Method number:	PV2062
Matrix:	Air
Target concentration:	5 ppm (25.14 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through standard size (6-mm o.d.,100/50-mg sections) coconut shell charcoal (CSC) tubes. Samples are desorbed with a mixture of 99/1 (v/v) carbon disulfide (CS_2)/dimethylformamide (DMF) and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended air volumes and sampling rate:	12 L at 0.1 L/min
Reliable quantitation limit:	0.004 ppm (0.020 mg/m^3)
Status of method:	Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History

The OSHA Salt Lake Technical Center recently received a set of field samples that requested analysis for 2-bromopropane. This analyte is being used as a replacement chemical for Freon 113 due to the belief that freon is destroying the stratospheric ozone layer. This evaluation was undertaken to establish a suitable sampling and analysis procedure for 2-bromopropane.

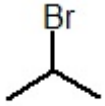
1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

A recent case study on the mass intoxication of workers at an electronic factory in Korea indicated that 2-bromopropane was the possible causative chemical for reproductive and hematopoietic toxicity. The case report indicated several female workers showed ovarian dysfunction accompanied by amenorrhea and severe anemia, and several male workers had oligospermia or azoospermia. One worker with azoospermia also had pancytopenia (Ref. 5.1). Workers exposed to 2-bromopropane complained of headache, vertigo, low back pain, neuralgia, paresthesia, anemia, purpura and amenorrhea (Ref. 5.2).

1.1.3 Workplace exposure (Ref. 5.2)

2-bromopropane has been used mostly as an intermediate for medicines and pesticides. It is also used as a substitute for freon 113 as a cleaning solution in the process of assembling tactile switches in an electronics product factory.

1.1.4 Physical properties and other descriptive information (Ref. 5.3 unless otherwise indicated).

Synonyms:	Isopropyl bromide
CAS number:	75-26-3
IMIS:	R289
RTECS:	TX4111000 (Ref. 5.4)
Molecular weight:	123.0 (Ref. 5.2)
Boiling point:	59.0°C
Melting point:	-89.0°C
Flash point:	22°C (72°F) (CC) (Ref. 5.4)
Vapor pressure:	236.3 mm Hg @ 25 °C
Density:	1.31 @ 20°C
Properties:	Clear, colorless to slightly yellow flammable liquid.
Solubility:	0.286 wt% in water (18°C), soluble in acetone, methanol, carbon tetrachloride, carbon disulfide and aromatic hydrocarbons. (Ref. 5.2)
Molecular formula:	C_3H_7Br
Structural formula:	

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 0.13 µg per sample (0.002 ppm or 0.011 mg/m³). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank.

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient, and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$

A = analytical sensitivity (slope)

therefore

$$DLOP = \frac{(Y_{DLOP} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 0.995 µg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the background response for the sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE)

for the calculation of the DLOP. Values of 3897 and 93.4 were obtained for A and SEE respectively. DLOP was calculated to be 0.072 µg/sample (0.001 ppm or 0.006 mg/m^3).

Table 1.2.1
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
0.181	863
0.271	1202
0.362	1537
0.452	1992
0.543	2227
0.633	2600
0.724	2928
0.814	3266
0.905	3451
0.995	4101

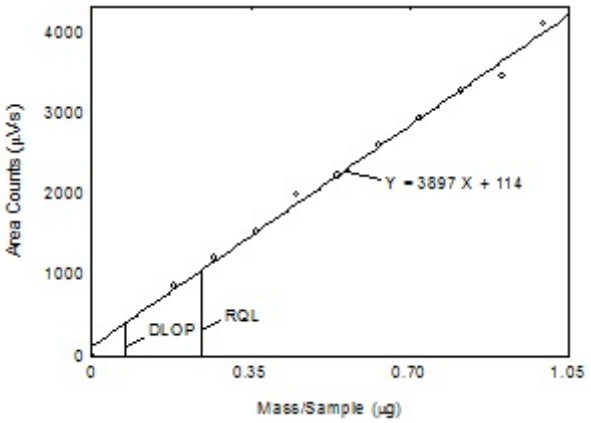


Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 0.24 µg per sample (0.004 ppm or 0.020 mg/m^3). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements.

The RQL is determined from the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

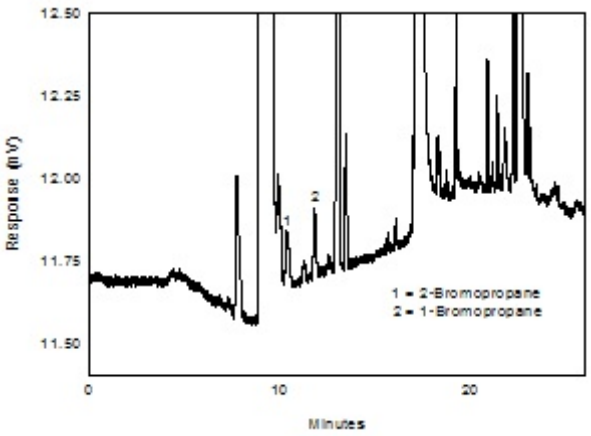


Figure 1.2.3. Chromatogram of the RQL.

RQL = 0.24 µg per sample (0.020 mg/m^3).The recovery at the RQL is 96.4%.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

2.1.2 Samples are collected using solid sorbent sampling tubes containing coconut shell charcoal (CSC). Each tube consists of two sections of charcoal separated by a urethane foam plug. The front section contains 100 mg of charcoal and the back section, 50 mg. The sections

are held in place with glass wool plugs in a glass tube 4-mm i.d. x 70-mm length. For this evaluation, SKC Inc. charcoal tubes (catalog number 226-01, Lot 2000) were used.

2.2 Technique

2.2.1 Immediately before sampling, remove the caps from the sampling tubes. All tubes should be from the same lot.

2.2.2 Attach the sampling tube to the pump with flexible tubing. It is desirable to utilize sampling tube holders which have a protective cover to sheild the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the front section of the tube first.

2.2.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.2.4 Attach the sampler vertically with the front section pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.2.6 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

2.2.7 Record the sample volume (in liters of air) for each sample, along with any potential interferences.

2.2.8 Ship any bulk samples in separate containers from the air samples.

2.2.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.3 Desorption efficiency

The desorption efficiency of 2-bromopropane was determined by liquid-spiking the charcoal tubes with the analyte at 0.1 to 2 times the target concentration. The loadings on the tubes were 30.17, 150.8, 301.6 and 603.2 µg of 2-bromopropane. These samples were stored overnight at ambient temperature and then desorbed and analyzed by GC-FID. The average desorption efficiency over the studied range was 97.7%.

Table 2.3.1
Desorption Efficiency of 2-Bromopropane From CSC

Tube #	% Recovered			
	0.1 × 30.16µg	0.5 × 150.8µg	1.0 × 301.6µg	2.0 × 603.2µg
1	104.8	100.9	100.0	97.6
2	101.7	96.9	99.9	99.1
3	103.6	96.8	97.7	100.1
4	100.0	97.3	99.5	99.6
5	106.5	96.4	99.3	98.9
6	97.8	99.4	99.5	98.8
$\overline{X}$	102.4	98.0	99.3	99.0
overall $\overline{X}$	99.7			
SD	±1.90			

2.4 Retention efficiency

The sampling tubes were spiked with 603.2 µg (50.3 mg/m^3 based on a 12 L air sample) 2-bromopropane, allowed to equilibrate overnight at room temperature, and then 12 L humid air (80% RH at 25°C) was drawn through them at 0.1 L/min. The sampling tubes were opened and the front section and the back section were each put in separate vials. The samples were desorbed and analyzed by GC-FID. The retention efficiency averaged 98.9%.

Table 2.4
Retention Efficiency of 2-Bromopropane

Tube #	Front Section	Back Section	Total
1	76.2	23.1	99.3
2	74.6	24.4	99.0
3	71.8	27.7	99.5
4	75.8	23.5	99.3
5	74.2	24.2	98.4
6	73.2	24.8	98.0
		$\overline{X}$	98.9

2.5 Sample storage

The adsorbing sections of twenty-four sampling tubes were each spiked with 301.6 µg (5.0 ppm or 25.1 mg /m^3 based on a 12 L air sample) of 2-bromopropane. They were sealed and stored at room temperature. The next day 12 L of humid air (80% RH at 25°C) was drawn through each tube at 0.1 L/min. Half of the tubes were stored in a drawer at ambient temperature and the other half were stored in a refrigerator at 0°C. After 7 days of storage six samples from the tubes stored under refrigeration and six samples from ambient storage were analyzed. The remaining samples were analyzed after 15 days of storage. The average recovery of the ambient and refrigerated storage samples was 99.6%.

Table 2.5
Storage Test for 2-Bromopropane

Ambient Storage		Refrigerator Storage	
Time (days)	% Recovered	Time (days)	% Recovered
7	99.5	7	99.9
7	101.9	7	101.7
7	100.8	7	98.8
7	98.2	7	97.1
7	98.4	7	102.2
7	96.4	7	101.5
15	99.9	15	99.3
15	97.7	15	100.0
15	99.5	15	101.3
15	98.3	15	99.5
15	97.8	15	98.5
15	98.5	15	103.5
$\overline{X}$	98.9	$\overline{X}$	100.3

2.6 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 12 L air samples should be collected at a sampling rate of 0.1 L/min.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of 2-bromopropane on coconut shell charcoal tubes. In general, the presence of other contaminants in the air will reduce the capacity of the sampling tube to collect 2-bromopropane.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

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 of the Chemical Hygiene Plan that apply to the work area being sampled.

2.8.3 Wear eye protection at all times while in the work areas.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A gas chromatograph equipped with a flame ionization detector. A Hewlett Packard model 5890 was used in this study.

3.1.2 A GC column capable of separating the analyte from any interferences. The column used in this study was a 60-meter Rtx-volatiles fused silica capillary column with a 1.5-µm film thickness and 0.32-mm i.d.

3.1.3 An electronic integrator or some suitable method of measuring peak areas. A Hewlett Packard model 3396A and the Waters Millennium Data System was used in this study.

3.1.4 Four milliliter vials with Teflon-lined caps.

3.1.5 A 10-µL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. A 2-mL Labindustries dispenser was used in this study.

3.1.7 Volumetric flasks - 10-mL and other convenient sizes for preparing standards.

3.1.8 A balance for weighing 2-bromopropane in standard preparation. A Ohaus Galaxy 160D was used in this evaluation.

3.2 Reagents

3.2.1 GC grade nitrogen, hydrogen and air.

3.2.2 2-Bromopropane (CAS 75-26-3). 2-Bromopropane, 99+%, was obtained from Aldrich Chemical Company, Lot 01220ER.

3.2.3 Carbon disulfide (CAS 75-15-0). Carbon Disulfide, 99.99%, was obtained from EM Science, Lot 970338.

3.2.4 N,N-Dimethyl formamide (CAS 68-12-2). N,N-Dimethyl formamide, 99.5%, was obtained from Fisher Chemical, Lot 933764.

3.2.5 ρ-Cymene (CAS 99-87-6). ρ-Cymene, 99%, was obtained from Aldrich Chemical Company, Lot 11703TR.

3.2.6 The desorbing solvent consists of 99/1 (v/v) carbon disulfide/N,N-dimethyl formamide containing ρ-cymene internal standard at a concentration of 0.25 µL/mL.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by weighing a quantity of 2-bromopropane and diluting with desorbing solution. The concentration of these stock standards was approximately 30.16 mg/mL.

3.3.2 Dilutions of these stock standards were prepared to bracket the samples. The range of the standards used in this study was from 30.16 to 603.2 µg/mL.

3.4 Sample preparation

3.4.1 Sample tubes are opened and the front section and back section of each tube are placed in separate 2-mL vials. Discard glass wool and foam plugs.

3.4.2 Each section is desorbed with 1 mL of desorbing solution.

3.4.3 The vials are sealed immediately and allowed to desorb for one hour on a mechanical rotator or the vials are shaken vigorously by hand several times during the desorption time.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size:	1 µL
Flow rates (mL/min)	
Nitrogen (make-up):	30
Hydrogen (carrier):	2
Hydrogen (detector):	40
Air:	420
Temperatures (°C)	
Injector:	200
Detector:	275
Column:	45 °C for 4 min, 10°/min to 200 °C, hold for 8 min at 200 °C.

Chromatogram:

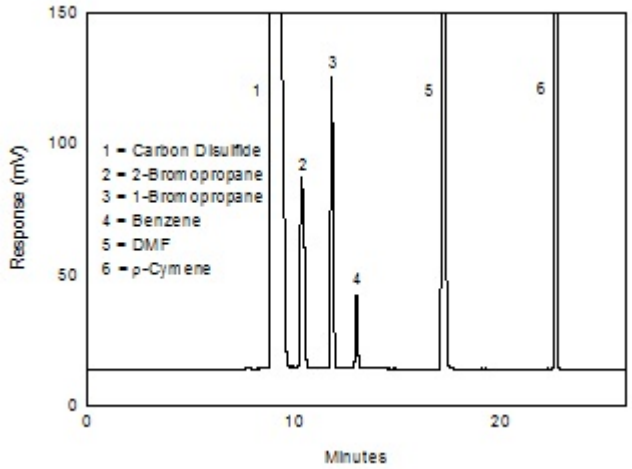


Figure 3.5.1 Chromatogram at the target concentration.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound that produces an FID response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte. Using the analytical conditions in this method, 1-bromopropane does not interfere.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by a GC-mass spectrometer or by another analytical procedure.

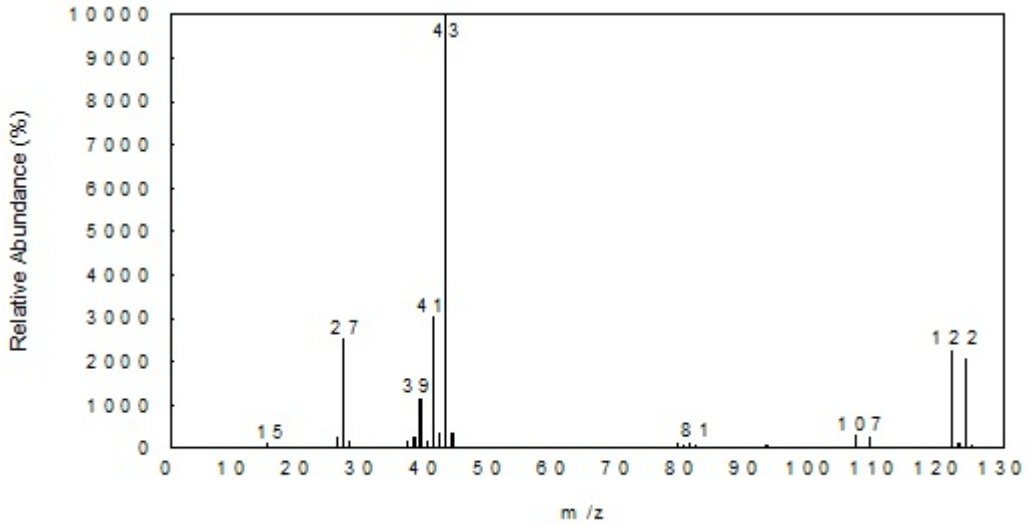


Figure 3.6.2 Mass spectra of 2-bromopropane

3.7 Calculations

3.7.1 The calibration curve was made from at least four standards at different concentrations bracketing the samples.

3.7.2 The values for the samples are obtained from the calibration curve.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\frac{(\mu g/mL)\ (\text{desorption volume})}{(\text{desorption efficiency})} = \text{mass of analyte in sample}$$

$$\frac{(\text{mass of analyte in sample})}{\text{molecular weight}} = \text{number of moles of analyte}$$

$$\left(\begin{array}{l}\text{number of moles}\\ \text{of analyte}\end{array}\right)\left(\begin{array}{l}\text{molar volume}\\ \text{at 25°C \& 760mm Hg}\end{array}\right) = \left(\begin{array}{l}\text{volume the analyte will}\\ \text{occupy at 25°C and 760mm Hg}\end{array}\right)$$

$$\frac{(\text{volume analyte occupies})\ (10^6)}{(\text{air volume})} * = \text{ppm}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to the following formula.

$$\frac{(\mu g/mL)\ (DV)\ (24.46)\ (10^6)\ (g)\ (mg)}{(\text{Liters})(DE)\ (MW)(1000mg)(1000\mu g)} = \text{ppm}$$

μg/mL = Concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25°C and 760mm Hg
MW = Molecular weight (g/mole)
DV = Desorption volume
Liters = Liters of air sample
DE = Desorption efficiency

3.7.5 To calculate the mg/m^3 of analyte in the sample:

$$\frac{(\mu g/mL)\ (DV)\ (mg)\ (1000\ L)}{(Liters)\ (DE)\ (1000\ \mu g)\ (m^3)} = mg/m^3$$

where:
µg/mL = Concentration of analyte in sample or standard
DV = Desorption volume
Liters = Liters of air volume
DE = Desorption efficiency

3.7.6 This calculation is done for each section of the sampling tube and the results added together after a blank correction is performed, if necessary.

3.8 Safety precautions

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan (which is mandated by the OSHA laboratory standard).

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

4. Recommendations for Further Study

Collection studies should be performed with controlled test atmospheres.

5. References

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5.2 Takeuchi, Y., G. Ichihara and M. Kamijima: A Review on Toxicity of 2-Bromopropane: Mainly on its Reproductive Toxicity. *Journal of Occupational Health.* **1997***,* Vol. 39, pp. 179-191.

5.3 OSHA Computerized Information System Database, Material Safety Data Sheets (CCOHS Trade Names) Database; 2-Bromopropane; Revision Date: 02/08/99; OSHA SLTC, Salt Lake City, UT 84115-1802.

5.4 Sweet, D., "Registry of Toxic Effects of Chemical Substances", 1985-86 ed., U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 4, Index Number TX4111000, p.3754.