



## Project Summary

# Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water

William C. Glaze and C.-C. Lin

This report describes a study of a liquid-liquid extraction (LLE) procedure for the analysis of volatile organic compounds (VOC's) in water. The method consists of a single step extraction with n-pentane in a closed vial, followed by gas chromatographic (GC) analysis of the compounds in the extract. Several aspects of the procedure have been investigated, including extraction efficiencies, precision, accuracy, and speed. Solvent: water ratio, pH, and ionic strength of the samples were the principal variables. In initial studies, four trihalomethanes (THM's) were used as analytes; but in later work, several other C<sub>1</sub> and C<sub>2</sub> organohalides were added. Subsequently, the method was extended to aromatic compounds such as benzene, toluene, and the xylenes. As the list of compounds grew, packed column GC was found to be inadequate, so open tubular capillary columns were adopted. Combined with electron capture (EC) and flame ionization detection (FID), capillary columns allow one to use LLE for mixtures of these compounds. Method detection limits (MDL) were below 1 µg/L for most organohalides, except for chloroform (2.9 µg/L), which was determined by blank values, and haloaromatics and 1,2-dichloroethane (8 µg/L), which have low responses to the EC detector. FID aromatics are in the range of 15-40 µg/L. Limits of detection may be enhanced by increasing the water:solvent ratio; however, lowered extraction efficiencies ultimately limit this option.

While not without deficiencies, LLE is a speedy and convenient procedure for the analysis of VOC's in water. The

method has been shown to be capable of precise and accurate measurements for the compounds used in this study.

*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).*

### Background

The report describes a laboratory study of LLE methods for the analysis of VOC's in water. The objectives of the study were to examine various method variables, including choice of solvent; solvent to water ratio; matrix pH and ionic strength; and the presence of quenching agents and methanol. The initial phase of the study emphasized optimization of the LLE method for a group of four THM's and other organohalides; but in latter portions of the study, the list of potential analytes was enlarged to include other organohalides and certain aromatics. This necessitated the exploration of capillary chromatographic techniques for the analysis of complex mixtures of the analytes.

### Description of the LLE Method Used

The method may be used for the following compounds:

<i>dibromochloromethane</i>	
<i>toluene</i>	<i>carbon tetrachloride</i>
<i>ethylbenzene</i>	<i>1,2-dichloroethane</i>
<i>xylenes</i>	<i>bromodichloromethane</i>
<i>dichlorobenzenes</i>	<i>1,1,2-trichloroethane</i>
<i>chloroform</i>	<i>tetrachloroethylene</i>

*bromoform*      *benzene*  
*1,1,1-trichloroethane*

The method may also be extended to other nonpolar organic compounds, particularly those with boiling points above chloroform, but is not recommended for very volatile compounds such as vinyl chloride and the dichloroethylenes, although with special care and some modification of the method these substances may be included. The method will also measure the dihaloacetonitriles and dichloriodomethane, but the analyst should be aware of the difficulties associated with the preparation and preservation of standards, and with the stability of these substances in water. If trihalomethane formation potential is to be measured, a procedure similar to that described by Glaze *et al.* should be used, in which the chlorination reaction is carried out in the vial used for the extraction. At the conclusion of the time required for reaction, quench may be added and the THM's analyzed as described below.

The extraction procedure is carried out in 25-mL (6 dram) borosilicate vials with screw caps, the tops of which have a 10 mm i.d. perforation. A silicone rubber liner with a Teflon coating on one side is used in conjunction with the cap so that a syringe needle may pierce the liner in order to withdraw or add materials to the vial. The Teflon face of the liner is placed in contact with the sample inside the bottle.

The water sample to be analyzed is usually added to the bottle in such a way as to avoid excessive loss of volatiles, i.e. without much bubbling. The vial is completely filled so that a convex meniscus is seen above the lip of the bottle. For samples which have residual chlorine present or suspected, a chlorine quenching agent is added to the vial before it is filled with sample. The nominal amount of quench used in this work was 0.25 mL of a solution containing 0.04 M Na<sub>2</sub>SO<sub>3</sub>. Care should be taken in filling the bottle to ensure that the quench is not washed out. No buffer is required if the sample is to be analyzed directly, i.e. without further chlorination.

On the day samples are to be analyzed, the GC system is properly calibrated using standards prepared by the procedure dictated by EPA. A solvent blank should be run to ensure adequate purity before the extractions are performed.

Extractions are carried out by first removing 5.0 mL of water from the vial, then adding 1.0 mL of *n*-pentane. These manipulations are carried out using

syringe withdrawal and injection techniques, while the bottle remains closed.

The pentane used for the extractions should be free of excessive interferences and should contain an internal standard at an appropriate concentration level. For THM's, the standard used in this work is 1,2-dibromoethane. Other internal standards which may be used with the ECD are bromotrichloromethane, 1,4-dibromobutane, and 2-bromo-1-chloropropane. *n*-Decane may be used with the GC/FID method.

Following addition of the pentane, the sample is shaken vigorously in order to reach liquid-liquid equilibrium. Shaking for one minute by hand, or thirty seconds with a vortex shaker is sufficient. The vial is then allowed to stand for a few minutes until the two layers thoroughly separate. While awaiting analysis, vials should be stored with topsides down. Calibration standards and water blanks should be treated and extracted by exactly the same procedure as samples.

GC analysis is carried out by carefully removing a 1-2  $\mu$ L aliquot from the pentane layer in the vial, and injecting it into the GC. In case the laboratory is warm, the vial should be cooled in a refrigerator prior to taking of the aliquot.

For THM analysis, a 10% squalane on Chromosorb A/AW column is recommended. (Column temperature, 80°C; injection port temperature, 100°C; <sup>63</sup>Ni EC temperature 300°C; attenuation, 2<sup>12</sup>; flow rate of helium, 21 mL/min; retention times: 1.43 chloroform; 2.36 bromodichloromethane; 4.30 dibromochloromethane; 5.29 1,2-dibromoethane (internal standard); 8.29 bromoform).

An SP-1000 or 6% OV-11/4% SP-2100 mixed-phase column is recommended for confirmation purposes. (Column temperature, 45°C, 12 min, 1°C/min to 70°C, <sup>63</sup>Ni ECD; retention times: 4.91 chloroform; 5.72 1,1,1-trichloroethane; 6.37 carbon tetrachloride; 7.00 1,2-dichloroethane; 9.11 trichloroethane; 10.96 bromodichloroethane; 21.01 tetrachloroethylene; 23.14 dibromochloromethane; 39.38 bromoform).

Organohalides, except THM's or in combination with THM's, may be analyzed with the mixed phase column, or in some cases with the squalane column. For capillary work, an SE-54 fused silica column is used with splitless injection of sample. (Temperature program; 0°C, 3 min, 3°C/min to 120°C; column: 30M x 0.25 mm, SE-54 wall coating; splitless injection with 0.5 min purge delay). Quantification of the analytes is carried out by the internal standard method with

EC and FI detectors for organohalides and aromatics respectively. Peak areas may be measured by one of several methods, but an electronic integrator is recommended. The detector used should be shown to give a response which is linearly proportional to the concentration of the analyte in the range of concentrations measured.

### **Effect of Matrix Variables**

Extraction efficiencies at the 20:1 water to solvent ratio are in excess of the 60% recovery minimum recommended as good laboratory practice. Table 1 shows values for nine organohalides using a drinking water matrix. Detailed studies have shown that extraction efficiencies are affected by added sodium chloride only at salt concentrations above 0.5M (Table 2). Methanol and sodium sulfite had no observable effect up to concentrations of 1.0% and 126 mg/L respectively; extraction efficiency was invariant from pH 4 to 10.

### **Precision and Accuracy of the Method**

Table 3 shows data which illustrate typical precision obtained by the method for THM analyses, using isothermal packed column GC/ECD. In other studies, the method has proven to be a speedy and reliable method for THM analysis.

There is considerably less experience available for judging the precision of the capillary GC method with temperature programming. Table 4 shows results of replicate analyses of solutions near the detection limit for each of 11 organohalides. These data show the capillary GC/ECD procedure including the extraction step has a precision of approximately 20%. Average values of S.D., the standard deviation of replicate analyses, was 19% with a range of 5% (o-dichlorobenzene at 9.68  $\mu$ g/L to 44% tetrachloroethylene at 0.20  $\mu$ g/L). Variances, defined as the absolute value of the spiked value minus the mean of measured values (on a percentage basis), averaged 10% with a range of 0% (carbon tetrachloride at 0.16  $\mu$ g/L) to 27% dibromochloromethane at 1.08  $\mu$ g/L). Given the fact that these data are near the detection limit, one presumes the precision and accuracy of the method would be superior at higher concentration values.

Another measure of the precision and accuracy of the capillary GC/LLE method may be obtained from the results of an EPA Quality Control Check (WP 1278). Table shows the data obtained for this check which consisted of two blind checks

**Table 1. LLE Extraction Efficiencies (20:1) Of Nine Volatile Halides From Denton Tap Water<sup>a</sup>**

Compound	Blank <sup>b</sup> (ppb)	Spike Concentration (ppb)	N <sup>c</sup>	Average Efficiency (%)
Chloroform	22 48	19 90	4	72 ± 2
			3	71.0 ± 0.4
			Weighted Average <sup>d</sup>	
1,1,1-Trichloroethane		10 49	4	80.3 ± 0.6
			3	91.4 ± 0.6
			Weighted Average	
Carbon tetrachloride	0.1 0.3	10 50	4	85.8 ± 0.6
			3	83.6 ± 0.5
			Weighted Average	
1,2-Dichloroethane		400 1890	4	62 ± 3
			3	73 ± 1
			Weighted Average	
Trichloroethylene		16 71	4	80.2 ± 0.8
			3	94.0 ± 0.5
			Weighted Average	
Bromodichloromethane	20 33	20 90	4	89.2 ± 0.7
			3	63 ± 2
			Weighted Average	
Tetrachloroethylene	0.5 0.4	23 105	4	73 ± 2
			3	84 ± 4
			Weighted Average	
Dibromochloromethane	15 22	21 98	4	84 ± 4
			3	61 ± 4
			Weighted Average	
Bromoform	1.6 3.1	12 58	4	78 ± 3
			3	70 ± 5
			Weighted Average	

<sup>a</sup>Determined on the HP 5840A with the mixed phase column vs. pentane standards.

<sup>b</sup>Unpurged tap water with pH of 7.0 to 7.6 and conductivity of 435 to 460 micromhos/cm.

<sup>c</sup>Number of replicate extractions at each spike level.

<sup>d</sup>Each individual mean was weighted inversely proportional to its variance.

**Table 2. Effect Of Ionic Strength Variations Upon Denton Tap Water Spiked With Five Volatiles\***

Ionic Strength**	(pH = 5.8)				
	CHCl <sub>3</sub> †	CHBrCl <sub>2</sub> †	CHBr <sub>2</sub> Cl†	C <sub>2</sub> Cl <sub>4</sub> †	CHBr <sub>2</sub> †
0.1	582.2	2420	2192	3348	829.6
	555.5	2326	2104	3159	797.2
	633.5	2657	2409	3680	915.4
	Avg. s	590.4 ±46	2468 ±200	2235 ±180	3396 ±310
0.5	532.2	2203	1990	2936	754.4
	631.9	2637	2383	3506	902.4
	548.7	2302	2068	3086	779.0
	Avg. s	571.0 ±59	2381 ±260	2147 ±230	3176 ±340
1.0	666.6	2759	2495	3703	946.2
	724.0	2991	2699	4051	1024.0
	554.0	2319	2075	2991	779.0
	Avg. s	648.2 ±100	2690 ±400	2423 ±370	3583 ±630

†Data in integrator counts x 10<sup>3</sup>.

\*Concentration of 40µg/L spiked into unpurged water.

\*\*NaCl added to yield this ionic strength, neglecting natural ionic strength.

different concentration levels. Concentration values are reported as determined by the internal standard method with 1,2-dichlorobutane as the internal standard. The following solvent blank values were subtracted from the observed concentrations: CHCl<sub>3</sub> (0.84 µg/L); 1,1,1-trichloroethane (0.08 µg/L); 1,2-dichloroethane (3.4 µg/L); carbon tetrachloride (0.01 µg/L); tetrachloroethylene (0.04 µg/L).

As expected, the accuracy of the method for 1,2-dichloroethane was poor, and the compound could not be verified at the 1.5 µg/L level. The variance for bromoform at the 10.4 µg/L is also higher than one would prefer. However, for all other cases, the accuracy of the method is quite acceptable. In all cases the precision of duplicate runs was within ± 10%.

### Method Detection Limit (MDL)

Detection limits for the LLE method with FSOT capillary GC/ECD are shown in Table 6. Values in µg/L for aromatic hydrocarbons using GC/FID are as follows: benzene (16); toluene (32); ethyl benzene (19); p- or m-xylene (23)\*; o-xylene or styrene (26)\*; and 1,2-dichlorobenzene (39).

These values were determined by the procedure recommended by EPA/EMSL as reported by Glaser *et al.* which defines MDL's in terms of a test that the data show values greater than zero at the 99% confidence level.

### Analysis of Samples of Drinking Water

In the latter stages of this study, five samples were obtained from the EPA project officer for analysis by the LLE method. Results of this study are shown in Table 6.

The samples were extracted by the 20:1 n-pentane method and analyzed by FSOT capillary GC with SE-54 column. Both EC and FI detectors were used; however, no evidence of aromatic hydrocarbons was observed from the LLE analysis.

Also in Table 6, concentrations are tabulated for those compounds identified by the HP 5840A data system as having retention times within a window ± 5% of the calibrated value. Solvent blank values were subtracted from the measured concentration values, and no data were reported if the observed value was below the MDL.

Table 6 goes on to list concentrations of the organohalides measured with Hewlett-Packard 7675A Purge and Trap (P/T)

\*Unresolved using the SE-54 column and temperature program conditions described above.

Module, using the EC detector. The P/T procedure is inherently more sensitive than the LLE method, and combined with the <sup>63</sup>Ni detector, P/T is a powerfully sensitive method for organohalides. Studies of the P/T: ECD combination show that the linear range for the organohalides is quite limited. Therefore, in the analysis of the samples listed in Table 6, dilution of the water samples was required. By necessity, this is a trial and error procedure which is time consuming and which leads to larger uncertainties than the usual P/T: Hall method.

Table 6 shows reasonably good agreement between the P/T and LLE methods with some notable irregularities. The trichloroethylene values for sample 0880-35-09 are badly out of agreement, and there are other similar cases involving bromoform and tetrachloroethylene.

### Conclusions

The pentane LLE method may be used with confidence for the analysis of THM's and certain organohalides and aromatic compounds. Precision is generally better than  $\pm 20\%$ , and check samples show an acceptable accuracy in most cases. For

compounds which do not have a higher electron capture sensitivity, the MDL's are high ( $>5 \mu\text{g/L}$ ). The MDL for chloroform is limited by the blank values in pentane and in water used to prepare calibration standards. The method is not recommended for very volatile compounds such as vinyl chloride, but with minor modifications it can be used for less volatile compounds such as chlorinated benzenes. When complex mixtures are suspected, the method must be used with capillary GC techniques which requires more precision on the part of the analyst. Comparison of the method with the Hewlett-Packard 7675A P/T module usually gave similar values for nine organohalides in drinking water samples from six U.S. sources.

**Table 3.** Precision Of LLE Method For Trihalomethanes In Actual Water Samples<sup>a</sup>

	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
<i>Texas and Louisiana Cities Waters<sup>b</sup></i>				
Conc. Range (ppb)	0.7 to 56	0.16 to 40	1.7 to 22	0.65 to 2.0
Median RSD (%)	7.4	14	12	21
N <sup>c</sup>	8	6	4	4
<i>Denton, Texas Water</i>				
Conc. Range (ppb)	4 to 90	2 to 50	2 to 25	1.5 to 2.4
Median RSD (%)	7.8	5.7	10	10
N <sup>c</sup>	8	8	8	4

<sup>a</sup>Analyzed on the 12.5% squalane column isothermally at 80° with internal standard, 1,2-dibromoethane.

<sup>b</sup>Drinking and other water samples from eight cities in Texas and Louisiana.

<sup>c</sup>Number of pairs of samples analyzed.

**Table 4.** Variance and Precision Of Replicate Capillary GC Analysis of Spiked Standards of Organohalides In Water

Compound	Low Concentration Range					Upper Concentration Range				
	N	Si	Sm	S.D.%	V%	N	Si	Sm	S.D.%	V%
Chloroform	7	2.76	2.53	7	8	8	5.52	5.36	18	3
1,1,1-Trichloroethane	7	0.35	0.32	16	9	9	0.70	0.74	28	5
1,2-Dichloroethane	7	0.57	0.53	9	7	9	1.14	1.24	12	9
Carbon Tetrachloride	7	0.16	0.16	31	0	10	0.32	0.37	27	16
Trichloroethylene	6	0.40	0.39	23	3	10	0.80	0.82	26	3
Bromodichloromethane	6	0.46	0.47	6	2	9	0.92	1.08	19	17
1,1,2-Trichloroethane	—	0.57	nm	nm	nm	9	1.14	1.19	18	4
Dibromochloromethane	5	0.54	0.59	8	9	9	1.08	1.37	19	27
Tetrachloroethylene	6	0.20	0.18	44	10	9	0.40	0.47	15	18
Bromoform	7	0.40	0.53	25	18	9	0.80	0.98	20	22
o-Dichlorobenzene	nm	4.84	nm	nm	nm	4	9.68	10.01	5	3

N: number of replicate analyses; Si: spiked concentration ( $\mu\text{g/L}$ ); Sm: measured value (mean of N determinations with GC data system calibrated at Si); S.D.: standard deviation, %;  $V = \frac{Sm - Si}{Si} \times 100$ ; S.D.V.: standard deviation of variance, %; nm: not measureable at this concentration.

**Table 5.** Analysis of EPA Quality Control Check Sample #WP 1278 by the Pentane LLE Method With FSOT Capillary GC Analysis

	$\mu\text{g/L}$							
	Sample No. 1				Sample No. 2			
	EPA Value	Sm	% Dev.	% Var.	EPA Value	Sm	% Dev.	% Var.
1,2-Dichloroethane	1.5	b	—	—	20.0	13.6	4	32
Chloroform	11.0	11.0	10	0	45.6	51.2	7	12
1,1,1-Trichloroethane	1.1	0.9	12	18	14.0	12.3	6	12
Trichloroethylene	2.6	2.5	1	4	13.0	12.9	3	0.8
Carbon Tetrachloride	2.3	2.2	1	4	9.4	9.9	5	5
Tetrachloroethylene	1.1	1.0	5	9	5.6	6.0	2	7
Dibromochloromethane	1.7	1.7	0	0	8.6	10.0	4	16
Chlorodibromomethane	2.4	2.2	5	8	12.0	12.2	3	2
Bromoform	2.8	2.9	1	4	10.4	13.6	8	31

Sm: mean of duplicate runs (separate extractions and analysis); % Dev: percent deviation of duplicate runs; % Var:  $\frac{EPA\ Value - Sm}{EPA\ value} \times 100$ ; b: below blank level [FSOT capillary column with SE-54 phase, 0°C, 3 min; 3°/min 120°C; splitless injection, other conditions in text.]

**Table 6. LLE/Capillary GC and Purge/Trap Analysis of Drinking Water Samples**

Compound	Detection Limit		Blank Value		µg/L									
					0202-13-13		0618-07-02		0737-38-13		0314-16-11		0880-35-09	
	LLE	P/T	LLE	P/T	LLE	P/T	LLE	P/T	LLE	P/T	LLE	P/T	LLE	P/T
Chloroform	2.9	0.4	0.8	0.4	—	—	—	—	—	0.73 ± 0.02	3.6 ± 0.4	4.2	4.7 ± 4	4.7 ± 0.1
1,1,1-Trichloroethane	0.6	0.1	0.08	0.1	1.9 ± 0.1	1.7 ± 0.4	1.7 ± 0.1	2.0 ± 0.06	10.5 ± 0.6	9.0 ± 0.6	—	a	—	0.4 ± 0.03
1,2-Dichloroethane	8	0.05	8	0.05	—	0.25 ± 0.03	1.6 ± 0.1	3.4 ± 0.03	—	0.1 ± 0.02	2.3 ± 0.09	0.45 ± 0.02	2.8 ± 0.2	2.2 ± 0.2
Carbon Tetrachloride	0.3	0.1	0.01	0.1	—	—	—	—	—	—	3.9 ± 0.2	4.0 ± 0.2	—	—
Bromodichloromethane	0.6	0.06	—	0.06	—	—	—	0.16 ± 0.004	1.1 ± 0.1	1.23 ± 0.03	14.0 ± 0.9	11.9 ± 0.1	7.2 ± 0.1	3.0 ± 1
Dibromochloromethane	0.8	0.2	—	0.2	—	—	—	0.7 ± 0.02	3.0 ± 0.3	4.7 ± 0	30.1 ± 1.8	33.3 ± 0.2	6.2 ± 0.4	5.6 ± 0.1
Trichloroethylene	0.6	0.2	—	0.2	4.32 ± 0.03	1.7 ± 0.1	—	0.20 ± 0.01	2.76 ± 0.03	3.5 ± 0.05	—	0.74 ± 0.01	29.7 ± 0.8	4.1 ± 1
Tetrachloroethylene	0.2	0.01	0.04	0.01	0.39 ± 0.02	0.38 ± 0.04	—	0.12 ± 0.02	2.7 ± 0.3	2.9 ± 0.4	1.8 ± 0.5	0.9 ± 0.2	0.28 ± 0.02	1.10 ± 0.05
Bromoform	0.6	0.005	—	0.005	—	—	12.3 ± 0.6	5.7 ± 0.3	3.8 ± 0.3	3.4 ± 0.1	28.1 ± 1.7	16.6 ± 1.6	3.1 ± 0.1	1.0 ± 1
Benzene	—	—	—	—	—	0.89 ± 0.05	—	7.1 ± 0.8	—	1.0 ± 0.1	—	—	—	—
Toluene	—	—	—	—	—	—	—	0.12 ± 0.04	—	0.08 ± 0.001	—	—	—	—
O-Dichlorobenzene	—	—	—	—	—	—	—	0.33 ± 0.02	—	—	—	—	—	—

LLE: 20/L Pentane microextraction with GC/ED or GC/FID, 30 m x 0.25 mm i.d. FSOT/SE-54; 0°, 3 min, 3°/min to 120°  
P/T: 5 mL sample, 10 min He purge at 40 mL/min; desorption, 250°; 0.2% Carbowax 1500 on 80/100 Carbopac, organohalides: column at 60°, 3 min, 8°/min to 130°, ECD; aromatics: column at 130°, 3 min, 15°/min to 160°, FID.

Blank values subtracted. No values reported below detection limits listed in Tables 30 and 31 of the full report

William C. Glaze and C.-C. Lin are with the University of Texas at Dallas, Richardson, TX 75080.

Thomas A. Bellar is the EPA Project Officer (see below).

The complete report, entitled "Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water," (Order No. PB 84-112 937; Cost: \$14.50, subject to change) will be available only from:

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

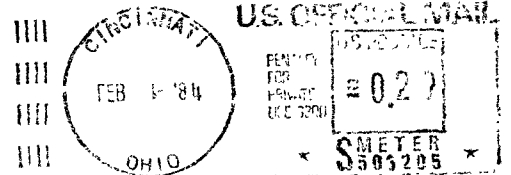
The EPA Project Officer can be contacted at:  
Environmental Monitoring and Support Laboratory  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

---

Official Business  
Penalty for Private Use \$300



PS 0000329  
U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBORN STREET  
CHICAGO IL 60604