Journal of Chromatography, 212 (1981) 187–197
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,812

EVALUATION OF A LIQUID–LIQUID EXTRACTION TECHNIQUE FOR WATER POLLUTANTS

REIN OTSON* and DAVID T. WILLIAMS
Bureau of Chemical Hazards, Environmental Health Directorate, Health Protection Branch, Health and Welfare Canada, Environmental Health Centre, Tunney's Pasture, Ottawa, Ontario K1A 0L2 (Canada)
(Received March 20th, 1981)

SUMMARY

A simple liquid–liquid extraction technique was evaluated and judged to be useful for semiquantitative determination of 37 organic pollutants present in water at concentrations of 50 μg/l or better. Gas chromatographic analysis of hexane extracts showed detection limits of $\leqslant 5$ μg/l for 30 compounds, recoveries of $\geqslant 80\%$ for 20 compounds and, generally, peak area precision of better than $\pm 5\%$ for triplicate sample analyses. Storage of aqueous standard solutions at 4°C for 4 weeks did not significantly affect recovery values.

INTRODUCTION

A wide range of organic compounds has been found in potable water supplies[1–4] and there is concern that ingestion of water containing these compounds may pose a potential hazard to human health. To aid in the health hazard assessment, Canadian potable water supplies have been surveyed[5–7] for the occurrence of selected organic contaminants. An analytical method for the determination of semi-volatile organic compounds ranging in boiling point up to 200°C was required to complement the head space and XAD-2 macroreticular resin analytical techniques which were used for these surveys. As part of its master scheme for the analysis of 114 organic priority pollutants[8], the U.S. Environmental Protection Agency has proposed a number of methods utilizing liquid–liquid extraction (LLE) as the first step of the analytical procedure. Water samples are extracted three times with methylene chloride and the combined extracts are reduced to a small volume while the solvent is changed to hexane. Simple, one step, liquid–liquid extraction methods employing pentane[9–11], hexane[9,12–14], isooctane[9,11], methylcyclohexane[9,15], cyclohexane–diethyl ether[16] and benzene–hexane[17] as the extractant have been reported for the determination of trihalomethanes and a few other organics. We now report the evaluation of a single step, LLE method of analysis for a representative group of 41 semi-volatile organic pollutants. The compounds investigated have either been listed as compounds of concern[8,18] or have been found in potable water supplies[1–4].

0021-9673/81/0000–0000/$02.50

EXPERIMENTAL

Equipment

All analyses were performed on a Hewlett-Packard Model 5840 gas chromatograph equipped with a ^{63}Ni electron-capture detector (ECD), a flame ionization detector (FID) and a Tracor Model 310 Hall electrolytic conductivity detector (HElCD). The signal from the HElCD was processed by a Spectra-Physics 4000 chromatography data system. The HElCD was operated in the chloride mode with the furnace temperature at 840°C, a hydrogen flow-rate of 10 ml/min and a 2-propanol–water (50:50, v/v) electrolytic solvent flow-rate of 0.2 ml/min. The ECD and FID were held at 300°C and hydrogen and air flow-rates respectively for the flame were 20 ml/min and 250 ml/min. Columns were attached to a Hewlett-Packard capillary column inlet system, held at 180°C and operated in the splitless mode. An inlet nitrogen gas purge at 75 ml/min was initiated 0.25 min after each injection for FID analyses. Nitrogen passed through Oxiclear and molecular sieve traps was used as column carrier, inlet purge and detector makeup gases. Makeup gas flows of about 25 ml/min were used for the FID and ECD. A Varian Model 8020 autosampler was interfaced with the gas chromatograph and injected 4-μl sample aliquots for FID and 2-μl sample aliquots for ECD and HElCD analyses.

The GC columns and conditions were:

(i) an OV-17 support-coated open tubular (SCOT) stainless-steel column (15 m × 0.5 mm I.D.) with a carrier gas flow of about 4 ml/min. After each injection the column temperature was maintained at 60°C for 3 min and was then raised at a rate of 8°C/min to 150°C where it was maintained 18 min before the oven was cooled;

(ii) a nickel column (1.8 m × 2 mm I.D.) packed with 0.1% SP-1000 on Carbopack C (80–100 mesh), and with a carrier gas flow-rate of about 20 ml/min. After each injection the column temperature was maintained at 100°C for 3 min and was then raised at a rate of 15°C/min to 220°C where it was maintained for 28 min before the oven was cooled.

Confirmatory analyses were performed on a Model 4000 Finnigan mass spectrometer–gas chromatograph coupled with a Model 6000 data system and utilizing a glass column (1.8 m × 2 mm I.D.) packed with 3% OV-17 on Gas-Chrom Q (100–120 mesh). A Burrell Model 75 wrist action shaker set at 3° was used for mechanical agitation of containers during solvent extraction procedures. A Brinkmann 5-ml capacity Dispensette was used to deliver hexane aliquots with a precision of better than ±0.1%. Culture tubes (capacity 32 ml), amber glass bottles (capacities 120, 500, 1000 and 4000 ml), autosampler vials (capacity 2 ml) and other glass containers were heated at 400°C for several hours, cooled to about 50°C and then sealed with PTFE-coated silicon disks and screw caps with centered holes.

Reagents

Purified water (pH 5.9) was prepared by irradiating distilled, deionized water for 5 h at 254 nm in a 5-l capacity vessel[19]. Stock tap-water (pH 8.7) was allowed to stand 2 days in an open container before use. The purity of all organic compounds was determined by analysis of hexane solutions on at least two chromatographic systems.

Primary standard solutions in methanol (25.0 ml) and containing 0.20 g/l of the

compounds listed in Table I were prepared in sealed culture tubes. Such primary standard solutions containing one compound only (single component), a group of compounds (groups A, B, C, D, E, F, G and H) and all compounds (multicomponent, groups A–H) were used to prepare corresponding aqueous standard solutions and standard solutions in hexane. Aqueous standard solutions containing 1, 5, 20 and 100 μg/l of each compound in water were prepared in sealed glass bottles or a volumetric flask. Standard solutions containing 0.01, 0.04, 0.20, 0.80 and 4.0 mg/l of each compound in hexane were prepared in sealed culture tubes. All aqueous solutions were prepared in bottles containing thiosulphate so as to provide 8.3 mg $Na_2S_2O_3 \cdot 5\ H_2O$ per 100 ml aqueous solution.

Procedures

Appropriate blanks were prepared and analyzed during all tests. Duplicate samples (two bottles) were used during exploratory tests and triplicate samples were used for recovery tests. Single component solutions in hexane were used for peak identification during chromatographic analyses and, where necessary, gas chromatography–mass spectrometry (GC–MS) was applied for confirmation. Multicomponent aqueous standard solutions and the OV-17 SCOT column with the ECD were used for the exploratory tests.

Choice of extraction solvent. A 5-ml aliquot of the aqueous solution (20 μg/l, in purified water) was removed from each full, 120-ml capacity, bottle and a 3-ml aliquot of pentane, hexane, hexane saturated with methanol, 15% (v/v) acetone in hexane, isooctane or benzene was added to the bottle. Extractions were completed by shaking the bottles for 30 min, storing them for 3 days at 25°C and transferring the organic phase into autosampler vials.

Hexane–water ratio. A portion (4, 7, 7 and 15 ml respectively) of the aqueous solution (1 μg/l, in purified water) in full 120, 500, 1000 or 4000 ml capacity bottles was removed from and a measured volume (3, 5, 5 and 10 ml respectively) of hexane was added to each bottle. Extractions were completed by the foregoing procedure.

Extraction technique. Aqueous standard solutions (5 μg/l, in tap-water) were prepared in 120-ml capacity bottles and in a 2-l volumetric flask. Within 24 h of preparation the solution in the volumetric flask was distributed into 120-ml capacity bottles. The full bottles were stored 0, 24 or 72 h before a 5-ml aliquot of the aqueous solution was withdrawn from and a 3-ml aliquot of hexane was added to each container. Extractions were completed by shaking the bottles for 1, 4 or 24 h, storing them for 0, 24 or 72 h and then transferring the organic phase into autosampler vials. Selected containers were drained and the inner walls were rinsed with measured volumes of hexane which were subsequently analyzed.

Storage effect. Aqueous standard solutions (20 μg/l, in pure water) were prepared in six, 120-ml capacity, bottles. Three bottles were stored 24 h at 25°C before a 5-ml aliquot of the aqueous solution was removed from, and a 3-ml portion of hexane was added to each bottle. Extraction was completed by shaking each bottle for 24 h, storing it for 24 h and transferring the organic phase for analysis in an autosampler vial. The remaining three bottles were stored at 4°C for 4 weeks and stored at 25°C for 24 h before extraction and analysis of the extracts.

Recovery studies. Aqueous solutions, each containing a group of compounds at concentration levels of 1, 5, 20 or 100 μg/l in pure water were prepared and extracted

in 120-ml capacity bottles for recovery studies utilizing the OV-17 SCOT column. Solutions containing groups A + B + C, groups D + E + F, group H + chloroform + trichloroethylene + 1,1,1-trichloroethane or group G + isophorone at the 20-μg/l concentration level only were prepared in both pure and tap-water in 120-ml capacity bottles for recovery studies utilizing the 0.1 % SP-1000 column. Extractions were conducted as described for the storage effect test.

Quantitative determination. Calibration curves were constructed by plotting concentration against peak area obtained for analyses of standard solutions in hexane. Percent recovery of an extracted compound was determined by comparing the mean peak area from analyses of extracts from triplicate solutions with the calibration curve peak area corresponding to the concentration calculated from 100% recovery of the compound in the organic layer. In some instances peak height was used for quantitation. Detection limits were estimated from the results of recovery studies.

RESULTS AND DISCUSSION

Since the FID, ECD and HElCD were used for compound identification, the choice of extractant was limited to those solvents which were compatible for use with all three detectors. Six solvent systems were evaluated for extraction of the compounds in groups A–H (Table I). It was found that their extraction efficiency decreased in the order pentane $\geqslant$ hexane $>$ hexane saturated with methanol $>$ isooctane $>$ 15% (v/v) acetone in hexane $\geqslant$ benzene, as estimated by comparison of the sum of peak areas. Also, pentane and hexane peaks showed the least interference with standard peaks during gas chromatography. Hexane was selected as the extraction solvent since the volatility of pentane makes it difficult to handle, particularly when it is used with an automatic injector[13].

Although use of larger sample bottles permitted an increase in the water–hexane volume ratio and, hence, an increased compound concentration in the hexane extract, it was considered that the 120-ml capacity bottles would be most convenient for shipping, storage and extraction of large numbers of survey samples. Also, extractions utilizing the latter containers allowed detection on the ECD of many compounds when present in water at a concentration of 1 μg/l. In order to minimize the number of manipulations and the loss of analyte, the hexane extraction was conducted in the sample bottle. Removal of 5 ml of water from the sample bottle and addition of 3 ml hexane allowed adequate mixing of the liquid phases, easy removal of the hexane for subsequent GC analysis and a potential concentration factor of 115/3.

A variety of short-term storage conditions and extraction procedures were investigated for fortified (5 μg/l) water samples and some results are shown in Table II. Percent recoveries obtained for extractions conducted with 4-h and 24-h agitation periods were essentially the same for any particular compound, whereas only 1 h of agitation resulted in considerably lower recoveries. Storage of contents after 24 h of agitation did not significantly change recovery values. With the exception of the 1,1,2,2-tetrachloroethane results, percent recovery values for any particular compound were essentially the same, whether tap-water was spiked directly in the extraction vessel or in a volumetric flask from which the solution was distributed into

TABLE I

COMPOUNDS INVESTIGATED

Formula	*Compound*	*Formula*	*Compound*
Group A		*Group F*	
C_6H_6	Benzene	$C_{10}H_8$	Naphthalene
$C_6H_5CH_3$	Toluene	$(CH_3CH_2CH_2)_2NNO$	N-Nitrosodi-*n*-propylamine
$C_6H_5C_2H_5$	Ethylbenzene	$(CH_3)_2NNO$	N-Nitrosodimethylamine
o-$C_6H_4(CH_3)_2$	*o*-Xylene	$CH_2ClCH_2OCHCH_2$	2-Chloroethyl vinyl ether
m-$C_6H_4(CH_3)_2$	*m*-Xylene	$CCl_2CClCClCCl_2$	Hexachlorobutadiene
p-$C_6H_4(CH_3)_2$	*p*-Xylene		
		Group G	
Group B		C_6H_5OH	Phenol
C_6H_5Cl	Chlorobenzene	2-ClC_6H_4OH	2-Chlorophenol
o-$C_6H_4Cl_2$	*o*-Dichlorobenzene	2,4-$Cl_2C_6H_3OH$	2,4-Dichlorophenol
p-$C_6H_4Cl_2$	*p*-Dichlorobenzene	2,4,6-$Cl_3C_6H_2OH$	2,4,6-Trichlorophenol
1,2,4-$C_6H_3Cl_3$	1,2,4-Trichlorobenzene		
$C_6H_5NO_2$	Nitrobenzene	*Group H*	
		$(CH_2ClCH_2)_2O$	Bis(2-chloroethyl) ether
Group C		$(CH_2Cl)_2O$	Bis(chloromethyl) ether
CCl_2CCl_2	Tetrachloroethylene		
$CHCl_2CH_2Cl$	1,1,2-Trichloroethane	*Other*	
$CHCl_2CHCl_2$	1,1,2,2-Tetrachloroethane	CH_2Cl_2	Dichloromethane
CCl_3CCl_3	Hexachloroethane	$CHCl_2CH_3$	1,1-Dichloroethane
		CCl_3CH_3	1,1,1-Trichloroethane
Group D		$CHCl_3$	Chloroform
$CH_2ClCHClCH_3$	1,2-Dichloropropane	CH_2ClCH_2Cl	1,2-Dichloroethane
$CH_2ClCHCHCl$	1,3-Dichloropropene	CCl_2CHCl	Trichloroethylene
$CHCl_2CClCHCl$	1,2,3,3-Tetrachloropropene	$C_9H_{14}O$	Isophorone
$CCl_2CClCHCl_2$	1,1,2,3,3-Pentachloropropene	2-$ClC_{10}H_7$	2-Chloronaphthalene
Group E			
$CHBr_2Cl$	Chlorodibromomethane		
$CHBr_3$	Bromoform		
C_5Cl_6	Hexachlorocyclopentadiene		

extraction vessels. This indicated that sorption of the detected compounds onto glass walls of a flask containing an aqueous standard solution was negligible. Since rinses of used extraction vessels and the empty stock solution flask were shown to be devoid of tested compounds, significant retention of these organics on container walls is unlikely. The relatively low recovery of 1,1,2,2-tetrachloroethane from aqueous solutions prepared in the extraction vessel as compared to recovery from the stock solution distributed into the extraction vessel could not be explained. For the chosen extraction technique, *i.e.*, 24-h agitation followed by 24-h storage, precision of peak area values from duplicate sample analyses were usually within $\pm 5\%$ of the mean peak area value.

Since survey samples may be stored for some time before analysis, the effect of sample storage on recovery values was investigated. Table III reports the effect of storage on recovery values for fortified (20 μg/l) water samples stored for either 1 day at 25°C or 4 weeks at 4°C. Percent recoveries for the two sets of samples were

TABLE II

EVALUATION OF HEXANE EXTRACTION PROCEDURE

Duplicate sample extracts analyzed on OV-17 SCOT column and ECD.

Treatment details	*Time (h)*						
Stored	24*	24*	72*	24	24	24	24
Agitated	1	24	24	1	4	24	24
Stored	24	24	24	24	24	24	72
Compound	*Recovery (%)*						
$CH_2ClCHCHCl$	50	59	50	44	56	52	51
$CCl_2CCl_2 + CHCl_2CH_2Cl$	75	82	86	56	78	78	76
$CHBr_2Cl$	58	72	78	59	76	75	74
$CHBr_3$	48	63	68	51	70	68	69
$CHCl_2CHCl_2$	36	48	42	45	63	63	64
$CHCl_2CClCHCl$	42	62	66	40	65	66	65
p-$C_6H_4Cl_2$	28	44	53	24	43	49	50
$CCl_3CCl_3 + o$-$C_6H_4Cl_2 + CHCl_2CClCHCl$	47	69	75	45	69	70	68
$CCl_2CClCHCl_2$	50	73	76	48	72	74	72
1,2,4-$C_6H_3Cl_3 + CCl_2CClCClCCl_2$	45	68	73	43	69	68	67

* Fortified in bottle.

TABLE III

EFFECT OF STORAGE ON RECOVERY

Hexane extracts analyzed on OV-17 SCOT column and ECD.

Compound	*24 h storage (25°C)**		*4 weeks storage (4°C)**	
	Recovery (%)	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*
$CH_2ClCHCHCl$	64	5.9	56	7.1
$CCl_2CCl_2 + CHCl_2CH_2Cl$	77	2.2	102	10.1
$CHBr_2Cl$	74	1.8	80	8.4
$CHBr_3$	70	1.3	73	7.3
$CHCl_2CHCl_2$	70	2.9	50	1.2
$CHCl_2CClCHCl$	74	2.4	63	9.3
$CCl_3CCl_3 + o$-$C_6H_4Cl_2 + CHCl_2CClCHCl$	89	1.3	91	4.8
$CCl_2CClCHCl_2$	76	2.8	80	12.0
1,2,4-$C_6H_3Cl_3 + CCl_2CClCClCCl_2$	88	0.8	83	13.7

* Three bottles.

generally in good agreement, thus indicating that storage at 4°C maintains the integrity of the water sample. It has previously been shown that bottled water samples may be stored for at least a few weeks without a significant change in trihalomethane[20] or total organic carbon[21] values.

TABLE IV

RETENTION TIMES AND DETECTION LIMITS FROM HEXANE EXTRACT ANALYSES OF 41 AQUEOUS POLLUTANTS

Retention times are relative to injection time. Detection limits refer to the concentration of compounds in purified water which gave clearly defined peaks upon analysis of the hexane extract. ND = Not detected at ≤ 100 μg/l; NA = not analyzed.

Compound	*OV-17 SCOT column*				*0.1% SP-1000 column*		
	Retention time (min)	*Detection limit (μg/l)*			*Retention time (min)*	*Detection limit (μg/l)*	
		FID	*ECD*	*HElCD*		*FID*	*ECD*
CH_2Cl_2	2.2	ND*	ND*	<1	–	ND	ND
$CHCl_2CH_3$	2.4	ND*	ND*	<1	–	ND	ND
$CHCl_3$	3.2	ND*	<1	<1	1.4	ND*	<1
CCl_3CH_3	3.6	ND*	<1	10	2.0	ND*	<1
CH_2ClCH_2Cl	4.0	ND*	20	2	–	ND	ND
CCl_2CHCl	4.6	ND*	<1	2	3.9	ND*	2
C_6H_6	–	ND	ND	ND	–	ND	ND
$CH_2ClCHClCH_3$	5.0	50	5	5	3.1	ND*	20
$C_6H_5CH_3$	5.3	5	ND	ND	8.6	5	ND
$CH_2ClCH_2OCHCH_2$	5.3	50	ND	NA	–	ND*	–
CCl_2CCl_2	5.8	10	<1	5	7.8	ND*	<1
$CH_2ClCHCHCl$	5.9	20	5	5	3.4, 4.4**	ND*	5
$CHCl_2CH_2Cl$	6.0	20	<1	<1	4.4	ND*	10
$CHBr_2Cl$	6.4	50	<1	<1	4.5	ND*	<1
C_6H_5Cl	7.6	5	ND	1	9.0	10	ND
$C_6H_5(C_2H_5)$	7.6	2	ND	ND	10.3	5	ND
m-$C_6H_4(CH_3)_2$	7.7	2	ND	ND	11.6	5	ND
p-$C_6H_4(CH_3)_2$	7.7	2	ND	ND	11.9	5	ND
o-$C_6H_4(CH_3)_2$	8.4	2	ND	ND	11.9	5	ND
$CHBr_3$	8.9	50	<1	1	6.1	ND*	<1
$CHCl_2CHCl_2$	9.6	5	<1	<1	7.4	ND*	<1
p-$C_6H_4Cl_2$	11.4	2	5	<1	13.7	10	2
$(CH_2ClCH_2)_2O$	11.9	20	ND	1	9.5	20	20
CCl_3CCl_3	12.0	10	<1	<1	9.0	ND	1
o-$C_6H_4Cl_2$	12.1	2	5	<1	13.7	10	2
$CHCl_2CClCHCl$	12.1, 10.5**	10	<1	1	9.6, 8.8**	50	1
$CCl_2CClCHCl_2$	12.5	10	<1	<1	11.7, 12.5**	ND	5
$C_6H_5NC_2$	14.5	5	20	ND	12.8	10	5
$CCl_2CClCClCCl_2$	14.6	5	<1	NA	12.3	50	1
1,2,4-$C_6H_3Cl_3$	14.8	2	<1	<1	26.7	10	5
$C_{10}H_8$	15.5	2	ND	ND	34.8	20	ND
$(CH_3)_2NNO$	–	ND	ND	NA	9.1	50	ND
$(CH_3CH_2CH_2)_2NNO$	–	ND	ND	NA	11.7	50	ND
C_6H_5OH	–	ND	ND	ND	9.7	10	ND
2-ClC_6H_4OH	–	ND	ND	ND	11.5	20	20
2,4-$Cl_2C_6H_3OH$	–	ND	ND	ND	21.0	20	5
2,4,6-$Cl_3C_6H_2OH$	–	ND	ND	ND	56.4	ND	10
$C_9H_{14}O$	17.9	ND	ND	ND	14.5	10	20
C_5Cl_6	–	ND	ND	ND	–	ND	ND
$(CH_2Cl)_2O$	–	ND	ND	ND	9.0	ND	ND
2-$ClC_{10}H_7$	21.3	ND	ND	ND	–	ND	ND

* Interference by hexane peak.

** Two peaks; major peak listed first.

TABLE V

PERCENT RECOVERY AND R.S.D. OBTAINED FOR HEXANE EXTRACTION OF AQUEOUS STANDARD SOLUTIONS

Italicized values were obtained on the SP-1000 column and are listed only for instances when corresponding OV-17 SCOT column results were not available. Results were calculated for triplicate sample analyses. NA = Not analyzed; D = detected but not quantitated. Values obtained from peak height measurements are given in square brackets.

Compound	*Detector*	*1 μg/l*		*5 μg/l*		*20 μg/l*		*100 μg/l*	
		Recovery (%)	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*
$CHCl_3$	ECD	NA	–	NA	–	*83*	3.3	NA	–
CCl_3CH_3	ECD	NA	–	NA	–	*91*	4.5	NA	–
CCl_2CHCl	ECD	NA	–	NA	–	*94*	5.3	NA	–
$CH_2ClCHClCH_3$	FID	–	–	–	–	–	–	36	16
	ECD	–	–	–	–	D	–	84	3.2
$C_6H_5CH_3$	FID	–	–	D	–	[83]	1.2	D	–
$CH_2ClCH_2OCHCH_2$	FID	–	–	–	–	–	–	[29]	12
CCl_2CCl_2	FID	–	–	D	–	D	–	[88]	1.8
	ECD	D	–	D	–	*78*	1.7	D	–
$CH_2ClCHCHCl$	FID	–	–	–	–	–	–	35	2.7
	ECD	–	–	–	–	43	9.9	41	2.4
$CHCl_2CH_2Cl$	FID	–	–	–	–	D	–	57	5.1
	ECD	D	–	D	–	*60*	25	D	–
$CHBr_2Cl$	FID	–	–	–	–	–	–	[90]	5.3
	ECD	D	–	68	3.1	70	1.9	80	0.5

C_6H_5Cl	FID	–	–	D	–	[91]	2.1	[94]	1.9
$C_6H_5C_2H_5$	FID	–	–	80	5.2	83 [85]	2.3, 2.3	81	1.4
m-$C_6H_4(CH_3)_2$ / p-$C_6H_4(CH_3)_2$	FID	–	–	85	1.7	85 [84]	2.2, 1.6	78	1.4
o-$C_6H_4(CH_3)_2$	FID	–	–	93	8.1	96 [85]	5.9, 1.5	80	1.3
$CHBr_3$	FID	–	–	–	–	–	–	29 [90]	12, 5.3
	ECD	30	1.0	70	3.0	77	2.4	68	1.6
$CHCl_2CHCl_2$	FID	–	–	–	–	49	4.4	68 [70]	2.3, 2.0
	ECD	75	36	70 [75]	3.6, 2.7	86	22	69	0.2
p-$C_6H_4Cl_2$	FID	–	–	99	7.0	89 [86]	1.7, 0.9	91 [92]	1.5, 2.2
	ECD	–	–	–	–	79 [93]	22, 4.7	92 [100]	2.4, 1.8
o-$C_6H_4Cl_2$	FID	–	–	77	18	94 [85]	4.3, 2.6	90 [92]	1.3, 2.8
	ECD	–	–	–	–	88 [92]	17, 6.9	94	2.3
$(CH_2ClCH_2)_2O$	FID	–	–	–	–	–		[16]	4.8
CCl_3CCl_3	FID	–	–	–	–	89	3.7	84 [87]	0.8, 1.5
	ECD	103	38	90	3.1	97	4.7	94	0.4
$CHCl_2CClCHCl$	FID	–	–	–	–	69	3.7	82 [84]	0.6, 2.3
	ECD	96	11	39	24	70	2.3	87	1.4
$CCl_2CClCHCl_2$	FID	–	–	–	–	72	5.3	92 [90]	5.2, 2.7
	ECD	102	9.0	46	18	82	2.0	90	1.4
1,2,4-$C_6H_3Cl_3$	FID	–	–	87	48	87 [90]	5.7, 2.6	85 [95]	6.0, 2.4
	ECD	76	16	86	21	94	13	93	2.1
$C_{10}H_8$	FID	–	–	54	14	69 [75]	0.9, 0.5	69	1.0
2,4-$Cl_2C_6H_3OH$	ECD	–	–	–	–	*20*	11	–	–
2,4,6-$Cl_3C_6H_2OH$	ECD	–	–	–	–	*18*	4.7	–	–
$C_6H_5NO_2$	FID	–	–	D	–	39 [40]	2.5, 4.7	36 [37]	6.1, 5.0
	ECD	–	–	–	–	*27*	0.7	38	31
$CCl_2CClCClCCl_2$	FID	–	–	D	–	68 [86]	6.1, 2.2	81	5.2
	ECD	133	21	93	2.7	97	1.7	99	1.9

Results listed in Table IV show that a detection limit of $\leqslant 5$ μg/l was obtained for many of the compounds in fortified water. Blank analysis results generally showed no significant interfering peaks for purified water. Percent recoveries obtained for hexane extraction of aqueous standard solutions fortified at 1, 5, 20 and 100 μg/l are reported in Table V for those compounds whose detection limit (FID or ECD) was below 100 μg/l. Benzene could not be quantitated since it coeluted with hexane on the GC columns. Hexachlorocyclopentadiene which is believed to degrade quickly in solution[22] could not be quantitated in the aqueous solution or in the hexane extract. Analyses conducted on the 0.1% SP-1000 column generally gave similar recovery values as those reported (Table V) for the OV-17 SCOT column. Recovery values calculated from peak height values were comparable to those calculated from peak areas and were usually more precise (Table V). When all results obtained at well above the detection limit, *i.e.*, usually at 20 and 100 μg/l, and with a precision of $\leqslant 6\%$ R.S.D. were considered, then twenty compounds showed recoveries of $\geqslant 80\%$. For the remaining compounds, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and naphthalene had recoveries of 57–75%, and 2-chloroethyl vinyl ether, bis(2-chloroethyl) ether, 1,3-dichloropropene, nitrobenzene, 2,4-dichlorophenol and 2,4,6-trichlorophenol had recoveries of $\leqslant 41\%$. For compounds which were also extracted from fortified tap-water, the recovery values were similar to those obtained for extractions from purified water.

The variations in recovery values for a particular compound at several concentration levels (Table V) was usually due to inconsistent and/or inaccurate integration of peak areas. This sometimes occurred for analyses at concentrations well above the compound detection limit and when the peak shape appeared to be clearly defined. These difficulties were primarily due to the fact that integration parameters had to be set at the beginning of the automated GC analyses and, therefore, could not be optimized for each sample and compound. This does not appear as a problem in those studies[9–17] where only a small number of compounds were being investigated and integration parameters and GC conditions could easily be optimized. For the 41 compounds investigated in this study GC conditions could not be optimized for each component. Among several columns tested, no single GC column could be found which would resolve all 41 compounds, but the use of two columns, an OV-17 SCOT column and a column packed with 0.1% SP-1000–Carbopack C, did permit resolution of most of the compounds. In addition the use of three different GC detectors also aided in compound identification and quantitation (Table V).

Compound identification and quantitation can be simplified by the use of concentration and fractionation procedures as reported for the U.S.A. priority pollutants master scheme[8] and/or by use of GC–MS. However, these procedures are less amenable for use in large scale surveys or for laboratories lacking the specialized equipment required.

CONCLUSION

The single step LLE procedure, although considered to give quantitative results for studies involving a limited number of compounds, has some limitations when applied to water samples containing large numbers of compounds. Analytical results for the latter type of sample are likely to be semiquantitative and require careful

evaluation. The hexane extraction procedure is, however, very useful as a simple, rapid, screening method which can be applied to complement other methods for the analysis of organic pollutants in potable water.

ACKNOWLEDGEMENTS

Technical assistance by P. D. Bothwell is gratefully acknowledged. We thank F. M. Benoit for GC–MS analyses, M. Malaiyandi and G. L. LeBel for in-house review of the manuscript and J. Ireland for typing the manuscript.

REFERENCES

1 W. M. Shakelford and L. H. Keith, *Frequency of Organic Compounds Identified in Water*, *EPA-600/4-76-062*, U.S. Environmental Protection Agency, Springfield, VA, December 1976.
2 A. W. Garrison, *Ann. N.Y. Acad. Sci.*, 298 (1977) 2.
3 J. A. Cotruvo and C. Wu, *J. Amer. Water Works Assoc.*, 70 (1978) 590.
4 J. M. Symons, T. A. Bellar, J. K. Carswell, J. De Marco, K. L. Kropp, G. G. Robeck, D. R. Seeger, C. J. Slocum, B. L. Smith and A. A. Stevens, *J. Amer. Water Works Assoc.*, 67 (1975) 634.
5 D. T. Williams, R. Otson, P. D. Bothwell, K. L. Murphy and J. L. Robertson, in B. K. Afghan and D. Mackay (Editors), *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*, Plenum, New York, 1980, p. 503.
6 F. M. Benoit, G. L. LeBel and D. T. Williams, *Bull. Environ. Contam. Toxicol.*, 23 (1979) 774.
7 D. T. Williams, F. M. Benoit, E. E. McNeil and R. Otson, *Pest. Monit. J.*, 12 (1978) 163.
8 *Guidelines establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations*, *Fed. Reg.*, 44 (1979) 69464.
9 M. M. Varma, M. R. Siddique, K. T. Doty and A. Machis, *J. Amer. Water Works Assoc.*, 71 (1979) 389.
10 J. E. Henderson, G. R. Peyton and W. H. Glaze, in L. A. Keith (Editor), *Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1976, p. 105.
11 J. J. Richard and G. A. Junk, *J. Amer. Water Works Assoc.*, 69 (1977) 62.
12 J. F. J. Van Rensburg, J. J. Van Huyssten and A. J. Hassett, *Water Res.*, 12 (1978) 127.
13 H. Norin and L. Renberg, *Water Res.*, 14 (1980) 1397.
14 R. Otson, D. T. Williams and P. D. Bothwell, *Environ. Sci. Technol.*, 13 (1979) 936.
15 J. P. Mieure, *J. Amer. Water Works Assoc.*, 69 (1977) 60.
16 G. J. Piet, P. Slingerland, G. H. Bijlsma and C. Morra, in B. K. Afghan and D. Mackay (Editors), *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*, Plenum, New York, 1980, p. 69.
17 A. J. Bergasser and J. F. Colaruotolo, *Anal. Chem.*, 51 (1979) 1588.
18 *Priority Chemicals*, *The Canada Gazette*, Part 1, December 1, 1979, p. 7365.
19 M. Malaiyandi, M. H. Sadar, P. Lee and R. O'Grady, *Water Res.*, 14 (1980) 1131.
20 *National Survey for Halomethanes in Drinking Water*, *77-EHD-9*, Health and Welfare Canada, Ottawa, 1977.
21 R. Otson, D. T. Williams, P. D. Bothwell, R. S. McCullough and R. A. Tate, *Bull. Environ. Contam. Toxicol.*, 23 (1979) 311.
22 F. M. Benoit and D. T. Williams, *Bull. Environ. Contam. Toxicol.*, in press.