California Environmental Protection Agency

AIR RESOURCES BOARD

Method 422

Determination of Volatile Organic Compounds in Emissions from Stationary Sources

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TABLE OF CONTENTS
METHOD 422

General Information Page

422 Determination of Volatile Organic Compounds In Emissions from Stationary Sources 3

Sampling Methods

422.1. Standard Operating Procedure for the Sampling of Volatile Organic Compounds in Emissions from Stationary Sources into Tedlar Bags 9

Analysis Methods

422.101. Standard Operating Procedure for the Gas Chromatographic Analysis of Volatile Halogenated Organic Compounds from Stationary Source Samples Collected in Tedlar Bags 26

422.102. Standard Operating Procedure for the Gas Chromatographic Analysis of 1,3-Butadiene in Emissions from Stationary Sources 29

422.199. Calibration and Quality Control Procedures for Analysis Methods 39

TABLE OF CONTENTS

METHOD 422

GENERAL INFORMATION

1 INTRODUCTION 3

2 APPLICABILITY 3

3 PRINCIPLE 4

4 DEFINITIONS AND ABBREVIATIONS 4

4.1 Response Factor 4

4.2 Performance Evaluation Sample 4

4.3 Calibration Check 4

4.4 Analytical Limit of Detection (LOD) 4

4.5 Analytical Limit of Quantitation (LOQ) 5

4.6 Reporting Limit (RL) 5

4.7 Field Blank 5

4.8 Field Spike 5

4.9 Laboratory Replicate Samples 5

5 RANGE AND SENSITIVITY 5

5.1 Range 5

5.2 Sensitivity 6

6 PRECISION AND ACCURACY 6

7 PRESURVEY 7

7.1 Pretest 8

7.1.1 Test Protocol 8

7.1.2 Pretest Sampling 8

7.1.3 Pretest Analysis 8

7.1.4 Protocol Review 8

LIST OF TABLES

Table 1 Average Audit Bias 6

METHOD 422

Determination of Volatile Organic
Compounds In Emissions from Stationary Sources

GENERAL INFORMATION

1. INTRODUCTION

Method 422 is designed to provide sampling and analysis techniques for measurement of volatile organic compounds (VOC) in emissions from stationary sources.

The following format is intended to aid the user by dividing the method into the following sections; general information, source sampling, and analysis. The first section is aimed at the source test planner. The second section is geared to the needs of the field sampling team, who prepare for the test, collect the samples and deliver the samples to a laboratory. The third section contains the analytical protocols to be followed by a chemist in analyzing the source test samples and reporting the results.

This method should not be attempted by persons unfamiliar with the performance characteristics of chromatography, nor by those persons who are unfamiliar with source sampling. This method does not apply where equipment is operated in potentially explosive atmospheres.

2. APPLICABILITY

This method applies to the sampling and analysis of volatile organic species. Listed below are the compounds specified for use with method 422.

	Synonym
dichloromethane	methylene chloride
chloroform	trichloromethane
1,1,1-trichloroethane	methyl chloroform
trichlorofluoromethane	fluorotrichloromethane
carbon tetrachloride	tetrachloromethane
1,2-dichloroethane	ethylene dichloride
trichloroethene	trichloroethylene
1,2-dibromoethane	ethylene dibromide
tetrachloroethene	perchloroethylene
1,3-butadiene	butadiene

This method cannot be used to determine compounds that (1) are polymeric (high molecular weight). (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

Alternative sampling and analytical methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or the Executive Officer (Air Pollution Control Officer) of the Air Pollution Control District/Air Quality Management District at whose request the test is conducted. The Executive Officer may require the submission of test data or other information showing that the alternate method is equivalent to method 422. Any modifications to the sampling and analytical procedures described must also be approved in writing by the Executive Officer.

3. PRINCIPLE

A sample of source gas containing one or more organics is subjected to gas chromatographic (GC) analysis.

4. DEFINITIONS AND ABBREVIATIONS

4.1 Response Factor

The response of the gas chromatograph detector to a known amount of standard.

4.2 Performance Evaluation Sample

A sample prepared by EPA, ARB, or other laboratories containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are usually known to the analyst.

4.3 Calibration Check Sample

A standard, normally the midpoint of multipoint calibrations (see section 422.199.4.1), which is analyzed each shift to monitor detector drift. The values of all analytes must be within 30% of the mean values established in the multipoint calibration or a new calibration curve must be prepared.

4.4 Analytical Limit of detection (LOD)

The lowest level at which detector response can be distinguished from noise. Refer to section 4.1.6 of method 422.199 for more detail.

4.5 Analytical Limit of Quantitation (LOQ).

The lowest level at which a compound can be accurately quantified. This value is 3.3 times the Limit of Detection.

4.6 Reporting Limit (RL)

The reporting limit (RL) is the lowest level that can be reliably quantitated within specified limits of precision and accuracy during routine analyses of source samples. Reporting limits will be based on parameters such as sampling volumes, dilutions, sample injection volume and chromatographic interferences. The reporting limit will also be based on the level of Tedlar bag contamination as determined during pretest bag checks (see Appendix A, method 422.1) and field blanks. The level of contamination is multiplied by a factor of 5 to calculate the RL. Contamination levels below the LOQ are assigned the value of the LOQ, with the minimum RL equal to 5 times LOQ. Thus, in the absence of any other interferences or dilutions, 5 times the LOQ will be the minimum amount that can be reported in field samples.

4.7 Field Blank

A field blank is taken in the same way as a sample is taken except that pure air or nitrogen is used as a sample. The field blank is used to determine background levels in the sampling system. The gas used for blank runs should be certified by the gas supplier or laboratory to contain concentrations less than the limit of detection for the analytes of interest.

4.8 Field Spike

A gas standard of the target compounds is sampled in the same way as the sample is taken. The purpose of the field spike is to determine any anomalies in sampling and analysis.

4.9 Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples are analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift.

5. RANGE AND SENSITIVITY

5.1 Range

The range of the specific method is given in Table 1.

5.2 Sensitivity

The limits of quantitation (LOQ), as determined by ARB analyses, are given in Table 1. Each laboratory that uses method 422 is required to calculate LOD's, LOQ's, and RL's. The values listed in Table 1 are to be used as a general guide for comparing laboratory performance.

6. PRECISION AND ACCURACY

The precision, as determined from multipoint analyses, and accuracy, as determined by audit analyses, of method 422.101 are given in Table 1.

Table 1

ACCURACY
Average Audit Bias

COMPOUND	ACCURACY[1]	PRECISION[2]	LOD (PPB)[3]
TRICHLOROFLUOROMETHANE	4.3%	10.1%	0.050
DICHLOROMETHANE	NA[4]	NA[4]	NA[4]
CHLOROFORM	3.9%	8.8%	0.54
1,1,1-TRICHLOROETHANE	4.7%	5.4%	0.15
CARBON TETRACHLORIDE	6.3%	12.9%	0.055
1,2-DICHLOROETHANE	NA[4]	NA[4]	NA[4]
TRICHLOROETHENE	5.6%	9.1%	0.92
1,2-DIBROMOETHANE	7.3%	9.7%	0.40
TETRACHLOROETHENE	5.4%	13.8%	0.075

1. Seven audits were performed between February 1987 and March 1989. The average results are listed in the Table 1. The levels of the audits ranged from 4-120 ppb (v/v). The source of the audit cylinders were Research Triangle Institute and the National Institute of Standards and Technology. The accuracy values represent averages of absolute values (bias) as determined from the seven audits. Note that the accuracy values reflect only the analytical process.

2. Precision values derived from multipoint analysis conducted in August, 1989.

3. Refer to Section 4.1.6 of method 422.199 for the equation used to calculate the LODs. The values listed were calculated from multipoint analyses conducted in August, 1989.

4. Standards were not available at the time the multipoint analyses were performed.

7. PRESURVEY

Perform a pre-survey for each source to be tested. The purpose of the pre-survey is to obtain source information so as to select the appropriate sampling and analysis parameters for that source. Potential interferences may be detected and resolved during the presurvey. In some cases, lack of source information could require actual source samples to be collected and analyzed.

The following information must be collected during a presurvey before a test can be conducted. The information can be collected from literature surveys and source personnel. A copy of the presurvey results must be forwarded to the chemist performing sample analyses.

1. Determination of moisture content. Moisture is determined by ARB method 4. The purpose of knowing the moisture content is to determine the need for heat trace line and/or the need for predilution of Tedlar bags. If the moisture content is high then the bags are prediluted. Also this information will help avoid problems in the analytical system.

2. Determination of stack gas temperature. The purpose for determining stack gas temperature is to select the proper probe for sampling. Also stack gas temperature is needed in order to calculate if moisture will condense at ambient temperatures.

3. Determination of corrosives (i.e. $Ca(OH)_2$). Corrosives may affect the analytical system.

4. Determination of amount of acids (i.e. HCl). Acids are scrubbed out of the sample stream by the use of an NaOH impinger.

5. Safety for personnel including exposure of test crew to unsafe or unhealthy levels of toxic substances.

6. Determine if sampling is in a potentially explosive atmosphere. This method does not apply to sampling in a potentially explosive atmosphere.

7. Determine approximate levels of target compounds. This information is needed to establish parameters for the analytical system. See Section 8.1.

The following information is important to the analytical chemist, and it is recommended that this information be obtained during a presurvey.

1. Determination of Static Pressure. This is to be done in accordance with ARB method 3. If the static pressure of the stack is negative, care should be taken to avoid dilution of the stack gas sample with ambient air. If the static

pressure is positive, care should be taken to avoid exposure of test crew to toxic gases.

2. Determination of levels of criteria pollutants. This information is important in determining staff safety.

3. Determination of amount of total organics. This measurement will give the upper limit in target compound levels. This will allow for an estimate of the amount of sample needed per injection.

4. Adequate power to operate source test equipment.

5. Adequate space to operate source test equipment.

6. Determination of representative sampling sites.

7.1 Pretest

If information on target compound concentrations and stack gas composition is unknown a pretest is recomended. The pretest will require that a sample of stack gas is collected and analyses for the target compounds performed.

7.1.1 Test Protocol. A draft protocol should be completed before the pretest. The purpose of the pretest is to determine the appropriate use of method 422.

7.1.2 Pretest sampling. The pretest sampling method should be done in the same way as proposed in the test protocol. Sample transport and storage should also follow the protocol.

7.1.3 Pretest Analysis. The pretest analysis is done to determine target compound levels.

7.1.4 Protocol Review. Information from the presurvey will then be used to fine tune the source test method.

State of California
Air Resources Board

Method 422.1

Standard Operating Procedure for
the Sampling of Volatile Organic Compounds in
Emissions from Stationary Sources into Tedlar Bags.

METHOD 422.1

Standard Operating Procedure for the Sampling of
Volatile Organic Compounds in Emissions from Stationary Sources

Page

1 APPLICABILITY 12

2 LIMITATIONS 12

3 EQUIVALENCY 12

4 APPARATUS 13

4.1 Probe 13

4.2 Alkaline Impinger 13

4.3 Water Impinger 13

4.4 Sample Line 13

4.5 Teflon Valves 13

4.6 Sample Bags 13

4.7 Rigid Containers 13

4.8 Pump 14

4.9 Flow Meter 14

4.10 Shipping Containers 14

4.11 Expendable Materials 14

4.11.1 Standard Gas Mixture 14

4.11.2 Pure Distilled Water 14

4.11.3 Reagent Grade Sodium Hydroxide Solution 14

4.11.4 99.999% N_2 or Zero Air 14

5 PROCEDURE.....14

6 QUALITY CONTROL.....17

6.1 Sampling Runs, Time and Volume 17

6.1.1 Sampling Runs.....17

6.1.2 Sample Time.....17

6.1.3 Sample Volume.....17

6.2 Routine Sampling Quality Control.....17

6.2.1 Field Blank Samples 18

6.2.2 Field Spike Samples 18

6.2.3 Collocated Samples 18

6.2.4 Tedlar Bag Contamination Checks.....18

Appendix A: Procedure for Production, Cleaning, and Contamination Testing of Tedlar Bags.....23

List of Figures

Figure 1 Tedlar Bag Sampling Train 19

Figure 2 Chain of Custody, Sample Record Form 20

Figure 3 Chain of Custody, Log Book Form.....21

Figure 4 Field Data Sheet 22

METHOD 422.1 STANDARD OPERATING PROCEDURE FOR THE SAMPLING OF VOLATILE ORGANIC COMPOUNDS IN EMISSIONS FROM STATIONARY SOURCES INTO TEDLAR BAGS.

INTRODUCTION

This method should not be attempted by persons unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. APPLICABILITY

This sampling method will use a Tedlar bag to collect volatile organic compounds (VOCs) samples from applicable source emissions and source-impacted ambient air. This sampling method is approved for use with the compounds (with exceptions) referenced in Table 1 (general information). Tedlar bags cannot be used to collect 1,3-butadiene samples from combustion sources.

The procedure described herein is applicable to the sampling of volatile organics in approximately the 0.001 to 200 ppm range. The lower limit is determined by bag cleanliness, the upper limit may depend on compound vapor pressure and sample matrix.

2. LIMITATIONS

2.1 This method is not applicable where the gases are occluded in particulate matter. Entrainment of gases from the particulate trap (in probe) into the sample gas stream has not been investigated.

2.2 Sampling efficiencies in actual source gas matrices have not been evaluated.

2.3 Source gas samples collected in Tedlar bags must be analyzed within 72 hours.

2.4 This method is not applicable to the collection of samples where there is a potential for explosion.

3. EQUIVALENCY

Alternative sampling methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer. The Executive Officer may require the submission of test data or other information showing the alternate method is equivalent to method 422. Any modifications to the sampling procedures described must also be approved in writing by the Executive Officer.

4. APPARATUS

Apparatus required for sampling is described below. It is recommended that all equipment which comes in contact with sampled gas be made of ceramic, glass, Teflon, or Tedlar unless these materials are found unsatisfactory and other materials demonstrated suitable in specific situations.

4.1 Probe. Pyrex glass, ceramic or Teflon as appropriate for stack temperature, equipped with a silanized glass wool plug to remove particulate matter.

4.2 Alkaline Impinger. An impinger with alkaline solution may be required to trap acid gases in certain cases; if used it will be located between the probe and the sample line as shown in Figure 1. A Wheaton micro-impinger is recommended. Acid knockout is necessary due to potential for matrix effects (for some compounds) in Tedlar bag samples in the presence of strong acids. In addition, acids may damage analytical equipment, ie., corrode tubing and degrade columns.

4.3 Water Impinger. A water impinger is required to control liquid carry over from the alkaline impinger. A Wheaton micro-impinger is suitable.

4.4 Sample Line. Teflon tubing, 6.4 mm (1/4 inch) outside diameter, of minimum length sufficient to connect the probe to bag and not longer than 10 feet. If the sample line must be longer than 10 feet, then the sample line shall be heated and insulated and capable of operation at above 100°C (212°F).

4.5 Teflon valves or fittings shall be used to connect sample train components. Mininert Teflon valves are recommended.

4.6 Sample Bags. Bags shall be made of Tedlar film, at least 0.002 in. thick.

4.6.1 Mininert Teflon valves are recommended.

4.6.2 Refer to Appendix A for apparatus used in Tedlar bag manufacture, cleaning, and contamination testing.

4.7 Rigid container(s) for filling sample bags by application of vacuum.

4.7.1 The container shall be airtight when sealed.

4.7.2 The container shall be opaque except that a small window to check the condition of the bag within is permissible.

4.7.3 The container shall be fitted with couplings to mate with sample bags, sample line and vacuum line and a flow control valve capable of shutting off flow to the bag.

4.7.4 Sample bags may be fabricated with rigid containers as an integral unit.

4.7.5 An appropriate vacuum relief valve is suggested to protect bags and rigid container.

4.8 Pump, leak free, with capacity of at least 2 liters per minute.

4.9 Flow meter, rotameter type or equivalent, with measurement range of 0.05 to 1.0 liters per minute for observing sampling rate.

4.10 Shipping containers to protect bags in transport shall be opaque to protect bags from ultraviolet light. Containers shall have no staples, sharp edges or metal closures which might damage bags. The rigid container for filling bags may be used for bag transport; any window in the container shall be covered with opaque material during such transport.

4.11 Expendable Materials

4.11.1 Standard gas mixture for field spikes. Appropriate cylinder gases containing the pollutant(s) of interest in known concentration.

4.11.2 Pure distilled water.

4.11.3 Reagent grade sodium hydroxide solution, 0.1 Normal.

4.11.4 99.999% N_2 or zero air.

5. PROCEDURE

The following describes the procedure for collecting samples from stacks. A field blank and a field spike must be obtained for each source test (Refer to section 6 for discussion).

5.1 (Optional) Determine stack moisture content by ARB Method 4; if moisture content is above the 60°F saturation level, then dilution of the sample bag may be required. If moisture content of stack gas is not determined, then Tedlar bag shall be monitored for condensation during sampling (see Section 5.7).

5.1.1 Procedure for Sample Bag Dilution. Bags should be pre-filled with 99.999% nitrogen or zero air to approximately one-third the final

sample volume. The exact volume of dilution gas must be recorded to allow for correction of data. If condensation still occurs, increase dilution as necessary.

5.2 Determine sample gas acid content with universal pH paper; if pH is less than 4, a knockout impinger containing 10 ml of 0.1 N NaOH is required. A water impinger containing 5 ml of distilled water is required to control carryover from the alkaline impinger.

5.3 Assemble the sampling train at the sampling site as shown in Figure 1, using impingers when appropriate. The impingers will be placed in the sampling line between the Tedlar bag and the probe.

5.4 Leak check the sample train. If impingers are used, they and the required rotameter must be installed prior to the leak test. If impingers are not used, a rotameter must still be installed at the inlet of the box in line with the probe. To start the leak check, connect the sample line to the bag, making sure the valve on the bag is closed. Place the bag in the rigid container and close as if for sampling. Turn on the vacuum pump until a reading of 15 inches H_2O is maintained. Make sure that the probe line is not plugged and that the ON/OFF valve is open. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before the leak check continues. Turn the pump off, break the vacuum on the rigid container and open the mininert valve on the Tedlar bag. Place the bag back in the container and close as if for sampling. Plug (leak tight) the end of the probe. Turn on the vacuum pump and adjust until a reading of 15 inches H_2O is maintained. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before sampling continues. If impingers are used, extreme care must be used when applying and removing the vacuum to avoid carry over of the liquids in the impingers.

5.5 Break the vacuum on the rigid container. Unplug the end of the probe and place the end of the probe in the stack away from the walls. Care should be taken to avoid dilution of the stack gas sample with ambient air by sealing the open port area around the probe, especially in stacks with negative static pressure.

5.6 Make sure the sampling train is configured correctly, the valve on the sample bag is open and the ON/OFF valve is closed. Turn the vacuum pump on and adjust until a reading of the 15 inches H2O is maintained. Begin sampling by opening the ON/OFF valve. Record the sample start time on the field data sheet.

5.7 Monitor the container vacuum and sample flow rate and adjust as necessary. After sampling for the planned interval, close the ON/OFF

valve noting the time on the field data sheet. Bags should be filled no more than half full. If condensation occurs, discard sample and resample as per 5.1.1.

5.8 If impingers are used, the sampling apparatus is purged with 99.999% nitrogen into the Tedlar bag at the same flow rate as normal sampling but for 1/3 the actual sample time. Disconnect the probe line from the ON/OFF valve and connect the purge gas line. Open the ON/OFF valve and record the purge flow rate and time on the field data sheet.

5.9 After sample purge is complete, close the ON/OFF valve, turn the pump off, break the vacuum on the rigid container and close the mininert valve on the bag.

5.10 Attach a label to each Tedlar bag sample (and impinger if used) containing the following information:

Job #
Date
Time
Sample/Run #
Plant Name
Sample Location
Log #
Initials of Sampler Operator

5.11 Promptly place the sealed bag in a shipping container; close the container to prevent possible degradation of the sample by ultraviolet light. Several bags may be placed in the same shipping container.

5.12 If impingers were used, promptly place impinger solutions in vials with no air space, cap and enclose in a shipping container (or wrap with aluminum foil to prevent possible degradation of the sample by ultraviolet light). Store impinger solutions on ice. Impinger solutions may be analyzed if suspected to contain analytes of interest. EPA purge and trap protocols for VOC analysis of water samples should be used (i.e., Method 624).

5.13 Fill out the Chain of Custody-Sample Record, Log Book Data sheets, and Field Data sheets. Copies of these forms are attached as Figures 2, 3 and 4.

5.14 Sample Bag Transport Procedure

5.14.1 Transport sample bags in opaque shipping containers.

5.14.2 Airborne transport could potentially result in rupturing of bags containing toxic samples. Surface shipment is advised. If airborne transport is unavoidable then bags should not be filled more than half way to avoid bag rupture.

5.14.3 Deliver bags to laboratory for analysis promptly. Check analysis method for allowable sample holding times.

6. QUALITY CONTROL

6.1 Sampling Runs, Time and Volume

6.1.1 Sampling runs. The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3) runs per source test.

6.1.2 Sample time. Integrated bag sampling. The sampling must be of sufficient duration to provide coverage of the average operating condition of the source. However, the minimum sampling time shall not be less than 20 minutes.

6.1.3 Sample volume. The sample volume will be based on the facility's permitted emission rate of the target analytes and the amount needed to meet the specific analyte's LOD. The volume may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{l}{C} \times n$$

Where:

A = The analytical LOD in ng
B = The percent (%) of the sample required per analytical run
C = Allowable stack emissions (ng/l)
n = multiplier to insure that sufficient sample is collected for additional analytical runs; must be ≥ 3.

The calculated sample volume is in liters.

6.2 Routine Sampling Quality Control. This section outlines the minimum quality control operations necessary to assure accuracy of data generated from samples collected in Tedlar bags. These QC operations are as follows:

* Field blank samples
* Field spike samples

* Collocated samples (optional)
* Tedlar bag contamination checks

6.2.1 Field blank samples. At least one field blank sample will be taken per source test. At the discretion of the tester, more blank samples may be taken. Air or nitrogen from a compressed gas cylinder, which contains levels of contaminants less than criteria stated in Appendix A (Tedlar bag contamination testing), is collected in the bag in the manner described in section 5 of this method. If impingers are used in the source sampling, then ultrapure air or nitrogen gas must be drawn through the impingers prior to the bag. This blank sample is transported and analyzed along with the stack gas samples. If field blank values are greater than 20% of the stack gas values, then the data will be flagged. Field blank values will be reported along with the stack gas results.

6.2.2 Field spike samples. At least one field spike sample will be taken per source test. At the discretion of the field engineer, more spike samples may be taken. Pure air or nitrogen containing known concentration(s) of the pollutant(s) of interest is drawn from one bag to another through the sampling apparatus. If impingers are used in the source sampling, then they must be included in the spike test. The spiked sample is transported and analyzed along with the stack gas samples. Spike sample recoveries will be reported along with the source test results.

6.2.3 Collocated samples. Collocated sampling will be performed at the discretion of the tester. Samples are collected through two identical sampling systems simultaneously from the same stack sampling port. The analysis results of collocated samples are used to estimate method precision.

6.2.4 Tedlar bag contamination checks. Tedlar bags will be tested for contamination as outlined in Appendix A of this document.

FIGURE 1

TEDLAR BAG SAMPLING TRAIN

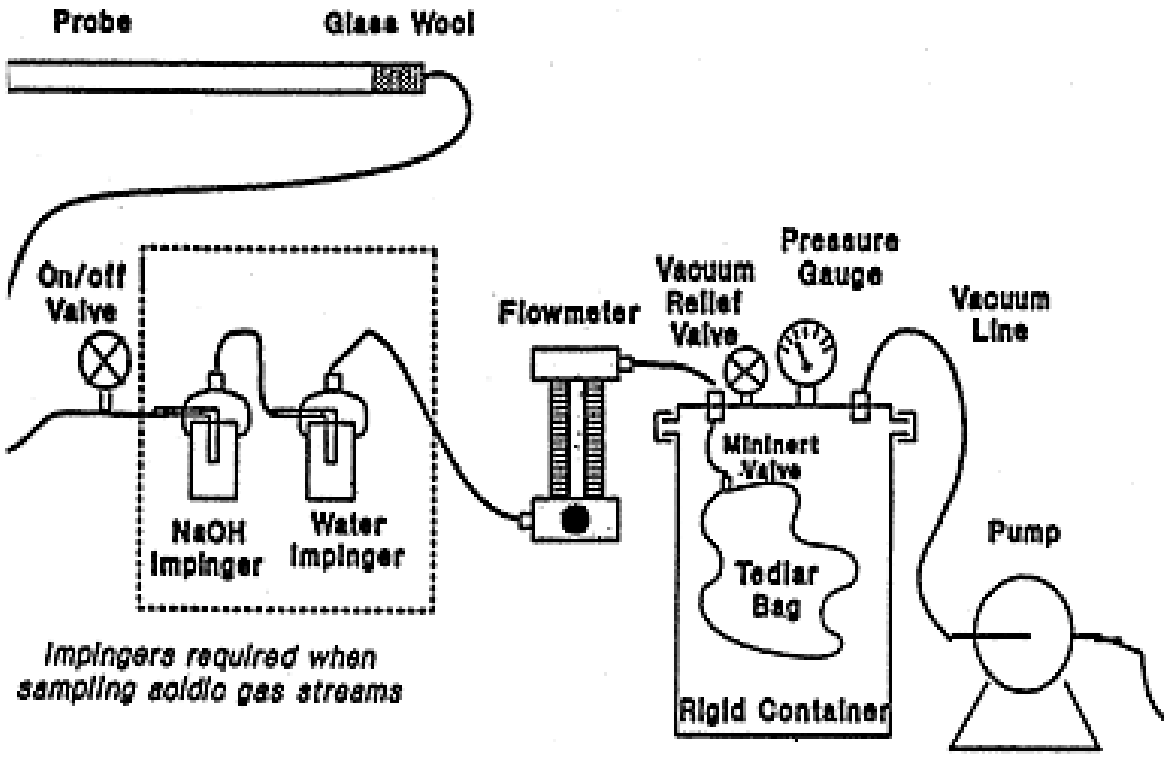


FIGURE 2

CHAIN OF CUSTODY

SAMPLE RECORD

Job Date: _____ Time: _____

Sample/Run # _____

Sample Location _____

Type of Sample _____

Log # _____ Fitting # _____ Initials _____

Action Taken	Start Date	Time	Given By	Taken By

Related I. D. #s	Description

FIGURE 3

CHAIN OF CUSTODY

LOGBOOK Project No._____

Log No.	Sample I. D.	Date	Time	Comment	Valve I. D. Bag Sample	Given By	Taken By

FIGURE 4

FIELD DATA SHEET

Project Name _____

Date _____ Sample ID: _____

LOG ID: _____

Sample Type: _____

BAG QUALITY ASSURANCE

Bag ID No. _____ Initial Bag Leak Check _____

Bag Check Analysis (List Results of Bag check Analysis):

IMPINGERS

no. of impingers _____

Impinger #1 solution type _____
Impinger #2 solution type _____

Volume of solution in Imp #1 _____
Volume of solution in Imp #2 _____

FLOWMETERS

Flowmeter ID _____

Date of Flow Meter Calibration Check _____

Sampler ID _____ Sampler Leak check _____

SAMPLE TIME

Time					Total time

Flowrate					Average Flow

COMMENTS _____

_____

_____

Method 422.1

Appendix A

Procedure for production, Cleaning and Contamination
Testing of Tedlar Bags

1. Production of Tedlar Bags

New bags are recommended for each sample. Previously-used bags may be used again if cleaned and checked for leaks and contamination as specified below. Tedlar bags may also be purchased already assembled, but must be certified to specified contamination levels before use.

1.1 Materials and Equipment

1.1.1 Tedlar, 0.002 inch thickness

1.1.2 Fittings for connection to sample line. Mininert Teflon valves are recommended. Quick-disconnect Swagelock fittings are commonly used, but are suspected of possible interferences at low ppb concentrations. Fittings should be composed of inert materials, teflon and stainless steel are recommended.

1.1.3 Septum fitting for injection of surrogates or removal of sample by syringe.

1.1.4 Cork borers for installation of fittings.

1.1.5 Lay-out Table to measure and cut Tedlar to size.

1.1.6 Heat-Seal Apparatus for making seams in Tedlar. Vertrod Thermal Impulse Heat Sealing Machinery or similar device. May require compressed air cylinder.

1.1.7 Pump for evacuation of bags during purging operations, together with fittings or manifold system to connect pump to bags.

1.1.8 Ultrasonic bath for cleaning fittings.

1.1.9 Oven for drying fittings

1.1.10 99.999% Nitrogen for purging bags.

1.1.11 Distilled water.

1.2 Clean Fittings

Use of organic solvents is not recommended due to possible contamination of bags.

1.2.1 Clean fittings by placing them in soapy water in ultrasonic bath for about one hour. Rinse fittings thoroughly with clean water, followed by a rinse with distilled water.

1.2.2 Bake fittings in a 100°F oven for at least 8 hours.

1.3 Manufacture of Tedlar bag

Tedlar bags should be constructed in a clean area, with care taken to avoid contamination such as exposure to chemical fumes, solvent vapors or motor exhaust.

1.3.1 Cut one piece of Tedlar film from roll on lay-out table using a razor blade. A sheet of Tedlar measuring about 54” by 30” will make about a 30 Liter capacity bag (15 L at half-full).

1.3.2 Fold Tedlar sheet in half and make two seams using heat-seal apparatus. Seams should be at least ½ inch from edge.

1.3.3 Place piece of cardboard inside bag. Use cork borer to make appropriate size hole for fittings, using cardboard to protect other side of bag. Tedlar film should fit snugly around base of fitting.

1.3.4 Attach previously cleaned sample line fitting. Use Teflon washers on inside and outside of bag to secure fitting.

1.3.5 Attach septum fitting if necessary. (Mininert valves have septum and sample line connections all on one fitting)

1.3.6 Seal remaining seam using heat-seal apparatus.

2. Leak Test

Check all sample bags for leaks by inflating with 99.999% nitrogen to a pressure of 2 to 4 inches of water. Good bags should hold constant pressure as indicated by a manometer for 10 minutes or (alternative test) should remain taut and inflated overnight. A small weight (e. g. Kimwipe box) may be placed on top of bag for the overnight leak check. Report bag acceptability on field data sheet (figure 4); destroy or repair and retest defective bags.

3. **Bag Cleaning**

Purge the bag with 99.999% nitrogen repeatedly until acceptable contaminant values are attained. ARB staff experience has shown that 3 to 8 purges are needed to meet the target contamination levels of <1 ppb for most VOCs of interest.

4. **Bag Contamination Check**

4.1 Check bags for contamination by filling them halfway (so that check volume approximates actual sample volume) with 99.999% nitrogen, allow to equilibriate for 24 hours, then analyze for the pollutant(s) of interest. Refer to appropriate Method 422 analysis procedure.

4.2 Acceptable contamination levels may vary depending on the expected sample concentration. However, bags which contain contaminants at levels greater than 20% of the desired reportable limit should be rejected. Thus, the minimum reportable limit will be 5 times the LOQ.

4.3 Label bags and record contamination levels. Also record contamination levels on field data sheets.

State of California
Air Resources Board

Method 422.101

Standard Operating Procedure for the Gas Chromatographic Analysis of Volatile Halogenated Organic Compounds from Stationary Source Samples Collected in Tedlar Bags

Method: 422.101	VOLATILE HALOGENATED ORGANIC COMPOUNDS
SAMPLING	MEASUREMENT
SAMPLING: Tedlar bag; evacuated carton ARB method 422.1	TECHNIQUE: Gas Chromatography, Electron Capture Detector.
	ANALYTE: Volatile Halogenated Organic Compounds
SHIPMENT: Opaque shipping carton, surface shipment recommended	INJECTION: 10 ul to 500 ul (gas tight syringe) 1/12 split (split/splitless injector)
SAMPLE STABILITY: 72 hrs.	TEMPERATURE --INJECTION: 200 C --DETECTOR: 250 C --COLUMN: see below
	CARRIER GAS: helium (99.999%) linear velocity 35 cm/sec, N_2 makeup at 15 cc/min
	COLUMNS: fused silica, 30m x 0.32-mm ID DB-624; 55 C for 5 min., 5 C/min to 100C, hold for 5 min., 15 C/min to 180 C for 8 min
	CALIBRATION: compressed gas cylinder standard, refer to method 422.199
	ESTIMATED LOD: see Table 2
	PRECISION: see Table 2

PRINCIPLE: A Tedlar bag sample of source gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using an electron capture detector.

APPLICABILITY: The method is applicable to the measurement of the following halogenated organics; chloroform, carbon tetrachloride, 1, 2-dichloroethane, tetrachloroethene, 1,2-dibromoethane, trichloroethene, 1,1,1-trichloroethane, trichlorofluoromethane and dichloromethane.

LIMITATIONS: This method is not applicable where the gases are occluded in particulate matter. Entrainment of gases, from the particulate trap in the sampling probe, into the sample gas stream has not been investigated. Also, sampling efficiencies and sample stability in actual source gas matrices have not been evaluated. Losses of ethylene dibromide may occur within 72 hours even in “clean” sample matrices.

INTERFERENCES: In sources where there is high moisture content a large peak elutes before chloroform. The tail of the peak can interfere with chloroform analysis. Methylene chloride and trichlorofluoromethane have short retention times. Because of the short retention times the analyst should especially note potential interfences for these two compounds.

REFERENCED METHODS: This method is based on sample collection in Tedlar bags; ARB method 422.1.

REAGENTS:*
1. Halogenated organics, @1000 ppb, 100, and 10 ppb in compressed gas cylinders.
2. Helium, 99.999%
3. Air, purified, to be used for dilutions, blank preparation, and standard preparation.

EQUIPMENT:*
1. Gas chromatograph, electron capture detector, intergrator, and columns.
2. Syringes, gas tight, 100-, 250-, 500- uL
3. Flow meters; rotameter type, 0 to 100 ml/min.
4. Gas regulators, stainless steel, dual stage with metal or teflon diaphrams.

* Refer to ARB method 422.1 for reagents and equipment used in Tedlar bag sampling

SAMPLING:
Refer to ARB method 422.1 for procedures used in Tedlar bag sampling.

CALIBRATION AND QUALITY CONTROL:
Refer to ARB method 442.199 for multipoint and daily calibration and quality control procedures.

TABLE 2

ACCURACY
Average Audit Bias

COMPOUND	ACCURACY[1]	PRECISION[2]	LOD (PPB)[3]
TRICHLOROFLUOROMETHANE	4.3%	10.1%	0.050
DICHLOROMETHANE	NA[4]	NA[4]	NA[4]
CHLOROFORM	3.9%	8.8%	
1,1,1-TRICHLOROETHANE	4.7%	5.4%	0.54
CARBON TETRACHLORIDE	6.3%	12.9%	0.15
			0.055
1,2-DICHLOROETHANE	NA[4]	NA[4]	NA[4]
TRICHLOROETHENE	5.6%	9.1%	0.92
1,2-DIBROMOETHANE	7.3%	9.7%	0.40
TETRACHLOROETHENE	5.4%	13.8%	0.075

1. Seven audits were performed between February 1987 and March 1989. The average results are listed in Table 1. The levels of the audits ranged from 4-120 ppb (v/v). The source of the audit cylinders were Research Triangle Institute and the National Bureau of Standards. The accuracy values represent averages of absolute values (bias) as determined from the seven audits. Note that the accuracy values reflect only the analytical process.

2. Precision values derived from multipoint analysis conducted in August, 1989.

3. Refer to Section 4.1.6 of method 422.199 for the equation used to calculate the LOD's. The values listed were calculated from multipoint analyses conducted in August, 1989.

4. Standards were not available at the time the multipoint analyses were performed.

State of California
Air Resources Board

Method 422.102

Standard Operating Procedure for the Gas Chromatographic Analysis of 1,3-Butadiene in Emissions from Stationary Sources

Method 422.102	1,3 BUTADIENE
PROPERTIES: gas M.W.: 54.09 B.P.: -4.4 C; V. P.: 280 kPa (26 psig) @ 25 C; vapor density: 1.9 (air = 1); explosive range: 2.0 to 11.5 % v/v in air	
SAMPLING	MEASUREMENT
SAMPLER: Field (portable) GC; Method 422 impinger train precedes the GC when conditions warrant. Refer to Appendix B and method 422.1 for details of use of the impinger train. NOTE: see Appendix C for the Tedlar bag sampling alternative.	TECHNIQUE: Field gas chromatography, flame ionization detector (PID optional). (see Appendix B for details of field GC) (see Appendix C for recommended analysis of Tedlar bag samples) ANALYTE: 1,3 butadiene INJECTION: 10 ul to 1000 ul; gas tight syringe or sampling loop. TEMPERATURE –INJECTION: 100C (suggested) --DETECTOR: 150 C (suggested) --COLUMN: isothermal 50 C CARRIER GAS: ultrazero air, 15 cc/minute COLUMNS: fused silica, 10m x 0.52-mm ID Al203/KCl PLOT with a 4” x 1/8”, 6.6% CSP 20M on Carbopack B, packed, backflushable precolumn. CALIBRATION: compressed gas cylinder standard, refer to method 422.199 ANALYTICAL RANGE: .005 to 100 ppm (PID) ANALYTICAL LOQ: .005 ppm (PID)
PRINCIPLE: A portable gas chromatograph is used at the emission site to perform a multi-dimensional GC analysis, using a flame ionization (FID) or photoionization detector (PID) APPLICABILITY: This method is applicable to the measurement of 1,3-butadiene from source emissions and source impacted ambient air. LIMITATIONS: The Tedlar bag sampling and analysis method described in Appendix C is not suitable for monitoring of 1,3-butadiene in combustion source emissions.	
INTERFERENCES: Pentane methyl acetylene, or vinylidene chloride may chromatographically interfere at high levels.	
REFERENCED METHODS: This method is based on NIOSH method 1024 (GC analysis).	

REAGENTS:	EQUIPMENT:
1. 1,3-Butadiene** @ 100 ppm and .10 ppm in compressed gas cylinders 2. Helium, 99.999% 3. Air, purified, to be used for dilutions, blank preparation, and standard preparation.	1. Gas chromatograph, flame ionization detector, integrator, and columns (see Appendices B & C). 2. Syringes, gas tight, 10-, 100-, 250-, and 500 ul.
** SPECIAL PRECAUTIONS: 1,3-Butadiene is a potential carcinogen, teratogen, and reproductive hazard. Work should be performed in a well ventilated fume hood.	
CALIBRATION AND QUALITY CONTROL: Refer to ARB method 422.199 for multipoint and daily calibration and quality control procedures.	

APPENDIX B: DESCRIPTION OF FIELD GAS CHROMATOGRAPHY SYSTEM

The following discussion describes the Photovac 10S70 analytical system and chromatographic operating conditions. Program events as listed below are specific to the Photovac system. However, mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. Other portable or field gas chromatographic systems are commercially available and may be substituted for the Photovac. However, the chromatographic system used must have backflushable precolumn capability to avoid contamination and degradation of the AL_2O_3-KCl PLOT analytical column. NIOSH method 1024 provides a detailed description and diagram of a pre-column backflush system.

Analytical system:

Figure 422.102.A shows the diagrams of the Photovac analytical system in the standby/backflush, sample loop fill, precolumn foreflush, and sample loop bypass configurations. These diagrams are provided as a guide for laboratories using equipment other than Photovac. The following table lists programmed events.

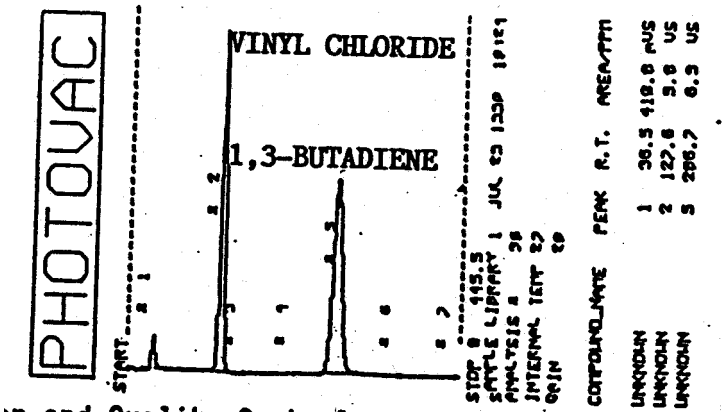
AUTOMATED (PROBE) EVENTS sec.

Event	ON	OFF	Description
1	0	10	sample pump switch
2	0	0	
3	10	30	sample loop inject (ON), backflush start (OFF)
4	0	10	probe and sample loop purge
5	20	30	end sample loop inject (ON), backflush start (OFF)

Chromatogram:

The chromatogram below was generated using the following conditions: 4” x 1/8”, 6.6% CSP 20M on Carbopack B precolumn; 10m x 0.52mm ID Al_2O_3/KCl fused silica PLOT analytical column; ultrazero air carrier gas at 15 cc/min.; 50 C isothermal; approximately

1cc (10 second sample loop flush) of 100 ppb 1,3-butadiene compressed gas standard; gain = 20; chart speed = .5 cm/sec.



Field Calibration and Quality Control:

Refer to Method 422.199., "Calibration and Quality Control Procedures for Analysis Methods", for a detailed description of initial performance evaluation and routine calibration procedures. Due to the nature of direct sampling though, routine calibration procedures are somewhat different. The sequence of calibration, QC, and sample runs as listed below is recommended when performing on-site GC analyses.

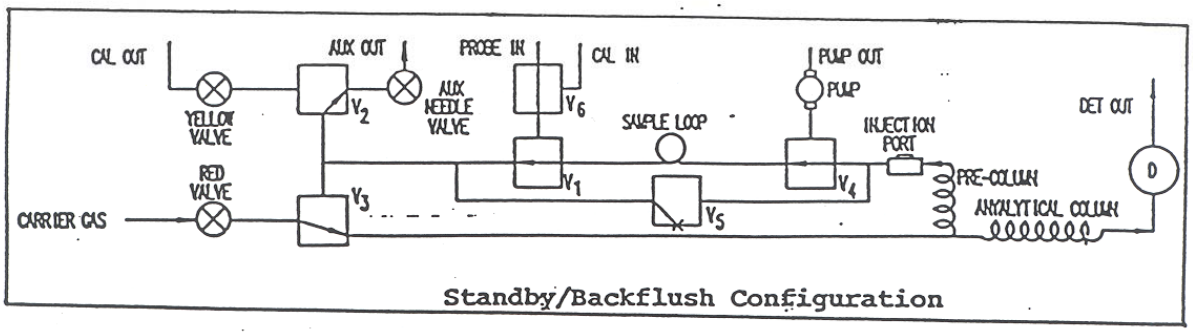
1. 3 point multipoint calibration bracketing the expected sample concentration.
2. blank run using ultrazero air.
3. field samples.
4. calibrate every 5th run (using the standard closest to sample concentrations).
5. blank run using ultrazero air at end of sampling.

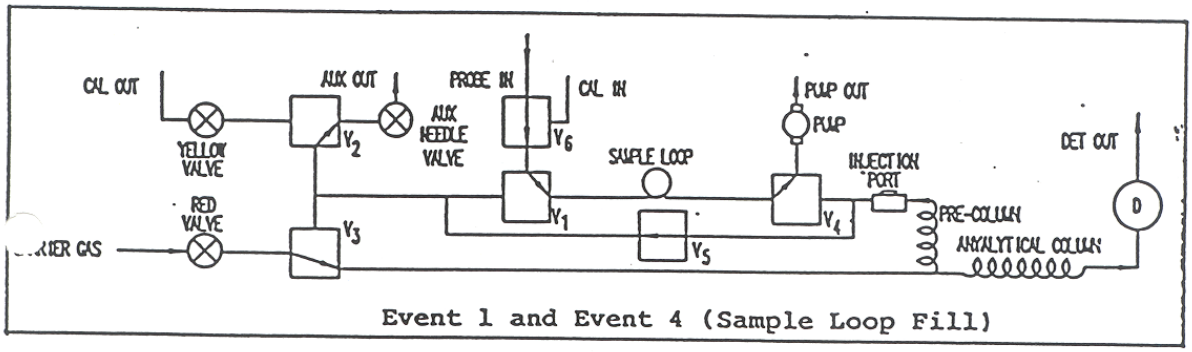
Sample probe and method 422.1. impinger train:

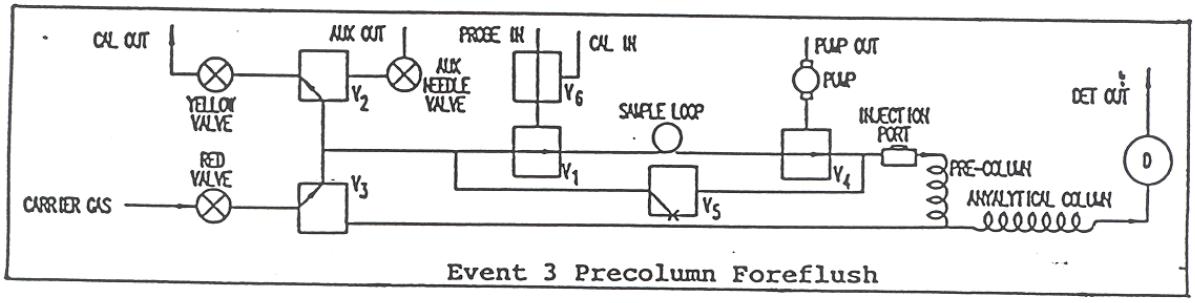
When acid and moisture knockout is required (refer to method 422.1, section 5), the impinger train and probe as described in method 422.1 will be used. In this case the 1/8" teflon sample inlet probe from the GC should be "Tee'd" into the ¼" telon impinger train line (after knockouts). A sample pump (fitted with a carbon trap) and rotameter are used to maintain a source gas flow of at least ~~100~~ 200 cc/minute through the impinger train and ¼" transfer lines. The pump would be located dowstream of the GC sample inlet probe "Tee". Alternatively, as diagrammed in Figure 422.102.B, an evacuated container/Tedlar bag set-up may be used to maintain source gas flow through the impinger train. Thus, the source emission sample collected in the bag may be used for the analysis of other VOC's.

When moisture and acid knockouts are not required, a 1/8" teflon line is used as the sample probe. If using the Photovac 10S70, the probe line should not exceed 8 feet.

FIGURE 422.102.A
PHOTOVAC ANALYTICAL SYSTEM







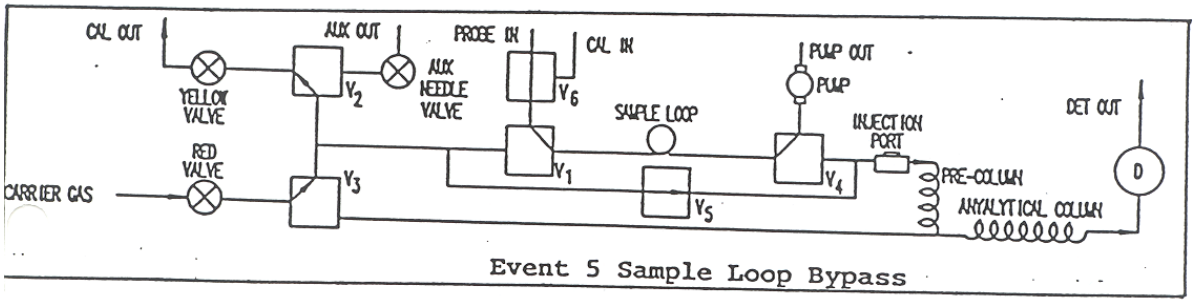
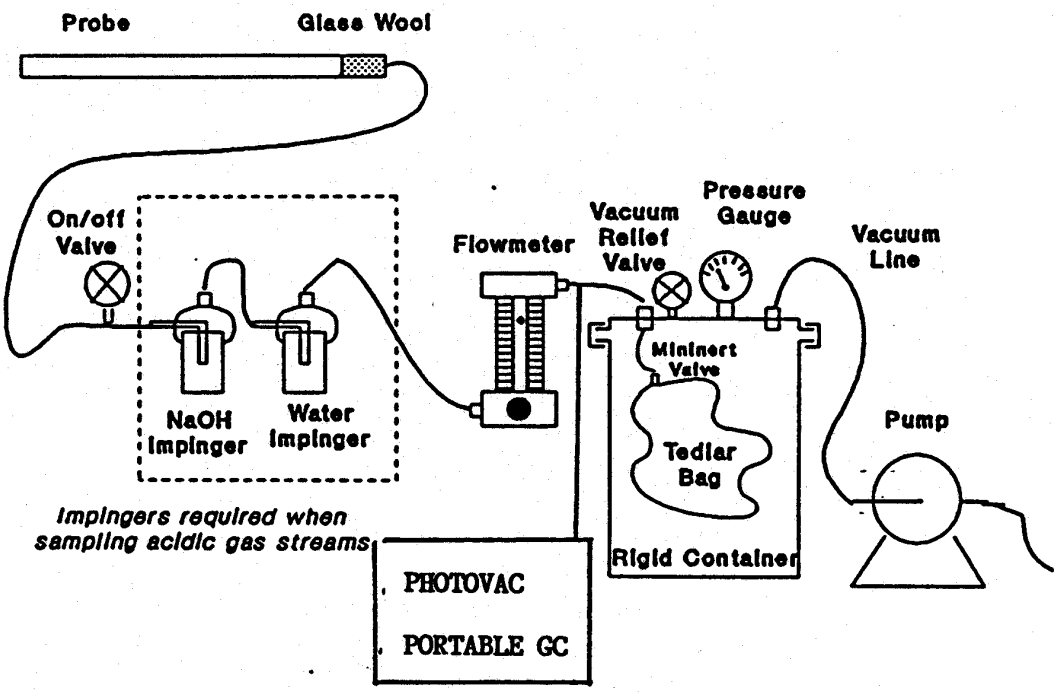


FIGURE 422.102.B
METHOD 422 IMPINGER TRAIN/FIELD GC SET-UP



APPENDIX C: TEDLAR BAG SAMPLING (METHOD 422.1) AND ANALYSIS ALTERNATIVE

Emissions from sources other than the combustion type (i.e., waste incineration, internal combustion engines, etc.) may be sampled using CARB method 422.1, which is an evacuated container/Tedlar bag procedure. If the tester is unsure of the sample stability, the tester should conduct a stability test. Validation tests performed by ARB staff have shown that 1,3-butadiene is not stable in bag samples collected from waste incinerators and IC engines. Decomposition of 1,3-butadiene in these type of samples tends to be too fast to allow even for a strict time requirement on bag analysis. Thus, for combustion type sources, the direct sampling/analysis described in Appendix B is necessary.

Recommended Analytical Procedure:

NIOSH method 1024 describes a method of GC analysis for 1,3-butadiene using a 50-m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) analytical column coated with Al_2O_3/KCl (Cat. #7515, Chrompack, Bridgewater, NJ) along with a 10-m x 0.5-mm ID fused silica CP Wax 57 CB precolumn (Cat. # 7648, Chrompack, Bridgewater, NJ). The Al_2O_3 column provides a very efficient separation of 1,3-butadiene from other C_4 to C_6 hydrocarbons at temperatures above ambient. The backflushable precolumn allows light hydrocarbons to pass through, but water, and polar or high boiling compounds are retained and can be backflushed. The precolumn is especially necessary when using the Al_2O_3/KCl column because water from the samples would deactivate the aluminum oxide, reducing the retention times, and high boiling or polar substances could accumulate on the column and irreversibly degrade the separation.

The chromatography in NIOSH method 1024 is set up for syringe injection of solvent extracted samples. In order to accomodate whole air samples, some modification of the system may be required. For source samples with relatively high levels of 1,3-butadiene (i.e., 1 ppm and above), gas tight sringes or sample loops would be appropriate for sample transfer to the GC. However, to achieve detection limits in the low ppb range, some means of sample preconcentration is required. A modified version of the NIOSH method has been used by ARB and is presented below. The only significant changes are the addition of a cryogenic preconcentrator (to handle whole air samples and get adequate detection limits) and the use of a poraplot Q precolumn. Refer to Figures 422.201.C & D for a diagram of the analytical system, list of programmed events and chromatogram.

Technique: gas chromatography, PID; column pressure switching system

Preconcentration: 18 cc, 9cc/min for 2 minutes, controlled by mass flow controller; cyrotrapped on a 5” x 0.32-mm ID GSQ capillary

column (Cat. # 115-3432, J&W Scientific, Folsom, CA) with liquid CO_2.

Injection: trap is thermally desorbed by the column oven at 80 C.

Columns: 50-m x 0.32-mm I.D. Al_2O_3/KCl PLOT analytical column;
10-m x 0.32-mm I.D. Poroplot Q precolumn.

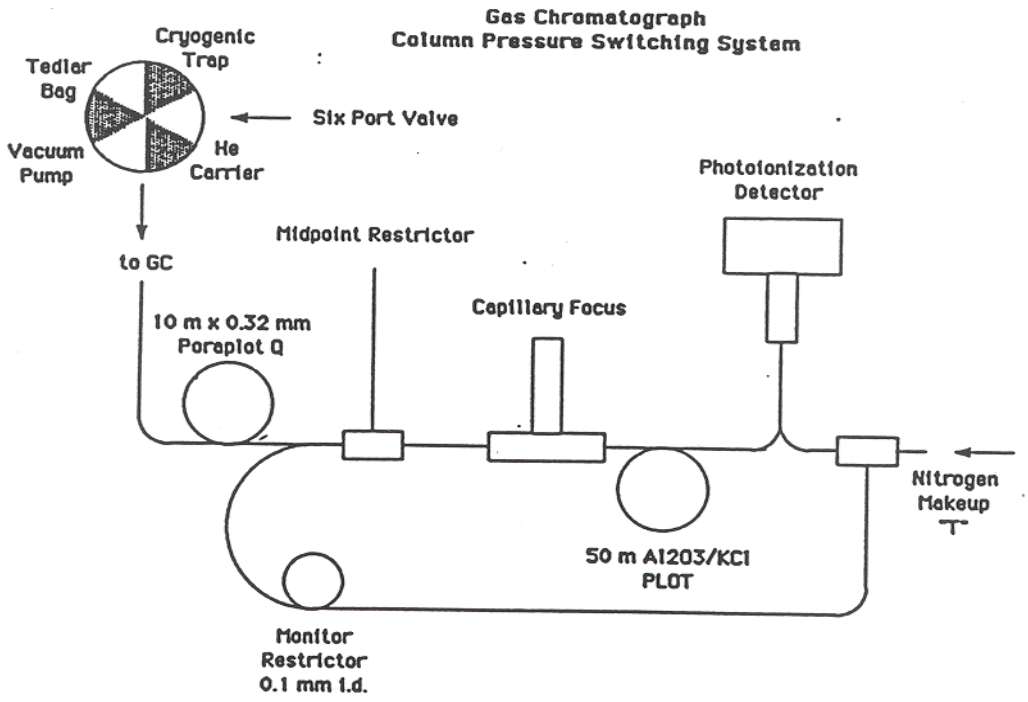
Carrier gas: 99.999% helium at 35 cm/sec.

Makeup gas: nitrogen at 30 cc/min.

Temperature program: 80 C for 8 minutes, 4 C/min to 120 C, 50 C to 200 C, hold 15 minutes.

NOTE: longer column bake-out times may be necessary to stabilize retention times.

FIGURE 422.102.C
ANALYTICAL SYSTEM
AND PROGRAMMED EVENTS

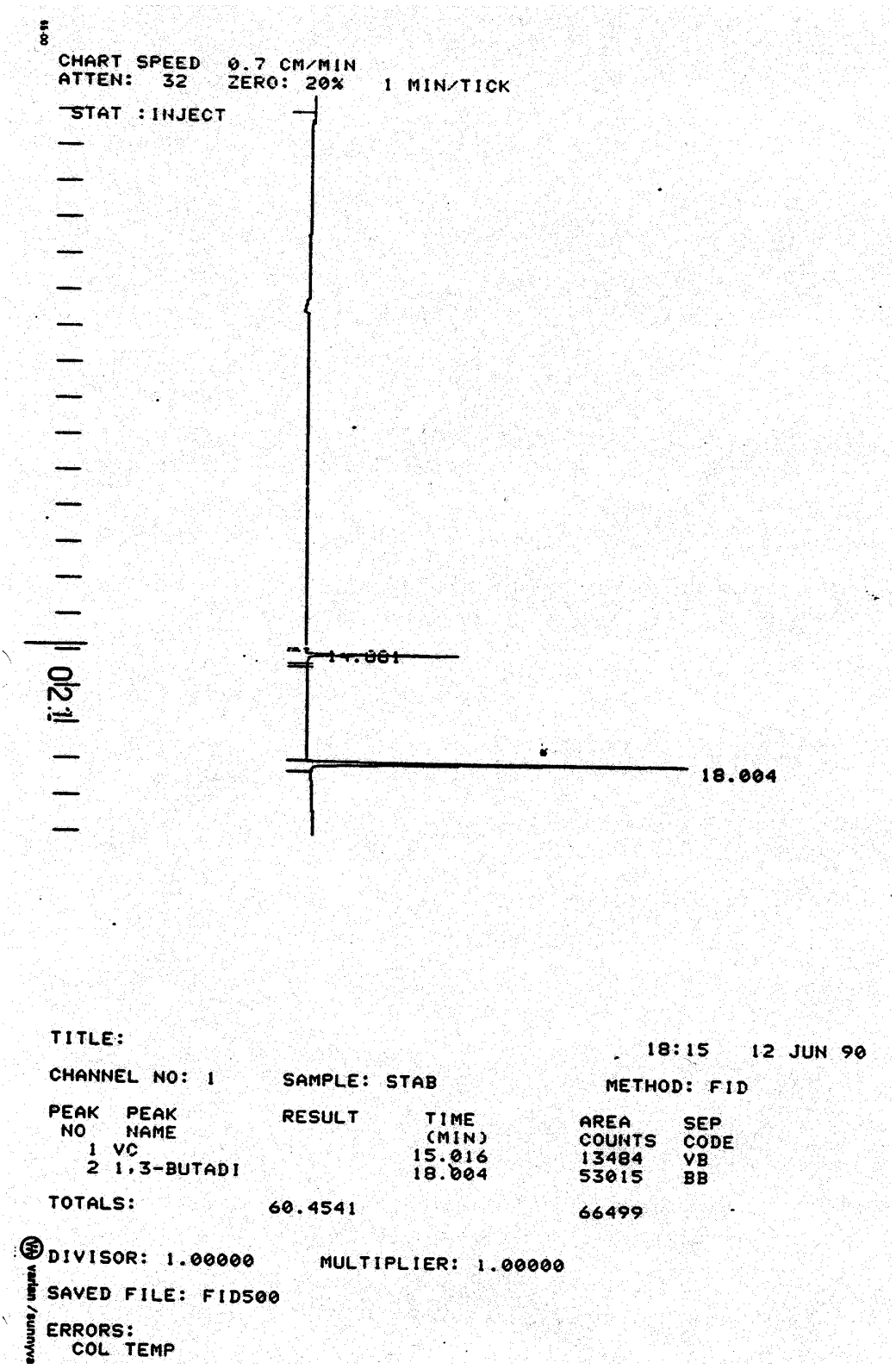


Programmed Events

Program	On	Off
Cold trap cryogen	:02	3:00
Valve to load	1:00	------
Valve to Inject	3:00	------
Capillary focus cryogen	5:30	10:20
Heartcut to analytical col.	5:30*	10:20
Precolumn backflush-splitter valve opens	10:30	25:00

* This program allows for the additional analysis of vinyl chloride.

FIGURE 422.102.D
CHROMATOGRAM



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METHOD 422.199

Calibration and Quality Control Procedures For Analysis Methods

Method 422.199

Calibration and Quality Control Procedures
for Analysis Methods

Page

1 INTRODUCTION 42

2 APPARATUS 42

3 REAGENTS 42

4 INITIAL PERFORMANCE EVALUATION 42

4.1 Multipoint calibration 43

5 ROUTINE CALIBRATION PROCEDURE 44

5.1 Option 1, Linear Regression 44

5.2 Option 2, Response Factor 45

6 ROUTINE QUALITY CONTROL 45

6.1 Analytical Blanks 45

6.2 Laboratory Replicate Samples 45

6.3 Calibration Check Sample 46

6.4 Performance Evaluation Samples 46

6.5 Qualitative Analysis Criteria 46

6.6 Quantitation Criteria 47

7 REPORTING 47

7.1 Complete Identification 47

7.2 Date of Submittal 47

7.3 The Raw and Calculated Data 47

7.4 The Calibration Data 47

7.5 Data Used to Define the Reporting Limit.....47

List of Figures

Figure 5 Preparation of Standards in Tedlar Bags, Data Sheet 50

Figure 6 Two-stage Calibration Gas Dilution system 51

Figure 7 Single-stage Calibration Gas Dilution System 52

Appendix D Preparation of Standards from High Concentration Standards ...48

Appendix E Calculations.....53

METHOD 422.199 CALIBRATION AND QUALITY CONTROL PROCEDURES FOR ANALYSIS METHODS

1. INTRODUCTION

Each laboratory that uses a procedure listed in method 422 is required to operate a formal quality control program. The minimum quality control requirements of this program consists of an initial demonstration of laboratory capability and an ongoing program of routine calibration and analysis of performance check samples to evaluate and document data quality. Two options are provided for routine calibration; calculation by linear regression or average response factor. The laboratory must maintain records of all performance checks to document the quality of generated data.

2. APPARATUS

2.1 Flowmeter, 100 sccm.

2.2 Tedlar bags, 10 L.

3. REAGENTS

3.1 Calibration standards can be obtained commercially in specially treated compressed gas cylinders. Concentrations of the minor components in each mixture must be traceable to the National Institute of Standards & Technology (NIST) or to a national measurement system approved by the Executive Officer of the Air Resources Board. NIST traceability may be accomplished by the specialty gas vendor via several methods:

(1) By analyzing the gas mixture directly against a NIST Standard Reference Material (SRM). This alternative can be utilized when an SRM with a proper component is available and the concentration is within a factor of two (2) from the gas mixture concentration.

(2) If SRM's are not available, analyzing the gas mixture against well characterized Gas Manufacturer Primary Standards (GMPS). These GMPS mixtures are analyzed against internal laboratory standards, gravimetric or volumetric, traceable to NIST.

4. INITIAL PERFORMANCE DEMONSTRATION

The following steps must be followed before the analytical method may be used. The performance evaluation must be repeated at least every six months. NOTE: Two options are provided for daily calibration (see Section 5). If response factor

method (5.2) is used, both Option 1 and 2 (4.1.2 and 4.1.4) must be conducted during initial performance evaluation.

4.1 Multipoint calibration

4.1.1 Standards are analyzed at least three times at four different concentrations. Refer to Appendix D for procedures for the preparation of serial standards from a high-concentration compressed gas cylinder standard. The concentration levels should be five times the limit of detection on the low end, approximately midway in the linear response range of the method, and near the high concentration end of the linear response limit. Results of the multipoint analyses must be documented and shall include data on intercept, slope, correlation of fit, relative standard deviations, range of concentrations tested, response factor and limit of detection calculations.

4.1.2 Option 1, Least Squares Fit. The least squares analysis of the data should produce a correlation coefficient of at least 0.98. Blank values shall not be subtracted from the raw data and the origin (0.0, 0.0) will not be used in the calculations. If the intercept deviates significantly from zero, the analysis must be reviewed for possible system contamination or other problems.

4.1.3 Standard deviations are calculated at each level of the multipoint and must be comparable to those published for the method.

4.1.4 Option 2, Response Factor. For each calibration target compound, calculate the pooled mean response factor (RF) from the set of four multipoint levels. Calculate the standard deviation and the percent relative standard deviation. The laboratory must demonstrate that RF values over the working range for the target compounds are constant. The percent relative standard deviations of the mean RF's must not exceed 15%. The equation for calculating the pooled mean response factor is listed below.

$$RF_{(pooled)} = (RF_{1a} + RF_{1b} + RF_{1c} + RF_{2a} + \ldots\ldots RF_{4b} + RF_{4c}) / 12$$

where 1a through 4c represent the individual response factors calculated from the 12 multipoint runs.

4.1.5 Analytical Limits of Detection (LOD) must be calculated. The LOD for each method must be calculated by the following equation:

$$LOD = |A| + 3S$$

where

A is the least squares intercept calculated from the multipont data (section 4.1.1).

S is the standard deviation of replicate determinations of the lowest standard. At least 3 replicates are required. The lowest standard must be run at 1 to 5 times the estimated detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:

$$S = RSD \times A$$

where RSD is the relative deviation of the lowest standard analyzed.

The equation as listed above was obtained from the Compendium of Methods for the Determination of Toxic Organics in Ambient Air, Research Triangle Park, North Carolina: U.S. Environmental Protection Agency; April 1984: Method T01. Publication No. EPA-600/4-84-041.

4.1.6 The Limit of Quantitation (LOQ) must be calculated by the following equation:

$$LOQ = 3.3 \times LOD$$

No analysis results will be reported below the LOQ.

5. ROUTINE CALIBRATION PROCEDURE

Routine users of the method, ie. daily, will use one of the following options for calibrations and result calculations. Compound concentrations used in the calibration curves must bracket levels found in stationary source emission samples.

5.1 Option 1, Least Squares Fit

A least squares fit, i.e. as determined with the initial multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every eight hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration as a check. The GC response of all analytes must be within 30% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The GC responses are recorded and inspected to check for

trends which indicate the degradation of standards or instrument performance.

5.2 Option 2, Response Factor

The average response factors, i.e. as determined with the multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every eight hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration (see section 4.1) as a check. The measured RF's of all analytes must be within 30% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The response factors are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

For non-routine users of the method, ie. 1 test per month or less, calibration involves generation of at least a 3 point curve during each analysis day and a midpoint calibration check after every 10 samples. Either linear regression or mean response factor calculations can be used. The initial performance evaluation is still required.

6. ROUTINE QUALITY CONTROL

6.1 Laboratory Blanks

A laboratory method blank is a volume of ultra high purity gas carried through the entire analytical scheme (preconcentration and analysis). The gas used for blank runs should be certified by the gas supplier or laboratory to contain less than the analytical limit of detection (LOD) of the analytes of interest. The laboratory blank volume must be equal to the sample volumes being processed. Laboratory blanks are analyzed each shift before the analysis of samples may proceed. A blank is also analyzed after the analysis of a sample containing components with concentrations greater than the most concentrated standard used. The laboratory blank results will be reported along with raw sample data in final reports. Sample results should not be corrected for blank contribution. Note that a field blank analysis may be used in place of the laboratory blank. However, if the results of the field blank are greater than LOQ, a laboratory blank will be run to isolate the source of contamination.

6.2 Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples, or at least one sample per batch, will be analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift. The precision ($|\text{Ave.} - X_1|/\text{Ave.}) \times 100$) of duplicate

analyses must fall within predetermined limits, i.e, 3 × RSD as established during the initial performance evaluation.

6.3 Calibration Check Sample

The midpoint standard used in multipoint calibrations must be analyzed every eight hours, or every ten samples, whichever is more frequent, to check instrument performance. The GC response of all analytes must be within 30% of the mean values established in the multipoint calibration or a new calibration curve must be generated. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

6.4 Performance Evaluation Samples

To demonstrate data quality, performance evaluation samples may be analyzed periodically. At the discretion of the Executive Officer, periodic analysis of performance evaluation samples may be required. Such materials for this method will be available for purchase through private vendors (e.g., Scott Specialty Gases' facilities in San Bernardino (714-887-2571) and Fremont (415-659-0162) California). The vendor should be informed of the component of interest and the concentration range expected. The vendor will forward the gas mixture and gas delivery equipment.

If analysis of performance evaluation samples is required by the Executive Officer, the analyses shall be conducted in the following manner. The performance evaluation material shall be used to evaluate both sampling and analytical systems. Performance evaluation samples shall be analyzed at a frequency dependent on how often the method is used. If the method is used on a daily basis, the performance evaluation sample must be analyzed twice a month. If the method is used less frequently, the performance evaluation sample must be analyzed once a month or whenever the method is used (whichever is less). A value of ±20% of the stated concentration of the performance evaluation sample must be recovered for the analyte of interest. The results of these analyses must also be recorded and placed on permanent file for at least three years and shall be made available to the Executive Officer upon request. All performance evaluation samples will be labeled with an expiration date and may be re-certified by the vendor if they contain sufficient volume (i.e. greater then 60% residual).

6.5 Qualitative Analysis Criteria

The retention time of the target compound must be within 0.06 RRT units of the standard RRT.

6.6 Quantitation Criteria

The column resolution criteria of 20% valley (as measured from the baseline to valley minimum) between a target compound and an interfering compound must be achieved before any quantitation can be allowed. When a compound interferes with the target compound and the degree of the interferences exceeds the column resolution criteria the compound can still be quantified if the following criteria is met. Set the reporting limit for the lowest amount that can be quantified high enough such that the interfering compound accounts for less than 10% of the area of the target compound. If integrations are done automatically as in automated data systems or integrators the baseline must be checked. Any improper baseline assignments must be corrected.

7 REPORTING

Each report of analyses shall be in the following format and will include the following information. Refer to Appendix E for result calculations format.

7.1 Complete identification of the samples analyzed (sample numbers and source). Pertinent information should be submitted to the analytical laboratory via a chain of custody record.

7.2 Date of submittal of the sample, date and time of GC analysis. The latter should appear on each chromatogram included with the report.

7.3 The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).

7.4 The calibration data, including average response factors calculated from the calibration procedure described in Section 5. Include the relative standard deviation, and data showing that the midpoint response factors have been verified at least once during each 8-hour period of operation or with each seperate set of samples analyzed.

7.5 All relevant data used to define the reporting limit will be reported. This will include parameters such as sampling volumes, sample injection volume, chromatographic interferences, and Tedlar bag contamination levels. In no case will results be reported below the established reporting limit. Test reports should include a table summarizing reporting limits (per sample) including a description of causes of variation.

APPENDIX D: PREPARATION OF STANDARDS FROM HIGH CONCENTRATION STANDARDS

Obtain enough high concentration cylinder standards to represent all the organic compounds expected in the source samples.

Use these high concentration standards to prepare lower concentration standards by dilution, as shown by Figures 6 and 7.

To prepare the diluted calibration samples, calibrated rotameters are normally used to meter both the high concentration calibration gas and the diluent gas. Other types of flowmeters and commercially available dilution systems can also be used.

Calibrate each flowmeter before use by placing it between the diluent gas supply and suitably sized bubble meter, spirometer, or wet test meter. Record all data shown on Figure 5. While it is desirable to calibrate the cylinder gas flowmeter with cylinder gas, the available quantity and cost may preclude it. The error introduced by using diluent gas for calibration is insignificant for gas mixtures of up to 1,000 to 2,000 ppm of each organic component.

Once the flowmeters are calibrated, connect the flowmeters to the calibration and diluent gas supplies using 6-mm Teflon tubing. Connect the outlet side of the flowmeters through a connector to a leak-free Tedlar bag as shown in Figure 7. (See Section 7.1 for bag leak-check procedures.) Adjust the gas flow to provide the desired dilution, and fill the bag with sufficient gas for GC calibration. Be careful not to overfill and cause the bag to apply additional pressure on the dilution system. Record the flow rates of both flowmeteres, and the laboratory temperature and atmospheric pressure. Calculate the concentration (Cs) in ppm of each organic in the diluted gas as follows:

$$C_s = 10^6 \times \frac{X \times Q_c}{Q_c + Q_d} \qquad \text{Eq. 18-1}$$

where:

10^6 = Conversion to ppm.

X = Mole or volume fraction of the organic in the calibration gas to be diluted.

Q_c = Flow rate of the calibration gas to diluted

Q_d = Diluent gas flow rate.

Single-stage dilutions should be used to prepare calibration mixtures up to about 1:20 dilution factor.

For greater dilutions, a double dilution system is recommended, as shown in Figure 2. Fill the Tedlar bag with the dilute gas from the second stage. Record the laboratory temperature, barometric pressure, and static pressure readings. Correct the flow reading for temperature and pressure. Calculate the concentration (Cs) in ppm of the organic in the final gas mixture as follows:

$$C_s = 10^6 \times \frac{Q_{c1}}{(Q_{c1} + Q_{d1})} \times \frac{Q_{c2}}{(Q_{c2} + Q_{d2})} \qquad \text{Eq. 18-2}$$

where:

10^6 = Conversion to ppm.

X = Mole volume fraction of the organic in the calibration gas to be diluted.

Q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.

Q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.

Q_{d1} = Flow rate of diluent gas in stage 1.

Q_{d2} = Flow rate of diluent gas in stage 2.

FIGURE 5

Preparation of Standards in Tedlar Bags
and Calibration Curve

	Standards		
	Mixture #1	Mixture #2	Mixture #3
Standards Preparation Date:			
Organics _____	_____	_____	_____
Bag number or identification	_____	_____	_____
Dry gas meter calibration factor	_____	_____	_____
Final meter reading (liters)	_____	_____	_____
Initial meter reading (liters)	_____	_____	_____
Metered volume (liters)	_____	_____	_____
Average meter temperature (°K)	_____	_____	_____
Average meter pressure, gauge (mm Hg)	_____	_____	_____
Average atmospheric pressure (mm Hg)	_____	_____	_____
Average meter pressure, absolute (mm Hg)	_____	_____	_____
Syringe temperature (°K) (Section 6.2.2.1)	_____	_____	_____
Syringe pressure, absolute (mm Hg) (Section 6.2.2.1)	_____	_____	_____
Volume of gas in syringe (ml) (Section 6.2.2.1)	_____	_____	_____
Density of liquid organic (g/ml) (Section 6.2.2.2)	_____	_____	_____
Volume of liquid in syringe (μl) (Section 6.2.2.2)	_____	_____	_____
GC Operating Conditions:			
Sample loop volume (ml)	_____	_____	_____
Sample loop temperature (°C)	_____	_____	_____
Carrier gas flow rate (ml/min)	_____	_____	_____
Column temperature			
Initial (°C)	_____	_____	_____
Rate change (°C/min)	_____	_____	_____
Final (°C)	_____	_____	_____
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hr clock)	_____	_____	_____
Distance to peak (cm)	_____	_____	_____
Chart speed (cm/min)	_____	_____	_____
Organic retention time (min)	_____	_____	_____
Attenuation factor	_____	_____	_____
Peak height (mm)	_____	_____	_____
Peak area (mm^2)	_____	_____	_____
Peak area x attenuation factor (mm^2)	_____	_____	_____
Calculate concentration (ppm) (Equation 18-3 or 18-4)	_____	_____	_____

Plot peak area x attenuation factor against calculated concentration to obtain calibration curve.

Standards prepared in Tedlar bags
And calibration curve.

Flowmeter Calibration

Flowmeter number or identification _____

Flowmeter type _____

Calibration device (x): Bubble meter _____ Spirometer _____ Wet test meter _____

Readings at laboratory conditions:

Laboratory temperature (T_{lab}) _____°K

Laboratory barometric pressure (P_{lab}) _____ mm Hg

Flow data:

Flowmeter			Calibration device		
reading (as marked)	temp. (°K)	pressure (absolute)	Time (min)	gas volume[a]	flow rate[b]

a = Volume of gas measured by calibration device, corrected to standard conditions (liters).

b = Calibration device gas volume/time.

Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a "family" of calibration curves that cover the operating pressure and temperature ranges of the flowmeter.

While the following techniques should be verified before application, it may be possible to calculate flow rate readings for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{750 \times T_{lab}}{P_{lab} \times 298}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (standard conditions)

Flowmeter calibration.

FIGURE 6

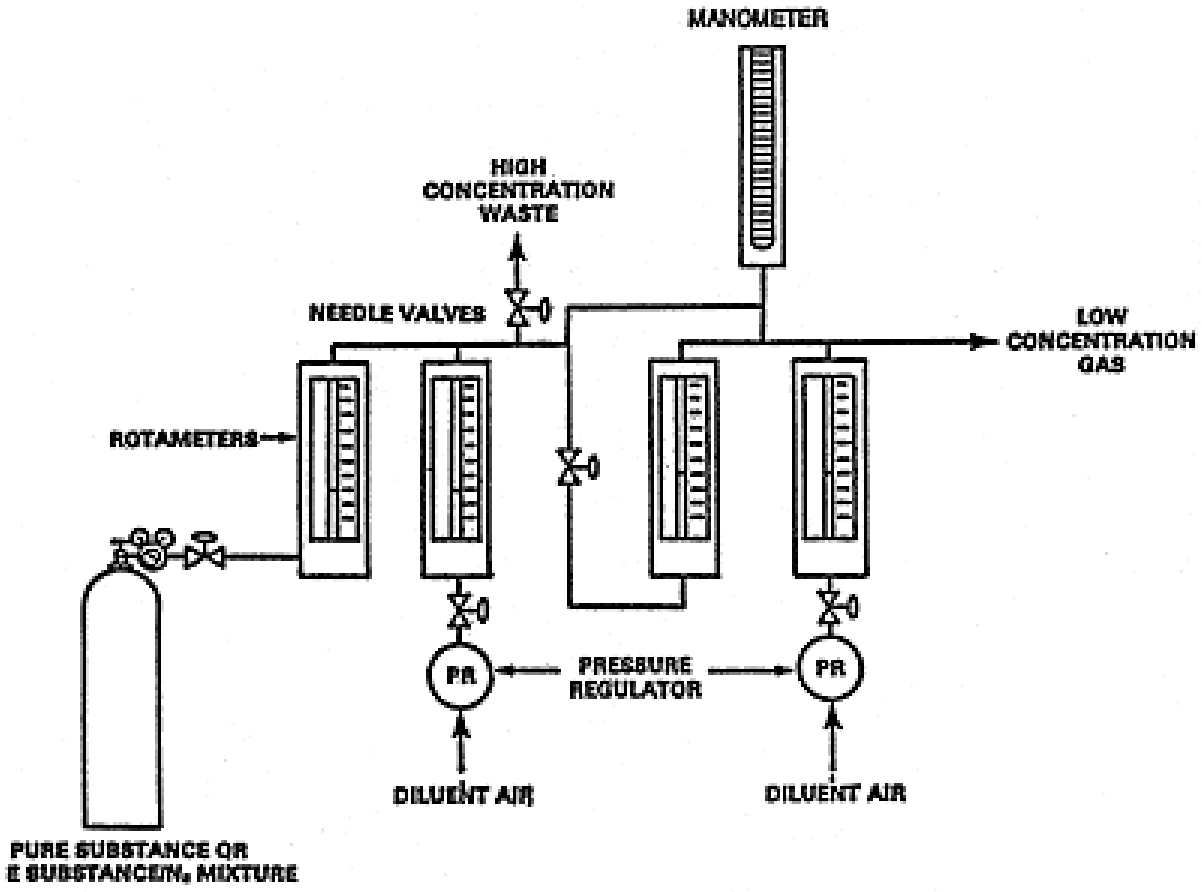
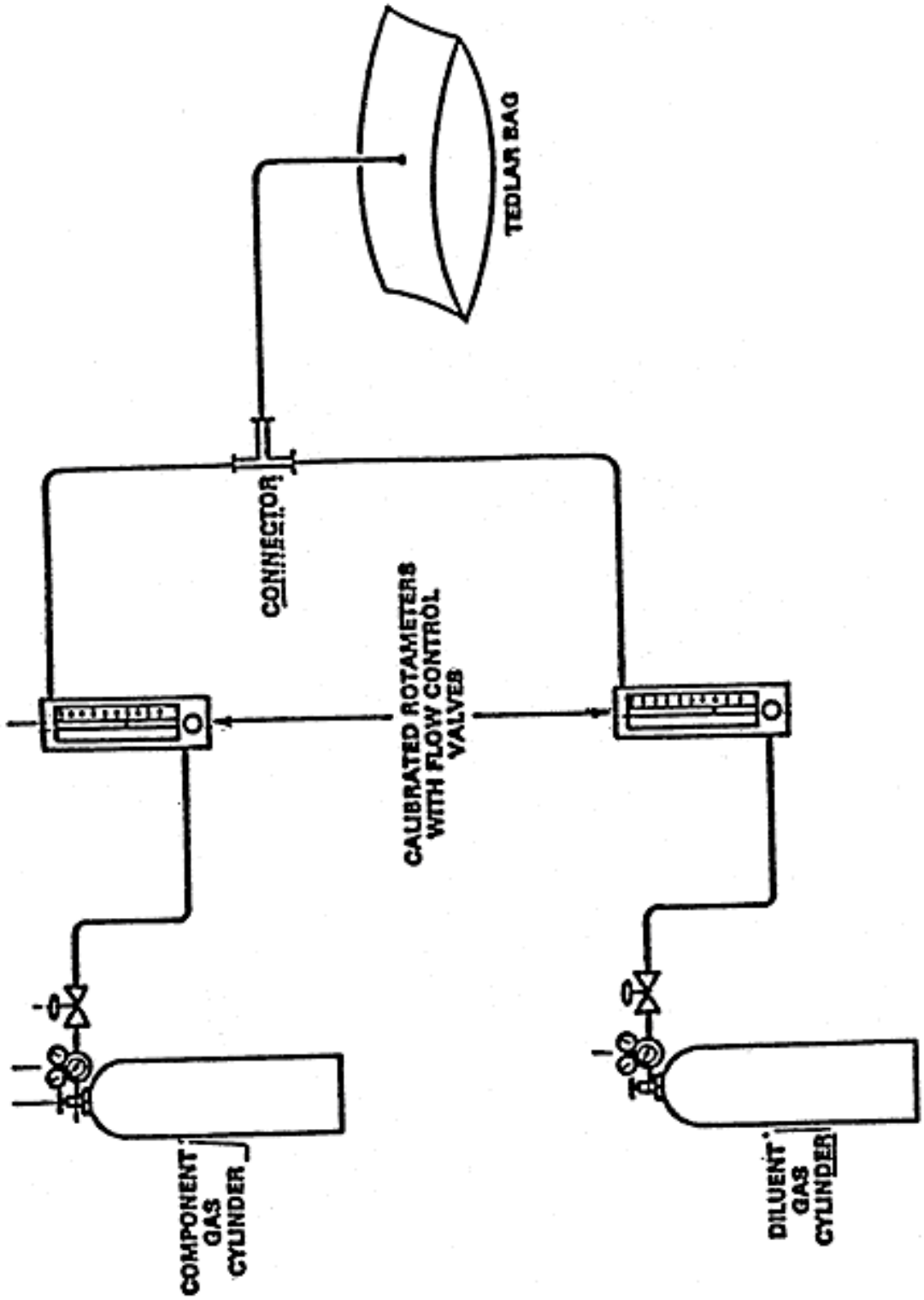

MANOMETER
HIGH CONCENTRATION WASTE
NEEDLE VALVES
LOW CONCENTRATION GAS
ROTAMETERS
PR
PRESSURE REGULATOR
PR
DILUENT AIR
DILUENT AIR
PURE SUBSTANCE OR
E SUBSTANCE/N₂ MIXTURE

FIGURE 7 Single-Stage calibration gas dilution system.



APPENDIX E: CALCULATIONS

Carry out calculation retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

Emission Calculations. From the average calibration curve described in Section 7.1.5., select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample as follows:

$$C_c = C_s P_r T_i F_r D\, E / P_i T_r (1 - B_{ws})$$

where:

C_s = concentration of the organic from the calibration curve, ppm.

P_r = Reference pressure, the barometric pressure or absolute sample loop pressure (if applicable) recorded during calibration, mm Hg.

T_i = Sample loop or syringe temperature at the time of sample analysis, “K”.

F_r = Relative response factor (if applicable, see Section 6.4).

P_i = Barometric or absolute sample loop pressure (if applicable) at the time of analysis, mm Hg.

T_r = Reference temperature, the temperature of the sample loop (if applicable) recorded during calibration, “K”.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.

D = Correction factor for the impinger purge volume.

E = Correction factor for dilution volume if bag was pre-filled with dilution air before sampling.