

# 1,3-BUTADIENE



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Method no.: 56

Matrix: Air

Target concentration: 1 ppm (2.21 mg/m<sup>3</sup>)

Procedure: Air samples are collected by drawing known volumes of air through sampling tubes containing charcoal adsorbent which has been coated with 4-tert-butylcatechol. The samples are desorbed with carbon disulfide and then analyzed by gas chromatography using a flame ionization detector.

Recommended air volume and sampling rate: 3 L at 0.05 L/min

Detection limit of the overall procedure: 90 ppb (200 µg/m<sup>3</sup>)

Reliable quantitation limit: 155 ppb (343 µg/m<sup>3</sup>)

Standard error of estimate at the target concentration: 6.5%  
(Section 4.6.1)

Special requirements: The sampling tubes must be obtained from the Salt Lake City Analytical Laboratory. Collected samples should be stored in a freezer.

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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## 1. General Discussion

### 1.1 Background

#### 1.1.1 History

This work was undertaken to develop a sampling and analytical procedure for 1,3-butadiene at 1 ppm. The 1 ppm target concentration was selected in anticipation of a possible reduction in the current OSHA PEL of 1000 ppm. NIOSH has recently recommended that 1,3-butadiene be treated as a potential occupational carcinogen, teratogen and as a reproduction hazard. (Ref. 5.1)

The current method recommended by OSHA for collecting 1,3-butadiene uses activated coconut shell charcoal as the sampling medium (Ref. 5.2). This method was found to be inadequate for use at low 1,3-butadiene levels because of sample instability (Sections 4.5.2 and 4.6.2).

The stability of collected samples has been significantly improved through the use of a specially cleaned charcoal which is coated with 4-tert-butylcatechol (TBC). TBC is a polymerization inhibitor for 1,3-butadiene (Ref. 5.3).

#### 1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

Symptoms of human exposure to 1,3-butadiene include irritation of the eyes, nose and throat. It can also cause coughing, drowsiness and fatigue. Dermatitis and frost-bite can result from skin exposure to liquid 1,3-butadiene. (Ref. 5.1)

NIOSH recommends that 1,3-butadiene be handled in the workplace as a potential occupational carcinogen. This recommendation is based on two inhalation studies that resulted in cancers at multiple sites in rats and in mice. 1,3-Butadiene has also demonstrated mutagenic activity in the presence of a liver microsomal activating system. It has also been reported to have adverse teratogenic and reproductive effects. (Ref. 5.1)

#### 1.1.3 Potential workplace exposure

In 1984, 2.53 billion pounds of rubber grade butadiene were produced. This amount was only 3.7% less than the average yearly amount produced during the past decade of 1974-1984. In 1984, butadiene ranked 36th of the top 50 chemicals produced in the United States. (Ref. 5.4) About 80% of the 1,3-butadiene produced in the United States is a by-product of the manufacture of ethylene. The remaining 20% is produced by the dehydrogenation of n-butene and n-butane. (Ref. 5.1)

About 90% of the annual production of 1,3-butadiene is used to manufacture styrene-butadiene rubber and polybutadiene rubber. Other uses include: polychloroprene rubber, acrylonitrile-butadiene-styrene resins, nylon intermediates, styrene-butadiene latexes, butadiene polymers, thermoplastic elastomers, nitrile resins, methyl methacrylate-butadiene-styrene resins and chemical intermediates. (Ref. 5.1)

A NIOSH survey, that was conducted from 1972 to 1974, estimated that approximately 65,000 workers were potentially exposed to 1,3-butadiene. About 70% of this total was employed in chemical and chemical products occupations. Another 25% of the total was employed in work places which included: rubber and rubber products industries miscellaneous business services and miscellaneous manufacturing industries. (Ref. 5.1)

#### 1.1.4 Physical properties (Ref. 5.1)

CAS no.: 106-99-0

molecular weight: 54.09  
appearance: colorless gas  
boiling point: -4.41 °C (760 mm Hg)  
freezing point: -108.9 °C  
vapor pressure: 2 atm at 15.3 °C  
5 atm at 47.0 °C  
explosive limits: 2 to 11.5% (by volume in air)  
odor threshold: 1.3 ppm  
structural formula: 

synonyms:biethylene;  
bivinyI; butadiene; divinyl; buta-1,3-diene; alpha-gamabutadiene; erythrene; NCI-C50602;  
pyrrolylene; vinyIethylene.

1.2 Limit defining parameters (The analyte air concentrations listed throughout this method are based on an air volume of 3 L and a desorption volume of 1 mL. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg.)

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure was 304 pg per injection. This was the amount of 1,3-butadiene which gave a measurable response relative to the interferences present in a standard. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure was 0.60 µg per sample (90 ppb or 200 µg/m<sup>3</sup>). This amount was determined graphically. It was the amount of analyte which, when spiked on the sampling device, would allow recovery approximately equivalent to the detection limit of the analytical procedure. (Section 4.1.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit was 1.03 µg per sample (155 ppb or 343 µg/m<sup>3</sup>). This was the smallest amount of analyte which could be quantitated within the limits of a recovery of at least 75% and a precision ( $\pm 1.96$  SD) of  $\pm 25\%$  or better. (Section 4.2)

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The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

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1.2.4 Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.6 to 2 times the target concentration, based on the recommended air volume, was 387 area units per µg/mL. This value was determined from the slope of the calibration curve. (Section 4.3) The sensitivity may vary with the particular instrument used in the analysis.

1.2.5 Recovery

The recovery of 1,3-butadiene from samples used in storage tests remained above 77% when the samples were stored at ambient temperature for 17 days, and above 94% when the samples were stored at refrigerated temperature for 18 days. These values were determined from regression lines which were calculated from the storage data. (Section 4.6) The recovery of the analyte from the collection device must be at least 75% following storage.

#### 1.2.6 Precision (analytical method only)

The pooled coefficient of variation obtained from replicate determinations of analytical standards over the range of 0.6 to 2 times the target concentration was 0.011. (Section 4.3)

#### 1.2.7 Precision (overall procedure)

The precision at the 95% confidence level for the refrigerated temperature storage test was  $\pm 12.7\%$ . (Section 4.6.1) This value includes an additional  $\pm 5\%$  for sampling error. The overall procedure must provide results at the target concentrations that are  $\pm 25\%$  at the 95% confidence level.

#### 1.2.8 Reproducibility

Samples collected from a controlled test atmosphere and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The average recovery was 97.2% and the standard deviation was 6.2%. (Section 4.7)

### 1.3 Advantages

1.3.1 The sampling and analytical procedure permits determination of 1,3-butadiene at low levels.

1.3.2 Samples are relatively stable following storage at ambient temperature for 17 days.

### 1.4 Disadvantage

The recommended sampling tubes must be obtained from the Salt Lake City Analytical Laboratory.

## 2. Sampling Procedure

### 2.1 Apparatus

2.1.1 Samples are collected by use of a personal sampling pump that can be calibrated to within  $\pm 5\%$  of the recommended 0.05 L/min sampling rate with the sampling tube in line.

2.1.2 Samples are collected with laboratory prepared sampling tubes. The sampling tube is constructed of silane-treated glass and is about 5-cm long. The i.d. is 4 mm and the o.d. is 6 mm. One end of the tube is tapered so that a glass wool end plug will hold the contents of the tube in place during sampling. The opening in the tapered end of the sampling tube is at least one-half the i.d. of the tube (2 mm). The other end of the sampling tube is open to its full 4-mm i.d. to facilitate packing of the tube. Both ends of the tube are fire-polished for safety. The tube is packed with 2 sections of pretreated charcoal which has been coated with TBC. The tube is packed with a 50-mg backup section, located nearest the tapered end, and with a 100-mg sampling section of charcoal. The two sections of coated adsorbent are separated and retained with small plugs of silanized glass wool. Following packing, the sampling tubes are sealed with two 7/32-in. o.d. plastic end caps. Instructions for the pretreatment and coating of the charcoal are presented in Section 4.8. of this method.

### 2.2 Reagents

None required

### 2.3 Technique

2.3.1 Properly label the sampling tube before sampling and then remove the plastic end caps.

- 2.3.2 Attach the sampling tube to the pump using a section of flexible plastic tubing such that the large front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing ahead of the sampling tube. The sampling tube should be attached in the worker's breathing zone in a vertical manner such that it does not impede work performance.
- 2.3.3 After sampling for the appropriate time, remove the sampling tube from the pump and then seal the tube with plastic end caps. Wrap the tube lengthwise with an official OSHA seal (Form 21).
- 2.3.4 Include at least one blank for each sampling set. The blank should be handled in the same manner as the samples with the exception that air is not drawn through it.
- 2.3.5 List any potential interferences on the sample data sheet.
- 2.3.6 The samples require no special shipping precautions under normal conditions. The samples should be refrigerated if they are to be exposed to higher than normal ambient temperatures. If the samples are to be stored before they are shipped to the laboratory, they should be kept in a freezer. The samples should be placed in a freezer upon receipt at the laboratory.

- 2.4 Breakthrough (Breakthrough was defined as the relative amount of analyte found on the backup section of the tube in relation to the total amount of analyte collected on the sampling tube.)

Five-percent breakthrough occurred after sampling a test atmosphere containing 2.0 ppm 1,3-butadiene for 90 min at 0.05 L/min. At the end of this time 4.5 L of air had been sampled and 20.1 µg of the analyte was collected. The relative humidity of the sampled air was 80% at 23 °C. (Section 4.4)

Breakthrough studies have shown that the recommended sampling procedure can be used at air concentrations higher than the target concentration. The sampling time, however, should be reduced to 45 min if both the expected 1,3-butadiene level and if the relative humidity of the sampled air are high. (Section 4.4)

- 2.5 Desorption efficiency

The average desorption efficiency for 1,3-butadiene from TBC coated charcoal over the range of from 0.6 to 2 times the target concentration was 96.4%. The desorption efficiency was essentially constant over the range studied. (Section 4.5)

- 2.6 Recommended air volume and sampling rate

- 2.6.1 The recommended air volume is 3 L.
- 2.6.2 The recommended sampling rate is 0.05 L/min for 1 h.

- 2.7 Interferences (sampling)

There are no known interferences to the sampling method.

- 2.8 Safety precautions (sampling)

- 2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.
- 2.8.2 Follow all safety practices that apply to the work area being sampled.

### 3. Analytical Procedure

### 3.1 Apparatus

- 3.1.1 A gas chromatograph (GC), equipped with a flame ionization detector (FID). A Hewlett-Packard Model 5840A GC was used for this evaluation. Injections were performed using a Hewlett-Packard Model 7671A automatic sampler.
- 3.1.2 A GC column capable of resolving the analytes from potential interferences. A 20-ft × 1/8-in. o.d. stainless steel GC column containing 20% FFAP on 80/100 mesh Chromosorb W-AW-DMCS was used for this evaluation.
- 3.1.3 Two milliliter glass vials with Teflon-lined caps.
- 3.1.4 Disposable Pasteur-type pipets, volumetric flasks, pipets and syringes for preparing samples and standards, making dilutions and performing injections.

### 3.2 Reagents

- 3.2.1 Carbon disulfide. Fisher Scientific Company A.C.S. Reagent Grade solvent was used in this evaluation. The benzene contaminant that was present in the carbon disulfide was used as an internal standard (ISTD) in this evaluation.
- 3.2.2 Nitrogen, hydrogen, and air, GC grade.
- 3.2.3 1,3-Butadiene of known high purity. Matheson Gas Products, CP Grade 1,3-butadiene was used in this study.

### 3.3 Standard preparation

- 3.3.1 Prepare standards by diluting known volumes of 1,3-butadiene gas with carbon disulfide. This can be accomplished by injecting the appropriate volume of 1,3-butadiene into the headspace above the 1 mL of carbon disulfide contained in sealed 2-mL vial. Shake the vial after the needle is removed from the septum. A standard containing 7.71 µg/mL (at ambient temperature and pressure) was prepared by diluting 4 µL of the gas with 1 mL of carbon disulfide.
- 3.3.2 The mass of 1,3-butadiene gas which was used to prepare standards can be determined by use of the following equations:

$$MV = (22.41)(760/BP)(273+T)/(273)$$

where: 22.41 = molar volume at STP  
MV = ambient molar volume  
BP = ambient barometric pressure  
T = ambient temperature

$$\mu\text{g}/\mu\text{L} = 54.09/MV$$

$$\mu\text{g per standard} = (\mu\text{g}/\mu\text{L})(\mu\text{L})(p)$$

where: µg/µL = ambient density of 1,3-butadiene gas  
µL = µL of 1,3-butadiene used to prepare standard  
p = purity of 1,3-butadiene, (decimal form)

### 3.4 Sample preparation

- 3.4.1 Transfer the 100-mg section of the sampling tube to a 2-mL vial. Place the 50-mg section in a separate vial. If the glass wool plugs contain a significant amount of charcoal, place them with the appropriate sampling tube section.

- 3.4.2 Add 1 mL of carbon disulfide to each vial.
- 3.4.3 Seal the vials with Teflon-lined caps and then allow them to desorb for 1 h. Shake the vials by hand with vigorous force several times during the desorption time.
- 3.4.4 If it is not possible to analyze the samples within 4 h of desorption, separate the carbon disulfide from the charcoal, using a disposable Pasteur-type pipet, following the 1-h desorption time. This separation will improve the stability of desorbed samples. (Tables 4.5.1.2 and 4.5.1.3)
- 3.4.5 Save the used sampling tubes to be cleaned and re-packed with fresh adsorbent.

### 3.5 Analysis

#### 3.5.1 GC Conditions

column temperature: 95°C  
injector temperature: 180°C  
detector temperature: 275°C  
carrier gas flow rate: 30 mL/min  
injection volume: 0.80 µL  
GC column: 20-ft × 1/8-in. o.d. stainless steel GC column containing 20%FFAP on 80/100 Chromosorb W-AW DMCS

#### 3.5.2 Chromatogram See Section 4.9

- 3.5.3 Use a suitable method, such as electronic integration or peak heights, to measure detector response.
- 3.5.4 Prepare a calibration curve using several standard solutions of different concentrations. Prepare the calibration curve daily. Program the integrator to report the results in µg/mL.
- 3.5.5 Bracket sample concentrations with standards.

### 3.6 Interferences (analytical)

- 3.6.1 Any compound with the same general retention time as the analyte and which also gives a detector response is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist.
- 3.6.2 GC parameters (temperature, column, etc.) may be changed to circumvent interferences.
- 3.6.3 A useful means of structure designation is GC/MS. It is recommended that this procedure be used to confirm samples whenever possible.

### 3.7 Calculations

- 3.7.1 Results are obtained by use of calibration curves. Calibration curves are prepared by plotting detector response against concentration for each standard. The best line through the data points is determined by curve fitting.
- 3.7.2 The concentration, in  $\mu\text{g/mL}$ , for a particular sample is determined by comparing its detector response to the calibration curve. If any analyte is found on the backup section, this amount is added to the amount found on the front section. Blank corrections should be performed before adding the results together.
- 3.7.3 The 1,3-butadiene air concentration can be expressed using the following equation:

$$\text{mg/m}^3 = (A)(B)/(C)(D)$$

where    A =  $\mu\text{g/mL}$  from Section 3.7.2  
          B = desorption volume  
          C = liters of air sampled  
          D = desorption efficiency

- 3.7.4 The following equation can be used to convert results in  $\text{mg/m}^3$  to ppm:

$$\text{ppm} = (\text{mg/m}^3)(24.46)/54.09$$

where     $\text{mg/m}^3$  = result from Section 3.7.3  
          24.46 = molar volume of an ideal gas at 760 mm Hg and 25 °C

### 3.8 Safety precautions (analytical)

- 3.8.1 Avoid skin contact and inhalation of all chemicals.
- 3.8.2 Restrict the use of all chemicals to a fume hood whenever possible.
- 3.8.3 Wear safety glasses and a lab coat in all lab areas.

## 4. Backup Data

### 4.1 Detection limit data

#### 4.1.1 Detection limit of the analytical procedure

The injection size recommended in the analytical procedure (0.80  $\mu\text{L}$ ) was used in the determination of the detection limit for the analytical procedure. The detection limit of the analytical procedure was 304 pg per injection. This was the amount of 1,3-butadiene which gave a measurable response relative to interferences present in a standard. This detection limit was determined by the analysis of a standard containing 380  $\text{ng/mL}$  of 1,3-butadiene

in carbon disulfide. Figure 4.1.1 is a chromatogram of the detection limit of the analytical procedure.

#### 4.1.2 Detection limit of the overall procedure

The injection size recommended in the analytical procedure (0.80  $\mu\text{L}$ ) was used in the determination of the detection limit of the overall procedure. 1,3-Butadiene was diluted for use in this study by adding the pure analyte to a sealed, silanized vial containing air and a few crystals of TBC. Samples were prepared by injecting 100-mg portions of TBC coated charcoal with appropriate amounts of the diluted 1,3-butadiene.

The samples were stored in a freezer overnight before analysis to allow complete adsorption of the analyte. Each result is the average of at least 2 samples. The results of this study are presented in Table 4.1.2 and in Figure 4.1.2.

The detection limit of the overall procedure was determined graphically (Figure 4.1.2) from the data in Table 4.1.2. This amount was 0.60  $\mu\text{g}$  per sample.

#### 4.2 Reliable quantitation limit data

The recommended injection size of 0.80  $\mu\text{L}$  was used in the determination of the reliable quantitation limit (RQL). The amount of 1,3-butadiene which provided a recovery of 75% from the sampling media was determined graphically (Figure 4.2.1) from the data in Table 4.1.2. This amount was 1.03  $\mu\text{g}$ . A chromatogram of the RQL is presented in Figure 4.2.2. Six samples were used to determine the precision at the RQL. The samples were prepared in a similar manner as those in Section 4.1.2. The results of this study are presented below and in Figure 4.2.1.

Table 4.2  
Reliable Quantitation Limit Data

sample number	$\mu\text{g}$ spiked	$\mu\text{g}$ recovered	percent recovered
1	1.03	0.854	82.9
2	1.03	0.754	73.2
3	1.03	0.829	80.5
4	1.03	0.779	75.6
5	1.03	0.836	81.2
6	1.03	0.836	81.2
$\bar{X}$	1.03	0.815	79.1
			SD = 3.8
			1.96 SD = 7.4

#### 4.3 Sensitivity and precision (analytical method only)

The sensitivity and precision of the analytical procedure were evaluated by performing multiple injections of analytical standards at 0.6, 1, and 2 times the target concentration. The standards were prepared by injecting appropriate amounts of 1,3-butadiene gas diluted with carbon disulfide. The data are presented in Table 4.3 and also in Figure 4.3. The ISTD data are the results of an internal standard calibration using the benzene contaminant present in carbon disulfide as the internal standard.

Table 4.3  
1,3-Butadiene Sensitivity and Precision Data

0.6×		1×		2×	
3.86 µg/sample		6.75 µg/sample		13.5 µg/sample	
ISTD	area	ISTD	area	ISTD	area
3.85	1332	6.66	2371	13.4	5190
3.89	1509	6.73	2386	13.5	5167
3.85	1507	6.78	2369	13.7	5076
3.81	1345	6.78	2393	13.5	5097
3.81	1416	6.86	2529	13.6	5045
3.95	1354	6.75	2327	13.3	5087
X = 3.86		6.76		13.5	
CV = 0.0138		0.00977		0.0105	
CV = 0.011					

The sensitivity for 1,3-butadiene was 387 area counts per µg/mL.

#### 4.4 Breakthrough data

Breakthrough was defined as the relative amount of 1,3-butadiene found on the 50-mg sampling tube section in relation to the total amount collected on the sampling tube.

Three breakthrough studies were performed at twice the target level with the recommended air sampler. The test atmospheres were generated by diluting the effluent of a gas cylinder containing 100 ppm of 1,3-butadiene with humid air. The concentrations of the test atmospheres were determined by direct injection of the atmosphere into a gas chromatograph. The gas chromatograph was calibrated using 1,3-butadiene from another source that had been diluted with dry air in a Teflon gas bag. The average concentration of the test atmospheres was 2.0 ppm. The average relative humidity of these test atmospheres was 80% at 23 °C. The sampling rates were about 0.05 L/min. The results of these studies are presented in Table 4.4.1.

Table 4.4.1  
1, 3-Butadiene Breakthrough at Twice the Target Concentration

sampling time (min)	amt on 100-mg section (µg)	amt on 50-mg section (µg)	% breakthrough
91	23.4	0.0	0.0
124	27.8	3.1	10.0
155	30.4	6.1	16.7
60	14.6	0.0	0.0
91	21.6	1.2	5.3
121	25.5	3.5	12.1
50	8.6	0.0	0.0
76	13.0	0.0	0.0
92	14.4	0.6	4.0
105	15.7	2.2	12.3
125	17.0	2.4	12.4

When the results of the three studies were combined, 5% breakthrough occurred after sampling for 90 min. The air volume sampled after this time was 4.5 L and the amount of 1,3-butadiene collected was 20.1 µg.

Additional breakthrough studies were performed at concentrations higher than twice the target level in order to determine if the recommended sampling procedure would be reliable at those concentrations. The test atmospheres used in these studies were generated and their concentrations were determined using the techniques previously described. Percent recovery values were calculated using sample results and the actual concentration of the test atmospheres. The sampling rates were about 0.05 L/min. The results of these studies are presented in Tables 4.4.2 through 4.4.4.

Table 4.4.2  
1,3-Butadiene Breakthrough Study at 7.3 ppm  
(Relative Humidity = 77% at 22 °C)

sampling time, min	air volume sampled, L	percent breakthrough	percent recovery
15	0.73	0.0	80.2
30	1.6	0.0	94.2
45	2.2	0.0	96.8
60	3.1	0.0	99.4
75	3.5	0.6	96.7
90	4.5	8.4	95.8

Table 4.4.3  
1,3-Butadiene Breakthrough Study at 32 ppm  
(Relative Humidity = 47% at 24 °C)

sampling time, min	air volume sampled, L	percent breakthrough	percent recovery
15	0.71	0.0	87.3
46	2.3	0.0	87.2
60	3.2	0.0	91.2
90	4.3	0.0	94.8
105	5.2	0.0	95.0
120	6.3	0.0	97.5
155	8.2	0.0	93.0

Five-percent breakthrough occurred after sampling for 84 min. At the end of this time, 4.2 L of air had been sampled and 68 µg of 1,3-butadiene had been collected.

No breakthrough was observed, even after sampling for 155 min. This data shows that, at low relative humidity, the recommended sampling media has considerable capacity for 1,3-butadiene.

Table 4.4.4  
1,3-Butadiene Breakthrough Study at 36 ppm  
(Relative Humidity = 90% at 21 °C)

sampling time, min	air volume sampled, L	percent breakthrough	percent recovered
36	1.9	0.0	105.8
47	2.2	0.0	98.8
60	3.0	21.6	90.2
75	3.9	30.0	96.0
90	4.3	30.6	76.4
105	5.8	32.1	57.6
121	6.3	31.1	56.7

It is apparent from the data in Tables 4.4.2 through 4.4.4 that the recommended sampling and analytical method can be used at 1,3-butadiene levels higher than the target concentration. The relative humidity of the sampled air has a significant effect on the ability of the sampling device to retain the analyte.

#### 4.5 Desorption efficiency and stability of desorbed samples

#### 4.5.1 Pretreated charcoal coated with TBC

The desorption efficiency of 1,3-butadiene was determined by injecting the gas onto 100-mg portions of the recommended collection medium. The samples were spiked and then stored in a freezer overnight prior to analysis. The average desorption efficiency over the range of 0.6 to 2 times the target concentration was 96.4%. The individual results are presented in Table 4.5.1.1.

The stability of desorbed samples was investigated by re-analyzing the target concentration desorption samples at various times after carbon disulfide addition. Freshly prepared standards were used for each analysis. The sample vials were resealed immediately after each analysis. The results of this study are presented in Table 4.5.1.2. The percent recovery is based on the theoretical amount of 1,3-butadiene added to the original samples.

Table 4.5.1.1  
Desorption Efficiency  
of 1,3-Butadiene from Charcoal Coated with TBC

× target conc. µg/sample	0.6× 3.86	1× 6.75	2× 13.5
desorption efficiency, %	94.3	100.0	97.5
	95.4	97.0	97.5
	96.4	102.0	95.8
	96.9	96.0	95.2
	94.8	64.3	93.4
	96.9	98.8	92.5
	95.8	98.0	95.3
X	95.8	98.0	95.33

Table 4.5.1.2  
The Stability (% Recovery) of 1,3-Butadiene  
After Desorption from Charcoal Coated with TBC

time, h	1	2	3	4	5	6	$\bar{X}$
1	100.0	97.0	102.0	96.0	94.3	98.8	98.0
4	98.7	95.1	97.7	89.0	88.6	87.4	92.8
9	90.2	89.4	92.2	88.7	88.0	89.4	89.6
16	84.2	82.2	84.1	81.3	80.3	86.6	83.1
24	82.4	76.8	79.7	76.6	72.3	79.0	77.8
58	66.8	50.4	52.3	61.5	60.6	64.2	59.3

To determine if the stability of desorbed samples could be improved, the following experiment was performed: twelve samples were prepared by injecting 1,3-butadiene gas, at the target concentration, onto 100-mg portions of the recommended sampling media. The samples were spiked and then stored in a freezer overnight prior to analysis. Following desorption and analysis, the carbon disulfide was separated from the charcoal for six of the samples. The other six samples were not separated. All of the samples were re-analyzed using freshly prepared standards and the results of this study are shown below.

Table 4.5.1.3  
Effect of Charcoal on the Stability of Butadiene in CS<sub>2</sub>

storage time hours	CS <sub>2</sub> /charcoal separated				CS <sub>2</sub> /charcoal not separated			
	1	2	3	$\bar{X}$	1	2	3	$\bar{X}$
6	93.1	91.8	93.5	92.8	93.6	91.3	93.1	92.7
28	88.9	90.1	92.4	90.5	76.8	74.0	76.2	75.7

It appears that the stability of desorbed samples can be improved by separating the carbon disulfide from the charcoal.

#### 4.5.2 Untreated charcoal

The desorption efficiency of 1,3-butadiene was also determined for untreated SKC, Inc. Lot 120 coconut shell charcoal in the same manner as used for the recommended medium. The average desorption efficiency over the range of 0.6 to 2 times the target concentration was 60.4%. The individual results are presented in Table 4.5.2.1.

The stability of 1,3-butadiene desorbed from untreated SKC, Inc. Lot 120 charcoal was investigated in the same manner as was the recommended medium. The results of this study are presented in Table 4.5.2.2.

Table 4.5.2.1  
The Desorption Efficiency  
of 1,3-Butadiene from SKC, Inc. Lot 120  
Charcoal

× target conc. µg/sample	0.6×	1×	2×
	3.86	6.75	13.5
desorption efficiency, %	61.6	67.3	67.1
	66.7	64.1	65.0
	61.5	61.7	62.8
	54.4	62.0	61.4
	52.3	57.9	58.7
	51.7	53.3	58.8
X	58.0	61.0	62.3

Table 4.5.2.2  
The Stability of 1,3-Butadiene After Desorption  
from SKC, Inc. Lot 120 Charcoal (% recovery)

storage time	sample number						
hours	1	2	3	4	5	6	$\bar{X}$
5	43.8	44.0	40.1	40.6	38.8	38.4	41.0

These data show that SKC, Inc. Lot 120 charcoal is inadequate for this application because of sample instability.

#### 4.6 Storage data

##### 4.6.1 Pretreated charcoal coated with TBC

The test atmosphere was generated by diluting the effluent of a gas cylinder, containing 100 ppm 1,3-butadiene, with humid air. The resultant atmosphere contained 1 ppm 1,3-butadiene, the relative humidity of the air was 75% and its temperature was 25 °C. The 1,3-butadiene content of the test atmosphere was determined by direct injection of 100 µL of the atmosphere into a gas chromatograph. The gas chromatograph was calibrated using 1,3-butadiene from another source which had been diluted with dry air in a Teflon gas bag. Samples were collected, using the recommended method, and they were stored either at -25 °C or at ambient temperature. The results of the storage test are presented in Table 4.6.1 and also in Figures 4.6.1.1 and 4.6.1.2.

Table 4.6.1  
1,3-Butadiene Storage Test Using TBC Coated Charcoal

storage time (days)	% recovery (ambient)	storage time (days)	% recovery (refrigerated)
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0	102.2	102.2	99.1	0	97.0	101.8	97.8
3	97.8	93.3	93.3	4	99.5	96.9	98.7
6	100.9	98.7	100.9	7	93.2	104.9	102.2
10	93.8	87.5	83.9	11	98.6	94.6	92.4
13	82.1	88.8	80.8	14	104.1	96.9	98.2
17	81.2	76.3	76.8	18	84.3	94.6	96.4

#### 4.6.2 Untreated charcoal

An additional ambient temperature storage test was performed using untreated SKC, Inc. Lot 120 charcoal as sampling media. The test atmosphere was generated and its concentration determined in the same manner as was used for the recommended method. The concentration of the test atmosphere was 1 ppm. The relative humidity of this atmosphere was 70% at 23 °C. Sampling was performed at 0.05 L/min for 1 h. The results of this study are presented in Table 4.6.2 and also in Figure 4.6.2.

Table 4.6.2  
1,3-Butadiene Ambient Temperature  
Storage Test Using SKC, Inc. Lot 120 Charcoal

storage time, days	% recovery		
0	33.5	36.3	33.5
3	31.3	30.1	29.0
6	17.9	12.8	14.9
10	29.0	22.5	22.6
13	25.2	23.8	19.9
17	18.2	19.8	17.4

#### 4.7 Reproducibility data

Samples were collected from a test atmosphere which was generated by diluting the effluent of a gas cylinder, containing 100 ppm 1,3-butadiene, with humid air. The resultant atmosphere contained 1 ppm 1,3-butadiene and the relative humidity of the air was 84% at 23°C. The 1,3-butadiene content of the test atmosphere was determined by the direct injection of 100 µL of the atmosphere into a GC. The GC was calibrated using 1,3-

Table 4.7 Reproducibility	
% recovery	statistics
100.0	
102.9	
100.5	$\bar{X} = 97.2$
98.0	$SD = 6.2$
96.6	
85.4	

butadiene, from another source, which had been diluted with dry air in a Teflon gas bag. The samples and a draft copy of this evaluation were given to a chemist unassociated with this work. The samples were analyzed after 3 days storage at reduced temperature. The results are presented in Table 4.7.

#### 4.8 A procedure to prepare specially cleaned charcoal coated with TBC

##### 4.8.1 Apparatus

- Magnetic stirrer and stir bar.
- Tube furnace capable of maintaining a temperature of 700°C and equipped with a quartz tube that can hold 30 g of charcoal. A Lindbergh Type 55035 tube furnace was used in this evaluation.
- A means to purge nitrogen gas through the charcoal inside the quartz tube.
- Water bath capable of maintaining a temperature of 60 °C.
- Miscellaneous laboratory equipment: One-liter vacuum flask, 1-L Erlenmeyer flask, 350-mL Buchner funnel with a coarse fritted disc, 4-oz brown bottle, rubber stopper, Teflon tape, etc.

##### 4.8.2 Reagents

- a) Phosphoric acid, 10%, by weight, in water. "Baker Analyzed" Reagent grade was diluted with deionized water for use in this evaluation.
- b) 4-tert-Butylcatechol (TBC). The Aldrich Chemical Company 99% grade was used in this evaluation. CAUTION- The bottle was labeled: Sensitizer! Severe irritant! Toxic! Refrigerate!
- c) Specially cleaned coconut shell charcoal, 20/40 mesh. Specially cleaned charcoal (Lot number 482338) was obtained from Supelco, Inc. for use in this evaluation. The cleaning process used by Supelco is proprietary.
- d) Nitrogen gas, GC grade.

#### 4.8.3 Procedure

Weigh 30 g of charcoal into a 500-mL Erlenmeyer flask. Add about 250 mL of 10% phosphoric acid to the flask and then swirl the mixture. Stir the mixture for 1 h using a magnetic stirrer. Filter the mixture using a fritted Buchner funnel. Wash the charcoal several times with 250-mL portions of deionized water to remove all traces of the acid. Transfer the washed charcoal to the tube furnace quartz tube. Place the quartz tube in the furnace and then connect the nitrogen gas purge to the tube. Fire the charcoal to 700°C. Maintain that temperature for at least 1 h. After the charcoal has cooled to room temperature, transfer it to a tared beaker. Determine the weight of the charcoal and then add an amount of TBC which is 10% of the charcoal, by weight. CAUTION- TBC is toxic and should only be handled in a fume hood while wearing gloves. Carefully mix the contents of the beaker and then transfer the mixture to a 4-oz bottle. Stopper the bottle with a clean rubber stopper which has been wrapped with Teflon tape. Clamp the bottle in a water bath so that the water level is above the charcoal level. Gently heat the bath to 60°C and then maintain that temperature for 1 h. Cool the charcoal to room temperature and then transfer the coated charcoal to a suitable container.

The coated charcoal is now ready to be packed into sampling tubes. The sampling tubes should be stored in a sealed container to prevent contamination. Sampling tubes should be stored in the dark at room temperature. The sampling tubes should be segregated by coated adsorbent lot number.

#### 4.9. Chromatograms

The chromatograms were obtained using the recommended analytical method. The chart speed was set at 1 cm/min for the first three min and then at 0.2 cm/min for the time remaining in the analysis.

Figures 4.2.2 and 4.9.2 are chromatograms of 1,3-butadiene desorbed from the recommended sampling media. The peak which eluted just before 1,3-butadiene is a reaction product between an impurity on the charcoal and TBC. This peak is always present, but it is easily resolved from the analyte. The peak which eluted immediately before benzene is an oxidation product of TBC.

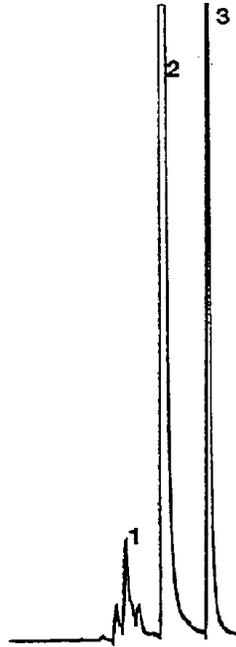


Figure 4.1.1 Chromatogram of detection limit of the analytical procedure. Peak identification was as follows: 1) 1,3-butadiene; 2) carbon disulfide; 3) benzene.

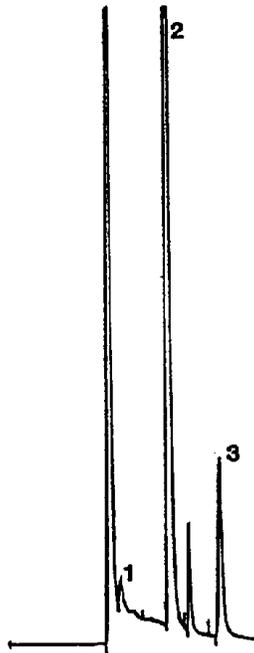


Figure 4.2.2 Chromatogram of the reliable quantitation limit. Peak identification was as follows: 1) 1,3-butadiene; 2) carbon disulfide; 3) benzene.

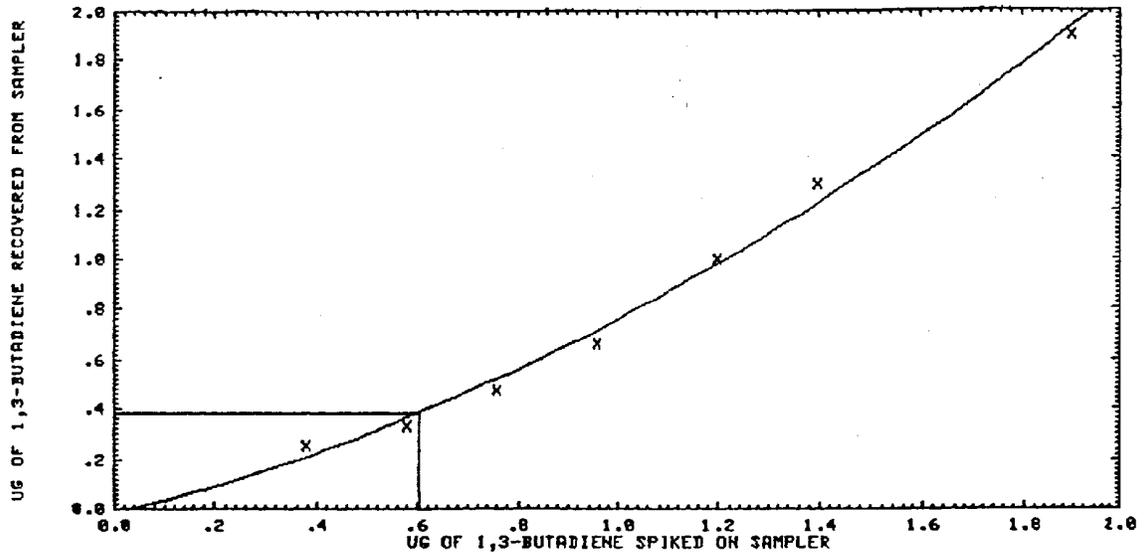


Figure 4.1.2 Determination of the detection limit of the overall procedure.

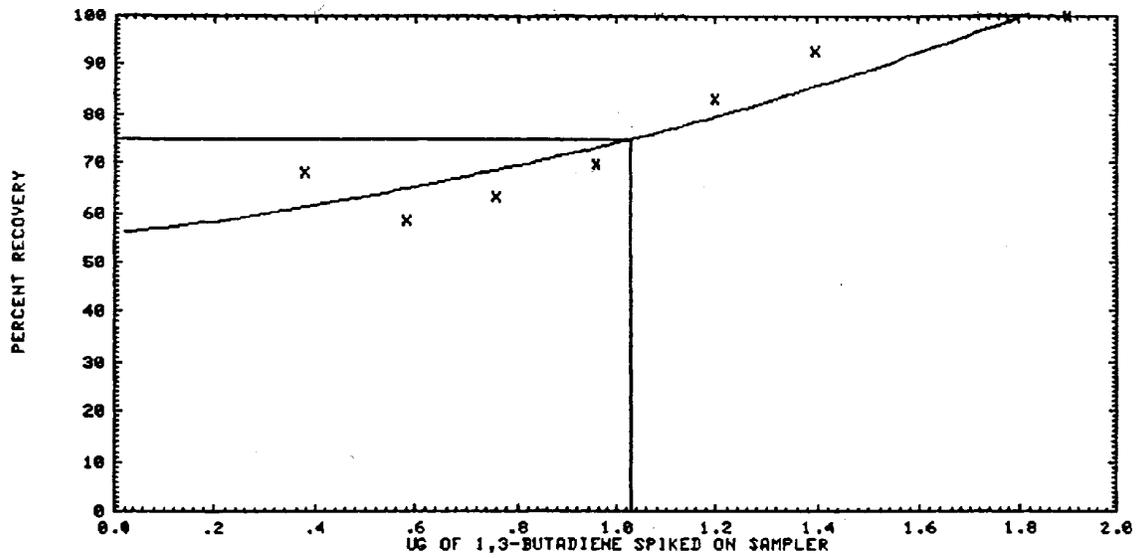


Figure 4.2.1 Determination of the reliable quantitation limit.

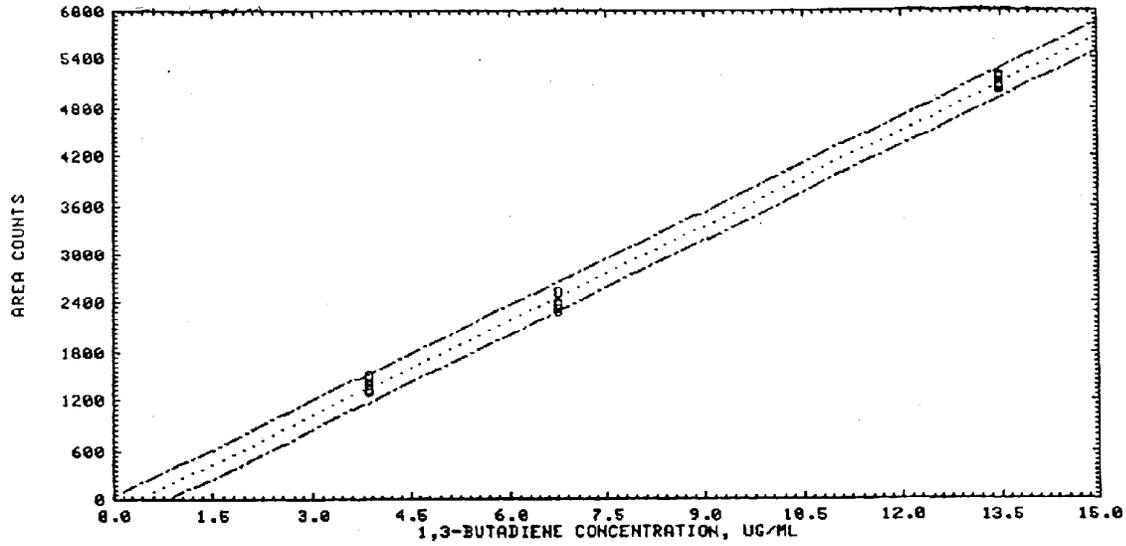


Figure 4.3. 1,3-Butadiene calibration curve.

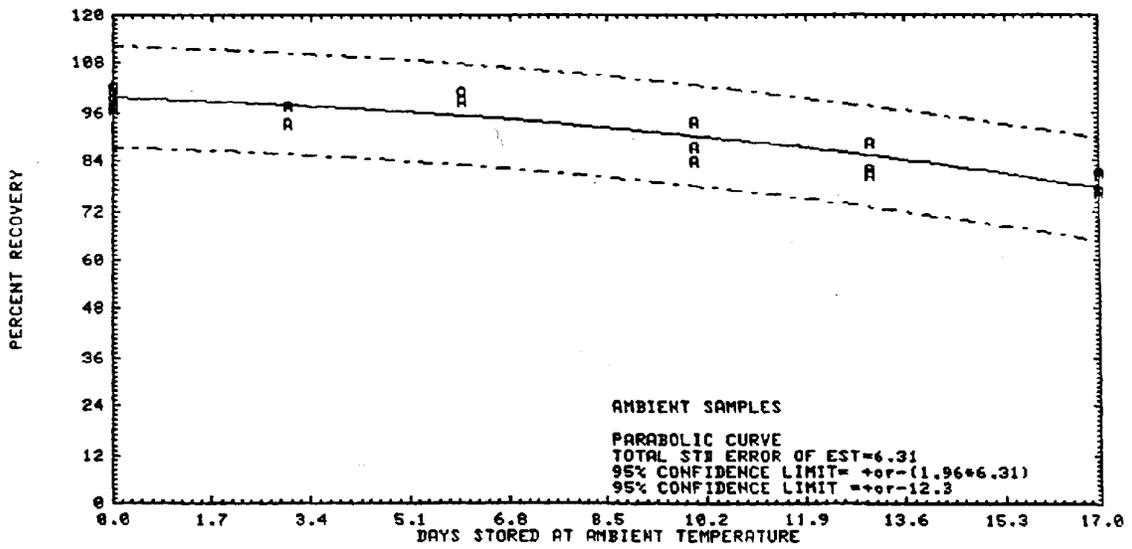


Figure 4.6.1.1 Ambient temperature storage test for 1,3-butadiene collected on TBC coated charcoal.

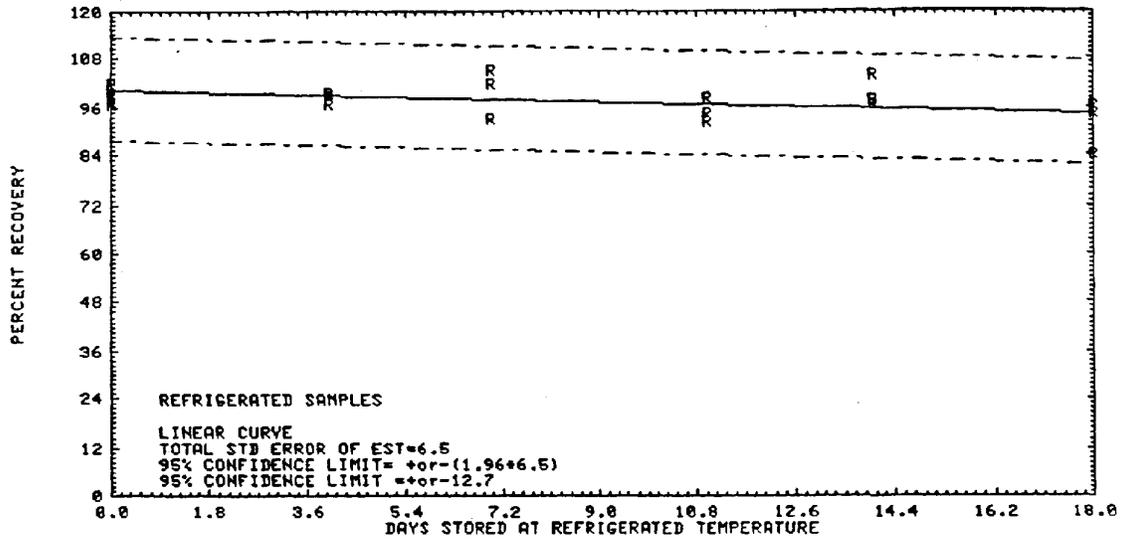


Figure 4.6.1.2 Reduced temperature storage test for 1,3-butadiene collected on TBC coated charcoal.

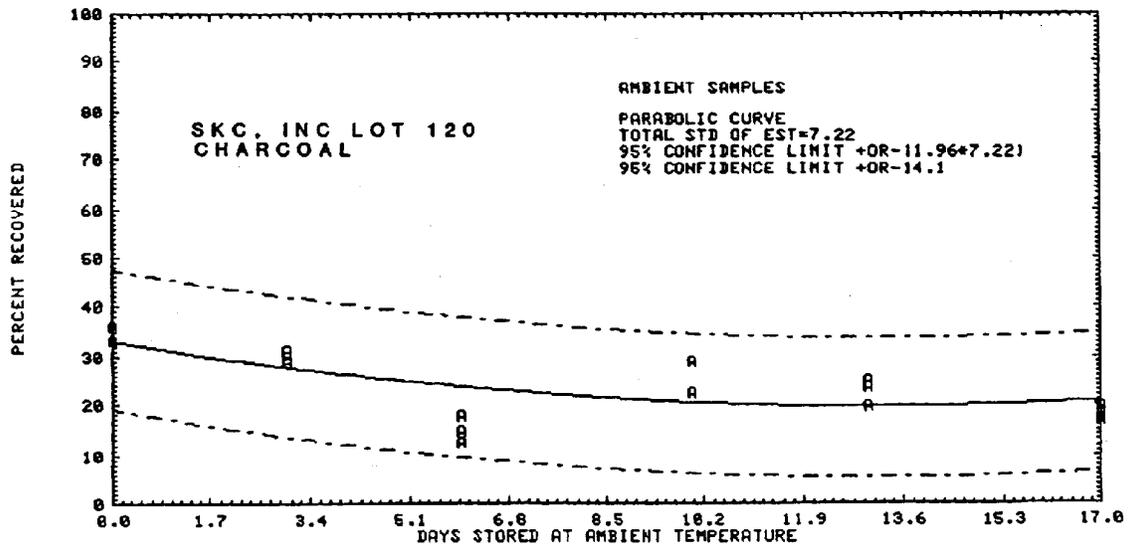


Figure 4.6.2 Ambient temperature storage test for 1,3-butadiene collected on untreated charcoal.

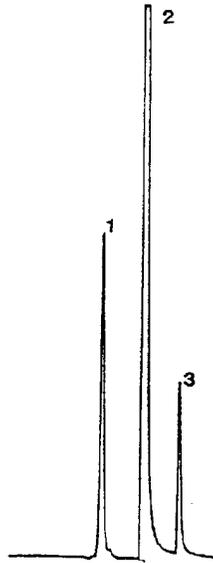


Figure 4.9.1 Chromatogram of a standard. Peak identification was as follows:  
1) 1,3-butadiene; 2) carbon disulfide; 3) benzene.

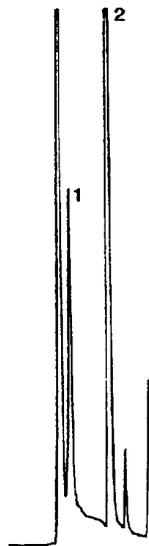


Figure 4.9.2 Chromatogram of a sample. Peak identification was as follows:  
1) 1,3-butadiene; 2) carbon disulfide; 3) benzene.

## 5. References

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