AP42 ref 60
EFD Ref. 94

Data Qual. = C

No Field Data.

LANDFILL METHANE RECOVERY

PART II: GAS CHARACTERIZATION

Also published as Argonne National Laboratory Report ANL/CNSV-TM-118

FINAL REPORT

(December 1981 to December 1982)

Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631

50272-101

Attachment E

REPORT DOCUMENTATION PAGE

1. REPORT NO. GRI - 81/0105

2.

3. Recipient's Accession No.

4. Title and Subtitle

LANDFILL METHANE RECOVERY PART II:
GAS CHARACTERIZATION

5. Report Date December, 1982

6.

7. Author(s) G.R. Lytwynyshyn, R.E. Zimmerman, N.W. Flynn, R. Wingender, V. Olivieri

8. Performing Organization Rept. No. 544

9. Performing Organization Name and Address

ESCOR, Inc.
1845 Oak Street Suite 14
Northfiled, Illinois 60093

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.

(C) 5080-351-0343

(G)

12. Sponsoring Organization Name and Address

Gas Research Institute
8600 West Bryn Mawr
Chicago, Illinois 60631

13. Type of Report & Period Covered

Final Report
12/81 - 12/82

14.

15. Supplementary Notes

Prepared in cooperation with:
Argonne National Laboratory

16. Abstract (Limit: 200 words)

This study developed standardized landfill gas sampling and analytical procedures, and evaluated the feasibility of implementing the procedures at different laboratories. It developed a data base on the amounts of volatile organic compounds and volatile mercury in raw, processed and surface landfill gas; and determined whether human pathogenic viruses and bacteria are present in the gas. Surface gas flux measurements were also made.

Results from this project provide an information base for the landfill methane recovery industry from which an increased understanding and resolution of the environmental issues can be achieved.

17. Document Analysis a. Descriptors

Methane, landfills, gas characterization, gas sampling procedures, landfill gas, volatile organics, volatile mercury, gas flux sampling.

b. Identifiers/Open-Ended Terms

Tenax, gas cylinders, trace chemical analysis, GC/MS analysis.

c. COSATI Field/Group

18. Availability Statement:

Release unlimited

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages 144

22. Price

(See ANSI-Z39.18)

See Instructions on Reverse

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

LANDFILL METHANE RECOVERY PART II: GAS CHARACTERIZATION

FINAL REPORT
December 1981 to December 1982

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GAS RESEARCH INSTITUTE
CONTRACT No. 5080-351-0343

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In cooperation with

ARGONNE NATIONAL LABORATORY
USDOE CONTRACT No. W-31-109-Eng-38

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December, 1982

NOTICE

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RESEARCH SUMMARY

Title: Landfill Methane Recovery Part II:
Gas Characterization

Contractor: ESCOR, Incorporated
GRI Contract No. 5080-351-0343
Cofunded by U.S. Department of Energy

Principal Investigator: R. E. Zimmerman, Ph.D.

Report Period: December, 1981 - December, 1982
Final Report

Objective: The objectives of this study were to develop standardized landfill gas sampling and analytical procedures, to evaluate the feasibility of implementing the procedures at different laboratories. To develop a data base on the amounts of volatile organic compounds and volatile mercury in raw and processed landfill gas, and to determine whether human pathogenic viruses and bacteria are present in the gas.

Technical Perspective: Methane produced during anaerobic decomposition of urban refuse in sanitary landfills is an immediately available alternative fuel that can be removed from existing landfills, processed, and utilized with available technology. Estimates place the quantity of gas ultimately available at 1% of the nation's annual energy needs, or approximately 5% of current natural gas utilization in the U.S. Several GRI member companies are involved with major landfill gas recovery and processing projects.

One of the major impediments to commercialization of this technology has been the lack of specific knowledge of the environmental and safety aspects (including the benefits) of landfill methane recovery (LMR) operations. One tangible benefit is that the processing and removal of gas from a landfill has the net effect of improving local air quality by reducing gaseous emissions, especially hydrocarbons, from the landfill site.

RESEARCH SUMMARY

The objective of the GRI/DOE Landfill Methane Recovery Research Program is to document the net effect of LMR on the environment.

Results:

A national survey was conducted in which gas samples were collected at nine sites and tested for trace volatile organic constituents (VOC), trace volatile mercury, and human pathogenic viruses and bacteria. Surface flux, i.e. the emanation of gaseous emissions through the landfill cover, was also measured at the landfill sites.

Qualitative results obtained from two analytical laboratories indicate consistent agreement on the types of environmentally significant compounds found in the gas. Quantitative analytical results indicate ranges in site-specific concentrations of these compounds over time. The general trend of the data shows a reduction in VOC concentrations from inlet (i.e. raw landfill gas) to product (i.e. processed landfill gas) to surface gas. The data also demonstrate a general trend of decreased VOC concentration with increased levels of gas processing.

Results from the mercury analyses show that mercury is not present in raw or treated gas in environmentally significant quantities at the sampled sites. Mercury concentrations were 3 to 5 orders of magnitude below the threshold limit value for inorganic mercury.

No indicator bacteria or human enteric viruses were recovered in any of the samples of inlet and outlet landfill gas. No pathogenic microorganisms were detected. Results indicate that neither bacterial nor viral content should be of concern in the development of landfill gas recovery.

Results from the surface flux measurements were inconclusive. The surface flux measurements suggest that the commonly used flux box technique using commercially available methanometers is not precise enough for this type of measurement.

The study presents a number of research recommendations. Major recommendations include: expand the existing VOC data base; perform a detailed statis-

RESEARCH SUMMARY

	tical analysis of this expanded data base; identify equipment and instrumentation needs of the LMR industry and for GRI member companies interested in LMR; review surface flux research in other industries, including a summary of the theoretical basis of surface flux modeling, and develop surface flux measuring methodologies and instrumentation, if needed, which will allow for collection of more accurate surface flux information.
Technical Approach:	Gas samples for VOC characterization were taken using Tenax-GC adsorbent resin. Samples for mercury characterization were taken using a trap consisting of gold coated quartz beads. At least two, and in some instances three, sampling visits were made to every site to determine the best sampling procedures and to adequately characterize the trace volatile organic and total mercury composition of landfill gas. The landfill gas was sampled at three locations: the collection system or inlet gas, the post-processing or product gas, and on the surface to measure gaseous emanations (flux) through the landfill cover. A sample of the ambient air was also collected. In addition, methods to sample and analyze the inlet and product gas for viral and bacterial content were developed and implemented. Surface flux measurements were made to test the use of a flux box to determine the flux rate of gas at the surface of landfills.
Project Implications:	Results from this project provide an information base for the landfill methane recovery industry from which an increased understanding and resolution of the environmental issues can be achieved. This project will continue as Part III, implementing selected research tasks recommended in this report.

GRI Project Manager
D.O. Johnson
Assistant Director, Environment and Safety Research

TABLE OF CONTENTS

SECTION 1 INTRODUCTION

SECTION 3 SCOPE OF STUDY

TABLE OF CONTENTS

SECTION 4 RESULTS AND CONCLUSIONS

TABLE OF CONTENTS

REFERENCES

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AA	Atomic Absorption
AGI	All Glass Impinger
AMU	Atomic Mass Units
ANL	Argonne National Laboratory
BUG	Brooklyn Union Gas Company
^{o}C	Degrees Centigrade
cm	Centimeter
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
ft^2	square-feet
gal	gallon
GC	Gas Chromatograph
GRI	Gas Research Institute
in	inch
i.d.	internal diameter
JHU	Johns Hopkins University
L	Liter
LMR	Landfill Methane Recovery
LN_2	Liquid Nitrogen
m	meter
mm	millimeter
min	minute
MPN	Most Probable Number
mV	milli-volt
MS	Mass Spectrometer
m/z	mass to charge ratio
N	Normal Solution
NBS	National Bureau of Standards
ng	nanogram
nm	nanometer
o.d.	outer diameter
PFU	Plaque Forming Units
PG&E	Pacific Gas and Electric Company
pH	Negative log of hydrogen ion concentration -- degree of acidity or alkalinity --
psi	pounds per square inch (gauge)
SAI	Science Applications, Inc.
scf	standard cubic foot
VOC	Volatile Organic Compound
Vppb	Volume parts per billion (concentration)
Vppm	Volume parts per million
Vpptr	Volume parts per trillion
torr	one millimeter of mercury (vacuum)

FOREWORD

This study, "Landfill Methane Recovery Part II: Gas Characterization", was jointly funded by the Gas Research Institute (GRI), through ESCOR, Inc., and by the U.S. Department of Energy (DOE), through the Argonne National Laboratory (ANL) Energy from Municipal Wastes (EMW) Program. This study is second of a series of GRI sponsored studies. The first study of the GRI series in the subject area -- "Landfill Methane Recovery Part I: Environmental Impacts" -- was completed by ESCOR, Inc. under GRI sponsorship. Additional studies in the subject area are planned under singular or joint funding.

ACKNOWLEDGEMENTS

This work is the collective effort of many individuals from ESCOR, Inc., Science Applications, Inc., and Argonne National Laboratory (ANL). Encouragement and support for this work was provided by Dr. Donald Johnson and Ms. Cindy Cahill of GRI, and members of the GRI Landfill Methane Task Force.

In addition, the authors would like to thank: Ms. Jean Bogner (ANL) for her critical review of the report and support; Dr. Joseph Stetter (ANL) for his review and management support; Mr. Robert Taylor (SAI) for technical and field support; Mr. John Taylor (ANL) for technical and field support; Dr. R. Duke (IHS) for advice and technical consultation throughout the project; Mssrs. John Nemmers, Gary Smith and Rusty Sims (SAI) for their expert instrumentation skills; Dr. Leo A. Raphaelian (ANL) for analytical GC/MS/DS support; Dr. Ralph Bane (ANL) for the mercury analyses and helpful comments on the collection and analytical protocols; Dr. Sidney Bourne (ANL) for help in processing analytical data; Drs. Deon Ettinger and Amrit Boparai (ANL) for their assistance in equipment operation in times of need; Ms. Marge Ravasz (ANL) for data processing support; and Mrs. Helen Grilli (ESCOR) for typing and review.

EXECUTIVE SUMMARY

Methane produced during anaerobic decomposition of urban refuse in sanitary landfills is an immediately available alternative fuel that can be removed from existing landfills, processed, and utilized with available technology. Estimates place the quantity of gas ultimately available at 1% of the nation's energy needs, or approximately 5% of the current natural gas utilization in the U.S. Currently, GRI member companies are involved in major landfill gas recovery and processing projects in California, Illinois, New Jersey, and New York. Additional projects are under consideration/development in these and other states.

One of the major impediments to commercialization of this technology has been the lack of specific knowledge of the environmental and safety aspects (including the benefits) of landfill methane recovery (LMR) operations.

One benefit of LMR is that processing and removal of gas from a landfill has the net effect of improving local air quality by reducing the emanation of gaseous emissions, especially hydrocarbons, from the landfill site. The objective of the GRI/DOE Landfill Methane Recovery Research Program is an effort to document the net effect of LMR on the environment.

This study addresses field sampling, analytical testing, and data generation for the characterization of both raw and processed landfill gas. Standardized protocols were developed for the sampling and anal-

ysis of the landfill gas for trace constituents and are presented as Appendices A-C. A nationwide survey was conducted in which gas samples were collected at nine landfill sites and tested for trace volatile organic compounds (VOC), trace volatile mercury, and human pathogenic viruses and bacteria. Surface-gas flux measurements at the landfill surface were also made.

The analysis of samples for VOC's and volatile mercury was performed at two analytical laboratories, Argonne National Laboratory (ANL) and Science Applications, Inc. (SAI), La Jolla. A third laboratory, Johns Hopkins University, evaluated selected samples for the presence of human pathogenic viral and bacterial organisms.

Repetitive sampling and analysis for each of the nine sites provided the opportunity to evaluate agreement (or variations) within a laboratory and between the two analytical laboratories. Sampling and analytical protocols used by both laboratories were identical, however the analytical hardware and interpretive computer hardware and software were different. The most significant variations in analytical results between the two laboratories were observed during the early portions of the program, and are probably attributed to the use of a procedure new to one laboratory, differing interlaboratory standards, and possible systematic variations in sampling and analytical procedures. Later in the program these differences were reduced, and the data indicate good agreement between laboratories. The level of confidence that can be applied to the quantitative analyses is within an order of magnitude.

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EXECUTIVE SUMMARY

The qualitative analytical results obtained from the two laboratories indicate consistent identification of volatile components. There was consistent agreement in results from the analyses of environmentally significant compounds (target compounds) and of other (non-significant) compounds.

The quantitative analytical results indicate that a range of concentrations for environmentally significant compounds occurs at different landfill sites and different sampling trips, when samples are analyzed by the same laboratory.

The general trend of the data shows a reduction in trace VOC concentrations from inlet gas to product gas and to surface gas. Minor variations from this general trend may be due to constituent concentration from the removal of carbon dioxide (i.e., reducing the volume of the gas), or by reactions during the processing of the gas, or other unknown factors. The data also demonstrate a general trend of decreasing VOC concentrations corresponding to an increased level of gas processing.

The study shows that mercury is not present in raw or treated gas in environmentally significant amounts at the tested sites. Mercury concentrations observed in this study are very low, especially compared to the "Threshold Limit Value" of 0.1 mg per meter^3 (11.1×10^{-3} Vppm) for inorganic mercury. The average values for mercury concentrations range from 134×10^{-6} Vppm for inlet gas to 37×10^{-6} Vppm for gas sampled at the surface of the landfill.

No indicator bacteria or human enteric viruses were recovered in

any of the samples of inlet and processed landfill gas. No pathogenic microorganisms were detected.

The surface flux measurements suggest that the commonly used flux box technique employing commercially available methanometers is not precise or sensitive enough for this type of measurement.

The study presents a number of research recommendations, including:

- Expand the existing VOC data base using available data and perform a detailed statistical analysis of this expanded data base.
- Identify equipment and instrumentation needs for the LMR industry and for GRI member companies interested in LMR.
- Review surface flux research in other industries, including a summary of the theoretical basis of surface flux modeling, and develop surface flux measuring methodologies and instrumentation, if needed, which will allow for collection of more accurate surface flux information.

1 INTRODUCTION

1.1 OVERVIEW

This final report presents the results of the Gas Research Institute (GRI) and U.S. Department of Energy (DOE) study of Landfill Methane Recovery Part II: Gas Characterization. This study is a continuation of the Part I study of the environmental impacts of landfill methane recovery (LMR).

Part I reviewed the state-of-the-art and environmental effects of LMR and developed a research plan for the subject area. Four high priority research projects were recommended in Part I. Part II addresses two of the four recommended projects:

- Standardize the sampling and analysis procedures.
- Establish a nationwide survey of the trace components in both inlet (raw) and processed (product) landfill gas.

Methane produced during anaerobic decomposition of urban refuse in sanitary landfills is an immediately available alternative fuel. This gas can be removed from existing landfills, processed, and utilized with technology currently available or under development. Estimates place the quantity of gas ultimately available at 1% of the nation's energy needs, or approximately 5% of current natural gas utilization in the U.S. Currently, GRI member companies are involved in major landfill gas recovery projects in California, Illinois, New Jersey, and New York. Additional projects are under consideration or development in these and other states.

One of the major impediments to commercialization of this technology has been a lack of specific knowledge of the environmental and safety aspects (including the benefits) of LMR operations. Conclusions from Part I of this study indicated that the range of landfill gas end-uses and the relative simplicity of the process make this technology suitable for development by GRI member companies. The LMR industry believes that removing and processing gas from a landfill has the net effect of improving local air quality and reducing the discharge of both gas and condensate from the landfill site. Recovery also reduces the area source impact of hydrocarbon emissions. The objective of the GRI/DOE Landfill Methane Recovery Research Program is to document the net effect of LMR on the environment.

1.2 TECHNICAL BACKGROUND

In order to identify the trace components in landfill gas and the net effect of landfill gas processing on the environment, GRI has initiated a multiphase research program. A previous characterization study (Flynn, et.al., 1981) at a single landfill methane recovery and processing facility identified over 100 trace volatile compounds (VOC's) in raw landfill gas. Based on this study and the Part I of the present study, the GRI Landfill Methane Task Force recognized the need to survey the trace chemical composition of landfill gas and to establish standardized sampling and analytical techniques in order to be able to compare the analyses of landfill gas between sites and over time at the same site.

1.3 OBJECTIVES

The objectives of this study are to:

- Develop and evaluate standardized landfill gas sampling procedures and analytical techniques.
- Develop a data base on the amounts of volatile organic compounds and volatile mercury in raw and

processed landfill gas.

- Evaluate the feasibility of implementing standardized sampling and analysis protocols at different laboratories.
- Determine the presence of human pathogenic viruses or bacteria in the gas.
- Develop further research recommendations.

1.4 STATEMENT OF WORK

The original work plan developed for this project consisted of the following eight tasks:

Task 1: <u>Program Plan Design/Technical Liaison.</u> Project team responsibilities and resources required for the joint study performed during this program were designated.

Task 2: <u>Site and Sampling Selection.</u> Potentially cooperative LMR facilities in the United States were identified. The willingness of these landfill and gas recovery operators to take part in the sampling program was confirmed, and the specific sampling locations at each recovery site were established.

Task 3: <u>Sampling and Testing Protocol.</u> A review and evaluation of the available sampling and analytical techniques used to characterize trace VOC's and volatile mercury in landfill gas was conducted. Based on this review, the sampling and analytical protocols were further refined for testing VOC's and volatile mercury.

Task 4: <u>Field Sampling.</u> Sampling of raw, processed, and surface gas and ambient air was conducted at the sites selected in Task 2 using procedures developed in Task 3.

Task 5: <u>Analytical Testing.</u> Laboratory analyses were performed on the samples collected at the landfill sites using the protocols developed in Task 3. The comparability and consistency of results between the two analytical laboratories were evaluated.

Task 6: Corrosion/Combustion Characteristics. Corrosion characteristics of both combusted and non-combusted landfill gas were to be examined by ANL. This task was eliminated from the project by ANL because of DOE budget cuts.

Task 7: Technology Review. Original plans were made to review European technology for control of landfill gas emissions. Portions of the Part I GRI report were to be updated as necessary. A preliminary assessment of European technology indicated that this task was not germane to Part II. Therefore, with approval from GRI, this task was eliminated and resources were allocated to the other tasks.

Task 8: Conclusions and Recommendations. Conclusions and recommendations based on the tasks carried out in this study are presented.

1.5 PROJECT SCOPE

The characterization of components of landfill gas in this study includes both the identification and concentrations of volatile organic compounds present in the gas. The primary purpose of this study was to characterize the constituents of landfill gas at several sites and establish the consistency of this characterization on a repetitive basis. In this study characterization included:

- Determination of the most common trace VOC's present in the three phases of landfill gas at the recovery operation (i.e. gas emanating at surface, raw gas and processed gas).
- "Order-of-magnitude" concentration determination of trace constituents in landfill gas.

The scope of this study required sampling and analytical testing for a broad range of constituents. Thus the accuracy of the results of the VOC determinations is limited due to the number of components that were analyzed by a single procedure. In order to establish more accurate data, compound-specific sampling and analysis is required. A discussion of the limitations of the sampling and analytical methods in this study is presented in Section 3 of this report.

1.6 BENEFITS

This study has produced a number of applicable tools and procedures useful to GRI, the gas industry, and the scientific and engineering community, including:

- Development of a nationwide data base of trace VOC's present in both raw and processed landfill gas;
- Development and refinement of field sampling equipment and procedures that are planned for future use in standardizing industry methodology.
- Refinement and evaluation of the analytical and chemical procedures for the analysis of trace VOC's and volatile mercury in landfill gas;
- Development of sampling and analytical procedures and examination of the pathogenic bacteria and viruses in both raw and processed landfill gas;
- Presentation and ranking of additional research recommendations in the subject area.

2 PROJECT ORGANIZATION

This study was jointly funded by GRI, through ESCOR, Inc. and by the DOE through Argonne National Laboratory (ANL). ESCOR was the primary contractor to GRI. Science Applications, Inc. (SAI) was a subcontractor to ESCOR and assisted in the GRI-funded field sampling and analytical tasks. The Methane Recovery from Landfills Program at ANL conducted a parallel analytical program with funding by DOE. The ANL analytical data are an integral part of this report. In addition, the School of Public Health and Hygiene at Johns Hopkins University (JHU) assembled the sampling equipment and the protocols that were used to analyze the landfill gas streams for pathogenic bacteria and viruses.

ESCOR, Inc. was responsible for the overall organization, management, task implementation and final report preparation. Principal investigators at ESCOR were: R. Eric Zimmerman and George R. Lytwynyshyn. Dr. Zimmerman was project director and was responsible for the overall study. Mr. Lytwynyshyn served as project manager and was responsible for the daily activities and reporting requirements.

SAI was responsible for the development and use of field sampling and analytical procedures. The principal investigator for SAI was Norman W. Flynn. SAI's responsibilities included development and implementation of field sampling and analytical protocols, field sampling, sample analysis, data presentation, and assistance in final report preparation.

ANL assisted in protocol development, field sampling, and sample analysis. The principal investigator for ANL was Dr. Ronald Wingender. Prior to this study, ANL had not used the procedures that were developed by SAI. Therefore, ANL was in the unique position to evaluate the laboratory requirements for the analytical procedures and to comment on the efficacy of the procedures. Argonne's primary responsibilities included implementation and evaluation of the sampling and analytical protocols, field sampling, data analysis and interpretation, and report preparation.

JHU acted as a consultant to ESCOR and investigated the presence of bacteria and viruses in the landfill gas stream. The principal investigator at JHU was Dr. Vincent Olivieri, Professor, School of Public Health and Hygiene. Dr. Olivieri's primary responsibilities were to develop and apply procedures to determine the presence of pathogenic bacteria and viruses in the inlet and product landfill gas.

3 SCOPE OF STUDY

3.1 SAMPLING SITE SELECTION

The primary criteria for selecting LMR sampling sites were based on:

- The ability to obtain raw and processed landfill gas samples in order to develop a nationwide data-base.
- The need to obtain and compare chemical and microbiological data on medium and high Btu gas from LMR systems.

In an effort to obtain data from the widest selection of sites, landfills with and without processing facilities were selected for gas evaluation. Nine LMR sites were selected for participation in the sampling program. Of these, three produce medium-Btu gas, four produce high-Btu gas, and two had no gas processing facilities.

Sampling locations at each facility were selected to provide characterization of the landfill gas at three stages:

1. At a point where the collected raw gas enters the processing plant.
2. As the gas emerges from the processing plant as product gas.
3. As the gas emanates from the landfill surface.

In addition, ambient air samples were collected upwind from the LMR facility. No samples were collected downwind from the LMR facility as these could contain non-factorable emissions attributable to the landfill and gas recovery process.

Due to site-specific arrangements, the LMR operator does not always control the landfill gas from recovery through processing and delivery of the product gas. Consequently, at some sites, collection of a complete set of samples was not possible. A complete set of samples was obtained at six of the nine LMR sites. Generally, two separate sampling trips were made to each site. Two sites were sampled three times, and two other sites were sampled only once.

3.2 VOLATILE ORGANIC COMPOUND CHARACTERIZATION

3.2.1 Background

Purpose. The purpose of the VOC characterization portion of the study was three-fold:

1. To initiate and develop a nationwide characterization of VOC data that is representative of raw (inlet) gas, processed (product) gas, and gas emanating from the landfill surface.
2. To use the resultant data from this study to review and recommend modifications to the sampling and analysis protocols (see Appendices A and B).
3. To evaluate the proficiency with which another laboratory can implement the sampling and analytical protocols developed by SAI.

Selection of Sampling and Analytical Methods. Landfill gas, which is predominantly composed of methane (50 to 60%) and carbon dioxide (40 to 50%), contains less than 1% organic and inorganic constituents, of which some may have potential environmental significance. It is this 1% of the total landfill gas that is the subject of this portion of the study.

The gas industry has long been aware that landfill gas contains detectable levels of aromatic and chlorinated VOC's. When the industry became involved in the characterization of landfill gas, these compounds became the focal point of their interest. At that time, a number of sampling and analytical procedures were considered for adoption as a standard protocol. The major considerations for this methodology included:

- The amenability of the sampling and analysis procedures to a wide range of VOC's.

- The ability of the sampling and analysis procedures to handle order-of-magnitude differentials in component concentrations.

- The simplicity of operation and portability of the sampling equipment.

An adsorbent resin VOC sample collection and combined gas chromatography/mass spectrometry (GC/MS) analysis was selected as the analytical tool for this study. Adsorbent resin columns, packed with Tenax-GC (diphenylene oxide) and Silica Gel, were chosen as the sample collection media because of their applicability to the compound types found in landfill gas and because of the precedent that has been set by the U.S. Environmental Protection Agency (EPA) (CFR Vol. 44, No. 233). GC/MS was chosen as the analytical method because of its ability to provide the ultimate reliability for compound identifications. An additional procedure which involves sample collection using a stainless steel cylinder was studied to evaluate the equivalence of the two sampling and analysis procedures.

The Tenax-GC/Silica Gel adsorbent resin (Tenax) sampling procedure's strength is its selective adsorption of VOC's. Carbon dioxide and methane are not adsorbed by Tenax and therefore are excluded from the analytical scheme. It is advantageous to use a sample collection technique that does not concentrate these two compounds, since they are present in concentrations of three or more orders-of-magnitude greater than the designated target analytes. In most cases the ambient air analyte levels of VOC's are not adequate for detection by GC/MS without sample concentration. The applicability of the Tenax procedure includes compounds with boiling points between that of the dichloroethenes (1,1 and 1,2-trans isomers) to that of naphthalene and trimethylbenzene.

Compound Selection. SAI originally became involved in the characterization of trace components in landfill gas in 1979. At that time landfill gas samples were collected from inlet and plant process stages. The resulting data were evaluated by submitting representative mass spectra to a computerized National Bureau of Standards (NBS) library search routine. From these data, recurring identifications of "priority pollutant" compounds and known carcinogenic compounds were used to establish a target compound list. Additional normal-alkanes were added to this list to provide data important to the gas industry. Due to the complexity of the sample matrices, a procedure for processing samples that would yield the maximum amount of information regarding the compounds of potential environmental and health significance was developed.

There are VOC's that are of environmental significance that are not included in this target compound listing. Vinyl chloride is one such compound; it is extremely volatile and is not collected efficiently on Tenax. In addition, heavier compounds which exhibit lower volatilities are not amenable to the Tenax collection method. Compounds of both these types require specific analytical techniques to detect their presence and concentration in landfill gas.

Identification and Quantification. Sophisticated analytical procedures are required to analyze the complex matrix of compounds (more than 100 in some samples) that are present in landfill gas. Development of capillary column GC techniques has provided the additional resolution necessary for improved compound identification and has made compound specific quantitation less ambiguous.

One of the strengths of the sampling and analytical methods used for this research project is the ability to provide both qualitative and quantitative determinations. For this study, the sample sources were known to contain significantly differing concentrations of the various compounds. Therefore, the use of a single method with a wide dynamic range was important. Sampling of gas and ambient air using Tenax enables collection of sample volumes of a few milliliters to many hundreds of milliliters. Assuming an instrument detection limit of 1 to 10 nanograms (ng), the level of detection can range from between 10^{-2} Vppb to 10^{1} Vppm. Other techniques limit analysis to relatively concentrated sample matrices. Volume parts per million results (Appendix B) are reported in this study.

Method Application. The sampling and analysis protocols described in Appendices A & B have a wide range of application with regard to sample types. Gas streams as complex as natural gas or raw landfill gas were of main interest in the development of these protocols. Ambient air samples and gas migrating from the landfill surface are also amenable to these techniques. Application of these methods covers a wide range of sample concentrations, since the volume of gas sampled and therefore the detection limit can be modified to meet the needs of the analysis. These methods are applicable to only a narrow range of compound volatility.

3.2.2 Volatile Organic Compound Sampling Procedures

Summary of Procedures. The origin and development of the methods used to collect VOC's for analysis in this study evolved from prior research programs (Flynn, et.al., 1981) that attempted to characterize the components of landfill gas. In this work, samples were collected using a laboratory vacuum pump at sampling locations under negative or ambient pressure and a corrosion-resistant, Teflon-lined two-stage gas regulator for sampling gas under positive pressure. From these studies and the interest that was generated within the gas industry, it became apparent that continuing sampling and analysis programs were needed. As a result, a gas sampler was constructed (see Appendix A) that includes the following features:

- Contain all necessary equipment within a single module.
- Provide flow-controlled sampling of gases.
- Allow operation from both AC and DC electrical sources.
- Weigh less than 32 Kg (70 lb) for ease of handling and shipping.

The sampling protocol presented in Appendix A describes two methods (vacuum pump and pressure reduction) for VOC collection using adsorbent resin traps and one method for VOC sample collection using stainless steel cylinders.

Sampling Method Selection by Location. Four types of samples were collected during the course of this study. The sampling procedure used for the collection of Tenax samples remained consistent with only one exception: inlet (raw) gas samples were sometimes collected using the two-stage regulator, or, in some cases, only the fine-metering valve normally used downstream of the regulator. This latter arrangement was used only if the inlet gas was under positive pressure when the LMR system was not operational. Product gas samples that were under positive pressure were always collected using the two-stage regulator. Surface gas samples and ambient air samples were always collected using the vacuum sampling system.

Rationale for Use of Tenax and Stainless Steel Cylinder Sample Collection Methods. Traditionally, several procedures have been used to collect gas samples. The most simple technique, and the one sometimes used by scientists working in the field of trace VOC chemistry, makes use of a cylinder or an evacuated container. The gas sample is either pumped into the cylinder if the gas stream is under negative or ambient pressure or is collected directly if the gas is under positive pressure.

The various sampling procedures used should be evaluated for consistency or equivalence during the developmental stages. In this study, a set of experiments was designed to compare the Tenax and cylinder sampling procedure. Product-gas samples were chosen for these experiments, mainly due to the expected component concentrations that fall within the dynamic range of the GC/MS. The results of these experiments are presented in Section 4.1.

3.2.3 Volatile Organic Compound Analysis

SAI Analytical Instrumentation. The evaluation of samples from product, inlet, surface, and ambient air locations for VOC's was conducted using combined GC/MS operated under computer control. Flow controlled thermal desorption was used to transfer the VOC's from the Tenax trap to the capillary GC column. The resultant GC effluent was detected by MS. The MS was operated in the electron-impact ionization mode. Mass spectra were collected by repetitive scan and stored on magnetic discs for subsequent data reduction. Automated computer search routines provided both compound identification and quantitative determinations. Data archiving was accomplished using magnetic tape. The following describes, in detail, the apparatus that was used by SAI for analysis of VOC's.

(1) Tekmar Liquid Sample Concentrator (LSC-2): An automated purge-

and-trap device was used to transfer VOC's from the Tenax adsorbent resin trap to the GC/MS. The LSC-2 was designed for the analysis of VOC's in waste water. The EPA has described a procedure (CFR Method 624) for the analysis of VOC's that is readily adaptable to the LSC-2. The LSC-2 uses an inert gas to purge VOC's from an aqueous sample (5-25 ml); VOC's are trapped on Tenax and later desorbed onto the capillary GC column. The analytical scheme that was used for analysis of LMR samples in this study modifies the normal LSC-2 procedure by eliminating the aqueous sample purge step. In the procedure described in Appendix B, Tenax traps were placed directly into the heater jacket of the desorption unit, and the VOC's were transferred by thermal desorption to the capillary GC column.

(2) Finnigan Model 4021 GC/MS Data System: This instrument, used for the analyses of VOC's, consists of a GC, quadrupole MS, and a dedicated computer system. Each of these modules is described in further detail below.

The GC system is composed of a microprocessor-controlled inlet system, heated chromatographic oven, and transfer lines that direct the sample effluent to the MS. The inlet system is designed for both packed and capillary column GC. The capillary inlet system, operated in the splitless mode, was used for the analyses of VOC's described in this report. The temperature of the chromatographic oven is controlled by a microprocessor, isothermal and programmed temperature-controlled analyses may be selected. The chromatographic interface consists of a heated oven that is also microprocessor controlled. A schematic diagram of the GC/MS system is presented in Appendix B.

The detector system (i.e., MS) provides ionization using an electron-impact ionization source. A quadrupole mass analyzer is used for mass-to-charge (m/z) ratio separation, and a continuous-dynode electron multiplier detects ion current. The mass analyzer is differentially pumped using an oil diffusion pumping system that is capable of achieving vacuum of 10^{-7} torr; operational vacuum is typically 10^{-6} torr. The MS ion-source voltages and electron multiplier voltage are controlled by a series of potentiometers. The MS is tuned manually by adjusting mass spectral peak shape and intensity using a standard calibration compound (perfluorotributylamine). The integrity of manual adjustments is evaluated by statistical observation via computer software programs.

The MS data system consists of a Data General minicomputer and two disc drives. Communication with the computer is accomplished through a Tektronix terminal, and hard copy is generated using a Printronix line printer. The MS can be operated under manual or computer control. When under computer control, mass spectra are recorded on magnetic discs as specified by operator-selected acquisition parameters. Detailed descriptions of the analytical procedures are presented in the following section.

Summary of SAI Analytical Methods. Analyses of VOC's were performed by placing the Tenax traps, which had remained sealed since collection, in the heater jacket of the Tekmar LSC-2. The Tenax traps were heat-desorbed onto the GC column at the start of the analysis. A capillary GC column (30-m x 0.25-mm id, DB-5 fused-silica, supplied by J&W Scientific) was used for all analyses. This column was connected directly to the ion source of the MS. During desorption of VOC's from the Tenax trap, the GC oven was held at 30° C. A portion of the initial capillary column was placed in a Dewar containing liquid nitrogen (LN_2). The function of the LN_2 Dewar is to cryogenically focus (i.e., to trap) volatile compounds that range from a molecular weight of approximately 40 to 150 Atomic Mass Units (AMU). The cryogenic focal area of the column was maintained at 6 cm, which provides for extremely narrow chromatographic bands during analysis. The GC oven was held at 30° C for 5.5 min. following completion of the desorption and removal of the LN_2 Dewar. The oven door was then closed and the GC oven was programmed from $30^{\circ}C$ to $65^{\circ}C$ at $4^{\circ}C/min$. The time required for chromatographic analysis was 22.5 min.

From the onset of the analysis, when thermal desorption of volatile compounds from the sample trap was initiated, the MS was repetitively scanned from m/z 35 to 275. The resultant mass spectra are stored on disk until data reduction is complete.

SAI Data Reduction Methods. Calibration was performed prior to sample analysis, by purge and trap analysis of standard known VOC's mixtures that were added to 5 mL of organic free water. From these analyses, a calibration curve was established for all the target compounds listed in the VOC analysis protocol (Appendix B). This calibration curve was used to provide response factors for the quantification of the target compounds. The sample data files were submitted to quantitative data reduction using automated programs written by Finnigan Corporation for the INCOS data system. Concentration data from automated data reduction were verified by an MS operator and the data were converted to Vppm using SAI software written for an Apple computer.

Qualitative determinations are achieved using another portion of the INCOS software package. Background-subtracted mass spectra were compared to reference spectra in the NBS Mass Spectral library (approximately 28,000 entries). A complex algorithm was used to compare the spectral information from the gas sample to each of these entries. The "best fit" selected by the computer was written to a file. This process was conducted repetitively on each chromatographic peak (time vs. intensity) selected for identification. When all chromatographic peaks were processed in this manner, a listing of the tentative compound identifications was printed in a report format.

ANL Analytical Instrumentation. ANL used the same basic approach as SAI for gas sample analysis. Because of some hardware and software differences between the two laboratories, the following descriptions are provided for clarification:

(1) A Tekmar Liquid Sample Concentrator (LSC-1) was used to desorb VOC's from the Tenax trap and transfer them via a heated line to the injection port of a Hewlett-Packard Model 570 GC. The purge-and-trap capability of the LSC-1 was used for analyzing standards to calibrate the instrumentation. The calibration procedure consisted of: (1) placing 5 mL of organic-free water in the purge vessel, followed by several uL of a standard solution of the target VOC's (20 ng/uL) in methanol, and (2) initiating an 8-min, 20 mL/min purge sample cycle. At the conclusion of this step, the VOC's are desorbed from the Tenax trap by heating to 180°C for 3.5 min. The desorbed VOC's are then transferred to a Hewlett-Packard 18740B Grob-type GC injection port. For both the standard and sample runs, the VOC's were cryogenically focused on the capillary GC column prior to the temperature programmed analysis. The GC effluent was transferred directly into the MS ion source.

(2) A Hewlett-Packard Model 5933A computer-controlled GC/MS system was used for the qualitative and quantitative analysis. This quadrupole MS was modified to enable effluent from a capillary column

to be directed into the MS ion source via a heated transfer line.

The MS was operated in the electron-impact ionization mode, with the quadrupole providing the mass-to-charge selection and a continuous-dynode electron multiplier providing detection of ion current. The vacuum system provides an operating range of 10^{-6} to 10^{-5} torr. The MS is manually tuned by adjusting the ion source potentials to optimize the response of a standard calibration compound (perfluorotributylamine).

The MS data system consisted of a Hewlett-Packard 2100S computer with 16K, 16-bit-word core memory and a 7900A dual disk drive. Communication with the computer was via a Tektronix 4012 graphic control terminal, and hard copy was generated with a Tektronix 4631. The MS can be operated under manual or computer control. Under computer control, a selected mass range is scanned repetitively and the resulting ion current is recorded on magnetic disc. The recorded data were processed using both manual and automated procedures.

Summary of ANL Analytical Methods: Sample analyses period were initiated by first analyzing several standards GC/MS system calibration. All standards were analyzed using the splitless injection mode. Sample traps were maintained at room temperature until just before analysis. The trap "end-caps" were removed and the trap was quickly placed in the heater-jacket of the LSC-1. A 1.8 cm portion of a 30-m x 0.25-mm i.d. J&W fused-silica SE-54 capillary column was immersed in LN_2 prior to the 3.5-min thermal desorption period. The injector was operated in the split mode (split ratio 30:1) for analysis of most inlet, product, and surface gas samples, and in the splitless mode for the ambient air samples. These procedural differences were used to prevent column overloading and to maintain the concentrations of organic components entering the MS within the linear range of the detector. After the desorption step, the column was quickly removed from the cryogenic trap and the GC temperature program -- 30° C for 2 min, followed by a programmed rate of 4° C/min -- was started. The time required for analyses was usually less than 20 min.

At the commencement of the GC temperature program, the MS was repetitively scanned from 47 to 200 AMU. The mass spectral data were stored by the computer on magnetic disks. Data reduction is discussed in the following subsection.

ANL Quantitative Data Reduction Methods. Prior to daily sample analyses, instrument calibration data were acquired by analyzing a standard mixture of target compounds. Additional standard analyses were made during the remainder of the operating day to provide a continuing check on instrument response. The response for each of the three most significant mass-ions of each standard compound was determined to insure that the normalized response of these ions agreed with known values. The response for the major ion of each standard compound was then computed as area counts per nanogram analyzed. This value was regenerated daily and, after the same procedure was applied to each of the target compounds present in the standard, the value (i.e., response factor) was used to compute the quantity of target compounds in the LMR sample.

The above procedure insures that the target compound, rather than one with similar mass spectra and retention time, is being quantitated in the sample. Linearity of the instrument was checked manually by observing the response of the major ion as a function of nanograms injected.

ANL developed quantification software specifically for this study. The initial ANL program required some manual interpretations. These are summarized in the following text:

1) Each standard and sample data file was examined using the Hewlett-Packard SPEED program to determine the retention times for each compound. Single-ion chromatograms were used to locate the methylbenzene and xylene peaks, which were present in almost all samples. Through comparison of the known relative retention times of the target compounds to those of methylbenzene and the xylenes, absolute retention times of each compound in the specific standard or sample were calculated.

2) Each standard was analyzed for response of each compound. The tabular data for ion intensity vs. scan number were examined in the expected compound retention-time window. The single-ion intensities for three selected ions and total-ion intensity for each compound were examined. The range of scans in which the three selected ions each formed a peak was identified by confirming against known standard retention times.

3) Triplicate standard compound response factors were calculated using the known concentration of the standard compound and the three ion intensities.

4) Each sample was analyzed in a similar manner. The integrated ion intensities were divided by the corresponding response factors to give the amount of compound in the sample.

5) Component concentrations (Vppm) were calculated, based

on the instrument gain relative to that for the standard, the split ratio of the sample, the volume of sample pumped through the sample tube, and the response factors for that day.

Data interpretation relied on extensive use of computer programs that presented the data in tabular form for examination and assisted in the mathematical manipulations. However, since the raw data were rough in places, all judgements of peak placement and validity were performed manually. When the concentrations calculated from the three ions of a compound were not internally consistent, the raw data were examined and a judgment was made as to the best value for the concentration.

Not all of the standards were available for each day that samples were analyzed. During January and February two Supelco (Purgable A and B) standards were used; each contained several, but not all, of the 20 target compounds. In March, a third standard solution was prepared which contained the additional target compounds not contained in the Supelco standards. In May, SAI provided a standard that contained all 20 of the target compounds. Thus, for the data gathered before May, only a subset of the 20 target compounds were analyzed as standards. The raw data were stored on magnetic discs and reanalyzed in May when information on all of the standards was available. Daily response factors for standards not analyzed the same day as a given sample were estimated from the later data and applied "after-the-fact" to the samples.

ANL analyzed 53 samples when only two Supelco standards were available for calibration. Once the 20 target compound standards were obtained, this mixture was used to perform all instrument calibrations. At this time it became necessary to analyze newly collected samples using the old software because the improved software was not yet totally debugged. Thus, an additional group of 54 samples were quantitated by this means.

The improved software required a Hewlett-Packard 21mx computer with 32K, 16-bit-word core memory and a Hewlett-Packard Model 9876A line printer. This software was developed to process the data obtained during the use of the 20-compound standard. This software performed the following tasks:

1) Searched GC/MS standard data files and determined retention time, relative abundances, and response factors for each of the standard compounds.
2) Averaged the results (relative abundances and response factors) of a number of GC/MS standard analyses.
3) Allowed the operator to correct the results (relative abundances and response factors) of a GC/MS standard analysis or averaged data from GC/MS standard analyses.
4) Searched GC/MS sample data files and, based on results from standard GC/MS analyses, located compounds and determined weight and volume of gas.
5) Allowed the operator to correct (or insert) the sample data results (weight and volume data).
6) Tabulated and performed statistical analysis on sample data obtained from a number of analyses.

With this software, there is a high degree of interaction with the operator during data reduction; therefore, corrections or additions can be easily made. Up to 100 GC/MS standard or sample data files can be evaluated at one time. Finally, the program inserts data that was missed by the GC/MS and prints out results both with and without the inserted data.

3.2.4 ANL VOC Protocol Implementation

One of the objectives of this study was to determine the effort required to implement the analytical protocols at a laboratory that had GC/MS capability, but no experience with landfill gas analysis. ANL met these requirements, and although they had equipment identical to SAI (Finnigan GC/MS) they elected to use their Hewlett-Packard GC/MS for this study. Thus, a test of the approved protocols with equipment variations was conducted.

Although the hands-on experience for conducting GC/MS analyses existed at ANL, no application experience existed for the analysis of VOC's collected on Tenax-GC/Silica gel adsorbent resin traps. ANL had little experience using a Tekmar Liquid Sample Concentrator and the one that was available, a Tekmar LSC-1, required modification to accommodate the adsorbent resin traps recommended in the SAI protocol. Chromatographic analyses involving cryogenic focussing of sample components had not been used at ANL, and, although it is reasonably straightforward, considerable experience is required to insure consistent retention times for the target VOC's. In addition, the type of software required for data reduction was not available for the Hewlett-Packard equipment and thus, required development by ANL.

The modification of the Tekmar LSC-1 and its incorporation into the existing GC/MS system was straightforward. Similarly, the cryogenic focussing technique was easily established, but took considerable experience to obtain the required in retention time and quantitative precision. The consistency developed gradually through establishment of a set, timed routine for the execution of the following steps: (1) thermal desorption, (2) cryogenic focussing, and (3) removal of the cryogenic trap from the capillary GC column and initiation of the GC temperature program.

The major difficulty of these analyses was due to the variable concentration of VOC's contained in the landfill gas samples. Even the smallest gas sample volumes (25-30 mL) sometimes contained high concentrations of VOC's, which led to analytical system overloading. Specifically, methylbenzene and the dimethylbenzenes (xylenes) were usually present in much higher concentrations than the other compounds. As experience was gained in the analyses of these samples, it was necessary for ANL to split the sample during thermal desorption to avoid overloading the analytical system. This was accomplished by adjusting the appropriate flows for the GC Grob-injector system. By trial and error, the optimum split ratio was established at about 30:1. That is, for every part of the sample that was cryogenically focussed on the column, 30 parts were vented off. While this split ratio was not practical for the analysis of all samples, a degree of flexibility was provided by selecting samples with higher collection volumes (50, 100, and 600 mL) or by using the Grob-injector in the splitless mode for more accurate sample quantitation. Better instrument performance was achieved because the amount of material entering the MS ion-source could be maintained within the linear range of the instrument.

The first data reduction programs developed by ANL provided quantitative results that assumed day-to-day variation in instrument response was the same for all of the 20 target compounds. The second set of programs included the ability to perform daily instrument calibration. These programs required retention time and ion response ratios of sample compounds that conformed to standard compounds as criteria for identification.

One of the problems affecting precision of the standard data was found to be trap-to-trap variation. Although all the traps were packed similarly, by weighing a 100 mg quantity of Tenax-GC and silica gel, some variation was experienced. Another factor affecting both precision and accuracy of this method was due to the use of an external standard calibration procedure. The use of an internal standard technique is highly desirable but difficult to incorporate into this protocol.

3.3 MERCURY CHARACTERIZATION

3.3.1 Background

Purpose. The presence of heavy metals in processed landfill gas is of concern to the gas industry. Of the heavy metals, mercury is the most volatile. The unknown dumping history of most landfills in this country means that this highly toxic, heavy metal may exist, as the free metal or as a complex, in raw and product gas obtained from LMR systems. The purpose of the sampling and analysis protocols summarized below and presented in detail in Appendices A and C is to provide mercury concentration data for raw, product, and surface gas and to compare these concentrations to those found in urban ambient air.

Selection of Sampling and Analytical Procedures. Selection of a procedure for the determination of mercury in gaseous samples required consideration of a number of criteria. The sample collection procedure should be simple, straightforward, and consistent with the methods previously described for the collection of VOC's. The method that was chosen uses the same equipment for sample collection that is used for VOC sampling and provides for the collection of positive, negative, and ambient pressure samples.

A review of the available literature revealed a method used to determine particulate and vapor-phase mercury in coastal and remote marine atmospheres (Fitzgerald and Gill, 1979). This method uses a two-stage gold amalgamation adsorbent trap for gas sample collection and subsequent analysis by thermal desorption flameless atomic absorption (AA) spectrophotometry. Fitzgerald and Gill state that the coefficient of variation for the determination of 0.5 ng mercury is 4% and that 0.06 ng of mercury can be measured with confidence.

The method described by Fitzgerald and Gill was adopted for analysis of volatile mercury from landfill gas and ambient air samples in 1979, by SAI, in a study supported by PG&E. Results of those analyses suggested that landfill gas could contain volatile mercury and that further investigation was warranted. Subsequent field investigations using these procedures have provided additional improvements, particularly with regard to the development of sampling hardware. Flow-controlled vacuum pumps with increased stability have been adapted to an integrated sampling device that provides on-line leak testing, calibration, and sample collection with a minimum of hardware replacement or modification. In addition, modifications to the original procedure have been made. During this early study, SAI replaced the flameless AA spectrophotometer with a cold-vapor AA spectrophotometer. This instrument offers the same capability as the flameless AA unit, but has a much lower initial purchase and continuing maintenance cost.

Level of detection. The detection limits for this method, like those for the method described for determination of VOC's, is mainly dependent on the volume of gas passed through the adsorbent trap. For this study the detection limit for mercury in the environment was established at 0.2 ng. Sample volumes collected for analysis of volatile mercury ranged from one to eight liters of landfill gas or ambient air.

3.3.2 Volatile Mercury Sampling Methods

Summary of Procedure. Gas samples were collected, with an adsorbent trap consisting of quartz beads coated with a gold amalgam, using either the vacuum sampling system (for negative or ambient locations) or using the teflon two-stage regulator (for collection of positive pressure samples). The sampling procedures are presented in Appendix A. At the conclusion of the sampling, the trap was removed from the sampling train, plastic caps were replaced at each end and the trap was placed in a screw-cap vial for storage until analysis.

3.3.3 Volatile Mercury Analysis

The sample trap was placed in a desorption unit and volatile mercury was transferred to the analytical trap by heating the sample trap to 600° C and by using a flow through the column of 300 mL/min of inert nitrogen gas. The sample components were then thermally desorbed from the analytical trap using the same conditions as for the transfer. This intermediate step was incorporated into the procedure to increase the precision and accuracy of the results, because the desorption characteristics of each of the sample traps were determined to be non-equivalent. Precision of the analysis was increased by providing consistency at the time of the analytical desorption and detection. The amount of volatile mercury collected in the gold coated quartz-bead analytical traps was determined by thermal desorption cold-vapor AA spectrophotometry at a wavelength of 254 nm. Peak intensity was recorded using a 10 mV laboratory strip chart recorder.

Calibration of the analytical system was accomplished before sample analysis by using vapor phase additions of mercury saturated air. The standard was prepared by allowing a known volume of elemental mercury to come to equilibrium with air in a glass container. Vapor pressure data were used to calculate the amount of mercury in air delivered from calibrated syringes to the analytical system. A typical calibration curve ranged from 0.2 to 200 ng mercury. Quantification of mercury in unknown samples was determined from peak intensities observed at the analytical wavelength of 254 nm. The calibration curve was used to make final sample concentration determinations.

3.4 BACTERIA AND VIRUS CHARACTERIZATION

3.4.1 Background

In addition to their normal contents of solid waste and debris, sanitary landfills also receive human fecal material and have, in the past received hospital wastes. The primary source of human feces in sanitary landfills is disposable diapers used for infants and toddlers; in some cases raw sewage sludge may also contribute fecal material. Infants and toddlers have a high incidence of gastrointestinal diseases due to their poor sanitary habits and the limited development of the host immune system. The gas industry has expressed concern for disease transmission through gas collected from LMR systems. The presence of pathogenic microorganisms must be demonstrated before the route of disease transmission can be established. The objective of this study was to (1) determine the presence and levels of selected indicator and pathogenic microorganisms in the inlet and product gas collected from landfills and (2) evaluate the health implications.

Since the diseases of concern follow the anal-oral route of transmission, the indicators of fecal contamination, rather than specific bacterial pathogens were selected for analysis. These indicators include total coliform, fecal coliform, and fecal streptococci; such microorganisms are easily assayed and behave in a manner similar to the enteric bacterial pathogens in the environment. The presence of these indicator microorganisms generally suggests recent fecal contamination. Human enteric viruses were also selected for analysis since they generally survive longer in the environment.

3.4.2 Bacteria and Virus Sampling Procedures

Liquid Samples. Condensate samples were collected at designated landfills by transferring the liquid into sterile 19-L (5 gal) containers which were sealed and shipped to the JHU Environmental Health Engineering Laboratories in Baltimore. These samples were then analyzed for selected bacteria and viruses. All samples were stored at 4°C upon arrival at the laboratory and processed within twenty-four hours.

Gas Samples. Samples of inlet and product landfill gas were collected using the procedure described by Decker et al. (1969). Minor modifications were incorporated into this procedure. The glass cyclone scrubber employed was described by Fannin and Vana (1981) and is shown in Figure 3-1. Large-volume gas samples were passed through the cyclone scrubber at high flow rates. Collection fluid (distilled water) used to minimize foaming, was aspirated to a mist (flow rate of 2 to 5 mL/min) through a 20-gauge syringe needle inserted perpendicular to the gas flow just prior to the entrance of the cyclone. The mist droplets collected on the wall of the cyclone, thus creating a

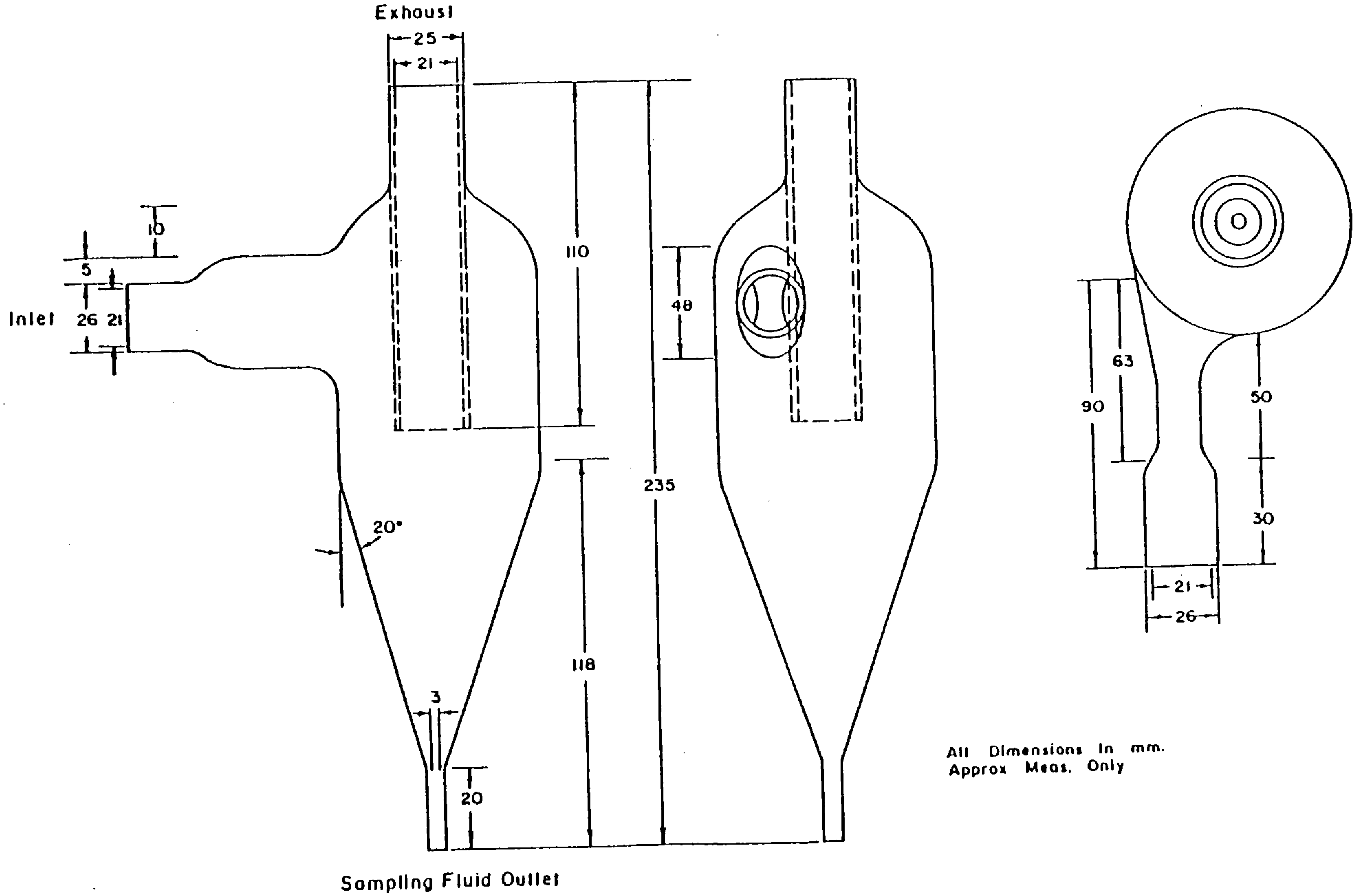


FIGURE 3-1: Schematic of Glass Cyclone Scrubber Aerosol Sampler. (Fannin and Vana 1981)

wet surface for the collection of the aerosol. The collection fluid moved helically toward the lower apex of the cyclone into a flask. Immediately after sample collection, sterile phosphate-buffered saline solution was added to the collection fluid to provide osmotic stability. The stabilized collection fluid was stored on ice, transported to the laboratory, and analyzed for indicator bacteria and human enteric viruses.

Gas-sample flow rates were determined by measuring the velocity at the point where the gas was released to the atmosphere after passing through 30 diameters of rigid plastic pipe. For gas lines under pressure, samples were taken directly from a 1.25 or 1.9 cm (0.5 or 0.75 inch) tap and the flow was set to approximately 1000 L/min. For high-pressure gas lines, the pressure was reduced with a two-stage regulator to facilitate sample collection. For lines under negative pressure, a Cadillac model HP33P pump was placed in the sample train downstream of the cyclone.

3.4.3 Microbiological Assays

Indicator Bacteria Analysis. Total coliforms were determined by the multiple-tube dilution technique described in Standard Methods for the Examination of Water and Wastewater, 15th Edition (1980). Lactose broth was the presumptive medium. All positive lactose tubes were confirmed by transfer to brilliant green lactose broth with 2% bile.

Fecal coliforms were determined by confirmation of positive presumptive tubes on EC medium of 44.5 +/- 0.2° C according to Standard Methods (1980).

Fecal streptococci were determined by pour plates on KF streptococcus medium as described in Standard Methods (1980).

Human Enteric Viruses. Viruses were concentrated and assayed by the microporous filter adsorption-elution method described in Standard Methods (1980). Minor modifications to the method are as follows: the pH of 20 to 40 L of sample was adjusted to 3.5 with 1.0-N HCl and filtered through a Baltston Type C filter. Viruses were eluted from the filter with pH-9.0 3% beef extract. The beef extract was then adjusted to pH 3.5 and the resulting floc containing the virus was collected by centrifugation at 300 x G for 10 min, then resuspended in 0.15-N phosphate buffer and adjusted to pH 7.0. Aliquots were assayed for viruses by the plaque-assay technique on Buffalo Green Monkey (BGM) kidney cells.

Low-volume samples (50 to 500 mL collecting fluid from the cyclone scrubber) were adjusted to pH 3.5 with 1.0 N-HCl and passed through a millipore type HA filter of 0.45 um. Viruses adsorbed to the filter were eluted with pH-9.0, 3% beef extract, then neutralized to pH 7 and assayed for viruses by the plaque-assay procedure described by Dahling, et al. (1974).

3.5 SURFACE-GAS FLUX CHARACTERIZATION

3.5.1 Background

One of the overall objectives of GRI's Methane from Landfills Research Program is to determine the net environmental effects of LMR. To properly qualify and quantify the net environmental effects, an understanding of the mass movements into and out of the landfill environment must be gained. Within the scope of this study, the purpose of the surface flux measurement was to obtain a characteristic flux rate gas emanating from the landfill surface.

The rate of gas flux at the landfill surface is dependent upon many variables. Factors such as atmospheric conditions, type of cover material, moisture conditions of the cover, and other physical aspects (e.g. cracks, thickness, microstructure, etc.) of the cover affect the rate and pattern of gas flux at the surface. Previous investigations have shown that flux rates are variable at different locations on a landfill (Cagliostro and Gargano, 1979).

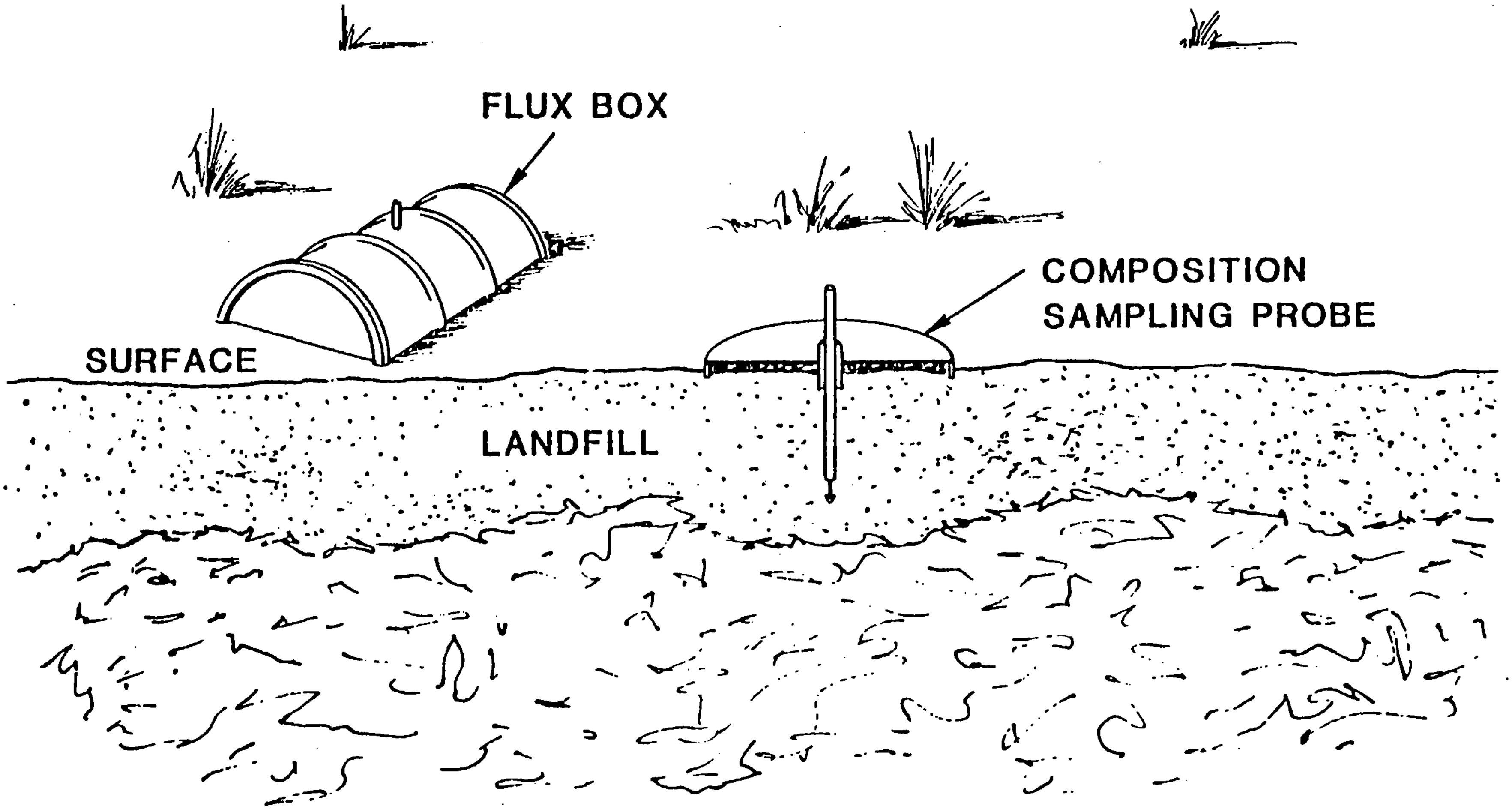
Measurement of gas flux at the landfill surface consists of monitoring one of the primary components (carbon dioxide, methane, oxygen, or nitrogen) in landfill gas. Such measurement must result in minimal disturbance to surface properties. Previous studies have measured the rate of gas flux by capturing the gas in an enclosed volume container and measuring the concentration of carbon dioxide or methane within the enclosed volume (Cagliostro and Gargano, 1979). A "flux-box" method similar to the one used in the Brooklyn Union Gas (BUG)/NYSERDA study (Kunz and Lu, 1980) was chosen for the purposes of this study.

The flux box used in this study consisted of a 114-L (30 gal) steel drum cut in half, parallel to its cylindrical axis (Figure 3-2). A 1.25 cm (0.5 in) wide strip of sheet metal was welded along the cut perimeter of the drum. A 0.6 cm (0.25 in) o.d. sampling port consisting of a metal tube was welded into the drum. Another 0.6 cm hole was drilled at one end of the drum under the cover lip. This hole served to equilibrate the pressure in the drum with atmospheric pressure.

3.5.2 Methods

The drum was embedded 1.25 cm (0.5 in) into the landfill surface to minimize intrusion of outside air. Care was taken to keep the pressure-equilibration port facing away from the wind. Immediately after the flux box was placed over the landfill surface, a methano-

FIGURE 3-2: Surface Flux Testing/Sampling Equipment



meter was attached to the sampling port via a 1.5 m (6 ft) long sampling tube. The methanometer (MSA Model 60) was similar to that used by gas utilities to measure percent volume concentrations of natural gas in air. The instrument has two dial settings that read to the nearest 0.1% in the 0 to 5% range and to the nearest 2% in the 0 to 100% range. Samples were drawn through the instrument via a hand-aspirated bulb.

Methane-concentration readings commenced immediately after the flux box was placed over the landfill surface. An initial reading, followed by readings every 1 to 2 minutes, were taken for 20 minutes. Measurements were taken for at least three locations on the landfill surface.

In addition to measurements of the flux rate of methane concentration in the flux box, a separate sample of the surface gas was taken near the flux box. This sample was taken using the surface gas sampling probe and was submitted to GC analysis to determine the relative concentrations of the primary components (carbon dioxide, methane, oxygen, and nitrogen) of the landfill gas at the surface. This data could then be combined with the methane venting rates to approximate the total gas flux at the surface.

A schematic of the surface gas probe is shown in Figure 3-2. The sampling tube consisted of a 2.5 cm o.d. (1.9 cm i.d.) stainless steel tube. The top end of the tube was capped by welding a 0.6 cm thick by 5 cm diameter circular stainless steel plate that served as the driving surface. The bottom end of the tube was tapered to facilitate penetration. A removable sampling port was tapped into the tube approximately 2.5 cm (1 in) below the end cap. The tube was inserted through an apron, to reduce air intrusion into the sampler. The apron was constructed from 0.6 cm (0.25 in) steel plate, with a diameter of 50 cm (20 in) and a 1.7 cm (0.7 in)lip around the edge of the plate (to reduce air intrusion). The sampling tube passed through the center of the plate through a raised opening. In the opening, an O-ring made an airtight seal between the sampler and the apron. A setscrew held the tube in position.

Before the sampler was driven into the surface, a 1.25 cm x 2.5 cm (0.5 in x 1 in) carriage bolt was inserted into the bottom of the sampling tube and manually held as the bottom of the tube was placed against the landfill surface. This sacrificial bolt kept soil out of the tube and dropped away from the tube as it was slightly lifted before sampling. For sampling purposes the tube was driven 7.6 to 18 cm (3 to 7 in) into the landfill surface, then raised 1.25 to 2.5 cm (0.5 to 1 in). Before sample collection, three to five volumes of air were evacuated from the tube. A sample was collected with an evacuated (-25 psi) can (volume 250 mL) and a hypodermic needle. A sample was collected until the vacuum measured in the can was zero (approximately 2 min). The location and date were recorded, and the can was shipped to ANL for analysis by standard GC thermal conductivity procedures to determine concentrations of oxygen, methane, carbon dioxide, and nitrogen.

Relative barometric pressure at the site was recorded using a Base Microbarograph (American Paulin System, Model SMB5) during surface flux measurements. Wherever possible, readings were initiated 8 to 12 hours before flux measurements in order to record barometric fluctuations that may affect surface gas emanation. Results from the surface flux measurements are presented and discussed in Section 4.4.

4 RESULTS

This study consists of four major sections that covered the sampling and analysis of:

- Trace volatile organic compounds in landfill gas.
- Volatile mercury in landfill gas.
- Bacterial and viral content of landfill gas and primary landfill gas condensate.
- Surface flux and bulk surface gas composition at the landfill.

Analytical results from the four major sections are described in the following sections.

4.1 RESULTS OF VOLATILE ORGANIC COMPOUND ANALYSES

4.1.1 Introduction and Summary

The results of the VOC analyses indicate that:

> Consistent identification of volatile components was obtained from the two laboratories. There was consistent agreement for the analyses of environmentally significant compounds (target compounds) and of compounds not found on the EPA "priority pollutant" list.
>
> A range in quantitative analytical results for environmentally significant compounds occurred at different landfill sites for samples collected during different sampling trips, even when samples were analyzed by the same laboratory. Occasional variations in excess of an order-of-magnitude were observed.
>
> Quantitative results from an independent GC/MS analysis (performed by a nationally known research facility) showed agreement with the trace VOC's present in gas sampled concurrently with this study. However, there was limited correlation of qualitative data for specific compounds reported in this study.

4.1.2 Interlaboratory Data Comparison

SAI and ANL performed repetitive sampling and analyses for each of the nine sites investigated. Trace analyses provided the opportunity to evaluate the data within a laboratory and between laboratories. The sampling and analytical techniques used by both laboratories were similar. However the analytical hardware and interpretative computer hardware and software were different.

The most significant variations in analytical results obtained by the two laboratories occurred during the early portion of the program. These discrepancies were attributed to the use of a new procedure by ANL, different vendor sources for standard compounds, and possible systematic variations in sampling and analytical procedures. Table 4-1 shows a statistical tabulation of the data generated by both laboratories during early and late stages in the program. Table 4-2 summarizes the comparison of data between the two laboratories.

Concentration differences of up to two orders-of-magnitude can be observed in the early data. Later in the program these differences were reduced, and the data indicate good agreement between laboratories. Analytical standards were interchanged by SAI and ANL for the analyses performed later in the program. Generally, the component concentration data reported by ANL show significantly higher concentrations than those reported by SAI. The level of confidence that can be applied to the quantitative analyses is within an order-of-magnitude.

4.1.3 Results of Qualitative Analyses of Gas Samples

Qualitative identifications of compounds other than those listed on the target compound list were made. A list of compounds in landfill gas which were identified in this study is provided in Table 4-3. The large number of individual compounds normally observed in landfill gas samples, and the empirical similarity of these compounds

Table 4-1

INTERLABORATORY COMPARISON OF QUANTITATIVE VOC ANALYSES IN EARLY AND LATE STAGES OF THE STUDY

(Volume parts per million)

	Early						Late					
	ANL			SAI			ANL			SAI		
	N[a]	$\overline{X}$[b]	S[c]	N	$\overline{X}$	S	N	$\overline{X}$	S	N	$\overline{X}$	S
Pentane	4	1.2	2.35	0	NA	NA	9	15.0	32.44	0	NA	NA
1,1-dichloroethylene	4	0.1	0.11	3	0.9	0.12	9	1.9	5.67	2	ND	NA
Dichloromethane	4	6.5	4.96	2	2.2	1.42	9	<0.1	<.01	2	<0.1	0.01
1,2-dichloroethene (Trans)	4	1.6	1.34	3	0.4	0.06	9	ND	NA	1	ND	NA
1,1-dichloroethane	4	3.7	2.75	3	0.7	0.04	9	ND	NA	2	ND	NA
Hexane	4	2.0	1.34	3	0.3	0.02	9	7.0	11.52	2	0.1	<.01
Benzene	4	5.4	1.57	3	0.8	0.10	9	1.1	1.62	2	0.2	.02
Iso-octane	4	0.6	0.85	3	0.5	0.45	9	ND	NA	1	0.1	NA
Trichloroethene	4	8.1	3.68	3	0.6	0.03	9	ND	NA	2	<0.1	0.0
Methylbenzene	4	112	67.3	3	0.7	0.05	9	2.2	3.33	2	0.1	0.01
1,1,2-trichloroethane	4	ND[d]	NA	3	ND	NA	9	ND	NA	2	ND	NA
Tetrachloroethene	4	15.0	13.5	3	0.4	0.03	9	<0.1	<.01	2	<0.1	<.01
Chlorobenzene	4	0.6	0.52	3	<0.1	0.02	9	ND	NA	2	ND	NA
Ethylbenzene	4	32.0	18.5	3	0.6	0.13	9	<0.1	0.15	2	0.2	0.01
m,p-xylene	4	19.0	19.9	3	0.2	0.32	9	0.5	0.67	2	0.3	0.04
o-Xylene	4	14.0	9.54	3	0.3	0.09	9	0.2	0.23	2	0.1	0.07
Nonane	4	69.0	4.90	3	0.1	0.04	9	0.3	0.50	2	0.1	0.0
Iso-propylbenzene	4	2.4	1.00	3	<0.1	0.02	9	0.1	0.26	2	<0.1	0.02
Propylbenzene	4	2.1	1.23	3	ND	NA	9	<.01	0.06	1	<0.1	NA
Naphthalene	4	ND	NA	3	ND	NA	9	ND	NA	2	ND	NA

a) N = Number of observations
b) $\overline{X}$ = Mean value of observations
c) S = Standard deviation
d) ND = Not detected
e) NA = Not applicable

Table 4-2

SUMMARY OF INTERLABORATORY COMPARISON OF VOC ANALYSES

(Volume parts per million)

	Early		Late	
	ANL	SAI	ANL	SAI
	$\overline{X}$[a]	$\overline{X}$	$\overline{X}$	$\overline{X}$
Pentane	1.2	NR[c]	15.0	NR
1,1-dichloroethylene	0.1	0.9	1.9	ND
Dichloromethane	6.5	2.2	<0.1	<0.1
1,1-dichloroethylene	1.6	0.4	ND	ND
1,1-dichloroethane	3.7	0.7	ND	ND
Hexane	2.0	0.3	7.0	0.1
Benzene	5.4	0.8	1.1	0.2
Iso-Octane	0.6	0.5	ND	0.1
Trichloroethene	8.1	0.6	ND	<0.1
Methylbenzene	112	0.7	2.2	0.1
1,1,2-trichloroethane	ND[b]	ND	ND	ND
Tetrachloroethene	15.0	0.4	<0.1	<0.1
Chlorobenzene	0.6	<0.1	ND	ND
Ethylbenzene	32.0	0.6	<0.1	0.2
m,p-xylene	19.0	0.2	0.5	0.3
o-xylene	14.0	0.3	0.2	0.1
Nonane	69.0	0.1	0.3	0.1
Isopropylbenzene	2.4	<0.1	<0.1	<0.1
Propylbenzene	2.1	ND	<0.1	<0.1
Naphthalene	ND	ND	ND	ND

a) $\overline{X}$ = Mean value
b) ND = Not detected
c) NR = Not reported

Table 4-3

REPRESENTATIVE LIST OF ORGANIC COMPOUNDS IDENTIFIED IN LANDFILL GAS

Pentane
Dichloromethane
Hexane
Iso-octane
Methylbenzene
Tetrachloroethene
Ethylbenzene
Nonane
Propylbenzene
Tetramethylhexane
Methylpentane
Dimethylpentane
Methylhexane
Heptane
Trimethylcyclopentane
Dimethylhexane
Dimethylcyclohexane
Octane
Dimethylhexene
Dimethylcyclohexane
Trimethylcyclohexane
Cyclohexyl-eicosane
Ethylpentene
Ethylmethylbutene
Tetramethylpentane
Diethylcyclohexane
Tetramethylbutane
Methylnonene
Tetramethylcyclopentane
Ethylmethylcyclohexane
Methylpropylpentanol
Dichlorofluoromethane
Heptanol
Decane
Decahydronaphthalene
Dichloroethene
Dichloroethane
Benzene
Trichloroethene
Trichloroethane
Chlorobenzene
Dimethylbenzene
Isopropylbenzene
Naphthalene
Methylpentylhydroperoxide
Methylcyclopentane
Hexene
Dimethylcyclopentane
Cycloheptane
Tetrahydrodimethylfuran
Methylheptane
Ethylmethylcyclopentane
Tetramethylcyclopentane
Dimethylheptane
Ethylcyclohexane
Ethylmethylcyclohexane
Methylpropylpentanol
Iso-octanol
Octahydromethylpentalene
Dimethyl(methylpropyl)cyclohexane
Ethylmethylheptane
Methylene-butanediol
Tetramethylhexene
Methylpropylpentanol
Nonyne
Methyl(methylethenyl)-cyclohexene
Hexadiene
Ethylbutanol
Butylcyclohexane

limit the ability to make isomer-specific identifications with the analytical procedures used in this study. The data collected by the two laboratories suggest excellent agreement regarding the qualitative presence of environmentally significant compounds in landfill gas.

4.1.4 Results of Quantitative Analyses of Gas Samples

Introduction. Quantitative volatile organic compound analysis was accomplished for the 20 target compounds listed in Table 4-4. Vinyl chloride was not generally detected using the described procedures, although it has been reported by others in compound-specific analyses performed at many landfill sites. Tenax adsorbent resin does not efficiently trap vinyl chloride in gas samples collected in the field. A vinyl chloride analysis using an adsorbent trapping material such as Carbopak C/0.19% picric acid or gas cylinder should be examined in order to develop a compound-specific method.

The quantitative data were reviewed and submitted to statistical analysis (e.g. minimum and maximum values, mean, standard deviation, number of observations) using the "Statistical Analysis System" (SAS Institute, Inc.) provided by ANL. This software package consists of a data-base management system and associated statistical software that is used to analyze subsets of a data base.

Table 4-5 summarizes and compares the average VOC concentrations to the reported Threshold Limit Values (American Conference of Governmental Industrial Hygenists, Inc., 1982) for the twenty target VOC's. The data show that the average concentrations of trace VOC's in processed landfill gas are one to two orders of magnitude below the TLV's of significant health hazards. The general trend of the data shows a reduction in trace VOC concentrations from inlet gas to

Table 4-4

TARGET COMPOUNDS
QUANTIFIED IN VOC ANALYSIS

Pentane
1,1-dichloroethylene
Dichloromethane
1,2-dichloroethylene
1,1-dichloroethane

1,1,2-trichloroethane
Tetrachloroethene
Chlorobenzene
Ethylbenzene
m,p-xylene

Hexane
Benzene
Iso-octane
Trichloroethene
Methylbenzene

o-xylene
Nonane
Isopropylbenzene
Propylbenzene
Naphthalene

Table 4-5

SUMMARY OF AVERAGE VOC CONCENTRATIONS AND THRESHHOLD LIMIT VALUES

(Volume parts per million)

Compound	Inlet	Product[a]	Surface	TLV[b]	STEL[c]
Pentane	0.4	0.8	0.3	600	750
1,1-dichloroethylene	0.1	0.2	<0.01	5	20
Dichloromethane	0.9	0.6	0.2	100	500
1,2-dichloroethylene	0.7	0.8	0.2	200	250
1,1-dichloroethane	0.4	0.2	0.3	200	250
Hexane	1.8	8.3	0.3	50	NR[e]
Benzene	1.7	0.7	0.3	10	25
Iso-octane	0.4	0.7	1.0	300	375
Trichloroethene	0.8	0.7	1.0	NR	NR
Methylbenzene	9.6	2.9	0.3	100	150
1,1,2-trichloroethane	<0.01	<0.01	ND[d]	10	20
Tetrachloroethene	1.3	0.8	0.3	NR	NR
Chlorobenzene	0.4	0.1	ND	75	NR
Ethylbenzene	3.0	1.1	0.2	100	125
m,p-xylene	3.7	1.2	0.8	100	150
o-xylene	1.3	0.4	0.1	100	150
Nonane	0.9	0.7	0.2	200	250
Isopropylbenzene	0.7	0.5	<0.01	50	75
Propylbenzene	0.1	0.2	<0.01	NR	NR
Naphthalene	<0.01	<0.01	ND	10	15

a) Including a high - and medium - Btu gas

b) Threshhold Limit Value - American Conference of Governmental Industrial Hygenists, Inc., (ACGIH), 1982

c) Short Term Exposure Limit - ACGIH, 1982

d) ND = not detected

e) NR = not reported

product gas and to surface gas. Minor variations from this general trend are probably due to constituent concentration resulting from the removal of carbon dioxide (i.e. reducing the volume of the gas), by reactions occurring during gas processing, or other unknown factors.

Results of Inlet Gas Analyses. Results of quantitative analysis indicate that inlet gas exhibits higher concentrations of target VOC's than does product and surface gas. A total of 75 samples of inlet gas were analyzed. The data obtained from these analyses are shown in Table 4-6. The maximum concentration levels of aromatic hydrocarbons (benzene and methylbenzene) range from 23 (1.7 Vppm mean value) to 210 Vppm (9.6 Vppm mean value) respectively. Maximum values for chlorinated hydrocarbons range from 1.1 (0.1 Vppm mean value) to 12.0 Vppm (0.9 Vppm mean value).

Results of Product Gas Analyses. A total of 68 product gas samples were analyzed for the target VOC's. Table 4-7 presents the summary data from these analyses. The maximum concentration levels of aromatic hydrocarbons (benzene and methylbenzene) range from 5.2 (0.7 Vppm mean value) to 53 Vppm (2.9 Vppm mean value); maximum values for chlorinated hydrocarbons range from 0.9 (0.1 Vppm mean value) to 10.0 Vppm (0.8 Vppm mean value).

The selection of LMR facilities for this study offered the opportunity to evaluate both highly and moderately processed landfill gas. Highly processed gas is defined as that gas which has been processed to remove both water and carbon dioxide. Moderately processed landfill gas is defined as that gas which has undergone only moderate, if any processing; in essence, only water is removed from the inlet gas.

The data presented in Table 4-8 show the maximum and mean values of target VOC's found in highly processed gas. Table 4-9 shows the

Table 4-6

DATA SUMMARY FOR VOLATILE ORGANIC COMPOUND ANALYSIS OF INLET GAS

(Volume parts per million)

Compound	Observations	Maximum Value	Mean Value	Standard Deviation
Pentane	59	5.0	0.4	1.2
1,1-dichloroethylene	75	1.1	0.1	0.3
Dichloromethane	74	12.0	0.9	1.7
1,2-dichloroethylene	68	3.6	0.7	1.0
1,1-dichloroethane	75	7.5	0.4	1.2
Hexane	74	28.0	1.8	4.9
Benzene	75	23.0	1.7	4.1
Iso-octane	69	4.1	0.4	0.8
Trichloroethene	75	8.1	0.8	1.8
Methylbenzene	75	210.0	9.6	29.2
1,1,2-trichloroethane	75	0.1	<0.01	0.0
Tetrachloroethene	75	35.0	1.3	4.2
Chlorobenzene	75	11.0	0.4	1.6
Ethylbenzene	75	54.0	3.0	10.1
m,p-xylene	75	91.0	3.7	13.5
o-xylene	75	25.0	1.3	4.0
Nonane	74	12.0	0.9	2.4
Isopropylbenzene	74	28.0	0.7	3.5
Propylbenzene	75	3.5	0.1	0.4
Naphthalene	75	0.1	<0.01	0.0

Table 4-7

SUMMARY DATA FOR QUANTITATIVE VOLATILE ORGANIC COMPOUND ANALYSIS OF PRODUCT GAS

(Volume parts per million)

Compound	Observations	Maximum Value	Mean Value	Standard Deviation
Pentane	50	8.1	0.8	2.0
1,1-dichloroethylene	67	0.9	0.2	0.3
Dichloromethane	66	3.8	0.6	0.9
1,2-dichloroethylene	60	4.3	0.8	1.2
1,1-dichloroethane	68	2.9	0.2	0.6
Hexane	64	62.0	3.3	9.1
Benzene	68	5.2	0.7	1.0
Iso-octane	63	3.7	0.5	0.9
Trichloroethene	68	10.0	0.7	1.7
Methylbenzene	67	53.0	2.9	8.2
1,1,2-trichloroethane	68	0.1	<0.01	0.0
Tetrachloroethene	68	7.9	0.8	1.7
Chlorobenzene	68	4.1	0.1	0.5
Ethylbenzene	67	12.7	1.1	2.6
m,p-xylene	68	11.2	1.2	2.2
o-xylene	60	8.0	0.4	1.1
Nonane	60	4.7	0.7	1.1
Isopropylbenzene	60	9.4	0.5	1.6
Propylbenzene	67	2.3	0.2	0.5
Naphthalene	68	1.1	<0.01	0.2

Table 4-8

RESULTS OF VOLATILE ORGANIC COMPOUND ANALYSIS

FOR HIGHLY PROCESSED GAS

(Volume parts per million)

Compound	Observations	Maximum Value	Mean Value	Standard Deviation
Pentane	33	0.3	<0.01	0.0
1,1-dichloroethylene	46	1.0	0.1	0.3
Dichloromethane	47	2.8	0.5	0.7
1,2-dichloroethylene	46	3.6	0.6	0.9
1,1-dichloroethane	47	1.8	0.1	0.3
Hexane	44	62.0	3.6	10.7
Benzene	47	5.2	0.5	1.0
Iso-octane	46	2.7	0.4	0.7
Trichloroethene	47	2.6	0.3	0.5
Methylbenzene	47	20.0	0.9	3.0
1,1,2-trichloroethane	47	0.1	<0.01	0.0
Tetrachloroethene	47	4.5	0.3	0.8
Chlorobenzene	47	0.1	<0.01	0.0
Ethylbenzene	46	1.4	0.2	0.3
m,p-xylene	47	5.7	0.4	0.9
o-xylene	47	1.5	0.1	0.3
Nonane	47	4.7	0.4	0.9
Isopropylbenzene	47	0.2	<0.01	0.0
Propylbenzene	46	0.8	<0.01	0.1
Naphthalene	47	0.1	<0.01	0.0

Table 4-9

RESULTS OF VOLATILE ORGANIC COMPOUND ANALYSIS

FOR MODERATELY PROCESSED GAS

(Volume parts per million)

Compound	Observations	Maximum Value	Mean Value	Standard Deviation
Pentane	13	8.1	1.7	3.2
1,1-dichloroethylene	17	0.9	0.3	0.3
Dichloromethane	15	3.8	1.1	1.2
1,2-dichloroethylene	14	4.3	1.5	1.7
1,1-dichloroethane	17	3.0	0.6	0.9
Hexane	16	15.0	3.1	4.2
Benzene	17	3.0	1.3	1.0
Iso-octane	14	3.7	1.2	1.4
Trichloroethene	17	10.0	1.9	3.0
Methylbenzene	16	53.0	8.5	16.4
1,1,2-trichloroethane	17	ND[a]	ND	0.0
Tetrachloroethene	17	7.9	2.0	2.8
Chlorobenzene	17	4.1	0.5	1.0
Ethylbenzene	17	12.7	3.5	4.4
m,p-xylene	17	11.2	3.3	3.2
o-xylene	17	8.0	1.3	2.0
Nonane	17	3.7	1.4	1.4
Isopropylbenzene	17	9.4	1.7	2.9
Propylbenzene	17	2.3	0.8	0.7
Naphthalene	17	1.1	0.2	0.4

a) ND = not detected

same data for samples of moderately processed gas. A summary comparison of these two data sets, shown on Table 4-10, indicates that the VOC concentrations can be significantly reduced or, in some cases, eliminated by processing of landfill gas. Further evaluation of this data representative of different scrubber technologies is not within the scope of this program.

Results of Surface Gas Analysis. Results from surface gas sample analyses were highly variable. A total of 83 surface gas samples were analyzed. The results of the surface gas analyses are presented in Table 4-11. In many cases, these results show VOC concentrations almost equal to those observed in raw landfill gas (Table 4-5). The levels of VOC's in surface gas show that these components migrate through the landfill and that the variable concentrations observed within a landfill site may be dependent on the type of landfill cover and other unknown site-specific factors.

Results of Ambient Air Analysis. Table 4-12 presents the summary data for the analysis of ambient air samples. Only four compounds in the target compound list were observed at concentrations greater than 0.01 Vppm. Of these four compounds, dichloromethane had the highest maximum observed concentration -- 0.2 Vppm. All other average VOC concentrations in ambient air were less than 0.01 Vppm. Dichloromethane is a common laboratory solvent and the concentrations observed in these analyses may result from contamination within the two laboratories.

Results of VOC Sample Trap Archive Study. An important issue concerning sampling and analysis is the holding-time from sample collection to analysis. An experiment was designed to demonstrate the holding-time characteristics of the Tenax resin procedure used in this

Table 4-10

SUMMARY OF AVERAGE VOC CONCENTRATIONS FOR INLET GAS AND MODERATELY AND HIGHLY PROCESSED LANDFILL GAS

(Volume parts per million)

Compound	Inlet	Moderately Processed	Highly Processed
Pentane	0.4	1.7	<0.01
1,1-dichloroethylene	0.1	0.3	0.1
Dichloromethane	0.9	1.1	0.5
1,2-dichloroethylene	0.7	1.5	0.6
1,1-dichloroethane	0.4	0.6	0.1
Hexane	1.8	3.1	3.6
Benzene	1.7	1.3	0.5
Iso-octane	0.4	1.2	0.4
Trichloroethene	0.8	1.9	0.3
Methylbenzene	9.6	8.5	0.9
1,1,2-trichloroethane	<0.01	ND[a]	<0.01
Tetrachloroethene	1.3	2.0	0.3
Chlorobenzene	0.4	0.5	<0.01
Ethylbenzene	3.0	3.5	0.2
m,p-xylene	3.7	3.3	0.4
o-xylene	1.3	1.3	0.1
Nonane	0.9	1.4	0.4
Isopropylbenzene	0.7	1.7	<0.01
Propylbenzene	0.1	0.8	<0.01
Naphthalene	ND	0.2	<0.01

a) ND = not detected

Table 4-11

DATA SUMMARY FOR VOLATILE ORGANIC COMPOUND ANALYSIS OF SURFACE GAS

(Volume parts per million)

Compound	Observations	Maximum Value	Mean Value	Standard Deviation
Pentane	61	3.3	0.3	0.9
1,1-dichloroethylene	83	0.6	<0.01	0.0
Dichloromethane	83	10.0	0.2	1.1
1,2-dichloroethylene	81	1.4	0.2	0.3
1,1-dichloroethane	83	13.0	0.3	1.6
Hexane	81	8.5	0.3	1.0
Benzene	83	7.1	0.3	1.1
Iso-octane	78	1.2	<0.01	0.1
Trichloroethane	81	74.0	1.0	8.2
Methylbenzene	82	10.0	0.3	1.2
1,1,2-trichloroethene	82	ND[a]	ND	0.0
Tetrachloroethene	83	15.0	0.3	1.7
Chlorobenzene	83	0.4	<0.01	0.0
Ethylbenzene	77	9.7	0.2	1.2
m,p-xylene	78	35.0	0.8	4.4
o-xylene	83	5.2	0.1	0.6
Nonane	83	3.4	0.2	0.5
Isopropylbenzene	81	3.0	< 0.01	0.3
Propylbenzene	83	1.6	<0.01	0.2
Naphthalene	82	ND	ND	0.0

a) ND = not detected

Table 4-12

DATA SUMMARY FOR VOLATILE ORGANIC COMPOUND ANALYSIS OF AMBIENT AIR

(Volume parts per million)

Compound	Observations	Maximum Value
Pentane	29	0.1
1,1-dichloroethylene	37	ND[a]
Dichloromethane	37	0.2
1,2-dichloroethylene	37	ND
1,1-dichloroethane	36	ND
Hexane	37	ND
Benzene	37	ND
Iso-octane	37	ND
Trichloroethene	37	0.1
Methylbenzene	37	0.1
1,1,2-trichloroethane	37	ND
Tetrachloroethene	37	ND
Chlorobenzene	37	ND
Ethylbenzene	37	ND
m,p-xylene	37	ND
o-xylene	37	ND
Nonane	36	ND
Isopropylbenzene	36	ND
Propylbenzene	37	ND
Naphthalene	37	ND

a) ND = not detected

study. Criteria that affect the shelf life of gas samples following collection in the field may include:

- Reactive nature of sample matrix within the adsorbent resin trap.
- Fugitive escape of sample components from the adsorbent resin trap.
- Time dependent equilibrium shifts in adsorption/desorption characteristics.

Both SAI and ANL laboratories performed similar holding-time experiments. During the initial sampling trip a series of product gas samples were collected by both laboratories. These samples were analyzed by each of the laboratories at intervals varying from three weeks to six months following collection. The data for these archive analyses is presented in Table 4-13 and Table 4-14.

The data show excellent consistency. SAI data (Table 4-13) show that aromatic compounds, such as benzene and methylbenzene agree to within a factor of 3 to 4 for holding-time up to six months. The scatter in the holding-time data is equal to the scatter between individual samples, and is within the overall level of confidence of the quantitative analysis procedure.

Other aromatic VOC's, such as ethylbenzene and the xylenes, are more inconsistent in the concentration results obtained by both laboratories. Chlorinated compounds were observed by both laboratories at very low levels and do not provide adequate information to provide holding-time recommendations. Overall, the data suggest that extended holding-time may be acceptable when compound specific analyses of benzene and methylbenzene is desired. Since extremely low levels of chlorinated compounds were observed in these experiments, no comment on the limitations of holding time can be made regarding these

Table 4-13

RESULTS OF SAI SAMPLE TRAP HOLDING-TIME EXPERIMENTS

(Volume parts per million)

Compound	Date Analyzed			
	1/27	1/18	4/19	7/20
1,1-dichloroethylene	ND[a]	ND	ND	ND
Dichloromethane	<0.01	0.02	0.20	0.1
1,2-dichloroethene	ND	ND	ND	ND
Hexane	0.84	0.13	0.69	ND
Benzene	0.15	0.19	0.52	0.23
Methylbenzene	0.43	0.15	0.02	0.57
Tetrachloroethene	ND	0.01	<0.01	ND
Ethylbenzene	<0.01	0.21	ND	0.01
m,p-xylene	<0.01	0.25	ND	0.02
o-xylene	<0.01	0.14	ND	<0.01
Nonane	0.62	0.08	ND	0.69
Naphthalene	<0.01	ND	ND	<0.01

a) ND = not detected

Table 4-14

RESULTS OF ANL SAMPLE TRAP HOLDING-TIME EXPERIMENTS

(Volume parts per million)

Compound	Date Analyzed				
	2/12	3/1	3/24	4/17	4/16
1,1-dichloroethylene	ND[a]	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	ND	ND
Hexane	5.6	3.3	6.4	0.50	37.0
Benzene	0.73	1.0	1.4	ND	5.2
Methylbenzene	0.40	0.28	1.0	1.6	5.8
Tetrachloroethylene	ND	ND	ND	ND	ND
Ethylbenzene	ND	0.012	0.021	0.12	ND
m,p-xylene	0.55	0.066	0.069	0.43	1.4
o-xylene	0.19	0.019	0.017	0.16	0.33
Nonane	ND	0.072	0.024	0.27	1.5
Naphthalene	ND	ND	ND	ND	ND

a) ND = not detected

compounds.

Based on these experiments, it is recommended to limit holding-time to two weeks following sample collection. Additional data is required to make recommendations for the holding-time for chlorinated VOC's.

Comparison of Results from Gas Samples Collected Using Tenax Traps and Stainless Steel Cylinders. The two most accepted procedures for gas sample collection are adsorbent resins and evacuated cylinders. Two experiments were conducted to evaluate the equivalence of these two sample collection procedures. In these experiments, product gas samples were collected in stainless steel cylinders and on sample traps at 50 mL for experiment A and 175 mL for experiment B. The results of these experiments are presented in Table 4-15. The data show that the two procedures are generally qualitatively equivalent and are quantitatively equivalent within an order-of-magnitude.

For ambient air samples, the sample volume on adsorbent resin traps must be 500 to 700 mL -- the GC/MS is not sensitive enough to analyze concentrations of compounds found in this study utilizing a 1 mL air sample from a cylinder. The use of Tenax sampling traps provides for concentration of a sampled gas stream, thereby adjusting the sample volume for limitations in instrument sensitivity.

4.2 RESULTS OF MERCURY ANALYSES

A total of 164 mercury samples were analyzed during this study. The results (Table 4-16) indicate that, at the sites tested, mercury is not present in raw or treated gas in environmentally significant amounts. Mercury concentrations observed in this study are very low, especially compared to the "Threshold Limit Value" (American

Table 4-15

RESULTS OF THE SAI COMPARISON OF STAINLESS STEEL CYLINDER AND TENAX GC/SILICA GEL ADSORBENT RESIN GAS SAMPLE COLLECTION PROCEDURES

(Volume parts per million)

	Experiment A		Experiment B	
Compound	Cylinder	Adsorbent Resin	Cylinder	Adsorbent Resin
1,1-dichloroethylene				
1,1-dichloroethane	1.6	2.0	ND[a]	ND
Hexane	ND	2.9	4.4	1.34
Benzene	2.0	2.2	0.72	0.30
Trichloroethene	22.9	2.1	ND	ND
Methylbenzene	112.0	10.7	0.29	0.71
1,1,2-trichloroethane	ND	ND	ND	ND
Tetrachloroethene	36.3	3.6	ND	ND
Chlorobenzene	1.3	1.9	ND	ND
Ethylbenzene	48.4	9.2	0.01	0.05
m,p-xylene	96.2	4.5	0.06	0.06
o-xylene	28.3	9.4	ND	0.01
Isopropylbenzene	6.0	3.0	ND	<0.01

a) ND = not detected

Table 4-16

CONCENTRATIONS OF TOTAL MERCURY

(Volume parts per million)

	SAI		ANL		BOTH	
	Range	Average	Range	Average	Range	Average
Inlet	.0000007-.00023	.000044	.000001-.000879	.000253	.0000007-.000879	.000134
Product	.0000007-.00027	.000029	.000005-.000501	.000099	.0000007-.000501	.000057
Surface	.0000007-.00019	.000021	.000001-.00013	.000052	.0000007-.00019	.000037
Air	.0000003-.0001	.000002	.000001-.00016	.000031	.0000003-.00016	.000015

Conference of Governmental Industrial Hygenists, 1982) of 0.1 mg per meter^3 (11.1×10^{-3} Vppm) and 0.05 mg/m^3 (5.6×10^{-3} Vppm) for inorganic mercury and mercury vapor respectively. The average values for mercury concentrations range from 0.000134 Vppm for inlet gas to 0.000037 Vppm for gas sampled at the landfill surface. The average concentration of mercury in ambient air at the sites tested was 0.000015 Vppm.

The data presented in Table 4-16 show the range and average mercury concentrations for samples of inlet gas, product gas, surface gas, and ambient air. The data are presented separately by laboratory and for both laboratories grouped together. A single high mercury concentration of 0.0028 Vppm was observed by SAI at a product gas sampling location. This data point seems to be uncharacteristically high, especially since both laboratories did not record any other similarly high values. In addition, the ANL results for the same sampling event did not reflect a similar elevated concentration. Therefore, statistical summaries omit this data point.

4.3 RESULTS OF BACTERIA AND VIRUS ANALYSIS

Initially, a trial of two potential sampling procedures was conducted at a LMR facility to evaluate the efficiency of recovery of microorganisms from landfill gas. The two techniques tested were the cyclone scrubber and the all glass impinger (AGI) system. The data are shown in Table 4-17 (sample numbers 1-3). No indicator bacteria or human enteric viruses were recovered using either procedure in the three samples. The sample volume for the AGI samples is a fraction of that which was collected with the cyclone. Fannin and Vana (1982) compared several viable microbial air samplers. They reported that the efficiency of the cyclone scrubber compared to the AGI is 152% for

Table 4-17

LEVELS OF INDICATOR BACTERIA AND HUMAN ENTERIC VIRUSES IN GAS COLLECTED AT LANDFILLS

					Indicator Bacteria		Human Enteric Virus	
		Gas Temp. °F	Gas. Vol. (m^3)	Total Coliform (MPN/m^3)[a]	Fecal Coliform (MPN/m^3)	Fecal Streptococci ($\#/m^3$)	Plaques Observed	(PFU/m^3)[b]
1.	Outlet	92	4.8	<2.8[c]	<2.8	<2.8	0	<0.2
2.	AG1 inlet	92	0.85	<2.5	<2.5	<2.5	0	<1.2
3.	AG1 outlet	92	0.85	<0.8	<2.5	<2.5	0	<1.2
4.	Inlet	92	31.5	<0.8	<0.8	<0.8	0	<0.03
5.	Outlet	92	27.3	<0.3	<0.3	<0.3	0	<0.04
6.	Outlet	74	13.9	<2.4	<2.4	<2.4	0	<0.07
7.	Inlet	74	32.8	<1.3	<1.3	<1.3	0	<0.03
8.	Outlet	70	20.6	<1.6	<1.6	<1.6	0	<0.05
9.	Inlet	70	28.8	<1.1	<1.1	<1.1	0	<0.04
10.	Outlet	70	17.9	NR[d]	NR	NR	0	<0.06

a) MPN = Most Probable Number (Standard Methods, 1980)

b) PFU = Plaque Forming Units (Standard Methods, 1980)

c) < = Less than - The number indicates the lower sensitivity limit for the assay given the volume sampled. No microorganisms were detected.

d) NR = not reported, data lost due to incubator malfunction.

spores of Bacillus subtilis var. niger, 150% for Serratia marcescens, 176% for f2 bacterial virus, and 192% for polio virus type 1. The cyclone scrubber was chosen for sample collection based on: (1) the preliminary trial, which demonstrated that the cyclone scrubber was a manageable system in the field; (2) the relative efficiency reported by Fannin and Vana; and (3) the larger sample volume.

The levels of indicator bacteria and human enteric viruses found in inlet and product landfill gas samples collected with the cyclone scrubber are shown in Table 4-17 (samples 4-10). No indicator bacteria or human enteric viruses were recovered in any of the samples. The data are reported as "less-than" a given number and indicate the lower sensitivity limit for the microbiological assay, given the volume of gas sampled. No pathogenic microorganisms were detected.

The landfill gas samples contained significant amounts of moisture. In a methane recovery plant, moisture in the raw landfill gas is collected in condensate traps prior to the gas compression stage. Samples of this condensate were collected from the condensate trap, since this would be a likely point where microorganisms in the landfill gas would accumulate. Table 4-18 shows the levels of indicator bacteria and human enteric viruses in the condensate. Low levels of total coliforms were found in four of five condensate samples (two samples were lost). One sample contained less than 2400 coliform per 100 mL. None of the coliforms recovered were fecal coliforms. Low levels of fecal streptococci were found in one of four samples.

The low level presence of fecal-contamination indicators in the landfill condensate was not unexpected. Tables 4-19 and 4-20 show the geometric mean levels of indicator bacteria in surface streams and storm runoff collected in Baltimore. Surface waters and streams in

Table 4-18

LEVELS OF INDICATOR BACTERIA AND HUMAN ENTERIC VIRUS IN LANDFILL GAS CONDENSATE

Initial pH	Total Coliform (MPN/100 mL)[a]	Indicator Bacteria		Human Enteric Virus		
		Fecal Coliform (MPN/100 mL)	Fecal Streptococci (#/1-- mL)	Liters Processed (L)	Plaques Observed	(PFU/m^3)[b]
6.5	90	NR[c]	NR	16	0	<0.06
3.5	<2.2[d]	<2.2	<2.2	8	0	<0.12
6.5	4	<2.2	<2.2	1	0	<1.0
6.5	NR	NR	NR	8	0	<0.12
-	NR	NR	NR	8	0	<0.12
-	<2400	<2.2	<2.2	1	0	<1.0
4.5	120	<2.2	<2.2	8	0	<0.12

a) MPN = Most Probable Number (Standard Methods, 1980)

b) PFU = Plaque Forming Units (Standard Methods, 1980)

c) NR = not reported, data lost due to incubator malfunction.

d) < = Less than - The number indicates the lower sensitivity limit for the assay given the volum sampled. No microorganisms were detected.

Table 4-19

GEOMETRIC MEAN DENSITIES OF SELECTED PATHOGENS AND INDICATOR MICROORGANISMS IN BACKGROUND SAMPLES COLLECTED IN BALTIMORE

	Raw Sewage	Herring Run	Jones Falls	Gwynns Falls	Lock Raven
Enterovirus (PFU/10L)[a]	8.7×10^{2}	2.8×10^{1}	6.0×10^{1}	1.3×10^{1}	5.9×10^{1}
Salmonella sp. (MPN/10L)[b]	5.0×10^{2}	$.46\times10^{1}$	$.91\times10^{1}$	1.5×10^{1}	ND[c]
P. aeruginosa (MPN/100 mL)	2.3×10^{5}	2.9×10^{2}	2.1×10^{3}	4.7×10^{2}	$.31\times10^{1}$
Staph. aureus (MPN/100 mL)	2.6×10^{2}	$.32\times10^{1}$	$.95\times10^{1}$	$.45\times10^{1}$	$.25\times10^{1}$
Total coliform (MPN/100 mL)	2.3×10^{7}	4.8×10^{3}	4.0×10^{4}	4.0×10^{4}	2.6×10^{1}
Fecal coliform (MPN/100 mL)	6.3×10^{6}	1.1×10^{3}	1.5×10^{4}	5.9×10^{3}	1.5×10^{1}
Fecal strep. (#/100 mL)	1.2×10^{6}	1.6×10^{3}	1.6×10^{4}	1.7×10^{3}	1.0×10^{1}
Enterococci (#/100 mL)	5.4×10^{5}	5.9×10^{2}	4.9×10^{3}	8.9×10^{2}	$.2\times10^{1}$

a) PFU = Plaque Forming Units (Standard Methods, 1980)

b) MPN = Most Probable Number (Standard Methods, 1980)

c) ND = not detected

Table 4-20

GEOMETRIC MEAN DENSITIES OF SELECTED PATHOGENS AND INDICATOR MICROORGANISMS IN STORMWATER SAMPLES COLLECTED IN BALTIMORE

	Stoney Run	Glen Ave.	Howard Park	Storm Drain	Bush St.	Northwood
Enterovirus (PFU/10L)[a]	1.9×10^{2}	7.5×10^{1}	2.8×10^{2}	3.0×10^{1}	$.69\times10^{1}$	1.7×10^{2}
Salmonella sp. (MPN/10L)[b]	3.0×10^{1}	2.4×10^{1}	1.4×10^{2}	2.5×10^{1}	3.0×10^{1}	$.57\times10^{1}$
P. aeruginosa (MPN/100 mL)	1.3×10^{3}	3.3×10^{3}	5.2×10^{3}	6.6×10^{3}	2.0×10^{3}	5.9×10^{2}
Staph. aureus (MPN/100 mL)	1.2×10^{1}	1.4×10^{1}	3.6×10^{1}	4.0×10^{1}	1.2×10^{2}	1.2×10^{1}
Total coliform (MPN/100 mL)	4.8×10^{4}	2.4×10^{5}	1.2×10^{6}	2.9×10^{5}	3.8×10^{5}	3.8×10^{4}
Fecal coliform (MPN/100 mL)	1.9×10^{4}	8.1×10^{4}	4.5×10^{5}	1.2×10^{5}	8.3×10^{4}	6.9×10^{3}
Fecal strep. (MPN/100 ml)	4.1×10^{4}	6.6×10^{5}	2.4×10^{5}	2.8×10^{5}	5.6×10^{5}	5.0×10^{4}
Enterococci (#/100 mL)	1.4×10^{4}	2.1×10^{5}	5.9×10^{4}	8.7×10^{4}	1.2×10^{5}	2.1×10^{4}

a) PFU = Plaque Forming Units (Standard Methods, 1980)

b) MPN = Most Probable Number (Standard Methods, 1980) populated areas are found to almost always contain low levels of fecal indicators. Thus, the presence of low levels of fecal indicators in the gas condensates shows little adverse health implication.

No human enteric viruses were recovered from any of the condensate samples even though 1 to 16 L of sample were concentrated and assayed. Seeded experiments in JHU laboratories, where polio virus was added to surface waters and storm run-off, indicated that the recovery of viruses by the methods suggested in Standard Methods (1980) was 10% to 40%. This value was similar to other data reported in the literature.

Several factors are responsible for the absence of microorganisms in the landfill gas. Enteric pathogens, when introduced into the environment, do not generally survive. There are very few environments outside the human gastrointestinal tract where temperature, nutrients, moisture, and other conditions will allow proliferation of enteric bacteria. Human enteric viruses are obligate parasites and will not grow outside the host. Thus, any enteric pathogenic microorganisms introduced into the landfill will decrease in numbers with time. Landfills used for gas recovery are generally inactive, and extended periods of time exist (often years) between the last application of waste and the recovery of gas. During this time the microorganisms, including viruses, are dramatically reduced in numbers.

An additional consideration when evaluating the health implications of gas recovery from landfills is that the recovered gases are generally compressed at least once before utilization. During compression, the gas temperature often increases several hundred degrees Celsius. The compression stage may therefore functionally pasteurize or sterilize the gas, depending on the temperature and contact time, before use.

4.4 RESULTS OF SURFACE FLUX TESTING

Testing of the surface flux consisted of two measurements: 1) measuring the emanation of methane using the flux box, and 2) taking a sample of the surface gas using the surface gas sampling probe, and analyzing the gas sample for bulk gas components (CH_4, CO_2, N_2, O_2, H_2O). These methods are described in section 3.5.

The results from the surface flux measurements are summarized in Table 4-21. The data show that, with the exception of two measurements (B1 and B2), no significant rates of methane permeating the surface of the landfill were observed throughout the course of this study. Many of the methane concentration readings which were made were at or near the detection limit of the methanometer (0.1%). Therefore, based on the accuracy of the methanometer, the actual flux rates may be different from the observed flux by a factor of 0.5 to 2.

Flux rate values varying from 0 to 15.6 standard-cubic-feet per square-foot per day ($scf/ft^2/day$) were observed. If the two high flux rate values (14.8 and 15.6 $scf/ft^2/day$) are omitted, then the range of observed flux rate values changes to from 0 to 0.28 $scf/ft^2/day$. The flux rate data reported in this study can be compared to similar surface gas flux data reported by other investigators (Cagliostro and Gargano,1979 and Kunz and Lu,1980). Methane venting rates have been observed in other studies, ranging from 0 to 6.6 $scf/ft^2/day$ and averaging from 0.4 to 0.8 $scf/ft^2/day$.

Two occurrences (sites B4 and B7) of relatively high methane concentrations in surface gas samples showed no corresponding increase in flux rate. At these sites, the soil cover was much thinner than at

Table 4-21

SURFACE FLUX DATA

Site	Methane Flux-rate scf/ft^2 day	Surface Gas Vol %				
		CH_4	CO_2	N_2	O_2	H_2O
A-1	0.07	0.02	0.04	77.5	20.5	0.7
2	0.05	-	-	-	-	-
3	0.06	0.2	0.6	77.4	20.3	0.8
B-1	14.8	22.2	14.7	48.3	13.0	1.1
2	15.6	-	-	-	-	-
B-3	ND[a]	0.07	1.0	76.1	20.2	1-1
4	0.03	8.8	15.6	64.6	10.1	0.1
5	ND	0.3	0.7	77.1	20.8	0.2
6	0.6	0.8	0.3	77.3	20.4	0.3
7	0.05	6.8	4.6	69.1	18.4	0.3
C-1	0.08	0.02	0.07	77.5	20.9	0.6
2	0.03	0.03	0.1	77.6	20.8	0.6
3	ND	0.02	0.3	77.4	20.6	0.8
D-1	ND	-	-	-	-	-
2	ND	-	-	-	-	-
3	ND	-	-	-	-	-
4	0.08	-	-	-	-	-
5	0.20	-	-	-	-	-
6	0.12	0.07	1.0	78.3	19.5	0.2
7	0.05	-	-	-	-	-
8	ND	-	-	-	-	-
9	0.20	-	-	-	-	-
10	0.10	0.03	0.2	77.4	20.5	1.0
11	0.10	0.01	0.2	77.6	21.0	0.3
12	0.20	-	-	-	-	-
13	0.10	-	-	-	-	-
14	0.0	-	-	-	-	-
15	ND	-	-	-	-	-
16	0.16	0.04	0.2	77.7	21.0	0.3
17	0.20	-	-	-	-	-
18	0.20	-	-	-	-	-
AIR 1		<0.05	0.06	77.7	21.0	0.3
2		<0.04	0.2	78.0	20.6	0.2
3		<0.02	0.2	78.0	20.6	0.2

a) ND = not detected

the other sites. The sampler may have penetrated the cover, and taken a sample from the upper layer of refuse.

Two incidents of high flux-rate (B1 and B2) were recorded one day after a heavy rainfall (4 to 5 cm); three surface flux readings were taken that day (B1, B2, and B3). The high readings were taken over puddles where gas bubbles were seen emanating from 0.6 to 2.5 cm fissures in the landfill surface. The reading where no flux was measured was taken near the area of puddles, but not directly over water.

The results of the flux rate testing are inconclusive for characterizing the rate of gas flux through the landfill surface. Additional instrumentation, protocol development, and controlled testing is necessary to properly measure the characteristic rate of gas emanation at the landfill surface.

5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 CONCLUSIONS

This research study has addressed a number of elements of interest to GRI, DOE, and the LMR industry. Analyses of VOC's, volatile mercury, and microorganisms have been conducted on samples collected from methane recovery systems representing high and moderate landfill gas processing. Surface flux measurements have also been made.

Based on this study, the following general conclusions are made:

VOC Analyses

Implementing the technology necessary to sample and accurately analyze VOC's from methane recovery systems can be accomplished. Implementation requires considerable time, experience and computer data processing capabilities.

Qualitative analytical results obtained from the two laboratories indicate consistent identification of volatile components. There was consistent agreement in these analyses for environmentally significant target compounds and for compounds not included on the EPA "priority pollutant" list.

Quantitative analytical results have established a characteristic range of trace VOC concentrations in raw landfill gas, product gas, surface gas, and ambient air.

Quantitative results indicate ranges in VOC concentrations up to an order-of-magnitude. Further protocol development to include compound-specific data applicable to regulatory criteria may be indicated.

The observed average values of VOC concentrations for processed landfill gas are up to 2 orders of magnitude below the TLV; and 1/2 to 1 order of magnitude below the TLV for raw gas.

Mercury Analysis.

The observed average values of mercury in the landfill gas are two to three orders-of-magnitude less than the TLV. Therefore, mercury in processed landfill gas should not be considered as a major impediment to the development of the LMR industry.

Bacteria and Virus Analyses

Samples of raw and processed landfill gas and condensate from the raw gas were analyzed for bacteria and viral content. No human enteric viruses were recovered from any samples. Indicator bacteria were not recovered from the gas samples and low levels of total coliform and fecal streptococci were found in some condensate samples. No fecal coliforms were detected. The data indicate that the risk of transmission of enteric diseases from landfill gas is very low and should not hinder the development of this resource.

Surface Flux Analyses

Data collected in this study on flux rates of gas emanating from the landfill surface is inconclusive. The rate of gas emanation from a landfill surface is dependent on many variables. A complete study of these variables is crucial but not within the scope of this study. Surface flux rates combined with other landfill gas data can yield important mass balance information on landfill gas generation, migration and control.

The major goals of the program have been met. Within the limits of the applied sampling and analysis techniques, the trace VOC's inherent in landfill gas have been identified and quantified, and protocols have been developed and documented. As in any research program, the results suggest questions that should be addressed by future studies.

5.2 RECOMMENDATIONS FOR FUTURE RESEARCH

5.2.1 Mass Balance Studies

The surface flux measurements and bulk surface gas measurements performed in this program were undertaken as a preliminary study. The flux box information derived during this research program indicates that there are measurable emissions of gas from the landfill surface. Extremely low levels of methane were detected using the methanometer and flux box apparatus. Whether the methane that was detected is representative in composition of trace components of gas at the wellhead is unknown. Additional research is indicated to establish how landfill gas recovery mitigates surface emissions and whether the emissions originating from the landfill are comparable in trace compound composition to raw landfill gas. This research is especially important in regard to odoriferous and reactive hydrocarbon components in landfill gas.

The following areas of research are suggested:

- Evaluation of the various techniques for obtaining surface flux measurements.
- Testing of the surface flux and bulk gas composition of a landfill during periods when the recovery plant is both operational and shut-down.
- Determination of the variations in trace VOC's at the wellhead and landfill surface.
- Evaluation of the difference between the surface flux with and without landfill cover.

5.2.2 Laboratory Analysis

This study has verified the suspected wide compositional range of trace VOC's in landfill gas. It is uncertain to what degree variations in test results are based on the natural composition of the gas, or on the accuracy of the analytical techniques. Two alternative bench scale testing programs and a field sampling/testing program are proposed to examine this problem:

- Testing of a known complex mixture of gases in the laboratory.
- Repetitive testing of a single sample of landfill gas.
- Continuous sampling and testing of a single landfill gas stream.

Laboratory Bench Scale Analyses. The results of the VOC analyses performed in this study indicate a broad range and concentration of VOC's. The limited scope of this program did not provide the opportunity to address the reasons for this variability. Based on the results presented in this study, it is reasonable to assume that the composition of trace compounds in landfill gas do not result in a homogeneous gas stream to the methane recovery system. This assumption should be tested by performing a series of experiments. A more detailed knowledge of constituent levels in landfill gas may help to: (1) determine how well landfill operations meet current regulations, and (2) evaluate realistic and credible regulations for landfill gas recovery.

- Bench-scale experiments involving sampling and analysis of a known complex gas stream and a single sample of landfill gas are required to establish the validity of the method.
- Spike and recovery experiments, can be used to establish the quantitative limits of the analytical protocol.

Field Analyses. This study developed a nationwide survey of nine landfill gas recovery sites. As expected, a wide variation in the gas composition was observed. Based upon this observation, confirmatory field sampling and analysis, designed to determine the homogeneity of landfill gas trace composition, involving repetitive sampling of a single landfill source (both inlet and product gas) is necessary.

5.2.3 Additional Protocol Development

Additional development of analytical procedures is required before protocols can be used as an industry standard for determinations of more precise VOC levels in landfill gas.

The Tenax sampling procedure employed for analysis of landfill gas VOC's was adopted for this study because of its capability to efficiently collect a broad range of EPA target VOC constituents and to confirm their concentration within an order-of-magnitude. The final decision for adoption of any procedure should hinge upon the intent of the results. Sampling for a specific trace volatile components in the gas might use the stainless steel or glass cylinder sampling technique. Also, GC/MS might be replaced by the gas chromatography electron capture or photoionization detection analysis, if specific compound results are mandatory. These techniques would provide less overall information, but might be more suitable for meeting special regulatory requirements.

5.2.4 Additional Areas of Research

A number of additional research areas were recognized during the course of this study, they include:

Instrumentation

- Develop, test, and validate an accurate field technique to collect and determine hydrogen sulfide and vinyl chloride in landfill gas.
- Evaluate the variation of the major components of a single landfill gas recovery stream.

Statistical Data Analysis

- The study developed a data base that contains nearly ten thousand data entries. This data base could be combined with other data, and complete statistical analysis (which was not within the scope of this program), could be undertaken as a separate study.

Mass Balance

- Develop an engineering model and testing program for mass balance evaluations at active landfill gas recovery sites.
- Determine and develop the necessary instrumentation to ascertain the bulk mass movement of gas within and out of a landfill for specific compounds such as: hydrogen sulfide, nitrogen, hydrocarbons and others.

APPENDIX A:

SAMPLING PROTOCOL
FOR COLLECTION OF VOLATILE ORGANIC AND VOLATILE MERCURY COMPOUNDS

SAMPLING PROTOCOL
FOR COLLECTION OF VOLATILE ORGANIC AND VOLATILE MERCURY COMPOUNDS

1. SCOPE AND APPLICATION

1.1 The methods described herein are for collection of samples for volatile organic compound (VOC) and volatile mercury analysis. The methods are designed to meet the present and future monitoring requirements of landfill gas producing industries, the Gas Research Institute, State and Federal regulatory agencies, and independent analytical laboratories.

1.2 These methods are based on field sampling experience and represent proven procedures which obtain the best possible adsorbent resin and cylinder collected samples for laboratory analysis of VOC's and volatile mercury.

1.3 The methods described specify:

<u>Tenax-GC Adsorbent Resin Stainless Steel Columns</u> (2-mm I.D. x 25-cm length). Packed with 80-mg of Tenax-GC (60-80 mesh) and 20-mg of Silica Gel (60-80 mesh).

<u>Evacuated Stainless Steel Cylinders</u>. Either 300- or 500-cc (cubic centimeter) volume, double ended with valves. These cylinders are made from seamless 304 stainless steel.

<u>Quartz Bead Columns</u> (4-mm i.d. x 130-mm length). Quartz columns packed with gold coated quartz chips (30-40 mesh).

For these landfill sampling sites:

<u>Inlet Gas</u> (definition) - a sampling site located at a well head or downstream of a manifold system prior to entry into the methane recovery plant. This sampling site is generally under negative pressure when the plant is operational and under ambient or slight positive pressure when the plant is not operational.

<u>Product Gas</u> (definition) - any sampling site that is located either within the plant processing stages or at the exit of the plant.

Surface Gas (definition) - a sampling site that is located on the landfill surface. Surface samples are collected by pumping gas from 3 to 6 inches below the landfill surface with a sample collection pump.

Ambient Air (definition) - any sampling site located upwind of the methane recovery plant that is representative of ambient air.

2. EQUIPMENT

Field Sampling Module. A portable field sampling unit that is capable of running on direct or alternating current is used for collection of VOC and volatile mercury samples. The field sampling unit should be constructed to maintain constant flow for the duration of the sampling. Attachment A describes this sampling unit.

Toggle-type Shut-off Valves. These valves isolate the trap and provide accurate sampling times and volumes.

Gas Chromatography-type Bubble Flow Meter. This device is used to calibrate the flow of gas through the sample traps both at set-up and during sample collection. This device is attached to a ring stand or is equipped with another self-standing support. A 10 cc flow meter is recommended for volatile organic compound sampling; a larger volume (100 cc) should be used during collection of volatile mercury samples.

Two Stage Pressure Regulator. This regulator is used when sampling pressurized gas lines. It should be constructed of stainless steel with teflon coated internal parts. It should be capable of handling pressures up to 500 psig and reducing them to less than 10 psig.

Stopwatches. Two stopwatches are required, one for recording the sample duration time and one for checking flow at initial calibration and during the sampling period.

Miscellaneous Tools and Assorted Swage-lok Fittings. A spare parts box is recommended to store the necessary fittings required for sample collection. Miscellaneous tools including screwdrivers, adjustable and open end wrenches, tubing cutters, teflon tape, etc. are required. Experience will direct the parts and tool inventory needed for specific types of sampling.

Tubing. Teflon (or Polyethylene) tubing (0.25-in. o.d.) is used to make connections between sampling ports, the sampler, and the sampling traps. Special plumbing hookups are sometimes required when taking tandem or duplicate samples. Extra tubing (20 to 30 ft.) must always be available during sampling for emergency replacement needs.

Field Notebook. A laboratory notebook is used to record all pertinent sampling data.

3. STANDARDS

3.1 Trap Preparation. Sample traps must be prepared in the laboratory prior to use in the field. Refer to the analytical protocols for trap preparation procedures.

3.2 Replicate Sampling. More than a single sample should be taken at a sampling location to insure acceptable data. Sampling with adsorbent traps results in only a single analytical opportunity in the laboratory. When a sample is desorbed, and analyzed by GC/MS (e.g. VOC analysis), or cold-vapor Atomic Absorption Spectrophotometry (e.g. volatile mercury analysis), that sample cannot be re-analyzed.

At a minimum, duplicate samples should be collected for all VOC and volatile mercury sample sites. In cases where conditions may exist such as high moisture, extremely concentrated or complex gas streams, gas stream with very low loading, etc., a triplicate sample may be necessary.

Duplicate sampling with stainless steel cylinders is not necessary. A 300- or 500-cc volume cylinder contains adequate volume to provide repetitive instrumental analysis.

3.3 Sample Volume. The size of the sample collected on adsorbent resin may be variable and depends on the component concentration at the site that is being sampled.

When sampling a previously non-sampled site, samples should be collected at various volumes. The recommended volumes are shown in Table A-1. Various sample volumes serve to provide a sample that supplies sample compound to the analytical instrument within its dynamic range.

If a site has been previously sampled, the volume of the sample that is necessary may be determined from the prior analytical results for that site.

3.4 Field Notes. A permanent log of field sampling must be maintained. The data which should be logged and a recommended format is shown in Table A-2.

PROCEDURES

4.1 Overview

4.1.1 The general sampling procedures for volatile organic compounds and volatile mercury are similar, although the size (i.e. volume) and flow rates are different.

4.1.2 A portable field sampler is used for collection of inlet and surface gas, and ambient air. It is generally not necessary to use this device when sampling product gas. Product gas is usually under pressure greater than 100 psig and can be easily sampled using the two stage stainless steel regulator described in Section 2.

4.1.3 Label and set aside a trap for VOC (Tenax) and volatile mercury (quartz) sampling calibration. These traps will be used to set the rate of gas flow through the trap at every site for the respective type of sampling.

4.1.4 Prior to sampling each site, determine the volume and number of samples to be collected. Set aside the necessary number of traps. In addition, set aside a VOC (Tenax) and volatile mercury (quartz) sample trap and label each trap "field blank". Record these traps in the notebook as such. Use a large ziplock bag to store this trap and the other traps as samples are collected. Handle all the traps in a similar manner. The Field blank will be analyzed in the laboratory.

4.2 Inlet Gas, Ambient Air and Surface Gas

4.2.1 Tenax and Quartz Traps

Select the location at which samples will be collected. Determine the type of plumbing required at each sampling site and install the necessary fittings so that the tubing can be connected. Prior to installation of the tubing, insure that all sampling connections are free of dirt and moisture. Ambient air samples should be collected in an area away from heavy vehicular traffic and dust conditions.

Leak test the sampling system.

A) Leak testing of the sampling line must be done when setting up at a new sampling location.

B) Connect the teflon tubing as shown in Figure A-1A, without a trap in place.

C) Close the toggle valve and turn on the pump.

D) Check if flow is detected by using the bubble-flow meter when the flow controller valve is fully opened.

E) If flow is detected, check the entire sampling system for leaks. Replace teflon tape or Swage-lok fittings at suspected leak points. Re-check for leaks.

F) If a "no-flow" condition is detected using the bubble-flow meter, then the system is leak free. Proceed to the calibration step.

Calibrate the trap.

A) Calibrate the flow rate when starting a sample collection series.

B) Close the toggle valve.

C) Attach the calibration trap into the sampling line. Use Teflon Swage-lok fittings with quartz traps, and stainless steel or brass Swage-lok fittings with Tenax traps.

D) Turn on the pump.

E) Open the toggle valve.

F) Calculate the flow rate by timing the rise of the bubble in the flow meter. Adjust the flow using the flow controller valve on the sampler to obtain the required flow rate. A flow rate of 25 to 30 ml/min should be used with Tenax traps, and a flow rate of 100 ml/min should be used with quartz traps. Reproduceable triplicate readings of the bubble flow meter establish calibration conditions.

G) Close the toggle valve.

H) Shut off the pump.

I) Remove the calibration trap. DO NOT CHANGE THE SETTING OF THE FLOW VALVE ON THE SAMPLING PUMP.

J) Proceed to the sampling step.

Sampling.

A) Select a sample trap, record the identification number in the notebook, and install the trap in the sampling line.

B) DO NOT CHANGE THE SETTING OF THE FLOW VALVE ON THE SAMPLING PUMP WHILE THE SERIES OF SAMPLES ARE BEING COLLECTED.

C) Determine and record the required sample volume.

D) Turn on the pump.

E) Open the toggle valve and start the stopwatch (one of two) to measure elapsed sample collection time.

F) Time the flow through the bubble flow meter using the second stopwatch.

G) Calculate the sampling time required to obtain the desired sample volume.

H) Monitor the flow using the dual range flowmeter on the sampler (if equipped) and by repetitive bubble-flow meter readings during the sampling period.

I) Shut off the toggle valve at the time determined in Step G.

J) Remove and tightly cap the trap.

K) Reset the elapsed time clock/stopwatch.

L) Repeat the above steps until all samples have been collected.

M) Shut off the pump.

4.2.2 Stainless Steel Cylinder Sample Collection

The set-up procedures for stainless steel cylinder sampling are similar to those for Tenax and quartz traps (Section 4.2.1). Inlet gas samples are collected via the vacuum pump which is used to obtain Tenax and quartz trap samples.

A) Follow leak-test procedures if necessary.

B) Set flow rate on sampling pump using flow control valve to provide a flow in excess of 100-ml/min.

C) Turn off pump.

D) Connect the gas cylinder into the sampling line as shown in Figure A-1A, using stainless steel or brass Swage-lok fittings. It is not necessary to connect the toggle valves. If these valves are in place, leave them in the open position.

E) Turn on pump.

F) Open the valves on the cylinder, SIMULTANEOUSLY.

G) Collect a sample equal to or greater than three volumes of the cylinder (3 minutes for a 300 ml cylinder, and 5 minutes for a 500-ml cylinder -- at a flow rate greater than or equal to 100-ml/min.)

H) Close the valves on the cylinder -- SIMULTANEOUSLY.

I) Turn off the pump.

J) Remove the cylinder from the sampling line and label for shipment to the laboratory.

4.3 Product Gas

4.3.1 Tenax and Quartz Traps

Select the location at which the sample will be collected.

A) Connect the sampling line as shown in Figure A-1B without a sample trap in place.

B) Close the toggle valve and adjust the two stage regulator for a final pressure of 10-psig.

C) Check if flow is detected using the bubble-flow meter.

D) If flow is detected, check the entire sampling system for leaks. Liquid Snoop can be used to identify leaks in this system. Repair leaks and re-test for leaks.

E) If no leaks are detected, proceed to the calibration step.

Calibration of gas sampling flow.

A) Calibrate the flow before starting each series of samples.

B) Close the toggle valve.

C) Attach the calibration trap. (Note: Use teflon Swage-lok fittings to connect the volatile mercury sampler.)

D) Open the two stage regulator.

E) Open the toggle valve.

F) Adjust the flow using the regulating valve so that a flow of 25 to 30 ml/min (VOC) and 100 ml/min (volatile mercury) is established.

G) Close the toggle valve.

H) Remove the calibration trap.

I) DO NOT CHANGE SETTING OF THE REGULATING VALVE.

Sampling

A) Select a sample trap and connect it into the sampling line. Record the number of the trap in the notebook.

B) Determine and record the required sample volume.

C) Open the toggle valve and start the stopwatch (one of two) to measure elapsed sampling time.

D) Calculate the flow through the bubble flow meter using the second stopwatch.

E) Calculate the time required to obtain the appropriate sample volume.

F) Shut off the toggle valve at the time determined in Step E.

G) Remove and tightly cap the sample trap and place in storage with the other traps.

H) Repeat the above steps until all samples have been collected.

4.3.2 Stainless Steel Cylinder (Product Gas)

A) Follow leak-test procedures if necessary.

B) Connect the gas cylinder into the sampling line as shown in Figure A-1B.

C) The product gas sample is collected by purging the cylinder with sample with a minimum of three cylinder volumes. The exit valve of the cylinder is closed before the inlet valve to provide a sample that has been collected under pressure.

D) Remove the cylinder from the sampling line and label for shipment to the laboratory.

4.4 Handling

All traps and sampling devices should be subject to similar handling and storage conditions.

A chain-of-custody from sample trap preparation through analysis and recycling should be established and strictly enforced. This chain-of-custody must limit the number of persons and times a trap is handled and should prevent the trap being handled in a manner where knowledge of storage/handling conditions is uncertain for extended periods of time. Wherever possible, in transit, the sampling traps should accompany the field technician on the same conveyance.

TABLE A-1

Recommended Sample Sizes

Site/Location	Type of Sample	Size (cc)
Inlet	Tenax	30, 50, 100
	Gold/Quartz Trap	8000
Outlet	Tenax	30, 50, 100
	Gold/Quartz Trap	8000
Ambient Air	Tenax	600, 200
	Gold/Quartz Trap	8000
Surface	Tenax	600, 200
	Gold/Quartz Trap	8000

TABLE A-2

Sample Field Data Format

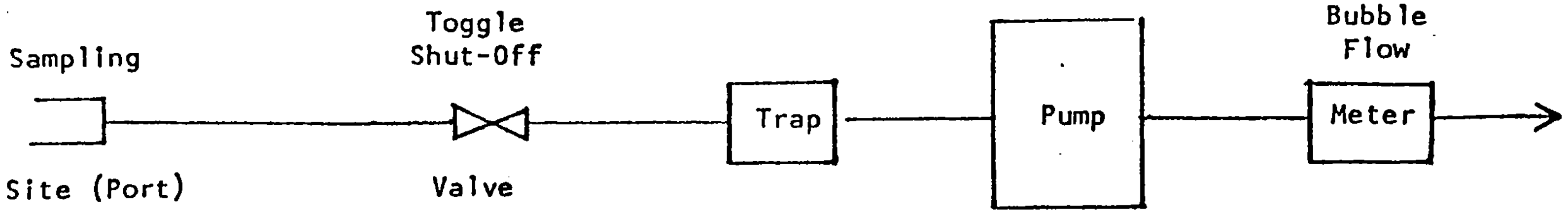
Trap No.	Elapsed Time for 10cc (sec.)	Flow Rate (mL/min)	Flow Meter Reading	Total Sample Time	Sample Volume	Sample Type Location*

* i.e., Tenax - Product, Mercury - Inlet, etc.

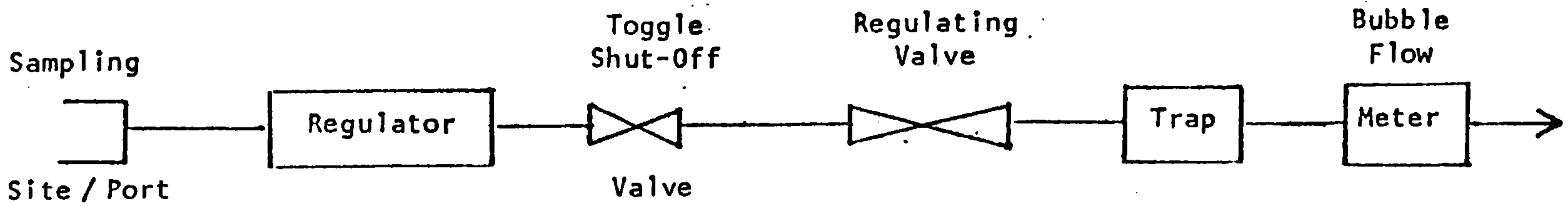
FIGURE A-1

Sampling Line Set Up

A. Inlet, Ambient, Surface



B. Product Gas



ATTACHMENT

DESCRIPTION OF FIELD SAMPLER DESIGNED FOR COLLECTING AND CONCENTRATING VAPORS FROM AMBIENT AIR AND PROCESS GAS STREAMS

A field sampler is described that enables collection and concentration of organic compound vapors onto Tenax-GC, and volatile mercury onto gold coated glass beads. The sampler is capable of operating with 110 volts AC line voltage or 12 volts DC from a vehicle battery. The sampler contains a differential flow controller, a fine metering needle valve and a dual range flowmeter for accurately achieving and maintaining the desired sampling flow rate. The flow rate is set with the fine metering needle valve and is monitored with a bubble flow meter and the in-line dual range flow meter. The power converter/charger can be used for charging a battery while AC is used to provide power. Connection to a sampling trap is via the inlet bulkhead union (1/4" tube, Swage-lok).

Schematics of the electrical and pneumatic systems of the field samples are shown on the following pages.

FIGURE A-2

ELECTRICAL DIAGRAM FOR FIELD SAMPLER

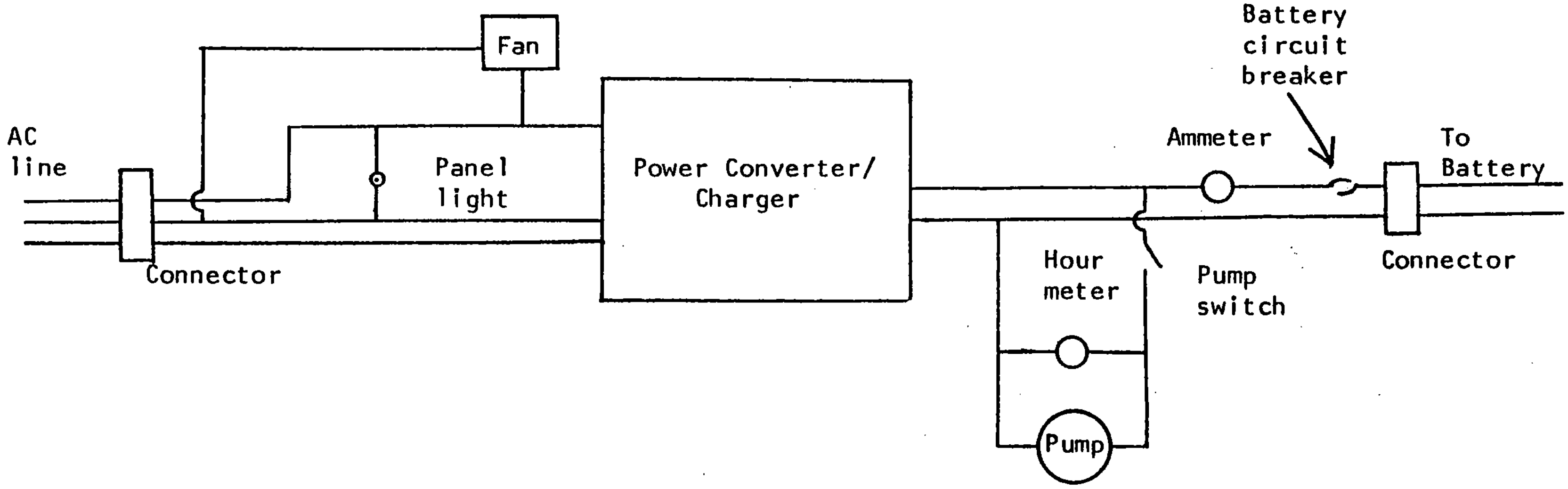


FIGURE A-3

PNEUMATIC DIAGRAM FOR FIELD SAMPLER

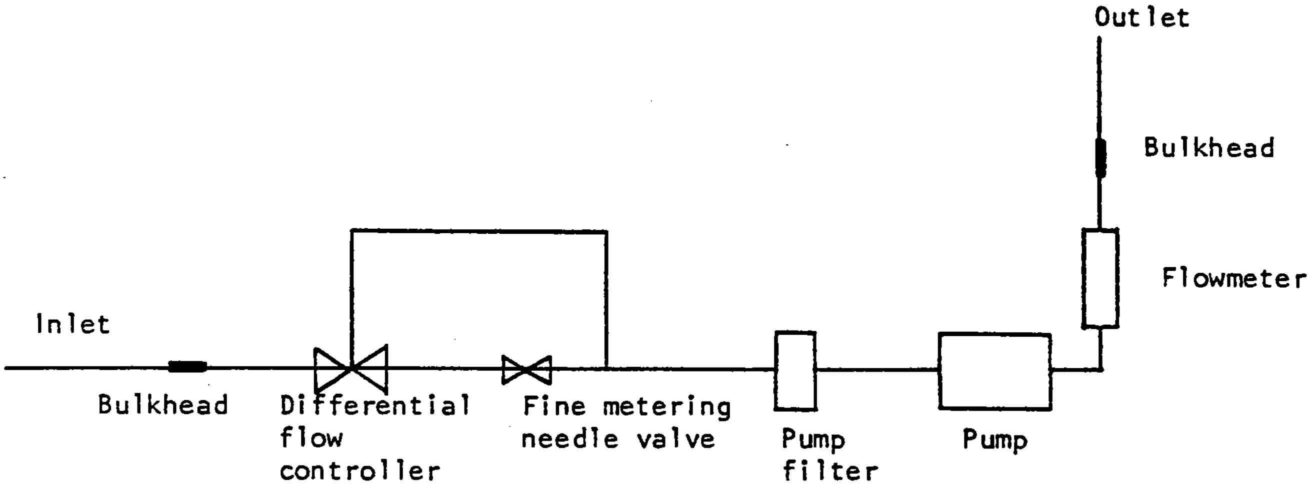
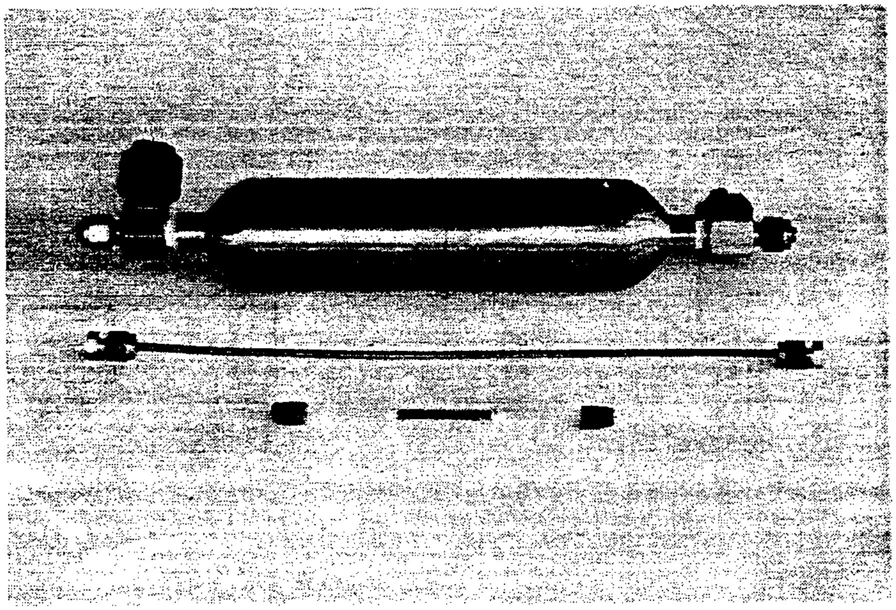


FIGURE A-4: SAMPLING TRAPS



Landfill gas sampling traps (from top to bottom): stainless steel cylinder, Tenax trap, and quartz bead trap.

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APPENDIX B:

ANALYTICAL PROTOCOL
FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

ANALYTICAL PROTOCOL
FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

1. SCOPE AND APPLICATION

1.1 This method is designed to determine volatile organic compounds (VOC) which are generally amenable to the purge and trap method (EPA Method 624). The parameters listed in Table B-1 may be determined by this method.

1.2 This method is applicable to the determination of compounds (Table B-1) in raw landfill gas, process gas, or landfill surface gas and ambient air. It is designed to meet the future monitoring requirements of gas producing industries, the Gas Research Institute, and Federal and State regulatory agencies.

1.3 The detection limit using adsorbent resin collected samples is usually dependent upon the level of interference and volume of sample collected rather than instrumental limitations. Absolute limit of detection is approximately 5 nanograns (ng) per compound at the analytical system. Samples collected in stainless steel cylinders have a detection limit of 5 ng regardless of the lower (1-10cc) GC/MS gas injection volume.

2. SUMMARY OF THE METHOD

Prior to sample analysis, the analytical system is calibrated by analyzing a standard compound mixture (see Table B-1) by the purge and trap technique. Calibration of the analytical system assumes 100% purging efficiency (see Section 9.4). This calibration procedure (purge and trap) is necessary because of the potential of even small volumes of solvent or water to form a plug in the gas chromatographic column during the desorption/cryogenic focusing step. This results in peak broadening during the chromatographic stages of the analysis.

2.1 Adsorbent Resin Collected Samples. A gas sample (raw, process, surface, or ambient air) is collected using an adsorbent

Tenax-GC/Silica gel (Tenax) trap (see Sampling Protocol for Collection of Volatile Organic Compounds). The Tenax trap is positioned in the purge and trap device (Tekmar LSC-2 or equivalent) with leak tight Swage-lok fittings. The trap is back-flushed while being rapidly heated to thermally desorb the components into the inlet of the gas chromatograph. VOC's are cryogenically focused using liquid nitrogen (LN_2), in the first loop of the capillary column, during the desorption step. Cryogenic focusing is required to maintain narrow chromatographic bands during subsequent chromatography. The components are separated via the gas chromatograph and detected by mass spectrometry. The mass spectrometer provides both qualitative and semi-quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters follow in Section 10.

2.2 Stainless Steel Cylinder Collected Samples. Inlet or product gas samples collected using stainless steel cylinders are analyzed in much the same manner as adsorbent resin collected samples. A 5-ml gas-tight luer-lok syringe is used to transfer the gas sample from the stainless steel cylinder to the gas chromatograph. During injection of the gas sample into the gas chromatograph, the first loop of the capillary column is cooled with LN_2. Cryogenic focussing is maintained throughout injection; the GC temperature program is initiated at the completion of sample injection.

3. INTERFERENCES

3.1 Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis. Method blanks are analyzed by charging the purging device with organic free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants or flow-controllers with rubber components in the purging device should be avoided.

3.2 Cross-contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross-contamination, it is recommended that a blank trap be analyzed to demonstrate that the system is free from contamination. Whenever an unusually concentrated sample is encountered it should be followed by the analysis of a blank Tenax trap to ensure a contaminant-free system for the subsequent sample.

4. APPARATUS AND MATERIALS

4.1 Purge and Trap Device. The purge and trap equipment consists of three separate pieces of apparatus (purging device, Tenax trap, heated desorber). The adsorbent trap consists of 2-mm i.d. (1/8-in o.d.) x 250-mm long stainless steel tubing packed with 80-mg of Tenax-GC (60-80 mesh) and 20-mg of Silica gel (60-80 mesh). The trap should be conditioned, after initial packing, for one hour at 210°C while being back-flushed at 20 mL/min with an inert gas. The purging device should hold 5 mL of liquid with complimentary gas lines for sparging the liquid and transfer to the Tenax trap. The heated desorber jackets the Tenax trap which is operated at 180°C for desorb and 210°C for bake-out. The complete device is available commercially from several vendors. Stainless steel cylinders are prepared for sampling by conditioning with a solution of Hexamethyldisilazane (HMDS) as recommended by the manufacturer of the solution for glassware. Evacuate the cylinder with a pump to remove any residual reagent and seal the cylinder at, or just below, ambient pressure.

4.2 Gas Chromatograph. The analytical system should contain a temperature programmable gas chromatograph with a split/splitless injector for capillary gas chromatography.

4.3 Chromatographic Column. A 30-m x 0.25-mm i.d. SE-54 or DB-5 open tubular gas chromatography column (J&W Scientific or equivalent) is recommended. Quartz capillary (fused silica) is recommended to facilitate the cryogenic focusing aspects of the analysis.

4.4 Syringes: Glass, 5-mL with Luer-lok tip.

4.5 Micro-Syringes: 10-, 25-, 100-uL (Hamilton or equivalent).

4.6 Mass Spectrometer. The mass spectrometer system should be capable to scan from mass to change ratio 20 to 285 in one-half second at 70 electron volts and produce a recognizable mass spectrum at unit resolution from 50-ng of 4-Bromofluorobenzene (4-BFB) when injected through the GC inlet. The mass spectrometer must be interfaced to a gas chromatograph. The GC/MS interface can be direct coupled, by passing the quartz capillary column through the conductance line, directly to the ion source. The GC/MS interface may utilize any configuration that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table B-1.

4.7 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic analysis. The computer system should also be equipped with mass storage devices for saving all data from GC/MS analyses. There must be computer software available to allow searching any GC/MS data file for specific ions and plotting the intensity of the ions with respect to time and scan number. The ability to integrate the area under a specific-ion plot peak is essential for quantitation.

4.8 In order to realize the advantage of capillary columns for VOC analyses, it is necessary that a portion of the column be cryogenically cooled during sample desorption from the Tenax trap or syringe injection from the stainless steel cylinder. This is done so that desorbed compounds will be trapped in a narrow band at the head of the column prior to GC analyses. This can be effectively accomplished by cooling the first coil of the column in a Dewar flask filled with LN_2. The method of cryogenic focusing must demonstrate the efficient chromatography (i.e., chromatographic peaks 4 seconds or less at peak half-height) of VOC's.

4.9 The desorption time and flow rate are somewhat dependent on the efficiency of cryogenic cooling and should be chosen to demonstrate quantitative transfer of VOC's from the Tenax trap to the capillary column without breakthrough or overloading (band broadening).

5. REAGENTS

5.1 Adsorbent Trap Materials:

5.1.1 Tenax-GC (2,6- diphenylene oxide) 60-80 mesh chromatographic grade.

5.1.2 Silica gel - (60-80 mesh).

5.2 Organic Free Water: Organic free water is defined (see EPA Method #624, CFR Vol. 44, No. 233, pg. 69533) as water free from interference when employed in the purge and trap procedure described herein. It may be prepared by boiling distilled water for a period of approximately 40 minutes.

5.3 Standards: The working standards are prepared from commercially available standard solutions. All standards must be prepared in methanol. The working standards are prepared in such a fashion that 20-, 50-, and 100-ng per compound may be added to organic-free water in a volume of methanol less than 20-uL. Volumes in excess of 20-uL may alter the purging efficiency of VOC's from water. The use of 20-uL or less aids in standardizing procedures used in different laboratories.

6. CALIBRATION

6.1 The calibration procedure used to prepare the GC/MS system for analysis of adsorbent resin collected samples and stainless steel cylinder collected samples is identical.

6.2 The external standard method is used for quantitation (see Section 11.3). Prepare a master calibration curve using a minimum of three (3) standard concentrations. Plot concentrations vs. integrated areas using characteristic ions (see Table B-1) for each compound. One point on each curve should approach the detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by analysis of at least one standard concentration. If significant drift has occurred, a new calibration curve must be established.

6.4 A GC/MS system calibration check is accomplished daily and checked every eight hours. Fifty nanograms (50-ng) of 4-BFB is injected into the GC/MS system through the GC inlet as a calibration check. A 50-ng sample should give ion abundances as indicated in Table B-3.

7. QUALITY CONTROL

7.1 Before analyzing any samples, the analyst should daily demonstrate through the analysis of an organic free water method blank that the entire analytical system is free from contamination and interference.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate precision of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix.

8. SAMPLE PRESERVATION AND HANDLING

8.1 Gaseous samples collected using adsorbent Tenax traps and stainless steel cylinders must be sealed, immediately following collection, with Swage-lok fittings. The sample is labeled appropriately with site designation and volume of gas sampled (in mL). The sample is immediately stored in a cool dry container. Care should be taken with regard to the integrity of the air-tight seal and the storage location should avoid direct contact with heated surfaces. If the ambient temperature is expected to rise above 80°F (26.5°C) during shipment or storage, the samples should be placed in a container that can be environmentally controlled.

8.2 Sample analysis should be performed as soon as possible following collection. All analyses should be completed within fourteen (14) days following receipt of samples in the laboratory.

9. STANDARD AND SAMPLE ANALYSIS OF ADSORBENT RESIN COLLECTED VOC SAMPLES

9.1 Remove standards and samples from storage and allow them to equilibrate to room temperature. Traps may be stored at room temperature 70°F (20°C) prior to analysis.

9.2 Analyze a blank sample by using the methodology described in this Section. Remove the plunger from a 5-mL syringe and attach a closed syringe valve (or seal temporarily with Teflon tape). Carefully pour organic free water into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0-mL.

9.3 Introduce sample into purge vessel.

9.4 Purge the sample for 8.0 min. This purge time is generally sufficient to liberate VOC's from the aqueous media. Each laboratory or analyst should demonstrate this hypothesis by purging the same spiked water and observing the volatile compound response in the subsequent chromatogram. A carry-over of 5% or less is acceptable.

9.5 Following the purge cycle, place a small section of the capillary column in the cryogenic focusing device (a small Dewar flask containing liquid nitrogen). Desorb the sample from the adsorbent trap for 3.5 min.

9.6 Initiate desorption by rapidly heating the trap to 180°C. The desorption flow should be 20-mL/min. For the initial 1.5-min of the 3.5-min desorption time, the injection is splitless. The remaining 2.0 min is split at 10:1.

9.7 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe (some units may provide for automatic draining). Wash the chamber with two (2) 5-mL flushes of organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next Blank or Standard.

9.8 After desorption, remove the cryogenic focusing device and begin the GC temperature program. (NOTE: The oven door is open during the desorb cycle which allows the operator to maintain the level of LN_2 in the Dewar.) The GC temperature program is 30°C for 5.5-min followed by a temperature program to 160°C at 8°C per minute.

9.9 Following the desorption step, recondition the trap at 210°C for 8-min. When cool (30°C), the trap is ready for the next sample. (NOTE: If this bake-out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration and potential shutdown of the system.)

9.10 Following the completion of the blank analysis, repeat Section 9.2 through 9.9 with the exception that a standard mixture of VOC's (see Table B-1) is added to the organic free water at the end of 9.2).

9.11 Analysis of blank organic free water (system blank) ensures that the analytical system is free of background material. Analysis of the organic-free water spiked with standard compounds provides the data necessary for quantitation of known compounds observed in field samples. The limitations of this method of standardization include the lack of ability to correct for purging efficiency of individual compounds and selective absorption on the Tenax trap. All standard response factors assume that a 100% purging efficiency is maintained for all compounds.

10. STANDARD AND SAMPLE ANALYSIS OF STAINLESS STEEL COLLECTED VOC SAMPLES

10.1 Standard VOC mixture analysis, in preparation for analysis of stainless steel cylinder collected VOC samples, is accomplished by the steps described in Section 9.

10.2 Analysis of stainless steel cylinder collected VOC samples and blanks is accomplished by transferring 1- to 5-cc of gas sample from the sample cylinder to a gas-tight luer-lok syringe. Insert the needle of the gas sampling syringe through a septum seal attached to the stainless steel cylinder. Draw 1- to 5-cc of sample into the cylinder, and allow one minute for the sample to equilibrate. Withdraw the syringe and adjust to desired volume by purging the excess sample.

11. GAS CHROMATOGRAPH - MASS SPECTROMETRY

11.1 Table B-2 summarizes the recommended gas chromatographic column materials and operating conditions for the instrument. Included in Table B-1 are estimated retention times and sensitivities that should be achieved by this method.

11.2 GC/MS Determination. Suggested analytical conditions for determination of the components amenable to purge and trap are given in Table B-2. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

11.3 Mass Spectrometer Parameters.

Electron energy - 70 ev (nominal)
Mass range - 35-285 amu (atomic mass units)
Scan time - 0.45 sec (0.05 sec hold between scans)

11.4 Calibration of the Gas Chromatography/Mass Spectrometry (GC/MS) System. Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of 4-BFB.

11.4.2 If the system performance criteria are not met for this test, the analyst must retune the mass spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

12. QUALITATIVE AND QUANTITATIVE DETERMINATION

12.1 To qualitatively identify a compound, obtain an Extractable Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table B-1. The criteria below must be met for a qualitative identification.

12.1.1 The characteristic ions for the compound must be found to maximize in the same scan or within one scan of each other.

12.1.2 The retention time at the experimental mass spectrum must be within 10 sec of the retention time of the standard compound.

12.1.3 The ratios for the three (3) EICP peak areas must agree within 20% of the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC/MS system or from a reference library.

12.2 <u>External Standard Quantitation Calculations:</u> The concentration of the unknown can be calculated from the slope and intercept of the multiple point calibration curve. The unknown concentration can be determined using the following equation:

$$\text{ng} = \frac{(A)(B)}{(C)}$$

Where A = area of the unknown
B = concentration of standard ng
C = area of the standard

12.3 The external standard method of quantitation described in Section 12.2 results in nanogram concentrations for Table 1 compounds analyzed in the Tenax trap. The gas producing indsutries prefer that reporting units are in volume parts per million (Vppm). Using the volume of gas drawn through the Tenax trap (see sampling methodology), Vppm may be calculated as follows (assuming ambient temperature and pressure; where T = 0°C and P = 1 atmosphere):

$$V_{ppm} = \left(\frac{\text{ng (calculated in Section 11.2)}}{\text{cm}^3 \text{ gas drawn through Tenax trap}} \right) \left(\frac{\text{1 mole}}{\text{MWT component in ng}} \right) \left(\frac{22{,}400 \text{ cm}^3 \text{ component}}{\text{mole}} \right) \times 10^6$$

12.4 For the case where 10 cm^3 of gas sampled yields 1000 ng of Benzene:

$$V_{ppm} = \left(\frac{1000 \text{ ng}}{10 \text{ cm}^3} \right) \left(\frac{\text{1 mole}}{(78 \times 10^9 \text{ ng})} \right) \left(\frac{22{,}400 \text{ cm}^3}{\text{mole}} \right) \times 10^6 = 29$$

12.5 Report all results to two significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported.

TABLE B-1: Standard Compound Identification

Compound Name Mwt., Empirical formula (ion, relative abundance)	Retention Time (min)	Detection Limit (ng)
Pentane 72 C5.H12 (43, 1000) (57, 125) (58, 292)	4:30	5
1,1 Dichloroethylene 96 C2. H2. Cl2 (61, 1000) (96, 656) (98, 411)	4:32	5
Dichloromethane 84 C. H2. Cl2 (49, 1000) (84, 770) (86, 486)	4:34	5
1,2-Dichloroethene (Trans) 96 C2. H2. Cl2 (61, 1000) (65, 577) (98, 368)	4:41	5
1,1-Dichloroethane 98, C2. H4. CL2 (63, 1000) (65, 313) (83, 110)	4:44	5
Hexane 84 C6. H12 (43, 631) (56, 463) (57, 1000)	4:50	5
Benzene 78 C6. H6 (52- 998) (77, 195) (78, 1000)	5:18	5
Iso-Octane 114 C. H18 (43, 173) (56, 281) (57, 1000)	5:36	5
Trichloroethene 130 C2. H. Cl3 (95, 928) (130, 1000) (132, 962)	5:44	5
Methyl Benzene 92, C7. H8 (91, 1000) (92, 633)	6:29	5
1,1,2 Trichloroethane 132 C2. H3. Cl3 (83, 1000) (85, 631) (97, 966)	6:34	5

TABLE B-1 Continued

Compound Name Mwt., Empirical formula (ion, relative abundance)	Retention Time (min)	Detection Limit (ng)
Tetrachloroethene 168 C2. H2. Cl4 (129, 800) (131, 795) (166, 1000)	7: 04	5
Chlorobenzene 114, C6. H5. Cl (77, 566) (112, 1000) (114, 313)	7:42	5
Ethylbenzene 106 C8. H10 (91, 1000) (106, 325)	8:00	5
M,P-Xylene 106 C8. H10 (91, 1000) (105, 222) (106, 533)	8:10	5
O-Xylene 106 C8. H10 (91, 1999) (105, 189) (106, 502)		
Nonane 128 C9. H20 (43, 1000) (56, 187) (57, 725)	8:50	5
Isopropyl Benzene 120 C9. H12 (77, 155) (105, 1000) (106, 83)	9:18	5
Propyl Benzene 120 C9. H12 (91, 1000) (92, 102) (120, 245)	9: 58	5
Napthalene 128 C10. H8 (127, 99) (128, 1000) (129, 66)	15:13	5

TABLE B-2

Operational Parameters for Desorption of Field Samples and Purge and Trap of Standard Compounds for Instrument Calibration

Sample size (for calibration)	5 mL
Purge time (for calibration)	8 min
Purge and desorb gas	He (99.999% purity)
Desorption time	3.5 min
Desorption temperature	180°C
Purge / desorption flow rate	20 mL / min
Cryogenic focusing	Dewar w / LN_2
Trap condition time	8 min
Trap condition temperature (bake out)	210°C
GC column (capillary)	DB-5 or SE-54 - cryogenically cooled during desorption
Trap support medium	Tenax-GC (60-80 mesh) 80 mg Silica Gel (35-60 mesh) 20 mg
Trap dimensions	2 mm (1/8" O.D.) I.D. x 250 mm long

TABLE B-3: BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	20 - 40% of mass 95
75	50 - 70% of mass 95
95	base peak, 100% relative abundance 5 - 9% of mass 95
173	less than 1% of mass 95
174	70 - 90% of mass 95
175	5 - 9% of mass 95
176	70 - 90% of mass 95
177	5 - 9% of mass 95

All ions listed must be present in the spectrum

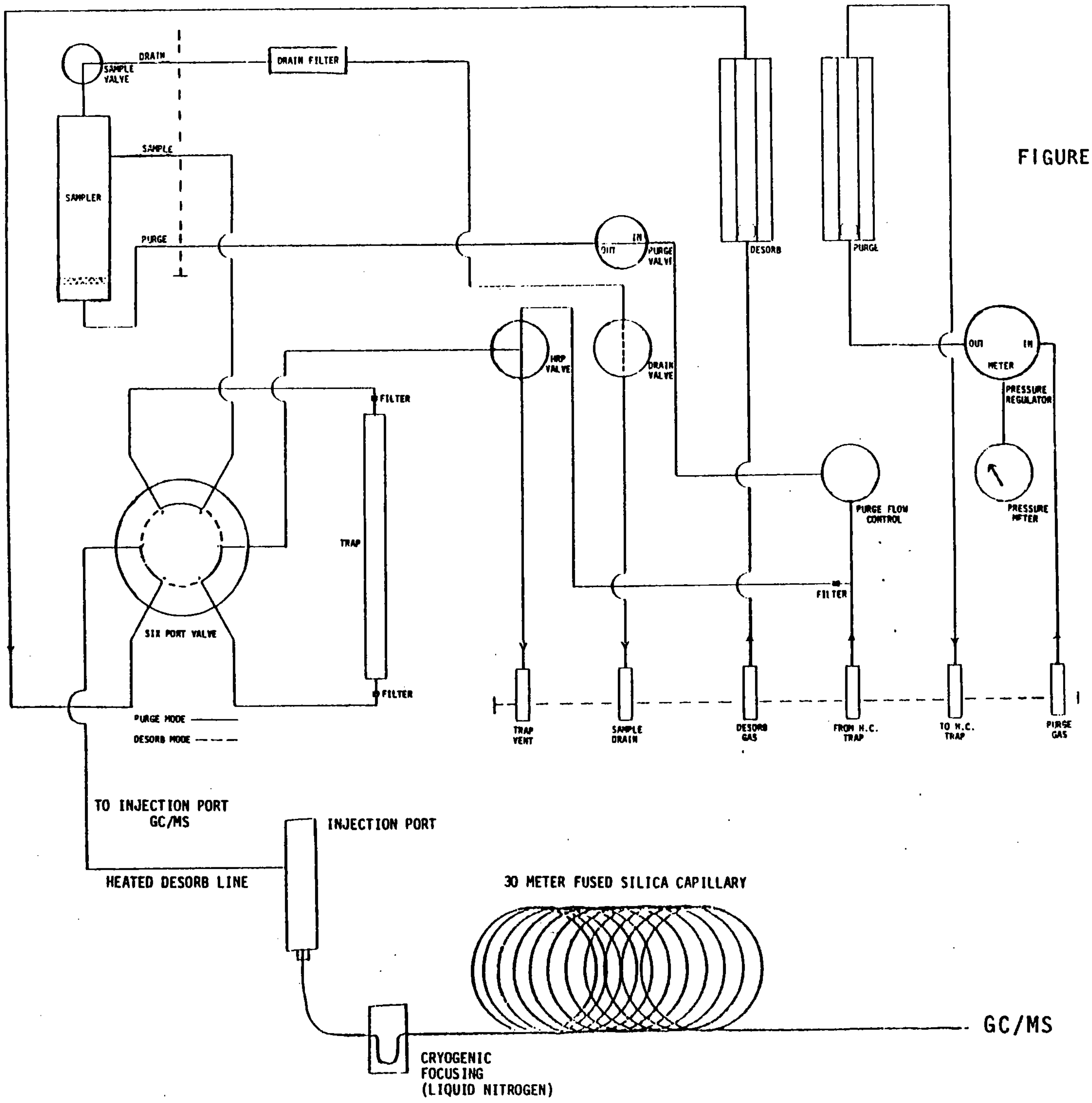

FIGURE B-1: Gas Flow System

APPENDIX C:

ANALYTICAL PROTOCOL FOR DETERMINATION OF VOLATILE MERCURY COMPOUNDS

ANALYTICAL PROTOCOL
FOR DETERMINATION OF VOLATILE MERCURY COMPOUNDS

1. SCOPE AND APPLICATION

1.1 This method is designed to determine not only total volatile mercury, but also speciate between inorganic and organic forms as well. This method is a modification of the one used by Fitzgerald and Gill (1979) and applies a two-stage gold and/or silver amalgamation followed by subsequent thermal desorption.

1.2 This method is applicable to the determination of volatile mercury in raw landfill, process gas stream, sales gas, ambient air and work space air (industrial hygiene). It is designed to meet the present and future monitoring requirements of gas producing industries, the Gas Research Institute, and Federal and State regulatory agencies.

1.3 Because of the method used in collecting the mercury (amalgamation as opposed to a charcoal based sorbent), there is little or no interference in the analysis stage. The absolute detection limit is approximately 0.05 nanograms (ng) of mercury. However, due to the ubiquitous nature of small levels of mercury and the chance of environmental contamination when determining such small concentrations, a more realistic detection limit approaches 0.2 ng of mercury.

2. SUMMARY OF THE METHOD

2.1 Volatile mercury samples are collected on gold and/or silver filled quartz columns by amalgamation. The sample columes are then capped and stored in screw cap culture tubes until time for analysis. Upon arrival at the laboratory, samples and blanks are thermally desorbed and the resultant mercury vapor is analyzed by cold vapor atomic absorption spectrophotometry (CVAAS) at a wavelength of 254 nm.

2.2 Gas samples (raw, process, sales, ambient air or work space air) are collected by amalgamation using quartz columns (4 mm I.D. x 6.5 mm O.D. x 130 mm length) which have been packed with gold or silver coated quartz chips. The active length of the packing is approximately 40 mm (Figure 1). Silver columns are used for the collection of inorganic (elemental) mercury. Gold columns are used for the collection of total (organic and inorganic) mercury.

3. INTERFERENCES AND CONTAMINATION

3.1 Gold and/or silver amalgamation, as a method for trapping mercury and its compounds, has minimal interferences: Carbon based sorbents, such as Carbosieve, which is used to trap alkyl forms of mercury, also traps a wide variety of inorganic and organic compounds. Upon thermal desorption, these compounds absorb at the same wavelength (254 nm) as mercury. Thus, they interfere to the degree, that at best, a series of from 5 - 15 peaks register on the recorder and one ends up with a chromatogram of several unresolved peaks. When gold and/or silver amalgams are thermally desorbed, only one highly resolved mercury peak is measured.

3.2 Although interferences are not serious problems when using the amalgamation technique, a possible limitation is the extreme sensitivity of the method. Gold and silver amalgams are so readily formed that a "blanked" uncapped column may take up as much as 0.1 ng mercury per hour, if left undisturbed, but exposed to ambient laboratory room air. Thus, the columns must be handled carefully to avoid contamination. (Braman and Johnson, 1974 and Fitzgerald and Gill, 1979).

3.3 To avoid contamination, all labware (tubing, fittings, caps, etc.) used should initially be cleaned in 2N HNO_3 for 48 hours followed by soaking and rinsing in deionized water for 24 hours. The labware should then be covered and allowed to dry in a clean area at ambient laboratory temperature. Only teflon (TFE) tubing and fittings should be used. Column caps should be of polyethylene or vinyl.

4. INSTRUMENTATION AND MATERIALS

4.1 UV Mercury Monitor: Samples are analyzed by CVAAS using a laboratory Data Control #1235 mercury monitor equipped with a Perkin-Elmer #023 strip chart recorder or equivalent. Alternate mercury analysis systems include Coleman #MAS-50 or MAS-50A. The Coleman instruments have detection limits comparable to the #1235 mercury monitor.

4.2 Preparation of Gold Traps: Quartz chips (30 - 40 mesh) are coated with an elemental gold paste (Liquid Gold Bright, Englehard Industries or Dupont) and then baked in a muffle furnace at 600°C for 30 minutes. Upon drying, a thin coating of elemental gold is plated on the quartz chips. After repeating this procedure four times, it is estimated that the surface of the quartz chips are 98 - 100% coated with gold. Next quartz columns are prepared. The dimensions of the columns are 4 mm I.D. x 6.5 mm O.D. x 130 mm long. The columns are packed with the gold coated quartz chips so that the active length of the packing is approximately 40 mm. The chips are held in the columns with 10 mm plugs of quartz wool. The packing is centered in the columns (Figure C-1).

4.3 Preparation of Silver Traps: The procedure is identical to the one described in Section 4.2 with the exception that elemental silver paste is used in place of the gold paste.

4.4 Micro-syringes: 50, 100, 250, 500, 100 ul (Hamilton or equivalent).

4.5 Standards: Calibration of the analytical system is accomplished using vapor phase additions of a Hg^{O} - saturated air standard. This standard is prepared by allowing approximately 10 mL of elemental mercury to come to equilibrium in a 250 mL amber glass bottle fitted with a silicon/teflon rubber septum. Vapor pressure data are used to calculate the amount of mercury in air delivered from the microsyringes used (Table C-1).

5. QUALITY CONTROL

5.1 Before samples are collected, all gold traps should be "blanked" by thermal desorption and the values recorded to insure that the traps are "clean" at the time of sample collection. (Note: "New" gold traps may contain as much as 500 ng Hg before they are blanked). The traps should then be capped with acid cleaned polyethylene or vinyl column caps (Supelco) and placed in labeled individual screw top culture tubes. The threads of the culture tubes should be wrapped in teflon (TFE) tape before capped in order to insure a tighter seal. The culture tubes may be made of glass or plastic. The gold traps are further sealed in Ziploc storage bags and stored until samples are collected. (Note: If the time interval between trap "blanking" and sample collection exceeds two weeks, the traps should be re-blanked before samples are collected).

5.2 Standard quality assurance practices should be used. Field replicates should be collected to validate the overall precision of the technique. Laboratory replicates should be analyzed to validate the precision of the analysis.

5.3 Field blanks and spiked traps should accompany the sample traps to insure no gain or loss of mercury in sample collection and transportation.

5.4 When performing sample analysis the method of standard additions should be used in conjunction with instrument calibration.

6. SAMPLE PRESERVATION AND HANDLING

6.1 Gaseous mercury samples collected using gold traps must be sealed immediately following collection with acid cleaned plastic column caps. The traps are placed in their original screw top culture tubes and labeled (site designation and volume of gas sampled). Next the samples are placed in Ziploc plastic storage bags and stored under refrigeration.

6.2 Upon arrival at the laboratory, the samples should be analyzed as soon as possible. If samples are not immediately analyzed, they should be stored frozen. All analyses should be completed within ten (10) days following receipt of samples in the laboratory.

7. CALIBRATION

7.1 Assemble the necessary tubing, fittings, valves, standard injection chambers, variable transformers, pyrometers, thermocouples, furnaces and traps along with the mercury analyzer and recorder in a manner similar to the schematic shown in Figure C-2. The operating parameters are presented in Table C-2.

7.2 Before calibration, it is first necessary to purge the analytical system of any residual mercury by turning on the sample N_2 carrier gas at a flow of 300 mL per minute for approximately three (3) minutes (Fitzgerald and Gill, 1979). This step should be repeated daily. Next a known amount of Hg^o gas, from the vapor phase standard, is injected into the standard injection port upstream and nearest the analytical gold trap. The N_2 carrier gas should have a flow of approximately 300 mL per minute. The mercury is allowed to amalgamate on the analytical gold trap for one minute. The mercury is then thermally desorbed at 600°C for one (1) minute. The resultant peak height is measured on the strip chart recorder (peak integration is more desirable, however, peak height is quite reproducible). The analytical gold trap is cooled via compressed air and the above procedure is repeated with at least three (3) additional standard concentrations, such that the standards bracket the suspected range of sample concentrations. This procedure is repeated at the beginning and end of each daily run. Typical standard calibration curves range from 0.2 - 200 ng mercury (depending on the range of the samples). If significant drift occurs in the linearity and individual standard peak height from one daily calibration curve to the next, a new calibration curve must be established.

8. SAMPLE ANALYSIS

8.1 Remove standards and samples from storage and allow them to equilabrate to room temperature (21°C).

8.2 Clean N_2 gold trap by purging with nitrogen and heating to 600°C simultaneously for one minute. Cool and reconnect N_2 gold trap. (Note: A silver trap may be used in place of gold.)

8.3 Set sample N_2 flow to 300 mL per minute and the reference N_2 flow to 500 mL per minute.

8.4 Clean entire analytical train by purging with N_2 for 3 - 5 minutes.

8.5 Calibrate instrument (see Section 7.2).

8.6 Turn sample N_2 flow to off (Note: Always leave reference flow on). Loosen teflon nuts on the swagelok unions. Uncap sample (or blank) gold trap and slip the quartz furnace (nichrome wire) over the active area (e.g., quartz wool and chips) of the trap. Insert both ends of trap into the teflon unions and tighten the nuts only finger tight. (Note: Tighten nuts just so the gold trap is not loose.)

8.7 Make sure valves are adjusted to insure direction of flow goes from the sample (field) gold trap to the analytical gold trap. (Note: In order to obtain reproducible results, the same analytical gold trap should be used for all standard and sample analyses.) Turn on sample N_2 flow (300 mL/min.) Turn on the variable transformer controlling the sample (field) quartz furnace. (Note: The necessary voltage needed to obtain a quick maximum temperature of 600°C should be previously determined. Once this is done, do not make further adjustments. Use only the on/off switch when operating the transformer.) Watch pyrometer reading to make sure temperature is within proper range (600°C ± 20°C). Heat sample trap for one minute, then turn off the transformer. Let flow continue for an additional minute. Leaving the sample N_2

flow on, switch on the transformer controlling the analytical quartz furnace. (Note: It surrounds the analytical gold trap.) This thermally desorbs the mercury from the analytical trap. Heat for one (1) minute at 600°C (Note: Watch pyrometer) or until the mercury signal begins returning to the baseline. Turn off the analytical transformer. While purging, cool both the sample and analytical traps to room temperature using compressed air. Turn the sample N_2 flow to off.

8.8 Repeat Sections 8.6 and 8.7 for each sample. As soon as the sample trap is analyzed and cooled, remove and cap with clean column caps. The trap is now ready to be used for additional sampling. (See Section 5.1 for storage time interval for "blanked" traps.)

8.9 Perform standard additions on 50% of the samples. This is done by injecting a known mass of mercury vapor into the standard injection port upstream and nearest the sample gold trap (field gold trap, Figure 1). Next, perform the steps described in Section 8.7.

9. QUANTITATIVE DETERMINATION

9.1 External Standard Quantitation Calculations - the mass of an unknown can be calculated from the slope and intercept of a multiple point calibration curve. However, since mercury standards are linear over five orders of magnitude, an unknown can also be calculated based on one standard using the following equation.

$$ng = \frac{(A)(B)}{(C)}$$

Where A = peak height of the unknown
B = mass of the standard (ng)
C = peak height of the standard

9.2 The external standard method of quantitation described in Section 9.1 results in nanogram mass values for mercury samples analyzed by gold or silver trap amalgamation/thermal desorption. Using the ng value, the volume of gas sampled and the molecular weight of mercury, the reporting units may be converted to volume parts per million (Vppm), volume parts per billion (Vppb) or volume parts per trillion (Vpptr). Using the volume of gas drawn through the gold trap (see sampling methodology) Vppm may be calculated as follows (assuming ambient temperature and pressure; where T = 0°C and p = 1 atmosphere):

$$\text{Vppm} = \left(\frac{\text{ng (calculated in Section 9.1)}}{\text{volume of gas sampled (L)}}\right)\left(\frac{\text{1 mole}}{\text{molecular weight component (ng)}}\right)\left(\frac{22.4\text{L}}{\text{mole}}\right) \times 10^{6}$$

likewise:

$$\text{Vppb} = \left(\frac{\text{ng (calculated in Section 9.1)}}{\text{volume of gas sampled (L)}}\right)\left(\frac{\text{1 mole}}{\text{molecular weight component (ng)}}\right)\left(\frac{22.4\text{L}}{\text{mole}}\right) \times 10^{9}$$

and:

$$\text{Vpptr} = \left(\frac{\text{ng (calculated in Section 9.1)}}{\text{volume of gas sampled (L)}}\right)\left(\frac{\text{1 mole}}{\text{molecular weight component (ng)}}\right)\left(\frac{22.4\text{L}}{\text{mole}}\right) \times 10^{12}$$

9.3 Example: 5 L of gas sampled yields 2 ng of mercury.

Since the mass/volume concentration of mercury is very low, we choose to calculate Vpptr instead of Vppb or Vppm.

$$\text{Vpptr} = \left(\frac{2\ \text{ng}}{5\text{L}}\right)\left(\frac{1\ \text{mole}}{201 \times 10^{9}}\right)\left(\frac{22.4\text{L}}{\text{mole}}\right) \times 10^{12} = 45$$

9.4 Report all results to two (2) significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported.

REFERENCES

Braman, R. S. and D. L. Johnson: "Selective adsorption tubes and emission technique for determination of ambient forms of mercury in air." Envir. Science and Tech. 8, 996-1003 (1974).

Fitzgerald, W. F. and G. A. Gill: "Subnanogram determination of mercury by two-stage amalgamation and gas phase detection applied to atmospheric analysis." Analytical Chemistry. 51, 1719-1720 (1979).

TABLE C-1

CONCENTRATION OF MERCURY VAPOR AS A FUNCTION OF TEMPERATURE USING THE IDEAL GAS LAW (PV = NRT)

(CONCENTRATION IN ng Hg/ml gas)

Temperature °C	Hg Concentration in ng/mL
20	13.2
22	15.6
24	18.3
26	21.5
28	25.2
30	29.5

TABLE C-2

OPERATING CONDITIONS AND PARAMETERS FOR ANALYSIS OF SAMPLES FOR VOLATILE MERCURY

Parameter	Description
Mercury Analyzer	Laboratory Data Control UV mercury Monitor #1235
Data Recorder	Multiple input (range) strip chart recorder, Perkin - Elmer #023
Method of Analysis	Thermal desorption of Hg-Au amalgam followed by CVAAS
Sample Size Range	0.5 - 200 ng Hg
Purge / Desorption Time (Calibration)	1 minute for amalgam formation (trap cold) 1 minute for thermal desorption from analytical trip (analytical furnace on)
Purge / Desorption Time (Sample Analysis)	1 minute for thermal desorption from sample trap (sample furnace on) 1 minute for amalgamation onto cold analytical trap (both sample and analytical furnaces off) 1 minute for thermal desorption from analytical trap (analytical furnace on)
Purge and Desorb Gas	N_2 (99.99%) purity; prefiltered through Ag or Au trap
Desorption Temperature	600°C
Purge / Desorption Flow Rate	300 mL / minute
Trap Composition	Quartz columns filled with gold coated quartz chips (30 - 40 mesh)
Trap Dimensions	4 mm I.D. x 6.5 mm O.D. x 130 mm long (active length of Au packing 40 mm)

QUARTZ COLUMN DIMENSIONS

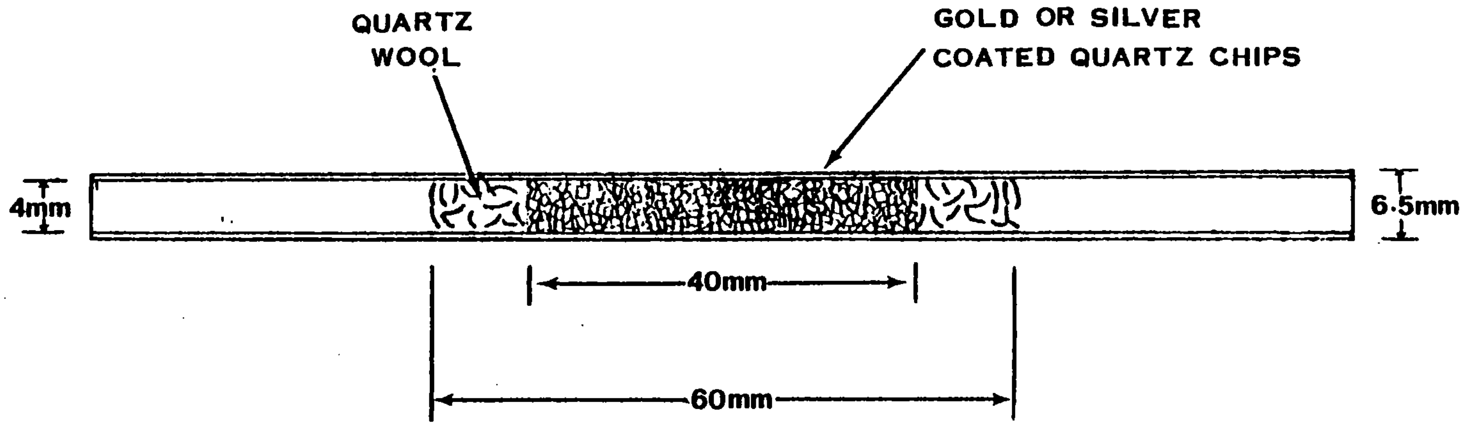

FIGURE C-1

MERCURY SYSTEM SCHEMATIC

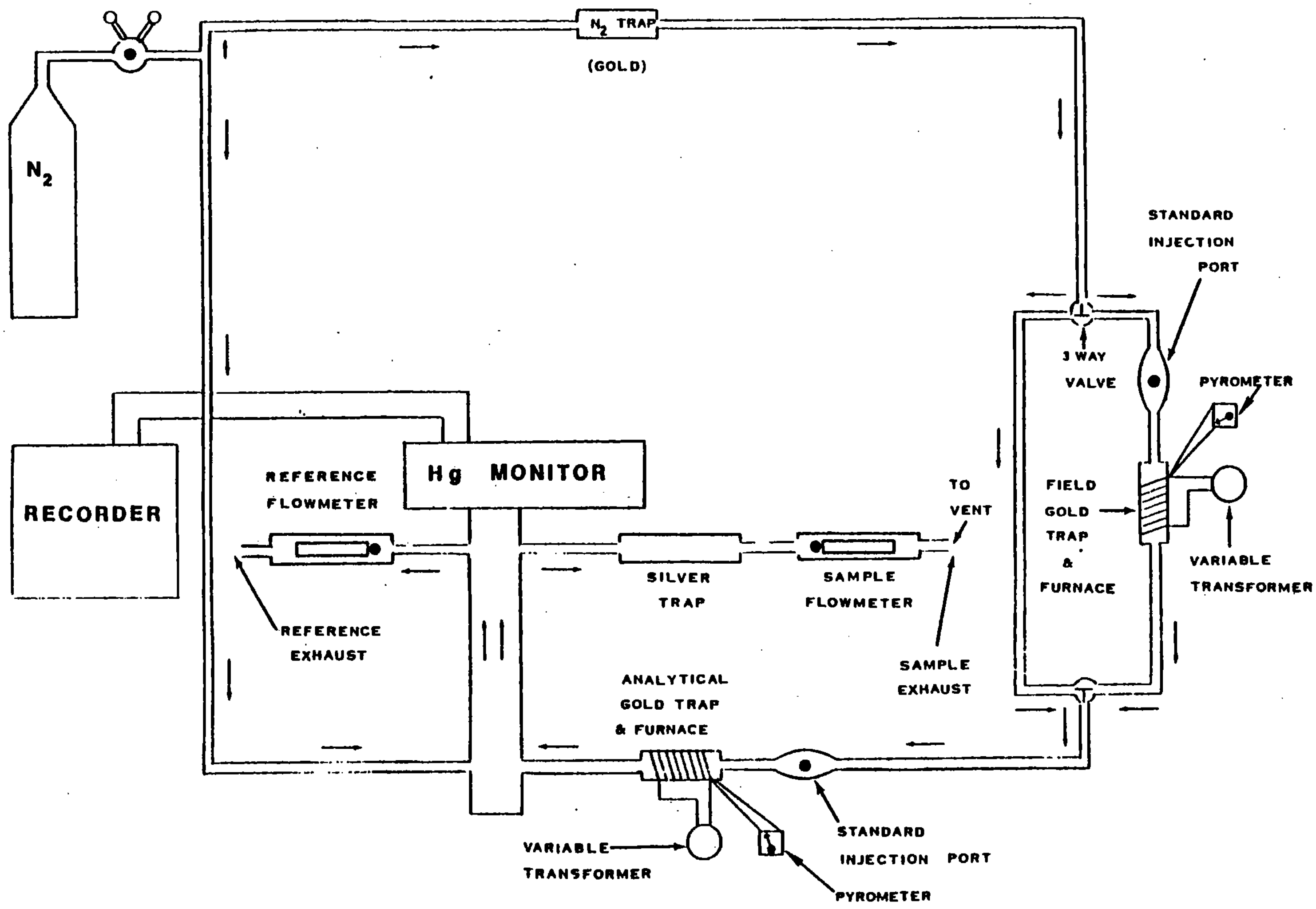

FIGURE C-2