



## *Project Summary*

# Determination of Haloethers in Industrial and Municipal Wastewaters

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This document describes an analytical method, not based on gas chromatography/mass spectrometry, for the analysis of haloethers in water and wastewater.

The following haloethers were originally included in this study: 2-chloroethyl vinyl ether, bis(2-chloroisopropyl) ether, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, and (bischloromethyl) ether. The 2-chloroethyl vinyl ether and the bis(chloromethyl) ether were later deleted from the project because of extreme volatility and hydrolytic instability, respectively.

A literature search was conducted to acquire published information on the hydrolytic stability of the haloethers, methods for the detection of haloethers in water, and methods for the isolation, concentration, and analysis of haloethers. Gas chromatography studies were completed to compare different packings for use with haloethers and to compare the results obtained using a Hall electrolytic conductivity detection with those obtained using an electron capture detector. Various solvents were evaluated for use in extracting haloethers from wastewater. Sample preservation was studied at various pH and residual chlorine levels and different temperatures. The stability of haloethers stored in acetone and in methanol was observed. Chromatographic cleanup

procedures were investigated for the removal of potential interferences.

The workable method developed in this program for the analysis of haloethers in wastewater consisted of a liquid/liquid extraction using methylene chloride, an evaporation step using Kuderna-Danish (K-D) evaporators, a column chromatographic clean-up procedure using Florisil, another K-D evaporation of the fraction from the Florisil column, and subsequent analysis by gas chromatography using an electrolytic conductivity detector.

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*This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Under provisions of the Clean Water Act, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 em-

phasize the control of toxic pollutants as well as declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigates the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement.

The following haloethers were originally in this study: 2-chloroethyl vinyl ether (CEVE), bis(2-chloroisopropyl ether (BCIPE), bis (2-chloroethyl) ether (BCEE), bis(2-chloroethoxy) methane (BCEXM), 4-chlorophenyl phenyl ether (CPPE), 4-bromophenyl phenyl ether (BPPE), and bis(chloromethyl) ether. The 2-chloroethyl vinyl ether and the bis(chloromethyl) ether were later deleted from the project because of extreme volatility and hydrolytic instability, respectively.

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### Gas Chromatography Studies

Gas chromatography studies were conducted to determine the optimum

column and conditions for use with haloethers. In addition, electron capture and electrolytic conductivity detectors were studied to determine the most selective and sensitive detector for use with the haloethers.

Initial studies of the gas chromatography of the haloethers resulted in the selection of SP-1000 on Supelcoport over Tenax-GC as the column of choice. Early studies of detector sensitivity showed that the electron capture detector was more sensitive than the electrolytic conductivity detector. Unfortunately, bis(2-chloroisopropyl) ether was found to contain a large number of electron capturing impurities, while showing no significant impurities with either the electrolytic conductivity detector or the flame ionization detector. Because of the BCIPE electron capturing impurities, work was continued on the electrolytic conductivity detector. With this modified detector, sensitivity was approximately equal to electron capture and flame ionization detectors, but with much greater specificity.

Figure 1 illustrates the results achieved with the SP-1000 column. Column

conditions and retention times for both columns are described in Table 1.

### Extraction Studies

Extraction studies for the six haloethers using spiked laboratory samples were conducted at pH 2, 7, and 10 using three solvents: methylene chloride, 15% ethyl ether in hexane, and pentane.

The analytical results of the extraction studies are presented in Table 2. Each value listed for "percent recovered," represents an average of three different extractions at a given pH and for a given solvent. These results were analyzed using analysis of variance (ANOVA). For CEVE, pH was the only variable which contributed significantly to the total variance. For BCIPE, both pH and solvent were significant contributors to the variance. For the four other haloethers, only the solvent contributed to the variance. These ANOVA results, in addition to the data presented in Table 2, indicate the best average recoveries of the haloethers are achieved by using methylene chloride as a solvent.

Column: 3% SP-1000 on Supelcoport  
Program: 60°C-2 minutes 8°/minute to 230°C.  
Detector: Hall electrolytic conductivity

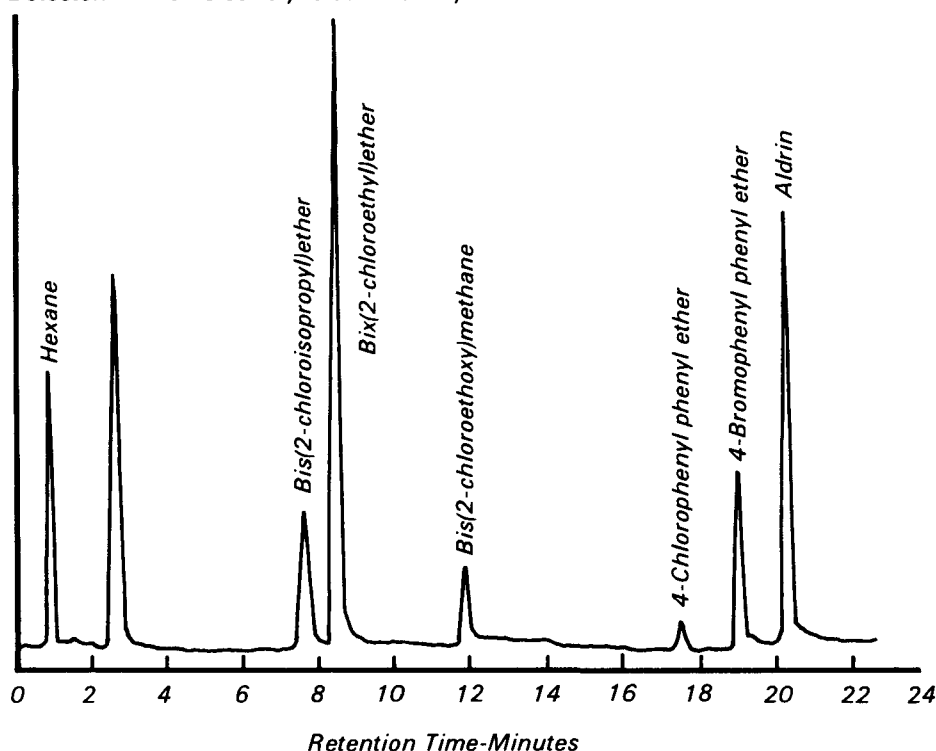


Figure 1. Gas chromatogram of haloethers.

## Preservation Studies

Preservation studies were conducted by spiking one liter solutions of buffered deionized water at pH 2, 7, and 10 with the standard solution of five haloethers, CEVE, BCEE, BCEXM, CPPE, and BPPE, in acetone. The studies were conducted at residual chlorine levels of 0 parts per million and 2 parts per million and storage temperatures of 4°C and 25°C.

Storage time was seven days. Extraction of the stored solutions was performed using methylene chloride.

The analytical results of the preservation studies are presented in Table 3. The "average percent recovered" values listed represent an average of three separate extractions.

The data in Table 3 and ANOVA analysis show the only precaution

needed for sample preservation is an adjustment of the pH to at least 7, due to the sensitivity of CEVE to acid hydrolysis and the reaction between residual chlorine and BPPE and CPPE at acid pH. Closer examination of Table 3 shows very little difference, if any, between preservation at pH 7 or pH 10. The table shows little difference between preservation at 4°C or 25°C, although the buffer solutions analyzed were not biologically active.

The stability of acetone and methanol solutions of CEVE, BCPE, BCEE, BCEXM, and BPPE were also studied. The results showed that while CEVE is very unstable in methanol, the other four haloethers were stable for at least 90 days in either solvent.

## Resin Studies

Studies were completed to evaluate the Amborsorb XE-340 and XAD-2 resins for use as concentrators. The two resins were Soxhlet extracted with acetonitrile overnight, and again with methanol overnight. They were packed into 10 mm ID columns to a depth of 6 cm. One liter portions of buffer solutions at pH 2, 7 and 10 were then spiked with the haloethers and passed through the resin beds. The beds were then eluted

**Table 1.** Chromatographic Conditions

Parameter	Retention Time (min.)	
	Column 1	Column 2
Bis(2-chloroisopropyl) ether	8.4	9.7
Bis(2-chloroethyl) ether	9.3	9.1
Bis(2-chloroethoxy) methane	13.1	10.0
4-Chlorophenyl phenyl ether	19.4	15.0
4-Bromophenyl phenyl ether	21.2	16.2

Column 1 conditions: Supelcoport (100/120 mesh) coated with 3% SP-1000 packed in 1.8 m long x 2 mm ID glass column with helium carrier gas at a flow rate of 40 mL/min. Column temperature: 60°C for 2 minutes after injection then program at 8°C/min to 230°C and hold for 4 minutes. Under these conditions the retention time for Aldrin is 22.6 minutes.

Column 2 conditions: Tenex-GC (60/80 mesh) packed in a 1.8 m long x 2 mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature: 150°C for 4 minutes after injection then program at 16°C/min to 310°C. Under these conditions the retention time for Aldrin is 18.4 minutes.

**Table 2.** Results of Extraction Studies

pH	Haloether	Solvent					
		15% Ethyl ether in hexane		Methylene chloride		Pentane	
		Percent recovered (average)	RSD, %	Percent recovered (average)	RSD, %	Percent recovered (average)	RSD, %
2	CEVE	29.6	32.4	31.3	9.5	37.8	32.1
	BCIPE	66.4	21.8	51.2	21.5	22.1 <sup>b</sup>	—
	BCEE	66.9	16.3	69.7	20.3	43.4	9.8
	BCEXM	55.9	15.0	83.2	11.2	50.5	13.9
	CPPE	67.3	9.8	82.9	12.7	62.8	20.0
	BPPE	57.4	8.7	68.9	14.6	55.8	21.3
7	CEVE	65.9	16.5	70.7	31.5	61.7	47.3
	BCIPE	88.5	7.6	61.6	8.2	76.2	10.7
	BCEE	63.7	3.1	93.2	1.6	46.1	8.7
	BCEXM	68.0	14.5	88.0	7.3	43.3	27.8
	CPPE	65.1	12.5	85.6	6.8	61.1	12.5
	BPPE	57.1	12.7	81.3	6.3	63.1	6.5
10	CEVE	44.2	29.8	55.0	41.2	30.7	13.8
	BCIPE	61.7 <sup>c</sup>	—	92.1	5.2	63.0	10.8
	BCEE	59.9	20.8	101.6	8.1	42.7	5.3
	BCEXM	54.5	24.7	75.3	8.5	38.4	6.4
	CPPE	54.4	30.8	93.2	4.3	66.1	2.3
	BPPE	52.7	30.4	82.9	1.9	67.3	0.56

<sup>a</sup>RSD = relative standard deviation.

<sup>b</sup>Value for one extraction.

<sup>c</sup>Average of two extractions.

**Table 3.** Preservation Study Results

pH	Chlorine, ppm	Haloether	At 4°C		At 25°C	
			Percent recovered (average)	RSD, <sup>a</sup> %	Percent recovered (average)	RSD, <sup>a</sup> %
2	0	CEVE	*	*	*	*
		BCEE	61.7	23.2	76.6	2.6
		BCEXM	75.7	22.0	71.0	3.5
		CPPE	78.7	9.5	86.9	3.8
		BPPE	90.6	7.6	91.9	4.6
2	2	CEVE	10.4	32.3	12.5	20.4
		BCEE	78.3	6.9	66.0	12.4
		BCEXM	66.2	22.3	89.0	9.7
		CPPE	20.2	60.5	16.4	61.0
		BPPE	18.7	70.2	11.5	25.2
7	0	CEVE	25.3	31.1	28.7	25.3
		BCEE	66.9	13.0	61.4	8.1
		BCEXM	65.3	24.0	71.4	5.7
		CPPE	80.3	10.3	74.0	8.0
		BPPE	87.9	8.8	76.5	2.6
7	2	CEVE	*	*	*	*
		BCEE	59.4	26.5	68.7	17.5
		BCEXM	68.1	10.1	54.9	20.8
		CPPE	73.2	5.4	70.3	7.6
		BPPE	79.3	9.8	72.5	6.6
10	0	CEVE	37.7	17.8	26.8	19.3
		BCEE	69.8	26.0	53.4	10.1
		BCEXM	63.8	26.0	54.0	20.3
		CPPE	66.6	22.3	63.3	1.5
		BPPE	78.4	18.2	57.3	8.0
10	2	CEVE	74.6	10.5	68.6	13.7
		BCEE	55.5	15.7	80.2	6.5
		BCEXM	78.8	4.0	70.2	16.9
		CPPE	68.2	8.2	76.9	9.2
		BPPE	60.8	42.0	77.1	0.76

<sup>a</sup>RSD = relative standard deviation.

\* = none detected.

using 150 mL of ethyl ether for the XAD-2 and 150 mL of acetone for the Amborsorb SE-340.

Both resins showed the ability to remove the haloethers from water. However, we were unable to strip the haloethers from the Amborsorb XE-340 using either acetone or methanol. The XAD-2 resin, though, worked well on both counts. At pH 7, the following average percent recoveries and standard deviations were obtained: BDIPE,  $71 \pm 11$ ; BCEE,  $51 \pm 7$ ; BCEXM,  $69 \pm 9$ ; BPPE,  $72 \pm 9$ . Due to the high volatility of CEVE, no appreciable amount of this compound was recovered. Analysis of the data showed no significant variation in the percent recovery at any of the three pH values used.

### Column Chromatography Studies

Column chromatography studies were conducted to find a chromato-

graphic medium sufficient for the removal of potential interferences that may be encountered in actual industrial wastewaters.

Four columns were packed with Florisil and eluted with 200 mL of 6% ethyl ether in petroleum ether followed by 200 mL 15% ethyl ether in petroleum ether. Most of the haloethers eluted in the 6% ethyl ether fraction, with only 10% of BCEXM eluting in the 15% ethyl ether fraction. Further studies showed at 300 mL of 6% ethyl ether in petroleum ether was sufficient to remove all the haloethers from the column, including BCEXM.

Other columns with 2 cm ID were slurry packed with 20 grams of 60-200 mesh silica gel. The haloether samples were then charged on the head of the column and eluted with varying concentrations of 5, 10, 20, 30, and 50% of methylene chloride in hexane. An experiment was conducted with four

identical samples charged on four columns. The FID analyses of the resulting fractions were so erratic, the analyses were repeated. These results and a third attempt were also very erratic. Therefore, Florisil appeared to be the preferred packing for the sample cleanup. The use of silica gel was not explored further as a column cleanup media.

### Application of Method to Wastewater Samples

Wastewater samples were obtained from a municipal secondary waste treatment plant and three industrial sites. Each of the four samples was divided into one liter portions and analyzed as received, or spiked with six haloethers. After problems with a computer integrater were encountered during the analysis of the first sample, all results were calculated using peak heights. The experimental design served as a check on the liquid extraction procedure, the XAD resin extraction technique, and sample stability for seven days at 4°C and 25°C. Three replicates of each sample were analyzed under each of five conditions as described in Table 4.

The samples described in the first three conditions were extracted with three 60 mL portions of methylene chloride. These portions were combined, dried with sodium sulfate, concentrated with hexane, and eluted from Florisil using 300 mL of 6% ethyl ether in petroleum ether. Then, the samples were again concentrated using K-D evaporator, the volume adjusted to 10 mL, and the samples were ready for analysis. Table 4 shows that the XAD resin sorption method was also used to prepare samples for analysis. In this procedure, the wastewater samples were spiked and run through the resin procedure described earlier. The samples were then either stripped and analyzed immediately, or stored for seven days at 4°C and then stripped and analyzed. All the analyses were done using the Hall electrolytic conductivity detector with a column packed with 3% SP-1000.

The blank samples, with the exception of industrial source #3, had no response on the Hall detector at retention times which interfered with the haloethers. Source #3 had several interferences which could not be removed with the Florisil cleanup. These interferences were so large and eluted so close to some of the haloethers that they

**Table 4. Percent Recoveries of Haloethers from Industrial and Municipal Wastewater**

Sample	As received		Stored at 25°C for 1 week		Stored at 4°C for 1 week		XAD-2		XAD-2 stored for 1 week	
	Percent recovered	Percent RSD	Percent recovered	Percent RSD	Percent recovered	Percent RSD	Percent recovered	Percent RSD	Percent recovered	Percent RSD
<i>Industrial #1</i>										
BCIPE	68.0	0.4	70.9	4.6	71.2	3.2	76.9	1.4	72.6	2.6
BCEE	56.5	0.6	67.1	5.3	59.8	5.8	66.4	3.1	61.3	3.8
BCEXM	60.2	2.0	70.7	6.3	67.6	5.5	69.1	2.5	63.8	5.2
CPPE	73.3	2.8	74.1	3.0	77.1	2.7	77.5	1.8	75.4	2.6
BPPE	82.9	3.2	79.8	2.6	89.4	4.5	79.2	1.2	84.4	4.7
<i>Industrial #2</i>										
BCIPE	62.9	1.2	64.6	3.0	65.3	3.4	76.2	2.4	77.7	2.9
BCEE	51.2	1.7	53.0	5.6	52.7	4.2	64.8	1.2	66.5	2.1
BCEXM	51.4	1.6	54.3	4.1	56.0	5.8	69.3	3.0	70.7	2.0
CPPE	70.1	0.4	71.4	1.4	72.5	1.4	77.3	3.5	77.3	1.7
BPPE	71.7	1.0	72.1	0.2	73.3	1.4	76.3	1.7	77.8	1.5
<i>Industrial #3<sup>a</sup></i>										
<i>Municipal #1</i>										
BCIPE	67.9	14.3	60.8	7.6	73.7	1.2	58.2	4.6	63.8	2.3
BCEE	64.6	17.3	58.3	7.1	71.3	1.9	47.3	5.6	60.6	6.4
BCEXM	68.4	19.2	59.6	9.3	74.3	1.3	56.0	4.1	61.1	4.3
CPPE	73.2	16.2	64.6	7.1	76.7	2.0	64.4	0.3	68.8	4.1
BPPE	81.3	8.8	72.0	7.3	75.6	1.2	73.8	5.5	74.9	5.1

<sup>a</sup>Unable to obtain recovery data because of interferences.

overshadowed all compounds near them. The data for recovery of the haloethers from the wastewaters are shown in Table 4.

Observation of the data from Table 4 seems to indicate that on the whole, there is not much difference in the samples extracted initially and those stored at 25°C and 4°C. There is, however, a difference in the samples analyzed using extraction as opposed to those using the XAD-2 resin. For the two industrial waters, the data indicate XAD concentration results in better recoveries than methylene chloride extraction for most of the haloethers.

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The complete report, entitled "Determination of Haloethers in Industrial and Municipal Wastewaters," (Order No. PB 81-232 290; Cost: \$9.50, subject to change) will be available only from:

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:  
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