



n-Butane

Method number: PV2010

Target Concentration: 800-ppm (1900 mg/m³) ACGIH Threshold Limit Value (TLV).

Procedure: Samples are collected by drawing known volumes of air through two Carbosieve S-III tubes in series. Samples are desorbed with desorbing solution (carbon disulfide/internal standard) and analyzed by gas chromatography (GC) using a flame ionization detector (FID).

Recommended air volume and sampling rate: 60 minutes at 0.05 L/min (3 Liters)

Detection limit of the overall procedure: 0.79 ppm (1.88 mg/m³) (Based on the recommended air volume and the analytical detection limit)

Status of method: Partially evaluated method. This method has been partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken to develop a sampling and analytical procedure for n-Butane at the ACGIH TLV 800 ppm level (Ref. 5.1).

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

n-Butane is a simple asphyxiant and irritant. It is an anesthetic at high concentrations. (Ref. 5.2 and Ref. 5.3)

1.1.3 Potential workplace exposure

The following paragraph is excerpted from the book Kirk-Othmer Encyclopedia of Chemical Technology, (Ref. 5.2)

Butanes are used primarily as gasoline blending components and less so as liquefied fuel and in the manufacture of chemicals. n-Butane and small amounts of isobutane are used for direct blending in motor-fuel gasoline to control the volatility of the finished product. The butane content of motor gasoline is ca 6-8 vol%. United States consumption of butane for this purpose was ca 84% of supply in 1977. Nonmotor-fuel uses of butanes represent ca 10% of the total consumption. Liquid petroleum gas (LPG) is a mixture of butane and propane, typically in a ratio of 60:40 butane-propane. LPG is consumed as fuel in engines and in home, commercial, and industrial applications. n-Butane also is used as a solvent in liquid-liquid extraction of heavy oils in deasphalting processes (Ref. 5.2). No data is available on the extent of work place exposure.

1.1.4 Physical properties (Ref. 5.2 and 5.3)

CAS number:	106-97-8
IMIS number:	0420
Molecular weight:	58.12
Molecular formula:	C ₄ H ₁₀
Freezing point:	- 138.3 °C at 101.3 kPa (760 mmHg)
Boiling point:	- 0.5 °C at 101.3 kPa (760 mmHg)
Flash point:	- 60 °C
Autoignition point:	405 °C at 101.3 kPa (760 mmHg)
Explosive limit:	1.9 to 8.5% by volume
Vapor density:	2.07 (air = 1)
Appearance:	colorless and flammable gas

Structure: CH3-CH2-CH2-CH3

1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 15:1 split ratio, is 0.333 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

2 Sampling Procedure

2.1 Apparatus

- 2.1.1 Samples are collected by using a personal sampling pump that can be calibrated to within $\pm 5\%$ of the recommended flow rate with the sampling device in line.
- 2.1.2 Samples are collected with two Carbosieve S-III tubes in series each containing 130 mg adsorbing section with a 65 mg backup section separated by silanized glass wool, with a silanized glass wool plug before the adsorbing section and after the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., Supelco tubes (ORBO-91) or equivalent.

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

- 2.3.1 The ends of the Carbosieve S-III tubes are opened immediately before sampling.
- 2.3.2 Connect two Carbosieve S-III tubes in series with a short piece of flexible tubing. Connect the second tube to the sampling pump with flexible tubing.
- 2.3.3 Attach the sampler vertically in the employee's breathing zone in such a manner that it does not impede work performance or safety.
- 2.3.4 After sampling for the appropriate time, remove the sampling device and seal the tube with plastic end caps.
- 2.3.5 Wrap each sample end-to-end with a Form OSHA-21 seal.
- 2.3.6 Record the air volume for each sample and list any possible interference.
- 2.3.7 Submit at least one blank with each set of samples. Handle the blank in the same manner as the other samples, except that no air is drawn through it.
- 2.3.8 If bulks are submitted for analysis, they must be shipped in a container separate from the samples.

2.4 Desorption efficiency

An amount of adsorbent equal to the sampling section (130 mg) of a Carbosieve S-III tube was placed in each of twelve 2-mL vials. They were divided into four groups of three vials each. The vials were vapor spiked respectively with 0.27, 1.4, 2.7 and 5.0 mL of n-butane (density = 2.09 mg/mL). These amounts represent 0.1 \times , 0.5 \times , 1.0 \times , and 2.0 \times the target concentration. The vials were sealed with polytetrafluoroethylene (PTFE)-lined caps and allowed to equilibrate overnight in a drawer at room temperature. The vials, along with a blank vial, were desorbed with 1.0 mL of the desorbing solution (CS₂/p-Cymene), and analyzed as in Section 3. The average desorption efficiency was 103.8%. The results are listed in table 2.4.

table 2.4
desorption efficiency

sample #	mg spiked	mg found	% recovered
1	0.564	0.599	106.2
2	0.564	0.606	107.4
3	0.564	0.617	109.4
average of 0.1 x TLV = 107.7%			
4	2.926	2.940	100.5
5	2.926	3.046	104.1
6	2.926	3.088	105.5
average of 0.5 x TLV = 103.4%			
7	5.643	5.768	102.2
8	5.643	5.772	102.3
9	5.643	5.716	101.3
average of 1.0 x TLV = 101.9%			
10	10.450	10.698	102.4
11	10.450	10.356	99.1
12	10.450	10.954	104.8
average of 2.0 x TLV = 102.1%			

2.5 Retention efficiency

Three Carbosieve S-III tubes were each vapor spiked with 2.7 mL (1× TLV) of n-butane. Five tubes were each vapor spiked with 5.0 mL (2× TLV) of n-butane. The tubes were allowed to equilibrate overnight in a drawer at room temperature. Each tube was connected in series with another Carbosieve S-III tube. Three liters of humid air (~80% relative humidity) were drawn through each tube at 0.05 L/min. The tubes, along with a blank tube, were desorbed with 1.0 mL of desorbing solution, and analyzed as in Section 3. There was no n-butane found on the backup sections of the second tubes. The average retention efficiency was 101.6%. The results are listed in table 2.5.

table 2.5
retention efficiency

sample #	% recovered				total
	front tube		back tube		
	'A'	'B'	'A'	'B'	
1	98.9	0.0	0.0	0.0	98.9
2	88.7	12.2	0.0	0.0	100.9
3	90.8	8.3	0.0	0.0	99.1
average of 1.0 x TLV = 99.6%					
1	95.4	8.6	0.0	0.0	104.0
2	72.5	19.3	14.9	0.0	106.7
3	74.1	17.7	8.2	0.0	100.0
4	67.0	22.8	16.5	0.0	106.3
5	64.8	25.3	10.2	0.0	100.3
average of 2.0 x TLV = 103.5%					

2.6 Sample storage

Eight Carbosieve S-III tubes were each vapor spiked with 2.7 mL (1× TLV) of n-butane. Each tube was connected in series with another Carbosieve S-III tube. Three liters of humid air (~80% relative humidity) were drawn through each tube at 0.05 L/min. The eight tubes were divided into two groups of four each. The first group was stored in a drawer at ambient temperature, and the second group was stored in a freezer (- 5 °C). After seven days, they were extracted and analyzed as in Section 3. No analyte was observed in backup sections of the second tubes. The results are given in Tables 2.6.1 and 2.6.2.

table 2.6.1
ambient storage

days stored	mg spiked	mg found	% recovered
7	5.643	5.333	94.5
7	5.643	5.512	97.7
7	5.643	5.097	90.3
7	5.643	4.754	84.2

average = 91.7%

table 2.6.2
freezer storage

days stored	mg spiked	mg found	% recovered
7	5.643	5.506	97.6
7	5.643	5.564	98.6
7	5.643	5.544	98.2
7	5.643	5.427	96.2

average = 97.7%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 3 L.

2.7.2 The recommended flow rate is 0.05 L/min.

2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of n-butane. Any suspected interferences should be reported to the laboratory with submitted samples.

2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical Procedure

3.1 Apparatus

- 3.1.1 A GC equipped with an FID. A Hewlett-Packard 5890A GC equipped with both an FID and a Hewlett-Packard 7673A Autosampler was used in this evaluation.
- 3.1.2 A GC column capable of separating n-butane from any interference. A 60-m × 0.32-mm i.d. (1.0-µm df) DB-1 capillary column was used in this evaluation.
- 3.1.3 An electronic integrator or some other suitable means to measure detector response. A Waters 860 Networking Computer System was used in this evaluation.
- 3.1.4 Volumetric flasks, pipettes, and syringes for preparing standards, making dilutions and performing injections.
- 3.1.5 Vials, 2-mL with PTFE-lined caps.

3.2 Reagents

- 3.2.1 Hydrogen, air and nitrogen, GC grade.
- 3.2.2 n-Butane. The n-butane used in this evaluation was 99.9% pure and purchased from Matheson CO., Inc.
- 3.2.3 Carbon disulfide. Reagent grade or better. The carbon disulfide used in this evaluation was purchased from EM Science.
- 3.2.4 p-Cymene. The p-Cymene used as an internal standard (ISTD) was purchased from Aldrich Chemical Company Inc.
- 3.2.5 Desorbing solution. The desorbing solution is prepared by adding 250 µL of p-Cymene to 1 L of carbon disulfide.

3.3 Standard preparation

- 3.3.1 Standards are prepared by diluting a known quantity of n-butane with the desorbing solution. A standard of 1000 µL/mL n-butane in the desorbing solution at 664 mmHg and 23 °C would be 2.06 mg/mL. This was calculated as follows:

$$2.06 \text{ mg / mL} = \frac{(MW)(P)(K + T)(Vol)(\%)}{(24.46)(760)(K)(DV)}$$

Where

- 24.46 = Molar volume (liters/mole) at 760 mmHg and 25 °C (ntp)
- 760 = Atmospheric pressure (mmHg) at sea level
- MW = Molecular weight = 58.12 g/mole of n-Butane
- T = Room temperature = 23 °C
- K = Kelvin temperature = 298 K at 25 °C
- P = Atmospheric pressure at lab = (664 mmHg)
- Vol = Volume of gas used
- % = % purity of gas
- DV = Dilution volume

3.3.2 At least two separate standards should be made. A third standard at higher concentration should be prepared to check the linearity of the detector response for n-butane.

3.4 Sample preparation

3.4.1 The front and back sections of each tube are placed in separate 2 mL vials.

3.4.2 Each section is desorbed with 1.0 mL of the desorbing solution.

3.4.3 The vials are sealed immediately with PTFE-lined septa and allowed to desorb for 30 minutes with occasional shaking.

3.5 Analysis

3.5.1 Instrument conditions

<u>Column:</u>	60 m × 0.32 mm i.d., (1.0 µm di) DB-1
<u>Head pressure:</u>	8.5 psi
<u>Temperature:</u>	
Injector temperature:	150 °C
Detector temperature:	250 °C
Column temperature:	50 °C (initial temp.)
Temperature program:	Hold initial temp 5 min. Increase temp at 10 °C/min to 170 °C. Hold final temp 1.5 min
<u>Detector gas flow:</u>	
Hydrogen flow rate:	30 mL/min
Air flow rate:	240 mL/min
Nitrogen flow rate:	30 mL/min
Injection volume:	1 µL
Split ratio:	15:1
<u>Retention time:</u>	3.4 min (n-Butane), 17.3 min (p-Cymene – Internal standard)

3.5.2 Chromatogram (See Figure 1)

3.5.3 Measure detector response using a suitable method such as electronic integration.

3.6 Interferences (analytical)

3.6.1 Any collected compound which produces an FID response and has a similar retention time as n-butane or the internal standard (p-cymene) is a potential interference.

3.6.2 GC conditions may generally be varied to circumvent interferences.

3.6.3 Retention time on a single column is not proof of chemical identity. Analysis by an alternate GC column and confirmation by GC/Mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 An ISTD calibration method is used. The linear nature of the FID allows the use of single level calibration, but bracketing of samples with analytical standards is a good practice.

3.7.2 Determine the $\mu\text{g/mL}$ of n-butane in both sections of each sample and blank from the calibration curve. If n-butane is found on the backup section, it is added to the amount found on the front section. Blank corrections should be performed before adding the results together.

3.7.3 Determine the air concentration by using the following formulae.

$$\text{mg} / \text{m}^3 = \frac{(\mu\text{g} / \text{mL, blank corrected})(\text{desorption volume, mL})}{(\text{air volume, L})(\text{desorption efficiency, decimal})}$$

$$\text{ppm} = \frac{(\text{mg} / \text{m}^3)(24.46)}{(58.12)}$$

Where: air volume = sample air volume collected, (L)
 24.46 = molar volume at 25 °C and 760 mmHg
 58.12 = molecular weight of butane (g/mole)
 $\mu\text{g/mL}$ = concentration of n-butane from calibration curve

3.8 Safety precautions (analytical)

3.8.1 Avoid air exposure to n-butane.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses in laboratory.

4 Recommendation for Further Study

This method needs to be fully validated.

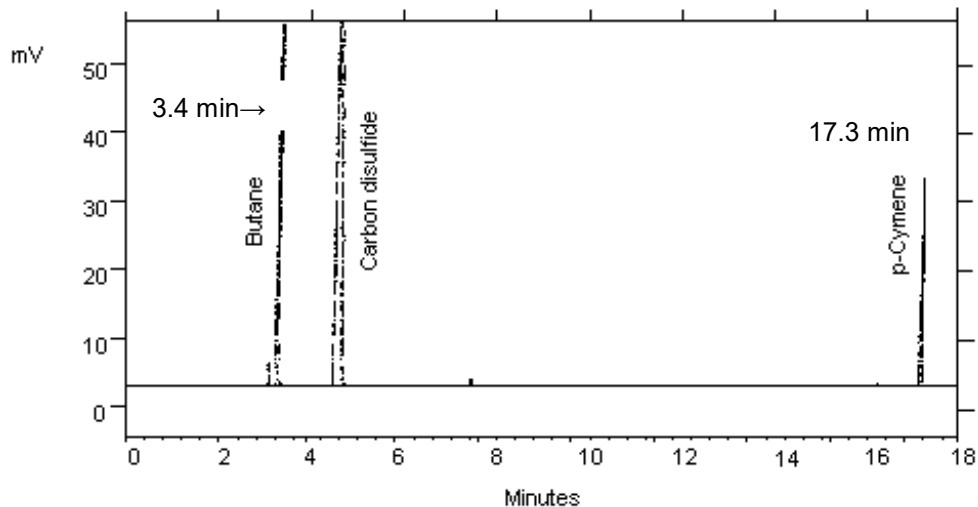


Figure 1
 Chromatogram of n-Butane at 0.5 x TLV.

5 References

- 5.1 "Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices," ACGIH, 1991-1992.
- 5.2 Grayson, M., Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., John Wiley & Sons Inc., New York, 1983; Vol. 12, pp. 910-919.
- 5.3 Windholz, M., Budavari, S., Blumetti, RF., and Otterbein, E., The Merck Index, 10th ed., Merck & CO., Inc., Rahway, N.J., 1983; p 210.