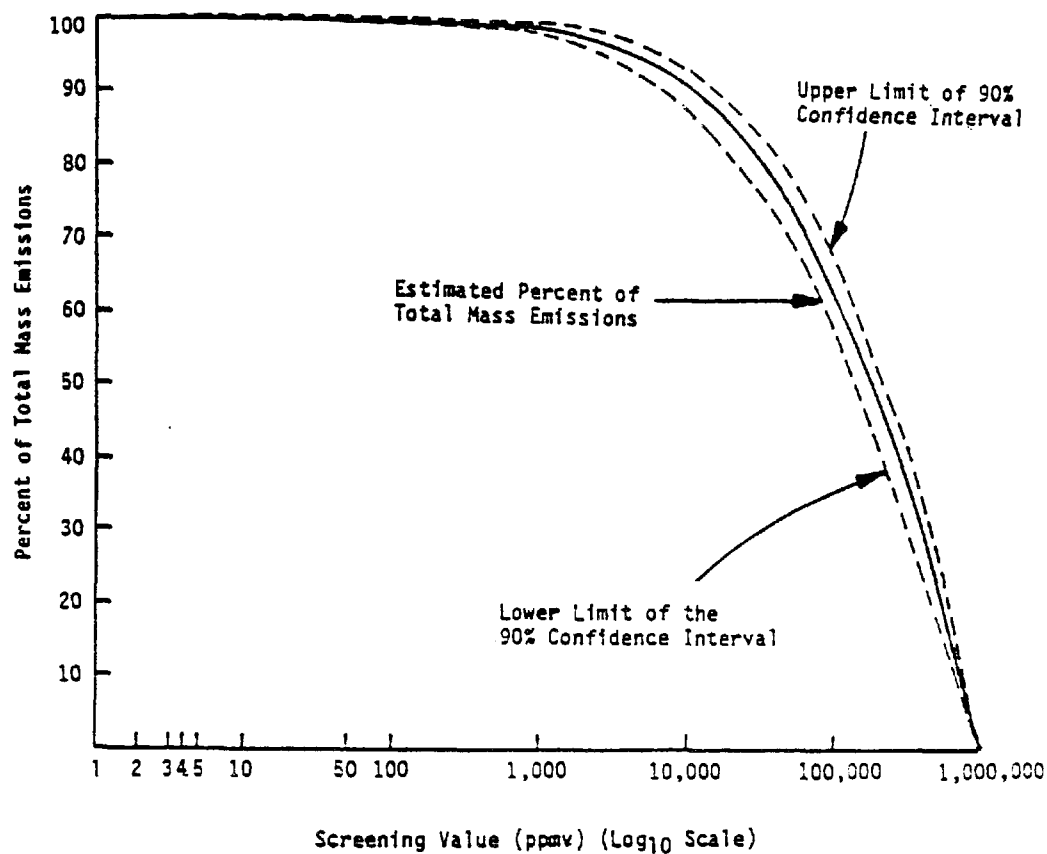
Percent of Total Mass Emissions - indicates the percent of total emissions
                                  attributable to sources with screening values
                                  greater than the selected value.

Figure 19B.   Cumulative Distribution of Source and Total
              Emissions by Screening Values for Pump Seals -
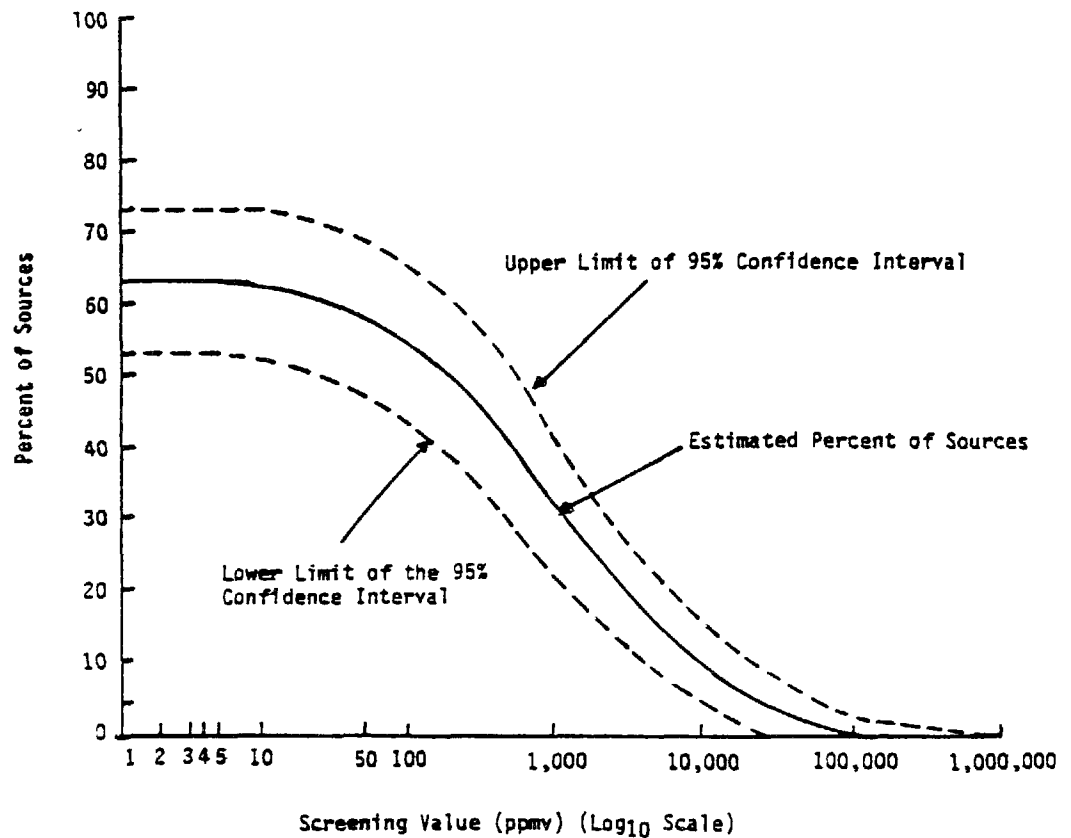   Light Liquid/Two-Phase Streams.

Figure 20A. Cumulative Distribution of Sources and
Total Emissions by Screening Values for
Pump Seals – Heavy Liquids

Figure 20B. Cumulative Distribution of Source and
Total Emissions by Screening Values for
Pump Seals – Heavy Liquids

Figure 21A. Cumulative Distribution of Sources and
Total Emissions by Screening Values for
Flanges.

F. G. Mesich

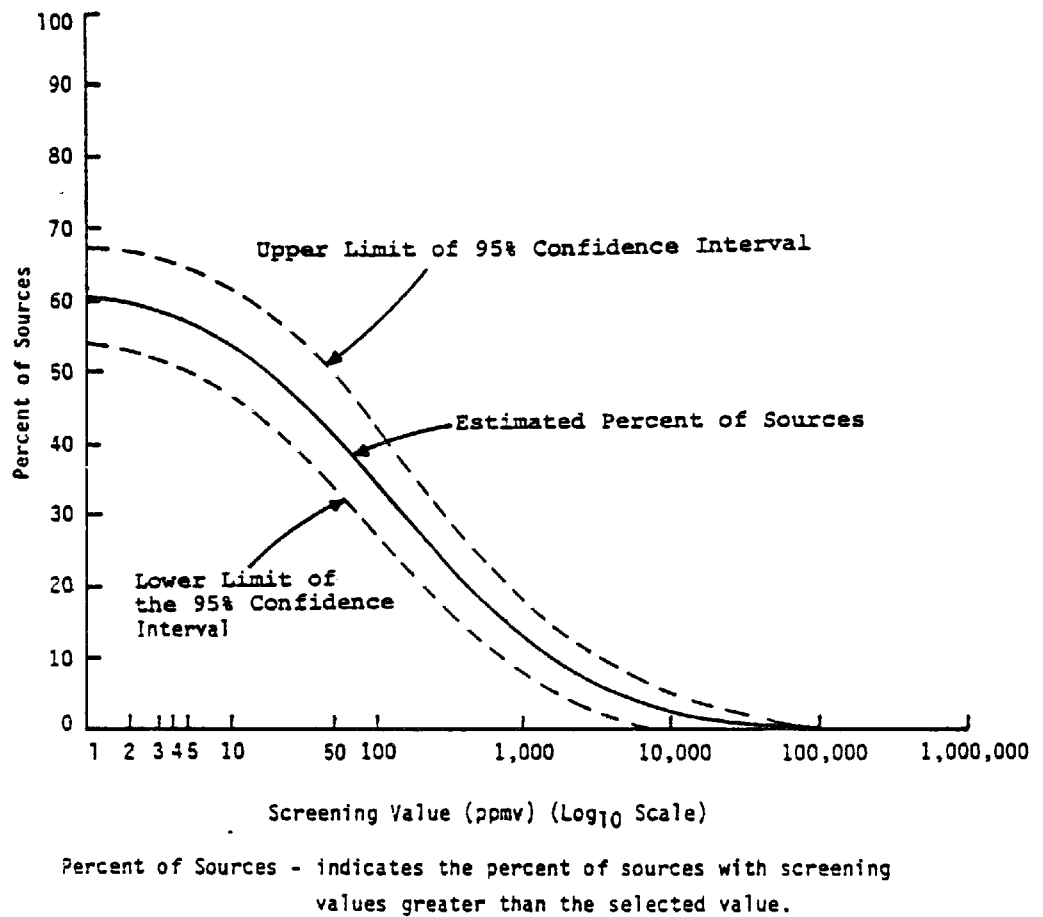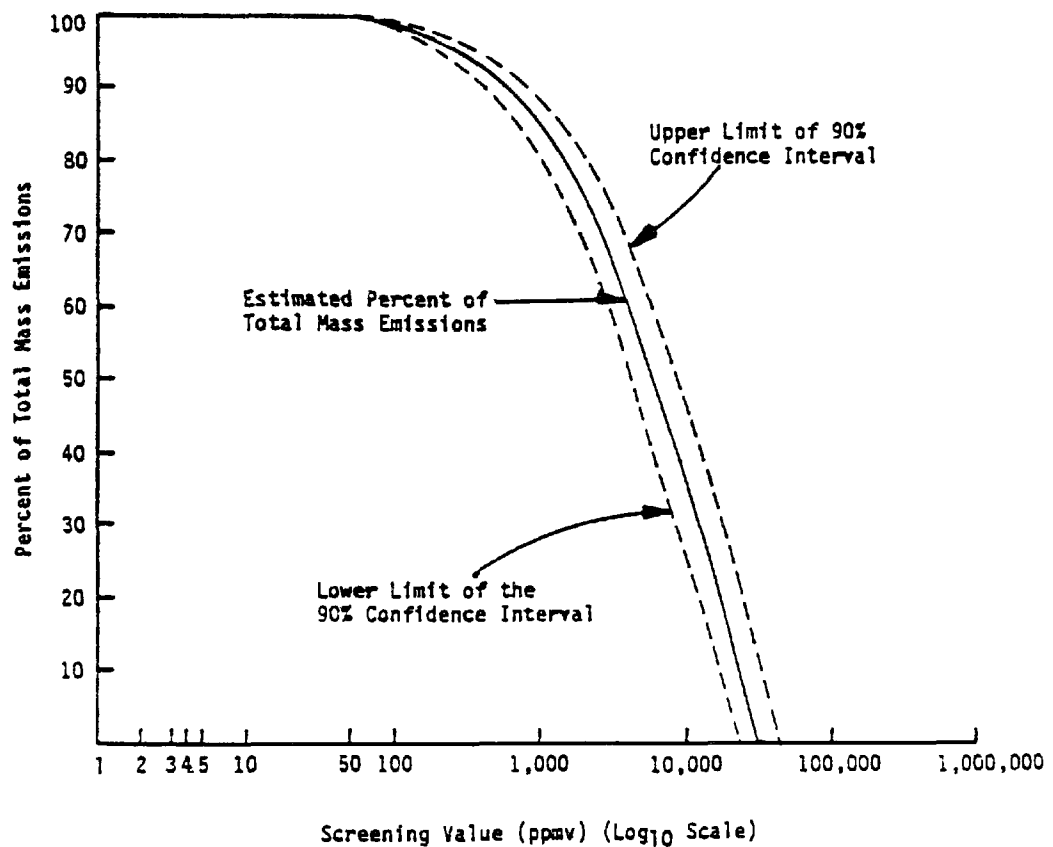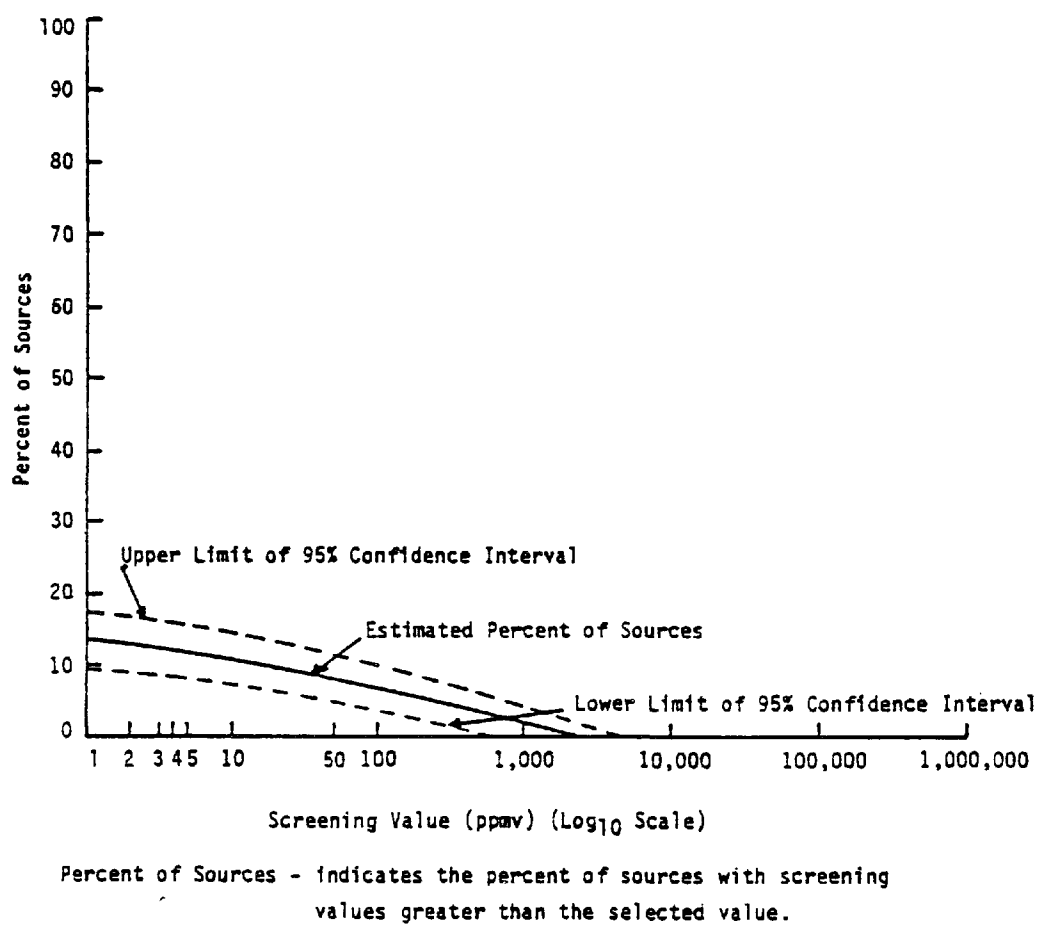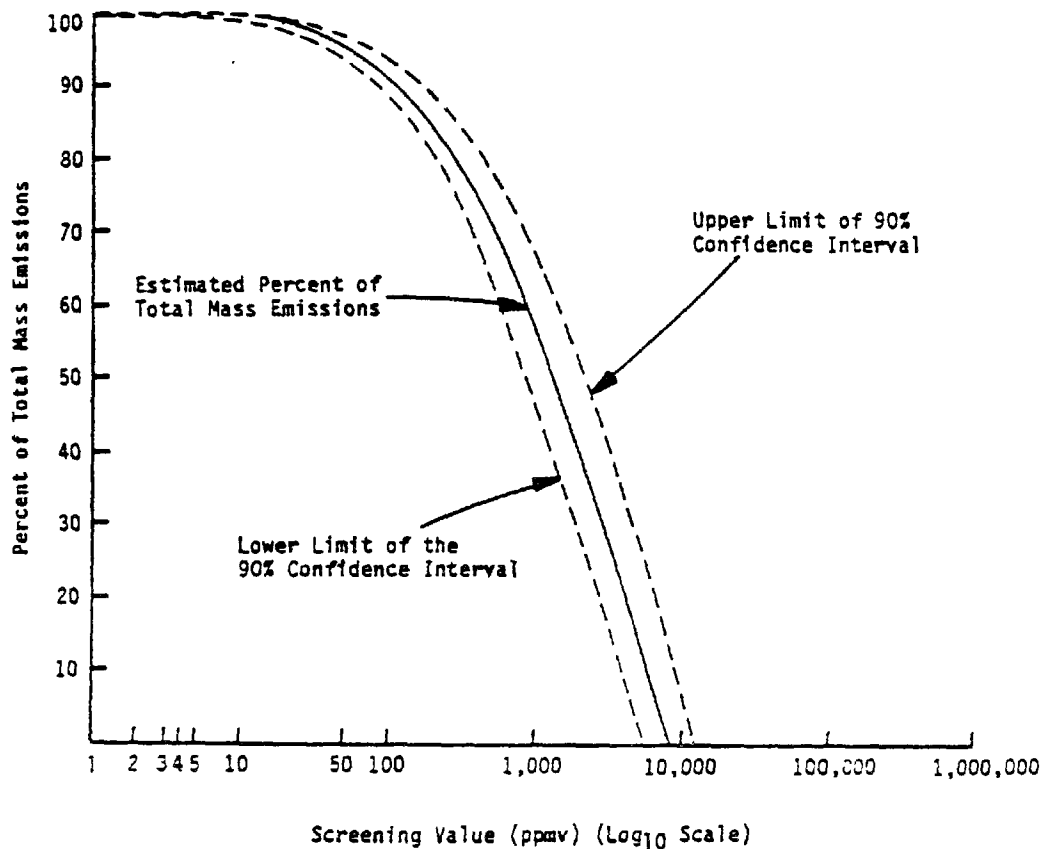Figure 21B. Cumulative Distribution of Source and
Total Emissions by Screening Values
for Flanges.

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nomographs will be conservative (i.e., they will identify more sources to achieve a given level of reduction on total emissions than would be identified through sampling). In a practical sense, however, it is unreasonable to expect that every source with a screening value exceeding a specific level could be bagged and sampled. Since, at this time, there is no better method than screening for identifying sources for maintenance, the nomographs are appropriate for evaluating maintenance and control options.

The nomographs are therefore useful in evaluating the potential effectiveness of maintaining and repairing sources for reducing emissions. For example, approximately 50 percent of valves in gas vapor stream service can be expected to have screening values above 50,000 ppmv. However, these 5 percent of the valves are responsible for an estimated 95 percent of the mass emissions. Similarly, for a screening value of 10,000 ppmv, the percent of sources and percent of emissions are 9 percent and 99 percent, respectively.

COOLING TOWERS AND WASTEWATER TREATMENT SYSTEMS

During the course of this program, extensive effort was expended in an attempt to directly determine the hydrocarbon emissions from open sources such as cooling towers and wastewater treatment systems. This was an exceedingly difficult task in that the composition of materials within these sources was highly variable and the sources consisted of large areas exposed to the atmosphere. Enclosing of these sources was either impractical from a size standpoint or hazardous from an explosion standpoint. A material balance technique was used in an attempt to quantify the loss of volatile hydrocarbons.

Cooling Towers

Thirty-one (31) cooling towers were sampled, eight (8) of which had statistically significant emissions. Streams from five (5) towers were analyzed by both TOC analysis and purge analysis; therefore, streams from a total of 21 towers were analyzed by TOC and 15 by purging. Because purge values were judged to be the more precise, they were chosen to represent the towers analyzed by both methods in the calculations of mean emissions for all towers. A summary of the emissions and the Δ ppm values for these towers is given in Table 9.

The magnitude of the sampling/analytical variation caused some problems in quantifying the low levels of emissions from the towers. The standard deviation for replicate TOC analyses was 4.2 ppm. If two tests were run each day, the standard deviation for the average would be 3.0 ppm. The between day standard deviation (after averaging replicate samples and analyses) using the TOC analyses was 3.61 ppm. Since this is close to the analytical standard deviation when replicate samples are averaged, it appears most of the variation in the TOC data is due to the analytical technique or the homogenity of replicate samples.

TABLE 9. SUMMARY OF COOLING TOWER EMISSIONS

Cooling Towers Sampled	31
Cooling Towers Having Statistically Significant Emissions	8
Range of Cooling Tower Circulation Rates	714 to 58,000 GPM

Results (estimate with 95% confidence interval)

Mean Cooling Tower Δ HC Concentration

From Emitting Towers Both Analyses	0.101 ± 0.19 ppm	(negligible, 0.29 ppm)
From All Towers Sampled		
TOC Analysis	1.25 ± 1.24 ppm	(0.01, 2.5 ppm)
Purge Analysis	0.0130 ± 0.0299 ppm	(negligible, 0.043 ppm)
Both Analyses[a]	0.0173 ± 0.058 ppm	(negligible, 0.075 ppm)

Mean Cooling Tower Emissions

From Emitting Towers Both Analysis	0.00088 ± 0.0016 lb/1000 gal	(negligible, 0.0025 lb/1000 gal)
From All Towers Sampled		
TOC Analysis	0.0124 ± 0.0123 lb/1000 gal	(0.0001, 0.025 lb/1000 gal)
Purge Analysis	0.000108 ± 0.00025 lb/1000 gal	(negligible, 0.000261 lb/1000 gal)
Both Analyses[a]	0.000151 ± 0.00051 lb/1000 gal	(negligible, 0.00066 lb/1000 gal)

Range of Measurable Emissions	0.36 to 8.46 lb/hr

[a]Calculated for 15 towers analyzed by TOC only plus 16 towers analyzed by purge. The 5 towers analyzed by both methods were represented only by the purge values, considered more accurate than TOC values.

The analytical standard deviation for the purge method is 80 percent of the concentration (averaging about 0.1 ppm). The between day standard deviation calculated here was 0.12 ppm so again most of the variation in the purge data is due to the analytical method. But, since the levels reported by the purge method were at least an order of magnitude smaller than the TOC values, the absolute variation is much smaller for towers evaluated using the purge techniques.

Since sampling was only done on five to seven days for most towers, and emissions from the towers were found to be relatively low, it was not surprising to get some negative values as estimates of emissions for a particular tower. The negative estimates are as follows:

Analytical Method	Number of Towers	Towers with Negative Estimate	
		Number	Percent
TOC	21	7	33.3
Purge	15	2	13.3
Combined	31	8	25.8

The negative estimates are due primarily to the analytical variation. In order not to bias the average emission calculation for cooling towers, these negative values have been used rather than setting the estimate to zero.

The mean emissions for the 16 towers analyzed by TOC only and the 15 analyzed by purge were 0.00015 lb/1000 gal with 95 percent confidence interval of ± 0.00051 (negligible, 0.00066 lb/1000 gal). Mean emissions for the eight towers with statistically significant emissions were 0.00088 ± 0.0016 lb/1000 gal (negligible, 0.0025 lb/1000 gal). Mean emissions for the 21 towers analyzed by TOC were 0.0124 ± 0.0123 lb/1000 gal (0.0001, 0.025 lb/1000 gal). For the 15 towers analyzed by the purge method, mean emissions were 0.000108 ± 0.00025 lb/1000 gal (negligible, 0.00026 lb/1000 gal).

Where values obtained by TOC analysis and values obtained by purging were combined to obtain a mean value, the confidence limit was sometimes larger than the obtained value.

Because of the varying precision of the methods, the upper confidence limit for each estimate may be a more useful value than the estimated average for many purposes. These values which give a "worst-case" estimate for the magnitude of hydrocarbon emissions from cooling towers are as follows:

Analytical Method Used	"Worst-Case" Estimate of Average Emissions from Cooling Towers
TOC	0.025 lb/1000 gal
Purge	0.0003 lb/1000 gal
Combined	0.0007 lb/1000 gal

Even these values are small relative to other sources of emissions from refineries.

WASTEWATER SYSTEMS

Wastewater treatment is usually accomplished in three stages: primary, secondary, and tertiary treatment. Primary treatment facilities are principally involved in physically upgrading the wastewater by removal of oil, oily sludge, and grit. Thus, primary treatment facilities will be the principal sources of fugitive hydrocarbon emissions from the waste treatment plant. Oil removal equipment includes API separators, corrugated plate interceptors, flocculation units, and dissolved air flotation units. The latter are also used for suspended solids removal.

Table 10 summaries the average emissions per gallon of material throughout for all sampled devises by refinery. Unfortunately, the data from the cooling tower and wastewater treatment systems are not sufficiently reproducible to develop usable emission factors. Cooling towers appear to be minor sources of emissions while oil/water separators require more work to determine the significance of the emissions.

TABLE 10. DESCRIPTION OF SAMPLED DEVICES – WASTE OIL/WATER SYSTEMS

Refinery	Device	Covered/Uncovered	Average Hydrocarbon Emissions	
			Losses from Oil Phase, lb/gal slop oil	Losses from Water Phase, lb/gal water
1	R Rectangular API Separator	C	1.6 ± 2	$2.7 \times 10^{-4} \pm 1.8 \times 10^{-4}$
	Circular DAF	U	$0.07\overline{3} \pm 0.4$	$8.2 \times 10^{-5} \pm 1.5 \times 10^{-4}$
2	Rectangular API Separator	C	1.84 ± 1.11	$-3.01 \times 10^{-6} \pm 1 \times 10^{-5}$
3	Corrugated Plate Interceptor	C	-1.5 ± 0.08	--
	Corrugated Plate Interceptor	C	-0.11 ± 0.06	--
4	Rectangular API Separator Forebay Covered	U	0.12 ± 1.3	$2.2 \times 10^{-4} \pm 2.7 \times 10^{-4}$
5	Surge Tank	U	0.45	
	Two Rectangular Separators	U	--	$1.6 \times 10^{-5} \pm 3 \times 10^{-6}$
	Rectangular DAF	U	--	$-2.4 \times 10^{-5} \pm 2.7 \times 10^{-5}$
6	Rectangular API Separator	U	-1.1 ± 0.74	$1.5 \times 10^{-4} \pm 2.4 \times 10^{-4}$
7	Rectangular API Separator	U	0.14 ± 0.4	$6.5 \times 10^{-4} \pm 1.9 \times 10^{-4}$
	Rectangular DAF	U	--	$1.1 \times 10^{-4} \pm 1.3 \times 10^{-4}$
8	Circular Separator	U	0.48 ± 0.61	$3.4 \times 10^{-4} \pm 1.8 \times 10^{-4}$
	Circular DAF	U	--	$1.4 \times 10^{-5} \pm 1.7 \times 10^{-5}$

REVIEW

by

James J. Morgester
California Air Resources Board
Sacramento, California

on

RESULTS OF MEASUREMENT AND CHARACTERIZATION OF
ATMOSPHERIC EMISSIONS FROM
PETROLEUM REFINERIES

RESUME

James Morgester attended the University of Washington and the
University of California at Berkeley specializing in physical science
and environmental law. Jim is the author of over 30 technical papers on
air and water pollution control and has 20 years experience in the fields.
He is presently chief of enforcement for the California Air Resources
Board.

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The thirteen-refinery study that has been conducted by Radian
Corporation for the Environmental Protection Agency (EPA) and summarized
in this paper is probably the best work, on the national level, done to
date on fugitive emission quantification in general and valve, flange,
pump, and compressor leakage in particular. However, since the sample
population for which the results are published in this paper was taken
from refineries in various regions of the U.S. (four refineries on the
West Coast), it is questionable whether the study statistics are directly
applicable to refineries in California or any specific region. In addi-
tion, the sample size for each source (valve, flange, pump, etc.) was less
than that sampled in previous California studies (e.g. 13,685 valves were
inspected in the Air Resources Board's 1978 California study, whereas
Radian examined 2,244 valves). This means that generalizing from Radian's
sample results is not as well supported as generalizing based on a larger
data base.

The most startling findings of the Radian study have been the high
occurrence of leakage found in valves and flanges (27 percent for valves
and 3 percent for flanges, overall), and the high average mass emission
rates for valves (approximately 0.55 lb/day/valve depending on the assumed
line-service profile at the refinery). The Air Resources Board's 1978 study
of valve and flange leakage in California refineries indicated nominal leak
frequencies of about 9 percent for valves and about 0.4 percent for flanges.
Furthermore, in 3 previous valve and flange studies in California (includ-
ing the Air Resources Board study), the overall mass emission rate for
valves was calculated to be in the 0.11 - 0.15 lb/day/valve range. Compari-
son of this emission rate with that found by Radian for valves indicates
the possibility of significant differences in inspection methods and/or the

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existing preventative maintenance programs of California refineries versus other U.S. refineries.

The specific results of Radian's California refinery inspections have not been published to date so it is impossible to make any comparison between those results and the data obtained in other regions of the U.S. It has been our experience that significant differences can exist among refineries in overall valve and flange leakage and in the leakage at similar process units, indicating a cause for leaks other than the nature of valve and flange service. It was evident to the Air Resources Board field personnel during our 1978 inspections of 7 major refineries and 6 chemical plants in California that variations of 6 percent to 18 percent valve leakage in refineries and 0.3 percent and 22 percent in chemical plants were largely due to the priority and emphasis given to routine maintenance of valves and flanges by each facility. In chemical plants it was clear that the priority given to routine maintenance was directly influenced by the costs of products being lost to leakage.

If the Radian study results which are summarized in this paper by Mr. Mesich are indicative of results to be expected on the regional level (although I have reservations about this being true), then past estimates of hydrocarbon emissions from valves and flanges in refineries may have been understated by as much as factor of five. Using your emission factors for valves and flanges, I calculate that emissions from valves in refineries in the South Coast Air Basin would be 64.1 tons/day and from flanges 3 tons/day. Accordingly, previous estimates of the emission reduction and cost savings achieveable by the implementation of effective and enforceable valve and flange emission control rules may have also been vastly under-estimated. In the coming era of higher and higher costs for petroleum products, such rules may very well come to be viewed as the most cost effective ever implemented.

If such rules have been logically implemented 20 years ago, after the 1958 joint study, the cumulative product savings in California refineries alone would have amounted to about 880,000 tons, or the equivalent of over 300,000,000 gallons of gasoline. At today's wholesale prices for gasoline the total cost savings would be $220,000,000.

Obviously, the Radian study has been long overdue, and the data generated from it probably will provide air quality analysts and control strategists working on the national level with a valuable tool in the years to come.

QUESTIONS AND ANSWERS

Q. James Stone/Louisiana Air Control Commission - On slide 23 you show that your flanges don't have any leaks greater than 1 pound per hour and at some other point in the talks they told me that you had included heat exchangers and things like that in the flanges and if I have seen a large leak that was not going to be stopped from a flange it was a heat exchanger. Does that mean that you did not include these in your study?

A. - No! All flanges measured are included in the data base. I would like to state for the record that visual inspection is not a good way to estimate the magnitude of a leak. For example, in several instances that I was personally involved in, things that had liquid leaks were screening and bagging very low in terms of air emissions, again showing the dependence on the volatility of material that was leaking from the line. And further, one of the largest sources our study identified was not recognized by the crew until they screened it and put a bag around it and the bag just about blew out. It was not visually or audibly apparent.

Q. James Stone/Louisiana Air Control Commission - The one refinery I am thinking about has a whole bank of exchangers. I have given them violations on opacity from smoke because of the drips from the exchangers. And I think those would probably qualify as bigger than one.

A. - All we can speak from is the data base of the thirteen refineries that we were in. And every flange that we measured is in that data base somewhere.

Q. Paul Harrison/Engineering-Science - I think that both the CARB study and the Radian study may be accurate, depending upon how you count. For example, I've seen an oven with maybe 3,000 components on one oven. A hydrogen oven where you have a lot of process gas entering; each one has a burner, each one has a valve, each one has a union and has them on both sides. And, if you start counting that way your percentage of leakers goes down. The value 0.5 pounds per day for unmaintained valves is not bad. I have found that the percentage of leakers was something like 2 percent for a new refinery and 6 percent for an old refinery, but that is including everything, including flanges, valves, compressors seals all in the same pot. I did not differentiate with valves. So, I could easily believe the CARB study. In any one unit I could believe the Radian study. In certain process units it is probably easily 25 percent with that stringent kind of study. In addition, my study was conducted at 5 cm as opposed to the 1 cm so I could easily double it as well up to 12 percent which is more like the CARB study. One more comment about heat exchangers. I caution you

that just because you have visible smoke coming out of a heat exchanger does not mean that it is detectable as VOC. That could be particulates and "heavies" which are dripping out. Many times those "heavies" aren't very volatile and you can barely see them on a detector. So, they would not get through the screening. The thing about visual leaks is that many times there are "heavies" that get into the ground, and maybe they are volatilizing over a long period. But many times screening devices will not pick them up.

A. - That is correct. Two other very brief comments. One is that I don't know whether our percentage of leakers is really different from California's or not. In that ours is based on the 200 ppm level at the surface. We presented a little data looking at the soap bubble technique. The data are really insufficient at this point to correlate between the two methods of detecting leaks. I tend to prefer the direct measurement to a somewhat subjective interpretation of the formation of bubbles, but I certainly would not make the statement that the latter method would be ineffective. Jim Morgester evidenced a concern that there would be large differences between refineries. Lloyd presented a slide this morning that pretty graphically shows that among the thirteen refineries, we found twelve that the differences between refineries were not a variable in terms of influencing our data, and I believe one refinery did have a small effect in the variance analysis. So, we basically did not see large differences, when you aggregate the data base.

COMMENT/Rosebrook - I think there are two other things that should be said. The first, deals with the differences in the data. I recall during some testimony about six weeks ago in San Francisco when we introduced the screening data which was collected at the six Bay Area refineries. This included the screening of some 25,000 valves. Our data then began to differ when we used a different cutoff. We used the California screening approach of one centimeter with the proper calibration gas and so forth and reported it as they wished to have it reported. I do not remember whose data was which but one of us found 10 percent leaking and the other one found 8 percent leaking. So, basically we are talking in terms of how we define a leak. Once we came close to using the same definition, I think we found approximately the same percentage of leaking fittings. Thus, we are not talking about the difference between 6 and 30. Given the proper basis these numbers do agree. The second point is that anyone having access to the raw data could compare two processing units or two refineries (if one takes only two of them) and find that there is indeed a difference. But insofar as its effect on our overall data base no refinery had a significant contribution which would skew the data base. We definitely found refineries where our random samples tended to give emission rates which were much higher than they were in other refineries.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - Based on what you were showing us Frank, you are saying that if we had a 50,000 barrel a day refinery and 300,000 barrel a day refinery and they had the same number of process units we should have the same amount of emissions from each one?

Because the number of valves is pretty constant like a FCC has the same number of valves, a little FCC and a big FCC has the same number of valves.

A. - Within the confidence limits yes.

COMMENT/Dan Martin/Union Carbide Corporation - The data presented here is for existing units in refineries or in chemical plants. It has only been in the last 12 to 18 months that the concern for fugitive losses has come out. On units now being built, should there be much concern about this because now we are addressing ourselves to valve and piping specifications that we never did before. We found a lot of valves in the past that came in improperly packed and were put in the system. Under the new standards I wonder when building a new unit if fugitive losses would be a problem in a permitting process rather than going back as some sort of a RACT or back up and correct the existing units. In addition, a plant that is now operating today has to be more concerned about occupational health. We are already going in now and doing a lot of correction on fugitive losses where you have employee exposure. We have never been concerned about that in the past and are tightening up things. Is fugitive loss really going to be that big of a problem in the future? And I have one last comment and answer. If a person has over 30,000 ppm coming out of something particularly a VOC you better be careful because you've got a flammable situation. You have got a time bomb. And even though the wind is blowing, some day you are going to have a fire on your hands.

COMMENT/K. C. Hustvedt/USEPA-RTP - From the plants that I have been in, the benzene unit is the one area where I think occupational health was already a factor. We haven't seen much difference in the leak incidence from our testing in those plants or elsewhere. It is a problem where you can't see the leaks. The plants are doing what they can for the ones they know about, but it is the ones they don't know about that cause the leaks that have created the emission factors we now have. Another point that will be shown in some of the correlations we see tomorrow is that it is not so much a factor of the type of equipment put in and how it is installed, but more how it is maintained once it is inline. You can see that the percent of sources, creating 90 percent of the emissions is a very small percent of the sources. It is the few that aren't properly maintained where something has gone wrong and they haven't been able to detect it. So, I think with even better design in the future and better installation you are still going to have problems. Vibration; you will still have incorrect specification; and, still have to do some level of monitoring to find these as they happen and correct the problem.

One other point you were talking about. The 30,000 ppm having an explosive problem. I think when you get right down to a source, 30,000 ppm sounds like a big number but it really isn't much. Sometimes you can have 30,000 ppm at the source and step back a foot and not see anything, if it is a pinhole type leak and you have a lot of wind.

COMMENT/Rosebrook - Jim Morgester would you care to address that question also, from a state's standpoint and whether you see any difference in the future on the types of enforcement problems and the types of regulations and so forth.

COMMENT/James J. Morgester/California Air Resources Board - Well, you have two different issues you have to look at. California's standpoint is, number one, we have a number of refineries there on-line now and it is clear to me that this problem was demonstrated in 1958. The problem is still with us twenty-two years later. Maybe it is worse than what we estimated in 1958, so there has got to be a clear motivating mechanism to make the people that are the decision makers aware of the issue and the problem and take care of it. That is for existing facilities. I think that it is a little optimistic to think that any significantly different type of valve arrangement is going to be used in a new unit. I think that the valves are shelf items and that most design engineers simply pull this valve off the shelf and unfortunately I think you are going to see the same type of valve configuration twenty years in the future that we have seen twenty years in the past. So, there is going to be a need for this type of regulations, strictly looking at it from a parochial narrow vision enforcement standpoint. My only objective is to make the stakes high enough that the management of the oil refineries cause these emissions sources to be looked at.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - About two weeks ago we had inspected a vinyl chloride plant with a VOC instrument, even though they had an ambient network in the plant to pick up fugitive emissions leaks. We found leaks over a 1,000 ppm, which was as high as this machine had been calibrated to go that day. They were picking up nothing on their ambient network. We found nothing coming out of the pump seals, which have double mechanicals with oil flush for each shaft, and the compressor seals and the relief valves, which have rupture disks. These people were very shocked to find leaks out of flanges and sampling valves, well over 1,000 ppm. Obviously since their networks weren't picking it up they weren't checking.

COMMENT/ Jim A. Mullins/ Shell Oil Company - I would like to respond to the comment on the vinyl chloride plant. In particular I think it is totally a function of not only the placement of area monitors but the level of detection those area monitors are set to detect and the option levels where repairs are done. In our particular plants we have such an action level that the area monitors will detect. For example, in a period of six months they detected 150 leaks, which were repaired. At the end of that six month period every flange, valve and seal in the plant was checked item by item and we found two leaks. And that was over 5,000 valves, pumps, flanges. So, I think it is totally a function of how the system is designed and should not be interpreted as a general indictment of area monitoring.

Q. Michael Scherm/Union Carbide Corporation - Did you make any distinction
in your data base of the difference between a daily operated type valve and
a valve that is simply in-line and rarely turned or rarely used?

A. (By Rosebrook) - There is a distinction which rests primarily on the
emission rates which we found for control valves, as opposed to any type
of block valves. We found that if there is a difference in the emission
rates for control valves, it is not statistically significant. We made
no attempt to determine for each of the valves that we monitored, any
frequency of use, other than breaking them up by putting control valves
in a separate category.

Q. Greg David/Dow Chemical Oyster Creek Division - I would just like to
point out that I think that on your examples or predictions for hypotheti-
cal refineries that you should have put somewhere on that piece of paper
that that is worst case. You have the number of valves to be 90 and you
estimate emissions in pounds per hour to equal 5. However, in your
screening phase you found somewhere around 27 percent of those valves to
be leakers, and I think that you should put a qualifier on that page.

A. - Actually I wish that were true, but the emission factors are based on
the total valve population and not only on leaking valves. In other words,
the zeroes are counted in and used as a devisor for determining emission
factors. Otherwise the emission factor wouldn't be very useful.

REFINERY AIR EMISSIONS CONTROL TECHNOLOGY

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ABSTRACT

Selected refinery process and fugitive emission sources and controls are discussed. Emission data from a recent study by Radian Corporation of selected emission sources in thirteen refineries are discussed. Pollution control technologies are described and evaluated. Specific topics discussed include sulfur recovery, catalyst regeneration, process boilers and heaters; valve and pump seals and packings; wastewater and cooling water systems.

RESUME

Mr. Phillips (B.S. - Chemical Engineering, Texas Tech, 1955) is employed by Radian Corporation. He has twenty years process industry experience which began with his return from military service in 1959. Experience includes (chronologically) refinery production engineering (3+ years); chemical company research, development and project engineering of principally oxidation reaction systems (12+ years); environmental and energy system research and development, Radian Corporation (3 years). Professional Affiliation: American Institute of Chemical Engineers.

REFINERY AIR EMISSIONS CONTROL TECHNOLOGY

INTRODUCTION

Background

Radian's refinery emissions study was conducted in thirteen refineries. Although fugitive emission testing within process battery limits was emphasized, twenty process stacks (process heaters, CO boilers, SRU tail gas, etc.) and off-site cooling towers and primary wastewater facilities were surveyed.

Objectives

Objectives of this paper are to:

- Review state-of-the-art of process and fugitive emission controls.

- Discuss available control technology.

Scope

Discussion of process emissions for purposes of this paper has been narrowed relative to that which appears in Radian's final Refinery Emissions Report. Focus will be on sulfur recovery, catalytic cracking regenerator control, and process heater control.

Certain low-impact fugitive air emission sources will be discussed only briefly. Emissions from loading, unloading and storage tanks were not measured as part of the original field study, so are omitted from discussion here.

PROCESS EMISSIONS

Table 1 lists process emissions by source and type. Emission sources in this table are coded to indicate which were field-measured and reported in the recent refinery study.

The major sources of atmospheric process emissions are sulfur recovery, regeneration of fluid catalytic cracker catalyst and process heaters and boilers. This section focuses on these sources.

The major types of atmospheric process emissions from refineries are hydrocarbons, sulfur oxides, particulates and carbon oxides.

TABLE 1. PROCESS EMISSIONS BY SOURCE AND TYPE

Source	Emissions						
	HC	P	SO_x	CO	Aldehydes	NH_3	NO_x
Sulfur[a] Recovery			X	X			
Catalyst[a] Regeneration (CO Boiler Vent)	X	X	X	X	X	X	X
Boilers and[a] Process Heaters	X	X	X	X	X		X
Vacuum[b] Distillation	X						
Coking[a]	X	X					
Air Blowing[b]	X						
Chemical Sweetening[b]	X						
Acid Treating[b]	X		X				
Blowdown[b]	X						
Compressor[b] Engines	X	X	X	X			X

[a] Detailed results are in Refinery Assessment Report.

[b] Emission not measured in this study.

Process heaters and boilers are used in a number of different refinery processes. Therefore, they will be discussed, not by process, but collectively as a separate emission source.

Sulfur Recovery

The amount of sulfur in various product streams depends directly on the sulfur content of the crude oil. As the oil is fractionated initially sulfur tends to become more concentrated in the heavier cuts because of the low volatility of its various compounds. The sulfur content of crude can vary from less than 0.1 weight percent to more than 5 weight percent. Any crude oil with more than 0.5 weight percent sulfur is generally considered to be a sour crude and its products are subjected to sulfur removal processing.[1] If not removed, the sulfur can cause corrosion, pollution and catalysis problems during refining or when the products are used as fuel or as petrochemical feedstocks.

Sulfur removal from whole crude is not generally economical.[2] Intermediate stock streams routinely subjected to sulfur removal include the outlet streams from crude distillation and cracking units.[3] Sulfur components in these streams are converted to hydrogen sulfide by hydro-processing with hydrogen over a nickel-molybdenum catalyst at an elevated temperature. Resulting H_2S boils between ethane and propane, so must be selectively removed from the sour gas stream and concentrated by one of several means, the most common of which is absorption by monoethanolamine (MEA) or diethanolamine (DEA) followed by steam stripping.

With increasing use of hydro-processing of ever increasing sulfur-containing crude stocks, it has become environmentally and economically sound to introduce a process for removal of H_2S generated by hydro-processing. The Claus process presently dominates. Tail gas from a Claus unit can be a major source of SO_2 emissions in a refinery. In the Claus process, some H_2S feed is oxidized to form SO_2 and water. Additional H_2S reacts with SO_2 to form elemental sulfur and water.

Claus unit tail gas contains H_2S, SO_2, CS_2, COS and S_x. The emission rates of these sulfur compounds depends on the concentration of the H_2S stream to the Claus unit and the efficiency of the unit. Tail gas from a typical three-stage Claus unit, 95 to 96 percent efficient, can be expected to contain about 7000-12,000 parts per million by volume sulfur compounds.[4,5] The tail gas also contains carbon monoxide formed from small amounts of hydrocarbons and carbon dioxide in the feed stream. Typical compositions of Claus unit feed and product gases are found in Table 2.

Catalyst Regeneration

Catalysts are used in several petroleum refining operations, including fluid catalytic cracking, moving bed catalytic cracking (known as Thermofor catalytic cracking or TCC), catalytic hydrocracking, reforming, and various oil desulfurizations. These catalysts become coated with carbon and

TABLE 2. TYPICAL COMPOSITIONS OF FEED STREAM AND TAIL GAS
FOR A 94 PERCENT EFFICIENT CLAUS UNIT[6]

Component	Sour Gas Feed, Volume Percent	Claus Tail Gas, Volume Percent
H_2S	89.9	0.85
SO_2	0.0	0.42[a]
S_8 Vapor	0.0	0.10 as S_1
S_8 Aerosol	0.0	0.30 as S_1
COS	0.0	0.05
CS_2	0.0	0.05
CO	0.0	0.22
CO_2	4.6	2.37
O_2	0.0	0.00
N_2	0.0	61.04
H_2	0.0	1.60
H_2O	5.5	33.00
HC	0.0	0.00
	100.0	100.00
Temperature, °F	104	284
Pressure, psig	6.6	1.5
Total Gas Volume[b]	–	3.0 x feed gas volume

[a] NSPS requires an emission of less than 250 ppmv (0.025 percent) SO_2, zero O_2, dry basis if Claus unit tail gas is oxidized last as a control step, or, 300 ppmv SO_2 equivalent reduced compounds (H_2S, COS, CS_2) and 10 ppm SO_2 if the tail gas is reduced as the last process step.

[b] Gas volumes compared at standard conditions.

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metals and must be regenerated to restore their activity. During regeneration, the carbon is oxidized to carbon monoxide and carbon dioxide and the hydrocarbons are burned incompletely.

In most applications, a catalyst must be regenerated only a few times a year. Emissions during these episodes may include catalyst fumes, oil mist, hydrocarbons, ammonia, SO_x, chlorides, cyanides, NO_x, CO, and aerosols.[7] Though there may be significant emissions during the regeneration of one of these catalysts, the total emissions over the course of the year are not significant.

Catalytic cracking catalyst regeneration is a continuous process. Uncontrolled cracking catalyst regeneration is one of the major sources of air pollution in a petroleum refinery. Flue gases from catalytic cracker regenerators contain particulates, SO_x, carbon monoxide, hydrocarbons, NO_x, aldehydes and ammonia.

Emission factors for uncontrolled regeneration of FCC and TCC catalysts are reported in AP-42 and are listed here in Table 3. These factors are from a 1956 stack sampling survey of FCC and TCC units in Los Angeles County.[8] The survey involved six FCC units and nine TCC units.

TABLE 3. EMISSION FACTORS FOR UNCONTROLLED REGENERATION
OF THE CATALYTIC CRACKING CATALYST[9]

Process	Emission Factor, lb/1000 bbl Fresh Feed						
	Particulate	SO_x as SO_2	CO	Total Hydrocarbon	NO_x as NO_2	Aldehydes	NH_3
Fluid Catalytic Cracking (FCC)	242	493	13,700	220	71	19	54
Moving Bed Catalytic Cracking (TCC)	17	60	3,800	87	5	12	6

These factors indicate that the uncontrolled emissions from FCC units are several times greater than from TCC units. The term "uncontrolled emission" here implies conventional regeneration without any external control. Radian believes that these 1956 emission factors should be reviewed because of advances in technology, especially the FCC particulates emission factor (242) because of the following:

1. FCC regenerator cyclone technology has advanced since the 1956 survey. Catalyst losses from properly designed two-stage regenerator cyclone systems in the range of 80-100 $lb/10^3$ bbl of fresh feed are typical.

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2. Five out of six of the FCC units surveyed in 1956 had emission factors of 50 lb/10^3 bbl fresh feed or less. The sixth may have been troubled by condensation at low stack temperature of high concentrations of SO_3. The individual emission factors were 181, 50, 43, 35, 27, and 24 (average: 60).

3. For several of the TCC units in the survey, emissions for the entire unit were extrapolated from measurements made on one stack. This method can produce errors, because TCC units employ several dissimilar stacks.

Boilers and Process Heaters

Most refineries use steam boilers to provide steam for direct use in various processes, for heating and for driving steam turbines. Large amounts of steam are needed for light ends strippers, vacuum steam ejectors, process heat exchangers and reactors. About 40 pounds of steam are required by a typical refinery per barrel of refining feed. This steam demand requires a boiler size of 53,000 Btu per barrel of refining feed.[10] Some steam is also generated in waste heat boilers, the largest of which is, in some refineries, a carbon monoxide boiler used to control emissions from the regeneration of the catalytic cracking catalyst. Another carbon monoxide control technique is high temperature catalyst regeneration at approximately 1300°F minimum. Most process steam generated is low pressure steam.

Process heaters are the largest combustion source of hydrocarbons in a refinery. Total process heater demand in a modern refinery is approximately 270,000 Btu per barrel of refining feed. Older, less efficient refineries may require 600,000 Btu per barrel of refining feed.[11]

Refining boilers and heaters are fired with the most available fuel, usually purchased natural gas, refinery fuel gas (mostly methane), or residual fuel oil. Ordinarily, the refinery gas supplies approximately one-half the fuel needs; natural gas is used in the summer months and residual oil in the cooler months when natural gas supplies go to preferred residential customers. These estimates vary with the individual refinery. Emission factors for burning of natural gas and residual fuel are found in Table 4.

In addition to combustion emissions, there are also emissions associated with the decoking of heaters. At intervals of about six months to three years, each heater must be flushed with a steam-air mixture to remove interior coke deposits. Emissions are similar to those from decoking operations on delayed coking units, but less.

Existing Control Technology

Most of the process emissions described previously can be controlled. This section describes control methods that are now in use or might be adapted to refinery use.

TABLE 4.   EMISSIONS FROM REFINERY BOILERS AND HEATERS[12]

Pollutant	Fuel	
	Natural Gas, $lb/10^6$ std ft^3	Fuel Oil, $lb/10^3$ gal
Hydrocarbons (as CH_4)	3	1
Particulates	5–15	$-^a$
SO_x as SO_2	0.6^b	$157 \, S^c$
CO	17	5
NO_x as NO_2	$120-230^d$	60^e

[a]A function of fuel oil grade and sulfur content
   For Grade 6: $lb/10^3$ gal = 10 S + 3
   For Grade 5:   10 $lb/10^3$ gal
   For Grade 4:   7 $lb/10^3$ gal

[b]Based on average sulfur content of natural gas of 2000 $gr/10^6$ Std Ft .

[c]S equals percent by weight of sulfur in fuel.

[d]Uses first number for tangentially fired units, second for horizontally fired units.

[e]Strongly dependent on the fuel nitrogen content.

"Existing" controls included are those considered to be in relatively common usage in refining. "Available" controls, which will be discussed following this section, are those which have had only limited application or which have not yet been applied. Those controls which have been used in other industries and which might be applicable to the refining industry, are included in the section following available controls.

Sulfur Recovery

The Claus unit is the accepted method for sulfur removal in a modern refinery. However, because it is not totally efficient in producing elemental sulfur, it is a major source of emissions. Much progress has been made in recent years in the control of emissions from Claus units. This discussion will consider first the Claus unit itself, then methods for cleaning up the Claus unit tail gas. Incineration is an integral part of several of these methods, so it is discussed immediately after the Claus unit.

More than 70 methods have been proposed for treatment of the Claus unit tail gas.[13] These methods may be continuations of the Claus reaction or add-on processes with chemistry quite different from that of the Claus reaction. Incineration is sometimes used alone to clean Claus unit tail gas, sometimes to prepare the tail gas for further treatment, and sometimes after that treatment.

The Claus Process--

The Claus process is recognized as a very effective control device. Since implementation of the Environmental Pollution Act in 1970, Claus has been used to remove sulfur from refinery process streams at an average efficiency exceeding 95 percent.

The overall Claus reaction is as follows:

$$H_2S + \tfrac{1}{2} O_2 = \left(\frac{1}{n}\right) S_n + H_2O \tag{1}$$
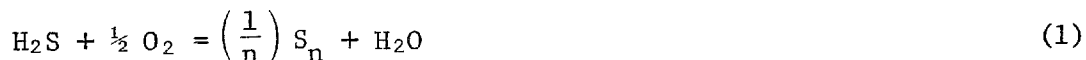
where n represents the various molecular forms of sulfur vapor. The two most popular designs of Claus units are illustrated in Figure 1. In the "once-through" design, the incoming H_2S-rich stream is burned in a limited amount of air to convert one-third of the H_2S to SO_2 according to the following reaction:

$$2H_2S + 2O_2 = SO_2 + S + 2H_2O \tag{2}$$

The hot gases from this reaction are then passed over a bauxite, alumina, or cobalt-molybdenum catalyst, to react the sulfur dioxide with unburned H_2S according to the following reaction:

$$2H_2S + SO_2 = 3S + 2H_2O \tag{3}$$
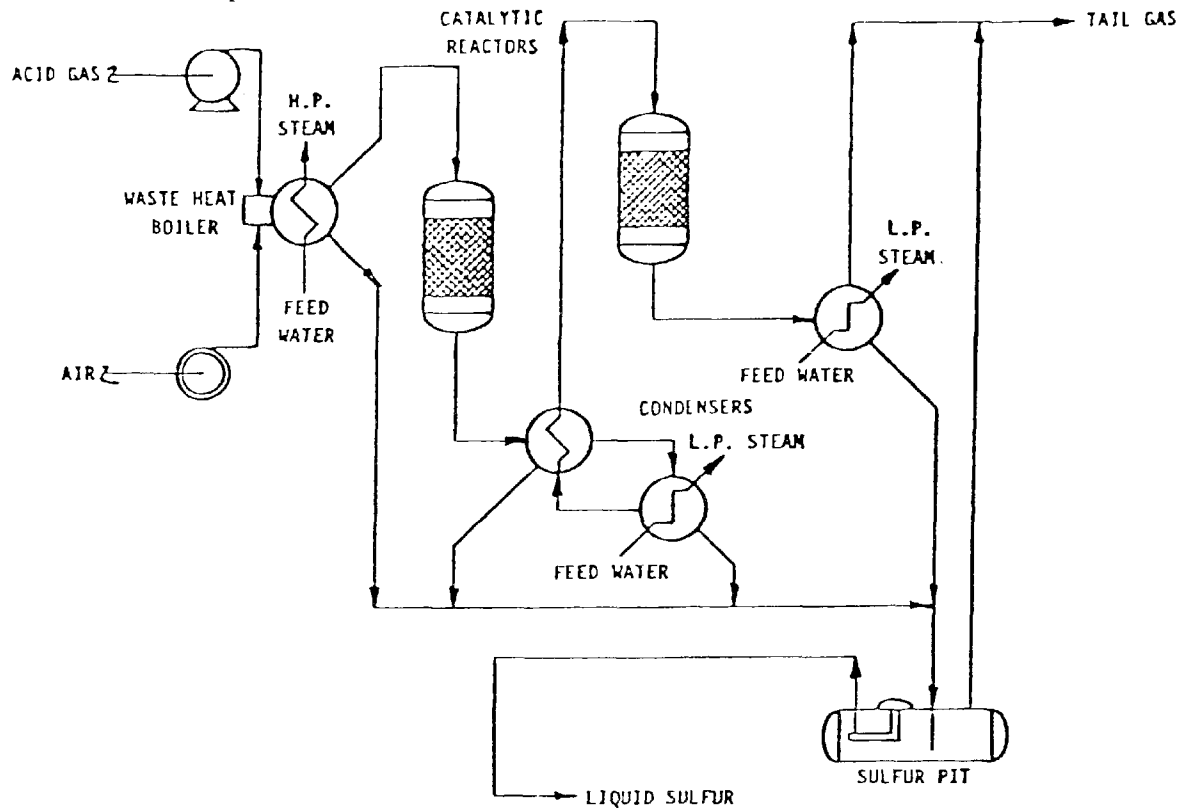
STRAIGHT THROUGH CLAUS PROCESS
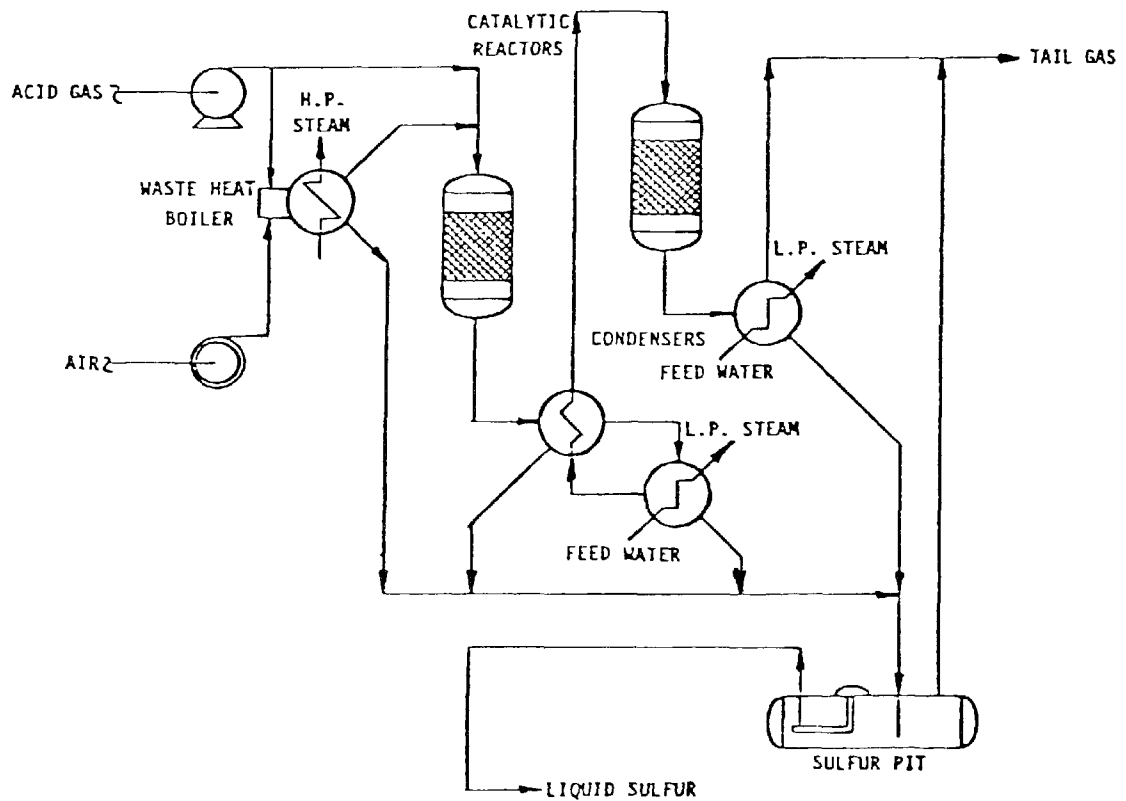
SPLIT FLOW CLAUS PROCESS

Figure 1.   The Claus Process.

If the "split-stream", or "by-pass", design is used, one-third of the incoming stream is separated and burned more completely according to the following reaction:

$$H_2S + \tfrac{3}{2}O_2 = SO_2 + H_2O \qquad\qquad (4)$$

The remaining H_2S is reacted over a catalyst with the hot gas from the furnace to form elemental sulfur according to reaction (3) above.

The "direct oxidation" design is for streams with lower concentrations of H_2S. In this design the incoming stream is preheated, mixed with air, and then passed over the bauxite or alumina catalyst.

The Claus designs described above with one pass through the catalytic reactor convert 80 to 86 percent of the H_2S to elemental sulfur.[14,15] This efficiency can be greatly enhanced by repeating the catalytic stage one or more times. Thus, two-stage Claus units can achieve 92 to 95 percent efficiency; three stages, 95 to 96 percent; and four stages, 96 to 97 percent.[16] Conversion is ultimately limited by the reverse reaction. Recovery rates for various feed compositions are found in Table 5.

These efficiencies, once considered sufficient, do not meet new regulations. Further treatment of the Claus unit tail gas is discussed in succeeding sections.

Incineration of Claus Unit Tail Gas--

The tail gas from the Claus unit is often incinerated before it either passes to the atmosphere or is subjected to further treatment. This incineration takes place at temperatures of about 1200°F or above in refractory-lined vessels with one or more burners.

Auxiliary fuel such as natural gas or fuel oil provides the heat necessary for incineration since the heating value of the tail gas is low. Excess air levels of 20 to 30 percent are used.

The objective of tail gas incineration is to convert all sulfur compounds in the tail gas to SO_2, but this conversion is incomplete. Typical compositions of a sour gas feed stream and the corresponding Claus unit tail gas before and after incineration are given in Table 6.

Tail Gas Clean-Up--

Each of the six tail gas clean-up methods listed in Table 7 has three or more commercial installations to its credit. The first three processes--Amoco's CBA process, the Sulfreen process, and the IFP process--are continuations of the Claus reaction under more favorable conditions. The second three processes--the Beavon process, the SCOT process, and the Wellman-Lord process--are add-on units with higher efficiencies than the first three.[17]

TABLE 5. TYPICAL CLAUS PLANT SULFUR RECOVERY FOR VARIOUS FEED COMPOSITIONS[18]

Hydrogen Sulfide in Sulfur Plant Feed (Dry Basis), %	Calculated Percentage Recovery[a]		
	Two Reactors	Three Reactors	Four Reactors
20	92.7	93.8	95.0
30	93.1	94.4	95.7
40	93.5	94.8	96.1
50	93.9	95.3	96.5
60	94.4	95.7	96.7
70	94.7	96.1	96.8
80	95.0	96.4	97.0
90	95.3	96.6	97.1

[a]Assumes 1 mole percent hydrocarbon contamination, conventional temperatures and reheat techniques, average organic by-products and entrainment allowance.

TABLE 6. TYPICAL COMPOSITIONS OF FEED STREAM AND TAIL GAS STREAMS
FROM A 94 PERCENT EFFICIENT CLAUS UNIT AND INCINERATOR[19]

Component	Sour Gas Feed, Volume Percent	Claus Tail Gas, Volume Percent	Thermally Incinerated Tail Gas, Volume Percent
H_2S	89.9	0.85	0.001
SO_2	0.0	0.42	0.89
S_8 Vapor	0.0	0.10 as S_1	0.00
S_8 Aerosol	0.0	0.30 as S_1	0.00
COS	0.0	0.05	0.02
CS_2	0.0	0.05	0.01
CO	0.0	0.22	0.10
CO_2	4.6	2.37	1.45
O_2	0.0	0.00	7.39
N_2	0.0	61.04	71.07
H_2	0.0	1.60	0.50
H_2O	5.5	33.00	18.57
HC	0.0	0.00	0.00
	100.0	100.00	100.00
Temperature			
°C	40	140	400
°F	104	284	752
Pressure			
Kilopascals	150	110	100
Psig	6.6	1.5	0
Total Gas Volume[a]	—	3.0 x Feed Gas Volume	5.8 x Feed Gas Volume

[a]Gas volumes compared at standard conditions.

TABLE 7.   ESTABLISHED METHODS FOR REMOVAL OF SULFUR FROM CLAUS TAIL GAS

Name	Developer	Description	Efficiency (Claus + Add-on)	Product	Cost (Percent of Claus	Number in[20] Commercial Production
CBA	Amoco	Claus reaction continued at low temperature; removal of condensed sulfur drives reaction. Bed regenerated with hot gas from Claus unit.	98-99.5 percent 1500 ppmv S	S_0	50-150	3
Sulfreen	SNPA/Lurgi	Claus reaction continued at low temperature as in CBA. Bed regenerated with hot nitrogen.	99 percent 1500-2000 ppm S	S_0	50-150	19
IFP-1500	Institut Francais du Petrole	Claus reaction occurs in a solvent.	1000-2000 ppm S	S_0	Variable	25
BSRP	Ralph M. Parsons & Union Oil Co. of California	All sulfur compounds reduced to H_2S which is processed in a Stretford unit.	250 ppm S or less	S_0	100	36[a]
SCOT	Shell	All sulfur compounds reduced to H_2S which is recycled to Claus.	200-500 ppmv H_2S	Feed to Claus	75-100	35
Wellman-Lord	Wellman Power Gas	SO_2 in incinerator gas contacted with $NaSO_3$ to form $NaHSO_3$. $NaSO_3$ regenerated in evaporator/crystallizer.	200 ppmv SO_2	$NaSO_4$/ $NaSO_3$ Crystals	130-150 for 100 lt/d Claus unit	7

[a]Figure includes plants in operation, under construction or being designed.

These six processes are discussed in more detail in Radian's refinery emissions report.

FCCU Catalyst Regeneration

Regeneration of the catalyst in fluid catalytic cracking units (FCCU's) produces three principal types of atmospheric emissions: SO_x, particulates, and CO_x. Lesser emissions include hydrocarbons, NO_x, aldehydes, and ammonia. SO_x is typically controlled by feedstock desulfurization; particulates by cyclones and electrostatic precipitators; and CO by a CO boiler. No single process can control all three.

SO_x Emissions--

Hydrodesulfurization (HDS) of feedstock to FCCU's has been practiced for years, since it increases the yield of salable products.

In HDS of FCCU feedstock, the ratio of weight percent sulfur in the coke over the weight percent sulfur in the desulfurized feedstock increases with the degree of desulfurization. The result is that very high levels of hydrodesulfurization are needed to achieve 90 percent or higher reduction in SO_x emissions. For a feedstock with 2.3 weight percent sulfur, for example, 92 to 95 percent desulfurization of the feed is necessary for a 250 ppm SO_x concentration in the flue gas.[21]

Particulates (Catalyst Fines)--

Before exiting the regenerator, gases pass through a series of cyclones that remove the small catalyst particles (fines) present in the exit gas. Some refineries have additional cyclones downstream of the regenerator.

Particles smaller than 5 microns are ordinarily not collected by cyclones. The majority of refineries use electrostatic precipitators to remove these catalyst fines from the flue gas.

The collecting efficiency of ESP's for catalyst fines is commonly 99.5 percent of the particles that escape the cyclones.[22] In most cases, final disposal of the waste particles is by burial in a sanitary landfill.

CO Emissions--

All methods of controlling the CO content of flue gas from FCC regeneration involve combustion of CO to CO_2. A typical unit with "conventional" regeneration burns off the coke from spent catalyst to, roughly, a 50-50 mixture of CO and CO_2.

The majority of refineries--66 percent in 1976-- used a CO boiler to recover part of the energy from hot FCCU flue gases and to reduce CO emissions.[23] The flue gas goes to the furnace of a CO boiler and external heat is applied to raise the temperature high enough ($\sim$1300°F) to achieve

near complete combustion (99.5 percent or more). The heat of combustion is recovered as steam, often used to drive the regenerator air blower as well as for other refinery operations.

In all but small refineries, the cost of CO boilers can be recovered in a few years. Small refineries may find it more economical to control CO emissions with flares, even though no energy recovery is possible.

Other Catalyst Regeneration

Because emissions from TCC catalyst regeneration are significantly less than those from FCCU catalyst regeneration, use of a CO boiler may not be justified. Flue gases from TCC catalyst regenerators are usually released directly to the atmosphere.

Flue gases from other catalyst regenerations may also be incinerated in a process heater or flared, but use of these control methods is not widespread because these emission sources are typically insignificant.

Control Technology Available in Refineries

Controls with limited application and those which have not yet been applied are included in this section. Information available on new technologies is often limited.

Controls chosen for inclusion in this section are those which have been proposed for consideration by the industry. Inclusion here merely indicates that it is worthy of consideration, and not necessarily a good choice.

Sulfur Recovery

A number of alternatives to the Claus method of sulfur removal have been proposed in recent years. Some are applicable only to Claus tail gas treatment, while others may be applied to other problem sulfur-bearing streams as well. Also being tested are one alternative to the Claus unit and an integrated Claus tail gas process. These alternatives would produce no objectionable tail gas stream. Tail gas treatment methods are found in Table 8.

UOP Sulfox Process[24]

The UOP Sulfox process is an alternative to the Claus process. Initially, aqueous ammonia, instead of an amine solution, is used to scrub H_2S from refinery feed gas. The ammonia is then scrubbed from the gas with purified water.

The rich solution is mixed with air and sour water and passed over a catalyst. Elemental sulfur is formed according to the following reaction:

$$NH_4HS + \tfrac{1}{2} O_2 = S_0 + H_2O + NH_3 \tag{5}$$

TABLE 8. AVAILABLE METHODS FOR REMOVAL OF SULFUR FROM CLAUS TAIL GAS

Name	Developer	Description	Efficiency or Outlet Concentration	Product	Cost (Percent of Claus)
IFP-150[25]	Institut Francais du Petrole	Gas from IFP-1500 scrubbed with ammonia; SO_2-laden ammonia mixed with H_2S in a glycol to form elemental sulfur and water.	<200 ppm SO_2	S_0	Variable
Cleanair[26,27]	Pritchard	Claus reactors operated at high temperature to reduce COS and CS_2 levels; SO_2 and elemental sulfur removed by aqueous scrubbing; H_2S removed by Stretford Process.	50 ppmv S	S_0	100
Trencor-M[28]	Trentham	All sulfur compounds reduced to H_2S. H_2S absorbed by amine solution and returned to Claus.	100-200 ppmv SO_2	Feed to Claus	150
Aqua-Claus[29,30]	Stauffer	SO_2 from incinerator mixed with H_2S-rich Claus feed; Claus reaction occurs in aqueous phase.	<100 ppmv SO_2	S_0 Na_2SO_4	125-135
Sulfoxide[31]	Alberta Sulfur Research, Ltd.	Claus reaction occurs in an organic sulfoxide medium.	<1000 ppmv S, Typically <500 ppmv S	S_0	Not Available
Topsoe[32]	SNPA/ Topsoe	SO_2 from incinerator oxidized to SO_3 which is converted to H_2SO_4.	90 Percent	H_2SO_4	Not Available

Continued

TABLE 8. Continued

Name	Developer	Description	Efficiency or Outlet Concentration	Product	Cost (Percent of Claus)
SFGD[33,34]	Shell	SO_2 in gas from incinerator absorbed by CuO bed which is regenerated with hydrogen.	90 Percent	Feed to Claus	250
Westvaco[35,36]	Westvaco	SO_2 in gas from incinerator removed and catalyzed to H_2SO_4 in activated carbon bed which is regenerated with H_2S.	<200 ppmv SO_2	S_0 or Feed to Claus	Not Available
Ammonium Bisulfate/ Ammonium Thiosulfate[37]	Pritchard	SO_2 in gas from incinerator absorbed in aqueous ammonia and converted to ammonium thiosulfate.	<900 ppmv SO_2	Ammonium Thiosulfate	75
BSR/ Selectox I[38]	Union Oil	All sulfur compounds reduced to H_2S which is then oxidized to S.	>98 Percent	S_0	≤200
Limestone Slurry[39]	Mineral & Chemical Resource Company	SO_2 in incinerator gas absorbed by limestone slurry.	>99.9 Percent	$CaSO_3$/ $CaSO_4$/ limestone solids	Not Available
Catalytic Incineration[40]	Institut Francais du Petrole	Catalyst promotes oxidation of sulfur compounds to SO_2 in incinerator.	<200 ppmv S	SO_2	Not Available

With ammonia and sulfide present, the elemental sulfur remains in solution as polysulfide. The liquid product from this reaction is then heated above the melting point of sulfur, mixed with air, and passed over a second catalyst where any remaining sulfide is oxidized to elemental sulfur. With no sulfide remaining to solubilize the sulfur as polysulfide, the sulfur exists as a separate molten product.

Tail gas is scrubbed with water to remove ammonia. Hydrogen sulfide content in the treated gas is 10 to 100 ppm. Although it is possible to design a Sulfox unit which will achieve 1 ppm H_2S in the tail gas, the new source performance standard requires only 250 ppmv SO_2 or less from a final oxidizing step.

Capital costs for a Sulfox system and a Claus unit are approximately equivalent, not including the cost of tail gas cleaning. Sulfox utility costs are approximately 60 percent of those of a Claus unit.

Union Carbide UCAP Process[41]

This newly publicized integrated Claus/tail gas treatment process requires only one Claus reactor stage to achieve the NSPS requirement of less than 250 ppmv of SO_2. The process converts H_2S to SO_2, absorbs it in triethanolamine and recycles the SO_2 to the Claus unit. Economics are not yet available. The process appears to be a strong candidate for new integrated plant installations.

Catalyst Regeneration

SO_x emissions may be controlled by flue gas scrubbing systems. Exxon presently operates four such scrubber systems installed in its coastal refineries in Texas, Louisiana and New Jersey.

Exxon's operations have shown that 95 percent of the SO_x and 90 percent of the particulates can be removed by a scrubber.[42] They believe that the cost of controlling both particulates and SO_x by scrubbing is less costly both in initial investment and maintenance than a combination of desulfurization and ESP's. The space requirements are also less.

The scrubbers may be the once-through or regenerable type. A non-regenerable process has been used for FCCU flue gas, and the resulting spent scrubbing liquid is handled by conventional wastewater treatment. It contains a high concentration of dissolved solids and salts and has a high chemical oxygen demand (COD). To date, scrubbers for controlling SO_x from FCC regeneration have been used only where wastewater can be discharged into the ocean after treatment. A 50,000 bbl/d FCCU charging a feed with 2 weight percent sulfur would generate as much as 60-70 tons of sludge per day.[43]

Boilers and Process Heaters--SO_x Removal

Emissions of SO_x from boilers and process heaters can be minimized by routing the flue gas to an integrated sulfur removal facility. Post-combustion removal of SO_x from boiler and heater flue gases using an integrated collection system of course poses serious safety and economic barriers. Pre-startup firebox purging would be extremely difficult and time consuming. Cost of ducting would probably be economically prohibitive. Two such units are the IFP-150 and the Aqua-Claus process described in Table 8.

NO_x Removal

NO_x emissions may be reduced in the tail gas by any of three methods. These methods are 1) gas scrubbing, 2) catalytic reduction, and 3) thermal reduction with added ammonia. Post-combustion NO_x removal tends to be more expensive than combustion modification because of the high temperature of the gas, the low NO_x concentration, interference from other pollutants, and high power consumption. Only thermal reduction appears economically promising.[44]

Controlled addition of ammonia and oxygen containing flue gas under strictly controlled conditions at 1300 to 1900°F can selectively reduce 50 to 70 percent of the NO_x remaining after combustion. This "thermal denox" process is a balance between two gas-phase reactions: ammonia reduces NO to N_2 in the presence of the oxygen in the flue gas and ammonia is simultaneously oxidized to NO. When conditions are carefully controlled, a major portion of the NO_x can be reduced with little ammonia left over. This process is more expensive than combustion modification but can supplement these modifications should stricter control of NO_x be required.

Control Technology from Other Industries

Control methods developed primarily for other industries can also be used in the petroleum refining industry with some degree of adaptation. This is especially true of methods developed by the electric utility industry for flue gas desulfurization. Some can be applied to the flue gas from a Claus incinerator; another with accompanying NO_x control can be adapted to the flue gases from process heaters; still others might be used to control sulfur emissions from FCC regenerators.

Sulfur Recovery

Table 9 outlines several sulfur recovery processes from other industries which might be adapted to Claus tail gas sulfur recovery. These sulfur recovery processes are described in greater detail in Radian's refinery emissions report. They do not uniformly meet NSPS for SO_2 emission.

TABLE 9. POTENTIAL CLAUS TAIL GAS SULFUR RECOVERY PROCESSES FROM OTHER INDUSTRIES

Process	Characteristics	H_2S or SO_2 Removal (%)		Treated Flue Gas SO_2 Concentration (ppmv)
Chiyoda Thoroughbred 101[45]	Gypsum product.	97	(SO_2)	>500
USBM Citrate[46]	Elemental sulfur product; capital = 250 percent of Claus cost. Not commercialized.	–	(SO_2)	–
Townsend[47,48]	Elemental sulfur product. Does not remove CS_2. Not commercialized.	–	(H_2S)	–
Lucas[49,50]	SO_2 product is recycled. Capital = 57–80 percent of Claus cost. Semi-commercial.	–	(SO_2)	200 (+ COS, CS_2)
Takahak[51]	Elemental sulfur product. Allegedly low capital cost.	≤99.9	(H_2S)	

Catalyst Regeneration

Several FGD methods used by the utility industry have been proposed for use on FCC regenerators.[52] In addition to the ones described below are some of the regenerable processes touched on earlier, as applicable for treatment of the Claus unit tail gas. One of the processes described below simultaneously removes SO_X and particulates from the flue gas.

The Lime/Limestone Flue Gas Desulfurization Process[53]--

Lime or limestone flue gas desulfurization processes are the most widely used FGD systems. The systems are very similar; they consume large quantities of feed material and produce large quantities of waste sludge, but have relatively low operating costs and are highly reliable. An SO_2 removal efficiency of greater than 90 percent has been demonstrated.

The economics of large lime/limestone FGD systems has been treated in great detail.[54]

The Dual Alkali Flue Gas Desulfurization Process[55]--

The dual alkali (or double alkali) flue gas desulfurization process can be used to overcome the scaling problem inherent in lime/limestone FGD systems while retaining the convenience of solid waste disposal. There are 53 operating dual alkali systems in the United States and Japan; several more are under construction.

These systems can achieve SO_2 removal efficiencies of greater than 90 percent. The capacity for more than 99 percent removal of SO_2 has been demonstrated. The dual alkali process itself is capable of greater than 98 percent particle removal.

Dual alkali systems are economically competitive with lime/limestone systems; however, a larger disposal area will be required than for a lime/limestone system because of the higher moisture content of dual alkali sludge.

Boilers and Process Heaters

The Shell flue gas desulfurization process (SFGD) can be used to remove SO_X and NO_X simultaneously from all stack gas in process heaters, providing they can be collected and sent to one or two stacks. The SFGD process can also be used to remove sulfur from the vent of fluid cat crackers, as well as from Claus units.[56,57,58]

The Shell flue gas treatment process has demonstrated SO_2 and NO_X removal efficiencies of greater than 90 percent. The efficiency of the system is not affected by variations in the SO_2 or NO_X concentration. Costs for an integrated SFGD system are not available, because such a system has not yet been built at a U.S. installation.

The processes proposed for control of SO_2 emission from FCCU regenerators may possibly be applied to flue gases from boilers and process heaters as well as from a Claus unit.

Emission Reduction Through Alternative Operating Practices and Conditions

Refinery operations are routinely modified to meet product specification requirements, product marketing trends, feedstock availability constraints, and operating cost goals. The operating choices made include both deliberate actions concerning processing alternatives (such as which catalyst to use or which cut point to pick) and more subtle actions, mainly in the energy conservation areas (such as attention to steam leaks or furnace efficiency). These choices can also affect the overall refinery emissions.

This subsection summarizes the effects on emissions of some of these alternative operating practices.

High Temperature FCCU Catalyst Regeneration[59,60,61,62,63]

In older FCCU regenerators, the highly exothermic oxidation of CO to CO_2 is avoided because the resulting high temperature can damage regenerator equipment, permanently deactivate the catalyst, and damage downstream equipment. To avoid this oxidation, the flue gas from the regenerator generally contains little oxygen and large, nearly equal, amounts of CO and CO_2.

With high temperature regeneration, coke is burned from the catalyst more efficiently, therefore yield from the FCC unit is increased. The carbon monoxide level in the exit gas from the regenerator can be reduced to well below 500 ppm; in many instances a CO boiler is no longer necessary for emission control. Because the catalyst to the FCC unit is hotter, preheat of the feed to the unit may not be necessary. (Five hundred ppm of CO corresponds to the NSPS limit.)

Several new catalysts, or promoters, have been introduced in the last several years to promote the combustion of CO to CO_2. A promoter may be chosen to promote complete combustion or partial combustion where metallurgy cannot withstand the higher temperatures. Partial combustion can also be used in situations where the CO is needed as fuel.

One type of noble metal promoter is made part of the catalyst recipe. A second type is a liquid injected into the regenerator combination zone. The third is a solid added to makeup catalyst.

In situations where partial combustion is needed, it is possible to combine high temperature regeneration with the CO boiler. For this combined operation, the degree of high-temperature regeneration, and the final temperature, can be controlled by the amount of promoter used. Higher regenerator outlet temperature partially compensates for the reduced quantity of CO reaching the CO boiler. Supplemental fuel to

the boiler is still required, but its cost is offset by the increased product yields in the FCC unit.

In 1975, the cost of converting a relatively modern FCCU with stainless steel cyclones to high-temperature regeneration was $50,000 to $300,000. Cost of a CO boiler for the unit was perhaps $2 million to $3 million.

SO_x Removal in the FCC Regenerator

Amoco has developed a catalyst which prevents sulfur from leaving the regenerator as SO_2. The catalyst holds the sulfur until it is returned to the reactor, where it is released and converted to H_2S. The H_2S leaves the reactor with the cracked product and is later converted to sulfur in the Claus plant; the regenerated catalyst returns to the regenerator.

Cost for a 60-75 percent reduction in SO_x emissions with this method in a new facility is estimated at $0.03/bbl, compared to $0.22-0.24/bbl for stack-gas scrubbing and up to $0.27/bbl for feed hydrodesulfurization. The use of the catalyst for SO_x control is also less expensive than other methods in retrofit applications.

Combustion Modification for Control of NO_x[64,65,66]

Of the oxides of nitrogen, only NO and NO_2 are of environmental concern. In combustion sources, NO may be produced either by the fixation of atmospheric nitrogen in the flame (thermal NO_x) or by the oxidation of a portion of the nitrogen in the fuel (fuel NO_x). NO_2 from combustion sources is produced as the NO combines with oxygen in the atmosphere. Refining sources of thermal NO_x and fuel NO_x are given in Table 10.

A number of specific combustion modifications for NO_x control have been devised. Those for refinery boilers are summarized in Table 11. Combinations of these methods have been shown to yield a smaller effect than the sums of the effects from the individual technologies. The effectiveness of some of the individual methods and some combinations at different boiler loads are shown in Table 12.

The subject of combustion modification is covered in greater detail in the refinery emissions report.

CONTROL OF FUGITIVE EMISSIONS

Sources of Fugitive Emissions

Sources Tested in This Study

The hydrocarbon (HC) emission factors developed in this study for valves, flanges, pump seals, compressor seals, drains and relief valves have reasonable confidence limits. Confidence limits for oil-water separator and

TABLE 10. REFINING SOURCES OF THERMAL NO_x AND FUEL NO_x

Classification	Source	Thermal NO_x	Fuel NO_x
High Temperature	Power boilers firing - gas	Present	Possible
	Power boilers firing - oil	Present	Present
	Power boilers firing - coal	Present	Strong
Internal Combustion	Engines	Present	Unlikely
	Turbines	Strong	Possible
Moderate Temperature	CO boilers	Present	Present
	Coke and residual fuels	Present	Present
	Catalyst regeneration	Unlikely	Present
	Incineration	Present	Present
	Process Heating		
	Gas cracking	Present	Possible
	Oil cracking	Unlikely	Possible
	Oil heating	Unlikely	Possible

TABLE 11.   BOILER COMBUSTION MODIFICATIONS FOR REDUCTION OF NOx EMISSIONS

METHOD	EFFECTS	GAS FIRED UNITS	OIL FIRED UNITS
Low excess air	Rating	Good	Good
	Advantages	Improved efficiency; less power	Improved efficiency; less power; less chance of cold end deposits
	Disadvantages	More complex ducts and controls	More complex ducts and controls
Flue gas recirculation	Rating	Excellent	Good
	Advantages	Very effective; does not upset combustion	In moderation does not upset combustion
	Disadvantages	High initial cost; high operating cost; additional controls	High initial cost; high operating cost; additional controls; works mainly on thermal NO_x
Staged combustion	Rating	Excellent	Very good
	Advantages	Inexpensive; very effective	Inexpensive; moderately effective
Two-stage combustion with over-fire air ports	Disadvantages	Longer flames; slight increase in excess air	Longer flames; slight increase in excess air

(Continued)

TABLE 11. Continued

METHOD	EFFECTS	GAS FIRED UNITS	OIL FIRED UNITS
Staged combustion (Cont'd)	Rating	Very good	Good
	Advantages	No power; effective	No power; moderately effective
Off-stoichiometric or Biased firing			
	Disadvantages	Slightly longer flames; small increase in excess air	Slightly longer flames; small increase in excess air
	Rating	Fair	Fair
Direct cooling Lower preheat or Water injection	Advantages	Simple; no power	Simple; no power
	Disadvantages	Reduced unit efficiency; require equipment	Reduced unit efficiency; require equipment
	Rating	Very good	Very good
Reduced load or Oversized fire box	Advantages	Simple; no power	Simple; no power
	Disadvantages	High initial cost	High initial cost; more radiant super-heater
	Rating	Good	Very good
Burner modifications	Advantages	Simple; no power	Simple; no power
	Disadvantages	None	None

TABLE 12. REDUCTIONS OF NO_x EMISSIONS WITH COMBUSTION MODIFICATIONS AT VARIOUS BOILER LOADS[67]

| Combustion Modification (Percent Full Load) | | Percent Reduction in NO_x Emissions | | | | | | | | | | | | | | |
| Fuel Fired | Burner Arrangement | Low Excess Air | | | Staging | | | Low Excess Air and Staging | | | Flue Gas Recirculation | | | Possible Combined[a] Modifications | | |
		85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60
Gas	Front Wall Horizontally	13	24	7	37	30	30	48	42	36	–	–	–	43	42	36
	Opposed	17	15	32	54	35	59	61	48	68	–	–	20	73	52	72
	Tangential	–	–	–	–	–	–	–	–	–	–	60	–	66	65	–
	Average	16	19	26	45	31	52	54	44	52	–	60	20	64	51	60
Oil	Front Wall Horizontally	27	20	28	29	20	20	39	32	21	46	31	–	50	41	21
	Opposed	10	16	12	34	34	47	35	44	42	–	–	–	38	35	55
	Tangential	28	22	–	–	17	–	–	45	–	10	13	–	–	59	–
	Average	19	19	18	30	22	34	38	37	37	28	23	–	47	42	38

[a]Possible combination of modifications on the boilers tested.

cooling tower emission factors were considerably broader; as a result, data from other sources have been substituted in Table 13 for results from the latter two systems.

Relative Importance of Fugitive Emission Sources

Table 13 lists emitting sources in refineries. All the types of emission sources listed were field-monitored except for numerically rare items or those sources otherwise deemed insignificant. Table 14 ranks the eight most important emission sources according to the total estimated HC losses from a hypothetical refinery.[68] Emission factors are compared to current literature values. Results show that process valves are typically the largest fugitive emission source because of their great number in the refinery.

The oil-water separator is ranked second in importance in fugitive hydrocarbon emissions based upon previous work (see Table 14 footnotes). Additional field measurements and/or improved analytical techniques may be required to obtain satisfactory confidence limits for separator emission factors because of the variability of waste oil vapor pressures, composition, rates, wind effects, etc. from day to day and from refinery to refinery. Controlled testing of a covered simulated separator gave results which would lower the estimated emission from the AP-42 based value of 110.5 lb/hr to 20.6 lb/hr.[69]

Cooling towers are also temporarily ranked high in HC emissions. The broad emission factor confidence limits found may be a result of real differences among cooling towers tested, or may reflect analytical imprecision resulting from having to analyze water-dissolved hydrocarbons in the 1-5 ppm range. Additional field work in this area may be justified.

Pump and compressor seal emission factors are averages for their respective arrays, as listed in Table 13. Types include packed gland, mechanical face, labyrinth and oil seals, for both rotary and reciprocating shaft types, where applicable. There were an average of about 1.4 seals per pump in the refineries surveyed, and 2.0 seals per compressor.[70]

The emission factor for equipment drains is a useful addition to the literature (0.070 lb/(hr-drain)) because no other factor has been available except in combination with one for oil-water separators.

Pipe flanges constitute the next to smallest fugitive emission source, even with the largest estimated total number of devices. The emission factor is 0.00058 lb/(hr-flange).

Relief valves contribute the least total HC emission, because of their relatively small number, but have a significant emission factor (0.190 lb/(hr-relief valve).

TABLE 13. FUGITIVE EMISSION SOURCES

System or Device	Number of Devices	Estimated Total Emissions, [a] lb/hr[b]
Process Piping System		
Valves	11,650	289.50
Flanges	46,520	26.98
Safety Relief Valves	106	20.14
Agitator Seals (Hydraulic, lip, packed, mechanical)	Not Measured	
Pump Seals	353[c]	57.63
Rotaty Shaft		
Mechanical Face		
Packed Gland		
Reciprocating Shaft		
Packed Gland		
Compressor Seals	68[d]	45.46
Rotary Shaft		
Labyrinth		
Oil		
Mechanical Face		
Reciprocating Shaft		
Packed Gland		
Water Systems		
Wastewater Systems		
Drains - Process and Storm	647	45.29
Primary Treatment - API separator, CPI[e] (covered)	1	21[e]
Intermediate Treatment - Air flotation, holding basin	Air Flot. Units tested; results statistically inconclusive	
Secondary Treatment - Biological oxidation processes	Not Tested	
Tertiary Treatment - Carbon absorption, filtration, ion exchange, reverse osmosis		
Cooling Water System - Cooling Towers	∿5[a]	113.3[f]
Solid Waste System Alternatives	Not Tested	
Land Farming	1 Site	0[g]
Total Fugitive HC Emissions, lb/hr		618.3
(lb/bbl feed)		(0.045)

[a] Estimated from data in Reference 71.
[b] Basis: 330,000 BCD hypothetical refinery, Reference 72.
[c] Basis: 1.4 seals (Av.) per pump, Reference 73.
[d] Basis: 2.0 seals (Av.) per compressor, Reference 74.
[e] Data from Reference 69.
[f] Based on 6 lb HC/10^6 gal H_2O (Reference 76) and 0.954 gpm circ. ÷ B/D crude feed (Reference 77).
[g] Reference 78.

TABLE 14.   FUGITIVE AIR EMISSION RANKINGS - HYPOTHETICAL 330,000 B/D REFINERY

Item (Device or System)	This Study		Emission Factor, lb/hr-item	
	Total HC Emission, lb/hr	Number of Items	This Study	Other Source
Process Valves	289.5	11,650	0.0248	0.00625[a]
Oil-Water Separator Uncovered	178	1	12.9 lb/10^3 bbl[i]	252 lb/10^3 bbl[b,c,i]
Oil-Water Separator Covered	20.6	1	1.5 lb/10^3 bbl[i]	9.6 lb/10^3 bbl[b,c,i]
Cooling Towers	2.04[g,h]	5[d]	0.408	22.7[b,d]
Pump Seals	57.63	353	0.163	0.175[a]
Compressor Seals	45.46	68	0.669	0.354[a]
Drains	45.29	647	0.070	N/A
Pipe Flanges	26.98	46,520	0.000580[f]	0.00625[e]
Relief Valves	20.14	106	0.190	0.100[e]

[a]Reference 79.
[b]Reference 80.
[c]Reference 81.
[d]Reference 82.
[e]Reference 83.
[f]The pipe flange emission factor is in units of lb/hr-flange pair.
[g]Based upon purge method.
[h]Equivalent to 0.108 and 12.4 lb HC/10^6 gal C.W. circulation and 0.954 gpm circulation of C.W./B/D crude oil feed.
[i]Bbl implies bbl of refinery crude oil feed.

Control Technology - Fugitive Emissions

Process Valves

Existing Levels of Control in Refineries: Process Valves--

Types of Valves--Process valve technology, per se, will not be covered here; instead, the focus will be on valve seals. Excellent recent valve technology review articles are available; one such is recommended.[84] With the exception of the check, plug, and diaphragm valve, valves are generally equipped with packed stem seals to prevent the working fluid from leaking to the atmosphere.

Packed Stem Seals--Figure 2 is a simplified diagram of the type of packed seal used for valve stems. In practice, the stuffing box is filled with rings of one or more types of compliant packing material. The packing gland is gently forced against the packing by tightening the bolts or studs connecting the packing gland to the stuffing box flange (bolts not shown). Upon being compressed, the packing material is forced against the stem or shaft, forming a snug seal face (see figure). This concentric contact seals the working fluid from the atmosphere.
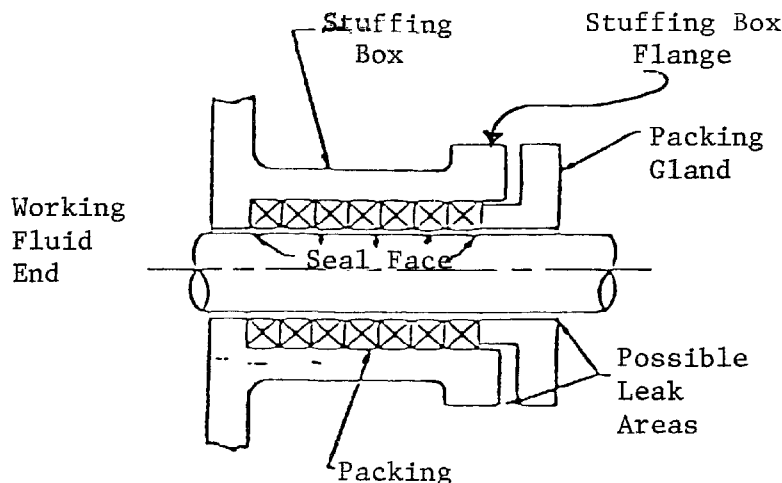
Figure 2. Simple packed seal.

Packing Materials--Table 15 shows the diversity of materials used alone or in combination.[85] The following trends in packings have been noted:

- Asbestos packing may continue to be used in high temperature service, especially with metal wire core, but is being displaced by TFE, TFE-filled glass fibers, etc., up to about 450-500°F (TFE = "Teflon"®).

- Graphite "ribbon" packing, which may be die-formed or formed in the stuffing box, is currently used in high temperature, high pressure service up to 4000 psi and 1200°F.

Control Valve Packings (High Temperature Steam Service)--One investigator reported poor results using ribbon graphite packing alone. The sliding stem of the control valve, after gland tightening, was roughened, friction was excessive, and after as few as 800 cycles, leakage exceeded the target limit of 0.5 cc/hr for a 0.5 in diameter stem.[86] By sandwiching laminated rings of graphite packing between layers of braided graphite filament packing, the former acting to control fluid loss parallel to, and along, the stem, and the latter acting to polish the stem, the life of the packing was extended to over 47,000 cycles before leakage exceeded 0.5 cc/hr. This cycle endurance is roughly equivalent to the mechanical life of many valves, so such a valve might never require repacking of the stem.[87]

Frequency of Application: Valves--

Process Valve Types--Table 16 lists the approximate distribution of Battery Limits refinery valves within two broad categories (manual and control) and by valve configuration. Radian's battery limits survey shows that 86 percent of all manual valves are gate valves, and 92 percent of the control valves are globe-type. The nine-refinery survey shows that these two categories, manual gate valves and controlled globe valves, make up 88 percent of all refinery valves.

Packed Seals--Radian's refinery observations further showed that all the gate-, globe- and butterfly valves catalogued had packed-gland stem seals. These packed-stem valves constitute an estimated 94.2 percent of the process valve population. On the basis of emission factors found in Table 14, it can be shown that, on the average, 95.5 percent of the total emission from a flanged in-line valve will be from the packing gland, and only 4.5 percent from the two flanges. Hence, the emphasis in valve emission control for existing valves must be to select proper monitoring, operating, and maintenance schedules and procedures, as well as suitable packings, for the packed-stem seals.

Effectiveness of Existing Levels of Control: Valves--

Factors Affecting Emission Rate--An established plant with a valve emission problem will seldom in practice solve it by changing the fluid conditions or the valve type. The valve originally selected will instead have been

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TABLE 15. PACKING MATERIALS - PROCESS VALVES[88]

Packing Material	Form	Used For	Temperature
Flexible, all metallic	Spiral wrapping. Thin ribbons of soft babbit foil.	Valve stem	Up to 450°F.
Flexible metallic packings (aluminum).	Spiral wrapping. Thin ribbons of soft annealed aluminum foil loosely around a small core of pure dry asbestos.	Hot oil valves, diphenyl valves.	Up to 1000°F.
Flexible metallic packing (copper).	Soft annealed copper foil loosely around a small core of pure dry asbestos.	Hot oil valves, diphenyl valves.	Up to 1000°F.
Long-fiber pure asbestos and fine lubricating graphite (nonmetallic).	Graphite special long-fiber asbestos binder.	Extreme resilience.	Up to 750°F.
Closely braided asbestos yarn, top jacket reinforced with Inconel wire; core: long fiber asbestos.	Spools, die-formed rings.	High-temperature valves.	Up to 1200°F.
Pure asbestos yarn with an Inconel wire insert around a resilient asbestos core impregnated with graphite.	Spool form, die formed.	Valve stem for air, water steam and mineral oil.	Stuffing box temperature up to 1200°F.
Twisted long fiber Canadian asbestos.	Spool form, die formed.	Valves handling, high and low pressure steam.	Up to 500°F.

(Continued)

TABLE 15.   Continued

Packing Material	Form	Used For	Temperature
Asbestos, graphite and oilproof binder.	Spool form, die formed.	Shutoff valves.	Up to 550°F.
Solid, braided TFE.	Coil, spool, ring.	Valve shaft for highly corrosive service.	100°F to 500°F.
Braided asbestos with complete impregnation of TFE.	Coil, spool, ring.	Valve stems in mild chemical or solvent service.	100°F to 600°F.
Braided of high quality wire-inserted asbestos over a loose core of graphite and asbestos.	Coils, spools.	Valve stems, steam, air, mineral oil.	Up to 1200°F.
Braided of high quality wire-inserted asbestos over a loose core of graphite.	Coils, spools.	Stainless-steel valve stems, air, steam, water.	Up to 1200°F.
Braided of long-fiber Canadian asbestos yarn each strand impregnated with heat-resistant lubricant.	Coils, spools.	Valves for steam, air, gas and mild chemicals.	Up to 550°F.
Long-fiber Canadian asbestos yarn, each strand treated with a synthetic oilproof binder and impregnated with dry graphite.	Coils, spools.	Refinery valves.	To 750°F.

(Continued)

TABLE 15. Continued

Packing Material	Form	Used For	Temperature
Braided/overbraided, wire-inserted, white asbestos packing impregnated with a heat-resistant lubricant.	Coils, spools.	Valve stems, for valves handling steam, air, gas cresylic acid.	Up to 750°F.
Braided white asbestos yarn impregnated with TFE suspensoid.	Coils, spools.	Valve stems.	100°F to 600°F.
Braided or bleached TFE multi-filament yarn.	Spools, coils.	Valve stems for highly corrosive liquids.	12°F to 500°F.
Braided TFE multifilament yarn impregnated with TFE suspensoid.	Spools, coils.	Valve stems for corrosive chemicals, solvents, gases.	120°F to 600°F.
Asbestos jacket, braided over a dry-lubricated plastic core of asbestos graphite and elastomers.	Spools and coils.	Valve stems, for valves handling superheated steam, hot gases.	Up to 850°F.

TABLE 16. APPROXIMATE DISTRIBUTION OF REFINERY PROCESS VALVES[a]
BY TYPE AND SERVICE

| Type Valve | Service | | Total |
	Manual	Control	
Gate	64.7	0.0	64.7
Globe	3.8	23.3	27.0
Plug	5.7	0.0	5.7
Butterfly	0.6	1.8	2.5
Diaphragm	0.0	0.1	0.1
Total	74.8	25.2	100.0

[a] Check and sample system valves excluded. No dry-service slide valves surveyed (Radian statistical survey basis).

chosen to fit the fluid flow conditions. It will further have been based upon economy of operation and safety in accordance with API code. The latter factor of safety, particularly with regard to potential failure in a fire, cannot be overemphasized.

Actions most apt to be used to solve or attenuate leakage, listed in increasing order of cost, are as follows:

1) Tighten packing gland;

2) Lubricate lantern ring (packed stem valve) or plug (plug valve);

3) Replace or change type of packing;

4) Replace or change type of valve.

Operations/Maintenance Cooperation--Many companies require operating personnel to check all major equipment once per shift or per day for leaks for purposes of economy and safety. Tightening and lubricating valves is routine.

Replacing valve packing is considered routine even though not all maintenance personnel are skilled at it. A change in type of packing materials is not generally costly. The cost breakdown for machinery packing (probably a pump) outage is:[89]

Item	Percent of Cost
Packing Material	3
Labor to Pack	13
Fluid Loss	21
Downtime	63
Total	100

Statistical Results and Rationale for Results--Table 14 showed the average valve emission factor for the valve mix in a 330,000 BPCD refinery to be 0.0248 lb/(hr-valve). Emission rate was interestingly only weakly dependent on valve size. Rationale might be:

1) Small valves have shallower stuffing boxes than large valves, so leak more for their stem size than large valves.

2) Large valves may get more maintenance and operation attention than small valves.

3) Large valves may be manufactured to closer tolerances than small valves.

Point 1 may be an area for improvement in valve design. Aside from retooling costs, the overall cost of small valves should not be increased significantly by deepening the stuffing box. Points 2 and 3 are speculative.

Available Control Technology for Fugitive Emissions in the Refining Industry: Valves--

Types of Controls Available for Valves: "Packless" Seals--The following types of valve seals are not apparently used in refineries based upon our survey:

• Diaphragm bonnet seal,

• Bellows bonnet seal.

These packless seals when correctly applied in noncritical, low-stress conditions of temperature, pressure or corrosivity (in the case of the bellows seal) should approach zero leakage. The diaphragm material in the first valve shown limits operation to about 50 psi pressure differential.[90] This type valve has definite limitations in refinery use; it would fail catastrophically upon overheating of the elastomer diaphragm, so use would not include hydrocarbon service where a fire could be fed by failure. The bellows-sealed valve, because of the corrosion and fatigue failure potential of the bellows, is limited in its use by combined temperature-pressure-corrosivity stress, which level is best defined by the valve manufacturer. Back-up stem packing would appear to be absolutely necessary for these valves in case of diaphragm or bellows failure.

Valve Maintenance Programs--Valve monitoring and maintenance programs can be an effective method for reducing valve emissions. These programs and their effectiveness are discussed in detail in another paper of this symposium.

Energy Requirements: Valves--No primary energy cost would result from substitution of a very limited number of packless valves for conventional packed-stem, bonnet-sealed valves. As to a valve maintenance program, incremental manpower requirement would probably be necessary if refineries not already doing so were to begin comprehensive periodic inspections.

Cost-Available Refinery Technology--Estimates for the substitution of packless valves for packed-stem valves range from 150-367 percent[91] to 1000-2000 percent[92] of packed stem valve cost. Application of packless valves (diaphragm-sealed; bellows-sealed) in critical services is not seen as probable because of problems associated with valve failure, so economic impact is correspondingly nil.

Because the long-term effects of valve maintenance are not yet clearly defined, costs of a valve maintenance program have not been developed. Any valve maintenance program would probably be more burdensome to the small

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refiner, because the number of valves inspected/maintained per unit throughput
will be higher for small refineries.

Control Technology from Associated Industries: Valves--

Ball valves may possibly find broad use in refining, but with TFE
and TFE-filled fiber seats, are limited to use below about 450°F. They were
not available in statistically significant numbers in this study, so their
field-tested emission factors are not available.

Development Needs: Valves--Short-term, there appears to be a need for a
small packed-stem valve with a deeper stuffing box than is currently
available.[93]

Pump Seals

Existing Levels of Fugitive Emission Control in Refineries: Pump Seals--

Types of Pump Seals--This survey showed that refinery pump-seal combinations
almost exclusively fall into one of three broad categories:

		Percent of Population
A.	Centrifugal Pump - Mechanical Seal	82.1
B.	Centrifugal Pump - Packed Seal	11.5
C.	Reciprocating Pump - Packed Seal	6.4
	Total	100.0

These seals are depicted in rudimentary form in Figure 3.

The packed seal, Figure 3(A), is used to seal both rotary and
reciprocating shafts against leakage of liquid from the "working fluid" end
of the shafts to the atmosphere. Compressed packing in the stuffing box
forms a contact seal against the moving drive shaft. High-speed friction
resulting from this contact requires that either the working fluid be
allowed to leak from the stuffing box housing the packed shaft, or a
supplementary liquid be introduced to remove frictional heat. A typical
leak rate would be 60 drops per minute ($\sim$3 ml per minute).[94]

Mechanical seal application, contrary to the broader applicability
of packed seals to both rotating and reciprocating shafts, is limited to use
on rotary shafts. Mechanical seals may be used to seal both pump and com-
pressor shafts, but are more universally applied to pumps, specifically
centrifugal pumps.

Packings - Service limits for selected packings are found in
Table 17.

a. Mechanical packing
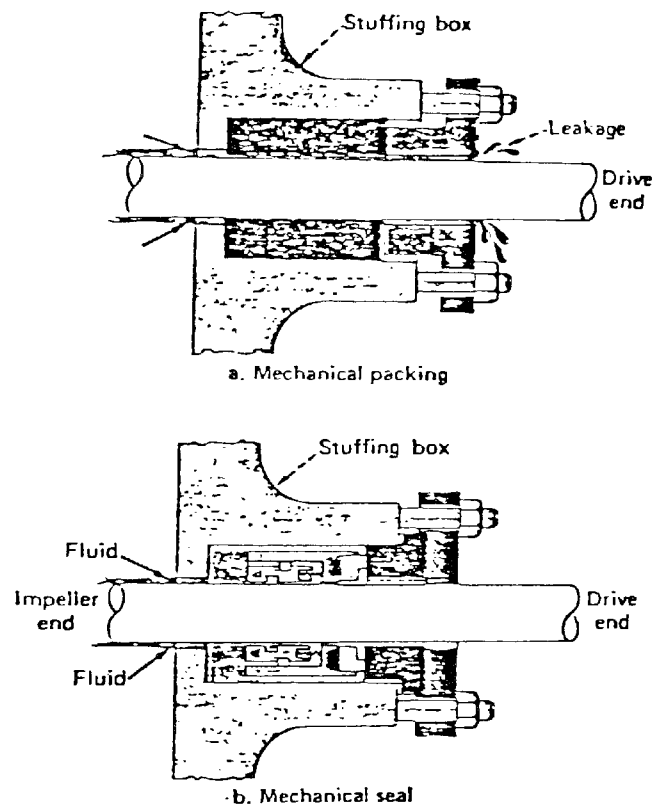
b. Mechanical seal

Figure 3. Common pump seals - simplified.

TABLE 17. SERVICE LIMITS FOR SELECTED MECHANICAL PACKINGS[a,95]

Packing	Break-In Leakage[b] (drops/min)	Running Leakage[b] (drops/min)	Maximum Temperature[c] (°F)	Pressure at Maximum Temperature[c] (psig)	Maximum Pressure[c] (psig)	Temperature At Maximum Pressure[c] (°F)
Asbestos/TFE	120	60	500	50	200	100
TFE (lubed)	120	60	500	50	200	100
Asbestos/Graphite		60	400	50	250	100
Graphite-Fiber		60	1000 (600)[d]	50	350	300
Graphite-Ribbon		60	1000 (600)[d]	50	350	‚300
Lead		60	350	50	400[e]	100
Aluminum		60	800 (500)[d]	50	400[e]	200
Inconel-Reinforced Asbestos Over Resilient Core[f]			1200	Unknown		

[a] Basic data: 2-in shaft, 3550 rpm. Controlled leakage for 720 hr Pumped liquid is water. Assumes maximum ΔT of 100°F (50°F for flax) due to shaft friction. Satisfactory results can be expected by using these maximum limits and following FSA (Fluid Sealing Assn.) Test Procedure #1.

[b] Leakage rate: 1 ml/min = 10 to 20 drops/min.

[c] Temperature is product temperature; pressure is stuffing-box pressure.

[d] Larger number is nonoxidizing environment; smaller number is oxidizing environment.

[e] Assumes rings are die-formed.

[f] For low-speed shafts only. (Green, Tweed and Company).

Lubricants for packings include the following substances:[96]

- Mica and talc

- Graphite

- Molybdenum disulfide (MoS_2)

- Hydrocarbon type lubricants (greases, tallow, petroleum oils)

- Tungsten disulfide

- TFE

- Silicone oils.

Mechanical seals – The mechanical seal in its many forms is the predominant pump seal today. At the time of the Los Angeles County, California study twenty years ago, mechanical seals made up only 42 percent of the seals in use there.[97] Radian's survey revealed that by 1978, approximately 82 percent of the refinery pump seals were mechanical type.

Mechanical seals are prefabricated assemblies which shift the point of wear from the drive shaft, as with packed seals, to easily-replaced pairs of rings, one of which is attached to the pump shaft, and the other to the gland plate or its equivalent. Seal faces are perpendicular to the shaft as shown in Figure 4. Faces are typically lapped to a flatness of two microns which accounts for their typically low leak rate when carefully installed, started up and flushed properly.

Double mechanical seals provide a margin of protection against seal failure not offered by single mechanical seals.

If the inner seal should fail, the outer seal prevents escaping fluid from reaching the atmosphere; in case of accidental pressure loss in the seal liquid system, however, the pumped liquid will contaminate the seal liquid. If the seal liquid is contained within a pressurized "seal pot" system, the problem of contaminated seal liquid cleanup is minimized.

Frequency of Application of Pump Seals--The hypothetical refinery mentioned much earlier in this paper (Table 14) was seen to emit an estimated 57.63 lb/hr from 353 pump seals for a weighted emission factor of 0.163 lb/(hr-pump seal). This total HC emission rate places pump seals fourth in importance among the process-related fugitive emissions studied by Radian.
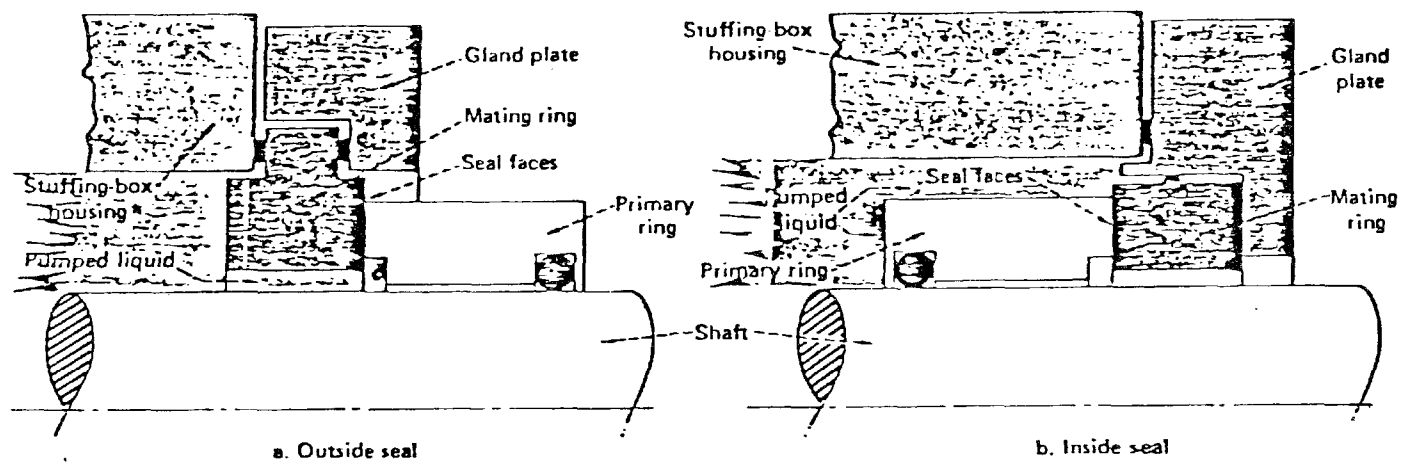
Figure 4. Location of primary ring determines seal type.

Table 18 is a comparison of seal distributions and emission factors taken from the 1958 California Study[98] and the current refinery survey.[99] In 1958, the percentages of mechanical and packed seals on pumps clearly favored packed seals:

Centrifugal Pumps, Packed Seals	34.7%
Reciprocating Pumps, Packed Seals	23.1
Subtotal Packed Seals	57.8
Centrifugal Pumps, Mechanical Seals	42.2
Total	100.0

By 1978 the percentage of mechanical seals used in refineries had almost doubled; approximately 82 percent of the seals were by then mechanical type. The Radian survey showed this percentage to be further subdivided into approximately 67 percent single mechanical seals and 15 percent double mechanical seals. No further subdivisions were made.

Effectiveness of Existing Levels of Control in Refineries--Table 18 reveals that the overall pump seal emission factor has improved slightly over 20 years from 0.17 lb/hr-seal to 0.16 lb/hr-seal.

Pump seal emission factors as shown in Table 18 should not be used injudiciously without referring to the detailed results and statistical analyses as found in the Final Report of this study. To illustrate the reasoning behind this statement, refer to Table 19. First, there is little doubt that pump seals in light liquid service emit hydrocarbons at a higher rate than those in heavy liquid service (0.256 vs. 0.046). The two emission factor confidence intervals do not overlap, adding validity to the estimated factors (0.17-0.39 vs. 0.02-0.11). By contrast, the emission factor confidence intervals for the three major seal types do overlap, meaning that within the limits of certainty (95 percent), all three classes of pump seals could have identical emission factors. These broad confidence limits were characteristic of the emission factors statistically separated according to type of seal, regardless of whether the emission factors were analyzed within stream types (light vs. heavy hydrocarbons) or not. One factor in the history of mechanical seal applications should not be overlooked. Typically, they were applied first in those services which presented the greatest emission problems: especially high pressure, high vapor pressure liquids with little self-lubrication.

Available Control Technology in the Refining Industry: Pump Seals--

Types--Application of the types of pump seals already described is relatively uniform within the refining industry. This may be the result of a greater uniformity of feedstocks and products than, say, the chemical industry uses and produces. The application of standards published by the American Petroleum Institute (API) has also undoubtedly led to uniformity among

TABLE 18. DISTRIBUTION OF TYPES OF, AND EMISSION FACTORS FOR, REFINERY PUMP SEALS

Seal Type	(Source) 1958[a]		(This Study) 1978[b]	
	Distribution (%)	Emission Factor (lb/hr-seal)	Distribution (%)	Emission Factor (lb/hr-seal)
Rotary Shaft (Centrifugal)				
Mechanical - Single			67.1	0.19[c]
Mechanical - Double			15.0	0.15[c]
Subtotal	42.2	0.13	82.1	0.19
Packed	34.7	0.20	11.5	0.071
Reciprocating Shaft				
Packed	23.1	0.22	6.4	0.14
Total	100.0	0.17	100.0	0.16

[a]California joint refinery study among federal, state and Los Angeles District agencies.

[b]Percentages are based upon complete process unit surveys within each of nine refineries, but without random selection of unit types. Units selected are lsited in Interim Report. Emission factors are average from operational and standby pumps.

[c]Emission factor confidence limits for the three basic types of seals (centrifugal-packed, centrifugal-mechanical, reciprocating-packed) overlap to the extent that all three classes of seals could have identical emission factors.

TABLE 19. PUMP SEAL EMISSION FACTORS

Source Type	Total Number Screened	Total Leaking	Percent Leaking	97.5 Percent Confidence Interval	Estimated Emission Factor	95 Percent Confidence Interval For Emission Factor
Stream 2[a]	466	298	63.9	(58.9, 68.9)	0.256	(0.17, 0.39)
Stream 3[b]	290	66	22.7	(17.2, 28.2)	0.046	(0.02, 0.11)
Total	756					
Seal Type CM[c]	621	312	51.0	(46.5, 55.5)	0.187	(0.13, 0.29)
Seal Type CP[d]	87	32	36.8	(24.6, 47.8)	0.071	(0.02, 0.22)
Seal Type RP[e]	48	20	41.7	(24.8, 60.0)	0.141	(0.057, 0.69)
Total	756					
Stream 2 – CM	404	264	65.3	(59.9, 70.6)	0.263	(0.18, 0.41)
Stream 2 – CP	37	17	45.9	(26.3, 66.6)	0.082	(0.013, 0.34)
Stream 2 – RP	25	17	68.0	(41.9, 87.8)	0.248	(0.04, 1.2)
Total	466					
Stream 3 – CM	217	48	22.1	(15.7, 28.4)	0.044	(0.02, 0.12)
Stream 3 – CP	50	15	30.0	(15.6, 47.9)	0.041	(0.0083, 0.17)
Stream 3 – RP	23	3	13.0	(1.8, 38.5)	0.013	$(10^{-5}, 7.2)$
Total	290					

[a] Light liquids
[b] Heavy liquids
[c] CM = Centrifugal pump – mechanical seal
[d] CP = Centrifugal pump – packed seal
[e] RP = Reciprocating pump – packed seal

devices used to control fugitive emissions, not only from pumps, but also other devices surveyed by Radian.

Effectiveness--All refinery pump seal emission technology believed to be available today was found among the thirteen refineries surveyed, and the control effectiveness by seal type was reported in the preceding section. A detailed account of emission factor statistics is found in the Final Report of this study.

Energy Requirements and Relative Costs--Industry experience has shown that mechanical seals lose less frictional energy than packed seals. One seal manufacturer[100] reports the following relative friction losses:

Type Pump Seal	Average Power Requirement, kW	Annual Electrical Cost, $*
Balanced Single Mechanical	0.333...	105
Unbalanced Single Mechanical	0.400	126
Packed	2.00	630

* Cost Basis: 4¢/kWh, 90 percent stream factors, 24 hr/day (7884 hr operation/yr), seal frictional cost only.

The saving in energy from using mechanical seals is in addition to the savings from lower maintenance and operating attention expenses.

Control Technology from Associated Industries: Pumps--

Types--The only type of pump emission control expected, but not actually found, in the survey is exemplified by the hermetically-sealed, or "canned", centrifugal pump. The canned pump has both pump and (typically) electric driver sealed in one container, with pumped liquid circulating in coolant cavities for purposes of heat removal. Manufacturers advertise canned pumps ranging from 1 to 250 hp, heads to 1000 ft, capacities to 2,000 gpm, and fluid temperatures to 450°F.[101] The canned pump is not covered by API Standard 610 for pumps, which may in part explain their absence from refineries. Canned pumps are, however, used in other industries, particularly where emissions would be wasteful, hazardous, or polluting.[102]

If canned pumps are to be used in the refining industry, they must be proven performers in terms of leak-tightness, reliability, maintainability, useful life and safety; i.e., they must be overall cost effective.

Cost--The original cost of canned pumps is approximately 110-115 percent of the cost of a centrifugal pump with conventional seals.[103] This type of pump should prove leakproof. No data are available to discern differences among the other true costs of running conventionally-sealed vs. canned pumps.

Applicability to Refining Industry--The hermetically-sealed, or canned, pump may be applicable to refinery services assuming that this type pump has a

satisfactory long-term performance history. It would probably be necessary for the API to take a positive position on the inherent design and performance of this type pump before refiners would be willing to apply them.

Wastewater Systems

Existing Levels of Control in Refineries: Wastewater Systems--

Refinery wastewater systems vary tremendously in volume of process water, storm water, particulates, oil and grease, and other contaminants. Refinery wastewater systems also vary from one refinery to the next. About the only common denominator is an oil and water separator of the API or CPI type. As a result of variations in wastewater, reliable data for hydrocarbon emissions from refinery wastewater systems do not exist.

Variation in wastewater composition causes corresponding differences in fugitive emission rates. This was seen in emission measurements as reported in Radian's fugitive emissions report.

Despite the lack of reliable emissions data, control of fugitive emissions is not complex, because emissions consist primarily of hydrocarbons released from the collection system and oil-water separator.[104]

Characterization of Existing Wastewater Systems--Refinery wastewater systems have evolved over the years as people have become aware of water pollution problems, and as various treatment systems have been developed. The basic treatment steps may be summarized as follows:[105]

- Primary Separation - The removal of oil by gravity separation. Normally an API or CPI type separator is used.

- Intermediate Separation - The removal of suspended solids and additional oil by chemical sedimentation or air flotation.

- Secondary Treatment - The reduction of the biological oxygen demand (BOD) with some type of biochemical oxidation.

- Tertiary Treatment - Removal of dissolved organics which will not degrade with biological treatment methods. Carbon adsorption is the most common form of tertiary treatment.

Only the collection and primary separation systems will be discussed. Losses from intermediate, secondary, and tertiary treatment systems are small in comparison.

Since the fugitive emissions from refinery wastewater systems consist almost exclusively of hydrocarbon losses from the collection system and the oil and water separator, measurement and control strategies should be limited to these two areas. (One additional potential source of air pollution is the vent gas from the carbon regeneration system.[106] This

source probably does not produce a significant amount of fugitive emissions, but should be investigated more fully as the number of refineries using carbon adsorption increases.)

Estimated Hydrocarbon Losses to the Air--In 1958, hydrocarbon emissions from wastewater separators in existing refineries in the Los Angeles County area were estimated to range from 10 lb/1000 bbls refinery capacity to 200 lb/1000 bbls refinery capacity.[107]

The third edition of report AP-42 (August 1977) lists the relevant hydrocarbon emission factors as follows:

Process Drains

Uncontrolled	210 lb/1000 bbl wastewater
Vapor Recovery or Separator Covers	8 lb/1000 bbl wastewater

The relationship between wastewater flow rate and crude oil throughput has been shown to vary widely among refineries. Newer or updated refineries do a better job of segregating process water from storm water. The following ratios have been reported.[108]

Refinery Classification	Bbl Wastewater/Bbl Crude
Older	6.0
Typical	2.4
Newer	1.2

Another source gives a ratio of 0.8 barrels of wastewater per barrel of crude.[109] The original 1958 Los Angeles factors and the current AP-42 factors are very similar when a ratio of wastewater to crude of slightly over one is used.

Table 14 of this report ranks hydrocarbon emissions from oil and water separators as the second largest source of fugitive emissions from a refinery. This ranking is based on the emission factor for uncovered separators according to Litchfield.[110] Litchfield's reported emission rates for covered and uncovered separators were obtained under controlled conditions, and are reasonable bases (with modifications which are to be shown) for revising the AP-42 emission factors.[111]

Using the most recent information available, Arthur D. Little employed characteristics of raw and treated process wastewater to generate models of two base case refineries.[112] For a 200,000 BPD East/Gulf Coast refinery, the oil and grease in the API separator effluent was given as 1920 lb/day, or 9.6 lb/1000 bbls refinery capacity. For the 330,000 BPD hypothetical refinery in Radian's study, this factor gives 132 lb/hr oil and grease in the separator effluent water to the dissolved air flotation unit.

Separator removal efficiencies are reported to be 60 to 99 percent,[113] and 50 to 87 percent.[114] Using 87 percent as a typical high efficiency number, oil and grease rate to the separator becomes 1015 lb/hr, or 74 lb/10^3 bbl of crude oil to the refinery.

In a 1971 study (using laboratory data from a simulated API separator) by D. K. Litchfield of American Oil Company, evaporative losses of oil from API separators were found to average 16 volume percent without covers and two volume percent with covers of a cellular glass insulation (manufactured by Pittsburgh Corning) floating directly on the oil.[115] The two volume percent loss with covers is not affected significantly by air temperature because of the insulating effect of the cover. The evaporative oil loss from uncovered separators was found to vary with ambient temperature, influent temperature, and the 10 percent true boiling point of the oil. The 16 percent volume loss reported is for an average ambient temperature of 40.1°F, an average separator water temperature of 140°F, and an average 10 percent true boiling point of the oil of 300°F.

The average ambient temperature of 40.1°F is low for an estimate of maximum hydrocarbon emissions, so an average ambient temperature of 80°F will be used. Using an evaporation factor of 0.0319 volume percent per °F increase, the oil evaporation from an uncovered separator is 17.3 volume percent and the oil loss with covers remains around two volume percent.

These loss rates give hydrocarbon evaporation rates from the 330,000 BPD refinery of 178 lb/hr for uncovered separators and 20.6 lb/hr for covered separators. If these more recent studies are more representative than the initial work beginning with the Los Angeles studies, then the wastewater system hydrocarbon emission factors should be:

12.9 lb/1000 bbl crude for uncovered API separators,

1.5 lb/1000 bbl crude for covered API separators.

Separator covers may therefore be expected to reduce emissions approximately 89 percent. These factors show that the fugitive hydrocarbon emissions from wastewater systems with covered separators should rank well down on the list of total emissions, and that API separator covers produce significant emissions reductions.

Collection System – Process and Storm Sewers—

The contribution of the wastewater collection system to the overall refinery fugitive hydrocarbon emissions is shown as 45.29 lb/hr in Table 15 for the hypothetical 330,000 BPD refinery. These emissions result mainly from allowing oil or oily water to be exposed to the air in the process areas or in the drains and sewers.

In general, available controls for reducing fugitive emissions from existing process and storm sewers and collection systems consist of

relatively minor modifications such as sealing open sewer systems, altering pump bases for better drainage, recurbing some process areas for separation of oily water, and improving housekeeping. These changes should be made wherever applicable.

Changes which involve substantial capital outlays (or which may be nearly infeasible from a construction standpoint) such as major revisions to existing underground sewer systems or installation of vapor recovery systems do not represent best available technology economically achievable.

Primary Treatment - Oil and Water Separator--

The primary treatment of process water is the oil and water separator which is usually of the API or CPI type (corrugated-plate interceptor). All U.S. refineries have facilities for gravity separation of oil and water.[116] These separators are effective in removing free oil from water, but will not separate substances in solution or break up emulsions.[117]

Covering the oil and water separator is the only effective and economical means of reducing hydrocarbon emissions from refinery wastewater treatment systems. If the separator is operated properly, then hydrocarbon emissions from the downstream equipment will be negligible, and if the separator is covered, then hydrocarbon emissions from that source will be effectively controlled.

API separators are covered by floating pontoons or double-deck type covers which are sealed against the outer walls of each bay. A CPI separator normally will have a fixed roof cover.[118]

Using an API separator as an example, the economic incentive of reducing oil losses to the atmosphere by covering the bays will be examined here. Conservative economics here will show the minimum return on investment for installing covers.

Sources indicate separator cover requirements of 0.028 an 0.050 ft^2 per BPD wastewater flow.[119,120] Corresponding costs escalated by the M&S equipment cost index (Chemical Engineering Magazine) to third quarter 1979 are $15.84 and $14.85 per ft^2, respectively. A capital cost of $265,000 is obtained for a 330,000 BPD refinery using $16.00/ft^2 and 0.050 ft^2/BPD.

A typical refinery installing covers would see evaporative oil losses of approximately 17 percent reduced to less than 2 percent. For the 330,000 BPD theoretical refinery this means a savings of 157 lb/hr or 12 BPD at an assumed specific gravity of 0.87. At $16 per barrel this savings is worth $70,000 per year. If annual maintenance costs of $5000 are incurred on the covers, then the net savings is $65,000 per year. This savings yields a before tax discounted cash flow (DCF) rate of return of 28 percent assuming a 20-year economic life and no investment tax credits.

The economic incentive to install covers on oil and water separators combined with the resultant reduction of fugitive hydrocarbon emissions make a strong case for all separators to be covered. As of January 1977, 80 percent of the refining capacity was located in states where these covers are required.[121]

Cooling Towers

Existing Levels of Cooling Tower Control in Refineries--

Types--At the time of the 1958 Los Angeles County California Emissions Study,[122] "atmospheric sections" (splash-cooled heat exchanger tubes) could still be found in refinery cooling towers, although they were prone to leak and were difficult to repair. Chromates and chlorine were used to control corrosion and biological growth, respectively. The emission factor for cooling towers was estimated to be 6.2 lb hydrocarbons/10^6 gal cooling water circulation.

By 1978, wetted "atmospheric" sections had, generally, been phased out of refineries, organo-phosphates had replaced chromates for corrosion control, and biological growth was being controlled by combinations of chlorine and, often, nonoxidizing biocides.

Today, as in 1958, makeup water ranges from near-pristine snow-based surface water to sea water. Some refineries now recycle water from sour water strippers, which tends to reduce total plant water effluent and retain phenols in the plant. If recycled to a cooling tower, the aeration encourages oxidation of phenols from the stripper bottoms water.[123]

Emission factors determined during this study have been based upon two analytical methods: Total Organic Carbon (TOC) Analysis, and a purge technique. These results bracket the 1958 emission factor of 6.2 lb/10^6 gal cooling water:

Analytical Technique	Emission Factor lb HC/10^6 gal C.W.
TOC	12.4
Purge	0.108

The purge technique is more precise and accurate than the TOC technique based upon standardization runs, so one concludes that there is a high probability that progress has been made in reducing cooling tower hydrocarbon losses.

Cooling Tower Control Technology Available in Refineries and Associated Industry--

Types and Effectiveness--Forced-draft cooling towers characterize refineries and organic chemical plants. The greater heat release rates of power

industry plants make parabolic, natural-draft towers more economical. There
is no inherent advantage to either basic type of tower in terms of primary
air emission control.

Air monitoring and water monitoring instruments for the purpose of
leak detection are common to all the process industries; no analytical
problems of a refinery water system may be considered unique.

Costs--As industries tighten restrictions on water emissions, the likelihood
of having to deal with a broader array of recycle water types increases.
This will probably require progressively more attention to materials of
construction of cooling towers, heat exchangers and water piping. Also,
more complex treatment chemicals and application systems may be called for.
Changes in the circulating water may of course affect levels of air emissions
as a result of corrosion-induced leaks. Air emissions may also increase from
use of cooling towers as bio-oxidation devices, as in the case of recycled
phenols already mentioned. The overall impact of these forecast changes on
air emission control costs has not been addressed, to the best of our
knowledge.

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REVIEW

by

J. A. Mullins
Shell Oil Company
Houston, Texas

on

REFINERY AIR EMISSION CONTROL TECHNOLOGY

RESUME

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SUMMARY

This paper had as its objectives to review the state-of-the-art of selected process and fugitive emission controls and to discuss available control technology. In order to meet these objectives, three selected process emission sources are described and the emissions are at least qualitatively discussed. Because of the vast differences which exist between refineries and because of their complexity, it is recognized that it is difficult to present a single simplified description or evaluation of emissions. In general, while there has been presented a lengthy listing of conceivable controls, we do not believe that there has been a proper evaluation of those technologies nor their applicability to petroleum refineries.

The classification system chosen for control technologies is misleading to the reader since it leaves one with the impression that many technologies can be readily applied to reduce atmospheric emissions when that is not the case.

We would readily agree that the controls listed as "existing" have been applied in petroleum refineries and are in usage at many locations. This fact, however, should not be interpreted that such controls are economic at all refiners or even necessary to meet ambient air quality standards.

The second listed grouping of control technology is incorrectly titled as "available." We believe this to be a poor grouping of possible processes which contains control technologies that have actually been applied in a limited number of refineries and those which have been considered but never applied. The use of the word "available" implies that

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all the processes listed could be used at least to some extent. Although there are general statements as to cost and sometimes safety, we believe that the review and discussion given these systems is far too shallow to justify the classification of "available."

The third classification of process emission control technology--namely technology transfer--again implies that the process discussed can be used in the refining industry. We disagree with the presumption that limited success and usage in some application classifies a process for transfer to another industry.

The portion of the paper dealing with fugitive emissions and the techniques for controlling them appears to have more technical backup than the process emission section and does a reasonable job of defining the potential leakage rates of various sources. The paper, in no way, however, attempts to place in perspective the relative importance of fugitive emissions to the overall hydrocarbon emission potential. As pointed out in the report, the second and third highest fugitive emission sources in the hypothetical refinery are based upon old or questionable testing data. Since these two sources alone would be judged to account for over 35 percent of the total fugitive emissions, additional studies are certainly indicated before any major conclusions can be made.

DETAIL COMMENTS

I would like to point out some of the specific areas where we believe clarification or correction may be warranted.

Process Emissions

Although the discussion section of the Claus process indicates the presence of hydrocarbon in the unit feed gas, Table 2 fails to indicate that a typical feed gas contains $1 \pm 0.5\%$ hydrocarbon. This can cause control problems with a Claus unit and sometimes results in excessive temperatures in a tail gas incineration device.

The discussion of catalytic cracking emissions would indicate that no new emission factors were determined in this study, and that, in the previous study, "uncontrolled" emission factors excluded control devices such as cyclone separators. Justification is presented to review these old emission factors because of changes in control technology. This presents a confusing picture to the reader and should be clarified. A second reason for review of the 1956 emission factors seems to be a concern that one of the six tested units may have been atypical, and that, if this unit were excluded, an average emission factor of under 50 pounds per 1,000 barrels of feed would result. Since the excluded factor is 181, we do not understand how the published factor 242 was arrived at. This entire question requires further review and clarification.

Because of vast differences in complexity of refineries, we do not believe that average steam and fuel usages are meaningful. As energy conservation projects are implemented these factors will also change. Emissions from the boilers and heaters are strongly dependent upon the mix of fuels used and this also varies significantly from refinery to refinery. The emissions factors shown in Table 4 are not in agreement with those in AP-42 and the reference for these factors was not indicated.

Existing Control Technology

In the sulfur recovery discussion, the inclusion of Claus tail gas incineration as a clean-up device is misleading since it only converts the sulfur compounds to a different form. In the discussion and accompanying table for tail gas incineration there are discrepancies which should be corrected. Incineration temperature is generally 950 - 1150°F rather than the 1200°F stated in the discussion or the 752°F shown in Table 6. Temperatures below about 900°F will not convert the H_2S and temperatures above about 1100°F are unnecessary and consume large quantities of fuel. Excess air is also more likely to be 100 percent or greater since most of these devices are natural draft with manual control.

Although hydrodesulfurization of feedstock to catalytic crackers is not generally practiced for purposes of SO_x contol, it does occur in about 20 percent of the cracking feed in the United States. We believe that an estimate of the degree of control achieved by this technology should be stated. It is implied in the discussion that the degree of desulfurization used today is 92 to 95 percent. This level is commercially uneconomical and rarely, if ever, achieved. More commonly levels of 60 to 70 percent are practiced.

In the discussion of FCCU particulate removal, a collection efficiency for ESP's of 99.5 percent is stated to be a common occurrence. Again, we believe this to be rarely, if ever, achieved in practice. The more likely long-term efficiencies are in the range of 90 to 95 percent.

Control of CO emissions by CO boilers is, as stated, a fairly common practice; however, the required combustion temperature is usually 1800 to 2000°F rather than the 1300°F indicated.

Available Control Technology

As discussed earlier, we disagree with the use of the term "available" since it implies a greater degree of assurance that the technology can be used than is justified. Examples of this are the UOP Sulfox Process and the Union Carbide UCAP Process which are reported as only being in the testing stage. The use of many of the alternative methods of Claus tail gas clean-up shown in Table 8 are also questionable. The Catalytic Incineration process does not by itself reduce sulfur compound emissions and should not be listed as a clean-up device.

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The system of SO_x removal discussed for boilers and process heaters is not realistic. The concept of ducting all furnace and boiler flue gases to an integrated sulfur removal facility is purely theoretical and cannot be justified either technically or economically. The safety barriers pointed out in the discussion would only be the "tip of the iceberg" if this practice were to be implemented. Even if such a centralized treatment system were feasible, the suggested processes for SO_x removal would not be the likely choice.

For NO_x removal (or reduction) from boiler and furnace flue gases, three add-on techniques are suggested with the conclusion that only the thermal process appears promising. We question not including combustion modifications in this discussion. In fact, we believe it would be more appropriate if all of the techniques included in the section devoted to changes in operating practices were discussed and classified as "existing," or "available" technology. We see no reason to consider these pollution reduction methods in a different light than the add-on techniques described in the earlier sections. Many of them may be more cost-effective than the proposed add-on devices and should be considered.

Concerning the "thermal denox" process, we believe the stated 50 to 70 percent reduction is optimistic and would, on a long-term basis, be in the range of 40 to 50 percent. Since some of the possible combustion modifications appear capable of achieving near the same reduction, the use of add-on techniques may not be justified at this time. Also, the temperature range cited for the thermal denox process is incorrect by a factor of 10. The proper temperature range is 1300 to 1900°F.

In the discussion of technologies that could be transferred from other industry for SO_x and/or particulate removal from boiler and furnace flue gases, several processes that are either in commercial use or test for flue gas scrubbing are suggested. I would not disagree that this may be possible from a technical point of view, but I question the economics and reliability of such schemes. It is stated that the lime/limestone SO_x removal process is highly reliable. Considering the recent comments of the utility industry relative to the SO_x scrubber requirements under the revised NSPS for utility boilers, I would question this conclusion. It is especially important when you consider that refinery catalytic crackers are expected to operate with very high stream factors.

Alternative Operating Practices

As discussed earlier, I believe that the various techniques described in this section should be placed, as appropriate, in the sections of the paper where technology is described as "existing" or "available." I see no reason to attempt to segregate things like catalyst changes from add-on scrubbing when considering the potential to reduce emissions and evaluating the economics of such changes.

In the discussion of high temperatures FCCU catalyst regeneration, it is stated that the CO level can be reduced to well below 500 ppm. In our experience the 500 ppm level is about the lower limit. We are not aware of any catalyst supplier or vessel designer that would guarantee CO levels of less than 500 ppm. A recent Federal Register notice also states that 500 ppm CO is the lower limit for high temperature regneration.

The newly developed catalysts which prevent sulfur from leaving the regenerator offer great promise for SO_x emission reduction. We would, however, question the costs cited as realistic. The estimate of $0.03 per barrel of feed appears to be taken from an Amoco study in early 1977. Escalation of these costs should be made as well as some allowances made for increased size and operating costs of the Claus unit required to handle the additional load that will be generated.

FUGITIVE EMISSIONS

As discussed initially, much of the emission data for fugitive emissions appears to be on a sounder basis. A significant effort by Radian to quantify the emissions was made and is the subject of another paper at this conference. It does concern me, however, that the second and third highest fugitive emission losses in the hypothetical refinery are stated to be the two categories of sources that had the lowest confidence limits of the study and were therefore estimated on the basis of previous work. The recommendation that these two potential sources be investigated further is certainly justified.

Even though a separate paper is being presented on the subject of fugitive emissions, I believe it should be made clear in this paper that the emission factors given for a particular type of source represent average leakage or loss, and that by far the majority of fugitive emissions are the result of a relatively few leaking sources. It is this fact which makes some type of leak detection and maintenance program a viable alternative of control. As was discussed, the use of "leak-proof" equipment such as diaphram values does not offer a reasonable or even achievable solution to the problem.

Of significant interest was the finding that, despite a great increase in the usage of mechanical pump seals in the past 20 years, the average emission factor for all pumps has essentially not changed. This would indicate that the proposals to require mechanical seals in certain processes would not result in emission reductions commensurate with the costs involved. Double mechanical seals of the tandem type are described. The other type of double seal operates with the seal fluid pressure higher than the pump suction and leakage is therefore into pump. Leakage across the outer seal to the atmosphere will occur; however, in limited cases this could be a nonhydrocarbon.

"Canned" pumps for horsepowers up to 250, heads to 3,000 feet, flow to 50,000 GPM and temperatures to 340°F are suggested. We are not aware of

any such applications and believe that the few that are used in refineries are near 30 HP, 200 feet of head, 100 GPM and temperatures of 100°F. It may be that confusion exists between the sealless "canned" pump and the vertical can pump which is sealed by mechanical seals. We would agree, however, that general refinery usage of sealless pumps will not occur until these pumps have met API standards.

QUESTIONS AND ANSWERS

COMMENT/Rosebrook - I would like to make a comment at this time, because I think something has happened which makes a point. Too often the only information available to consulting firms such as ourselves, to enforcement agencies, to many other types of firms, is information which we glean from the literature, and attempt to appraise based on sound engineering principles. But it is people like Jim Mullins and Shell Chemical, and Mobil and Exxon and others, who tell you that it is not 1300°, it is 1800. It really makes a difference in the economics of that control technology and the effectiveness of the control technology, if indeed as opposed to the literature, practical experience, day-to-day running in the field, shows that instead of giving 90 percent efficiency they give 60 percent or 70 percent.

Q. Joseph Zabago/Mobil Oil - Perhaps you can elucidate Table 13 and 14, where you are making an attempt to prioritize sources with specific reference again to Mullins' commentary on the oil/water separators and the cooling towers. I am not as interested in your answer to the question as I am in applying the question to a paper that will be given tomorrow, where people will be talking about dispersion analysis for an entire refinery. Table 13 and 14 are the first place that I have seen in the document where one has taken the whole A. D. Little hypothetical refinery and turned out a number. We got a number based on all those numbers that Lloyd told us about this morning, and I like them, in terms of what he has already done, but then we have wastewater separators and cooling towers and they just blow Table 13 and 14 out of the water. It is my way of saying that I don't think the tables are consistent, and I think they should be strongly qualified as one is based on a study and one is a paper study. One is based on empirical work and the other is totally a paper study.

A. - First of all, on the oil/water separators, as I originally said, I tried to put these emission factors and total emissions from a hypothetical refinery in some sort of pecking order. Well, for the oil/water separator, you can see it only fits into the table if you will look at the uncovered or uncontrolled oil/water separator. The emission in pounds per hour is 178, but if you look at a covered separator, which I am beating the drum for here, it drops clear to the bottom of the table. So, it is there in

position number 2 only by virtue of what it will do if it is uncovered. Now, as to the data that went into that, those who did the separator simulation, actually took a body of water and an oil layer and covered it and uncovered it and took their temperatures and samples and so forth. We feel like that is probably better than the original work that went into the AP-42 numbers represented here as 252 pounds per 1,000 barrels. Well, anyway, not only are those numbers lower than the original AP-42 numbers, but I think they were done in a controlled manner. As to cooling towers, the values which I show you here for Table 14 include both the values that we got using our purge method and our TOC method. I don't believe it appears in your copy. The original order here was established by the values given by the TOC results for cooling towers of 234. It was only after going through the data, going through the procedures, looking at both the precision and the accuracy of the two methods that we concluded that the lower values based upon the purge method were what we should go with. Now, obviously in that case that would drop cooling towers way down in the table. So, your point is well taken. Those two, if they are covered, in the first case, and if we use the purge method in the second, which we feel is the more reliable of the two numbers, then certainly those two sources of emissions are out of the running for being important. Incidentally, we did take a look at rough economics of covering the API separator. It is a runaway first choice for doing what was mentioned earlier today, namely holding onto some of those good hydrocarbons that you really don't want in the air, that you would like to recycle into your refinery. There is a high return I won't mention it because someone will hang his hat on it.

COMMENT / Joseph Zabago/Mobil Oil - Thank you! The 234 is not included in our copies. That clarifies my total confusion in figuring out why number 3 was the lowest, I now understand that and why a number of cooling towers should be, say 2.04, put at the bottom of the priority list, and I appreciate your clarifying the business on the oil/water separators. The commentary about the economics is still premature pending the data that we determined from studies that were talked about earlier.

CORRELATION OF FUGITIVE
EMISSION RATES FROM BAGGABLE
SOURCES WITH REFINERY
PROCESS VARIABLES

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ABSTRACT

The effects which refinery process variables have on fugitive emission rates are discussed in this paper. Correlations are presented for both continuous and discrete process variables. Continuous variables include temperature, pressure, size, age, etc. Discrete variables may relate to function, type, manufacturer, etc. The only dominating correlation observed was for stream composition; components containing higher volatility process fluids tend to have higher emission rates. Factors which affect the observed correlations or lack of correlation are also presented.

RESUME

Russell Honerkamp is a Staff Chemical Engineer at Radian Corporation. He received his B.S. degree in Chemical Engineering from the University of Texas at Austin in 1975. Since 1976, he has worked on several projects at Radian pertaining to atmospheric emissions of VOC from industrial processes. He is currently working on a contract with EPA to support and develop New Source Performance Standards for fugitive emission sources in the Synthetic Organic Chemical Manufacturing Industry.

R. L. Honerkamp

CORRELATION OF FUGITIVE EMISSION RATES FROM BAGGABLE
SOURCES WITH REFINERY PROCESS VARIABLES

INTRODUCTION AND OBJECTIVES

Refinery process variables can be categorized as continuous or
discrete variables. Continuous variables exist over a range with common
unit(s) of measure which describe the range. Continuous variables include
pressure, temperature, size, age, capacity, etc. Discrete variables include
function, type, manufacturer, configuration, etc. Discrete variables must
be compared individually and no interpolation between levels of the variables
is possible. Some variables, such as stream composition, can be treated as
either continuous or discrete depending on how they are defined. The objec-
tive of this paper is to present and explain the correlations observed in
this study between process variables and fugitive leak rates.

There are two primary reasons for investigating the effects of
process variables on fugitive emission rates. The more important reason is
to provide useful information for developing fugitive emission control strat-
egies. If certain classes of emission sources do not leak due to the effects
of process variables, these sources can be excluded from emission reduction
maintenance programs. If changes in certain process variables increase
emission rates significantly, more intensive maintenance programs might be
indicated for the higher emission rate sources. Alternatively, changes in
design, construction, or operation of these source types could be applied to
counteract the emission rate increase caused by the process variables. The
second reason for examining these correlations is that numerous correlation
theories were proposed at the outset of the sampling program. Many people
felt that these effects would be borne out by sampling data "without a doubt".
Thus far, the surprises have outnumbered the expected effects.

One constraint which complicates the effort to relate emission
rates and process variables is the accuracy of recorded process variables.
A large number of process variables were collected for each source screened
or sampled. (Figure 1). The amount of time and effort that could be expended
in collecting these variables was limited by the schedule and budget, and
sometimes the information simply was not available. Age is a good example
of this problem. The "best" age to record for a source would be the age
since maintenance or installation. But often the only estimate of age
available was the age of the process unit. For a large number of diverse
sources (especially valves) it was impossible to obtain accurate process
variable information.

DATA SHEET - PUMP SEAL   500

1. Radian ID# [| | |P| | | |]
                1 2 3 4 5 6 7 8

2. Unit _____

3. Refinery ID# _____

Note: Space 5 should be seal identification letter (A,B,C etc.). Use same ID on sampling sheet.

☐ I - Inboard
9 Ø - Outboard

☐ In-Service/Out of Service (I/Ø)
10

VARIABLES:

4. Discharge pressure, psig [| | |]
                              11 12 13 14

5. Temperature, °F [| | |]
                    15 16 17 18

6. Pump/seal type ⎡ CM - centrifugal/mech. ⎤ [|]
                  ⎢ CP - centrifugal/packed ⎥ 19 20
                  ⎣ RP - recip/packed ⎦

7. RPM or strokes PM [| | | |]
                      21 22 23 24 25

8. Stroke length (Recip, in) [| | |]
                              26 27 28 29

9. Capacity, GPM [| | | |]
                  30 31 32 33 34

10. Seal/lube ⎡ P - product leakage ⎤ [ ]
              ⎢ W - water ⎥   35
              ⎣ H - hydrocarbon lubricant ⎦

11. Gland type ⎡ N - no quench gland ⎤ [ ]
               ⎢ Ø - oil quench ⎥   36
               ⎣ W - water quench ⎦

12. Single or double (S, D) [ ]
                             37

13. Shaft diameter, in _____ [|]
                               38 39

14. Age, yrs [|]
              40 41

15. Manufacturer _____ [|]
                         42 43

16. Mtls of constr _____ [|]
                           44 45

17. Horizontal or vertical (H, V) [ ]
                                   46

PROCESS FLUID DESCRIPTION:

18. Name [| | | | | | | | | |] _____
          47 48 49 50 51 52 53 54 55 56

SCREENING DATA:

19. Date of screening [| | | | |]
                       57 58 59 60 61 62

20. Screening team [|] ___/___
                    63 64

21. Max TLV [| | | | |]
             65 66 67 68 69 70

22. Liquid leak? (Y, N) [ ]
                         71

23. TLV data _____

LEAK PREDICTION DATA:
IF max TLV reading is > 200 ppm, record all screening values below

Radian ID# [| | | | | |]   Screening [| | | | |]   Screening [|]
            1 2 3 4 5 6 7 8   Date   9 10 11 12 13 14 Team   15 16

Screening Concentration, ppm
[| | | | |] [| | | | |] [| | | | |] [| | | | |]
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

5 Cm Reading [| | | | |]   ⎡S⎤
              65 66 67 68 69 70   80

REMARKS:

Figure 1   Process Variable Data Collection Sheet

CONCLUSIONS

The only dominating effect on emission rate that has been observed is related to stream composition. This effect became evident in the early stages of the program. One problem with this effect was related to the units used to describe stream composition. Refinery streams are primarily multi-component hydrocarbon mixtures with wide variations of vapor pressure, molecular weight, chemical class (paraffins, aromatics), viscosity, etc. Since stream composition changes numerous times within a single process unit, it was im-possible to determine complete stream composition variables for each emission source screened or sampled. The most available type of stream identification available was the "stream name", such as atmospheric overhead, debutanizer bottoms, reformer reactor outlet, etc. The actual composition of streams with the same name may vary considerably between refineries depending on crude composition, desired products, operating conditions, and other factors. Radian developed a stream identification code system to categorize streams based on the most volatile class present in $\geq$ 20 weight percent. (Figure 2). Analysis of emission rates showed three distinct "stream classifications". Highest emission rates were observed for sources containing gases or vapors. Lower emission rates were observed for sources containing light liquid or two phase streams, and sources in heavy liquid service had the lowest emission rates. The split between "light" and "heavy" liquids is approximately between heavy naphtha and kerosene. This corresponds to a vapor pressure of about 0.1 psia @ 100°F. Examination of other process variables was performed after separating stream categories in order to separate the stream composition effect from effects of other variables.

For all other process variables, no major significance was observed. In some cases a statistically significant correlation coefficient was ob-served, but no dominating effects, other than stream composition, were seen. The lack of significant correlations may be due to the dominating effect of stream composition, the inaccuracy of measuring process variables, the variability of leak rates and measurement techniques, or combinations of all of these. The only conclusion that can be made is that stream composition is the only dominating variable. Other correlations either don't exist, or the data base isn't accurate enough to identify them.

PRESENTATION OF RESULTS

COMPLICATING FACTORS

There are several peculiarities of fugitive emissions and/or this particular data base which make it difficult to draw conclusions about ob-served correlations. These factors include:

● The extreme skewness of the leak rate data with a large percentage of most source types not leaking

● The variability of leaks and leak measurement techniques

STREAM GROUP[1]	HYDROCARBON STREAM DESCRIPTION[2]
Gas/Vapor	C_1-C_2 Hydrocarbons
	C_3-C_4 Hydrocarbons
	C_5-C_9 Hydrocarbons
	C_{10}+ Hydrocarbons
	Mixed Molecular Weight Hydrocarbon Streams
	Aromatic Hydrocarbons
	Miscellaneous Organic Compounds
	Hydrocarbon Streams Containing H_2, H_2S, and H_2O
Light Liquids/Two-Phase	C_2 Hydrocarbons
	C_3-C_4 Hydrocarbons
	C_5-C_6 Hydrocarbons
	C_7-C_9 Hydrocarbons
	Naphtha
	Light Distillate
	Aromatic Hydrocarbons (low molecular weight)
	Miscellaneous Streams
Heavy Liquids	Kerosene, Diesel, Heating Oil
	Gas Oils
	Atmospheric Resid/Vacuum Gas Oil
	Vacuum Resid/Asphalt
	Aromatics/Polymers
	Mixed Molecular Weight Streams
	Non-distillate Solvents
	Miscellaneous Organic Streams

[1]Stream group is determined by the stream conditions within the process lines

[2]The most volatile stream component present at a concentration of 20% or more determines the stream classification.

FIGURE 2. PROCESS STREAM CLASSIFICATION BY GROUP

- The dominating effect of stream composition on leak rates

- The inaccuracy or unavailability of process variable data

The effects of the first two factors listed above were minimized by transforming the data to $\log_{10}$. This normalized the data and gave homogeneous variability for all levels of $\log_{10}$ leak rates.

Any discussion of the effect of process variables is complicated by the confounding between variables in the data base. This confounding is due to the lack of independence between process variables as they naturally occur and the fact that all combinations of levels of many variables could not be obtained in the study. A fractional factorial experimental design was followed in selecting sources with selection based on key process variables. This design allowed the estimation of the main effects of important variables, but not all variable interaction effects could be estimated. Most second order interactions (such as stream type by line size, by source type) and higher order interactions are either confounded or there are not enough replicate data to quantify by their effects with any precision. This means that it is difficult to break sources down by more than two variables at a time to determine emission factors or effects.

A good example of the difficulty introduced by the distribution of leak rates is the effect of line size on flange emission rates. The percent of flanges leaking, mean leak rate, and emission factor estimate are shown as a function of line size in Figure 3. Although there are significant differences in percent leaking and a significant effect of line size on leak rate, the confidence intervals for the five emission factors all overlap. Since this effect of overlapping confidence intervals occurs for many other source and variable interactions, comparison of emission factors is not a good way to determine significance of process variable effects. For continuous variables, the simple correlation coefficient "r" is an indicator of statistical significance of the correlation. Discrete variables can be compared visually by preparing "box and whisker" diagrams.

CONTINUOUS VARIABLES

At the beginning of the sampling program, several trends were expected to be present. The process variables which were expected to show greatest significance were:

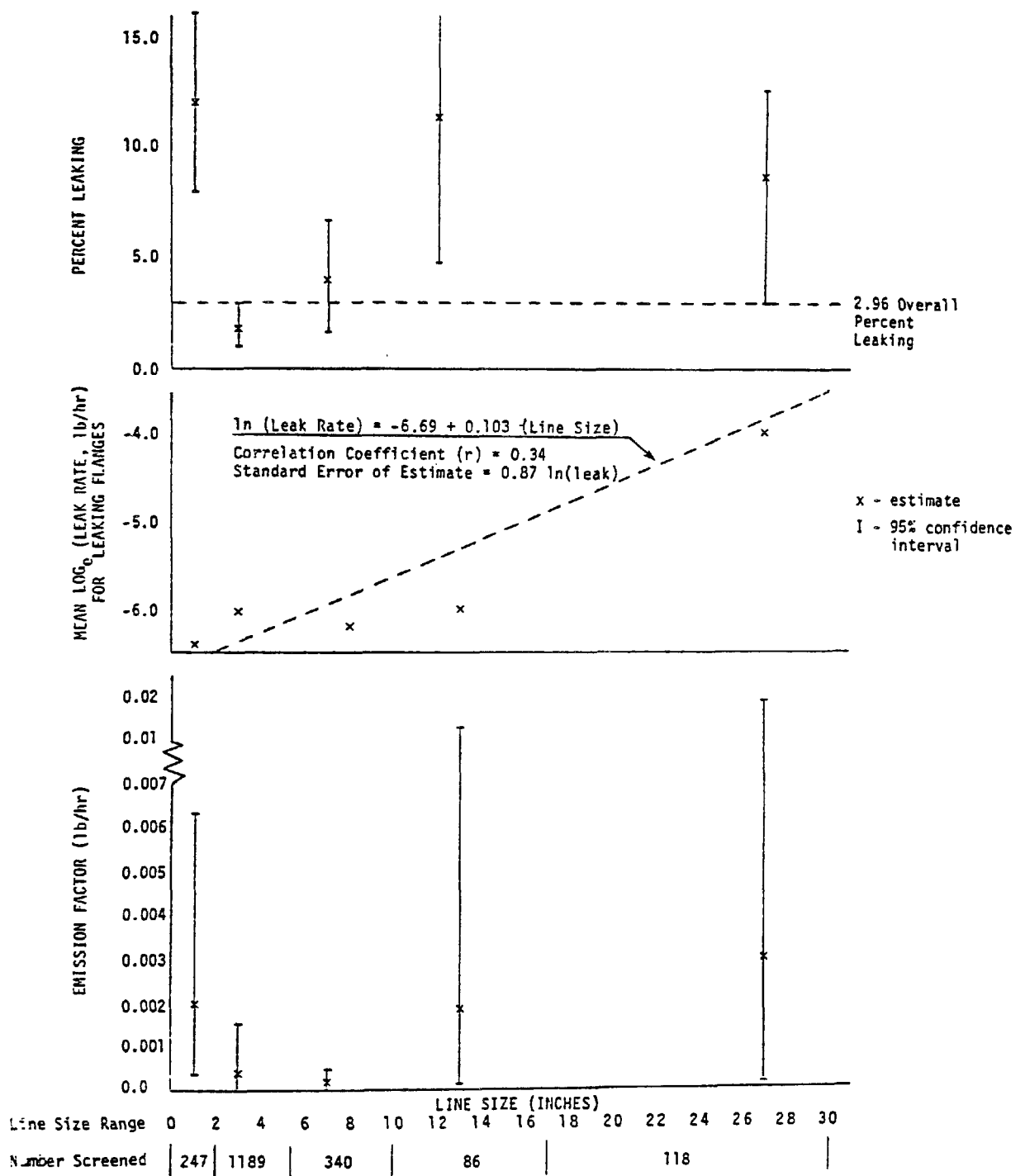- Pressure

- Temperature

- Size

- Age

Figure 3 Effect of line size on emissions from flanges

Increasing pressure might provide increasing driving force for emissions through the sealing element. Temperature extremes might adversely affect the degradation rate of sealing elements. Larger sizes would be expected to have larger potential emission area, and therefore greater emission rates. Age or time since last maintenance was also expected to result in increased degradation of the sealing element. None of these expected results has been conclusively determined from the data base.

The inaccuracies in determining some of the process variables reduce the sensitivity of the correlation analysis. For instance, the variable "age" recorded was usually the age of the unit. A more useful age determination would have been the years in service of each individual source, or possibly the time since last maintenance was done, but it was impractical to obtain this information for the large number of sources studied. Therefore, the conclusions concerning process variables pertain to the variables as measured or determined in this study.

Table 1 lists the simple correlation coefficients between the log leak rate and the appropriate continuous process variables for each source type and stream classification. Correlations significantly different than zero are noted. The simple correlation coefficient is a statistical measure of the linear relationship between two variables. The correlation between "X" and "Y" is computed as:

$$r_{XY} = \frac{\sum_i (X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\sum_i (X_i - \overline{X})^2 \ \sum_i (Y_i - \overline{Y})^2}}$$

and is bounded: $\quad -1 < r_{XY} < 1.$

The value of r^2 indicates the approximate percentage of the total variation in the log leak rate that is accounted for by the relationship of the leak rate with the correlating variable. For instance if $r = 0.50$, then $r^2 = 0.25$ and about 25 percent of the variation in the leak rate is attributable to the relationship with the process variable. The remaining 75 percent of the variation is due to other variables and random variation.

The sampling distribution of values of r is highly dependent on the sample size. Small values of r (0.1-0.2) may be statistically significant for large sample sizes while large values of r (0.4-0.7) may not be significant for small sample sizes. Statistically significant refers to a statistical test of the hypothesis that the correlation is equal to zero , i.e., no relationship between the variables. A significant correlation therefore does not imply a large value of r, since values of r < 0.2 may be significant for large sample sizes.

TABLE 1 CORRELATIONS BETWEEN CONTINUOUS VARIABLES AND LOG_{10} LEAK RATE

	Pressure	Temperature	Age	Line Size	Diameter	Area	RPM	Capacity	Load	Stroke Length
Valves										
Gas/Vapor Streams	.230*	.077	.263*	.150*	–	–	–	–	–	–
Light Liquid Streams	.103*	.051	.096	.143*	–	–	–	–	–	–
Heavy Liquid Streams	-.351*	.144	.220	.046	–	–	–	–	–	–
Hydrogen Service	-.088	.129	-.531*	.288*	–	–	–	–	–	–
Open-Ended	.236	.242	.230	-.078	–	–	–	–	–	–
Pump Seals										
Light Liquid Service	.088	-.012	.062	–	.021	–	-.064	–	–	–
Heavy Liquid Service	.097	-.098	.237	–	.128	–	-.182	–	–	–
Flanges	.072	.021	-.180	.336*	–	–	–	–	–	–
Compressor Seals										
Hydrocarbon Service	.346*	.218*	.105	–	.278*	–	-.143[a]	-.138	-.087	-.012
Hydrogen Service	.398*	.312*	.052	–	.343*	–	-.034	.218	-.099	-.074
Drains	–	-.408*	–	–	-.039	-.191	–	–	–	–
Relief Valves	.045	.096	–	-.075	–	–	–	–	–	–

* Correlation Coefficient statistically different from zero (P > .90).

[a] Log_{10} RPM was correlated with log_{10} leak rate.

The correlation coefficient, r, can sometimes be misleading for the following reasons:

- r does not describe how much Y changes for a given change in X, what the shape of the curve connecting Y and X is, or how accurately Y can be predicted from X.

- A correlation between X and Y may be due to their common relation to other variables.

- Outliers and highly skewed data can distort the frequency distribution of r.

- Selecting values of X at which Y is measured can distort the frequency distribution of r.

- r may be unduly high because of sampling from two different populations instead of one.

In order to examine the actual data used in calculating the correlations presented here, scatter plots of the log leak rate data (in pounds per hour) and the process variables were developed. Several of these plots have been selected to illustrate the "best" correlations observed. (Figures 4 through 18). Each plot selected shows a correlation that was considered to be statistically significant, and although the correlations are statistically significant, the data show a lot of scatter throughout the range. Each plot shows a line representing the mean value of the correlation. A one order of magnitude change in leak rate is indicated by two solid dots on the line. In all cases, the variation of leak rates at given values for the process variable is at least one order of magnitude, while the variation in mean leak rate across the entire range of the process variable is often less than one order of magnitude. These plots represented the process variables which showed the most significant correlations. All other continuous variables for all other source types showed more scattering and less statistical correlation. Several examples of this scattering are shown in Figures 19 through 25. These figures show how the expected correlations were not observed in the data base.

DISCRETE VARIABLES

Unlike continuous variables, correlation coefficients are not easily interpreted for discrete variables versus leak rate. A visual method for comparing the relationships between levels of the variable and leak rate is the schematic plot. On each plot, the level of the variable is represented by a "box and whisker" figure that identifies the mean, median, upper and lower quartile and range of values. Because of small sample sizes and overlapping values, most of the correlations with discrete variables are not considered to be significant.
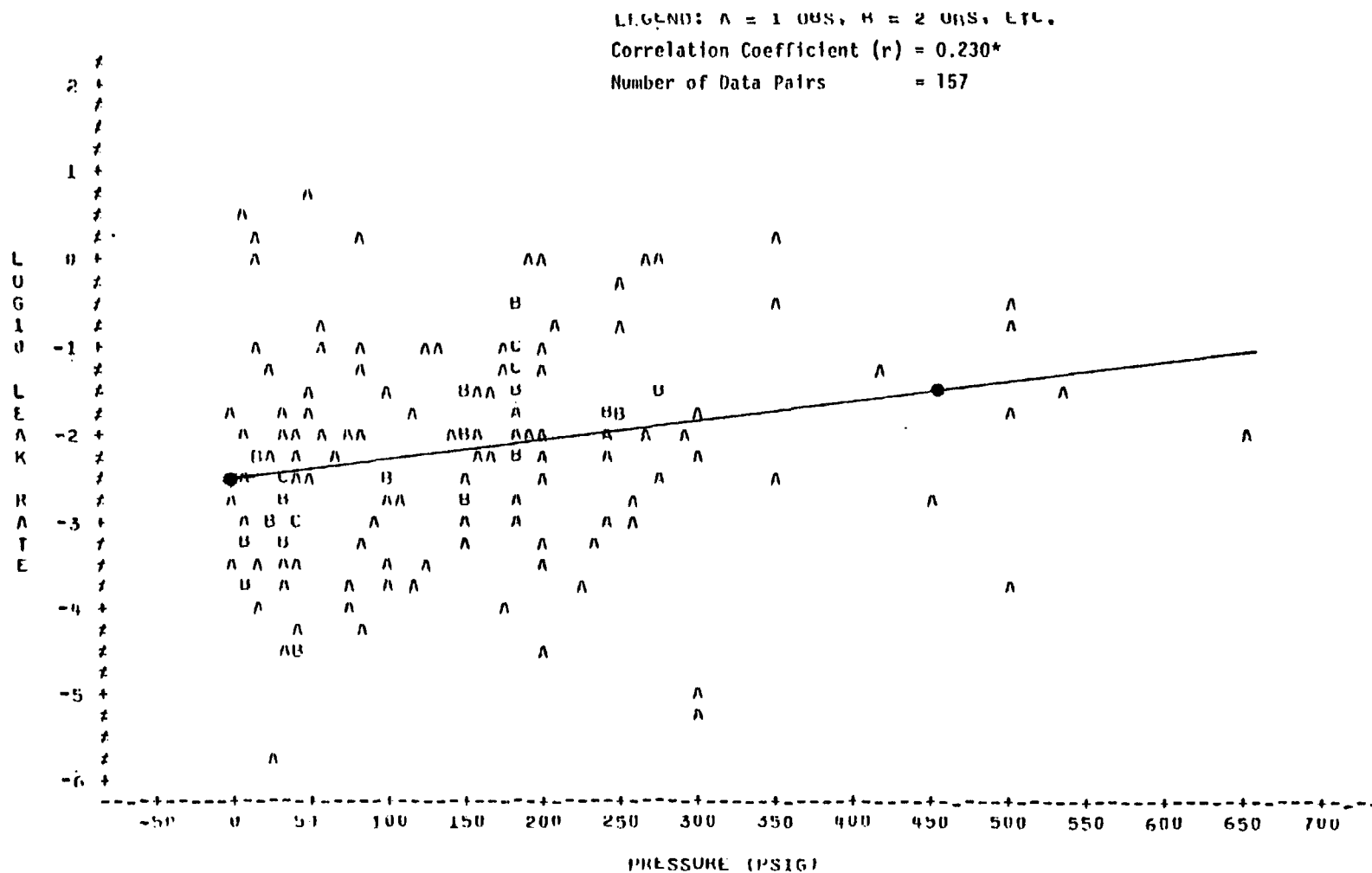
Figure 4   Leak rate vs. pressure - valves, gas/vapor streams.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Coefficient (r) = 0.150*

Number of Data Pairs   = 156

LINE SIZE (INCHES)
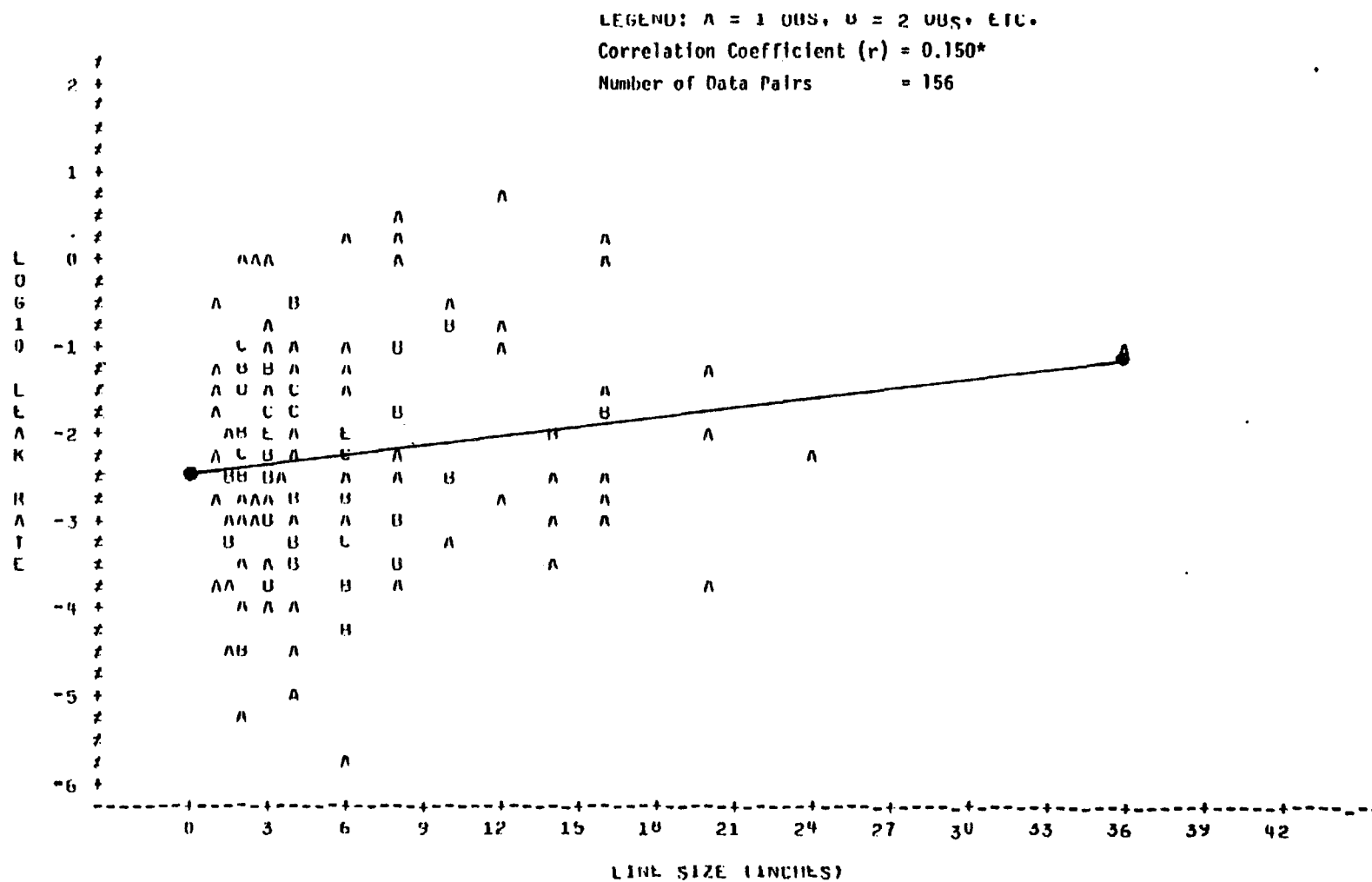
Figure 5   Leak rate vs. line size - valves, gas/vapor streams.
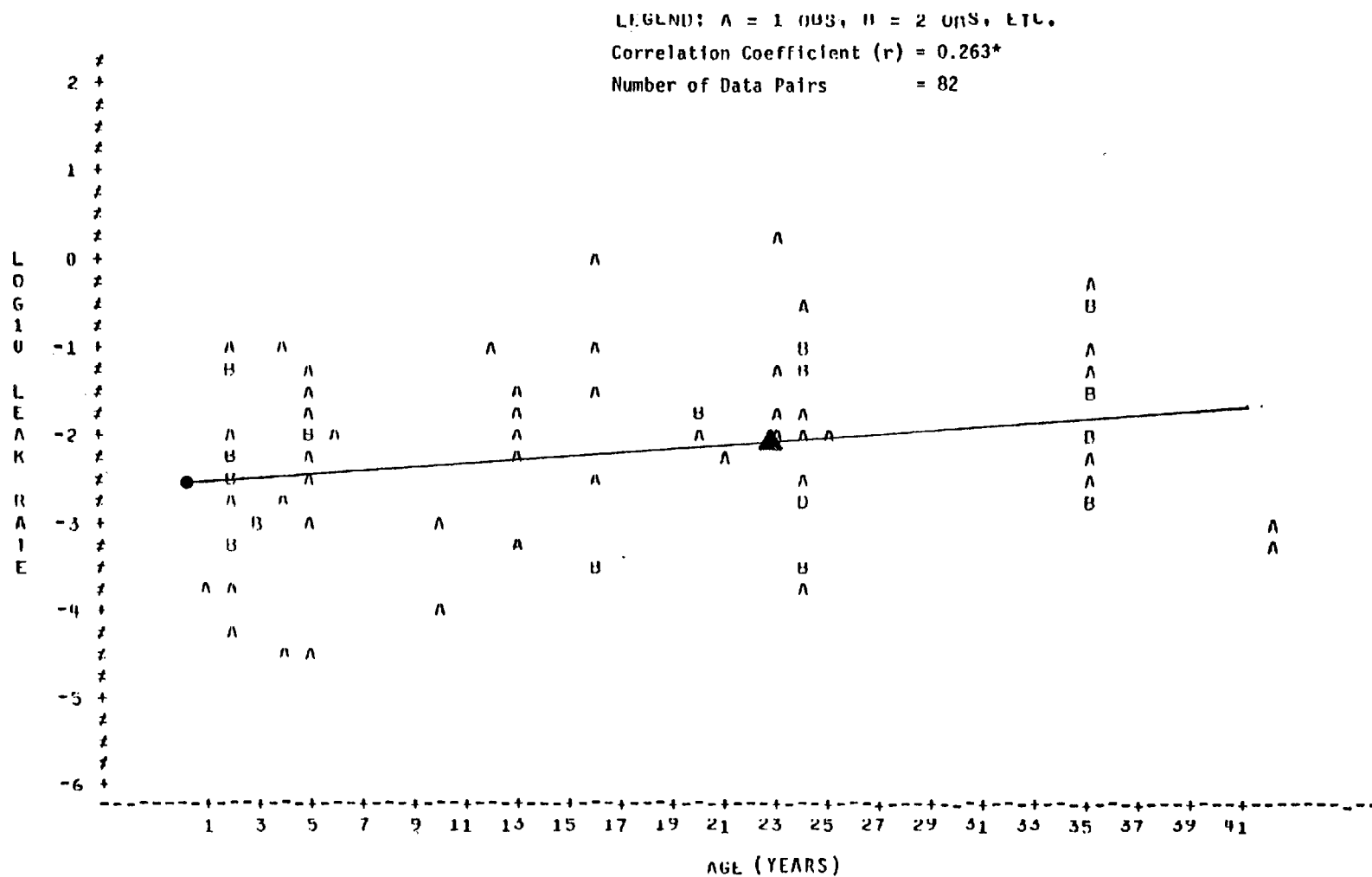
Figure 6   Leak rate vs. age - valves, gas/vapor streams.
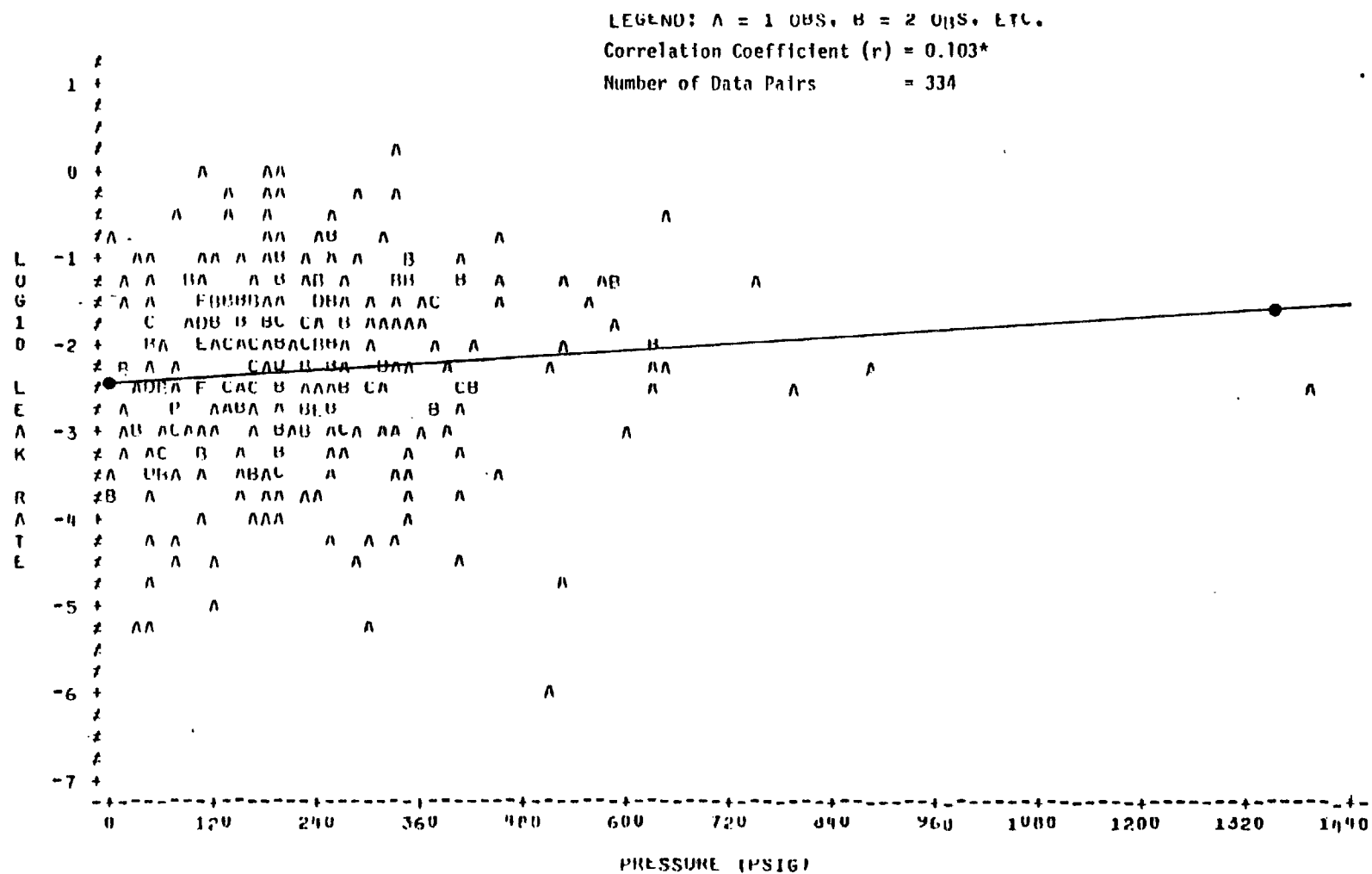
Figure 7   Leak rate vs. pressure - valves, light liquid/two phase streams.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
Correlation Coefficient (r) = 0.143*
Number of Data Pairs   = 326
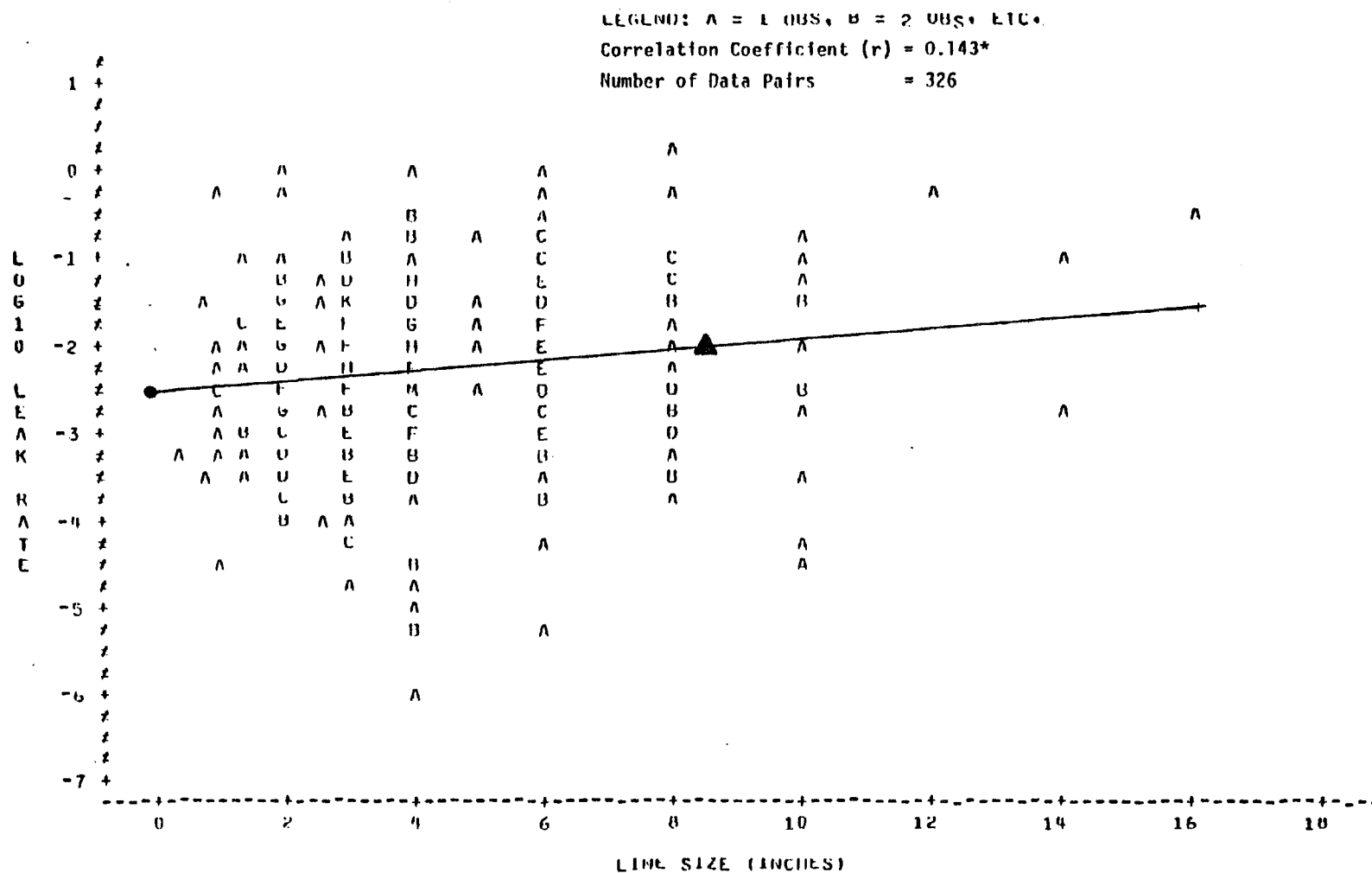
Figure 8   Leak rate vs. line size - valves, light liquid/two phase streams.
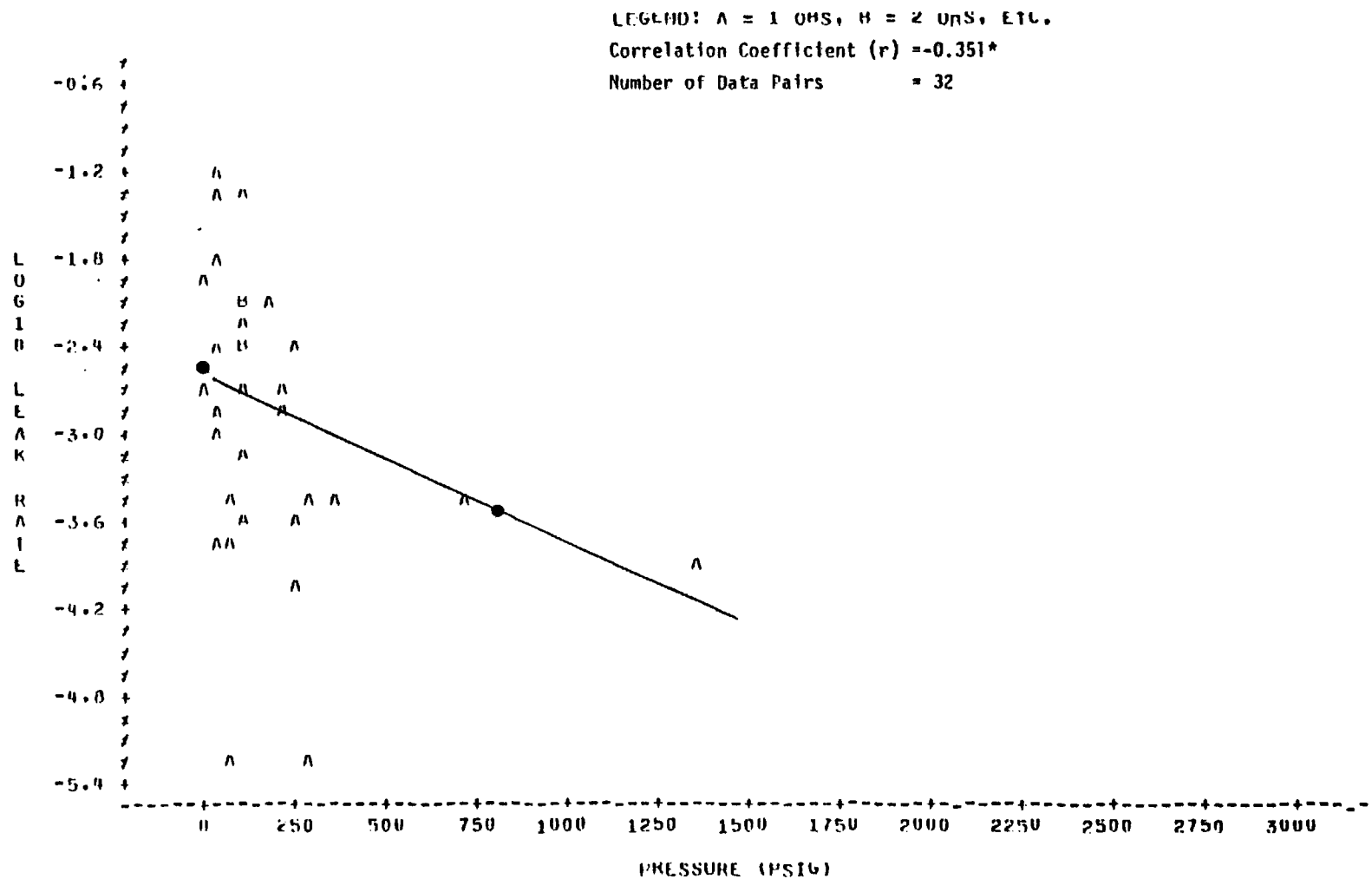
Figure 9   Leak rate vs. pressure - valves, heavy liquid streams.
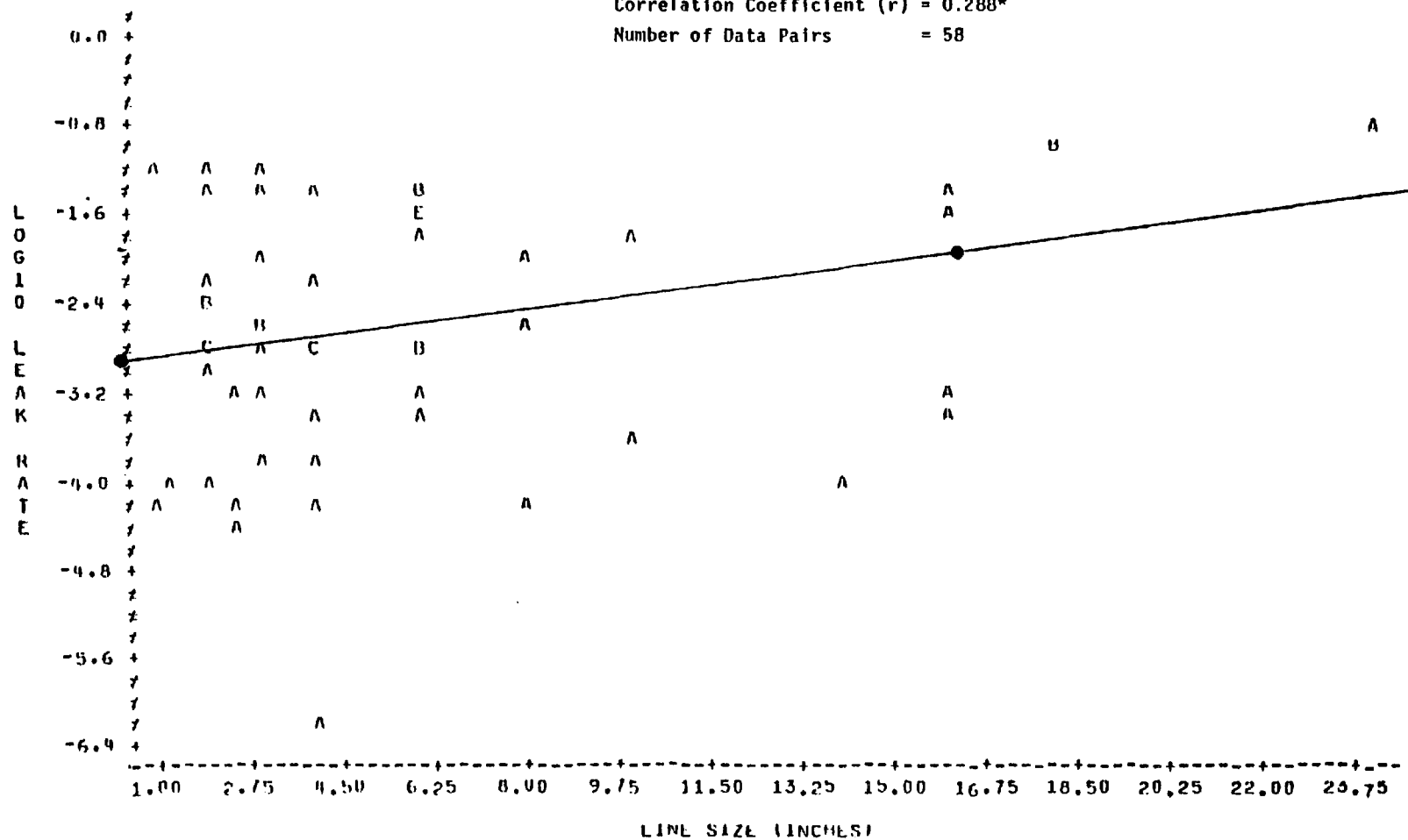
Figure 10   Leak rate vs. line size - valves, hydrogen streams.
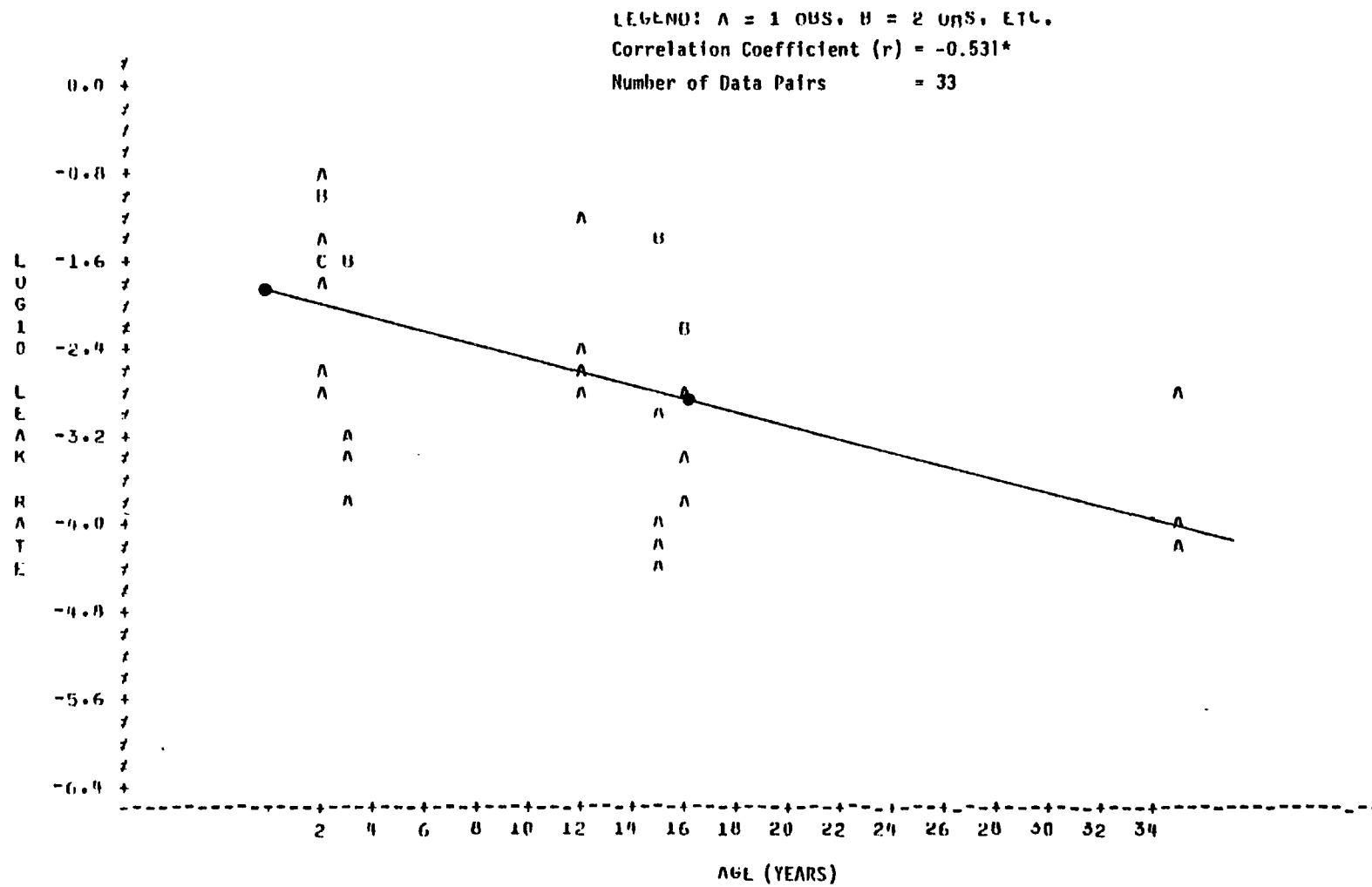
Figure 11   Leak rate vs. age - valves, hydrogen streams.
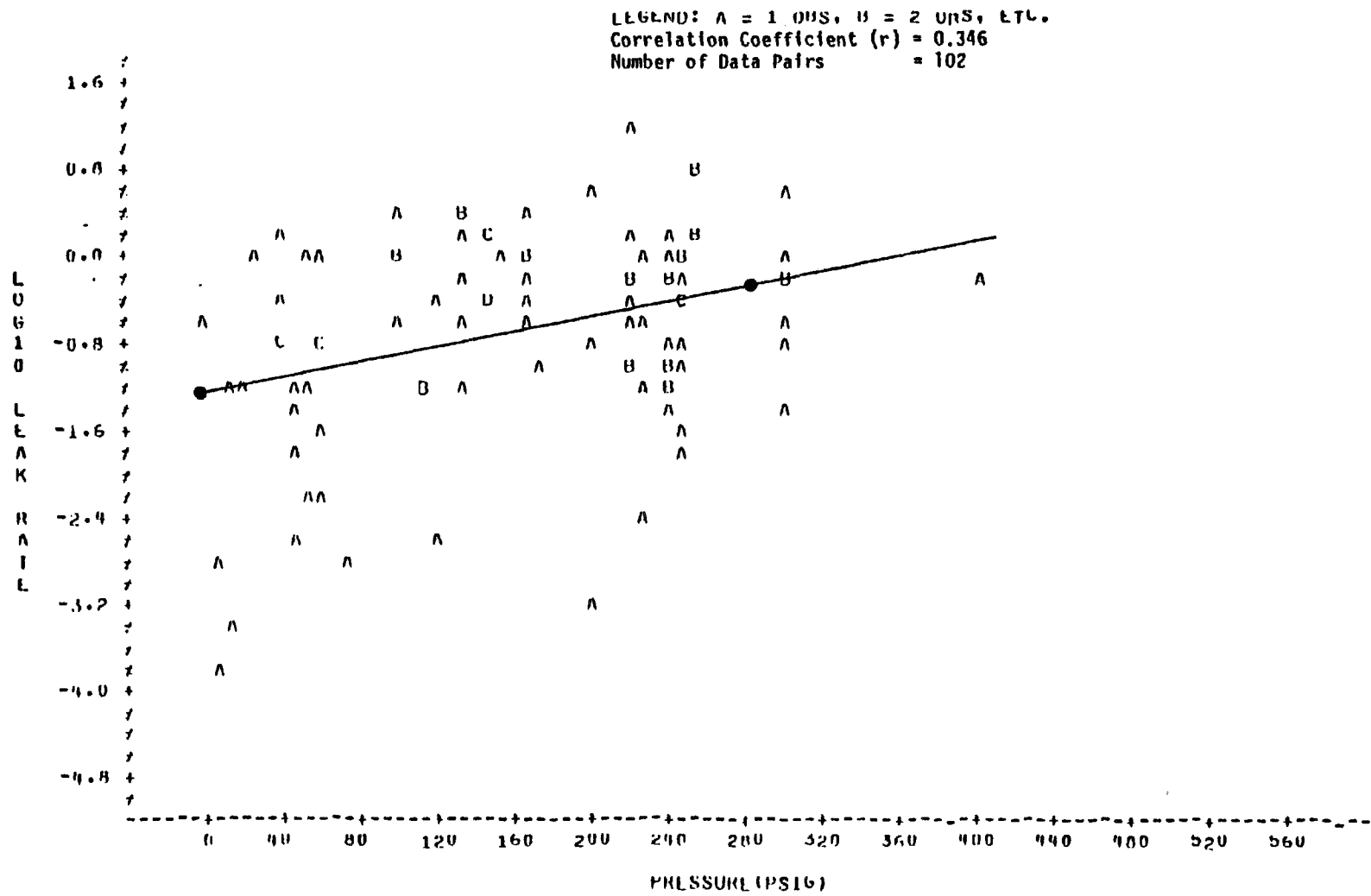
Figure 12   Leak rate vs. pressure - compressor seals, hydrocarbon service.
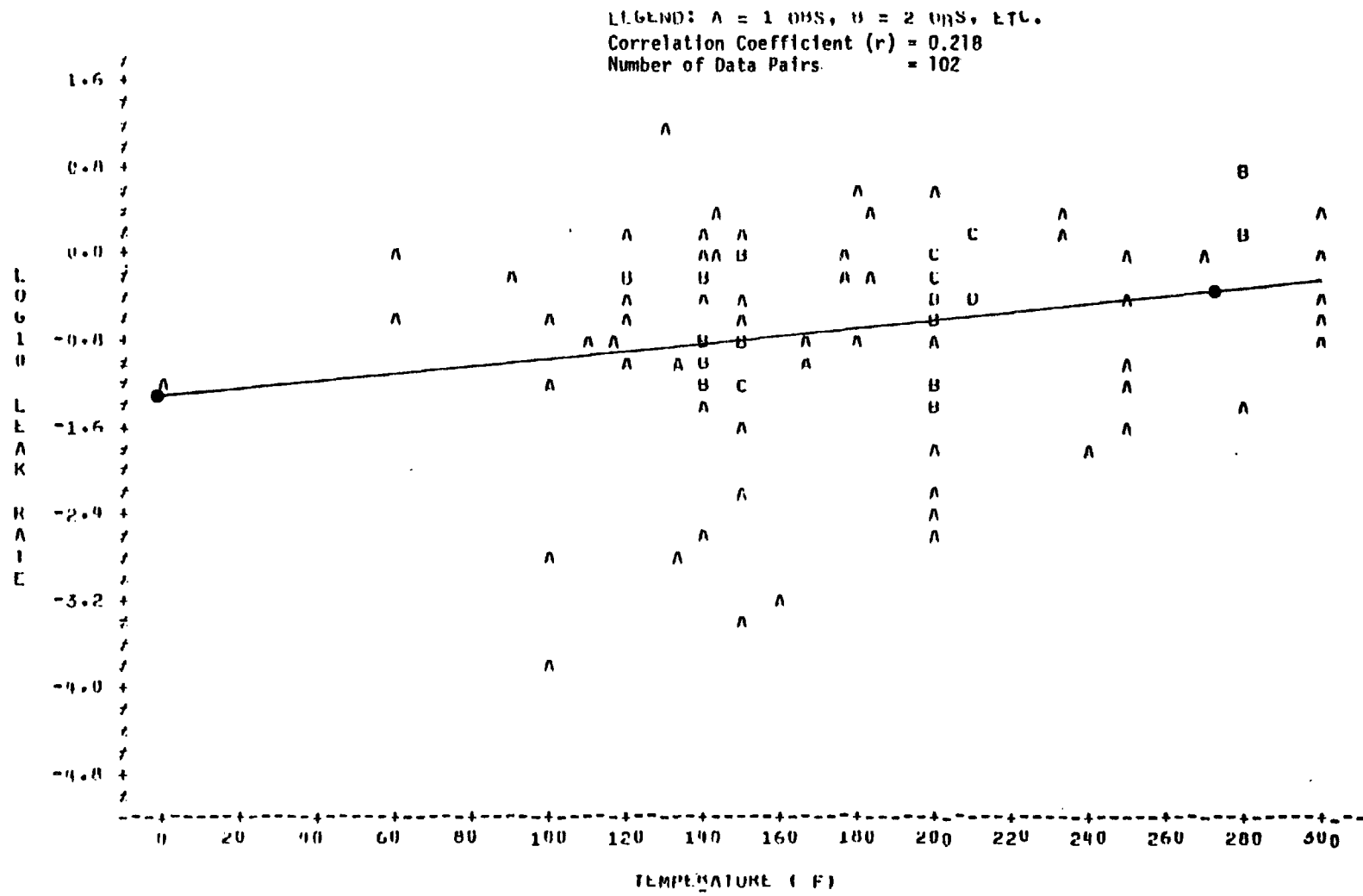
Figure 13 Leak rate vs. temperature - compressor seals, hydrocarbon service.
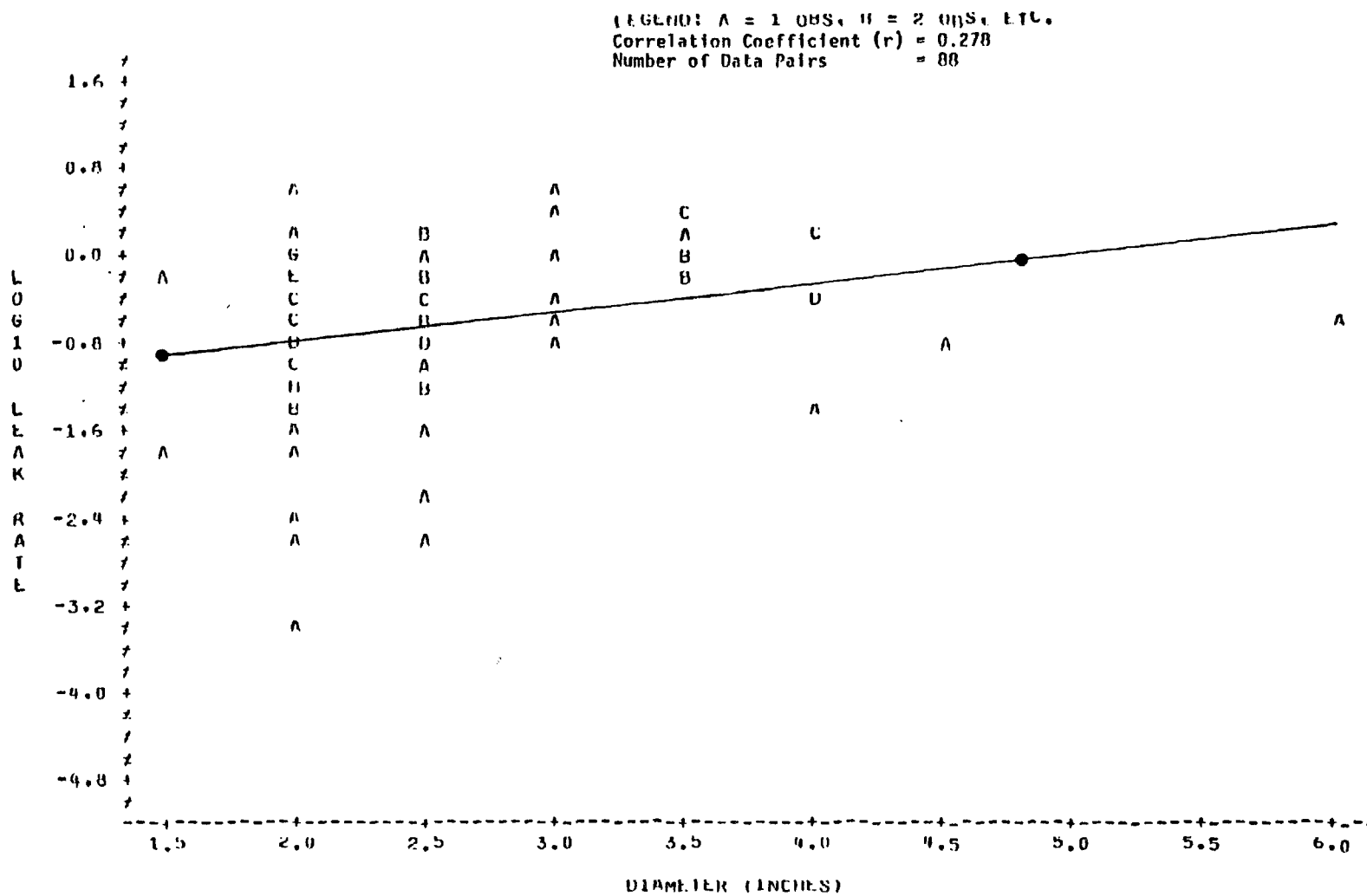
Figure 14   Leak rate vs. diameter - compressor seals, hydrocarbon service.

Figure 15 Leak rate vs. pressure - compressor seals, hydrogen service.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.
Correlation Coefficient (r) = 0.311
Number of Data Pairs   = 59

Figure 16   Leak rate vs. temperature - compressor seals, hydrogen service.

Figure 17   Leak rate vs. diameter - compressor seals, hydrogen service.
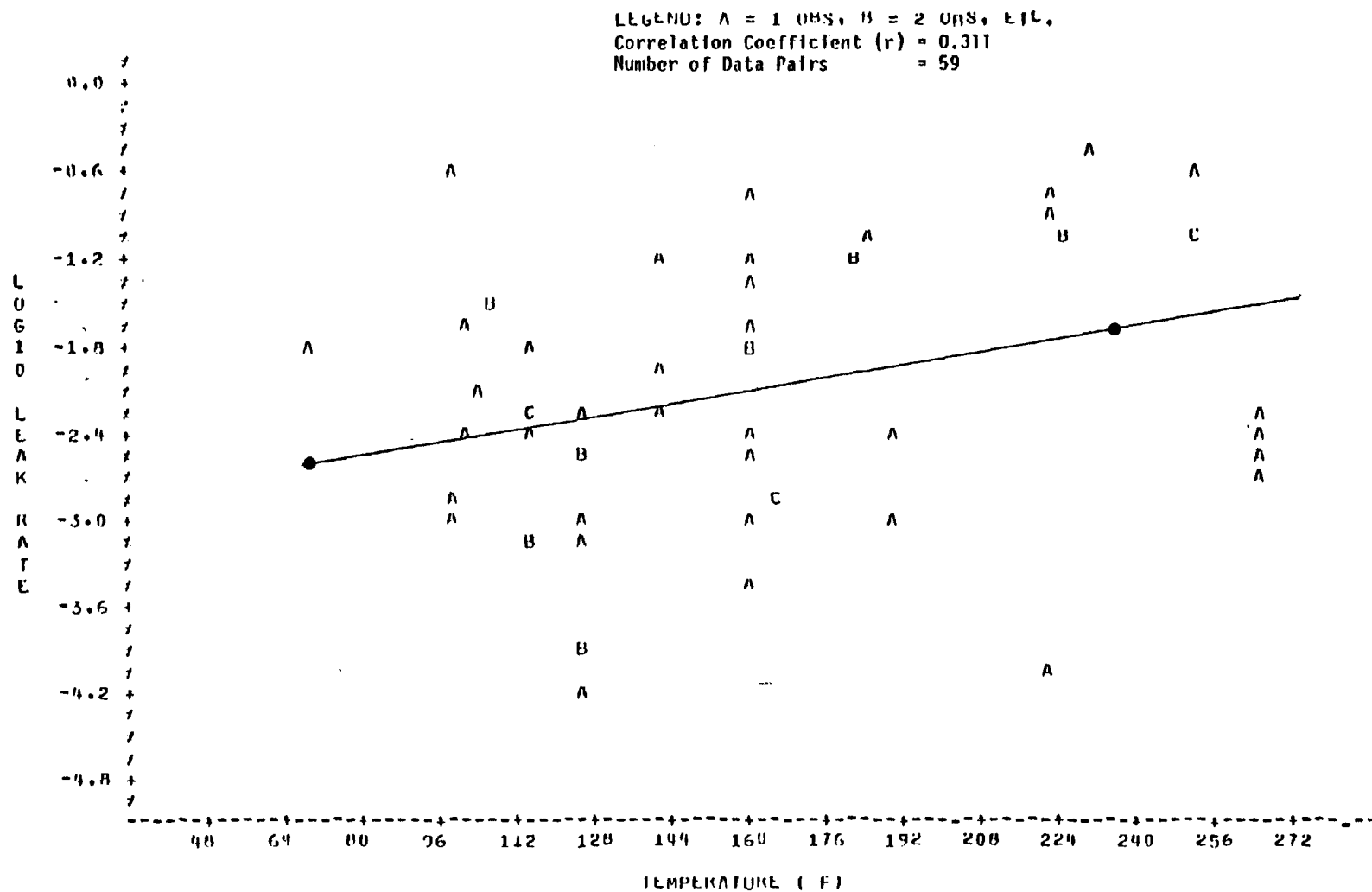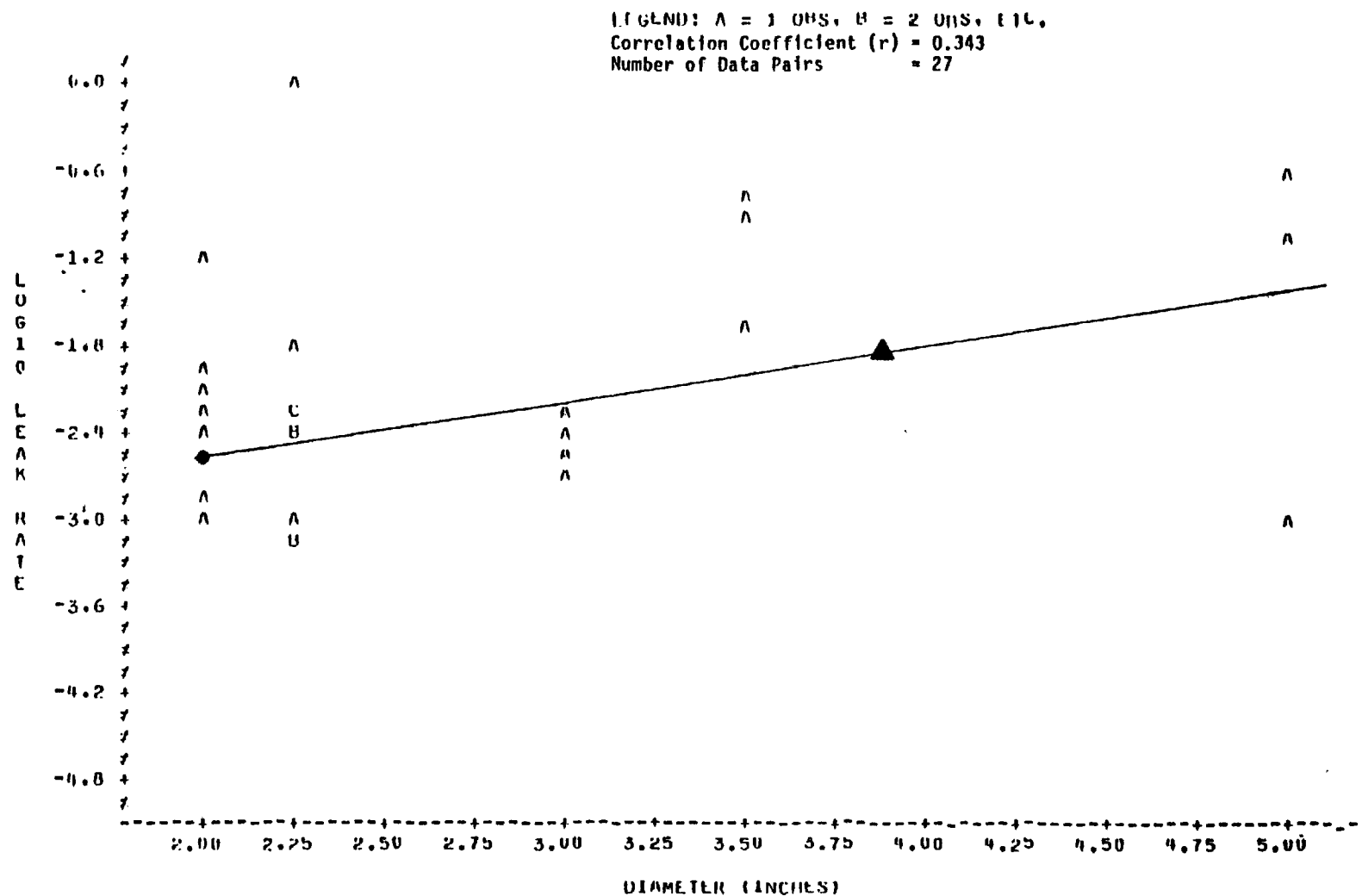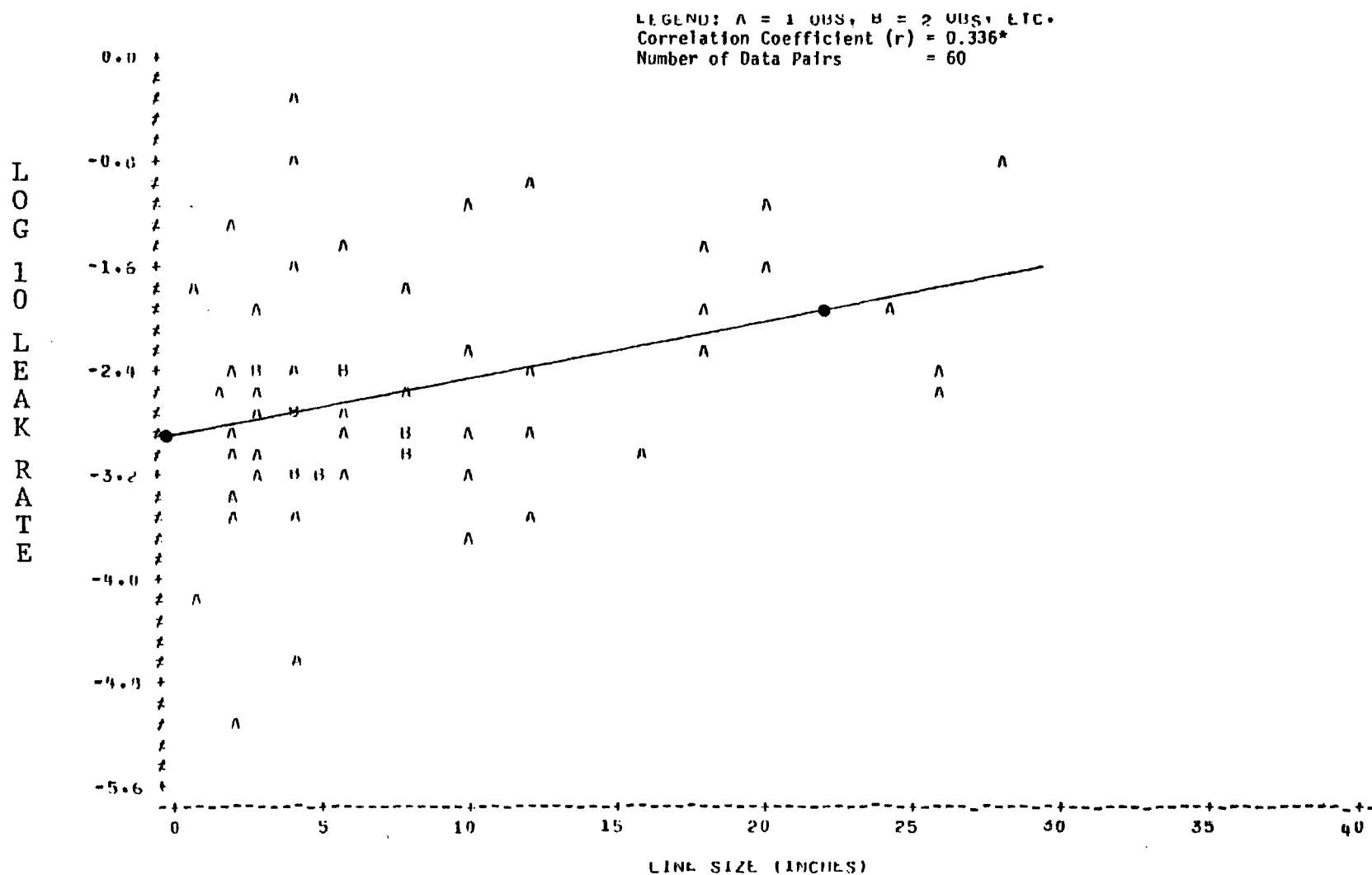
Figure 18   Leak rate vs. line size - flanges.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Coefficient (r) = 0.096

Number of Data Pairs = 181

290
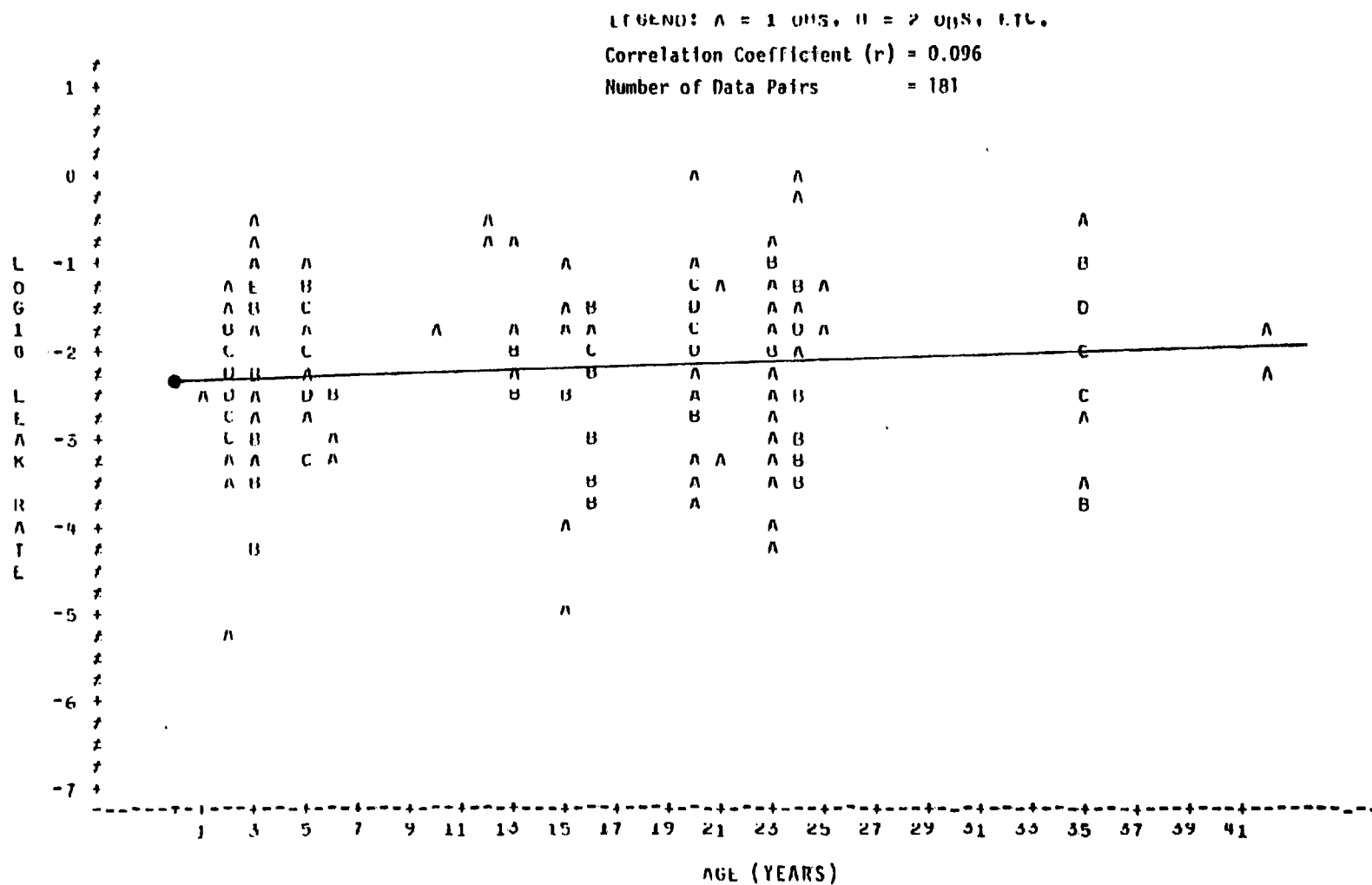
Figure 19 Leak rate vs. age - valves, light liquid/two phase streams.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Correlation Coefficient (r) = -0.012

Number of Data Pairs   = 291

```
      f
  2 + f
      f
      f
      f
  1 + f                          A
      f              A               A
      f              B  AB      A         A
      f     A  A  A       A
  0 +A    A  A     A    B   A  A     A
L     f   A   A      BC   A  B      A
O     fA     AABA  B   BBA    A  A     A    A
G     f  A  CFCA  AA  CBBABA  B   A         A  A
1 -1 +        AACAB   DBA  ABAB          A  A              A
O     fAA   A  A  BA  ABBE  C  A  A  B             A              A
      fAA   A  LAA  A   BBAA   AA  B   A     A  AB
L     fABABACAB  ABAABBAA  AAA    A        A   A      A
E -2 +        ABEAA  A  C  BA   BA           B  A
A     f    A  CBA  AAA  ABCB  AA      A       B     A
K     fABAA  B  AA   A  A      AA       A           A
      fE     AACAAB  AAA  AA  A                A
R -3 +        BA  A    A        A              A          A
A     f          A  BLA       A
T     f       A   A     A  A  A
E     f  A  AA
 -4 +    A                A
      f
      f
      f
 -5 +    A  A
      f
      f    A
      f
 -6 +
      f
    -+-------+-------+-------+-------+-------+-------+-------+-------+-------+-------+-------+-------+-
     0    160    320    480    640    800    960   1120   1280   1440   1600   1760   1920
```

PRESSURE (PSIG)

Figure 20   Leak rate vs. pressure - pump seals, light liquid service.

LLGEND: A = 1 OBS, B = 2 OBS, LTC.

Correlation Coefficient (r) = -0.012

Number of Data Pairs   = 294

Figure 21 Leak rate vs. temperature - pump seals, light liquid service.
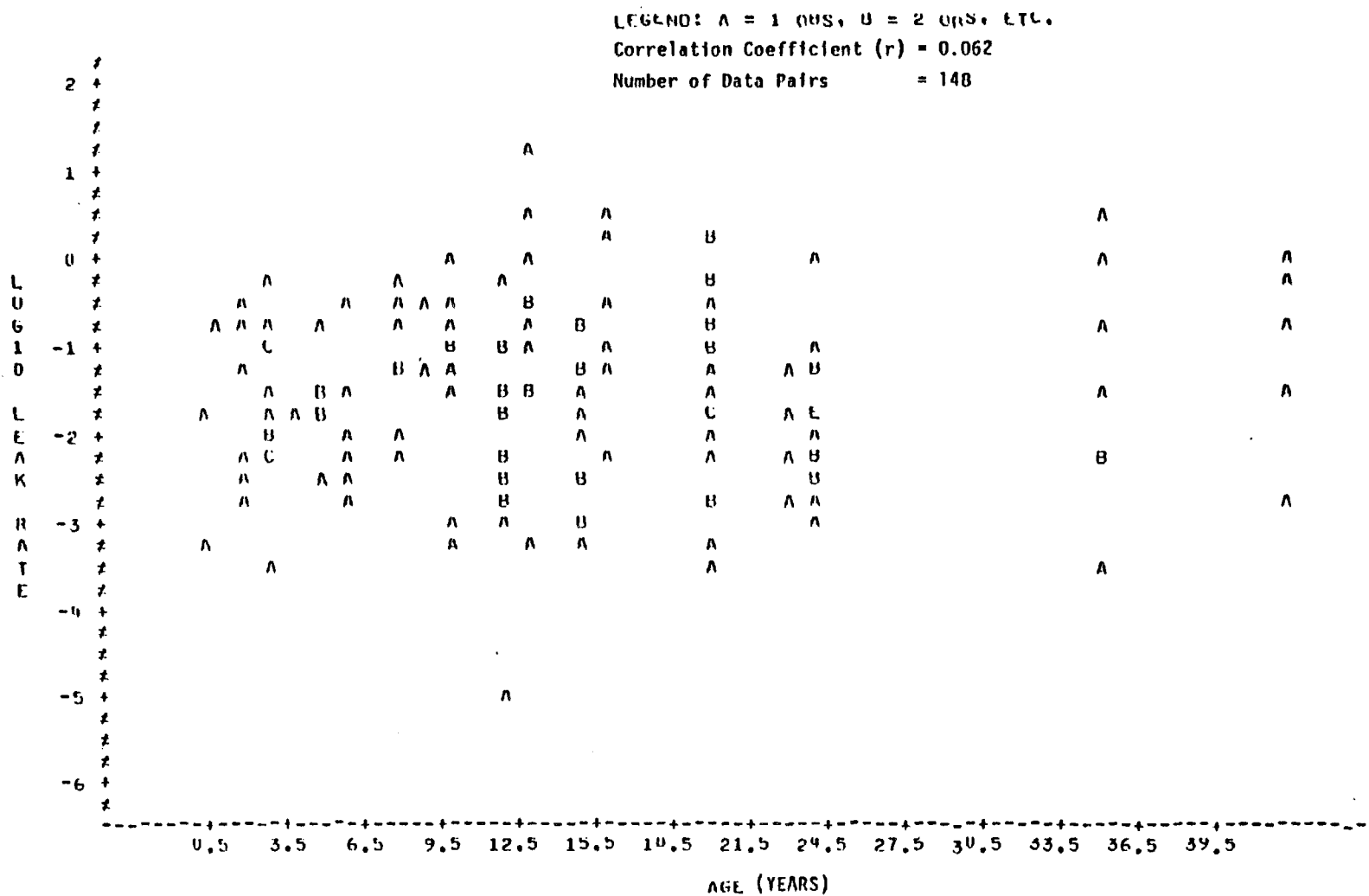
Figure 22   Leak rate vs. age - pump seals, light liquid service.
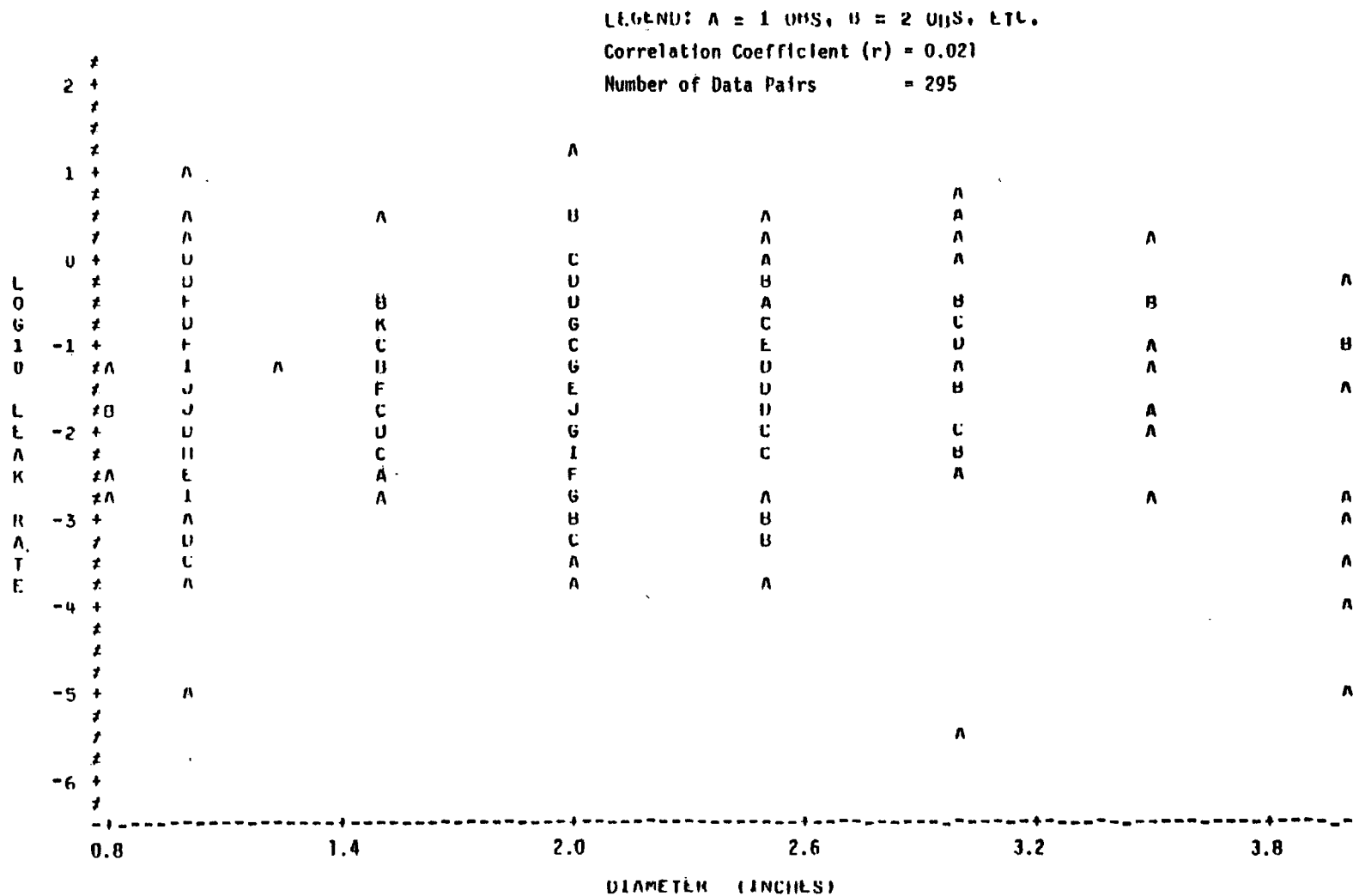
Figure 23 Leak rate vs. diameter - pump seals, light liquid service.
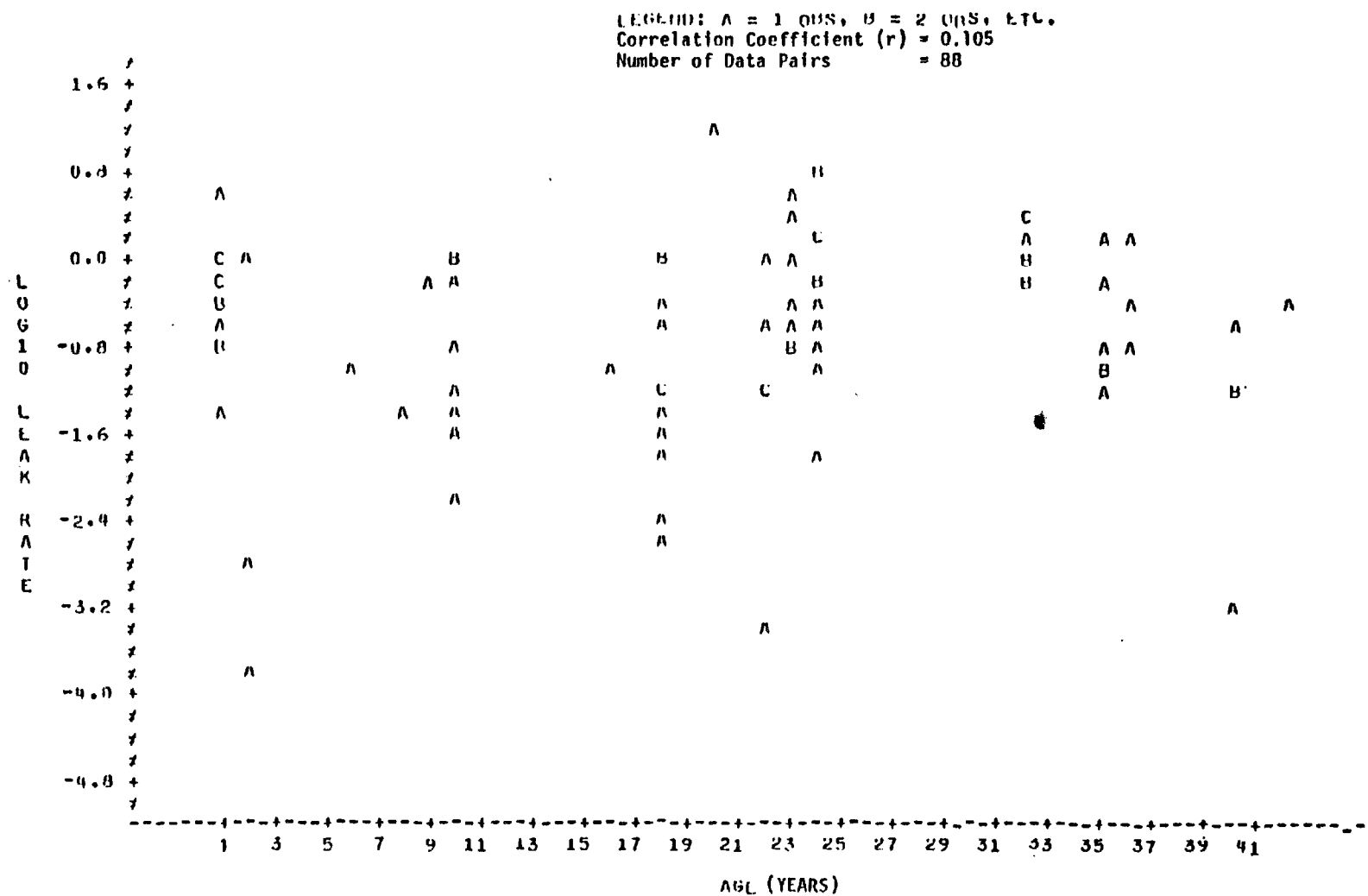
Figure 24   Leak rate vs. age - compressor seals, hydrocarbon service.

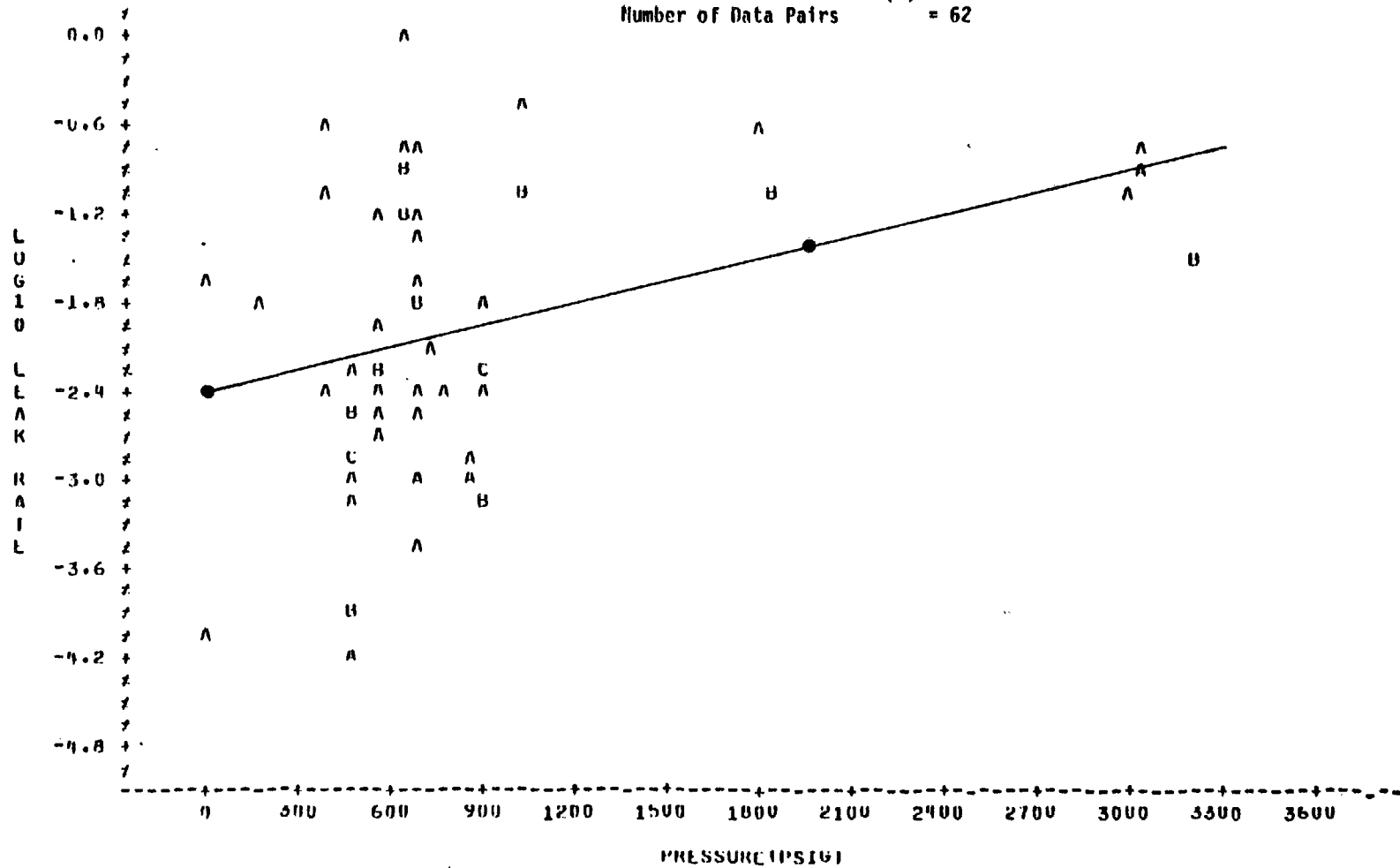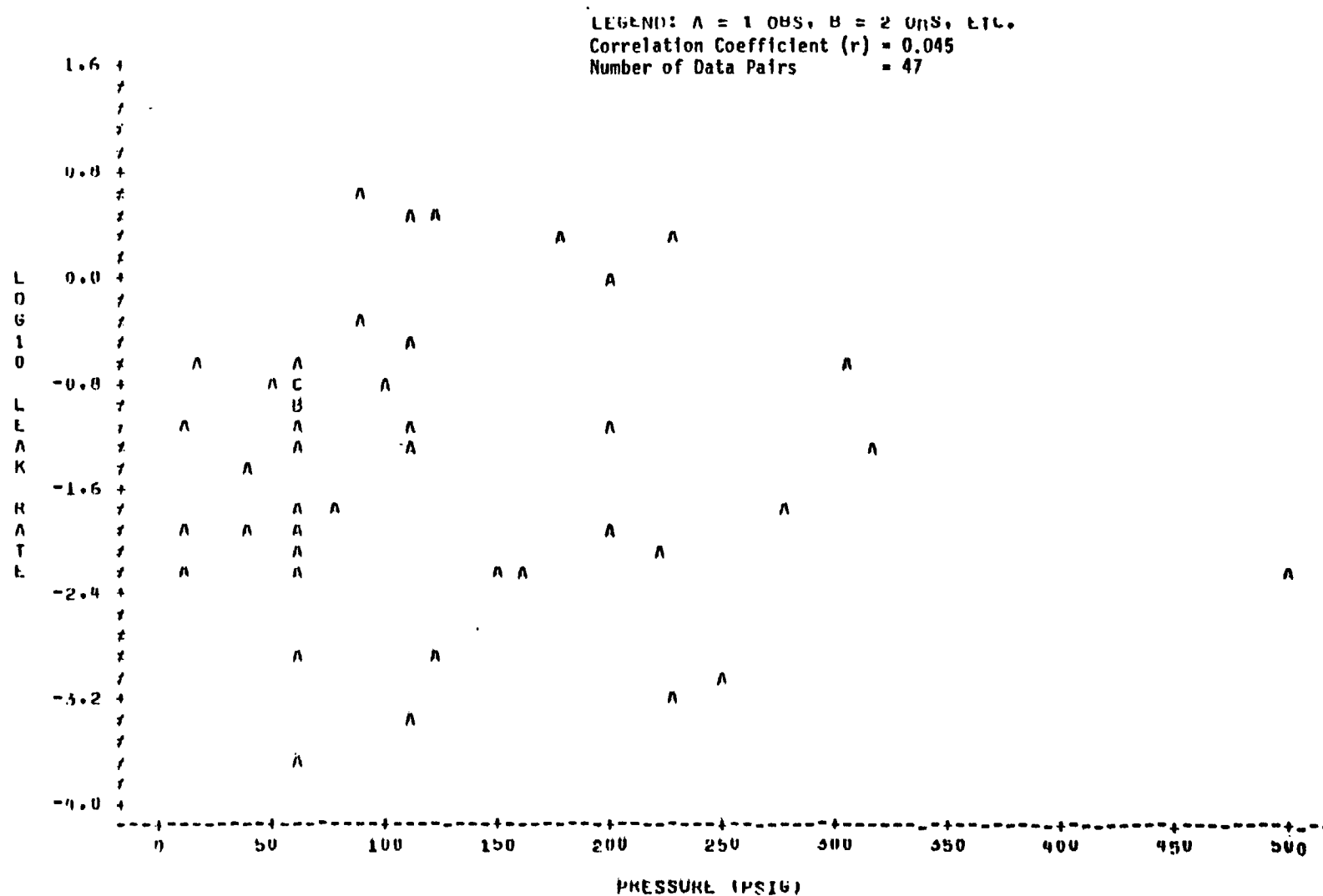Figure 25   Leak rate vs. pressure - relief valves.

Several trends were expected to exist for discrete variables. Control valves were expected to leak more then block valves because of a higher frequency of operation. Vibration was expected to be directly proportional to leak rate. Packed, single mechanical, and double mechanical seals were expected to represent the range of highest to lowest emission rates. It was also speculated that sources made by different manufacturers would exhibit different emission rates. Several examples of discrete variable correlations are shown in Figures 26 through 34.

CONCLUDING REMARKS

Even the "most significant" correlations observed showed a lot of scattered data and the correlations were not dramatic. The only exception to this is the effect observed for stream composition. These results do not necessarily indicate that correlations between emission rates and process variables are nonexistent. There were several factors discussed previously which probably explain why no significant correlations were observed, and therefore no conclusions can be drawn from the observed results. As fugitive emissions become subject to regulatory constraints, additional data may be collected by the regulated industries. This expanded data base may eventually reveal significant correlations between process variables and fugitive emission rates.
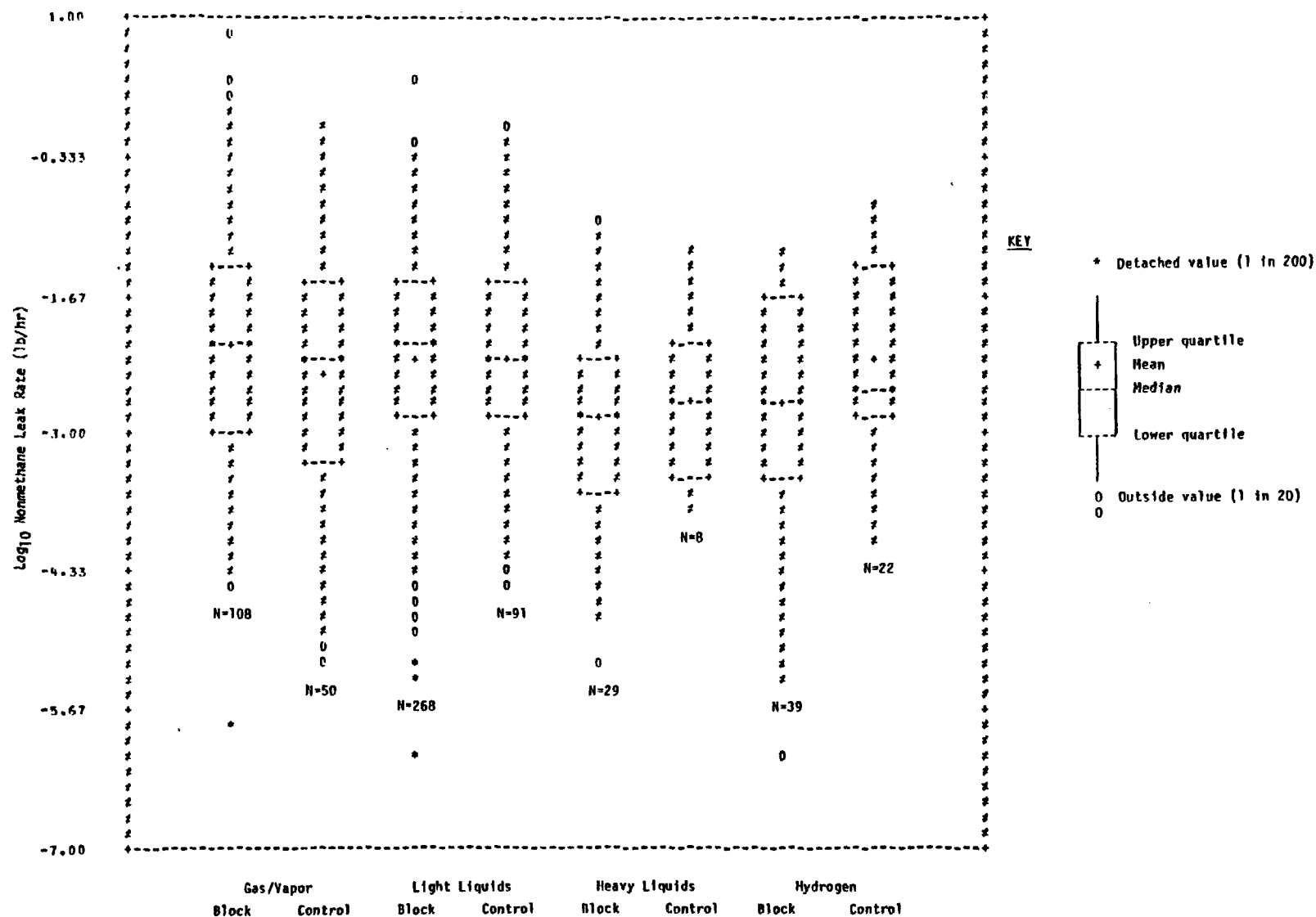
Figure 26   Schematic plot for valves by block/control variable.
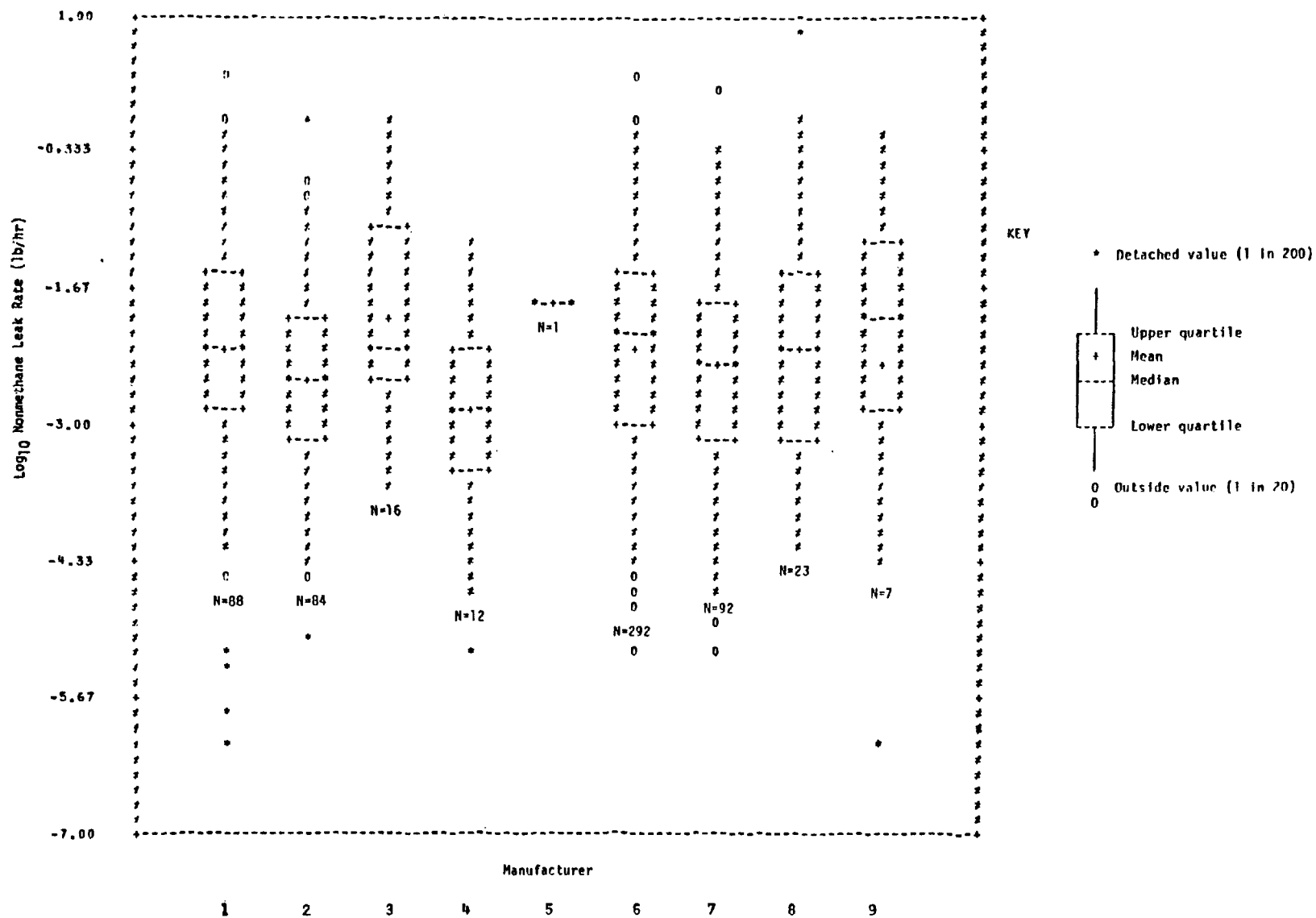
Figure 27   Schematic plot for valves by manufacturer variable.
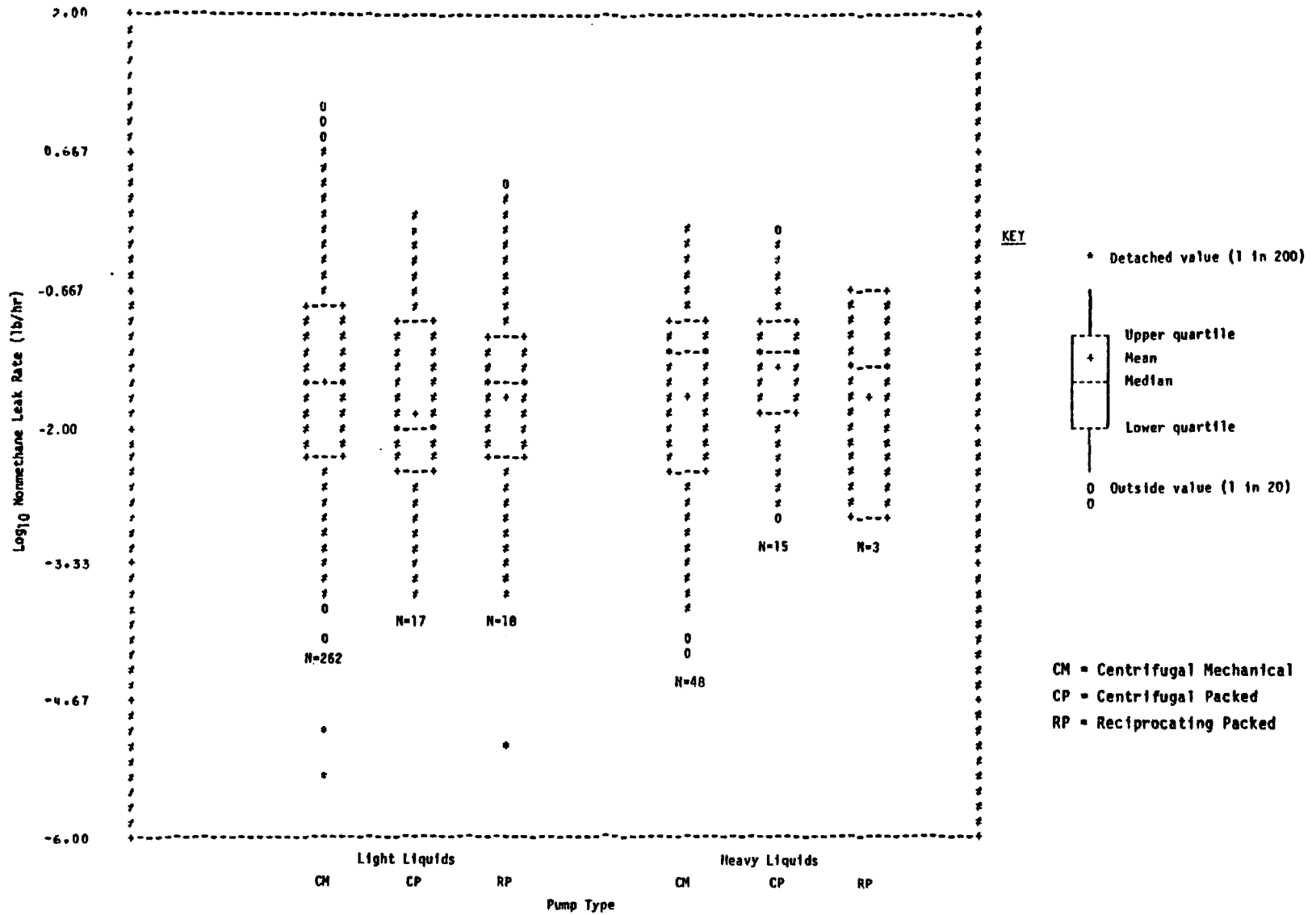
Figure 28   Schematic plot for pumps by pump type variable.
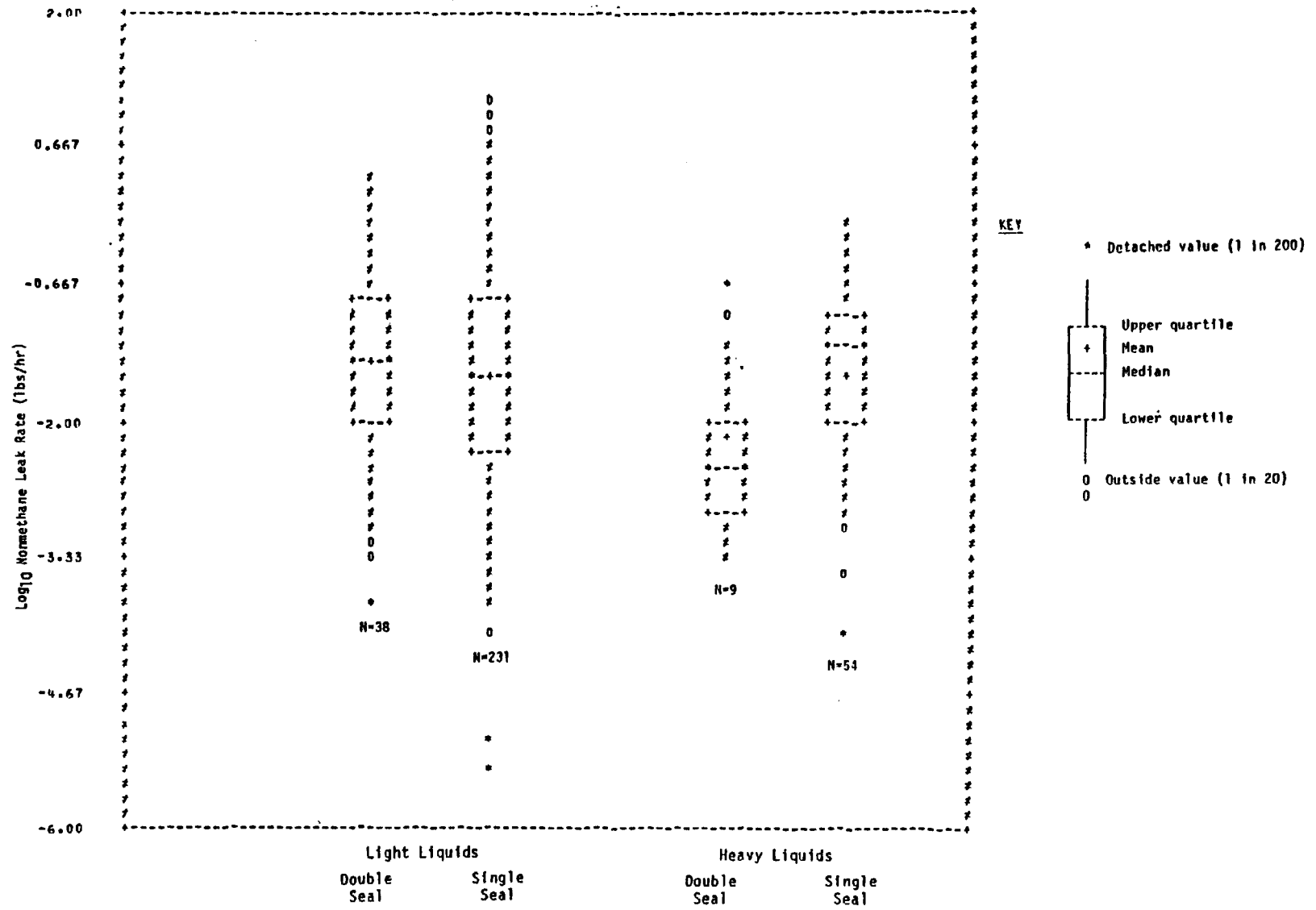
Figure 29   Schematic plot for pumps by seal variable.
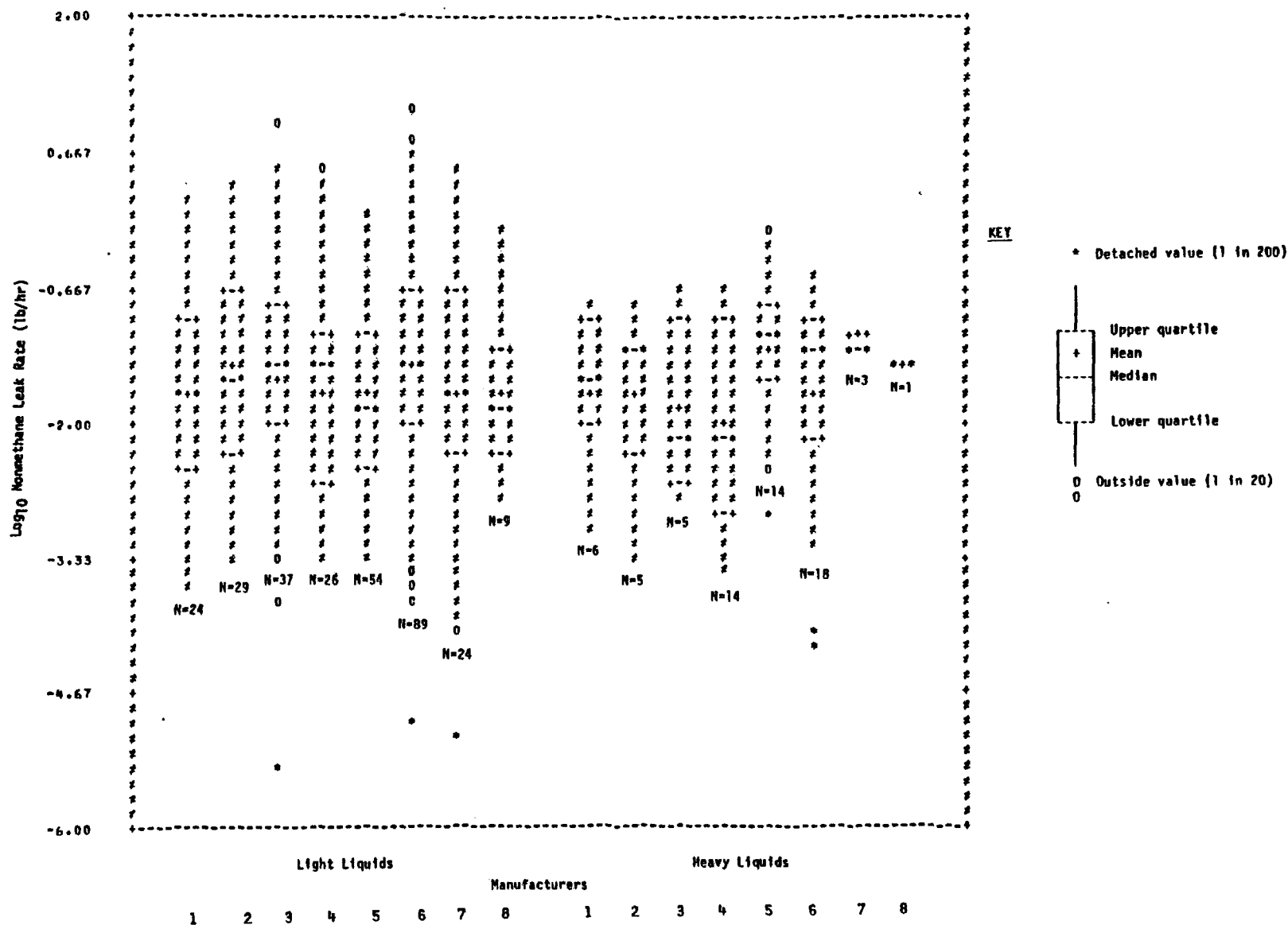
Figure 30   Schematic plot for pumps by manufacturer variable.
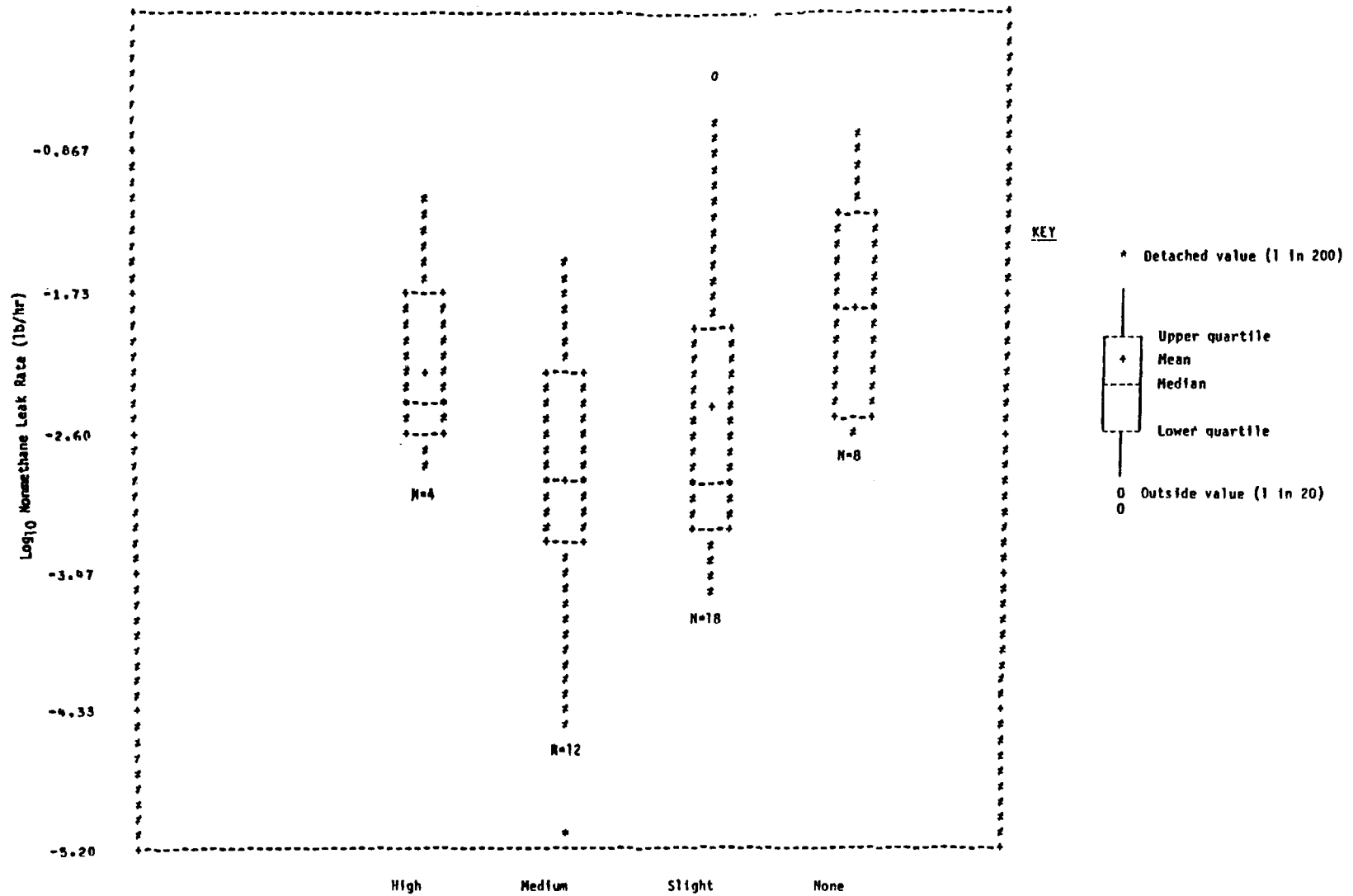
Figure 31   Schematic plot of flanges by vibration variable.
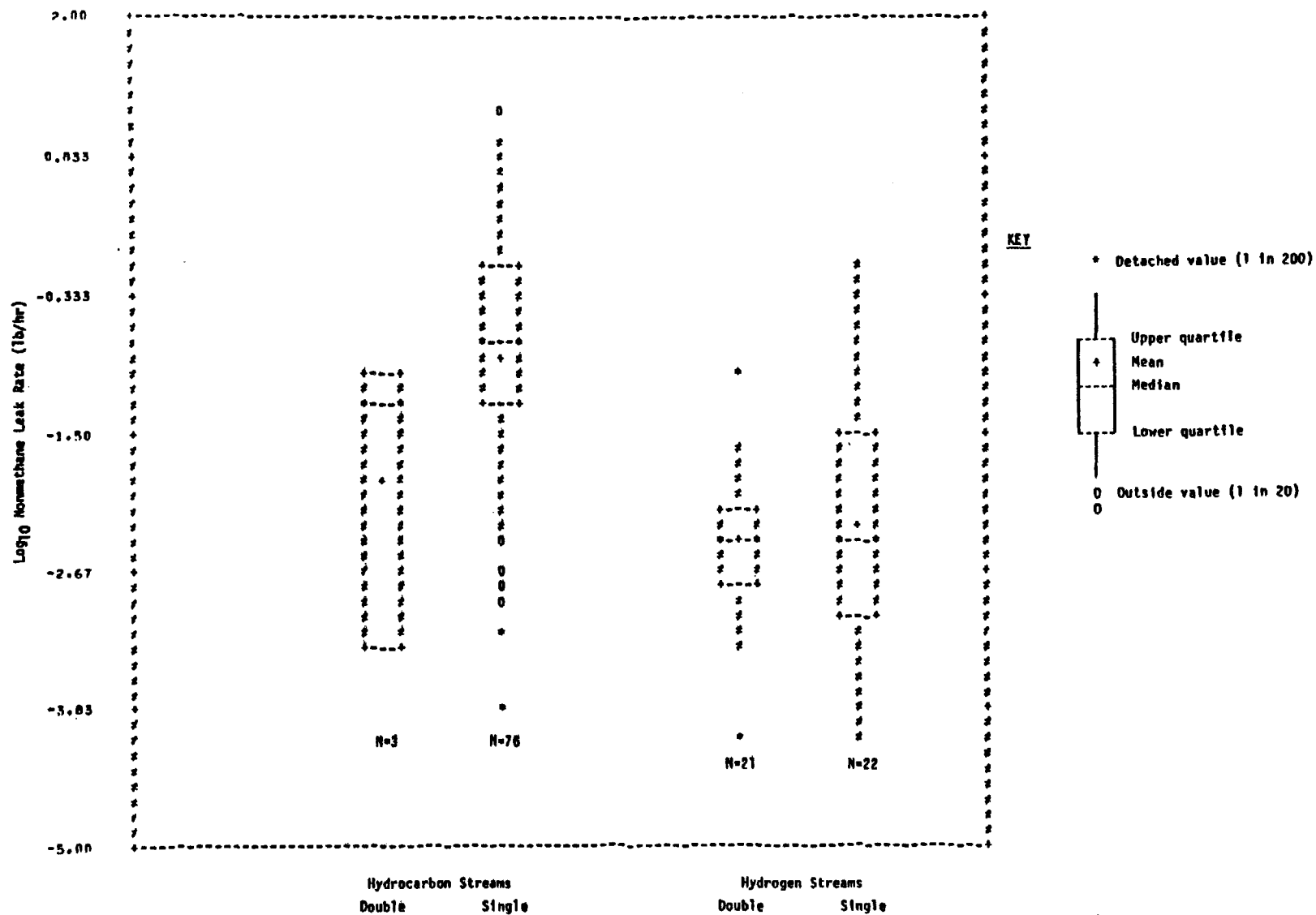
Figure 32   Schematic plot for compressor seals by single/double seal variable.
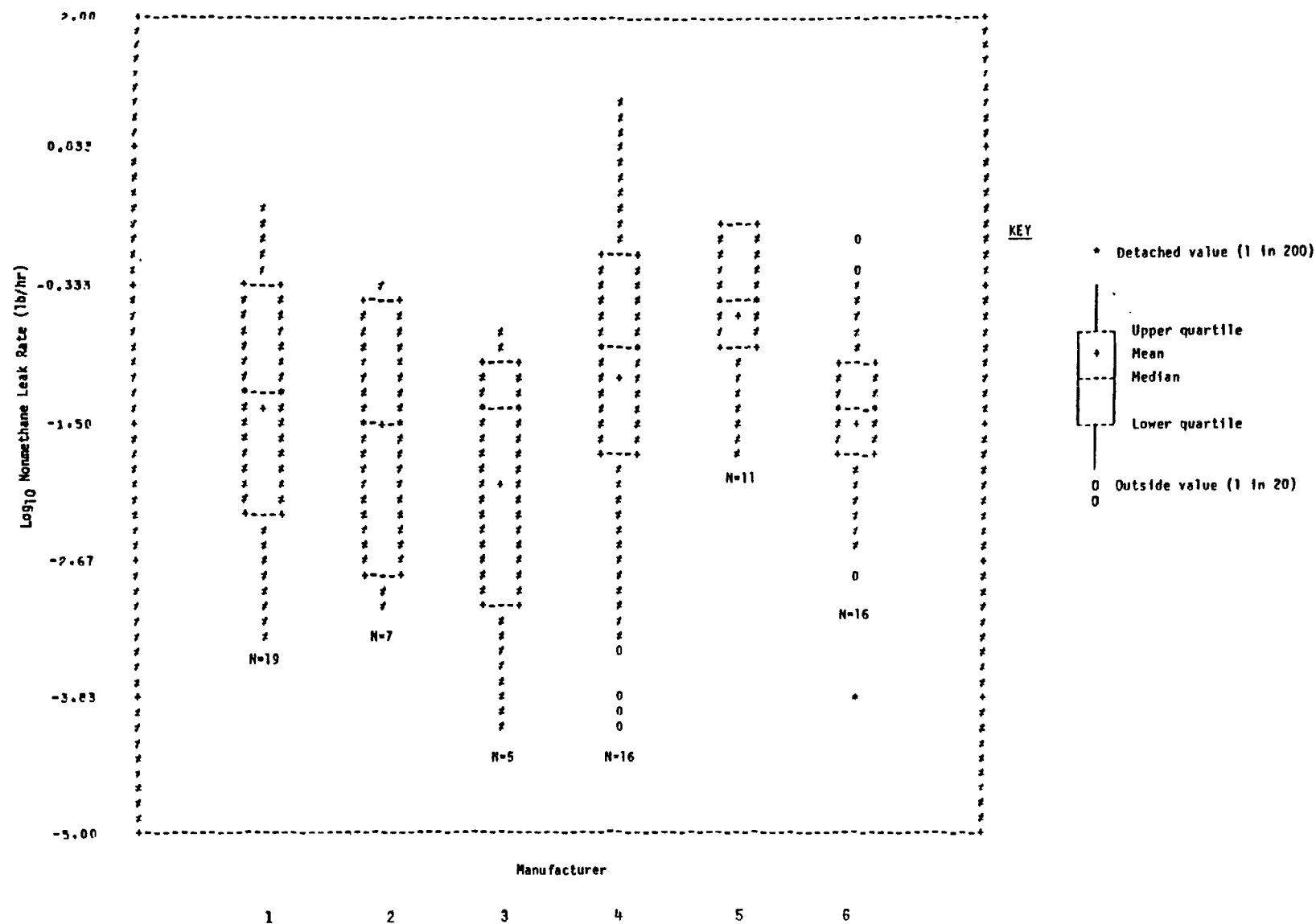
Figure 33   Schematic plot for compressor seals by manufacturer variable.
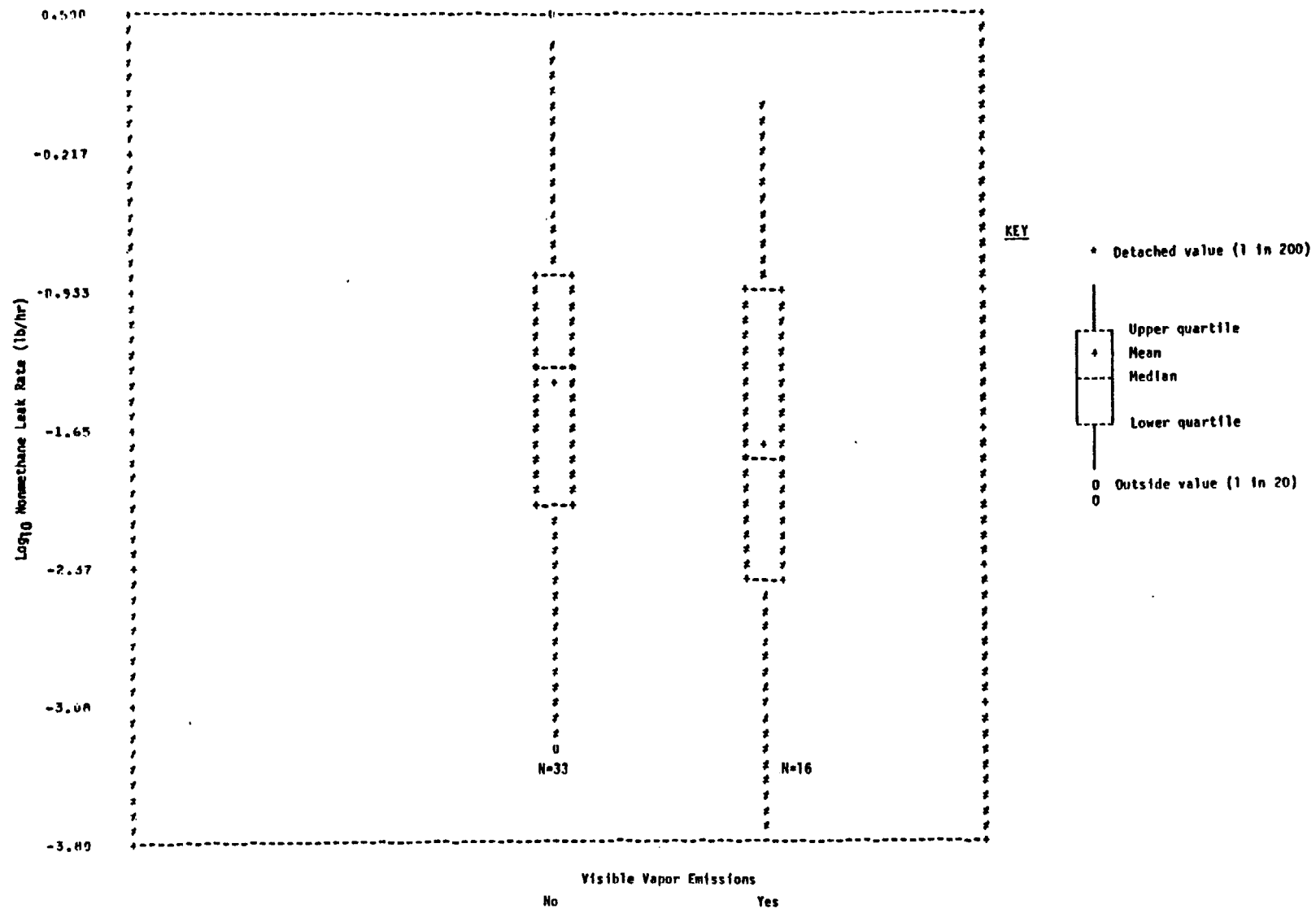
Figure 34   Schematic plot of drains by visible vapor variable.

REVIEW

by

A. F. Pope
ARCO Petroleum Products Company
A Division of
Atlantic Richfield Company
Los Angeles, California

on

CORRELATION OF FUGITIVE EMISSION RATES FROM BAGGABLE
SOURCES WITH REFINERY PROCESS VARIABLES

RESUME

Arthur F. Pope is the Manager, Environmental Policy and Planning, for ARCO Petroleum Products Company, a division of Atlantic Richfield Company. He received his B.S. degree in Mechanical Engineering from the University of Detroit in 1969. Since 1974, he has worked for Atlantic Richfield as a Project Engineer, Manager, Air and Water Conservation, and Manager, Environmental and Energy Conservation, at the Watson refinery, Carson, California. He has participated in the several projects conducted by EPA and the California Air Resources Board which attempted to ascertain atmospheric emissions of VOC from refinery sources, including valves, during his assignments at the Watson refinery.

REVIEW

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A. F. Pope
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CORRELATION OF FUGITIVE EMISSION RATES FROM BAGGABLE
SOURCES WITH REFINERY PROCESS VARIABLES

INTRODUCTION

Refinery fugitive VOC emissions have been studied a number of times, starting in 1957 with the Joint Study[1] of the then Los Angeles County Air Pollution Control District and culminating most recently with the completion of the EPA/RADIAN program under discussion at this Symposium. The Atlantic Richfield Watson refinery has been involved in each of these studies except the recent RADIAN effort. Therefore, the observations made in these previous studies should be useful in comparing the results from our experiences with the results from facilities examined by RADIAN. I will limit my discussion to the subject of R. L. Honerkamp's paper, "Correlation of Fugitive Emission Rates From Baggable Sources With Refinery Process Variables."

The data I will present corroberates what Honerkamp found--the dominating correlation is stream composition. I will also suggest that, for refinery valves at least, process unit designations may be more suitable and are certainly more practical than specific stream composition in designing inspection and maintenance programs for refinery fugitive VOC sources.

DISCUSSION

As reported by J. H. Nakagama[2] at a previous EPA/RADIAN workshop on this subject at Jekyll Island, Georgia, in 1978, Atlantic Richfield Company undertook a study of all the valves and fittings in one of its crude oil distillation units. The objective of this study was to assess the costs that would be incurred for the inspection of all valves and fittings for the detection of any leaks, using a soap-solution method. Of the more than 11,000 potential leak sources checked in this 38,000 B/D crude unit, 38 leaks were discovered. Thirty-one leaks were repaired with the unit on-stream.

Subsequent to this study, the California Air Resources Board, using enforcement personnel, conducted a two-week study of refinery valves and flanges in the South Coast Air Basin including Watson. Upon reinspection of this same crude oil distillation unit, using soap-solution methods, no leaks were found. Approximately eight months had elapsed between studies.

Some conclusions that can be reached are: (1) once repaired, crude oil distillation unit valves and fittings will not begin to leak for at least eight months, and (2) crude oil distillation unit process stream conditions of pressure, temperature, stream composition, etc., collectively yield a low probability that a component will be found to be leaking, whenever it is inspected.

In each of the studies mentioned, virtually all valves and flanges were examined. As a result, it would be more accurate to say that these studies had characterized the emission factor for the valves for that specific crude oil distillation unit, rather than the emission factor for the category of valves in general. Indeed, the data ought not be considered in statistical analysis, since the valves were not selected on a random basis. Therefore, it is not possible to compare these results directly with results obtained by RADIAN.

However, these data and that which I am about to describe generally support the finding that stream composition is an appropriate variable to consider when developing fugitive emission control strategies and that, as noted in the crude oil distillation unit case, the composite effect of the process variables associated with a process unit may be more practical in identifying those refinery sources which have a higher probability that an individual component within that process unit will be found to be leaking.

While Atlantic Richfield Company disagreed[3] with the inspection methodology and the conclusions reached by the California Air Resources Board enforcement personnel, some insight on the composite effect of process variables can be gleaned from the data obtained during this effort. The process units inspected at Watson included the crude oil distillation unit mentioned previously, two additional crude oil distillation units, an alkylation unit, a super fractionation and isomerization (SFIA) unit, and LPG storage vessels and associated transfer piping.

The refinery obtained duplicate gas samples of each component which was bagged by CARB and analyzed the sampes for VOC. Using the CARB leak rate measurement and the mass spectrometer results from the refinery laboratory, the following estimated emission factors were developed for the valves and flanges associated with each specific process unit:

UNIT TYPE	VOC EMISSION FACTOR LB/DAY/VALVE	LEAKING MATERIAL
Crude	0	N/A
Alkylation	0.0299	Butanes
SFIA	0.0362	Light Gasoline Components
LPG	0.0596	LPG

These emission factors incorporate all the variables possible for each process unit without the need to determine their individual influence. In general terms, these factors also indicate that the stream composition plays a significant part in the unit emission factor, i.e., the lighter and higher pressure streams exhibited higher leak rates.

A crude oil distillation unit will have many different streams at different temperatures, compositions, and pressures. This type of unit was found not to have any leaks. At the other end of the spectrum, the LPG facilities handle a single stream at relatively constant temperature and pressure and was found to leak most. If one were to consider all streams within a process unit and determine an "average" stream, the stream composition effect is easily seen.

CONCLUSIONS

Several conclusions concerning fugitive VOC emissions result from the preceding discussion:

1. Process unit VOC emission factors for valves corrolate well with "average" stream composition.

2. Process unit designation offers a more practical method for evaluating fugitive emission control strategies than stream type.

3. Process unit designation minimizes the problem of attempting to correlate a multiplicity of process variables, including component age, line size, pressure, temperature, and stream composition.

4. The data discussed support the conclusion of R. L. Honerkamp that the dominating correlation is stream composition.

REFERENCES

1. "Joint District, Federal, and State Project for the Evaluation of Refinery Emissions," Los Angeles Air Pollution Control District, 1957.

2. "Inspection and Monitoring Concepts for Refinery Fugitive Emissions," J. H. Nakagama, 1978.

3. Letter, N. E. Pennels (Atlantic Richfield Company) to J. J. Morgester (California Air Resources Board), May 5, 1978.

R. L. Honerkamp

QUESTIONS AND ANSWERS

Q. James Stone/Louisiana Air Control Commission - The first question, maybe frivolous. Did you assess operator motivation as a variable? In other words, in an HF alkylation unit, he is very likely to see to it that any leak is repaired immediately, while in some other units, like a coker nothing dripping is going to hurt him, so he wouldn't go after the leak quite as fast.

A. - No! We did not attempt to assess that particular variable. The results that I presented here were not really a documentation of any existing maintenance practices, but based on the entire data base collected from the thirteen refineries nation-wide. All sources in the stream composition service shown pose the effect of the process variables on the emission rate. But, perhaps looking at it on a unit basis, as Art Pope suggested, might show differences that could be attributable to that factor. But, I don't have any data that I could present that would show how that effect could be quantified. Art, do you have anything else?

COMMENT/A. F. Pope/ARCO Petroleum Products Company - One of the units in the study that I did not present any information on was that in our plant we happened to have a benzene unit and there were no high VOC emissions from that unit. There were some hydrogen leaks, but there were no VOC leaks. So, that might tend to answer your question.

Q. James Stone/Louisiana Air Control Commission - The second question is that you have been putting a lot of effort into your statistical evaluation of the data. Do you think that a statistical approach would have validity in regulations which we might write to cover maintenance of this type?

A. - I think it certainly might, although I don't think that any of the correlations presented here this morning other than stream compositions are significant enough to warrant such attention. All the variations that we saw were primarily about an order of magnitude variation in leak rate throughout the entire range of the variable. Although there were much greater variations than that at individual values. So, based on that I don't think we can conclude that any particular temperature range or pressure

range should have more or less frequent inspection of maintenance. Although the effect does seem to be there as far as stream composition.

Q. James Stone/Louisiana Air Control Commission - What I really mean is that we have a regulation in Louisiana that says that best practical maintenance shall be used at all times in a refinery. And, as we inspect the place, if we pick a statistical number of valves rather than try to inspect everything on paper, and if we find that below a certain number is leaking, they are in compliance, and above a certain number, they would be considered to be in violation of that regulation.

A. (By Rosebrook) - Lloyd Provost has a very definite view on that. The line of reasoning is that he can, given a sufficient data base for the enforcement people to work with, he can set confidence intervals based on the time since the refinery last did their inspection and maintenance in a particular unit, he feels very strongly a set of numbers could be developed which would allow you to come in and for example screen 100 valves or 200 valves, rather than screening the entire unit. If you find a certain number leaking then you could call it a violation with some kind of confidence, if you find some leaking but not the limiting number then it should not be a violation. I can't go through that explanation near as well as Mr. Provost, and perhaps we can at least have you get together with him to answer that question.

A. (By Honerkamp) - One thing that such a scheme does require is that several variables be understood. Those variables will be discussed in greater detail in the final paper that EPA will present this afternoon, those include: what level of repairs are achievable; and, how long after repair do the leaks reoccur. You must know, with confidence, what those factors are before you can attempt to develop the statistical enforcement program.

COMMENT/Person unknown - I encourage the regulators not to write that number as zero. The data that you have seen would tell you that on any given day, in any given plant, there is going to be at least one component that is going to leak to some degree or another. And, what I am trying to tell you is that if you have a nonattainment area and you have a source requesting a permit, and that source has to certify that he is in compliance with all federal, state, and local regulations, under penalty of perjury, how can he do that if you have a regulation that requires all discrete components in a plant, not to leak. That is a no growth regulation.

Q. Nancy A. Kilbourn/PEDCo Environmental, Inc. - My first question is how
much did it cost Atlantic Richfield to monitor all the valves? And, my
second question is how much do you think that you will save after you
establish an I and M (inspection and maintenance) program?

A. (By Pope) - We are subject to California regulation now and have been
for almost a year to conduct I and M in the Southern California area at our
Watson refinery, and we have utilized the resources of a contractor to do
that inspection and minor maintenance work. The costs this year are going
to run on the order of $100,000 to do the inspection and perhaps another
$50,000 to do some special repairs on-line, to avoid shutting down unit to
make that repair. The State of California regulation for your information,
has a maintenance provision in it. It allows two working days from the
discovery of a leak to repair it to a no-leak condition. And, a leak in
this case is 10,000 ppm at 1 cm. A repair is 1,000 ppm at 1 cm.

Q. R. L. Honerkamp/Radian - Do those numbers include regular maintenance or
is that just special maintenance?

A. (By Pope) - No, that is just special maintenance for this program.
There would be additional costs to the number that I gave you for the
contractors costs to us, the internal cost of our own people. I'm really
not sure what they are at this point. It would be more.

Q. Nancy A. Kilbourn/PEDCo Environmental, Inc. - How much do you think you
would save then in recovering your volatile organic compounds?

A. (By Pope) - I don't have a number for you.

Q. James Stone/Louisiana Air Control Commission - Just going to follow-up
on that same question. When your contractor does that sampling, do they
sample all valves or flanges or do they use some percentage to work by?

A. (By Pope) - No, the regulation we are subject to, requires a comprehen-
sive inspection of all valves. Flanges are not included.

Q. James Stone/Louisiana Air Control Commission - How many is that? How
many valves for your facility?

A. (By Pope) - I think we estimated, since we don't really have a complete
count with a high degree of accuracy, something on the order of 100,000 to
130,000 components. They are $1.60 a piece to check if you want.

Q. K. C. Hustvedt/US-EPA-RTP - On the whisker diagrams, looking at the difference between the block valves and the control valves, the emission factors before you crossed the lines looked like the same for all three process stream variables; the gas, the light liquid, and the heavy liquid. I think that it has biased the diagrams by excluding the nonleakers from them. You are showing emission factors that are not the real emission factors.

A. - But I am showing leak rates for the ones that did leak. As I pointed out in the beginning, the combination of that effect plus the effect on the percent that leaks, i.e. how many that don't leak at all, is what results in the emission factor. But rather than look at emission factors for my presentation I looked at just the effect on the ones that were leaking. Since there were no dramatic effects that were going to be shown at all, I felt that it would be more interesting to look at the effect on the ones that did leak, rather than whether or not they leaked at all. That effect has been split out in the stream category designation.

Q. K. C. Hustvedt/US-EPA-RTP - To completely compare the two between block and control valves you have to know what your total population looked like, not just some arbitrary subset, say over 200 ppm, to be able to compare the effects of those if 90 percent of the block valves did not leak and 50 percent of the control valves did not leak. Just comparing their average emission factors for leakers doesn't tell you on the average if block valves or control valves leak more or less. You have to look at the total population, I would think, to see what a real true comparison between what the effect of those two is, not a subset based on an arbitrary cutoff.

A. - We weren't looking at the effect on emission factor, but the effect on the ones that leaked. It is true that if such an effect did exist that emission factors were significantly different for block and controlled valves, that would have been the incorrect presentation to look at. I don't believe such an effect, on emission factors does exist, as far as block and control valves. That is, I think the confidence intervals probably do overlap significantly, if you look at emission factors. But it is true, that what we looked at were just the ones that were leaking.

Q. A. F. Pope/ARCO Petroleum Products Company - I would like to encourage you not to think just of the components, as I mentioned in my discussion. I think you will be better served in looking at this whole spectrum of things that need to be done on a practical level. The people out there like myself have to implement something. If you can focus on getting to where you want

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to go in a practical manner, some of these discrete things you might like
to evaluate would be good to know, and perhaps will be helpful in
redesigning components for minimizing losses from those components. But
in terms of I & M programs, I don't think that they are really worthy of
the significant effort to characterize them in a very discrete manner.

THE EFFECT OF MAINTENANCE PROCEDURES ON THE REDUCTION OF
FUGITIVE HYDROCARBON EMISSIONS FROM VALVES IN
PETROLEUM REFINERIES

R. G. Wetherold and S. L. Preston
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Austin, Texas

ABSTRACT

Regulations pertaining to the screening and maintenance of refinery process valves are being proposed by regulatory agencies. Under an EPA contract, Radian has studied the effect of simple maintenance practices on the reduction of hydrocarbon emissions from refinery valves. The results are presented here. Included in the study were block and control valves in the major types of refinery process stream services. The reduction in hydrocarbon emissions after maintenance was determined for valves having initial leak rates ranging from large to small. The merits of hydrocarbon monitoring during the performance of maintenance were evaluated. Finally, the effectiveness of valve maintenance over short (one week) and long (six months) time periods was investigated.

RESUME
R. G. Wetherold

Robert G. Wetherold is a Senior Staff Engineer at Radian Corporation in Austin, Texas. He is currently Project Director for several programs associated with the study of fugitive emissions from petroleum refineries and chemical plants. He received his B.S. in chemical engineering from Texas A&I University, a M.S. in chemical engineering from Texas A&M University, and his Ph.D. from the University of Texas at Austin. Before coming to Radian, he was employed as an Associate Engineer in the Process Development Division of Mobil Chemical Company. He also worked in the Process Design Division of Chevron Research Company. He is a member of AIChE.

Sheryl L. Preston

Sheryl Preston is a Data Management Specialist at Radian Corporation. She has a B.S. from the University of Arizona, and is currently in a Masters program at the University of Texas. She is a member of ASQC. For the past 3 years she has managed the Fugitive Emissions from Petroleum Refining data base at Radian and contributed in data analysis.

R. G. Wetherold/S. L. Preston

THE EFFECT OF MAINTENANCE PROCEDURES ON THE REDUCTION OF
FUGITIVE HYDROCARBON EMISSIONS FROM VALVES IN
PETROLEUM REFINERIES

The effects of relatively simple maintenance procedures on the reduction of fugitive emissions must be defined to evaluate the cost effectiveness of inspection and maintenance procedures. The reduction of fugitive hydrocarbon emissions from valves as a result of maintenance has been studied as part of the EPA's program for the environmental assessment of petroleum refineries. The emission reduction study is described in this paper. The results of the study are presented.

OBJECTIVES

The objectives of this maintenance study are given below:

- To select for the program those fugitive hydrocarbon emission sources which could be studied in the most cost-effective manner.

- To define a group of the selected emission sources which would provide a representative sample for the maintenance study.

- To determine the immediate effects of directed and undirected maintenance activities on the reduction of hydrocarbon emissions.

- To define the short and long-term effects of maintenance procedures on the reduction of fugitive hydrocarbon emissions.

MAINTENANCE PROCEDURES

The six "baggable" sources were all considered for maintenance studies in this program. These sources include valves, flanges, pump seals, compressor seals, relief valves, and drains. The types of maintenance considered for each source are described below. They are listed in order of increasing difficulty, complexity, and generally, cost.

The majority of valves in refineries are gate valves (on/off) and globe valves (control). Plug valves are also present. The types of maintenance considered for valves include:

- Tightening packing gland nuts (gate and globe valves)

- Adding grease (plug valve)

- Replacing the valve packing

- Injecting sealant into the packing area

- Replacing the entire valve

Pump seals are either of the packed or mechanical types. The maintenance procedures applicable to these seals are:

- Tightening of the packing gland nuts (packed seal)

- Replacement of the packing (packed seal)

- Replacement of the mechanical seal

The maintenance of compressor seals takes the same form as that of pump seals. Included are:

- Tightening of the packing gland nuts (packed seal)

- Replacement of the packing

- Replacement of the mechanical seal

Repair of flange leaks can generally be accomplished by one of these procedures:

- Tightening of the flange bolts

- Replacing the flange gasket

- Replacement of the flange or flange face

Those pressure relief valves venting to the atmosphere were also considered for maintenance studies. If these devices are leaking through the valve seat to the atmosphere, mechanical repairs are generally required. If a dual relief or manual bypass system is available, the more simple mechanical repairs might be made with the valve in the line but blocked out of service. In many cases, however, the entire valve must be removed and repaired.

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There is generally no simple maintenance procedure that can be used to reduce emissions from open drains. The drainage system must be revamped to include items such as covers and traps.

EXPERIMENTAL DESIGN OF THE MAINTENANCE STUDY

It was not possible to study the effectiveness of various types of maintenance on all six baggable source types. The study was limited by time, funds, and practical considerations in an operating refinery. As an aid in the definition of a useful but limited program, the total emissions from the six source types in the major process units of a refinery were estimated. The Gulf Coast Cluster Model Refinery developed by A. D. Little, Inc.[1] was used as a basis to these estimates. The number of sources in each unit were developed from source counts made during the course of the sampling program or from source counts of relatively similar process units.

The estimated total number of baggable source types in each major process unit is shown in Table I. In Table II the estimated percentage of leaking source types and the relative emission contribution of these sources are presented. The most numerous source types are valves and flanges. However, the percentage of flanges that leak is quite low, and their contribution to the total emissions is small. A considerable amount of time would be required to locate a sufficient number of leaking flanges for a satisfactory sample size.

Valves are quite numerous, over a third of them leak, and they contribute 60 percent of the baggable source emissions. Preliminary studies indicated that a significant reduction in valve emissions could be achieved through simple maintenance.

Nearly half of all inspected pump seals leaked to some degree. With the exception of valves, pump seals contribute more emissions than any other source type. In the case of packed seals, simple maintenance consists of tightening the packing gland. This can be done while the pump is in service. Leaking mechanical seals must be replaced. The pump must be taken out of service to make this replacement. Refineries generally have spare pumps which can be quickly placed in service in place of many of the more important pumps. Thus, in many cases, a pump can be taken out of service for maintenance without disrupting the process.

The majority of compressor seals leak. Because there are relatively few of them, however, their emissions are only 9 percent of the total baggable source emissions. Additionally, maintenance of packed seals and replacement of mechanical seals can be a major procedure. In many cases, the process would have to be shut down to repair or replace the compressor seals.

Maintenance of relief valves is also not an insignificant effort. While over a third of the inspected relief valves leaked, the emissions only make up 4 percent of the total baggable source emissions.

TABLE I. ESTIMATED DISTRIBUTION OF FUGITIVE EMISSION SOURCE TYPES IN MAJOR PROCESS UNITS OF A HYPOTHETICAL REFINERY[a]

Process Unit	Valves	Flanges	Pump Seals	Compressor Seals	Relief Valves	Drains
Atmospheric Distillation:						
Unit 1	890	3560	43	2	6	69
Unit 2	890	3560	43	2	6	69
Vacuum Distillation	500	2000	21	–	6	35
Light Ends/Gas processing	190	760	4	4	6	11
HDS – Reformer Feed:						
Unit 1	650	2600	14	6	6	22
Unit 2	650	2600	14	6	6	22
HDS – Light Gas Oil	650	2600	14	6	6	22
HDS – Light Cycle Oil	650	2600	14	6	6	22
HDS – Vacuum Gas Oil	650	2600	14	6	6	22
HDS – Coker Naphtha	650	2600	14	6	6	22
Fluid Catalytic Cracking	1300	5200	42	6	6	65
Hydrocracking	940	3760	31	6	6	58
Catalytic Reformer:						
Unit 1	690	2760	20	6	6	49
Unit 2	690	2760	20	6	6	49
Aromatics Extraction	600	2400	17	0	6	41
Allaylation	570	2280	15	0	6	41
Coking	310	1240	13	0	6	28
Hydrogen Production	180	640	3	6	4	8
	11650	46520	456	74	106	655

[a]Hypothetical refinery units taken from Arthur D. Little Gulf Coast Cluster Model Refinery with a capacity of 330,000 BPD.

TABLE II. ESTIMATED DISTRIBUTION OF FUGITIVE HYDROCARBON EMISSIONS FROM SIX SOURCE TYPES IN THE MAJOR PROCESS UNITS OF A HYPOTHETICAL REFINERY[a]

Source Type	Estimated Percent Leaking	Emissions Contributed By Each Source Type, Percent of Total
Valves	27	60
Flanges	3	6
Pump Seals	48	12
Compressor Seals	76	9
Relief Valves	39	4
Drains	19	9
		100

[a]Arthur D. Little: Gulf Coast Cluster Model Refinery – 330,000 BPS.

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It was decided that the most cost effective sources to study were valves and pump seals. Furthermore, the maintenance study would concentrate on valves, since they represent the greatest emission source of the baggable source types.

The maintenance to be performed on valves consisted of:

- Simple adjustment/tightening of the packing gland, or

- Injection of grease into the fittings of plug valves.

Additionally, some valves were to be monitored for extended time periods to determine the effectiveness of valve maintenance over an extended period of time.

The number of valves required to make the above evaluations was limited through selective experimental design. The wide variation in leak rates between valves was circumvented by using paired measurement schemes for maintenance evaluations. Only valves with particular selected leak rates were studied.

The factors that were considered in selecting valves for the maintenance study were:

- Process stream group (gas/vapor streams, light and two-phase streams, and heavy liquid streams.

- Valve type (block/gate, block/other, control/globe, control/other).

- Leak rate or screening value range (500 – 5000 ppm screening value, 5001 – 50,000 ppm screening value, and > 50,000 ppm screening value).

In addition, data were collected on all of the parameters normally included in the program.

A total of 28 valves were proposed for study at each refinery. The distribution of these valves is shown in Table III.

Pump seals were to be selected for the maintenance study in a manner similar to that for valves. The factors that were considered in the selection included:

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TABLE III. DISTRIBUTION OF VALVES TO BE STUDIED IN EACH REFINERY[1]

Process Stream Group	Valve Type	Low (500–5,000 ppm)	Medium (5001–50,000 ppm)	High (≥ 50,000 ppm)	Total X's
I Gas–Vapor Streams	BG	XO	XO □	XO	
	BO	0	X	X	10
	CG	X	X	X □	
	CO	0	X	X	
II Light Liquid & Gas–Liquid Streams	BG	XO	XO	XO □	
	BO	0	X	X	10
	CG	X □	X	X	
	CO	0	X □	X	
III Kerosine & Heavier Streams	BG	X	X	X	
	BO	0	X	0	8
	CG	X	X □	X	
	CO	0	0	0	
Total X's		6	12	10	28

[1] Determined by maximum "TLV Sniffer" reading.

BG = Block, gate; BO = Block, any type other than gate;
CG = control valve, globe; CO = control valve, other than globe.
□ = control point, i.e. select a valve but do no maintenance.
X = select a valve here if possible; 0 = secondary choice for valve selection.

- Leak rate category (medium leak = 0.5 - 1.0 lbs/hr, high leak rate = > 1.0 lb/hr).

- Pump type (centrifugal-packed, centrifugal-single mechanical seal, centrifugal-double mechanical seal, centrifugal-packed, etc.).

It was hoped that 10 leaking pump seals suitable for a maintenance study could be found in each of four refineries.

PROCEDURE

The steps below were generally followed during the maintenance studies:

- screening to locate potential sources

- rescreening of selected sources

- sampling of sources

- performance of maintenance

- resampling of sources

- additional short and long-term screening

- application of quality control procedures

A Bacharach "TLV Sniffer," a sensitive hydrocardon detector, was used to locate and select sources for study. With a dilution probe, the range of this instrument is 0 - 100,000 ppmv. The TLV Sniffer is calibrated with hexane. For source selection the TLV Sniffer probe was placed as close as possible to the points of potential leakage (valve stem and gland, pump seal). Readings were taken at eight different points around valve stems and glands and at four points around pump seals. The maximum reading was taken as the basis for estimating the leak rates. Leaking valves which fit into the desired distribution (Table III) were tagged for further consideration. Selected pump seals were similarly tagged.

When all the required valves and pump seals were located, preparations were made for measuring their leak rate. Each selected source was rescreened immediately prior to sampling. All data were recorded. The leaking source was then enclosed in plastic. A sampling train was attached to the enclosure and the leak rate from the source was determined.

After the initial leak rate was measured, maintenance was performed on the leaking source. This maintenance was defined as either "directed" or "undirected." Directed maintenance involves simultaneous maintenance and

screening of the source with a hydrocarbon detector. Maintenance activities are continued until no further reduction in hydrocarbon concentration can be achieved. Undirected maintenance consisted of the normal maintenance procedures without any hydrocarbon concentration monitoring during the activity.

When the maintenance procedures were completed, the maintained source was again screened and sampled. The leak rate immediately after maintenance was thus determined.

Whenever possible each maintained source was rescreened several times during a period of one to two weeks immediately following the maintenance. The purpose of this activity was to get an indication of the short-term effectiveness of directed and undirected maintenance.

Arrangements were made at some refineries to obtain some data regarding the long-term effects of maintenance on the reduction of emissions. In these cases, refinery personnel agreed to monitor selected maintained valves at intervals of one week to one month for a period of six months.

As part of the experimental study, quality control procedures were implemented. These generally consisted of replicate and multiple source screening, replicate source sampling, accuracy testing of the sampling train, frequent calibration checks, and frequent analysis of standard gases in the laboratory.

RESULTS

A total of 120 valves were included in the maintenance study. Eighty-six of these actually underwent maintenance. The remaining 34 valves were not maintained. They were screened, however, and were also, in some cases, sampled. The unmaintained group provided data on the variability of screening values and the change in leak rate as a function of time.

Twenty-seven valves underwent directed maintenance. Fifty-nine valves were subjected to undirected maintenance procedures.

No maintenance studies were performed on pump seals. Difficulties were encountered in locating leaking pump seals in the proper leak rate categories. In addition some pumps that were found to be leaking could not be adequately isolated for seal replacement. In some cases, there were no spare pumps available to replace the leaking pump. In other cases, it was felt that the time required and the cost incurred for seal replacement was not justified by the size of the leak.

The effect of maintenance procedures on leak rates can be expressed as a percentage reduction in leak rate. The percentage reduction can be calculated from Equation 1.

$$R = \frac{L_B - L_A}{L_B} \times 100$$

(1)

where

R = leak rate reduction, %

L_B = leak rate before maintenance, lb/hr

L_A = leak rate after maintenance, lb/hr.

Negative percentage reductions in leak rates can be obtained if the leak rate is higher after maintenance than it was before maintenance. The highest achievable positive reduction is 100%. It is possible, however, to get negative percentage reductions that are much greater than 100 percent. Thus is particularly true if the original leak rate, L_B, is very low.

The effect of maintenance procedures on the leak rates of the individual valves involved in this study are tabulated in Tables IV and V. The data are plotted in Figures 1 and 2 where the effect of maintenance can be seen more clearly. In these figures the leak rate of the individual valves after maintenance is plotted as a function of the valve leak rate before maintenance. This is done for both undirected and directed maintenance procedures. The valves exhibiting a reduction in leak rate from maintenance activities are indicated by those points that fall below the diagonal line drawn in each figure. Those valves whose leak rate increased after maintenance are represented by the points which fall above the diagonal line. It can be seen that the points in Figure 2 generally fall further below the diagonal and closer to the horizontal axis than those plotted in Figure 1. It appears from these figures, then, that directed maintenance procedures are generally more effective than undirected maintenance activities in reducing valve emissions. Also, a smaller fraction of valves exhibit an increase in emission rate after directed maintenance than after undirected maintenance.

The data are plotted in the form of histograms in Figure 3. The results of the directed and undirected maintenance studies are shown. The greater effectiveness of the directed maintenance procedures is clearly shown in this figure.

The effects of the valve maintenance studies are summarized in Table VI. The results are shown for both the directed and the undirected maintenance programs, and are grouped according to the level of emission rates. Two results are noteworthy. It is evident that the average percentage leak reduction for those valves that were subjected to directed maintenance is considerably greater than that of the valves which underwent undirected maintenance.

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TABLE IV. THE EFFECT OF UNDIRECTED MAINTENANCE PROCEDURES ON LEAK RATES
FROM INDIVIDUAL VALVES

Valve ID	Valve Function	Measured Leak Rate, lb/hr of Nonmethane Hydrocarbons		Reduction After Maintenance, Percent
		Before Maint.	After Maint.	
1	Block	0.0320	0.00001	100
2	Block	0.0437	0.00002	100
3	Block	0.0158	0.00028	98
4	Block	0.1476	0.0051	97
5	Block	0.6572	0.0231	96
6	Block	0.5801	0.0481	92
7	Block	0.0018	0.00015	92
8	Block	0.0327	0.0031	90
9	Block	0.0871	0.0094	89
10	Block	0.1963	0.0288	85
11	Block	0.1071	0.0168	84
12	Block	0.0026	0.00045	83
13	Block	0.0109	0.00191	83
14	Block	0.1673	0.0365	78
15	Block	0.0019	0.00047	76
16	Block	0.0449	0.0174	61
17	Block	0.0381	0.0192	50
18	Block	0.0295	0.0157	47
19	Block	0.1256	0.0767	39
20	Block	0.0023	0.0015	34
21	Block	0.1995	0.1354	32
22	Block	0.1019	0.0714	30
23	Block	0.0264	0.0198	25
24	Block	0.1761	0.1328	25
25	Block	0.0015	0.0012	20
26	Block	0.0614	0.0508	17
27	Block	0.00049	0.00054	− 10
28	Block	0.0034	0.0044	− 29
29	Block	0.0083	0.0174	−110
30	Block	0.0182	0.0462	−153
31	Block	0.0293	0.1398	−377
48	Control	0.2703	0.0009	100
49	Control	0.6235	0.0045	99
50	Control	0.2253	0.0017	99
51	Control	0.0923	0.0012	99
52	Control	0.0227	0.0018	92
53	Control	0.0286	0.0023	92
54	Control	0.5863	0.0553	91

Continued

TABLE IV. Continued

Valve ID	Valve Function	Measured Leak Rate, lb/hr of Nonmethane Hydrocarbons		Reduction After Maintenance, Percent
		Before Maint.	After Maint.	
55	Control	0.0058	0.0008	86
56	Control	0.0054	0.0007	87
57	Control	0.0161	0.0029	82
58	Control	0.0063	0.0013	79
59	Control	0.0514	0.0202	61
60	Control	0.0039	0.0018	54
61	Control	0.1641	0.0758	54
62	Control	0.0276	0.0141	49
63	Control	0.00037	0.00026	29
64	Control	0.0009	0.00065	28
65	Control	0.0055	0.0040	27
66	Control	0.00063	0.00049	22
67	Control	0.0127	0.0115	9
68	Control	0.0234	0.0244	− 4
69	Control	0.0119	0.0133	− 12
70	Control	0.0027	0.0035	− 30
71	Control	0.0015	0.0024	− 60
72	Control	0.0011	0.0027	− 145
73	Control	0.00031	0.00078	− 152
74	Control	0.00013	0.00085	− 550
75	Control	0.0019	0.1673	−8745

TABLE V. THE EFFECT OF DIRECTED MAINTENANCE PROCEDURES ON LEAK RATES FROM
INDIVIDUAL VALVES

Valve ID	Valve Function	Measured Leak Rate, lb/hr of Nonmethane Hydrocarbons		Reduction After Maintenance, Percent
		Before Maint.	After Maint.	
84	Block	0.0011	0.0000	100
85	Block	0.0111	0.0002	98
86	Block	0.0891	0.0017	98
87	Block	0.1396	0.0028	98
88	Block	0.0075	0.0002	97
89	Block	0.0383	0.0017	96
90	Block	0.0126	0.0009	93
91	Block	0.0115	0.0008	93
92	Block	0.0307	0.0025	92
93	Block	0.0032	0.0004	87
94	Block	0.0045	0.0007	84
95	Block	0.0800	0.0124	85
96	Block	0.00066	0.00013	80
97	Block	0.0014	0.00039	72
98	Block	0.00078	0.00032	59
99	Block	0.00197	0.00106	46
100	Block	0.00055	0.00090	− 63
101	Block	0.0053	0.0130	−145
109	Control	0.0095	0.0000	100
110	Control	0.0181	0.0004	98
111	Control	0.0065	0.0003	95
112	Control	0.0173	0.0010	94
113	Control	0.0126	0.0011	91
114	Control	0.0025	0.0003	88
115	Control	0.0021	0.0005	76
116	Control	0.0005	0.0003	40
117	Control	0.0016	0.0035	−119

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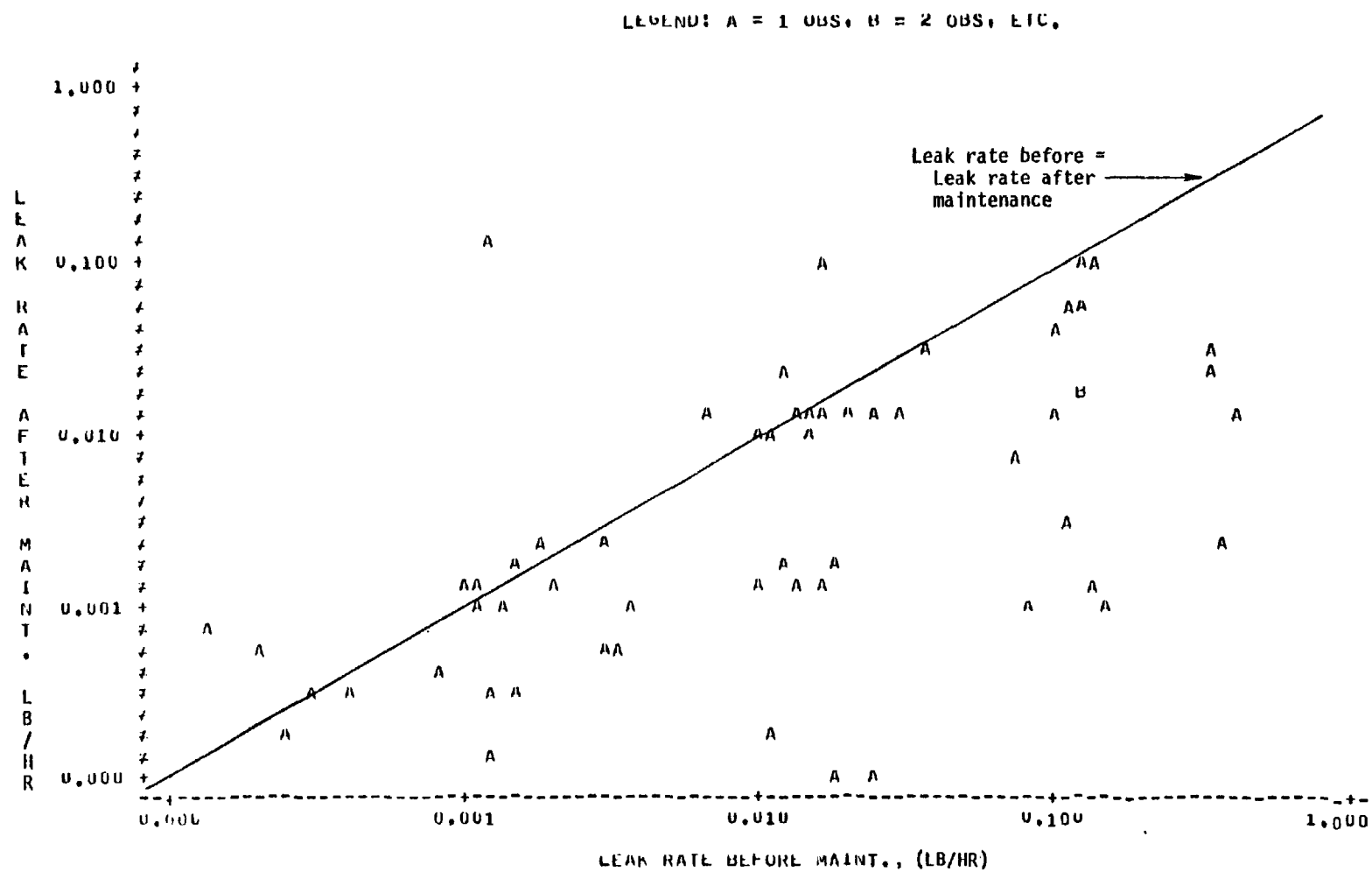
Figure 1.   The Effect of Undirected Maintenance on the Leak Rate From Valves

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Leak rate before = Leak rate after maintenance

LEAK RATE AFTER MAINT., LB/HR

LEAK RATE BEFORE MAINT., LB/HR
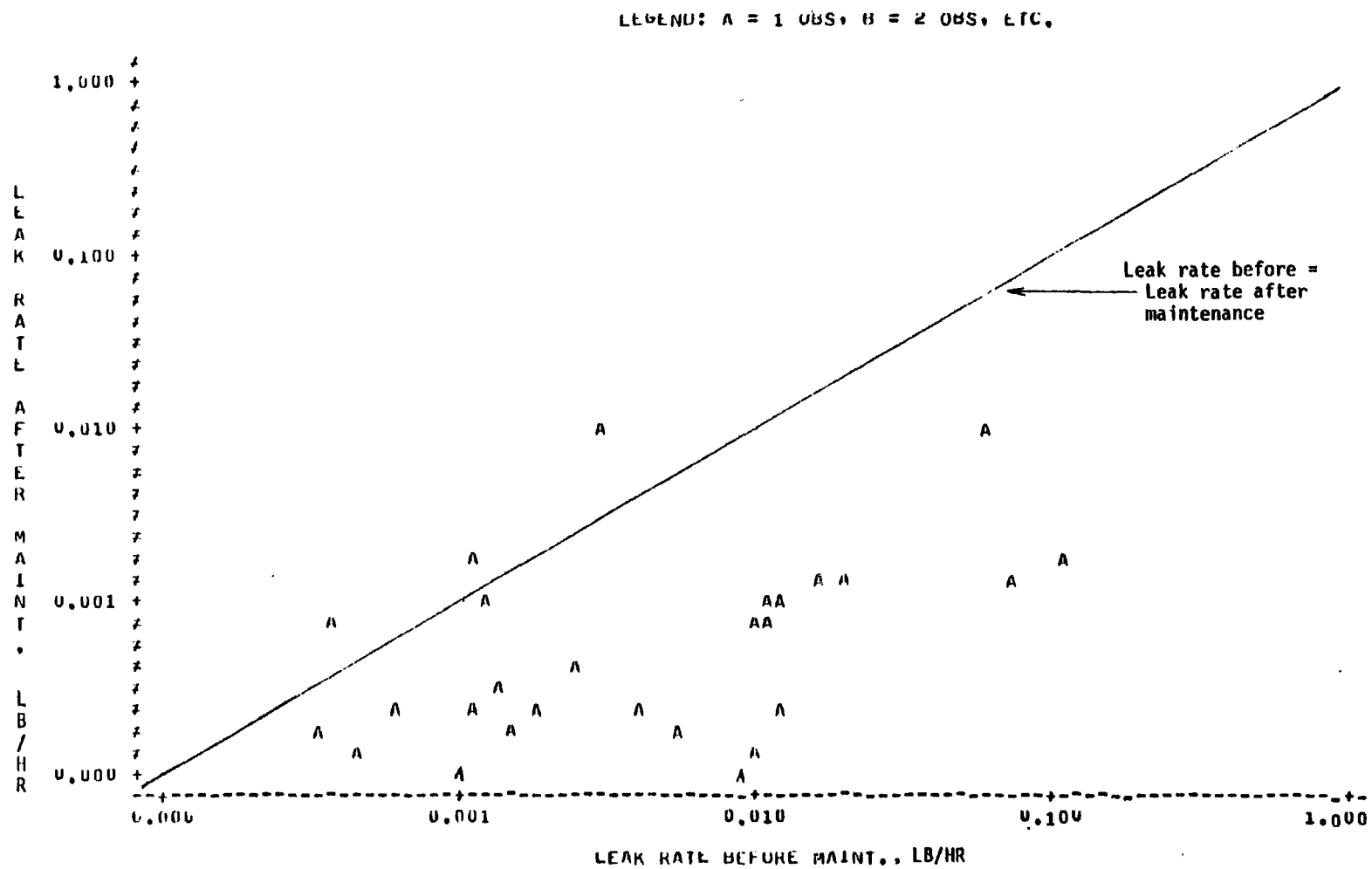
Figure 2.   The Effect of Directed Maintenance on the Leak Rate From Valves
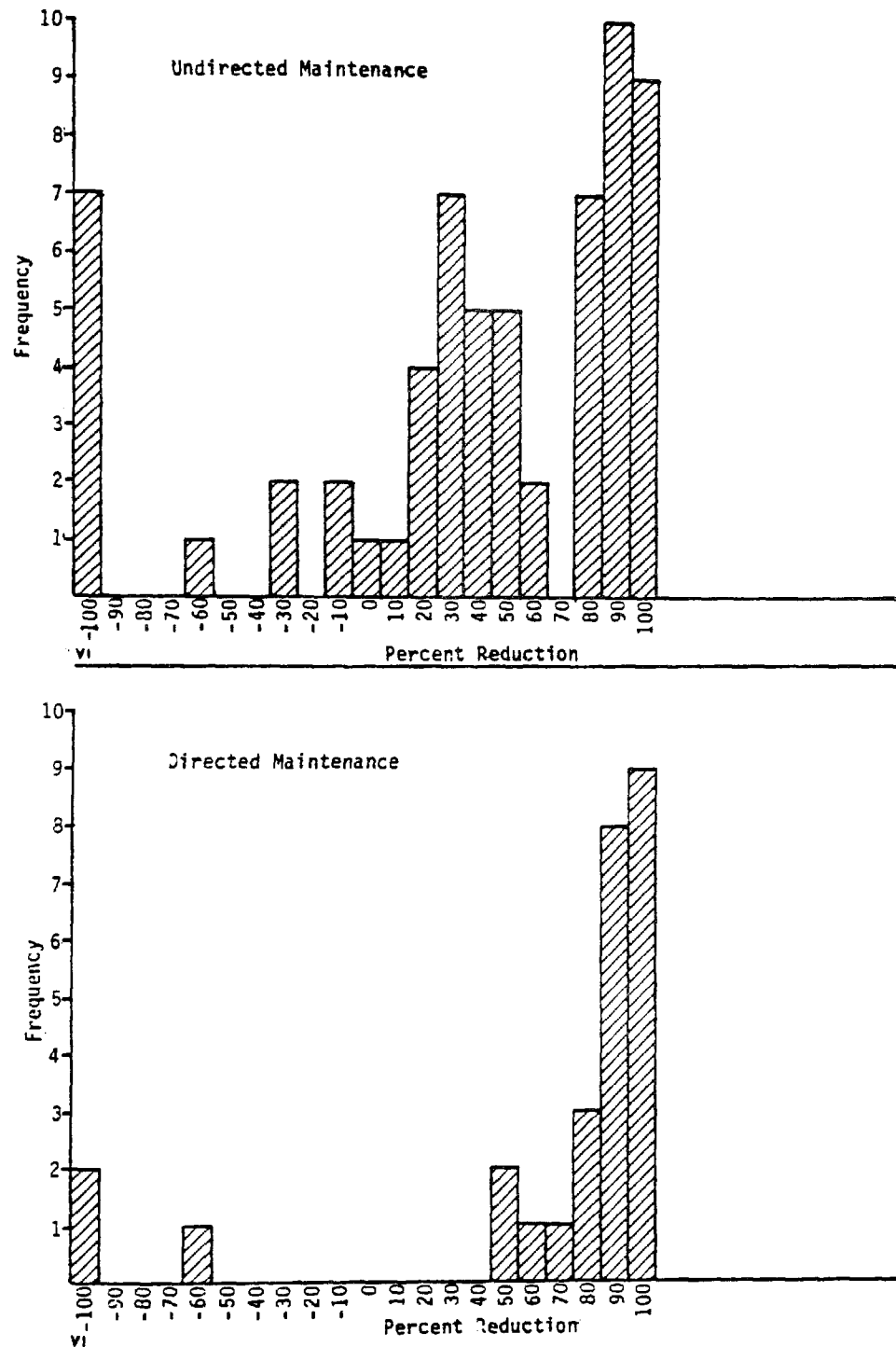
Figure 3. Histograms for Percent Reduction in Leak Rate
From Directed and Undirected Maintenance

TABLE VI. SUMMARY OF MAINTENANCE REDUCTION BY LEAK RATE LEVEL

Level	Original Leak Rate Range (lb/hr)		Directed Maintenance	Undirected Maintenance
1	≤ 0.001	n	4	6
		$\overline{p}$	30.7	− 105.5
		pw	35.2	− 26.3
		pm	52.6	5.6
2	0.001 − 0.01	n	12	16
		$\overline{p}$	48.7	− 530.0
		pw	56.9	− 276.4
		pm	86.2	30.4
3	0.01 − 0.1	n	10	22
		$\overline{p}$	93.8	31.7
		pw	93.0	45.1
		pm	93.8	60.9
4	> 0.1	n	1	15
		$\overline{p}$	98.0	73.4
		pw	98.0	83.5
		pm	98.0	85.4

n = Number of valves maintained

$\overline{p}$ = Average percent reduction = $\Sigma P_1/n$, where $P_1 = \dfrac{(\text{leakage before} - \text{leakage after maintenance})}{\text{leakage before maintenance}} \times 100$

pw = Weight percent reduction = $\dfrac{\Sigma \text{leakage before maintenance} - \Sigma \text{leakage after maintenance}}{\Sigma \text{leakage before maintenance}} \times 100$

pm = Median percent reduction

It is also apparent that the level of the initial leak rate has a marked effect on the percentage reduction in emission rate for both directed and undirected maintenance. The percentage reduction achieved by maintenance is lower for the initially small leak rates. In the low initial leak ranges, ≤ 0.01 pounds per hour, the average and weight percent reduction in emissions was actually negative for undirected maintenance.

It should be noted that as the magnitude of the leak rate becomes smaller, both the average percent reduction and weight percent reduction decrease rapidly. Both of these parameters are dependent on the magnitude of the initial leak rate and are highly influenced by extremes within the leak rate range. The median percent reduction, however, is a more definitive measure of central tendency and cannot be affected by the very large negative values of percent reduction encountered at low leak rates with undirected maintenance.

The median percent reduction does show the same pattern as the average and weight percent reductions. The comparison between the median percent reductions for the two types of maintenance indicates that directed maintenance yields a higher reduction in leak rate. Undirected maintenance appears to be even less reliable at low leak rate levels (< 0.001 lb/hr). This type of maintenance appears to have a greater potential for producing an increase in valve emissions after maintenance.

The percent reduction from the two maintenance methods was plotted against the original screening value in Figures 4 and 5. The positive percent reductions with directed maintenance generally appear to be higher than the reductions achieved with undirected maintenance. Also, a greater percentage of the valves undergoing undirected maintenance appears to have increased in leak rate (compared to those subjected to directed maintenance) after being maintained. Table VII bears out these observations. The median percent reduction with directed maintenance (91.2 percent) is significantly higher than that with undirected maintenance (53.8 percent).

The valves are grouped by function (block or control) in Table VII. Control valves which had directed maintenance had a slightly higher median percent reduction in leak rate than block valves which had the same type of maintenance. However, the opposite is true for valves which underwent undirected maintenance. Again, even within the block/control groupings, directed maintenance appears to yield a higher percent reduction in leak rate than undirected maintenance.

It should be noted that leaking valves in some categories of the original experimental design were not found. Very few valves in the heavy liquid stream classification were found to be leaking, particularly at the higher rates. Valves in some categories were found in some refineries, but not in others. In many cases, substitutions from other categories were made to provide an adequately sized data base.

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

Note: 3 values were out of range
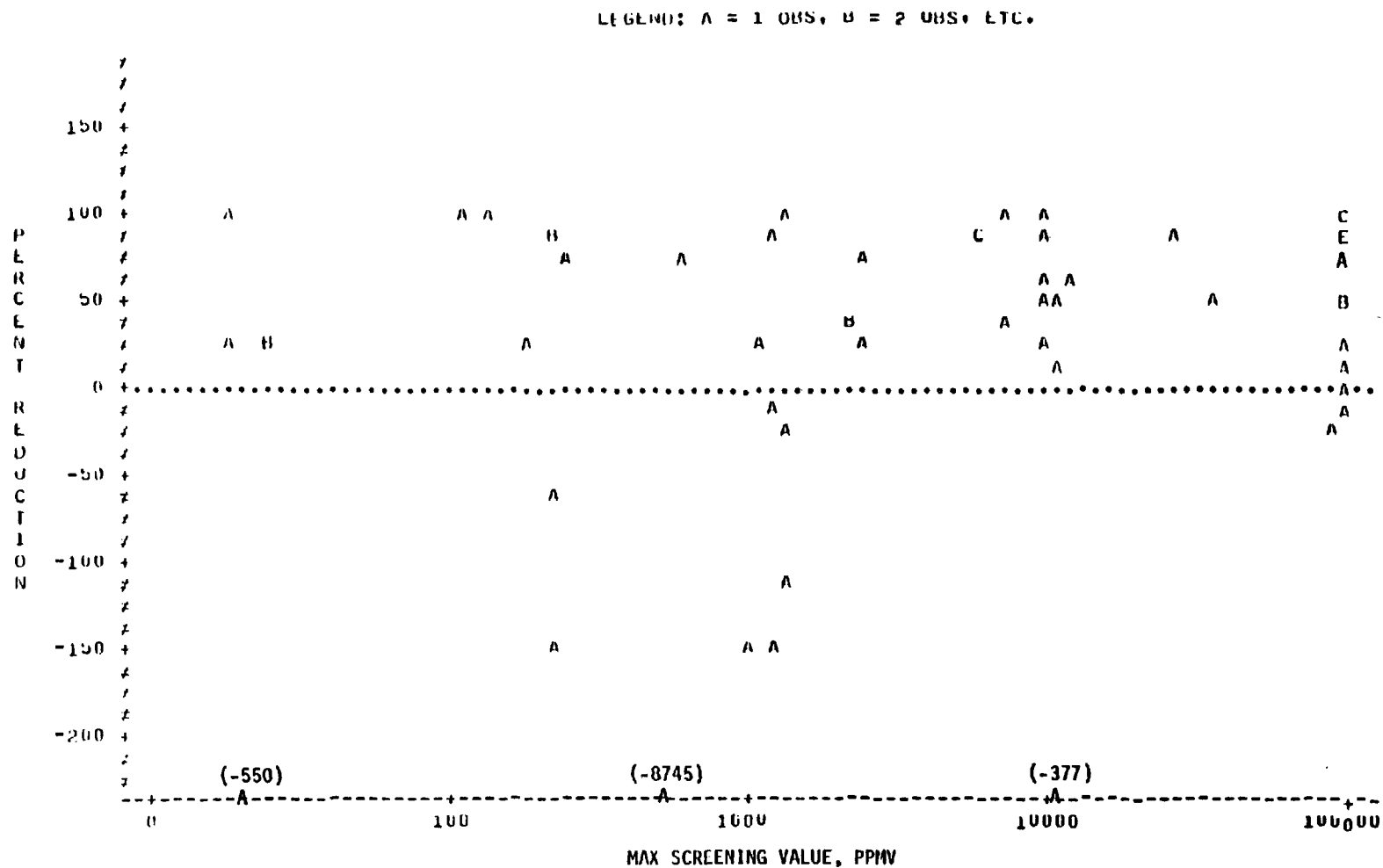
Figure 4. Undirected Maintenance – Percent Reduction in Emissions as a Function of Initial Screening Values

Figure 5. Directed Maintenance – Percent Reduction in Emissions as a Function of Initial Screening Values

TABLE VII. STATISTICAL SUMMARY OF MAINTENANCE DATA - PERCENT REDUCTION

Directed Maintenance

Screening Value Range (ppmv)	Block Valves G/V Stream	LL Stream	HL Stream	Total* Block	Control Valves G/V Stream	LL Stream	HL Stream	Total Control	Total* All Valves
<5K	2 58.8 / 56.5 / 58.8	5 63.1 / 90.5 / 93.1	0	7 61.8 / 86.5 / 87.3	0	4 39.5 / 84.9 / 89.8	0	4 39.5 / 84.9 / 89.8	11 53.74 (3.7,100) / 85.6 (72,99) / 88.4 (18,98)
5K-50K	2 76.1 / 90.7 / 76.1	4 89.8 / 89.0 / 90.1	0	6 85.2 / 89.1 / 88.7	1 45.7 / 45.7 / 45.7	1 95.0 / 95.0 / 95.0	0	2 70.4 / 91.5 / 70.4	8 81.5 (65,98) / 89.2 (69,100) / 88.7 (-55,96)
>50K	3 93.8 / 97.8 / 98.0	2 -26.4 / 56.7 / -26.4	0	5 45.7 / 92.3 / 91.7	1 77.2 / 77.2 / 77.2	2 97.2 / 96.4 / 97.2	0	3 90.5 / 95.0 / 94.5	8 62.5 (-7.9,100) / 92.6 (81,100) / 93.1 (-33,99)
				18 64.2 (32,96) / 91.0 (82,99) / 86.2 (75,97)				9 66.8 (12,100) / 89.7 (79,99) / 91.2 (9.3,98)	27 64.6 (38,91) / 90.7 (83,98) / 91.2 (79,95)

(Continued)

*Numbers in parentheses indicate an approximate 95% confidence interval for the average reduction for the three different estimations.

Code for Each Cell in Table:

1	2
	3
	4

1 = Number of valves maintained

2 = Average of percent reduction where percent reduction $= \dfrac{100 \times (\text{leak before} - \text{leak after maintenance})}{\text{Leak before maintenance}}$

3 = Weight percent reduction $= \dfrac{\Sigma\text{leak rate before maintenance} - \Sigma\text{leak rate after maintenance}}{\Sigma\text{leak rate before maintenance}}$

4 = Median percent reduction

TABLE VII. Continued

Undirected Maintenance

Screening Value Range (ppmv)	Block Valves C/V Stream	LL Stream	HL Stream	Total* Block	Control Valves C/V Stream	LL Stream	HL Stream	Total Control	Total* All Valves
<5K	6 54.0 / 52.2 / 65.2	6 42.6 / 58.9 / 76.9	4 -26.1 / -43.4 / 7.37	16 29.7 / 48.5 / 33.1	7 -1320 / - 717 / -58.4	5 5.2 / 91.1 / 26.56	0	12 - 769 / -50.5 / 24.1	28 -312 (-950,100) / 33.0 (-39,100) / 28.9 (-0.5,79)
5K-50K	4 69.8 / 47.8 / 82.6	4 -64.9 / - 9.0 / 28.2	0	8 2.4 / 20.2 / 50.1	2 54.2 / 53.8 / 54.2	4 87.8 / 96.9 / 95.6	1 82.1 / 82.1 / 82.1	7 77.4 / 90.2 / 82.1	15 37.4 (-28,100) / 67.4 (34,100) / 82.1 (42,88)
>50K	3 75.3 / 88.4 / 84.3	4 81.3 / 93.0 / 90.9	0	7 78.7 / 91.1 / 85.4	8 29.4 / 81.3 / 19.3	1 90.6 / 90.6 / 90.6	0	9 36.2 / 87.0 / 29.5	16 54.8 (31,78) / 89.6 (81,98) / 67.0 (21,92)
				31 33.7 (-1.8,69) / 68.7 (48,89) / 61.1 (31,85)				28 298 (-940,100) / 81.0 (64,98) / 51.4 (13,85)	59 -124 (-410,100) / 73.9 (69,88) / 53.8 (29,82)

*Numbers in parentheses indicate an approximate 95% confidence interval for the average percent reduction for the three different estimations.

Code for Each Cell in Table	1	2
		3
		4

1 = Number of valves maintained

$$2 = \text{Average of percent reduction where percent reduction} = \frac{100 \times (\text{leak before} - \text{leak after maintenance})}{\text{Leak before maintenance}}$$

$$3 = \text{Weight percent reduction} = \frac{\text{Eleak rate before maintenance} - \text{Eleak rate after maintenance}}{\text{Eleak rate before maintenance}} \times 100$$

4 = Median percent reduction

A comparison of emission reduction by range of screening value can also be made. For directed maintenance, the median percent reduction stays approximately constant across the screening value range. However, for the undirected maintenance group the median percent reduction increases dramatically with increasing screening values. The median percent reduction is very low, only 28.9 percent, for those valves having low screening values. This may indicate that undirected maintenance at this screening level is not effective at all. For the middle screening value range, the median percent leak reduction for valves which underwent directed maintenance increases to 82.1 percent, almost as high as the reduction with directed maintenance (88.7 percent). However, the median percent leak reduction with directed maintenance is somewhat lower (67 percent) for the valves in the high screening value range. The effectiveness of the maintenance program appears to be much more consistent when the directed maintenance method is used rather than the undirected method.

The differences in percent reduction discussed above should be considered as trends. Confidence intervals were calculated for the key values and these are presented in Table VII. Differences in the percent emission reduction cannot be considered statistically significant if confidence limits for the estimates overlap.

A graphical representation of the differences between the effect of maintenance on block and control valves is shown in the next several figures. The leak rates before and after maintenance are plotted for block and control valves in Figures 6 and 7. The percent reduction in leak rate for each valve is plotted against the original screening value for block and control valves in Figures 8 and 9.

Finally, Figures 10 and 11 are histograms of percent reduction for block and control valves for directed and undirected maintenance. While no large differences between valve function are obvious, the differences between the percent reduction in emissions for valves undergoing directed and undirected maintenance can be seen. The advantages of directed maintenance are apparent.

THE SHORT AND LONG TERM EFFECTS OF VALVE MAINTENANCE

A number of the valves which underwent maintenance were screened several times during a one week period following the maintenance. The results are summarized in Table VIII. The advantage of directed maintenance can be clearly seen. Fifty percent of those valves with initial screening values $\geq$ 10,000 ppmv still had screening values in excess of 10,000 ppmv immediately after undirected maintenance. By the end of one week, 60 percent of these valves had exhibited screening values above 10,000 ppmv.

By contrast, only 2 of the 10 valves subjected to directed maintenance had screening values in excess of 10,000 ppmv. One additional valve developed a screening value above 10,000 ppmv by the end of the week.

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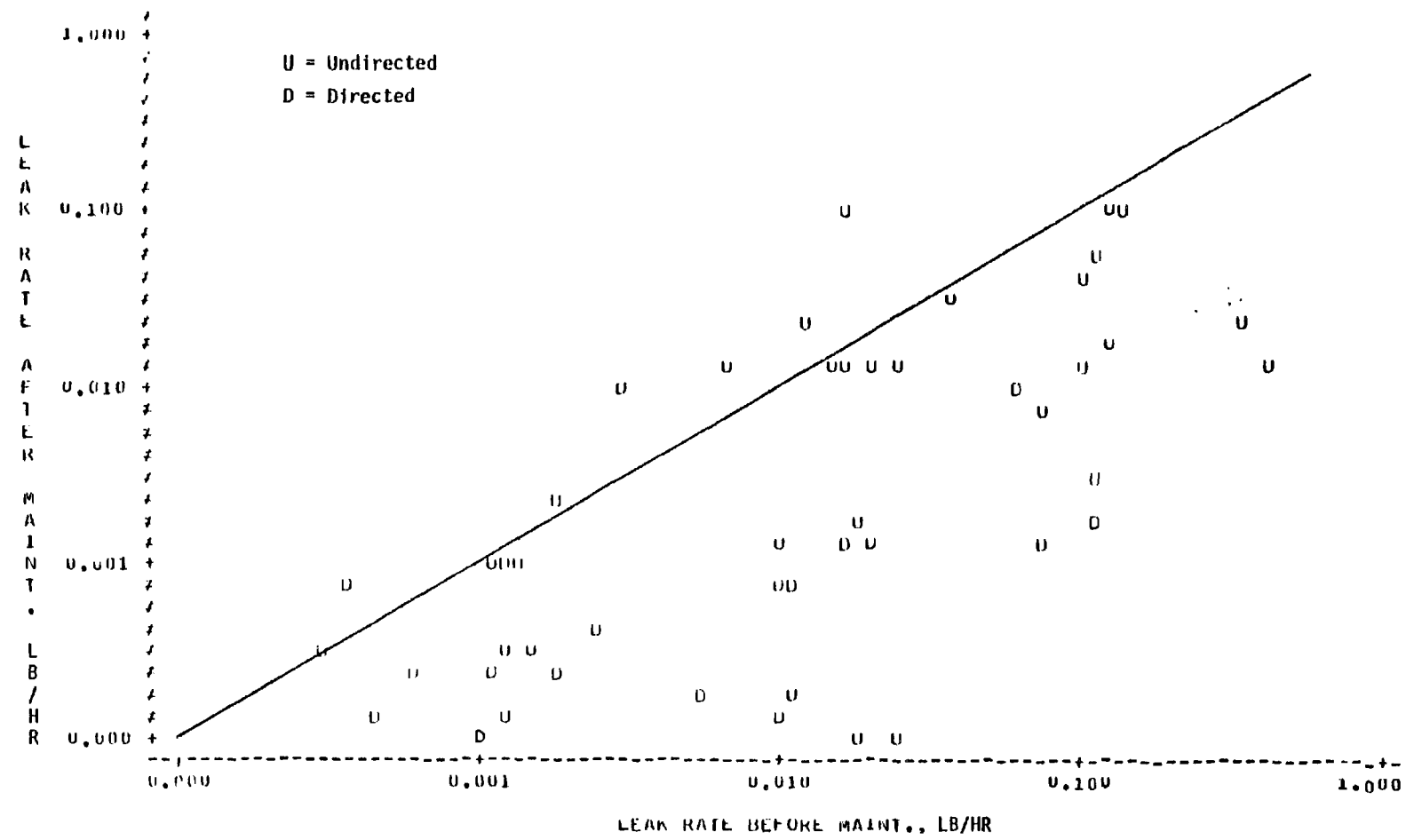
Figure 6.   Directed and Undirected Maintenance – Leak Rate After Maintenance as a Function of the Leak Rate Before Maintenance – Block Valves.
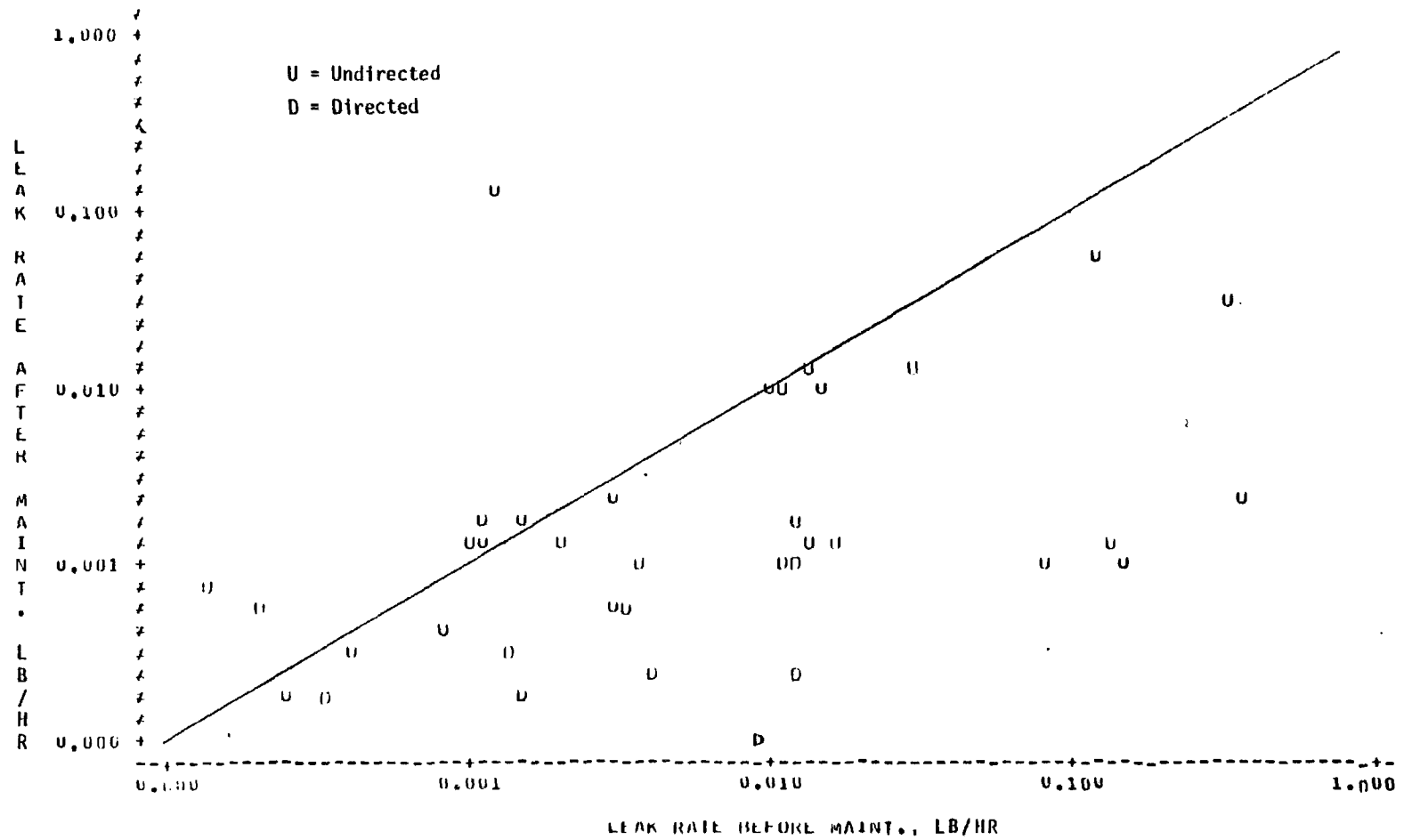
Figure 7.   Directed and Undirected Maintenance - Leak Rate After Maintenance as a Function of the Leak Rate Before Maintenance - Control Valves

Figure 8. Directed and Undirected Maintenance – Percent Reduction in Emission Rate as a
Function of the Screening Value – Block Valves
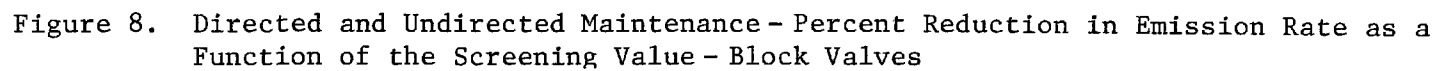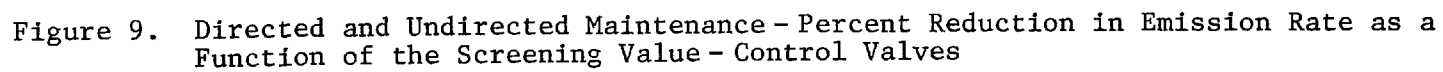
Figure 9. Directed and Undirected Maintenance – Percent Reduction in Emission Rate as a Function of the Screening Value – Control Valves

R. G. Wetherold/S. L. Preston
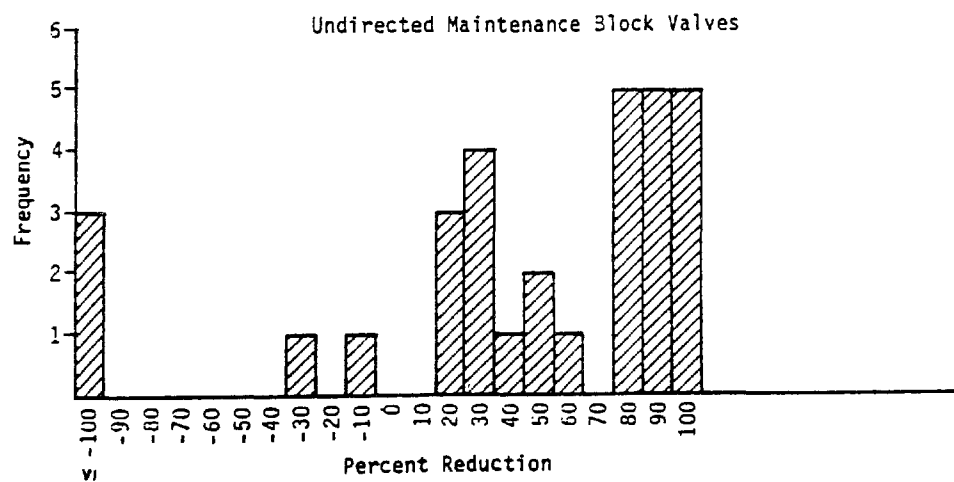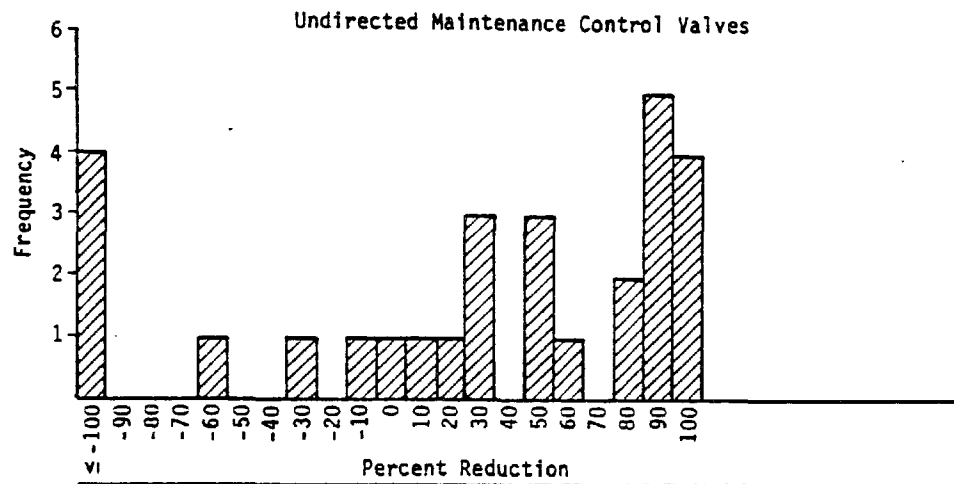
Figure 10.   Histograms for Percent Reduction in Leak Rate –
Undirected Maintenance

Directed Maintenance Control Valves

Directed Maintenance Block Valves
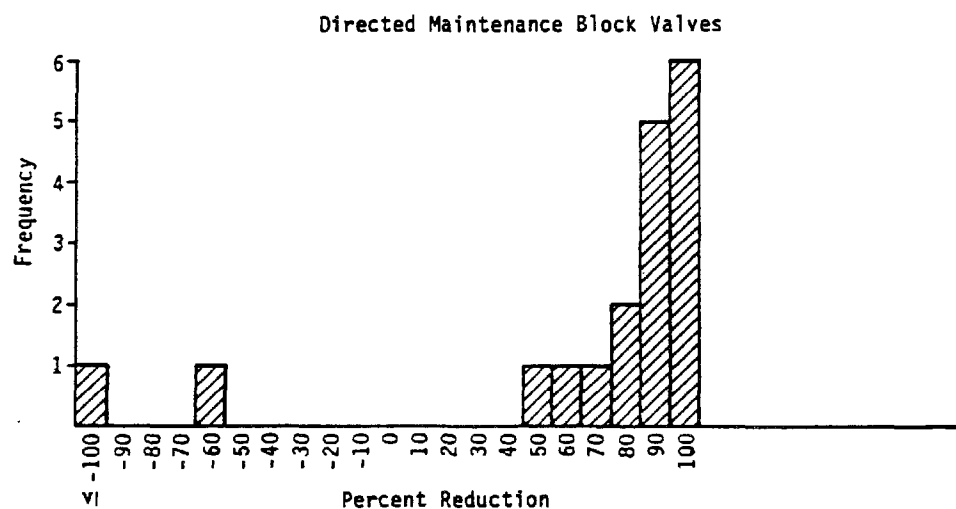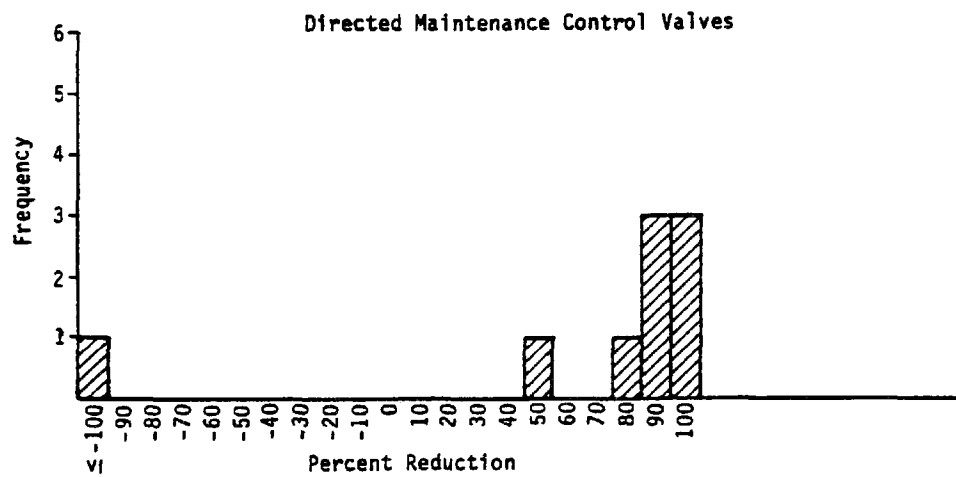
Figure 11.   Histograms for Percent Reduction in Leak Rate –
Directed Maintenance

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TABLE VIII. EFFECT OF MAINTENANCE ON VALVES OVER A SHORT PERIOD OF TIME FOLLOWING THE MAINTENANCE

Type of Valve Maintenance	Valve Function	Valves With Screening Values $\geq$ 10,000 ppmv Before Maintenance			Valves With Screening Values $\geq$ 1,000 ppmv Before Maintenance		
			Valves With Screening Values $\geq$ 10,000 ppmv			Valves With Screening Values $\geq$ 1,000 ppmv	
		Total Valves Maintained	Immediately After Maintenance	Within One Week Of Maintenance	Total Valves Maintained	Immediately After Maintenance	Within One Week Of Maintenance
Undirected	Block	10	4	4	16	12	14
Directed	Block	7	2	2	14	9	11
Undirected	Control	10	6	8	14	12	14
Directed	Control	3	0	1	8	3	6

Eighty percent of the valves with initial screening values ≥ 1,000 ppmv which underwent undirected maintenance had screening values ≥ 1,000 ppmv immediately after maintenance. This percentage increased to 93% within one week. Fifty-five percent of the valves subjected to directed maintenance had screening values above 1,000 ppmv immediately after maintenance. Within one week, 77% of these valves developed screening values ≥ 1,000 ppmv. These results indicate the difficulty of reducing screening values to very low levels.

Several oil refineries are participating in a study of the effectiveness of valve maintenance over a 6 - 9 month period following the maintenance. The study is still continuing, but a limited amount of data have been received from one refinery. These results are presented in Figure 12. A total of 23 valves are being screened at this refinery on a weekly basis. In Figure 12, the valves screening above 10,000 ppmv and 1,000 ppmv immediately after undergoing undirected maintenance are shown as a function of the time elapsed since the maintenance.

There does not appear to be any significant increase with time in the number of valves screening above the selected values in any given week. The percentage of valves screening above 10,000 ppmv is lower than the percentage screening above 1,000 ppmv during the initial weeks. During the last 6 weeks, however, these percentages are not substantially different.

It is not unusual for a given valve to have screening values that are highly variable over a period of time. Screening values for 3 selected valves taken at intervals over a thirty week period are shown in Figure 13. The screening values of valve 20 span nearly three orders of magnitude. In contrast, the screening values of valves 10 and 14 lie within one order of magnitude. Thus, it is very possible for a valve to have screening values that occasionally and periodically rise above any selected screening limit. The causes of the reported variability of screening values have not been clearly defined. A few possible causes are

- weather conditions (excessive wind, rain, etc.)

- variations in the valve leak rate

- operator interpretation of indicator readings

- operator technique

- malfunctioning or miscalibrated instrument

- miscellaneous errors

The effects of the screening variability can be seen in Figure 14. The percent of the maintained valves with screening values that exceed either 1,000 or 10,000 ppmv for one or more times over the elapsed weeks are shown.
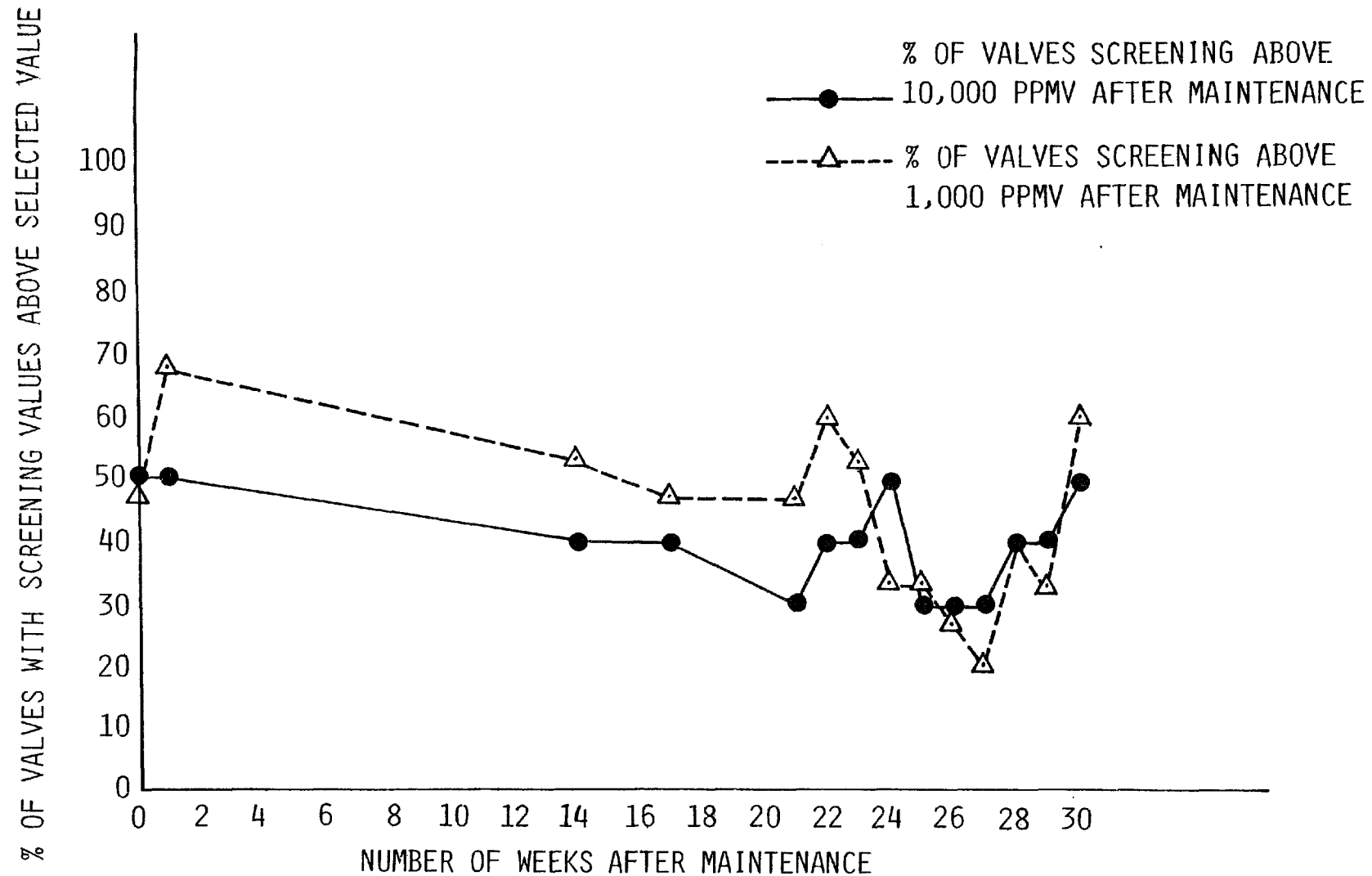
Figure 12

EFFECT OF UNDIRECTED MAINTENANCE ON LEAKING VALVES OVER A LONG TIME PERIOD
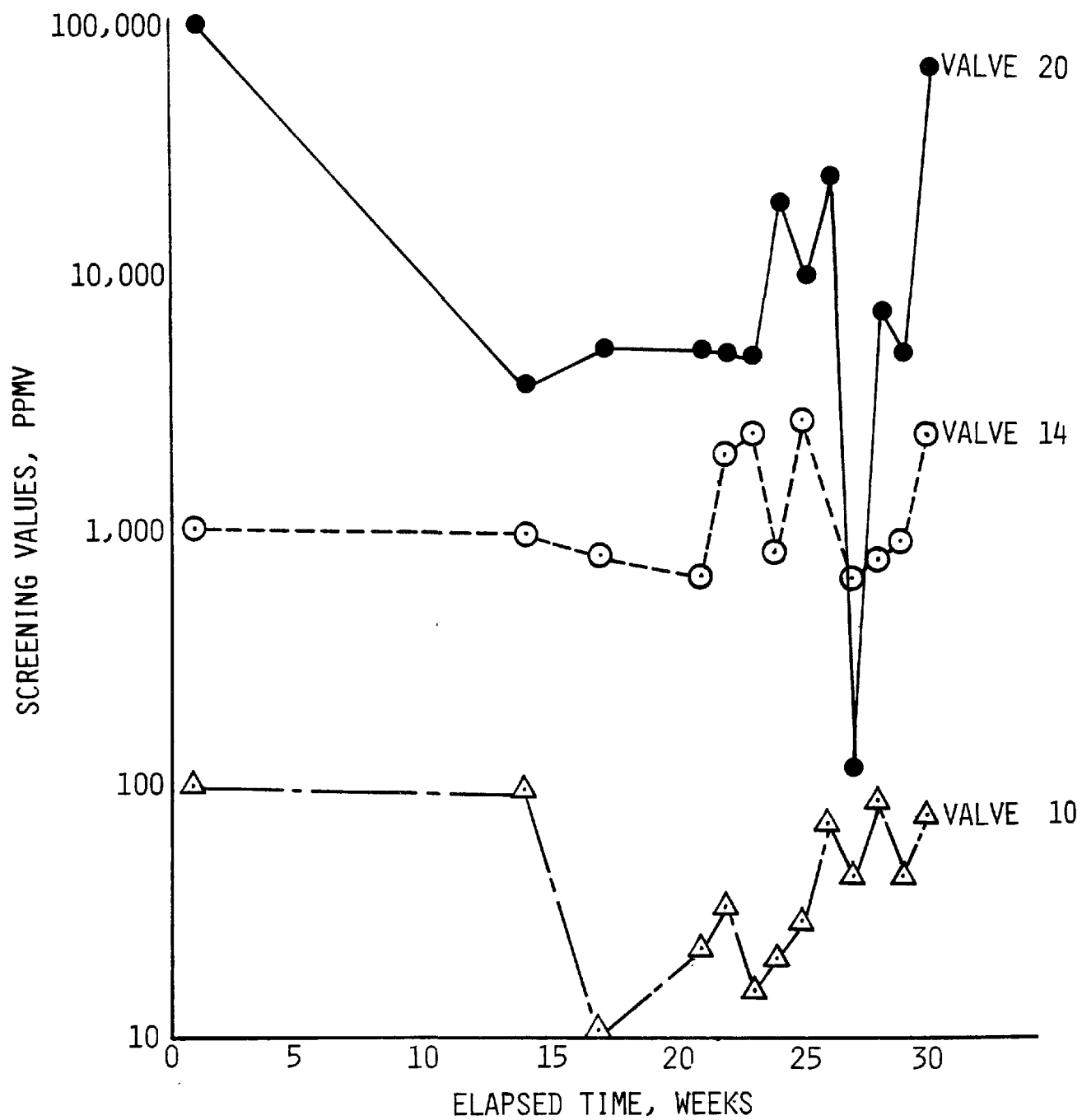
Figure 13

SCREENING VALUES OF SELECTED VALVES OVER A PERIOD OF 30 WEEKS
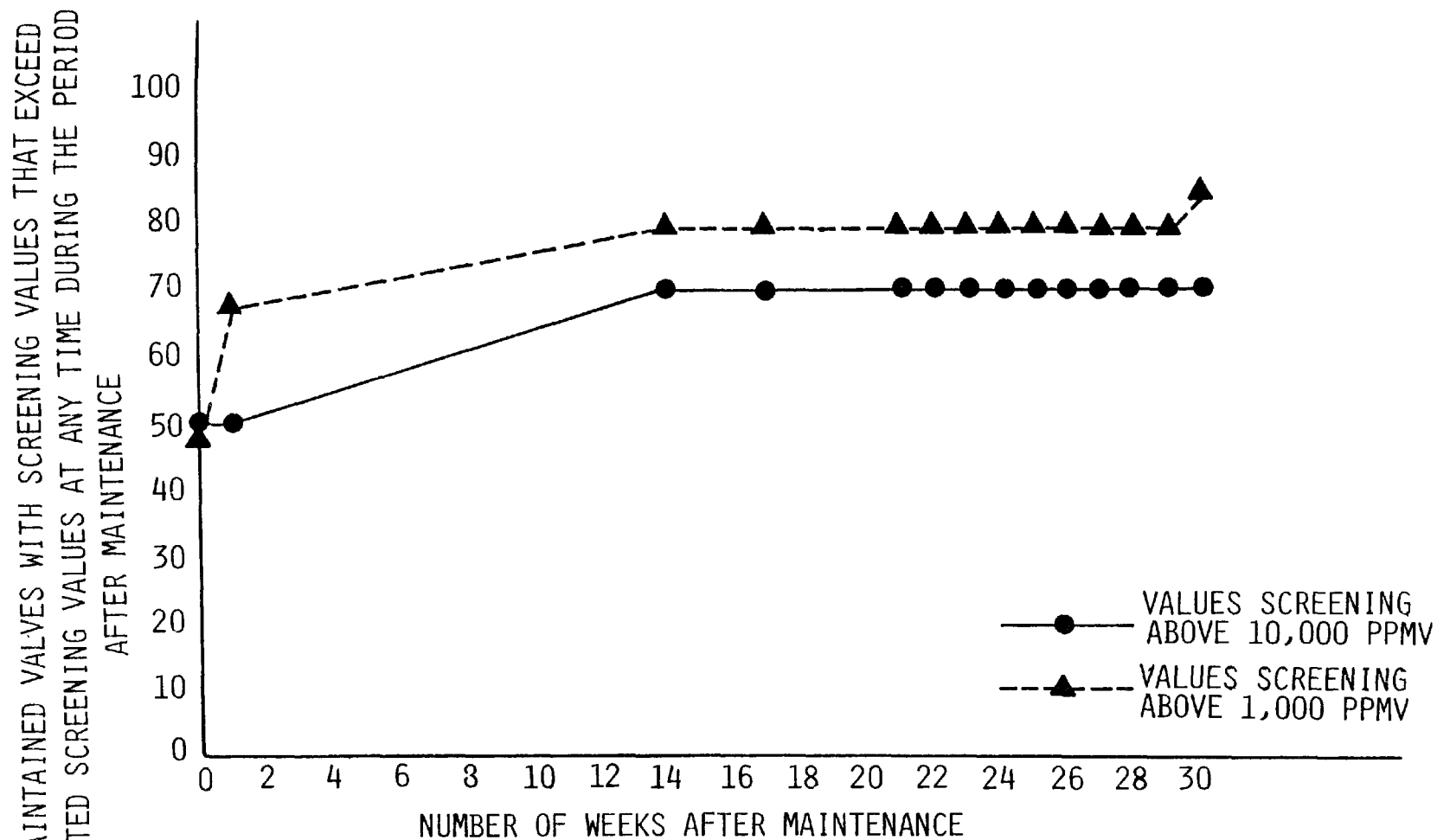
Figure 14
EFFECT OF UNDIRECTED MAINTENANCE ON
VALVE SCREENING VALUES

The percentage of these valves increases moderately during the first 14 weeks after maintenance. However, only a small percentage of the remaining valves exhibited a screening value above the limits at any time during the remaining 16 weeks.

The variability of screening values is evident when Figures 12 and 14 are compared. For example, in the 27th week only 20% of the selected valves have screening values above 1,000 ppmv (Figure 12). Yet, by that time 79% of these same valves have had at least one screening value above 1,000 ppmv (Figure 14).

CONCLUSIONS

The results obtained during the study of the effects of simple valve maintenance support the following conclusions.

- Simple valve maintenance is effective in reducing valve emissions.

- Maintenance is most effective for valves with high initial leak rates. The effectiveness decreases with decreasing initial leak rates.

- Directed maintenance provides significantly greater reduction of valve emissions than does undirected maintenance.

- Directed maintenance is equally effective in reducing emissions from both block and control valves.

- Emission reductions of more than 90% can be achieved with directed maintenance of valves leaking at a rate of 0.01 lbs. per hour or more.

- The data are as yet too sparse to support conclusions regarding the short and long term effects of valve maintenance.

REFERENCE

1. Arthur D. Little, Inc.

REVIEW

by

M. R. Olson
Union Oil Company of California
San Francisco Refinery
Rodeo, California

on

THE EFFECT OF MAINTENANCE PROCEDURES ON THE REDUCTION OF
FUGITIVE HYDROCARBON EMISSIONS FROM VALVES
IN PETROLEUM REFINERIES

RESUME

Mike Olson is Supervisor of Environmental Control Engineering at Union Oil Company's San Francisco Refinery. He received his B.S. degree in Mechanical Engineering from California Polytechnic State University. He has also worked for Union in Project Engineering and Instrumentation Maintenance. He is a Registered Professional Engineer in California and is a member of the American Society of Mechanical Engineers, the Instrument Society of America, and the Air Pollution Control Association.

REVIEW

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M. R. Olson
Union Oil Company of California
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THE EFFECT OF MAINTENANCE PROCEDURES ON THE REDUCTION OF
FUGITIVE HYDROCARBON EMISSIONS FROM VALVES
IN PETROLEUM REFINERIES

INTRODUCTION

The control of fugitive emissions from valves in petroleum
refineries has been the subject of much regulatory activity in the last
year or so. Already, some regulations call for the reduction of valve
emissions through maintenance, although, to my knowledge, no previous
independent work has been done to evaluate the potential of maintenance
to achieve the required reductions. As other Radian Corporation work has
contributed to the assessment of fugitive emissions from valves, this
study is a significant addition to the available knowledge in this area
and a large step toward understanding how such emissions can be reduced.

My primary objective in reviewing this study was to find answers
to the following questions: (1) How were the valves maintained? (2) How
much did this maintenance reduce valve emissions? (3) How long did the
emission reductions last? (4) How much would this maintenance cost?
(5) On what results are the answers to the preceeding questions based?

COMMENTS ON STUDY OBJECTIVES

The list of study objectives appeared to be sufficient to provide
answers to all the above questions, except that cost was not studied. All

the stated objectives were achieved except the definition of short and long-term effects of maintenance on emission reductions. This was reportedly due to insufficient data.

COMMENTS ON STUDY DESIGN AND PROCEDURE

The two types of maintenance which were to be compared were introduced as directed and undirected maintenance. Directed maintenance was essentially in-service tightening of valve packing while monitoring the valves' emissions. Undirected maintenance was in-service tightening of valve packing without the aid of emission-monitoring equipment. The bulk of the study seems to be taken up with the comparison of these two methods of maintenance. The directed approach is obviously superior in reducing emissions and this fact is firmly established. Because of this fact, however, the majority of the data, which was collected through undirected maintenance, is of reduced value to the remainder of the study. For this reason, most of my additional comments are based on the data obtained through directed maintenance.

Neither method of maintenance considered the ability of the valve to function properly following maintenance. It is very possible to tighten valve packing to the point where the valve physically cannot be operated. Smooth operation is especially important in control valves where even slight overtightening of packing can cause the valve to stick, upsetting unit operations. Our refinery is presently involved in a valve maintenance program for the control of fugitive emissions. Valve maintenance is performed with the aid of a hydrocarbon detector. Valve packing is tightened until the required emission reduction is achieved. Each valve is then checked for free operation following maintenance. This is essentially a directed maintenance approach, which insures the valve against overtightening.

The maintenance procedures used in the study included the screening of each selected valve to determine leak concentration, followed by leak testing of each valve to determine mass emission rate. Although it does not appear in the report, Radian has developed mathematical correlations to determine leak rate from screening value. The use of these correlations in place of leak testing would have saved considerable time, allowing the size of the data set to be increased.

COMMENTS ON STUDY RESULTS

The study shows that valves which leak at low rates are improved less by maintenance than those leaking at higher rates; and, some valves leaking at low rates may actually leak at a higher rate following maintenance. The data is interpreted, however, using the Median Percent Reduction which is unaffected by these large emission increases from some valves. This seems to be in effect a biasing of the data. The Average Percent Reduction may give a more realistic picture of the overall emission reduction.

Keep in mind that any percent reduction figure applies only to those valves which undergo maintenance. This may be considerably less than the total population of leaking valves for the following reasons. Many types of block valves have no provision for in-service packing adjustment. Maintenance of these valves may require that operating equipment be shut down. In addition to obviously great cost and lost production, this could result in greater emissions than the valve repairs would prevent. Also, many valves are in locations which make access difficult. Inspection and repair of these valves would be much more time-consuming and may often result in unsafe working conditions. As mentioned previously, control valves, especially, must be left in a freely-operating condition following maintenance. This factor may limit the amount of packing adjustment possible.

The valve repair experience at our refinery to date has been based on a population of 2,138 valves in a hydrocracking/reforming complex. Inspection yielded 77 leaking valves. Of these valves, 27 were block valves of types which have no provision for in-service packing adjustment. Another 8 were control valves which are difficult to adjust in-service because this could cause the valve to stick. The remaining 42 valves (only 55% of the leaking valves) were able to be repaired in-service.

COMMENTS ON SHORT AND LONG-TERM EFFECTS OF VALVE MAINTENANCE

The variability of leak rates from valves has been the subject of much discussion throughout the recent regulatory activity. Radian has produced previous information indicating the high variability which may occur in leaking valves prior to maintenance. This study provided the vehicle to extend this information to variability following repair.

The short and long-term effects of valve maintenance must be evaluated since no maintenance program will be successful if the emission reductions do not last a reasonable length of time.

It is unfortunate that the majority of the valves investigated for short-term effects and all valves investigated for long-term effects had apparently undergone undirected maintenance, which was shown to be less effective than directed maintenance. However, Figure 15 shows that within 14 weeks of maintenance, 70 percent of the valves exceeded 10,000 ppm and 80 percent exceeded 1,000 ppm. Also, 10 valves which had undergone directed maintenance were included in the short-term effects study. Of these valves, three leaked in excess of 10,000 ppm within 1 week of maintenance.

COMMENTS ON STUDY CONCLUSIONS

The conclusion that directed maintenance provides greater emission reduction than undirected maintenance is, of course, well supported by the study results. However, it should be kept in mind that while we would agree with the superiority of the directed approach, any valve maintenance procedure must leave the valve in a freely-operating state following packing adjustment.

The conclusion that directed maintenance is equally effective on block and control valves is also well established immediately following repair. This would be expected if both valve types are similarly maintained since similar packing geometry is found in most gate-type block valves and globe-type control valves. The danger in treating block and control valves similarly in a maintenance program is that, as stated previously, control valves have a particular need to operate freely to insure a safely-operating facility.

The major conclusion appears to be that emission reductions of more than 90 percent are achievable with directed maintenance for valves leaking at 0.01 lbs/hr. or more. This conclusion appears to be based upon the results of 11 valves which appear in Table VI. While this amount of reduction may well be possible, it would likely be reduced in an actual fied maintenance program by several factors mentioned previously. These factors include valves with limited access, valves with no provision for in-service packing adjustment, and allowances which may be necessary to permit valves to operate freely. In addition, it seems premature to state that large emission reductions are achievable when no conclusive information is available on how long such emissions reductions last.

Finally, the lack of sufficient data to support a conclusion on short and long-term effects of maintenance is unfortunate. This is a very key point in the study of valve maintenance since the cost and success of a maintenance program would depend on how long the achieved emission reductions last. Although more data may become available on long-term effects, a volume of short-term effects data sufficient to insure a conclusion should have been obtained at the time of the study.

CONCLUSION

Overall, the study presents and supports sound conclusions that simple maintenance can significantly reduce fugitive valve emissions and that a directed maintenance approach would be the preferred method. However, such a maintenance program must take into consideration the fact that a valve is more than a source of fugitive emissions to be controlled. Each valve is a necessary piece of operating equipment which must be maintained in a condition which allows it to function properly.

The study is a good first step toward defining the effects of maintenance; however, more work is needed. In particular, the effects of in-service maintenance on the ability of the valve to operate safely in its intended manner, the short and long-term effects of valve maintenance, and the cost of such a maintenance program, must be investigated in more detail.

QUESTIONS AND ANSWERS

Q. James Stone/Louisiana Air Control Commission - In your Figure 13, which is on page 349, or one of your slides, is a directed maintenance versus undirected maintenance chart. The valves over 10,000 ppm leaking exceed the valves over 1,000. How is that possible? On weeks 24, 27 and 29? I thought anything that leaked 10,000, would at least leak 1,000.

A. (By Wetherold) - They are different valves. If you will note, that those are valves which initially leaked greater than 10,000 and valves which initially leaked greater than 1,000.

Q. James Stone/Louisiana Air Control Commission - So it is different sets?

A. (By Rosebrook) - Yes! Remember the study was set up to look at valves in categories 1,000 to 10,000, 10,000 to 50,000, so that we are talking about different valves.

Q. H. M. Walker/Monsanto - In most units a large number of the valves are simply there to permit you to start up, shut down, or various nonregular operating procedures. So, in many cases it is probable that valves go for months, and maybe even years without ever being turned or operated in any way. I would like to ask the people that did the study, whether any cognizance was taken of this factor, or any effort to keep statistics on these valves to determine whether they were actually used at all between observations?

A. (By Wetherold) - As far as I know, there was really no attempt to do that. All the valves were screened. Those which fell in the proper categories were selected for the study. So, we really did not attempt to add an additional variable, having to do with the frequency of use. However, one thing that you can notice is we really didn't see much difference between control and block valves, and control valves are in constant motion, although a somewhat different mechanism. There is no rotary motion.

Q. Joseph Zabaga/Mobil Oil - First, quickly, I think that, my company would like to endorse the comments made by Union. Most particularly the point of

looking at the average versus the median data, as it affects the conclusions
that you are drawing Robert. The information that you have come up with so
far is powerful and it is one that everyone is waiting for. I am enthusias-
tic and understanding of what you have here, but I am overwhelmed by the
data that you presented. It prevents my presenting a comprehensive
commentary on what I think the effects are. So, therefore, I can only
comment on a very brief scan of the data. And I think that I will concen-
trate on just one point. On page 352 (of the paper) you list your con-
clusions. Conclusion number 5 bothers me. Let me move to another field
that we haven't even discussed at this conference, but with which I am
connected all the time, vapor recovery in marketing terminals. Some years
ago, an arbitrary number of 90 percent was presented by someone, as a control
level that might be desirable. Since then the regulatory agencies have
realized that a mass emission control level is far more appropriate for
properly controlling emissions and achieving goals that both industry and
agencies are interested in achieving. However, to this day there persists
an incredible amount of misinterpretation and misunderstanding on this
arbitrary 90 percent. It doesn't belong in regulations, in that particular
arena and I suggest that it doesn't belong here. And, I was a little dis-
turbed by seeing the fact that we would take eleven valves, and I think
that is what we do have in here, and make a statement to that effect. I
wonder whether the commentary is appropriate. Your conclusion 5 could have
said, here is what happened with directed maintenance, and here is what
happened with undirected maintenance. You didn't make the comparison. You
made a pronouncement. I think a comparison might be deserved. If one does
make that comparison, the effects might not be as pronounced. Moreover,
suggesting that there is an arbitrary level that one might direct oneself
towards, I think is inappropriate. I think that while this study is a very,
very important part of the entire effort, we are simply too early in the
game to write down levels of leak rate and the amounts of control that might
be obtained, based on eleven valves over a very short time span. I think
that it is something that will come days from now, some months from now,
possibly some years from now, but certainly it is too premature right now.

A. (By Wetherold) - That can be reworded, I think, to say that we have seen
that kind of reduction with some valves. And so it is possible, but I don't
think that should be, based on this data, any kind of target value, to shoot
for.

COMMENT/Rosebrook - I would like to say that I think that is probably a very
good comment Joe. We have in the past, attempted to avoid making statements
appear overly positive until we had the data. We attempted to avoid making

statements that could be misconstrued and then try to explain ourselves in the clearest possible terms backed up by sufficient amount of data. This is one case where we can get some preliminary indications, based on the amount of work that was done and we have perhaps made that statement too positive.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - Are you getting any kind of contracts to continue to see what the effect of an I & M program is on overall emission reduction in the refinery versus individual valves?

A. (By Rosebrook) - At this time there is no such contract in the works. There is further work being undertaken, which is being done in the chemical industry. That study is to do valve maintenance with a broader data base, with all directed maintenance, bagging, not only immediately, but bagging to get absolute emission rates after periods of time up to four months.

Q. Thomas C. Ponder, Jr./PEDCo Environmental, Inc. - Are you planning in that program to go through a plant periodically with like an OVA or TLV and see once they start their I & M program, if the number of instances of leakers goes down versus the amount of emissions?

A. (By Rosebrook) - No, we are not. We are going to select a somewhat larger data base of valves which screen less than 1,000, and follow those valves as often as we possibly can every time we are near that particular unit to determine the instances of leak occurrence from nonleaking fittings. And once again, we are going to be subject to the variation that is introduced just by using the screening device, but we will attempt to take enough readings to determine if, indeed, things are beginning to leak.

COMMENT/Bruce A. Tichenor - I appreciate the comments by Mike Olson regarding the data that are being collected by the oil refinery people. And I think that we all would be served if as soon as these data become available, it could be made available to other people for analysis. I agree one hundred percent we don't have enough information and in my paper this afternoon that will be pointed out again. As the I & M programs are instituted, as the data becomes available and distributed, I think we will all get better answers to some of these questions. I don't necessarily think it is EPA's responsibility to collect all the data.

ENVIRONMENTAL ASSESSMENT OF ATMOSPHERIC EMISSIONS FROM

PETROLEUM REFINERIES

G. E. Harris and M. W. Hooper
Radian Corporation
Austin, Texas

ABSTRACT

The objective of this study was to perform an environmental impact
assessment based on the new emission data generated in the EPA funded program
entitled "The Assessment of Environmental Emissions from Oil Refining." This
was done by:

- defining a hypothetical refinery,

- calculating its emissions,

- performing atmospheric dispersion modeling of those emissions
  to determine ground level concentrations, and

- comparing those concentrations to quantifiable toxicity data
  to determine the possibility of a public health hazard.

The results of this analysis are discussed in terms of their significance to
the hypothetical refinery and of their potential for generalization.

RESUME

Graham E. Harris

Mr. Harris holds a B.S. degree in Chemical Engineering from Texas
A&I University. He was employed as a process engineer at Texaco's Port
Arthur refinery for six years. Since joining Radian, he has worked on a
variety of projects, but has maintained a specialization in petroleum
processing and the measurement/control of Volatile Organic Carbon emissions.
He participated in all phases of the subject refinery sampling program.

Michael W. Hooper

Mr. Hooper holds a B.S. in Engineering Physics from the University
of Colorado and an M.A. in Ecology from The University of Texas. He was
previously employed by U.S. Army Materiel Commands at White Sands Missile Range
as a mathematical modeler for seven years. While employed at Radian he has
been envolved on numerous projects involving air quality impact prediction
(i.e., dispersion modeling) and analysis. Projects included the impacts due
to strip mines, sulfur plants, automobile traffic, agriculture, heavily
industrialized area, etc.

G. E. Harris/ M. W. Hooper

ENVIRONMENTAL ASSESSMENT OF ATMOSPHERIC EMISSIONS FROM A HYPOTHETICAL PETROLEUM REFINERY

INTRODUCTION

This environmental assessment is, in many ways, the culmination of more than three years work in petroleum refineries. It brings together many diverse pieces of information which seemed totally independent during the sampling and analysis phase. And it bridges the gap from cause to effect, from source sampling to ambient pollutant levels. In addition, it will attempt to use known toxicity data to evaluate the potential effect of these ambient pollutant concentrations on the public.

This type of analysis is particularly important for fugitive emissions, where hydrocarbons are the only significant pollutant species. The rationale behind controlling hydrocarbon emissions is based on two diverse effects: the formation of photochemical oxidants and the toxic effects of some hydrocarbon species. Only through atmospheric modeling (or the even more expensive ambient monitoring) can the latter effects be assessed.

OBJECTIVES

The objectives of this study can be summarized as follows:

- To determine the impacts of both criteria pollutants and selected hydrocarbon species emitted from a hypothetical refinery.

- To perform a sensitivity analysis on the primary variables.

- Based on the sensitivity analysis, to determine if any generalizations can be drawn about the potential environmental impacts of refineries.

- To assess the utility of the modeling approach as a means of determining the impacts of potentially hazardous pollutants.

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G. E. Harris/M. W. Hooper

APPROACH

The approach used to accomplish these objectives is relatively straightforward, but it is complicated by the large number of independent inputs. Figure 1 shows a block diagram of the steps involved in this assessment. Input variables include:

- description of the model refinery,

- emission factors,

- fitting counts,

- stream analyses,

- toxicity data, and

- ambient air quality requirements.

The various operation steps include:

- calculation of emissions,

- atmospheric dispersion modeling,

- characterization of unit emissions by streams,

- characterization of unit emissions by selected hydrocarbon components, and

- adaptation of industrial hygiene toxicity data to a general public basis.

There are some intermediate results which are of interest in themselves, but are also used in further operations steps to achieve final results. These factors include the various ground level concentrations of criteria pollutants, total hydrocarbons, and selected hydrocarbon species.

The final results are the source severity factors for criteria pollutants and hydrocarbon species. Although this concept will be described more fully later, a brief explanation is in order here. Monsanto Research Corporation worked under contract to the EPA to develop a standard method for calculating the environmental impacts of potentially hazardous atmospheric emissions. They defined a source severity factor as the ratio of the maximum ground level concentration of a pollutant in a "standard receiving atmosphere" to the "acceptable pollutant concentration," as shown in Table 1. This acceptable concentration is derived from either National Ambient Air Quality Standards (NAAQS) or from Threshold Limit Values (TLV's).
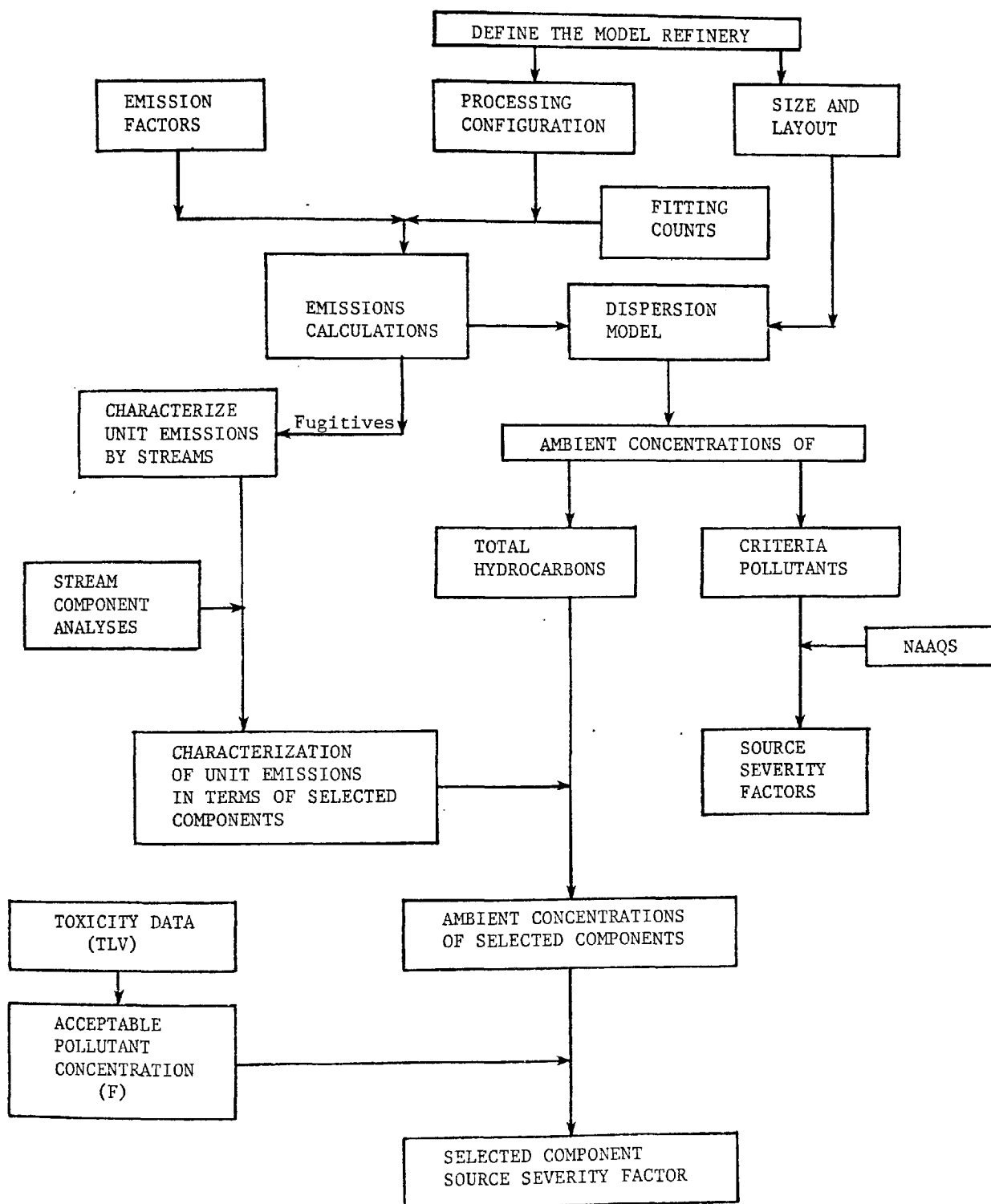
Figure 1. Block diagram of the approach.

If the resulting ratio is greater than 1.0, then control technology development is probably needed. If the ratio is below about 0.01, then further control is probably not needed. Intermediate values are in a gray area where technology may or may not need to be developed.

TABLE 1. SOURCE SEVERITY

$$S = \frac{\overline{\chi}_{max}}{F}$$

where:

S is the Source Severity Factor

$\overline{\chi}_{max}$ is the Maximum Ground Level Concentration of the Pollutant

F is the Acceptable Pollutant Concentration

Description of the Model Refinery

The first element to be examined is the development of the model refinery. The requirements of this model are much broader than most, because not only the refinery processing must be characterized, but also its physical configuration. There is ample documentation of the difficulties involved in trying to synthesize a "typical representative refinery." Refineries are very diverse, and only a very rough approximation can be achieved with a single model. When size and layout are added to the model, the task goes from difficult to impossible. Therefore, it should be noted throughout this discussion that this is not a model that attempts to represent the industry, but rather a model of one hypothetical refinery that reflects as much of the "real world" as possible.

The source for the model refinery is an EPA report prepared by Pacific Environmental Services[1] in which they gave detailed descriptions of the processing and physical layouts of several types of refineries. The large existing refinery was chosen as the model for this study because it is essentially the worst case. If the results show minimal environmental impact for this type of refinery, then smaller, less complex, or more efficient grass roots refineries should create an even lesser impact.

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Figure 2 shows the basic processing configuration of the model refinery. All of the normal refinery unit operations are represented including:

- atmospheric and vacuum crude distillation,

- extensive hydrotreating of all ranges of product streams (such as naphtha, middle distillate, gas oils, and resid),

- catalytic reforming,

- aromatics extraction and separation of BTX,

- hydrogen manufacturing,

- fluid catalytic cracking with ESP and CO boiler,

- sulfuric acid alkylation,

- sulfur recovery and tail gas treating,

- gas processing,

- delayed coker,

- rerun stills for recovered oils, and

- many miscellaneous treating, brightening, etc., types of processing.

Again, it should be stressed that this configuration is not intended to represent the industry. But it is a reasonable example of a modern fuels refinery supplying low sulfur products.

The plot plan of the refinery (shown in Figure 3) will give evidence of the detail which was presented in the PES report. The functions of the various refinery modules are detailed in Table 2. It should be noted that this environmental assessment does not include the effects of emissions from storage tanks, but only from the refinery processes. The process areas tend to form two clusters, probably the result of a stage-wise expansion over a period of many years. Considerable detail has been included in the physical model. All of the appropriate vital functions have been accounted for and distributed in a realistic manner. These are critical points in achieving meaningful results from the atmospheric dispersion model.

Fuel Gas and LPG

LPG and Gas

Gas Treating

Sulfur Recovery

Tail Gas Treating

Sulfur

Naphtha

Naphtha

Hydro-treating

Catalytic Reforming

BTX

Aromatics Extraction

Gasoline

Middle Distillates

Reformate

Solvents

Hydro-treating

Heavy Atm. Gas Oil

Catalytic Cracking

Gasoline

Aviation Fuels

Cycle Gas Oils

Diesels

Hydro-Treating

Heating Oils

To Hydrotreaters

Aromatics

Atmospheric Distillation

Vac. Gas Oil

H₂ Plant

H₂

Petrochemical Feedstocks

P R O D U C T S

Vac. Gas Oil

Hydro-treating

Asphalts

Industrial Fuels

iC₄

Alkylation

Alkylate

C₃⁼/C₄⁼

Refinery Fuel Oil

Vacuum Distillation

Asphalt Plant

Resid Hydro-Treating

Delayed Coking

Gasoline, Naphtha, Middle Distillates

Coke

Figure 2. Block flow diagram of model refinery.

LARGE CAPACITY EXISTING REFINERY

W = 1865 m

L = 2775 m

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Figure 3. Model refinery layout.

TABLE 2. LARGE CAPACITY EXISTING REFINERY MODULE KEY.

Module No.	Description	Module No.	Description
L1	Buffer Zone	L36	Catalytic Reformer
L2	Feedstock Storage	L37	Aromatics Extraction
L3	Crude Oil Storage	L38	Catalytic Cracking
L4	Feedstock Storage	L39	Para-Xylene Plant
L5	Feedstock Storage	L40	Delayed Coker
L6	Crude Oil Storage	L41	Barrel Storage
L7	Feedstock and Product Storage	L42	Barrel Reconditioning
		L43	Feedstock Storage
L8	Crude, Feedstock, and Product Storage	L44	Storm Water Impound Basin
L9	Crude, Feedstock, and Product Storage	L45	Warehouse
		L46	Gas Holder/Blowdown Stack
L10	Oil-Water Separator		
L11	Product Storage	L47	Gas Holder/Blowdown Stack
L12	Product Storage		
L13	Distillation and Gas Recovery Unit	L48	Fire Prevention Training Facility
L14	Jet Hydrofiner/Catalytic Reformer	L49	Oil-Water Separator
		L50	Asphalt Plant
		L51	Solvent Treating Plant/ Boiler House
L15	Naphtha Hydrotreater		
L16	Hydrotreater (Lt Cycle Oil)	L52	SO$_2$ Treating Plant/ Tanks
L17	Hydrogen Manufacturing	L53	Lube Oil Packaging
L18	Partial Oxidation Unit	L54	Coke Storage
L19	Future Expansion	L55	Crude Oil Storage
L20	Cooling Tower	L56	Feedstock Storage
L21	Flares	L57	Tanks/Impound Basin
L22	Feedstock and Product Storage	L58	Administration
		L59	Oil-Water Separator
L23	Naphtha Hydrotreater	L60	Gasoline Sweetener/ Crude Distillation
L24	Vacuum Gas Oil Unit		
L25	Benzene Fractionation	L61	Crude Distillation/ Crude Desalter
L26	Steam Rerun Stills		
L27	Future Expansion	L62	Specialty Crude Distillation
L28	Crude Distillation		
L29	Catalytic Reformer	L63	Speciality Crude Distillation/Condenser Box
L30	Vacuum Residuum De-sulfurizer		
L31	Hydrogen Manufacturing	L64	Gasoline Fractionating Unit
L32	Alkylation		
L33	Distillate Hydrodesul-furization (Hvy Gas Oil)	L65	Tank Loading/Truck Loading/Vapor Recovery
L34	Sulfur Recovery	L66	Buildings
L35	Tanks/Cooling Towers	L67	LPG Storage and Blending
L68	Vapor Recovery/Gasoline Rectifier/Tanks		
L69	Main Pump House		
L70	Product Storage		
L71	Wastewater Treatment		
L72	Building		
L73	Product Storage		
L74	Shops and Warehouse		
L75	Crude Oil Storage		
L76	Crude, Feedstock, and Product Storage		

The oil/water separator in Module L10 treats aqueous discharge from Modules L1-L21.

The separator located in Module L59 treats aqueous streams from Modules L58-L60, L70, L71, and L73-L76.

The wastewater separator in Module L49 treats discharges from the remaining modules.

Emissions Calculations

Once the model refinery is defined, the next step is to calculate its emissions. The emission factors used for these calculations were derived primarily from the results of testing on this program, but they were supplemented by emission factors from other sources (such as AP-42) as needed. Table 3 shows a summary of emission factor sources.

The refinery processing configuration and the emission factors are sufficient to define point source emissions, but the fugitive source emission factors are given on a per source basis. Therefore, fitting counts and their distribution in various types of service (gas phase, light liquids, heavy liquids, or hydrogen) had to be established. Radian made fitting counts on a number of process units during the field testing phase and the results are shown in Table 4. These counts were not used directly, however, since they do not show the service distribution. The PES report gave a detailed listing of all the pumps on each unit. Radian data were used to generate ratios of valves per pump which, when applied to the PES pump list, yields a count of valves in each type of service. The number of compressors and some previous estimates from the 1950's Los Angeles study were used to estimate the number of valves in gas service.

Applying all of these factors, a slate of refinery emissions was generated. Table 5 is a summary of those emissions by pollutant type.

Description of the Dispersion Model

The air quality impacts of the model refinery were then predicted with RAM, an EPA guideline model.[2] It is capable of predicting a 1- to 24-hour average concentration of relatively unreactive pollutants. A maximum of 250 point and 100 area sources can be modeled. Concentrations are predicted at a maximum of 150 selected locations (receptors).

RAM uses Gaussian steady-state dispersion algorithms for areas where one wind vector for each hour is a good approximation. Concentrations are calculated hour by hour as if the atmosphere had achieved a steady-state condition.

Inputs to the model are hourly meteorological data consisting of:

- wind speed,

- wind direction,

- temperature

- stability class (i.e., atmospheric turbulence), and

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TABLE 3. EMISSION FACTORS

Emitting Source Type	Emission Factor Reference
Baggable Fugitives and Cooling Towers	Radian Refinery Assessment
API Separator, Flares, FCC, Sulfur Recovery	AP-42
Heaters and Boilers	EPA Report: A Program to Investigate Various Factors in Refinery Siting

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TABLE 4. ESTIMATED NUMBER OF INDIVIDUAL EMISSION SOURCES[2] IN
15 SPECIFIC REFINERY PROCESS UNITS.

Process Unit	Estimated Number of Sources Within Battery Limits of Process Units					
	Valves	Flanges	Pumps[3]	Compressors[4]	Drains	Relief Valves
Atmospheric Distillation	890	3540	31	1	69	6
Vacuum Distillation[1]	500	2000	16	0[1]	35	6
Fuel Gas/Light Ends Processing	180	760	3	2	11	6
Catalytic Hydroprocessing	650	2600	10	3	24	6
Catalytic Cracking	1310	5200	30	3	65	6
Hydrocracking	930	3760	22	3	58	6
Catalytic Reforming	690	2760	14	3	49	6
Aromatics Extraction[1]	600	2400	18[1]	0[1]	41	6
Alkylation	680	2280	11	0	41	6
Delayed Coking[1]	300	1240	9[1]	0[1]	28	6
Fluid Coking	300	1240	9	4	28	6
Hydroealkylation[1]	690	3760	14[1]	3[1]	58	6
Treating/Dewaxing	600	2290	18	1	44	6
Hydrogen Production	180	640	5	3	17	4
Sulfur Recovery[1]	200	800	6[1]	0[1]	20	4

[1] Sources were not counted in process units of this type. The number of sources was estimated.
[2] Only those sources in hydrocarbon (or organic compound) service.
[3] Number of pump seals = 1.4 x number of pumps.
[4] Number of compressor seals = 2.0 x number of compressors.

TABLE 5.   SUMMARY OF EMISSIONS FROM THE MODEL REFINERY

Pollutant	Emissions in g/sec (TPY)		
	Point Sources	Fugitives	Total
Particulates	111.8 (3,886)	0	111.8 (3,886)
SO_x	356.6 (12,397)	0	356.6 (12,397)
CO	23.3 (809)	0	23.3 (809)
NO_x	405.6 (14,100)	0	405.6 (14,100)
Hydrocarbons	27.8 (966)	256.7 (8,924)	294.5 (9,891)

- mixing height (the layer of atmosphere in which the pollutant can freely disperse).

Also required as inputs are the emission data. For point sources this consists of:

- source coordinate,

- emission rate,

- physical height,

- stack diameter,

- stack gas exit velocity, and

- stack gas temperature.

Area source parameters consist of the:

- coordinates of the southwest corner,

- side length,

- total area emission rate, and

- effective height.

Concentrations from the point sources are a function of the distance downwind and cross wind from the source to the receptor. In order to save computation time, concentrations due to area sources are calculated using the narrow plume approximation. This neglects diffusion in the crosswind direction and assumes that an area source consists of many narrow plumed point sources. As a result, any receptor that has no area sources directly upwind receives no contribution to its predicted concentration from area sources. This approximation is good when modeling large urban area sources.[3]

Basic Dispersion Assumptions Used in RAM Algorithms

The Gaussian-plume model is derived from the basic diffusion equation which describes the flow of mass from a region of high concentration to one of lower concentration. The diffusion equation is solved for steady-state conditions, i.e., there is no change in concentration at any location for the hour being considered. The following assumptions are also made in order to facilitate the solution of the equation:

- There is no vertical wind component.

- There is no downwind diffusion, only vertical and horizontal diffusion.

- The maximum concentration is the plume centerline. The concentration distribution in the vertical and horizontal is Gaussian.

- The wind speed and direction is constant for each hour and over the entire area in question.

- When the plume hits the ground all its matter is reflected back.

- The terrain in the area of interest must be relatively flat.

The dispersion coefficients (the Gaussian σ's in the vertical and horizontal directions) are empirically-determined as functions of atmospheric turbulence, distance from the source and the concentration averaging time. Thus the spread of the plume is dependent on these three factors. The atmospheric turbulence is defined by stability classes. These classes, which range from very unstable to neutral to very stable atmospheres, are determined by wind speed and insolation during the day, or wind speed and cloud cover during the night. This relationship is presented in Table 6. The most unstable class is A with F the most stable.

Dispersion coefficients are largest in unstable conditions and smallest in stable conditions. This means the plume disperses more rapidly in the vertical and horizontal directions during usntable conditions (i.e., one to two hours after sunrise) than in stable conditions.

Application of RAM to Hypothetical Refinery

RAM has a rural and an urban version. The vertical and horizontal dispersion coefficients are smaller in the rural version of RAM than they are in the urban version. This is due to the fact that urban areas contain numerous heat sources which tend to increase dispersion. The rural version of RAM was used to describe the worst case.

Fugitive emissions were modeled by three different methods:

- as a single point source originating in the center of the process unit plot,

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TABLE 6. RELATIONSHIP BETWEEN STABILITY CATEGORIES AND
SURFACE METEOROLOGICAL CONDITIONS (4).

| Surface Wind Speed (at 10 m), m/sec | Day | | | Night | |
| | Incoming Solar Radiation | | | Thinly Overcast or | $\leq 3/8$ |
	Strong	Moderate	Slight	$\geq 4/8$ Low Cloud	Cloud
< 2	A	A-B	C		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
> 6	C	D	D	D	D

- as a pseudo-area source (where the single point
  source was divided into three point sources
  distributed across the unit in a plane perpen-
  dicular to the worst case wind direction), and

- as area sources.

It was hoped that the point source approximation would not significantly
affect the results, since this type of calculation requires much less com-
puter time.

Meteorological inputs for 24 hours consisted of C stability; a
wind speed of 4.5 m/sec; three alternating wind directions (5 degrees either
side of and including the worst-case wind direction); a temperature of 25°C;
and a mixing height of 500 meters. This mixing height allowed all the sour-
ces' plumes to rise to their maximum height without causing them to be trap-
ped above the mixing height or have them reflect off it. The worst-case
wind direction is dependent on source geometry and emission parameters.
The worst-case direction was determined by modeling with the wind coming
from 16 directions for one hour each and comparing the predicted concentra-
tions.

Modeling runs were also conducted to determine concentration sen-
sitivity to atmospheric conditions. One run was made with a more stable
atmosphere (D stability) and one run was made with a slower wind speed (3.5
m/sec).

The locations of a series of permanent receptor sites were also
input to the model. The locations consisted of a grid placed in the area
of greatest impact as predicted by the worst-case wind direction. The model
then calculated the 24-hour average concentration at each receptor. From
these data maximum concentrations were determined. Also, isopleths (lines
of equal concentration) were plotted. Not only can the total ambient con-
centration be displayed for each receptor, but these concentrations can be
broken up into their component contributions from each of the sources. All
the meteorological conditions, except wind direction, are constant for the
24 hours. The wind directions are repeated in sequence every 3 hours. Thus
the predicted 24-hour concentration would be the same as the 8-hour and 3-
hour concentrations.

Annual concentrations can be predicted with Larsen statistics.[5]
Using empirically determined ratios, maximum annual concentration can be
determined from mean concentrations for shorter averaging times. These
ratios, for converting from averaging times of 1 second to 1 month, are
functions of the standard geometric means (SGM) of the shorter averaging
times.

Using data collected in 1977 by the Texas Air Control Board, a typical SGM of 1.85 per 24-hour NO_x concentration was determined. Using this value, Larsen's model estimates the ratio of average 24-hour concentration to the expected maximum annual concentration to be 4.85.

Modeling Results

Three of the pollutants showed no violation of the NAAQS, those being particulates, oxides of sulfur, and carbon monoxide. The maximum ground level concentration of particulates was 68 $\mu g/m^3$. It should be noted that this considers only process particulates (which result primarily from the FCC and oil fired heaters), and does not include fugitive dust from unpaved roads, construction activities, or coke handling. The point of maximum concentration occurred due west of the refinery center at a distance of 1.5 kilometers from the fence line, as shown in Figure 4.

The maximum concentration of SO_x was found to be 288 $\mu g/m^3$ as compared to the NAAQS of 365 $\mu g/m^3$. The maximum point was due west of the sulfur recovery complex and occurred at one half kilometer from the refinery boundary, as shown in Figure 5.

The maximum 1-hour concentration of CO was predicted to be 17 $\mu g/m^3$ as compared to an NAAQS of 10,000 $\mu g/m^3$. The maximum point occurred due west of the refinery center and at a distance of 1.25 kilometers from the boundary line, as shown in Figure 6.

The maximum 24-hour average NO_x concentration was found to be 269 $\mu g/m^3$, which is well in excess of the NAAQS value of 100 $\mu g/m^3$, as shown in Figure 7. The NAAQS is expressed as the maximum annual average concentration. By applying the Larsen statistics, the predicted annual average NO_x concentration is reduced to 55 $\mu g/m^3$. This brings the refinery well within attainment of the NAAQS, as shown in Figure 3-8.

The total hydrocarbons were also found to be in excess of the 160 $\mu g/m^3$ standard, with a maximum concentration of 9644 $\mu g/m^3$. This point was located on the refinery boundary and due west of the main processing area. Although the concentrations fell off rapidly from the maximum, the 160 $\mu g/m^3$ isopleth extends about 3.5 kilometers downwind and encompasses about four square kilometers, as shown in Figure 9.

Hydrocarbon Component Characterization

Criteria pollutant modeling is now quite common and is included in most permit applications. The site-specific models used are probably much more accurate than this generalized case, but this level does provide the input to further characterize the emissions and the resulting ambient concentrations.

250   500

250 meters

500 meters

750

1000

No violations of either the primary
or secondary NAAQS

1250

$\bar{\chi}_{max} = 68 \ \mu g/m^3$

1500

1750

2000

2250

2500

2750

Pollutant: Particulates
NAAQS: Primary 260 $\mu g/m^3$; Secondary 150 $\mu g/m^3$.
Area in Non-Attainment: 0

East

South
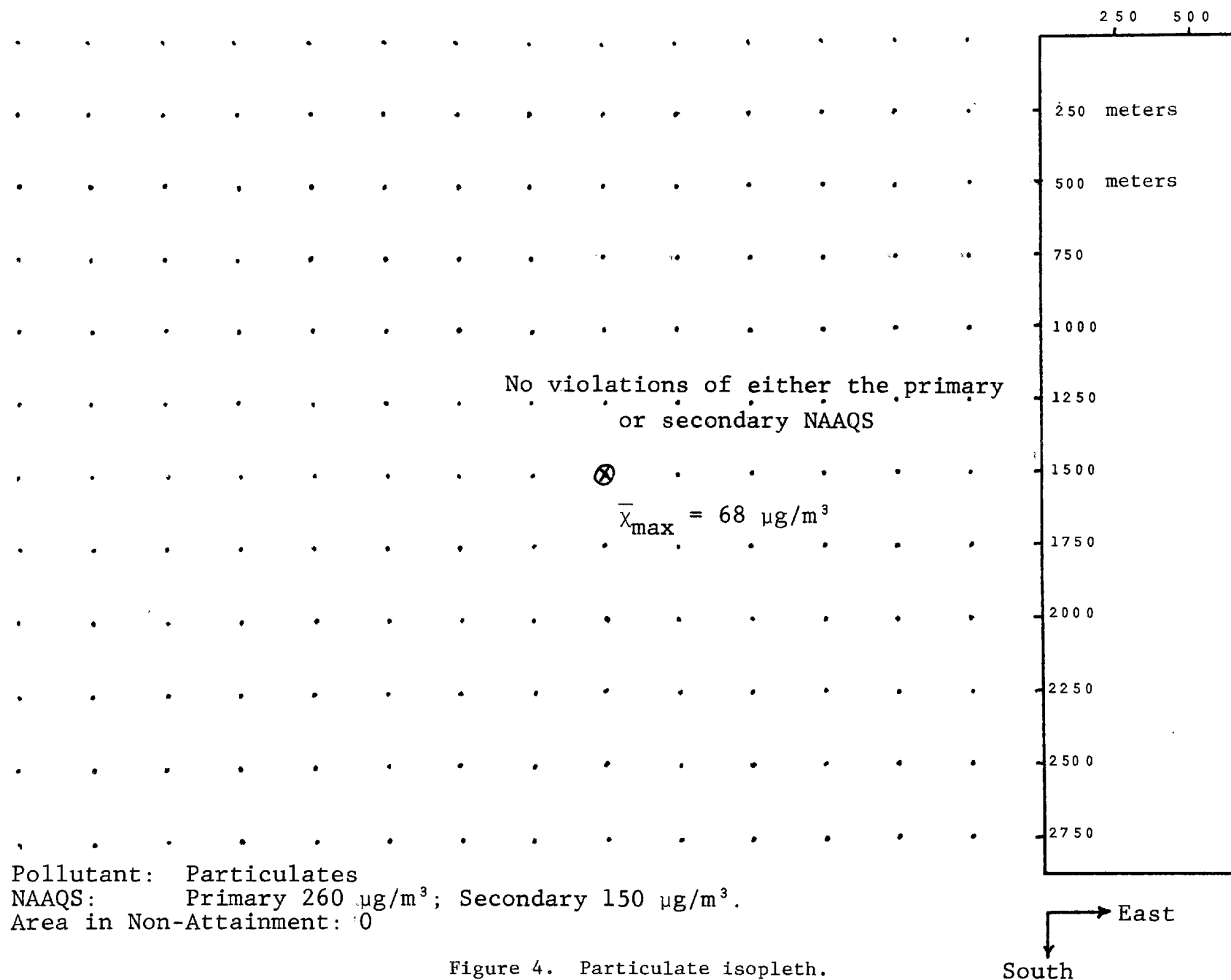
Figure 4.   Particulate isopleth.

No violation of NAAQS

$\overline{X}_{max}$ = 288 µg/m³

Pollutant: SO_x
NAAQS = 365 µg/m³
Area in Non-Attainment: 0

East

South

Figure 5. SO_x isopleth.

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No violations of NAAQS

$\overline{\chi}_{max} = 16.9 \ \mu g/m^3$

Pollutant: CO
NAAQS: 10,000 $\mu g/m^3$
Area in Non-Attainment: 0

East

South

250   500

250

500

750

1000

1250

1500

1750

2000

2250

2500

2750

Figure 6. CO isopleth.

Scale
1 km

250 500 750

250

500

750

1000

1250

1500

1750

2000

2250

2500

2750

Refinery

$\overline{X}_{max}$ = 268.5 µg/m³

Pollutant: NO$_x$ (24-hour average)
NAAQS: 100 µg/m³ (based on an annual average)
Area in Non-Attainment: 5.24 km² (2.02 mi²)

East

South

Figure 7. NO$_x$ isopleth, 24-hour average.

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$$\overline{X}_{max} = 55 \ \mu g/m^3$$

250   500

250

500

750

1000

1250

1500

1750

2000

2250

2500

2750

East

South

Pollutant: NO$_x$ (annual average based on Larsen's statistics)
NAAQS: 100 $\mu g/m^3$ (based on an annual average)
Area in Non-Attainment: 0

Figure 8. NO$_x$ isopleth, annual average.

Figure 9. Hydrocarbon isopleth.

Pollutant: HC
NAAQS: 160 μg/m³
Area in Non-Attainment: 4.05 km² (1.57 mi²)

$\overline{X}_{max} = 9644\ \mu g/m^3$

East

South

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Next it is desired to characterize the total hydrocarbon emissions in terms of selected components. This requires one new piece of input data and two computation steps. The input data is a set of stream analyses for the selected components. The emissions were calculated on a unit basis, however, so first the unit emissions must be broken down into the streams characteristic of that unit. As an example, Table 7 shows the breakdown for the fluid catalytic cracker. First the characteristic streams must be selected:

- atmospheric gas oil (feedstock),

- proylene/butylenes,

- cracked naphtha,

- light cycle gas oil, and

- heavy cycle gas oil.

Although this does not include every possible product or intermediate stream, it is detailed enough to allow a reasonably good characterization. The next step is to estimate the percentage of total fittings in each stream service. These are engineering estimates based on familiarity with the unit operations. The next important variable is the mean emission factor for each stream (which is determined by classifying the stream as gas phase, light liquid, heavy liquid, or hydrogen) and applying the emission factors presented earlier. If these two factors are multiplied together, the resulting product is in proportion to each stream's tendency to cause fugitive emissions. By summing these products and determining each product as a percentage of the sum, the total unit emissions can be allocated to each stream by that percentage.

Then the component analyses can be applied to these stream emissions. The component analyses come primarily from GC-MS work done on samples collected in the refineries during fugitive testing. This was supplemented where necessary with data from a previous Radian literature survey,[6] an API medical research report,[7] and engineering estimates. Tables 8 and 9 are examples of a GC-MS data sheet and a stream quality summary, respectively.

It was necessary to consolidate these component analyses to minimize calculations and to yield reasonable data. This consolidation was done on the basis of the availability of both discrete concentration data and quantifiable toxicity data for any given component. If both were available, then the component was treated individually. If either was missing, the component was lumped into a family of components such as "other alkylbenzenes." This resulted in a list of discrete components which included:

TABLE 7. DISTRIBUTION OF UNIT FUGITIVE EMISSIONS BY STREAM.

Stream	Percent of Fittings in That Service (A)	Mean Emission Factor in That Service (B) lb/hr/source	Product (A) x (B)	Percent of Unit Fugitive Emissions in That Service
Atmospheric Gas Oil	15	0.0016	0.024	1
Fuel Gas	10	0.059	0.59	30
Olefinic LPG	15	0.030	0.45	23
Cracked Naphtha	30	0.030	0.9	45
Lt. Cycle Gas Oil	20	0.0016	0.032	1
Hvy Cycle Gas Oil	10	0	0	0
Totals	100	N.A.	1.996	100

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TABLE 8.   EXAMPLE STREAM COMPONENT ANALYSIS-CRACKED NAPHTHA.

Peak Number	Compounds (In Retention Order)	Bulk Liquid (ppm)	Vapor on XAD (µg)	Vapor on Tenax (µg)
1	Benzene	6,600	260	0.72
(IS)	d_6-Benzene	--	--	(0.035)
2	Toluene	47,700	8,100	25.3
3	Ethylbenzene	10,600	4,400	4.0
4	m→p-Xylene	57,200	8,000	21.3
5	o-Xylene	21,300	7,500	8.7
6	Isopropylbenzene	--	130	0.21
7	n-Propylbenzene	3,000	850	
8	3- + 4-Ethyltoluene	32,500	7,100	19.8
9	1,3,5-Trimethylbenzene	15,100	2,800	
10	2-Ethyltoluene	7,100	1,280	
11	1,2,4-Trimethylbenzene	46,000	6,150	13.3
12	1,2,3-Trimethylbenzene	9,600	880	3.2
13	C_4-Alkylbenzene	--	72	0.33
14	Indan	4,000	250	1.2
15	C_4-Alkylbenzene	17,200	1,000	
16	C_4-Alkylbenzene	19,600	960	7.8
17	C_4-Alkylbenzene	2,400	210	
18	C_4-Alkylbenzene	13,200	520	4.1
19	C_4-Alkylbenzene	13,600	480	
20	2- +Methylindan	2,500	85	0.41
21	C_4-Alkylbenzene	2,000	32	0.74
22	C_4-Alkylbenzene	19,600	340	2.3
23	Methylindan	2,500	10	0.22
24	Methylindan	2,800	30	0.24
25	C_4-Alkylbenzene	2,800	--	0.49
26	C_5-Alkylbenzene	27,000	--	1.2
27	C_5-Alkylbenzene	2,700	--	0.44
28	Naphthalene	15,600	66	0.03
29	C_4-Alkylbenzene	1,200	--	--
30	C_2-Alkylindane	2,400	--	0.11
31	C_4-Alkylbenzene	600	--	--
32	C_5-Alkylbenzene	4,000	--	1.2
33	C_5-Alkylbenzene	1,700	--	0.46
34	C_2-Alkylindan	400	--	--
35	C_2-Alkylindan	600	--	--
36	C_2-Alkylindan	400	--	--
37	C_2-Alkylbenzene	100	--	--
38	C_5- Alkylbenzene	1,000	--	--
39	2-Methylnaphthalene	8,700	--	0.03
40	1-Methylnaphthalene	3,600	--	0.01
(IS)	d_{10}-Anthracene (IS)	(100)	(1000)	--

TABLE 9. SUMMARY OF STREAM QUALITY DATA (PPMW).

Compound or Functional Family	LPG Olefins	Alkylate	Cracked Naphtha	FCC Light Cycle Gas Oil	FCC Heavy Cycle Gas Oil	Heavy Aromatics Extract (SO_2 Plant)
Benzene	0	0.1	2880	0	740	0
Toluene	0	0.3	89780	40	10000	0
Ethylbenzene	0	0.1	21430	0	1200	0
Xylenes	0	1.1	171450	610	11800	0
Other Alkylbenzenes	0	3.3	243470	26670	38200	750000
Napthalene	0	0.3	10950	59000	14000	0
Anthracene	0	0	0	10270	0	0
Biphenyl	0	0	0	10180	0	0
Other PNA's	0	2.2	6480	624480	22500	200000
n-Hexane	0	96	11830	0	0	0
Other Alkanes	400000	998956	204110	190800	701560	45000
Olefins	600000	930	170740	36750	50000	0
Cycloalkanes	0	11	66880	41200	150000	5000
Other Compounds Indicated Present	Thiols		Pyridines Thiols Sulfides Quinolines	Phenols Carbonyls Pyridines Thiols Sulfides Quinolines	Pyridines Carbonyls Thiols Sulfides Quinolines	
Reference Sources	3	1,3	1,3	1,3	1,3	3

Reference 1: Radian Data

Reference 2: Sampling and Analytical Strategies for Compounds in Petroleum Refinery Streams

Reference 3: Engineering Estimates

- benzene,

- toluene,

- ethylbenzene,

- mixed xylenes,

- naphthalene,

- anthracene,

- biphenyl, and

- hexane.

The general family groups included:

- other alkylbenzenes,

- other polynuclear aromatics,

- other alkanes,

- olefins, and

- cycloalkanes.

It is not really meaningful to talk about the toxicity of such a broad group as olefins or cycloalkanes. These were included to allow a consistent closed analysis to be synthesized from several diverse sources.

The dispersion model inputs emissions on a unit basis, so the next step is to combine the stream breakdown with the stream analyses to get a component analysis of unit emissions. An example of this process is shown for the FCC in Table 10.

A similar operation was performed separately on relief valves, since they are not distributed uniformly across the streams. Relief valves are usually placed at the top of a fractionating column or reactor vessel, and thus are exposed primarily to lighter streams. Table 11 shows the allocation of relief valves for the Aromatics Fractionation Unit. The total number of relief valves in each stream service was then totalled, and the stream analyses were applied to the emissions, as shown Table 12.

Still a different procedure was required to characterize the hydrocarbons emitted from the API separators. Analyses were available of the inlet oil to the separator and the recovered oil. A hydrocarbon material balance was then made to determine the composition of the evaporative emissions from the separator, as shown in Table 13. The available analyses

TABLE 10. FLUID CATALYTIC CRACKING – FUGITIVE EMISSION CHARACTERIZATION.

Stream	% of unit fugitives attributable to that stream	Weighted Contribution of each Component to Unit Emissions, in PPMW													
		Benzene	Toluene	Ethylbenzene	Xylenes	Other Alkylbenzenes	Naphthalene	Anthracene	Biphenyl	Other Poly-nuclear Aromatics	n-Hexane	Other Alkanes	Olefins	Cycloalkanes	H_2
Atmos. Gas Oil	1	0	0	0	0	1	0	0	0	2	0	9495	0	500	0
Fuel Gas	30	0	0	0	0	0	0	0	0	0	0	276000	18000	0	6000
LPG Olefins	23	0	0	0	0	0	0	0	0	0	0	92000	138000	0	0
Cracked Naphtha	45	1296	40401	9644	77153	109562	4928			2916	5324	91850	76833	30096	0
Lt. Cycle Gas Oil	1	0	0	0	6	267	590	103	102	6245	0	1906	368	412	0
Hvy Cycle Gas Oil	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total		1296	40401	9644	77159	109830	5518	103	102	9163	5324	471251	233201	31008	6000
	Emiss. Rate lb/hr														
L38-1	59.8	.078	2.42	.577	4.61	6.57	.33	.006	.006	.548	.318	28.18	13.95	1.85	.359

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TABLE 11. RELIEF VALVE DISTRIBUTION

Example: Aromatics Fractionation Unit

Total Relief Valves = 6

Stream	No. of Relief Valves
Benzene	4
Toluene	2
Xylenes	0

TABLE 12. RELIEF VALVE SUMMARY - FUGITIVE EMISSION CHARACTERIZATION.

Total # Relief Valves in That Service	Stream	% of unit fugitives attributable to that stream	Weighted Contribution of each Component to Unit Emissions, in PPMW													
			Benzene	Toluene	Ethylbenzene	Xylenes	Other Alkylbenzenes	Naphthalene	Anthracene	Biphenyl	Other Poly-nuclear Aromatics	n-Hexane	Other Alkanes	Olefins	Cycloalkanes	H_2
(42)	H_2 Recycle Gas	22.5	0	0	0	0	0	0	0	0	0	0	146250	0	0	78750
(12)	Fuel Gas	6.5	0	0	0	0	0	0	0	0	0	0	59800	3900	0	1300
(58)	LPG	31.1	0	0	0	0	0	0	0	0	0	0	311000	0	0	0
(4)	LPG Olefins	2.2	0	0	0	0	0	0	0	0	0	0	8800	13200	0	0
(33)	S.R. Naphtha	17.6	45	461	156	286	2918	257	1	111	2637	6835	87932	0	74361	0
(13)	Cracked Naphtha	7.0	202	6285	1500	12002	17043	767	0	0	454	828	14288	11952	4682	0
(8)	Reformate	4.3	232	3341	1441	7349	13949	318	0	0	30	1032	15308	0	0	0
(2)	Extract	1.1	196	2824	1217	6210	528	1	0	0	1	1	21	0	0	0
(2)	Raffinate	1.1	1	8	3	17	25	1	0	0	1	693	10252	0	0	0
(4)	Benzene	2.2	21846	44	0	0	0	0	0	0	0	110	0	0	0	0
(2)	Toluene	1.1	11	10921	44	11	0	0	0	0	0	0	13	0	0	0
(4)	SO_2	2.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
(2)	Middle Distillate	1.1	0	0	0	1	9	1	0	0	61	0	9828	0	1100	0
	Totals	100.0	22533	23884	4361	25876	34472	1345	1	111	3184	9499	663492	29052	80143	80050
	Normalized Total		23040	24421	4459	26458	35247	1375	1	113	3256	9713	678416	29705	81946	81850

TABLE 13.   COMPONENT MATERIAL BALANCE AROUND THE API SEPARATOR*

Component	Inlet Rate lb/day	Outlet Rate lb/day	Evaporative Loss(lb/day)	Concentration of Loss
Benzene	290	58	232	696 PPMW
Toluene	2243	1500	743	2229
Ethylbenzene	598	400	198	594
Xylenes	2105	1408	697	2091
Alkylbenzenes	7979	5337	2642	7926
Naphthalene	2921	1954	967	2901
Anthracene	394	264	130	390
Biphenyl	1767	1182	585	1755
PNA's	20378	19868	510	1530
Alkanes	961325	634695	326630	979888
	1000000	666666	333334	1000000

*Assume an inlet oil flow of 1,000,000 lb/day.

Evaporative losses = 333,334; Skim Oil - 666,666.

showed only the aromatics components, so the balance of the oil was assumed to fall in the alkane family.

Ambient Hydrocarbon Component Concentration

The ambient concentration of any given hydrocarbon species can be determined by the following relationship:

$$\overline{X}_s = (\overline{X}_T) \; (PPMW_s) \; (10^{-6})$$

where

$\overline{X}_s$ = the mean hydrocarbon species ambient concentration,

$\overline{X}_T$ = the mean total hydrocarbon ambient concentration, and

$PPMW_s$ = the concentration in weight parts per million of the subject species in the emitting source.

This is based on the dispersion model assumption that all species will disperse at the same rate; or in other words, that atmospheric turbulence far outweights any difference in molecular diffusion between species.

The first point of interest is the receptor showing the largest total hydrocarbon concentration. Table 14 shows the component breakdown at that point. This maximum point is located directly downwind of the API separator (Source L-49), and 97.8 percent of the hydrocarbon species at that point came from the separator. The bulk of the hydrocarbons are from the alkane family (9380 $\mu g/m^3$ or 1.9 PPMV), but both the aromatics and polynuclear aromatics species are present at the part per billion level (PPB).

It is also desirable to find the point of maximum concentration for each hazardous component, if that should prove to be different from the point of maximum total hydrocarbons. A limited search was carried out to find these species maximum points by finding the maximum points for units with high concentrations of the subject species. For example in the case of benzene, the maximum point for each catalytic reformer, the aromatics extraction unit, the aromatics fractionation unit, and the fluid catalytic cracking unit were determined. A complete component breakdown was calculated at each point to detect unit interactions, and the point of maximum benzene concentration was selected. A similar procedure was carried out for each component, and the resulting maximum concentrations are summarized in Table 15.

It is interesting to note that all of the species maximum concentrations came from the two highest ranked points for total hydrocarbons. Five species (including benzene, naphthalene, anthracene, biphenyl, and the general polynuclear aromatics family) had their maximums adjacent to the API separator. The other species maximum values were found at a receptor on the west boundary about 1380 meters from the northeast corner. The largest

TABLE 14. HYDROCARBON SPECIES AMBIENT CONCENTRATION AT THE POINT OF
MAXIMUM TOTAL HYDROCARBON CONCENTRATION

Location: On the west boundary line at a point 1650 meters from the north-
west corner; directly downwind of source L49 (an API separator).

Component	Concentration, $\mu g/m^3$	Concentration, PPMV
Benzene	6.6	0.0019
Toluene	21.2	0.0051
Ethylbenzene	5.7	0.0012
Xylenes	19.8	0.004
Other Alkylbenzenes	102.2	0.017
Naphthalene	27.5	0.0047
Anthracene	3.6	0.0005
Biphenyl	16.5	0.0025
Other Polynuclear Aromatics	22.7	0.0030
n-Hexane	2.8	0.0007
Other Alkanes	9380.0	1.876
Olefins	0	0
Cycloalkanes	33.7	0.009
H_2	1.8	0.020
Total Hydrocarbons	9644.0 $\mu g/m^3$	1.95 PPMV

TABLE 15. MAXIMUM AMBIENT CONCENTRATION OF SELECTED HYDROCARBON SPECIES

Component	Ambient Concentration		Location
	$\mu g/m^3$	PPMV	On the West Boundary, XXXX meters from the Northeast Corner.
Benzene	6.6	0.0019	1650
Toluene	26.3	0.0063	1380
Ethylbenzene	10.7	0.0022	1380
Xylenes	53.6	0.0092	1380
Other Alkylbenzenes	105.5	0.0179	1380
Naphthalene	27.5	0.0047	1650
Anthracene	3.6	0.0005	1650
Biphenyl	16.5	0.0025	1650
Other Polynuclear Aromatics	22.7	0.0030	1650
n-Hexane	58.5	0.0152	1380
Olefins	37.6	0.010	1380
Cycloalkanes	365.8	0.099	1380

contributor to this point was the crude distillation unit (L28-1). Other significant contributing units included:

- two catalytic reformers (L36-1 and L29-1),

- aromatics extraction (L37-1),

- alkylation (L32-1),

- fluid catalytic cracker (L38-1),

- delayed coker (L40-1),

- hydrogen plant (L31-1), and

- resid HSD (L30-1).

The largest concentration for any single component examined was found to be hexane at a concentration of 15 PPBV.

Toxicity Data

To assess the impact of a given concentration of a pollutant species, quantifiable toxicity data must be available. The Monsanto approach uses the term "acceptable pollutant concentration" as the level at which there is a very low probability of adverse impacts on the general public. For criteria pollutants, the Primary Ambient Air Quality Standards are used as the acceptable pollutant concentrations. For other species, the acceptable concentration can be calculated from the TLV as shown in Table 16. The factor "G" is defined as a conversion factor to change a TLV into an "equivalent PAAQS," and G is calculated to be 1/300. This comes from two factors:

- the ratio $(\frac{8}{24})$ converts the TLV from an 8 hour per day basis to a 24-hour basis, and

- the factor $(\frac{1}{100})$ is a safety factor to account for the fact that the general public is more susceptible to illness than the industrial work force (for whom the TLV was set).

Table 17 shows a summary of the acceptable pollutant concentrations that result from this operation. Note that some of the values are in parentheses. These are values arbitrarily assigned to a family of chemicals, some of whose members have TLV's that average out to the assigned value. These values are interesting, but they should be used with caution. Not all of the members of such a family are equally toxic, nor is it certain that their effects would be additive. If the source severity factors based on these values

TABLE 16. DEFINITION OF "ACCEPTABLE POLLUTANT
CONCENTRATION," (F)

For Criteria Pollutants: F = PAAQS

For Other Pollutants: F = TLV (G)

where

$$G = (\frac{8}{24}) \ (\frac{1}{100}) = \frac{1}{300}$$

so

$$F = \frac{TLV}{300}$$

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TABLE 17. SUMMARY OF "F" VALUES.

Pollutant	F $\mu g/m^3$	Based on
Particulates	260	PAAQS
SO_x	365	PAAQS
CO	10,000	PAAQS
NO_x	100	PAAQS
Benzene	114	TLV = 10 PPM
Toluene	1,388	TLV = 100 PPM
Ethylbenzene	1,586	TLV = 100 PPM
Xylenes	1,586	TLV = 100 PPM
Other Alkylbenzenes	(488)	TLV = (25 PPM)
Naphthalene	194	TLV = 10 PPM
Anthracene	0.66	TLV = 200 $\mu g/m^3$*
Biphenyl	4.4	TLV = 0.2 PPM
Other Polynuclear Aromatics	(25)	TLV = (1 PPM)
n-Hexane	1,281	TLV = 100
Other Alkanes	(16,665)	TLV = (1,000)
Olefins	(12,344)	TLV = (1,000)
Cyloalkanes	(4,937)	TLV = (400)

*Based on "Coal Tar Pitch Volatiles" of which anthracene is a major component.

are low, then it can be said with some confidence that no damage will be done by those compounds. If the values are high, however, no conclusions can be drawn.

Source Severities for Criteria Pollutants

Table 18 shows a summary of the source severities for criteria pollutants. Taken at face value, these factors say that there is no problem, since none of the pollutants have a source severity greater than 1.0. But since there are uncertainties involved in determining the maximum ambient concentration, Monsanto recommends the decision levels shown in the lower part of the table. Based on these, CO would probably not require control; NO_x, SO_x, and particulates could go either way.

Besides the basic uncertainty that is involved in determining the maximum ambient concentrations, there is some doubt as to whether PAAQS represent the level at which medical danger to the general public will start. There are many areas of the country in non-attainment of PAAQS that show minimum impact on the health of the general public. But these decision levels must be set conservatively, so that if an error is made, it is in the direction of requiring control where it is not needed rather than omitting control where it is needed.

Source Severity Factors for Hydrocarbon Components

Taking the maximum ambient concentrations presented in Table 15 and the acceptable pollutant concentrations shown in Table 17, it is an easy matter to calculate source severity factors for each component. These factors are shown in Table 19.

Using Monsanto's recommended decision levels, it can be said that there is a strong probability that anthracene and biphenyl need further application of control technology. Several things should be noted in that context:

- the high concentrations were contributed by the API separator located on the downwind boundary line,

- the emissions from an API separator are highly variable in component breakdown (much more so than process unit emissions), and the species breakdown for that unit is based on several grab samples which may well not be reflective of "typical" operation, and

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TABLE 18.   SOURCE SEVERITY FACTORS FOR CRITERIA POLLUTANTS.

Pollutant	$\overline{X}_{max}$ µg/m^3	F µg/m^3	S
Particulates	68	260	0.26
SO$_x$	288	365	0.78
CO	16	10,000	0.0016
NO$_x$	55	100	0.55

Decision Levels

if S $\geq$ 1: Control Technology Probably Required

if 0.1* $\leq$ S < 1.0: May Require Control, May Not

if S < 0.1*: Control Technology Probably Not Required

*The lower critical value may need to be as low as 0.01 where large
uncertainties are involved.

TABLE 19.   SOURCE SEVERITY FACTORS FOR SELECTED HYDROCARBON SPECIES

Component	$\overline{X}_{max}$ $\mu g/m^3$	F $\mu g/m^3$	S
Benzene	6.6	114	0.06
Toluene	26.3	1388	0.02
Ethylbenzene	10.7	1586	0.007
Xylenes	53.6	1586	0.03
Other Alkylbenzenes	105.5	(488)*	(0.22)
Naphthalene	27.5	194	0.14
Anthracene	3.6	(0.66)	(5.5)
Biphenyl	16.5	4.4	3.8
Other Polynuclear Aromatics	22.7	(25)	(0.9)
n-Hexane	58.5	1281	0.05
Olefins	37.6	(12344)	(0.003)
Cycloalkanes	365.8	(4937)	(0.07)

*Values in parentheses are an average of the F values for several selected members of the family group, and are not true F values for the entire family.

- the technology to control API separator emissions
  is to cover the separator, a practice which is
  becoming standard on new installations.

It can also be stated that there is a very low probability of the
need for further control of ethylbenzene and the olefin family. All other
species fall into the range where no clear decision can be made. The un-
certainties involved in the calculation of these source severity factors
make it impossible to make clean cut decisions for the range from 0.01 to
0.99.

One other point should be noted here, that all of the quoted hydro-
carbon species maximum points occurred on the refinery boundary. Because
they are released close to the ground and with little velocity or thermal
buoyancy, the vapors tend to stay at ground level. Dispersion does proceed
at a relatively rapid pace when moving downwind. This establishes two in-
teresting points:

- the sphere of influence for hydrocarbon species
  that were noted as potential problems at the
  boundary line does not extend more than a few
  hundred meters, and

- this further suggests that buffering areas with
  a high potential for fugitive emissions could be
  effective in reducing or eliminating high source
  severities.

DISCUSSION OF RESULTS

Having now presented the results of this environmental assessment,
it is time to discuss their significance. The first step should be an ex-
amination of all the input variables to see how sensitive the results are to
changes in the assumptions that were made. The most significant variables
to consider are:

- refinery processing configuration,

- refinery layout,

- calculated emissions,

- atmospheric dispersion model choice,

- meteorological conditions,

- hydrocarbon component breakdown,

- basic toxicity data, and

- modified toxicity data.

Several of these can be considered in a group. A change in the calculated emission rates will produce a proportional change in the predicted maximum concentrations, and the emissions will vary with a change in refinery processing configuration, emission factors, or fitting counts. This in itself is enough to prevent a complete generalization of these results to the refining industry. A simple topping refinery, for instance, will have lower emissions and quite different component breakdowns, resulting in lower source severity factors.

The refinery layout may be even more critical than the complexity and the resulting overall emission rate, especially for the hydrocarbon speies. Fugitive emissions are released near ground level, and thus are subject to much less dispersion than stack emissions. A refinery layout with process units right on the boundary line (such as the model used here) will show much higher hydrocarbon concentrations than one with a buffer zone around the processing area.

The situation is further complicated when looking at individual species. For instance, a gas processing facility near the fence line would result in high concentrations of total hydrocarbons, but it would probably not cause any large source severity factors. On the other hand, a complex consisting of a reformer, an aromatics extraction unit, and a BTX fractionation unit would result in moderate to low total hydrocarbons, but they would probably result in high source severities for the aromatics components.

The choice of which type of dispersion model to use could affect the predicted pollutant concentrations somewhat, but most approved models (if properly applied) would give results in the same range. It was found that the handling of fugitive emissions was quite difficult. The use of single point sources created some very unrealistic situations at the plant boundary. For example, a receptor directly downwind of a fugitive source might read over 10,000 $\mu g/m^3$ while the receptors 100 meters on either side registered zero. This situation was tempered somewhat by splitting each fugitive source into a number of point sources distributed across a plane perpendicular to the wind direction. But this still did not produce satisfactory results. Only the time consuming area source modeling could produce realistic boundary line concentration profiles.

CONCLUSIONS

The conclusions drawn from this study can be summarized as follows:

- The results show that there is little chance of public hazards resulting from the emissions of this hypothetical refinery.

- Conversely, there is no certainty that it does not create a hazard.

- If any hazard exists due to hydrocarbon species, the most likely species to cause problems would be the polynuclear aromatics, specifically anthracene and biphenyl.

- This approach to an environmental assessment of a generalized source is not very useful. It can only give a reliable indication of the impact of sources that are either very bad or of negligible impact. Most real world sources will fall into the category that "may need further control technology development."

- If this approach were used to assess the impact of a specific plant, it might yield some useful results. The range of uncertainty would be much narrower because more of the input factors could be firmly defined.

G. E. Harris/M. W. Hooper

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REVIEW

by

S. S. Wise
Mobil Research & Development Corp.
Paulsboro, New Jersey

J. M. Pierrard - Du Pont
B. S. Bailey - Texaco

on

ENVIRONMENTAL ASSESSMENT OF ATMOSPHERIC EMISSIONS
FROM PETROLEUM REFINERIES

RESUME

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REVIEW

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ENVIRONMENTAL ASSESSMENT OF ATMOSPHERIC EMISSIONS
FROM PETROLEUM REFINERIES

The paper by Harris and Hooper is the seventh of a series of eight reports on characterization of refinery emissions. In it, the authors have attempted to capitalize on Radian's monumental measurement program to model the air quality impact of refinery emissions. In these comments we address both the general approach employed by Harris and Hooper, and some of the specific details of their analysis.

We endorse the concept employed by the authors of (1) defining a combination of emissions sources, (2) calculating the emissions, (3) modeling the air quality resulting from these emissions, and finally, (4) evaluating potential health hazards by comparing the air quality with allowable levels. Unfortunately, the uncertainties associated with these four steps preclude drawing definite conclusions. This was recognized by the authors when they stated as one of their conclusions.

> "This approach to an environmental assessment of a
> generalized source is not very useful. It can only
> give a reliable indication of the impact of sources
> that are either very bad or of negligible impact.
> Most real world sources will fall into the category
> that 'may need further control technology development.'"

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And, we would add, much work is required to identify and quantify emissions from the overwhelmingly dominant hydrocarbon source--the API separator--to improve upon the understandably crude estimate used in this study.

In order to model the impact on air quality of refinery hydrocarbon emissions in a meaningful way, emission factors for sources must be accurately known. Earlier presenters and commenters have sufficiently discussed Radian's measurements and hydrocarbon characterization techniques, and determinations of component emission factors. However, of the 9800 t/yr. hydrocarbon emissions of this model refinery it would appear that only 2500 to 3000 t/yr. can be assigned to these components (assuming that this refinery is similar to that outlined in Appendix B of Radian's "Detailed Results"). Over two-thirds of the emissions (approximately 7000 t/yr.) must be coming from the three API separators. Unfortunately, the authors give no data on throughput in the three separators, nor do they discuss how the material balance outlined in Table 13 was carried out. It would also appear that no chemical analysis of the vapor component of the separator was carried out, although composition of the liquid phases is discussed in detail. The authors acknowledge the uncertainty introduced by using AP-42 emissions estimates for the separators (5 lb vapor/1000 gal wastewater); still, they fail to comment on the additional uncertainty introduced when this factor was presumably used for each separator regardless of which refinery units were actually contributing to each of the three treatment plants.

We now wish to make several comments on the choice of the RAMR model used to predict emissions impact, and on the manner in which the model was used. First, we are certain the authors realize that the NAAQS is for NO_2 not NO_x as stated in the paper. However, since the NO_2 standard is used as basis for comparison and since NO is the predominant species formed in most combustion systems, it would be appropriate for the authors to comment on the additional conservatism introduced into the analysis by the implicit assumption of total conversion of NO to NO_2. Total conversion is impossible over the time/space dimension of this analysis.

Our second comment has to do with the decision to use RAMR (rural) rather than RAM (urban), which adds still further conservatism to the analysis. Although emissions traveling from and through a refinery would be expected to be further dispersed due to the heat island effect of the refinery and the added surface roughness of the varied structures, no credit was taken because of the choice of the rural dispersion parameters.

Recently, the American Petroleum Institute contracted with The Research Corporation of New England to assemble an extensive data base consisting of over 17 documented tracer release programs. Included were the tests from which both urban and rural dispersion coefficients were developed. Five "guideline" models were used to model each of the over 400 tracer tests. Two papers describing the results of this program have been submitted by R. Londergan, et al., TRC, for presentation at the joint APCA/AMS meeting to be held in New Orleans in March 1980. To illustrate the ability of the RAM and RAMR models to predict maximum impact for conditions similar to those modeled by the authors, we have tabulated the results for six ground level release programs selecting those tests with stable and neutral atmospheric conditions. The ratios of the sum of the 10 maximum predicted concentrations to the sum of the 10 maximum observed concentrations are selected as the best measure of the ability of the models to predict maximum impact.

As can be seen in Table 1, even in the rural areas in which these tests were carried out, the urban dispersion coefficients provided better prediction of maximum impact. RAMR indicated over-predictions of 2 to 14 times the measured highest values and over 3 times the RAM prediction. On average, RAM also over-predicted the highest values for these near ground level (1-2 m) releases. Addition of turbulence due to a large concentration of heat sources would favor the urban model even more.

In summary, the authors have attempted to provide a technical assessment of the impact of different refinery emissions sources on the area surrounding a model refinery. Then, by comparison with a conservative estimate of the socially acceptable impact level the authors try to indicate potential problem areas. However, because the authors have compounded the introduction of a very conservative model with the uncertainty of the emissions from their largest hydrocarbon source, the reader is left with little as a basis to make an informed judgment as to the usefulness of the analysis.

Table 1

Comparison of RAM and RAMR Using Ground Release Tracer Test Data,
Light Wind and Neutral/Stable Atmospheric Conditions. Rural Tests/
Flat Terrain, On-site Meterological Data.

PROGRAM	HANFORD 67	PRAIRIE GRASS[1]	GREEN GLOW	NRTS	TMI	OCEAN BREEZE
Tests at Conditions/ Total No. Tests Analysed	16/73	32/47	21/21[2]	9/9	9/9[2]	25/68
Average No. Monitors/ Test	132	120	183	52	16[3]	42
Performance Ratio*						
RAM	3.40	.75	1.80	1.03	3.27	1.15
RAMR	14.44	1.92	5.87	3.44	2.29	4.16

*Ratio = $\dfrac{\Sigma \ 10 \ \text{highest predicted receptors}}{\Sigma \ 10 \ \text{highest measured receptors}}$

Notes: (1) Results used in derivation of RAMR dispersion coefficients
(2) Stable conditions only
(3) Recepter grid pattern very sparse

QUESTIONS AND ANSWERS

Q. H. M. Walker/Monsanto - I would simply like to reiterate a point made. It appears, as I understood it, that the compositional data was obtained primarily from analyzing the liquid and not the air. And, I have some questions about those analyses. It appears to have been done by low voltage mass spectometry or something like that, which would only predominately pick the aromatics anyway, and would skip many other compounds. You have no real evidence that for example anthracene was getting into the air unless you did some air sampling and picked up anthracene. So, I think it is pretty dangerous to use your data in that manner, when all of your other data was not done by methods comparable. I believe the author stated there were only a few grab samples, which makes me reluctant to accept practically anything of the compositional data in that heavy aromatic range when there is no conclusive evidence that they are in the air. The use of TLV values and then taking a 300-fold conservatism from there, I think is a rather blind reach. I realize that Monsanto Research Corporation did come out with something like this, because EPA requested they do that. But, I find it very unsatisfying as a methodology, and I think one should keep in mind that the thrust of everything that has been going on the last few days--the formation of photo-chemical oxidants. This analysis did not touch on that at all.

A. (By Harris) - On the comment, as far as the polynuclear aromatics reaching the air, that really should be taken into account. If they did not evaporate at all then they should have been there in a higher percentage in the outlet oil stream. So, when you take a material balance approach, if they have been lost somewhere, you have to assume they have been lost to the atmosphere. And, as far as the unit component emissions we did have both bulk stream compositions as well as some confirming compositions of the vapor emissions from the baggable type fittings. We didn't have any vapor emissions over the API separators. You are correct in that remark.

Q. H. M. Walker/Monsanto - I am a little confused as to how you operated that material balance on those heavy aromatics. Would you explain that in a little more detail. You said if they were coming in they had to have gone somewhere, but how did you get it back?

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A. (By Harris) - We had an inlet oil composition that would show parts per million values of the heavier aromatics, and then outlet oil composition taken on that same separator, very shortly thereafter. They are going to have a concentrating effect due to the fact if they were not being lost as evaporative emissions there would be a concentration of these components due to the loss of other components to the atmosphere. And as you can see, by those two analyses, that indeed the concentration did not go up but it went down, indicating that there were evaporative losses even with those components.

Q. H. M. Walker/Monsanto - Did you compensate for the solubility of these materials in the water phase?

A. (By Harris) - No!

COMMENT/Rosebrook - I would like to make a comment to set the records straight on this. We have the same problem with using the data that we collected on API separators, in this sense, as we have using it to calculate the total fugitive emissions from separators. We suffer from exactly the same problem. Had we been able to get good data for one we would have had the data for the other one, so nobody is trying to sell you the idea that this is really the very latest word. I think part of EPA's new program is to collect samples which accurately reflect what is in the vapor phase, and hopefully some fifteen months from now the data will be available to more accurately assess what the impact of API separators is.

Q. James Stone/Louisiana Air Control Commission - How did the residence time in the API separator compare with the sampling time between your inlet and outlet samples in formulating your ideas on what was in and out?

A. (By Harris) - Basically it was just a rough approximation. At the point of time when you are taking those samples in the field you really don't know what all the flow rates are. Flow rates are being measured by accumulation in a slop oil tank. So, it is very rough at that point. That certainly is a point of uncertainty.

Q. James Stone/Louisiana Air Control Commission - You took out both the inlet and the outlet samples at the same time, then, rather then trying to space them according to the residence time of the device?

A. (By Harris) - They were spaced very roughly, but we had no real accurate idea of what that residence time was.

COMMENT/Ivan H. Gilman/Chevron USA Inc. - I would like to observe two things on the separator test. One is that the solubility of hydrocarbons is a very, very, important issue here. The other thing is that we have been dealing with closed API separators because of odor control for several years, where the big problems is keeping the vapor space saturated enough to keep it from being explosive. Now, if your hypothesis were correct, this would be no problem, and it is in fact. Another thing that you must observe is, that we made some radioactive tracer tests, with light and heavy hydrocarbons. We found that grab samples in and out never came close to the tracer tests as far as accuracy of what is going into the separator and what is coming out. I know that you took the best testing situation that you had, but I think that when you get back into it your long term test is going to show a completely different analysis of what happens in that API separator than what you have indicated.

Q. Steve Jones/Concoco Inc. - The EPA laboratory at Ada, Oklahoma has done some work, showing that some of these aromatics tend to concentrate in the sludge that precipitates out of the API separators. I think that is a likely area and may explain these large losses.

COMMENT/Rosebrook - That is a very good comment.

A. (By Harris) - I think that I would like to emphasize here at this point that I tried to bring out the uncertainties in these API separators emissions and you certainly pointed out some things that make that even more uncertain. The level of hydrocarbons at the point opposite the processing area was only very slightly lower--in the realm of 7,000 micrograms per cubic meter opposite the crude unit. So, perhaps we are focusing too much attention on the API separator itself, because you have very similar situations right down the road. Although none of those did result in source severity factors over one. I tried to bring that out when I discussed those factors themselves, and in the conclusions did not say that there was an indicated definite health hazard with polynuclear aromatics.

Q. R. C. Weber/US-EPA-IERL-Cincinnati - I'm a little bit confused by some-thing you said earlier in your presentation. I thought that I heard you say that you didn't include storage tanks in your calculations, is that correct?

A. (By Harris) - Yes, that is correct.

Q. R. C. Weber/US-EPA-IERL-Cincinnati - Can you explain why you reached that decision?

A.   (By Harris) – Basically, the storage tank emissions measurements has been excluded from the realm of this project from the very beginning. It could have been, I suppose, brought in with other factors, but we have had very low confidence in applying much of those. So, we were trying to model the results and the impact of the things that we felt we had some data to support.

COMMENT/Rosebrook – The consideration of tankage was specifically eliminated from this contract from the beginning, probably due to some estimate of how much that was going to cost.

Q. K. C. Hustvedt/US-EPA-RTP – The valve counts you have here from the counts you made in refineries are substantially different than almost all the other data I have seen on valve counts. Your hypothetical refinery has an average of 25 valves per pump and other data I have seen range from midsixties to mid-seventies. This has a large effect on, not only the total emissions from fugitives, but also on the relative strength of each of the different fugitive categories. If the higher number was used, it would make emissions from valves a much more substantial part of the total, and would make the other ones much less, which I think, if that is a true fact should be something that people should keep in mind, when they are developing a strategy to control the different sources.

A.   (By Harris) – As I said during the presentation, the ratio of valves to pumps was based on the counts that we made on the process units. Anytime you go out and count fittings whether you are doing it physically on the unit or from a detailed piping diagram, you are going to have to decide at some point which are the meaningful valves. Now we have seen data that is very, very high like you talked about, in the range of 60 to 70 valves per pump. We feel that those indicate some nonhydrocarbon service fittings and a heavy preponderance of valves for example around flow columns and things like this in the one-half to one inch range, that played a very, very small part in the total emission testing program. Our counts, we felt, are in line with the emission factors. The calculations would then be based on all hydrocarbon valves.

Q. K. C. Hustvedt/US-EPA-RTP – I think that leads to a problem in interpretation of the data. You do not state anywhere that you have excluded these valves from your data base. If in fact you did exclude them from the emission factor development they should be excluded from the counts to make emission estimates. But then your total emissions should be footnoted to show that they do not include emission from these sources, because you have not tested

them and you don't know what the emissions are. That leads into problems of interpreting regulations by enforcement people if we say go out and marginally repair all the valves. They are going to have to monitor and repair every valve. They can't say that it is not significant because Radian did not test it. They do not have that latitude. I think that if this data is going to be applied to regulations it has to be qualified as to how it can and can't be used and where it was and was not applied.

A. (By Harris) - Well, I don't think there is any problem in excluding nonhydrocarbons valves. I think that is one of the big differences in these counts. As far as the source of your counts possibly not showing every valve, that is another factor too. Some of the counting data was taken from piping and instrument diagrams. You have to work with what is there. We used the counts that we had the most confidence in at that point. I do not have any details on the mechanism that was used to generate the 60 to 70 count numbers that you are talking about. We could certainly get down and get on the basics of that and see what the differences are.

Q. K. C. Hustvedt/US-EPA-RTP - Does your data base exclude any size valves, one quarter inch, one-eighth inch, half inch, one inch? Is there any exclusion?

A. (By Harris) - There is not any intentional exclusion there, but there is a minimal amount of time that was spent actually doing these counts. And, as you are trying to go through three-dimensional space of a refinery unit you are inevitably going to miss some of the smaller sources. I think that really has a minimal impact on your data base. Most of these are very, very seldom used. They are blocked in one position or another. They are probably not going to have that much contribution.

Q. C. H. Schleyer/Marathon Oil Company - As a meterologist, I would like to say that I think that the modeling used was very inappropriate because a refinery is all sorts of structural obstacles. Most of these valves are not freely exposed to the wind as they were in all these tracer experiments and I think very little is known about the dispersion in a refinery. I think that you can draw almost no conclusions from this kind of modeling. You need some sort of ambient measurement. That is the only way really to get the health effect of these compounds.

A. (By Harris) - I think that that is our conclusion number 5. There is one mitigating effect because we found that the units closest to the boundary line had by far the major contribution to those levels. So that they are

going to have encountered the least turbulence in getting across their unit to the boundary. But your points are very well taken.

Q. C. H. Schleyer/Marathon Oil Company - Yes, but to get to the boundary the wind has to go across all the other units.

A. (By Harris) - But, I'm saying that if you assume that the wind had zero concentration coming into that last unit, you would still have seen 80 percent of the maximum concentration just because of the proximity of it.

COMMENT/Hooper - We used the RAM family of models since it was a short term EPA guideline model, this being more familiar than some of the numerical models that various consulting firms have come up with. We used RAM basically because of its conservatism. I was not familiar with some of these ratios here, but it is possible that we did over predict therefore taking some of the teeth out of it.

Q. Paul Harrison/Engineering-Science - I won't comment to the appropriateness of the model selected because really no model exists that fully takes into consideration a refinery. A refinery is a source of extreme heat island effect under low wind conditions. Some of you remember the Jekyl Island Meeting where we had a discussion about the use of downwind transects for characterizing total fugitives from refineries and the tracer experiment that was performed was performed in wind conditions of one to three miles per hour and we only had 10 percent of the tracer at the fence line. And, it was obvious that it was a heat island effect, which they did not consider during their test. If you have sufficient wind speed, the turbulent structure over the facility will actually carry fugitives from mezzanine levels down to the surface at the fence line. So, it is very complex and I think we just have to conclude that we used the best model we can, but we do not have an adequate model at this time. And, under different wind conditions we have definite nonlinearities. Under low wind conditions and proper vertical temperature profiles you will get zero at the fence line. It will just all go up and form a little cloud and get in the gradient wind. And that has been observed several times. But under proper wind conditions the dispersion as you say, is very good and that 80 to 100 percent of the fugitives nearest to the fence line will get to the ground. It is very complex and we have a lot of humility in selecting and interpreting these modes.

Q. P. L. Scupholme/BP-Environmental Control Center/ENGLAND - We have done some measurements in the UK upwind and downwind of separators, using total

hydrocarbon analyzers at ground level and at different altitudes. We are fairly confident that we can get a total mass balance across the separator. Secondly, at two refineries in Europe we have spent four months recording ambient hydrocarbon levels at different locations within the refinery boundary. We correlate the data with wind speed and direction. And eventually, we can identify the major sources of emission within the refinery and rank them. And, we conclude that the losses from the separators, the loading jetties, the storage tankage area, and the process units are roughly equivalent in magnitude. Thirdly, I would like to comment on the inconsistent use of units during the study. I've got very confused hearing pounds per hour, grams per second, miles, kilometers and so on. I make a plea for consistent use of imperial units.

Q. Karen Hanzevack/Exxon R&E - The comment I have amplifies what K. C. was getting at just a minute ago. I do not think it deals so very directly with this particular talk but it was a comment I wanted to make on the program in general. And, that is the development of emission factors is only useful to the extent that you know what number to multiply them by to get a total emission. And, that is the counts of components. Perhaps it is not within the scope of this program to provide a detailed count of components in everyone's facility, but surely it is within the scope to clearly define how you counted and what your emission factors really do or do not apply to. For example, if very small sampling valves are excluded, that should be very clearly said. I have the experience of trying to describe to process people how to take counts. It is next to impossible, given what I know about what you have done from what I have read. It's a grave point of confusion. And since that number is an equal multiplier with the emission factor it deserves more attention or at least clarification as to what your factors apply to and how the counts ought to be taken.

A. (By Harris) - Let me clarify that nothing was intentionally excluded from the basis of these counts. I was just discussing the possible things that can enter into the counting process and cause differences between individuals counts. The other thing that we ought to consider, what you have addressed here, is that it is really not valid to come up with a count and say that there are so many valves on a fluid cat cracker or vacuum pipe still or anything else. Each manufacturer and each consumer or each refiner is going to require slightly different facilities there. There are going to be variations in that and in these total ratios from one place to another. We have to be very careful in trying to come up with a set of these numbers that we say that everyone should use. I think that probably in administering fugitive emissions for your plant, that your own fitting counts are certainly the most meaningful.

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Q. Ronald R. Holten/Chevron USA Inc. - I would like to agree with what Karen
has said and in response to what Buzz said about caution in using these things.
I might point out that we're not always dealing with existing facilities.
That is sometimes, for example, in trying to estimate emissions from an
expansion project we don't have P and ID's to count from. Therefore, there
is a definite need in the industry for a sound basis from which to estimate
number of components. And I would, along with Karen, encourage that you at
least state your basis.

COMMENT/Rosebrook - There is a point I would like to raise to start off the
commentary. Something that would really be concerning me now if I were
Art Pope and I had stood up here today and said we have not seen any leak
recurrence in eight months in these things that we fixed and everyone else
stands up here and talks about the rate of recurrence. Would you care to
address that question?

COMMENT/Arthur F. Pope/Atlantic Richfield - The recurrence rate in the South
Coast areas is being determined right now for not only our refineries but
for all of the plants in the area. One of the things that I did not men-
tion on South Coast regulation is a six month interval for inspection at
the present time for refineries with a requirement for a recheck of a
component which is found to leak and is repaired at a three month interval.
That work is going on and the first year's data will have been collected by
the end of this year. Then we go to an annual inspection program for the
second year. And at the conclusion of two years of data collection by way
of this regulation the South Coast District staff is to get together with
the industry in the area and make the determinations that are being dis-
cussed right now. And that is, what is the appropriate cutoff for screen-
ing or repair? What is the appropriate monitoring interval? What can we
learn about recurrence of leaks? The degree of the recurrence? That work
is underway. But it is underway by way of a regulation. And maybe perhaps
Ivan can comment on Chevron's experience there. I can tell you that we were
successful repairing leaks to below 1,000, if they are 10,000 plus.

COMMENT/Rosebrook - I would like to point out that although we are very
proud of the work that we have done and the good results we are also very
cognizant of those areas where we did not get acceptable results. We have
attempted to bring those to the attention of industry, to the attention of
the EPA, and to all interested and involved parties. We hope that sometime
in the near future those gaps which are left in our data will be filled and
we will begin to answer the many questions which still remain.

CONTROLLING PETROLEUM REFINERY FUGITIVE EMISSIONS
VIA LEAK DETECTION AND REPAIR

by

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ABSTRACT

Petroleum refinery hydrocarbon fugitive emissions from valves, pump and compressor seals, and relief valves can be reduced via the implementation of a leak detection and repair program. The following factors are discussed relative to their impact on the effectiveness of such a program: monitoring methods, hydrocarbon screening techniques, directed versus undirected maintenace, repair effectiveness, repair waiting time, action level for repair, and monitoring interval. The difference between what is ideally obtainable and practically achievable is discussed, and a method f estimating the emission reduction is presented. The computational method accounts for the effect of imperfect repair, leak occurence/recurrence between repairs, and repair delay. Example calculations show how available data are used to make estimates of overall emission reductions. The effect of variations in critical variables (i.e., action level, repaired level, leak occurrence/recurrence, and monitoring interval) are shown graphically, as well as via a sensitivity analysis.

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RESUMES

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CONTROLLING PETROLEUM REFINERY FUGITIVE EMISSIONS
VIA LEAK DETECTION AND REPAIR

Introduction

The purpose of this paper is to present and discuss a method for estimating the efficiency of leak detection and repair programs to control petroleum refinery fugitive emissions of volatile organic compounds (VOC).

The papers presented previously have discussed the collection and analysis of the fugitive emission data developed by Radian in support of EPA's Petroleum Refinery Environmental Assessment Program. This paper will show how these data can be used to assess the effectiveness of a program for reducing fugitive emissions. Our discussion today will be limited to those sources which are amenable to detection and repair; namely, valves, pump seals, compressor seals, and relief valves. Emphasis will be placed on comparing theoretical maximum emission reductions to reductions which are realistically and practically achievable.

Leak Detection and Repair

The nature of fugitive emissions (i.e., large numbers of sources) generally precludes the use of pollution control hardware as a mechanism for reducing emissions. Exceptions include double mechanical seals for pumps and rupture disks upstream of relief valves. Once the myriad of potential fugitive emission sources are installed and operating within a refinery, the most practical method for controlling emissions is to find and repair the leaks.

In developing a strategy for a leak detection and repair program, several factors must be considered: monitoring methods, screening methods, repair methods, effectiveness of repair, repair waiting time, action level for repair, and monitoring interval.

1. Monitoring Methods

A number of methods for monitoring fugitive emissions have been proposed and used, including: fixed-point monitoring, unit area survey, and complete individual component survey.

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a. Fixed-Point Monitoring

The basic concept of the fixed-point monitoring system is that equipment can be installed at specific sites within the process area to monitor for leaks automatically. The ambient VOC concentration can be remotely and centrally indicated to the operator, who can respond appropriately when elevated levels are indicated.

b. Unit Area Survey

A unit area survey entails measuring the ambient VOC concentration within a given distance (e.g., 1 meter) of all ground level equipment within a processing area.

c. Complete Individual Component Survey

In a complete individual component survey, each potential leak source is screened to estimate the VOC concentrations at locations where leaks could occur.

While techniques a. and b., above, can be used to determine localized increases in VOC concentration, tying these increases to specific sources is difficult or, in some cases, impossible. Only by a source-by-source survey can one be assured of evaluating each potential fugitive emission location. Thus, while the other methods can be used to supplement a complete screening program, technique c. is suggested as the monitoring method of choice. An added benefit of the complete component survey is that it will result in an accurate count of all potential emission sources. This count can then be used with the emission factors to estimate total plant fugitive emissions and emission reductions.

2. Screening Methods

A number of methods for screening potential fugitive emission sources are available, including: visual, soap solution, and portable hydrocarbon detector. Visual inspections will not detect a significant number of vapor leaks, and the liquid leaks which are found may or may not be significant sources of vapor emissions. Soap solutions can be used effectively to find vapor leaks, but they are limited in their applicability. Soap solutions are difficult to use on hot or cold fittings, and they cannot differentiate between hydrocarbon and non-hydrocarbon (i.e., air, steam) leaks. Therefore, the portable hydrocarbon detector is the method of choice, since it is effective in finding hydrocarbon leaks and also provides an order of magnitude estimate of the leak rate.

3. Repair Methods - Directed Versus Undirected

The methods used to repair a leak will, of course, vary depending on the source and severity of the leak. In most instances, on-line repair procedures (e.g., tightening a valve gland) will be used. In some cases, removal and repair or replacement will be required.

When making repairs, it is clear that <u>directed</u> maintenance must be employed. Directed maintenance involves simultaneous maintenance and screening of the fitting until no further reduction in screening value can be obtained. Since the leaks being repaired are generally invisible, only by on-the-spot monitoring with a portable hydrocarbon detector can the repair personnel know whether or not their repair is effective. Radian has shown that undirected maintenance (i.e., maintenance without on-the-spot monitoring) is simply not as effective as directed maintenance in reducing emissions.

4. Effectiveness of Repair

How well can a given fugitive emission source be repaired? Data presented earlier show that the effectiveness of repair varies widely from source to source. In some cases, essentially all emissions were stopped; in other cases, the repair failed to reduce emissions significantly. Sometimes, the attempted repair actually increased emissions. Overall, directed maintenance does reduce emissions. Any estimate of the effectiveness of a proposed leak detection and repair program must account for the imperfect nature of the repair processes.

5. Repair Waiting Time

To be effective, a leak detection and repair program must limit the time interval between finding a leak and fixing it. This time interval reflects a trade-off in company resources being applied to production or to reducing emissions in a timely manner.

6. Action Level for Repair

At what screening value is a leak considered significant enough to repair? As has been shown in other papers in these proceedings, a small number of large leaks contribute the bulk of the total fugitive emissions. Thus, a cost effective leak detection and repair program must focus on controlling the large leaks. To accomplish this goal, one must select an <u>action level</u> which defines the screening value above which the source must be repaired. Those sources above the action level will include the large leakers which together make up a high percentage of the total fugitive emissions. In selecting this action level, one must take into account the cost and time required for repair. Setting the action level too low increases maintenance costs without significantly increasing emission reductions; setting the action level too high will not provide sufficient emission reductions.

7. Monitoring Interval

The frequency of monitoring for leaks will impact the success of a leak detection and repair program. Excessively long monitoring intervals will not be effective due to the development of new leaks and the recurrence of leaks repaired at the time of the last inspection. Monitoring intervals that are too short can be expensive and time consuming.

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Calculation Procedure

In estimating the effectiveness of a given leak detection and repair program, the factors discussed above must be considered. The calculation procedure presented herein takes into account the practical problems encountered in instituting an effective program.

The reduction of emissions achieved by leak detection and repair program can be expressed as:

1) Percentage reduction of fugitive emissions, or

2) Reduction in average fugitive emission rate.

The percentage reduction gives a quantitative picture of the program's efficiency, while the reduction in average emission rate provides an estimate of the actual decrease in mass emissions. For the purposes of this presentation, we will discuss the effectiveness of leak detection and repair in terms of percentage reduction.

We define percentage reduction (or reduction efficiency) as the percent decrease in mass emissions due to the operation of a regularly scheduled leak detection and repair program when compared to the emissions that would occur if the program were not used:

$$\% \text{ Reduction} = \frac{\text{Emissions w/o program} - \text{Emissions w/program}}{\text{Emissions w/o program}} \times 100\%$$

Figure 1 is a graphical representation of the effectiveness of a leak detection and repair program that illustrates and defines the computational procedure. Figure 1 represents the time history of fugitive emissions from sources being controlled by a leak detection and repair program, with the following simplifying assumptions:

1) Between inspection and repair intervals, emissions increase as a linear function of time.

2) At a given point in time, one is able to locate all sources with screening values over the action level. Although this is not precisely correct, it is implicitly considered in the heoretical minimum emission rate.

Since it is obvious that the emissions are not constant with respect to time, we must define effectiveness with respect to time. We have selected an annual cycle as the time interval over which percent emission reduction will be calculated. In terms of Figure 1, total annual uncontrolled emissions are simply the initial emission rate times 1 year. The emission reductions are represented by the area above the emissions curve (that is, from the emissions line up to the initial emission rate) for

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FIGURE 1. TIME HISTORY OF EMISSIONS
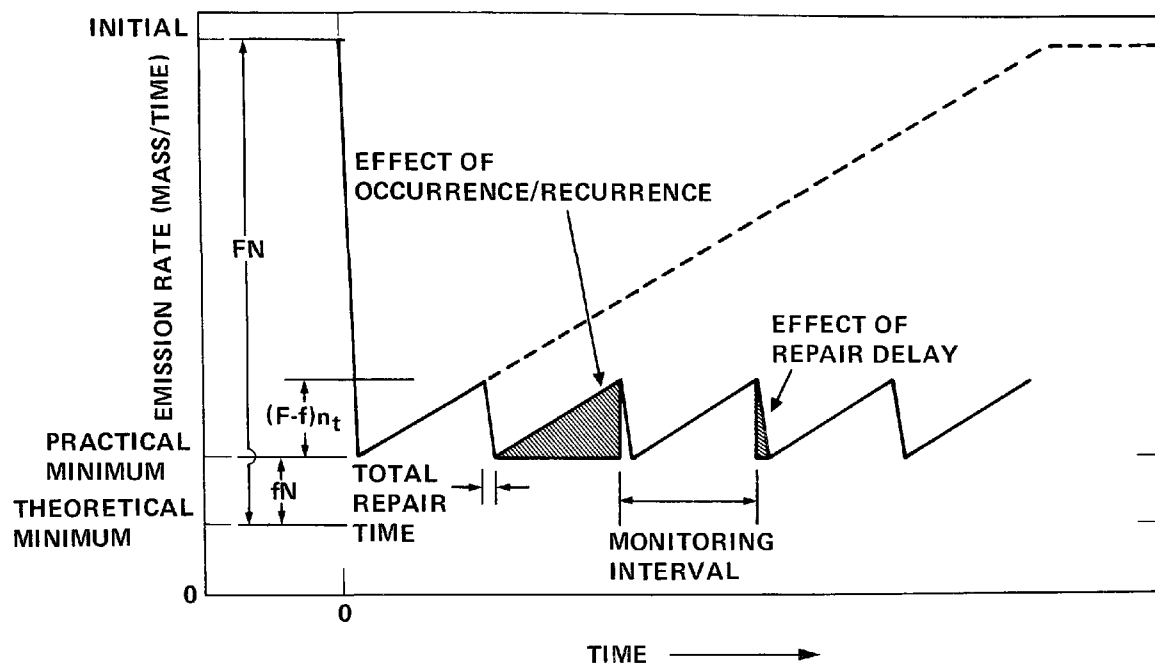
DEFINITIONS

F = AVERAGE EMISSION FACTOR FOR SOURCES AT OR ABOVE THE ACTION LEVEL.

f = AVERAGE EMISSION FACTOR FOR SOURCES AT THE AVERAGE SCREENING VALUE ACHIEVED BY REPAIR.

N = TOTAL NUMBER OF SOURCES INITIALLY AT OR ABOVE THE ACTION LEVEL.

n_t = NUMBER OF LEAKS WHICH OCCUR AND RECUR BETWEEN MONITORING INTERVALS.

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a period of 1 year. Therefore, percent reduction can be calculated as the ratio of the emission reductions over an annual cycle to the uncontrolled (initial) emissions over the same time period.

The following material provides a method for making this calculation:

1. Theoretical Minimum (The A Factor)

As Figure 1 indicates, there is a theoretical minimum emission rate achievable. This is defined as the fraction of total emissions due to sources screening at or below the action level. The lower the action level, the lower this theoretical minimum. In terms of percent reduction, we define:

A = Fraction of initial mass emissions reduced if all sources at or above the action level are repaired to zero leak rate.

A can also be expressed as the fraction of initial mass emissions at or above the action level. A is obtained from curves that relate percent of total mass emissions to screening value, as shown in Figure 2.

2. Practical Minimum (The D Factor)

As discussed previously, leak repair is imperfect. A repaired source will not, on the average, have a zero emission rate or zero screening value. For example, at an action level of 10,000 ppm, the average screening values for repaired sources may be 1,000 ppm. The effect of imperfect repair is calculated as follows:

D = Fraction of theoretical emission reduction achieved, accounting
for imperfect repair = $(FN - fN)/FN = (1 - \frac{f}{F})$

Where:

F = Average emission factor for sources screening at and above the action level (mass/time − source)*

f = Average emission factor for sources screening at the average screening value achieved by repair (mass/time − source)*

N = Total number of sources initially screened at or above the action level

3. Leak Occurrence and Recurrence (The B Factor)

If, after repair, no new leaks occurred and the repaired leaks remained fixed, no increase in emissions would occur. In reality,

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* F and f are further defined in 6. Example Calculation with follows.

FIGURE 2. CUMULATIVE DISTRIBUTION OF TOTAL EMISSIONS BY SCREENING VALUES — VALVES — GAS/VAPOR STREAMS (REF. 1)

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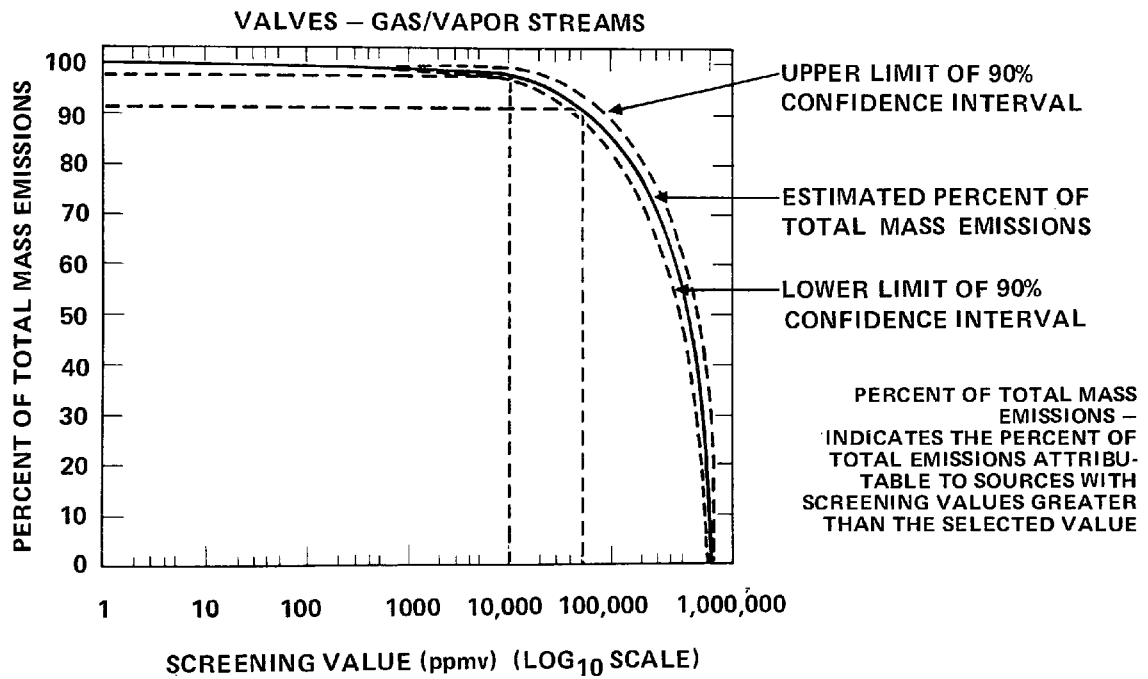
however, new leaks do occur and repaired leaks start leaking again.
Therefore, the number of sources with screening values above the action
level will tend to increase with time. Without additional leak detection
and repair at a later time, the emissions will eventually rise to the
original uncontrolled level, as illustrated by the dotted line in
Figure 1. Also, as shown in Figure 1, immediately after repair is completed,
the emissions start to increase. We do not know the true relationship
for the number of leak occurrences and recurrences as a function of time.
However, by making assumptions regarding this relationship, we can calculate
the effect of this phenomenon on overall reduction efficiency.

If we define n_t as the number of leaks which occur and recur
between monitoring intervals, including known leaks that couldn't be
repaired, where the subscript t refers to this interval, the quantity
$(F-f) n_t$ defines the increase in emissions which occurs over the monitoring
interval. (The expression $(F-f) n_t$ assumes that n_t sources would have been
emitting at an average rate f, in the absence of a trend of increasing
emissions with time.) Assuming a linear increase in emissions over this
time, the average increase in emissions is $(F-f) \bar{n}_t$, where $\bar{n}_t = n_t/2$.
In terms of percent reduction, we can then define:

B = Fraction of practically achievable leak reductions, accounting
for leak occurence and recurrence.

$$B = \frac{(FN - fn) - (F - f) \bar{n}_t}{FN - fn} = 1 - \frac{\bar{n}_t}{N}$$

Table 1 provides possible values of n_t, $\bar{n}_t$, and B as a function of the
monitoring interval and the number of initial leaks, N. We can illustrate
the interpretation of Table 1 using valves in gas/vapor service with an
action level of 10000 ppm and a 3 month monitoring interval. From
Figure 3, we see that, initially, 10% of these valves will be leaking
(i.e., N = 10% of the valves). At the end of each monitoring interval,
2% of the valves would be expected to be leaking (i.e., n_t = 0.2 N = 2%
of the valves). Since we assume a linear relationship between n_t and
time, 1% of the valves (i.e., $\bar{n}_t$ = 0.1N = 1%) would be leaking on the
average over the monitoring interval.

4. Repair Delay (The C Factor)

The effect of the delay between detection and repair is shown in
Figure 1. The longer the repair time, the greater the emissions which
occur due to the delay.

We assume that the total repair time will be short and that the
effect of repair delay will be minimal and can be disregarded. Therefore:

C = Fraction of achievable leak reduction accounting for repair
delay = 1.0

TABLE 1. n_t, $\bar{n}_t$, and B vs. MONITORING INTERVAL

MONITORING INTERVAL	n_t (1)	$\bar{n}_t$ (2)	B (3)
1 month	0.1N	0.05N	0.95
3 months	0.2N	0.1N	0.90
1 year	0.4N	0.2N	0.80

(1) n_t = TOTAL NUMBER OF LEAKS WHICH OCCUR, RECUR, AND REMAIN BETWEEN MONITORING INTERVALS.

(2) $\bar{n}_t$ = AVERAGE NUMBER OF LEAKS OVER THE MONITORING INTERVAL.

(3) B = CORRECTION FACTOR ACCOUNTING FOR LEAK OCCURENCE/RECURRENCE.

(4) N = NUMBER OF SOURCES INITIALLY ABOVE THE ACTION LEVEL

FIGURE 3. CUMULATIVE DISTRIBUTION OF SOURCES BY
SCREENING VALUES — VALVES — GAS/VAPOR STREAMS
(REF. 1)
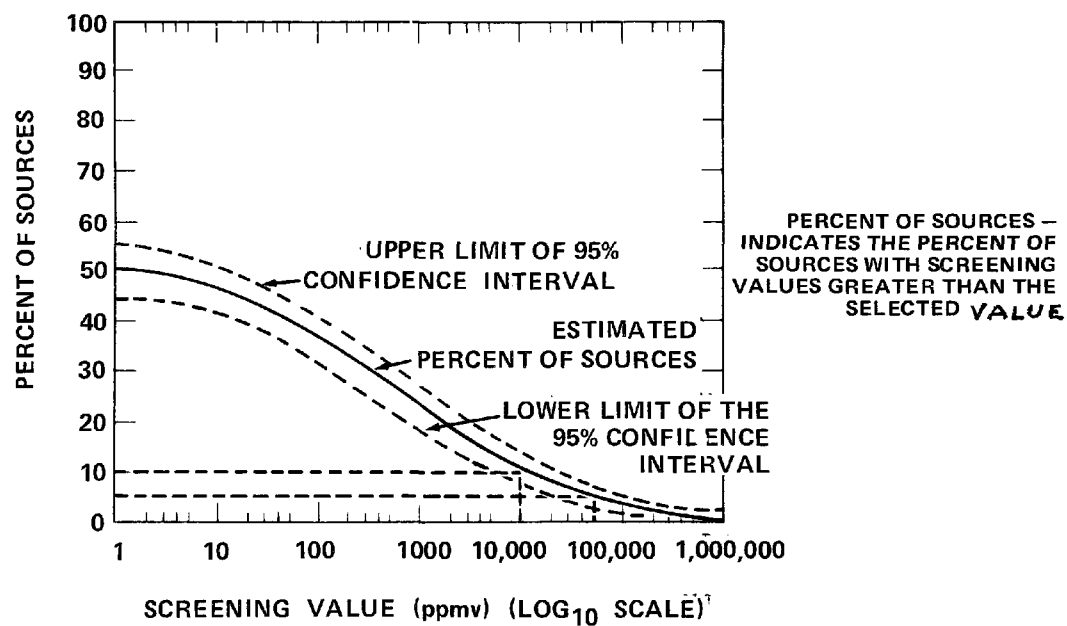
The effect of repair delay is greatest for the initial repair period (i.e., at time zero in Figure 1). This effect could be estimated if one wanted to evaluate the effectiveness of a leak detection and repair program's initial year. Also, if future experience with leak detection and repair programs provides adequate data on the effect of repair delay, the C value could be adjusted accordingly.

5. Overall Effectiveness

Using the definitions provided above, we can calculate the overall average annual effectiveness of a leak detection and repair program as:

Overall Percent Reduction = (A)(B)(C)(D)(100%)

6. Example Calculation

The example calculation on the next page illustrates the application of the procedure. Table 2 shows the results of this example, along with others.

Effect of Variations in Action Level, Repaired Level, and Monitoring Interval

In order to evaluate the effect of the various factors on overall detection and repair effectiveness, one can look at the influence of each variable separately.

1. Effect of Action Level

Figure 2 shows how A (the theoretical maximum reduction) changes with action level, with A (percent of total mass emissions) increasing as the action level (screening value) decreases.

2. Effect of Action Level and Repaired Level

$$D = 1 - \frac{f}{F}$$

The action level and repaired level influence D (correction factor accounting for imperfect repair) via their effects on the values of F and f. Figure 4 shows these effects for two source categories: valves in gas/vapor service and pump seals in light liquid service. In this example, valves in gas/vapor service are rather insensitive to changes in the repaired level, while pumps in light liquid service show marked changes in D with changes in repaired levels.

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EXAMPLE CALCULATION

GIVEN: 1) A LEAK DETECTION AND REPAIR PROGRAM TO REDUCE EMISSIONS FROM VALVES IN GAS/VAPOR SERVICE.

2) ACTION LEVEL = 10,000 ppm

3) AVERAGE SCREENING VALUE AFTER DIRECTED REPAIR = 1,000 ppm

4) LEAK DETECTION AND REPAIR INTERVAL (MONITORING INTERVAL) = 3 MONTHS

5) NUMBER OF VALVES HAVING NEW OR RECURRING LEAKS BETWEEN REPAIR INTERVALS, n_t = 0.2N (FROM TABLE 1)

A = 0.98 (FROM FIGURE 2)
B = 0.9 (FROM TABLE 1)
C = 1.0

$$D = (1 - \frac{f}{F})$$

$$F = \frac{A \ (\text{AVE. UNCONTROLLED EMISSION FACTOR})*}{\text{FRACTION OF SOURCES SCREENING} \geqslant 10,000 \ \text{ppm}**}$$

F = (0.98) (0.059)/0.10 = 0.578 lb/hr - SOURCE
f = EMISSION FACTOR AT 1000 ppm***
f = 0.003 lb/hr - SOURCE

$$D = (1 - \frac{0.003}{0.578}) = 0.995$$

OVERALL PERCENT REDUCTION = A x B x C x D x 100%
OVERALL PERCENT REDUCTION = (0.98) (0.9) (1.0) (0.995) (100%)
OVERALL PERCENT REDUCTION = 88%

* FROM REF. 2
** FROM FIGURE 3
*** FROM REF. 1

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TABLE 2. EXAMPLE CALCULATION RESULTS

SOURCE	SERVICE	A (% OF MASS EMISSIONS)	MONITORING INTERVAL	B	C	% OF SOURCES ≥ 10,000ppm	UNCONTROLLED* EMISSION FACTOR	F	f	D	OVERALL % REDUCTION
PUMP SEALS	LIGHT LIQUID	87	1 yr.	0.8	1.0	22	0.25	0.99	0.076	0.923	64
VALVES	VAPOR	98	3 mo.	0.9	1.0	10	0.059	0.58	0.003	0.995	88
VALVES	LIGHT LIQUID	84	1 yr.	0.8	1.0	10	0.024	0.20	0.009	0.955	64
RELIEF VALVES	VAPOR	69	3 mo.	0.9	1.0	7	0.19	1.9	0.076	0.960	60
COMPRESSOR SEALS	VAPOR	84	3 mo.	0.9	1.0	32	1.4	3.7	0.076	0.979	74

ASSUMPTIONS:

1) ACTION LEVEL = 10,000 ppm
2) REPAIRED LEVEL = 1000 ppm
3) $\bar{n}_t$ = 0.2N FOR MONITORING INTERVAL = 1 yr.
   $\bar{n}_t$ = 0.1N FOR MONITORING INTERVAL = 3 mo.

*UNITS = LB/HR − SOURCE

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FIGURE 4. ACTION LEVEL AND REPAIRED LEVEL vs. D*
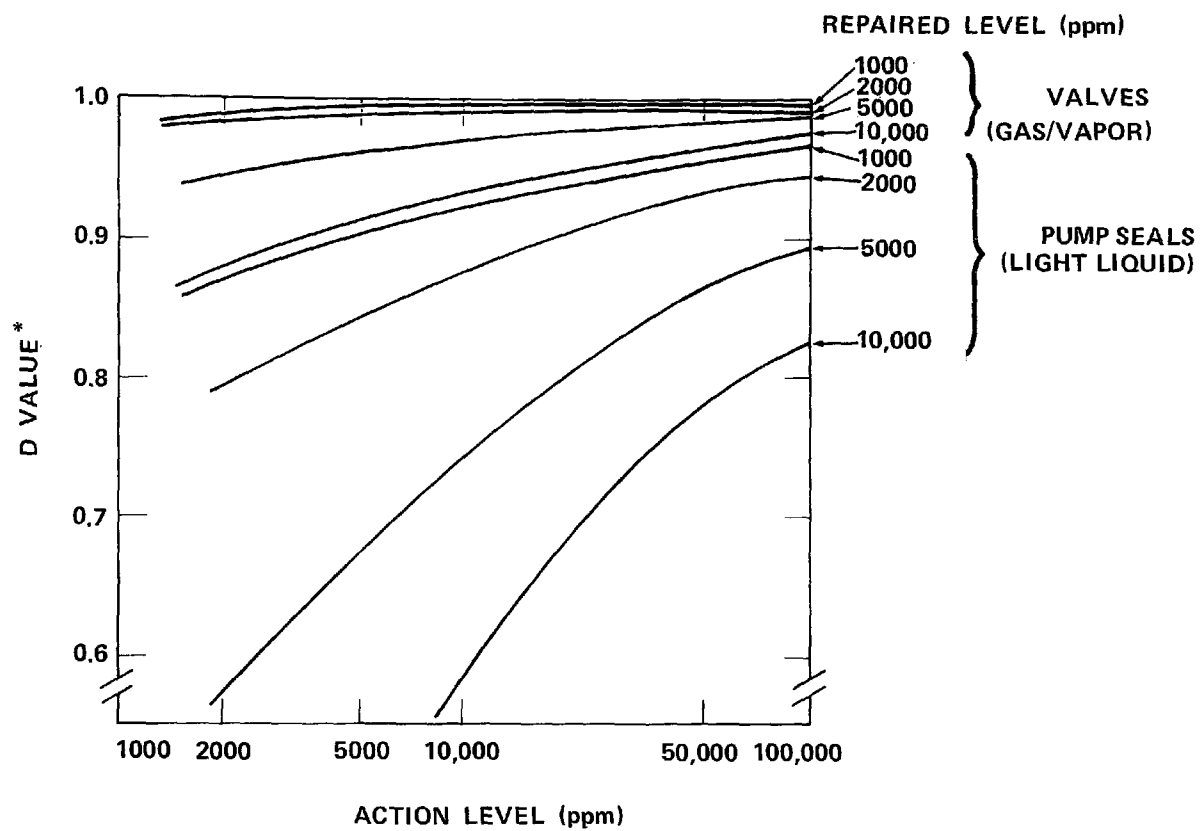
*D = IMPERFECT REPAIR CORRECTION FACTOR

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3. Effect of Monitoring Interval

$$B = 1 - \frac{\bar{n}_t}{N}$$, where $\bar{n}_t$ is a function of the monitoring interval.

Figure 5 shows how B (correction factor accounting for leak occurrence/recurrence) varies with monitoring interval. As indicated, when the frequency of monitoring increases, the B value (and thus the control effectiveness) also increases.

Sensitivity Analysis

A sensitivity analysis was performed to determine the effect of critical variables on the estimated reduction efficiency. The theoretical maximum reduction (A) is based on actual data and it is not affected by the assumptions of the calculation procedure. The effect of repair delay (C) has been fixed at 1. Values of both B and D, however, are determined by estimated values. Specifically, B is determined by estimating a value for n_t; D is determined by estimating a value for f (F is fixed by the selected action level). Thus, the sensitivity analysis was conducted to look at the effect of changing the values of n_t and f.

Table 3 provides the results of a sensitivity analysis for valves in gas/vapor service. The Base Case is for the values of n_t and f assumed in the previous example. Cases 1 and 2 show the change in % reduction (last column) due to a change in the value of n_t, the other variables being held constant; cases 3 and 4 illustrate the change in % reduction as a result of changing the repaired level (which determines f). The analysis shows that the results are rather insensitive to the assumed repaired level. However, changes in n_t have a more pronounced effect. For example, doubling the rate of leak occurrence/recurrence (Case 1) causes a 10% decrease in overall estimated efficiency.

Conclusions

The theoretical procedure described above provides a means of estimating the overall effectiveness of a petroleum refinery leak detection and repair program. The number of leaks which occur and recur between monitoring inspections (n_t) and the emission rate after repair (f) have been assumed. The results of the sensitivity analysis show the accuracy of these assumptions is important for n_t, but not for f. Therefore, the major data need for application of this calculation procedure is a time history of leaks; that is, how soon new leaks occur and repaired leaks recur. Bearing this limitation in mind, the calculation procedure can be used to derive estimates of controlled emissions and emission reductions for various leak detection and repair programs. These estimates have several uses, including:

1) Estimating the relative effectiveness of regulatory alternatives,

FIGURE 5. MONITORING INTERVAL vs. B*
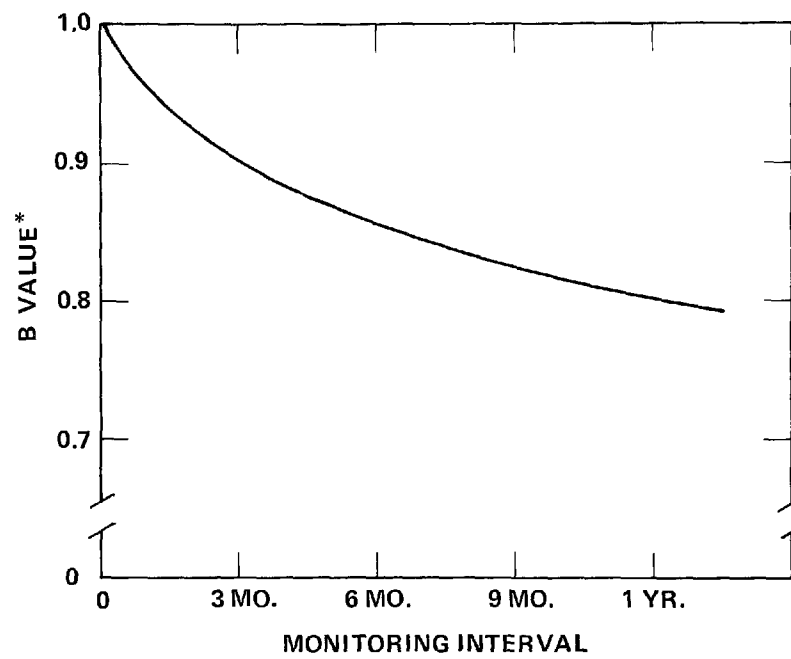
*B = LEAK OCCURENCE/RECURRENCE
   CORRECTION FACTOR

TABLE 3. SENSITIVITY ANALYSIS

CASE	A	C	n_t	B	REPAIRED LEVEL	f	D	OVERALL % REDUCTION	% (1) CHANGE
BASE	0.98	1.0	0.2N	0.9	1000 ppm	0.003	0.995	88	
1	0.98	1.0	0.4N	0.8	1000 ppm	0.003	0.995	78	−11
2	0.98	1.0	0.1N	0.95	1000 ppm	0.003	0.995	93	+6
3	0.98	1.0	0.2N	0.9	5000 ppm	0.017	0.971	86	−2
4	0.98	1.0	0.2N	0.9	500 ppm	0.001	0.998	88	0

(1) % CHANGE = $\dfrac{\text{% REDUCTION (CASE\#)} - \text{% REDUCTION (BASE CASE)}}{\text{% REDUCTION (BASE CASE)}}$

ASSUMPTIONS: 1) SOURCE — VALVES, GAS/VAPOR SERVICE
2) MONITORING INTERVAL — 3 MONTHS
3) ACTION LEVEL — 10,000 ppm. (F = 0.58)

B. A. Tichenor, K. C. Hustvedt, and R. C. Weber

    2) Quantifying reductions in product loss within process units, and

    3) Implementing programs to trade-off emisions from new construction.

References

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2. Radian Corporation, "Draft Appendix B: Detailed Results — The Assessment of Environmental Emissions from Oil Refining," August 1979. (Not Published — Final Draft will be an EPA report.)

Ivan H. Gilman

REVIEW

by

Ivan H. Gilman
Chevron U.S.A.
San Francisco, California

on

CONTROLLING PETROLEUM REFINERY FUGITIVE EMISSIONS
VIA LEAK DETECTION AND REPAIR

RESUME

Mr. Gilman is General Manager of Environmental Affairs for Chevron
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REVIEW

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INTRODUCTION

I believe both Radian Corporation and EPA deserve a great deal of
credit for their accomplishments with the refinery fugitive emission
program to date. They have developed an enormous body of quality emission
data that has permitted a realistic assessment of the magnitude of these
emissions to be made. In their paper, Tichenor, Hustvedt and Weber have
taken the next step by developing a model to predict the effectiveness of
screening and maintenance programs for reducing fugitive emissions.

I. Theoretical Model – Not a Correlation

The authors' model for predicting the dependence of emissions on
the specific requirements of a fugitive emission reduction program is con-
ceptually reasonable. Although it is based largely on theory and the pre-
dictions depend critically on several key assumptions, their model provides
an excellent framework for understanding the incremental benefits of
alternate strategies for controlling fugitive emissions. For example, the
authors have shown there is little to be gained either by requiring repair
of components whose leakage is found by screening to be below 10,000 ppm or
by lowering the post-repair screening value below 1,000 ppm. On the other
hand, selection of screening interval, especially as it relates to the leak
occurrence/recurrence rate, appears to be a key element in assuring signifi-
cant overall reductions of fugitive emissions. However, because the validity

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of some crucial assumptions is as yet unknown, I do not believe the model should be used to make quantitative estimates as it now exists.

II. Critical Role of Unquantified Assumptions

Unfortunately, very few data exist to assist the authors in predicting the occurrence and recurrence of leaks with time--and this, of course, is the most sensitive input to the model. In the absence of definitive data, the authors have assumed that components begin, or resume, leaking linearly with time. The linearity assumption is consistent with mathematical reliability theory for a large number of components. However, Table I and Figure 5 do not appear to be consistent with this assumption.

The authors have also assumed that the leak occurrence/recurrence rate will not change with improved maintenance procedures. As I will illustrate later, there are some types of repairs that are permanent and will prevent leak recurrence. When these types of repairs are made, the occurrence/recurrence rate will drop.

The authors should show how the length of the monitoring interval required to achieve a given program effectiveness is affected by changes in the leak occurrence/recurrence rate. As the rate drops, the monitoring interval can be extended without loss of program effectiveness.

Before the model can be used to determine the proper monitoring interval, the present leak occurrence/recurrence rate and its variability with improved maintenance must be established.

It would only be reasonable to assume an unchanging leak occurrence/ recurrence rate if leaks were due entirely to random events. In my experience, most leaks are due to explainable and sometimes predictable causes. The causes can vary greatly, but awareness of them holds the key to basic understanding of leak occurrence and recurrence and to improving the reliability of the model. Unfortunately, most of these external factors cannot be quantified and used in the predictive model. They result from a series of judgments and decisions made during the planning, design and construction phases of a project which are rarely all known and understood by the owners or managers of the project. I have worked on more than a dozen major refinery construction projects using a variety of contractors in at least six states. It is my experience that not even newly installed piping is completely free of leaks upon startup.

Depending on what is causing a component to leak, a repair may be a long-term success or be doomed to quick or chronic failure. I would like to cite some examples illustrating this.

Piping components frequently leak because of improper gasketing or because of improper or misapplied packing. Likewise, some components—especially the packing in small valves—can be damaged by excessive heat when the component is initially welded into place. In such cases proper replacement of the gasket or packing material would normally result in long-term, successful repair of the component. (I take this to mean that the component is not found to leak at levels above 10,000 ppm during future monitoring.)

Some of the reasons why a component may become a chronic leaker are:

- The component itself may only marginally meet the piping performance standard for the particular service and, thus, be more prone to leakage. (There is considerable latitude in the pressure/temperature service ratings of valves, flanges and pipe.) The quality of components will differ from refinery to refinery and sometimes even project to project within a refinery, depending upon the philosophies of the owner/manager and designer.

  The ASA piping standards, which form the basis most designers use for selection of valve and flange pressure ratings, flange facings, bolting requirements and other piping system components, have many areas of overlap. In these areas use of the lesser component may make the system more vulnerable to leakage than the conservative selection. Because there are significant cost differentials between these components, there is a great economic incentive for both owner and contractor to avoid overdesign. A typical large refinery construction project can save several million dollars by avoiding unnecessary overdesign.

  There is also a substantial variation in design among various manufacturers of standard components such as valves and flanges. A large project may have too great a demand to purchase only the "best" design. Price differentials will influence selection and application in this manner also.

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- Sometimes leaks occur because of piping strain caused by poor fabrication or improper design or construction allowance for expansion. Likewise, piping spools, assemblies of prefabricated pipe and components which are often times prepared at remote locations, may be damaged in transit or upon installation. Even if undamaged, the spools themselves may not fit properly unless the designer has specified the dimensions very accurately and these have been followed meticulously by the fabricator.

- The variations in temperature and types of stock handled may have a substantial effect on leakage. For example, ice can form on liquefied petroleum gas valves and flanges, which can score the closure area and result in leakage or failure.

- Improper design or performance of a vapor/liquid separation system can also result in chronic leaking of components. Liquid "hammer" in piping systems imposes considerable strain on the components and frequently causes leakage. This is especially common down-stream of an improperly designed heater or cooler where liquids accumulate in what should be a vapor line.

This myriad of physical variations in piping systems makes quantitative prediction of leakage by use of a model very difficult. Add to this uncertainty the many one-time events such as fires, power outages, emergency shutdowns, mechanical damage from maintenance activities and the quantitative prediction becomes impossible no matter how well done the model.

III. Recommendations and Conclusions

I believe the authors' model provides an excellent starting point for designing reasonable and cost-effective control requirements for reducing fugitive emissions. As it stands, it provides a basis for justifying the additional research that must be undertaken to determine the appropriate monitoring interval, occurrence/recurrence rate and effect of maintenance. However, until the predictions of the model are checked against a reasonable amount of long-term fugitive emission data in several refineries, I would caution against its use for quantitative purposes.

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16. ABSTRACT   The proceedings are a compilation of papers, formal discussions, and question and answer sessions from the EPA-sponsored Symposium on Atmospheric Emissions from Petroleum Refineries, November 5-6, 1979, in Austin, TX. The symposium focused on results of the petroleum refining environmental assessment program conducted by Radian Corporation under the sponsorship and direction of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC. The 4-year program cost $2.5 million and included extensive sampling of atmospheric emissions in 13 oil refineries throughout the U.S. Papers were presented by Radian and EPA on emissions measurement, quality control, and analysis and application of results. Emphasis was on fugitive emissions. Formal discussions of each paper were provided: discussors included petroleum industry representatives, environmental consultants, and state environmental regulatory personnel. Each paper and formal discussion was followed by a question and answer session between the audience and the presenter.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Measurement Petroleum Industry Quality Control Refineries Processing Refining Leakage Assessments Sampling	Pollution Control Stationary Sources Environmental Assessment Fugitive Emissions	13B 05C 14D 13I 13H 14B
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