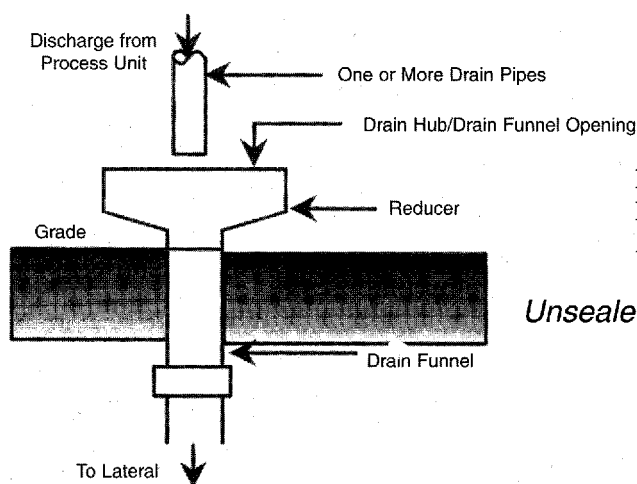


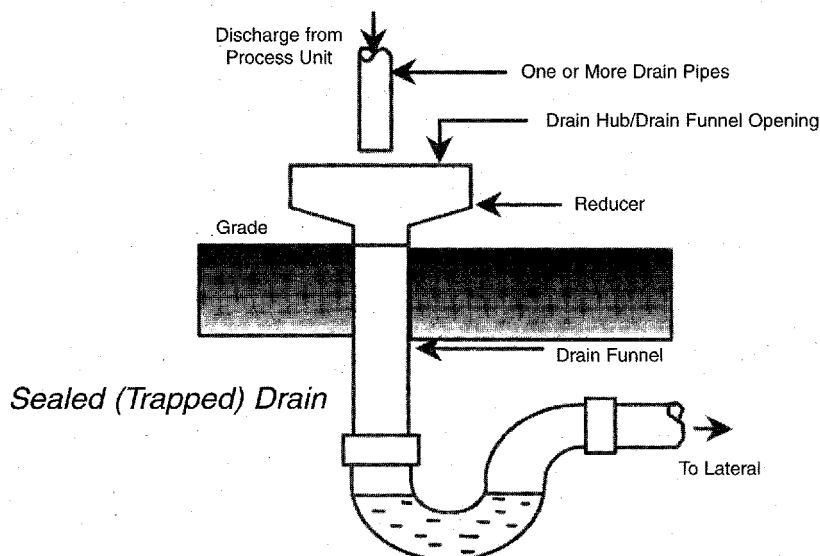
FUGITIVE EMISSIONS FROM REFINERY PROCESS DRAINS VOLUME I

FUGITIVE EMISSION FACTORS FOR REFINERY PROCESS DRAINS



HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4677
APRIL 1999

Unsealed Drain



Sealed (Trapped) Drain

American Petroleum Institute Environmental, Health, and Safety Mission and Guiding Principles

MISSION

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

PRINCIPLES

- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emission and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

Fugitive Emissions From Refinery Process Drains Volume I

Fugitive Emission Factors For Refinery Process Drains

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4677

PREPARED UNDER CONTRACT BY:

BROWN AND CALDWELL
100 WEST HARRISON STREET
SEATTLE, WASHINGTON 98119-4186

ENVIROMEGA LTD.
7 INNOVATION DRIVE
HAMILTON, ONTARIO
CANADA L9J1K3

APRIL 1999



Documents

Document Sharing Hub

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

All rights reserved. No part of this work may be reproduced, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the publisher, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005.

Copyright © 1999 American Petroleum Institute

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Paul Martino, Health and Environmental Sciences Department

MEMBERS OF THE REFINERY DRAINS EMISSIONS PROJECT GROUP

Nick Spiridakis, Chairman, Chevron Research and Technology

Karel Jelinek, BP Oil Company

Miriam Lev-On, Arco

Gary Morris, Mobil Technology Company

Chris Rabideau, Texaco

Manuel Cano, Shell Development Company

Achar Ramachandra, Amoco Corporation

Jeff Siegel, Exxon Research and Engineering

Ron Wilkniss, Western States Petroleum Association

Jenny Yang, Marathon Oil Company

Brown and Caldwell would also like to thank Hugh Monteith (Enviromega, Ltd.) for his assistance in the completion of this work.

PREFACE

The results of this study are presented in three separate reports.

- Volume I entitled "*Fugitive Emission Factors for Refinery Process Drains*" (API Publication Number 4677) contains simplified emission factors that can be used to quickly estimate total volatile organic compound (VOC) emissions from refinery process drains.
- Volume II entitled "*Fundamentals of Fugitive Emissions from Refinery Process Drains*" (API Publication Number 4678) describes theoretical concepts and equations that may be used in a model (APIDRAIN) to estimate speciated VOC emissions. The model can provide insight on how to change process drain variables (flow rate, temperature, etc.) to reduce emissions.
- Volume III entitled "*APIDRAIN Version 1.0, Process Drain Emission Calculator*" (API Publication Number 4681) is the computer model with user's guide to estimate emissions from refinery process drains. The software allows users to calculate VOC emissions based on the emission factors in Volume I and equations for speciated emissions in Volume II.

All three volumes of this study can be purchased separately; however, it is suggested that the user consider purchase of the entire set to gain a complete understanding of fugitive emissions from refinery process drains.

ABSTRACT

Fugitive emissions are estimated using USEPA's emission factors from the publication known as AP-42. The factor for refinery process drains was first developed in 1979. Drain modifications and sewer system improvements have reduced emissions, with the result that the AP-42 emission factor may overestimate drain emissions. The refinery process drain emission factor has also been applied to non-process drains, with the result that drain emissions are now a significant component of refinery emissions. This work was undertaken to address these concerns. Laboratory- and pilot-scale drain systems were constructed and tests were conducted to develop emission factors and to evaluate the mechanics of emissions from active, trapped process drains. A model was developed to estimate emissions from process drains.

Table of Contents

	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
1. INTRODUCTION	1-1
2. PILOT SCALE DETERMINATION OF DRAIN BAGGING PROTOCOL	2-1
EXPERIMENTAL PROCEDURE.....	2-1
Analyte Selection and Characteristics	2-1
Apparatus.....	2-2
No Bag	2-2
Vacuum Method	2-2
Blow-Through Method	2-3
Dosing Procedure.....	2-7
Wastewater Sampling and Analysis.....	2-7
OVA Calibration.....	2-7
Experimental Schedule.....	2-8
RESULTS	2-9
Sample Results for Each Experiment - Analysis of Duplicate Submissions	2-9
Percentage Emissions.....	2-9
Mass Emissions	2-11
Organic Vapor Analyzer Results.....	2-13
OVA Concentrations	2-13
Mass Emissions.....	2-14
Statistical Analysis of Results	2-15
DISCUSSION OF RESULTS	2-17
3. PILOT SCALE DETERMINATION OF STRIPPING EFFICIENCIES	3-1
EXPERIMENTAL PROCEDURE.....	3-1
Analyte Selection and Characteristics	3-1
Experimental Apparatus	3-2
Emission Factor Drain Structure	3-2
Emission Factor Drain Structure - No Bag	3-5
Emission Factor Drain Structure - Vacuum Method	3-5
Aligned Drain Structure.....	3-6
University of Texas Drain Structure	3-8
Dosing Procedure.....	3-9
Sample Analysis.....	3-9
OVA Calibration.....	3-10
Experimental Plan and Methodology	3-10
Drain Emission Factor Study	3-10
Aligned Drain Emissions.....	3-12
Duplication of University of Texas Experiments	3-12
Experimental Schedule.....	3-13


Documents

Document Sharing Hub

Table of Contents

	<u>Page</u>
RESULTS	3-14
Duplicate Sample Analysis	3-14
Discharge Column of Water Description	3-15
Drain Emission Factors Experiments (misaligned drain)	3-16
Calculation of Experimental Percentage Emissions	3-16
Emission Factor Tables	3-18
Organic Vapor Analyzer Results	3-20
Aligned Drain Structure	3-22
Duplication of University of Texas Experiments	3-23
DISCUSSION OF RESULTS	3-25
SIMPLIFIED EMISSION FACTOR TABLES	3-26
Using the Simplified Emission Factor Tables	3-31
Example Use of the Emission Factor Tables	3-32
User Input Data	3-32
User Input: Look-up Table Mass Emissions	3-33
Calculations	3-34
 4. CONCLUSIONS AND RECOMMENDATIONS	 4-1
 5. REFERENCES	 5-1
Appendix A	Analytical Data From Drain Bagging Protocol Experiments
Appendix B	QA/QC - Duplicate Sample Submission From Drain Bagging Protocol Experiments
Appendix C	Analytical Data From Stripping Efficiency Experiments
Appendix D	Emission Factors (Misaligned Drain) for Individual Contaminants From Stripping Efficiency Experiments
Appendix E	Degree of Saturation in Gas Phase During Bagged Experiments From Stripping Efficiency Experiments
Appendix F	Mass Emission Calculations Based on OVA Readings

Table of Contents

LIST OF TABLES

		<u>Page</u>
Table 2-1.	Henry's Law Coefficients for Test Compounds	2-2
Table 2-2.	Experimental Schedule	2-8
Table 2-3.	Summary of Drain Emissions (%) - No Bag	2-10
Table 2-4.	Summary of Drain Emissions (%) - Vacuum	2-10
Table 2-5.	Summary of Drain Emissions (%) - Blow-Through	2-11
Table 2-6.	Comparison of Blow-Through Bag Results for Phase 1 (API, 1996) and Phase 2 (Current Work)	2-11
Table 2-7.	Summary of Drain Emissions (µg/min) - No Bag	2-12
Table 2-8.	Summary of Drain Emissions (µg/min) - Vacuum	2-13
Table 2-9.	Summary of Drain Emissions (µg/min) - Blow-Through	2-13
Table 2-10.	Observed OVA Readings	2-15
Table 2-11.	Total Drain Emissions Based on OVA Measurements - Vacuum	2-15
Table 2-12.	Comparing Vacuum and Blow-Through Methods	2-16
Table 2-13.	Comparing Combined Vacuum and Blow-Through Methods To No Bag Method	2-17
Table 3-1.	Henry's Law Coefficients for Test Compounds	3-2
Table 3-2.	Drain Emission Factor Experimental Plan	3-11
Table 3-3.	Drain Emission Factor Experimental Process Variation	3-11
Table 3-4.	Inactive Drain Sampling Schedule	3-12
Table 3-5.	University of Texas Replication Experiments - Process Conditions	3-13
Table 3-6.	Experimental Schedule	3-13
Table 3-7.	Inactive Drain Liquid Temperature	3-16
Table 3-8.	Emission Factors: $1.23 \leq H_c \leq 7.17$	3-19
Table 3-9.	Emission Factors: $0.32 \leq H_c < 1.23$	3-19
Table 3-10.	Emission Factors: $0.13 \leq H_c < 0.32$	3-20
Table 3-11.	Emission Factors: $0.02 \leq H_c < 0.13$	3-20
Table 3-12.	Organic Vapor Analyzer Results	3-21
Table 3-13.	Drain Emissions Based OVA Measurements - Bagged Experiments	3-21
Table 3-14.	Aligned Drain Percentage Emissions	3-23
Table 3-15.	University of Texas Experiments - Percentage Emissions	3-24
Table 3-16.	Study Emissions and University of Texas Model Emissions	3-25
Table 3-17.	Simplified Emission Factor Table Summary of Drain Operating Conditions	3-28
Table 3-18.	High Volatility Compounds ($1.23 \leq H_c \leq 7.17$)	3-29
Table 3-19.	Medium Volatility Compounds ($0.13 \leq H_c < 0.32$)	3-29
Table 3-20.	Low Volatility Compounds ($\leq 0.02 H_c < 0.13$)	3-29
Table 3-21.	Simplified Emissions Factor Table - High Volatility	3-30
Table 3-22.	Simplified Emissions Factor Table - Medium Volatility	3-30
Table 3-23.	Simplified Emissions Factor Table - Low Volatility	3-30
Table 4-1.	Conservative Use of Emission Factor Tables	4-1

Table of Contents

LIST OF FIGURES

	<u>Page</u>
Figure 2-1 Schematic of Pilot Drain Structure	2-4
Figure 2-2 Vacuum Bag Apparatus	2-5
Figure 2-3 Pressure Bag Apparatus	2-6
Figure 3-1. Drain Emission Factor Drain Structure	3-3
Figure 3-2. Drain Emission Factor Hub Structure	3-4
Figure 3-3. Drain Emission Structure - Vacuum Bag	3-6
Figure 3-4. Aligned Drain Discharge	3-7
Figure 3-5. Replication of University of Texas Drain Structure	3-8
Figure 3-6. Mass Emissions as a Function of OVA Reading	3-22



Documents

Document Sharing Hub

EXECUTIVE SUMMARY

This investigation was initiated by the American Petroleum Institute (API) to update the AP-42 emission factor for refinery process drains, which may overestimate refinery process drain fugitive emissions. Changes in refinery process drains have been implemented in response to United States Environmental Protection Agency (USEPA) regulations, including benzene waste operations National Emission Standards for Hazardous Air Pollutants (NESHAP) and New Source Performance Standards (NSPS) Subpart QQQ. Sealed drains have led to lower refinery process drain emission conditions, compared with conditions when the AP-42 emission factor was developed. The results of this study indicate that the AP-42 emission factor for refinery process drains should be modified.

The work reported in this report is the second phase of an effort to develop new emission factors to improve the estimate of drain emissions. This report presents new emission factors based on the flow and loadings into laboratory- and pilot-scale process drains. The emission factors require a knowledge of the concentrations of various constituents in the process wastewater discharged to the refinery drains. Specific project activities are summarized below.

Protocols for field bagging and measuring drain emissions were tested. Results indicated that vacuum and blow-through bagging protocols give the same results. For the least volatile constituents, emissions were statistically greater for a drain with no bag than for a drain enclosed by a bag.

A series of emission factor tables were developed, which are more appropriate for estimating drain emissions than using a single emission factor. The emission factor tables require a knowledge of the volatility of the constituents discharged to the drain, the physical parameters of the drain, and the amount of time (hours per day) the drain is used. The emission factor tables were developed using the wastewater mass balance method, because it was shown to be more accurate than the gas sampling method during the pilot-scale studies. Experiments for the emission factor tables used the misaligned hub configuration to conservatively promote emissions.

A model was developed to describe drain emission mechanics. The model includes estimates of air entrainment, degree of chemical equilibrium, and gas- and liquid-phase mass transfer coefficients associated with volatilization across the surface of a water seal. The existing

USEPA model, WATER8, may significantly overestimate stripping efficiencies from process drains that contain water seals. The reader has the option of using either the model or the emission factor tables.

Field studies to test drain emissions were difficult to implement because of the impact of benzene waste operations NESHAP. Tests were conducted at one refinery, but the emissions were too low for any meaningful conclusions.

1. INTRODUCTION

This project develops a set of emission factor tables that can be used to replace the AP-42 emission factor for refinery process drains. The project also develops a two-phase model to predict the emissions from refinery process drains, and this model can also be used to replace the emission factors from AP-42. The AP-42 factor is only viable for process drains and for drains without a water seal. Many refinery drains have been retrofitted with a seal to reduce these emissions. New emission factors or approaches to develop new emission estimates are thereby warranted.

The project was completed in a number of tasks. Their significant activities and findings are presented below.

PILOT-SCALE VERIFICATION OF DRAIN BAGGING PROTOCOL

The results are presented in Chapter 2 of this report. The most significant finding was that emissions for five of the six compounds tested are statistically greater from a bagged drain than from a drain with no bag. The five compounds were all of the less volatile compounds.

PILOT-SCALE DETERMINATION OF STRIPPING EFFICIENCIES

The results are presented in Chapter 3 of this report. The stripping efficiency tests resulted in a series of emission tables that can be used instead of the AP-42 emission factor when wastewater composition and flow rate characteristics are known. These emission factor tables yield much lower emissions than the AP-42 emission factor when using realistic conditions of refinery drain activity.

MODEL PARAMETER ESTIMATION AND ANALYSIS OF EFFECTS OF AMBIENT CONDITIONS ON EMISSIONS

The results are presented in API Publication Number 4678. A two-zone model was developed for estimating volatile organic compound (VOC) emissions from refinery process drains. One zone was above the water seal and one zone was below. The laboratory investigations

developed factors based on fundamental mass transfer kinetics and allow for a range of operating conditions and environmental factors. A significant finding is that the existing EPA model may significantly overestimate emissions from refinery process drains that contain water seals. These results are presented in API Publication Number 4678.

FIELD DRAIN EMISSION MEASUREMENTS

This effort was begun but the field measurements were conducted at a refinery that had collected all its wastewater and sealed its drains in compliance with benzene waste operations NESHAP. Thus, there were no process drains that met even minimal levels (100 ppm VOCs) of emissions that could be used to test the bagging protocols, the emission factor tables, or the model. Thus, these tests were discontinued.

This effort highlighted the changes that refinery process drains have undergone in the 1990s. When the drains were first being included in emission inventories, the emission factor for refinery process drains was the only emission factor available. Thus, this emission factor was used for storm sewers, non-process sewers, indeed virtually any drain of any sewer in a refinery. This report presents an improved emission factor that more accurately reflects emissions from sealed, process drains in a petroleum refinery.

2. Pilot Scale Determination of Drain Bagging Protocol

The objective was to experimentally determine the impact of gas sampling procedures (that is, bagging) on emission rates from an active, aligned process drain sealed with a P-trap. Percentage emissions and mass emission rates were calculated using wastewater contaminant concentrations before and after the drain and wastewater flowrate. Emission rates were to be measured for three gas sampling conditions:

- drain bagged using the vacuum method
- drain bagged using the blow-through method
- drain not bagged

In addition, organic vapor analyzer (OVA) measurements of total organic vapor concentrations were to be made to compare to USEPA's correlation equation for predicting emission rates from "other components" (USEPA, 1995a).

EXPERIMENTAL PROCEDURE

Analyte Selection and Characteristics

The compounds used during this study and their Henry's Law coefficients are presented in Table 2-1. Compounds encompassing a wide range of volatilities were selected and, where possible, compounds used in *Phase 1 Report: Estimation of Fugitive Emissions from Petroleum Refinery Process Drains* (American Petroleum Institute, 1996) (hereinafter called the "Phase 1 Report") were used in this task.

A Foxboro 108 OVA was used to indicate total organic concentrations in the gas phase. Since the instrument is calibrated using methane, gas phase concentrations indicated by the Foxboro 108 for compounds other than methane must be corrected using a response factor. Response factors for a variety of compounds are presented in the *1995 Protocol for Equipment Leak Emission Estimates* (USEPA, 1995a) (hereinafter called the "1995 EPA Protocol"). Therefore, analyte selection was influenced by the need to select VOCs where a response factor was available.

Table 2-1. Henry's Law Coefficients for Test Compounds

Compound	H (m ³ _{liq} /m ³ _{gas}) @ 25°C
Cyclohexane	7.17
Tetrachloroethylene	0.72
1,1,1-Trichloroethane (methyl chloroform)	0.71
Ethylbenzene	0.32
Toluene	0.26
o-Xylene	0.20

Apparatus

A schematic of the drain structure is presented on Figure 2-1. All materials were constructed of carbon steel. The drain funnel consisted of a standard six to four inch reducer. The influent wastewater line was 1 inch in diameter and discharged 1 inch above the plane of the drain opening. Thus, there was a 1 inch air gap between the inlet line and the plane of the drain opening. The discharge line was centered over the drain funnel and therefore, wastewater did not splash onto the edge of the funnel or drain pipe. The drain funnel was connected to a P-trap with a 4 inch diameter pipe. Figure 2-1 also includes the relative position of the OVA which was placed near to the water surface.

No Bag. The experimental set-up for the no bag condition was similar to that shown on Figure 2-1. The inlet to the OVA was located approximately 2 cm from the water surface. A suitable distance was maintained to exclude water from the OVA air sample (water will skew OVA results). The air sample flowrate to the OVA was maintained at approximately 1.75 L/min.

Vacuum Method. A schematic of the vacuum bag sampling apparatus is presented on Figure 2-2. The procedure is based on that outlined in the 1995 EPA Protocol (USEPA, 1995a).

The tent enclosure was constructed of Tedlar™ sheeting, obtained from cutting a 24" x 24" Tedlar™ sampling bag, and was secured around the drain structure using duct tape. The gas volume enclosed by the tent was estimated to be 3 L. Nickel-plated valves were used

to connect the bag to a water manometer and a Viton™ line leading to a cold trap. A third connection was made to the bag for allowing the OVA to sample the bag for gas phase contaminants. A small hole was cut in the bag and the OVA sample port put inside the tent enclosure. The inlet to the OVA was located approximately 2 cm from the water entering the tent. A suitable distance was maintained to prevent water from being included in the air sample.

Flow through the cold trap was monitored by a rotameter and a target flow rate of 4 L/min was maintained. The air sample flowrate required by the OVA ranged from 1 to 3 L/min and was preset by the supplier at 1.75 L/min. The total flowrate drawn through the tent enclosure from the ambient air was, therefore, 5.75 L/min. This air flowrate was in the range presented by the 1995 EPA Protocol (USEPA, 1995a) where typical flowrates were recommended to be 60 L/min or less. In addition, the flowrate through the cold trap was, for results comparison purposes, chosen to be the same as that used in the Phase 1 Report (American Petroleum Institute, 1996).

A second water manometer was located at the inlet side of the rotameter. A carbon adsorption tube was placed on the outlet side of the rotameter to eliminate potentially explosive conditions from reaching the vacuum pump which immediately followed the adsorption tube. The vacuum pump was used to draw air through the system. The vacuum in the bag was maintained at vacuums of 0.1" or greater.

Blow-Through Method. A schematic of the blow-through bag sampling apparatus is presented on Figure 2-3. The procedure is based on that outlined in the 1995 EPA Protocol (USEPA, 1995a). The procedure was identical to that utilized in the Phase 1 Report (American Petroleum Institute, 1996).

A cylinder of ultra-high purity nitrogen provided the blow-through gas. The nitrogen proceeded through a desiccant trap for moisture removal. The gas flowrate was measured using a rotameter before entering the tent enclosure.

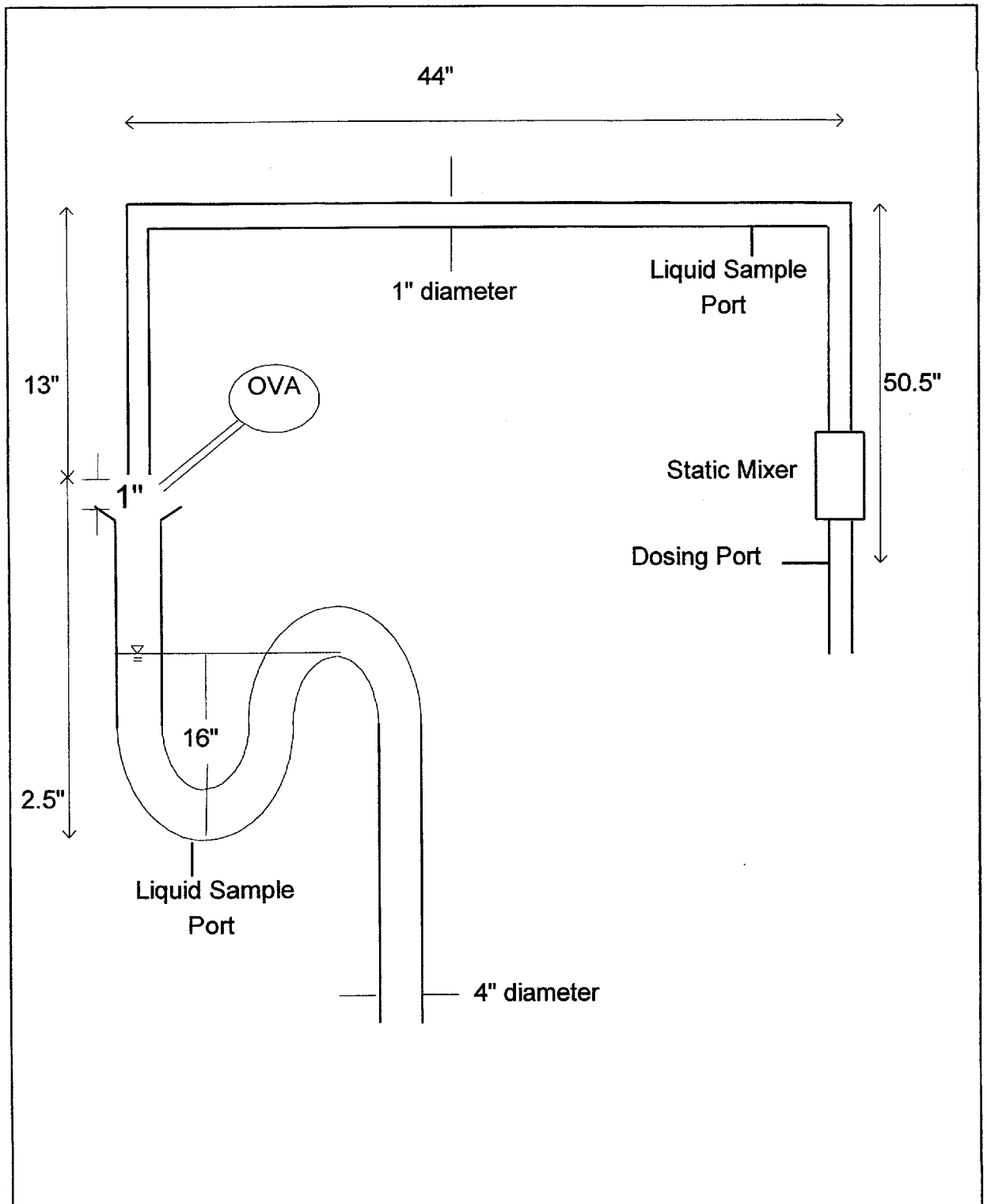


Figure 2-1. Schematic of Pilot Drain Structure

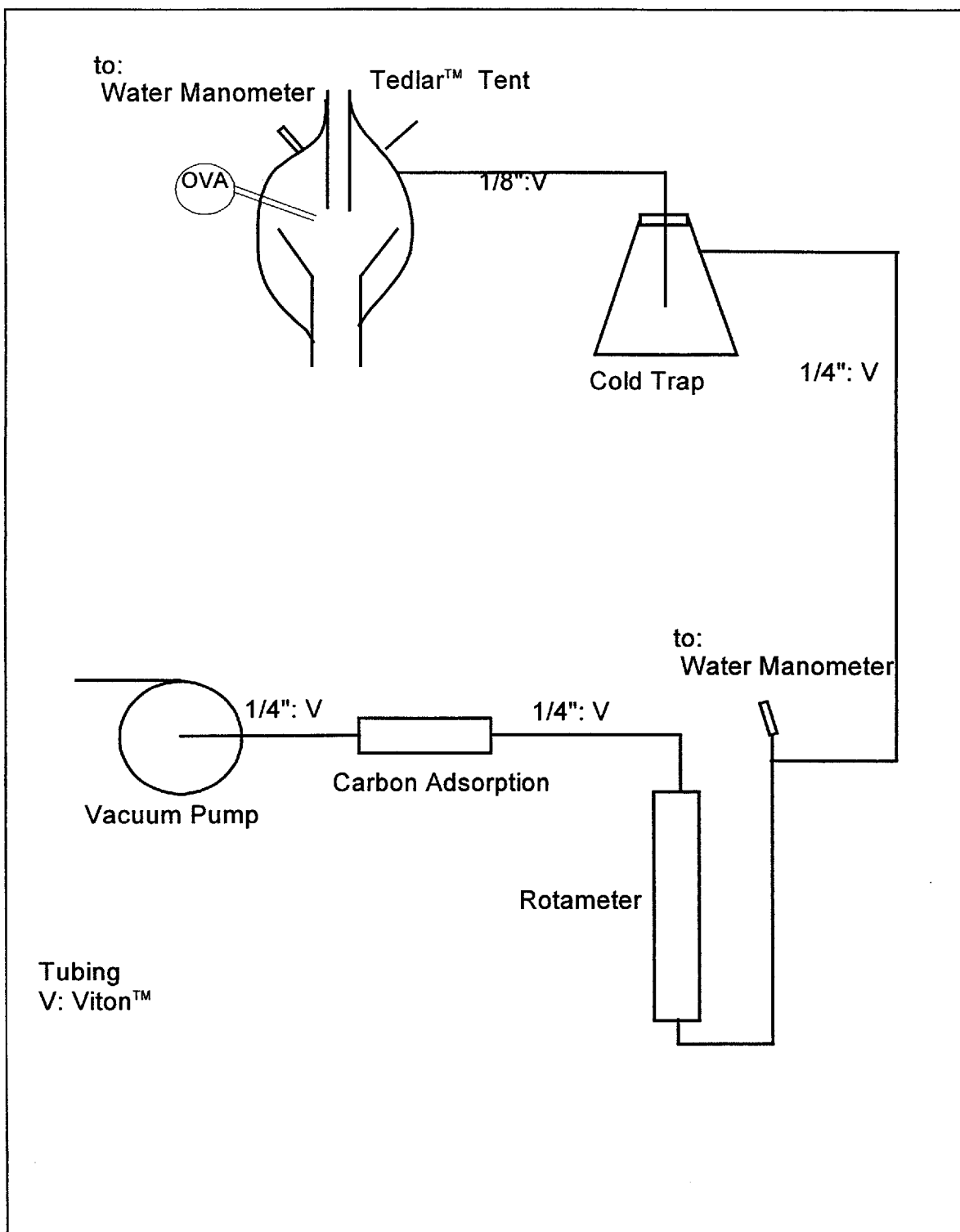


Figure 2-2. Vacuum Bag Apparatus

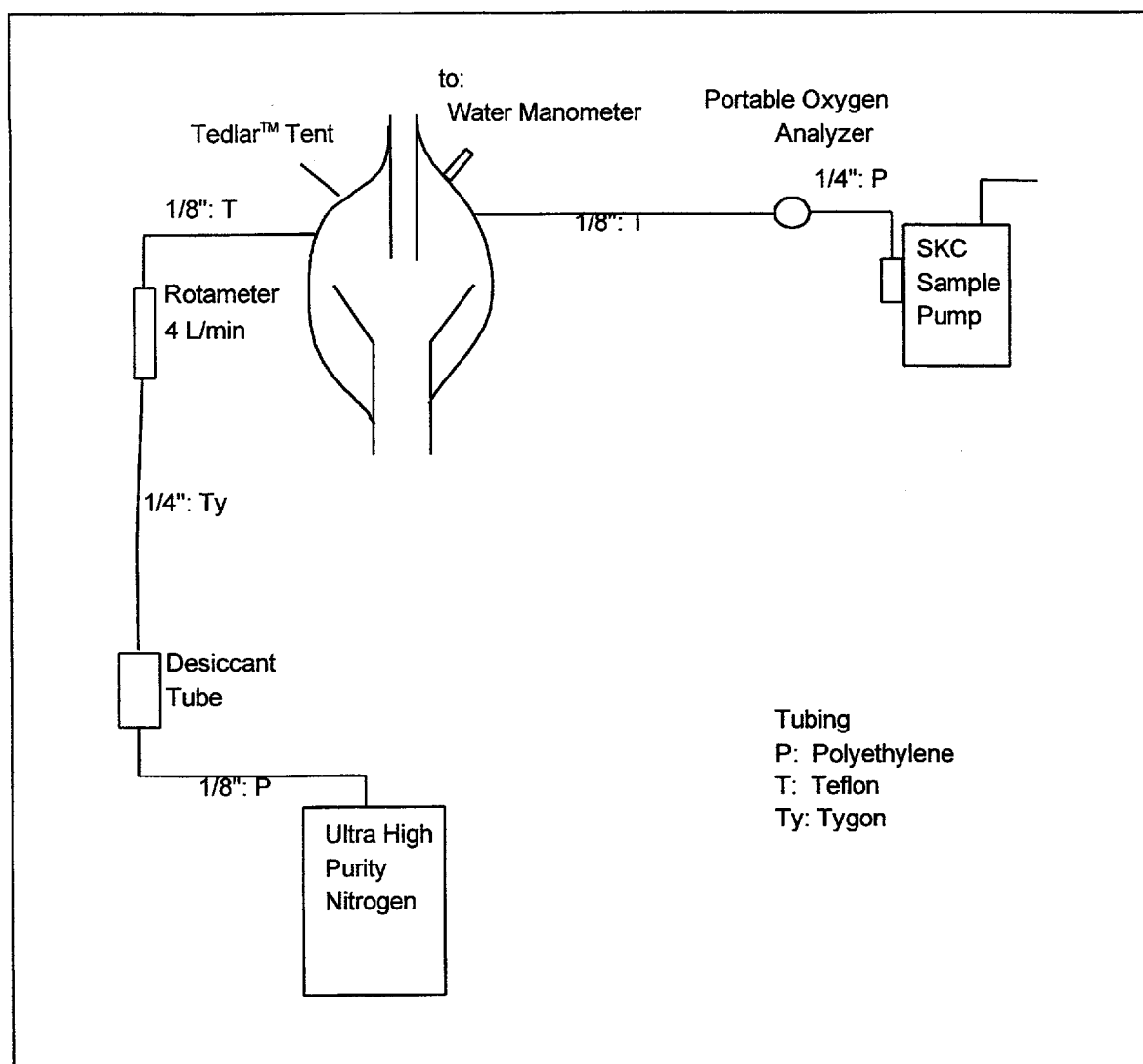


Figure 2-3. Pressure Bag Apparatus

The tent enclosure was constructed of Tedlar™ sheeting, obtained from cutting a 24" x 24" Tedlar™ sampling bag, and was secured around the drain structure using duct tape. The gas volume enclosed by the tent was estimated to be 3 L. Nickel-plated valves were used to connect the bag to a water manometer and a Viton™ line leading to an oxygen analyzer and ultimately to a SKC vacuum sample pump. In the Phase 1 Report (American Petroleum Institute, 1996), the SKC pump ensured that air from the tent enclosure was directed to the gas sampling apparatus. Although gas samples were not taken during this work, the SKC pump

was used to maintain experimental conditions identical to those of the Phase 1 Report (American Petroleum Institute, 1996).

The nitrogen gas flowrate was controlled to 4 L/min, as used in the Phase 1 Report (API, 1995). The flow of the SKC pump was set at 2 L/min. The difference between the two flowrates (2 L/min) escaped from the tent enclosure to the ambient atmosphere and the lower flowrate of the SKC pump ensured a positive pressure within the tent enclosure was maintained. A tent enclosure pressure of 0.1" or greater was maintained for all blow-through experiments.

Due to the absence of oxygen in the tent enclosure, the use of nitrogen as a carrier gas in the blow-through procedure prevents potentially explosive conditions from occurring. In addition, the absence of oxygen prevents the use of the OVA since oxygen is required to maintain the flame used to ionize the compounds in the influent OVA gas stream.

Dosing Procedure

The target influent wastewater consisted of potable water, heated to 30° C. The flowrate was measured, prior to dosing, using a rotameter. The 6 compounds selected for dosing were dissolved in water and contained in a Tedlar™ bag. The bag contents were pumped into the influent water stream, at a controlled rate, through Viton™ tubing. The dosing bag collapsed upon itself as the contents were pumped, preventing the formation of headspace in the bag. The compounds were pumped into a vertical section of pipe because the full pipe encouraged mixing and provided a gas seal for the system. A static, helical mixer was located immediately downstream of the point where the dosing chemicals entered the influent line.

Wastewater Sampling and Analysis

All wastewater samples were collected in 40 mL amber, teflon, septum-top bottles, and analyzed using EPA method 624. Samples of the wastewater entering the drain were collected from a sample port in the horizontal section of the influent pipe, downstream of the dosing location. The contents of the P-trap were collected from a sample port at the bottom of the trap. Samples were collected 1 hour after dosing was initiated.

OVA Calibration

The OVA was calibrated using a two-point procedure using methane standards supplied with the instrument.

Experimental Schedule

Three sets of four experiments (no bag, vacuum bag and blow-through bag) were conducted, for a total of twelve experiments. The experiments were conducted in a random order (Table 2-2). The water flowrate was turned off and contaminant dosing suspended between experiments. A new Tedlar™ enclosure was used for each experiment.

To ensure the experimental system was at a steady state condition, samples were taken one hour after the introduction of compounds to the influent wastewater. This time period was based on results from the Phase 1 Report (American Petroleum Institute, 1996).

Table 2-2. Experimental Schedule

Experiment Number	Date Test Conducted (1996)	Experimental Method
1	June 28	no bag
2	June 28	vacuum
3	June 29	blow-through
4	June 29	vacuum
5	June 29	no bag
6	June 30	no bag
7	June 30	blow-through
8	June 30	blow-through
9	June 30	no bag
10	June 30	blow-through
11	July 2	vacuum
12	July 2	vacuum

RESULTS

Sample Results for Each Experiment - Analysis of Duplicate Submissions

The analytical results for the twelve drain experiments are presented in Appendix A. For each experiment, between one and three samples were submitted of the influent water to the drain and the drain effluent. The number of samples were randomly submitted to meet the study budget. The influent and effluent sample averages and Coefficient of Variations (COV) for each experiment are presented in Appendix B. The COV was calculated as the ratio, expressed as a percentage, of the standard deviation of the samples to the sample average. If only one sample was submitted, the COV could not be determined. The majority (94%) of the COVs were less than 10% while more than half (52%) were less than 5%. These results indicate very good analytical repeatability.

Percentage Emissions

For each experiment, the average of the influent wastewater concentrations and the average of the effluent wastewater concentrations were used to calculate the percentage emissions from the drain. The percentage emissions were calculated using Equation 2-1.

$$\text{Emissions (\%)} = \left(\frac{C_{\text{influent}} - C_{\text{effluent}}}{C_{\text{influent}}} \right) \times 100\% \quad (2-1)$$

where:

C_{influent} = contaminant concentration before drain

C_{effluent} = contaminant concentration after drain

For each set of experiments, the average percentage emissions for the four experiments was calculated as well as the 95% confidence interval (two-tailed T-test) of the average. The results for each set of experiments are presented in Table 2-3, Table 2-4 and Table 2-5. In each of the tables, the compounds are listed from the most volatile (cyclohexane) to the least volatile (o-Xylene). Within each set of experiments, average percentage emissions were related to compound volatility (the greater the volatility, the greater the emissions).

A qualitative comparison of Table 2-4 and Table 2-5 suggests no consistent difference between emission rates for the set of experiments employing the vacuum and blow-through bagging procedures. A qualitative comparison of Table 2-3 to Table 2-4 and Table 2-5 suggests that emission rates were generally higher for the set of experiments employing no bag than the set of experiments using a bag (for the five less volatile compounds). There was no apparent difference for the most volatile compound, cyclohexane. Statistical analysis of the data is presented later.

The percentage emissions observed in the Phase 1 Report (American Petroleum Institute, 1996) (blow-through bag method only) and the blow-through bag results of this study are presented in Table 2-6. Cyclohexane and toluene, common compounds to both studies, had similar percentage emissions in both the Phase 1 Report (American Petroleum Institute, 1996) and this study.

Table 2-3. Summary of Drain Emissions (%) - No Bag

Compound	Expt 1	Expt 5	Expt 6	Expt 9	Avg	95% CI
Cyclohexane	43.6	34.8	37.0	39.7	38.8	±7.0
Tetrachloroethylene	36.8	31.2	33.9	32.4	33.6	±4.4
1,1,1-Trichloroethane	33.5	30.1	35.2	35.6	33.6	±4.6
Ethylbenzene	35.0	21.4	29.8	23.7	27.5	±11.3
Toluene	31.6	20.9	22.5	15.9	22.7	±12.0
o-Xylene	29.4	15.7	20.3	17.6	20.8	±11.1

Table 2-4. Summary of Drain Emissions (%) – Vacuum

Compound	Expt 2	Expt 4	Expt 11	Expt 12	Avg	95% CI
Cyclohexane	42.1	35.7	45.3	39.8	40.7	±7.4
Tetrachloroethylene	29.0	27.2	26.8	25.0	27.0	±3.0
1,1,1-Trichloroethane	27.7	32.1	33.3	21.8	28.7	±9.6
Ethylbenzene	20.5	17.0	14.8	15.2	16.9	±4.8
Toluene	19.3	11.2	13.4	16.2	15.0	±6.4
o-Xylene	17.0	14.2	9.9	13.2	13.6	±5.4

Table 2-5. Summary of Drain Emissions (%) - Blow-Through

Compound	Expt 3	Expt 7	Expt 8	Expt 10	Avg	95% CI
Cyclohexane	31.7	38.6	37.9	36.8	36.2	±5.7
Tetrachloroethylene	24.3	26.3	24.8	24.2	24.9	±1.8
1,1,1-Trichloroethane	21.6	16.5	29.5	31.2	24.7	±12.6
Ethylbenzene	14.2	12.2	16.8	23.5	16.7	±9.0
Toluene	16.1	11.5	12.4	17.0	14.2	±5.0
o-Xylene	11.0	9.4	15.1	10.8	11.6	±4.5

Table 2-6. Comparison of Blow-Through Bag Results for Phase 1 (American Petroleum Institute, 1996) and Phase 2 (Current Work)

Compound	H @ 25°C (m ³ _{liq} /m ³ _{gas})	Phase 1 Results ¹ (% emissions)	Phase 2 Results ² (% emissions)
Cyclohexane	7.17	39.0	36.2
Tetrachloromethane	1.23	26.4	—
Tetrachloroethylene	0.72	—	24.9
1,1,1-Trichloroethane	0.71	—	24.7
Ethylbenzene	0.32	—	16.7
Toluene	0.26	14.2	14.2
o-Xylene	0.20	—	11.6
1,4-Dichlorobenzene	0.13	7.6	—
Bromoform	0.02	2.0	—
1: Average of the three pilot scale experiments conducted in Phase 1 (Table 6-10 in Phase 1 Report - blow-through).			
2: Average of the four blow-through experiments conducted in Phase 2.			

Mass Emissions

The mass emissions for each experiment were determined using influent wastewater contaminant concentration, wastewater flowrate, and percentage emissions. The target wastewater flowrate set point for all of the experiments was 4 L/min with adjustment to the flow control device made when the indicated flowrate was greater or less than 5% (0.2 L/min) of the target flowrate (4 L/min). The equation used to calculate the mass emissions is presented in Equation 2-2 and results are presented in Table 2-7, Table 2-8, and Table 2-9.

$$\text{Mass Emissions} = C_o \times Q_o \times (\text{PE} / 100) \quad (2-2)$$

where:

mass emissions [$\mu\text{g}/\text{min}$] = contaminant mass transferred to the air

C_o = contaminant wastewater concentration before drain ($\mu\text{g}/\text{L}$)

Q_o = wastewater flowrate (4 L/min)

PE = contaminant percentage emissions

The total contaminant emission rate ranged from a low of 168.6 $\mu\text{g}/\text{min}$ (blow-through experiment #3) to a high of 335.2 $\mu\text{g}/\text{min}$ (no-bag experiment #6). Since emission rate is a function of contaminant concentration and contaminant percentage emissions and wastewater contaminant concentration varies, the emission rate varies. For example, cyclohexane, as indicated previously, had the greatest percentage emissions in all of the experiments and yet had the smallest mass emissions in all of the experiments. This is due to the lower influent cyclohexane wastewater concentration.

Table 2-7. Summary of Drain Emissions ($\mu\text{g}/\text{min}$) - No Bag

Compound	Expt 1	Expt 5	Expt 6	Expt 9
Cyclohexane	9.2	19.5	19.6	27.6
Tetrachloroethylene	51.7	66.4	72.0	71.2
1,1,1-Trichloroethane	55.6	73.8	84.8	101.2
Ethylbenzene	67.7	31.4	53.2	44.8
Toluene	70.5	57.4	57.6	46.0
o-Xylene	47.0	37.6	48.0	44.0
TOTAL	301.7	286.1	335.2	334.8

Table 2-8. Summary of Drain Emissions ($\mu\text{g}/\text{min}$) - Vacuum

Compound	Expt 2	Expt 4	Expt 11	Expt 12
Cyclohexane	8.2	21.8	39.8	32.8
Tetrachloroethylene	42.8	58.8	58.3	54.8
1,1,1-Trichloroethane	40.2	85.6	99.1	60.4
Ethylbenzene	30.6	25.6	32.5	28.4
Toluene	43.6	29.2	38.5	51.2
o-Xylene	29.2	35.2	24.5	33.6
TOTAL	194.6	256.2	292.7	261.2

Table 2-9. Summary of Drain Emissions ($\mu\text{g}/\text{min}$) - Blow-Through

Compound	Expt 3	Expt 7	Expt 8	Expt 10
Cyclohexane	7.2	24.4	26.4	24.2
Tetrachloroethylene	43.2	55.4	56.4	49.4
1,1,1-Trichloroethane	34.4	40.8	90.8	82.0
Ethylbenzene	23.0	20.6	41.6	48.6
Toluene	38.2	27.6	39.6	52.8
o-Xylene	22.6	22.0	41.6	27.0
TOTAL	168.6	190.8	296.4	284.0

Organic Vapor Analyzer Results

OVA Concentrations. The OVA was used during the set of experiments with no bag and vacuum bag. Ambient OVA and test OVA readings during the no bag and vacuum tests are presented in Table 2-10. Ambient OVA readings were recorded at various times before and after experiments. Since in the no bag and vacuum bag procedures ambient air is used as the carrier gas, the minimum expected OVA reading in the tent enclosure is the ambient OVA value. During the no bag and vacuum bag experiments this background concentration varied from 5 to 25 ppm. The reported test OVA values were recorded when the wastewater samples were collected (1 hour after commencing contaminant injection).

During the no bag experiments, OVA readings were generally near ambient levels (10 to 20 ppm). On two occasions (experiments 5 and 9) additional OVA readings were taken below the plane of the hub. These values were approximately 5 ppm greater than readings above the plane of the hub.

During the vacuum bag experiments, the increase in OVA readings ranged from 10 to 25 ppm. The variation in observed contaminant concentrations is postulated to be the result of variations in influent wastewater contaminant concentrations and instrument reading variation at these low values. During experiment 4, OVA readings of 25 ppm were recorded in the vacuum tent enclosure, prior to contaminant injection and with the wastewater flowing. This value is identical to ambient levels, indicating no reportable contamination of the air by the tent enclosure.

Mass Emissions. The OVA measurements for the vacuum bag experiments were converted to total mass emission rates following the procedure outlined in the 1995 EPA Protocol (USEPA, 1995a). The bagging procedure presented in the 1995 EPA Protocol (USEPA, 1995a) is reproduced in Appendix F and the total contaminant mass emissions calculated are presented in Table 2-11. In addition to the OVA based mass emissions, Table 2-11 contains the wastewater mass balance based emission rates and the ratios of the OVA to wastewater determined mass emissions. The OVA indicated greater emission rates ranging from a low of 120% to a high of 180% of that indicated by the wastewater mass balance method.

The mole fractions required for the calculation of the contaminant mixture's collective molecular weight and response factor were based on the wastewater analytical results.

Although OVA measurements for the no-bag condition were collected, the mass emission rate for the no-bag condition can not be determined due to an unknown airflow rate. OVA measurements for the blow-through method were not collected since the carrier gas (nitrogen) did not contain oxygen and, therefore, the OVA ionization flame could not ignite.

Table 2-10. Observed OVA Readings

Experiment	OVA Readings* (ppm)		Increase in OVA Reading
	Background	During Experiment	
No Bag Experiments			
1	10	10	0
5	18	20 (25*)	2
6	10	10	0
9	15	15 (20*)	0
Vacuum Bag Experiments			
2	10	20	10
4	25	40	15
11	5	30	25
12	10	25	15
●●●●The reported test OVA values were recorded when the wastewater samples were collected (1 hour after commencing contaminant injection). *: Reading taken below the plane of the hub.			

Table 2-11. Total Drain Emissions Based on OVA Measurements - Vacuum

Experiment	Total Mass Emissions (µg/min)		Ratio of OVA to Wastewater Methods
	OVA Based	Wastewater Based	
2	240.6	194.6	1.2
4	356.3	256.2	1.4
11	519.2	292.7	1.8
12	306.8	261.2	1.2

Statistical Analysis of Results

In order to determine if there is a statistical difference between the bagging methods, a statistical T-test was conducted. The first statistical test was conducted to determine if there is a difference between the vacuum bag and blow-through bag values. For the T-test, the average emission values for each of the experiments (4 no bag and 4 vacuum bag) were used.

The results are presented in Table 2-12 and indicate that for all of the compounds, values were not statistically different at a significance level of 0.1.

The second statistical test was conducted to determine if the vacuum bag and blow-through results were different from those observed during the no bag method. Since no difference was found between the vacuum and blow-through methods, their results were combined and then compared to the no bag method. The results of the test are presented in Table 2-13. For the five less volatile compounds, analysis indicates that the percentage emissions were statistically different at a significance level of 0.1. For the most volatile compound, cyclohexane, the percentage emissions were not statistically different at a significance level of 0.1.

Table 2-12. Comparing Vacuum and Blow-Through Methods

Compound	H ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) @ 25°C	Vacuum and Blow-through Experiment Averages Are The Same ? ¹ (Y or N) (level of significance = 0.1) ²
Cyclohexane	7.17	y
Tetrachloroethylene	0.72	y
1,1,1-Trichloroethane	0.71	y
Ethylbenzene	0.32	y
Toluene	0.26	y
o-Xylene	0.20	y
1: Based on 2-sided T-test. 2: corresponds to t ₉₅ .		

Table 2-13. Comparing Combined Vacuum and Blow-Through Methods To No Bag Method

Compound	H ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) @ 25°C	Bag and No Bag Experiment Averages Are The Same? ¹ (Y or N) (level of significance = 0.1) ²
Cyclohexane	7.17	y
Tetrachloroethylene	0.72	n
1,1,1-Trichloroethane	0.71	n
Ethylbenzene	0.32	n
Toluene	0.26	n
o-Xylene	0.20	n
1: Based on 2-sided T-test. 2: Corresponds to t ₉₅ .		

DISCUSSION OF RESULTS

Results indicate that there was no statistical difference in percentage emissions between the vacuum and blow-through drain bagging protocols. Results indicate that, for the five least volatile compounds, percentage emissions were statistically greater for the drain with no bag than for the drain enclosed by a bag. For the most volatile compound, cyclohexane, there was no difference.

The above observation may be consistent with an air entrainment mechanism. In the case of a drain with no bag enclosure, the air in the area of the drain hub would likely be continuously swept clean, (i.e., contaminant gas phase concentration equals zero). The contaminant mass transfer driving force (difference between the equilibrium and actual gas concentrations) from the liquid in the P-trap to the rising air bubble is thereby maximized. In the case of the bagged drain, the limited gas flow through the enclosure likely results in headspace gas, inside the bag contaminated with the organic compounds, being drawn back down into the water stream. Since the gas contains contaminants, the mass transfer driving force from the liquid to the rising gas bubble is reduced as compared to the non-bagged condition where the gas contains no contaminants. As contaminant volatility increases, more contaminant can be

transferred from the liquid to the gas before equilibrium conditions are obtained. As a result, the driving force for higher volatility compounds will not be reduced to the same extent as that for low volatility compounds. Higher volatile compounds, therefore, will be less sensitive to the effects of recirculated gas. The impact of the bag on emissions may be minimized by increasing the air flowrate through the bag although this has not received experimental verification.

3. PILOT SCALE DETERMINATION OF STRIPPING EFFICIENCIES

The objective was to develop emission factors for refinery process drains. The emission factors developed estimate drain emissions as a function of compound volatility under different operating conditions for both active and inactive drains. In addition to drain emission factors, this study:

- compared aligned and misaligned drain emissions
- repeated three experiments conducted at the University of Texas for a pilot scale verification of bench scale work
- compared drain mass emissions as a function of Organic Vapor Analyzer (OVA) values to those reported in literature.

EXPERIMENTAL PROCEDURE

Analyte Selection and Characteristics

The compounds used during this study and their Henry's Law coefficients are presented in Table 3-1. Compounds encompassing a wide range of volatilities were selected. Since the emission tables to be developed in this work were not compound specific but rather volatility dependent, the selection of compounds were based on availability and the ability of the OVA to detect the compounds.

A Foxboro 108 OVA was used to indicate total organic compounds (TOCs) in the gas phase. Since the instrument is calibrated using methane, gas phase concentrations indicated by the Foxboro 108 must be corrected using a response factor. Response factors were obtained from the 1995 EPA Protocol (USEPA, 1995a). If a contaminant's response factor was not available in the 1995 EPA Protocol, the manufacturer's response factor was used.

Table 3-1. Henry's Law Coefficients for Test Compounds

Compound	H ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) @ 25°C
Cyclohexane	7.17
Tetrachloromethane	1.23
Tetrachloroethylene	0.72
Ethylbenzene	0.32
Toluene	0.26
o-Xylene	0.20
1,4-Dichlorobenzene	0.13
Bromoform	0.02

Experimental Apparatus

Two distinct experimental drain structures were used during this study. Two sets of experiments were conducted on a drain structure similar to that used in previous API work (American Petroleum Institute, 1996) conducted by Enviromega. The first of these used a misaligned discharge configuration and the second used an aligned discharge configuration. The drain structure was then modified to duplicate experiments conducted at the University of Texas. Each experimental apparatus is discussed separately.

Emission Factor Drain Structure. A schematic of the emission factor drain structure is presented on Figure 3-1. All materials were constructed of carbon steel. The drain funnel consisted of a standard six to four inch floor drain. The influent wastewater line was one inch in diameter and discharged four inches and nine inches above the plane of the drain opening. The floor drain was connected to a liquid seal trap (6.8L) (often referred to as a P-trap or J-trap) using a 4 inch diameter pipe. As indicated on Figure 3-2, the discharge line was off-center over the drain funnel and discharged onto the angular section of the floor drain.

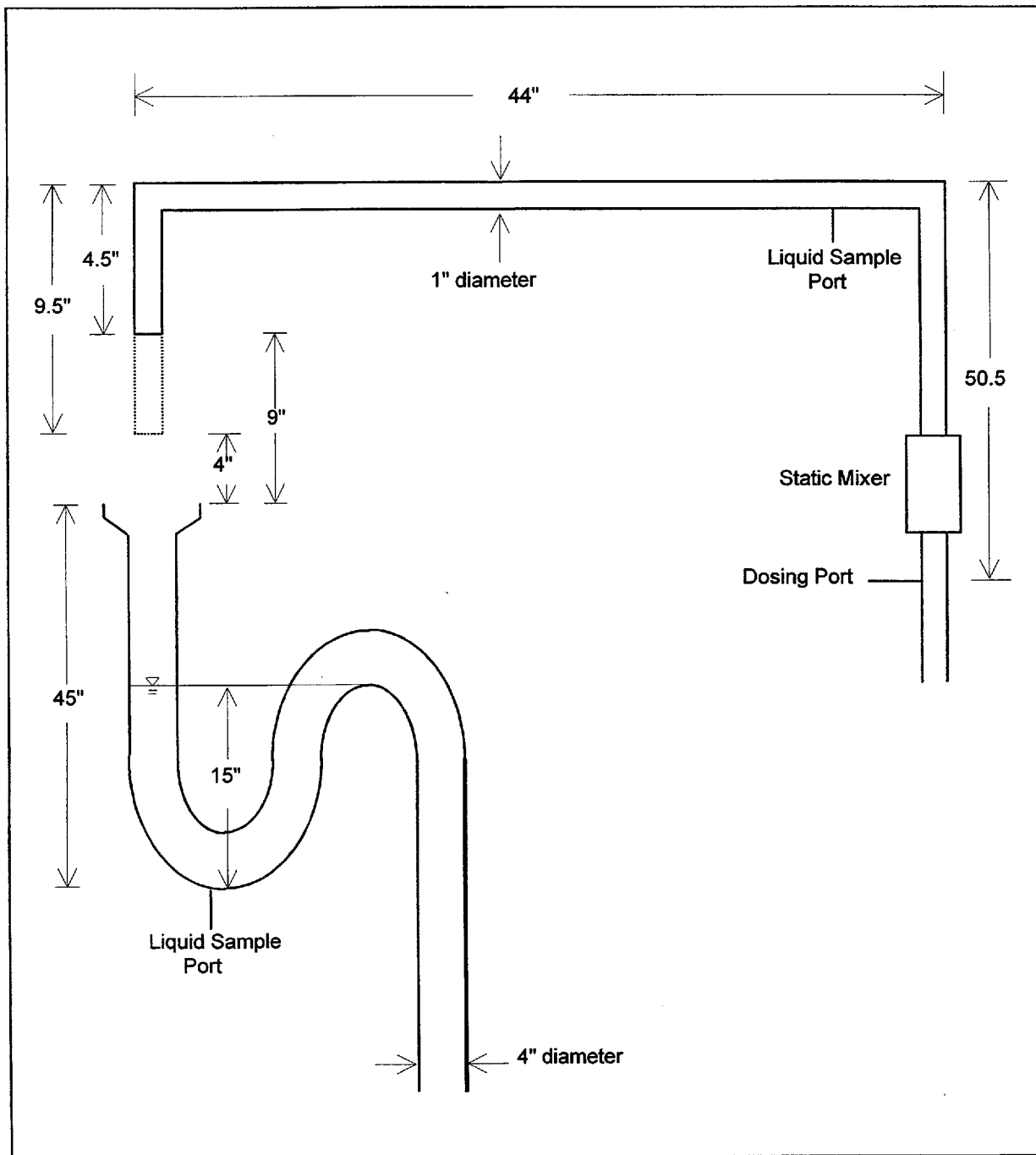


Figure 3-1. Drain Emission Factor Drain Structure