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# Sampling and Analysis of Butadiene at a Neoprene Producing Plant

Entropy Environmentalists, Inc., Research Triangle Park, NC

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# SAMPLING AND ANALYSIS OF BUTADIENE AT A NEOPRENE PRODUCING PLANT

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16. ABSTRACT

This document details a field study to validate a method for the sampling and analysis of butadiene emissions from a plant manufacturing neoprene from butadiene/chlorine mixtures. Gaseous samples were collected from the process vent of one such plant using a modification of the evacuated container sampling procedure, outlined in Section 7.1.1 of EPA Method 18. The samples were collected at a sampling rate of 0.04 L/min, rather than at 0.5 L/min as specified in the method. Sample collection at the lowered sampling rate yields a total sample volume of approximately 3 L, rather than the 30 L obtained when using the specified sampling rate. On-site analysis of samples was performed using a gas chromatograph equipped with a flame ionization detector.

The method precision was determined by collection and analysis of simultaneous, quadruplicate samples. The average relative standard deviation for quad-train samples collected at the lowered sampling rate was approximately 4% for emission levels ranging from about 2 to 40%$_v$.

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## FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

1,3-Butadiene is being evaluated for future emissions regulations because this and other alkenes are quite reactive under atmospheric conditions and exist as "central constituents in urban smog chemistry." Acceptable measurement methodology is critical for proper assessment of the impact on the environment of these emissions from stationary sources. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform development and validation work on a method for the quantification of butadiene emissions from stationary sources.

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## ABSTRACT

Butadiene has been listed as a hazardous air pollutant by the United States Environmental Protection Agency (EPA). This document details a field study which validates a method for the sampling and analysis of butadiene emissions from a neoprene producing plant. Butadiene emission samples were collected from the process vent of a plant manufacturing neoprene from chlorine and butadiene. Four Tedlar bag samples were collected simultaneously employing the evacuated container sampling procedure outlined in Section 7.1.1 of EPA Method 18. This procedure was modified to collect the samples at a flow rate of 0.04 liters per minute rather than the recommended sample flow rate of 0.50 liters per minute. On-site analysis of samples was performed using a gas chromatograph equipped with a flame ionization detector. The precision of butadiene concentrations from samples collected was determined. Statistical evaluation of mean values and precisions of butadiene emission samples collected simultaneously was conducted. With the exception of one quadruplicate-train (quad-train) run, all relative standard deviations were within the range of 1.70 - 6.40 percent. The relative standard deviation of the outlier was 13.5 percent. Twelve quad-train runs were conducted.

This report is submitted by Entropy Environmentalists, Inc. in fulfillment of EPA Contract No. 68-02-4442, Work Assignment No. 103.

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## ABBREVIATIONS

| | |
|---|---|
| butadiene | used synonymously with 1,3-butadiene |
| cm | centimeter(s) |
| cm $H_2O$ | pressure equivalent to that exerted by a water column of the indicated height |
| AREAL, QAD | Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division of the United States Environmental Protection Agency |
| Entropy | used synonymously with Entropy Environmentalists, Inc. |
| EPA | United States Environmental Protection Agency |
| FID | flame ionization detector |
| GC | gas chromatograph |
| GC/ECD | gas chromatograph equipped with an electron capture detector |
| GC/FID | gas chromatograph equipped with a flame ionization detector |
| hr | hour(s) |
| L | liter(s) |
| L/min | liter(s) per minute |
| m | meter(s) |
| mL | milliliter(s) |
| mL/min | milliliter(s) per minute |
| $ppm_v$ | parts per million by volume |
| quad-train | apparatus for simultaneous collection of quadruplicate samples |
| ul | microliter(s) |

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## SECTION 1

## INTRODUCTION

1,3-Butadiene (butadiene) is being evaluated for future emission regulations by the U. S. Environmental Protection Agency. This and other alkenes are quite reactive under atmospheric conditions and exist as "central constituents in urban smog chemistry."[1] In addition, butadiene has been listed as a hazardous air pollutant. Exposure to the substance could result in serious health effects, including cancer.[2] A wide variety of natural and manmade combustion processes produce the gas, but the compound is made commercially from dehydrogenation of butene or butane/butene mixtures.[3] Butadiene is widely employed as a polymer building block, particularly in the production of synthetic rubbers as a copolymer with styrene[4] and in the production of neoprene rubber. An analytical method for the measurement of butadiene emissions from polymer-producing processes, as well as from petroleum cracking operations, where the material is produced, is needed.

A modified version of EPA Method 18[5] has previously been proven acceptable for the sampling and analysis of butadiene at a synthetic rubber plant.[5] In an effort to broaden the use of the modified version of the method, the U. S. EPA commissioned Entropy Environmentalists, Inc. (Entropy) to conduct a field evaluation of the method at a neoprene producing plant.

### Flow Rate Modification of Method 18

EPA Method 18 is employed for the collection and analysis of gaseous organic compounds. Several procedures for sample collection are described in the method, with one of the most commonly used being the flexible bag procedure. The bag procedure as described in Method 18 requires a sample flow rate of 0.50 liters per minute (L/min). Collecting sample for one hour at this flow rate results in a final sample volume of approximately 30 liters, thus requiring a Tedlar bag of 40 liters or greater to contain a single emission sample. Less than a liter of the inconveniently large emission sample is

required for a number of replicate analyses using a gas chromatograph with flame ionization detection (GC/FID). In an effort to minimize the size of sample that is collected when the Method 18 bag procedure is employed, several studies have been conducted to compare the recommended flow rate of 0.50 L/min to a lesser flow rate of approximately 0.05 L/min. The low flow rate allows collection of the emission sample in a bag of only 5 liters resulting in more convenient sampling containers and easier transportation of the sample from the field to the laboratory. The compounds which have been evaluated and collected successfully at the lower flow rate are: butadiene, carbon tetrachloride, chloroform, perchloroethylene, and trichloroethylene.

Acurex Corporation, as part of a previous assignment for EPA's Quality Assurance Division of the Atmospheric Research and Exposure Assessment Laboratory Office of Research and Development (QAD, AREAL), developed a prototype gas sampling system, which utilized a reduced sampling rate of 0.050 L/min allowing use of the smaller bag size. Acurex evaluated application of this methodology to sampling and analysis of butadiene in a laboratory study.[7]

Two separate field test sponsored by QAD, AREAL Office of Research and Development have included evaluation of a lower sample flow rate using Method 18.

The first evaluation of the recommended flow rate verses a lower sampling rate was conducted while collecting butadiene emission samples at a synthetic rubber producing plant. During a dual quadruplicate-train (quad-train) sampling run, one of the quad-trains sampled at a rate of 0.30 L/min while the other sampled at a rate of 0.05 L/min. A variance ratio test, or F-test, showed that standard deviations obtained using the different bag sizes and flow rates were not significantly different at the 95% confidence level. When the average butadiene levels measured for the samples collected at the low flow rates were compared to those collected at the higher flow rate, they also were found to be equivalent at the 95% confidence level.

The second evaluation of the lower flow rate verses the recommended 0.50 L/min was conducted during an evaluation of Method 18 for high temperature high moisture sampling.[8] The compounds collected during this evaluation were; carbon tetrachloride, chloroform, perchloroethylene, and trichloroethylene. Four of sixteen of the samples collected were at the recommended higher sample

rate while the remaining twelve samples were collected at approximately 0.04 L/min. Comparison of the results from the larger bag to those of the smaller were again well within the 95% confidence level for measured concentration and standard deviations.

Because the two different sampling rates utilized for collection of bag samples during these studies did not statistically affect the values or precision of the determinations made, the lower flow rate, which yields a more convenient sample size than the sampling rate recommended in EPA Method 18 is acceptable for collection of bag samples.

Report Organization

This report describes the field study commissioned by AREAL, QAD, Research Triangle Park, North Carolina, which validates sampling and analysis of butadiene emissions from a neoprene producing plant using EPA Method 18, modified as described above.

Section 2 presents the conclusions and recommendations regarding use of Method 18 as a sampling and analysis technique for emissions of butadiene from a neoprene producing plant. Sections 3 and 4 discuss the experimental procedures and results of the field test, and quality assurance/quality control procedures, respectively.

## SECTION 2

## CONCLUSIONS AND RECOMMENDATIONS

The Method 18 sampling and analytical protocol was validated for use at neoprene producing plants incorporating the use of the lowered sampling rate for collection of emission samples in small Tedlar bags. The average relative standard deviation observed using the small bags was approximately 4.0%.

As a result of the field test, the following conclusions and recommendations can be made:

1. Low sample flow rates (approximately 0.05 L/min) are recommended for the collection of butadiene at neoprene plants. These lower flow rates have been proven to be acceptable at the 95% confidence level and they greatly reduce the sample size. This reduced sample size allows sample collection in much smaller more convenient sample containers.

2. The average precision for this method is 4% based on the average relative standard deviations obtained in the field evaluation.

3. The possible presence of butane/butene isomers in the sample stream necessitates the use of a chromatography column capable of separating butadiene from these potential interferents. A 2 m x 1/8-inch stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C was utilized during this investigation. Use of this column or another one of similar design capable of resolving butadiene from these potentially interfering hydrocarbons is highly recommended.

4. Sample stability is a concern when collecting butadiene at neoprene plants due to the high concentrations (2 - 40%) observed. Samples appear to be stable up to two weeks, but no longer. Rapid analysis of the samples is highly recommended and will eliminate the possibility of polymerization of butadiene before sample analysis.

### Hydrocarbon Interferent

The presence of several butane/butene isomers in the sample stream when this method was validated at a synthetic rubber producing plant necessitated the use of a chromatography column capable of separating butadiene from these potential interferents. To eliminate the possibility of the same interferents

at the neoprene plant, the column which had been proven effective for use at synthetic rubber producing plants was used. This column, a 2 m x 1/8-inch stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack, or another column similarly able to resolve butadiene from these potentially interfering hydrocarbons, is highly recommended. This system allowed accurate quantitation of butadiene in the observed sample matrix to be carried out in less than 4 minutes.

## SECTION 3

## SUMMARY OF EXPERIMENTAL PROCEDURES AND RESULTS

The primary objective of this field test was to evaluate Method 18 as applied to sampling and analysis of butadiene at a neoprene producing plant. The sampling and analytical field evaluation protocol was finalized based on the results of previous tests and the presurvey results.

### Facility Description

The site selected by Entropy and approved by QAD personnel was a plant which produces neoprene from isomers of chlorinated butadiene. In the production of neoprene rubber, chlorine is added to a stream of pure 1, 3-butadiene. When the butadiene and chlorine are mixed, chloroprene and isomers of dichlorobutene are produced. Caustic is added to the process to remove the chloroprene, and the dichlorobutene isomers are then dechlorinated and "washed." The resulting product is the basic component of neoprene rubber. The process is dry (less than 100 ppm moisture) up to the point of dechlorination.

### Sampling Location

Gas samples were collected from a single point in the process vent. Butadiene is mixed with chlorine and transported to where the dichlorobutene isomers are removed for use. A three inch stainless steel pipe is used to vent the process prior to "washing" the isomers. The process vent reaches approximately 30 feet above the 10-inch pipe which transports the reacted butadiene and chlorine to the caustic. Connected to the base of the three-inch process vent is a 3/8-inch stainless steel tube which is connected to plant nitrogen. Approximately four feet from the connection of the 3/8-inch stainless to the process vent is a sampling port installed by the plant. The sample port is 3/8-inch stainless tubing in-line from the process vent to the plant nitrogen.

Positive pressure flow is present at this point in the process, which allows a small amount of the emissions to be diverted to the sample port when the On/Off valve is in the proper position. The quad-train samples were collected from a teflon sample line inserted into the 3/8-inch stainless sample port. Figure 1 is a schematic of the sampling location.

A valve is also present to allow plant nitrogen into the emission path. This is a precautionary procedure taken in order to dilute the emission stream when there is danger of a lightning strike to the emission vent. Dilution of the process vent is necessary due to the presence of the highly explosive butadiene. During sampling, the plant nitrogen was not used because of the likelihood of interfering hydrocarbons.

Applicability and Principle

The principles of sampling and analysis followed the general procedures described in EPA Method 18, with the exception that emission samples were collected at flow rates of 0.04 L/min, rather than 0.5 L/min.

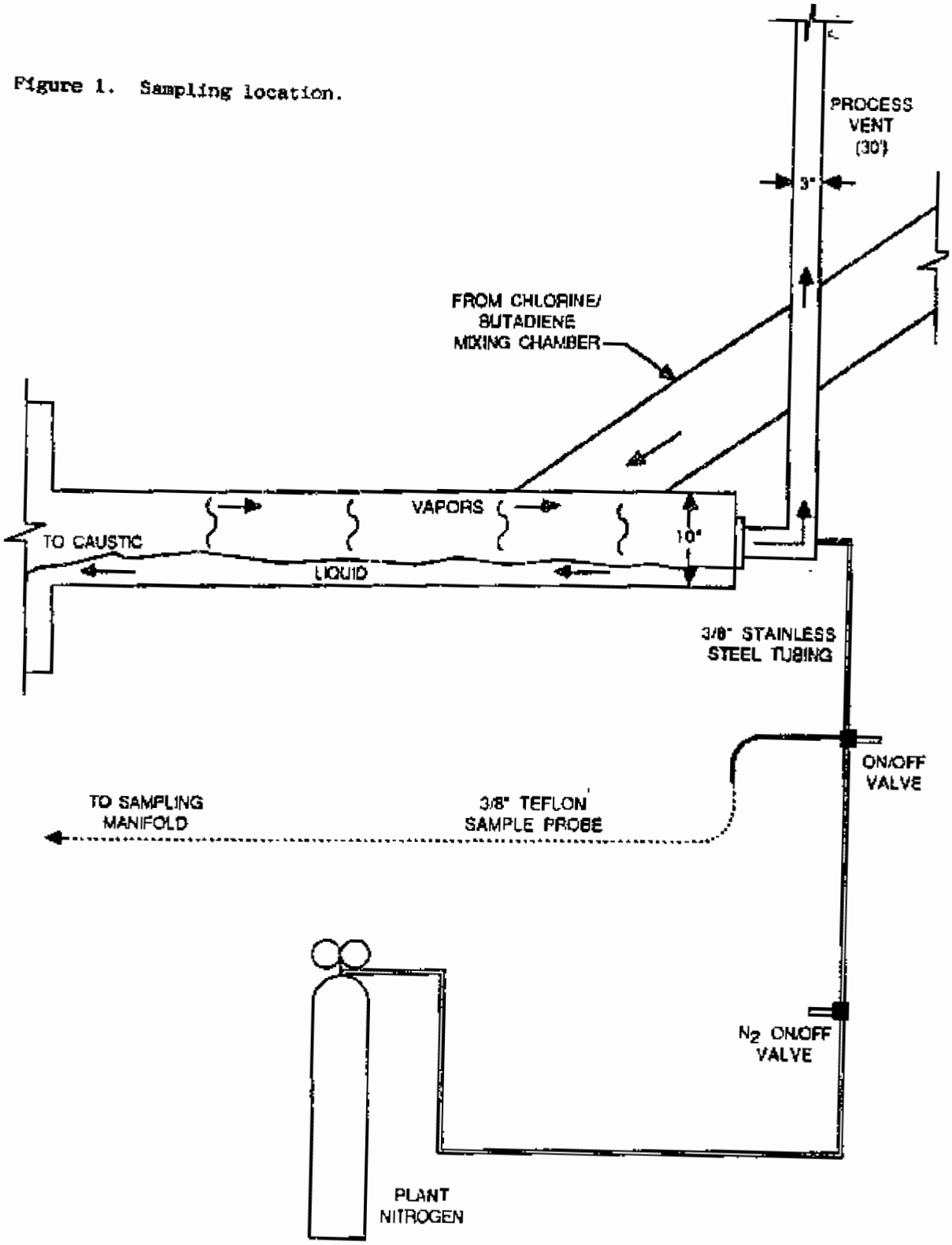
Range and Sensitivity

The range and sensitivity were determined for the Tedlar bag sampling technique prior to conducting the field test. An estimation of the limit of detection and quantifiable limit was carried out using a method that employs the chromatograph baseline noise and analyte response for these determinations.[9] Using a sample size of 1 mL, these values were determined to be 0.43 $ppm_v$ and 2.0 $ppm_v$, respectively. With sample dilution, or the use of smaller sample loops, there is no upper limit. Emission levels quantified in the field test ranged from approximately 2.5 - 41$\%_v$ . The FID was calibrated using a 1-ml sample loop and standards in the range of 0.20 - 3.8% butadiene by volume. The field samples were analyzed using a 100 ul sample loop.

Precision and Accuracy

Precision of the sampling and analysis techniques was determined using quad-train runs. For the field test, gases were withdrawn from a single point at the process vent approximately 30 feet from release of the emissions into the atmosphere. All bags were analyzed on-site, as was an audit sample. The results from analysis of the four bags collected simultaneously were averaged

Figure 1. Sampling location.



and a standard deviation was calculated for each run. The standard deviations were tested for level dependence by linear regression on the means, and a value of the y-statistic was calculated for the slope of the regression line. This value, 0.415, did not exceed the critical value of the t-statistic for 10 degrees of freedom and the 95% confidence level, 2.228. Thus, because the slope of the regression line was not significantly different from zero, the set of standard deviations were independent of level. Application of the Bartlett test[10] demonstrated that the variances were homogeneous. An estimate of the chi-squared statistic from the data yielded the value 9.05, which did not exceed the critical value of the statistic, 19.7, for 11 degrees of freedom and the 95% confidence level.[11]

As a result of these tests, it was possible to calculate a standard deviation from the combined variances that was more representative of the data than the standard deviation of any single run, 0.011 mole fraction. Thus, the coefficient of variation ranged between 3 - 7% for the 11 runs in the 0.16 - 0.41 concentration range. However, this combined standard deviation leads to a much higher $C_v$, 42%, for Run 10, which had a concentration an order of magnitude lower than the other points. Those data were included in the analysis to prevent the results from being biased, but additional data would be needed to correctly estimate the precision at that level. This information is summarized in Table 1.

Laboratory Precision

For individual bag samples, successive duplicate analyses were always well within 5% of their mean value as required by EPA Method 18. In fact, the duplicate analyses often differed from the mean by less than 1%.

One bag sample from each of the twelve sampling runs was returned to the base laboratory for reanalysis by Entropy. All bags collected during the final two sampling runs were also retained. These samples were analyzed 13 to 15 days following the original analysis. The reanalysis results for 14 of the samples are presented in Table 2. Samples reanalyzed after 13 days showed some signs of sample degradation. Several small peaks prior to the elution of butadiene from the column and one large peak following the butadiene peak which were not present in the original analyses were noted during reanalysis. Seventy-five percent of the samples analyzed on or before 13 days were within 10% of the original analyses.

TABLE 1. SUMMARY OF ANALYTICAL RESULTS AND PRECISION OF DATA

| Date | Run ID | Mean Conc. (%) | Coefficient of Variation (%) |
|---|---|---|---|
| 4/2/90 | 1 | 25.7 | 4.44 |
| 4/3/90 | 2 | 33.9 | 1.70 |
| 4/3/90 | 3 | 35.5 | 2.46 |
| 4/3/90 | 4 | 37.5 | 2.53 |
| 4/3/90 | 5 | 20.2 | 6.03 |
| 4/3/90 | 6 | 24.0 | 5.77 |
| 4/4/90 | 7 | 41.4 | 2.28 |
| 4/4/90 | 8 | 34.2 | 1.86 |
| 4/4/90 | 9 | 22.8 | 6.40 |
| 4/4/90 | 10 | 2.55 | 13.5 |
| 4/4/90 | 11* | 15.7 | 4.83 |
| 4/4/90 | 12 | 26.9 | 6.01 |

*One bag sample collected during this run was found to leak; the results from analysis of this bag are not included in any statistical evaluation of the data.

TABLE 2. COMPARISON OF FIELD AND LABORATORY ANALYSES

| Sample ID | Field Conc. (%) | Lab Conc. (%) | Percent Deviation | Age (days) |
|---|---|---|---|---|
| 1-C | 26.13 | 12.86 | - 34.05% | 15 |
| 3-B | 35.25 | 23.06 | - 20.92% | 14 |
| 7-B | 42.76 | 15.86 | - 45.88% | 13 |
| 8-A | 34.84 | 34.12 | - 1.05% | 13 |
| 9-C | 23.10 | 14.88 | - 21.63% | 13 |
| 10-A | 28.29 | 32.66 | + 7.18% | 13 |
| 10-B | 28.16 | 31.21 | + 5.14% | 13 |
| 10-C | 21.17 | 23.48 | + 5.19% | 13 |
| 10-D | 24.22 | 23.84 | - 0.78% | 13 |
| 11-A | 15.67 | 10.24 | - 20.96% | 13 |
| 11-B | 16.55 | 15.06 | - 4.73% | 13 |
| 11-C | 15.04 | 18.40 | + 10.06% | 13 |
| 12-B | 27.82 | 28.74 | + 1.63% | 13 |
| 12-C | 27.55 | 26.95 | - 1.11% | 13 |

## Between-Laboratory Precision

Following reanalysis at Entropy's base laboratory, selected bag samples were made available to AREAL, QAD personnel for independent verification of butadiene concentrations measured. These analyses were conducted after 15 days of collection of the samples, and a second peak not present in the original analyses was noted. The peak is believed to be a derivative of the polymerization of butadiene; therefore, the values obtained from the reanalysis of the samples are not consistent with the original values. Due to possible polymerization of the butadiene, the values obtained by QAD personnel were not used to determine between-laboratory precision.

## Audit Results

Accuracy of the butadiene determinations was examined by the on-site analysis of a blind audit sample provided by Research Triangle Institute, Research Triangle Park, North Carolina under EPA's performance audit program, which utilizes cylinder gases containing volatile organics in the $ppm_v$ range. The audit cylinders available were known to contain butadiene in the 5-60 $ppm_v$ range. Field and laboratory analyses of the cylinder provided a quality assurance check of the three-point calibration curves.

Several analyses of the audit cylinder were conducted while analyzing samples collected during the field test. The average value obtained for the concentration of the audit cylinder was approximately 51.7 $ppm_v$ while the actual audit value was 49.8, with a difference of 4%.

## Interferences

In the previous field test of butadiene emission samples, several other organic components, in addition to butadiene, were present in samples collected from the plant's process vent. Analysis of samples by the EPA Task Officer from the first field test on a megabore capillary column revealed the presence of several butane/butene isomers. The column chosen for use in the presence of these isomers was a 0.19% picric acid on 80/100 mesh Carbopack C. To eliminate the possibility of these isomers interfering during the analysis at the neoprene plant, the same picric acid column was used for this field test. Analysis of the presurvey samples on a megabore capillary column indicated that no other interferences were present.

Presurvey

Pretest samples were collected to determine any need for modification of the sampling or analysis procedures. After discussions with plant officials concerning the compounds present in the process vent stream, which included only butadiene and hydrogen chloride gas, optimum GC/FID conditions were determined. Two grab samples were collected and returned to the laboratory for analysis. The analyses on the GC/FID packed column indicated no interfering peaks, as did analyses on the megabore capillary column. The GC/FID conditions to be used in the field were determined and the final analyses procedures were developed based on the results of the presurvey test. The concentration of butadiene collected during the pretest survey was approximately 3.9%.

Sampling Procedures and Sampling Equipment

The test matrix was designed to evaluate GC/FID analysis of butadiene emission samples based on 12 quad-train sampling runs employing Tedlar bags for sample collection. During the field test, four samples were collected simultaneously in 5 L Tedlar bags.

All sampling was conducted according to EPA Method 18. The samples were collected over a one-hour period from a common manifold. Twelve sample runs were conducted during the test, generating 48 samples for analysis.

A schematic of the quad-train sampling system is presented as Figure 2. The sample probe, a 3/8-inch teflon line, was tapered at the end for easy insertion into the sample port. The probe was connected to a sampling manifold constructed of stainless steel fittings. Bag samples were collected from the manifold using individual 1/4-inch Teflon sample lines (approximately five feet in length). Before each sample run, the manifold was purged with stack gas for several minutes to allow equilibration of the system. The individual sampling systems were connected to a separate manifold, which in turn was connected to a vacuum pump. The vacuum allowed sample flow into the Tedlar bags through the sample line.

The sampling containers used during this field test were newly designed systems. They were developed in order to reduce the leakage problems associated with the rigid PVC bag sampling containers that have been previously used for sample collection. A schematic of the new system is presented as Figure 3. The sampling device is constructed of a low-cost, commercially available 9-liter

Figure 2. Quad-train sampling system.

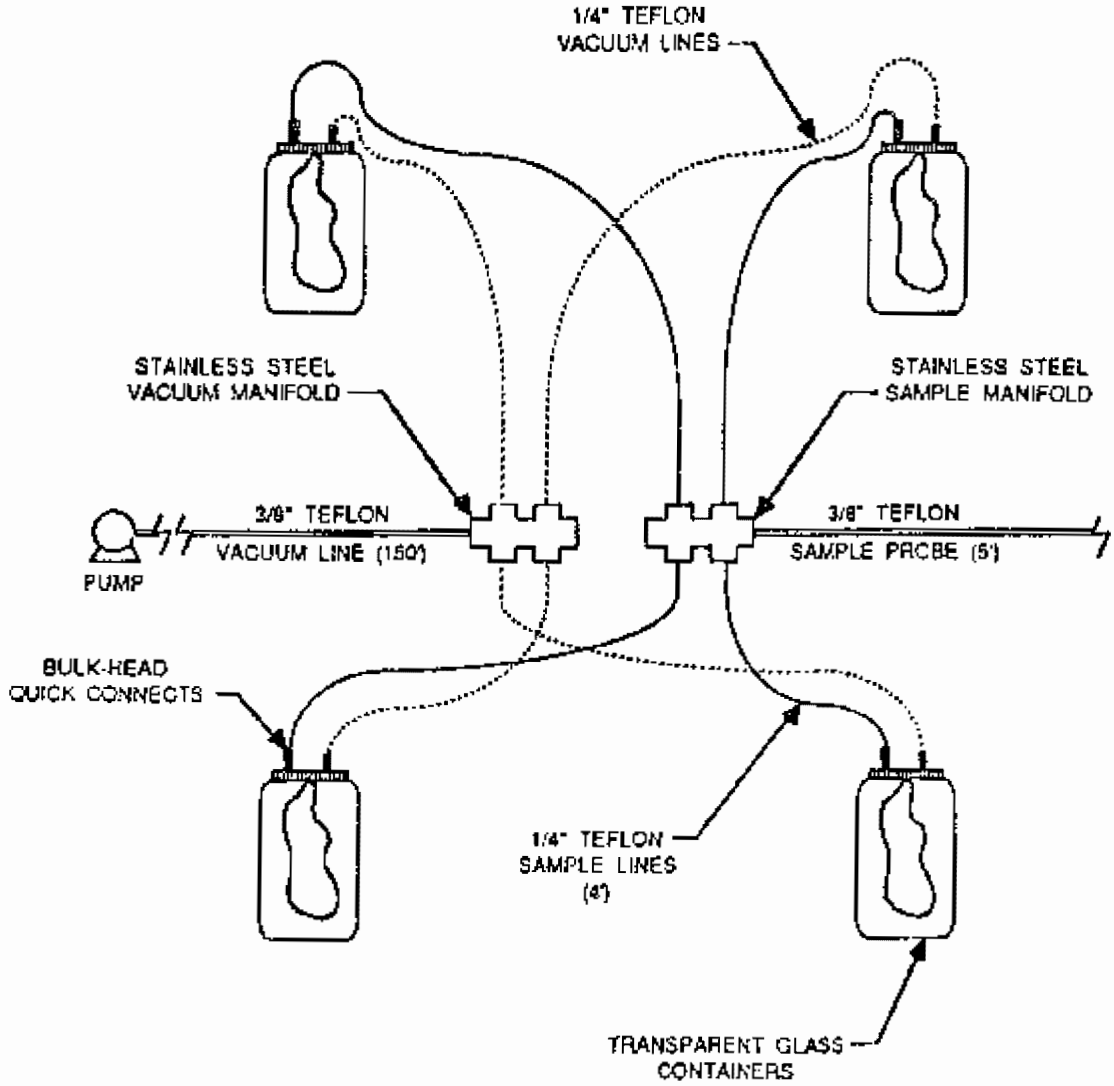
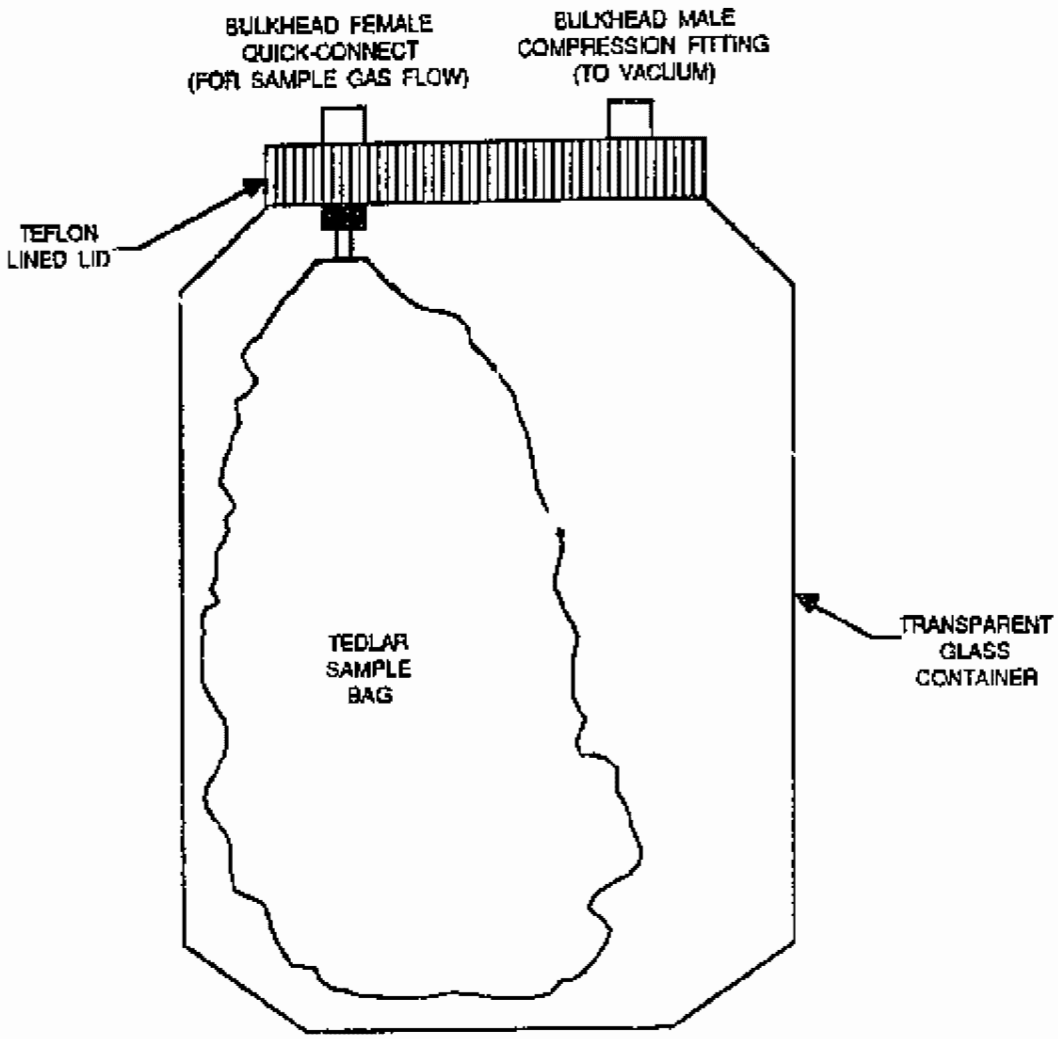


Figure 3. Sampling system.



glass container with a Teflon-lined, threaded metal lid. Minor modifications of the container lid consist of drilling holes which are fitted with bulkhead connections. One of the fittings has a female quick-connect on the outside of the lid for connection to the sample line. The Tedlar bag is connected on the inside of the lid. A male compression fitting is used to evacuate air space around the Tedlar bag in order to draw sample into the bag. Leak tests conducted on these devices have been encouraging. The containers have been shown to maintain a vacuum of 21 inches of water overnight. The glass containers also permit viewing of the Tedlar bag during sampling to assure that the bag is being filled. Each Tedlar bag and each sampling container was leak checked at 16 in. Hg in the laboratory and prior to use in the field.

Flow into each bag was moderated by individual critical orifices. The orifices were calibrated in the laboratory and the optimum vacuum was determined to be 15 in. Hg with orifice flows ranging from 37.9 - 39.2 cc/min. The orifices were connected in the evacuation lines from each lung sampling system with specific flow for each noted.

Double seamed Tedlar bags were fabricated using a bag sealer, and each bag was leak checked and blanked before being used to collect field samples. Bags were inflated to rigidity and allowed to stand overnight or longer. If a bag showed any loss of rigidity, it was discarded. During the field tests, bags to be reused were flushed four times with nitrogen to remove previous samples. They were then completely evacuated and allowed to stand for several minutes and examined for the intake of air in order to detect gross leaks. New bags were used for most of the samples to be retained for post-field test studies.

Analytical Procedures and Equipment

Two major concerns with all organic sampling and analytical procedures are (1) rapidity of sample analyses and (2) sample stability. Minimization of time required for the total elution of individually injected samples was considered in selection of GC conditions for analysis of field samples. Sample stability was assessed by reanalysis of field samples after "aging."

All field samples collected were analyzed by Entropy using a Perkin-Elmer 8210 gas chromatograph equipped with a flame ionization detector and a manually operated gas sampling valve. Peak areas were determined using an electronic integrator. The analyses were conducted isothermally at 80°C with a carrier gas flow rate of 30 milliliters/min (mL). The packed column used for sample

analysis was a Supelco 0.19% picric acid on 80/100 mesh Carbopack C. Duplicate analyses of bag samples could be completed within 10 minutes with this system.

Standards prepared by a commercial vendor were drawn from Tedlar bags into a 1 mL sample loop. The field samples were analyzed using a smaller (100 uL) sample loop due to the high concentrations of butadiene collected. Samples were drawn into the sample loop by a small pump at a rate of 60 cc/min. Calibration data were collected in the approximate range of 0.20 - 4.0%. Each calibration was audited using cylinders of butadiene provided by the QAD Division of EPA, Research Triangle Park, North Carolina.

Sample Stability

To assess the stability of the bagged samples, reanalysis of one sample from several of the runs and reanalysis of all samples from two of the runs were conducted. Table 2 shows the results obtained and the amount of time lapsed from the original analysis.

Data Analysis

The sample concentrations were obtained by comparison of the sample peak area to the curve obtained by linear regression analysis of the calibration gases.

The values obtained for each of the samples collected during a quad-train run were averaged, and a relative standard deviation (RSD) for the quad-train run was calculated.

One of the values obtained for relative standard deviation was not in the same range of the other values. This value was statistically eliminated using the Q-test for elimination of outliers. To determine whether the data point in question could be statistically eliminated from the averaged results, the following equation was used:

$$Q = Gap/Range$$

where:

Gap = Difference between the questionable value and the nearest point.

Range = Difference between the questionable value and the lowest point.

Q values associated with the degrees of freedom are given at the 90% confidence interval. The calculated value must be greater than the given value in order to eliminate the questionable data point. The actual calculation for eliminating the questionable data point for this test and the given Q values are presented in Appendix B.

Results

All four bags from each quad-train run were initially analyzed on-site by Entropy. For the samples collected, the successive duplicate analyses specified by Method 18 were generally well within 5% of their mean values as required by the method. In fact, the duplicate analyses often differed from the mean by less than 1%. The average relative standard deviation observed for the samples was 4.0%, if the outlier is statistically eliminated by the Q-test. A summary of the results is presented in Table 1.

The on-site analysis of cylinder audit gases provided by QAD allowed estimation of method accuracy. The audit performed in the 10 - 100 ppm range yielded 51.7 ppm, while the actual audit value was 49.8 ppm, resulting in a difference of only 4%.

Reanalysis of the bag samples resulted in 70% of the samples consistent with the original analyses. Due to the percentage of sample values that repeated after 13 days, it is evident that permeation of the butadiene through the walls of the Tedlar is unlikely. The number of samples whose values were not repeatable does, however, cause concern. It was determined that samples analyzed after 13 days from collection had compounds other than butadiene present. It is possible that butadiene in the percent levels is not stable over long periods of time; therefore, sample analyses should be conducted as soon as possible.

## SECTION 4
## QUALITY CONTROL

During each stage of the investigation every effort was made to guarantee the integrity of the data collected. Some of the important precautions observed are outlined below.

### Cylinder Standards

Analyzed cylinders containing approximately 10, 150, 2000 $ppm_v$, 1.08% and 3.8% of gaseous butadiene in nitrogen were purchased from a supplier of high purity gases. The cylinders were analyzed after final blending by the supplier, who certified the butadiene concentrations to $\pm$ 5 ppm. No other standards were necessary for completion of the field test or laboratory work.

### Calibration and Audit Procedures

Calibration standards were injected into the gas chromatograph until two successive injections disagreed by no more than 5%, as specified in EPA Method 18. Often duplicate injections of standards, and those of most samples, differed from their mean by less than 1%.

Instrument response was obtained from a least squares fit of the calibration data. An audit of these results was conducted daily by assaying the concentration of a blind audit sample provided under the EPA's performance audit program. The audit sample contained butadiene diluted with nitrogen gas at a concentration in the $ppm_v$ range.

### Retention of Butadiene by Tedlar Bags

Although the retention of butadiene by Tedlar bags was not rigorously evaluated, experiments were conducted to demonstrate that bags containing field samples could be reused after they had been blanked. Bags were emptied of sample by complete evacuation and flushed four times with compressed air before being filled to half their capacities. After allowing the bags to stand

overnight, analysis of the contained gas showed them to be essentially free of butadiene.

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4. Air Pollution Emission Factors. Report No. AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1973.

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## APPENDIX A

## STANDARD OPERATING PROCEDURES FOR THE SAMPLING AND ANALYSIS OF BUTADIENE EMISSIONS

### 1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. These procedures are applied in the determination of 1,3-butadiene (hereafter butadiene) present in waste gases emitted from a neoprene producing plants.

1.2 Principle. Gas samples are collected in Tedlar gas sampling bags from a conduit carrying gaseous emissions and analyzed using a gas chromatograph equipped with a flame ionization detector (GC/FID).

1.3 Potential Interferences. Several other organic components in addition to butadiene can be present in emission samples. The possible presence of several C4 and unsaturated C4 hydrocarbons in the emission samples necessitates the use of a chromatography column capable of separating butadiene from these potential interferents.

1.4 Precision. The within-laboratory relative standard deviation observed for the collection and analysis of quadruplicate samples during field validation of this method was approximately 4.0%.

1.5 Stability. Samples should be analyzed within two weeks of collection.

### 2. Summary

2.1 Sampling. Emission samples are collected in 5 L Tedlar bags housed in rigid, air-tight containers. Evacuation of the container void space surrounding the bag, at flow rates of 50 mL/min over a 1 hour period, draws a 3 L sample into the bag.

2.2 GC Analysis. Cylinders of dilute gaseous butadiene in nitrogen, commercially available from a supplier of high purity gases, are used as standards in calibration of the GC. The linear calibration curves generated from analysis of these standards are used to determine the concentration of butadiene in collected field samples.

### 3. Safety

Butadiene has been listed as a hazardous air pollutant in the Federal Register[1] since serious health effects result from exposure to the gas; therefore, inhalation of butadiene, and of other potentially harmful vapors present in source samples, must be rigorously avoided. The use of electrical equipment for sampling in potentially explosive areas requires additional precautionary measures.

## 4. Apparatus and Materials

4.1 Sampling Apparatus. The sampling train is shown in Figure A-1, and component parts are discussed below.

4.1.1 Probe. Teflon tubing, 3/8-inch OD. Attach to a port in the conduit carrying gaseous process emissions via appropriate connecting fittings.

4.1.2 Glass Wool. Borosilicate or quartz. Use a small wad of glass wool at the inlet of the probe to remove particulate matter, if present in the sample stream.

4.1.3 Primary Sampling Pump. Leak-free Teflon-coated diaphragm-type pump, or equivalent.

4.1.4 Sampling Manifold. Stainless steel, with the appropriate fittings necessary for acquisition of simultaneous samples and for connection of a manometer. In general, two or more samples are collected. Flow through all parts of the manifold should be unrestricted and uniform.

4.1.5 Manometer. 76 cm. U-tube water manometer, to measure pressure existing in the sampling manifold.

4.1.6 Sample Lines. Teflon tubing, 1/4-inch O.D., to conduct gas from the manifold to the Tedlar gas sampling bags.

4.1.7 Quick-connects. Stainless steel, self-sealing, male quick-connects. Attach to the bag end of each sample line. Mating female, stainless steel, bulkhead quick-connect, affixed in the lid of rigid, evacuable bag containers are adjoined on the underside of each container lid directly to an enclosed Tedlar gas sampling bag.

4.1.8 Rigid, Evacuable Bag Containers. Suitable rigid material, to house leak-free Tedlar gas sampling bags. The design of one such container is shown in Figure A-2.

4.1.9 Tedlar Gas Sampling Bags. Unused, double-seamed, with nominal capacities of 5 liters.

4.1.10 Auxiliary Sampling Pump. For evacuation of bag containers. Sample flow into each gas sampling bag is produced by controlled, partial evacuation of container void space surrounding the sample bags.

4.1.11 Critical Orifices. Glass or other suitable material, to fix the flow exiting the evacuable containers, and, in turn, to regulate the sample flow entering the sample bags. Sonic flow through each orifice should be approximately 0.050 L/min. Calibrate and place in-line between auxiliary sampling pump and bag.

4.1.12 Vacuum Tubing. To connect the rigid, evacuable bag containers to the auxiliary sampling pump.

4.1.13 Rate Meter. To be used in leak check procedures.

Figure A-1. Sample collection system.

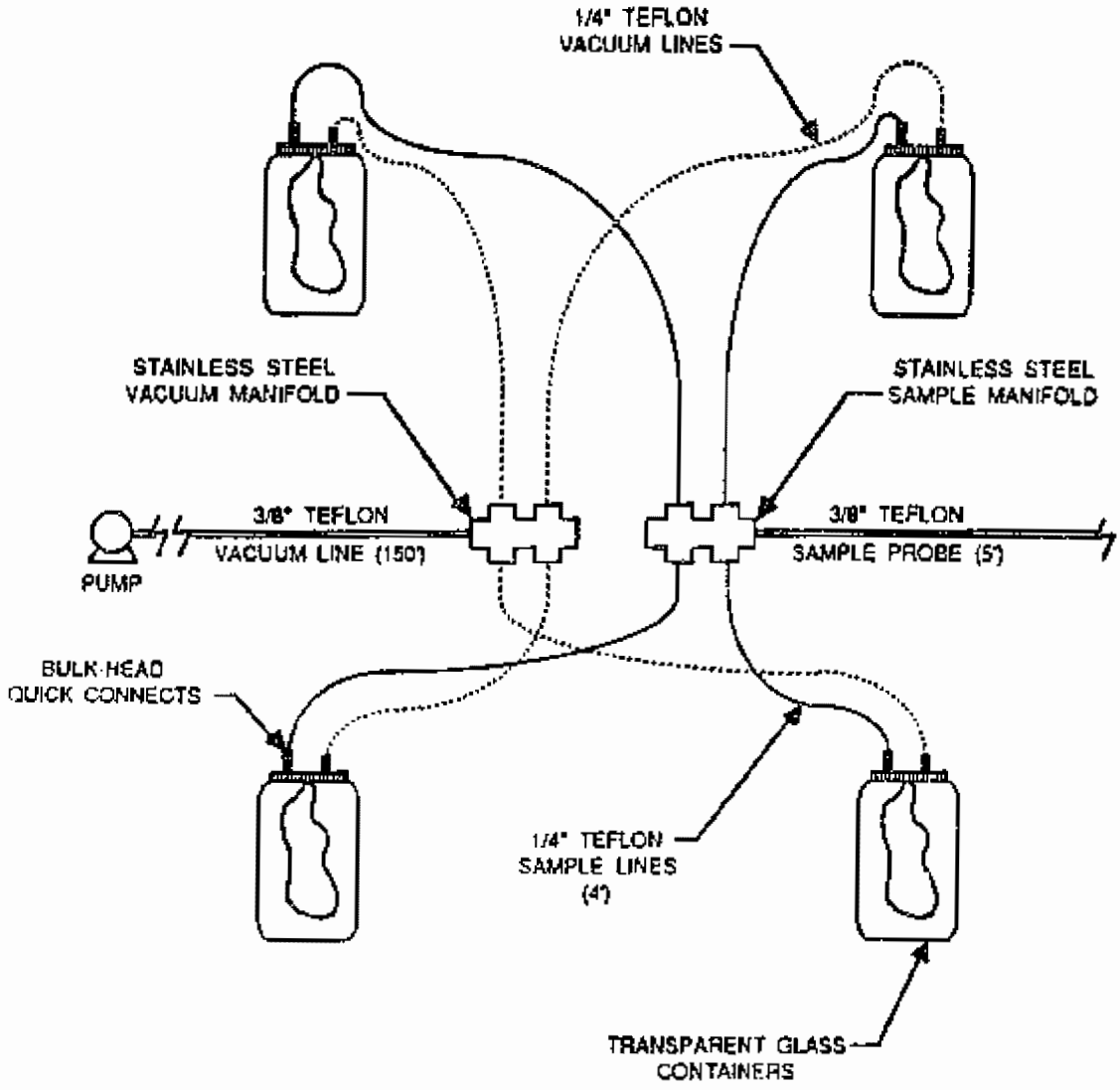
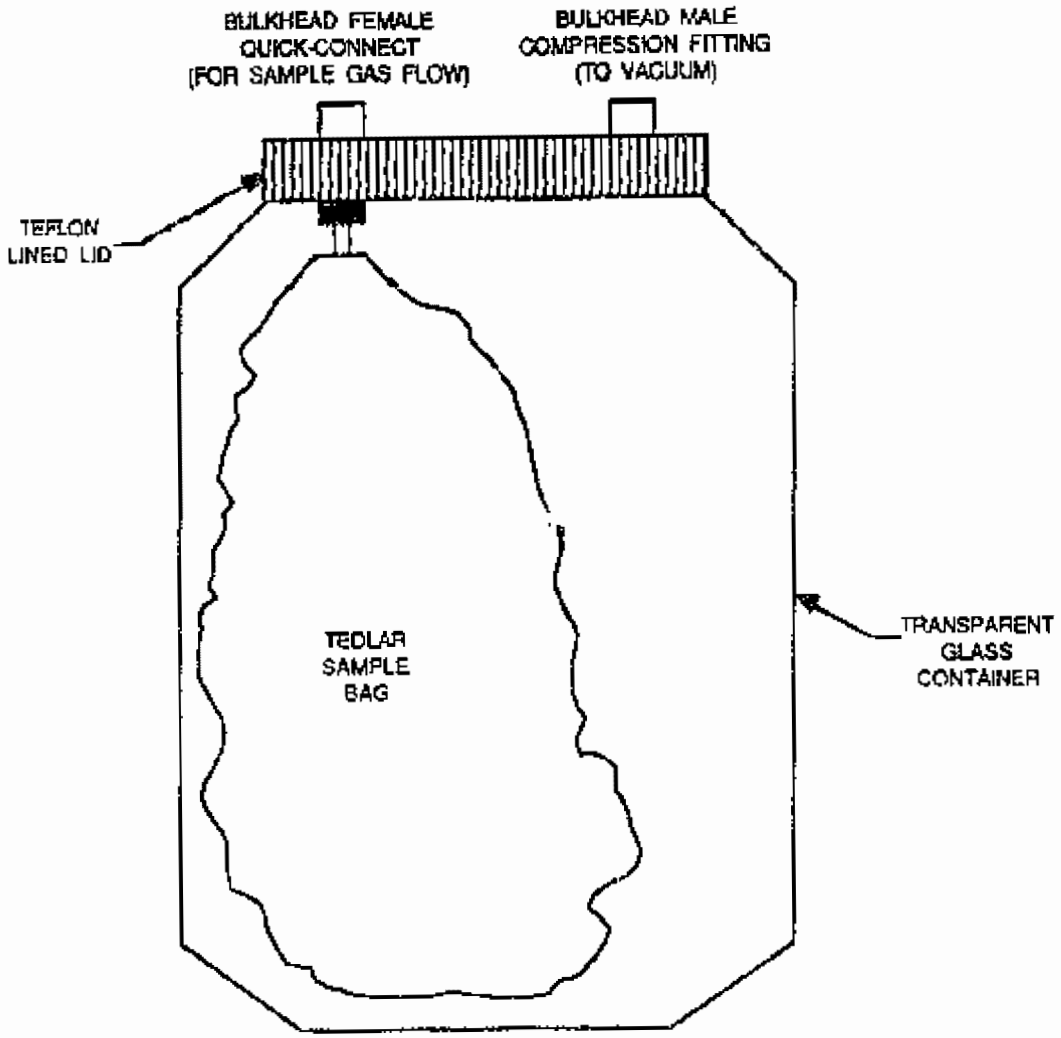


Figure A-2. Bag sampler.



4.2 Gas Standards. Dilute gaseous butadiene in nitrogen at concentrations certified to ± 2%, commercially available from suppliers of high purity gases. Purchase cylinders containing nominal butadiene concentrations to bracket the emission concentrations expected. Order the desired concentrations four or more weeks in advance of need to allow time for custom blending of gases by suppliers, when necessary.

4.3 Gas Chromatographic System. General criteria for the GC and peripheral hardware necessary for analysis of samples are outlined below.

4.3.1 Gas Chromatograph. Transportable, incorporating an FID, appropriate separation columns, a temperature-controlled gas sampling valve, and a column oven capable of maintaining stable temperatures of 30-100°C.

4.3.2 Carrier Gas. Oxygen-/hydrocarbon-free nitrogen gas for optimum performance of separation columns and noiseless operation of detector. Minimum acceptable purity specifications recommended for carrier gas are dependent on specific column(s) and specific brand of detector used.

4.3.3 Detector Feed Gases. High purity, hydrocarbon-free, compressed air and hydrogen for operation of FID. Minimum acceptable purity specifications recommended for detector feed gases are dependent on specific brand of detector used.

4.3.4 Recorder/Integrator. To record the output of the detector. If a strip chart recorder is used, provisions must be made for estimation of the recorded peak areas.

4.3.5 GC Columns. A 2 m x 1/8-inch stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C, or other column similarly able to resolve C4 and unsaturated C4 hydrocarbons.

4.3.6 Gas Sampling Valve. Stainless steel with the entire valve/column assembly maintained at a constant temperature in the GC column oven.

4.3.7 Gas Sample Loop. Stainless steel or Teflon. The sample loop's precise volume need not be known unless dilution is employed, but sample loop volumes of 0.1 to 1.0 mL are convenient for most analyses.

4.3.8 Gas Sample Loop Pump. To draw collected emissions samples from a gas sample bag through the sample loop at a nominal flow rate of 100 mL/min.

4.3.9 Rate Meter. To measure sample flow during loading of sample loop.

## 5. Sampling Procedure

5.1 Pre-test Leak Checks. The Tedlar gas sampling bags and the rigid, evacuable containers are leak checked before being transported to the test site.

5.1.1 Leak Check of Tedlar Gas Sampling Bags. Leak check each Tedlar bag before sealing it in an evacuable container. A compression fitting incorporated during construction of each bag allows direct connection of the bag to

the bulkhead female quick-connect fixed in the lid of individual evacuable containers. Screw the bags tightly to this quick-connect on the underside of the container lids and inflate bags to rigidity. Discard bags that show any loss of rigidity after standing overnight. Following leak check procedures, completely deflate the bags.

5.1.2 Leak Check of Rigid, Evacuable Containers. After ensuring that leak-free bags are attached to the lid of each evacuable container, screw the lids tightly in place. To leak check individual evacuable containers, attach a water manometer to the bulkhead, male, compression fitting that is imbedded in each container lid. This fitting provides access to the container void space surrounding the enclosed sample bag, and allows the pressure changes within the container to be monitored. Seal other "open" fittings, create a positive pressure of 25 cm $H_2O$ in the container by slowly filling the sample bag with a small volume of zero air via the female quick-connect connected to the enclosed bag. Any visible change in the level of the water in the manometer during a 30-second period indicates a leak. Isolate any leaks detected in the evacuable containers with a leak detection fluid.

5.2 Set-up of Sampling Apparatus. Attach the 3/8-inch O.D. Teflon probe line to the intake of the sampling manifold. Attach the 3/8-inch O.D. vacuum line to the vacuum manifold and the vacuum pump. Use Teflon tubing to return excess sample gas to the emission conduit, or when the concentrations of process gases present create no explosion risk, pass excess sample gas through an activated charcoal filter before venting to the atmosphere at a safe distance from sampling personnel. Attach sample lines to the steel manifold.

Place the evacuable containers used to house the Tedlar bags in position for connection to the manifold sample lines using the quick-connects affixed in their lids. Do not connect the rigid, evacuable bag containers to the sampling manifold or to the auxiliary sampling pump until leak-check procedures are completed.

5.3 On-Site Leak-Checks of Sampling Apparatus. The sampling apparatus is leak checked on-site in three sections.

5.3.1 Leak-Check of Evacuation System. Plug the open ends of the vacuum tubing used to evacuate the bag containers. Connect the flow meter to the outlet of the auxiliary sampling pump and start the pump. If the flow meter indicates any residual flow after a time sufficient to evacuate the vacuum lines, a leak is present. Shut off the pump and unplug the vacuum lines when the leak check is complete.

5.3.2 Leak-Check of Probe. Plug the open end of the probe and start the pump. If the flow meter indicates any residual flow after a time sufficient to evacuate the vacuum lines, a leak is present. Shut off the pump, and unplug the probe when the leak-check is complete.

5.3.3 Leak-Check of Delivery System. Visually inspect and tighten all connections. Position the probe to draw in ambient air, and start the pump. Adjust the flow exiting the sampling manifold to maintain a positive pressure of 25 cm $H_2O$, as measured by the water manometer connected to the sampling manifold. A leak detection fluid may be used to isolate suspected leaks. Shut off the pump when the leak-check is complete.

5.4 Final Assembly of Sampling Apparatus and Purge Procedure. Immediately prior to sampling, check the Tedlar gas sampling bags for residual gas and evacuate as necessary. A large volume of in-drawn ambient air indicates that the bag may have leaked during transport. Attach the vacuum lines to the evacuable containers. Insert the probe into the emission conduit.

5.5 Sample Collection. Following the purge of the delivery system, mate the quick-connects at the end of the manifold sample lines with the quick-connects joined to the gas sampling bags. Immediately start the auxiliary sampling pump to begin sampling. Adjust the sample flow at this point if the system pressure drops below approximately 4 cm $H_2O$, as measured by the water manometer. Rapid filling of an individual Tedlar bag indicates a leak in the surrounding container. Monitor the manifold pressure every 10 minutes, as a drop in system pressure indicates a leak has formed in the delivery system. At the end of the 60-minute sampling period, switch off the auxiliary pump and detach the manifold sample lines from the evacuable containers.

6. GC Analysis

6.1 Instrument Operating Parameters.

6.1.1 Operating Parameters for Detector. For all analyses, fix the hydrogen and air flows to the FID at rates that give a stable flame. If the GC used includes internal metering orifices, supplying these gases at constant regulator pressures will accomplish this. Optimization of detector response according to the instructions provided by the manufacturer is recommended.

6.1.2 Temperatures of Heated Components. When using the column listed in Section 4.3.5, set the oven to operate isothermally at 80°C. Maintain the detector temperature at 250°C.

6.2.3 Carrier Gas Flows. When using the columns listed in Section 4.3.5, set the forward flow through the column at approximately 30 mL/min.

6.3 GC Equilibration. Prior to sample analysis, establish a stable baseline. Inject a nitrogen blank to distinguish any peaks arising from sample injection.

6.4 Introduction of Samples. Draw samples from the Tedlar bags and through the sample loop at a flow rate of 60 mL/min using a small pump. During sample loop loading of either standard cylinder gases or bag samples, purge the sample loop for a minimum of one minute. After cessation of standard or sample gas flow, allow the sample loop pressure to equilibrate to ambient pressure over a 10 second period before injecting loaded samples.

6.5 Calibration Curve for Gas Chromatograph. Analyze the cylinder gas calibration standards as outlined in EPA Method 18. Use the peak areas resulting from analysis of these standards to establish a linear calibration curve relating detector response to the concentration of butadiene present in a sample.

6.6 Audit Analysis. Perform the analysis of audit samples during calibration of the detector response, as set forth in EPA Method 18.

6.7 Calculation of Measured Butadiene Concentrations. Calculate the concentration of butadiene in the field samples using the detector response, as set forth in EPA Method 18.

## 7. References


1. Federal Register, 51, No. 62, pp 11021-11022, April 1, 1986.

2. Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, 40 Code of Federal Regulations 60. July 1, 1987.

# APPENDIX B

## DATA SHEETS/AUDIT RESULTS

STATISTICAL CALCULATION FOR ELIMINATING OUTLIER

Relative standard deviations for test runs arranged from lowest to highest:

| | |
|---|---|
| 1.70 | 4.83 |
| 1.86 | 5.77 |
| 2.28 | 6.01 |
| 2.46 | 6.03 |
| 2.53 | 6.40 |
| 4.44 | 13.5 |

Q = Gap/Range

Gap = Difference between questionable point and the nearest value

= 13.5 - 6.40 = 7.07

Range = Difference between lowest point and questionable value

= 13.5 - 1.70 = 11.8

Q = Gap/Range = 7.07/11.8 = 0.54

The point may be eliminated if:

$$Q_{(observed)} > Q_{(tabulated)}$$

| $Q_{(tabulated)}$ | Degrees of freedom |
|---|---|
| 0.94 | 3 |
| 0.76 | 4 |
| 0.64 | 5 |
| 0.56 | 6 |
| 0.51 | 7 |
| 0.47 | 8 |
| 0.44 | 9 |
| 0.41 | 10 |

Twelve data points, the degrees of freedom is greater than 10; therefore, the observed Q value must be greater than 0.41.

Observed Q value for the test is 0.54; therefore, 13.5 may be statistically eliminated from the results.

Gas Chromatograpy Calibration Data

Job Name: Butadiene  Job Num. 4303
Analyst: Cheryl Davis  Date: April 3, 1990

Standard Calibration Curve by Linear Regression

| Cal Gas (ppm) | Peak Area Run 1 | Run 2 | Average | Predicted Gas Value | Percent Deviation from Actual |
|---|---|---|---|---|---|
| 1977 | 117.23 | 118.99 | 118.11 | 2112.21 | 6.84% |
| 10300 | 622.72 | 625.67 | 624.19 | 10324.17 | -1.71% |
| 38000 | 2382.22 | 2392.92 | 2387.57 | 38040.63 | 0.11% |

Standard Curve  Slope 0.0632 Intercept -15.3099

| Sample ID | Run 1 Area | Run 2 Area | Average | Percent Deviation | Detected Charge (PPM) | Dil Fac | Actual Conc (PPM) | Flow Rate (L/min) |
|---|---|---|---|---|---|---|---|---|
| Run Number: 5 | | Time: 15:16 - 16:16 | | | | | | |
| Run time 60 | | | | | | | | |
| 5-A | 1286.33 | 1287.62 | 1286.98 | 0.05% | 20617 | 10 | 206170 | 0.039 |
| 5-B | 1218.09 | 1071.00 | 1144.54 | 6.43% | 18362 | 10 | 183619 | 0.039 |
| 5-C | 1308.65 | 1291.47 | 1300.06 | 0.66% | 20824 | 10 | 208240 | 0.040 |
| 5-D | 1337.01 | 1273.20 | 1305.10 | 2.44% | 20904 | 10 | 209038 | 0.038 |
| Average | | | | | 20177 | | | |
| Standard Deviation | | | | | 1219.847 | | | |
| Coefficient of Variation | | | | | 6.046% | | | |
| Run Number: 6 | | Time: 17:07 - 18:07 | | | | | | |
| Run time 60 | | | | | | | | |
| 6-A | 1380.40 | 1377.11 | 1378.76 | 0.12% | 22070 | 10 | 220699 | 0.039 |
| 6-B | 1551.64 | 1536.95 | 1544.29 | 0.48% | 24690 | 10 | 246905 | 0.039 |
| 6-C | 1506.69 | 1501.71 | 1504.20 | 0.17% | 24056 | 10 | 240558 | 0.040 |
| 6-D | 1588.71 | 1570.29 | 1579.50 | 0.58% | 25248 | 10 | 252479 | 0.038 |
| Average | | | | | 24016 | | | |
| Standard Deviation | | | | | 1385.820 | | | |
| Coefficient of Variation | | | | | 5.770% | | | |

Gas Chromatograpy Calibration Data

Job Name: Butadiene — Job Num. 4303

Analyst: Cheryl Davis — Date: April 4, 1990

Standard Calibration Curve by Linear Regression

| Cal Gas (ppm) | Peak Area Run 1 | Run 2 | Average | Predicted Gas Value | Percent Deviation from Actual |
|---|---|---|---|---|---|
| 1977 | 127.16 | 129.24 | 129.20 | 2152.45 | 8.87% |
| 10300 | 632.75 | 630.79 | 631.77 | 10071.83 | -2.22% |
| 38000 | 2398.50 | 2416.41 | 2407.46 | 38052.72 | 0.14% |

Standard Curve Slope 0.0635 Intercept -7.3963

| Sample ID | Run 1 Area | Run 2 Area | Average | Percent Deviation | Detected Charge (PPM) | Dil Fac | Actual Conc (PPM) | Flow Rate (L/min) |
|---|---|---|---|---|---|---|---|---|
| Run Number 7 | | Time: 8:40-9:40 | | | | | | |
| Run time 60 | | | | | | | | |
| 7-A | 2606.41 | 2579.38 | 2592.89 | 0.52% | 40975 | 10 | 409748 | 0.039 |
| 7-B | 2698.84 | 2716.04 | 2706.44 | 0.35% | 42764 | 10 | 427640 | 0.039 |
| 7-C | 2548.45 | 2593.90 | 2571.17 | 0.88% | 40633 | 10 | 406325 | 0.040 |
| 7-D | 2622.23 | 2589.73 | 2605.99 | 0.62% | 41181 | 10 | 411812 | 0.038 |
| Average | | | | | 41388 | | | |
| Standard Deviation | | | | | 944.734 | | | |
| Coefficient of Variation | | | | | 2.283% | | | |
| Run Number: 8 | | Time: 10:36 - 11:36 | | | | | | |
| Run time 60 | | | | | | | | |
| 8-A | 2202.90 | 2204.21 | 2203.55 | 0.03% | 34840 | 10 | 348397 | 0.039 |
| 8-B | 1213.48 | 1077.04 | 1145.26 | 5.96% | 18163 | 10 | 181633 | 0.039 |
| 8-C | 2153.07 | 2166.59 | 2159.83 | 0.31% | 34151 | 10 | 341507 | 0.040 |
| 8-D | 2143.25 | 2093.24 | 2118.24 | 1.18% | 33495 | 10 | 334954 | 0.038 |
| Average | | | | | 34162 | | | |
| Standard Deviation | | | | | 633.787 | | | |
| Coefficient of Variation | | | | | 1.855% | | | |
| Run Number: 9 | | Time: 11:54-12:54 | | | | | | |
| Run time 60 | | | | | | | | |
| 9-A | 1495.21 | 1510.97 | 1503.09 | 0.52% | 23802 | 10 | 238019 | 0.039 |
| 9-B | 1308.54 | 1299.48 | 1304.01 | 0.35% | 20665 | 10 | 206648 | 0.039 |
| 9-C | 1454.96 | 1461.82 | 1458.39 | 0.23% | 23098 | 10 | 230975 | 0.040 |
| 9-D | 1489.86 | 1498.40 | 1494.13 | 0.29% | 23661 | 10 | 236607 | 0.038 |
| Average | | | | | 22806 | | | |
| Standard Deviation | | | | | 1499.704 | | | |
| Coefficient of V[illegible] | | | | | [illegible] | | | |

Gas Chromatograpy Calibration Data

Job Name:Butadiene — Job Num. 4303

Analyst: Cheryl Davis — Date: April 4, 1990

Standard Calibration Curve by Linear Regression

| Cal Gas (ppm) | Peak Area Run 1 | Run 2 | Average | Predicted Gas Value | Percent Deviation from Actual |
|---|---|---|---|---|---|
| 1977 | 129.16 | 129.24 | 129.20 | 2128.95 | 7.69% |
| 10300 | 632.75 | 630.79 | 631.77 | 10102.39 | -1.92% |
| 38000 | 2398.50 | 2387.59 | 2393.05 | 38045.66 | 0.12% |

Standard Curve Slope 0.0630 Intercept -4.9892

| Sample ID | Run 1 Area | Run 2 Area | Average | Percent Deviation | Detected Charge (PPM) | Dil Fac | Actual Conc (PPM) | Flow Rate (L/min) |
|---|---|---|---|---|---|---|---|---|
| Run Number 10 | | | Times 13:29-14:29 | | | | | |
| Run time 60 | | | | | | | | |
| 10-A | 172.54 | 174.07 | 173.31 | 0.44% | 2829 | 10 | 28287 | 0.039 |
| 10-B | 171.55 | 173.43 | 172.49 | 0.55% | 2816 | 10 | 28157 | 0.039 |
| 10-C | 132.43 | 124.39 | 128.42 | 3.14% | 2117 | 10 | 21166 | 0.040 |
| 10-D | 149.77 | 145.56 | 147.67 | 1.43% | 2422 | 10 | 24219 | 0.038 |
| | | Average | | | 2546 | | | |
| | | Standard Deviation | | | 342.750 | | | |
| | | Coefficient of Variance | | | 13.464% | | | |
| Run Number: 11 | | | Time 14:48 - 15:48 | | | | | |
| Run time 60 | | | | | | | | |
| 11-A | 962.95 | 982.30 | 982.62 | 0.03% | 15669 | 10 | 156688 | 0.039 |
| 11-B | 1036.41 | 1040.05 | 1038.23 | 0.18% | 16551 | 10 | 165511 | 0.039 |
| 11-C | 942.21 | 943.38 | 942.80 | 0.06% | 15037 | 10 | 150369 | 0.040 |
| 11-D | 398.45 | 399.52 | 398.99 | 0.13% | 6409 | bag leak | | 0.038 |
| | | Average | | | 15752 | | | |
| | | Standard Deviation | | | 760.504 | | | |
| | | Coefficient of Variance | | | 4.828% | | | |
| (Does not include leaky bag, 11-D) | | | | | | | | |
| Run Number: 12 | | | Times 16:22-17:22 | | | | | |
| Run time 60 | | | | | | | | |
| 12-A | 1542.42 | 1531.38 | 1536.90 | 0.36% | 24463 | 10 | 244626 | 0.039 |
| 12-B | 1730.71 | 1766.38 | 1748.55 | 1.02% | 27820 | 10 | 278205 | 0.039 |
| 12-C | 1732.99 | 1730.62 | 1731.81 | 0.07% | 27555 | 10 | 275549 | 0.040 |
| 12-D | 1747.45 | 1741.34 | 1744.40 | 0.18% | 27735 | 10 | 277546 | 0.038 |
| | | Average | | | 26890 | | | |
| | | Standard Deviation | | | 1627.592 | | | |
| | | Coefficient of Variance | | | 6.051% | | | |

PART B - To be filled out by audit supervisor:

I. Audit Results:

a. Cylinder ID: 328
b. Last Analysis: 1/89
c. psig pre-audit: 1680
d. psig after audit: 1600

| COMPOUND | AUDITEE CONC (ppm) | RTI CONC (ppm) | AUDIT % BIAS* |
|---|---|---|---|
| 1,3-Butadiene | 51.76 | 49.8 | +4 |

*Audit Accuracy expressed as % Bias $= \frac{\text{Auditee conc} - \text{RTI conc}}{\text{RTI conc}} \times 100$

Comments: If an audit gas is used to demonstrate the accuracy measurements during a compliance test for and EPA regulation, and if Method 18 (Gas Chromatography) is the measurement method, then the agreement between the auditee concentration and the assigned audit concentration should be as follows:

| For audit concentration | Agreement should be within |
|---|---|
| 5 to 20 ppm | ± 15% |
| > 20 ppm | ± 10% |

cc: Darryl von Lehmden, EPA/AREAL, RTP
Robert Lampe, EPA/AREAL, RTP

STATISTICAL CALCULATION FOR ELIMINATING OUTLIER

Relative standard deviations for test runs arranged from lowest to highest:

| | |
|---|---|
| 1.70 | 4.83 |
| 1.86 | 5.77 |
| 2.28 | 6.01 |
| 2.46 | 6.03 |
| 2.53 | 6.40 |
| 4.44 | 13.5 |

Q = Gap/Range

Gap = Difference between questionable point and the nearest value

= 13.5 - 6.40 = 7.07

Range = Difference between lowest point and questionable value

= 13.5 - 1.70 = 11.8

Q = Gap/Range = 7.07/11.8 = 0.54

The point may be eliminated if:

$$Q_{(observed)} > Q_{(tabulated)}$$

| $Q_{(tabulated)}$ | Degrees of freedom |
|---|---|
| 0.94 | 3 |
| 0.76 | 4 |
| 0.64 | 5 |
| 0.56 | 6 |
| 0.51 | 7 |
| 0.47 | 8 |
| 0.44 | 9 |
| 0.41 | 10 |

Twelve data points, the degrees of freedom is greater than 10; therefore, the observed Q value must be greater than 0.41.

Observed Q value for the test is 0.54; therefore, 13.5 may be statistically eliminated from the results.

# APPENDIX C

# EPA METHOD 18

Sampling Equipment. Environmental Protection Agency, Research Triangle Park, N.C. APTD-0576 March, 1972.

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8. Vollaro, R. F., A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, N.C. November, 1976 (unpublished paper).

9. Annual Book of ASTM Standards, Part 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials, Philadelphia, Pa. 1974, pp. 617-622.

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## METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

### *Introduction*

This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

### 1. *Applicability and Principle*

1.1 Applicability. This method applies to the analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources.

This method will not 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.

1.2 Principle.

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles.

The retention time of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

### 2. *Range and Sensitivity*

2.1 Range. The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

### 3. *Precision and Accuracy*

Gas chromatographic techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Duplicate analyses are within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

### 4. *Interferences*

Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately, is best dealt with by thorough purging of the GC sample loop between samples.

To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

### 5. *Presurvey and Presurvey Sampling*

Perform a presurvey for each source to be tested. Refer to Figure 18-1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

5.1 Apparatus. This apparatus list also applies to Sections 6 and 7.

5.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

5.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

5.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

5.1.4 Flowmeters. To measure flow rates.

5.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

5.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

5.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter sizes, calibrated, maximum accuracy (gas tight), for preparing calibration standards. Other appropriate sizes can be used.

5.1.8 Tubing Fittings. To plumb GC and gas cylinders.

5.1.9 Septums. For syringe injections.

5.1.10 Glass Jars. If necessary, clean-colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

5.1.11 Soap Film Flow Meter. To determine flow rates.

5.1.12 Tedlar Bags. 10- and 50-liter capacity, for preparation of standards.

5.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ±2 percent, for perparation of gas standards.

5.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

5.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

5.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD-2, etc.) for presurvey samples.

5.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

5.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

5.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

5.1.20 Barometer. To measure barometric pressure.

5.2 Reagents.

5.2.1 Deionized Distilled Water.

5.2.2 Methylene Dichloride.

5.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

5.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

5.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

5.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

5.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatability with the column.

5.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

5.3 Sampling.

5.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples can be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows. Remove the stopcocks from both ends of the flasks and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene dichloride. Clean all glass parts with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace and apply heat up to 500° C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Grease the stopcocks with stopcock grease and return them to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape.

Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into



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and purging the flask with a rubber suction bulb.

5.3.1.1 Evacuated Flask Procedure. Use a high vacuum pump to evacuate the flask to the capacity of the pump, then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

5.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in Section 5.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

5.3.2 Flexible Bag Procedure. Tedlar or aluminized Mylar bags can also be used to obtain the presurvey sample. Use new bags, and leak check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak check and sample collection procedures given in Section 7.1.

5.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 50° C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

5.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pilot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure, noting whether the reading is positive or negative.

5.5 Collection of Presurvey Samples with Adsorption Tube. Follow Section 7.1 for presurvey sampling.

6. *Analysis Development*

6.1 Selection of GC Parameters.

6.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

Most column manufacturers keep excellent records of their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations.

Plants with analytical laboratories may also be able to provide information on appropriate analytical procedures.

6.1.2 Preliminary GC Adjustment. Using the standards and column obtained in Section 6.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

6.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

6.1.4 Presurvey Sample Analysis. Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

Use the GC conditions determined by the procedures of Section 6.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 6.3) to obtain an estimate of the concentrations.

Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

6.2 Calibration Standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If available, commercial cylinder gases may be used if their concentrations have been certified by direct analysis.

If samples are collected in adsorbent tubes (charcoal, XAD-2, Tenax, etc.), prepare or obtain standards in the same solvent used for the sample extraction procedure. Refer to Section 7.4.3.

Verify the stability of all standards for the time periods they are used. If gas standards are prepared in the laboratory, use one or more of the following procedures.

6.2.1 Preparation of Standards from High Concentration Cylinder 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 18-5 and 18-6.

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 18-4. 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 the 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 18-5. (See Section 7.2 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 flowmeters, and the laboratory temperature and atmospheric pressure. Calculate the concentration $C_s$ in ppm of each organic in the diluted gas as follows:

$$C_s = \frac{10^6 \, (\bar{X} \, q_c)}{q_c + q_d} \qquad \text{Eq. 18-1}$$

where:

$10^6$ = Conversion to ppm.

$\bar{X}$ = Mole or volume fraction of the organic in the calibration gas to be diluted.

$q_c$ = Flow rate of the calibration gas to be 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 18-6. 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 $C_s$ in ppm of the organic in the final gas mixture as follows:

$$C_s = 10^6 \bar{X} \left(\frac{q_{c1}}{q_{c1} + q_{d1}}\right)\left(\frac{q_{c2}}{q_{c2} + q_{d2}}\right) \qquad \text{Eq. 18-2}$$

Where:

$10^6$ = Conversion to ppm.

$\bar{X}$ = Mole or 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.

Further details of the calibration methods for flowmeters and the dilution system can be found in Citation 21 in the Bibliography.

6.2.2 Preparation of Standards from Volatile Materials. Record all data shown on Figure 18-3.

6.2.2.1 Gas Injection Technique. This procedure is applicable to organic compounds that exist entirely as a gas at ambient conditions. Evacuate a 50-liter Tedlar bag that has passed a leak-check (see Section 7.1) and meter in 5.0 liters of air or nitrogen through a dry gas meter that has been calibrated in a manner consistent with the procedure described in Section 5.1.1 of Method 5. While the bag is filling use a 0.5-ml syringe to inject a known quantity of "pure" gas of the organic compound through the wall of the bag, or through a septum-capped tee at the bag inlet. Withdraw the syringe needle, and immediately cover the resulting hole with a piece of masking tape. In a like manner, prepare dilutions having other concentrations. Prepare a minimum of three concentrations. Place each bag on a smooth surface, and alternately depress opposite sides of the bag 50 times to mix the gases. Record the average meter temperature and pressure, the gas volume and the barometric pressure. Record the syringe temperature and pressure before injection.

Calculate each organic standard concentration C, in ppm as follows:

$$C_s = \frac{G_v \times 10^6 \frac{293}{T_s} \frac{P_s}{760}}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000}$$

$$= \frac{G_v \times 10^3}{V_m Y} \frac{P_s}{T_s} \frac{T_m}{P_m} \qquad \text{Eq. 18-3}$$

where:

$G_v$ = Gas volume or organic compound injected, µl.

$10^6$ = Conversion to ppm.

$P_s$ = Absolute pressure of syringe before injection, mm Hg.

$T_s$ = Absolute temperature of syringe before injection, °K.

$V_m$ = Gas volume indicated by dry gas meter, liters.

Y = Dry gas meter calibration factor, dimensionless.

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

$T_m$ = Absolute temperature of dry gas meter, °K.

1000 = Conversion factor, ml/liter.

6.2.2.2 Liquid Injection Technique. Use the equipment shown in Figure 18-8. Calibrate the dry gas meter as described in Section 6.2.2.1 with a wet test meter or a spirometer. Use a water manometer for the pressure gauge and glass, Teflon, brass, or stainless steel for all connections. Connect a valve to the inlet of the 50-liter Tedlar bag.

To prepare the standards, assemble the equipment as shown in Figure 18-8, and leak-check the system. Completely evacuate the bag. Fill the bag with hydrocarbon-free air, and evacuate the bag again. Close the inlet valve.

Turn on the hot plate, and allow the water to reach boiling. Connect the bag to the impinger outlet. Record the initial meter reading, open the bag inlet valve, and open the cylinder. Adjust the rate so that the bag will be completely filled in approximately 15 minutes. Record meter pressure and temperature, and local barometric pressure.

Allow the liquid organic to equilibrate to room temperature. Fill the 1.0- or 10-microliter syringe to the desired liquid volume with the organic. Place the syringe needle





into the impinger inlet using the septum provided, and inject the liquid into the flowing air stream. Use a needle of sufficient length to permit injection of the liquid below the air inlet branch of the tee. Remove the syringe.

When the bag is filled, stop the pump, and close the bag inlet valve. Record the final meter reading, temperature, and pressure.

Disconnect the bag from the impinger outlet, and either set it aside for at least 1 hour, or massage the bag to insure complete mixing.

Measure the solvent liquid density at room temperature by accurately weighing a known volume of the material on an analytical balance to the nearest 1.0 milligram. A ground-glass stoppered 25-ml volumetric flask or a glass-stoppered specific gravity bottle is suitable for weighing. Calculate the result in terms of g/ml. As an alternative, literature values of the density of the liquid at 20 °C may be used.

Calculate each organic standard concentration C, in ppm as follows:

$$C_s = \frac{\frac{L_v \rho}{M}(24.055 \times 10^6)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m} \qquad \text{Eq. 18-4}$$

where:

$L_v$ = Liquid volume of organic injected, µl.

$\rho$ = Liquid organic density as determined, g/ml.

M = Molecular weight of organic, g/g-mole.

24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.

$10^6$ = Conversion to ppm.

1000 = Conversion factor, µl/ml.

6.3 Preparation of Calibration Curves. Establish proper GC conditions, then flush the sampling loop for 30 seconds at a rate of 100 ml/min. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their average. The average value multiplied by the attenuator factor is then the calibration area value for the concentration.

Repeat this procedure for each standard. Prepare a graphical plot of concentration ($C_s$) versus the calibration area values. Perform a regression analysis, and draw the least squares line.

6.4 Relative Response Factors. The calibration curve generated from the standards for a single organic can usually be related to each of the individual GC response curves that are developed in the laboratory for all the compounds in the source. In the field, standards for that single organic can then be used to "calibrate" the GC for all the organics present. This procedure should first be confirmed in the laboratory by preparing and analyzing calibration standards containing multiple organic compounds.

6.5 Quality Assurance for Laboratory Procedures. Immediately after the preparation of the calibration curves and prior to the presurvey sample analysis, the analysis audit described in 40 CFR Part 61, Appendix C, Procedure 2, "Procedure for Field Auditing GC Analysis," should be performed. The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 18-3 and 18-7. The audit analyses should agree with the audit concentrations within 10 percent. When available, the tester may obtain audit cylinders by contacting: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided that (a) the gas manufacturer certifies the audit cylinder in a manner similar to the procedure described in 40 CFR Part 61, Appendix B, Method 106, Section 5.2.3.1, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined as an analysis performed by an individual other than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

7. *Final Sampling and Analysis Procedure*

Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 7.1, 7.2, 7.3, or 7.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique. If the source temperature is below 100°C, and the organic concentrations are suitable for the detector to be used, use the direct interface method. If the source gases require dilution, use a dilution interface and either the bag sample or adsorption tubes. The choice between these two techniques will depend on the physical layout of the site, the source temperature, and the storage stability of the compounds if collected in the bag. Sample polar compounds using direct interfacing or dilution interfacing to prevent sample loss by adsorption on the bag.

7.1 Integrated Bag Sampling and Analysis.

7.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight containers that hold the bags. Use a field sample data sheet as shown in Figure 18-10. Collect triplicate sample from each sample location.

7.1.1.1 Apparatus.

7.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with 6.4-mm OD Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

7.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

7.1.1.1.3 Needle Valve. To control gas flow.

7.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

7.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

7.1.1.1.6 Flowmeter. 0 to 500-ml flow range, with manufacturer's calibration curve.

7.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18-9. Leak check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack, or at a point no closer to the walls than 1 m, and start the pump with the needle valve adjusted to yield a flow of 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, 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. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18-10. Protect the Tedlar bag and its container from sunlight. When possible, perform the analysis within 2 hours of sample collection.

7.1.2 Direct Pump Sampling Procedure. Follow 7.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of stainless steel or some other material not affected by the stack gas. Leak check the system, and then purge with stack gas before the connecting to the previously evacuated bag.

7.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 7.1.1 except replace the pump with another evacuated can (see Figure 18-9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

7.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection, and maintain it at a suitably elevated temperature during all subsequent operations. (Note: Take care to leak check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the Tedlar bag.

In the first procedure, heat the box containing the sample bag to the source temperature, provided the components of the bag and the surrounding box can withstand this temperature. Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to source temperature until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

To use the second procedure, prefill the Tedlar bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 8.2.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or





Teflon positive displacement pump. Verify the dilution factors periodically through dilution and analysis of gases of known concentration.

7.1.5 Analysis of Bag Samples.

7.1.5.1 Apparatus. Same as Section 5. A minimum of three gas standards are required.

7.1.5.2 Procedure. Establish proper GC operating conditions as described in Section 6.3, and record all data listed in Figure 18-7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with gas from one of the three calibration mixtures, and activate the valve. Obtain at least two chromatograms for the mixture. The results are acceptable when the peak areas from two consecutive injections agree to within 5 percent of their average. If they do not, run additional analyses or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in the same manner. Prepare a calibration curve as described in Section 6.3.

Analyze the source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified for that bag. Follow the specifications on replicate analyses specified for the calibration gases. Record the data listed in Figure 18-11. If certain items do not apply, use the notation "N.A." After all samples have been analyzed, repeat the analyses of the calibration gas mixtures, and generate a second calibration curve. Use an average of the two curves to determine the sample gas concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by comparison to both calibration curves.

7.1.6 Determination of Bag Water Vapor Content. Measure and record the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in Section 7.1.4, determine the stack gas water content by Method 4.

7.1.7 Quality Assurance. Immediately prior to the analysis of the stack gas samples, perform audit analyses as described in Section 6.5. The audit analyses must agree with the audit concentrations within 10 percent. If the results are acceptable, proceed with the analyses of the source samples. If they do not agree within 10 percent, then determine the reason for the discrepancy, and take corrective action before proceeding.

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

$$C_c = \frac{C_i P_r T_i F_r}{P_i T_r (1 - B_{ws})} \qquad \text{Eq. 18-5}$$

where:

$C_c$ = Concentration of the organic from the calibration curve, ppm.

$P_r$ = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.

$T_i$ = Sample loop temperature at the time of sample analysis, °K.

$F_r$ = Relative response factor (if applicable, see Section 8.4).

$P_i$ = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.

$T_r$ = Reference temperature, the temperature of the sample loop recorded during calibration, °K.

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

7.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. Adhere to all safety requirements with this method.

7.2.1 Apparatus.

7.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as required by duct temperature, 6.4-mm OD, enlarged at duct end to contain glass wool plug. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining duct temperature.

7.2.1.2 Sample Lines. 6.4-mm OD Teflon lines, heat-traced to prevent condensation of material.

7.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

7.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

7.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

7.2.1.6 Needle Valve. To control gas sampling rate from the source.

7.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 2 liter/minute sampling rate.

7.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

7.2.1.9 Charcoal Adsorber. To absorb organic vapor collected from the source to prevent exposure of personnel to source gas.

7.2.1.10 Gas Cylinders. Carrier gas (helium or nitrogen), and oxygen and hydrogen for a flame ionization detector (FID) if one is used.

7.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

7.2.1.12 Recorder/Integrator. To record results.

7.2.2 Procedure. To obtain a sample, assemble the sampling system as shown in Figure 18-12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the source temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature of 0 to 3°C above the source temperature. While the probe and heated line are being heated, disconnect the sample line from the gas sampling valve, and attach the line from the calibration gas mixture. Flush the sample loop with calibration gas and analyze a portion of that gas. Record the results. After the calibration gas sample has been flushed into the GC instrument, turn the gas sampling valve to flush position, then reconnect the probe sample line to the valve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the sample using the same conditions as for the calibration gas mixture. Repeat the analysis on an additional sample. Measure the peak areas for the two samples, and if they do not agree to within 5 percent of their mean value, analyze additional samples until two consecutive analyses meet this criteria. Record the data. After consistent results are obtained, remove the probe from the source and analyze a second calibration gas mixture. Record this calibration data and the other required data on the data sheet shown in Figure 18-11, deleting the dilution gas information.

(NOTE: Take care to draw all samples, calibration mixtures, and audits through the sample loop at the same pressure.)

7.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

7.2.4 Quality Assurance. Same as Section 7.1.7. Introduce the audit gases in the sample line immediately following the probe.

7.2.5 Emission Calculations. Same as Section 7.1.8.

7.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the Section 7.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

7.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

7.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm type that can withstand being heated to 120°C and deliver 1.5 liters/minute.

7.3.1.2 Dilution Pumps. Two Model A-150 Kemmyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

7.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to 6.4-mm OD Teflon tubing.

7.3.1.4 Flowmeters. Two, for measurement of diluent gas, expected delivery flow rate to be 1,350 cc/min.

7.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

7.3.1.6 Heated Box. Suitable for being heated to 120°C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) The heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18-13.

(NOTE: Care must be taken to leak check the system prior to the dilutions so as not to create a potentially explosive atmosphere.)

The heated box shown in Figure 18-13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling value on the chromatograph.

7.3.2 Procedure. Assemble the apparatus by connecting the heated box, shown in Figure 18-13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple to the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3°C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds. Verify the operation of the dilution system by analyzing a high concentration gas of known composition through either the 10:1 or 100:1 dilution stages, as appropriate. (If necessary, vary the flow of the diluent gas to obtain other dilution ratios.) Determine the concentration of the diluted calibration gas using the dilution factor and the calibration curves prepared in the laboratory. Record the pertinent data on the data sheet shown in Figure 18-11. If the data on the diluted calibration gas are not within 10 percent of the expected values, determine whether the chromatograph or the dilution system is in error, and correct it. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop, bypassing the dilution system. If these analyses are not within acceptable limits, correct the dilution system to provide the desired dilution factors. Make this correction by diluting a high-concentration standard gas mixture to adjust the dilution ratio as required.

Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards. Repeat the analyses until two consecutive values do not vary by more than 5 percent from their mean value are obtained.

Repeat the analysis of the calibration gas mixtures to verify equipment operation. Analyze the two field audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

7.3.3 Determination of Stack Gas Moisture Content. Same as Section 7.2.3.

7.3.4 Quality Assurance. Same as Section 7.2.4.

7.3.5 Emission Calculations. Same as Section 7.2.5, with the dilution factor applied.

7.4 Adsorption Tube Procedure (Alternative Procedure). It is suggested that the tester refer to the National Institute of Occupational Safety and Health (NIOSH) method for the particular organics to be sampled. The principal interferent will be water vapor. If water vapor is present at concentrations above 3 percent, silica gel should be used in front of the charcoal. Where more than one compound is present in the emissions, then develop relative adsorptive capacity information.

7.4.1 Additional Apparatus. In addition to the equipment listed in the NIOSH method for the particular organic(s) to be sampled, the following items (or equivalent) are suggested.

7.4.1.1 Probe (Optional). Borosilicate glass or stainless steel, approximately 8-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-stack heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

7.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

7.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices to provide pumping rates from approximately 10 to 100 cc/min.

7.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within ± 1 percent, to calibrate pump.

7.4.1.5 Stopwatch. To time sampling and pump rate calibration.

7.4.1.6 Adsorption Tubes. Similar to ones specified by NIOSH, except the amounts of adsorbent per primary/backup sections are 200/200 mg for charcoal tubes and 1040/264 mg for silica gel tubes. As an alternative, the tubes may contain a porous polymer adsorbent such as Tenax GC or XAD-2.

7.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

7.4.1.8 Rotameter. 0 to 100 cc/min, to detect changes in flow rate during sampling.

7.4.2 Sampling and Analysis. It is suggested that the tester follow the sampling and analysis portion of the respective NIOSH method section entitled "Procedure." Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

Use a sample probe, if required, to obtain the sample at the centroid of the duct, or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. When more than one organic is present in the emissions, then develop relative adsorptive capacity information. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacture's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Analyze the audit samples (see Section 7.4.4.3), then the emission samples. Repeat the analysis of each sample until the relative deviation of two consecutive injections does not exceed 5 percent.

7.4.3 Standards and Calibration. The standards can be prepared according to the respective NIOSH method. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses. Prepare the calibration curve by using the least squares method.

7.4.4 Quality Assurance.

7.4.4.1 Determination of Desorption Efficiency. During the testing program, determine the desorption efficiency in the expected sample concentration range for each batch of adsorption media to be used. Use an internal standard. A minimum desorption efficiency of 50 percent shall be obtained. Repeat the desorption determination until the relative deviation of two consecutive determinations does not exceed 5 percent. Use the average desorption efficiency of these two consecutive determinations for the correction specified in Section 7.4.4.5. If the desorption efficiency of the compound(s) of interest is questionable under actual sampling conditions, use of the Method of Standard Additions may be helpful to determine this value.

7.4.4.2 Determination of Sample Collection Efficiency. For the source samples, analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and backup), repeat the sampling with a larger sampling portion.

7.4.4.3 Analysis Audit. Immediately before the sample analyses, analyze the two audits in accordance with Section 7.4.2. The analysis audit shall agree with the audit concentration within 10 percent.

7.4.4.4 Pump Leak Checks and Volume Flow Rate Checks. Perform both of these checks immediately after sampling with all sampling train components in place. Perform all leak checks according to the manufacturer's instructions, and record the results. Use the bubble tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

7.4.4.5 Calculations. All calculations can be performed according to the respective NIOSH method. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results by dividing by the desorption efficiency (decimal value). Report results as ppm by volume, dry basis.

7.5 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18-11 have been completed. Summarize this data on the data sheets shown in Figure 18-15.

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I. Name of company _____ Date _____
Address _____
_____
Contacts _____ Phone _____
_____ _____
Process to be sampled _____
_____
_____
Duct or vent to be sampled _____
_____

II. Process description _____
_____
_____
_____
_____
Raw material _____
_____
_____
Products _____
_____
_____
Operating cycle
Check: Batch _____ Continuous _____ Cyclic _____
Timing of batch or cycle _____
Best time to test _____

Figure 18-1. Preliminary survey data sheet.





III. Sampling site
A. Description
Site description _____
Duct shape and size _____
Material _____
Wall thickness _____ inches
Upstream distance _____ inches _____ diameter
Downstream distance _____ inches _____ diameter
Size of port _____
Size of access area _____
Hazards _____ Ambient temp. _____ °F

B. Properties of gas stream
Temperature _____ °C _____ °F, Data source _____
Velocity _____, Data source _____
Static pressure _____ inches $H_2O$, Data source _____
Moisture content _____ %, Data source _____
Particulate content _____, Data source _____
Gaseous components
$N_2$ _____ % Hydrocarbons _____ ppm
$O_2$ _____ % _____ _____
CO _____ % _____ _____
$CO_2$ _____ % _____ _____
$SO_2$ _____ % _____ _____
Hydrocarbon components
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm

Figure 18-1 (continued). Preliminary survey data sheet.

C. Sampling considerations

Location to set up GC _____

_____

Special hazards to be considered _____

_____

Power available at duct _____

Power available for GC _____

Plant safety requirements _____

_____

Vehicle traffic rules _____

_____

Plant entry requirements _____

_____

Security agreements _____

_____

Potential problems _____

_____

D. Site diagrams. (Attach additional sheets if required).

Figure 18-1 (continued). Preliminary survey data sheet.





| Components to be analyzed | Expected concentration |
|---|---|
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |

Suggested chromatographic column _____

_____

Column flow rate ____ ml/min Head pressure____ mm Hg

Column temperature:

Isothermal _____ °C

Programmed from _____ °C to ____ °C at ____ °C/min

Injection port/sample loop temperature _____ °C

Detector temperature _____ °C

Detector flow rates: Hydrogen _____ ml/min.

head pressure____ mm Hg

Air/Oxygen _____ ml/min.

head pressure____ mm Hg

Chart speed _____ inches/minute

Compound data:

| Compound | Retention time | Attenuation |
|---|---|---|
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

Figure 18-2. Chromatographic conditions data sheet.

Preparation of Standards in Tedlar Bags and Calibration Curve

| | Standards Mixture #1 | Mixture #2 | Mixture #3 |
|---|---|---|---|
| Standards Preparation Data: | | | |
| Organic: _____ | | | |
| 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 (ll) (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 ($mm^2$) | | | |
| Calculated concentration (ppm) (Equation 18-3 or 18-4) | | | |

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

Figure 18-3. Standards prepared in Tedlar bags and calibration curve.





Flowmeter Calibration

Flowmeter number or identification _____

Flowmeter type _____

Calibration device (s): 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 reading (as marked) | Flowmeter temp. (°K) | Flowmeter pressure (absolute) | Calibration device time (min) | Calibration device gas volume[a] | Calibration device 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 technique should be verified before application, it may be possible to calculate flow rate readings for rotameters at standard conditions $Q_{std}$ as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

| Flow rate (laboratory conditions) | Flow rate (standard conditions) |
|---|---|
| | |
| | |
| | |
| | |
| | |
| | |

Figure 18-4. Flowmeter calibration.

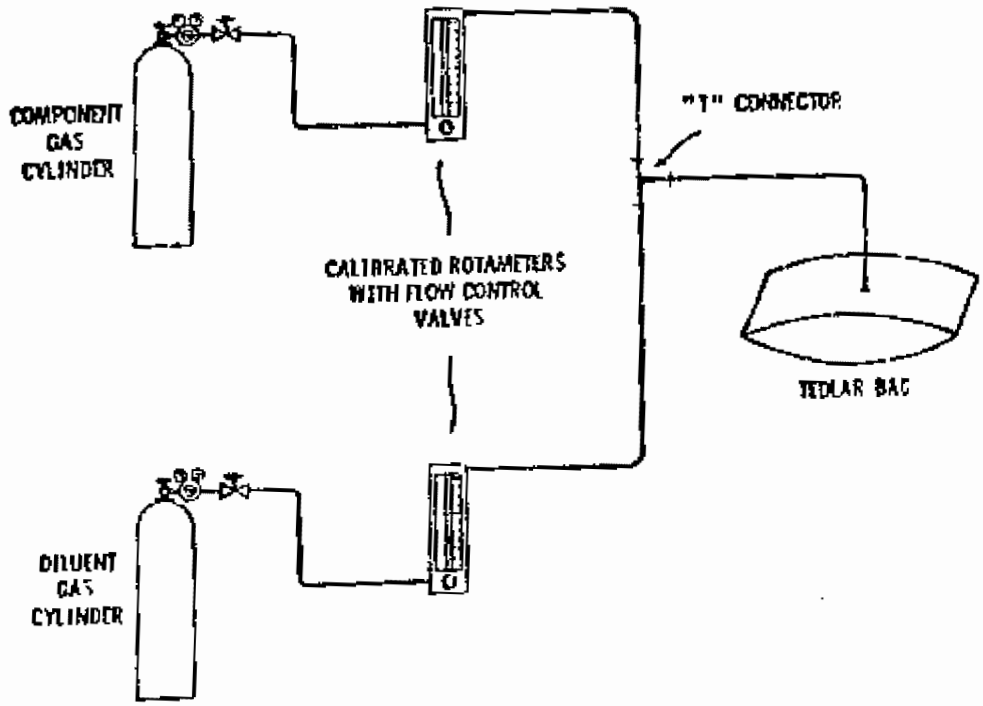


Figure 18-5. Single-stage calibration gas dilution system.



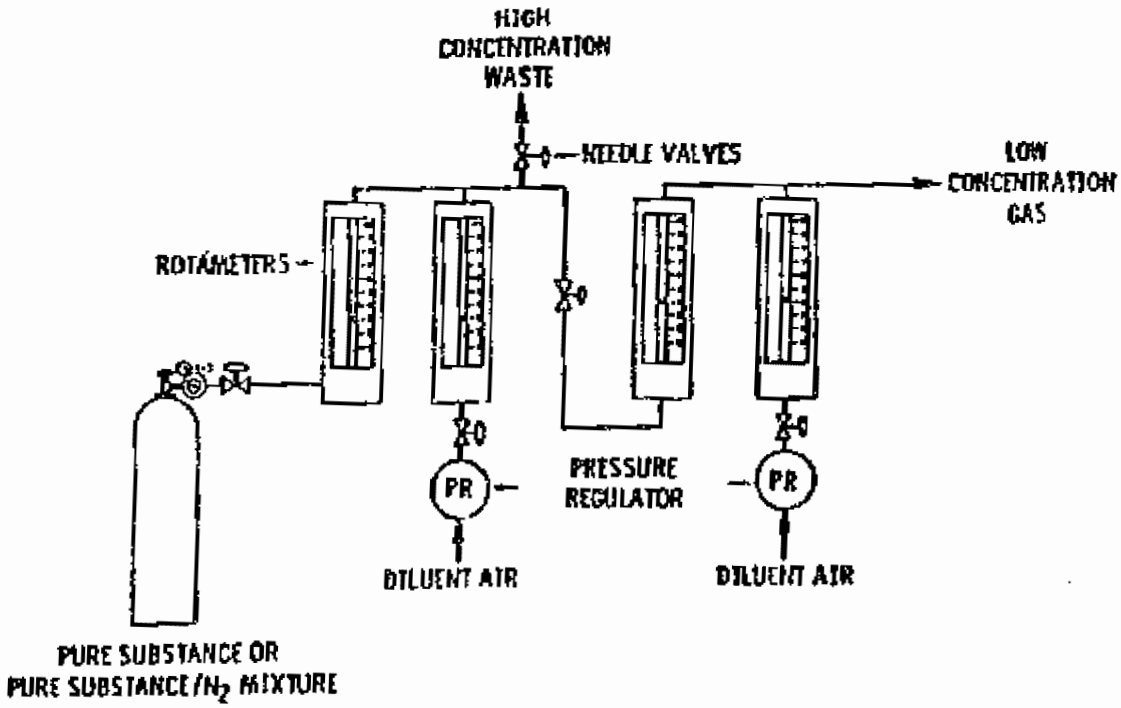


Figure 18-6. Two-stage dilution apparatus.

Preparation of Standards by Dilution of Cylinder Standard

Cylinder standard: Organic _____ Certified concentration _____ ppm

Standards Preparation Date: Date _____

| Stage 1 | Mixture 1 | Mixture 2 | Mixture 3 |
|---|---|---|---|
| Standard gas flowmeter reading | | | |
| Diluent gas flowmeter reading | | | |
| Laboratory temperature (°K) | | | |
| Barometric pressure (mm Hg) | | | |
| Flowmeter gage pressure (mm Hg) | | | |
| Flow rate cylinder gas at standard conditions (ml/min) | | | |
| Flow rate diluent gas at standard conditions (ml/min) | | | |
| Calculated concentration (ppm) | | | |
| **Stage 2 (if used)** | | | |
| Standard gas flowmeter reading | | | |
| Diluent gas flowmeter reading | | | |
| Flow rate stage 1 gas at standard conditions (ml/min) | | | |
| Flow rate diluent gas at standard conditions (ml/min) | | | |
| Calculated concentration (ppm) | | | |
| GC Operating Conditions: | | | |
| Sample loop volume (ml) | | | |
| Sample loop temperature (°C) | | | |
| Carrier gas flow rate (ml/min) | | | |
| Column temperature: | | | |
| Initial (°C) | | | |
| Program rate (°C/min) | | | |
| Final (°C) | | | |
| Organic Peak Identification and Calculated Concentrations: | | | |
| Injection time (24-hr clock) | | | |
| Distance to peak (cm) | | | |
| Chart speed (cm/min) | | | |
| Retention time (min) | | | |
| Attenuation factor | | | |
| Peak area ($cm^2$) | | | |
| Peak area x attenuation factor | | | |

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

Figure 18-7. Standards prepared by dilution of cylinder standard.





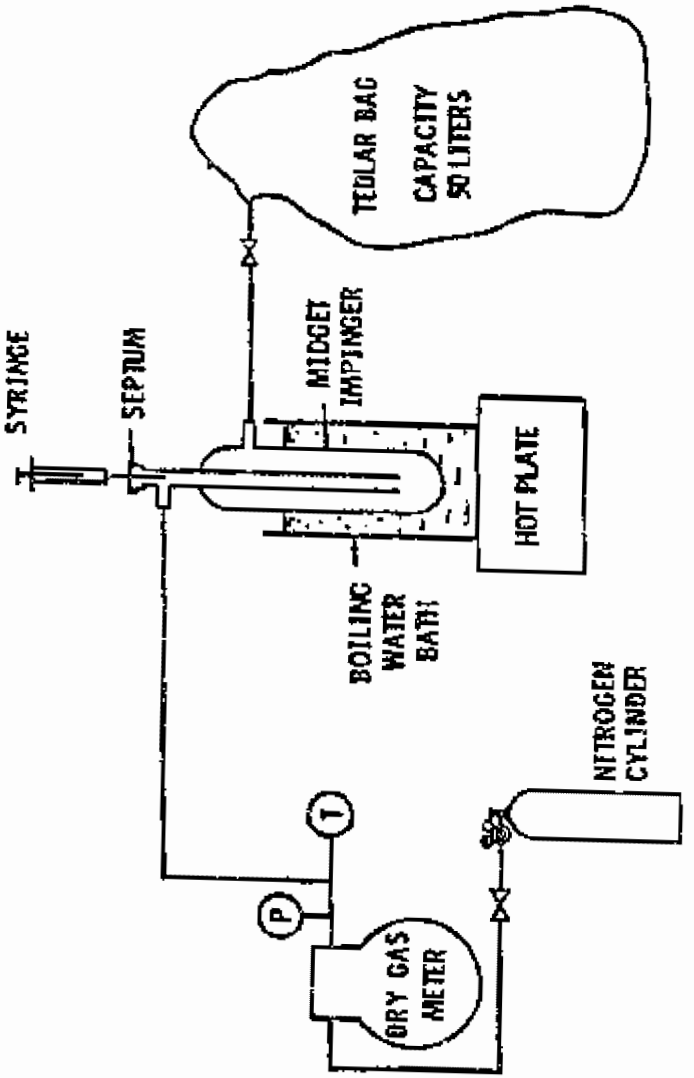


Figure 18-8. Apparatus for preparation of liquid materials.