FUGITIVE EMISSIONS - DETECTION, DISTRIBUTION AND REDUCTION

B. Tod Delaney
Fred C. Hart Associates
New York, New York

Introduction

There are many sources of volatile organic compounds (VOC) within the resins and plastics industry. Many of the VOC's associated with processes in this industry have been determined to be deleterious to health (e.g., benzene) in very small concentrations. VOC emissions also can play a signficant role in air quality degradation, especially through the formation of photochemical smog. The types of emission sources in the resins and plastics industry, as in the petroleum-petrochemical sector, can be divided into two categories: point sources (stack and vents) and non-point sources (fugitive emission sources comprised mainly of pump seals, valve seals, compressor seals, etc.). This paper will address fugitive emission sources and will use valves as a representative type of fugitive emission. The paper will generally cover the following three major areas:

- Leak detection and sampling.
- Distribution of leaks.
- Maintenance and reduction of leaks.

Leak Detection and Sampling

A fugitive emission can best be described as an atmospheric emission from an industrial operation that does not emanate from a process stack or vent. This definition includes such emission sources as leaking equipment, valve, pump and or compressor seals, storage tanks, loading/unloading facilities and cooling towers. Because fugitive emission sources do not emanate from an enclosure such as a stack or vent they have been difficult to quantify. Industry and EPA have generally accepted emission factors for these sources that were developed more than 20 years ago.(1)

In recent years, however, fugitive emissions have come to comprise a larger percentage of overall plant emissions due to improvements in industrial process emission controls. This increased importance has led recently to many studies.(2, 3, 4, 5) These recent studies have used screening techniques such as soap solutions sprayed on equipment as well as sensitive hydrocarbon detectors such as the J. W. Bacherach Instrument Company "TLV Sniffer" and the Century Systems Instruments "Organic Vapor Analyzer" (Model OVA-108) for leak detection. The process of detection, sampling and analysis can require a considerable effort in both manpower and time to acquire statistically significant data to be used for the determination of emission factors. After the leak is detected the source is enclosed usually by plastic or other suitable material and a sample is obtained for analysis.

Plant managers and industrial toxicologists are not primarily concerned with the development of emission factors but with the rapid detection and quantification of emissions within a processing area. The ideal instrument for survey work should be intrinsically safe, portable, provide rapid response, and provide both qualitative and quantitative information. Century Systems' Portable Organic Vapor Analyzer (OVA), mentioned earlier and shown in Figure 1, meets all of these criteria. The instrument was designed to measure small quantities (1-10,000 ppm) of organic material in air. The OVA can be used to obtain reliable data above the 10,000 ppm limit to almost any desired level with the use of a dilution system. The OVA uses a hydrogen flame ionization detector (FID) which has been used for many years as a detector for organic compounds. The portability of the OVA coupled with its intrinsic safety classification makes it an ideal instrument for field survey use, especially in areas where potentially hazardous concentrations (above the lower explosion limit) exist. The inclusion of a gas chromatographic (GC) option within the instrument increases its usefulness as a monitoring and detection instrument. With the GC option, not only can the magnitude of the leak be measured but composition can also be determined in the field, thus aiding in the location of the source.

The FID system used in the OVA (Figure 2) consists of a diffusion flame of pure hydrogen which is free of ions and is thus nonconducting. However, when a sample of organic materials is introduced into the flame, ions are formed and the flame becomes conductive. The conductivity of the flame can then be measured. The amount of conductivity that the flame exhibits with the introduction of organic compounds is related to many parameters, but is thought to be primarily based on the number of carbon atoms present and the efficiency of combustion.

In the typical laboratory FID (Figure 2) the sample to be analyzed is introduced and entirely mixed with the hydrogen prior to introduction to the burner. This premixing of sample with the hydrogen does not occur in the OVA. In the OVA, the sample is brought in with the combustion air (Figure 3). The sample contained in the combustion air is introduced into the combustion/detection chamber through a porous bronze filter which disperses the air and organic compounds around the hygrogen flame.

The method used in the OVA to introduce the sample to the hydrogen flame modifies the typical ion formation process and consequently changes the OVA's FID response to various compounds from that of a conventional FID. In the usual laboratory FID, a normal C_3 would have a response of three times the methane response (for the same 100 ppm_v) and a normal C_6 would have a response of six times that of methane. The OVA FID, however, has a response for nearly all commonly encountered hydrocarbons of between 50 percent and 150 percent the response of methane. Table 1 provides a sample of OVA responses for 100 ppm_v samples of common organics encountered in the petroleum petrochemical industry.

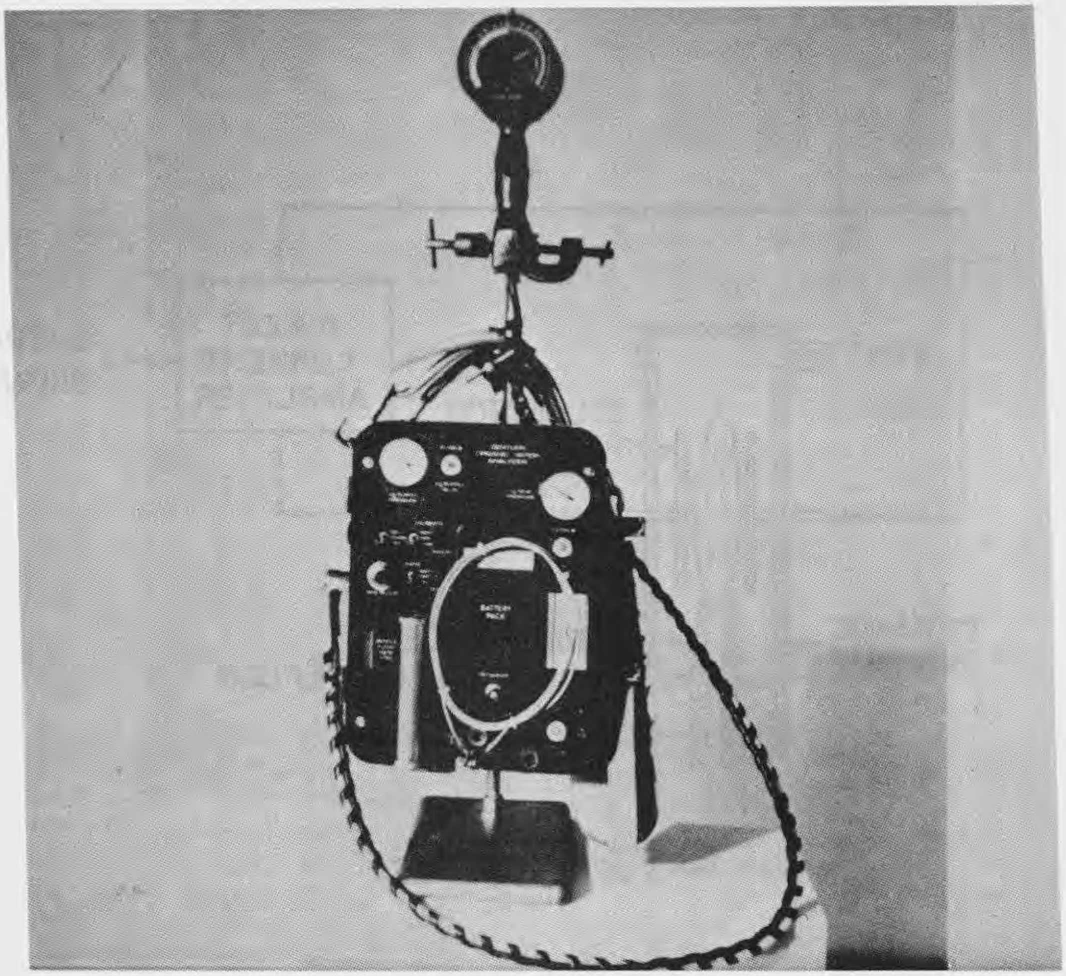

Figure 1. Century System's portable organic vapor analyzer (OVA).

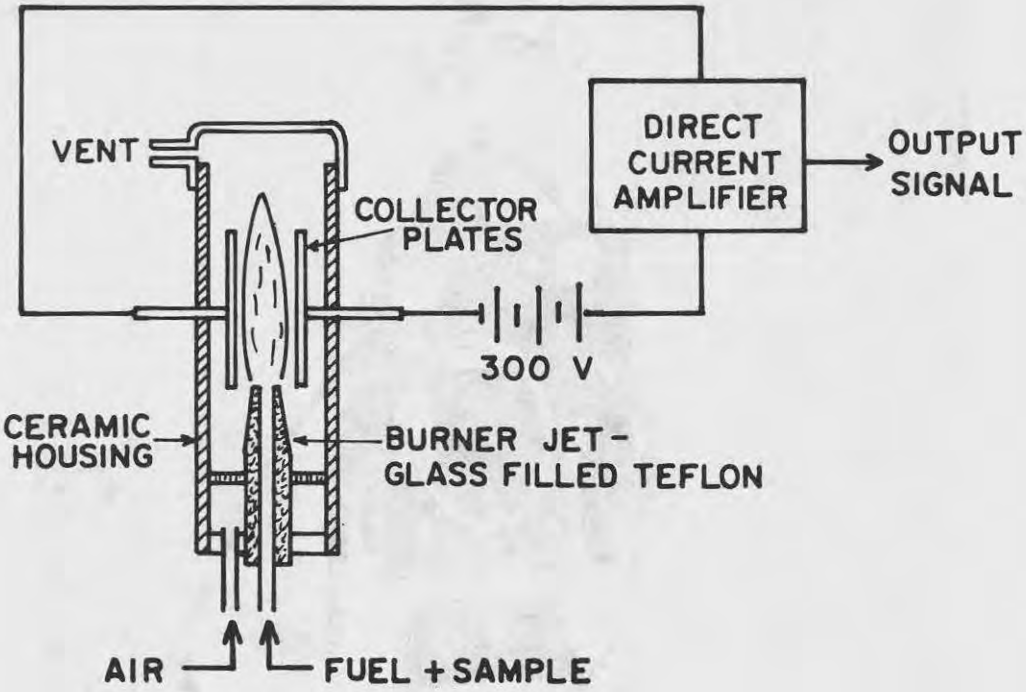

Figure 2. Flame ionization detector hydrocarbon analyzer burner-detector - standard type.

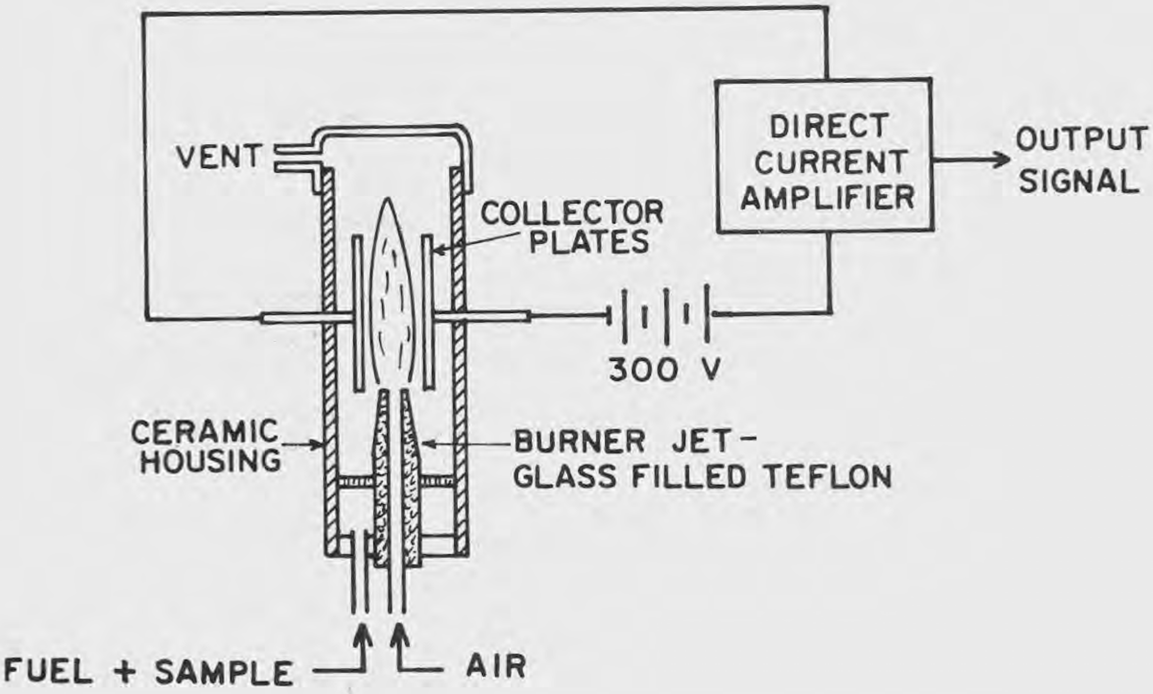

Figure 3. Flame ionization dector hydrocarbon analyzer burner-detector - OVA type.

Table 1. Relative responses at 100 ppm (V/V)

Compound	Meter Readout
Methane	100 (calibration sample)
Propane	85
Propylene	75
N-Butane	100
N-Penthane	100
Ethylene	65
Acetylene	225
N-Octane	150
Benzene	235
Toluene	150

The precise reason for the difference in response between the OVA and other FID's has not been completely determined. One hypothesis is that the size of the reaction envelope and the energy available from the hydrogen flame are altered by introducing the sample at the periphery of the flame reaction zone. This allows for less contact time, which reduces the number of ions formed, and consequently changes the response mechanism.

The Century Systems Organic Vapor Analyzer (OVA) will respond to almost all organic compounds. But since the responses of the OVA to the various compounds differ, it is necessary to calibrate the instrument with the organic compounds that are expected to be encountered in the field. Once the expected mixture of organics has been determined, a calibration curve for the mixture can be developed in the laboratory. The basic method for developing a calibration curve consists of recording the response of the OVA to a range of concentrations of the expected gas mixture. The OVA responses to the known hydrocarbon concentrations are then plotted to obtain a calibration curve for the test mixture. (An example of the curve is shown in Figure 4.)

After the calibration curve has been developed the OVA can be used to determine emission factors, the emission rate for a specific piece of equipment, or the concentration and composition of the ambient plant air. The test program can take many forms, such as a simple walk-through of the plant with the instrument or a detailed survey of each possible source of fugitive hydrocarbons in a specific process area. The level of effort is directly related to the data desired or required.

The GC option of the OVA greatly expands the instrument's analytical capabilities. With this option the OVA can obtain the concentration of specific compounds during field sampling in approximately 20 minutes. As with the total hydrocarbon analysis, a calibration curve has to be made. For GC operation, however, a curve has to be made for each compound tested. The curves are developed by measuring the peak heights from the portable strip chart recorder. Table II is an example of repeated measurements of benzene. Table III is the compilation of data from Table II, and Figure 5 is an example of a calibration curve of peak height and the test gas concentration.

Distribution of Leaks

Emission factors for valves and other sources of fugitive hydrocarbons which are of general use to agency officials and industry representatives have to be based on statistically valid data. Most fugitive emission factors published to date except for the valve data published by Exxon Research and Engineering(5), were not well grounded on statistical test programs or parameters. The general assumption had been that fugitive emission leak rates were normally distributed and that the arithmetic mean was the best descriptor of the population and would thus provide the best emission factor. This was not found to be the case. For valves and most other sources (for some sources the data base is not large enough as yet to make a definite statement) the log-normal distribution should be used.

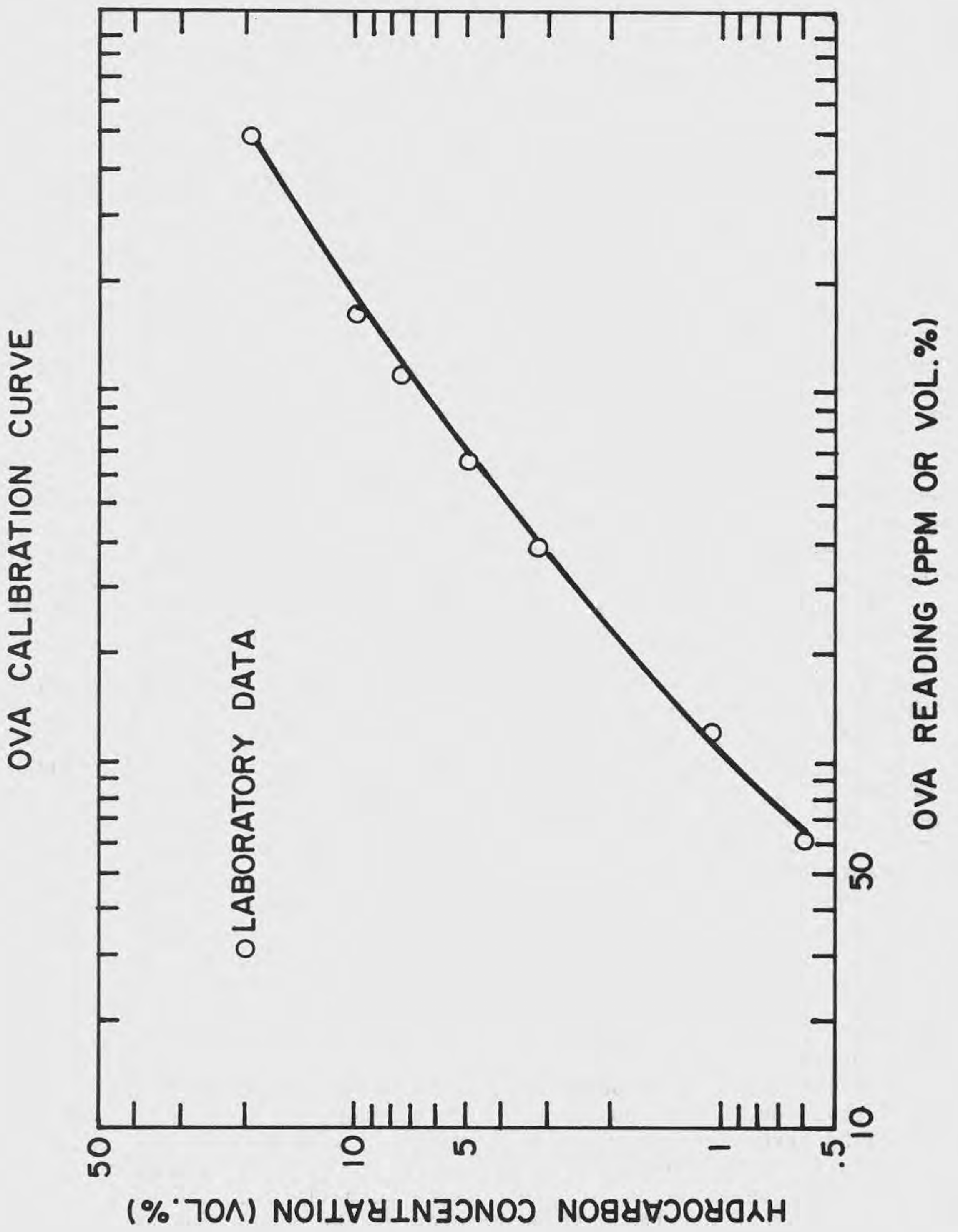
OVA CALIBRATION CURVE
○ LABORATORY DATA
50
10
5
1
.5
10
50
HYDROCARBON CONCENTRATION (VOL.%)
OVA READING (PPM OR VOL.%)

Figure 4.

Table 2. Tradewell Corporation benzene data.

Concentration	Peak Height	(mm)
2 ppm	6.25	
	6.20	
	6.22	$\tilde{x} = 6.238$
	6.22	$\sigma_{n-1} = 0.039$
	6.30	
4 ppm	12.06	
	12.10	$\tilde{x} = 12.062$
	12.12	
	12.05	$\sigma_{n-1} = 0.054$
	11.98	
5.33 ppm	16.46	
	16.37	$\tilde{x} = 16.452$
	16.52	
	16.45	$\sigma_{n-1} = 0.054$
	16.46	
8 ppm	24.82	
	24.80	$\tilde{x} = 24.884$
	25.51	
	24.72	$\sigma = 0.363$
	24.57	
10 ppm	30.72	
	30.46	$x = 30.292$
	30.45	
	30.36	$\sigma_{n-1} = 0.479$
	29.47	

Table 3. Benzene Data Courtesy Tradewell Corporation

Concentration	Mean Peak Height
2 ppmv	6.238 mm
4 ppmv	12.062 mm
5.33 ppmv	16.452 mm
8 ppmv	24.884 mm
10 ppmv	30.292 mm

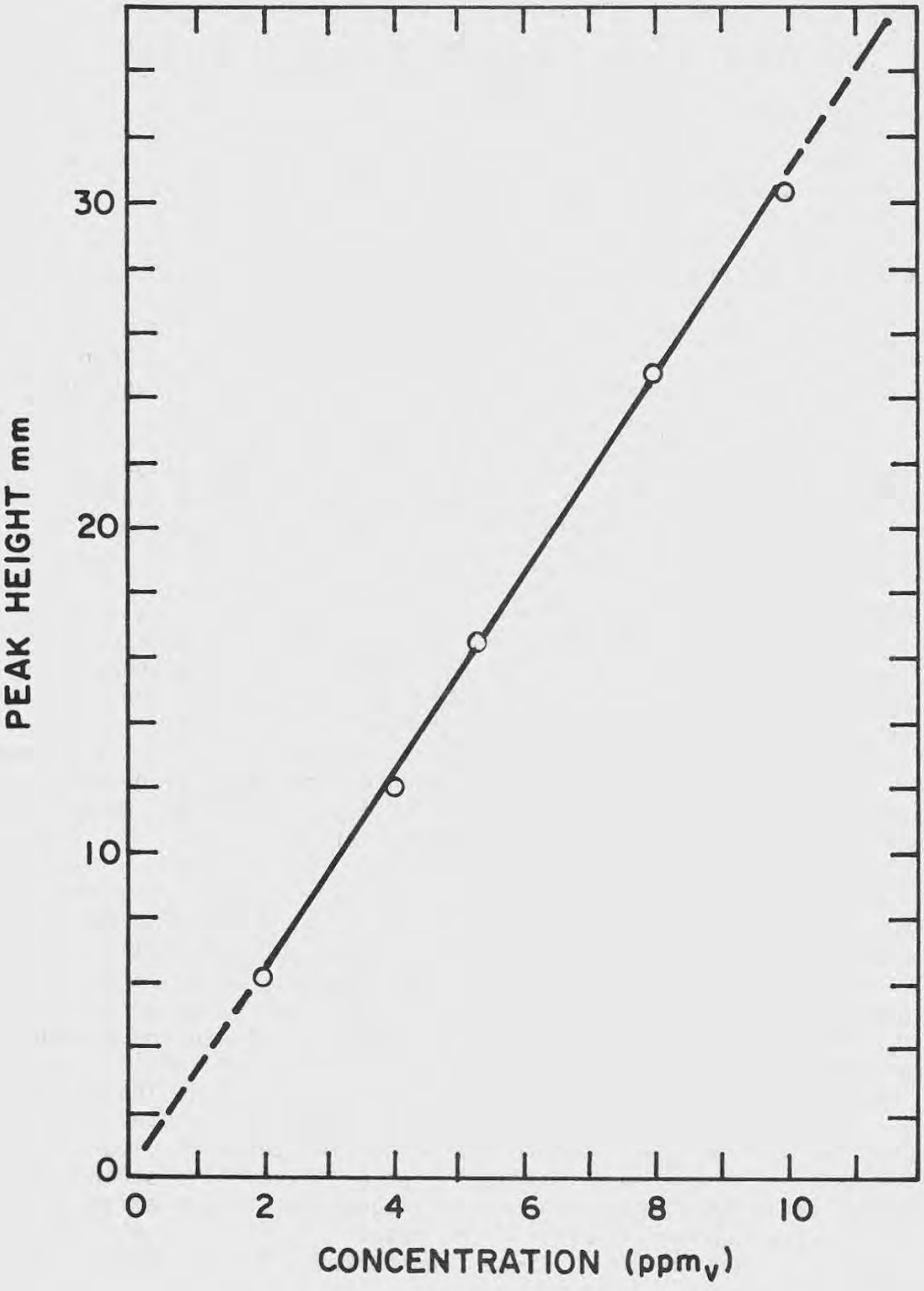

Figure 5. Peak height vs. concentration benzene (0-10 ppm)

Data Courtesy Tradewell Corporation

This conclusion can be best illustrated by briefly describing the test program I conducted for Exxon (referenced earlier). The objective of this test program was to verify and/or update emission factors used to estimate fugitive losses from valve stems, pump and compressor seals and atmospheric safety valves at a petrochemical facility. Valves are used as a representative source type. A stratified random sampling procedure was developed to assure that the pieces of equipment selected would provide the required statistical data base.

The sampling program was divided into two phases:

Phase I involved quantification of the number of valves in the plant. A random selection of about 10% of the total valves were then screened to determine the presence of leaks and an estimate of magnitude.

Phase II involved the stratified random sampling of a number of valves from the total data set developed under Phase I. The valves were bagged (enclosed in a plastic enclosure) and sampled. These valves reflected the same proportion and magnitude of leaks as determined from the initial screening.

The bagging involved enclosing the individual emission source with a plastic or aluminum foil enclosure. Figure 6 shows the equipment used. Plant instrument air was then passed through a dessicant and a charcoal filter at a predetermined flow rate. The flow rate was maintained so that a slight positive pressure would be maintained inside the enclosure. A sample of the air/hydrocarbon mixture was withdrawn from the enclosure outlet to a stainless steel cylinder for analysis by gas chromatography. The leak rate could then be easily calculated from the known flow rate and measured hydrocarbon concentration.

The initial approach for the analysis of the data was to calculate an average emission rate based on the arithmetic means of the entire data set. This preliminary analysis indicated that the number of small leakers far outnumbered the moderate and large leakers. In order to obtain a quantitative description, the measured emission rates were divided into 10 classes based on the total difference between the maximum and minimum emission rates measured. Figure 7 is a plot of the 10 classes. The preponderance of data falling in the first class indicated that the measured emission rates might not be normally distributed. Consequently, statistical tests were undertaken. The tests coupled with the positive skewing of the data indicated that a log-normal distribution would better describe the data. The natural logarithm of each emission rate was obtained. Figure 8 represents the result of using the natural logarithm for each emission rate. These transformed valued resemble very closely the familiar bell shaped curve.

A computer program was developed to convert the field data (flow-rate and concentration) to emission rates; the emission rates were then used to determine the geometric mean and standard deviation. The geometric mean and standard deviation were then used to obtain a population mean. This population mean then represents the emission factor for the component in question.

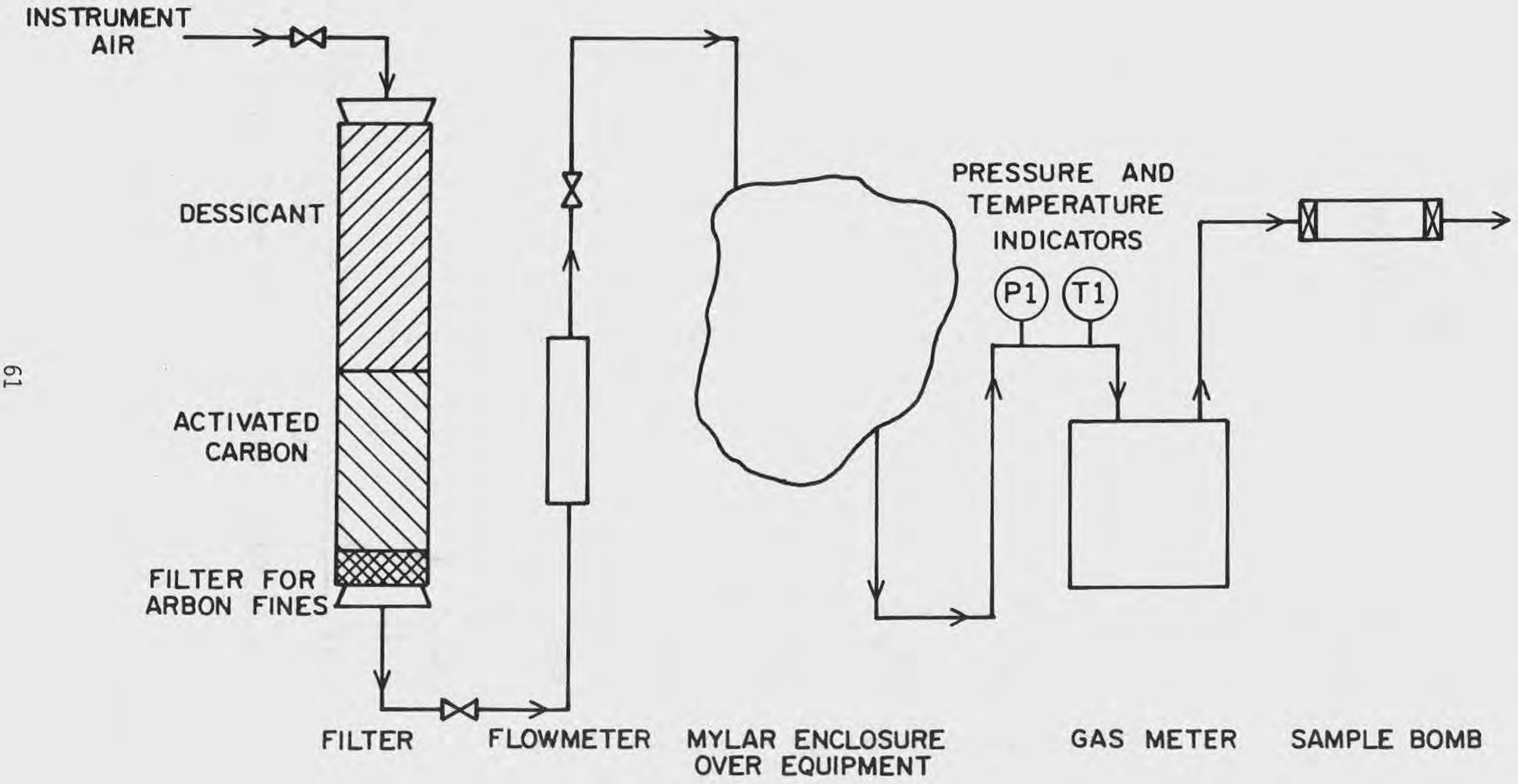

Figure 6. Fugitive emissions sampling train.

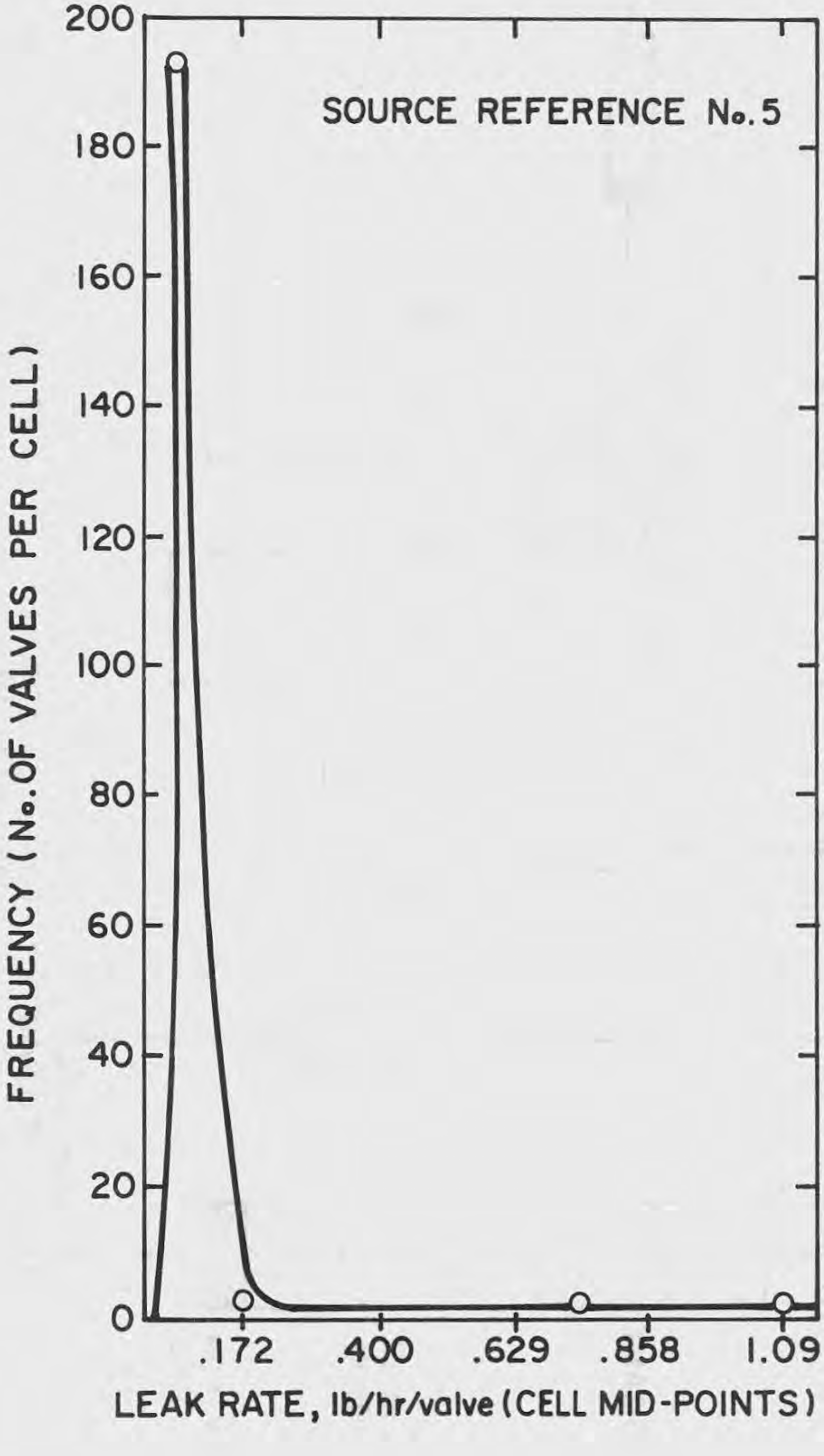

Figure 7. Frequency distribution of valve leak rate data.

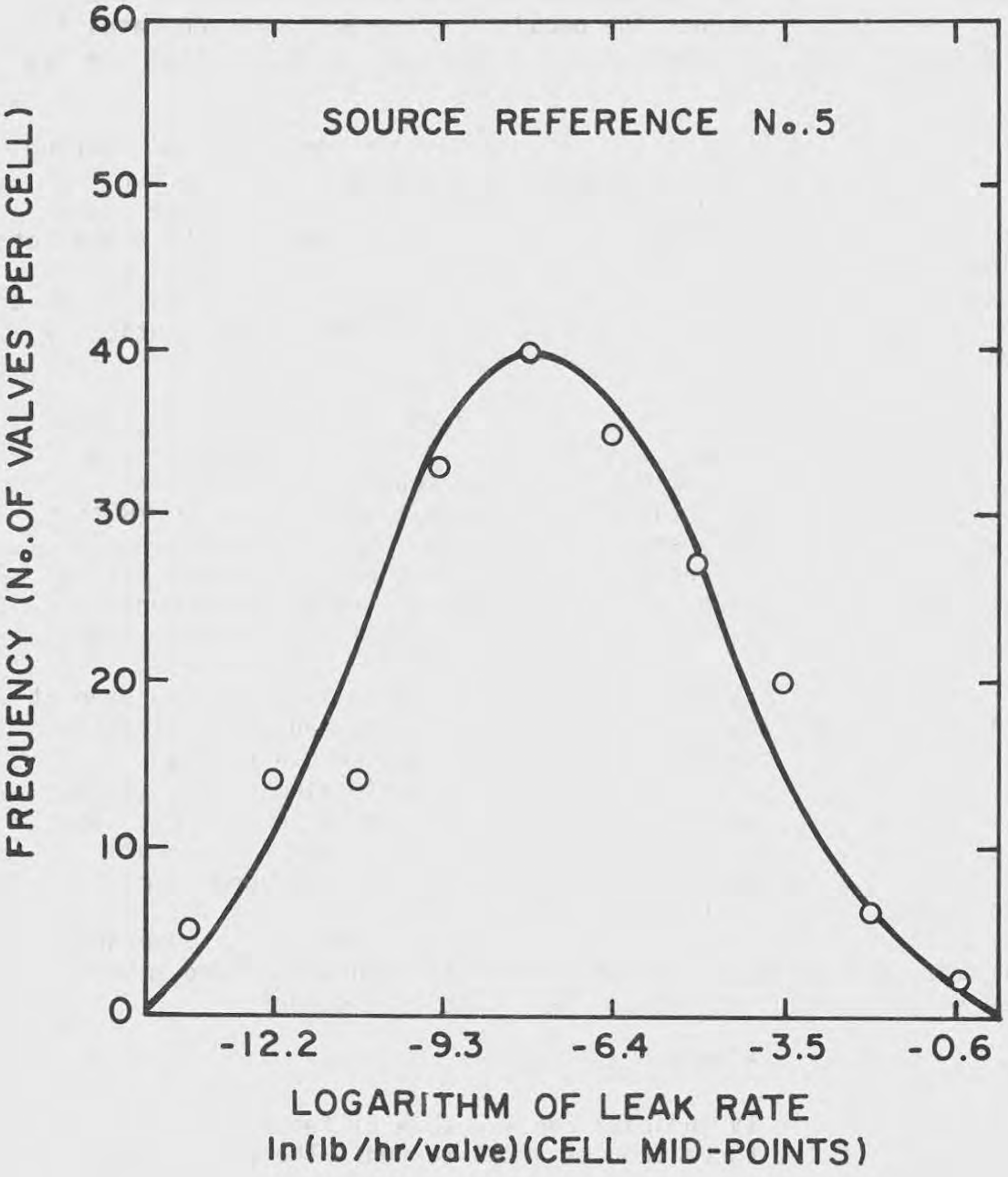

Figure 8. Frequency distribution of logarithms of valve leak rate data.

Table IV contains the emission factors obtained by following the above procedure for three different product lines at the petrochemical plant. When all of the data from each product line are used as single data set, a value of .64 lb/day per valve is obtained as an emission factor. This value represents the population average emission rates for leaking valves in the petrochemical plant during the period that the test program was conducted.

This emission factor has to be adjusted by the percentage of leaking valves in the plant to obtain a plant specific emission factor for valves. The initial screening of 10% of the total valves in the plant indicated that 15% leaked. Adjusting the emission rate for the number of valves leaking one obtains an overall emission factor for valves of approximately .11 lb/day. When used with the total number of valves at a plant this valve would provide an estimate of the total contribution by valves to the total fugitive emission burden.

The .11 lb/day compares well with the AP-42(6) emission factor for valves of .15 lb/day. But the .11 lb/day valve is considerably larger than recent values obtained by Meteorology Research, Inc.(MRI), at Atlantic Richfield's Elwood California Gas Treatment Facility. MRI's results were based on a very small size and the use of the arithmetic mean. Also, recent Radian results employing the geometric mean with a large data base obtained from their petroleum refinery measurement program compare well with the results obtained during the Exxon study.

Before any of the emission factors contained in Table IV are used at a specific plant, data has to be obtained on the percentage of leaking components. This data can be obtained by use of the OVA or soap solution. Once an estimate of the percentage of leaking components has been obtained, an estimate of the total quantity of material lost can then be calculated. For most calculations of this type the overall emission rate of .64 lb/day per leaking value should be used since it is supported by the largest data base. The result obtained by this precedure will provide a good indication of the quantity of hydrocarbon loss, but age, amount of maintenance, chemical composition and other variables will influence the actual leak rate considerably.

Maintenance and Reduction of Leaks

The values in Table IV indicate considerably different emission factors for each of the three product lines tested. These differences are a direct result of variations in individual maintenance programs. The maintenance programs for each line varied from routine maintenance to a special program designed to reduce unacceptable losses of a costly chlorinated hydrocarbon. The results show that a significant improvement in both the emission factor and the percent of leaking components can be obtained through a conscientous effort and desire to reduce losses.

A concise definition of what constitutes a good maintenance program is currently not available. Also the cost associated with maintenance

Table 4. Valve emission factors.

Source Sample Size	Leaking Source Emission (Factor (lb/hr/valve)		Percentage of Leaking Components	Plant Product Line Emission Factor (lb/day/valve)
	Mean Value	30 Confidence Limits		
Total Plant Valves (197)	0.031	0.017 - 0.057	15	.11
Product Lines:				
A-Routine maintenance (100)	0.032	0.014 - 0.076	17	.13
B-Improved maintenance (49)	0.019	0.008 - 0.047	16	.07
C-Special maintenance (48)	0.008	0.002 - 0.026	8	.014

Source Ref #5

programs has not as yet been developed. But the data indicates that inspection and maintenance of valves has the potential for considerable reduction of fugitive hydrocarbons in plants.

The magnitude of the reduction can be illustrated by assuming that a plant has 1000 valves. If the plant had a routine maintenance program, the amount of hydrocarbon lost per day would be approximately 130 lbs. If this same installation has a well executed maintenance program, this loss could be reduced to 14 lbs. Assuming that all 1,000 valves are located within a building having a volume of 100,000 ft^3 and that the leaking compound is benzene the 1,000 valves would contribute approximately 600 ft^3 of benzene per day to the plant atmosphere. If the air were changed 10 times per hour this would result in a daily concentration level of 25 ppm for a routine maintenance program and about 2.5 ppm for a well-executed maintenance program. Thus, the initiation of a valve maintenance program could be expected to reduce fugitive emissions by up to a factor of 10. Reduction by this magnitude could be sufficient to reduce the need for additional, more costly controls which may be required to meet some of the newer standards being proposed and instituted.

REFERENCES

1. Joint District, Federal, and State Project for the Evaluation of Refinery Emissions, "Emissions to the Atmosphere from Petroleum Refineries in Los Angeles County", 1957-1958, nine reports.

2. "Total Hydrocarbon Emission Measurements of Valves and Compressors at ARCO's Ellwood Facility," Report Number 911-115-1661, Meteorology Research, Inc., 1976.

3. "Assessment of Environmental Emissions from Oil Refining", (unpublished interim reports), Radian Corporation, EPA Contract No. 68-02-2665, in progress, March, 1976 to March, 1979.

4. Taback, H. J., "Petroleum Refinery Fugitive Emissions, Measurement, Emission Factors, and Profiles, KUB Inc., Paper Presented at Symposium/Workshop on Petroleum Refining Emission, Jekyll Island, Georgia, April 26-28, 1978.

5. Hanzevack, K. M. "Fugitive Hydrocarbon Emissions - Measurement and Data Analysis Methods", Paper presented at Symposium/Workshop on Petroleum Refining Emissions, Jekyll Island, Georgia, USEPA, April 26-28, 1978. (Note: The planning and analysis of the test program described in this paper were performed by Dr. Bernard T. Delaney and Paul H. Woods, Jr. Their contribution and that of others at Exxon were not recognized in the Authorship or in an acknowledgement at the time the paper was presented due to Exxon policy.)

6. "Compilation of Air Pollutant Emission Factors," AP-42, Third Ed. Plus Supplements, EPA, OAQPS, Research Triangle Park, NC.

* * *

MR. DONATO R. TELESCA: Mr. Ralph Barley will be giving the next talk. He is a Chemical Engineer with 25 years' industrial experience in operation and engineering design. He was recently involved in the redesign of an existing suspension PVC plant to bring it into compliance with the Federal regulations. His talk will be on the reduction of worker exposure during on-stream maintenance in a PVC plant.

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