Method number:	1017
Version:	1.0
Target concentration:	0.1 ppm (0.50 mg/m^3) 1-bromopropane 0.1 ppm (0.50 mg/m^3) 2-bromopropane
OSHA PEL:	none for 1-bromopropane none for 2-bromopropane
ACGIH TLV:	10 ppm (50.0 mg/m^3) 1-bromopropane none for 2-bromopropane
Procedure:	Active samples are collected by drawing workplace air through coconut shell charcoal tubes with personal sampling pumps. Samples are extracted with 99:1 (v/v) carbon disulfide:N,N-dimethylformamide (CS_2:DMF) and analyzed by gas chromatography using an electron capture detector (GC-ECD).
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12.0 L)
Reliable quantitation limit:	1.2 ppb (5.9 µg/m^3) 1-bromopropane 1.8 ppb (9.2 µg/m^3) 2-bromopropane
Standard error of estimate at the target concentration:	5.3% 1-bromopropane 5.1% 2-bromopropane
Special requirements:	Store samples in a refrigerator between sampling and analysis.
Status of method:	Fully validated method. This method has been subjected to the established validation procedures of the Methods Development Team.

September 2013

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1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact Salt Lake Technical Center (SLTC) at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

OSHA Method PV2061[1] (for 1-bromopropane) and OSHA Method PV2062[2] (for 2-bromopropane) were both developed in 1999 using a target concentration of 5 ppm for each analyte. Both of these methods utilize a gas chromatograph equipped with a flame ionization detector (GC-FID). The listed reliable quantitation limits for these methods were 0.007 ppm and 0.004 ppm respectively. The ACGIH did not have a TLV for 1-bromopropane at the time these methods were developed.[3]

In 2012 ACGIH included 1-bromopropane in the notice of intended changes table in preparation to change the TLV from 10 ppm (adopted in 2004) to 0.10 ppm.[4] This reduction in the TLV drew new attention to the compound.

GC-ECD methodology has several advantages over GC-FID methodology with regards to its sensitivity and selectivity to halogens such as bromine. These advantages justified the development of a sampling and analytical method that utilized GC-ECD in the determination of air concentrations of 1-bromopropane to replace the GC-FID method. The main objective of this work was to create a fully validated method for the sampling and analysis of 1-bromopropane that was sensitive enough to measure the proposed ACGIH TLV of 0.10 ppm. 2-bromopropane was included in this work because of its similar structure and properties, and because it is often found as a contaminant in 1-bromopropane.

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

The toxicity of 1-bromopropane has been proven in extensive animal inhalation studies including both rats and mice. In two week studies both rats and mice exposed to over 500 ppm 1-bromopropane exhibit decreased body weight and enlarged livers and kidneys, nasal lesions, and respiratory epithelial necrosis. Mice are less likely to survive the exposure when compared to a control group. Longer studies (3 months) demonstrate mild hepatotoxicity in rats (exposed to 500 ppm for males and 1000 ppm for females) and increased lesions in the nose, trachea, lungs, liver and adrenal cortex in mice (500 ppm). Two year studies of rats and mice exposed to 1-bromopropane have shown clear evidence of animal carcinogenic activity in females (based on increased adenoma of the large intestine, and increased neoplasms of the skin), and some evidence of carcinogenic activity in male rats (based on increased epithelial

[1] Potter, W. 1-Bromopropane (OSHA Method PV2061), 1999. U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/sltc/methods/partial/pv2061/2061.html (accessed Sept 2013).
[2] Potter, W. 2-Bromopropane (OSHA Method PV2062), 1999. U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/sltc/methods/partial/pv2062/2062.html (accessed Sept 2013).
[3] American Conference of Government Industrial Hygienists, ACGIH® Board of Directors. *1999 TLVs® and BEIs® Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*; Cincinnati, OH, 1999.
[4] American Conference of Government Industrial Hygienists, ACGIH® Board of Directors. *2012 TLVs® and BEIs® Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*; Cincinnati, OH, 2012.

neoplasms of the skin).[5] Similar rat studies show the potential toxic effects of 1-bromopropane to the nervous system, particularly to the myelin sheaths of peripheral nerves. Effects observed in similar studies include ataxic gait, paralysis, and degradation of peripheral nerves and myelin sheaths.[6]

The neurotoxicity of 1-bromopropane has been observed in human case studies as well. Exposure to 1-bromopropane has been linked to weakness in the lower extremities and hands, numbness, dysphagia, and urinary difficulties.[7] Three employees working with spray-on solvent adhesives (55% 1-bromopropane) in the manufacture of foam cushions were exposed to 1-bromopropane concentrations ranging from 60 to 261 ppm (daily TWA) for 5 to 12 months. Their symptoms included vertigo, light headedness, headaches, and feelings of intoxication.[8] Other employees performing similar tasks with similar exposures (91 to 176 ppm seven hour TWA), but over a period of three years experienced lower extremity pain and difficulty walking. Upon examination it was discovered these employees had developed spastic paraparesis, distal sensory loss, and hyperreflexia. The most affected employees showed very little improvement of function two years after exposure ended.[9]

Only very limited toxicological data were found for 2-bromopropane.

1.1.3 Workplace exposure[10,11,12]

1-Bromopropane is used as a substitute for perchloroethylene in many applications because it has less of an environmental impact than the chlorinated molecule. Its potential harm and toxicity has been noted by both government and industry, but it continues to find a wide variety of applications including: as a cleaning and degreasing agents for metals and electronics, as a solvent in dry cleaning, and as a component of adhesives used on foam cushions in furniture manufacture.

Workplace exposure to 1-bromopropane is increasing as it continues to be substituted for compounds that have been identified as suspected carcinogens or ozone depleting chemicals. High levels of 1-bromopropane have been measured in industrial settings in the United States, where 1-bromopropane is a high production volume chemical. U.S. production of 1-bromopropane between 1999 and 2000 was 1.5 million pounds with another 2.8 million additional pounds being imported.

The primary route of exposure to 1-bromopropane is inhalation, although dermal exposure is also possible. Occupational surveys in the U.S. show wide ranges of concentrations of 1-bromopropane in workers breathing zones from 18 to 381 ppm where 1-bromopropane is used in a spray-on solvent adhesive, 54 ppm in the dry

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[5] National Toxicology Program. *NTP Technical Report on Toxicology and Carcinogenesis Studies of 1-Bromopropane (CAS no. 106-94-5) in F344/N Rats and B6C3F1 Mice (Inhalation Studies)*; NTP TR 564; NIH Publication no. 11-5906: Research triangle Park, NC, August 2011.

[6] Yu, X.; Ichihara, G.; Kitoh, J.; et al. Preliminary Report on the Neurotoxicity of 1-Bromopropane, an Alternative Solvent for Chlorofluorocarbons. *J. Occup. Health.* **1998**, 40, 234-235.

[7] Sclar, G. *Case Report: Encephalomyeloradiculoneur-opathy Following Exposure to an Industrial Solvent*; Clin. Neurol. Neurosurg. **1999**, 101, 199-202.

[8] Ichihara, G.; Miller, J.K.; Ziolkokwska, A.; et al. Neurological Disorders in Three Workers Exposed to 1-Bromopropane. *J. Occup. Health*. **2002**, 44, 1-7.

[9] Majersik, J.J.; Caravati, E.M.; Steffens, J.D. Severe Neurotoxicity Associated with Exposure to the Solvent 1-Bromopropane (n-Propyl Bromide). *Clin. Toxicol*. **2007**, 45, 270-276.

[10] N-Propyl Bromide, Emerging Issues, OSTA, U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://oshapedia.osha.gov/mediawiki/index.php/N-Propyl_Bromide,_Emerging_Issues,_OSTA (accessed Sept 2013).

[11] Blando, J.D.; Schill, D.P.; De La Cruz, M.P.; Zhang, L.; Zhang, J. Preliminary Study of Propyl Bromide Exposure Among New Jersey Dry Cleaners as a Result of a Pending Ban on Perchloroethylene. *J. Air Waste Manag. Assoc.* **2010**, 60, 1049-1056.

[12] Hanley, K.W.; Petersen, M; Curwin, B.D.; Sanderson, W.T. Urinary Bromide and Breathing Zone Concentrations of 1-Bromopropane from Workers Exposed to Flexible Foam Spray Adhesives. *Ann. Occup. Hyg.* **2006**, 50, 599-607.

cleaning industry, and from 0.04 to 0.63 ppm where 1-bromopropane is used as a vapor degreaser.

No exposure data were found for 2-bromopropane.

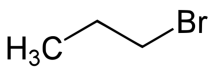
1.1.4 Physical properties and other descriptive information[13,14,15]

1-Bromopropane

synonyms:	bromopropane, n-bromopropane, 1-propyl bromide, n-propyl bromide, 1BP, nPB
tradenames for solvent mixtures:	Hypersolve, Abzol, Lenium, Contact Cleaner–NPB Heavy Duty, Leksol, Teksol, Ensolv, Solvon, Vapor Edge 1100, X-Cel, VDS-3000, Cobar-Clean NPB, No Flash Nu Electro Cleaner, Heavy Duty Degreaser II
tradenames for adhesives:	Whisper Spray, Soft Seam 640

IMIS[16]:	R290
CAS number:	106-94-5
boiling point:	71 °C (160 °F)
melting point:	-110 °C (-166 °F)
density:	1.35 g/mL @ 20 °C
molecular weight:	122.99
flash point:	24 °C (75 °F) (open cup)
molecular formula:	C_3H_7Br
appearance:	colorless liquid
lower explosive limit:	4.6% (by volume)
autoignition temperature:	490 °C (914 °F)
solubility:	2.5 g/L water; miscible with alcohol, carbon disulfide

structural formula:



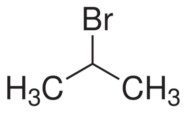
[13] *The Merck Index*; 14th ed.; O'Neil, M., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2006 pp 901, 7854.
[14] Chemical Book. http://www.chemicalbook.com/ProductMSDSDetailCB8341613_EN.htm (accessed Sept 2013).
[15] Chemical Book. http://www.chemicalbook.com/ProductMSDSDetailCB1854219_EN.htm (accessed Sept 2013).
[16] 1-Bromopropane (OSHA Chemical Sampling Information), 2010. U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_222006.html (accessed Sept 2013).

2-Bromopropane

synonyms: isopropyl bromide, 2BP

IMIS[17]:	R289
CAS number:	75-26-3
boiling point:	59-60 °C (138-140 °F)
melting point:	-89 °C (-128 °F)
density:	1.31 g/mL @ 20 °C
molecular weight:	122.99
flash point:	40 °C (104 °F) (open cup)
molecular formula:	C_3H_7Br
appearance:	colorless liquid
lower explosive limit:	4.6% (by volume)
solubility:	3.0 g/L water; miscible with alcohol, carbon disulfide

structural formula:



This method was validated according to the OSHA SLTC "Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[18]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations, and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

Samples are collected with 7 cm × 4 mm i.d. × 6 mm o.d. glass sampling tubes packed with two sections of coconut shell charcoal. The front section contains 100 mg and the back section contains 50 mg of coconut shell charcoal. The sections are held in place with glass wool and separated by urethane foam plugs. For this validation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-01, lot no. 2000).

A sampler tube holder is required to protect the worker from the sharp glass ends of the sampler tube.

[17] 2-Bromopropane (OSHA Chemical Sampling Information), 2010. U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_222008.html (accessed Sept 2013).

[18] Eide, M.; Hendricks, W.; Simmons, M. Validation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed Sept 2013).

Samples are collected using a personal sampling pump calibrated to within ±5% of the recommended flow rate with the sampling device in-line.

2.2 Reagents

None required

2.3 Technique

Immediately before sampling, break off both ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking ends. Use sampling tube holders to minimize the hazard to the worker from the broken ends of the tubes. All tubes should be from the same lot.

The smaller section of the adsorbent in the tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder (with the adsorbent tube) to the sampling pump so that the tube is in an approximately vertical position with the inlet facing down in the workers breathing zone during sampling. Position sampling pump, tube holder, and tubing so they do not impede work performance or safety.

Draw the air to be sampled directly into the inlet of the tube holder. The air being sampled is not to be passed through any hose or tubing before entering the sampling tube.

Sample for up to 240 min at 50 mL/min (12 L) to collect TWA (long-term) samples.

After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to end with a Form OSHA-21 as soon as possible.

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

Record sample air volume (L), sampling time (min), and sampling rate (mL/min) for each sample, along with any potential interferences on the Form OSHA-91A.

Submit the samples to the laboratory for analysis as soon as possible after sampling, preferably by overnight or express shipping. If delay is unavoidable, store the samples in a refrigerator.

Ship any bulk samples separate from the air samples.

3. Analytical Procedure

Adhere to the rules set down in your laboratory's Chemical Hygiene Plan[19] (for instance: OSHA SLTC adheres to the rules set down in the OSHA SLTC Chemical Hygiene Plan). Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analytical procedure. Follow all applicable quality assurance practices established in your laboratory's internal quality system (for instance: OSHA SLTC follows the quality assurance practices established in the OSHA SLTC Quality Assurance Manual).

3.1 Apparatus

Gas chromatograph equipped with an ECD. An Agilent 6890 GC System equipped with an automatic sample injector was used for this validation.

[19] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

GC injection port liner. An Agilent focus 4-mm × 6.3-mm × 78.5-mm injection port liner with glass wool (catalog no. 210-4004-5) was used in this validation.

GC column capable of separating 1-bromopropane and 2-bromopropane from the extraction solvent, potential interferences, and internal standard. An Agilent J&W DB-624 60-m × 0.32-mm i.d. (film thickness 1.8-µm) capillary column was used in this validation.

Electronic integrator or other suitable means of measuring GC detector response. A Waters Empower 3 Data System was used in this validation.

Glass vials with PTFE-lined crimp caps. In this validation 2.0-mL vials were used.

A dispenser capable of delivering 1.0 mL of extraction solvent to prepare standards and samples. If a dispenser is not available, 1.0-mL volumetric pipettes can be used.

Class A volumetric flasks of convenient sizes for standard preparation. In this validation 10-mL and 25-mL flasks were used.

Calibrated microliter syringes of convenient sizes for standard preparation. A Hamilton 800 series 25-µL syringe was used in this validation.

Mechanical shaker. An Eperbach 6000 shaker was used for this validation.

3.2 Reagents

Carbon disulfide (CS_2), [CAS no. 75-15-0]. The carbon disulfide used in this validation was >99.9% pure (lot no. STBB9382V) purchased from Sigma Aldrich (Milwaukee, WI).

N,N-Dimethylformamide (DMF), [CAS no. 68-12-2]. The N,N-dimethylformamide used in this validation was 99% pure (lot no. 1013944) purchased from Acros (Morris Plains, NJ).

2,2-Dichloropropane, [CAS no. 594-20-7]. The 2,2-dichloropropane used in this validation was 98% pure (lot no. 29598LJ) and obtained from Aldrich (Milwaukee, WI).

1-Bromopropane, [CAS no. 106-94-5]. The 1-bromopropane used in this validation was 99% pure (lot no. 04523CH) and obtained from Aldrich (Milwaukee, WI).

2-Bromopropane, [CAS no. 75-26-3]. The 2-bromopropane used in this validation was 99% pure (lot no. 08331AE) and obtained from Aldrich (Milwaukee, WI).

The extraction solvent used for this validation consisted of 99:1 (v/v) CS_2:DMF with 2,2-dichloropropane at a concentration of 0.002 µL/mL added as an internal standard (ISTD).

3.3 Standard preparation

Prepare a concentrated stock standard mixture of 1-bromopropane and 2-bromopropane in CS_2. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 2-mL vials containing 1.0 mL of extraction solvent delivered from the same dispenser used to extract samples.

Bracket sample concentrations with standard concentrations. If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

Due to the quadratic nature of the calibration curve, six working standards were prepared at 0.1, 0.25, 0.50, 1.0, 1.5, and 2.0 times the target concentration (from about 0.6 µg/mL to about 12 µg/mL) by injecting microliter amounts of concentrated stock standard mixtures into extraction solvent. For example: A stock standard can be prepared by injecting 11.5 µL of 1-bromopropane (density 1.354 g/mL, 99% pure) into 25 mL of CS_2 for a concentration of 616.6 µg/mL. This stock standard can be used to prepare a working standard at the target concentration (6.166 µg/mL) by adding 10.0 µL to 1.0 mL of extraction solvent in a 2-mL vial.

3.4 Sample preparation

Remove the plastic end caps from the sample tube and carefully transfer the media from the front and back sections to separate 2-mL glass autosampler vials. The sampling tube, foam plugs, and glass wool should be carefully inspected to ensure that all the media is transferred. Discard the glass tubes, the foam plugs, and glass wool.

Add 1.0 mL of extraction solvent to each vial and immediately seal the vials with crimp caps.

Immediately place the vials on a shaker for 60 min.

3.5 Analysis

3.5.1 Analytical conditions:

<u>GC column conditions</u>	
column:	Agilent J&W DB-624 60-m × 0.32-mm i.d. (film thickness 1.8-µm), or equivalent
flow:	4.2 mL/min (hydrogen)
column mode:	constant flow
initial average velocity:	61 cm/sec
<u>GC oven conditions</u>	
oven temperature:	60 ℃, hold 6 min, ramp to 190 ℃ at 25 ℃/min (hold 0 min)
run time:	11.2 min
<u>GC autosampler conditions</u>	
injection volume:	1 µL
<u>GC inlet conditions</u>	
liner:	Agilent focus 4-mm i.d. x 6.3-mm o.d. x 78.5-mm injection port liner with glass wool (catalog no. 210-4004-5)
temperature:	190 ℃
split ratio:	splitless
septum purge:	28.0 mL/min (hydrogen)
purge time	0.0 min
total flow:	38.5 mL/min
nominal inlet pressure:	16.8 psi
<u>GC detector conditions</u>	
temperature:	240 ℃
const col + makeup flow:	60.0 mL/min(nitrogen)
<u>GC signal conditions</u>	
zero:	150
range:	0

retention times

2-bromopropane:	4.32 min
ISTD:	5.14 min
1-bromopropane:	5.44 min

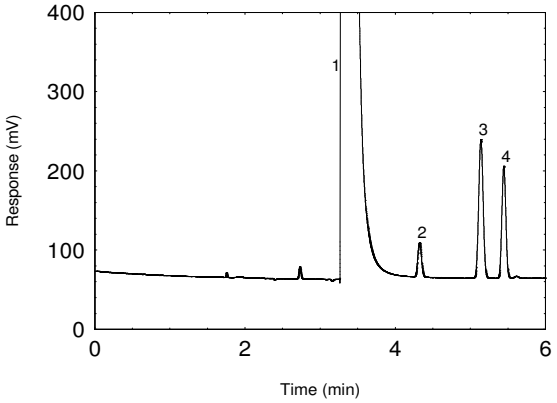


Figure 3.5.1. Chromatogram obtained at the target concentration with the recommended analytical conditions. (1: CS_2; 2: 2-bromopropane; 3: ISTD; 4: 1-bromopropane).

3.5.2 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over the range of concentrations.

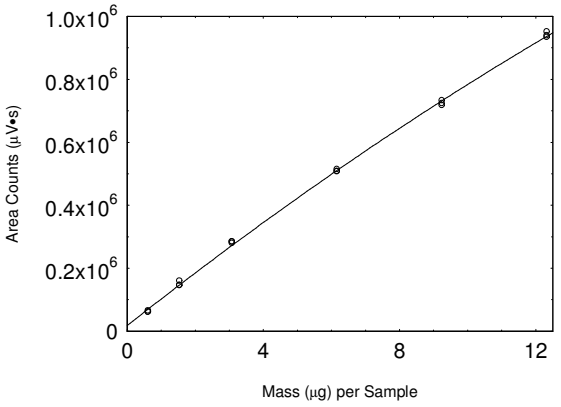


Figure 3.5.2.1. Calibration curve for 1-bromopropane ($y = -879x^2 + 8.53\times10^4x + 1.78\times10^4$).

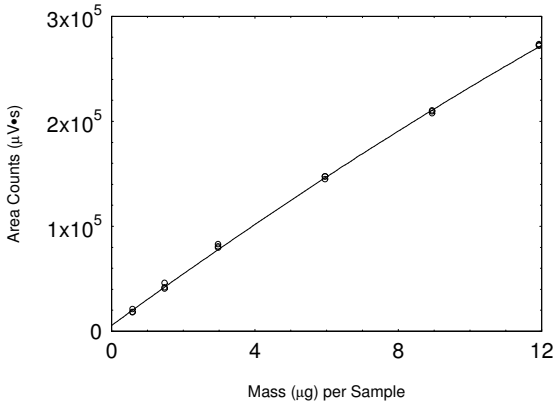


Figure 3.5.2.2. Calibration curve for 2-bromopropane ($y = -226x^2 + 2.49\times10^4x + 5532$).

3.6 Interferences (analytical)

3.6.1 Any compound that produces a GC response and has a similar retention time as the analyte or internal standard is a potential interference. *cis*-Dichloroethylene is a compound that produces a detector response and co-elutes with the internal standard. If *cis*-dichloroethylene is present, an external standard calibration can be used provided the standards and samples are each injected twice and averaged. If potential interferences, such as *cis*-dichloroethylene, were reported, they should be considered

before samples are extracted. Generally, chromatographic conditions can be altered to separate interferences from the analytes.

3.6.2 When necessary, the identity of an analyte peak can be confirmed with additional analytical data or procedures (Section 4.10).

3.7 Calculations

The amount of analyte per sample is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. The second section is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, it is added to the amount on the front section. If more than 20% of the total amount is found on the back section, report that the sampler may have been saturated on the Form OSHA-91B. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concn by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency in decimal form

$$C_V = \frac{C_M V_M}{M_r}$$

where C_V is concn by volume (ppm)
C_M is concn by weight (mg/m^3)
V_M is 24.46 (molar volume at NTP)
M_r is molecular weight (122.99 g/mol)

4. Method Validation

General instruction for the laboratory validation of OSHA sampling and analytical methods that employ chromatographic analysis is presented in "Validation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"[20]. These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. Air concentrations listed in ppm are referenced to 25 ºC and 760 mmHg (101.3 kPa).

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equally descending increments of analyte with the highest standard having a concentration that would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. These standards and the reagent blank were analyzed with the recommended analytical parameters (1-µL injection with no split). The data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 9.484×10^4 and 671.5 were obtained for the slope and standard estimate of error respectively for 1-bromopropane. For 1-bromopropane the DLAP was calculated to be 21.2 ng. Values of 2.924×10^4 and 425.8 were obtained for the slope and standard estimate of error respectively for 2-bromopropane. For 2-bromopropane the DLAP was calculated to be 43.7 ng.

[20] Eide, M.; Hendricks, W.; Simmons, M. Validation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed Sept 2013).

Table 4.1.1
Detection Limit of the Analytical Procedure
for 1-Bromopropane

concn (μg/mL)	mass on column (ng)	area counts (μV•s)
0	0	0
0.0308	0.0308	3657
0.0617	0.0617	7635
0.0925	0.0925	10250
0.1233	0.1233	12697
0.1542	0.1542	16068
0.1850	0.1850	19573
0.2158	0.2158	21299
0.2466	0.2466	23839
0.2775	0.2775	27700
0.3083	0.3083	29576

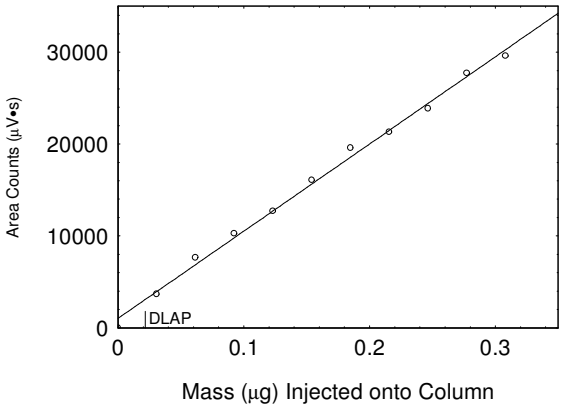


Figure 4.1.1. Plot of data to determine the DLAP for 1-bromopropane (y = 94843x + 1042.6).

Table 4.1.2
Detection Limit of the Analytical Procedure
for 2-Bromopropane

concn (μg/mL)	mass on column (ng)	area counts (μV•s)
0	0	0
0.0597	0.0597	2607
0.1194	0.1194	4235
0.1791	0.1791	5489
0.2388	0.2388	7605
0.2985	0.2985	8964
0.3582	0.3582	11160
0.4179	0.4179	12300
0.4776	0.4776	14005
0.5373	0.5373	15712
0.5970	0.5970	18616

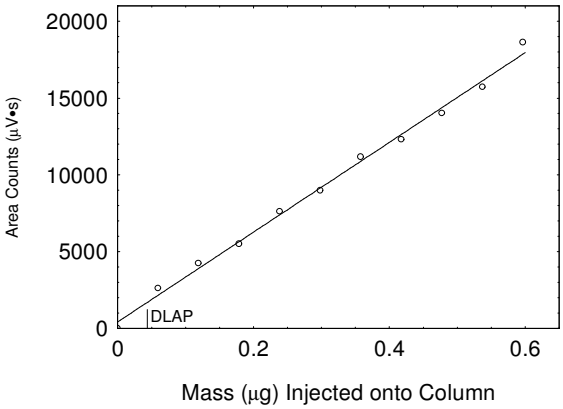


Figure 4.1.2. Plot of data to determine the DLAP for 2-bromopropane (y = 29235x + 427.8).

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

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 equally descending increments of analyte with the highest standard having a concentration that would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and slope) for the calculation of the DLOP. Values of 7.857×10^4 and 551.5 were obtained for the slope and standard estimate of error respectively for 1-bromopropane. For 1-bromopropane the DLOP was calculated to be 21.1 ng/sample (0.350 ppb or 1.76 μg/m^3). Values of 2.693×10^4 and 296.7 were obtained for the slope and standard estimate of error respectively for 2-bromopropane. For 2-bromopropane the DLOP was calculated to be 33.1 ng (0.549 ppb or 2.76 μg/m^3).

Table 4.2.1
Detection Limit of the Overall Procedure for 1-Bromopropane

mass per sample (µg)	area counts (µV•s)
0.0000	0
0.0308	3440
0.0617	5140
0.0925	7351
0.1233	11044
0.1542	13246
0.1850	15129
0.2158	17699
0.2466	20525
0.2775	22300
0.3083	24015

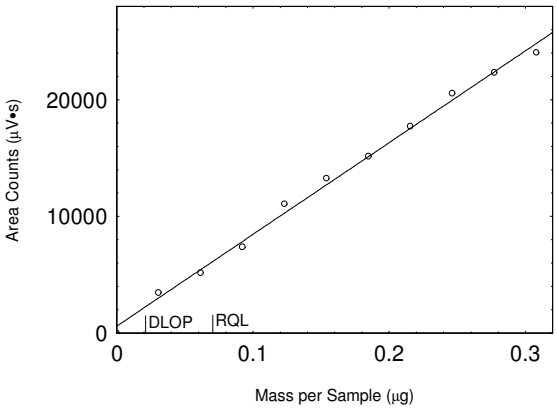


Figure 4.2.1. Plot of data to determine the DLOP/RQL for 1-bromopropane (y = 78569x + 605.5).

Table 4.2.2
Detection Limit of the Overall Procedure for 2-Bromopropane

mass per sample (µg)	area counts (µV•s)
0.0000	0
0.0597	1434
0.1194	3175
0.1791	4381
0.2388	6426
0.2985	7427
0.3582	9048
0.4179	11582
0.4776	12614
0.5373	14274
0.5970	16028

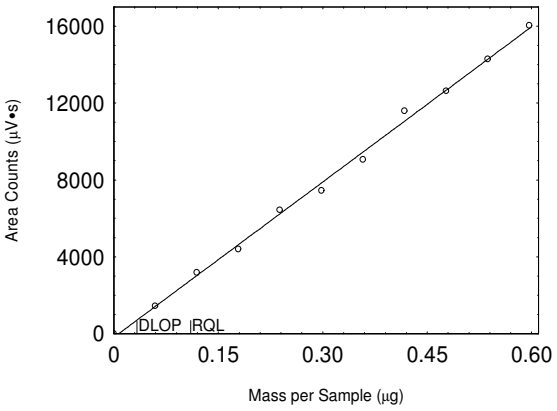


Figure 4.2.2. Plot of data to determine the DLOP/RQL for 2-bromopropane (y = 26929x – 184.7).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL for 1-bromopropane is 0.0702 µg per sample (1.16 ppb or 5.85 µg/m^3). Recovery at this concentration is 92.8%. The RQL for 2-bromopropane is 0.1102 µg per sample (1.83 ppb or 9.18 µg/m^3). Recovery at this concentration is 104.5%.

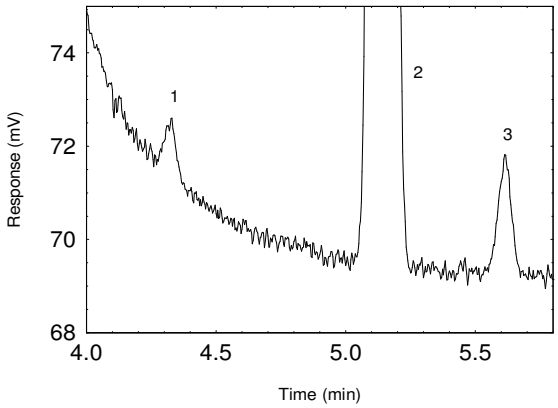


Figure 4.2.3. A chromatogram of the RQL of 1-bromopropane and 2-bromopropane. (1: 2-bromopropane; 2: ISTD; 3: 1-bromopropane).

4.3 Precision of the analytical method

The precision of the analytical method was measured as the mass equivalent to the standard error of estimate determined from the linear regression of data points from standards over a range that covers 0.1 to 2 times the target concentration for the sampler. A calibration curve was constructed and is shown in Section 3.5.2 from the three injections each of six standards. The standard error of estimate for 1-bromopropane is -0.104 µg. The standard error of estimate for 2-bromopropane is -0.128 µg.

Table 4.3.1
Instrument Calibration for 1-Bromopropane

× target concn	0.1×	0.25×	0.5×	1.0×	1.5×	2.0×
(µg/sample)	0.617	1.542	3.083	6.166	9.249	12.33
area counts	60476	159572	283344	513606	732498	950585
(µV·s)	65250	145598	279498	506636	716868	933480
	61292	146016	284537	507858	723024	938287

Table 4.3.2
Instrument Calibration for 2-Bromopropane

× target concn	0.1×	0.25×	0.5×	1.0×	1.5×	2.0×
(µg/sample)	0.597	1.493	2.985	5.970	8.955	11.94
area counts	17613	45530	80304	146980	209151	272913
(µV·s)	20816	41308	79066	144356	207184	271978
	18014	40230	82485	147096	209938	271619

4.4 Storage stability test

Refrigerated storage stability test samples for 1-bromopropane and 2-bromopropane were prepared by sampling a dynamically generated controlled test atmosphere using the recommended sampling parameters. The concentrations of 1-bromopropane and 2-bromopropane were the target concentrations (0.101 ppm or 0.508 mg/m^3 for both 1-bromopropane and 2-bromopropane), and the relative humidity was 80% at 24 ℃. Eighteen storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the tubes were stored at reduced temperature (4 ℃). At 3-4 day intervals, three samples were selected from the storage set and analyzed. Sample results are not corrected for extraction efficiency.

Ambient storage stability test samples were similarly prepared and analyzed with the exception that the samples were stored in a closed drawer at ambient temperature (about 23 ℃). The concentrations of 1-bromopropane and 2-bromopropane were the target concentrations (0.100

ppm or 0.503 mg/m^3 for both 1-bromopropane and 2-bromopropane), and the relative humidity was 80% at 25 ℃.

Table 4.4.1
Storage Test for 1-Bromopropane

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.2	94.9	95.8	93.4	94.8	94.0
3	93.3	95.0	94.5	94.0	97.8	96.8
7	90.4	90.5	91.0	95.8	95.9	96.7
10	89.8	93.9	96.8	96.5	97.8	96.1
14	90.1	92.5	90.5	97.4	96.7	94.1
18	89.5	87.4	89.1	97.1	92.8	94.9

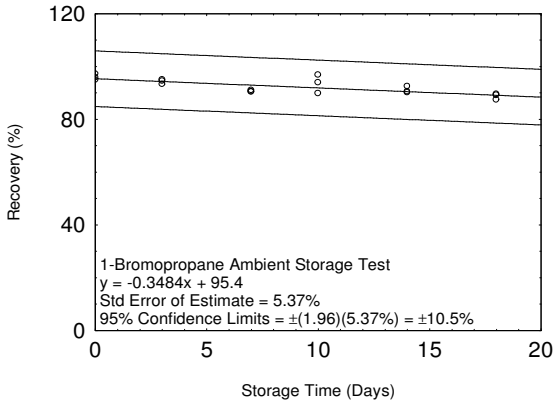


Figure 4.4.1. Ambient storage test for 1-bromopropane.

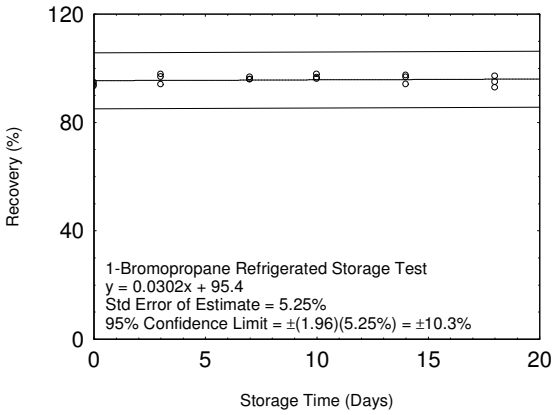


Figure 4.4.2. Refrigerated storage test for 1-bromopropane.

Table 4.4.2
Storage Test for 2-Bromopropane

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.9	101.0	102.9	101.6	101.6	102.5
3	101.9	101.5	105.1	101.3	101.5	100.6
7	101.0	100.9	100.1	100.0	100.3	101.4
10	100.8	101.0	101.2	101.8	101.0	102.3
14	101.8	102.7	101.7	102.5	101.1	102.1
18	100.9	99.2	102.3	101.8	102.3	99.1

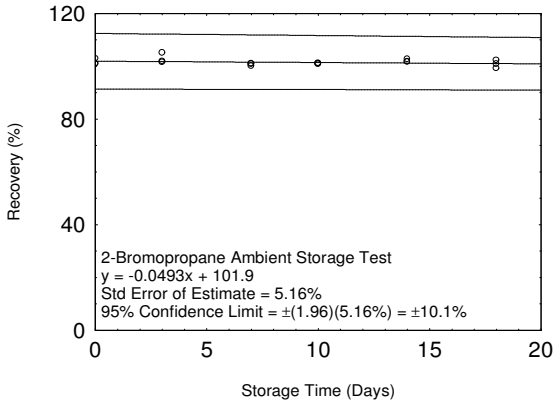


Figure 4.4.3. Ambient storage test for 2-bromopropane.

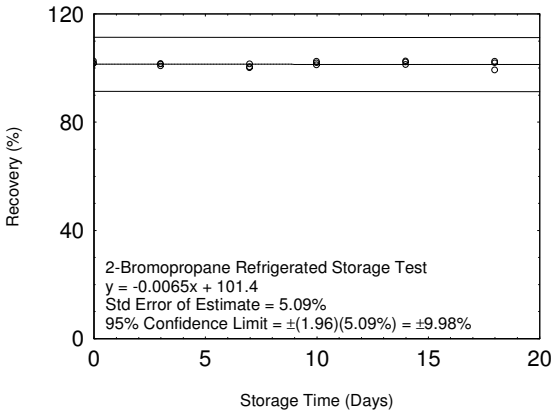


Figure 4.4.4. Refrigerated storage test for 2-bromopropane.

4.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). Ninety-five percent confidence intervals are drawn about the regression lines in the storage stability figures shown in Section 4.4.

4.5.1 Coconut Shell Charcoal Lot 2000 (SKC 226-01)

The precision for 1-bromopropane at the 95% confidence for the refrigerated temperature (4 °C) 18-day storage test was ± 10.3%. It contains an additional 5% for sampling pump error.

The precision for 2-bromopropane at the 95% confidence for the refrigerated temperature (4 °C) 18-day storage test was ± 9.98%. It contains an additional 5% for sampling pump error.

4.5.2 Recovery

The recovery of 1-bromopropane from samples used in an 18-day storage test remained above 95.9% when samples were stored at 4 °C.

The recovery of 2-bromopropane from samples used in an 18-day storage test remained above 101.3% when samples were stored at 4 °C.

4.6 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere similar to that used in the collection of the storage samples. The concentration of 1-bromopropane and 2-bromopropane in the test atmosphere was the target concentration (0.1014 ppm or 0.510 mg/m^3 for 1-bromopropane and 0.1016 ppm or 0.511 mg/m^3 for 2-bromopropane), and the relative humidity was 80% at 24 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed after being stored for 39 days at 4 °C. Sample results were corrected for extraction efficiency. No sample result had a deviation greater than the precision of the overall procedure determined in Section 4.5.

Table 4.6.1
Reproducibility Data for 1-Bromopropane

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
6.33	6.21	98.1	-1.9
6.38	5.94	93.1	-6.9
6.35	6.12	96.4	-3.6
6.11	5.93	97.1	-2.9
6.07	5.88	96.9	-3.1
5.99	5.83	97.3	-2.7

Table 4.6.2
Reproducibility Data for 2-Bromopropane

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
6.34	6.14	96.8	-3.2
6.39	5.94	93.0	-7.0
6.37	6.02	94.5	-5.5
6.12	5.92	96.7	-3.3
6.08	5.78	95.1	-4.9
6.00	5.86	97.7	-2.3

4.7 Sampler capacity

The sampling capacity of the front section of the sampling tube (with the back section of sorbent removed) of the recommended air sampler was tested by sampling a dynamically generated controlled test atmosphere containing 1-bromopropane and 2-bromopropane at two times the target concentration (0.200 ppm or 1.01 mg/m^3 for 1-bromopropane and for 2-bromopropane) and 80% relative humidity at 24 °C. The samples were collected at 50 mL/min. A second sampler was placed in a sampling train behind the front section of the first sampler. The percentage of the amount found on the second tube in relation to the concentration of the

test atmosphere was defined as breakthrough. There was no significant (<5%) breakthrough for either 1-bromopropane or 2-bromopropane observed after 8 hours of testing. This is equivalent to an air volume of 24 L. The recommended air volume is 12 L.

4.8 Extraction efficiency and stability of extracted samples

The extraction efficiency is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the guidelines.[21]

Extraction efficiency

The extraction efficiencies of 1-bromopropane and 2-bromopropane were determined by liquid-spiking four front sampling tubes of the recommended air sampler at each concentration level. These samples were stored overnight at ambient temperature and then analyzed. The overall mean extraction efficiency over the working range of 0.1 to 2 times the target concentration was 94.8% for 1-bromopropane and 98.5% for 2-bromopropane. The presence of water had no significant effect on extraction efficiency. The extraction efficiencies for the RQL and for the wet samplers are not included in the overall mean. Wet media were prepared by sampling humid air (81% RH at 24 ℃) for 240 min at 50 mL/min. The data obtained are shown in Table 4.8.1 and Table 4.8.2.

Table 4.8.1
Extraction Efficiency (%) of 1-Bromopropane

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	0.617	94.7	94.7	95.1	96.4	95.2
0.25	1.542	100.5	97.8	99.6	100.6	99.6
0.5	3.083	92.3	92.1	92.4	95.7	93.1
1.0	6.166	93.8	94.8	93.8	94.0	94.1
1.5	9.249	93.6	94.6	93.8	94.0	94.0
2.0	12.33	92.7	92.8	92.7	92.9	92.8
RQL	0.0925	92.3	92.5	95.3	94.8	93.7
1.0 (wet)	6.166	93.1	94.4	94.3	93.3	93.8

Table 4.8.2
Extraction Efficiency (%) of 2-Bromopropane

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	0.597	95.7	96.0	94.4	98.5	96.2
0.25	1.493	100.1	102.6	98.4	102.4	100.9
0.5	2.985	96.7	98.5	96.6	99.5	97.8
1.0	5.970	98.6	96.5	96.5	96.7	97.1
1.5	8.955	100.3	99.9	100.0	99.9	100.0
2.0	11.94	99.4	98.8	98.4	99.0	98.9
RQL	0.1194	101.4	100.5	99.9	98.3	100.0
1.0 (wet)	5.970	99.3	99.6	98.9	98.7	99.1

[21] Eide, M.; Hendricks, W.; Simmons, M. Validation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed Sept 2013).

Stability of extracted samples

The stability of extracted samples was examined by reanalyzing the target concentration samples 24, 48, and 72 h after the initial analysis. After the original analysis was performed two vials were recapped with new septa which were replaced after each analysis. The remaining two vials retained their punctured septa throughout this test. All samples were allowed to stand in the autosampler tray at room temperature. The samples were reanalyzed with freshly prepared standards. The difference between the initial analysis and the subsequent analysis is shown as percentage. Each septum was punctured 3 times for each analysis. The data obtained are shown in Table 4.8.3 and Table 4.8.4.

Table 4.8.3
Stability of Extracted Samples for 1-Bromopropane

punctured septa replaced							punctured septa retained						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
93.8	96.2	+2.4	94.0	+0.2	93.6	-0.2	94.8	95.9	+1.1	93.9	-0.9	92.0	-2.8
93.8	95.0	+1.2	93.9 (mean)	+0.1	92.6	-1.2	94.0	94.3	+0.3	92.4 (mean)	-1.6	90.3	-3.7
93.8	95.6	+1.8	94.0	+0.2	93.1	-0.7	94.4	95.1	+0.7	93.2	-1.2	91.2	-3.3

Table 4.8.4
Stability of Extracted Samples for 2-Bromopropane

punctured septa replaced							punctured septa retained						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
98.6	101.4	+2.8	99.7	+1.1	98.7	+0.1	96.5	100.1	+3.6	100.1	+3.6	98.8	+2.3
96.5	99.5	+3.0	100.7 (mean)	+4.2	100.4	+3.9	96.7	98.8	+2.1	99.8 (mean)	+3.1	99.3	+2.6
97.6	100.5	+2.9	100.2	+2.7	99.6	+2.0	96.6	99.5	+2.9	100.0	+3.4	99.1	+2.5

4.9 Sampling interferences

Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing 1-bromopropane and 2-bromopropane at two times the target concentration (0.199 ppm or 1.00 mg/m^3 for 1-bromopropane and 2-bromopropane) and 80% relative humidity at 25 ℃. The test atmosphere was sampled by six samplers at 50 mL/min for 60 min. After 60 min sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminate-free air. Contaminant-free air is laboratory conditioned air at known relative humidity and temperature but without any added chemical except water. Sampling was resumed with a set of three samples and contaminant-free air at 80% RH and 25 ℃ was sampled at 50 mL/min for 180 min and then all six samplers were analyzed. The data obtained are shown in Table 4.9.1 and Table 4.9.2.

Table 4.9.1
Retention of 1-Bromopropane

	recovery (%)			
set	1	2	3	mean
first	100.2	101.3	100.2	100.6
second	99.9	104.0	100.0	101.3
second/first				100.7

Table 4.9.2
Retention of 2-Bromopropane

	recovery (%)			
set	1	2	3	mean
first	104.7	109.6	103.6	106.0
second	107.0	108.8	105.4	107.1
second/first				101.0

Low humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (0.200 ppm or 1.01 mg/m^3 for 1-bromopropane and 0.199 ppm or 1.00 mg/m^3 for 2-bromopropane) and 21% relative humidity at 23 °C. The test atmosphere was sampled with three of the recommended samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Sample results were 96.0%, 99.4%, and 100.3% of theoretical for 1-bromopropane. Sample results were 98.2%, 102.6%, and 101.2% of theoretical for 2-bromopropane.

Low concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 0.1 times the target concentration (0.0099 ppm or 0.0498 mg/m^3 for 1-bromopropane and 0.010 ppm or 0.0503 mg/m^3 for 2-bromopropane) and 80% relative humidity at 24 °C. The test atmosphere was sampled with three of the recommended samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Sample results were 93.0%, 97.2%, and 97.5% of theoretical for 1-bromopropane. Sample results were 98.5%, 102.1%, and 106.3% of theoretical for 2-bromopropane.

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Chemical interference

The effect of potential chemical sampling interference(s) was tested by sampling a dynamically generated controlled test atmosphere containing the target concentration (0.0997 ppm or 0.501 mg/m^3 for 1-bromopropane and 0.0998 ppm or 0.502 mg/m^3 for 2-bromopropane) and 79% relative humidity at 25 °C. The test atmosphere also contained the interference perchloroethylene at 99.4 ppm or 674 mg/m^3. The test atmosphere was sampled with three of the recommended samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Sample results were 95.5%, 100.2%, and 101.9% of theoretical for 1-bromopropane. Sample results were 98.8%, 101.9%, and 104.5% of theoretical for 2-bromopropane.

4.10 Qualitative analysis

When necessary, the identity or purity of an analyte peak can be confirmed by GC-mass spectrometry or by another analytical procedure.

A chromatogram was obtained using an Agilent Technologies 7890A GC System with a 5975C Mass Selective Detector and is included as Figure 4.10.1. The mass spectra of 1-bromopropane and 2-bromopropane that are also shown as Figure 4.10.2 and Figure 4.10.3.

GC/MS conditions:

<u>GC column conditions</u>	
column:	Agilent J&W DB-624 60-m × 0.32-mm i.d. (film thickness 1.8-µm), or equivalent
flow:	3.4 mL/min (helium)
column mode:	constant flow
initial average velocity:	48 cm/sec
<u>GC oven conditions</u>	
oven temperature:	60 °C, hold 7.69 min, ramp to 190 °C at 19.5 °C/min (hold 0 min)
run time:	14.4 min

GC autosampler conditions

injection volume:	1 µL

GC inlet conditions

liner:	low pressure drop precision liner w/wool (Restek catalog no. 2309.1, or equivalent)
temperature:	190 °C
split ratio:	splitless
septum purge:	3.0 mL/min (helium)
total flow:	34.4 mL/min
nominal inlet pressure:	22.4 psi

MS conditions

transfer line temperature:	250 °C
MS source temperature:	250 °C
MS quad temperature	200 °C
ion masses:	25 – 300 amu

retention times

2-bromopropane:	5.35 min
ISTD:	6.34 min
1-bromopropane:	6.71 min

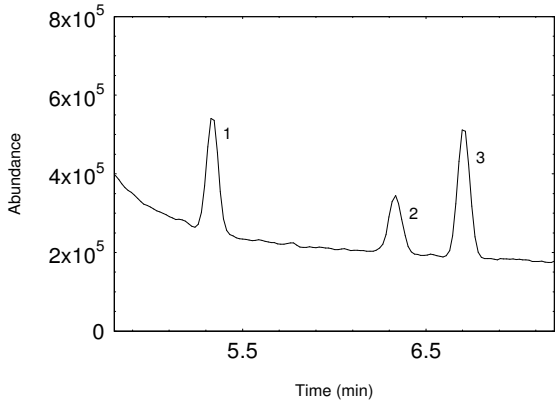

Figure 4.10.1. A chromatogram obtained by GC-MS of 1-bromopropane and 2-bromopropane at the target concentration. (1: 2-bromopropane; 2: ISTD; 3: 1-bromopropane).

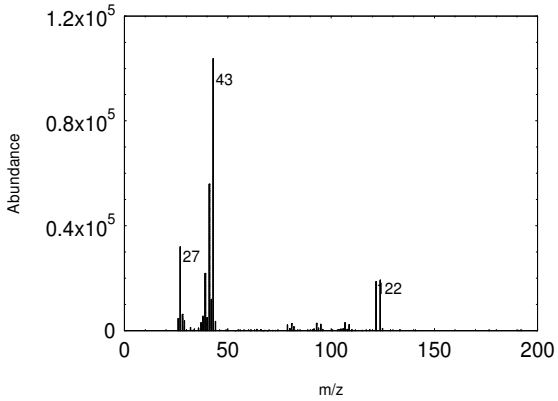

Figure 4.10.2. Mass spectrum of 1-bromopropane.

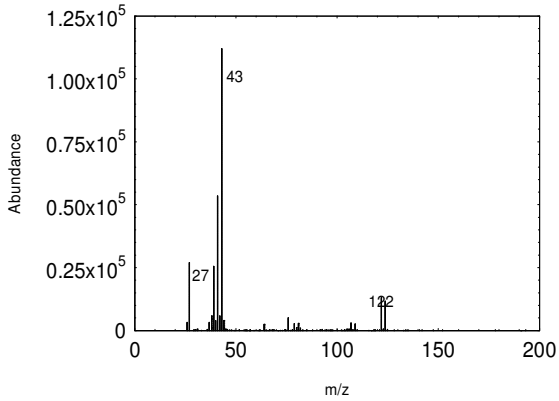

Figure 4.10.3. Mass spectrum of 2-bromopropane.

4.11 Generation of test atmospheres

The following apparatus was placed in a walk-in hood. The test atmospheres were generated by pumping microliter volumes (typically between 85 and 90 µL/min.) of a mixture containing 1-bromopropane and 2-bromopropane in perchloroethylene with an ISCO model 100DM syringe pump through a short length of 0.53-mm uncoated fused silica capillary tubing into a vapor generator where it was heated and evaporated into the dilution air stream (Figure 4.11). The vapor generator consisted of a 15-cm length of 5-cm diameter glass tubing with a side port for introduction of the capillary tubing. The vapor generator was heated with a variable voltage controlled heating tape to evaporate the mixture. The humidity, temperature, and volume of the dilution air were regulated by use of a Miller Nelson Model HCS-401 Flow-Temperature-Humidity control system. The dilution air volume was typically 200 L/min. The test atmosphere passed into a glass mixing chamber (76-cm × 15-cm) from the vapor generator, and then into a glass exposure chamber (76-cm × 12-cm). Active samplers were attached to glass ports extending from the exposure chamber. The humidity and temperature were measured at the exit of the exposure chamber with a Vaisala M170 temperature and humidity probe. During sampling, test atmosphere concentration and stability was monitored using a Gasmet DX-4015 FTIR Gas Analyzer. The theoretical concentrations were calculated from the temperature, pressure, ISCO pump flow rate, the concentration of mixture, and the air flow volumes. The theoretical concentrations were used throughout this validation.

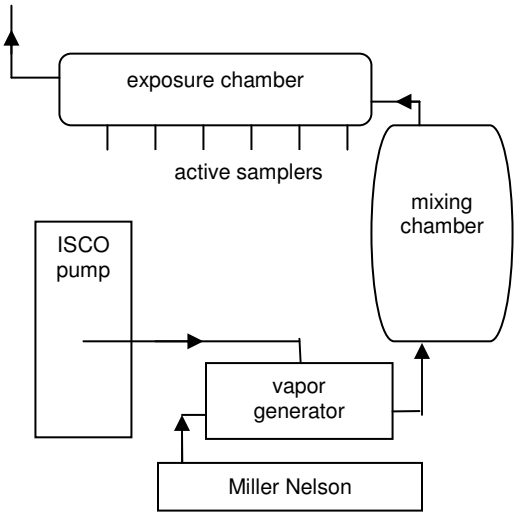

Figure 4.11. The test atmosphere generation and sampling apparatus.