United States
Environmental Protection
Agency

EPA-600/S2-81-080
May 1981
Report #1

EPA

Research and Development

EVALUATION OF MAINTENANCE FOR FUGITIVE
VOC EMISSIONS CONTROL

Prepared for

OFFICE OF AIR QUALITY PLANNING AND STANDARDS
EMISSIONS STANDARDS AND ENGINEERING DIVISION

Prepared by

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

United States
Environmental Protection
Agency

EPA-600/S2-81-080
May 1981

EPA

Research and Development

EVALUATION OF MAINTENANCE FOR FUGITIVE
VOC EMISSIONS CONTROL

Prepared for

OFFICE OF AIR QUALITY PLANNING AND STANDARDS
EMISSIONS STANDARDS AND ENGINEERING DIVISION

Prepared by

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EVALUATION OF MAINTENANCE FOR FUGITIVE VOC EMISSIONS CONTROL

By:

G. J. Langley and R. G. Wetherold
Radian Corporation
8501 Mo-Pac Blvd.
P.O. Box 9948
Austin, Texas 78766

Contract No. 68-03-2776

Project Officer

Robert C. Weber
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

DISCLAIMER

FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report, "Evaluation of Maintenance for Fugitive VOC Emissions Control," quantifies the effectiveness of simple on-line maintenance for reducing VOC emissions from in-line valves. The overall effectiveness of an inspection/maintenance program was examined by studying: the immediate reduction in mass emissions as a result of maintenance, the long-term emissions from those valves which were maintained, the recurrence rate of leaks from valves, and the rate at which new leaks occur, for both valves and pump seals. The time required for simple on-line maintenance was also studied, to aid in the estimation of maintenance costs.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

The U.S. EPA Office of Air Quality Planning and Standards (OAQPS) has the responsibility for formulating regulations for the control of fugitive emissions of volatile organic compounds (VOC). "Fugitive emissions" generally refers to the diffuse release of vaporized hydrocarbon or other organic compounds. Fugitive emissions originate from equipment leaks as well as large and/or diffuse sources. The study reported here was undertaken by the Office of Research and Development to assist OAQPS in the development of regulations.

The project was designed to quantify the effectiveness of routine (on-line) maintenance in the reduction of fugitive VOC emissions from in-line valves. An overall emission reduction of approximately 70% was achieved by tightening the bolts on the valve packing gland. This level of control was sustained for up to about six months. The rates of leak occurrence and recurrence were also evaluated, as well as the time required to conduct the on-line maintenance.

TABLE OF CONTENTS

Page

1.0 INTRODUCTION. 1

2.0 SUMMARY OF RESULTS. 2
2.1 Effect of Valve Maintenance. 2
2.2 Occurrence of Leaks. 3
2.3 Recurrence of Leaks. 3
2.4 Modelled Relationship-Leak Rate Versus Screening Value. 3
2.5 Time for Maintenance 4

3.0 DETAILED RESULTS. 5
3.1 Statistical Concepts and Models. 5
3.1.1 Weighted Percent Reduction. 5
3.1.2 Percent Sources Repaired. 6
3.1.3 Exponential Distribution Model. 6
3.1.4 Mixed Distribution Models 7
3.1.5 Correlation Coefficient 7
3.1.6 Analysis of Variance. 8
3.1.7 Analysis of Covariance. 8
3.1.8 Linear Regression (Least-Squares Fit) 8
3.1.9 Scale Bias Correction Factor. 9
3.2 Immediate Effect of Valve Maintenance. 9
3.2.1 Effectiveness of Valve Maintenance Based on Measured Leak Rates 10
3.2.2 Effectiveness of Maintenance Based on Screening Values. 17
3.3 Long-Term Effect of Maintenance on Emissions 26
3.4 Occurrence of Leaks. 30
3.5 Recurrence of Leaks. 44
3.6 Modeled Relationship - Leak Rate vs. Screening Value . . 46

TABLE OF CONTENTS (contd)

	Page
3.7 Maintenance Summary	81
REFERENCES	85
APPENDIX A - EXPERIMENTAL PROCEDURES	86
APPENDIX B - DATA HANDLING	123
APPENDIX C - QUALITY CONTROL	126
APPENDIX D - STATISTICAL CONSIDERATION	174
APPENDIX E - TWO-WAY TABLES OF SCREENING VALUES	195

LIST OF TABLES

Table		Page
3-1	IMMEDIATE EFFECT OF VALVE MAINTENANCE.	15
3-2a	PERCENT OF VALVES REPAIRED BASED ON INITIAL SCREENING VS. IMMEDIATELY AFTER MAINTENANCE SCREENING VALUES	22
3-2b	PERCENT OF VALVES REPAIRED BASED ON IMMEDIATELY BEFORE AND AFTER MAINTENANCE SCREENING VALUES	23
3-3	OCCURRENCE RATE ESTIMATES FOR VALVES AND PUMPS BY PROCESS.	32
3-4	OCCURRENCE RATE ESTIMATES FOR VALVES IN GAS AND LIQUID SERVICE BY PROCESS	33
3-5	OCCURRENCE RATE ESTIMATES FOR BLOCK AND CONTROL VALVES BY PROCESS.	34
3-6	SUMMARY OF RESULTS ON PAIRWISE COMPARISON OF OCCURRENCE RATE ESTIMATE.	43
3-7	VALVE LEAK RECURRENCE RATE ESTIMATES	44
3-8	ANALYSIS OF COVARIANCE FOR PUMPS AND VALVES USING OVA SCREENING VALUES	52
3-9	ANALYSIS OF COVARIANCE FOR PUMPS AND VALVES USING TLV SNIFFER SCREENING VALUES	53
3-10	MODELLING LEAK RATE VS. SCREENING VALUE COMPARING SOCMI AND REFINERY ESTIMATES	76
3-11	SUMMARY OF MAINTENANCE TIME DATA	82

LIST OF FIGURES

Figure		Page
3-1	Sequence of Emissions Measurements and Screening Values. . . .	11
3-2	Plot of Before vs. After Maintenance Leak Rates.	13
3-3	Plot of Before Minus After Maintenance Leak Rate vs. Before Maintenance Leak Rate.	14
3-4	Immediate Effect of Valve Maintenance.	16
3-5	Plot of Before Maintenance OVA Reading vs. the Measured Reduction in Emissions Due to Maintenance.	18
3-6a	Plot of Initial Before Maintenance vs. After Maintenance OVA Reading	20
3-6b	Plot of the Before vs. After Maintenance OVA Readings	21
3-7	Long-Term Effect of Maintenance vs. Control Group.	27
3-8	Long-Term Effect of Maintenance vs. Control Group.	28
3-9	Overall Occurrence Rate Estimates.	35
3-10	Occurrence Rate Estimates by Service	36
3-11	Occurrence Rate Estimate by Valve Type	37
3-12	Occurrence Rate Estimate for Cumene Process Units.	38
3-13	Occurrence Rate Estimate for Ethylene Process Units.	39
3-14	Occurrence Rate Estimate for Vinyl Acetate Process Units . . .	40
3-15	Occurrence Rate Estimate vs. Empirical CDF	42
3-16	Recurrence Rate Estimate vs. Empirical Distribution Function .	45
3-17	Log_{10} Leak Rate vs. Log_{10} OVA for All Valves - Zeroes Set to 1 for OVA or .000001 for Leak Rates.	47
3-18	Log_{10} Leak Rate vs. Log_{10} TLV Sniffer for All Valves - Zeroes Set to 1 for OVA or .000001 for Leak Rates	48
3-19	Log_{10} Leak Rate vs. Log_{10} OVA for Valves Screening < 10 and Leak = 0 Removed	49
3-20	Log_{10} Leak Rate vs. Log_{10} TLV Sniffer for Valves Screening < 10 and Leak = 0 Removed.	50
3-21	Log_{10} Leak Rate vs. Log_{10} OVA Reading for Pump Seals	57
3-22	Log_{10} Leak Rate vs. Log_{10} TLV Reading for Pump Seals	58
3-23	Log_{10} Leak Rate vs. Log_{10} OVA Reading for Valves - Gas Service.	59

LIST OF FIGURES (contd)

Figure		Page
3-24	Log_{10} Leak Rate vs. Log_{10} TLV Reading for Valves - Gas Service.	60
3-25	Log_{10} Leak Rate vs. Log_{10} OVA Reading for Valves - Liquid Service.	61
3-26	Log_{10} Leak Rate vs. Log_{10} TLV Reading for Valves - Liquid Service.	62
3-27	Modelled Relationship - Leak Rate vs. OVA for Pump Seals	64
3-28	Modelled Relationship - Leak Rate vs. TLV Sniffer for Pump Seals.	65
3-29	Modelled Relationship - Leak Rate vs. OVA for Valves in Gas Service.	66
3-30	Modelled Relationship - Leak Rate vs. TLV Sniffer for Valves in Gas Service	67
3-31	Modelled Relationship - Leak Rate vs. OVA for Valves in Liquid Service	68
3-32	Modelled Relationship - Leak Rate vs. TLV Sniffer for Valves in Liquid Service	69
3-33	Modelled Relationship - Leak Rate vs. OVA Individual and Mean Confidence Regions for Pump Seals	70
3-34	Modelled Relationship - Leak Rate vs. TLV Sniffer Individual and Mean Confidence Regions for Pump Seals	71
3-35	Modelled Relationship - Leak Rate vs. OVA Individual and Mean Confidence Region for Valves in Gas Service	72
3-36	Modelled Relationship - Leak Rate vs. TLV Sniffer Individual and Mean Confidence Region for Valves in Gas Service	73
3-37	Modelled Relationship - Leak Rates vs. OVA Individual and Mean Confidence Regions for Valves in Liquid Service	74
3-38	Modelled Relationship - Leak Rate vs. TLV Sniffer Individual and Mean Confidence Regions for Valves in Liquid Service.	75
3-39	SOCMI - Refinery Comparison - Pump Seals	78
3-40	SOCMI - Refinery Comparison - Valves - Gas	79
3-41	SOCMI - Refinery Comparison - Valves - Light Liquid	80
3-42	Distribution of Maintenance Time for Valves in Study	83

GLOSSARY

action level: A screening value obtained with a portable VOC monitor which indicates the need for repair.

"directed maintenance": Refers to a valve maintenance procedure whereby the hydrocarbon detector is utilized during maintenance. The leak is monitored with the instrument until no further reduction of leak is observed or the valve stem rotation is restricted.

fugitive VOC emissions: Generally refers to the diffuse release of vaporized hydrocarbon or other organic compounds. Fugitive emissions originate from equipment leaks as well as large and/or diffuse sources.

initial screening value: Refers to the maximum repeatable hydrocarbon concentration obtained from a source (e.g. valve, pump) during the initial unit visit by a screening team.

leak: A screening value of equal to or greater than 10,000 ppm.

leak rate: Refers to the actual mass emissions from a source with respect to time and can be referred to as the emission rate.

maintenance: For the purpose of this study maintenance refers to action by plant personnel in which an assigned worker tightens the valve packing gland pressure plate retention bolts nuts with a wrench to futher compress the packing material around the valve stem and seat.

occurrence of a leak: The appearance or initiation of a leak from a source which has not previously been leaking.

OVA: Refers to a portable hydrocarbon detection instrument (organic vapor analyzer) manufactured by Century Systems (now Analabs). It utilizes a flame ionization detector (FID) and an air pump.

process stream: Process fluid such as reactants, intermediate products, final products, by-products, etc. that is contained within pipes in a process unit. Steam, water, air, and other utility lines are not considered to be process streams.

process unit: Refers to equipment assembled to produce an organic chemical as an intermediate or final product. A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the final product.

recurrent leak: Refers to a leak which appears at some time after the leak has initially been repaired.

repair: For the purposes of this study repair is adjustment or alteration of a valve which reduces the screening value from greater than or equal to 10,000 ppmv to below 10,000 ppmv.

repeat screening value: Refers to the maximum repeatable hydrocarbon concentration observed during subsequent screening of a previously screened source.

screening: Refers to the act of measuring the hydrocarbon concentration of a source with a portable hydrocarbon detector.

screening value: The maximum repeatable hydrocarbon concentration (in ppmv) detected at a source with a portable hydrocarbon detector (such as a Century Organic Vapor Analyzer or a Bacharach TLV Sniffer) while traversing with the instrument probe around all the potential leak points of the source.

service: See type of service.

source type: Refers to process unit equipment components which may emit fugitive emissions. Common source types of fugitive emissions are valves, pump seals, flanges, compressors, couplings, etc.

statistically significant: Implies that the variation in the data is not just due to sampling or analytical error, but that there is a real difference between the actual result and what was expected to happen by chance alone. With any statistical test there is a level of uncertainty, usually called the significance level (α level). This is the probability of declaring that the difference is real when in fact it is not.

tenting: refers to the procedure of enclosing the source leak in an inert plastic (Mylar®, Tedlar®) enclosure. The sampling train is connected to the enclosure, and the fugitive emission leak rate is measured.

TLV "Sniffer": Refers to a portable hydrocarbon detection instrument manufactured by Bacharach, Inc. It uses a catalytic detector and air pump.

total hydrocarbons (THC): A summation of the concentration of all organic compounds detected in a sample of the fugitive emissions.

type of service: Refers to the physical state (gas, liquid, or both) of the material(s) contained in a specific pipeline or vessel.

volatile organic compound (VOC): Means any organic compound which participates in atmospheric photochemical reactions; or which is measured by Reference Method 21.

weighted percent reduction (WPR): An estimate of the percent that the total emissions were reduced due to maintenance.

$$WPR = \frac{\left(\sum^{n} \text{Mass emissions before maintenance} - \sum^{n} \text{Mass emissions after maintenance}\right)}{\sum^{n} \text{Mass emissions before maintenance}} \times 100$$

1.0 INTRODUCTION

The U.S. EPA Office of Air Quality Planning and Standards (OAQPS) is currently in the process of formulating New Source Performance Standards (NSPS) for the control of fugitive emissions of volatile organic compounds (VOC). This study was undertaken by the Office of Research and Development to assist OAQPS in this effort. This work effort was intended to develop data to determine the effectiveness of routine (on-line) maintenance in the reduction of fugitive VOC emissions from in-line valves. The overall effectiveness of an inspection/maintenance program was examined by studying:

- immediate emission reduction due to maintenance,
- the propagation of the leaks after maintenance, and
- the rate at which new leaks occur, for both pumps and valves.

This report contains three major sections and five appendices plus a reference section. The major conclusions of the program and the significant results which support these conclusions are presented in Section 2. The detailed results and statistical analyses are presented in Section 3. The various experimental procedures involved in this project are described in Appendix A. Appendix B contains details on data handling procedures. Quality control procedures and results are described in Appendix C. A detailed discussion of the statistical considerations and procedures used in developing Section 3 are given in Appendix D. Appendix E contains two-way table data summaries of screening values. A complete presentation of the data gathered for analysis for this project can be found in an unpublished technical note (Reference 6).

The screening data were developed with both the Century Systems OVA and the Bacharach TLV Sniffer, but most of the analyses presented in this report use the OVA data to be consistent with other studies in chemical plants.

2.0 SUMMARY OF RESULTS

Several important findings resulted from this study. The significant results are highlighted in this section. A more complete presentation of the results of this program is included in Section 3.

2.1 Effect of Valve Maintenance

Three aspects of the effect of valve maintenance on fugitive emissions were studied:

- the immediate effect based on measured leak rates,
- the long term effect based on measured leak rates, and
- the immediate effect based on screening values.

Analysis of the immediate effect of maintenance using measured leak rates produced an estimate of 71.3% reduction in fugitive emissions (95% confidence limits of 54% to 88%) immediately after maintenance.

Later sampling of the maintained sources to study the long term effect of maintenance indicated that the reduction estimates obtained for immediate effects of maintenance held for the length of the study (up to six months).

Analysis of the immediate effect of maintenance based on screening data and using a 10,000 ppmv action level, produced an estimate of 28.9% reduction in the number of leaking sources as a result of the maintenance. This indicates that 71% of the leaking sources could not be repaired (where repaired is defined as screening <10,000 ppmv after maintenance).

2.2 Occurrence of Leaks

The rate of occurrence of leaks was studied using those pumps and valves that initially screened at <10,000 ppmv and which were not maintained during the project. An exponential model was fitted to the data to develop occurrence rate estimates. The resulting estimate of the occurrence rate after 30 days is 1.3% for valves with a 95% confidence interval of 0.7% to 2.1%. For pump seals, the 30-day estimated occurrence rate is 5.5% with a 95% confidence interval of 2.2% to 10%. Thus, after 30 days from the time of screening, 1.3% of the valves and 5.5% of the pump seals which had screening values <10,000 ppm in the initial screening can be expected to have screening values >10,000 ppm.

2.3 Recurrence of Leaks

The rate of recurrence of leaks was studied using 28 valves which were repaired during maintenance. A statistical model was fitted to the data to develop recurrence rate estimates. The resulting estimate of the recurrence rate of leaks for valves 30 days after repair is 17.2% with an approximate 95% confidence interval of 5.1% to 37%. The recurrence rate for leaks is much higher than the occurrence rate.

2.4 Modelled Relationship-Leak Rate Versus Screening Value

Relationships between screening values and measured leak rates were established for both the OVA and the TLV Sniffer. Separate models were developed for pump seals, valves in gas service, and valves in liquid service, since statistically significant differences in the models were found between these categories. The slope and intercept for the valves in the liquid service model were found to be statistically different from those from the refinery study (Reference 8). The pump models were not found to be statistically different. The slope for the gas service valves was found to be statistically different from that developed in the refinery project, but, the intercept estimates were not statistically different. However, project constraints did not permit a thorough comparison between the relationships developed in this study and those from the refinery project.

2.5 Time for Maintenance

The time for maintenance of valves in this study averaged about ten minutes per valve. Maintenance during this study was restricted to tightening packing gland bolts. There was no difference in the time required to maintain block and control valves.

3.0 DETAILED RESULTS

The methodology and the results obtained from this study of the effects of maintenance on fugitive emissions are presented in this section. Statistical methods employed to analyze the data obtained are briefly presented first in Section 3.1. More detailed technical information concerning those methods is included in Appendix D. The methods are introduced first to aid the reader in following the methodology used to interpret the data presented in the subsequent sections.

Quantitative descriptions of the effects of maintenance on fugitive emissions from valves as determined in this study are presented in Sections 3.2 and 3.3. Section 3.2 presents the findings concerning immediate effects of maintenance, and Section 3.3 presents those findings for longer periods of time. Rates for occurrence of leaks in non-leaking pumps and valves and recurrence of leaks in valves which had been leaking and were repaired are presented in Sections 3.4 and 3.5. The relationship between screening values obtained with portable monitors and actual sampled leak rates is shown in Section 3.6. Finally, maintenance procedures in this study and other practices applicable to valves are discussed, and the time required in this study for maintenance of valves are presented in Section 3.7.

3.1 Statistical Concepts and Models

This section provides a brief description of the statistical methods employed in Section 3. Application of these methods is also discussed. Appendix D contains detailed discussions of these statistical methods.

3.1.1 Weighted Percent Reduction

The Weighted Percent Reduction (WPR) is an estimate of the percent that the total mass emissions were reduced due to maintenance:

$$WPR = \frac{\left(\sum^{n} \text{mass emissions before maintenance} - \sum^{n} \text{mass emissions after maintenance}\right) \times 100}{\sum^{n} \text{mass emissions before maintenance}}$$

This estimate was used to measure the effectiveness of valve maintenance based on measured leak rates (Section 3.2.1).

Confidence intervals for the WPR were constructed by fitting an appropriate t distribution after estimating the mean and variance for a ratio of random variables. These intervals were used to statistically compare the immediate effect of maintenance for the three processes and gas vs. liquid service.

3.1.2 Percent Sources Repaired

In analyzing the effect of maintenance based on screening values, the percent of sources repaired (P_r) was estimated using:

$$P_r = \frac{\text{Number of repaired sources} \times 100}{\text{Number of sources screened} \geq 10{,}000 \text{ Immediately Before Maintenance}},$$

where a repaired source refers to a source which screened below 10,000 ppmv immediately following maintenance (Section 3.2.2).

Confidence intervals for the percent of sources repaired were constructed by fitting an appropriate binomial distribution. The unknown true percent of sources in the population which would be repaired lies within the confidence limits with reasonable certainty.

3.1.3 Exponential Distribution Model

In evaluating the rate of occurrence of leaks in Section 3.4, an exponential model was used to approximate the actual distribution of the time to first occurrence of a leak. Once the occurrence rate was estimated from the data using this model, 30-day, 90-day, and 180-day occurrence rates by process for valves, pump seals, valves in gas service, valves in liquid service, block valves, and control valves were estimated. Corresponding 95% confidence intervals for the occurrence rates were also computed based on a chi-square distribution. A statistical test (F-ratio) was performed to test for significant differences in occurrence rate estimates.

In comparing the observed with the predicted occurrence rates, the empirical distribution function was computed from the data. A comparison of the plot of the empirical distribution with that of the cumulative distribution (Section 3.4) for the exponential model indicated that the exponential distribution provided an adequate model for estimating occurrence rates.

3.1.4 Mixed Distribution Models

In estimating recurrence rates of leaks after maintenance in Section 3.5, a mixed distribution model was employed. This mixed model consists of a uniform distribution for recurrence times within five days after repair and an exponential distribution for recurrence times greater than five days after repair.

Thirty-day, 90-day, and 180-day recurrence rate estimates were obtained from the model, including 95% confidence intervals, in similar fashion to the occurrence rate estimates reported in Section 3.4. A comparison of the empirical distribution with the cumulative distribution for the mixed model indicated that the mixed distribution provided an adequate model for estimating recurrence rates.

3.1.5 Correlation Coefficient

The correlation coefficient, r_{xy}, is a number between -1 and 1 which measures the strength of the linear relationship between two random variables x and y. It is applied in Section 3.6 to describe the goodness of fit of each linear regression of Log_{10} leak rate vs. Log_{10} mean screening value.

In this context, r^2_{xy} can be interpreted as the proportion of total variability of Log_{10} leak rate that is explained by Log_{10} mean screening value.

3.1.6 Analysis of Variance

The analysis of variance is a statistical technique that separates the variation that is present in a set of data into exclusive sums of squares due to one or more independent variables and then tests hypotheses about the effect of these variables on the data. The method was used to estimate the variance components described in Appendix C. A modification of this analysis, called the analysis of covariance, is described below.

3.1.7 Analysis of Covariance

The analysis of covariance is an extension of the analysis of variance that examines the joint linear relation between two variables as affected by one or more independent variables, where one of the two variables is considered the dependent variable and the other is termed the covariate. This method was applied in Section 3.6 to examine the relationship between emission rate (dependent variable) and either OVA or TLV sniffer mean screening values (covariates), as affected by process (cumene, ethylene, and vinyl acetate), service type (gas and liquid), and source type (valves and pump seals). The results of this analysis were used to determine whether the linear regression relationship between Log_{10} leak rate and Log_{10} mean screening value remained the same for various combinations of process, service type, and source type. Separate linear regression equations were subsequently fit for each combination yielding a statistically significantly different regression line for Log_{10} leak rate vs. Log_{10} mean screening value.

3.1.8 Linear Regression (Least-Squares Fit)

Linear regression refers to a statistical technique for fitting a straight line through a set of data points (pairs of values of two variables). The purpose is to be able to predict values of one variable from those of the other. The least squares criterion was used to obtain separate fitted lines for the regression of Log_{10} leak rate vs. Log_{10} mean screening value (OVA and TLV Sniffers separately), for each of the appropriate combinations of service type and source type: pump seals, valves in liquid service, and valves in gas service. See Section 3.6.

3.1.9 Scale Bias Correction Factor

A scale bias correction factor is a statistic required to obtain an unbiased estimate of the mean in the linear (original) scale when regression analysis is performed in the logarithmic scale. Its use may be illustrated by an example (Section 3.6): For pump seals, the linear regression equation for predicting Log_{10} leak rates from Log_{10} mean OVA screening value is given as:

$$Log_{10}\ (LEAK) = -5.29 + 0.88\ Log_{10}\ (Mean\ OVA).$$

and the bias correction factors were estimated to be 3.19. Converting to the linear scale, the prediction equation for the mean (non-methane) leak rate becomes:

$$Mean\ NM\ Leak\ Rate = 3.19\ (10^{-5.29})(OVA)^{0.88}$$

$$= 1.64\ (10^{-5})(OVA)^{0.88}$$

Observe that this equation is obtained from the regression equation by applying the exponential (inverse logarithm) function to both sides and them multiplying by the bias correction factor, 3.19.

3.2 Immediate Effect of Valve Maintenance

There are several ways to approach the topic of the effectiveness of maintnenace. The differentiating factor among the various approaches is the underlying question to be answered. If the question is "What is the effect of an in-service maintenance program on total emissions?", then a comparison of the total leak rate before maintenance versus the total leak rate after maintenance would be appropriate.

The question, "How well can leaking sources be maintained to screening value limits?", can be answered by examining the screening values immediately before and after maintenance.

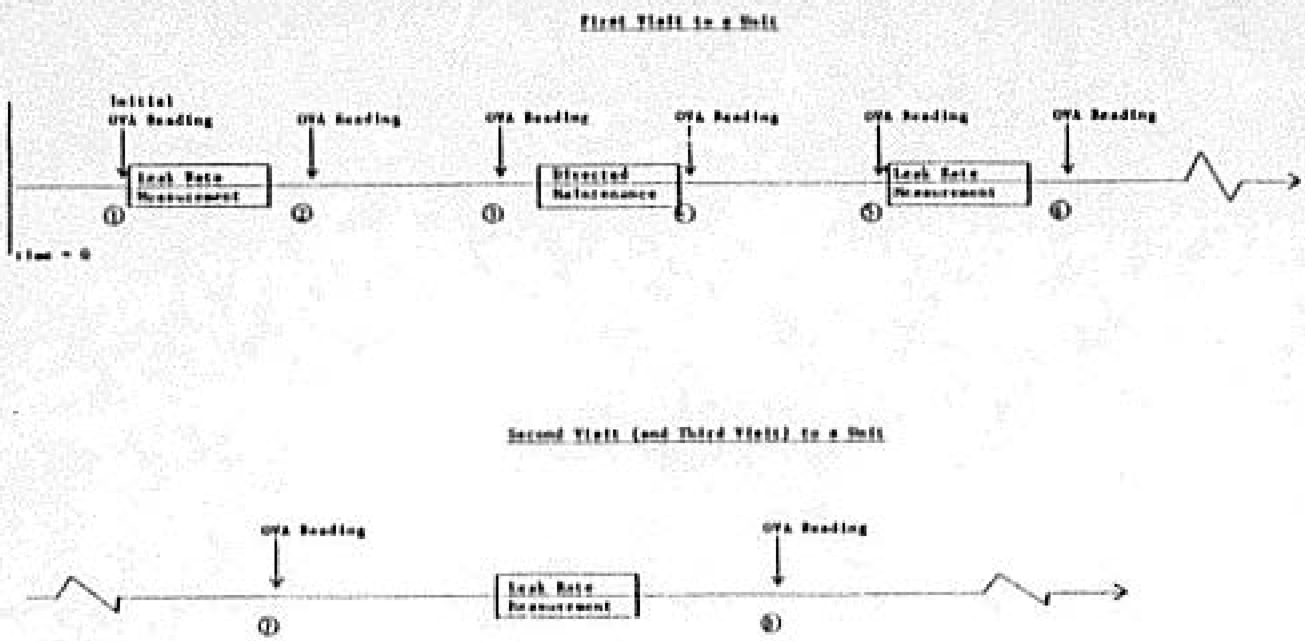
Consequently, answering either or both of these questions requires that the most appropriate measurements (screening value or leak rate) be chosen from the many data points collected. Figure 3-1 is a time line diagram showing the sequence of screening value and emissions measurements for the valves in this study. Measurements made during the second and third visits were used in evaluating the long-term effect of maintenance. The immediate effect of maintenance was evaluated using only first visit data.

3.2.1 Effectiveness of Valve Maintenance Based on Measured Leak Rates

To answer the question of "What is the effect of an in-service maintenance program on total fugitive emissions?", the weighted percent reduction (WPR) was used:

$$WPR = \frac{\left(\sum^{m} \text{Mass Emissions Before Maint.} - \sum^{m} \text{Mass Emissions After Maint.}\right)}{\sum^{m} \text{Mass Emissions Before Maint.}} \times 100,$$

where m is the number of valves maintained.



Legend

1. Initial before maintenance OVA reading.
2. After tenting, before maintenance OVA reading.
3. Before maintenance OVA reading - the screening value obtained immediately before maintenance
4. After maintenance, 1st OVA reading - the screening value obtained immediately after maintenance
5. Before tenting, after maintenance OVA reading
6. After tenting, after maintenance OVA reading
7. Before tenting OVA reading
8. After tenting OVA reading

Figure 3-1. Sequence of Emissions Measurements and Screening Values

To calculate the WPR, paired observations of measured leak rates from 155 attempts at maintenance were available. These sources were enclosed ("tented") and the mass emission rates (in pounds per hour) of total hydrocarbons were measured. Although it is not generally considered a VOC, methane was included in evaluating effectiveness of maintenance. It has been shown that the effectiveness of maintenance is virtually independent of process unit type. Therefore, it was assumed that the reduction in mass emissions due to maintenance is not dependent on the composition of the VOC being emitted. Within a few hours to a few days after the initial sampling, in-service maintenance was performed on the valves. This was followed by another sampling within a few days. The sampling methods are described in Appendix A.

Figures 3-2 and 3-3 present the resulting emissions data on logarithmic scales in two formats. Figure 3-2 is a plot of the before-maintenance leak rate versus the after-maintenance leak rate. Figure 3-3 is a plot of the difference between the before-maintenance and after-maintenance leak rates as a function of the before-maintenance leak rate. The latter plot shows two distinct groupings of observations; those where maintenance was successful (difference greater than zero) and those where the maintenance procedures appeared to worsen the leak. An examination of the many variables associated with each source failed to find reasons for the ineffectiveness of maintenance for this latter group of sources. However, for approximately one-third of these sources, the maintenance crew noted some conditions which may have prevented successful repair. Some of the conditions were:

- packing already compressed fully,
- rusted nuts, and
- gland cracked.

Weighted percent reductions were calculated for various groupings of the 155 attempts at maintenance. These WPR's are given in Table 3-1. A graphical presentation of these WPR estimates and their 95% confidence intervals is shown in Figure 3-4.

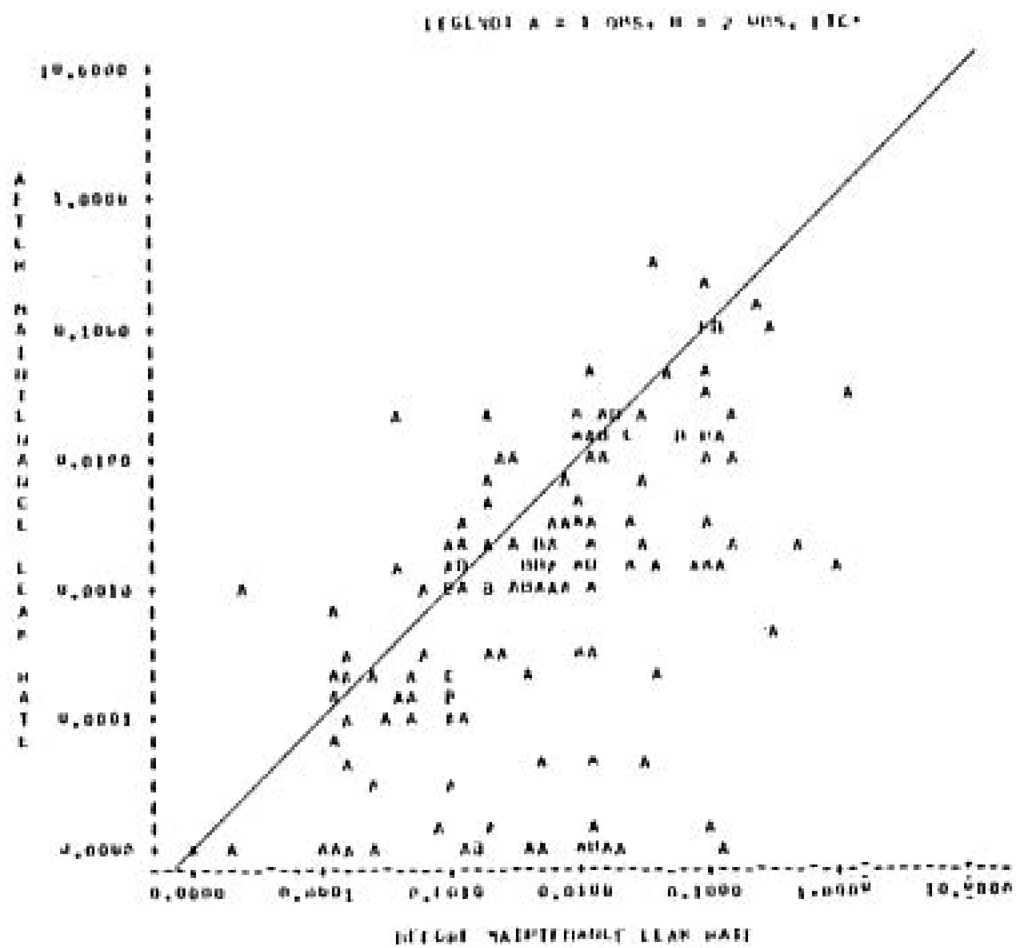


Figure 3-2. Plot of Before vs. After Maintenance Leak Rates

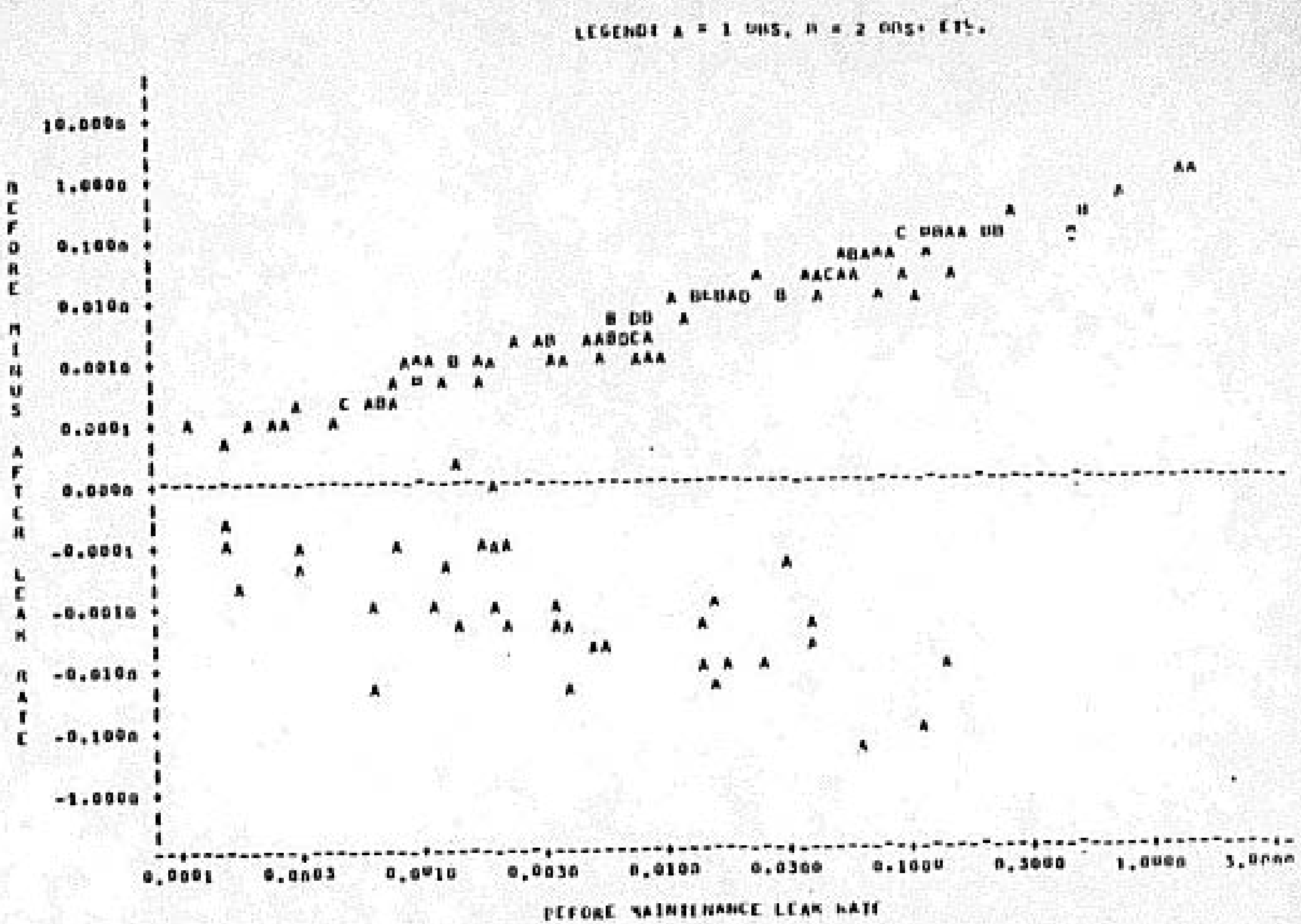
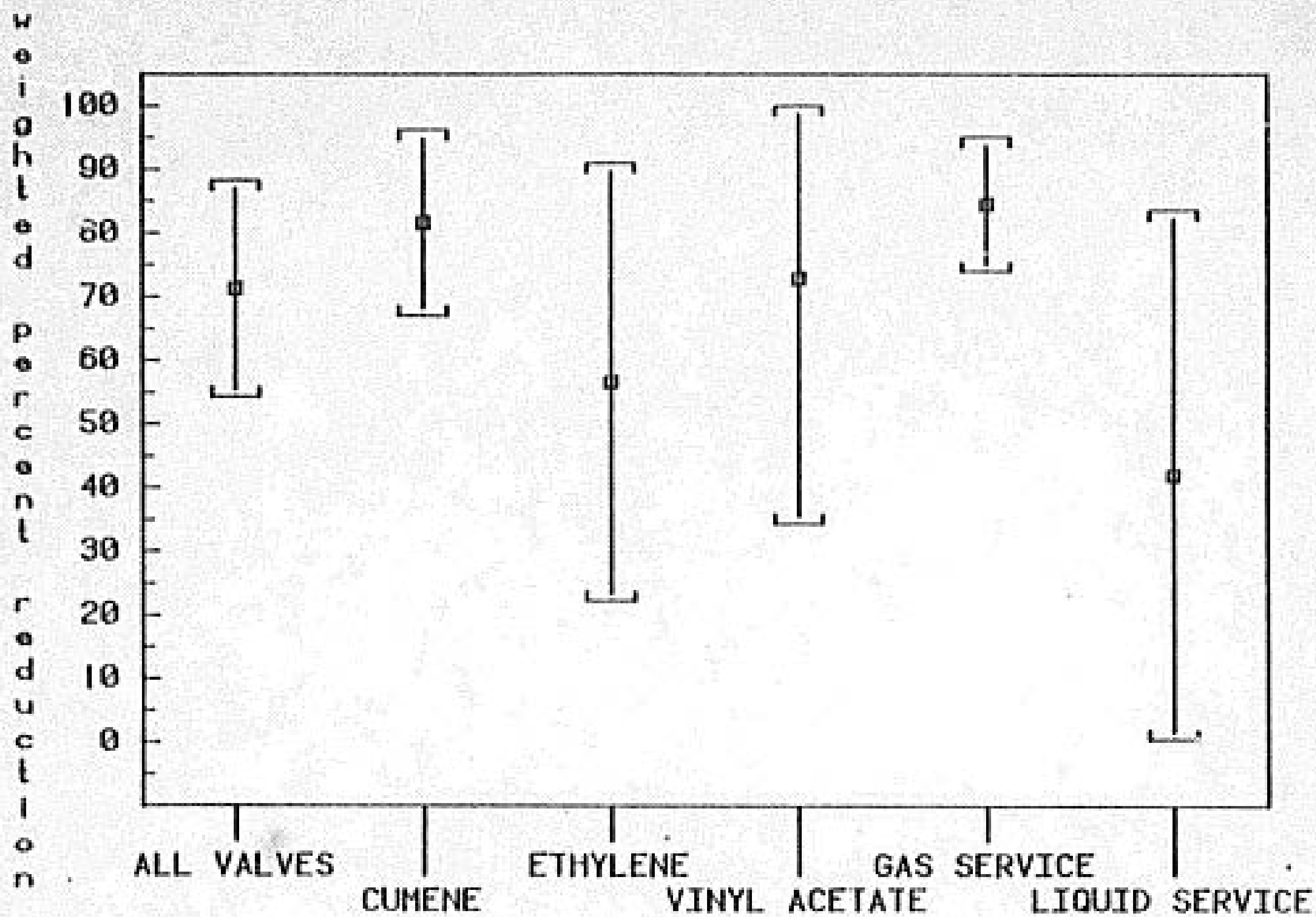


Figure 3-3. Plot of Before Minus After Maintenance Leak Rate vs. Before Maintenance Leak Rate

TABLE 3-1. IMMEDIATE EFFECT OF VALVE MAINTENANCE

	Number of Valves Maintained	Weighted Percent Reduction (WPR)	95% Confidence Limits for WPR
All Valves	155	71.3	(54, 88)
Cumene Units	54	81.6	(67, 96)
Ethylene Units	69	56.6	(22, 91)
Vinyl Acetate Units	32	72.9	(34, 100)
Gas Service Valves	71	84.5	(74, 95)
Liquid Service Valves	84	42.0	(0.4, 84)



Bracketed intervals are 95% confidence intervals.

Figure 3-4. Immediate Effect of Valve Maintenance

Since none of the WPR estimates are statistically different for any of the groupings, the overall estimate is the most appropriate estimate for application in other organic chemical units.

It was also of interest to investigate the change in the WPR estimates for varying screening action levels. Figure 3-5 is a plot of the before-maintenance OVA reading versus the reduction in measured emissions rates (pounds per hour) due to maintenance. When only valves with the immediately before maintenance screening values $\geq$10,000 ppmv were considered, the WPR estimate decreased slightly to 70.1% with a 95% confidence interval of 46% to 95%. This estimate is almost identical to the overall estimate of 71.3%. The WPR estimate for those sources where the before maintenance OVA reading was <10,000 was 82.4% with an approximate 95% confidence interval of 57% to 100%. These two WPR estimates are not statistically different.

3.2.2 Effectiveness of Maintenance Based on Screening Values

To answer the question of how well can leaking sources be maintained to screening value limits, three specific screening values for each maintained source were considered. They are the initial before-maintenance OVA reading (① on Figure 3-1), the OVA reading obtained immediately before maintenance (③ on Figure 3-1), and the OVA reading obtained immediately after maintenance (④ on Figure 3-1).

Two different analyses of these screening values were performed. The analyses were performed in a manner which would simulate two ways in which inspection/maintenance programs might be implemented. One way to implement an inspection/maintenance program would be having personnel go through the process unit screening emission sources, and then having a separate maintenance crew follow at another time to perform maintenance.

Another way in which an inspection/maintenance program might be established is by having the same crew perform screening and maintenance during one tour of the process unit.

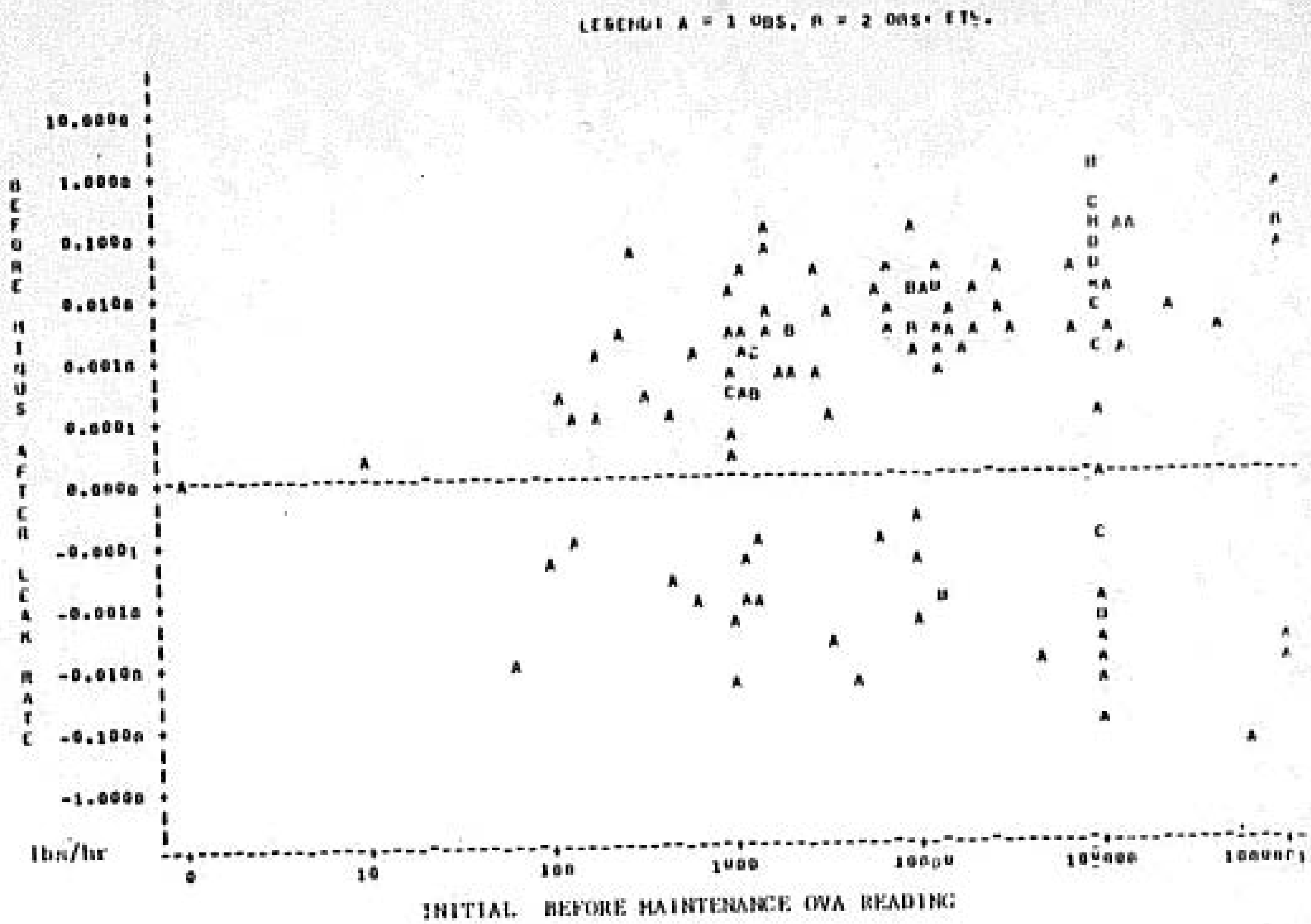


Figure 3-5. Plot of Before Maintenance OVA Reading vs. the Measured Reduction in Emissions Due to Maintenance

To analyze the effectiveness of the first type of program, comparisons were made between the initial before-maintenance OVA reading (① on Figure 3-1) and the OVA reading taken immediately after maintenance (④ on Figure 3-1). To analyze the effectiveness of a program of the second type, comparisons were made between the OVA reading taken immediately before maintenance (③ on Figure 3-1) and the OVA reading taken immediately after maintenance (④ on Figure 3-1). These comparisons are shown graphically in Figure 3-6a and b.

Tables 3-2a and b are summaries of analyses based on a screening value cut-off of 10,000 ppmv. In both cases, the percent repaired at maintenance is the percentage of those sources which screened above 10,000 ppmv and after directed maintenance, screened below 10,000 ppmv. The overall estimate for one type of maintenance program was 28.9 percent. For the other type it was 29.6 percent. These estimates can be interpreted to mean that about 70 percent of the sources could not be repaired (with the definition of repair being to screen at less than 10,000 ppmv). However, it should be pointed out that even though only about 30 percent were repaired (to action level of 10,000 ppmv), a significant reduction in emissions was achieved. (See Section 3.2.1.)

In addition to the summaries in Table 3-2, a&b for the two inspection/maintenance procedure scenarios, analyses on four screening value comparisons are given in Appendix E. Each of the screening values used in this analysis was classified in a screening range category according to the following ranges:

Screening Value (x) Range, ppmv	Category
$x = 0$	0
$1 \leq x \leq 999$	1
$1,000 \leq x \leq 9,999$	2
$10,000 \leq x \leq 49,999$	3
$50,000 \leq x$	4

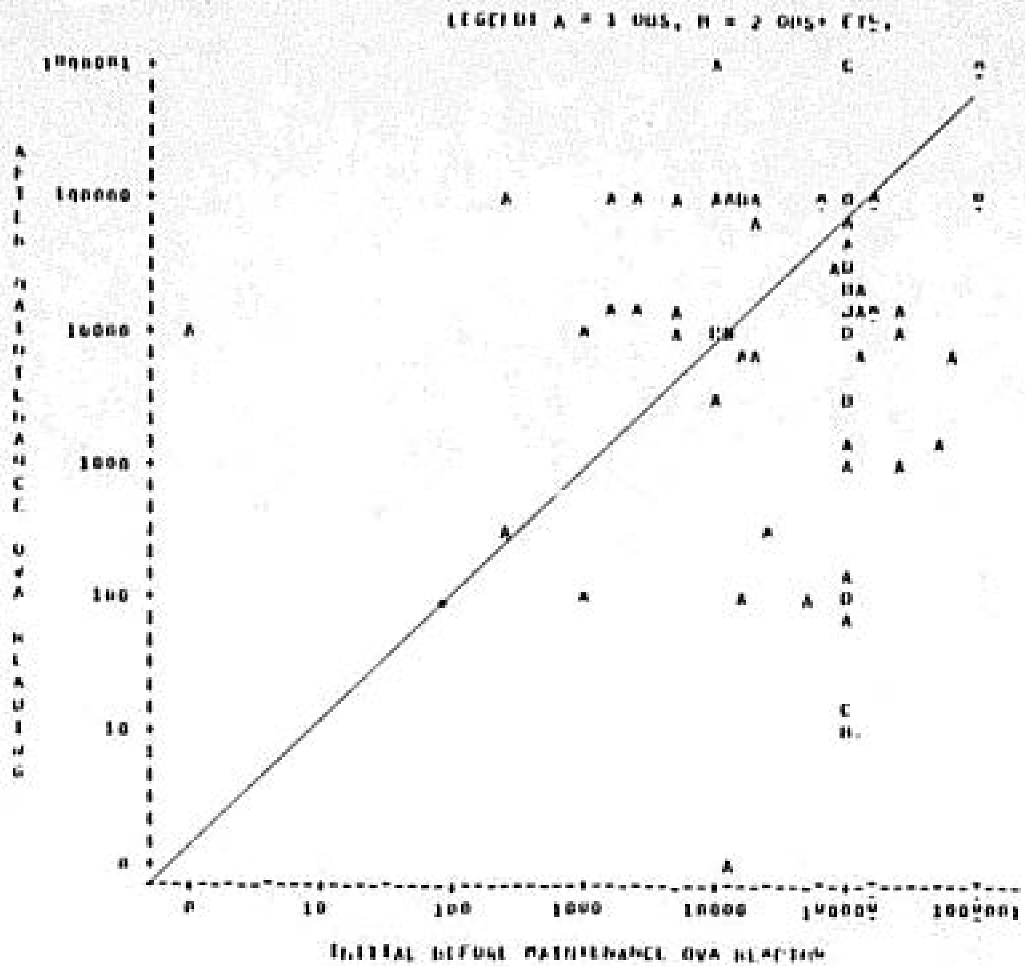


Figure 3-6a. Plot of Initial Before Maintenance vs. After Maintenance OVA Reading*

*Only for sources where the immediately before maintenance OVA reading ≥10,000 ppmv.

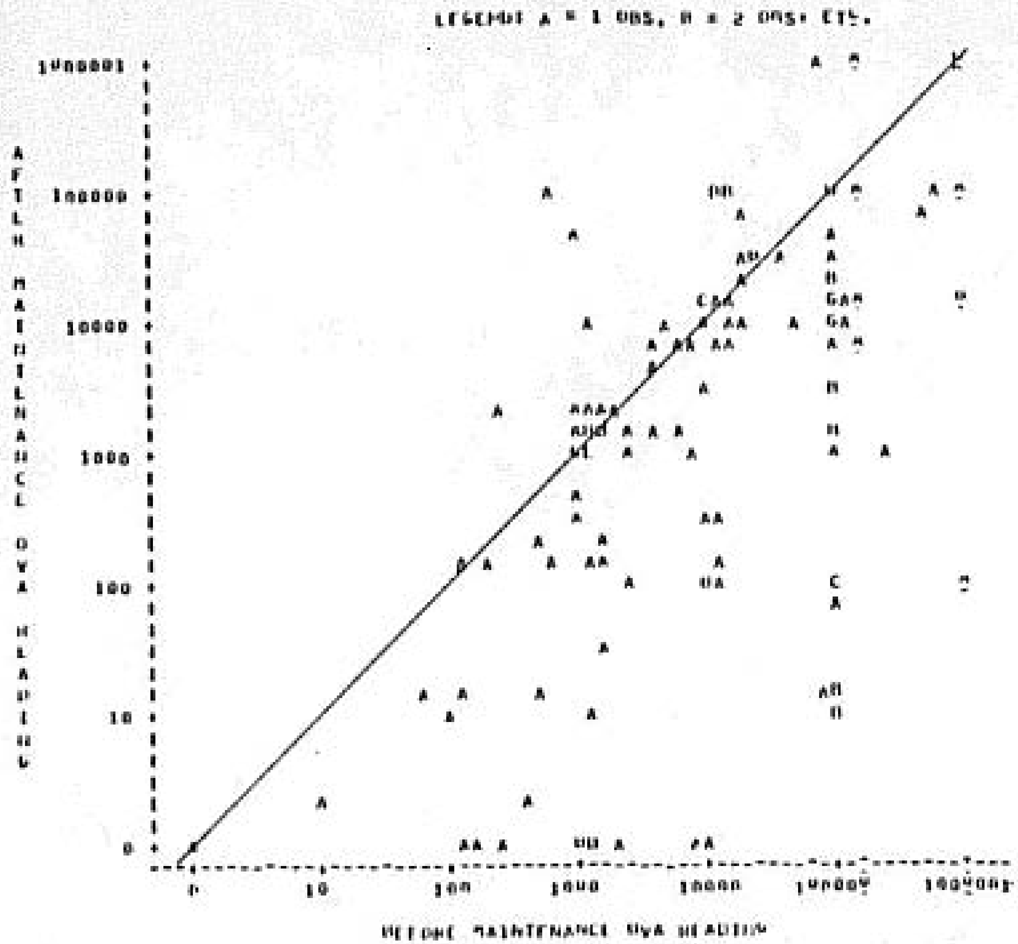


Figure 3-6b. Plot of the Before vs. After Maintenance OVA Readings

TABLE 3-2a. PERCENT OF VALVES REPAIRED* BASED ON INITIAL SCREENING VS. IMMEDIATELY AFTER MAINTENANCE** SCREENING VALUES

	Number of Valves Screening ≥ 10,000 at Initial Screening	Percent Repaired* at Maintenance	95% Confidence Interval on Percent Repaired*
All Valves	81	29.6	(20, 41)
Cumene	29	27.6	(13, 47)
Ethylene	38	26.3	(13, 43)
Vinyl Acetate	14	42.9	(18, 71)
Gas Service	40	32.5	(19, 49)
Liquid Service	41	26.8	(14, 43)
Block Valves	50	36.0	(23, 51)
Control Valves	31	19.4	(8, 38)

*Repaired means the source screened below 10,000 ppmv on the after-maintenance OVA reading.

**Only sources where the immediately before maintenance screening value was ≥10,000 ppmv.

Note: the percent repaired estimates for the various breakdowns are not statistically different at the 0.05 level of significance.

TABLE 3-2b. PERCENT OF VALVES REPAIRED* BASED ON IMMEDIATELY BEFORE AND AFTER MAINTENANCE SCREENING VALUES

	Number of Valves Screening ≥ 10,000 Immediately Before Maintenance	Percent Repaired* at Maintenance	95% Confidence Interval on Percent Repaired*
All Valves	97	28.9	(20, 39)
Cumene	32	25.0	(12, 43)
Ethylene	48	22.9	(12, 37)
Vinyl Acetate	17	52.9	(28, 77)
Gas Service	44	31.8	(19, 48)
Liquid Service	53	26.4	(15, 40)
Block Valves	58	36.2	(24, 50)
Control Valves	39	18.0	(7, 34)

*Repaired means the source screened below 10,000 ppmv on the after-maintenance OVA reading.

Note: the percent repaired estimates for the various breakdowns are not statistically different at the 0.05 level of significance.

To allow an assessment of the effects of different action levels on the number of valves which can be repaired, two-way tables were constructed using these screening value categories. The two-way tables show the following comparisons.

- Immediately before maintenance screening values versus the immediately after maintenance screening values

This comparison can be used to evaluate an inspection/maintenance program where the inspection team also performs the maintenance.

- Initial before maintenance screening values versus screening values obtained immediately before maintenance

This comparison can provide information concerning the percent of valves which cross an action level without maintenance.

- Initial before maintenance screening values versus screening values obtained immediately after maintenance

This comparison is useful in evaluating the effect of maintenance on reducing the percent of leaking sources if the level of the immediately before maintenance screening value is ignored.

- Initial before maintenance screening value versus screening values obtained immediately after maintenance only for those sources where the immediately before maintenance screening value is greater than or equal to 10,000 ppmv

This comparison provides an indication of the effect of an inspection/maintenance program where the maintenance crew follows the screening crew by several days.

The tables are presented in Appendix E and were constructed to allow analysis by the following breakdowns:

- overall,
- process type (Cumene, Ethylene, Vinyl Acetate),
- service (gas liquid), and
- valve type (block, control).

3.3 Long-Term Effect of Maintenance on Emissions

Valves that underwent maintenance in this study were observed periodically for up to eight months. Selected valves were resampled during this period to assess the long-term effects of maintenance on emission rates. This part of the study was not directly related to the main objectives of the program as described in the introduction. However, the effect of an in-service maintenance program on emissions over periods of several months is of obvious interest to all concerned.

To put the long-term effect of maintenance into perspective, it is helpful to compare the emissions from the maintained valves to those from a control group of unmaintained valves over a period of time. Figures 3-7 and 3-8 are graphic displays of this comparison.

Figure 3-7 shows the average emission rate in pounds per hour of fugitive emissions per source for three separate time categories. For a source to be selected for the analysis shown in Figure 3-7, it had to have a measured leak rate in each time category. The exception to this rule was for sources in the control group. Valves in the control population were not required to have an observtion in the "after maintenance" category since they were not maintained. In the first category, "initial samples", the average leak rates for 126 sources to be maintained and 60 sources designated as controls are displayed. In the second category, "after maintenance", the average leak rate of the 126 maintained sources immediately after maintenance is shown. Naturally, there are no observations for the control group for this category. In the third category, "21 to 225 days", the average leak rates for the 126 and 60 sources, measured at least 20 days after the initial sampling, are shown. In this category, the median sampling day since the initial sampling for the control group is 77 days. For the maintained group the median day since initial sampling is 110 days. The ranges of the days since initial sampling for the two groups are 21 to 216 and 41 to 225, respectively.

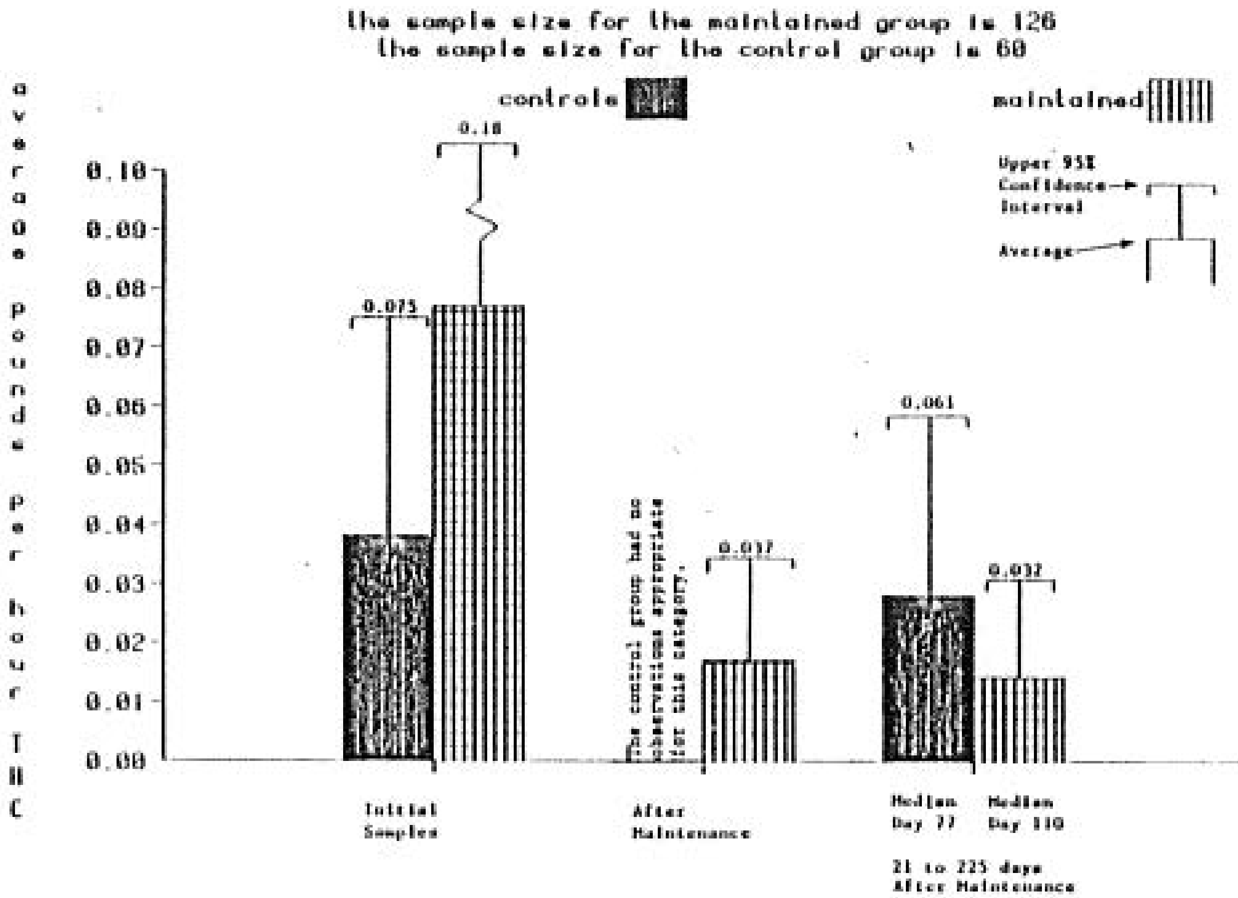


Figure 3-7. Long-Term Effect of Maintenance vs. Control Group

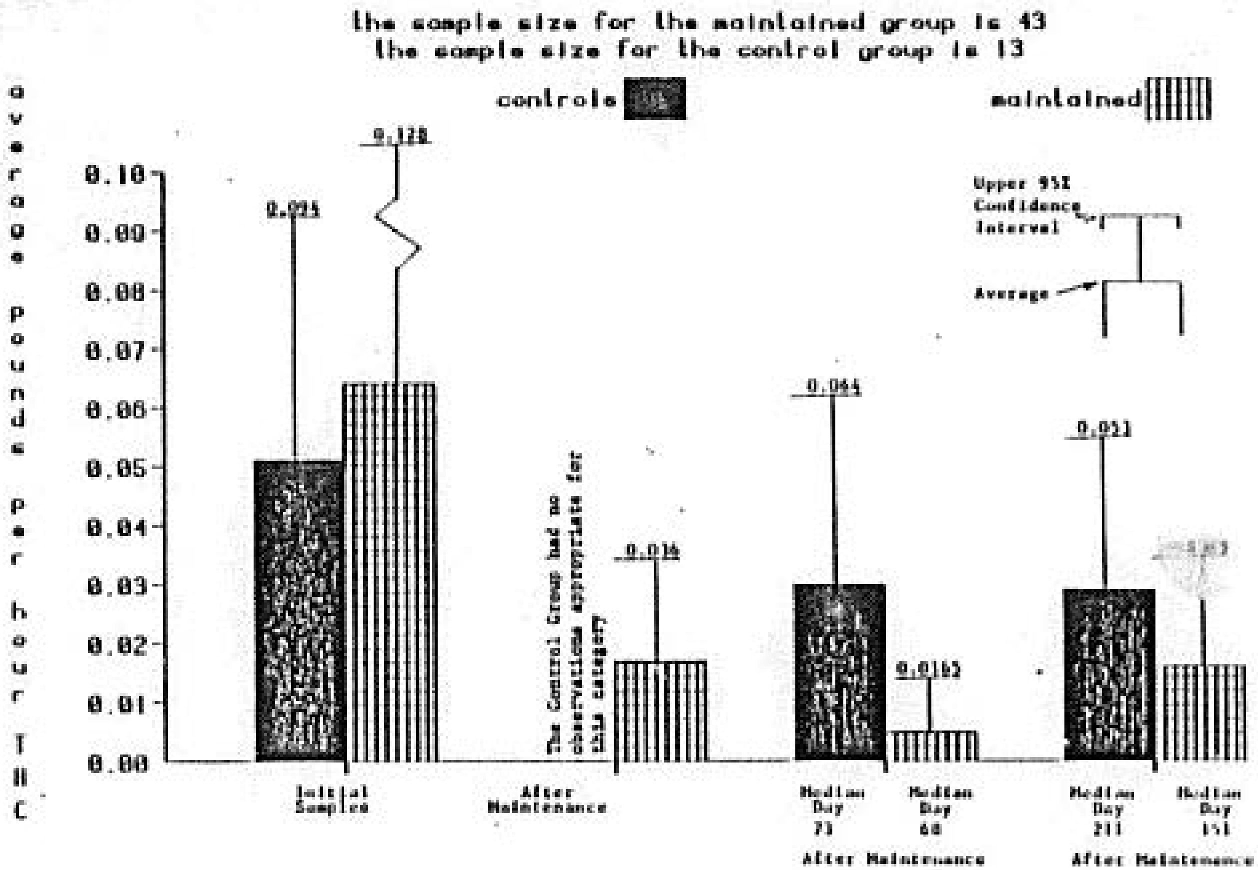


Figure 3-8. Long-Term Effect of Maintenance vs. Control Group

To provide a statement of confidence on the estimate of the average emission rate in Figures 3-7 and 3-8, an estimate of sampling variations, 23% (see Appendix C) was applied to each observation. It is appropriate to apply the estimate of sampling error (23%) to each measurement rather than a measure of source-to-source variability, since pairing of observations over time made source-to-source variability irrelevant. Since the same group of sources is sampled in each time category, the only source of variation pertinent to comparing the same group of sources over time is the sampling variation. The confidence limits displayed in Figures 3-7 and 3-8 are approximate, one-sided 95% confidence limits.

Figure 3-8 is similar to Figure 3-7 except that an attempt has been made to break the "21 to 225 days" category into two sub-categories. The sub-categories were defined to provide a higher resolution analysis of valve emission behavior over time. The major problem in this redefining of the time dimension is a reduction in sample size. Only 13 control sources could be matched into three sampling periods (initial, 15 to 105 days, and over 105 days). Only 43 maintained sources could be matched for the necessary four sampling periods (initial, after maintenance, 15 to 105 days, and over 105 days). The division at 105 days was selected to obtain the maximum number of sources in both groups.

The major conclusion that can be drawn from Figures 3-7 and 3-8 is that the immediate effect of maintenance discussed in Section 3.2 was sustained for the duration of the project. The minor changes in the control group and the maintenance group after the initial sampling visit (during which the maintenance occurred) are not statistically significant.

3.4 Occurrence of Leaks

The rate of occurrence of leaks was studied using pumps and valves that initially screened at <10,000 ppmv and were not maintained during the project. An exponential model was fit to the data in order to develop occurrence rate estimates. The resulting 30-day estimate for valves is 1.3% with a 95% confidence interval of 0.7% to 2.1%. For pumps, the 30-day estimate is 5.5% with a 95% confidence interval of 2.2% to 10%.

To evaluate the rate of occurrence of leaks, an exponential model was used to approximate the actual distribution of the time to first occurrence of a leak (screening value ≥10,000 ppmv). This model is widely used to summarize data similar in nature to leak occurrences if the assumption can be made that the occurrence rate remains constant. A major advantage of the exponential model over other statistical distribution models is that a single parameter fully and completely describes a given exponential distribution (see Appendix D for more detail).

The estimate of this single parameter (designated as λ) for the type of data obtained in this study is

$$\lambda = \frac{\text{number of leaks that occurred}}{\sum_{i=1}^{n} \text{Total time source } i \text{ was followed}}$$

where n = number of sources followed.

For purposes of this analysis a leak from a source was defined as having occurred if it initially screened <10,000 ppmv and at some later date screened ≥10,000 ppmv. Data on the occurrence of leaks were gathered from two separate groups of sources. Sources in a control group that initially screened between 1,000 - 10,000 ppmv were combined with the "low leaker" group (0 - 1,000 ppmv) in the development of occurrence rate estimates.

Combining the groups required proper weighting of the data in each group, based on the actual distribution of screening values. For each process and each source type, the fraction of all sources with screening values between 0 and 1,000 ppmv and between 1,000 and 10,000 ppmv were obtained from the complete screening of the plants documented in Reference 2. These fractional values appear in Appendix D. They were used in computing estimates of the occurrence rates and approximate upper and lower 95% confidence limits for these estimates (see Appendix D for more detail).

Tables 3-3 through 3-5 show the estimated 30-day, 90-day, and 180-day occurrence rates by process for valves, pump seals, valves in gas service, valves in liquid service, block valves, and control valves. For example, from Table 3-3 it is estimated that 29.0% of the pump seals will screen greater than or equal to 10,000 ppmv after 180 days. The confidence interval for this estimate is 13% to 47%. Apart from the estimates themselves, the main result is that pump seals have a statistically significant higher rate of occurrence than do valves.

Plots of the cumulative distribution functions are shown in Figures 3-9 through 3-14. The predicted occurrence rate for periods up to eight months can be obtained directly from these curves. The fact that the curves are not straight lines is a consequence of the effectively decreasing population size, since sources which begin leaking are no longer included in the population. It should be kept in mind that the underlying occurrence rates are always assumed to be constant, however.

As a check on the model, the observed and predicted occurrence rates were compared. The empirical distribution function (the actual data) was computed as

$$\bar{\bar{F}}(t) = 100 \times \frac{\text{Number of occurrences at time} \leq t}{\text{Number of sources observed over time } (0,t)}$$

The derivation of the denominator is explained in Appendix D.

TABLE 3-3. OCCURRENCE* RATE ESTIMATES FOR VALVES AND PUMPS BY PROCESS

	Number of Sources Followed							
	x < 1,000 ppmv	1,000 ≤ x < 10,000	30-Day Estimate	95% Confidence Interval	90-Day Estimate	95% Confidence Interval	180-Day Estimate	95% Confidence Interval
VALVES								
Cumene units	136	4	1.9	(0.2, 5.9)	5.6	(0.6, 17)	10.8	(1.3, 30)
Ethylene units	284	13	2.0	(0.9, 3.6)	6.0	(2.7, 10)	11.6	(5.3, 20)
Vinyl Acetate units	209	5	0.3	(0.0, 0.6)	0.8	(0.1, 1.9)	1.5	(0.3, 3.8)
All Units	629	22	1.3	(0.7, 2.1)	3.8	(2.0, 6.0)	7.4	(4.0, 12)
PUMPS								
Cumene units	12	3	5.8	(0.7, 20)	16.3	(2.1, 49)	30.0	(4.2, 74)
Ethylene units	31	2	18.4	(2.8, 42)	45.7	(8.2, 81)	70.5	(16, 96)
Vinyl Acetate units	39	2	2.8	(0.8, 6.2)	8.1	(2.2, 17)	15.6	(4.4, 32)
All Units	82	7	5.5	(2.2, 10)	15.7	(6.6, 27)	29.0	(12, 47)

*A leak from a source was defined as having occurred if it initially screened <10,000 ppmv and at some later date screened ≥10,000 ppmv.

TABLE 3-4. OCCURRENCE* RATE ESTIMATES FOR VALVES IN GAS AND LIQUID SERVICE BY PROCESS

	Number of Sources Followed**							
	x <1,000 ppmv	1,000 ≤ x <10,000	30-Day Estimate	95% Confidence Interval	90-Day Estimate	95% Confidence Interval	180-Day Estimate	95% Confidence Interval
GAS SERVICE								
Cumene units	59	2	2.8	(0.1, 9.5)	8.3	(0.4, 29)	15.9	(0.9, 45)
Ethylene units	123	6	0.9	(0.3, 2.6)	2.6	(0.9, 7.5)	5.1	(1.9, 15)
Vinyl Acetate units	46	3	0.7	(0.1, 1.9)	2.0	(0.2, 5.6)	4.0	(0.5, 11)
All Units	228	11	1.0	(0.4, 2.0)	3.1	(1.2, 6.0)	6.1	(2.4, 12)
LIQUID SERVICE								
Cumene units	77	2	0.6	(0.1, 10)	1.7	(0.2, 28)	3.4	(0.4, 48)
Ethylene units	130	7	4.1	(1.5, 7.8)	11.9	(4.5, 22)	22.4	(8.8, 39)
Vinyl Acetate units	63	2	0.2	(0, 1.0)	0.6	(0, 3.0)	1.3	(0, 5.9)
All Units	270	11	2.4	(1.2, 4.0)	7.0	(3.6, 11)	13.6	(7.1, 22)

*A leak from a source was defined as having occurred if it initially screened <10,000 ppmv and at some later date screened ≥10,000 ppmv.

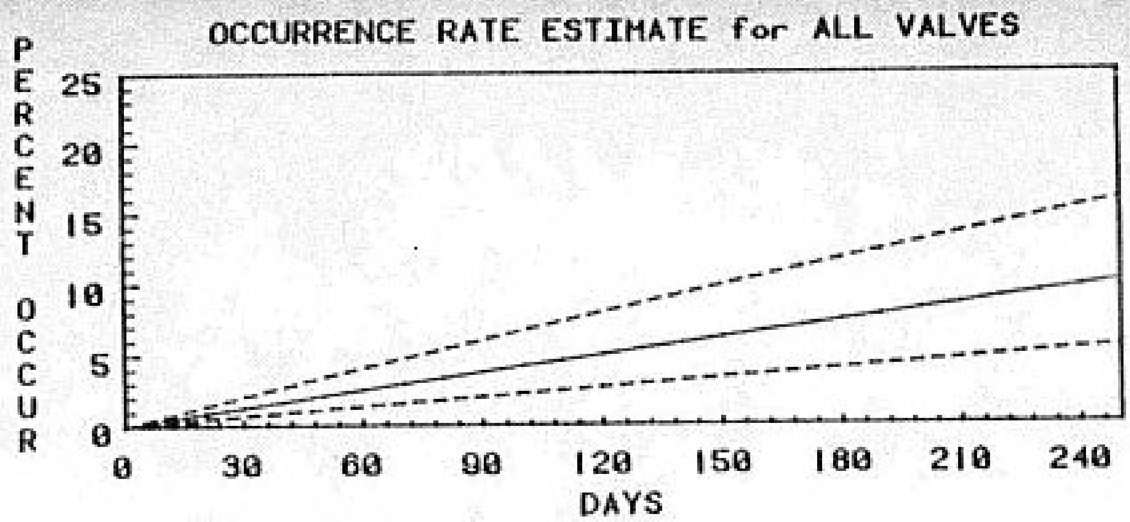
**Unit I sources were not identified by service type and therefore not included in this count.

TABLE 3-5. OCCURRENCE* RATE ESTIMATES FOR BLOCK AND CONTROL VALVES BY PROCESS

	Number of Sources Followed**							
	x <1,000 ppmv	1,000 ≤x <10,000	30-Day Estimate	95% Confidence Interval	90-Day Estimate	95% Confidence Interval	180-Day Estimate	95% Confidence Interval
BLOCK VALVES								
Cumene units	110	4	2.0	(0.3, 6.2)	6.0	(0.8, 18)	11.7	(1.5, 32)
Ethylene units	129	7	2.3	(0.8, 4.8)	6.9	(2.3, 14)	13.3	(4.6, 26)
Vinyl Acetate units	69	4	0	(0, 0.7)	0	(0, 2.1)	0	(0, 4.1)
All Units	308	15	1.2	(0.5, 2.2)	3.6	(1.6, 6.5)	7.0	(3.1, 13)
CONTROL VALVES								
Cumene units	25	0	0	(0, 2.6)	0	(0, 7.5)	0	(0, 15)
Ethylene units	123	6	1.7	(0.4, 3.9)	5.0	(1.2, 11)	9.7	(2.5, 21)
Vinyl Acetate units	40	1	1.3	(0.2, 3.2)	3.7	(0.7, 9.3)	7.3	(1.3, 18)
All Units	188	7	1.6	(0.5, 3.2)	4.6	(1.6, 9.3)	9.0	(3.1, 18)

*A leak from a source was defined as having occurred if it initially screened <10,000 ppmv and at some later date screened ≥10,000 ppmv.

**Unit 1 sources were not identified by valve type and therefore not included in this count.



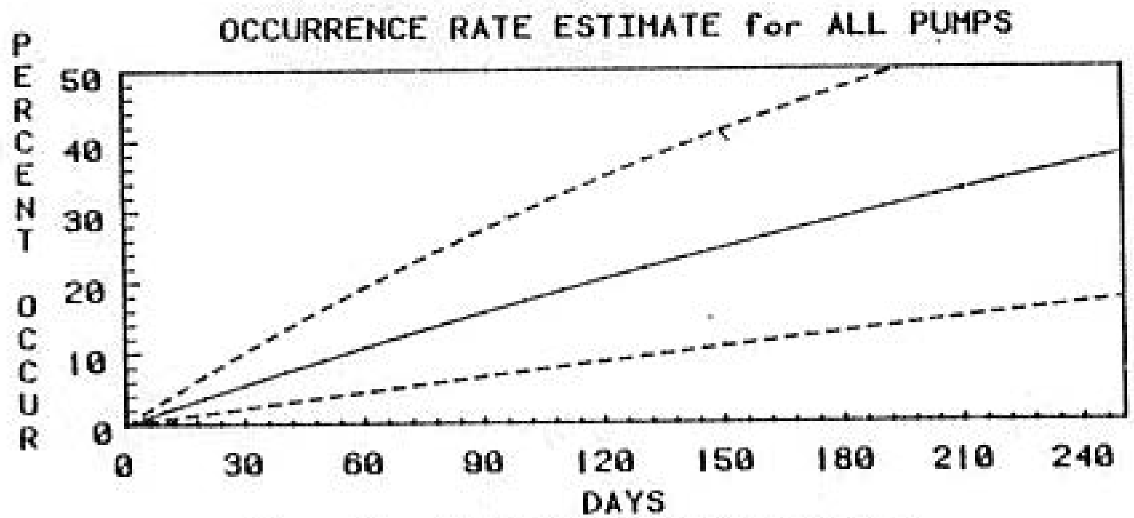


Figure 3-9. Overall Occurrence Rate Estimates

Note: Dashed lines indicate 95% confidence region.

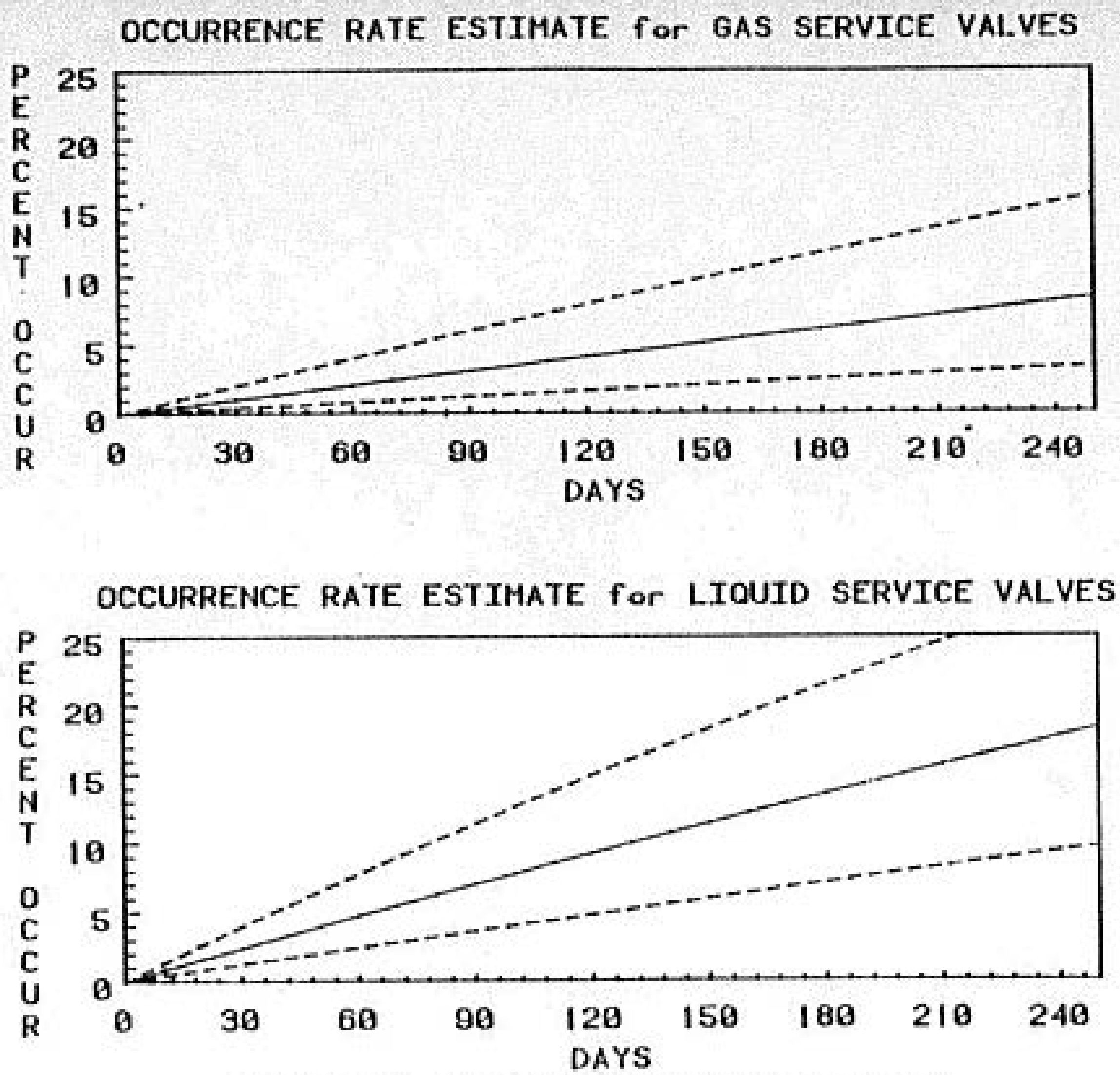


Figure 3-10. Occurrence Rate Estimates by Service

Note: Dashed lines indicate 95% confidence region.

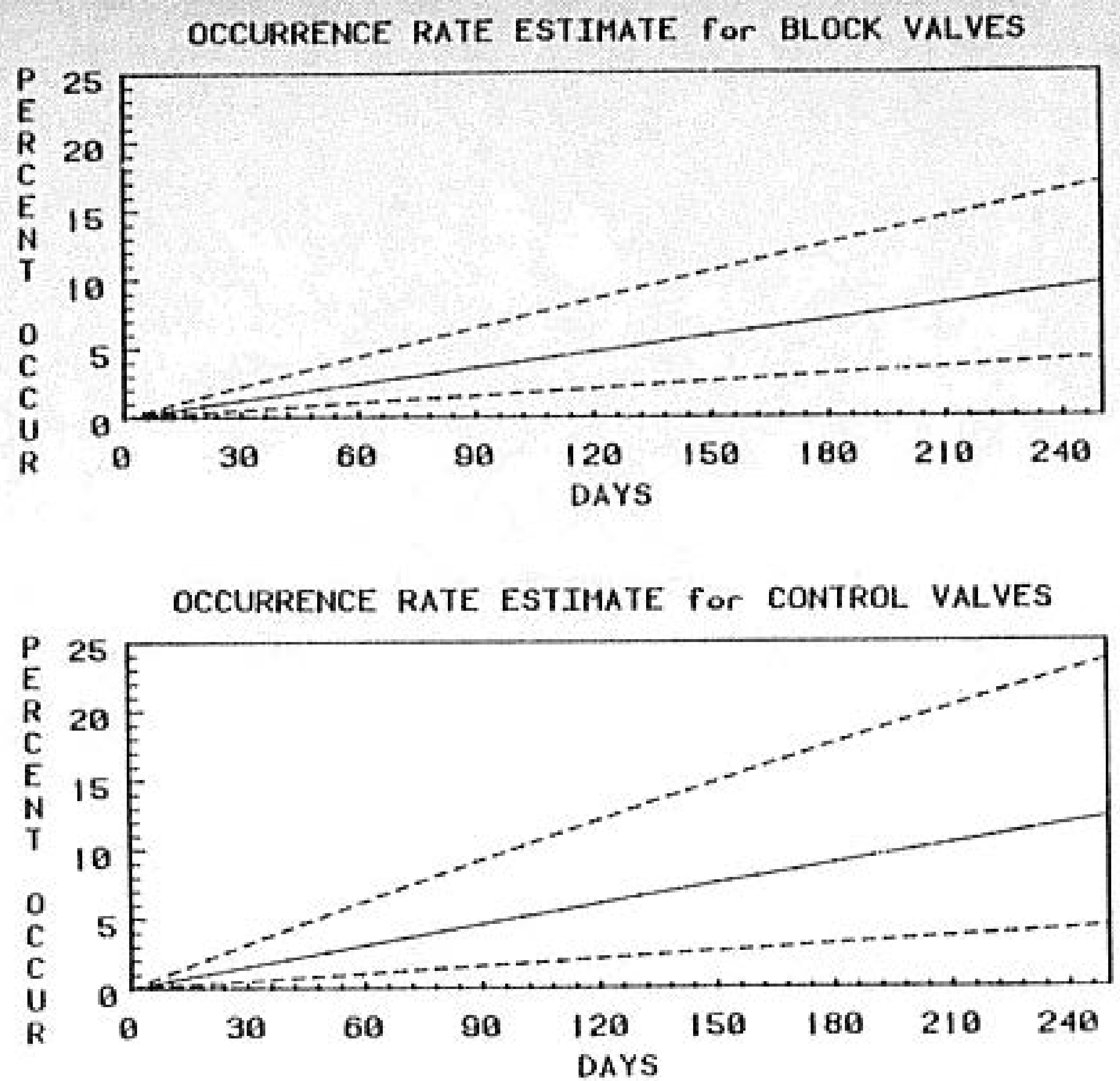
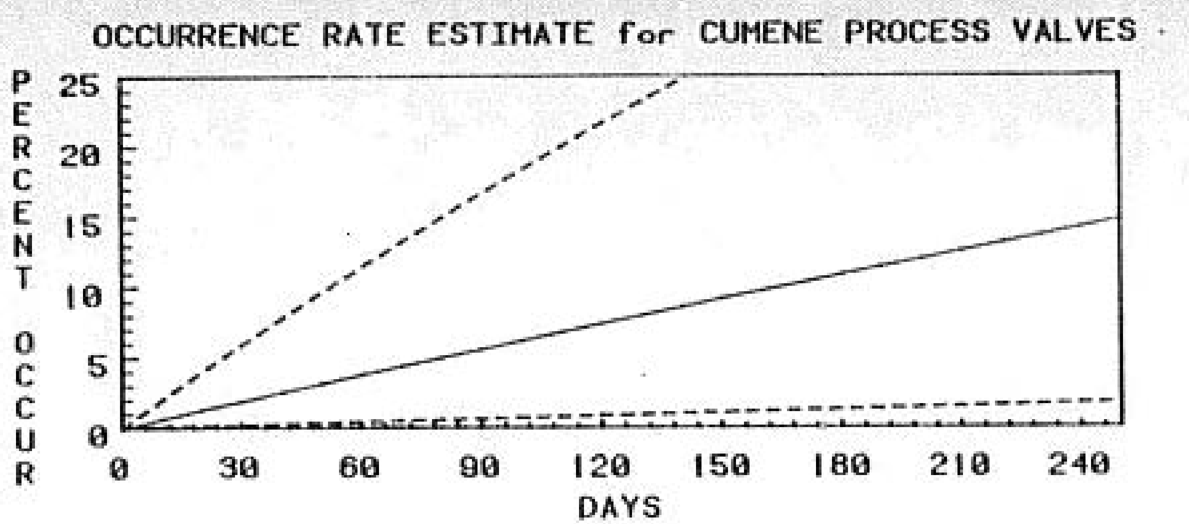


Figure 3-11. Occurrence Rate Estimate by Valve Type

Note: Dashed lines indicate 95% confidence region.



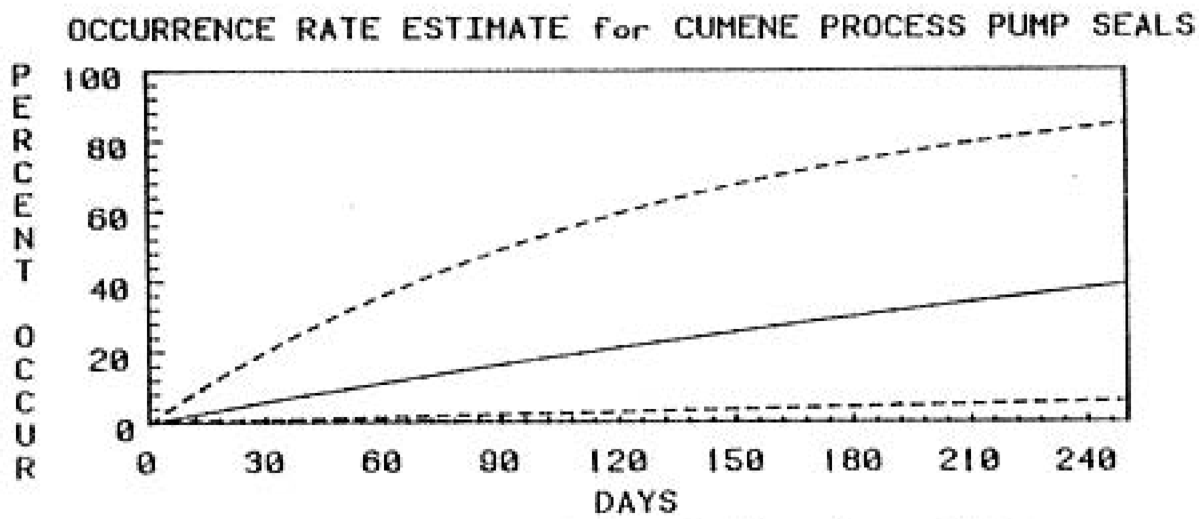


Figure 3-12. Occurrence Rate Estimate for Cumene Process Units

Note: Dashed lines indicate 95% confidence region.

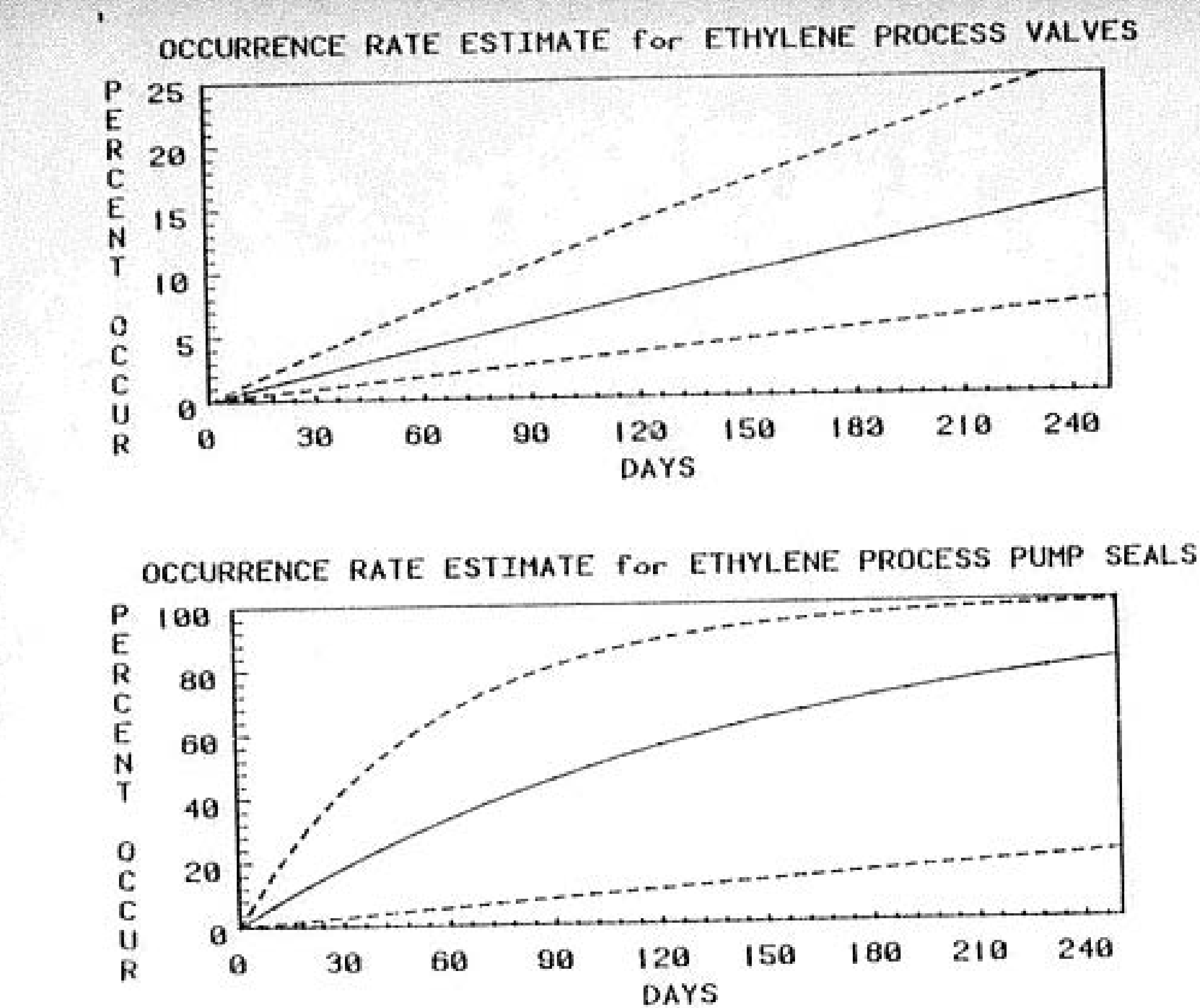


Figure 3-13. Occurrence Rate Estimate for Ethylene Process Units

Note: Dashed lines indicate 95% confidence region.

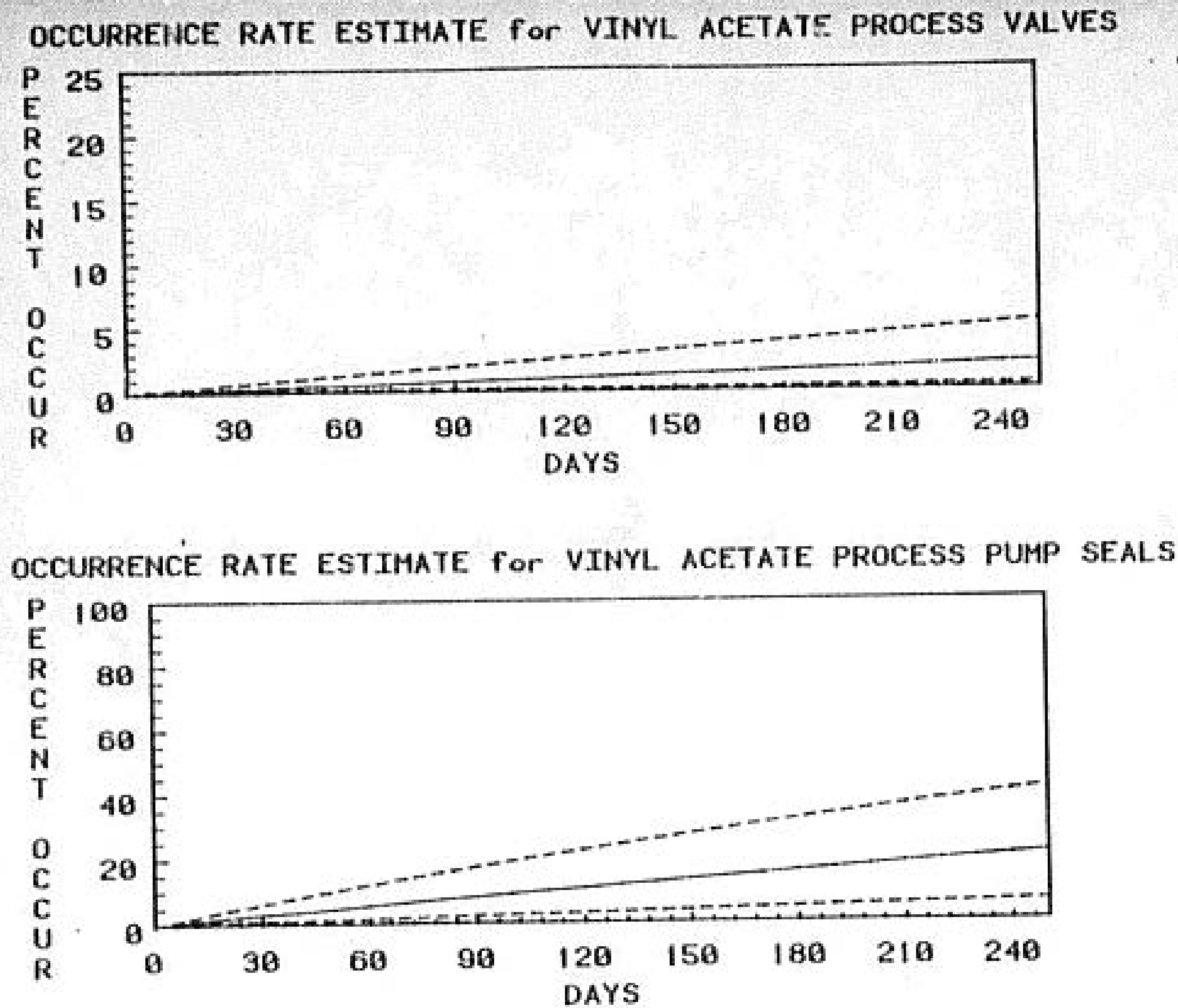
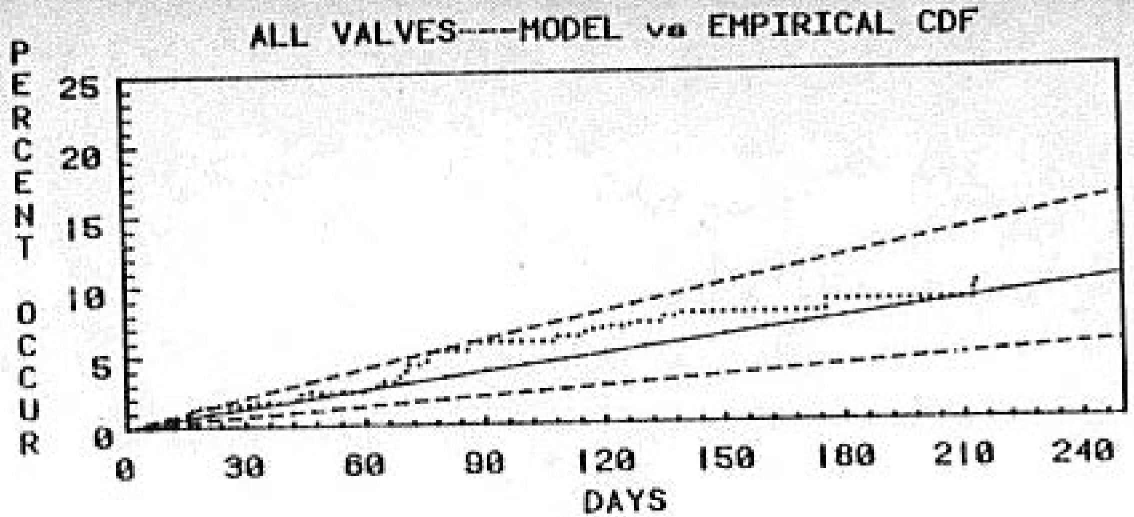


Figure 3-14. Occurrence Rate Estimate for Vinyl Acetate Process Units

Note: Dashed lines indicate 95% confidence region.

The resulting comparisons for valves and pumps are shown in Figure 3-15. The empirical distribution function is shown as a stair-step function, and the predicted models are the same as shown in Figure 3-8. Although the figure shows that the data stay above the predicted line for most of the time, most of the observations (steps) are within the 95% confidence regions (dashed lines). It was therefore, felt that the exponential distribution provided an adequate model for evaluating occurrence rates.

A statistical test was used to evaluate pairwise differences in occurrence rate estimates (see Appendix D for detail of the test). Table 3-6 presents the results of this analysis. The statistical tests showed that pump seals have a higher occurrence rate than valves. Similarly, valves in liquid service have a higher occurrence rate than those in gas service. Valves in the vinyl acetate process units have a lower occurrence rate than both those in ethylene process units and those in cumene process units. The pump seals in vinyl acetate units have a lower occurrence rate than the pump seals in the ethylene units.



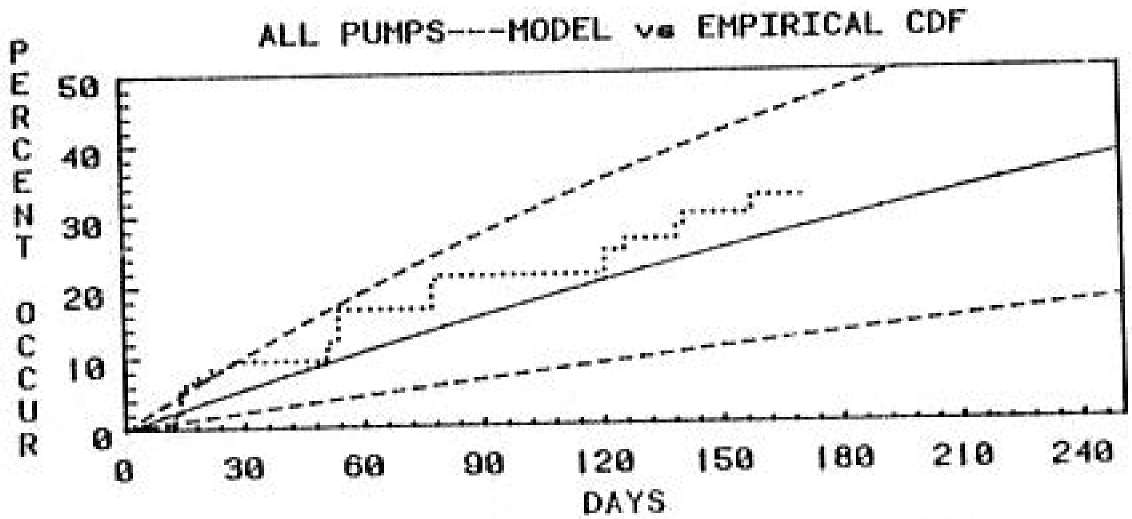


Figure 3-15. Occurrence Rate Estimate vs. Empirical CDF

Note: Dotted line is plot of actual data.

TABLE 3-6. SUMMARY OF RESULTS ON PAIRWISE COMPARISON OF OCCURRENCE RATE ESTIMATE

Test Grouping	Categories Being Tested for Statistically Different Occurrence Rates	Result of Test at the 0.05 Significance Level[a] for Each Test Grouping
1	Valves vs. Pump Seals	Significant
2	Block vs. Control Valves	Not Significant
3	Valves in Gas vs. Liquid Service	Significant
4	Valves - Ethylene vs. Cumene	Not Significant
	Valves - Ethylene vs. Vinyl Acetate	Significant
	Valves - Cumene vs. Vinyl Acetate	Significant
5	Pumps - Ethylene vs. Cumene	Not Significant
	Pumps - Ethylene vs. Vinyl Acetate	Significant
	Pumps - Cumene vs. Vinyl Acetate	Not Significant

[a]Means the probability of incorrectly classifying a difference within a category as significant.

3.5 Recurrence of Leaks

To study the recurrence of leaks after maintenance, data from the 155 attempts at maintenance were examined. Of these 155 attempts, 97 cases screened ≥10,000 ppmv immediately before maintenance. For this analysis, only those valves which screened ≥10,000 ppmv immediately before maintenance and screened <10,000 ppmv immediately after maintenance were considered as having a potential to recur. This eliminated all but 28 valves from the analysis. Of these 28 valves, eight were seen to recur (i.e., screen ≥10,000 ppmv at some time following the after-maintenance screening). Of the eight valves whose leaks recurred, four recurred within a few days after maintenance. The other four recurrences were spread over the study period (up to 7 months). Because of the two distinct groupings of recurrences over time, a mixed-model was used in estimating the recurrence rate. The exact form of the model used is described in Appendix D.

A graphical presentation of the modeled percentages for recurrence along with an approximate 95% confidence region is given in Figure 3-16. The empirical distribution function (actual data) is indicated by the dotted line.

In Table 3-7, 30-day, 90-day, and 180-day recurrence rate estimates are given along with their approximate 95% confidence limits. In comparison to occurrence rates, recurrence rates are much higher.

TABLE 3-7. VALVE LEAK RECURRENCE RATE ESTIMATES

	Recurrence Rate Estimate	95% Confidence Limits on the Recurrence Rate Estimate
30-day	17.2%	(5, 37)
90-day	23.9%	(7, 48)
180-day	32.9%	(10, 61)

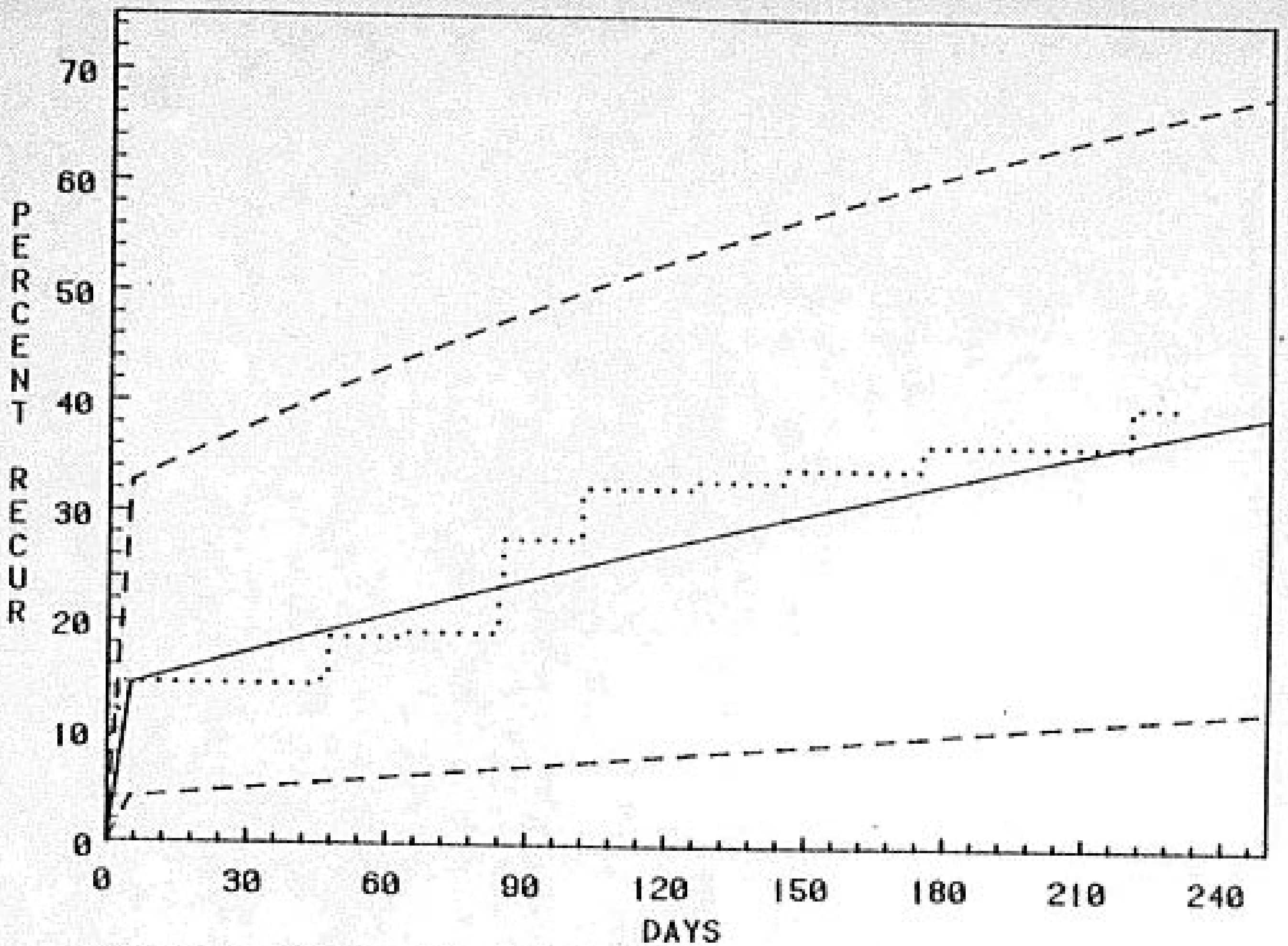


Figure 3-16. Recurrence Rate Estimate vs. Empirical Distribution Function

Note: Dotted line is actual data.
Dashed lines indicate a 95% confidence region.

3.6 Modeled Relationship - Leak Rate vs. Screening Value

To investigate the relationship between screening values and emission rates, a representative screening value was first chosen. Since two screening values for both the OVA and TLV Sniffer were taken with each sample, a more precise estimate of the relationship (model) could be developed using the means of the screening values. Therefore, the mean of the OVA readings and the mean of the TLV Sniffer readings were chosen as the representative screening values and were used in the model development.

The occurrence of zero screening values with large leak rates and large screening values with zero leak rates was investigated. Checks were made with field personnel and the original data sheets were reviewed in each of these cases. In some instances valves that had high screening values with zero leak rates also had very high ambient HC readings at the time of sampling. These cases account for many spurious points. Also, screening values of 10 ppmv and below are often inaccurate because of background concentrations. Screening value to emission rate relationships which include zero points are not usually of interest. That is, the range of interest for screening values is from about 1,000 to 1,000,000 ppmv. Another difficulty with using data points where either the screening value is zero or the measured leak rate is zero is that they do not naturally transform to the log scale used in the model development. In order to use these data points, they would have to first be set to some arbitrary positive value.

Plots of the data in log scale with the zero mean screening values first set to one and the zero non-methane leak rate estimates set to 10^{-4} lbs/hr are shown in Figures 3-17 and 3-18. Similar plots of the data with the "zero" data points deleted are shown in Figures 3-19 and 3-20. Although deleting the "zero" data points had very little effect on the parameter estimates, the overall precision of the model estimate was enhanced.

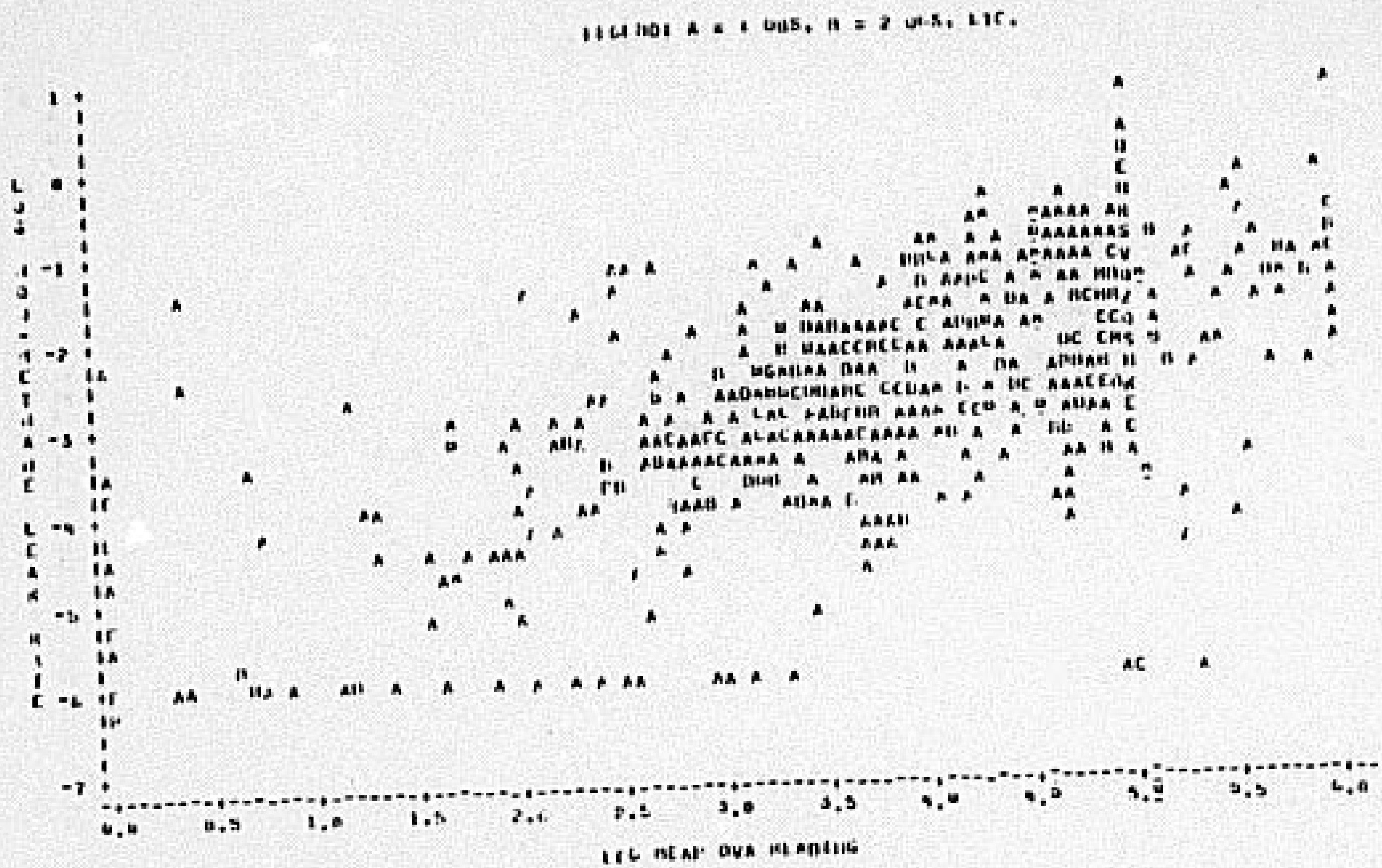


Figure 3-17. Log10 Leak Rate vs. Log10 OVA for All Valves - Zeroes Set to 1 for OVA or .000001 for Leak Rates

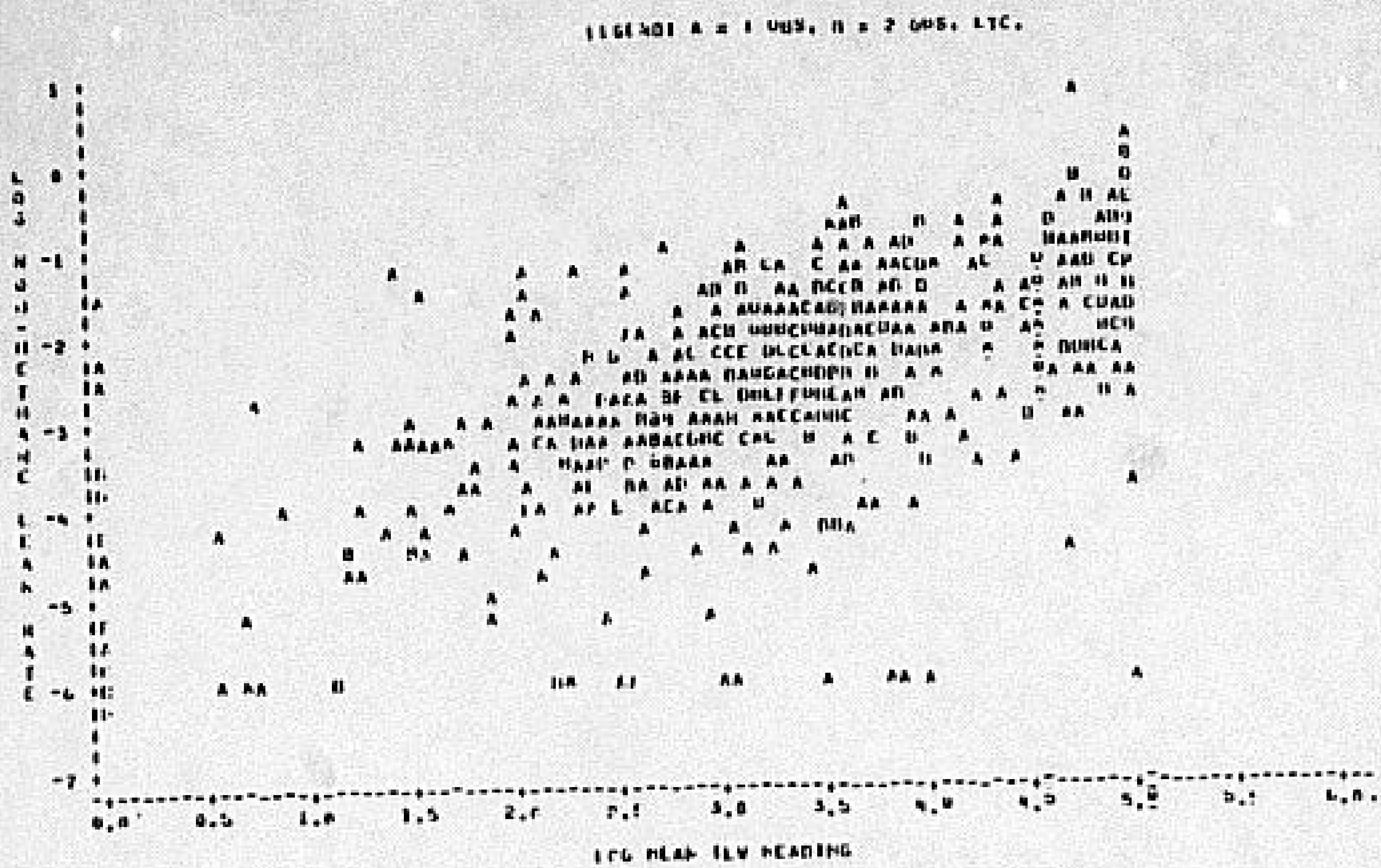


Figure 3-18. Log_{10} Leak Rate vs. Log_{10} TLV Sniffer for All Valves – Zeroes Set to 1 for OVA or .000001 for Leak Rates

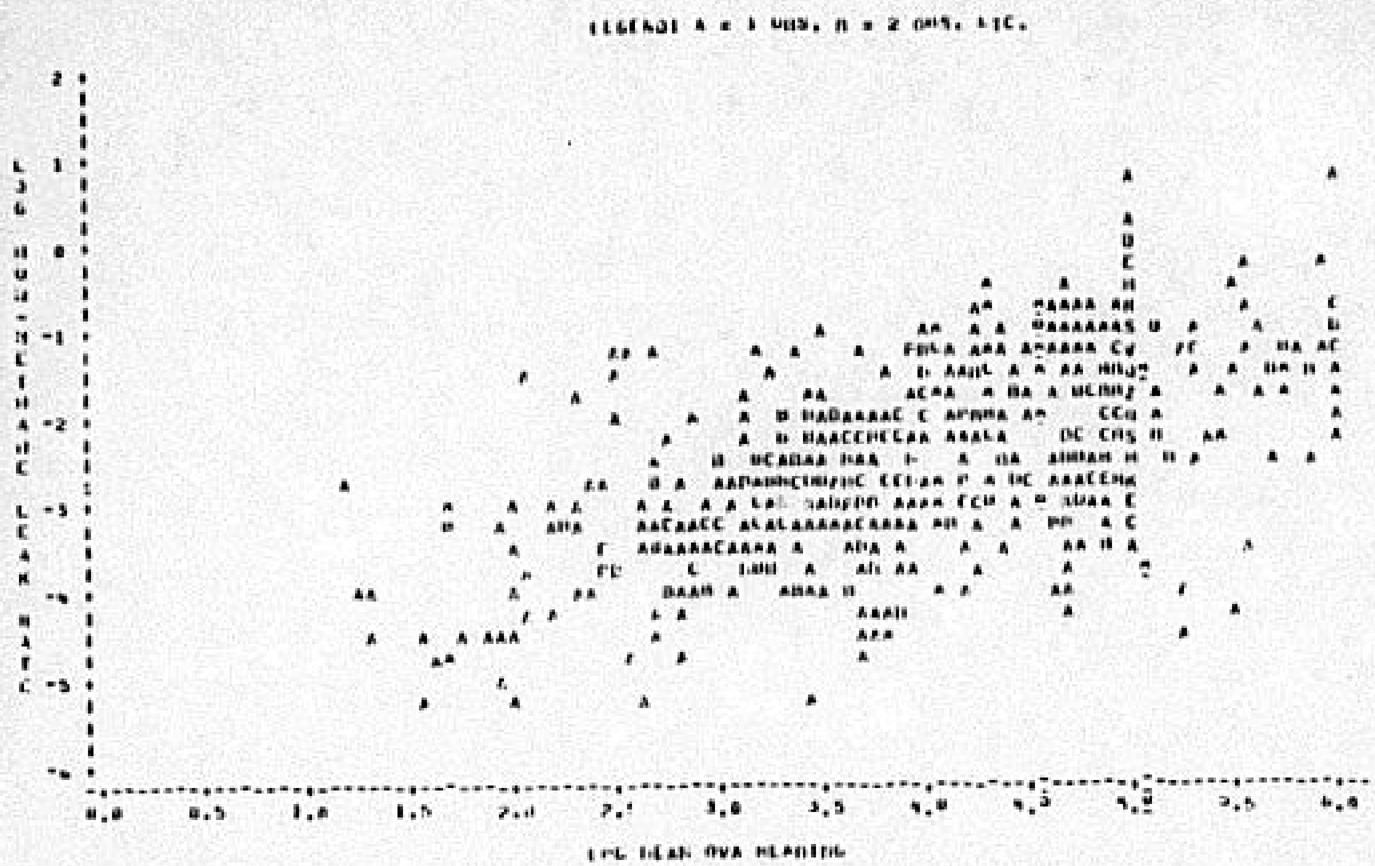


Figure 3-19. Log_{10} Leak Rate vs. Log_{10} OVA for Valves
Screening < 10 and Leak = 0 Removed

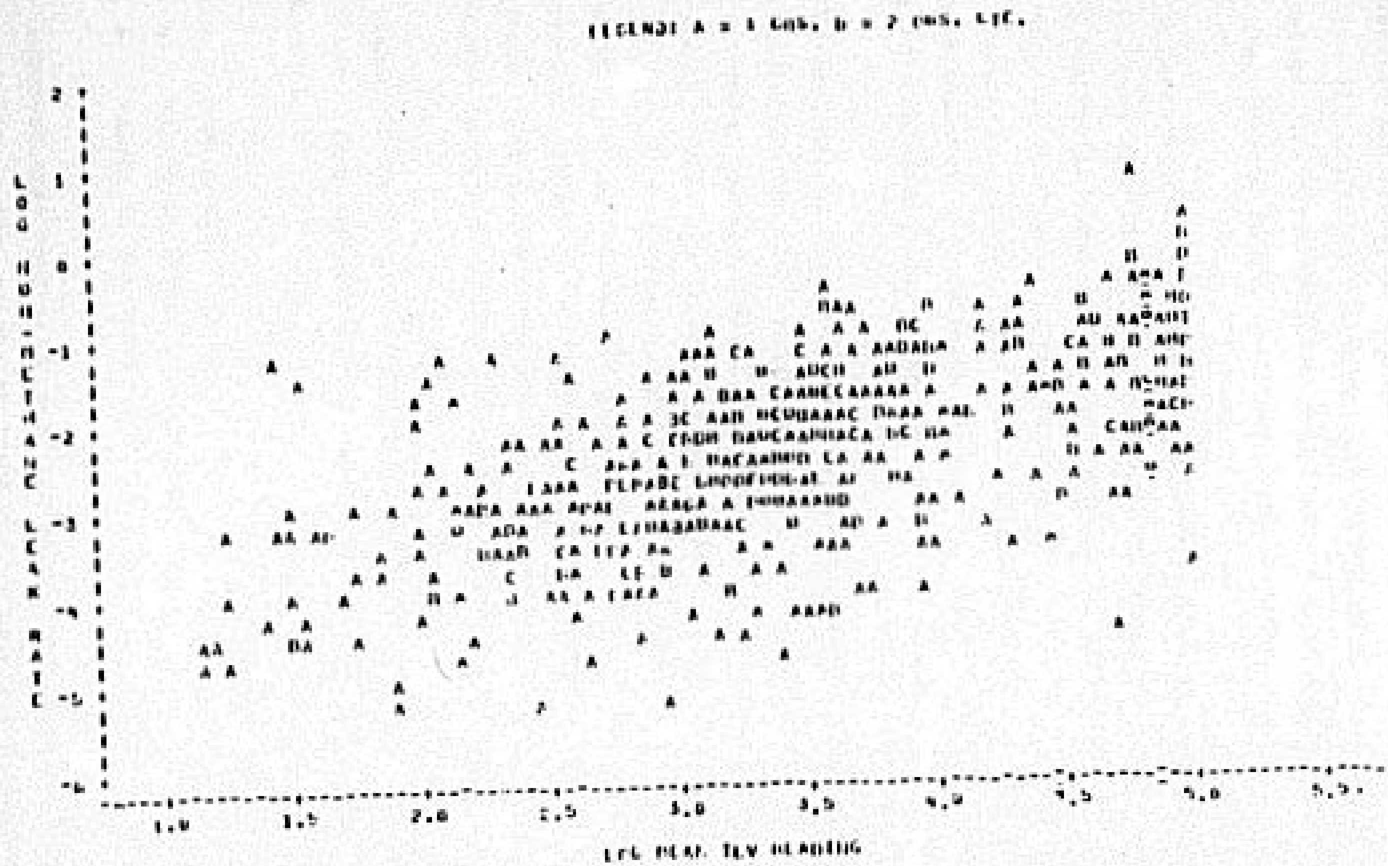


Figure 3-20. Log₁₀ Leak Rate vs. Log₁₀ TLV Sniffer for Valves Screening < 10 and Leak = 0 Removed

Because the parameter estimates were only slightly affected and because of the difficulty in including them in the model, all valves with screening values (OVA or TLV Sniffer) less than 10 ppmv and all zero leak rates were removed from further analyses of the relationships.

In developing a model for the screening value and emission rate relationship, data were first divided into two source types (pump seals and valves). A statistical analysis was performed to determine whether separate equations would be necessary for the various process units (cumene, ethylene, and vinyl acetate) and service (gas and liquid) types. Tables 3-8 and 3-9 present these analyses of covariance results for the OVA and TLV Sniffer, respectively. (Appendix D describes analysis of covariance procedures.)

Through the interaction terms (e.g., OVASERVICE), the slopes of the relationships for the various levels of the second variable (e.g., Service) are tested for significant differences. For example, the OVASERVICE category is found to be significant. This indicates that the slope of the screening value/leak rate relationship is different for gas and liquid service valves. The individual categories (i.e., SERVICE and PROCESS) can be interpreted as testing for differences in the intercepts within each classification. For example, in Table 3-8, gas service and liquid service models are seen to have different intercepts.

Based on the results of the analysis of covariance, the following breakdowns were deemed appropriate for model development for both OVA and TLV Sniffer:

- pump seals,
- valves in liquid service, and
- valves in gas service.

Least-squares regression analyses were done for each of these breakdowns. The logarithm of the nonmethane leak rate was regressed upon the logarithm of the mean screening value (OVA and TLV Sniffer).

TABLE 3-8. ANALYSIS OF COVARIANCE FOR PUMPS AND VALVES USING OVA SCREENING VALUES

Pumps Seals (n = 69)

	Degrees of Freedom	Sum of Squares	F Value	Pr > F
OVA	1	18.92	41.69	0.0001*
Process	2	0.76	0.83	0.44
OVAx Process	2	0.34	0.32	0.69

Valves (n = 651)

	Degrees of Freedom	Sum of Squares	F Value	Pr > F
OVA	1	253.75	470.43	0.0001*
Process	2	0.39	0.36	0.70
Service	1	5.71	10.59	0.001*
OVAx Process	2	0.99	0.92	0.40
OVAx Service	1	6.59	12.23	0.0005*

*Significant at α < 0.05

TABLE 3-9. ANALYSIS OF COVARIANCE FOR PUMPS AND VALVES USING TLV SNIFFER SCREENING VALUES

	Pumps Seals (n = 66)			
	Degrees of Freedom	Sum of Squares	F Value	Pr > F
TLV Sniffer	1	19.50	40.74	0.0001*
Process	2	0.15	0.16	0.86
TLV SnifferxProcess	2	0.65	0.68	0.51

	Valves (n = 592)			
	Degrees of Freedom	Sum of Squares	F Value	Pr > F
TLV Sniffer	1	256.4	506.21	0.0001*
Process	2	2.33	2.30	0.10
Service	1	1.89	3.72	0.05
TLV SnifferxProcess	2	0.03	0.03	0.97
TLV SnifferxProcess	1	1.27	2.51	0.11

*Significant at $\alpha < 0.05$

The resulting six equations (three OVA and three TLV Sniffer) are given below:

- **Pump Seals - OVA**

  Equation for Predicted Mean Line:
  Mean NM Leak Rate = $1.64\ (10^{-5})(\text{OVA})^{0.88}$

  Equation based on the following least squares equations:
  Log_{10} (LEAK) = $-5.29 + 0.88\ \text{Log}_{10}$ (Mean OVA)
  Correlation Coefficient of the estimate = 0.79
  Standard Deviation = 0.67
  95% Confidence Interval for Intercept = (-6.0, -4.6)
  95% Confidence Interval for Slope = (0.71, 1.04)
  Scale Bias Correction Factor = 3.19
  N = 69

- **Pump Seals - TLV Sniffer**

  Equation for Predicted Mean line:
  Mean NM Leak Rate = $1.15\ (10^{-4})(\text{TLV Sniffer reading})^{0.78}$

  Equation based on the following least squares equations:
  Log_{10} (LEAK) = $-4.47 + 0.78\ \text{Log}_{10}$ (Mean TLV Sniffer reading)
  Correlation Coefficient = 0.59
  Standard Deviation of the Estimate = 0.69
  95% Confidence Interval for Intercept = (-5.06, -3.89)
  95% Confidence Interval for Slope = (0.62, 0.95)
  Scale Bias Correction Factor = 3.39
  N = 66

- Valves - Gas Service - OVA

Equation for Predicted Mean Line:

Mean NM Leak Rate = 0.97 $(10^{-5})(\mathrm{OVA})^{.79}$

Equation based on the following least squares equations:

Log_{10} (LEAK) = -5.72 + 0.79 Log_{10} (Mean OVA)

Correlation Coefficient = 0.70

Standard Deviation of the Estimate = 0.73

95% Confidence Interval for Intercept = (-6.12, -5.32)

95% Confidence Interval for Slope = (0.70, 0.88)

Scale Bias Correction Factor = 4.06

N = 301

- Valves - Gas Service - TLV Sniffer

Equation for Predicted Mean Line:

Mean NM Leak Rate = 1.82 $(10^{-5})(\text{TLV Sniffer reading})^{.79}$

Equation based on the following least squares equations:

Log_{10} (LEAK) = -5.27 + 0.79 Log_{10} (Mean TLV Sniffer reading)

Correlation Coefficient = 0.74

Standard Deviation of the Estimate = 0.68

95% Confidence Interval for Intercept = (-5.60, - 4.95)

95% Confidence Interval for Slope = (0.71, 0.88)

Scale Bias Correction Factor = 3.39

N = 283

- <u>Valves - Liquid Service - OVA</u>

  Equation for Predicted Mean Line:
  Mean NM Leak Rate = 1.16 $(10^{-4})(\text{OVA})^{0.54}$

  Equation based on the following least squares equations:
  Log_{10} (LEAK) = −4.72 + 0.54 Log_{10} (Mean OVA)
  Correlation Coefficient = 0.55
  Standard Deviation of the Estimate = 0.83
  95% Confidence Interval for Intercept = (−5.08, −4.35)
  95% Confidence Interval for Slope = (0.46, 0.63)
  Scale Bias Correction Factor = 6.09
  N = 350

- <u>Valves - Liquid Service - TLV Sniffer</u>

  Equation for Predicted Mean Line:
  Mean NM Leak Rate = 1.20 $(10^{-4})(\text{TLV Sniffer reading})^{0.65}$

  Equation based on the following least squares equations:
  Log_{10} (LEAK) = −4.68 + 0.65 Log_{10} (Mean TLV Sniffer reading)
  Correlation Coefficient = 0.59
  Standard Deviation of the Estimate = 0.81
  95% Confidence Interval for Intercept = (−5.03, −4.33)
  95% Confidence Interval for Slope = (0.55, 0.75)
  Scale Bias Correction Factor = 5.73
  N = 309

The data used to develop these equations are shown in Figures 3-21 through 3-26. Each of these graphs shows the data and a plot of the regression equation with both variables on a logarithmic scale.

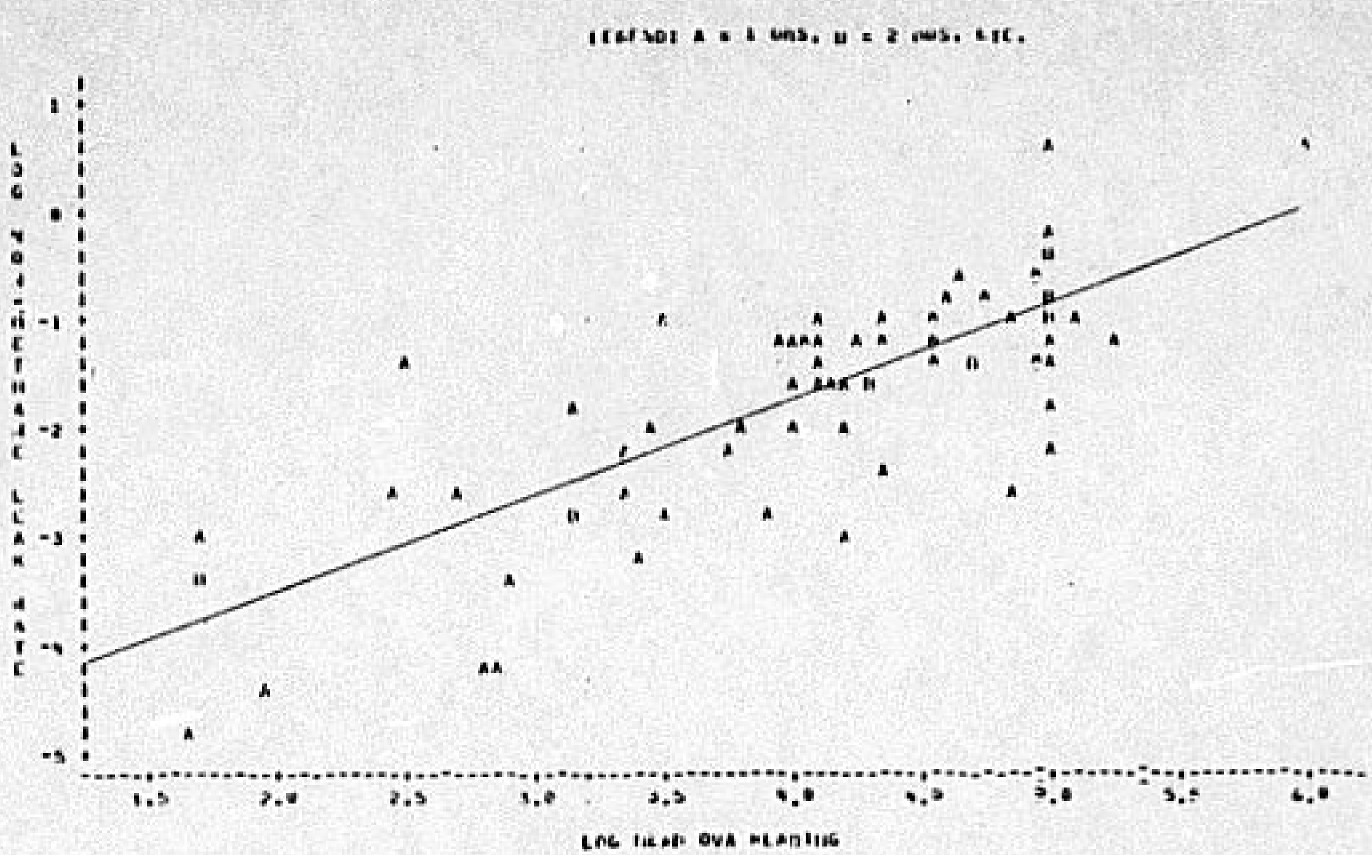


Figure 3-21. Log_{10} Leak Rate vs. Log_{10} OVA Reading for Pump Seals

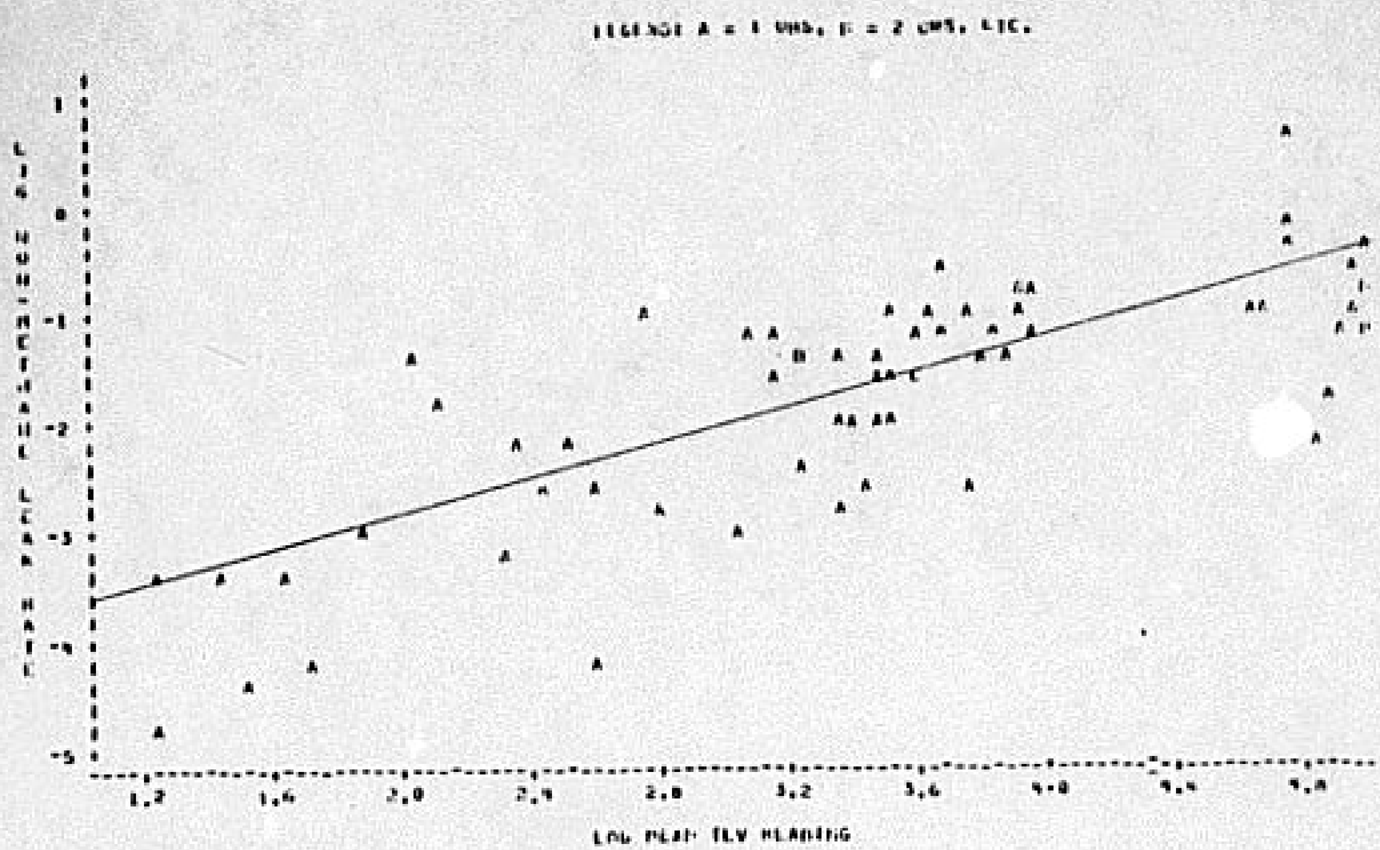


Figure 3-22. Log_{10} Leak Rate vs. Log_{10} TLV Reading for Pump Seals

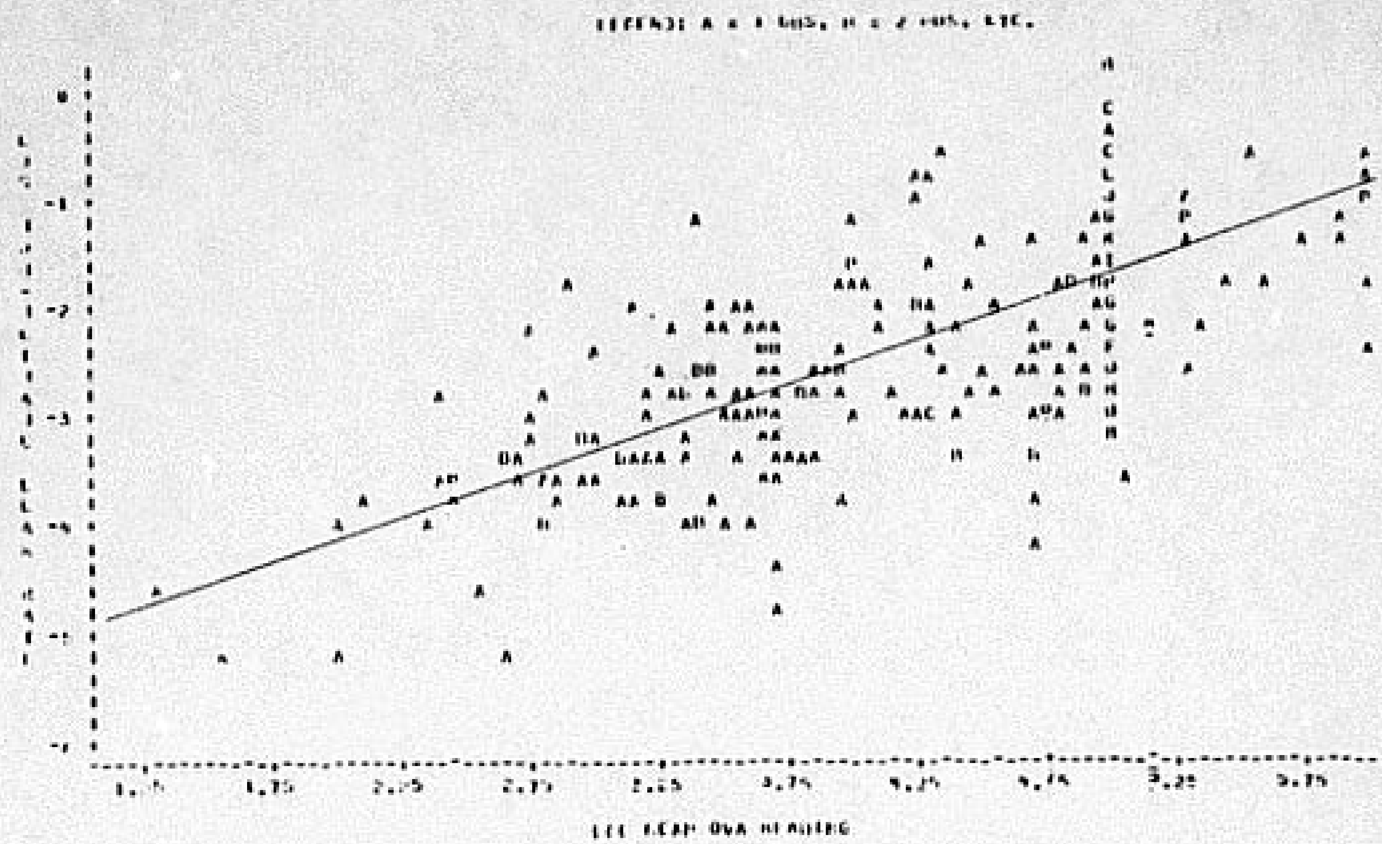


Figure 3-23. Log_{10} Leak Rate vs. Log_{10} OVA Reading for Valves - Gas Service

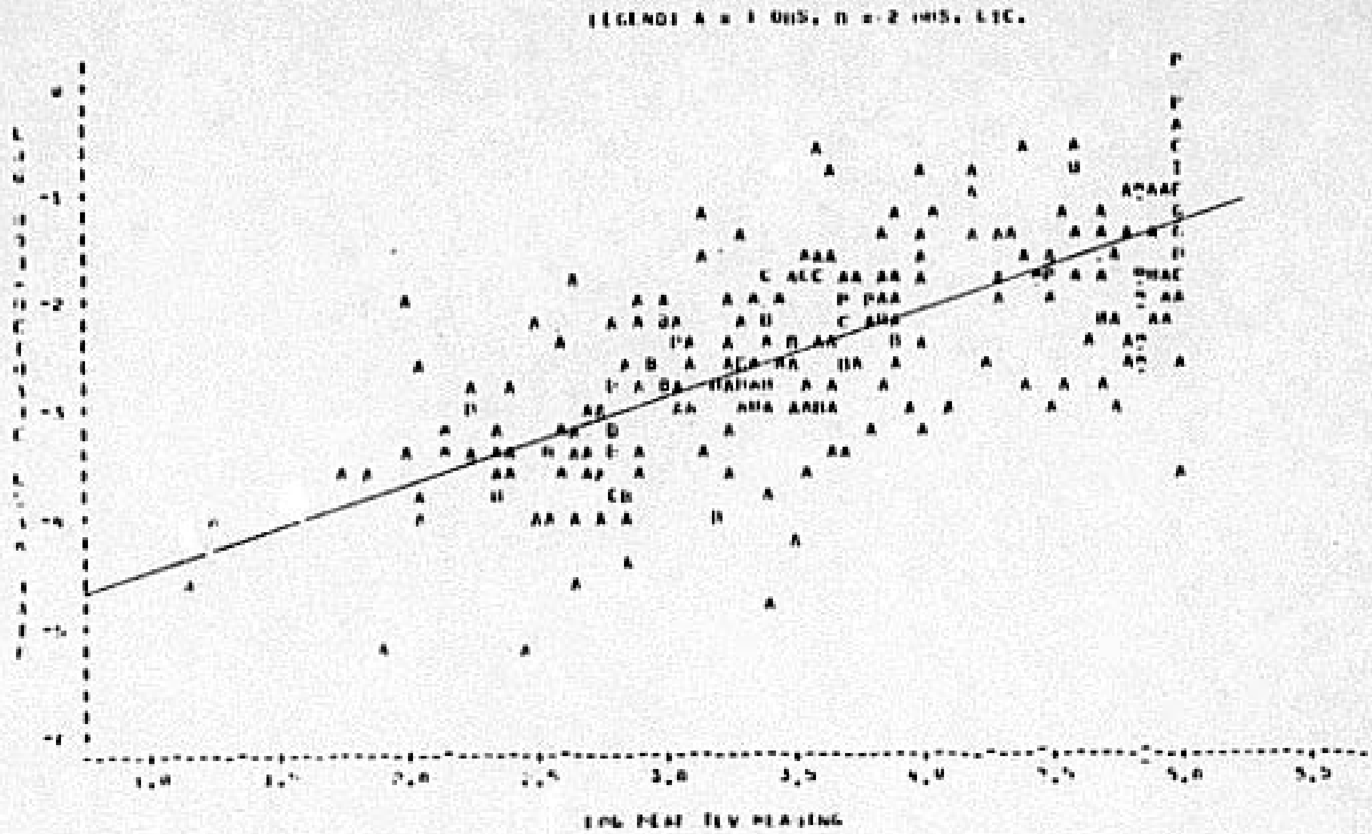


Figure 3-24. $\log_{10}$ Leak Rate vs. $\log_{10}$ TLV Reading for Valves – Gas Service

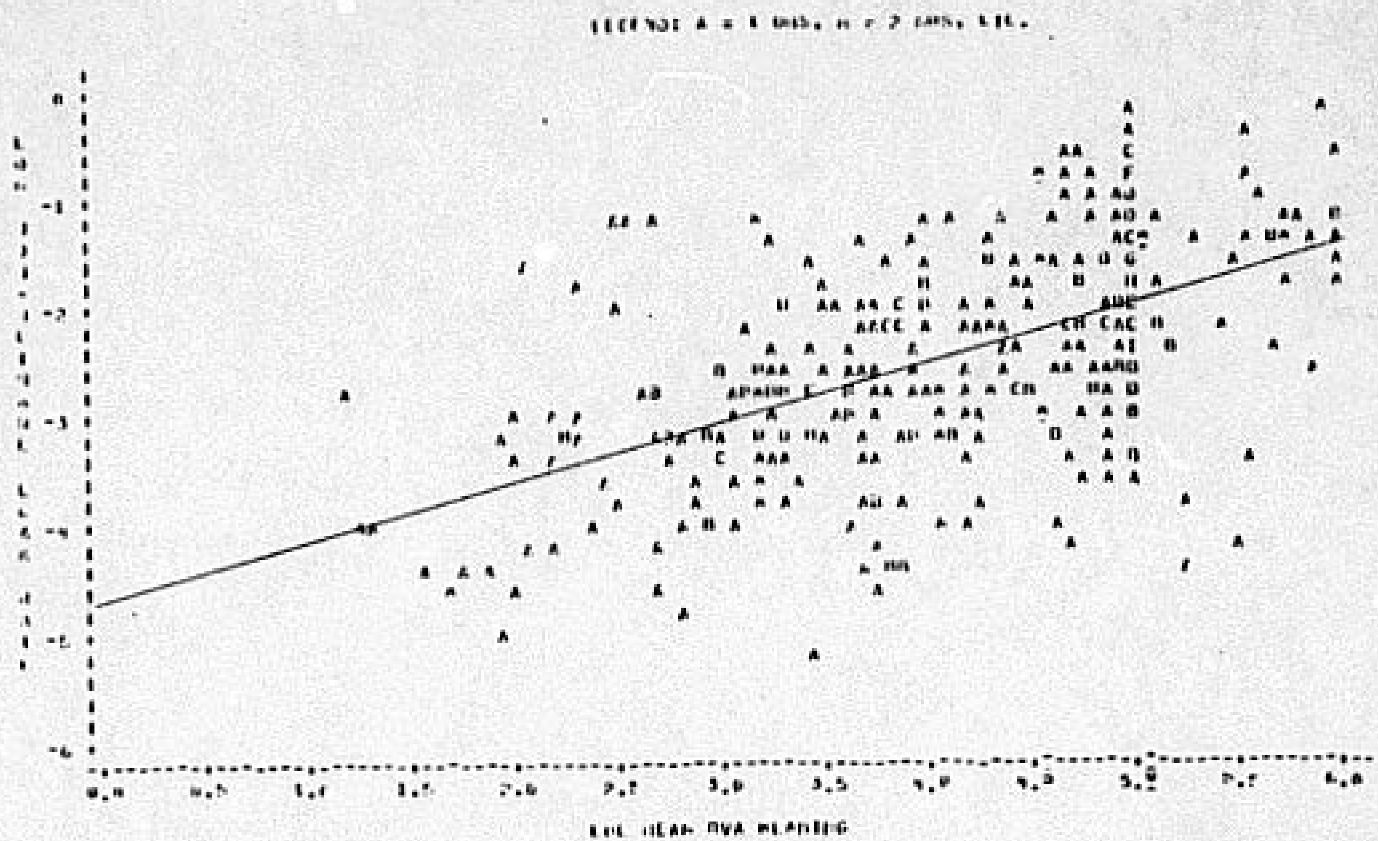


Figure 3-25. Log_{10} Leak Rate vs. Log_{10} OVA Reading for Valves – Liquid Service

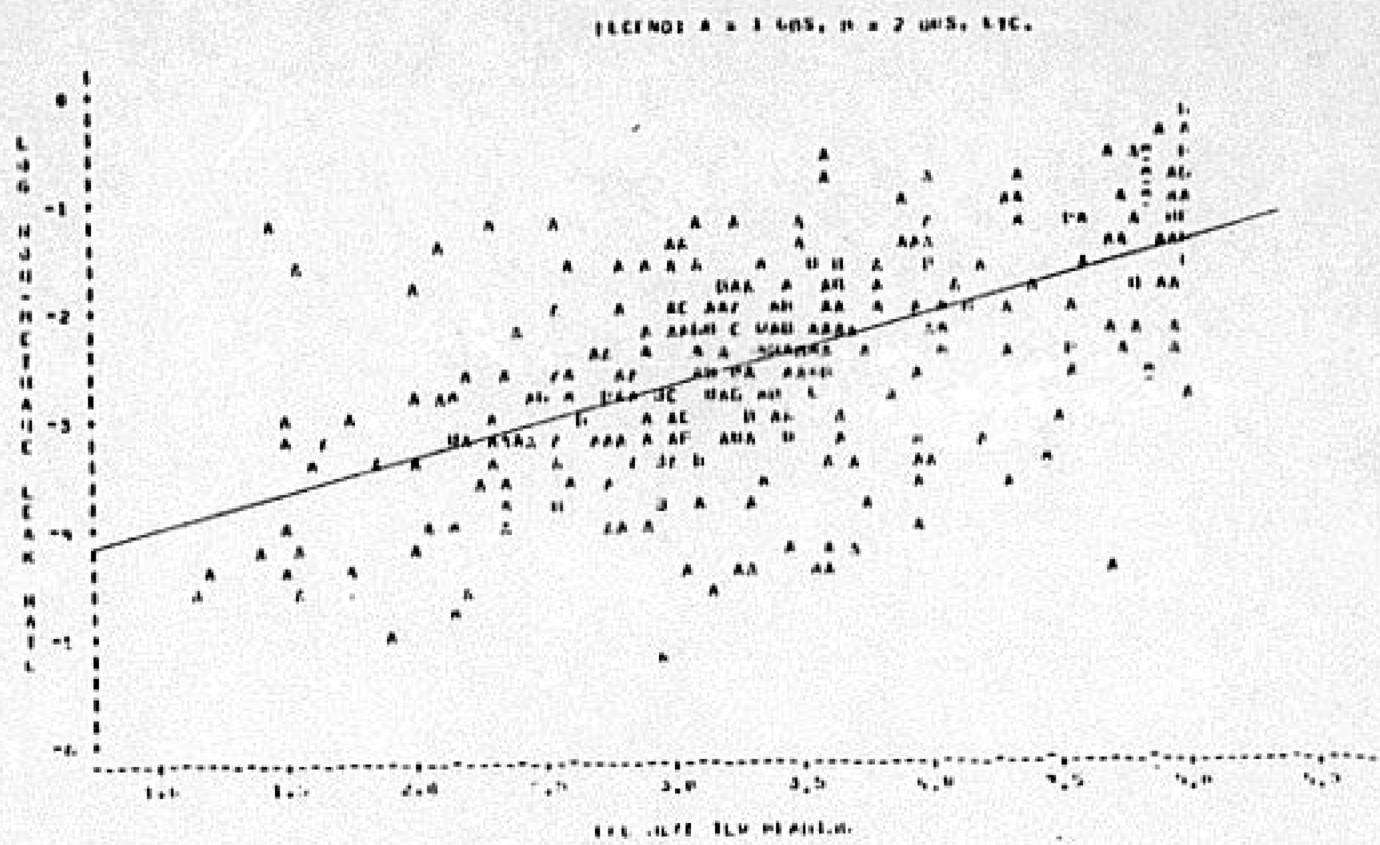


Figure 3-26. Log_{10} Leak Rate vs. Log_{10} TLV Reading for Valves – Liquid Service

The equations were used to develop graphs which relate the predicted leak rate to the screening values for the various source and service types. These graphs are shown in Figures 3-27 through 3-32. Each figure gives the predicted mean leak rate as a function of the screening values with either the TLV Sniffer or OVA.

Ninety-five percent confidence intervals are shown on the graphs for the predicted mean leak based on the given screening values. These confidence limits are for the mean leak rate and should not be confused with confidence intervals for individual source leak rates for given screening values. Figures 3-33 through 3-38 graphically demonstrate the difference between these two types of confidence intervals.

Although equations were developed on a logarithmic scale, the modelled relationships are shown on an arithmetic scale for ease in reading and interpolation.

The log-log linear models describing the leak rate and screening value relationship for the TLV Sniffer were compared to those developed in the refinery project (Reference 8, pp. 53-55). To compare the models in the log scale, t-tests were performed on the coefficients of the TLV Sniffer models. It should be noted that this is only a test of the coefficients of the log scale models and does not consider the bias correction factors for transforming to the arithmetic scale.

The intercept estimates and the slope estimates for values in gas/vapor service are statistically different at the 0.05 level of significance. The slope estimates in the models for liquid service valves were also found to be statistically different at the 0.05 level of significance. However, the intercept estimates were not significantly different. The coefficients for the pump seals models were not found to be different. Table 3-10 is a presentation of these various models.

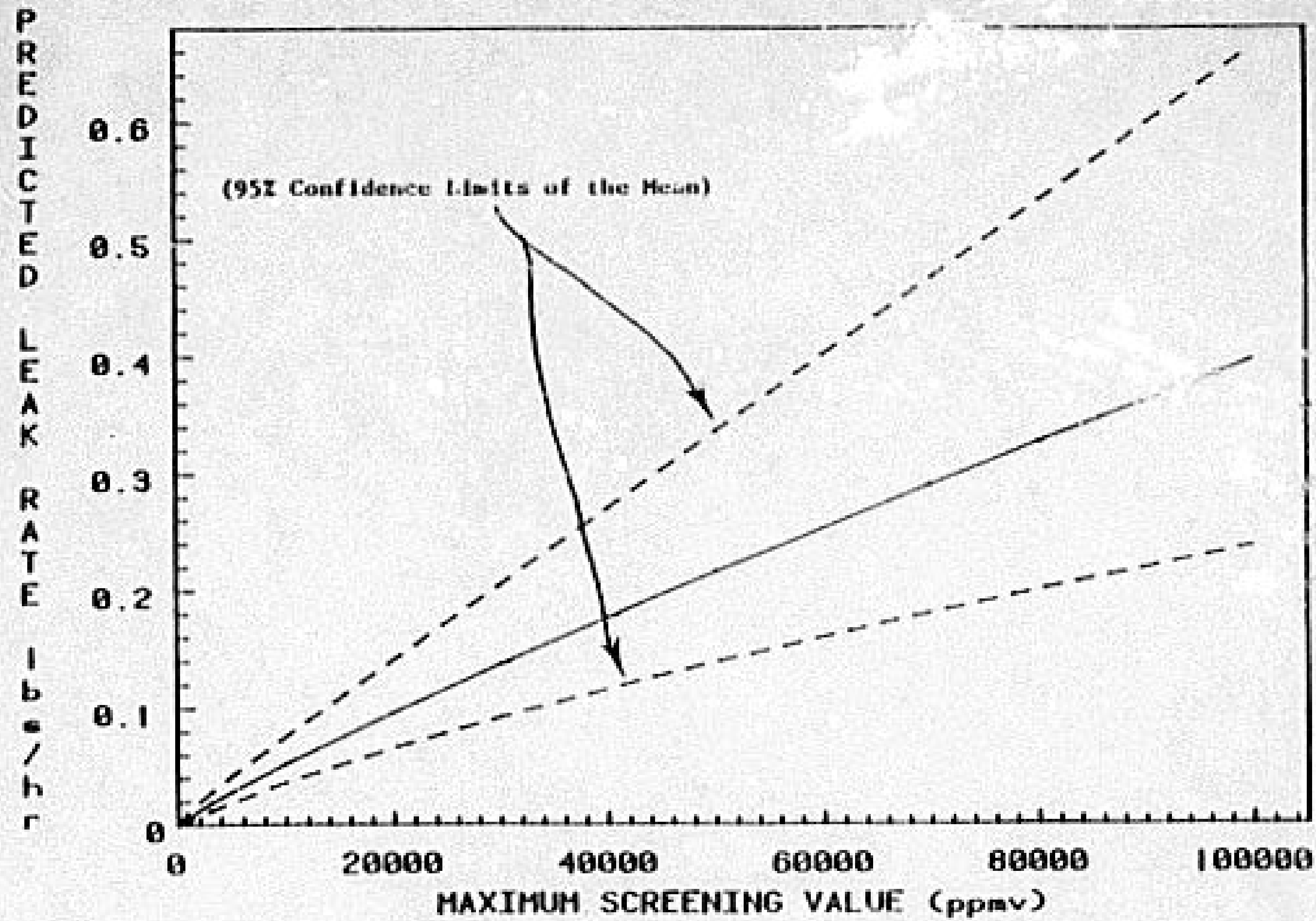


Figure 3-27. Modelled Relationship - Leak Rate vs. OVA for Pump Seals

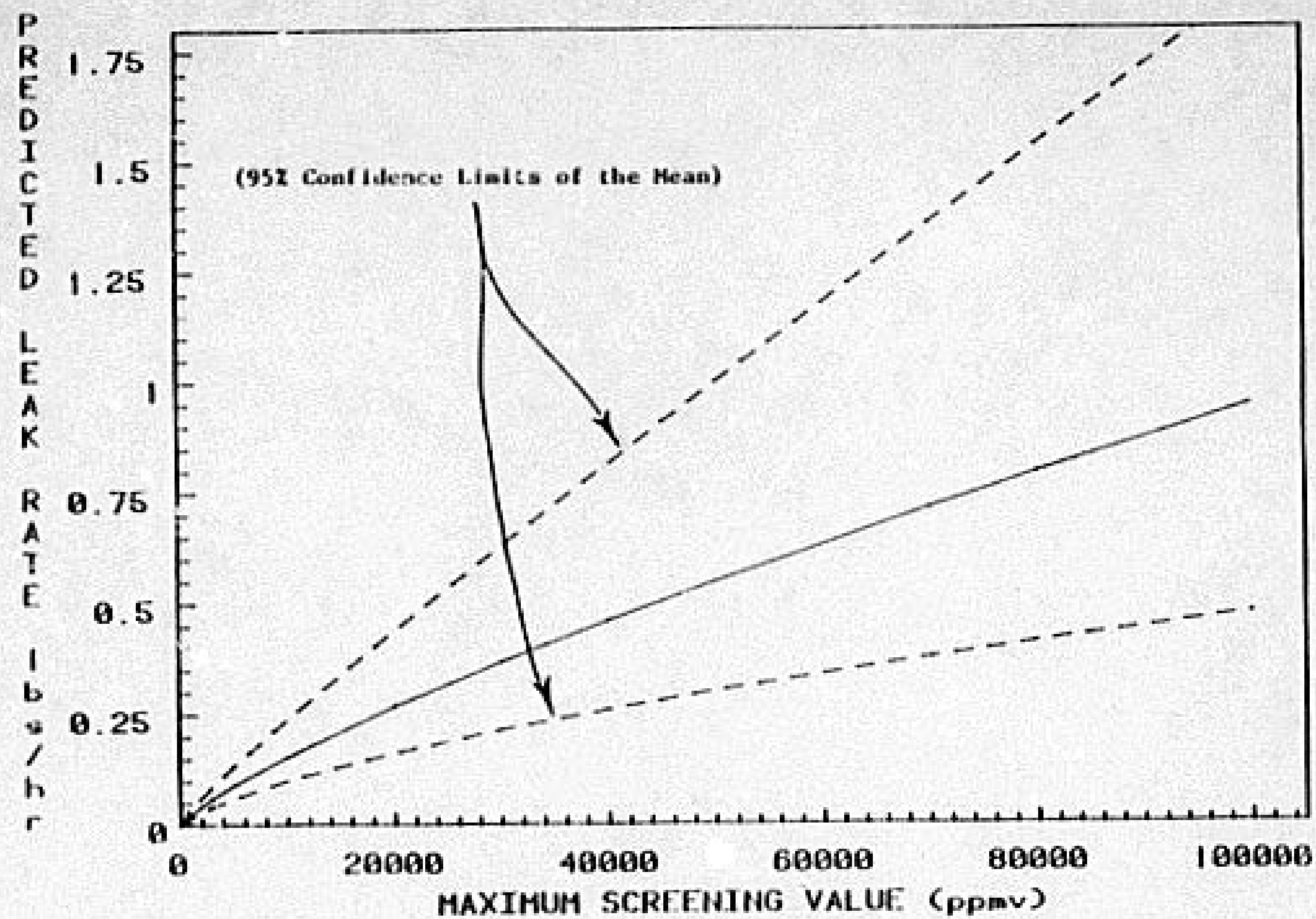


Figure 3-28. Modelled Relationship - Leak Rate vs. TLV Sniffer for Pump Seals

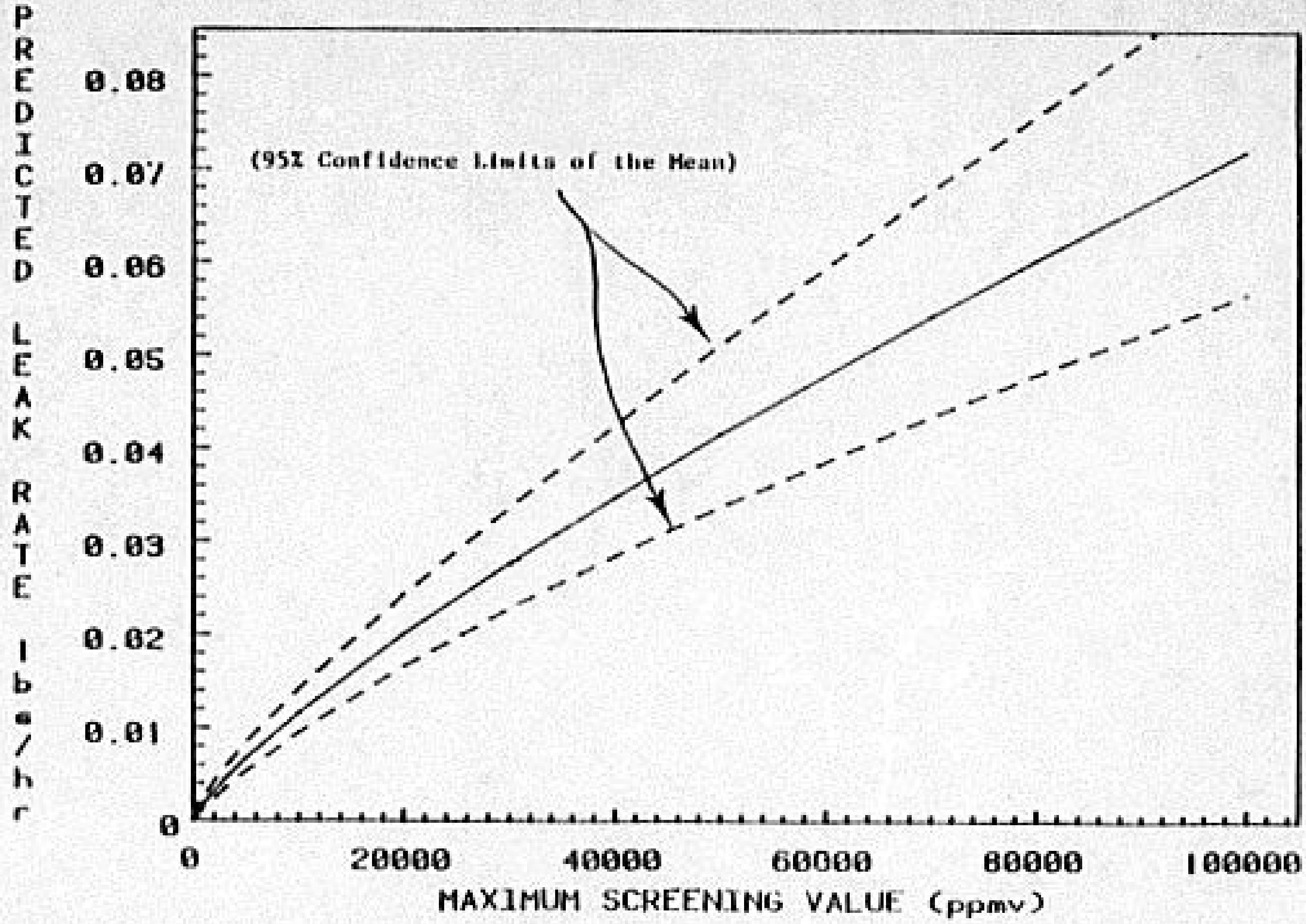


Figure 3-29. Modelled Relationship - Leak Rate vs. OVA for Valves in Gas Service

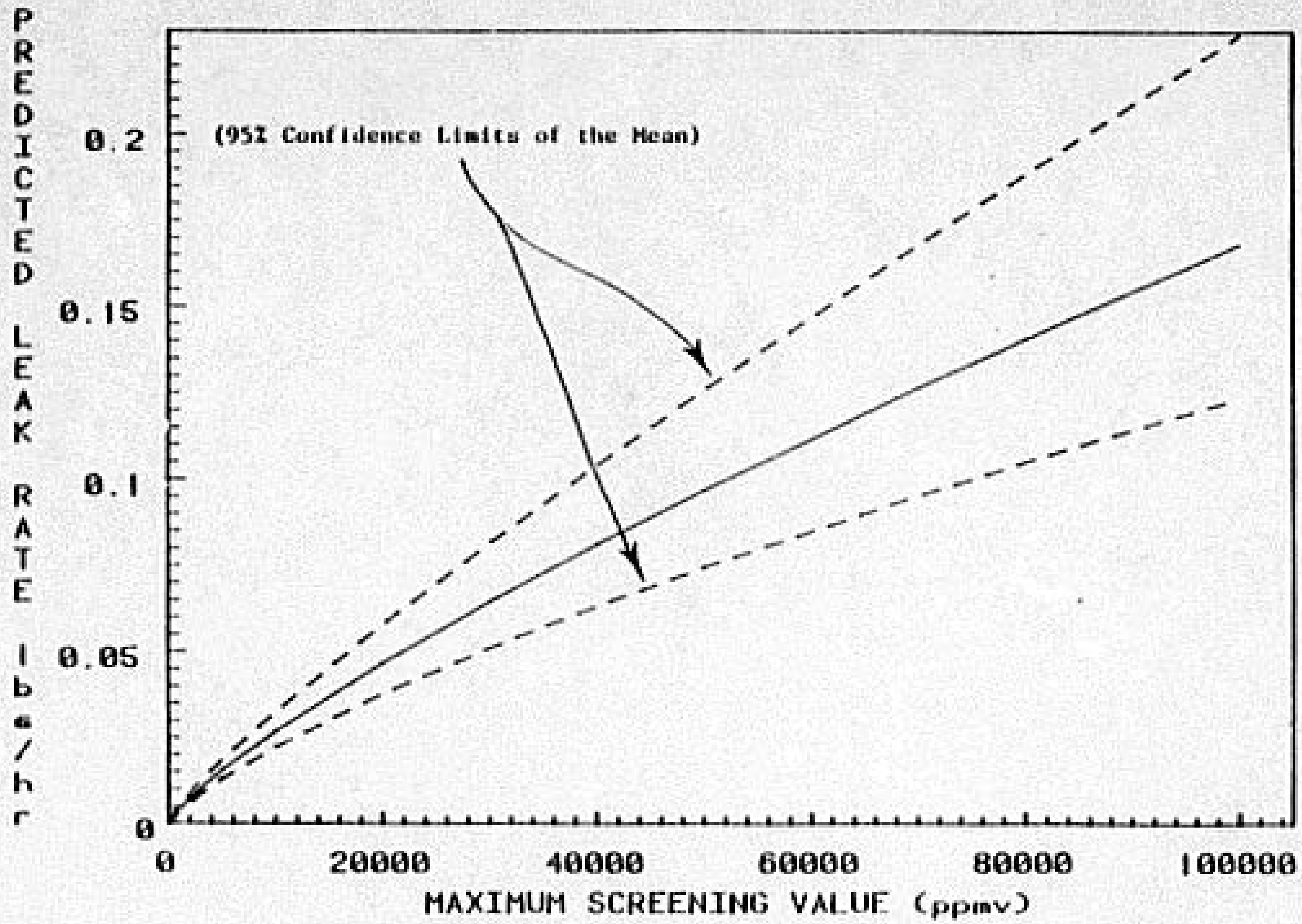


Figure 3-30. Modeled Relationship … Leak Rate … for Smaller Valves in Gas Service

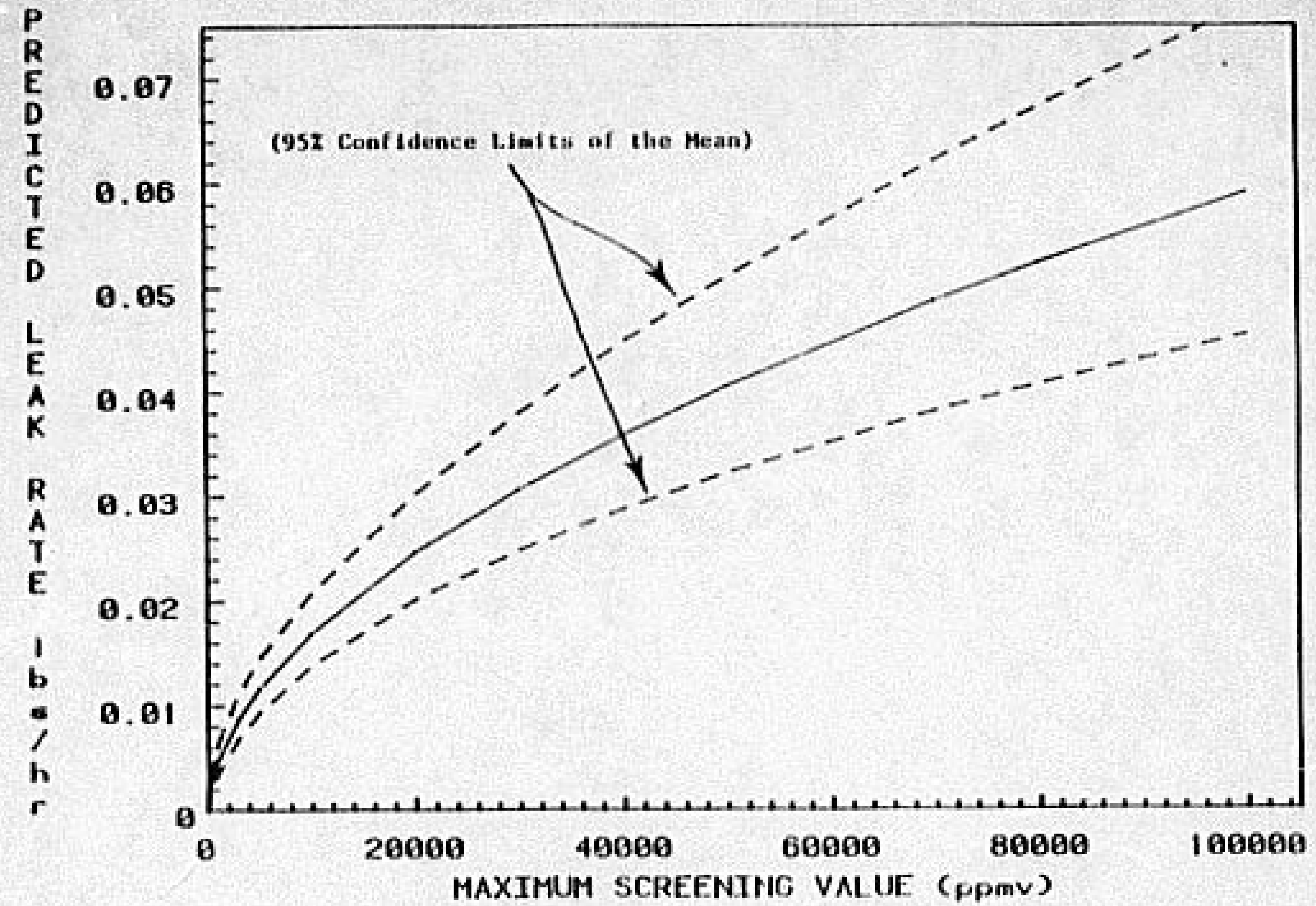


Figure 3-11. Modified Relationship [illegible] Leak Rate vs. OVA for Valves in Liquid Service

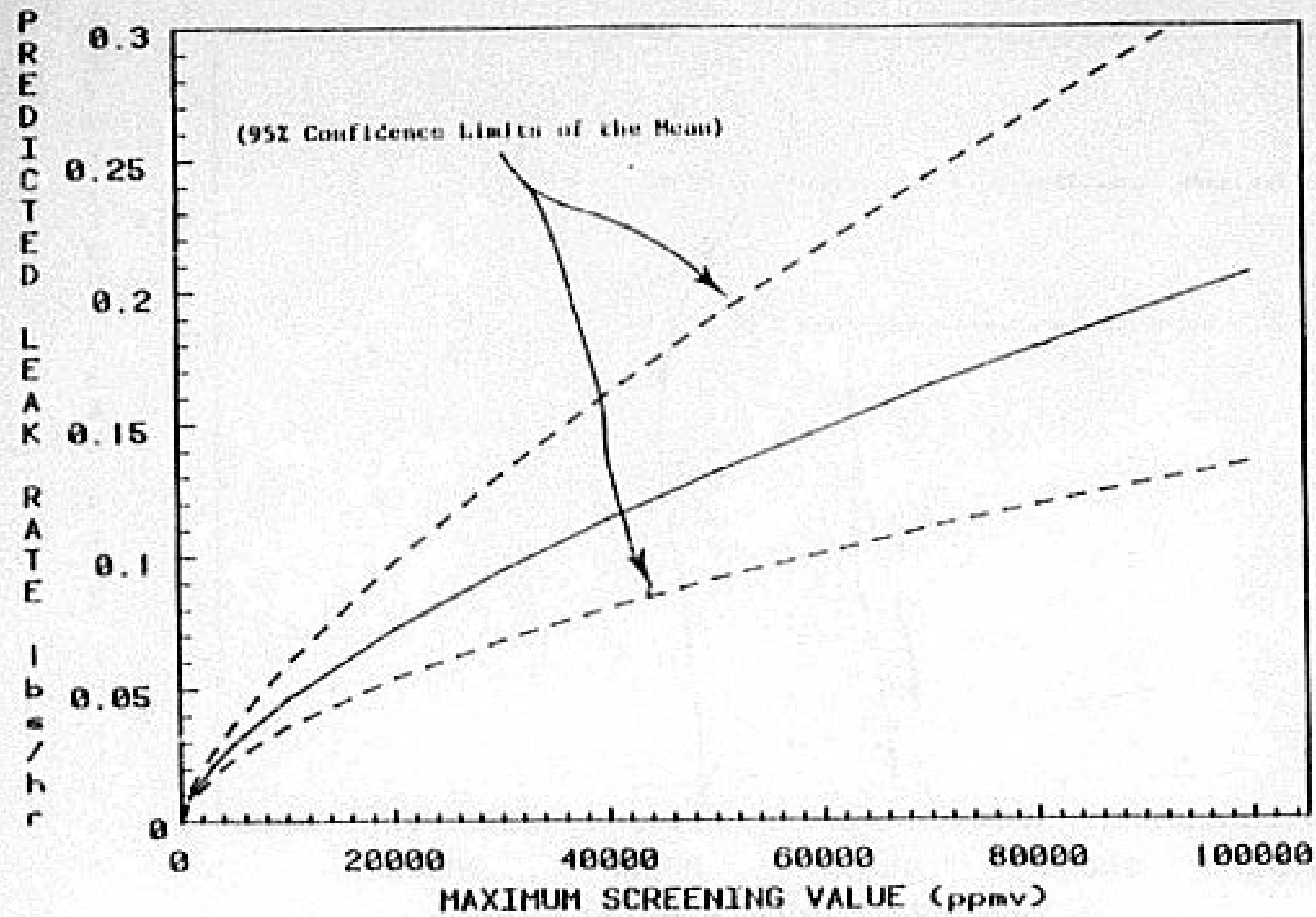


Figure 3-32. Modelled Relationship - Leak Rate vs. TLV Sniffer for Valves in Liquid Service

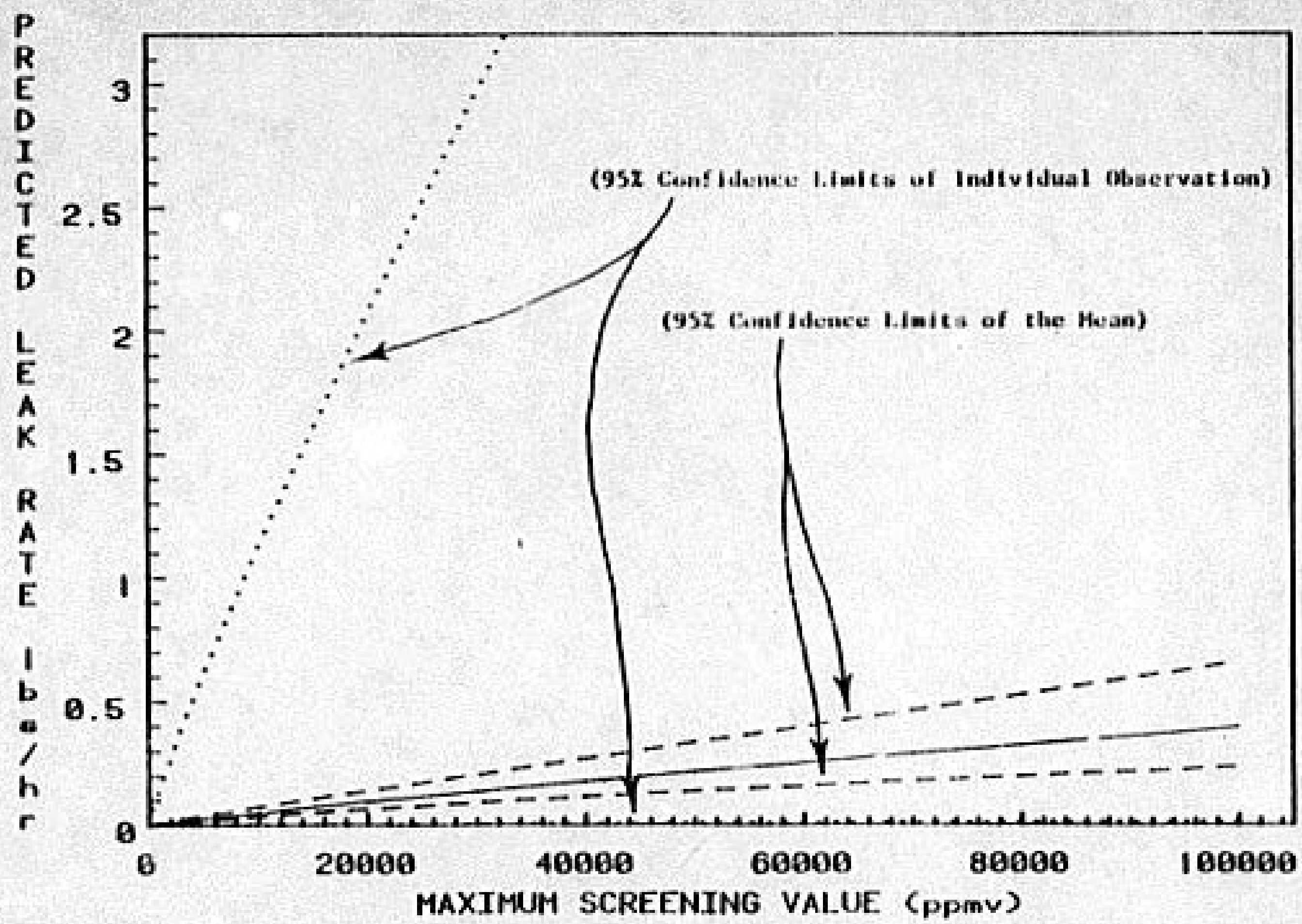


Figure 3-53. Modelled Relationship - Leak Rate vs. OVA Individual and Mean Confidence Regions for Pump Seals

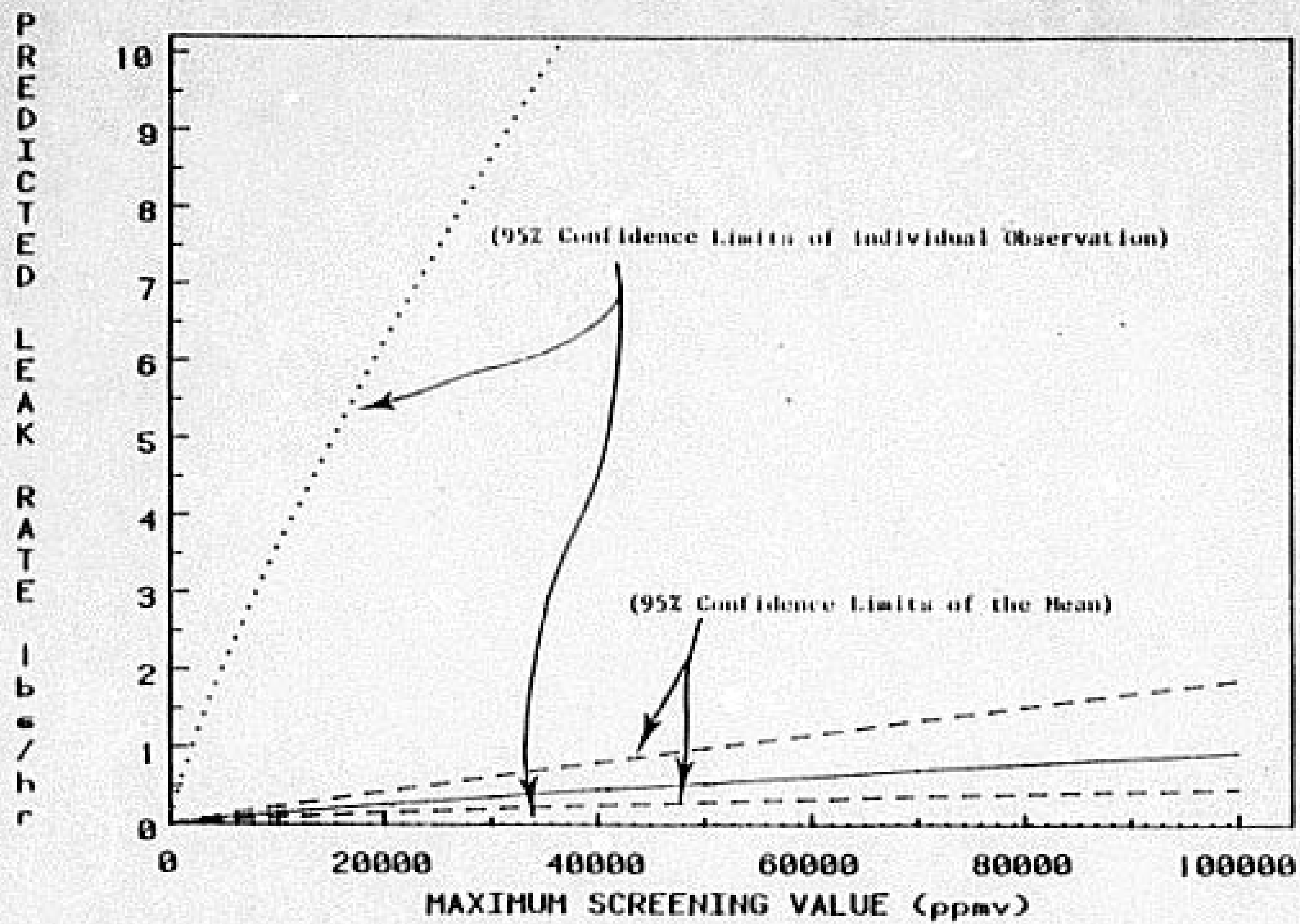


Figure 3-34. Modelled Relationship - Leak Rate vs. TLV Sniffer Individual and Mean Confidence Regions for Pump Seals.

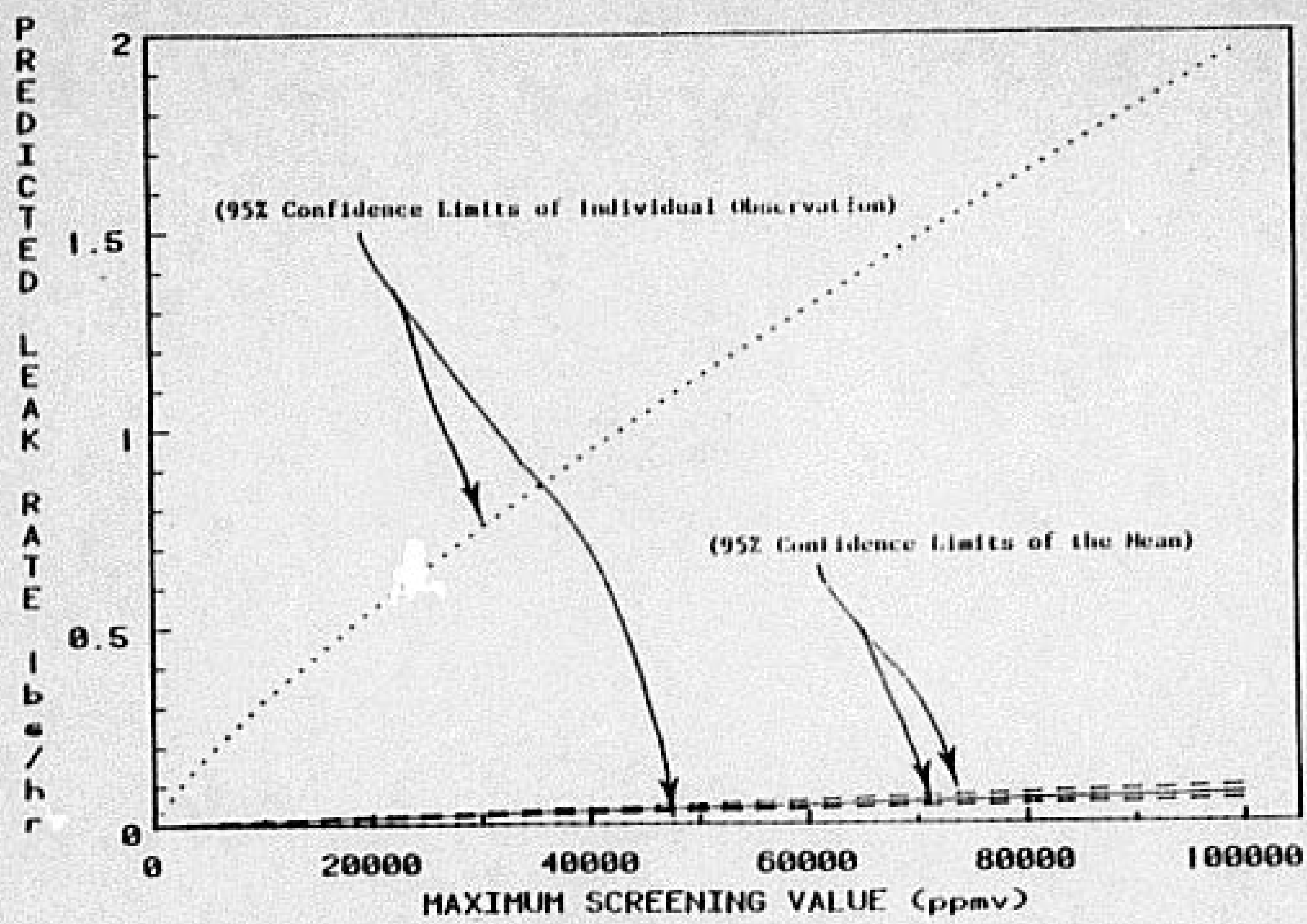


Figure 3-35. Modelled Relationship - Leak Rate vs. OVA Individual and Mean Confidence Region for Valves in Gas Service

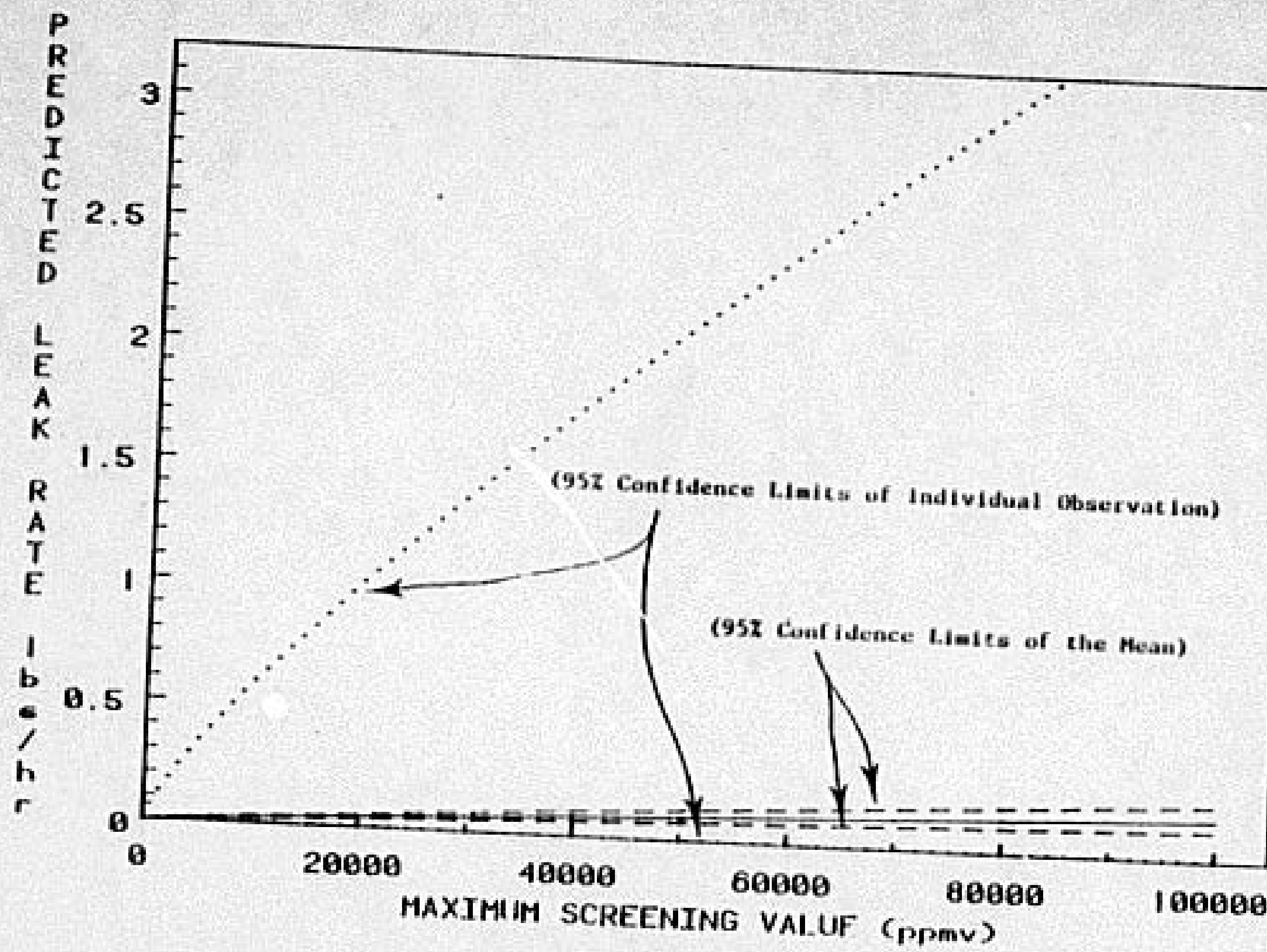


Figure 3-9. Modelled Relationship - Leak Rate vs. TLV Sniffer Individual and Mean Confidence Region for Valves in Gas Service

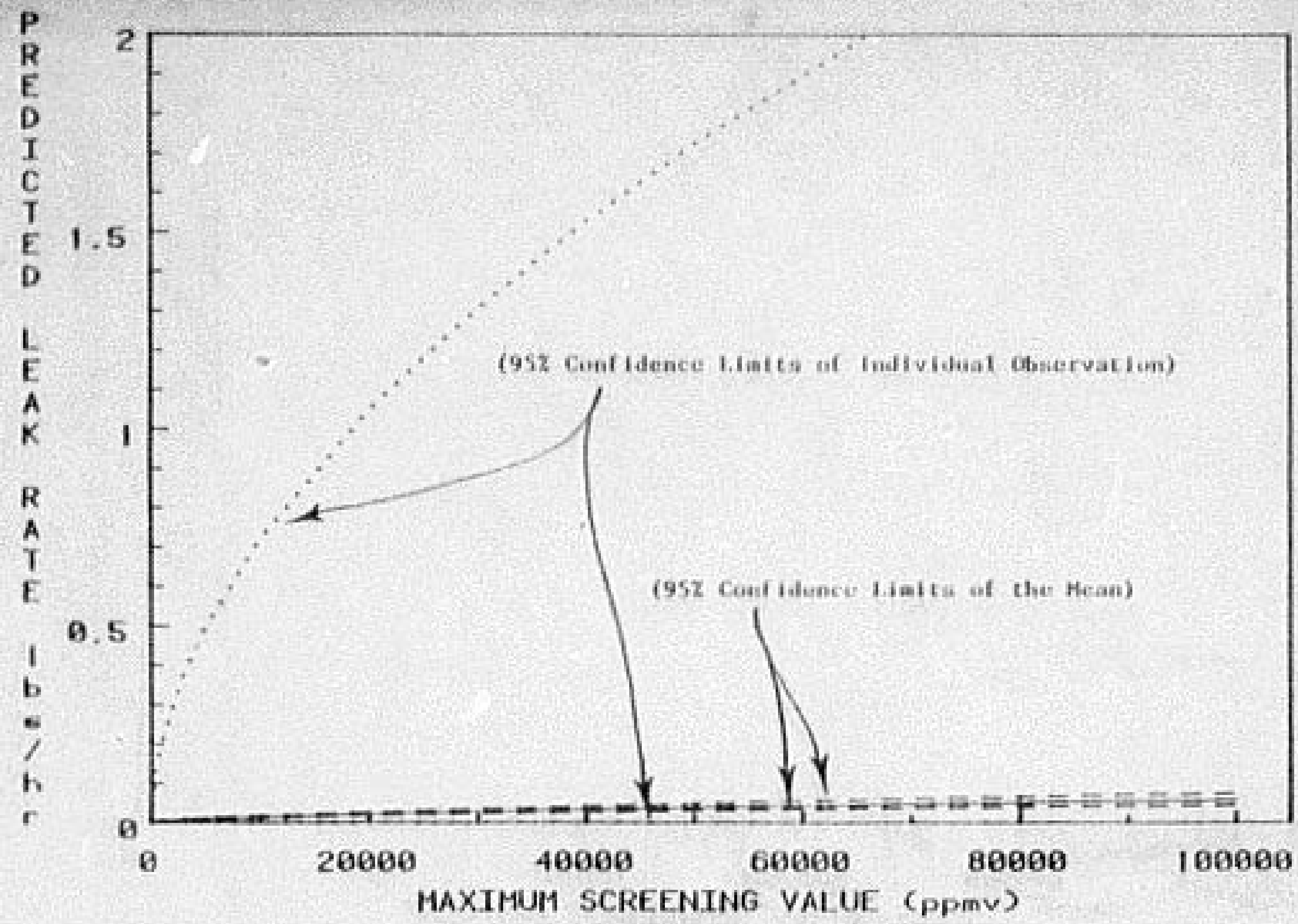


Figure 3-37. Modelled Relationship – Leak Rates vs. OVA Individual and Mean Confidence Regions for Valves in Liquid Service

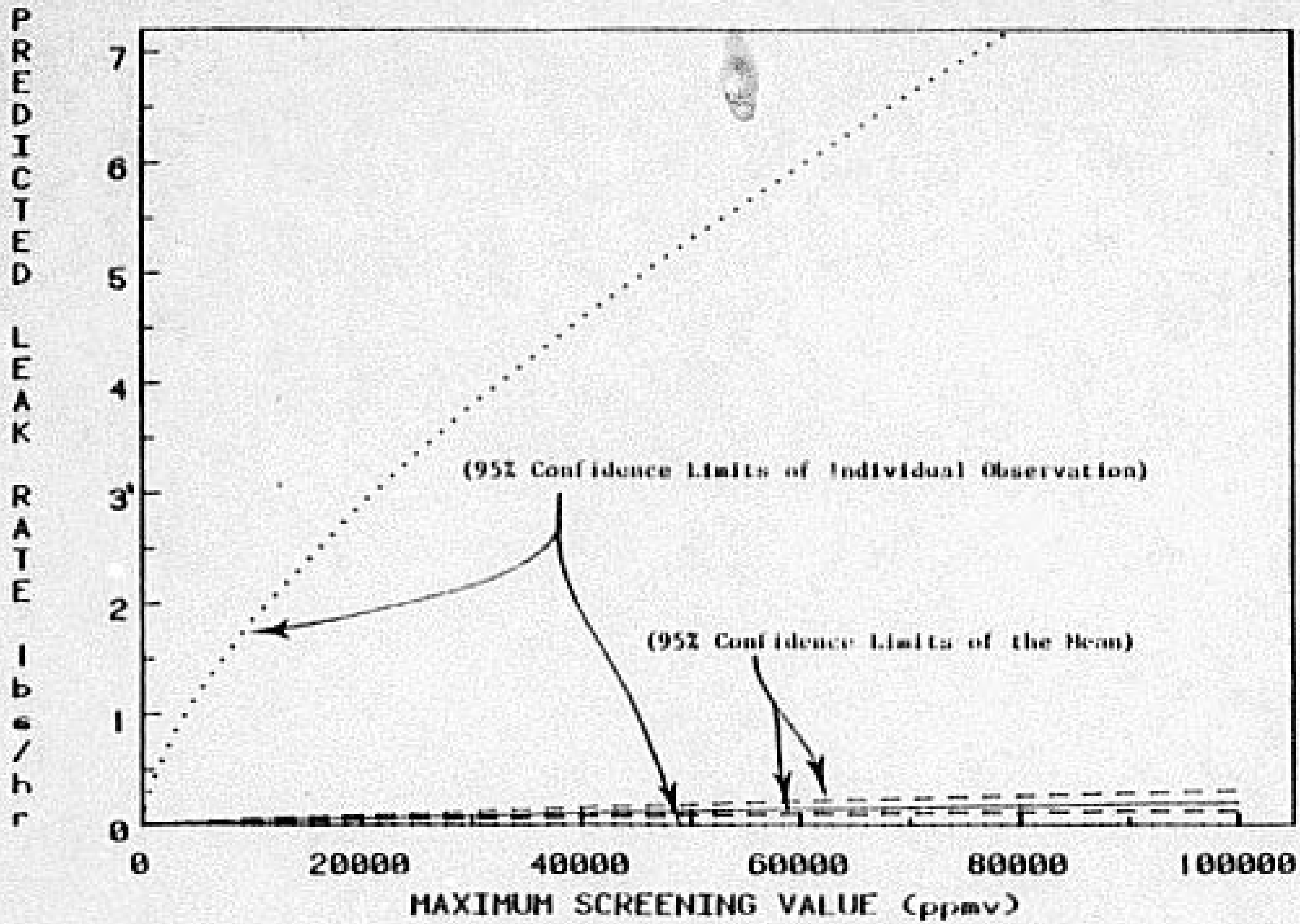
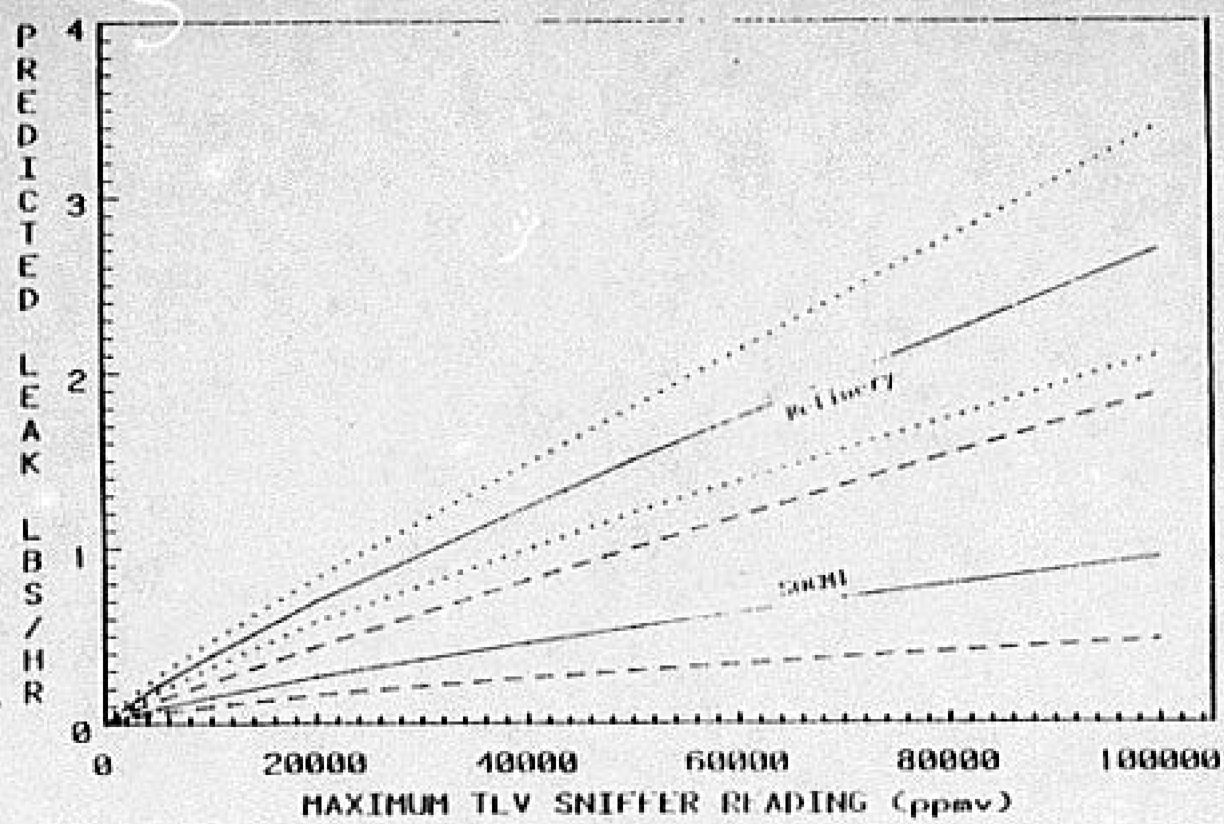


Figure 3-38. Modelled Relationship - Leak Rate vs. TLV Sniffer Individual and Mean Confidence Regions for Valves in Liquid Service

TABLE 3-10. MODELLING LEAK RATE VS. SCREENING VALUE COMPARING SOCMI AND REFINERY ESTIMATES

Source and Phase	Type of Screening Service	SOCMI Intercept (95% C.I.)	SOCMI Slope (95% C.I.)	Refinery Intercept (95% C.I.)	Refinery Slope (95% C.I.)
Valves - Gas/Vapor	OVA	-5.72 (-6.1, -5.3)	0.79 (0.70, 0.88)		
	TLV	-5.27 (-5.6, -5.0)	0.79 (0.71, 0.88)	-7.0 (-8.1, -5.9)	1.23 (0.99, 1.47)
Valves - Light Liquid	OVA	-4.72 (-5.1, -4.4)	0.54 (0.46, 0.61)		
	TLV	-4.68 (-5.0, -4.3)	0.65 (0.55, 0.75)	-4.9 (-5.3, -4.5)	0.80 (0.69, 0.91)
Pumps - Light Liquid	OVA	-5.29 (-6.0, -4.6)	0.88 (0.71, 1.04)		
	TLV	-4.47 (-5.1, -3.9)	0.78 (0.62, 0.95)	-4.4 (-4.9, -3.9)	0.83 (0.72, 0.94)

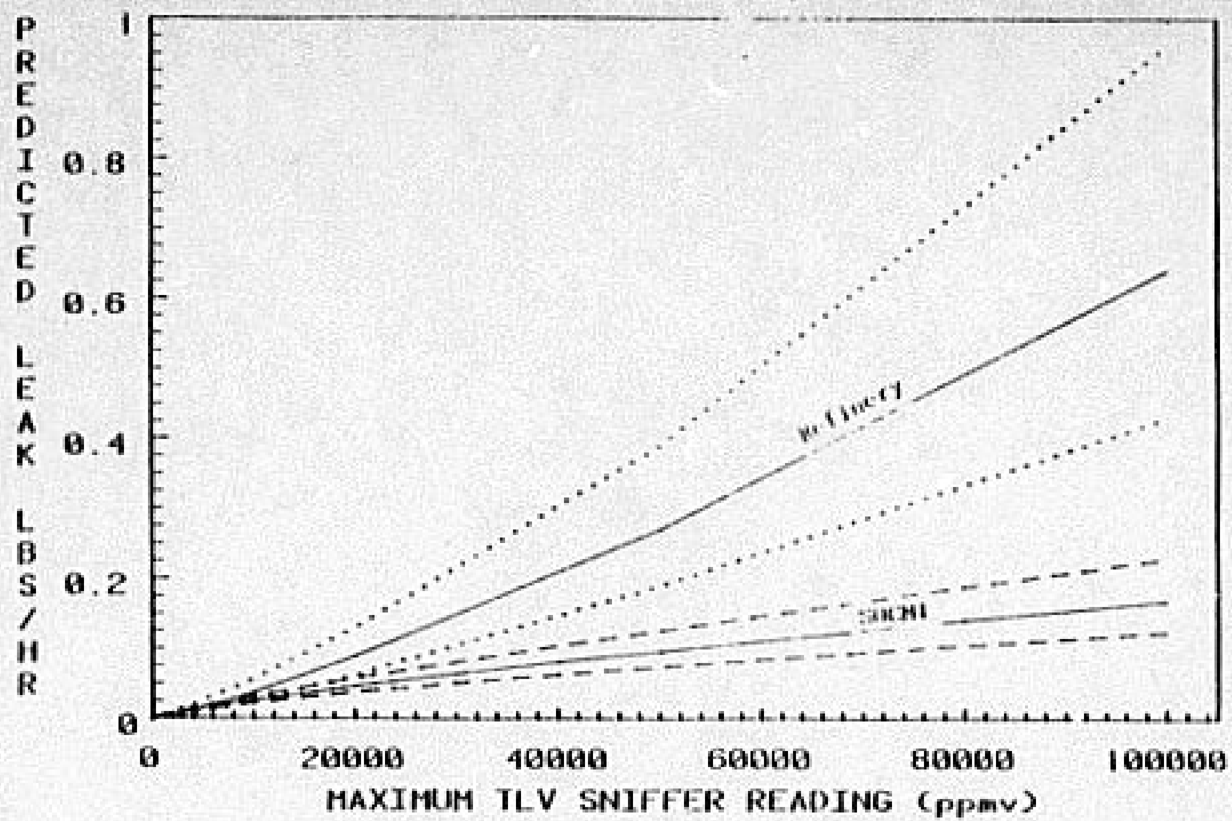
To compare the models in the arithmetic scale, plots were constructed for the three sets of models (Figure 3-39 through 3-41). The models from the refinery data can be seen to predict higher emissions for a given screening value in every case. For valves in gas service and pump seals the confidence regions do not overlap.



Dotted lines are 90% confidence bounds for the "Refinery" model

Dashed lines are 95% confidence bounds for the SOCMI model

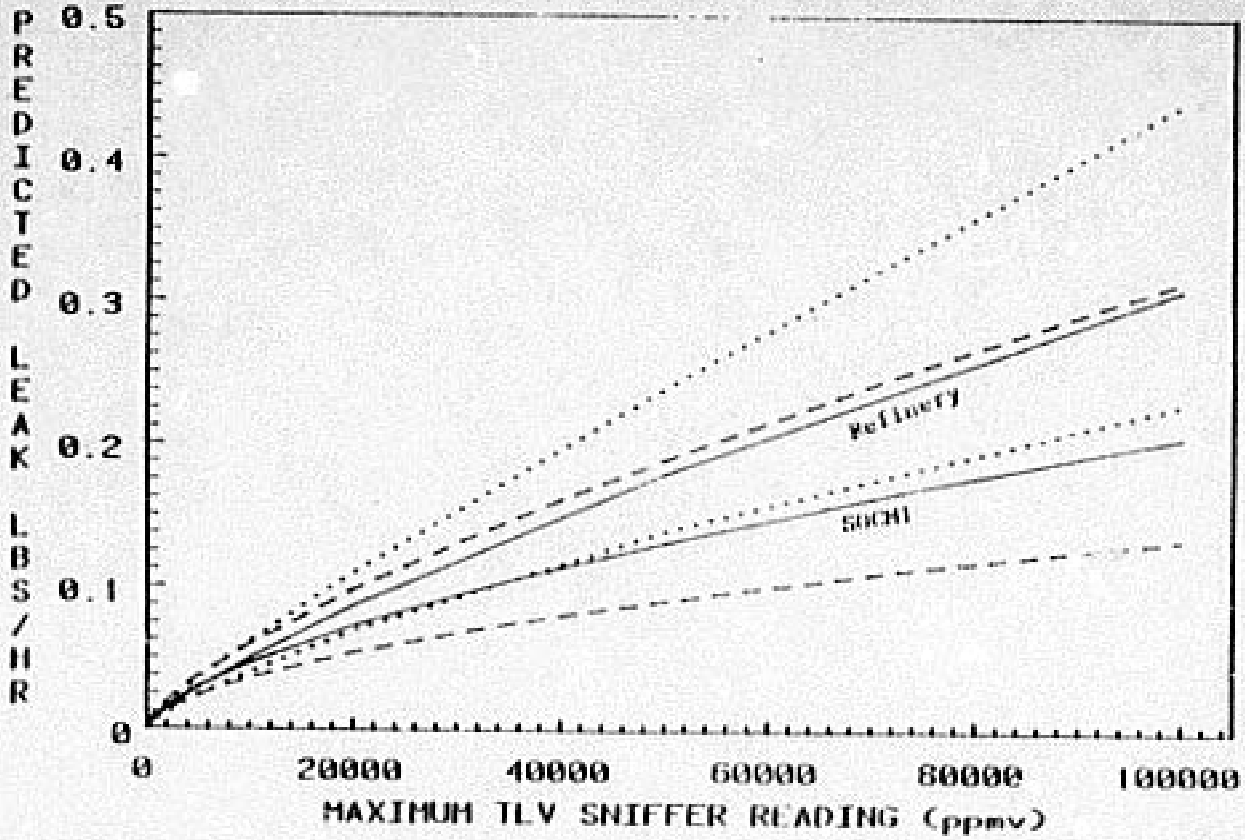
Figure 3-19. SOCMI-Refinery Comparison—Pump Seals



Dotted lines are 90% confidence bounds for the "Refinery" model

Dashed lines are 95% confidence bounds for the SOCMI model

Figure 3-40. SOCMI-Refinery Comparison---Valves-Gas



Dotted lines are 90% confidence bounds for the "Refinery" model

Dashed lines are 95% confidence bounds for the SOCMI model

Figure 3-41. SOCMI-Refinery Comparison---Valves-Light Liquid

3.7 Maintenance Summary

To aid in assessing the costs of valve maintenance, the total time (in minutes) associated with maintenance was recorded each time that a series of valves was maintained. There were a total of 14 times in six units visited in which a plant maintenance crew of one to three people (usually one) went out in the unit to maintain valves for this study. Table 3-11 summarizes the total time (man hours) spent on each series of valves. The maintenance time ranged from 3.7 minutes per valve to 28.7 minutes per valve with an average of 9.6 minutes per valve (95% confidence interval for average: 8.6 to 10.[illegible] minutes per valve). Figure 3-42 is a histogram showing the distribution of calculated maintenance times for the 172 scheduled maintenance attempts examined in this study. These data indicated that ten minutes per valve would be a reasonable maintenance time to use in assessing costs of valve maintenance.

Some conditions encountered in the field during this study prevented attempts at maintenance. There were originally 169 valves selected for maintenance, with 3 valves maintained twice. Seventeen valves were not maintained due to the physical condition or current service of the valve (leaving 155 cases of maintenance). However, because time was spent examining or attempting maintenance, the seventeen valves were included in the time estimates. Some of the conditions encountered were rusty bolts on the packing glands, cracked packing glands, and missing gland nuts. Maintenance of valves in these conditions was prevented because of the fear of causing catastrophic failure by disturbing them. Another problem encountered was the inability to tighten packing gland bolts due to the fact that epoxy had been painted over them. Finally, there were some valves in very critical service. These valves were not disturbed because of the fear that tampering with them might cause disruption of the process.

TABLE 3-11. SUMMARY OF MAINTENANCE TIME DATA

Unit	Maintenance Period	Number of Attempts	Total Time for Maintenance (minutes)	Average Maintenance Time per Valve (minutes)
1	1	10	180	18.1
		3		N.A.
2	1	13	201	13.4
	2	8 (2)*	287	28.7
		2		15.0
		2		N.A.
3	1	8	48	6.0
		5 (2)*	45	6.3
		4	15	3.7
4	1	18	125	6.9
		10 (2)*	60	5.0
		10 (1)*	80	7.3
		8	143	17.9
5	1	3 (1)*	70	17.5
	2	29 (3)*	129	4.0
6	1	8 (6)*	90	6.4
	2	13	125	9.6
		1		N.A.
TOTAL		149**(17)*	1,598	9.6

*Valves were not maintainted.
**Does not include valves for which no time information was available.

(N.A. - No information on time of maintenance available)

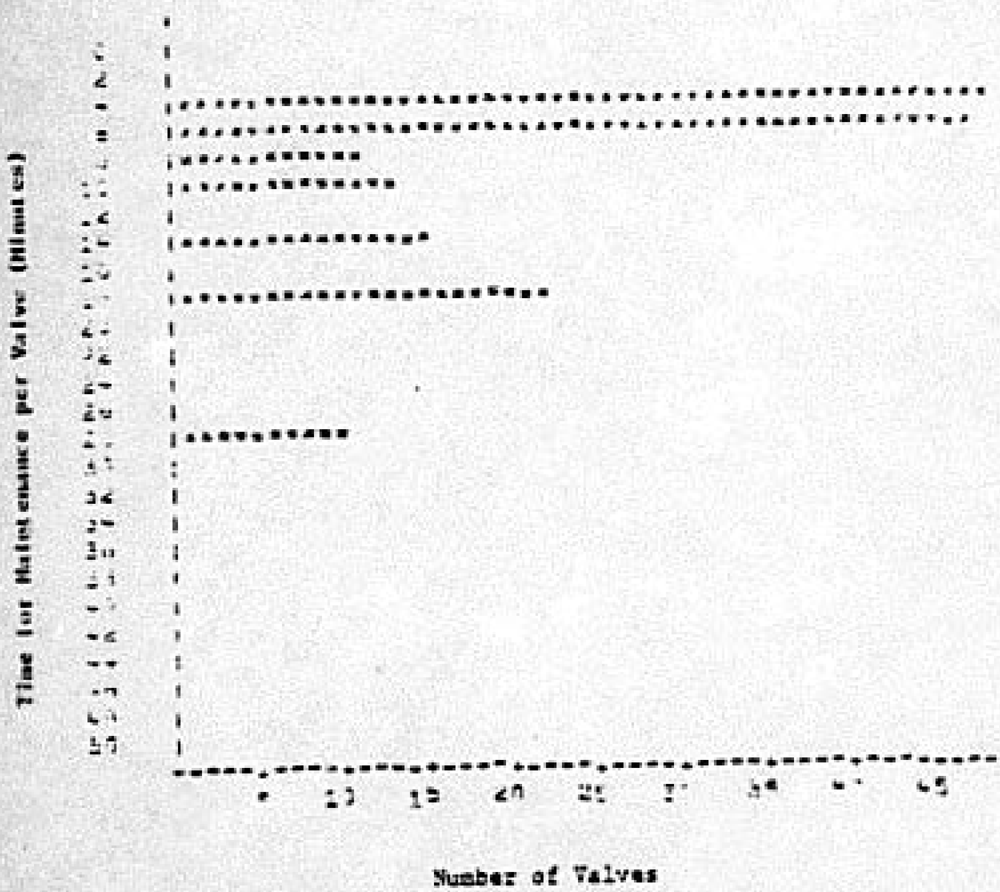


Figure 3-42. Distribution of Maintenance Time for Valves in Study

The activities included in maintenance for this study were restricted to tightening packing gland bolts to compress the packing material around the valve stem and seat while the valve was in service. This operation is a simple on-line maintenance procedure. In many cases after the packing gland bolts had been tightened, the valve was opened and closed. It was then screened again and further tightening was done, if necessary.

Normally, maintenance on control valves was performed by an instrument mechanic, and block valves were maintained by pipe fitters. There did not appear to be significant differences in the time required for maintenance between the two types of valves.

Other on-line maintenance procedures could have been used and are currently practiced in industrial plants. Although some of these other methods may be more time consuming, they have been demonstrated as effective. Some valves have lubricated packing and are equipped with fittings to inject lubricant into the packing gland while the valve is in service. There are also valves equipped with backseating capabilities which allow replacement of the packing without dismantling the valve. Also available are commercial leak sealing services which can inject sealant into a valve to seal the leak while the valve is in service. Finally, some process units have piping configurations which allow bypass or isolation of a valve for repacking while it is in place, even though it is not on-line.

REFERENCES

1. Bazovsky, I., Reliability Theory and Practice, Prentice-Hall, Inc., Inglewood Cliffs, New Jersey 1961.

2. Blacksmith, J. R., G. E. Harris, and G. J. Langley. Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units: Draft Final Report, EPA Contract No. 68-02-3171-1, Radian Corporation, Austin, Texas. August 1980.

3. Finney, D. J., "On the Distribution of a Variate Whose Logarithm is Normally Distributed," Journal of the Royal Statistical Society, Series B, 7 (1941), 155-161.

4. Mood, A. M., F. A. Graybill, and D. C. Boes, Introduction to the Theory of Statistics, Third Edition, McGraw-Hill Book Company, New York 1974.

5. Patterson, R. L., "Difficulties Involved in the Estimation of a Population Mean Using Transformed Sample Data: Technometrics 8, No. 3, (1966), 535-537.

6. Radian Corporation, Data Listing for EPA Project No. 68-03-2776, unpublished technical note, Austin, Texas, December 1980.

7. Searle, S. R., Linear Models, John Wiley & Sons, Inc., New York, 1971.

8. Wetherold, R. G. and D. D. Rosebrook, Environmental Assessment of Atmospheric Emissions from Petroleum Refinery, EPA NO. 600/2-80-075a, NTIS PB 80-225-253, Radian Corporation, Austin, Texas, 1980.

APPENDIX A

Experimental Procedures

EXPERIMENTAL PROCEDURES

This section describes the experimental approach which was taken to investigate the effectiveness of on-line maintenance as a means of reducing VOC emissions from valves in gas and light liquid services.

The selection of process unit types, the choice of individual sources within process units, the screening/sampling methodology, the analytical techniques, and the data-handling methods are all discussed in this section.

1.0 EXPERIMENTAL DESIGN

This section includes a description of the process unit selection and the method used to select sources within the units. The sampling schedule is also presented.

1.1 Process Selection

The selection of processes for testing in this project involved a compromise between sampling efficiency and the degree to which the study represented the population of chemical processes. There are more than 350 major high volume organic chemicals in production exhibiting a wide array of volatility, toxicity, corrosiveness, product value, process severity, production rate, and growth rate. There are benefits to sampling a large variety and number of processes. A wide selection of chemicals would be involved, equipment manufactured by a substantial array of manufacturers would be represented, and a broad range of processing parameters (pressure, temperature, corrosivity, etc.) could be tested. Obviously, however, the scope of testing is limited by both funding and time. It is inefficient to sample at a large number of sites if only a short period of time can be spent at each location. A certain amount of time is required for set-up and for packing at each location. Some time is required for familiarization in each unit (plant work practices, safety regulations, etc.). Additionally, a reasonable number of samples must be obtained at each location. The results from a very small sample set may be statistically insignificant. The choice of six process units to be sampled represents a compromise among the many inconsonant considerations.

Since any single process unit can exhibit unique characteristics, it is desirable to test several examples of each type of process. It was, therefore, decided to test two units of each process type. This resulted in a sampling plan in which two plants for each of three chemical processes were studied.

The three process types studied were ethylene, cumene, and vinyl acetate production. Ethylene was chosen because typically these units are large and widespread, operate with a wide range of process conditions, and handle very volatile materials. Cumene was of interest because this type of unit (one using the reaction of benzene and propylene) handles a hazardous air pollutant, benzene. Production of vinyl acetate from the reaction of ethylene and acetic acid was chosen because some of the process streams are corrosive.

1.2 Selection of Sources

The objectives of this study focused on the effect of routine on-line maintenance on valve emissions and the occurrence and recurrence of leaks from valves and pump seals. Valves and pump seals were selected from each process unit to study these issues.

Source selection relied heavily on a concurrent EPA project (Reference 2) in which all valve and pump sources in the selected process units were screened. Leaking sources were then tagged. The cells of the selection matrix (Table A-1) were filled by random selection from those sources found in the screening study.

TABLE A-1. MATRIX OF SAMPLING/SCREENING QUOTAS PER PLANT

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		M*	C**	M*	C**	C **
Gas	< 1,000	0	30***	0	30***	-
	1,000 to 9,999	2	2	2	2	-
	10,000 to 49,999	2	2	2	2	-
	> 50,000	2	2	2	2	-
Light Liquid	< 1,000	0	30***	0	30***	15***
	1,000 to 9,999	2	2	2	2	2
	10,000 to 49,999	2	2	2	2	2
	> 50,000	2	2	2	2	2

M* is the number of fittings to be maintained.

C** -is the number of fittings in the control group.

*** Fittings screening below 1000 ppm were not maintained. Approximately 30 were scheduled to be screened (not sampled) at least two times each per plant visit to determine the rate of new leak occurrence.

The random selection was performed by selecting approximately twice as many sources as were ultimately needed for each cell. The field crew then followed a selection protocol from these groups of potential sources for testing. The protocol allowed for the elimination of those potential sources which were deemed inaccessible for sampling or which could not be found. Valves selected for maintenance were picked first from the groups of potential sources. Those sources to be used as controls were picked from those that were left in the group. In some units, there were not enough sources to fill certain cells. These insufficiencies were corrected with additional samples in other units. Tables A-3 through A-8 outline the number of sources picked for each unit. Table A-2 summarizes the sampling matrix for the entire program.

1.3 Sampling Schedule

The sampling schedule for the plants in this program is shown in Table A-9. Because of constraints on time and funding, some of the second and third visits were shorter than originally planned. In the abbreviated visits, all screening of valves and pumps in the screening/sampling matrix was performed. However, some valve and pump emission measurements could not be completed during the shorter visits. Sampling priorities were given to those maintained valves which had the higher original screening values. Thus, the reduced sampling effort had a relatively small effect on defining the long-term effect of maintenance on total mass emission rates (or weighted percent reduction). There were, however, a smaller number of measured emission rates for the valves with lower screening values. As a result the confidence intervals associated with the recurrence rate and long term effects of maintenance are not quite as narrow as they might have been with additional mass emissions measurements.

TABLE A-2. MATRIX OF SAMPLING/SCREENING FOR ALL UNITS

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		H*	C**	H*	C**	C**
Gas	< 1,000	--	84***	--	161***	--
	1,000 to 9,999	11	4	15	10	--
	10,000 to 49,999	10	4	12	8	--
	> 50,000	14	7	14	11	--
Light Liquid	< 1,000	--	124***	--	165***	87
	1,000 to 9,999	13	5	21	10	11
	10,000 to 49,999	9	2	16	8	9
	> 50,000	13	6	21	9	6

H* Is the number of valves actually maintained.

C** Is the number of valves (or pumps) in the control group.

*** "low leaking" valves for Unit I could not be matched to their original process information since the identification tags were removed between the first and second visits. There were a total of 106 "low leaking" valves in Unit I.

TABLE A-3. MATRIX OF SAMPLING/SCREENING FOR UNIT 1 (VINYL ACETATE)

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		H	C	H	C	C
Gas	< 1,000	--	*	--	*	--
	1,000 to 9,999	2	--	--	--	--
	10,000 to 49,999	2	--	--	--	--
	> 50,000	2	--	4	2	--
Light Liquid	< 1,000	--	*	--	*	30
	1,000 to 9,999	3	1	--	--	2
	10,000 to 49,999	--	--	--	--	3
	> 50,000	--	--	--	--	--

* "Low leaking" valves for Unit 1 could not be matched to their original process information since the identification tags were removed between visits. There were a total of 106 "low leaking" valves in Unit 1.

TABLE A-4. MATRIX OF SAMPLING/SCREENING FOR UNIT 2 (ETHYLENE)

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		M	C	M	C	C
Gas	< 1,000	--	30	--	32	--
	1,000 to 9,999	2	2	2	2	--
	10,000 to 49,999	2	2	2	2	--
	> 50,000	2	2	2	2	--
Light Liquid	< 1,000	--	34	--	36	12
	1,000 to 9,999	2	2	3	2	1
	10,000 to 49,999	1	--	1	2	1
	> 50,000	2	2	4	2	2

TABLE A-5. MATRIX OF SAMPLING/SCREENING FOR UNIT 3 (VINYL ACETATE)

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		M	C	M	C	C
Gas	< 1,000	--	11	--	35	--
	1,000 to 9,999	2	--	2	2	--
	10,000 to 49,999	2	--	2	2	--
	≥ 50,000	2	--	2	2	--
Light Liquid	< 1,000	--	29	--	34 *	12
	1,000 to 9,999	--	--	2	2	--
	10,000 to 49,999	--	--	2	--	1
	≥ 50,000	1	--	2	1	--

TABLE A-6. MATRIX OF SAMPLING/SCREENING FOR UNIT 4 (ETHYLENE)

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		H	C	H	C	C
Gas	< 1,000	--	31	--	31	--
	1,000 to 9,999	2	2	2	2	--
	10,000 to 49,999	3	2	4	2	--
	> 50,000	2	2	2	2	--
Light Liquid	< 1,000	--	33	--	32	20
	1,000 to 9,999	3	2	6	2	5
	10,000 to 49,999	7	2	5	2	1
	> 50,000	6	2	6	2	3

TABLE A-7. MATRIX OF SAMPLING/SCREENING FOR UNIT 5 (CUMENE)

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		H	C	H	C	C
Gas	< 1,000	--	2	--	30	--
	1,000 to 9,999	1	--	7	2	--
	10,000 to 49,999	--	--	1	--	--
	≥ 50,000	1	--	2	1	--
Light Liquid	< 1,000	--	10	--	31	3
	1,000 to 9,999	1	--	8	3	3
	10,000 to 49,999	--	--	6	2	2
	≥ 50,000	2	--	7	2	1

TABLE A-8. MATRIX OF SAMPLING/SCREENING FOR UNIT 6 (CUMENE)

Stream Class	Initial Screening Value (ppm)	Number to be studied in each fitting type				
		Control Valves		Block Valves		Pump Seals
		H	C	H	C	C
Gas	< 1,000	--	10	--	33	--
	1,000 to 9,999	2	--	2	2	--
	10,000 to 49,999	1	--	3	2	--
	> 50,000	5	3	2	2	--
Light Liquid	< 1,000	--	18	--	32	10
	1,000 to 9,999	4	--	2	1	--
	10,000 to 49,999	1	--	2	2	1
	> 50,000	2	2	2	2	--

TABLE A-9. PROJECT SCHEDULING

Process/Plant ID	Process/Plant Screenings*		Process/Plant Sampling					
			Visit 1		Visit 2		Visit 3	
	Date Started	Date Completed	Date Started	Date Completed	Date Started	Date Completed	Date Started	Date Completed
A	1/21/80	1/30/80	1/31/80	3/7/80*	4/27/80	5/9/80	8/12/80	8/27/80
B	2/12/80	2/28/80	3/10/80	3/26/80	6/1/80	6/11/80	10/21/80	10/21/80
C	3/4/80	3/12/80	4/7/80	4/22/80	9/29/80	10/3/80	10/24/80	10/28/80
D	4/17/80	5/6/80	5/11/80	5/30/80	6/30/80	8/5/80	10/13/80	10/17/80
E	5/7/80	5/16/80	6/12/80	6/30/80	10/7/80	10/10/80	10/29/80	10/31/80
F	5/19/80	5/28/80	9/10/80	9/26/80	11/3/80	11/7/80	-	-

*Interrupted for > 10 days for unexpected plant shutdown

2.0 SCREENING METHODOLOGY

Brief descriptions of the screening procedures and instruments used during this program are presented in this section.

2.1 Instruments

Two types of sensitive portable hydrocarbon detectors were used to screen sources in this program. These were the Bacharach TLV Sniffer and the Century OVA-108.

The Bacharach Instrument Company J-W Model TLV Sniffer 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, 0-1,000 ppm, and 0-10,000 ppm, are built into this instrument. A dilution probe was used when the TLV readings exceeded 10,000 ppm. The probe allowed readings of up to 100,000 ppm. The instrument meter displays the result as ppm hexane by volume when calibrated with hexane. It is battery operated, self-contained, compact and portable.

The TLV Sniffer was calibrated daily with standard mixtures of hexane in air. Two standards were used. One contained 300 ppmv of hexane and the other contained 2000 ppmv of hexane. Details of the calibration procedures are given in a previous Radian report entitled "Assessment of Atmospheric Emissions from Petroleum Refining" (Reference 8).

The Century Systems Corporation Portable Organic Vapor Analyzer Model OVA-108 is a portable gas chromatograph which uses a hydrogen flame ionization detector to detect hydrocarbon concentrations from 1 to 10,000 ppmv. A dilution probe allowed concentrations as high as 100,000 ppmv to be measured (and, in some cases, up to 1,000,000 ppmv).

The electronics and detector were warmed-up for at least ten minutes before calibration. The sample lines were then checked for leaks by placing a finger over the end of the probe and making sure the flowmeter on the front panel chattered or stopped. The OVA was calibrated according to the instructions given in the OVA-108 Operating and Service Manual. The instrument was calibrated with methane. The methane standard was a bottled standard of 8000 ppmv methane in air. A Tedlar bag was fitted with surgical tubing, marked, and used exclusively for this gas standard. This bag was flushed daily and filled with the standard before calibrating.

2.2 Screening Procedures

Screening was done with a Century Systems Corporation OVA-108 and a Bacharach TLV Sniffer. The valves were screened by traversing 360 degrees around the stem seal and the seam where the packing gland merges with the valve bonnet. The point of maximum concentration was identified. The OVA-108 was used before the TLV to quickly identify the area of maximum concentration because of its faster response time. The sample probes were placed as close to the maximum leak as possible. The recorded screening value was the highest reading obtained twice during an interval of about one minute.

Pumps and compressors were screened at the outer shaft seals by completely traversing 360 degrees with the OVA to locate the point of maximum concentration. Occasionally a 12-inch Teflon extension was added to the OVA probe in order to extend past safety screens on vertical pumps.

3.0 Sampling Methodology

Sources were sampled by the flow-through method described previously (Reference 8). Dual sampling trains were used in order to sample different sources simultaneously or to dilute the steady-state concentration in the system to nonexplosion levels. Dilution was accomplished by operating the two trains in parallel on the same leak source. Two trains in parallel produced a dilution air rate which was twice as high as could be obtained with a single train.

3.1 Valve Emissions

The sampling procedure was:

- The valve was screened with the OVA-108 and TLV Sniffer and the values and time of day were recorded.
- The valve was tented with Mylar® and duct tape and sampled (see Reference 8).
- The tent was removed and the valve was rescreened as in the first step, above.

3.2 Pump Seal Emissions

Pump sampling was analogous to valve sampling. Due to the configurations of some pumps, it was difficult to construct small and/or well-sealed tents around the pump seal. Some pump seal (or seal areas) continually emit water, oil, or other seal flushing media. The tent must have an opening to allow drainage of this material. A large tent is often required to reach areas where the duct tape can make an adequate seal. Areas closer to the seal may be too hot or may be wet with water or flush oil. In some cases, it is simply not safe to allow the tent material to be close to the rotating shaft and seal area.

3.3 Emission Calculations

The emission rates can be calculated from the physical measurements recorded during the operation of the sampling train and with the analyses of the hydrocarbon content of the air passing through the sampling train. The basic equation is

$$L = \frac{k_1\ DF(P-\Delta P)M(C_T-C_A)}{460+T} \qquad \text{(A-1)}$$

where
- L = Hydrocarbon emission rate, lb/hr
- k_1 = 2.75×10^{-6}, a conversion constant
- D = Dry gas meter correction factor
- F = Flow rate, CFM
- P = Ambient atmospheric pressure, in. Hg
- ΔP = Pressure differential between ambient pressure and pressure at dry gas meter, in Hg.
- M = Average molecular weight of gas (essentially air) passing through dry gas meter
- C_T = Total hydrocarbon concentration in air passing through the dry gas meter, ppmw
- C_A = Total hydrocarbon concentration in air near the measured leak source, ppmw
- T = Temperature of gas (air) stream at the dry gas meter, °F

For example, assume a total hydrocarbon concentration of 19,000 ppmw was measured in the gas stream from a tent around a leaking source in an ethylene unit. The hydrocarbon would be assumed to be hexane (MW=86). The following values were recorded during the sampling

- F = 1.3 CFM
- P = 29.9 in.Hg
- ΔP = 2.0 in.Hg (at the dry gas meter)
- C_T = 19,000 ppmw
- C_A = 20 ppmw
- T = 73°F

and $D = 0.95$

Then $$M = \frac{10^6}{\frac{19,000}{86} + \frac{10^6 - 19,000}{29}} = 29.37$$

The emission rate L is then calculated from Equation (A-1)

$$L = \frac{(2.75 \times 10^{-6})(0.95)(1.5)(29.9 - 2.0)(29.37)(19,000 - 20)}{460 + 75}$$

$$L = 0.114 \text{ lb/hr.}$$

3.4 Species Emissions

Some organic species sampled were found to quickly degenerate through decomposition or reaction in the sample bags. To minimize this degradation, samples were taken in 1 ml Teflon® tubes with inert valves on each end. The sample gas was taken from the sampling train, but as close as possible to the tent. Teflon® fittings were used throughout to avoid degradation. An inert valve with Luer-Lok fittings was placed in the sampling train line and used as the sample point. The 1 ml Teflon® tubes were flushed with 200 ml of sample from this point using a gas-tight syringe. They were then closed to trap the gas sample, remove, and analyzed on the gas chromatograph within three minutes. This procedure was found to reduce sample degradation to a negligible level.

4.0 Valve Maintenance Procedures

Valve maintenance consisted of tightening packing glands while monitoring the leak. The term "directed maintenance" refers to this procedure when a hydrocarbon detector is used during the maintenance activity. The leak is monitored with the instrument until no further reduction of screening values is observed or until the valve stem rotation starts to be restricted. The type of maintenance personnel performing the repairs depended upon the type of valves that were to be maintained. Control valves required instrument personnel experienced with the process unit and with the precautions necessary to safely maintain operations while repairing control valves. Block valves were maintained by regular maintenance personnel such as pipefitters or boilermakers.

The maintenance procedures generally consisted of first screening the valve with the OVA-108 and recording the value. The packing gland nuts were then tightened a little at a time while monitoring the leak with the OVA. Tightening was continued to the point of either minimizing the leak, causing the stem movement to tighten or grab, or reaching the bottom of the packing bolts. The valve was then operated, if possible, and rescreened. If the leak remained or worsened, the packing was further tightened until the limits described were reached.

Certain valves could not be maintained due to their locations in the process stream. These were in critical locations where sticking, jamming, or breaking of the valve might precipitate a unit shutdown. This occurred with two valves in the six process units.

5.0 DATA COLLECTION

Data were collected and recorded on previously prepared data sheets. This facilitated the easy transfer of information in a concise format. The types and sources of information obtained in this study are discussed below.

5.1 Data Sources

Data sources for this project consisted of direct observations by Radian field personnel, verbal and written input from plant personnel, and input from process flow diagrams and piping and instrumentation diagrams supplied by plant personnel.

5.2 Data Collection and Recording

Process unit sources were screened and the data were reported on the Screening Data Form (Figure A-1). The Radian screening teams traced process lines and compared plant lines with those on flow diagrams. Temperatures, pressures, and primary and secondary stream compositions were generally supplied by plant personnel. The Screening Data form was reused for the screening of the sources in both the sample and nonleaking source matrices at each unit visit during the sampling phase of the program. Each stream component in every plant was assigned a code. This was recorded on the materials coding sheet (Figure A-2) for each process unit.

Sampling data were compiled on three forms: the Screening Data Sheet (Figure A-3), the Sampling Data Sheet (Figure A-4), and the Analysis Data Sheet (Figure A-5).

Valve maintenance procedures were recorded on the valve maintenance data form (Figure A-6). Required maintenance was reported as the number of turns for each nut on the packing gland compression plate bolts.

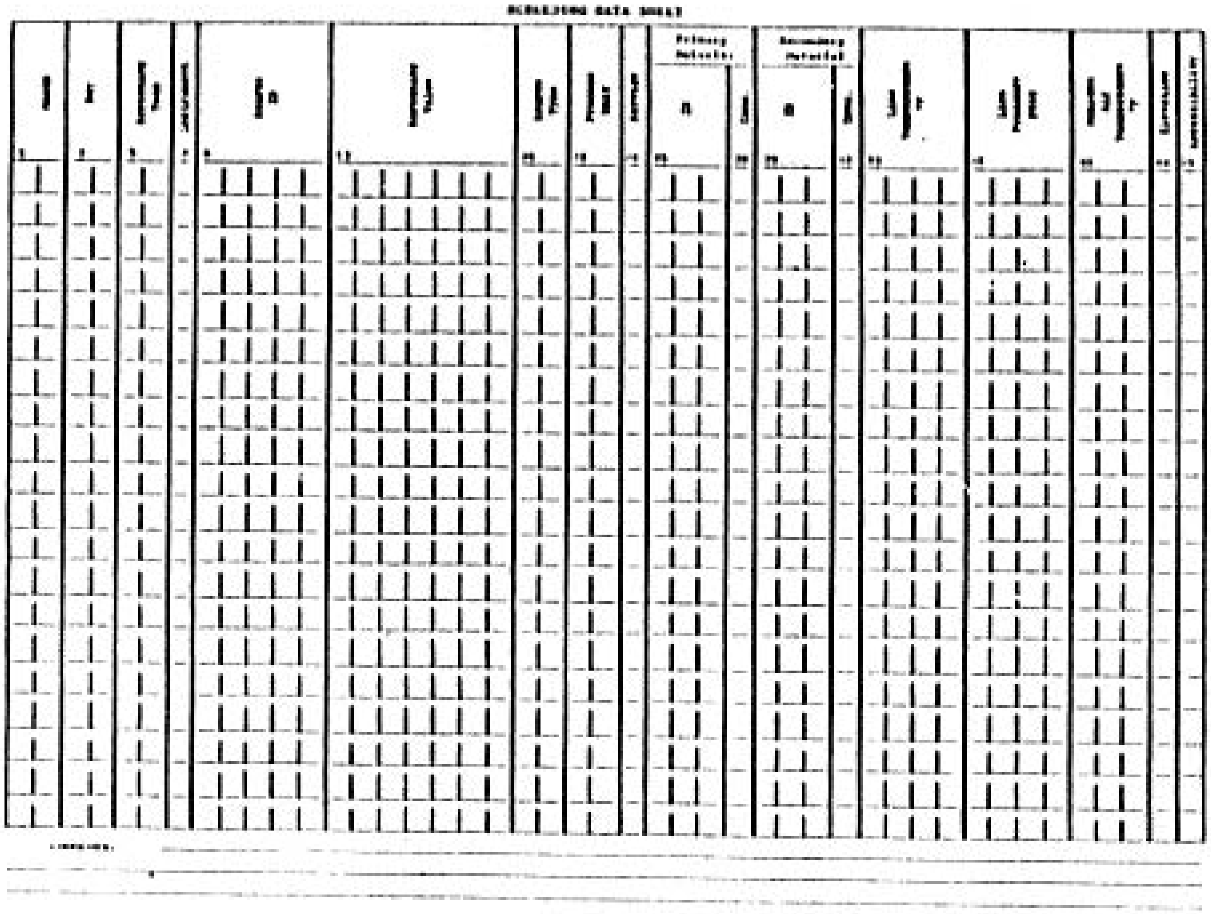


Figure A-1. Screening Data Sheet

MATERIAL CODING SHEET

Company Name: ____

Chemical*		ID	DO NOT CODE
	3		
	9		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
Repeat columns 1 and 2 —	3		
	9		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		
	[illegible]		

Figure A-1. Material Coding Sheet

SCREENING SHEET
FOR SAMPLE DATA

Card 1

1. Radian Valve/Pump ID # ________ 2. Unit/Process ________

3. Plant Name ________________________

---

4. Date (Mo. Day Yr.) ________ 5. Screener's ID ________

6. Before Testing Screening Time (Military Time) ________

7. Before Testing OVA Screening Value ________ TLV Screening Value ________

---

8. Screener's ID ________

9. After Sampling Screening Time (Military Time) ________

10. After Sampling OVA Screening Value ________ TLV Screening Value ________

Comment 1 ________ Comment 2 ________

Figure A-3. Screening Sheet for Sample Data

Card 1 [ ]

SAMPLE DATA SHEET

1. Radian Valve/Pump ID# [ ] 2. Unit/Process ______ _____

3. Plant Name ______________________________

---

4. Date [Mo. Day Yr.] 5. Sampler's Initials [ ]

6. Time [ ] (Military Time) 7. Card ID# [ ] 8. S.S.# ___ 9. Page # ___

10. Meter #1 [ ] 12. Meter #2 [ ]

11. Time #1 [ ] 13. Time #2 [ ]

14. Temp #1 °F [ ] 15. Temp #2 °F [ ]

16. Bar. Press., in. Hg. [ ] 17. ΔP, in. Hg. [ ]

18. DGM Correction Factor [ ] 19. Meter # ______________________

20. Vol. Org. Condensate ml [ ]

21. Coll. time, minutes [ ] 22. Specific Gravity of Organic Condensate [ ]

23. Comment [ ]

Figure A-4. Sample Data Sheet

ANALYSIS DATA SHEET
(AMBIENT AND BAG)

| 1 | A |
1

1. Radian Valve/Pump ID# [| | V | A | | | |] 3   2. Unit/Process ______________

3. Plant Name ______________________

4. Date (Mo. Day Yr.) [| | | | |] 11   5. Analyst's Initials [| |] 17

6. Time (Military) [| | |] 20   7. S.S. # ________   8. Page # ______

9. Instrument __________________ [ ] 24

AMBIENT AIR

	Component Code	PPM
1.	25	28
2.	43	46
3.	61	64

BAG SAMPLE

Component Code	PPM
34	37
52	55
70	73

Card 2 [2 | A] 1 Duplicate columns 3 through 10 from Card 1

	Component Code	PPM
4.	11	14
5.	29	32
6.	47	50

Component Code	PPM
20	23
38	41
56	59

Remarks:

Figure A-5. Analysis Data Sheet

VALVE MAINTENANCE RECORD SHEET

DATE ____________ TIME START __________ TIME END ________ PLANT ________ UNIT ________

Maintenance Team OP PT IM Screening Team ____________ Instrument ID __________

Valve ID	Valve Type C/S	OVA Screening Value		Type of Maintenance Person	Time Required in Minutes	Maintenance Performed
		BM	AM			

Figure A-6. Valve Maintenance Record Sheet

For the VOC leak sources in the sampling matrix, additional information was obtained and recorded on the process stream data form (Figure A-7) and the valve and pump data forms (Figures A-8 and A-9). These forms were completed by both Radian and plant personnel.

Daily calibrations of the TLV Sniffer and OVA were recorded on the calibration data form (Figure A-10) while repeat screening values were recorded on the form shown in Figure A-11. The repeat screening values are those screening values observed in subsequent screening of the same source by the same operator.

PROCESS STREAM DATA

1 P

Stream Name ____________________ Code [ ] 3 4 5

Radian Valve/Pump ID # [ ] 6 7 8 9 10 11 12 13

Company Valve/Pump ID # ____________________ [ ] 14

Stream Vapor Pressure [ ] 19 psia at [ ] 23 °C

Stream Phase at Process Conditions gas = 1/ liquid = 2/ 2-phase = 3/ [ ] 26

Stream Composition:

Component Weight % (1) or Volume % (2) [ ] 27

Component		
____________	[ ] 28	[ ] 31
____________	[ ] 35	[ ] 38
____________	[ ] 42	[ ] 45
____________	[ ] 49	[ ] 52
____________	[ ] 56	[ ] 59
____________	[ ] 63	[ ] 66
____________	[ ] 70	[ ] 73
____________		
____________		

Figure A-7. Process Stream Data

DATA SHEET - VALVES

1. Radian ID# [F A] (1)

2. Unit/Process______________________

3. Plant Name______________________

Valve ID (or description)______________________

VARIABLES:

4. Pressure, psig [ ] (9)

5. Temperature, °F [ ] (13)

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

7. Line size (inches) [ ] (18)

8. Block or control (B,C) [ ] (21)

9. Valve type [ ] (22)
   - GA - gate; PL - plug
   - GL - globe, DI - discharge
   - BF - butterfly; SL - slide
   - AN - angle; RM - ram

10. Time since last maintenance (months) [ ] (24)

11. Age, yrs [ ] (26)

12. Stem movement [ ] (28)
    - I - in/out
    - R - rotation
    - C - combination

13. Manufacturer [ ] (29) ______________

14. Seals of cover [ ] (31)
    - S - steel
    - O - other

15. In-line/Open-ended (I/O) [ ] (32)

16. Vibration [ ] (33)
    - N - none
    - S - slight
    - M - moderate
    - H - heavy

17. Open/Closed (O/C) [ ] (34)

18. Flow/No-Flow (F/N) [ ] (35)

Figure A-5. Data Sheet - Valves

DATA SHEET - PUMP SEAL

1. Radian ID# [| | F | S | | | |]

2. Unit/Process ______________________

Pump ID ______________________

3. Plant Name ______________________

[ ] I - Inboard
O - Outboard

[ ] Seal Symbol (A, B, C, etc.)

VARIABLES:

4. Discharge pressure, psig [| | |]

5. Temperature, °F [| | |]

6. Pump/seal type
   CM - centrifugal/mech.
   CP - centrifugal/packed
   RP - recip/packed
   [|]

7. RPM or strokes PM [| | | |]

8. Stroke length (Recip. in) [| | |]

9. Capacity, GPM [| | | |]

10. Seal/lube
    P - product leakage
    W - water
    H - hydrocarbon lubricant
    [ ]

11. Gland type
    N - no quench gland
    O - oil quench
    W - water quench
    [ ]

12. Single or double (1,2) [ ]

13. Shaft diameter, (in) [|]

14. Age, yrs [|]

15. Time since last maintenance (months) [|]

16. Manufacturer ______________ [|]

17. Mtls of constr
    S - steel
    O - other
    [ ]

18. Horizontal or vertical (H,V) [ ]

19. Pump running (Y,N) [ ]

Figure A-9. Data Sheet - Pump Seal

1 Month	3 Day	5 Instrument	6 Screening Team	8 ___ Low standard ppm calibration	14 ___ High standard ppm calibration	20 Dilution Probe Calibration

Comments: ____

____

____

____

Figure A-10. Calibration Checking Form

1 Month	3 Day	5 Screening Time	7 Instrument	8 Process Unit	10 Source ID	15 Screening Value	22 Ambient Air	33 [illegible]	[illegible]

Comments:

Figure A-11. Repeat Screening Form

6.0 ANALYTICAL TECHNIQUES

Two different analytical methodologies were used to quantitate VOC emissions in the three types of process units studied in this program. Total hydrocarbon analyses were performed on the emission streams in the ethylene and cumene units. This was satisfactory because hydrocarbons are nearly exclusively present in the process streams of these two types of units. The response of the flame ionization detector (FID) to these compounds is quite similar. Thus, an instrument such as the Byron Total Hydrocarbon Analyzer (THC) can be calibrated with a single representative hydrocarbon. The emission streams can then be analyzed for the total hydrocarbon content with reasonable accuracy.

However, the organic components of the streams in the vinyl acetate process unit do produce widely differing responses with an FID. Thus, a more comprehensive analysis to identify individual components must be performed. The gas chromatograph must be calibrated with the individual major components present in the streams.

6.1 Organic Species

Because of the wide variation of responses by weight to Flame Ionization Detection (FID) of the organic components encountered in the vinyl acetate unit process streams, analyses of the VOC samples were conducted on a HP 5730A Dual FID Gas Chromatograph (GC). Individual components were separated and quantified. Dual gas samples were introduced simultaneously onto separate columns with a Valco 10 port Hastalloy C Multipoint Valve installed immediately forward of the GC syringe injection ports. Component peak integrations were compiled on two HP 3380 A Electronic Integrators.

The parameters and their values used during the gas chromatographic analysis of emissions from the vinyl acetate units were:

- Porapak S in 6' x .25 inch O.D. 2 mm I.D. glass columns.
- Temperature = 170°C Isothermal,
- Flow rate of N_2 carrier = 90 ml/min.
- Run time = 10-15 minutes.

Excellent peak resolution was achieved for ethylene, acetaldehyde, methyl acetate, vinyl acetate, ethyl acetate and acetic acid.

The GC FIDs were calibrated to standards daily, and because of the number of standards involved, were generally limited to single point calibrations. Concentrations of the standard gases for the vinyl acetate units were:

		Permeation Tube	Cylinder
•	Ethylene	--	114,700 ppmw
		--	10,200 ppmw
•	Acetaldehyde	~ 1000 ppmw	7,870 ppmw
•	Methyl Acetate	~ 5000 ppmw	5,300 ppmw
•	Vinyl Acetate	~ 3000 ppmw	--
•	Ethyl Acetate	~ 1500 ppmw	30,000 ppmw
•	Acetic Acid	~ 1000 ppmw	--

Calibration standards, except ethylene, were initially generated for all the major components of the process VOC samples by means of a Metronics 230X Permeation Oven maintained at 100°C for all standards. Dry nitrogen carrier flow was kept in the 50-100 ml/min range. The permeation oven took up to several hours to re-establish equilibrium for the permeation standards when interrupted by changing flow rates, loss of temperature, or loss of oven chamber pressure when changing permeation tubes. Consequently, cylinder tank standards were used to corroborate and replace permeation standards whenever possible.

Two gas standards were always generated from the permeation oven due to great adsorption when exposed to metal surfaces. Thus, compositions of standard gases stored in metal cylinders were not reliable. The two gases which were found to adsorb were vinyl acetate and acetic acid.

Acetic acid standards from permeation tubes gave reproducible values of the ratio $\left(\frac{\text{integrator counts}}{\text{ppmw}}\right)$. However, the ratio for vinyl acetate declined at a rapid rate after the first day or two usage of vinyl acetate permeation tube. This decline was apparently due to the chemical's polymerization in the permeation tube at oven temperatures, despite the presence of hydroquinone inhibitor. The available permeation surface area thus decreased with increasing polymer gel formation. This property led to the steady reduction of response factor values $\left(\frac{\text{counts}}{\text{ppmw}}\right)$. This problem was circumvented by relating the maximum permeation rate measured with several new vinyl acetate tubes to the acetic acid tube permeation rate. Vinyl acetate responses were then determined by measuring the acetic acid response and applying relative response ratios to the acetic acid FID response for that day. This can be seen more clearly in Equation A-2, Below. The ethylene standard FID response factor was used for corroboration.

$$\left(\frac{I_{va}}{C_{va}}\right)_{\text{day } K} = \frac{\left(\frac{I_{va}}{C_{va}}\right)_{\text{day } n}}{\left(\frac{I_{aa}}{C_{aa}}\right)_{\text{day } n}} \left(\frac{I_{aa}}{C_{aa}}\right)_{\text{day } k} \qquad \text{(A-2)}$$

where: I_{va} = integrator counts for vinyl acetate of concentration C_{va}

I_{aa} = integrator counts for acetic acid of concentration C_{aa}

C_{aa} = concentration of acetic acid, ppmw

C_{va} = concentration of vinyl acetate, ppmw

day n = reference day of analysis when vinyl acetate permeation
tubes were new

day k = days on which subsequent calibrations are desired

Gas emission samples in the vinyl acetate unit are taken in small Teflon® tubes. These tubes are 0.125 OD, and capped at each end with Hamilton mini-inert two way valves. The tubes were prepared by flushing them with standard gases for two to five minutes. Then they were placed on the multi-port gas sampling valve on the inlet of the GC and the contents flushed for fifteen seconds onto the GC columns. The tubes were then flushed with carrier gas for approximately 30-60 minutes. The tubes were ready for use on the sampling train to catch emission samples.

When the tubes were filled with samples, they were placed on the multiport gas sampling valve and the contents flushed for fifteen seconds onto the GC columns. Analyses of VOC species occurred within three minutes of the time the samples were taken.

A measure of the accuracy of this sampling/analysis method can be found in the results of emission measurement accuracy checks made with ethyl acetate. The recovery of ethyl acetate ranged from 95 to 113 percent.

6.2 Total Hydrocarbons

Because of the exclusive presence of hydrocarbons in the ethylene and cumene process units, primary analysis of these fugitive volatile organic carbons (VOCs) was undertaken on a Byron 301C Total Hydrocarbon Analyzer (THC). Principles of operation and specifics to this particular application can be found elsewhere (Reference 8). Because of an upper limit of 20,000 ppmv for quantitation of the VOC samples on this instrument, dilutions of the relevant samples were made with a 1.5 liter gas-tight syringe.

Methane calibrations were carried out daily on the THC with an 8000 ppmv methane/air tank standard. Nonmethane hydrocarbon calibrations were also carried out daily on the THC with a 2000 ppmv hexane/air standard.

APPENDIX B

Data Handling

DATA HANDLING

Data were taken and recorded on specially prepared data sheets and handcarried to the data management team. Inconsistencies were resolved and the data keypunched and entered into the computerized data base.

1.0 FIELD PROCEDURES

Data were taken and values recorded directly into bound notebooks containing data sheets. Separate notebooks for screening, sampling and analytical parameters were used.

Information data sheets for pumps and valves were used to collect physical and historical data. These were submitted to the company contact and subsequently returned to Radian.

Raw data were always handcarried from the field to Austin and presented to the data management team. At that time, an attempt was made to fill in any missing data and to resolve any apparent inconsistencies. This was accomplished in a meeting between data base management personnel and a member of the field crew.

2.0 DATA EDITING AND KEYPUNCHING

Data sheets received from the field were logged into a data log sheet. Then the data were manually edited in order to eliminate obvious mistakes and inconsistencies. The edited data were keypunched and key-verified.

3.0 DATA BASE MANAGEMENT

Programs using the SAS software system were developed early in the project to input and perform a second edit on the data. Universal I.D.s were used in each data set so that complete cross-referencing was possible. Towards the end of the project, all the data were organized into a rectangularly structured disk file. Each time a source was screened, sampled or maintained a record was added to the file. All disk records were written to magnetic tape on a weekly basis to back-up the data files.

When field testing was completed and all data had been included in the disk files, computer listings of all data were prepared. These listings were audited by comparison to the original field data sheets and laboratory notebooks. All inconsistencies were corrected. The validated data base was then used for data summaries and statistical analysis.

APPENDIX C

Quality Control

1.0 OVERVIEW OF QUALITY CONTROL PROCEDURES

Comprehensive quality control was emphasized throughout the program. All phases of the sampling and analysis effort from experimental design to data reduction included specific quality control procedures. There were two major objectives of the quality control effort:

- to identify problems as they occurred in the field, and
- to measure and document occurring levels of accuracy and precision of all measurements.

Quality control guidelines were developed to be both cost effective and adequate to insure credible data. The quality control program for the sampling and analysis activities included the following elements:

- formatted data collection forms for direct keypunching of data recorded in the field,
- sampling and subsequent analysis of standard gas mixtures,
- daily calibration checks of the screening devices,
- daily testing of screening devices on the same source, and
- replicate sample analysis and blind standard analysis in the laboratory.

Using the above objectives and activity guidelines as a basis, this Appendix presents the various types of quality control data collected during the program. Table C-1 summarizes the accuracy and precision of the sampling and analysis procedures used in this program. The Quality Control results are presented in this appendix as follows:

Section 2.0 - Quality Control for Screening Devices

Section 3.0 - Quality Control for Sampling and Analytical Procedures

TABLE C-1. SUMMARY OF ACCURACY AND PRECISION OF SAMPLING AND ANALYSIS TECHNIQUES

	Screening Devices
Accuracy	90 percent of calibration checks were within ± 20 percent of the standard; no drifts or biases were noted in any of the instruments (see Section 2.1)
Repeatability	screening value for a given source with an average screening value of x can be expected to vary from x/5.6 to 5.6x within a short time period (see Section 2.2)
Percent of Variation in Data Attributable to Measurement	About 18 percent of the variability in the screening values from the selected sources with multiple readings can be attributed to the screening devices. More than 50 percent of the variation is attributable to differences between the sources (see Section 2.2)
	Sampling/Analysis
Accuracy	
Analysis	the average percent difference from standards for the two analytical systems used is 7.4 percent, indicating a slight positive bias in the analysis (see Section 3.1).
Sampling and Analysis	Average recovery for the non-benzene standards was 102 percent, indicating no biases in the total sampling/analysis system (see Section 3.2). The benzene checks do not impact the data in the report.
Repeatability	
Sampling and Analysis	The standard deviation from repeat samples from the same source was 23 percent, while the variability in the standard checks was 16 percent (see Sections 3.2 and 3.3). The difference is attributable to short-term variations in the actual leak rate and/or variations in process conditions.

2.0 QUALITY CONTROL FOR SCREENING PROCEDURE

The screening of sources was accomplished with six different instruments in use at various times in the program. These included five Century Instrument Company Organic Vapor Analyzers (Model OVA-108) and one J. W. Bacharach Instrument Company "TLV Sniffer." The corresponding instrument identification numbers are given below:

Device Type	Serial Number	Assigned ID Number
OVA	2158	1
OVA	1575	2
OVA	2159	3
OVA	2848	4
TLV	7E8A17	5
OVA	2254	6

Two quality assurance activities were used for the screening devices:

- calibration checks, and
- repeated screenings.

2.1 Calibration Checks

The OVA and TLV instruments were calibrated each day. Standards of 490-800 ppmv and 2990-8000 ppmv methane in air were used to obtain a two point calibration each day on the OVA; 200-300 ppmv and 1990-2000 ppmv hexane in air were used to calibrate the TLV. Before a recalibration was made each day, the values obtained from the instrument were recorded. This served two purposes:

- a check for instrument damage or malfunction, and

- documentation of the stability of the daily calibration.

In addition to the low and high standard calibrations, a dilution probe was occasionally attached to the instrument and another reading was taken. The probe was set at 10:1 or 100:1 dilution of the high standard concentration.

Figures C-1 through C-18 are the plots for the various calibration readings. They are plotted according to instrument and then by low, high and diluted standards. The symbols used to indicate the different screening values are the instrument ID numbers.

Most of the differences found were less than 20 percent of the known concentration, with a few between 20-30 percent. None of the devices gave any indication of a consistent bias (or drift) at either the high or low level. Based on this finding, it is concluded that the daily calibration of the screening devices at two levels using standard gases was adequate for obtaining consistent, unbiased readings.

2.2 Repeated Screenings

The repeatability of the screening devices and the variability of screening values from the same source over time were investigated by the performance of multiple screenings on the same source by the same operator each day that testing was done in a unit. These repeated screenings are useful in assessing:

- repeatability of screening measurements (difference between multiple readings on the same source within a short time period, i.e., less than five minutes); and

- variability in screening values from a particular source over time.

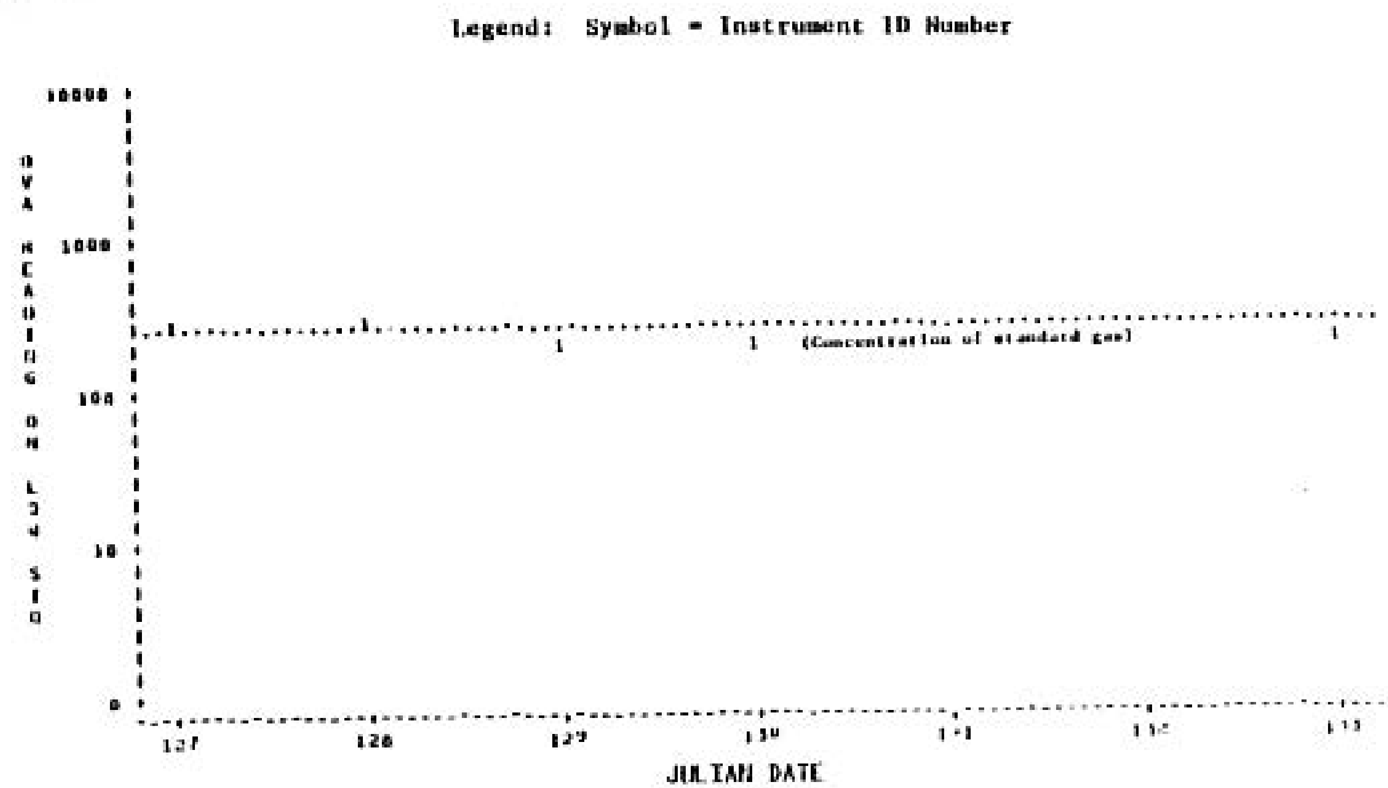


Figure C-1. Low Standard Calibrations for OVA
Instrument #1

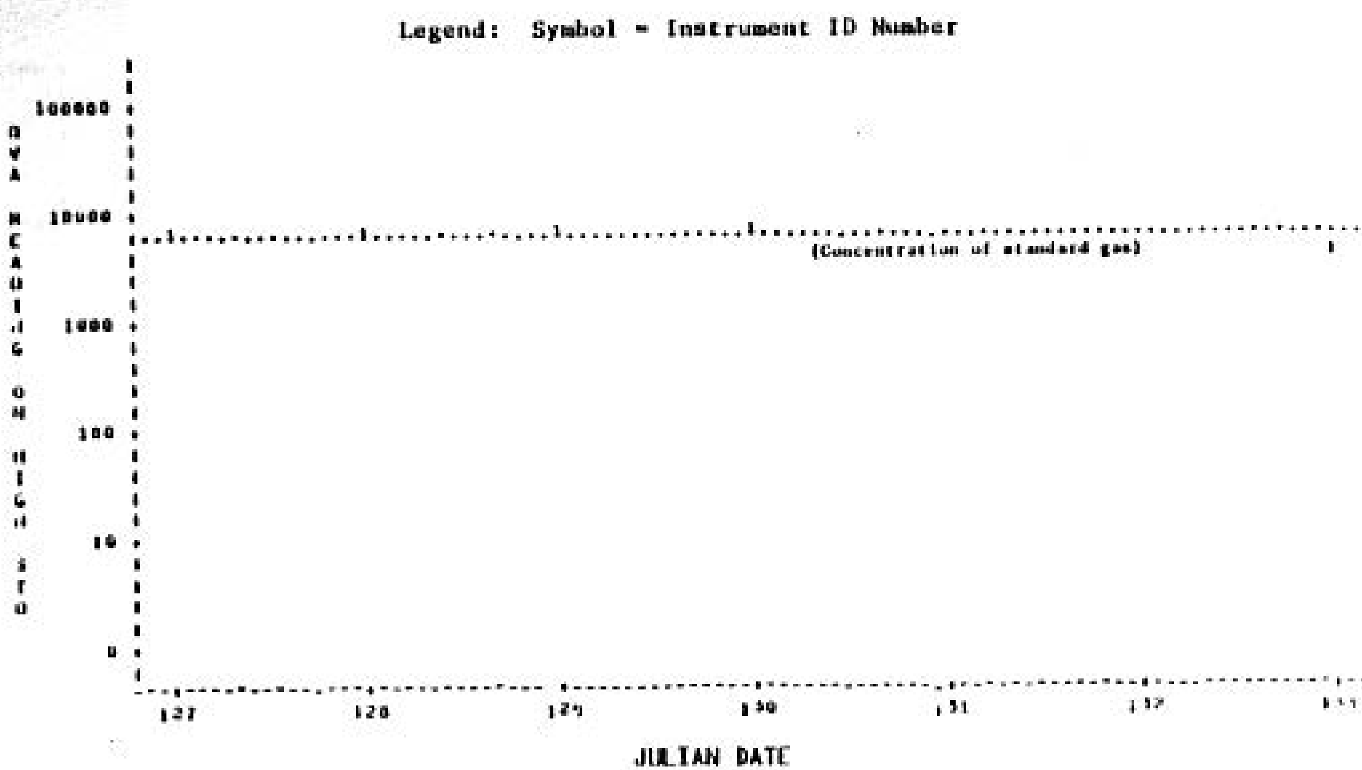


Figure C-2. High Standards Calibrations for OVA Instrument #1

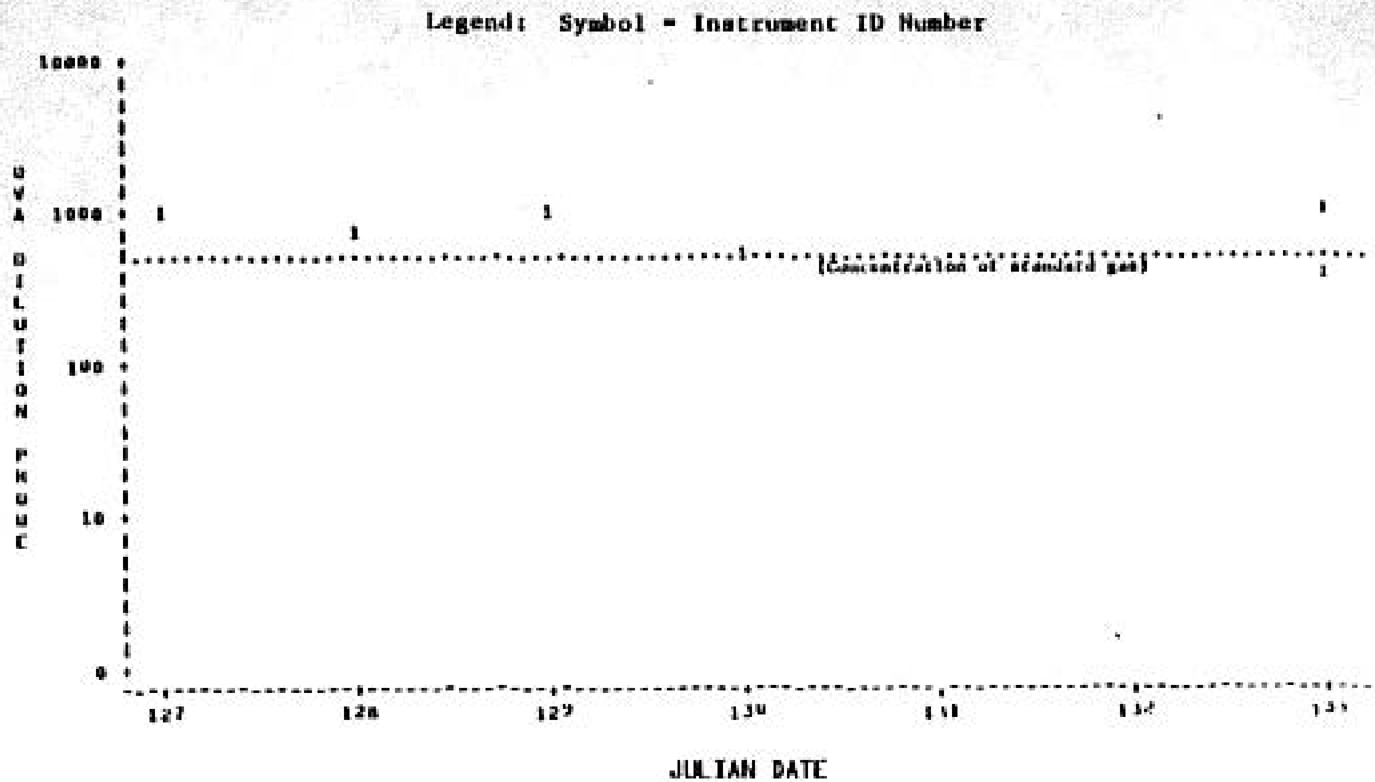


Figure C-3. Dilution Probe Calibrations for OVA Instrument #1

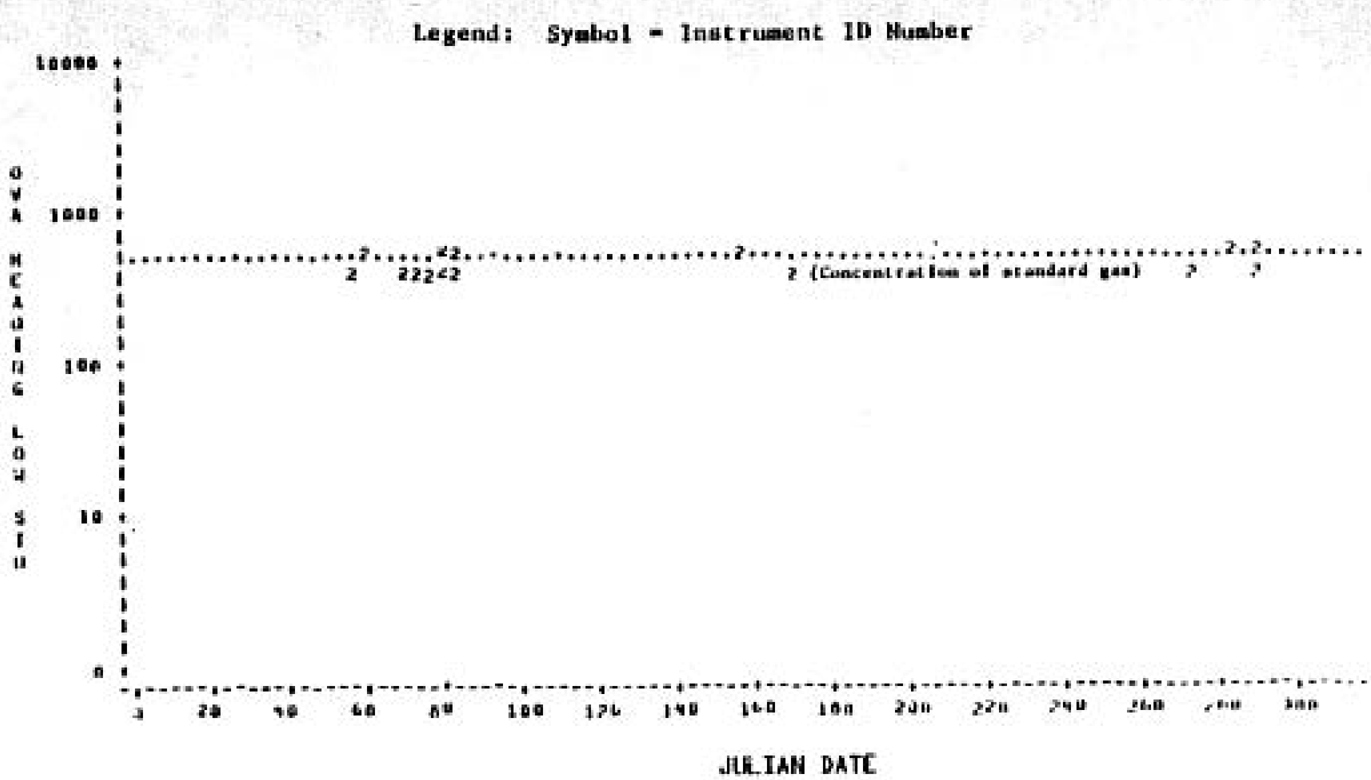


Figure C-4. Low Standards Calibrations for OVA Instrument #2

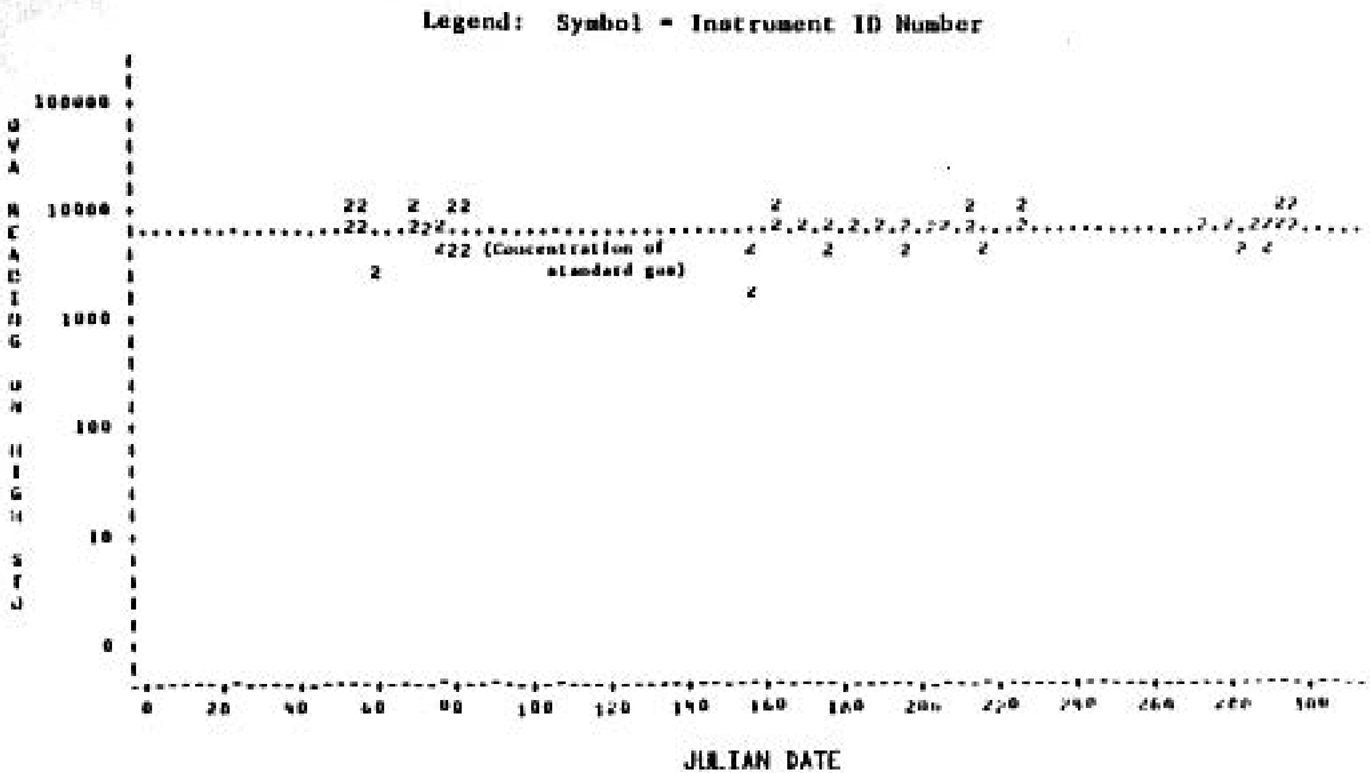


Figure C-5. High Standards Calibrations for OVA Instrument #2

Legend: Symbol = Instrument ID Number

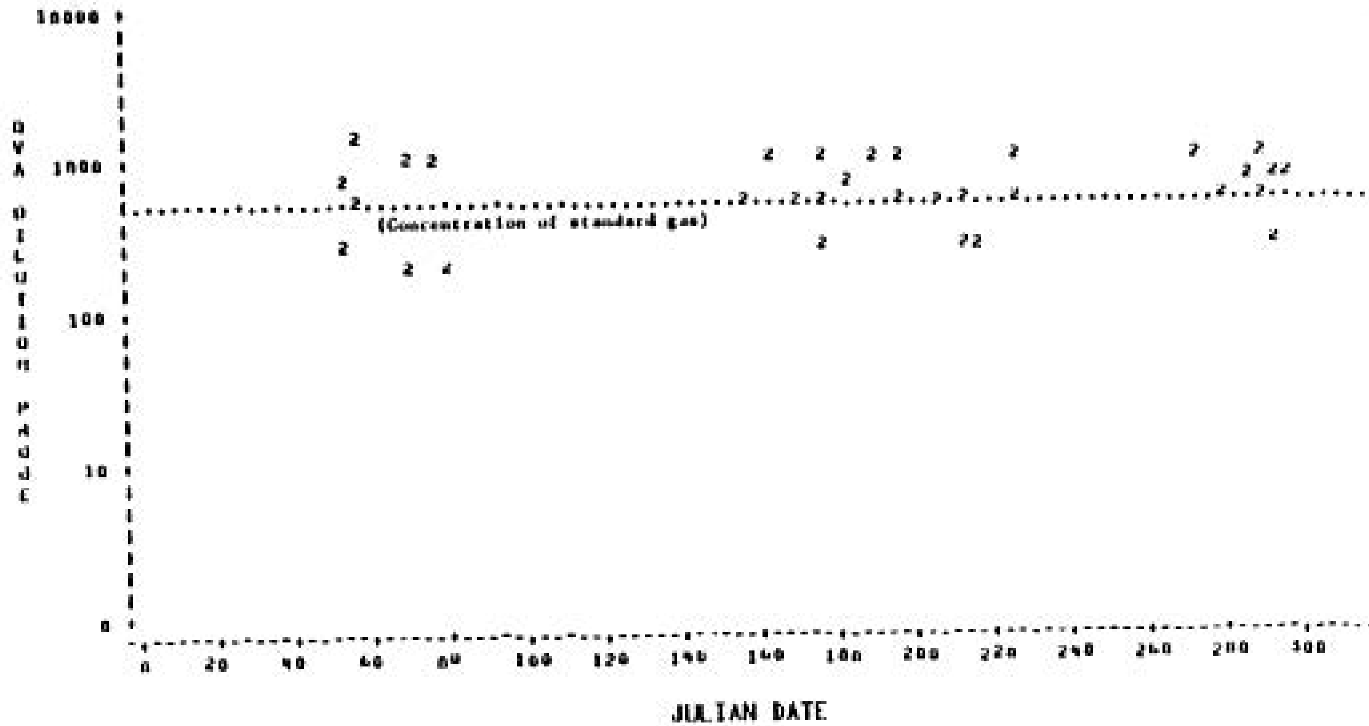


Figure C-6. Dilution Probe Calibrations for OVA Instrument #2

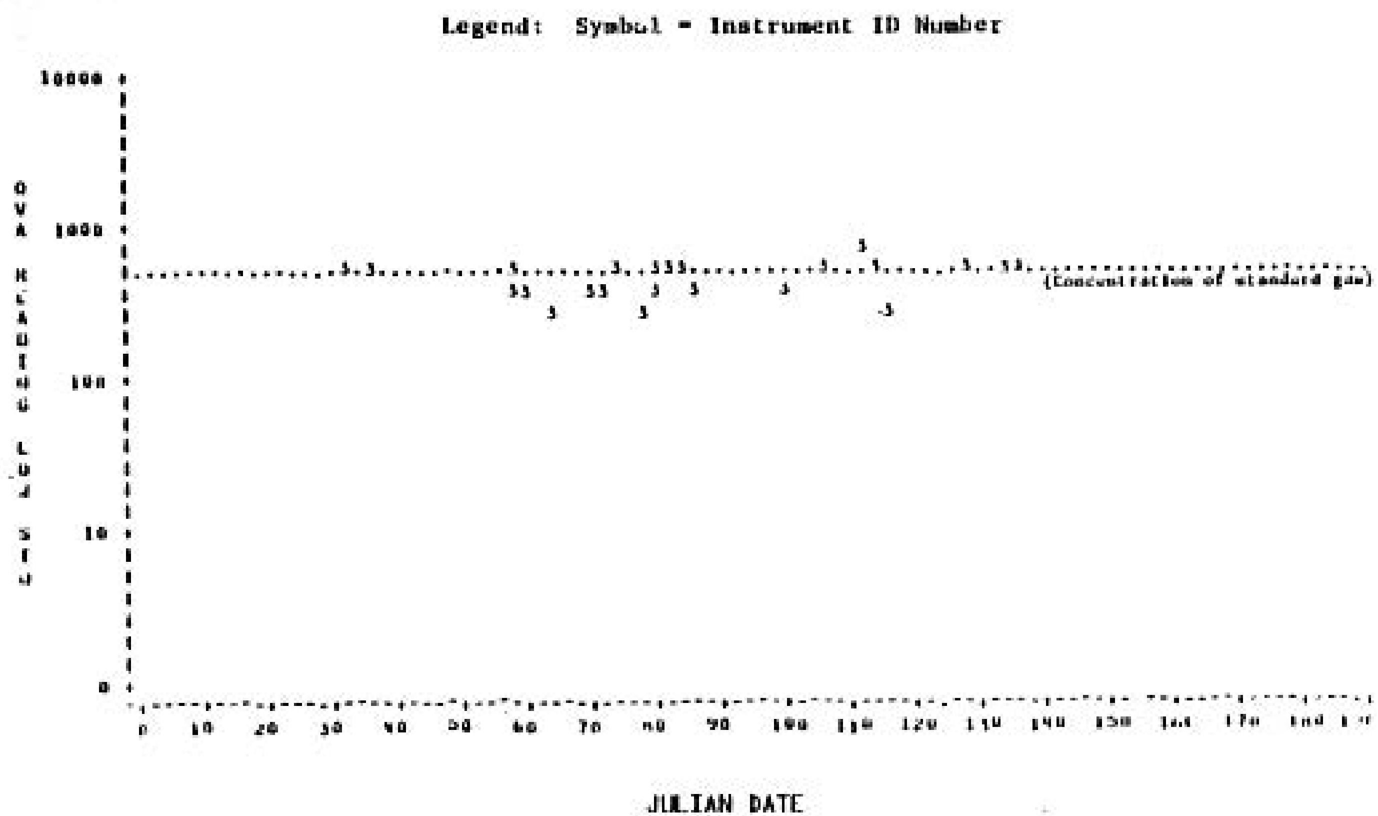


Figure C-7. Low Standards Calibrations for OVA Instrument #3

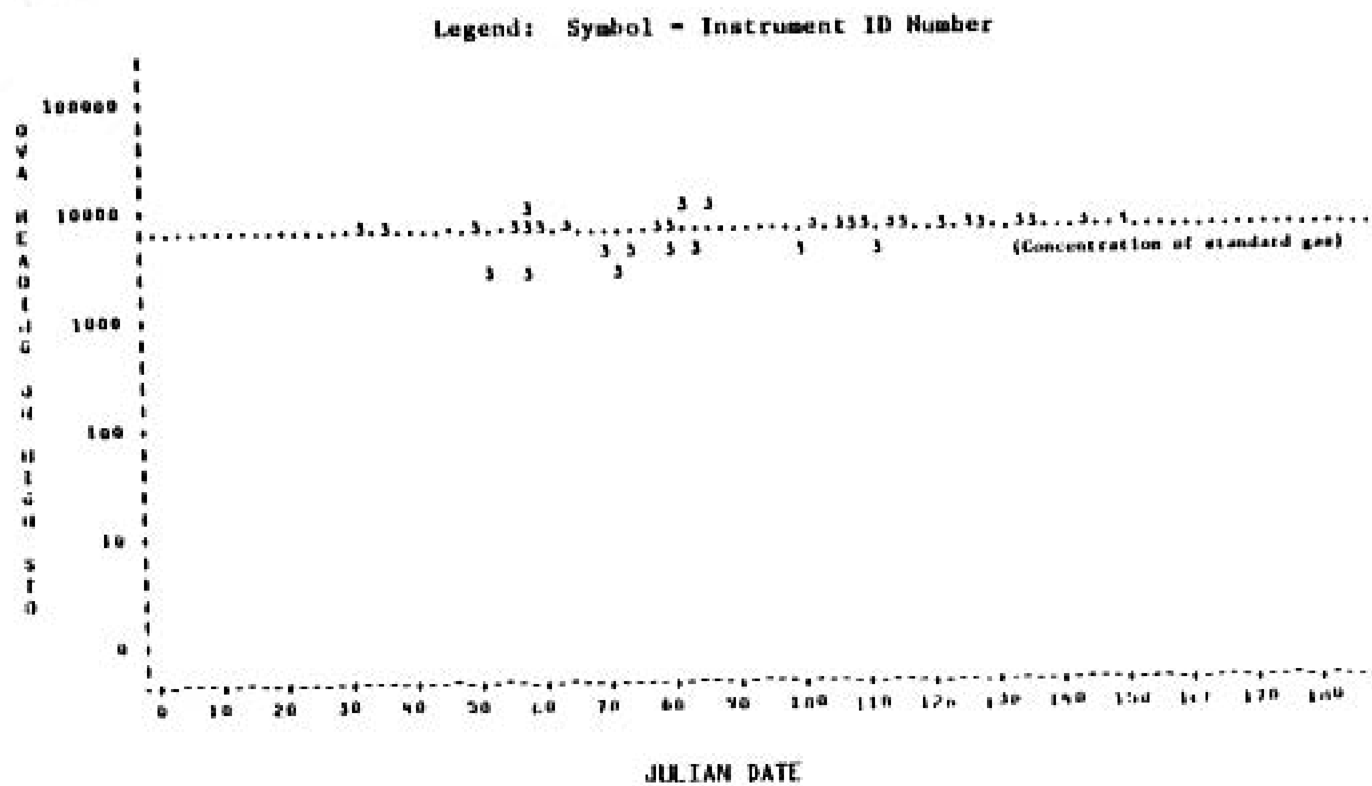


Figure C-8. High Standards Calibrations for OVA Instrument #3

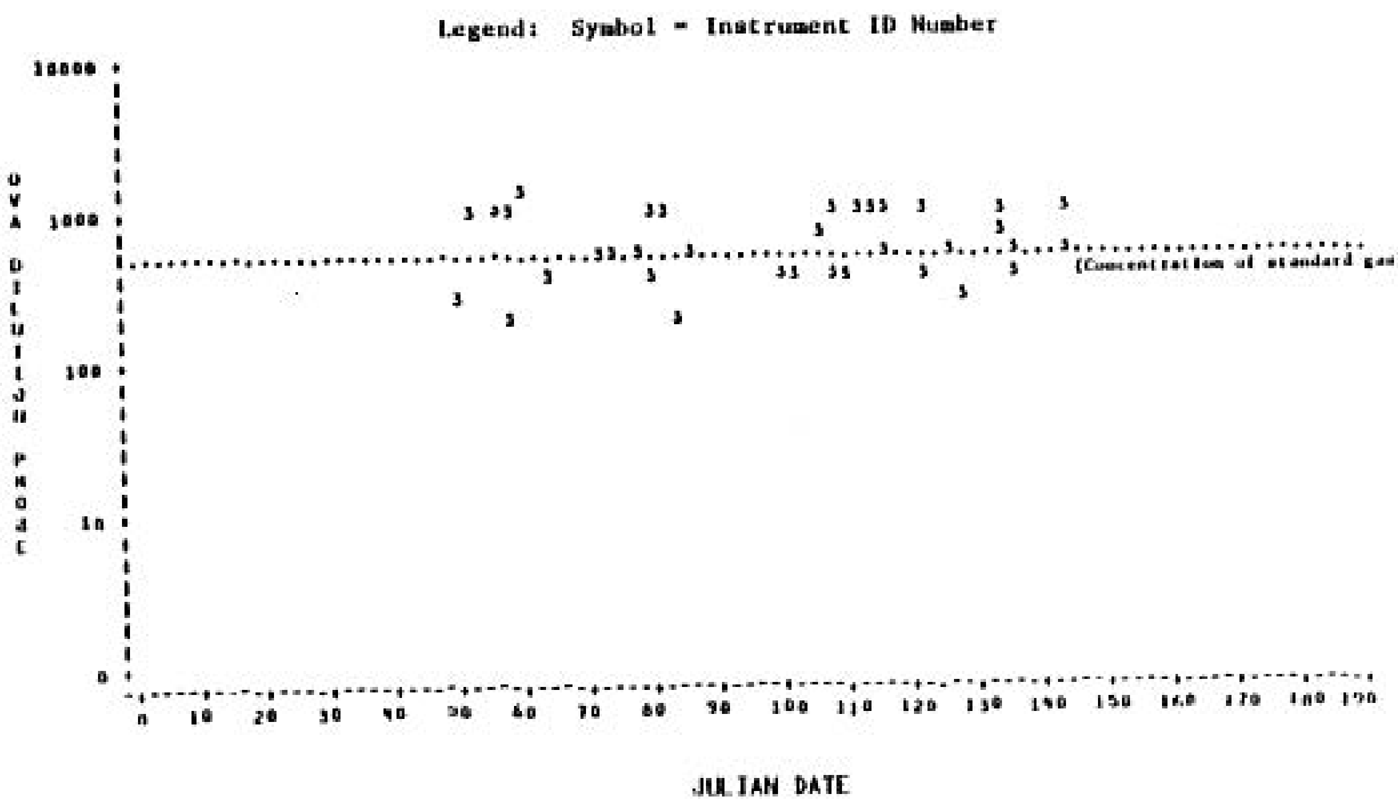


Figure C-9. Dilution Probe Calibrations for OVA Instrument #1

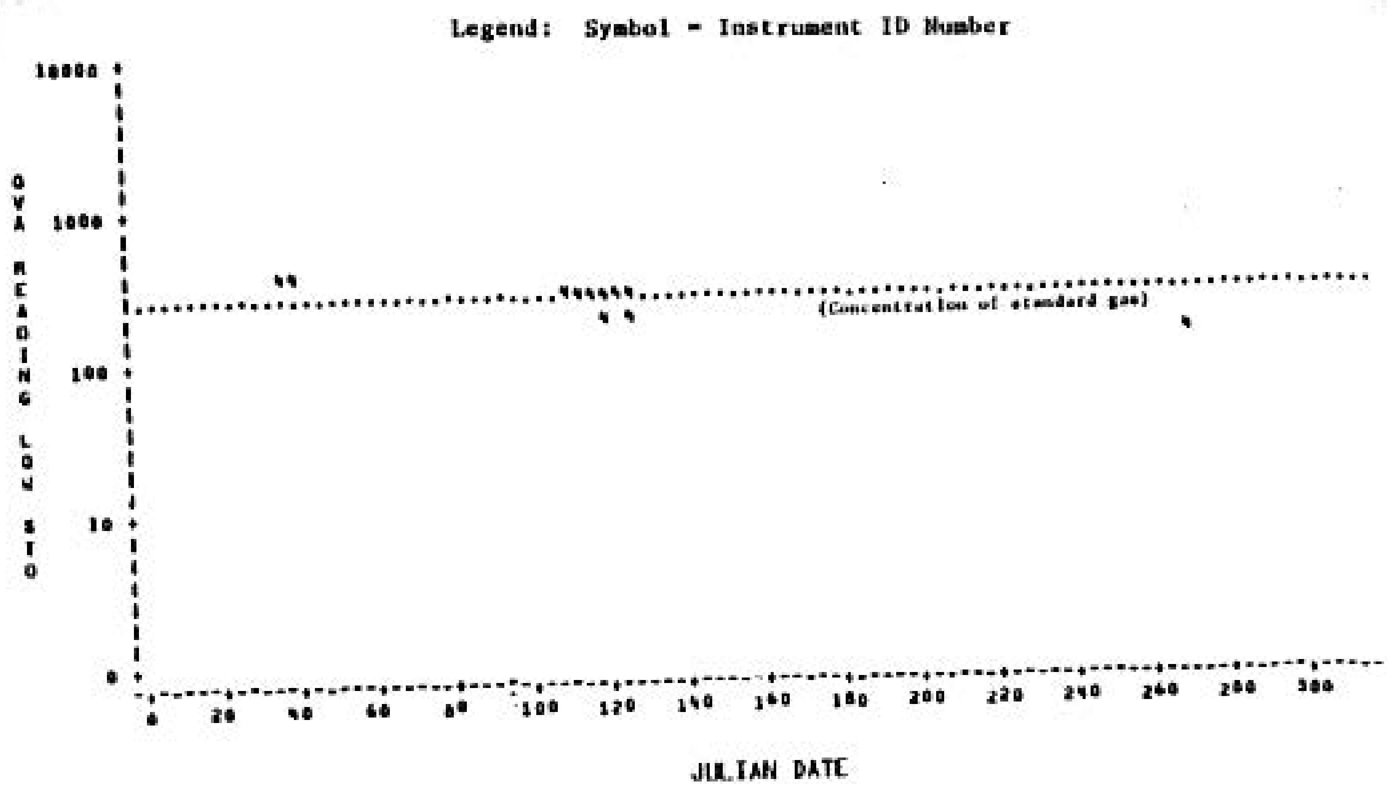


Figure C-10. Low Standards Calibrations for OVA Instrument #4

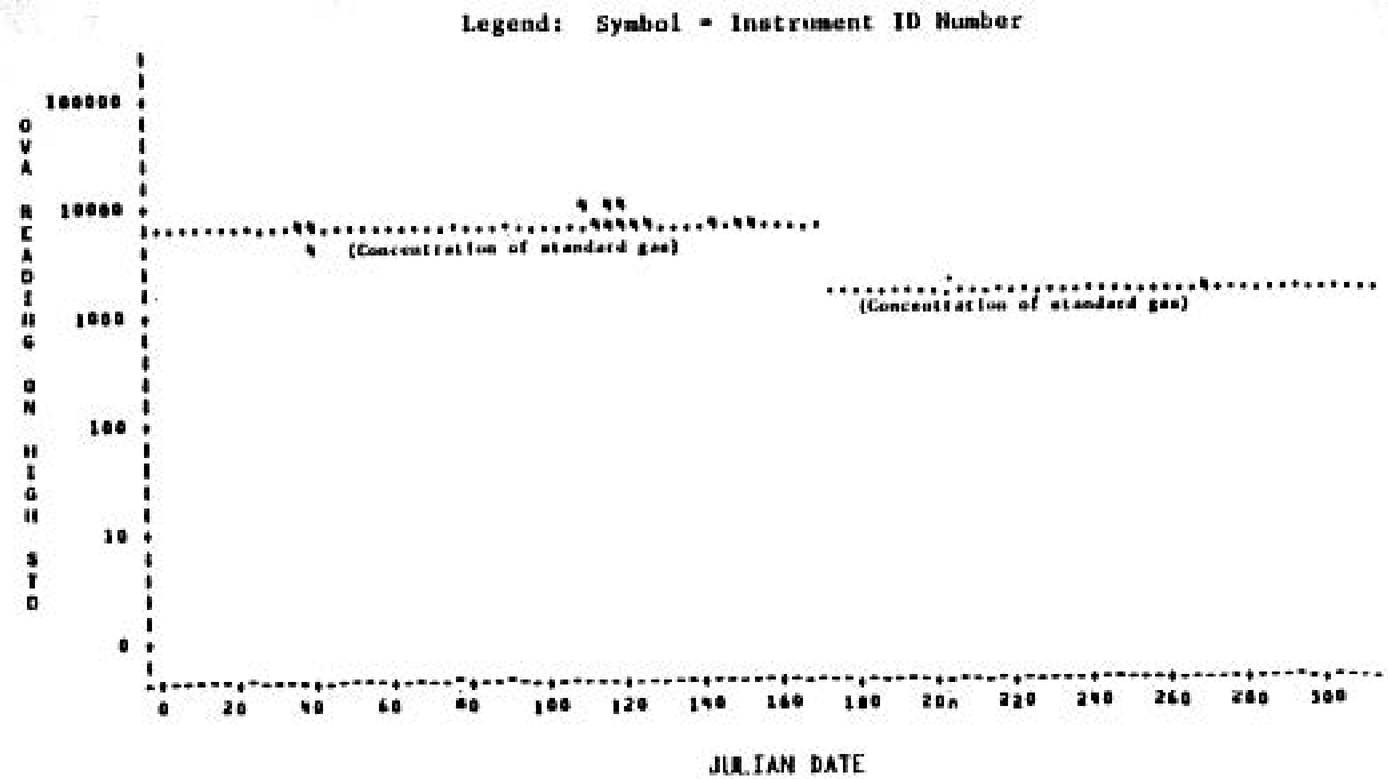


Figure C-11. High Standards Calibrations for OVA Instrument #4

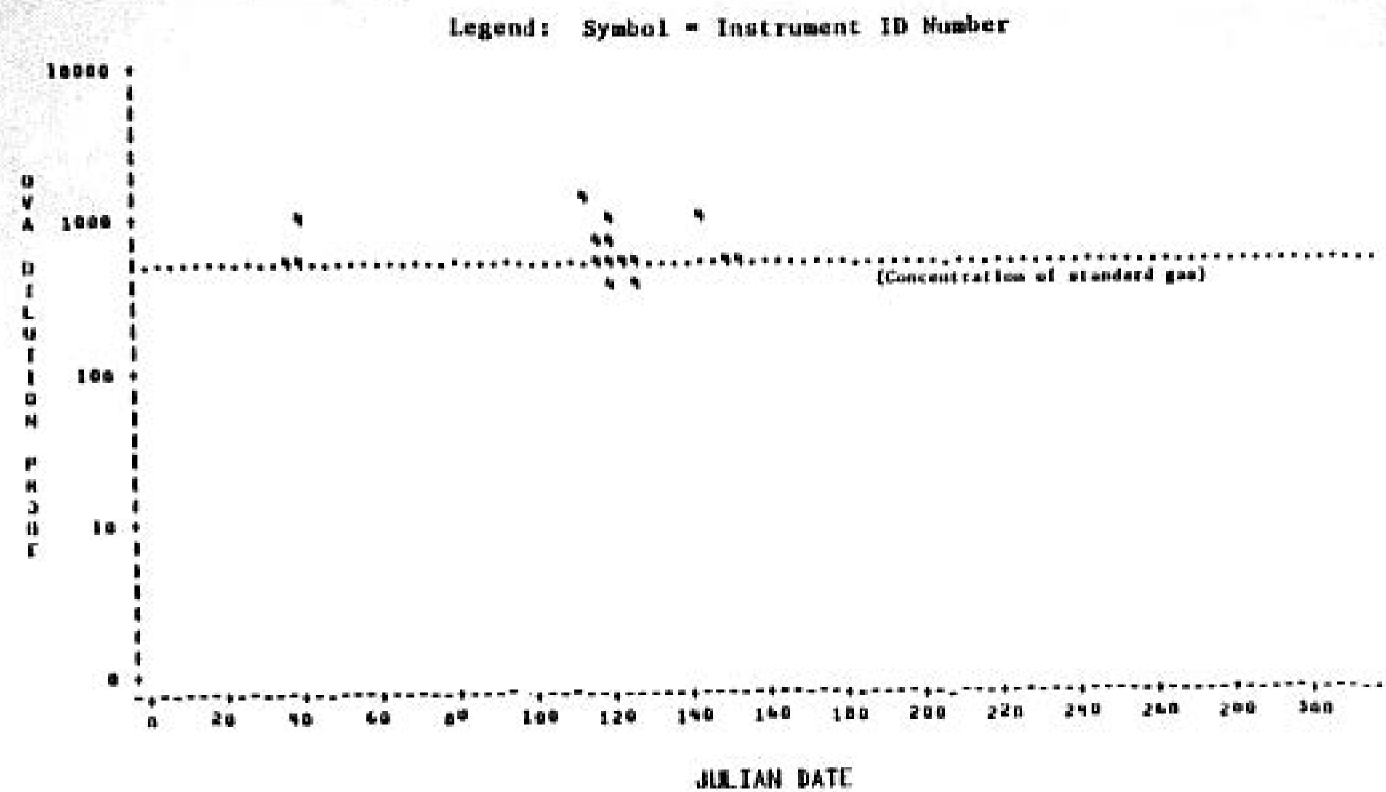


Figure C-12. Dilution Probe Calibrations for OVA Instrument #4

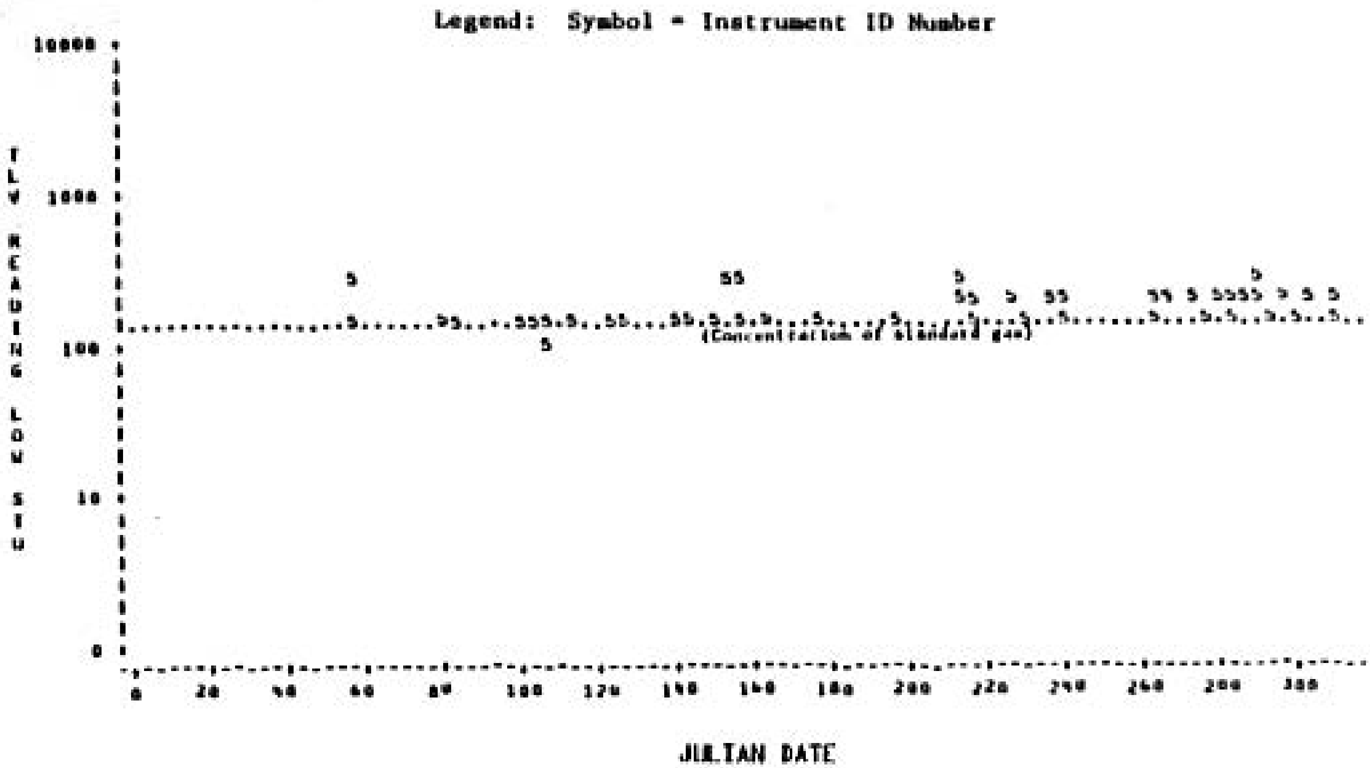


Figure C-13. Low Standards Calibrations for TLV Instrument #5

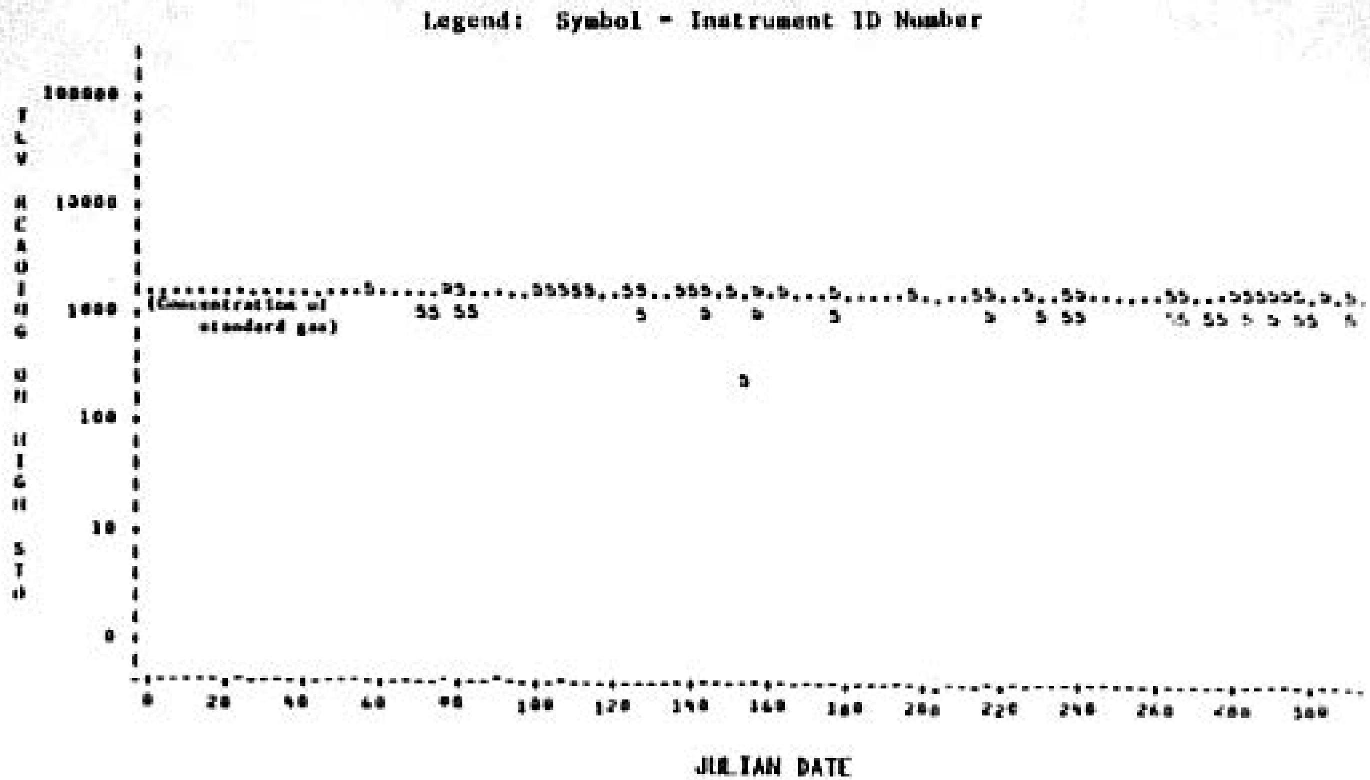


Figure C-14. High Standards Calibrations for TLV Instrument #5

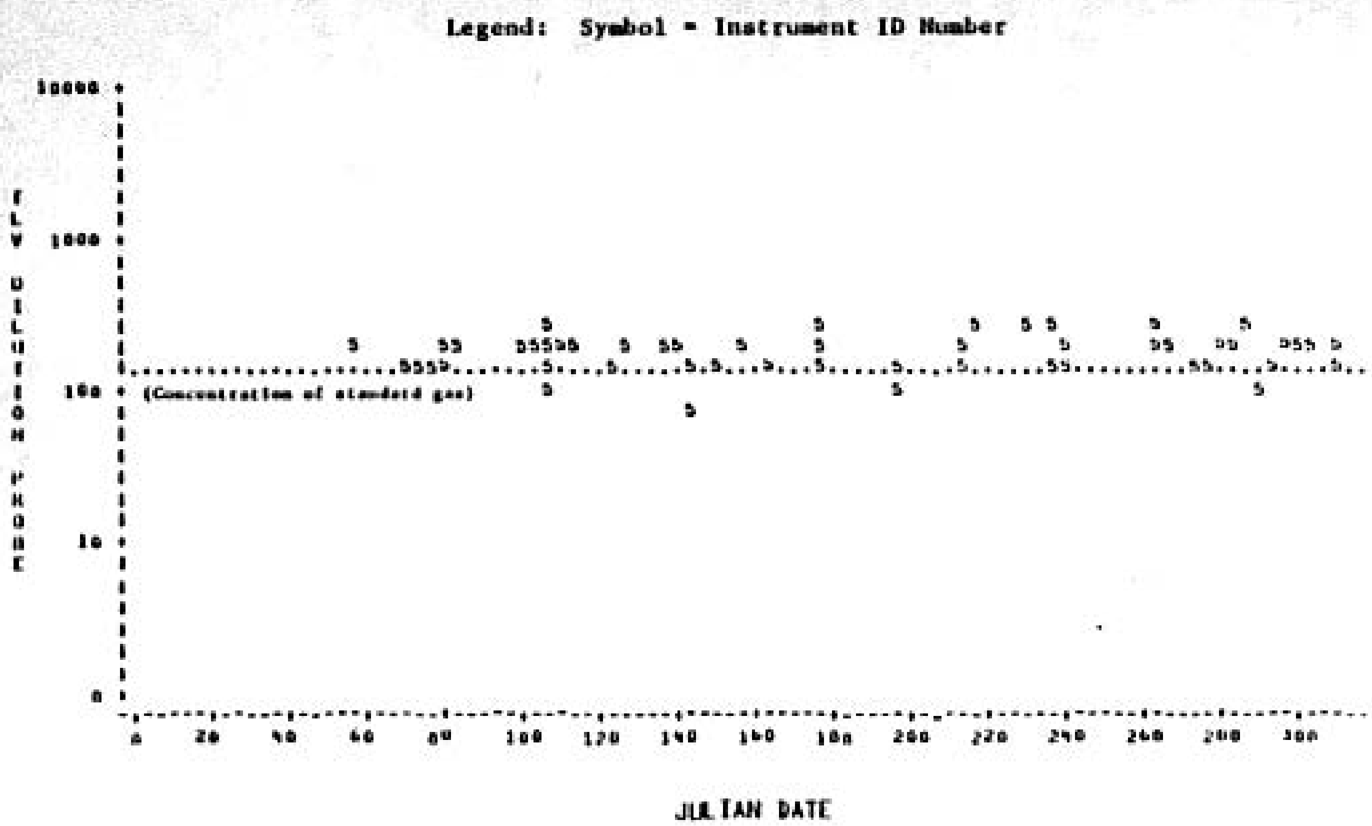


Figure C-15. Dilution Probe Calibrations for TLV Instrument #5

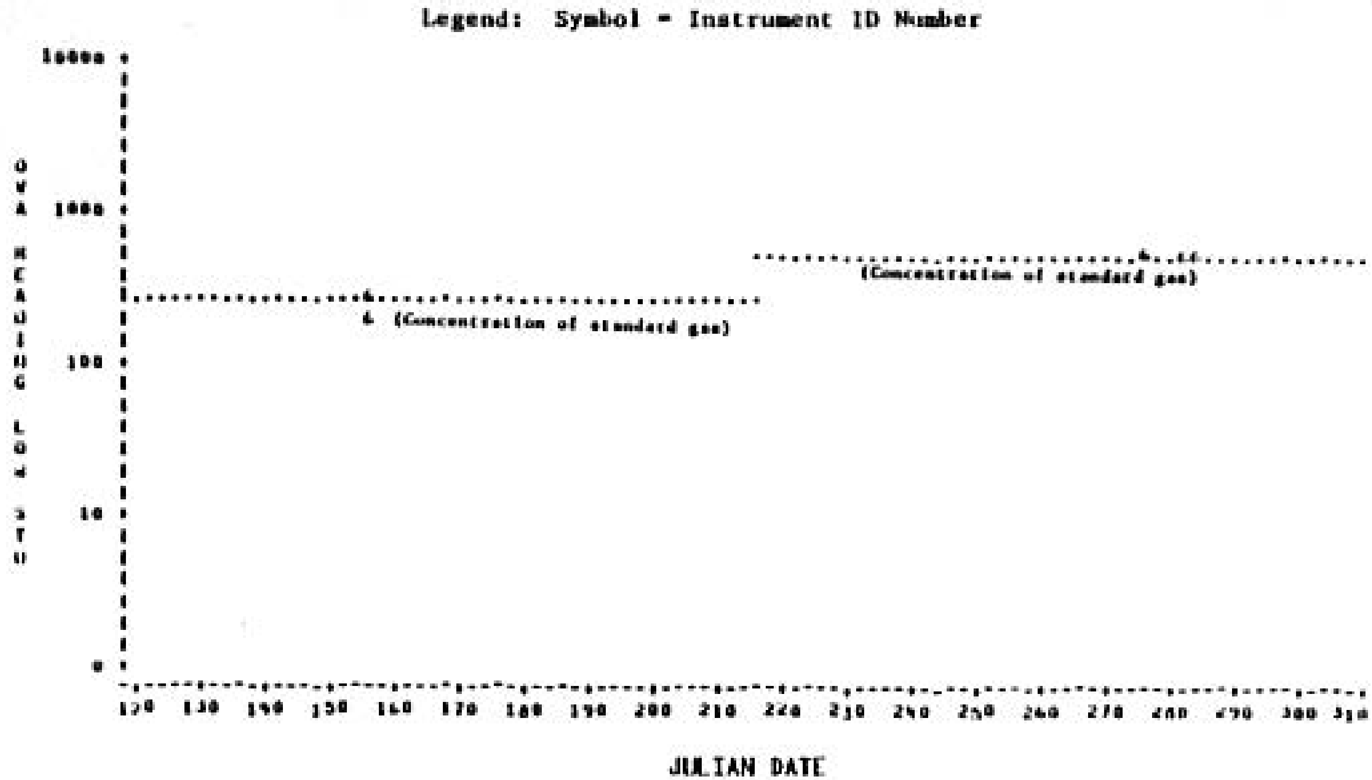


Figure C-16. Low Standards Calibrations for OVA Instrument #6

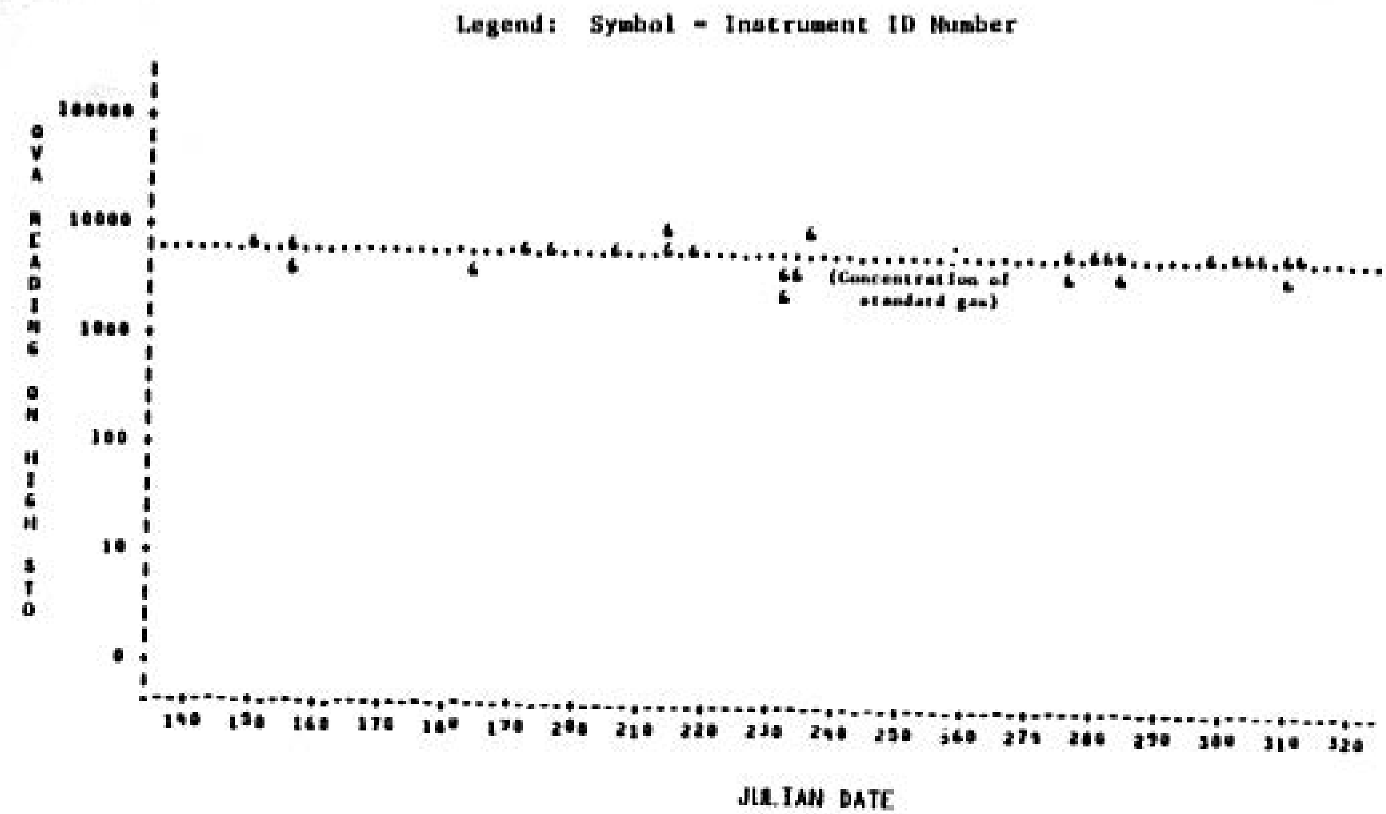


Figure C-17. High Standards Calibrations for OVA Instrument #6

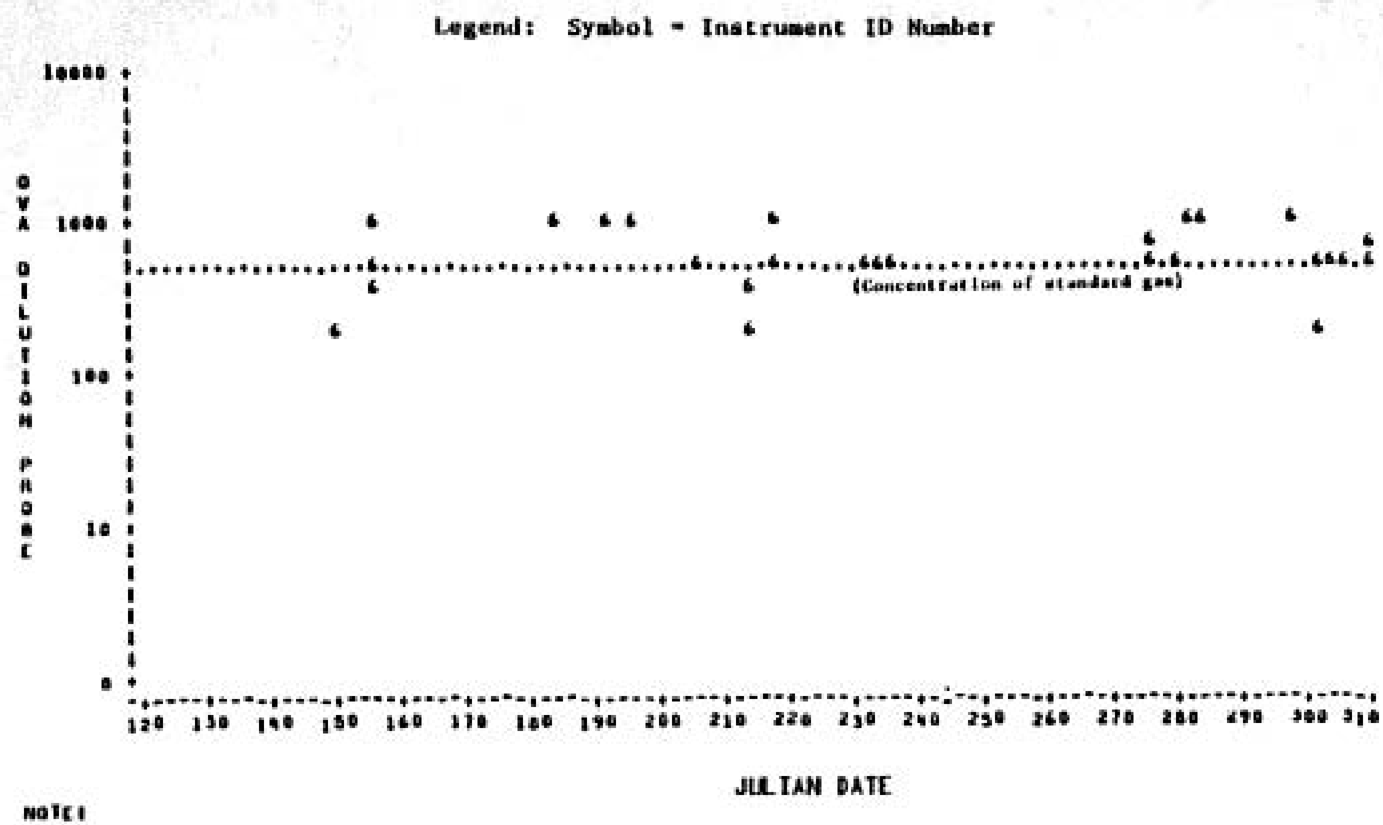


Figure C-18. Dilution Probe Calibrations for OVA Instrument #6

A total of fourteen valves were screened multiple times during the program. Plots of the repeated screening values for twelve valves with more than five screening values are shown in Figures C-19 through C-30. Each figure represents a separate valve. Screening values are plotted against the Julian date of screening. The symbols used to indicate the different screening values are the instrument ID numbers. The logarithm scale is used on all plots for ease of comparison.

To summarize the variation in screening values observed from these selected sources, a statistical analysis of variance was done. The analysis of variance procedure estimates variance components which shows the contribution to the variation in the screening measurements. Table C-2 summarizes this variance analysis. About 18 percent of the total variation in the screening values is attributable to the replicate readings obtained at the same time. The 50 percent of the variation attributable to the different valves shows that the screening device is capable of differentiating valve leaks, even after a period of time.

The variation in replicate screenings can be used to define the repeatability of the screening measurement. The 0.141 log $(ppm)^2$ variance component for replicate readings gives a standard deviation between replicate readings of 0.38 log (ppmv). Using this standard deviation, screening values ranging from X/5.6 to 5.6X can be expected (95 percent confidence) from a source with a mean screening value of X. For example, screening values from a source which has an average screening value of 8000 ppmv could expect to be between 1425 ppmv and 44,800, 95 percent of the time.

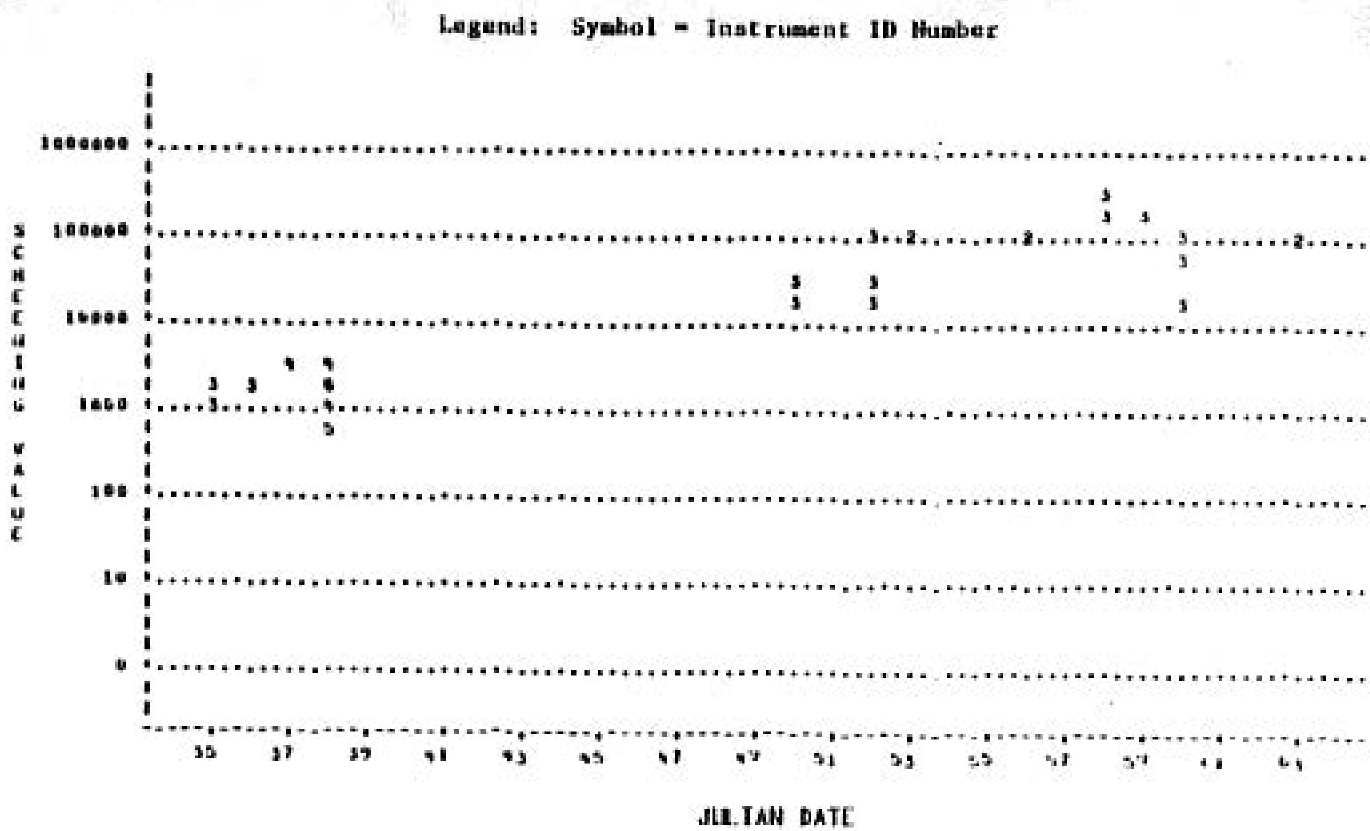


Figure C-19. Repeated Screenings Unit #1 ID #59

Legend: Symbol = Instrument ID Number

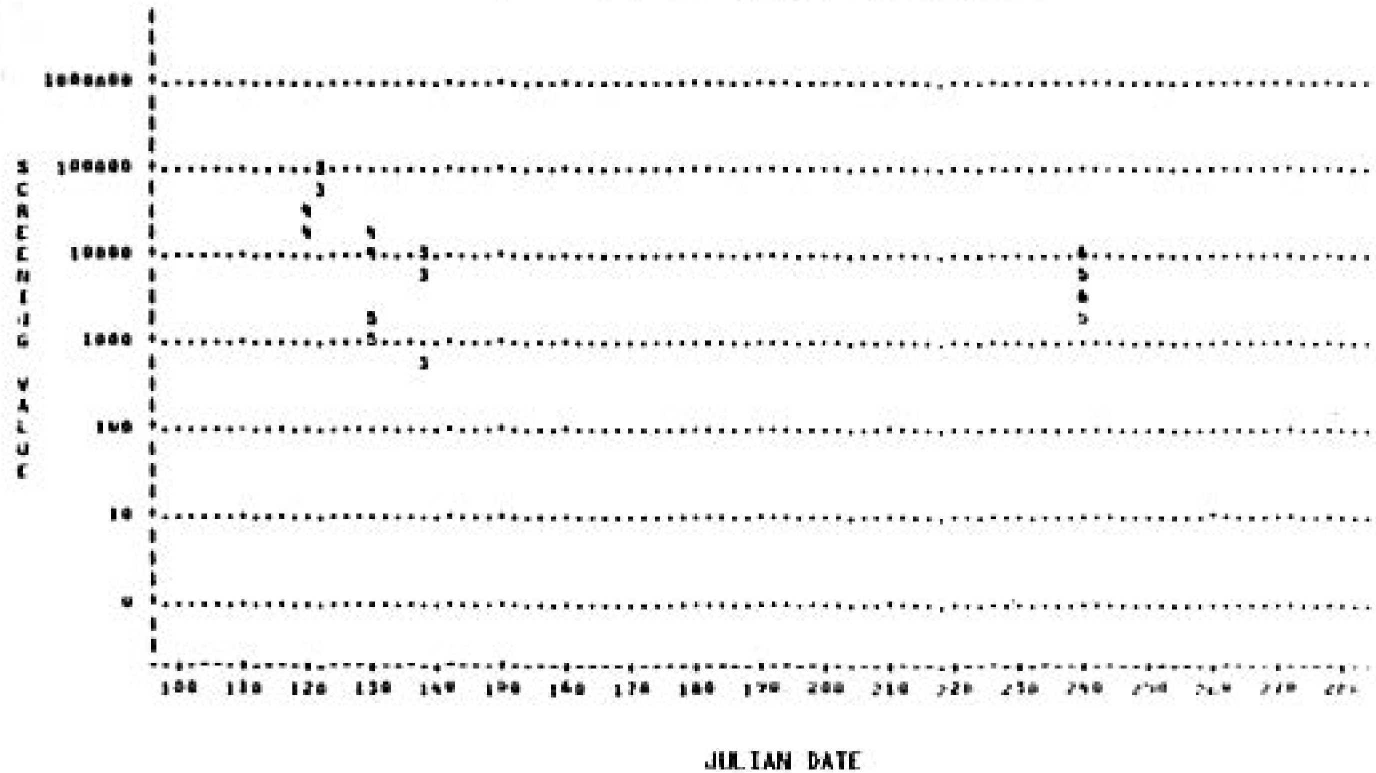


Figure C-20. Repeated Screenings Unit #1 ID #211

Legend: Symbol = Instrument ID Number

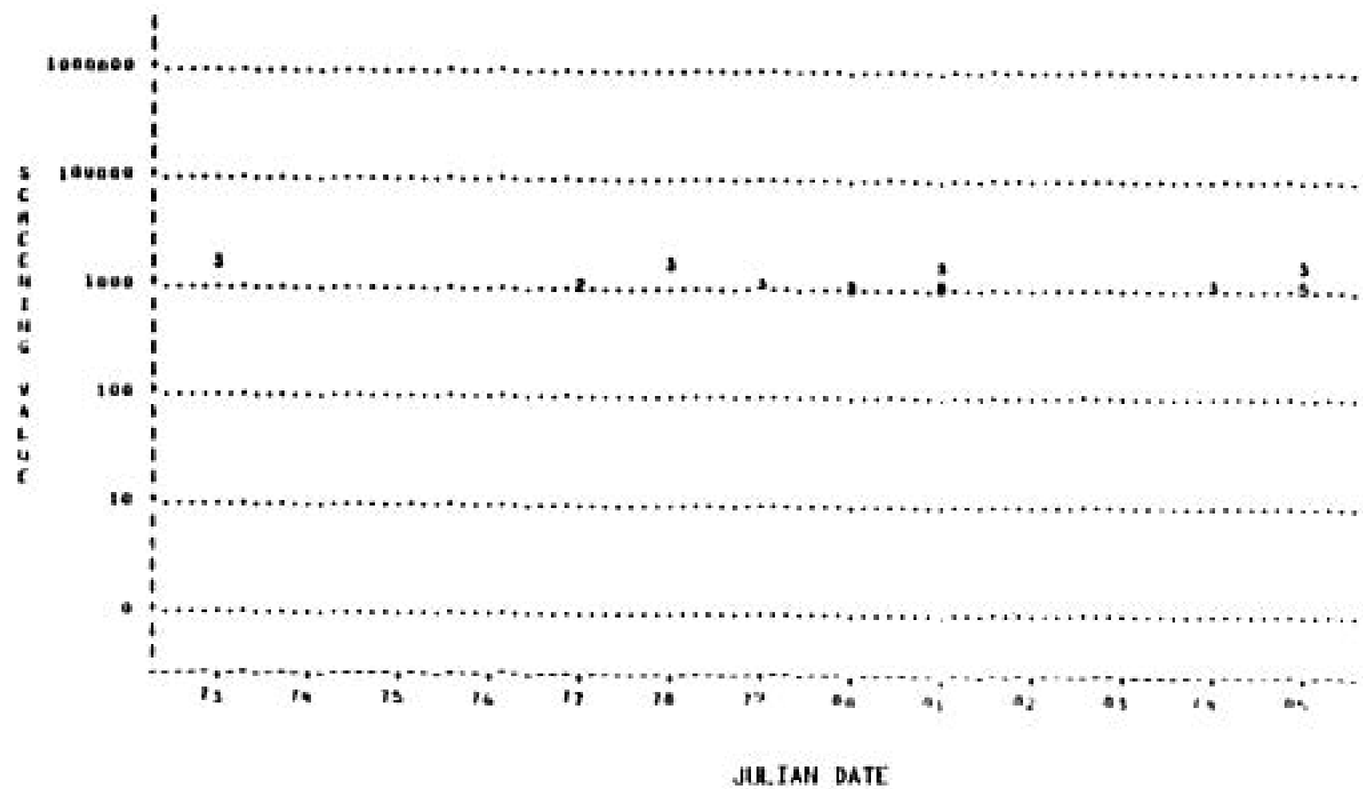


Figure C-21. Repeated Screenings Unit #2 ID #4232

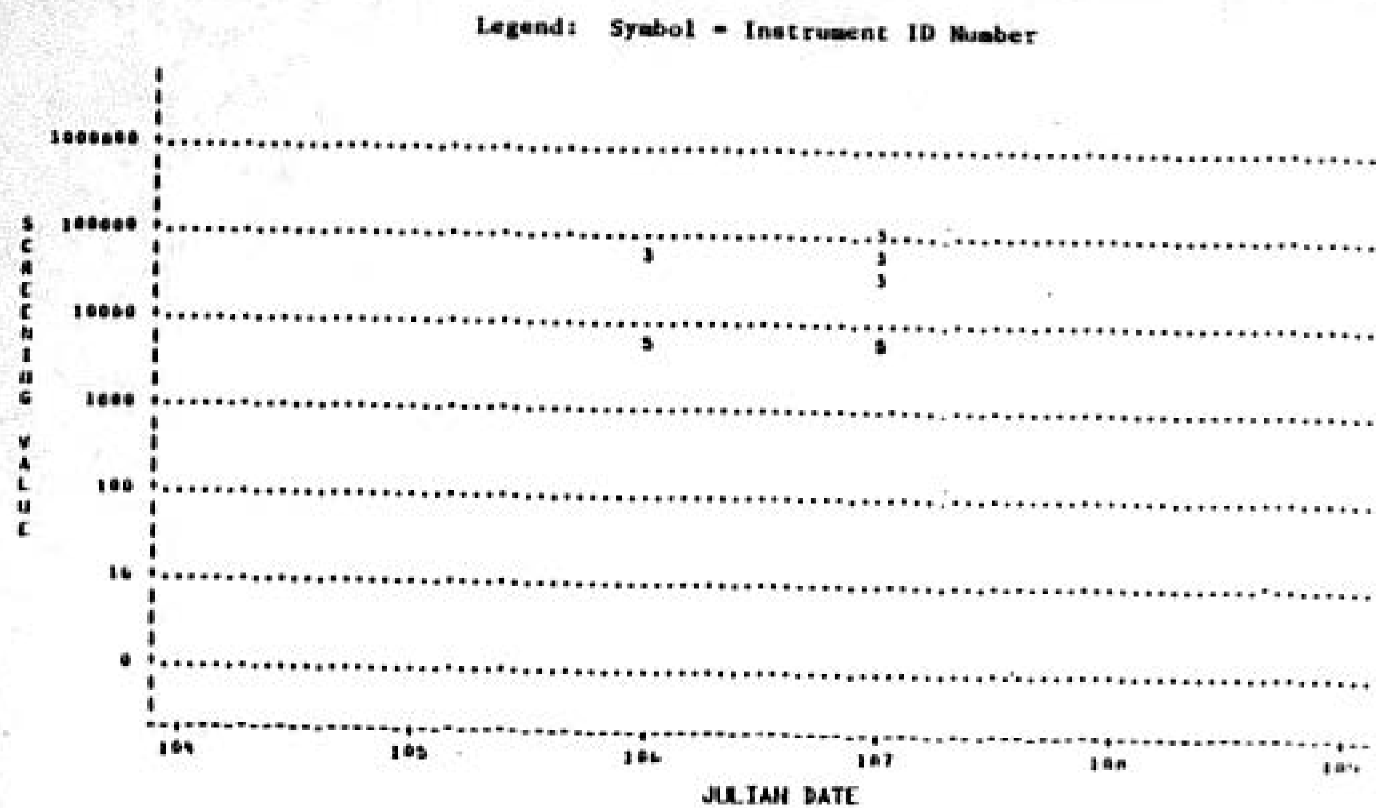


Figure C-22. Repeated Screenings Unit #3 ID #291

Legend: Symbol = Instrument ID Number

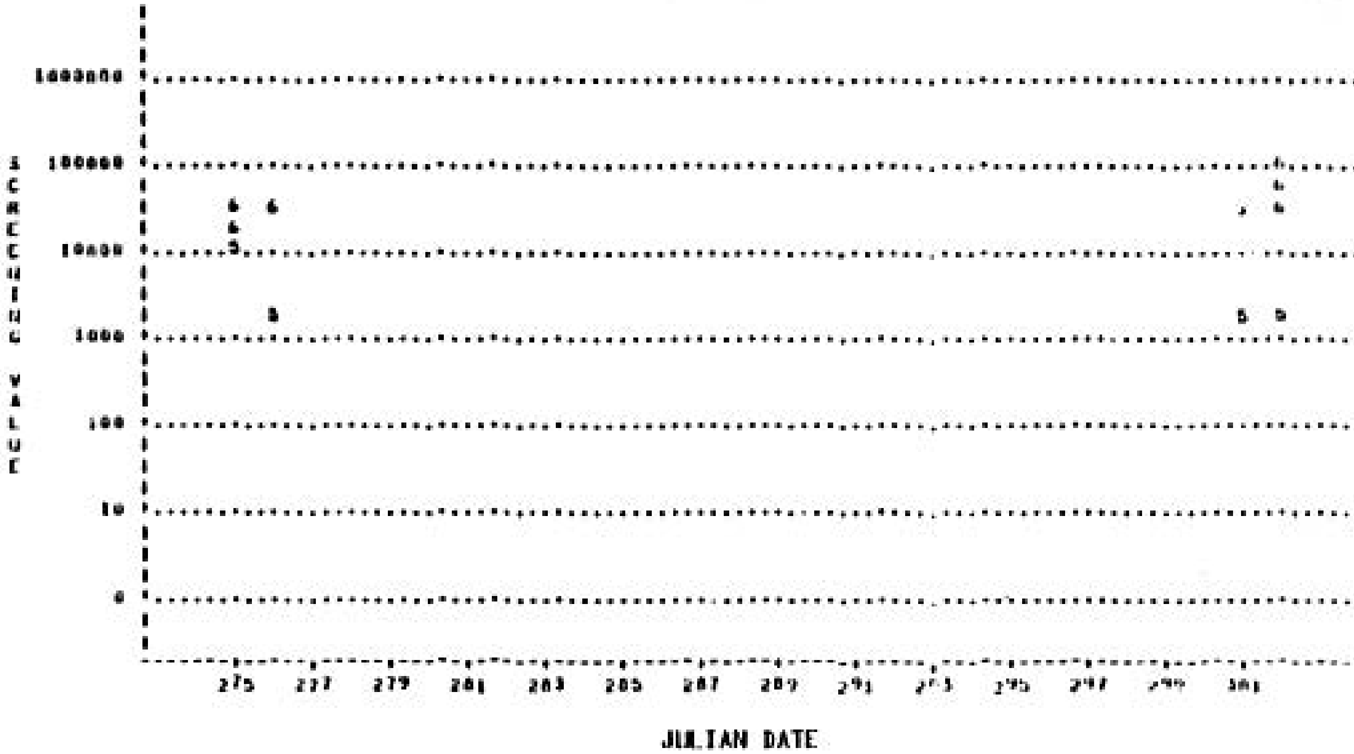


Figure C-23. Repeated Screenings Unit #3 ID #2857

Legend: Symbol = Instrument ID Number

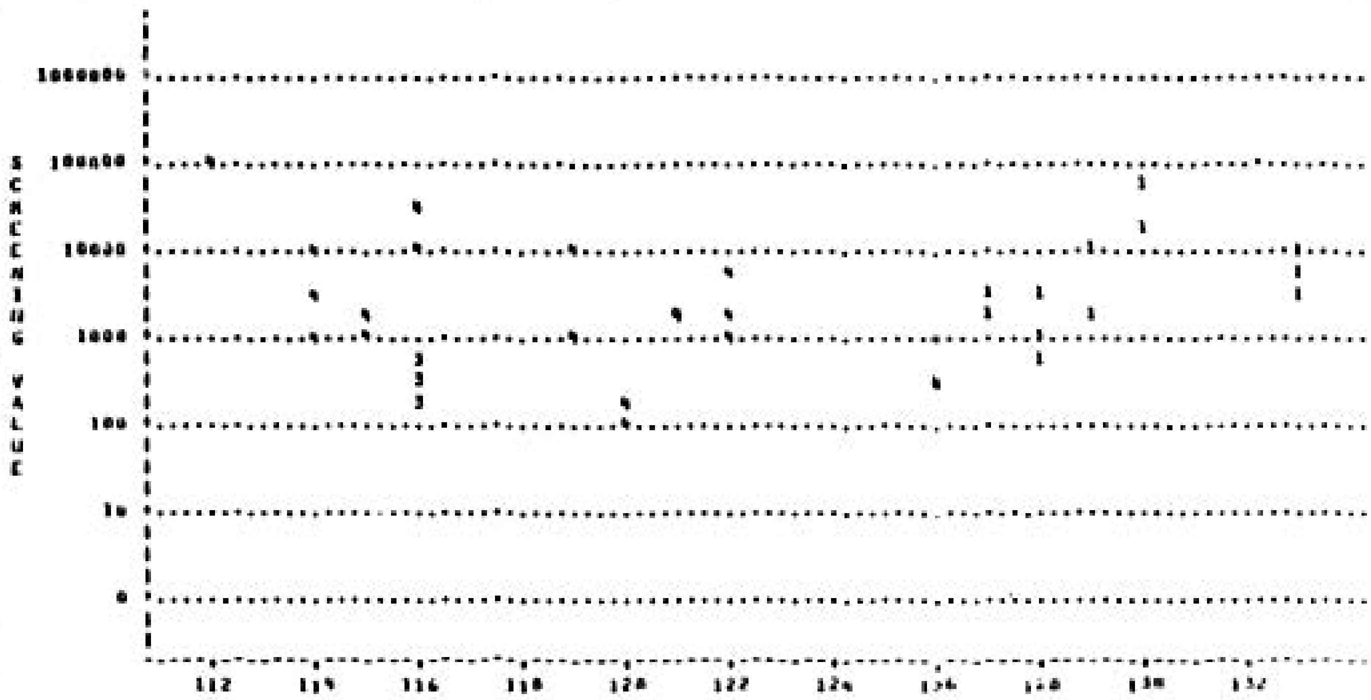


Figure C-24. Repeated Screenings Unit #4 ID #1

Legend: Symbol - Instrument ID Number

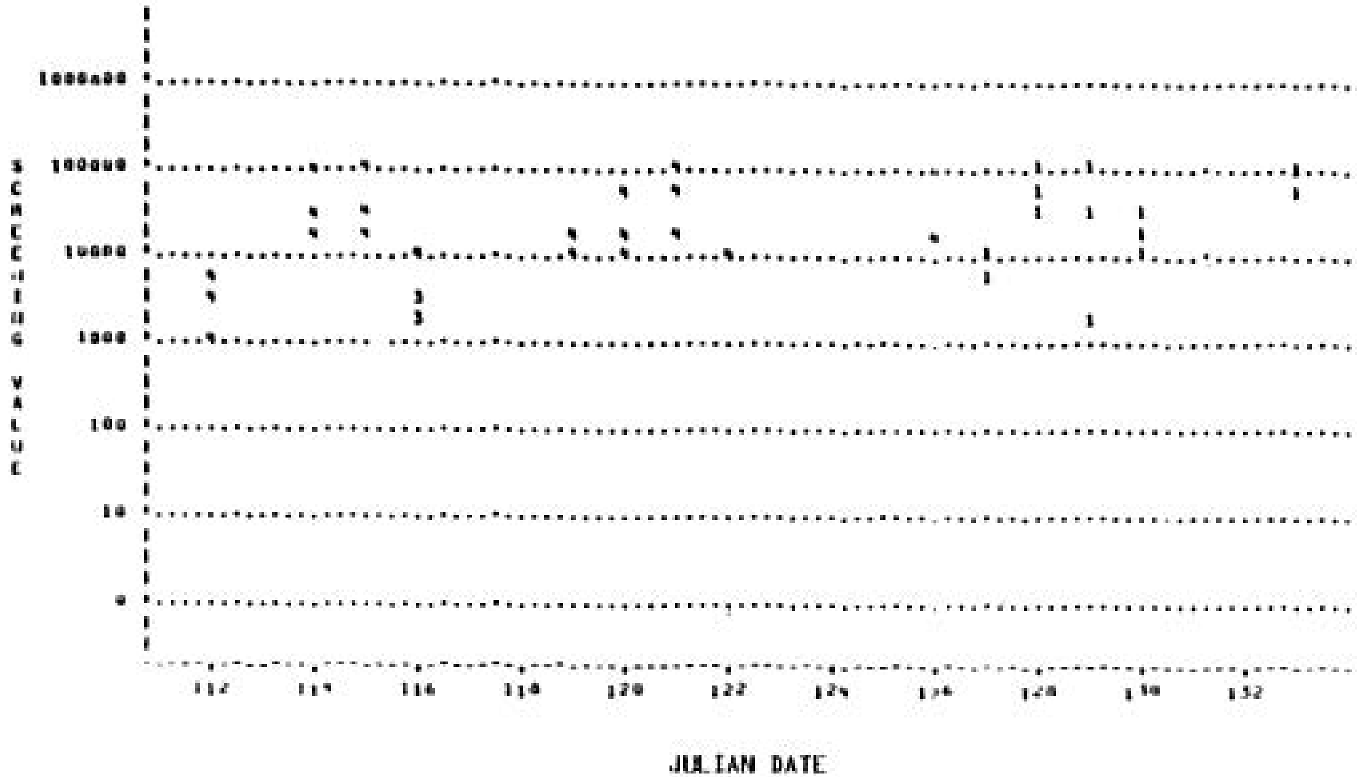


Figure C-25. Repeated Screenings Unit #4 ID #18

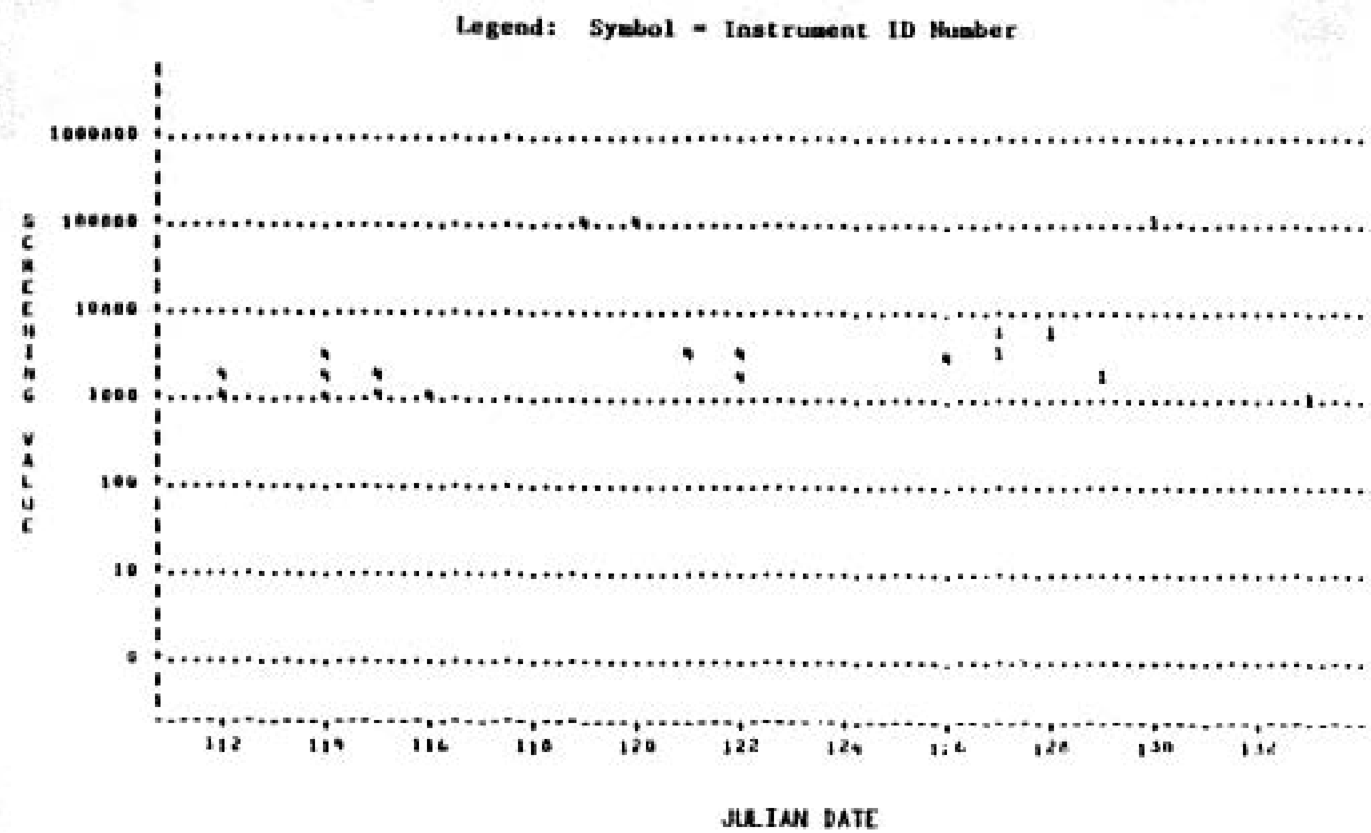


Figure C-26. Repeated Screenings Unit #4 ID #125

Legend: Symbol = Instrument ID Number

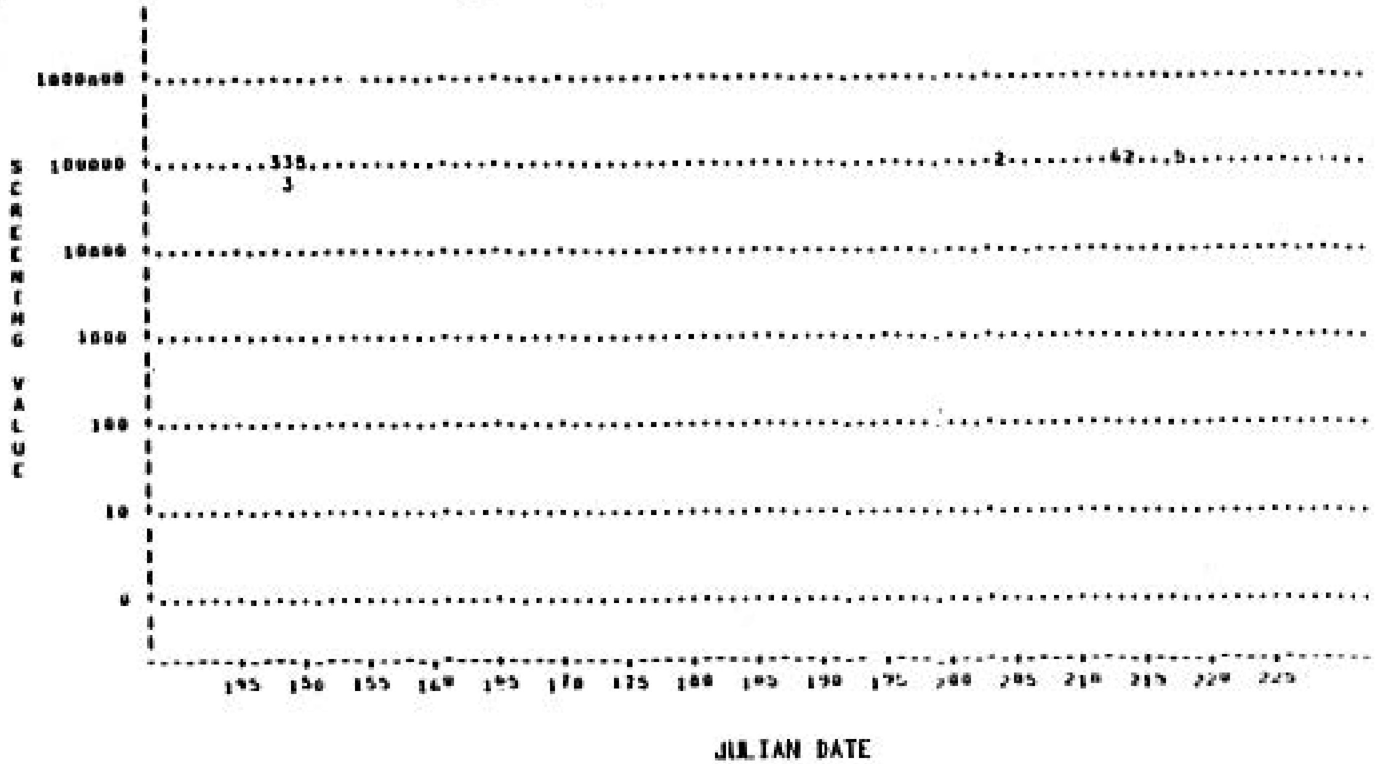


Figure C-27. Repeated Screenings Unit #4 ID #299

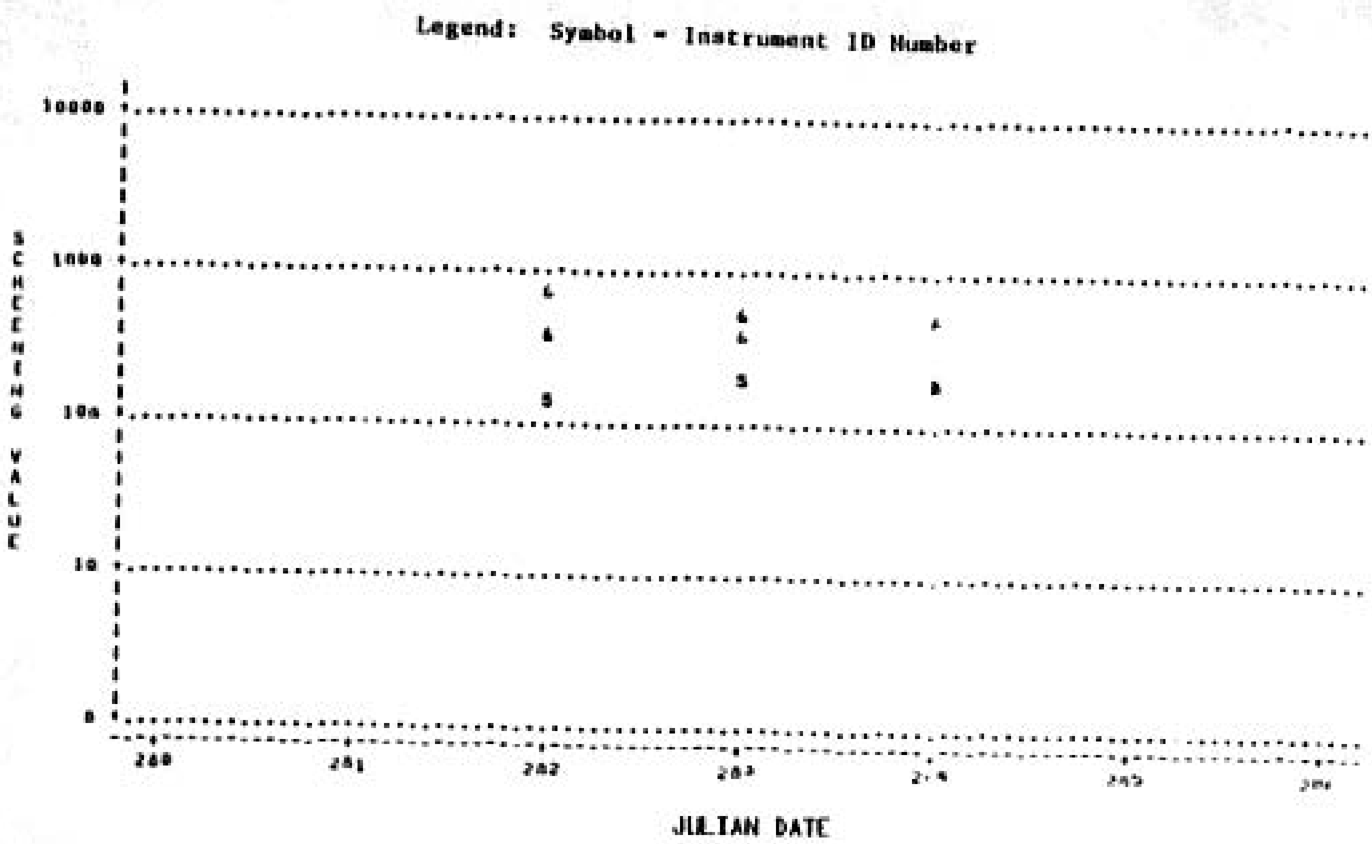


Figure C-28. Repeated Screenings Unit #5 ID #115

Legend: Symbol - Instrument ID Number

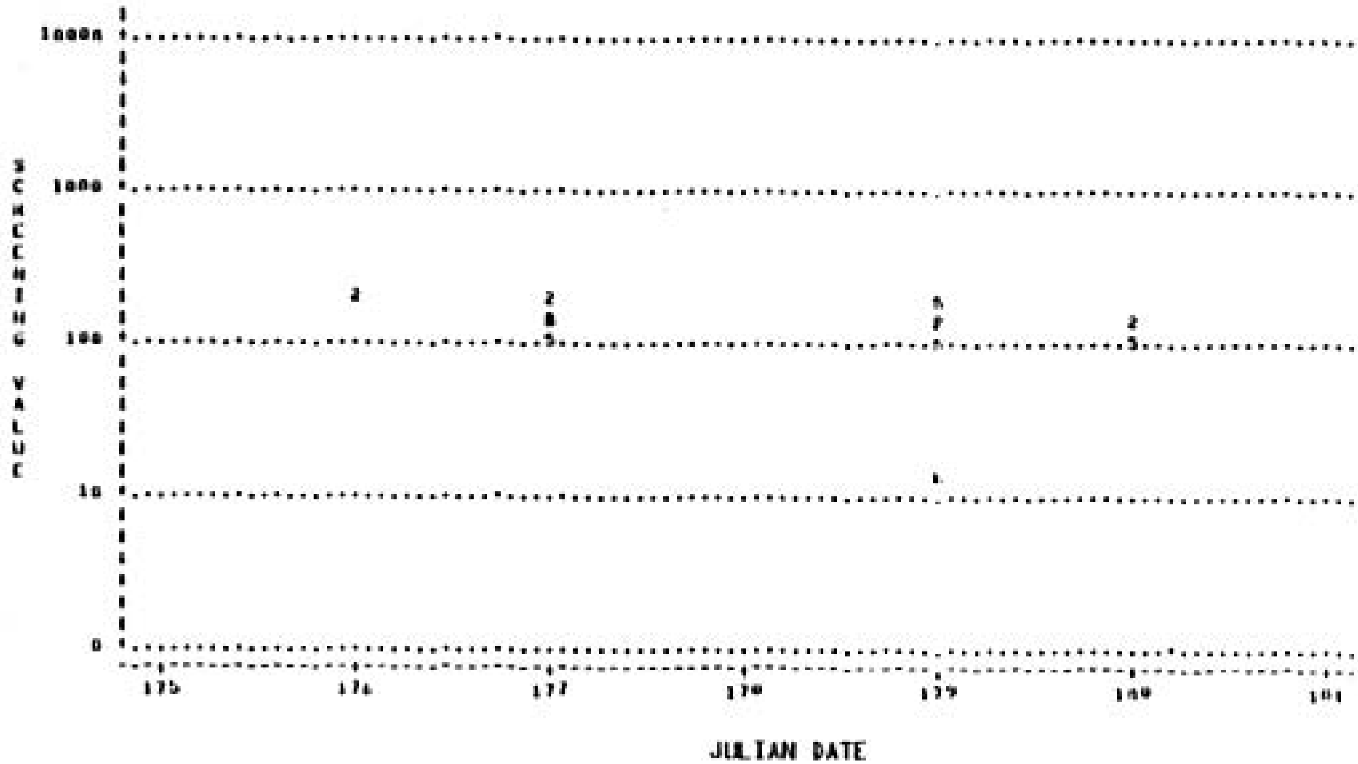


Figure C-29. Repeated Screenings Unit #5 ID #133

Legend: Symbol = Instrument ID Number

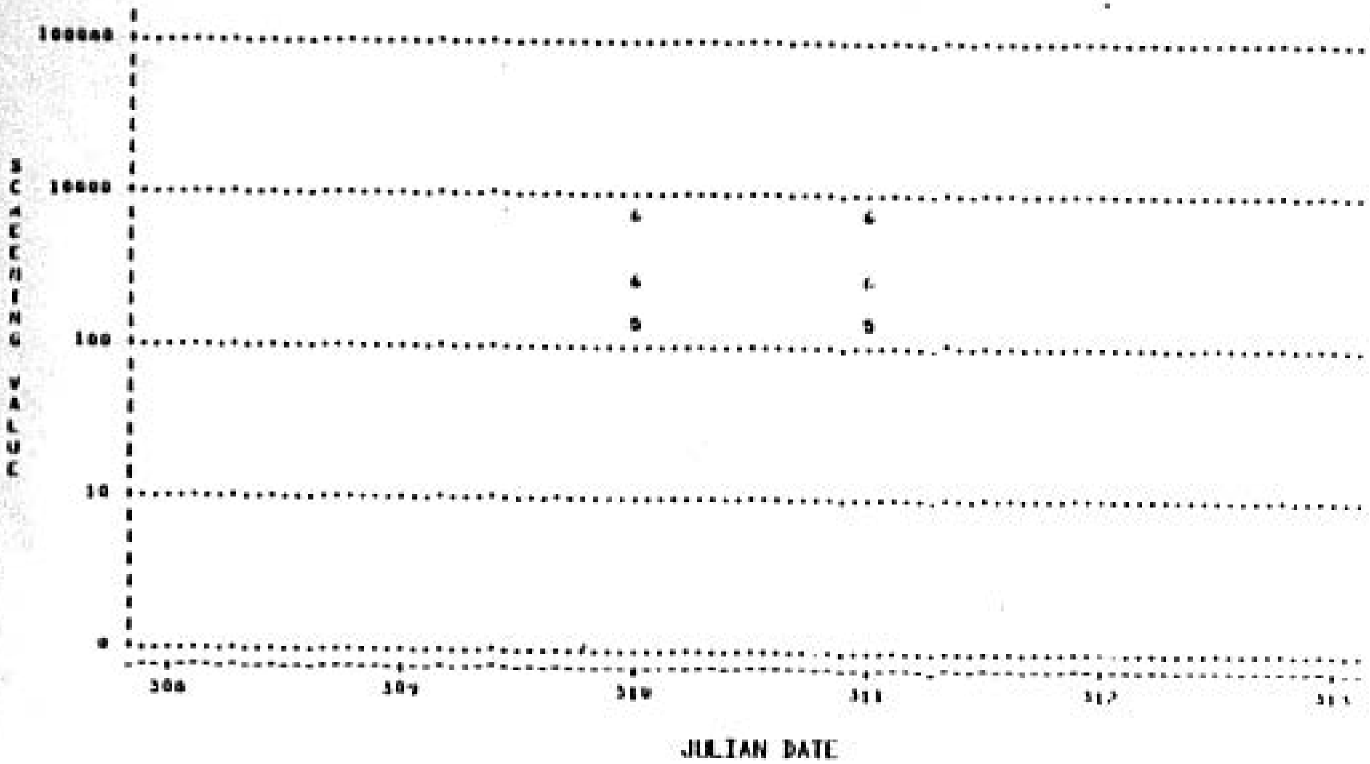


Figure C-30. Repeated Screenings Unit #6 ID #1260

TABLE C-2. VARIANCE COMPONENT ESTIMATES FOR OVA SCREENING MEASUREMENTS ON VALVES

Source of Variation	Degrees of Freedom	Log_{10} (screening value) Variance Component Estimate $log_{10}(ppmv)^2$	Percent of Total Variation In Screening Values
Total Variation	322	0.773	100
Variation Between Individual Values	13	0.384	49.7
Day-to-Day Variation (within a valve)	74	0.247	32.0
Variation From Replicate Screenings	235	0.141	18.3

(See Appendix D for an explanation of the analysis of variance procedure and to estimate the variance components.)

3.0 QUALITY CONTROL FOR ANALYTICAL AND SAMPLING PROCEDURES

Quality control procedures were implemented to ensure accurate, consistent and unbiased analytical and sampling techniques throughout the project. The procedures discussed in this section include:

- blind standards,
- accuracy checks, and
- repeated samplings.

3.1 Blind Standards

Regularly scheduled analyses of blind standards were used to evaluate both the Byron 301C Total Hydrocarbon Analyzer (THC) and the HP 5703A Dual FID Gas Chromatograph. The following standard gases were used for these checks:

Propane	147 ppmv
Hexane	89 ppmv-5,910 ppmv
Methane	245 ppmv
Ethylene	11,420 ppmv-46,525 ppmv

Table C-3 lists the data from 21 hydrocarbon standards analyses during the six month project. The difference between the prepared and measured concentration is shown as the percent difference. The percent difference is defined as:

$$\% \text{ DIFF} = (\text{Prepared}-\text{Measured}) \times 100/\text{Prepared}$$

TABLE C-1. BLIND STANDARDS DATA LISTING

INSTRUMENT	DATE	JULIAN	GASTYPE	SYMBOL	PREPARED	MEASURED	DIFF	PERCENT
HP	02/01/80	32	ETHYLENE	E	11940.0	971[illegible].0	1705.0	14.9
HP	02/05/80	36	ETHYLENE	E	46525.0	46929.0	-404.0	-0.9
THC	03/10/80	70	HEXANE	X	5884.0	540[illegible].0	482.0	8.2
THC	03/13/80	73	HEXANE	X	2923.0	232[illegible].0	601.0	20.6
THC	03/13/80	73	METHANE	M	245.0	21[illegible].2	29.0	12.2
THC	03/13/80	73	PROPANE	A	197.0	15[illegible].0	-7.0	-4.0
THC	03/13/80	73	PROPANE	A	197.0	15[illegible].0	-10.0	-6.0
THC	03/13/80	73	PROPANE	A	197.0	19[illegible].0	-1.0	-0.7
HP	04/14/80	105	PROPYLENE	P	74000.0	6473[illegible].0	9262.0	12.5
HP	06/16/80	168	HEXANE	X	508.7	45[illegible].9	129.8	27.0
HP	06/16/80	168	HEXANE	X	508.7	57[illegible].5	10.2	1.7
THC	06/16/80	168	HEXANE	X	508.7	65[illegible].5	-65.8	-11.2
HP	06/16/80	168	HEXANE	X	508.7	52[illegible].3	60.4	11.6
THC	06/16/80	168	HEXANE	X	363.2	30[illegible].5	55.7	14.0
HP	06/16/80	168	HEXANE	X	363.2	24[illegible].5	117.7	32.9
THC	07/14/80	196	HEXANE	X	5910.0	613[illegible].0	-220.0	-3.7
THC	07/14/80	196	HEXANE	X	591.0	43[illegible].0	153.0	21.9
THC	07/14/80	196	HEXANE	X	591.0	60[illegible].0	-11.0	-1.9
THC	07/14/80	196	HEXANE	X	591.0	57[illegible].0	17.0	2.9
THC	07/14/80	196	HEXANE	X	591.0	57[illegible].0	19.0	3.2
THC	07/25/80	207	HEXANE	X	69.0	67.3	1.7	1.9

Average: 7.4%
Standard Deviation: 11.6%

Figure C-31 contains plots of the percent difference by Julian date. The maximum percent difference found was 32.4 percent, ninety percent of the differences were within 20 percent of the standard concentration. No significant difference between the two analytical systems was noted from these standard analyses. The average percent difference was 7.4 percent (95 percent confidence interval of 2.1 percent to 13 percent), indicating a slight positive bias for the VOC analyses by the two systems.

3.2 Accuracy Checks

Accuracy checks were used to evaluate the overall accuracy of the bagging sampling and analysis technique. The detailed procedures used to perform these tests were developed by Radian (Reference 8).

Table C-4 lists the data from the 54 accuracy tests performed during the project. The measured leak rate, induced leak rate, and the percent recovery are shown. The percent recovery is defined as:

$$\% \text{ Recovery: } \frac{\text{Measured Leak rate}}{\text{Induced Leak rate}} \times 100$$

Figure C-32 contains plots of the percent recovery by Julian date.

The recoveries for the benzene standards tended to be more variable than the other standards. After the first benzene recovery of 285 percent was observed, the sampling/analysis system was investigated. A new benzene standard (Scott gas) was purchased and checked against the permeation tubes. The tubes were found to be inaccurate for calibration, so the Scott standard was used for all future calibrations. The nine additional benzene accuracy checks had an average recovery of 139 percent with a standard deviation of 42 percent. The benzene results were not used in the analysis for this report.

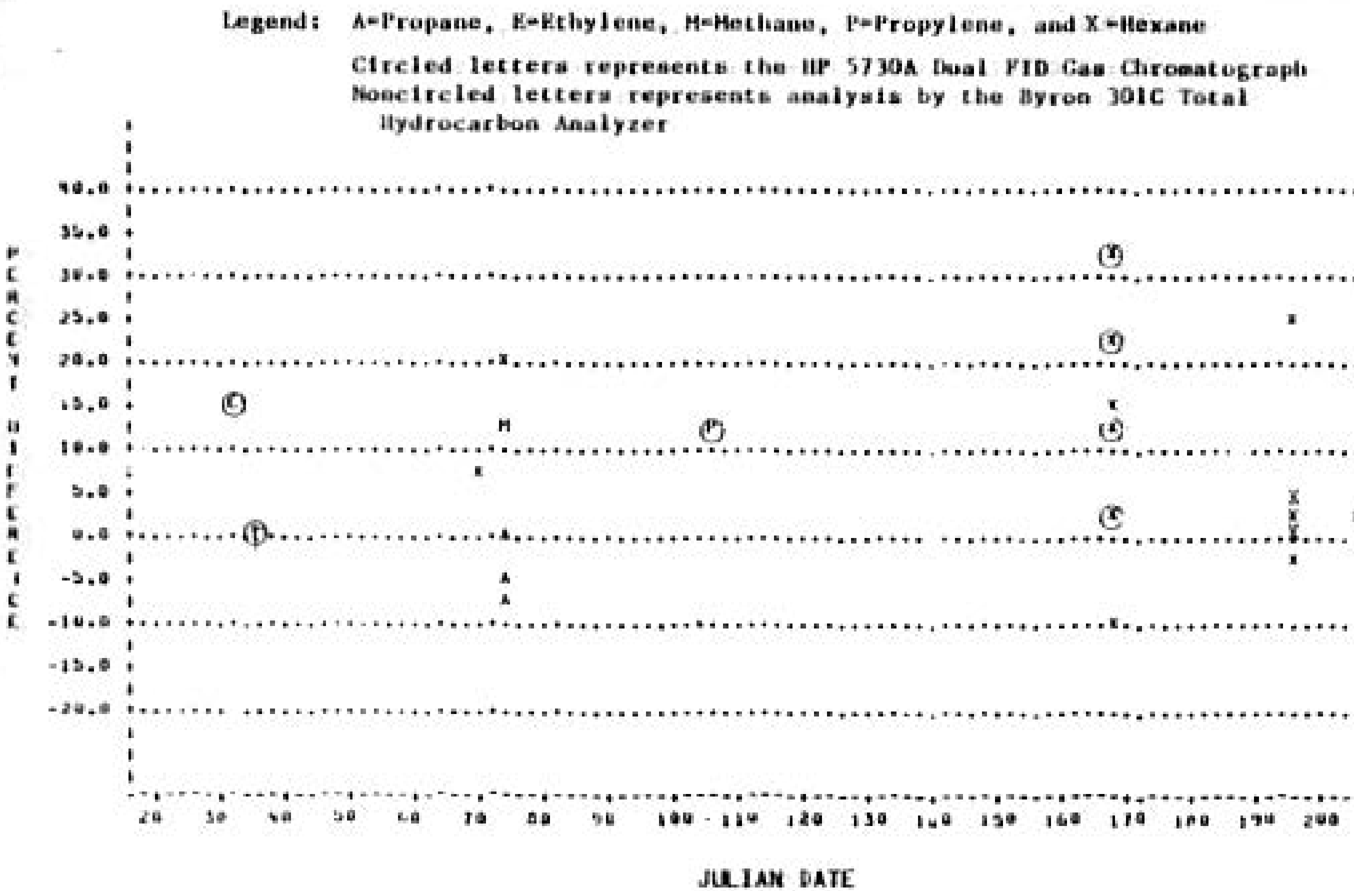


Figure C-31. Blind Standards Percentage Plots

TABLE C-4. ACCURACY CHECKS DATA LISTING

DATE	JULIAN DATE	STANDARD TYPE	SYMBOL	MEASURED LEAK RATE (lbs/hr)	INDUCED LEAK RATE (lbs/hr)	PERCENT RECOVERY
02/01/80	32	ETHYLENE	E	0.0329706	0.028000	117.8
02/05/80	36	ETHYLENE	E	0.0186849	0.021800	85.7
02/25/80	56	ETHYLENE	E	0.0243921	0.024800	98.4
02/25/80	56	ETHYLENE	E	0.0249186	0.025000	99.7
03/19/80	79	HEXANE	X	0.0011527	0.001099	104.9
03/21/80	81	HYDROCARBONS	C	0.0006484	0.000667	97.2
04/11/80	102	ETHYLENE	E	0.0131679	0.017700	74.4
04/14/80	105	PROPYLENE	P	0.0132968	0.014600	91.1
04/29/80	120	ETHYLENE	E	0.0213709	0.021000	101.8
04/30/80	121	ETHYL ACETATE	A	0.0064610	0.005700	113.4
04/30/80	121	ETHYL ACETATE	A	0.0064723	0.005700	113.5
05/15/80	136	HYDROCARBONS	C	0.0082724	0.011280	73.3
05/15/80	136	HYDROCARBONS	C	0.0084907	0.011510	73.8
05/15/80	136	HYDROCARBONS	C	0.0007843	0.000573	136.9
05/15/80	136	HYDROCARBONS	C	0.0006060	0.000559	108.4
05/15/80	136	HYDROCARBONS	C	0.0006672	0.000563	118.5
06/04/80	156	HYDROCARBONS	C	0.0010635	0.001130	94.1
06/04/80	156	HYDROCARBONS	C	0.0011994	0.001130	106.1
06/04/80	156	HEXANE	X	0.0010639	0.001130	94.1
06/04/80	156	HEXANE	X	0.0011994	0.001122	106.9
06/04/80	156	HEXANE	X	0.0012339	0.001122	110.0
06/11/80	163	HEXANE	X	0.0005113	0.000680	75.2
06/13/80	165	HEXANE	X	0.0007748	0.000808	95.9
06/13/80	165	HEXANE	X	0.0009197	0.000824	111.8
06/24/80	176	HEXANE	X	0.0008251	0.000880	93.8
07/02/80	184	HEXANE	X	0.0007276	0.000636	114.4
07/02/80	184	HEXANE	X	0.0006684	0.000635	105.3
07/25/80	207	HEXANE	X	0.0006852	0.000935	73.3
07/25/80	207	HEXANE	X	0.0015089	0.001013	149.0
07/30/80	212	HEXANE	X	0.0007954	0.000758	104.9
08/05/80	218	HEXANE	X	0.0007105	0.000811	87.6
08/06/80	219	BENZENE	B	0.0071350	0.003487	204.8
08/14/80	227	ETHYL ACETATE	A	0.0026139	0.002311	113.1
08/25/80	238	ETHYL ACETATE	A	0.0025971	0.002659	97.7
09/15/80	259	HEXANE	X	0.0005939	0.000572	103.8
09/16/80	260	BENZENE	B	0.0032978	0.003192	103.5

TABLE C-4. Continued

DATE	JULIAN DATE	STANDARD TYPE	SYMBOL	MEASURED LEAK RATE (lbs/hr)	INDUCED LEAK RATE (lbs/hr)	PERCENT RECOVERY
09/22/80	266	HEXANE	X	0.00060066	0.000601	99.9
09/22/80	266	BENZENE	B	0.00206862	0.002076	99.6
09/22/80	266	BENZENE	B	0.00192536	0.002125	90.6
09/22/80	266	HEXANE	X	0.00070336	0.000622	113.1
09/30/80	274	ETHYL ACETATE	A	0.00050595	0.000528	95.8
10/06/80	280	HEXANE	X	0.00066552	0.000600	110.9
10/07/80	281	BENZENE	B	0.00110123	0.000584	188.6
10/07/80	281	BENZENE	B	0.00103960	0.000512	202.1
10/10/80	284	BENZENE	B	0.00081051	0.000484	167.5
10/10/80	284	BENZENE	B	0.00074298	0.000478	155.3
10/10/80	284	BENZENE	B	0.00067767	0.000477	142.1
10/10/80	284	BENZENE	B	0.00047799	0.000467	102.2
10/14/80	288	HEXANE	X	0.00060654	0.000625	97.0
10/20/80	294	HEXANE	X	0.00096166	0.000763	126.0
10/21/80	295	HEXANE	X	0.00060969	0.000606	100.5
10/24/80	298	ETHYL ACETATE	A	0.00256030	0.002540	100.8
10/30/80	304	HEXANE	X	0.00072910	0.000699	104.3
11/04/80	309	HEXANE	X	0.00065043	0.000648	100.4

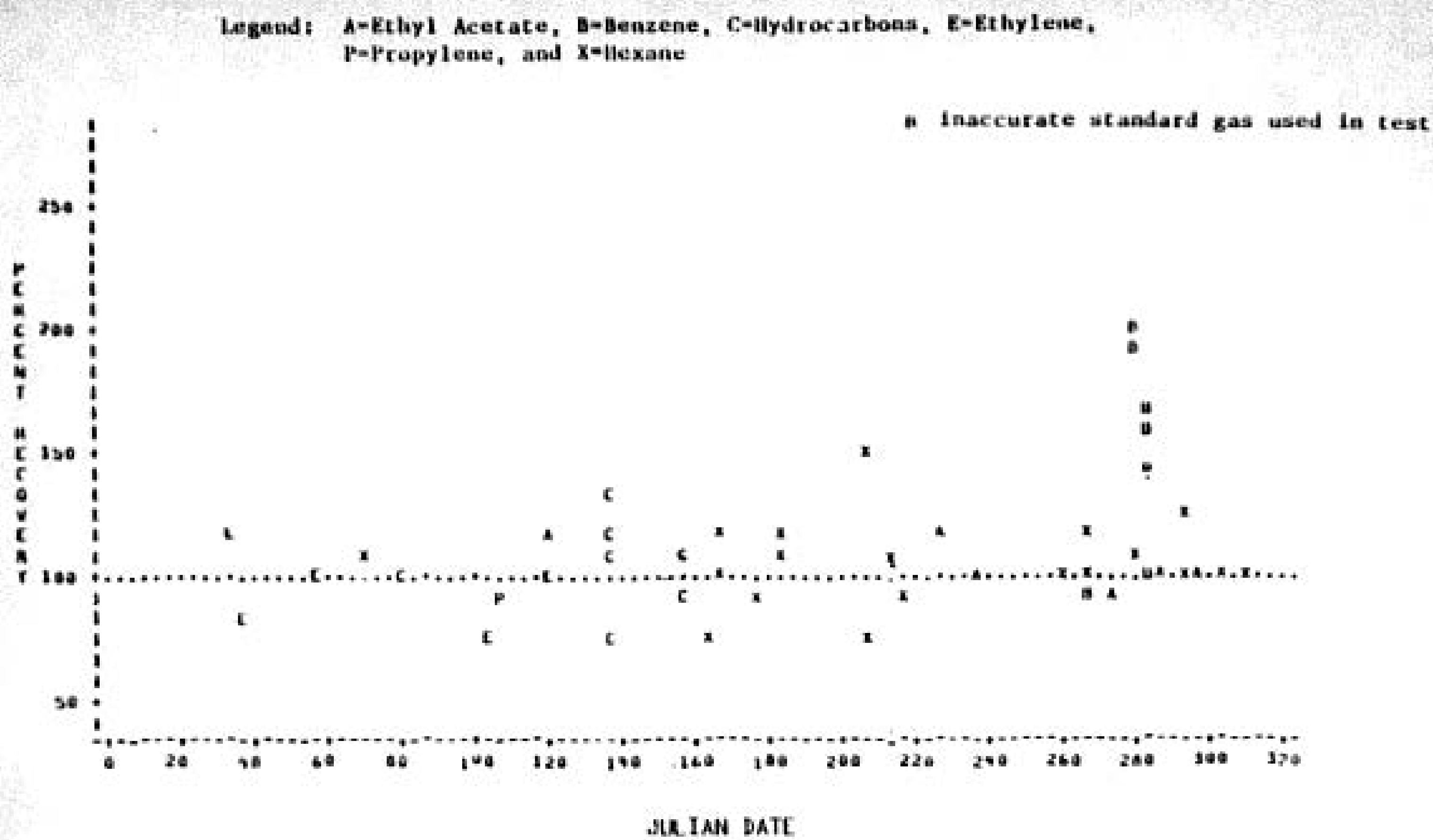


Figure C-32. Accuracy Checks Percent Recovery Plot

The 44 accuracy tests using standards other than benzene had an average recovery of 102.2 percent with a standard deviation of 15.6 percent. These values are comparable to results from 74 similar accuracy checks at refineries with an average recovery of 97.4 percent and a standard deviation of 17.2 percent (Reference 8).

3.3 Repeated Sampling of the Same Source

Repeated sampling was performed on six sources during the course of the study by taking multiple bagged samples from the source after tenting. The results of these tests are shown in Table C-5. Figure C-33 shows the individual percent difference plotted against the average leak rate for the bagged source. A maximum of 70 percent difference between samples was the original goal for the bagging sampling and analysis procedure. As can be seen, all but one of the checks were within these limits.

Considering both pumps and valves together, the average standard deviation of the repeated screenings is 23 percent. This would yield a confidence limit about a single test of $\pm$ 46 percent.

This standard deviation of 23 percent is composed of variation due to analysis, sampling train components, sampling team effect, and inherent short-term variability in the leak rate. No significant differences between sampling teams or sampling systems 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. These changes can be attributed to variations in process conditions and random variations in the actual leak rate. The 16 percent standard deviation for the accuracy checks (Section 3.2) is an estimate of the variability associated with just the sampling/analysis procedures.

TABLE C-5. SUMMARY OF REPEAT SAMPLING DATA

Unit	Source	Date	Nonmethane Leak Rate (lbs/hr)	Individual* % Difference	Pooled # Standard Deviation %
1	PU 154	3/5/80	0.08902		
			0.07134	22.1	11.1
1	PU 1148	8/22/80	0.00995		
			0.01070	-7.3	
			0.01068	-7.1	
			0.01196	-22.4	
			0.01135	-13.1	8.8
1	PU 1314	3/6/80	0.12543		
			1.67235	-122.1	
			0.17027	-30.3	71.3
1	VA 59	5/7/80	0.00132		
			0.00141	-6.6	
			0.00133	-0.7	
			0.00139	-5.2	
			0.00128	3.1	
			0.00135	-2.3	2.7
2	VA 2287	3/25/80	0.04871		
			0.06984	-35.6	19.1
			0.06882	-34.2	
4	PU 764	5/29/80	0.00089		
			0.00142	-45.9	22.9

*INDIVIDUAL DIFFERENCE = $\frac{\text{original leak rate} - \text{QC leak rate}}{(\text{original} + \text{QC leak})/2} \times 100$

#Pooled Standard Deviation - Percent standard deviation of leak rates for each ID

$$= \left[\frac{\sum_{i=1}^{n} (\text{Individual \% Diff})^2}{2n} \right]^{1/2} ,$$

where n is the number of samples for the source.

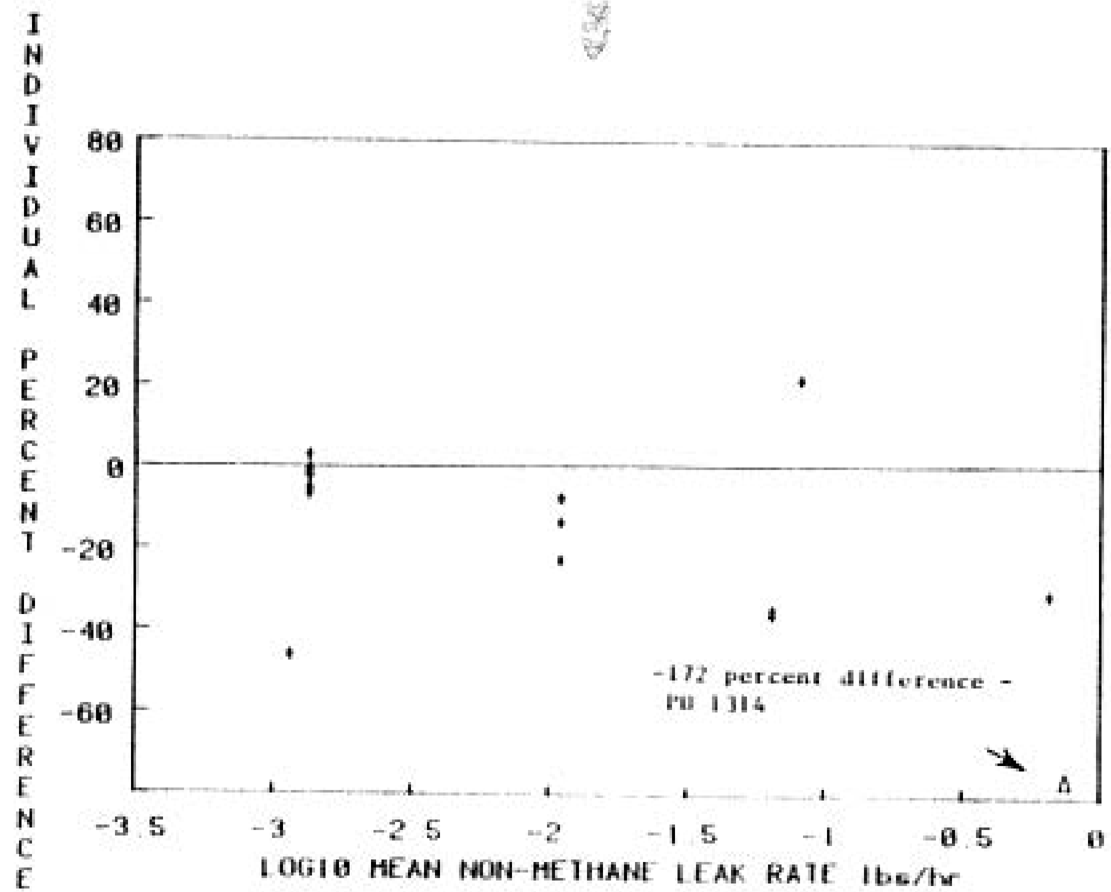


Figure C-33. Plot of Individual Percent Differences vs. Mean Leak Rate for Repeated Samples

APPENDIX D

Statistical Considerations

1.0 INTRODUCTION

Several different statistical techniques were applied during this study of fugitive emissions from the synthetic organic chemical industry. The basis for these techniques is discussed in this appendix.

The statistical methods were applied in the following areas:

- immediate effect of maintenance
- occurrence of leaks
- recurrence of leaks
- modelling leak rate vs. screening value

Special methods were developed for confidence intervals for weighted percent reduction (WPR) of mass emissions due to maintenance, weighting factors needed to combine the low leaking sources (<1,000 ppmv screening values) with the control sources (1,000-10,000 ppmv screening values) for estimating occurrence rates, development of a mixed model for the estimating recurrence rates, and correcting for transforming from a logarithmic to an arithmetic scale for predicting leak rates from screening values.

2.0 CONFIDENCE INTERVALS FOR WEIGHTED PERCENT REDUCTION

Confidence intervals for the weighted percent reduction were given in Section 3.2.1. These were computed following the Mood, Graybill and Boes (Reference 4) derivation of the variance of a ratio of random variables. Ninety-five percent confidence intervals were computed using:

$$\text{Lower limit} = W - t(n-2)\sqrt{S_W^2}$$

$$\text{Upper limit} = W + t(n-2)\sqrt{S_W^2}$$

where

W = estimated weighted percent reduction

$$= \frac{\sum^{n} B_i - \sum^{n} A_i}{\sum^{n} B_i} \cdot 100$$

S_W^2 = estimated variance of the weighted percent reduction

$$= \frac{100^2\ \bar{A}^2}{n\ \bar{B}^2}\left[\frac{S_A^{\,2}}{\bar{A}^2} + \frac{S_B^{\,2}}{\bar{B}^2} - \frac{2\sum^{n}(A_i - \bar{A})\ (B_i - \bar{B})}{(n-1)\ \bar{A}\ \bar{B}}\right].$$

Here, n is the number of leaking sources and t(n-2) is the .975 probability point of student's t distribution with n-2 degrees of freedom. The following notations were used:

B_i = before maintenance leak rate of the ith leaking source

A_i = after maintenance leak rate of the ith leaking source

$$\bar{B} = \frac{1}{n} \sum^{n} B_i$$

$$\bar{A} = \frac{1}{n} \sum^{n} A_i$$

$$S_A^2 = \frac{1}{(n-1)} \sum^{n} (A_i - \bar{A})^2$$

$$S_B^2 = \frac{1}{(n-1)} \sum^{n} (B_i - \bar{B})^2$$

The confidence intervals should be interpreted as follows:

> When we state that the true weighted percent reduction falls within the limits computed as described above, we expect to be correct about 95 percent of the time.

3.0 CONFIDENCE INTERVALS FOR PERCENT OF SOURCES REPAIRED

Confidence intervals for the percent of leaking sources repaired were computed using the binomial distribution. This distribution is used to model data when a random sample is selected and each item is classified into one of two categories (repaired or not repaired in Section 3.2). Exact confidence limits ((1-α) · 100%) for the estimate of percent repaired can be obtained by solving for P_ℓ in

$$\sum_{t=k}^{n} \binom{n}{t} P_\ell^{\,t} (1-P_\ell)^{n-t} = \frac{\alpha}{2}$$

for the lower limit and for P_u in

$$\sum_{t=0}^{k} \binom{n}{t} P_u^{t} (1-P_u)^{n-t} = \frac{\alpha}{2}$$

for the upper limit, where

n = number of sources screened above 10,000 ppmv before maintenance

k = number of leaking sources screened below 10,000 ppmv after maintenance (number repaired).

Assuming that the sources screened approximate a random sample from the population, these confidence intervals can be interpreted as follows:

> When we state that the true percent of sources in the population which are repaired lies within the confidence bounds, we expect to be correct about 95 percent of the time.

4.0 EXPONENTIAL DISTRIBUTION MODEL

The exponential distribution function given by

$$f(t) = \lambda \exp[-\lambda t],\ t \geq 0$$

where λ is a constant (occurrence rate) and t is time to first occurrence was used to approximate the actual distribution of the time to first occurrence of a leak (screening value $\geq$ 10,000 ppmv) in Section 3.4. The appropriate use of this distribution in modelling first leak occurrences is discussed in Bazovsky (Reference 1).

One advantage of this distribution is the ease with which a 30-day occurrence rate can be obtained once λ has been estimated from the data. The estimated cumulative distribution function

$$\hat{F}(t) = 100 \times (1 - \exp[-\hat{\lambda} t])$$

is evaluated at t = 30, where the maximum likelihood estimate of λ is given by

$$\hat{\lambda} = \frac{1}{\hat{m}}$$

where

$$\hat{m} = \frac{T}{r}$$

and T is sum of times for all sources to either (1) leak occurrence or (2) last screening (if no leak occurred), and r is the number of occurrences. Confidence intervals for λ are based upon percentage points of the chi-square distribution, since

$$\frac{2r\hat{\lambda}}{\lambda}$$

is distributed as a chi-square with 2r degrees of freedom (Reference 1). Thus

$$\hat{\lambda}_L = \frac{X^2_{1-\alpha/2}(2r) \cdot \hat{\lambda}}{2r}$$

and

$$\hat{\lambda}_U = \frac{X^2_{\alpha/2}(2r) \cdot \hat{\lambda}}{2r} .$$

Estimates of occurrence rates by process (and their confidence intervals) for valves vs. pumps, for gas vs. liquid service and for block valves vs. control valves were computed using $\hat{\lambda}$, $\hat{\lambda}_L$, and $\hat{\lambda}_U$ as shown above. Tables 3-3 through 3-5 of Section 3.4 show these estimated 30-day, 90-day and 180-day occurrence rates.

Corresponding confidence intervals for $F(t)$ are obtained by substituting $\hat{\lambda}_L$ and $\hat{\lambda}_U$ into the formula for $\hat{F}(t)$. The predicted occurrence rate for any time can be obtained from a plot of the cumulative distribution function.

To compare the observed with the predicted occurrence rates, the empirical distribution function was computed using

$$\tilde{F}(t) = 100 \times \frac{\text{No. of occurrences at times} \leq t}{\text{No. of sources observed over time } (0,t)} .$$

The denominator in the above formula is the sum of the number of occurrences in the interval (0,t) and the number of nonleaking sources observed over

(0,t). If a source was not observed over all of (0,t), then the fraction of (0,t) over which t was observed was used in the sum.

Sources in the control group that were screened at 1,000-10,000 ppmv were combined with the "low leaker" group (0-1,000 ppmv) in the development of 30-day occurrence rate estimates and in the generation of the empirical distribution function used to compare the data with the occurrence model. The proportion of all screened sources between 0 and 1,000 ppmv and between 1,000 and 10,000 ppmv for each process and each source type are given in Table D-1. These proportions were obtained from Reference 2. Combined estimates for the occurrence rates and for approximate upper and lower 95 percent confidence limits for the estimates were computed using these weights. For example, for the overall estimate for valves,

$$\hat{\lambda} = .918\ \hat{\lambda}\ (Z) + .082\ \hat{\lambda}\ (C),$$

$$\hat{\lambda}_U = .918\ \hat{\lambda}_U\ (Z) + .082\ \hat{\lambda}_U\ (C), \text{ and}$$

$$\hat{\lambda}_L = .918\ \lambda_L\ (Z) + .082\ \lambda_L\ (C),$$

where $\hat{\lambda}$ is the combined estimate of the occurrence rate from the 0-1,000 ppmv group (Z) and from the 1,000-10,000 ppmv group (C). The subscripts U and L denote the approximate upper and lower 95 percent confidence limits for the respective estimates, which were developed for the Z and C groups seperately according to the formulas presented above.

Pairwise comparisons of source type (valves vs. pump seals), service (gas vs. liquid), and valve type (block vs. control valves) were made using percentage points of the F-distribution. Since $2r\hat{m}/m$ is distributed as a chi-square with 2r degrees of freedom and $\lambda = 1/m$, $2r\lambda/\hat{\lambda}$ is also a chi-square with 2r degrees of freedom. If, for example, subscripts V and P denote valves and pumps, respectively, then

$$\left(\frac{\lambda_V}{\hat{\lambda}_V}\right) \Big/ \left(\frac{\lambda_P}{\hat{\lambda}_P}\right)$$

is distributed as an F with $2r_V$ and $2r_P$ degrees of freedom. Under the null hypothesis that $\lambda_V = \lambda_P$, $\hat{\lambda}_P/\hat{\lambda}_V$ is distributed as an F with $2r_V$ and $2r_P$ degrees of freedom. This was the criterion used to test H_o: $\lambda_V = \lambda_P$. H_o: $\lambda_G = \lambda_L$, and H_o: $\lambda_{BV} = \lambda_{CV}$, where G and L denote gas and liquid service, and BV and CV denote block valves and control valves, respectively, were tested similarly.

TABLE D-1. Weighting Factors Used to Construct Thirty (30)-Day Estimates From the Sources Screened at 0-1,000 ppmv (Z) and Those Screened at 1,000-10,000 ppmv (C).

Process	Valves		Pump Seals	
	Z	C	Z	C
Cumene	.877	.122	.762	.238
Ethylene	.890	.110	.800	.200
Vinyl Acetate	.987	.013	.976	.024
Overall	.918	.082	.901	.099

Note: These weights are the proportions of the total population of sources screened in the given category represented by Z (0-1,000 ppmv) and C (1,000-10,000 ppmv).

5.0 MIXED DISTRIBUTION MODEL

In order to estimate recurrence rates of leaks after maintenance (Section 3.5) a mixed distribution model of the following form was used:

$$f(t) = \begin{cases} (1-p)\ \lambda \exp\ [-\lambda(t-5)], & t > 5 \\ p/5, & 0 \leq t \leq 5 \\ 0, & t < 0 \end{cases}$$

where λ is developed using methods similar to those used for Section 3.4 (Exponential Distribution Model). The p is the proportion of valves which recur within five days of maintanance and (1-p) is the proportion that will follow an exponential distribution of time to recur.

To estimate p, the following equation was used:

$$\hat{p} = \frac{\text{Number recurring within 5 days}}{\text{Number of valves observed}} = \frac{4}{28} = 0.143.$$

The maximum likelihood estimate for λ was found to be

$$\hat{\lambda} = 1/\hat{m} = .0014$$

where

$$\hat{m} = \frac{\text{Total observation time past 5 days for all sources}}{\text{Number recurring after 5 days}}$$

$$= \frac{2827}{4} = 706.8 \text{ days.}$$

The resulting estimate of percent recurring over time is of the form:

$$\hat{F}(t) = 100 \times \begin{cases} 0.143 + 0.857\left(1-\exp\left[-0.0014\,(t-5)\right]\right), & t > 5 \\ 0.143/5, & 0 \leq t \leq 5 \\ 0, & t < 0. \end{cases}$$

6.0 CORRELATION COEFFICIENT

The sample correlation coefficient is a statistical measure of the linear relationship between two variables. The correlation between two variables, X and Y, is computed as

$$r_{XY} = \frac{\Sigma (X_i - \bar{X}) \cdot (Y_i - \bar{Y})}{\Sigma (X_i - \bar{X})^2 \cdot \Sigma (Y_i - \bar{Y})^2}$$

and is bounded:

$$-1 \leq r_{XY} \leq 1.$$

In section 3.6, X represents Log_{10} mean screening value and Y represents Log_{10} leak rate.

A value of r equal to -1 indicates a perfect linear relationship between the sample values of X and Y, with the value of Y decreasing as the value of X increases. A value of r equal to +1 also indicates a perfect linear relationship between the sample values, but one in which the value of Y increases as X increases. If there is no linear relationship between the sample values of X and Y, then r will have a value near zero.

7.0 ANALYSIS OF VARIANCE

Often it is desirable to design an experiment in such a way that several variables or populations can be studied simultaneously. There is a certain amount of variation present in every group of samples. The Analysis of Variance is a technique that separates the total variation present into separate independent components that may be attributed to one source or another. These separate components of the variance are then analyzed in such a manner that certain hypotheses can be tested. The assumptions that must be made are that (1) the data are random samples from normal distributions and (2) the normal populations all have equal variances. Analysis of Variance can also be used to estimate the actual variance components as in Appendix C.

8.0 ANALYSIS OF COVARIANCE

In describing the relationship between screening value and emission rate, a statistical Analysis of Covariance was first performed to determine whether different linear equations were required for each process and service type in Section 3.6. The Analysis of Covariance is a technique that combines the features of Analysis of Variance and regression. For each reading of Y, emission rate, we also have a reading of X, the screening value. Thus two separate Analyses of Variance are possible, one for each variable, and also a joint one analyzing the covariance between X and Y. Such an analysis in its complete form is called the Analysis of Covariance. This analysis was performed in the present study to determine which source, service, and process stream types should be combined for prediction purposes.

9.0 LINEAR REGRESSION (LEAST-SQUARES FIT)

While the sample correlation coefficient is a measure of the linear relationship between two variables X and Y, it does not tell us what the relationship is. It is often desirable to determine the relationship in order to predict the value of one variable from that of the other. Finding the equation that gives the relationship between Y and X is known as finding the regression line.

The equation of a straight line can be given in terms of its Y-intercept and its slope. The Y-intercept of a straight line is the Y-coordinate of the point where the line crosses the Y-axis. The slope of a line is the amount of change in Y per unit change in X. The equation of the line whose Y-intercept is the number a, and whose slope is the number b, is

$$Y = a + bX.$$

Transformations of the Y variable or the X variable can often "linearize" a nonlinear model. In developing a relationship between screening values and emission rate, logarithm (base 10) transformations were performed on both variables in Section 3.6.

Least squares estimators of the regression coefficients, a and b, minimize the sum of the squares of deviations of the predicted Y-values from the observed Y-values. Defining the best-fitting line in this manner it can be shown (Reference 7) that the equation of the best-fitting line is

$$\hat{Y} = \hat{a} + \hat{b}X$$

where

$$b = \frac{\Sigma (X_i - X)\, Y_i}{\Sigma (X_i - \bar{X})^2} = \frac{\Sigma X_i Y_i - n\bar{X}\bar{Y}}{\Sigma X_i^2 - n\bar{X}^2}$$

$$\bar{X} = \frac{\sum X_i}{n}, \quad \bar{Y} = \frac{\sum Y_i}{n},$$

and

$$\hat{a} = \bar{Y} - \hat{b}\bar{X}.$$

In the above expression $\hat{Y}$ represents a predicted value. The estimated regression coefficients are denoted $\hat{a}$ and $\hat{b}$.

10.0 CONFIDENCE INTERVALS FOR MODEL PARAMETERS OF A LEAST-SQUARES REGRESSION EQUATION

A confidence interval for a parameter θ is an interval

$$c < \theta < d,$$

where c and d are numbers calculated partially from sample data, within which we feel reasonably certain the unknown parameter lies. A confidence interval is derived from a probability statement that involves the unknown parameter θ. Confidence intervals were presented in section 3.6 along with the fitted linear least-squares regression equation for Log_{10} leak rate vs. Log_{10} mean screening value.

Confidence intervals are very powerful methods for assessing the accuracy of least squares estimates. Searle (Reference 7) describes the statistical concepts and models used in obtaining the following formulas for the confidence limits for the slope and the intercept.

Parameter	Confidence Interval
a (intercept)	$\hat{a} - t_{1-\alpha/2}(n-2)\hat{\sigma}_a \leq a \leq \hat{a} + t_{1-\alpha/2}(n-2)\hat{\sigma}_a$
b (slope)	$\hat{b} - t_{1-\alpha/2}(n-2)\hat{\sigma}_b \leq b \leq \hat{b} + t_{1-\alpha/2}(n-2)\hat{\sigma}_b$

$$\hat{\sigma}_a^2 = \hat{\sigma}^2 [n^{-1} + (\bar{X}/d_X)^2]$$

$$\hat{\sigma}_b^2 = \hat{\sigma}^2/d_X^2$$

$$d_X^2 = \Sigma (X_i - \bar{X})^2$$

$$\hat{\sigma}^2 = \Sigma (Y_i - \hat{a} - \hat{b}X_i)^2/(n - 2)$$

$$\bar{X} = \Sigma X_i/n$$

$t_{1-\alpha/2}(n - 2)$ is the $1 - \alpha/2$ probability point of student's t distribution with (n - 2) degrees of freedom.

The confidence intervals should be interpreted as follows:

> When we state that the parameter falls within the limits computed as described above, we expect to be correct about 100 x (1 - α) percent of the time.

11.0 STANDARD ERROR OF ESTIMATE

The standard error of estimate is a statistical measure of the amount of variation of the actual values of the dependent variable (of an estimating equation) from their estimated or computed values. Its formula may be written

$$S_Y = \sqrt{\frac{\Sigma (Y_i - \hat{Y}_i)^2}{n - 2}}$$

where

Y = observed (or actual) values of the dependent variable

$\hat{Y}$ = estimated Y values obtained by solving the estimating (or regression) equation

n = number of data pairs.

The standard error of the estimate was presented for each of the fitted regression equations in section 3.6.

12.0 SCALE BIAS CORRECTION FACTOR

In order to fit a linear least-squares regression equation to the leak rate vs. screening value data in section 3.6, both the leak rate and the screening value had to be transformed to a logarithmic scale. This was done to obtain a linear relationship between Log_{10} leak rate and Log_{10} mean screening value, and also to obtain approximately normally distributed leak rates.

Let X_i, $i = 1, \ldots, m$ be m screening values or leak rates. If

$$Y_i = \log_e X_i, \; i = 1, \ldots, m,$$

then

$$\bar{Y} = \sum_{i=1}^{m} Y_i/m,$$

and

$$S^2 = \sum_{i=1}^{m} (Y_i - \bar{Y})^2/(m - 1).$$

The estimated mean of the X-variate is computed as

$$\hat{\mu}_X = \exp(\bar{Y}) \cdot g\left(\frac{S^2}{2}\right),$$

where g(t) is the infinite series.

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

The function g(t) is a scale bias correction factor for the mean (Reference 3), needed to obtain an unbiased estimate of the mean of X, $\hat{\mu}_X$, in the original scale of X. Patterson (Reference 5) described how confidence intervals for the mean from a lognormal distribution can be computed:

$$CL_U = \exp\left[\bar{Y} + 1.96\ (S/\sqrt{m}\,)\right] \cdot g\left(\frac{S^2}{2}\right)$$

$$CL_L = \exp\left[\bar{Y} - 1.96\ (S\sqrt{m}\,)\right] \cdot g\left(\frac{S^2}{2}\right),$$

where S is the standard deviation of the logarithmically transformed data, m is the number of sources, and g(t) is the scale bias correction factor.

APPENDIX E

Two-Way Tables of Screening Values

To provide a basis for further investigation into the effect of maintenance based on screening values, two-way tables are presented in this appendix. (This is an extension of Section 3.2.2.)

Each of the screening values used in this analysis was classified in a screening range category according to the following ranges:

Screening Value (x) Range, ppmv	Category
$x = 0$	0
$1 \leq x \leq 999$	1
$1,000 \leq x \leq 9,999$	2
$10,000 \leq x \leq 49,999$	3
$50,000 \leq x$	4

To allow an assessment of the effects of different action levels on the number of valves which can be repaired, two-way tables were constructed using these screening value categories. The two-way tables show the following comparisons:

- Immediately before maintenance screening values versus the immediately after maintenance screening values

This comparison can be used to evaluate an inspection/maintenance program where the inspection team also performs the maintenance.

- Initial before maintenance screening values versus screening values obtained immediately before maintenance

This comparison can provide information concerning the percent of valves which cross an action level without maintenance.

- Initial before maintenance screening values versus screening values obtained immediately after maintenance

This comparison is useful in evaluating the effect of maintenance on reducing the percent of leaking sources if the level of the immediately before maintenance screening value is ignored.

- Initial before maintenance screening value versus screening values obtained immediately after maintenance only for those sources where the immediately before maintenance screening value is greater than or equal to 10,000 ppmv

This comparison provides an indication of the effect of an inspection/maintenance program where the maintenance crew follows the screening crew by several days.

The tables are presented in this appendix and were constructed to allow analysis by the following breakdowns:

- overall,
- process type (Cumene, Ethylene, Vinyl Acetate),
- valve type (block, control)

TABLE E-1. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR ALL UNITS

IMMEDIATELY BEFORE MAINTENANCE OVA READING: FREQUENCY / PERCENT / ROW PCT / COL PCT	IMMEDIATELY AFTER MAINTENANCE OVA READING: 0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	0.65	0.00	0.00	0.00	0.00	0.65
	100.00	0.00	0.00	0.00	0.00	
	9.09	0.00	0.00	0.00	0.00	
1	3	10	1	0	1	15
	1.94	6.45	0.65	0.00	0.65	9.68
	20.00	66.67	6.67	0.00	6.67	
	27.27	28.57	2.78	0.00	2.38	
2	6	9	24	2	1	42
	3.87	5.81	15.48	1.29	0.65	27.10
	14.29	21.43	57.14	4.76	2.38	
	54.55	25.71	66.67	6.45	2.38	
3	1	6	3	7	6	23
	0.65	3.87	1.94	4.52	3.87	14.84
	4.35	26.09	13.04	30.43	26.09	
	9.09	17.14	8.33	22.58	14.29	
4	0	10	8	22	34	74
	0.00	6.45	5.16	14.19	21.94	47.74
	0.00	13.51	10.81	29.73	45.95	
	0.00	28.57	22.22	70.97	80.95	
TOTAL	11	35	36	31	42	155
	7.10	22.58	23.23	20.00	27.10	100.00

TABLE E-2. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR ALL UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY BEFORE MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	1	2
	0.65	0.00	0.00	0.00	0.65	1.29
	50.00	0.00	0.00	0.00	50.00	
	100.00	0.00	0.00	0.00	1.35	
1	0	6	7	1	1	15
	0.00	3.87	4.52	0.65	0.65	9.68
	0.00	40.00	46.67	6.67	6.67	
	0.00	40.00	16.67	4.35	1.35	
2	0	7	19	6	7	39
	0.00	4.52	12.26	3.87	4.52	25.16
	0.00	17.95	48.72	15.38	17.95	
	0.00	46.67	45.24	26.09	9.46	
3	0	0	13	8	9	30
	0.00	0.00	8.39	5.16	5.81	19.35
	0.00	0.00	43.33	26.67	30.00	
	0.00	0.00	30.95	34.78	12.16	
4	0	2	3	8	56	69
	0.00	1.29	1.94	5.16	36.13	44.52
	0.00	2.90	4.35	11.59	81.16	
	0.00	13.33	7.14	34.78	75.68	
TOTAL	1	15	42	23	74	155
	0.65	9.68	27.10	14.84	47.74	100.00

TABLE E-3. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR ALL UNITS

Rows: BEFORE TENTING-BEFORE MAINTENANCE OVA READING. Columns: IMMEDIATELY AFTER MAINTENANCE OVA READING.

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	1	0	2
	0.65	0.00	0.00	0.65	0.00	1.29
	50.00	0.00	0.00	50.00	0.00	
	9.09	0.00	0.00	3.23	0.00	
1	1	9	3	0	2	15
	0.65	5.81	1.94	0.00	1.29	9.68
	6.67	60.00	20.00	0.00	13.33	
	9.09	25.71	8.33	0.00	4.76	
2	4	10	14	8	3	39
	2.58	6.45	9.03	5.16	1.94	25.16
	10.26	25.64	35.90	20.51	7.69	
	36.36	28.57	38.89	25.81	7.14	
3	5	4	10	4	7	30
	3.23	2.58	6.45	2.58	4.52	19.35
	16.67	13.33	33.33	13.33	23.33	
	45.45	11.43	27.78	12.90	16.67	
4	0	12	9	18	30	69
	0.00	7.74	5.81	11.61	19.35	44.52
	0.00	17.39	13.04	26.09	43.48	
	0.00	34.29	25.00	58.06	71.43	
TOTAL	11	35	36	31	42	155
	7.10	22.58	23.23	20.00	27.10	100.00

TABLE E-4. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR ALL UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	0	0	0	1	0	1
	0.00	0.00	0.00	1.03	0.00	1.03
	0.00	0.00	0.00	100.00	0.00	
	0.00	0.00	0.00	3.45	0.00	
1	0	1	0	0	1	2
	0.00	1.03	0.00	0.00	1.03	2.06
	0.00	50.00	0.00	0.00	50.00	
	0.00	6.25	0.00	0.00	2.50	
2	0	3	0	7	3	13
	0.00	3.09	0.00	7.22	3.09	13.40
	0.00	23.08	0.00	53.85	23.08	
	0.00	18.75	0.00	24.14	7.50	
3	1	2	3	4	7	17
	1.03	2.06	3.09	4.12	7.22	17.53
	5.88	11.76	17.65	23.53	41.18	
	100.00	12.50	27.27	13.79	17.50	
4	0	10	8	17	29	64
	0.00	10.31	8.25	17.53	29.90	65.98
	0.00	15.63	12.50	26.56	45.31	
	0.00	62.50	72.73	58.62	72.50	
TOTAL	1	16	11	29	40	97
	1.03	16.49	11.34	29.90	41.24	100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-5. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR CUMENE PROCESS UNITS

Rows: IMMEDIATELY BEFORE MAINTENANCE OVA READING; Columns: IMMEDIATELY AFTER MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	1.85	0.00	0.00	0.00	0.00	1.85
	100.00	0.00	0.00	0.00	0.00	
	100.00	0.00	0.00	0.00	0.00	
1	0	4	0	0	0	4
	0.00	7.41	0.00	0.00	0.00	7.41
	0.00	100.00	0.00	0.00	0.00	
	0.00	36.36	0.00	0.00	0.00	
2	0	3	12	2	0	17
	0.00	5.56	22.22	3.70	0.00	31.48
	0.00	17.65	70.59	11.76	0.00	
	0.00	27.27	75.00	13.33	0.00	
3	0	3	2	4	0	9
	0.00	5.56	3.70	7.41	0.00	16.67
	0.00	33.33	22.22	44.44	0.00	
	0.00	27.27	12.50	26.67	0.00	
4	0	1	2	9	11	23
	0.00	1.85	3.70	16.67	20.37	42.59
	0.00	4.35	8.70	39.13	47.83	
	0.00	9.09	12.50	60.00	100.00	
TOTAL	1	11	16	15	11	54
	1.85	20.37	29.63	27.78	20.37	100.00

TABLE E-6. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR CUMENE PROCESS UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY BEFORE MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	1.85	0.00	0.00	0.00	0.00	1.85
	100.00	0.00	0.00	0.00	0.00	
	100.00	0.00	0.00	0.00	0.00	
1	0	2	1	0	0	3
	0.00	3.70	1.85	0.00	0.00	5.56
	0.00	66.67	33.33	0.00	0.00	
	0.00	50.00	5.88	0.00	0.00	
2	0	2	9	3	0	14
	0.00	3.70	16.67	5.56	0.00	25.93
	0.00	14.29	64.29	21.43	0.00	
	0.00	50.00	52.94	33.33	0.00	
3	0	0	5	5	3	13
	0.00	0.00	9.26	9.26	5.56	24.07
	0.00	0.00	38.46	38.46	23.08	
	0.00	0.00	29.41	55.56	13.04	
4	0	0	2	1	20	23
	0.00	0.00	3.70	1.85	37.04	42.59
	0.00	0.00	8.70	4.35	86.96	
	0.00	0.00	11.76	11.11	86.96	
TOTAL	1	4	17	9	23	54
	1.85	7.41	31.48	16.67	42.59	100.00

TABLE E-7. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR CUMENE PROCESS UNITS

Row variable: BEFORE TENTING-BEFORE MAINTENANCE OVA READING
Column variable: IMMEDIATELY AFTER MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	1.85	0.00	0.00	0.00	0.00	1.85
	100.00	0.00	0.00	0.00	0.00	
	100.00	0.00	0.00	0.00	0.00	
1	0	2	1	0	0	3
	0.00	3.70	1.85	0.00	0.00	5.56
	0.00	66.67	33.33	0.00	0.00	
	0.00	18.18	6.25	0.00	0.00	
2	0	3	7	4	0	14
	0.00	5.56	12.96	7.41	0.00	25.93
	0.00	21.43	50.00	28.57	0.00	
	0.00	27.27	43.75	26.67	0.00	
3	0	3	6	2	2	13
	0.00	5.56	11.11	3.70	3.70	24.07
	0.00	23.08	46.15	15.38	15.38	
	0.00	27.27	37.50	13.33	18.18	
4	0	3	2	9	9	23
	0.00	5.56	3.70	16.67	16.67	42.59
	0.00	13.04	8.70	39.13	39.13	
	0.00	27.27	12.50	60.00	81.82	
TOTAL	1	11	16	15	11	54
	1.85	20.37	29.63	27.78	20.37	100.00

TABLE E-8. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR CUMENE PROCESS UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	1	2	3	4	TOTAL
2	0	0	3	0	3
	0.00	0.00	9.38	0.00	9.38
	0.00	0.00	100.00	0.00	
	0.00	0.00	23.08	0.00	
3	2	2	2	2	8
	6.25	6.25	6.25	6.25	25.00
	25.00	25.00	25.00	25.00	
	50.00	50.00	15.38	18.18	
4	2	2	8	9	21
	6.25	6.25	25.00	28.13	65.63
	9.52	9.52	38.10	42.86	
	50.00	50.00	61.54	81.82	
TOTAL	4	4	13	11	32
	12.50	12.50	40.63	34.38	100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-9. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR ETHYLENE PROCESS UNITS

IMMEDIATELY BEFORE MAINTENANCE OVA READING (rows) / IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
1	0	5	0	0	1	6
	0.00	7.14	0.00	0.00	1.43	8.57
	0.00	83.33	0.00	0.00	16.67	
	0.00	41.67	0.00	0.00	3.67	
2	3	3	9	0	1	16
	4.29	4.29	12.86	0.00	1.43	22.86
	18.75	18.75	56.25	0.00	6.25	
	100.00	25.00	56.25	0.00	3.67	
3	0	1	1	2	6	10
	0.00	1.43	1.43	2.86	8.67	14.29
	0.00	10.00	10.00	20.00	60.00	
	0.00	8.33	6.25	18.18	21.43	
4	0	3	6	9	20	38
	0.00	4.29	8.57	12.86	28.67	54.29
	0.00	7.89	15.79	23.68	52.63	
	0.00	25.00	37.50	81.82	71.43	
TOTAL	3	12	16	11	28	70
	4.29	17.14	22.86	15.71	40.00	100.00

TABLE E-10. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR ETHYLENE PROCESS UNITS

Rows: BEFORE TENTING-BEFORE MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	IMMEDIATELY BEFORE MAINTENANCE OVA READING 1	2	3	4	TOTAL
0	0	0	0	1	1
	0.00	0.00	0.00	1.43	1.43
	0.00	0.00	0.00	100.00	
	0.00	0.00	0.00	2.63	
1	3	4	0	1	8
	4.29	5.71	0.00	1.43	11.43
	37.50	50.00	0.00	12.50	
	50.00	25.00	0.00	2.63	
2	2	7	3	5	17
	2.86	10.00	4.29	7.14	24.29
	11.76	41.18	17.65	29.41	
	33.33	43.75	30.00	13.16	
3	0	5	2	5	12
	0.00	7.14	2.86	7.14	17.14
	0.00	41.67	16.67	41.67	
	0.00	31.25	20.00	13.16	
4	1	0	5	26	32
	1.43	0.00	7.14	37.14	45.71
	3.13	0.00	15.63	81.25	
	16.67	0.00	50.00	68.42	
TOTAL	6	16	10	38	70
	8.57	22.86	14.29	54.29	100.00

TABLE E-11. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR ETHYLENE PROCESS UNITS

Row variable: BEFORE TENTING-BEFORE MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	IMMEDIATELY AFTER MAINTENANCE OVA READING 0	1	2	3	4	TOTAL
0	0	0	0	1	0	1
	0.00	0.00	0.00	1.43	0.00	1.43
	0.00	0.00	0.00	100.00	0.00	
	0.00	0.00	0.00	9.09	0.00	
1	0	5	1	0	2	8
	0.00	7.14	1.43	0.00	2.86	11.43
	0.00	62.50	12.50	0.00	25.00	
	0.00	41.67	6.25	0.00	7.14	
2	2	3	5	4	3	17
	2.86	4.29	7.14	5.71	4.29	24.29
	11.76	17.65	29.41	23.53	17.65	
	66.67	25.00	31.25	36.36	10.71	
3	1	1	4	1	5	12
	1.43	1.43	5.71	1.43	7.14	17.14
	8.33	8.33	33.33	8.33	41.67	
	33.33	8.33	25.00	9.09	17.86	
4	0	3	6	5	18	32
	0.00	4.29	8.57	7.14	25.71	45.71
	0.00	9.38	18.75	15.63	56.25	
	0.00	25.00	37.50	45.45	64.29	
TOTAL	3	12	16	11	28	70
	4.29	17.14	22.86	15.71	40.00	100.00

TABLE E-12. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR ETHYLENE PROCESS UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) × IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	1	2	3	4	TOTAL
0	0	0	1	0	1
	0.00	0.00	2.08	0.00	2.08
	0.00	0.00	100.00	0.00	
	0.00	0.00	9.09	0.00	
1	0	0	0	1	1
	0.00	0.00	0.00	2.08	2.08
	0.00	0.00	0.00	100.00	
	0.00	0.00	0.00	3.85	
2	1	0	4	3	8
	2.08	0.00	8.33	6.25	16.67
	12.50	0.00	50.00	37.50	
	25.00	0.00	36.36	11.54	
3	0	1	1	5	7
	0.00	2.08	2.08	10.42	14.58
	0.00	14.29	14.29	71.43	
	0.00	14.29	9.09	19.23	
4	3	6	5	17	31
	6.25	12.50	10.42	35.42	64.58
	9.68	19.35	16.13	54.84	
	75.00	85.71	45.45	65.38	
TOTAL	4	7	11	26	48
	8.33	14.58	22.92	54.17	100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-13. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR VINYL ACETATE PROCESS UNITS

IMMEDIATELY AFTER MAINTENANCE OVA READING (columns); IMMEDIATELY BEFORE MAINTENANCE OVA READING (rows)

FREQUENCY PERCENT ROW PCT COL PCT	0	1	2	3	4	TOTAL
1	3 9.68 60.00 42.86	1 3.23 20.00 8.33	1 3.23 20.00 25.00	0 0.00 0.00 0.00	0 0.00 0.00 0.00	5 16.13
2	3 9.68 33.33 42.86	3 9.68 33.33 25.00	3 9.68 33.33 75.00	0 0.00 0.00 0.00	0 0.00 0.00 0.00	9 29.03
3	1 3.23 25.00 14.29	2 6.45 50.00 16.67	0 0.00 0.00 0.00	1 3.23 25.00 20.00	0 0.00 0.00 0.00	4 12.90
4	0 0.00 0.00 0.00	6 19.35 46.15 50.00	0 0.00 0.00 0.00	4 12.90 30.77 80.00	3 9.68 23.08 100.00	13 41.94
TOTAL	7 22.58	12 38.71	4 12.90	5 16.13	3 9.68	31 100.00

TABLE E-14. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR VINYL ACETATE PROCESS UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY BEFORE MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	1	2	3	4	TOTAL
1	1	2	1	0	4
	3,23	6,45	3.23	0,00	12.90
	25,00	50,00	25.00	0,00	
	20,00	22,22	25.00	0,00	
2	3	3	0	2	8
	9,68	9,68	0.00	6,45	25.81
	37,50	37,50	0.00	25,00	
	60,00	33,33	0.00	15,38	
3	0	3	1	1	5
	0,00	9,68	3.23	3,23	16.13
	0,00	60,00	20.00	20,00	
	0,00	33,33	25.00	7,69	
4	1	1	2	10	14
	3,23	3,23	6.45	32,26	45.16
	7,14	7,14	14.29	71,43	
	20,00	11,11	50.00	76,92	
TOTAL	5	9	4	13	31
	16,13	29,03	12.90	41,94	100.00

TABLE E-15. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR VINYL ACETATE PROCESS UNITS

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT		0	1	2	3	4	TOTAL
1	FREQUENCY	1	2	1	0	0	4
	PERCENT	3.23	6.45	3.23	0.00	0.00	12.90
	ROW PCT	25.00	50.00	25.00	0.00	0.00	
	COL PCT	14.29	16.67	25.00	0.00	0.00	
2	FREQUENCY	2	4	2	0	0	8
	PERCENT	6.45	12.90	6.45	0.00	0.00	25.81
	ROW PCT	25.00	50.00	25.00	0.00	0.00	
	COL PCT	28.57	33.33	50.00	0.00	0.00	
3	FREQUENCY	4	0	0	1	0	5
	PERCENT	12.90	0.00	0.00	3.23	0.00	16.13
	ROW PCT	80.00	0.00	0.00	20.00	0.00	
	COL PCT	57.14	0.00	0.00	20.00	0.00	
4	FREQUENCY	0	6	1	4	3	14
	PERCENT	0.00	19.35	3.23	12.90	9.68	45.16
	ROW PCT	0.00	42.86	7.14	28.57	21.43	
	COL PCT	0.00	50.00	25.00	80.00	100.00	
TOTAL		7	12	4	5	3	31
		22.58	38.71	12.90	16.13	9.68	100.00

TABLE E-16. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR VINYL ACETATE PROCESS UNITS

BEFORE TENTING—BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY PERCENT ROW PCT COL PCT	0	1	3	4	TOTAL
1	0 0.00 0.00 0.00	1 5.88 100.00 12.50	0 0.00 0.00 0.00	0 0.00 0.00 0.00	1 5.88
2	0 0.00 0.00 0.00	2 11.76 100.00 25.00	0 0.00 0.00 0.00	0 0.00 0.00 0.00	2 11.76
3	1 5.88 50.00 100.00	0 0.00 0.00 0.00	1 5.88 50.00 20.00	0 0.00 0.00 0.00	2 11.76
4	0 0.00 0.00 0.00	5 29.41 41.67 62.50	4 23.53 33.33 80.00	3 17.65 25.00 100.00	12 70.59
TOTAL	1 5.88	8 47.06	5 29.41	3 17.65	17 100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-17. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR GAS SERVICE VALVES

IMMEDIATELY AFTER MAINTENANCE OVA READING

IMMEDIATELY BEFORE MAINTENANCE OVA READING	FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	FREQUENCY	1	0	0	0	0	1
	PERCENT	1.39	0.00	0.00	0.00	0.00	1.39
	ROW PCT	100.00	0.00	0.00	0.00	0.00	
	COL PCT	11.11	0.00	0.00	0.00	0.00	
1	FREQUENCY	3	4	0	0	1	8
	PERCENT	4.17	5.56	0.00	0.00	1.39	11.11
	ROW PCT	37.50	50.00	0.00	0.00	12.50	
	COL PCT	33.33	22.22	0.00	0.00	4.76	
2	FREQUENCY	4	5	8	2	0	19
	PERCENT	5.56	6.94	11.11	2.78	0.00	26.39
	ROW PCT	21.05	26.32	42.11	10.53	0.00	
	COL PCT	44.44	27.78	66.67	16.67	0.00	
3	FREQUENCY	1	2	1	1	2	7
	PERCENT	1.39	2.78	1.39	1.39	2.78	9.72
	ROW PCT	14.29	28.57	14.29	14.29	28.57	
	COL PCT	11.11	11.11	8.33	8.33	9.52	
4	FREQUENCY	0	7	3	9	18	37
	PERCENT	0.00	9.72	4.17	12.50	25.00	51.39
	ROW PCT	0.00	18.92	8.11	24.32	48.65	
	COL PCT	0.00	38.89	25.00	75.00	85.71	
TOTAL		9	18	12	12	21	72
		12.50	25.00	16.67	16.67	29.17	100.00

TABLE E-18. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR GAS SERVICE VALVES

Row variable: BEFORE TENTING-BEFORE MAINTENANCE OVA READING

Column variable: IMMEDIATELY BEFORE MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	1.39	0.00	0.00	0.00	0.00	1.39
	100.00	0.00	0.00	0.00	0.00	
	100.00	0.00	0.00	0.00	0.00	
1	0	4	3	0	1	8
	0.00	5.56	4.17	0.00	1.39	11.11
	0.00	50.00	37.50	0.00	12.50	
	0.00	50.00	15.79	0.00	2.70	
2	0	3	9	1	2	15
	0.00	4.17	12.50	1.39	2.78	20.83
	0.00	20.00	60.00	6.67	13.33	
	0.00	37.50	47.37	14.29	5.41	
3	0	0	5	1	3	9
	0.00	0.00	6.94	1.39	4.17	12.50
	0.00	0.00	55.56	11.11	33.33	
	0.00	0.00	26.32	14.29	8.11	
4	0	1	2	5	31	39
	0.00	1.39	2.78	6.94	43.06	54.17
	0.00	2.56	5.13	12.82	79.49	
	0.00	12.50	10.53	71.43	83.78	
TOTAL	1	8	19	7	37	72
	1.39	11.11	26.39	9.72	51.39	100.00

TABLE E-19. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR GAS SERVICE VALVES

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	1.39	0.00	0.00	0.00	0.00	1.39
	100.00	0.00	0.00	0.00	0.00	
	11.11	0.00	0.00	0.00	0.00	
1	1	5	1	0	1	8
	1.39	6.94	1.39	0.00	1.39	11.11
	12.50	62.50	12.50	0.00	12.50	
	11.11	27.78	8.33	0.00	4.76	
2	3	4	5	3	0	15
	4.17	5.56	6.94	4.17	0.00	20.83
	20.00	26.67	33.33	20.00	0.00	
	33.33	22.22	41.67	25.00	0.00	
3	4	1	1	0	3	9
	5.56	1.39	1.39	0.00	4.17	12.50
	44.44	11.11	11.11	0.00	33.33	
	44.44	5.56	8.33	0.00	14.29	
4	0	8	5	9	17	39
	0.00	11.11	6.94	12.50	23.61	54.17
	0.00	20.51	12.82	23.08	43.59	
	0.00	44.44	41.67	75.00	80.95	
TOTAL	9	18	12	12	21	72
	12.50	25.00	16.67	16.67	29.17	100.00

TABLE E-20. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR GAS SERVICE VALVES

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
1	0	0	0	0	1	1
	0.00	0.00	0.00	0.00	2.27	2.27
	0.00	0.00	0.00	0.00	100.00	
	0.00	0.00	0.00	0.00	5.00	
2	0	1	0	2	0	3
	0.00	2.27	0.00	4.55	0.00	6.82
	0.00	33.33	0.00	66.67	0.00	
	0.00	11.11	0.00	20.00	0.00	
3	1	0	0	0	3	4
	2.27	0.00	0.00	0.00	6.82	9.09
	25.00	0.00	0.00	0.00	75.00	
	100.00	0.00	0.00	0.00	15.00	
4	0	8	4	8	16	36
	0.00	18.18	9.09	18.18	36.36	81.82
	0.00	22.22	11.11	22.22	44.44	
	0.00	88.89	100.00	80.00	80.00	
TOTAL	1	9	4	10	20	44
	2.27	20.45	9.09	22.73	45.45	100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-21. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR LIQUID SERVICE VALVES

IMMEDIATELY AFTER MAINTENANCE OVA READING

Rows: IMMEDIATELY BEFORE MAINTENENCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
1	0	6	1	0	0	7
	0.00	7.23	1.20	0.00	0.00	8.43
	0.00	85.71	14.29	0.00	0.00	
	0.00	35.29	4.17	0.00	0.00	
2	2	4	16	0	1	23
	2.41	4.82	19.28	0.00	1.20	27.71
	8.70	17.39	69.57	0.00	4.35	
	100.00	23.53	66.67	0.00	4.76	
3	0	4	2	6	4	16
	0.00	4.82	2.41	7.23	4.82	19.28
	0.00	25.00	12.50	37.50	25.00	
	0.00	23.53	8.33	31.58	19.05	
4	0	3	5	13	16	37
	0.00	3.61	6.02	15.66	19.28	44.58
	0.00	8.11	13.51	35.14	43.24	
	0.00	17.65	20.83	68.42	76.19	
TOTAL	2	17	24	19	21	83
	2.41	20.48	28.92	22.89	25.30	100.00

TABLE E-22. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR LIQUID SERVICE VALVES

BEFORE TENTING-BEFORE MAINTENANCE OVA READING	FREQUENCY / PERCENT / ROW PCT / COL PCT	IMMEDIATELY BEFORE MAINTENANCE OVA READING 1	2	3	4	TOTAL
0	FREQUENCY	0	0	0	1	1
	PERCENT	0.00	0.00	0.00	1.20	1.20
	ROW PCT	0.00	0.00	0.00	100.00	
	COL PCT	0.00	0.00	0.00	2.70	
1	FREQUENCY	2	4	1	0	7
	PERCENT	2.41	4.82	1.20	0.00	8.43
	ROW PCT	28.57	57.14	14.29	0.00	
	COL PCT	28.57	17.39	6.25	0.00	
2	FREQUENCY	4	10	5	5	24
	PERCENT	4.82	12.05	6.02	6.02	28.92
	ROW PCT	16.67	41.67	20.83	20.83	
	COL PCT	57.14	43.48	31.25	13.51	
3	FREQUENCY	0	8	7	6	21
	PERCENT	0.00	9.64	8.43	7.23	25.30
	ROW PCT	0.00	38.10	33.33	28.57	
	COL PCT	0.00	34.78	43.75	16.22	
4	FREQUENCY	1	1	3	25	30
	PERCENT	1.20	1.20	3.61	30.12	36.14
	ROW PCT	3.33	3.33	10.00	83.33	
	COL PCT	14.29	4.35	18.75	67.57	
TOTAL		7	23	16	37	83
		8.43	27.71	19.28	44.58	100.00

TABLE E-23. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR LIQUID SERVICE VALVES

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) / IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY PERCENT ROW PCT COL PCT	0	1	2	3	4	TOTAL
0	0 0.00 0.00 0.00	0 0.00 0.00 0.00	0 0.00 0.00 0.00	1 1.20 100.00 5.26	0 0.00 0.00 0.00	1 1.20
1	0 0.00 0.00 0.00	4 4.82 57.14 23.53	2 2.41 28.57 8.33	0 0.00 0.00 0.00	1 1.20 14.29 4.76	7 8.43
2	1 1.20 4.17 50.00	6 7.23 25.00 35.29	9 10.84 37.50 37.50	5 6.02 20.83 26.32	3 3.61 12.50 14.29	24 28.92
3	1 1.20 4.76 50.00	3 3.61 14.29 17.65	9 10.84 42.86 37.50	4 4.82 19.05 21.05	4 4.82 19.05 19.05	21 25.30
4	0 0.00 0.00 0.00	4 4.82 13.33 23.53	4 4.82 13.33 16.67	9 10.84 30.00 47.37	13 15.66 43.33 61.90	30 36.14
TOTAL	2 2.41	17 20.48	24 28.92	19 22.89	21 25.30	83 100.00

TABLE E-24. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR LIQUID SERVICE VALVES

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	1	2	3	4	TOTAL
0	0 0.00 0.00 0.00	0 0.00 0.00 0.00	1 1.89 100.00 5.26	0 0.00 0.00 0.00	1 1.89
1	1 1.89 100.00 14.29	0 0.00 0.00 0.00	0 0.00 0.00 0.00	0 0.00 0.00 0.00	1 1.89
2	2 3.77 20.00 28.57	0 0.00 0.00 0.00	5 9.43 50.00 26.32	3 5.66 30.00 15.00	10 18.87
3	2 3.77 15.38 28.57	3 5.66 23.08 42.86	4 7.55 30.77 21.05	4 7.55 30.77 20.00	13 24.53
4	2 3.77 7.14 28.57	4 7.55 14.29 57.14	9 16.98 32.14 47.37	13 24.53 46.43 65.00	28 52.83
TOTAL	7 13.21	7 13.21	19 35.85	20 37.74	53 100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-25. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR BLOCK VALVES

IMMEDIATELY AFTER MAINTENANCE OVA READING (columns); IMMEDIATELY BEFORE MAINTENANCE OVA READING (rows)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	0	1
	1.08	0.00	0.00	0.00	0.00	1.08
	100.00	0.00	0.00	0.00	0.00	
	12.50	0.00	0.00	0.00	0.00	
1	1	5	0	0	0	6
	1.08	5.38	0.00	0.00	0.00	6.45
	16.67	83.33	0.00	0.00	0.00	
	12.50	21.74	0.00	0.00	0.00	
2	5	6	14	2	1	28
	5.38	6.45	15.05	2.15	1.08	30.11
	17.86	21.43	50.00	7.14	3.57	
	62.50	26.09	63.64	9.52	5.26	
3	1	4	1	4	1	11
	1.08	4.30	1.08	4.30	1.08	11.83
	9.09	36.36	9.09	36.36	9.09	
	12.50	17.39	4.55	19.05	5.26	
4	0	8	7	15	17	47
	0.00	8.60	7.53	16.13	18.28	50.54
	0.00	17.02	14.89	31.91	36.17	
	0.00	34.78	31.82	71.43	89.47	
TOTAL	8	23	22	21	19	93
	8.60	24.73	23.66	22.58	20.43	100.00

TABLE E-26. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR BLOCK TYPE VALVE

Rows: BEFORE TENTING-BEFORE MAINTENANCE OVA READING. Columns: IMMEDIATELY BEFORE MAINTENANCE OVA READING.

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1	0	0	0	1	2
	1.08	0.00	0.00	0.00	1.08	2.15
	50.00	0.00	0.00	0.00	50.00	
	100.00	0.00	0.00	0.00	2.13	
1	0	3	4	0	0	7
	0.00	3.23	4.30	0.00	0.00	7.53
	0.00	42.86	57.14	0.00	0.00	
	0.00	50.00	14.29	0.00	0.00	
2	0	2	13	2	5	22
	0.00	2.15	13.98	2.15	5.38	23.66
	0.00	9.09	59.09	9.09	22.73	
	0.00	33.33	46.43	18.18	10.64	
3	0	0	9	5	6	20
	0.00	0.00	9.68	5.38	6.45	21.51
	0.00	0.00	45.00	25.00	30.00	
	0.00	0.00	32.14	45.45	12.77	
4	0	1	2	4	35	42
	0.00	1.08	2.15	4.30	37.63	45.16
	0.00	2.38	4.76	9.52	83.33	
	0.00	16.67	7.14	36.36	74.47	
TOTAL	1	6	28	11	47	93
	1.08	6.45	30.11	11.83	50.54	100.00

TABLE E-27. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR BLOCK TYPE VALVE

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
0	1 1.08 50.00 12.50	0 0.00 0.00 0.00	0 0.00 0.00 0.00	1 1.08 50.00 4.76	0 0.00 0.00 0.00	2 2.15
1	1 1.08 14.29 12.50	2 2.15 28.57 8.70	3 3.23 42.86 13.64	0 0.00 0.00 0.00	1 1.08 14.29 5.26	7 7.53
2	2 2.15 9.09 25.00	8 8.60 36.36 34.78	7 7.53 31.82 31.82	5 5.38 22.73 23.81	0 0.00 0.00 0.00	22 23.66
3	4 4.30 20.00 50.00	4 4.30 20.00 17.39	6 6.45 30.00 27.27	4 4.30 20.00 19.05	2 2.15 10.00 10.53	20 21.51
4	0 0.00 0.00 0.00	9 9.68 21.43 39.13	6 6.45 14.29 27.27	11 11.83 26.19 52.38	16 17.20 38.10 84.21	42 45.16
TOTAL	8 8.60	23 24.73	22 23.66	21 22.58	19 20.43	93 100.00

TABLE E-28. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR BLOCK TYPE VALVE

BEFORE TENTING-BEFORE MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	IMMEDIATELY AFTER MAINTENANCE OVA READING 0	1	2	3	4	TOTAL
0	0 0.00 0.00 0.00	0 0.00 0.00 0.00	0 0.00 0.00 0.00	1 1.72 100.00 5.26	0 0.00 0.00 0.00	1 1.72
2	0 0.00 0.00 0.00	3 5.17 42.86 25.00	0 0.00 0.00 0.00	4 6.90 57.14 21.05	0 0.00 0.00 0.00	7 12.07
3	1 1.72 9.09 100.00	2 3.45 18.18 16.67	2 3.45 18.18 25.00	4 6.90 36.36 21.05	2 3.45 10.18 11.11	11 18.97
4	0 0.00 0.00 0.00	7 12.07 17.95 58.33	6 10.34 15.38 75.00	10 17.24 25.64 52.63	16 27.59 41.03 88.89	39 67.24
TOTAL	1 1.72	12 20.69	8 13.79	19 32.76	18 31.03	58 100.00

*Only if before maintenance OVA reading was over 10,000.

TABLE E-29. IMMEDIATELY BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR CONTROL VALVES

IMMEDIATELY BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
1	2	5	1	0	1	9
	3.23	8.06	1.61	0.00	1.61	14.52
	22.22	55.56	11.11	0.00	11.11	
	66.67	41.67	7.14	0.00	4.35	
2	1	3	10	0	0	14
	1.61	4.84	16.13	0.00	0.00	22.58
	7.14	21.43	71.43	0.00	0.00	
	33.33	25.00	71.43	0.00	0.00	
3	0	2	2	3	5	12
	0.00	3.23	3.23	4.84	8.06	19.35
	0.00	16.67	16.67	25.00	41.67	
	0.00	16.67	14.29	30.00	21.74	
4	0	2	1	7	17	27
	0.00	3.23	1.61	11.29	27.42	43.55
	0.00	7.41	3.70	25.93	62.96	
	0.00	16.67	7.14	70.00	73.91	
TOTAL	3	12	14	10	23	62
	4.84	19.35	22.58	16.13	37.10	100.00

TABLE E-30. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY BEFORE MAINTENANCE OVA READING FOR CONTROL TYPE VALVE

Rows: BEFORE TENTING-BEFORE MAINTENANCE OVA READING

Columns: IMMEDIATELY BEFORE MAINTENANCE OVA READING

FREQUENCY / PERCENT / ROW PCT / COL PCT	1	2	3	4	TOTAL
1	3	3	1	1	8
	4.84	4.84	1.61	1.61	12.90
	37.50	37.50	12.50	12.50	
	33.33	21.43	8.33	3.70	
2	5	6	4	2	17
	8.06	9.68	6.45	3.23	27.42
	29.41	35.29	23.53	11.76	
	55.56	42.86	33.33	7.41	
3	0	4	3	3	10
	0.00	6.45	4.84	4.84	16.13
	0.00	40.00	30.00	30.00	
	0.00	28.57	25.00	11.11	
4	1	1	4	21	27
	1.61	1.61	6.45	33.87	43.55
	3.70	3.70	14.81	77.78	
	11.11	7.14	33.33	77.78	
TOTAL	9	14	12	27	62
	14.52	22.58	19.35	43.55	100.00

TABLE E-31. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING FOR CONTROL TYPE VALVE

BEFORE TENTING-BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	0	1	2	3	4	TOTAL
1	0	7	0	0	1	8
	0.00	11.29	0.00	0.00	1.61	12.90
	0.00	87.50	0.00	0.00	12.50	
	0.00	58.33	0.00	0.00	4.35	
2	2	2	7	3	3	17
	3.23	3.23	11.29	4.84	4.84	27.42
	11.76	11.76	41.18	17.65	17.65	
	66.67	16.67	50.00	30.00	13.04	
3	1	0	4	0	5	10
	1.61	0.00	6.45	0.00	8.06	16.13
	10.00	0.00	40.00	0.00	50.00	
	33.33	0.00	28.57	0.00	21.74	
4	0	3	3	7	14	27
	0.00	4.84	4.84	11.29	22.58	43.55
	0.00	11.11	11.11	25.93	51.85	
	0.00	25.00	21.43	70.00	60.87	
TOTAL	3	12	14	10	23	62
	4.84	19.35	22.58	16.13	37.10	100.00

TABLE E-32. BEFORE TENTING-BEFORE MAINTENANCE OVA READING VS. IMMEDIATELY AFTER MAINTENANCE OVA READING* FOR CONTROL TYPE VALVE

BEFORE TENTING - BEFORE MAINTENANCE OVA READING (rows) by IMMEDIATELY AFTER MAINTENANCE OVA READING (columns)

FREQUENCY / PERCENT / ROW PCT / COL PCT	1	2	3	4	TOTAL
1	1	0	0	1	2
	2.56	0.00	0.00	2.56	5.13
	50.00	0.00	0.00	50.00	
	25.00	0.00	0.00	4.55	
2	0	0	3	3	6
	0.00	0.00	7.69	7.69	15.38
	0.00	0.00	50.00	50.00	
	0.00	0.00	30.00	13.64	
3	0	1	0	5	6
	0.00	2.56	0.00	12.82	15.38
	0.00	16.67	0.00	83.33	
	0.00	33.33	0.00	22.73	
4	3	2	7	13	25
	7.69	5.13	17.95	33.33	64.10
	12.00	8.00	28.00	52.00	
	75.00	66.67	70.00	59.09	
TOTAL	4	3	10	22	39
	10.26	7.69	25.64	56.41	100.00

*Only if before maintenance OVA reading was over 10,000.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/S2-81-080	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Evaluation of Maintenance for Fugitive VOC Emissions Control		5. REPORT DATE May 1981 (issue) 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) G. J. Langley and R. G. Wetherold		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 8501 Mo-Pac Blvd. P.O. Box 9948 Austin, TX 78766		10. PROGRAM ELEMENT NO. 1AB604 11. CONTRACT/GRANT NO. 68-03-2776
12. SPONSORING AGENCY NAME AND ADDRESS U.S.EPA Industrial Environmental Research Laboratory Industrial Pollution Control Division Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

The EPA Project Officer was Robert C. Weber. He can be contacted at (513) 684-4481.

16. ABSTRACT

The U.S.EPA Office of Air Quality Planning and Standards (OAQPS) has the responsibility for formulating regulations for the control of fugitive emissions of volatile organic compounds (VOC). "Fugitive emissions" generally refers to the diffuse release of vaporized hydrocarbon or other organic compounds. Fugitive emissions originate from equipment leaks as well as large and/or diffuse sources. The study reported here was undertaken by the Office of Research and Development to assist OAQPS in the development of regulations.

The project was designed to quantify the effectiveness of routine (on-line) maintenance in the reduction of fugitive VOC emissions from in-line valves. An overall emission reduction of approximately 70% was achieved by tightening the bolts on the valve packing gland. This level of control was sustained for up to about six months. The rates of leak occurrence and recurrence were also evaluated, as well as the time required to conduct the on-line maintenance.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Fugitive Emissions Volatile Organic Compounds (VOC)	VOC (volatile organic compounds) fugitive emissions (equip. leaks)	engineering air pollution

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	21. NO. OF PAGES 241 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE