United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Research Triangle Park NC 27711

EPA-600/4-78-057
September 1978

Research and Development

The Use of Tedlar Bags to Contain Gaseous Benzene Samples at Source-Level Concentrations

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

THE USE OF TEDLAR BAGS TO CONTAIN GASEOUS BENZENE SAMPLES AT SOURCE-LEVEL CONCENTRATIONS

by

Joseph E. Knoll, Wade H. Penny, and M. Rodney Midgett
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Tedlar bags have been evaluated as containers for gaseous benzene samples at source-level concentrations. Sample stability over time periods typically required in field work, "memory" effects, decontamination procedures, and the temperature range over which the bags can be successfully used were subjects of this study. Benzene samples remained essentially unchanged for up to 17 days. Cooling to -40° C or heating to 70° C did not produce concentration changes. Above 105° C, decomposition of the bag seals was observed. No evidence of permeation loss at room temperature was observed, and absorptive loss could be observed only upon prolonged contact. Flushing the bags with nitrogen was sufficient to remove all traces of previous samples. Calibration mixtures were prepared in Tedlar bags by injecting measured quantities of liquid benzene while metering-in nitrogen gas. These bag standards were used to perform calibrations for the G.C. measurement of benzene-containing cylinders. Corroboration of these results by three other laboratories demonstrated that such bag samples are useful as calibration standards.

CONTENTS

Abstract ii

Figures. iv

Tables v

Acknowledgments vi

1. Introduction 1

2. Conclusions 3

3. Experimental 4

4. Results and Discussion 6

References 21

Appendix A 22

FIGURES

Number		Page
1	Double Tedlar bag assembly	14

TABLES

Number		Page
1	Freshly Filled Tedlar Bag Results as a Percent of the Master Cylinder Concentration	8
2	The Effect of Temperature on Benzene Concentration of Gas Mixtures Stored in Tedlar Bags	10
3	Variation of the Benzene Concentration of Gas Mixtures Stored in Tedlar Bags at Ambient Temperatures	13
4	Benzene Concentration Changes in Double Tedlar Bag	16
5	Benzene Concentration Values of Aluminum Cylinders as Determined by Various Corroborators	17
6	Interlaboratory Comparison of Benzene Concentration of Various Analyzed Components	18

ACKNOWLEDGMENTS

The authors acknowledge with thanks the help of Mr. William Lonneman of this Agency and Mr. Robert Denyszyn of the Research Triangle Institute for performing the corroborative analyses reported herein. They also wish to thank Mr. Lonneman for permission to use his bag sealing machine and Miss Susan Setzer for performing several analyses.

SECTION 1

INTRODUCTION

A frequent problem in gas analysis involves the collection of a representative and stable gas sample. Such problems are particularly important in environmental studies since pollutants are, by their nature, reactive materials that tend to undergo transformations with time. One method that has frequently been employed utilizes nonrigid plastic containers (1). Many studies have been made of the ability of such bags to preserve gas samples free from contamination and change. Schuette (2) has reviewed much of the earlier work in this area, and Seila, et al. (3) have discussed more recent studies and, in particular, the plastic Tedlar. This latter investigation studies the effects of simulated sunlight and radiation on the stability of hydrocarbon samples in Tedlar bags, in which they observed a series of contamination peaks released by the radiation and suggested that the origin of these peaks was manufacturing residues. Since most investigators work in this area, the study was concerned with concentrations at ambient air levels.

On the other hand, plastic bags have also been used for stationary source sampling. In this field, samples usually contain much higher concentrations and the major problems encountered result from sample cross-contamination or "memory" effects and from the extremes of temperatures that are encountered. Tedlar bags have been successfully employed in the source sampling method for vinyl chloride (4). Also, Schuetzle, et al. (5) have

compared various plastic materials and found Tedlar to be superior. This material is a polyvinylfluoride that is relatively inert to many other substances and that can be used to fabricate large containers. Flexibility of container size is an important advantage in source emission analysis where it may be necessary to collect gas over an extended period of time in order to obtain a representative sample.

Recently, a method for the analysis of benzene has been proposed that uses Tedlar bags for sample collection (see Appendix A). This method has been developed in the Test Support Section of the Emission Measurement Branch, ESED, EPA, and has been used to determine benzene concentrations in the effluent streams from chemical process plants (6). In view of the developing agency committments to control emissions of certain volatile organic compounds, the present investigation was undertaken to study the stability of benzene in Tedlar bags at source level concentrations. Specifically, it deals with time studies of the benzene concentrations in Tedlar bags that were held at room temperature and that were heated and cooled. Permeation and "memory" effects were investigated, and some information was also obtained on the utility of bag samples as standards. This work was carried out in the Source Section of the Quality Assurance Branch, EMSL, EPA, which has a program to evaluate and standardize source emission test methodology.

SECTION 2

CONCLUSIONS

This study of Tedlar bags containing benzene/nitrogen gas mixtures that were subjected to varying conditions yielded the following results:

When Tedlar bags were held at room temperature, the benzene concentration remained within 94% of its initial value after 17 days.

When Tedlar bags were cooled to -40° C for one hour, no concentration change could be detected.

When Tedlar bags were heated to 70° C for one hour, no concentration change could be detected. When they were heated to temperatures above 105° C, a decrease of 6-20% was observed, along with decomposition of the adapter and bag seals. The observed loss appeared to result from leakage.

There was no evidence of permeation loss at room temperature.

Flushing bags three times with nitrogen was sufficient to remove at least 99.9% of the previous samples, except when bags were held in contact with benzene for prolonged periods of time. Then, desorption of benzene was evident only after the bags were heated to 60° C for one hour.

Ten-liter bags had the same characteristics as 100-liter bags.

Tedlar bags are useful for preparing calibration gas mixtures from measured quantities of liquid benzene and nitrogen.

SECTION 3

EXPERIMENTAL

Tedlar bags were fabricated from 2-mil plastic sheets. The edges were sealed with a Vertrod Thermal Impulse Heat Sealing Machine (Model 48 EPS 1/4 WC). Connections to the bag were made using an O-Seal Straight Thread Adapter having a 1/4 in. o.d. tube and a 7/16-20 thread (Swagelok 401-A-OR), which was inserted through a 2 in. square piece of VisQueen polyethylene tape fixed to the outside surface of the bag. The adapter was held in place with an 0.058 in. Teflon washer (1/2 i.d. by 1 in. o.d.) and a 7/16-20 nut. A 7115G4B Hoke ball valve was connected to the adapter.

A 65 ppm benzene in nitrogen reference mixture in an aluminum cylinder was obtained from Airco, Inc. Two other such cylinders of benzene gas were obtained from Scott Research Laboratories and were standardized at the Research Triangle Institute. In one part of this study, benzene-nitrogen mixtures in Tedlar bags were prepared by injecting in liquid benzene while filling the bags with nitrogen. The nitrogen was measured using a No. 802 Singer dry gas meter; a No. 801, 10 microliter Hamilton syringe was used to measure the benzene. In all other instances, Tedlar bags were filled directly from the reference cylinder.

Benzene concentrations were determined using a Tracor Model 222 gas chromatograph equipped with dual flame ionization detectors (No. 12016) and a 1.0 ml sampling loop. The output was recorded using an Autolab Systems IV computing integrator. The chromatographic column consisted of an 8 ft. by

1/8 in. stainless steel helix packed with 10% TCEP (1,2,3 tris-(2-cyanoethoxy) propane) on 80/100 mesh Chromasorb P AW. The following operating conditions were employed: inlet temp., 105° C; column, 75° C; detector, 165° C; carrier gas, liquid air nitrogen at 20 ml/min. Under these conditions, benzene eluted with a Kovats retention index of 1066. Only a single peak could be observed.

Tedlar bags were sampled by drawing the gas through the chromatographic sampling loop using an Bell and Gossett LV 1/12 vacuum pump. The reference gas was forced through the sampling system under its own pressure and was used to normalize the gas chromatograph results.

SECTION 4

RESULTS AND DISCUSSION

STABILITY OF BENZENE VAPOR WHEN STORED IN TEDLAR BAGS

In this phase of the investigation, a study was made of the stability of benzene vapors that were contained in Tedlar bags for differing lengths of time and under a variety of temperature conditions. Although much information was available on the use of Tedlar bags in ambient air studies (3) and some also had been obtained that related to stationary source sampling (5), much data was missing that dealt with specific source problems. These problems not only included questions of sample stability over time periods typically required in field work, but also included "memory" effects, decontamination procedures and the temperature range over which such bags can be successfully used. While the conditions to which these bags were subjected are unlikely to occur in laboratory studies, our findings do hold important ramifications for those engaged in field work where extreme variations in temperature and concentration do actually occur.

To initiate this study several tests were made to determine whether contamination or "memory" effects result when benzene vapor interacts with Tedlar. Such effects could take place if benzene vapor is absorbed into the plastic material and slowly released thereafter. This would be a problem if the bag is refilled with another sample at a considerably lower benzene concentration. Thus, this part of the study was carried out not only to assure that "memory" effects did not cause errors in our results but also, because Tedlar bags would be expected to be reused many times during field studies, to

determine whether intercontamination of samples takes place. To determine this, new Tedlar bags were filled with 65 ppm benzene/nitrogen gas mixture, then the bag was flushed three times by repeatedly filling with nitrogen and evacuating. The bag was filled with nitrogen and, when analyzed, benzene could no longer be detected. (The detection limit of the GC system was less than 0.1 ppm.) The bag was left to stand at room temperature for several days, and, when reanalyzed, no detectable benzene could be observed. The experiment was repeated using a Tedlar bag that had contained the benzene gas mixture at room temperature for several days, one in which the bag containing the benzene gas mixture was heated to 65° C for one hour, and one that was cooled to -40° C for one hour. With only one exception, the flushing procedure described above was adequate to remove all detectable traces of benzene from the container.

As stated above, the memory effect was actually observed in one instance. A Tedlar bag that had contained 65 ppm benzene/nitrogen mixture for 17 days was evacuated, flushed, filled with nitrogen, and measured. At first no benzene could be detected in the bag's contents, but, when the bag was heated to 60° C for one hour, a benzene concentration of 1.7 ppm was measured. Apparently, benzene is slowly absorbed into the Tedlar plastic in amounts that can become appreciable after an extended period of time. Therefore, these results indicate that benzene-containing gas samples should not be left in contact with the Tedlar plastic for any longer than necessary, if "memory" effects are to be completely avoided.

In the stability study that is to be described below, the concentration of benzene in gas within Tedlar bags was determined by comparing the bags with a master cylinder from which the bags had been filled. Each time the bags were measured, the cylinder was run and used to calibrate the chromatograph.

The results in Table I show that this technique produced nearly identical values. Later, measurements made with a Hewlett-Packard Model 5830 GC confirmed these findings.

The effect of temperature on bag stability was carried out as follows. A bag was filled with the benzene/nitrogen mixture and measured. It was then subjected to the temperature in question for one hour, after which it was allowed to come to ambient temperature and was measured. The bag was evacuated, refilled with the benzene/nitrogen mixture, and remeasured. It was subjected to the temperature under consideration for an additional hour, after which it was brought to ambient conditions and measured again. The GC instrument was recalibrated using the master cylinder three times during each such run (at the initial fill, at the end of the first conditioning, and at the end of the second conditioning) to insure that the gas chromatograph was giving stable responses. The results (Table 2) indicate no appreciable change in benzene concentration over the range of temperatures studied, except that some losses appear just above 110° C.

In order to establish an upper limit to the temperature conditions over which Tedlar bags can be accurately employed in sampling procedures, bags filled with 65 ppm benzene in nitrogen were heated for one hour at either 110° or 115° C. At this latter temperature, the Tedlar material softened, became pliable, and the valve sealing tape melted, causing the valve fittings to loosen and leak. These decompositions at 115° C made it impossible to ascertain whether the drop in benzene concentration shown in Table 2 was the result of vapor seepage through the valve and edge seals, or due to permeation through the Tedlar material. As the results in Table 2 indicate, it is possible to expose benzene vapors contained in Tedlar bags to a temperature

Table 1. FRESHLY FILLED TEDLAR BAG RESULTS AS A PERCENT OF THE MASTER CYLINDER CONCENTRATION.

Run	Number of measurements	Percent
1*	2	96.8
2*	3	98.3
3†	4	101.2

*Samples introduced using syringe.

†Measurement made using Hewlett-Packard Model 5830.

Table 2. THE EFFECT OF TEMPERATURE ON BENZENE CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS.

Run	Temp. (C°)	Benzene concentration in ppm			
		Initial filling	After first hour	After refilling	After second hour
1	-41	65	64	67	66
2	70	65	64	65	65
3	80	65	63	64	64
4	110	65	61	66	60
5	110	65	61	--	--
6	110	65	60	--	--
7	115	65	52	--	--

-- Indicates that bags were not refilled.

approaching 110° C for short durations without incurring significant loss of sample, provided that the valve and bag seals remain intact. Above 110° C, however, the bags deteriorate rapidly and exhibit sample loss, so use above that temperature should be avoided.

It is important to emphasize here that the quality of the valve fittings and bag construction is essential in obtaining sample stability. Care must be taken that all three edges of the bag are heat-sealed without gaps or wrinkles. In some of our runs in the 110°-115° C range, double-sealed bags with reinforced valve ports were substituted for the typical single-sealed bags. This was done in an attempt to minimize sample loss at the higher temperatures. Slight improvements were noted.

During the study cited above, we observed that heating Tedlar bags produced several new peaks on the chromatograms. Such effects have been noted by other investigators (3). To determine whether heating caused the release of substances that would interfere with benzene measurements, a new Tedlar bag was filled with nitrogen and heated to 90° C for one hour. A chromatogram of the contents produced several peaks, but none of them fell within the integration range of benzene. If any substances were emitted in that range, they were below the 0.1-ppm detection sensitivity of our instrument. Thus, when making measurements of benzene at source-level concentrations, heating Tedlar bags to 90° C for one hour does not cause the Tedlar to release substances that interfere in the measurement of benzene, provided that the chromatographic column and parameters used in this study are employed.

The studies cited above all dealt with stability and "memory" effects that were observed over time periods of a few hours. We have also investigated the stability of benzene/nitrogen mixtures in Tedlar bags for longer periods

of time, for up to 408 hours. This work was done at ambient temperatures, and the results are listed in Table 3. The measurements show that very little change took place over the time periods that elapsed. They indicate that Tedlar bags will be useful for the storage and transport of benzene-containing samples.

Although these studies showed that benzene/nitrogen mixtures remain relatively stable in Tedlar bags, all of the measurements were concerned with demonstrating benzene loss by observing a concentration change. This is a relatively insensitive method that would not have enabled us to detect small changes if they had taken place. Further, it would not have given any information about the mechanism of such losses.

Table 3. VARIATION OF THE BENZENE CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES.

Bag No.	Elapsed time (hours)	Benzene conc. (ppm) Initial value	Final value
1	48	65	63
2	336	65	61
3	48	65	65
4	48	65	63
5	192	65	65
5	336	65	64
5	408	65	61

Therefore, in an attempt to determine whether small amounts of benzene were passing through the plastic, we constructed a Tedlar bag system having one bag within another (Figure 1). The inner bag was filled with the 65 ppm benzene/nitrogen gas mixture, and the outer bag was filled with an equivalent amount of pure nitrogen. Thus, it would have been possible to detect a much smaller loss of benzene from the inner bag, since our GC system had a sensitivity of at least 0.1 ppm. However, as the results in Table 4 show, no benzene could be detected in the outer bag after 48 hours. Of necessity, loss of benzene as a result of permeation through the plastic would have been less than 0.1% per day.

USE OF TEDLAR BAGS TO PREPARE BENZENE CALIBRATION GAS MIXTURES

For this study, benzene/nitrogen mixtures were prepared in Tedlar bags and employed as calibration standards. In one experiment, such bag standards were used to calibrate our gas chromatograph while measuring the concentration of benzene in aluminum cylinders. These results were checked by comparing them with values obtained by three other laboratories. The cylinders in question were prepared and measured by Scott Environmental Technology, Plumsteadville, Pa. They were subsequently measured again at the Research Triangle Institute (RTI), Research Triangle Park, N.C. and at the Environmental Sciences Research Laboratory (ESRL) at this center.

The values reported by these three laboratories, along with our results (QAB values), are listed in Table 5. They are consistent with respect to each other and show no trend over the time period that elapsed. Although the laboratories cited employed different methods of calibration and different chromatographic columns, those details have not been included here since it is not the purpose of this study to compare calibration and GC procedures.

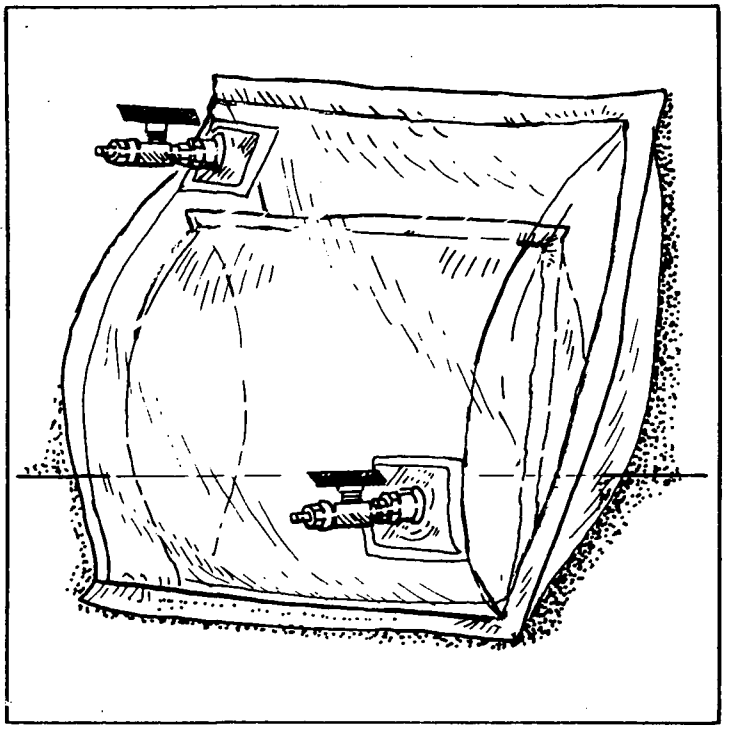

Figure 1. Double Tedlar bag assembly.

Table 4. BENZENE CONCENTRATION CHANGES IN DOUBLE TEDLAR BAG.

Bag component	Benzene concentration in ppm	
	Initial conc.	Final conc*
Inner bag	65	63
Outer bag	0	<0.1

*Elapsed time, 48 hours

Table 5. BENZENE CONCENTRATION VALUES OF ALUMINUM CYLINDERS AS DETERMINED BY VARIOUS CORROBORATORS.

Corroborator	Date of analysis	Benzene concentration (ppm) Cylinder BAL-107	Benzene concentration (ppm) Cylinder BAL-111
Scott	7/1/77	65	324
RTI	7/27/77	79	374
QAB*	11/23/77	76	365
RTI	12/9/77	74	336
ESRL	12/12/77	80	355

*Tedlar bag standards used for calibration

We feel that the consistency among the values obtained by the three laboratories is sufficient evidence for the accuracy of their results. QAB standards were prepared by injecting liquid benzene into Tedlar bags with a calibrated syringe while metering-in dry nitrogen gas. The quantity of nitrogen was measured using a dry gas meter that had been calibrated with a spirometer. Utilizing this procedure, two calibration standards were prepared that had benzene concentrations of 31.8 and 133 ppm, respectively. However, only one of the two cylinders under analysis fell within this calibration range; the other one fell beyond it. Since GC system response was linear over the range of the calibration standards employed, it was possible to carry out a linear extrapolation to determine the value of the second cylinder. Measurements made on both the high and the low concentration cylinders yielded results that fell within the range of values obtained by the three laboratories cited above.

Additional tests were carried out using benzene in Tedlar bags as standards. A series of four bags were prepared having benzene concentrations of 33.5, 60, 108, and 135 ppm, respectively. The 33.5 and the 135 ppm bags were employed as standards and were used in the analysis of the other two. These latter bags were then measured at the Research Triangle Institute and remeasured in our laboratory. All operations, including bag preparation and measurements, were carried out on the same day. The results are listed in Table 6. In another experiment, Tedlar bag standards were used for the analysis of a cylinder containing approximately 9.5 ppm benzene in nitrogen. Since the bag calibration standards were 31.8 and 133 ppm, it was necessary to assume system linearity below the calibration range. These results are also listed in Table 6.

Table 6. INTERLABORATORY COMPARISON OF BENZENE CONCENTRATION VALUES OF VARIOUS ANALYZED COMPONENTS.

Analyzed component	Benzene concentration in ppm			
	Prepared value	RTI value	ESRL value	QAB value
Tedlar bag	60	62	--	57
Tedlar bag	108	109	--	105
Cylinder, RB	9.5	10.1	9.5	9.7

Tables 5 and 6 show that, for each component analyzed, measurements made using Tedlar bag calibration standards fell within the range of values obtained by the corroborating laboratories. The data is therefore evidence that the calibrations were accurate and that useful standards may be prepared in Tedlar bags. It should also be noted that such systems are not difficult to prepare and are reasonably stable, as was shown elsewhere in this report. Thus, when used in the source level concentration range being considered here, benzene/nitrogen mixtures prepared in Tedlar bags make useful calibration standards for gas chromatographic measurements.

In several of the instances cited above, measurements have been made outside the range of the calibration standards that were employed. GC/FID systems are linear in a very large range of sample sizes, and it is common practice to assume that linearity persists below an established calibration range over which linearity has been demonstrated. On the other hand, it is risky to employ linear extrapolations in making measurements at sample sizes much greater than the highest calibration standard employed. It is not the purpose of this study to advocate that practice. Such results have been included here only because they add additional weight to our findings.

REFERENCES

1. Baker, R. A., and R. C. Doerr. Methods of Sampling and Storage of Air Containing Vapors and Gases. Int. J. Air Poll., 2:142-158, 1959.

2. Schuette, F. J. Plastic Bags for the Collection of Gas Samples. Atmos. Environ., 1:515-519, 1967.

3. Seila, R. L., W. A. Lonneman, and S. A. Meeks. Evaluation of Polyvinyl Fluoride as a Container Material for Air Pollution Samples. J. Environ. Sci., A-11(121-130), 1976.

4. Scheil, G. W. Standardization of Stationary Source Method for Vinyl Chloride. Environmental Monitoring Series EPA-600/4-77-026, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1977.

5. Schuetzle, D., T. J. Prater, and S. R. Ruddell. Sampling and Analysis of Emissions from Stationary Sources. J. Air Poll. Control Assoc., 25:925-932, 1975.

6. Feairheller, W. R., A. M. Kemmer, B. J. Warner, and D. Q. Douglas. Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. Monsanto Research Corporation EPA Contract 68-02-1404, Task 33, Dayton, Ohio, May 1977-January 1978.

APPENDIX A

METHOD FOR THE DETERMINATION OF BENZENE FROM STATIONARY SOURCES

METHOD 111. DETERMINATION OF BENZENE FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are 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 benzene, a carcinogen.

1. Principle and Applicability

1.1 Principle. An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

1.2 Applicability. The method is applicable to the measurement of benzene in stack gases only from specified processes. It is not applicable where the benzene is contained in particulate matter.

2. Range and Sensitivity

The procedure described herein is applicable to the measurement of benzene in the 0.1 to 70 ppm range. The upper limit may be extended by extending the calibration range or by dilution of the sample.

3. Interferences

The chromatograph columns and the corresponding operating parameters herein described have been represented as being useful for producing an adequate resolution of benzene. However, resolution interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior resolution of benzene without reducing the response to benzene as specified in Section 4.3.1.

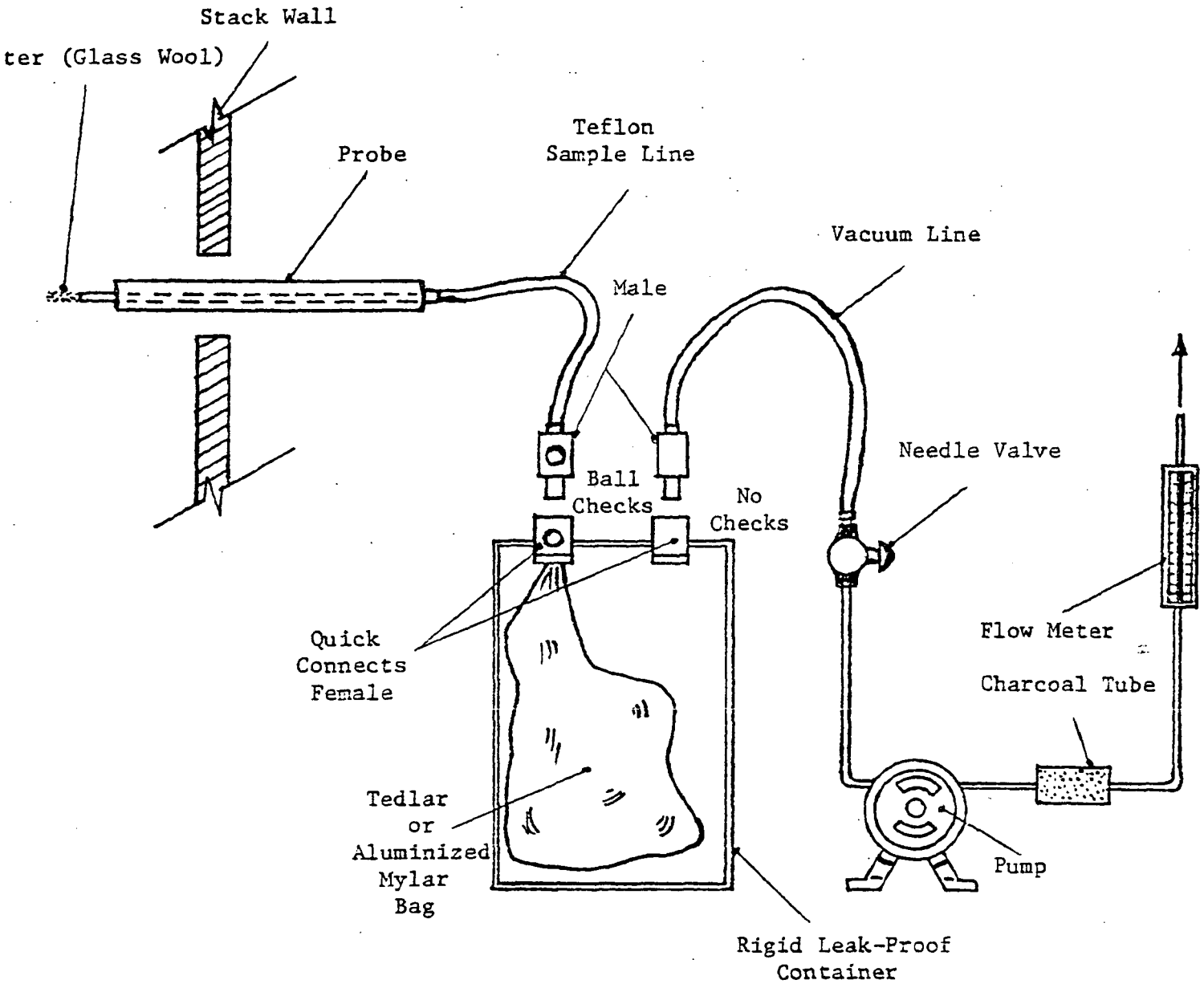

Figure 111-1. Integrated-bag sampling train. (Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.)

In any event, the chromatograph operator shall select a column which is best suited to his particular analysis problem, subject to the approval of the Administrator. Such approval shall be considered automatic provided that confirming data produced through a demonstrably adequate supplemental analytical technique, such as analysis with a different column or G.C./mass spectroscopy, is available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure III-1).

4.1.1 Probe. Stainless steel, Pyrex[1] glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Line. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick connects, with ball checks (one pair without) located as shown in Figure III-1.

4.1.4 Tedlar or aluminized Mylar bags, 100 liter capacity. To contain sample.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump--Leak-free. Minimum capacity 2 liters per minute.

[1]Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

4.1.8 Charcoal Tube. To prevent admission of benzene and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liters per minute.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sample train (Figure III-1).

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm benzene that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns other than those listed below can be used, provided that the precision and accuracy of the analysis of benzene standards are not impaired. Information confirming that adequate resolution of the benzene peak is accomplished should be available. Adequate resolution is defined as an area overlap of not more than 10 percent of the benzene peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromotographic Peak Resolution."

4.3.2.1 Benzene in the Presence of Aliphatics. Stainless Steel, 2.44 m x 3.2 mm, containing 10 percent TCEP on 80/100 Chromosorb P AW.

4.3.2.2 Benzene With Separation of the Isomers of Xylene. Stainless steel, 1.83 m x 3.2 mm, containing 5 percent SP 1200/1.75 percent Bentone 34 on 100/120 Supelcoport.

4.3.3 Flow Meters (2). Rotameter type, 0 to 100 ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump--Leak-free. Minimum capacity 100 ml/min.

4.3.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.3.8 to measure chromatograph peak areas.

4.4 Calibration. 4.4.2 through 4.4.6 are for section 7.1 which is optional.

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 1.0 µl, gas tight, individually calibrated, to dispense liquid benzene.

4.4.4 Syringe. 10 µml, gas tight, individually calibrated, to dispense liquid benzene.

4.4.5 Dry Gas Meter, With Temperature and Pressure Gauges. Accurate to ±2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flowrate used to prepare standards.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize benzene.

5. Reagents

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air as Required by the Detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Benzene, 99 Mol percent pure benzene certified by the manufacturer to contain a minimum of 99 Mol percent benzene; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50, 10, and 5 ppm benzene in nitrogen cylinders) for which the gas composition has been certified with an accuracy of ±3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change by greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified benzene concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer

to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.3.

5.2.3.1 Cylinder Standards Certification. The concentration of benzene in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a threepoint calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 50 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1 and using 99 Mol percent benzene, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards identical in preparation to those in Section 5.2.3 (benzene in nitrogen cylinders), except the concentrations are only known to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low concentration cylinder in the range of 5 to 20 ppm benzene, and one high concentration cylinder in the range of 100 to 300 ppm benzene. Audit cylinders may be obtained by contacting: EPA, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at EPA, an alternate source must be secured.

6. Procedure

6.1 Sampling. Assemble the sample train as in Figure 1. Perform a bag leak check according to section 7.4. Determine that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample Storage. Sample bags must be kept out of direct sunlight. Analysis must be performed within 24 hours of sample collection.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 80°C for column A or 75°C for column B, the detector temperature to 225°C, and the sample loop temperature to 70°C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having the retention time corresponding to

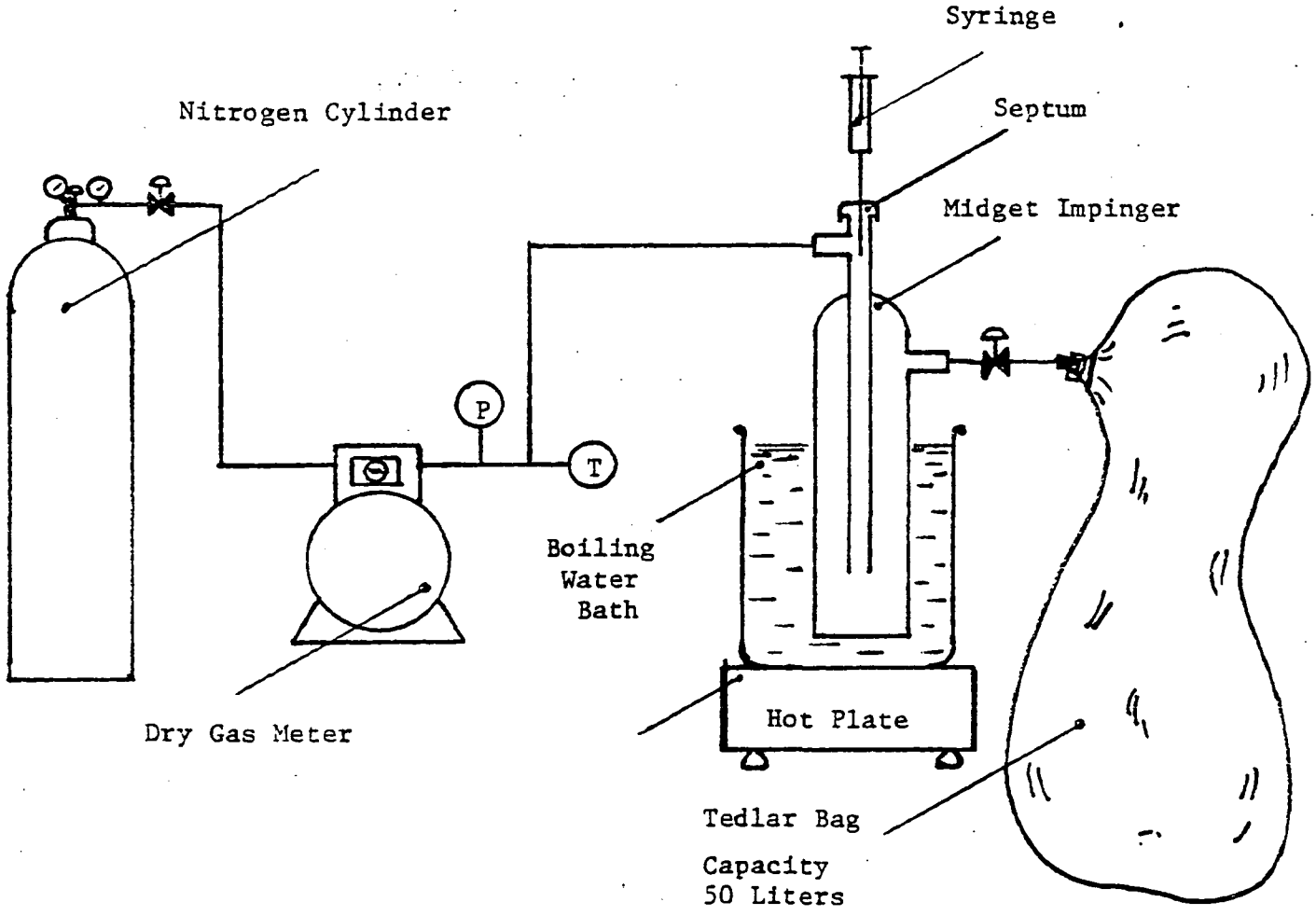

Figure 111-2. Preparation of Benzene Standards.
(optional)

benzene, as determined in Section 7.2. Measure the benzene peak area, A_m, by use of a disc integrator or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the benzene peak do not vary more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.5 Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Standards' Calibration and Quality Assurance

7.1 Standards.

7.1.1 Preparation of Benzene Standard Gas Mixtures. (Optional--delete if cylinder standards are used.) Assemble the apparatus shown in Figure 111-2. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.4) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling use the 10 µl syringe to inject 10 µl of 99 + percent benzene through the septum on top of the impinger. This gives a concentration of approximately 50 ppm of benzene. In a like manner, use the other syringe to prepare dilutions having approximately 10 and 5 ppm benzene concentrations. To calculate the specific concentrations, refer to section 8.1. These gas mixture standards may be used for four days

from the date of preparation, after which time preparation of new gas mixtures is required. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Benzene Retention Time. This section can be performed simultaneously with section 7.3. Establish chromatograph conditions identical with those in section 6.3, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of benzene. Maintain conditions, with the equipment plumbing arranged identially to section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the benzene calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to benzene. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the benzene peak retention time. Since it is quite likely that there will be other organics present in the sample, it is very important that positive identification of the benzene peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in section 5.2.3 or 7.1) using conditions identical with those listed in

Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c, the concentration of benzene injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values vs C_c. When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix E, Supplement B: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak

check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Optional Benzene Standards Concentrations. Calculate each benzene standard concentration prepared in accordance with Section 7.1 as follows:

$$C_c = \frac{B(.8787\ \text{mg})\ \frac{10^3\ \mu g}{mg}\ \frac{\mu g\ mole}{78.11\ \mu g}\ \frac{24.055\ \mu l}{\mu g\ mole}\ 10^6}{V_m\ Y\ \frac{10^6\ \mu l}{l}\ \frac{293}{T_m}\ \frac{P_m}{760}}$$

$$= \frac{B\ (270.6)}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 111-1}$$

Where:

C_c = Benzene standard concentration in ppm.

B = Number of µl of benzene injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

.8787 = Density of benzene at 293°A.

78.11 = Molecular weight of benzene.

24.055= Ideal gas at 293°A, 760 mm Hg.

10^6 = Conversion factor, ppm.

8.2 Benzene Sample Concentrations. From the calibration curve described in section 7.3, above, select the value of C_c that corresponds to A_c. Calculate C_s as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1-S_{wb})} \qquad \text{Equation III-2}$$

where:

S_{wb} = The water vapor content of the bag sample, as analyzed.

C_s = The concentration of benzene in the sample in ppm.

C_c = The concentration of benzene indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, °A.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, °A.

9. References

1. Feairheller, W. R.; Kemmer, A. M.; Warner, B. J.; and Douglas, D. Q. "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," EPA Contract No. 68-02-1404, Task 33 and 68-02-2818, Work Assignment 3. Jan., 1978.

2. Knoll, Joseph E.; Penny, Wade H.; Midgett, Rodney M.; Environmental Monitoring Series Publication in preparation. Stability of Benzene Containing Gases in Tedlar Bags. QAB/EMSL, U. S. Environmental Protection Agency.

3. Bulletins 743A, 740C, and 740D. "Separation of Hydrocarbons" 1974. Supelco, Inc. Bellefonte, Pennsylvania 16823.

4. Volume 10, No. 1 "Current Peaks," 1977. Carle Instruments, Inc., Fullerton, California 92631.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE THE USE OF TEDLAR BAGS TO CONTAIN GASEOUS BENZENE SAMPLES AT SOURCE-LEVEL CONCENTRATIONS.		5. REPORT DATE August 1978 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Joseph E. Knoll, Wade H. Penny and M. Rodney Midgett		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Quality Assurance Branch Environmental Monitoring and Support Laboratory U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO. 1HD621 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Final Report 14. SPONSORING AGENCY CODE EPA-ORD-600

15. SUPPLEMENTARY NOTES

To be published as an Environmental Monitoring Series Report.

16. ABSTRACT

Tedlar bags have been evaluated as containers for gaseous benzene samples for use in EPA Method 111 - Determination of Benzene from Stationary Sources. When such bags were used for storage, benzene samples remained essentially unchanged when held at ambient temperatures for up to 17 days, when cooled to -40° C for one hour or when heated to 70° C for one hour. At higher temperatures, some concentration changes were observed and above 105° C decomposition of the bag seals resulted. At room temperature, there was no evidence of permeation loss and absorptive loss could only be observed upon prolonged contact. Flushing bags three times with nitrogen was sufficient to remove all traces of previous samples.

Tedlar bags were also used to prepare gaseous mixtures for calibration purposes in gas chromatography. Such samples were prepared by injecting measured quantities of liquid benzene into a bag while metering-in nitrogen gas.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air pollution	Benzene Calibration	13 B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 37 22. PRICE

EPA Form 2220-1 (9-73)