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FREON FC-113, AN ALTERNATIVE TO METHYLENE CHLORIDE FOR LIQUID–LIQUID EXTRACTION OF TRACE ORGANICS FROM CHLORINATED DRINKING WATER*

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SUMMARY

Methylene chloride is the U.S. Environmental Protection Agency solvent of choice for the liquid–liquid extraction of base-neutral organic compounds from water. The presence of cyclohexene as a preservative in the methylene chloride becomes a serious constraint when a 10^5 concentration factor is needed to isolate ng/l amounts of the trace constituents for biological testing (*e.g.* Ames bioassay) and/or gas chromatographic (GC) and GC–mass spectrometric (MS) analysis of chlorinated water samples. Cyclohexene reacts with the residual free chlorine in the samples to produce many chlorinated and oxidized cyclohexene products. These artifacts mask large portions of the early chromatogram (Kovats index < 700–1300) of a capillary GC analysis on a non-polar stationary phase. Also, dechlorination by a reducing agent can affect any electrophiles present in the sample which are analyzed in the Ames procedures. This study evaluates the replacement of methylene chloride with freon FC-113 for the isolation of trace organics from chlorinated water samples that will be used for biological testing and/or GC and GC–MS analysis. Freon was found to minimize the interferences from solvent artifacts.

A continuous liquid–liquid extractor is used to compare the extraction efficiency of methylene chloride and freon. The results showed that the extraction efficiency of both solvents are comparable when 100–300 ng/l of non-polar organics are extracted and concentrated 1000-fold. Solvent blanks showed freon to have no contaminants at 200-fold concentration and, when used to extract chlorinated water, no byproducts were observed. Field sampling and quality assurance considerations show that freon is an acceptable alternative to methylene chloride for the isolation of trace organic compounds when large volumes of chlorinated waters are concentrated 10^5-fold for toxicity testing or GC and GC–MS analysis.

INTRODUCTION

The potentially hazardous ng–μg amounts of trace organic contaminants present in environmental water samples must be isolated and concentrated before they can be analyzed by gas chromatography–mass spectrometry (GC–MS) or tested for toxicity (e.g. Ames bioassay). A 10^5-fold concentration factor (100 l to 1 ml) for drinking water is needed for chemical identification by GC–MS and bioassay procedures. This translates into 1 ng/l in water being concentrated from 100 l to 0.1 μg/ml solvent or 0.5 ng/5 μl injected into a GC–MS system.

A major objective of the isolation and concentration methods are to assure minimum chemical alteration of the sample, and minimize blank artifacts of the method. This can be a difficult problem, especially when chlorinated drinking water is sampled, since free chlorine in water is very reactive. However, dechlorination by a reducing agent would react with electrophiles that may be in the sample. These electrophiles, in fact, are the compounds that would affect the Ames bioassay procedure. This study will consider 1,1,2-trichloro-1,2,2-trifluoroethane (freon FC-113) as an alternative to methylene chloride for the extraction of base–neutral organic compounds from water.

Methylene chloride is the solvent of choice for the liquid–liquid extraction of base–neutral organic compounds from water by EPA method 625[1] and the Master Analytical Scheme (MAS)[2]. The presence of cyclohexene as a preservative in the methylene chloride becomes a serious constraint for the extraction of chlorinated water samples[3]. Cyclohexene reacts with the residual free chlorine in the samples to produce many chlorinated and oxidized cyclohexene products[3]. The reaction products can mask a large portion of the beginning of a capillary GC chromatogram (Kovats index < 700–1300) therefore limit the quantification of compounds eluting in this region of the chromatogram. At the present time, attempts to separate cyclohexene from methylene chloride have failed and the use of a more appropriate preservative for methylene chloride has not yet been developed by manufacturers for commercial use.

Toxicological concern exists for methylene chloride. A national EPA toxicology program studying lifetime inhalation of methylene chloride showed carcinogenic effect on mice[4]. Accordingly, the highest time-weighed average (TWA) allowable air exposure limit was decreased from 500 ppm to 100 ppm[5].

Some of the general criteria for choice of solvent are: (1) stability and chemical reactivity, (2) solvent character (e.g. polarity), (3) solubility in water, (4) solvent handling (e.g. volatility, viscosity, etc.), (5) toxicity, (6) flammability and (7) cost. In the last few years, freon FC-113 was introduced as a solvent for today's needs[6]. For example, the TWA allowable exposure limit of FC-113 is 1000 ppm. Table I summarizes the physical properties of FC-113 and methylene chloride. FC-113 is stable, non-flammable and chemically inert which makes it attractive as a solvent. It does not react with strong acids (e.g. sulphuric acid), inorganic bases (e.g. sodium hydroxide) and oxidizing agents (e.g. perchlorates, N_2O_4, O_3, liquid O_2 and H_2O_2). Its low heat of vaporization allows evaporation with comparatively small amounts of energy. However, the lower solubility parameter (7.3 vs. 9.6 for methylene chloride) makes freon less efficient than methylene chloride for extracting polar organic compounds. Environmental concern related to the earth's ozone layer can associate with uncontrolled evaporation of either methylene chloride or freon[7]. However, recovery of the solvent from the distillation process can be achieved.

TABLE I

PHYSICAL PROPERTIES OF FREON FC-113 AND METHYLENE CHLORIDE[20,21]

	FC-113	Dichloromethane
Formula	CCl_2FCClF_2	CH_2Cl_2
Molecular weight	187.37	84.93
Boiling point (°C) at 1 atm	47.57	39.75
Latent heat of vaporization (cal/g)	35.07	78.6
Vapor pressure (Torr) at 25°C	330	436
Freezing point (°C)	− 36.4	− 95.14
Viscosity at 20°C (cP)	0.711	0.44
Liquid density at 25°C (g/ml)	1.564	1.317
Refractive index at 25°C	1.356	1.424
UV cutoff (nm)	231	250
Surface tension (dyn/cm) at 20°C	17.3	28.12
Solubility of water at 20°C (%)	0.009	0.24
Solubility in water at 20°C and saturation pressure (%)	0.017	1.60
Dielectric constant (ε) at 25°C	2.4	8.93
Hildebrand solubility parameter, δ	7.3	9.6

Trichlorotrifluoroethane (no exact structure given) has been used to extract organic solutes from water[8]. Comparative recovery data for extracting toluene by hexane, freon, carbon tetrachloride and chloroform was reported. Of the four solvents, freon gave the best extraction efficiency for toluene. Surprisingly, freon was more efficient than benzene, hexane and chloroform for the extraction of 2-pentanol, which is more polar than toluene. No comparative recovery data involving methylene chloride was reported.

This paper investigates the partitioning characteristics of both solvents and studies the possibility of using freon FC-113 as an alternative to methylene chloride for liquid–liquid extraction of non-polar trace organics from chlorinated drinking water samples.

Apparatus

The continuous liquid–liquid extractor (CLLE) developed and modified by Suffet and co-workers[9-15] to isolate and concentrate detectable amounts of trace organic compounds from water samples was further modified in this study. The CLLE glassware was redesigned by introducing the evaporative concentration system (EVACS)[16] as the evaporation chamber. A schematic diagram of the entire process is shown in Fig. 1. The new design of the CLLE glassware with the EVACS is shown in Fig. 2 and a photograph of the apparatus is shown in Fig. 3. The most significant changes of the present CLLE from the previous one used by Baker et al.[14,15] are as follows.

(1) The distillation chamber with the previous heating element is replaced by the EVACS with a Mica band heater (Watlow B1A1JN3) which allows smoother operation especially when used with a variable voltage supply (Variac) to have full control over the heater. The new heater eliminated the problem of cracking the glass tube surrounding the old heater (Fig. 4)[14]. The solvent loss during recycle in the system is reduced from 300 to 150 ml with the new design. The final volume of the extract after
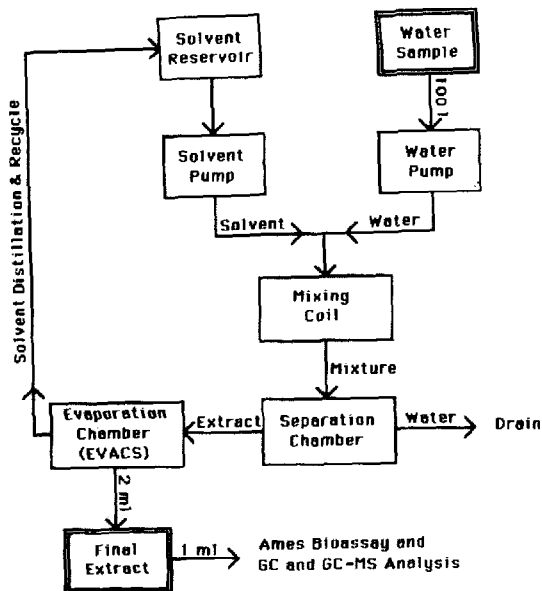
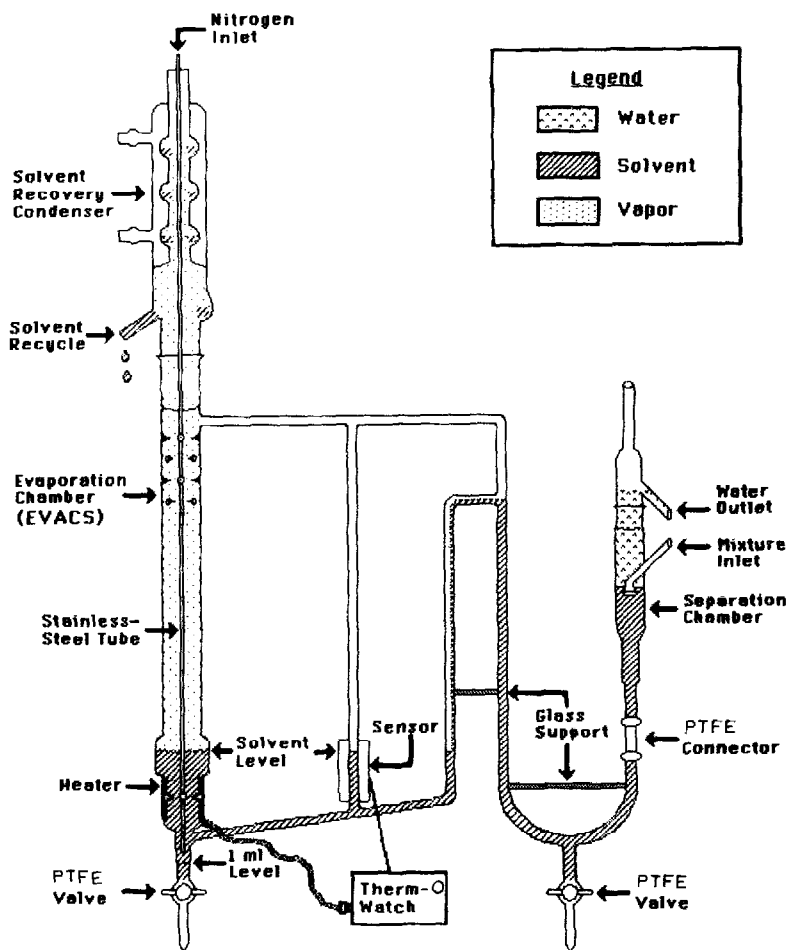Fig. 1. Schematic diagram of the CLLE process.

Fig. 2. Modified CLLE glassware.

introducing EVACS is 1 ml which can be injected directly in a GC or GC–MS system without any subsequent evaporation.

(2) The solvent level is sensed with a solid state sensor which uses conductance instead of the level sensor which was used with a glass-float containing copper wire wrapped in aluminum foil. The new sensor eliminated the operational problems of the
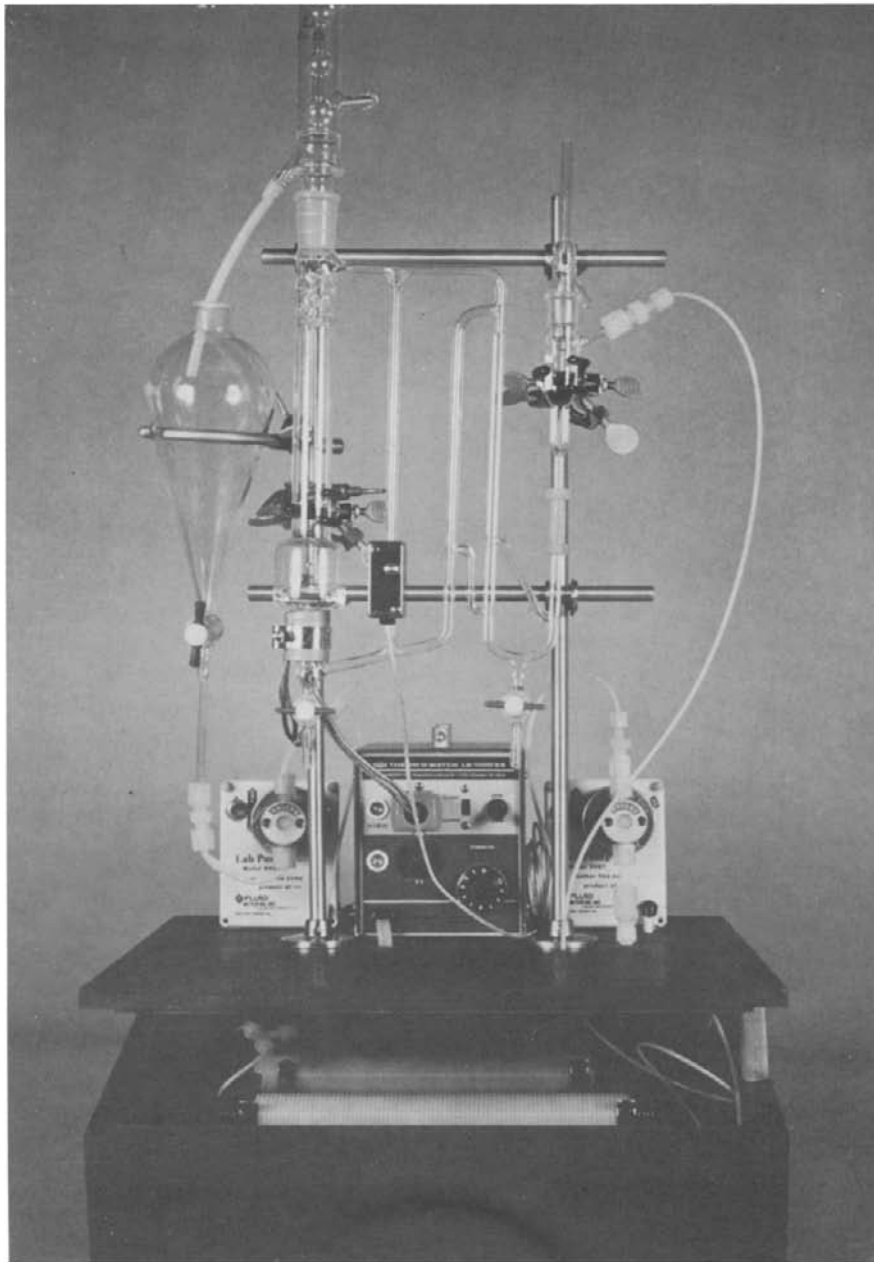

Fig. 3. Photograph of the CLLE apparatus made by E. M. Becker Co. (Philadelphia, PA, U.S.A.).
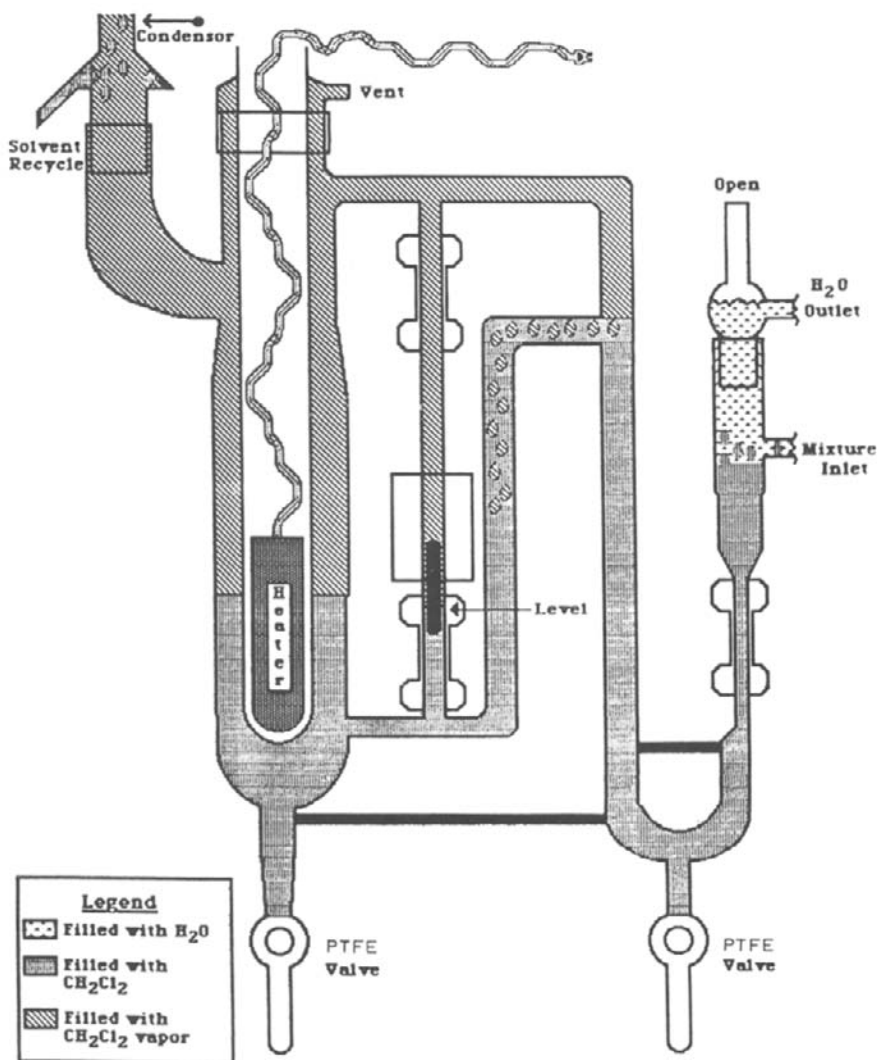
Fig. 4. Previous version of CLLE apparatus (Baker et al.[14]).

float with its adherence to the walls of the level tube. The manufacture states that the new solid state sensor is sensitive to liquids with dielectric constant (ε) greater than 4. However, it works for FC-113 with a dielectric constant of only 2.5.

(3) The positive displacement pumps Models RH1CKC and PG 20 (Fluid Metering, Oyster Bay, NY, U.S.A.) for water and solvent, respectively, were replaced by two identical positive displacement pumps Model RHSY1CKC (Fluid Metering). The new pumps are smaller in size, lighter in weight (4 instead of 9 lbs. for the old pumps) and safer in operation as they can operate dry.

The CLLE apparatus was designed to be run by one operator with minimum

downtime and adjustments. The latest unit made by E. M. Becker Co. (Philadelphia, PA, U.S.A.) was assembled on a rigid box with the two coils inside and the other parts (pumps, glassware, and Therm-O-Watch) outside (Fig. 3).

EXPERIMENTAL

The solvents used in the study were HPLC–GC-grade freon FC-113 from Burdick & Jackson (Muskegon, MI, U.S.A.) and distilled in glass LC–GC methylene chloride from EM Science (Cherry Hill, NJ, U.S.A.). The following laboratory experiments were conducted to study the extraction efficiency of FC-113.

(1) A 200-ml volume of FC-113 was evaporated to 1 ml in the EVACS[14] and analyzed by capillary GC for quality assurance.

(2) A set of organic compounds representing different functional groups and different polarities were used to evaluate the partitioning characteristics of FC-113 at pH 7. Table II lists those selected compounds, their functionality, boiling points and Kovats indices.

(3) A mixture of lower boiling compounds (Table III) was also used in a comparative study of FC-113 *versus* methylene chloride for extracting Milli-Q water samples. A 1-l volume of Milli-Q water was spiked with 5 μl of 1% solution (in acetone) of each of these compounds. Continuous liquid–liquid extraction of these spiked chemicals into FC-113 was completed using the modified CLLE (Fig. 3). At the end of each run the solvent was recycled in the system for 10 min to rinse the coils and separation chamber. Further concentration of the sample to 1 ml was continued in the evaporation chamber (EVACS). The sample was stored in a 1-ml vial with a PTFE-lined cap after adding 10 μl of 2000 ppm of six internal standards (C_8, C_9, C_{10},

TABLE II

ORGANICS SELECTED FOR EVALUATION OF FC-113

GC conditions: Carlo Erba 2150 gas chromatograph with flame ionization detector using a 60 m × 0.32 mm fused-silica column with a SE-30 bonded phase. Nitrogen carrier gas at a flow-rate of 0.4 ml/min and detector gases; air at 400 ml/min and hydrogen at 40 ml/min. Temperature program: isothermal at 50°C for 8 min; 5°C/min to a final temperature of 275 then isothermal at 275°C for 10 min; injector and detector temperatures were 250°C and 300°C, respectively. Sample size was 2.5 μl and split ratio was 20:1. Peak integration was done with a Spectra-Physics SP 4100 computing integrator using 1 cm/min chart speed and attenuation 4.

Compound	Functional group	Boiling point (°C)	Kovats index
Acetophenone	Ketone	202.6	1029.3
Isophorone	Ketone	214.0	1083.8
2,4-Dichlorophenol	Phenol	210.0	1143.1
Quinoline	Benzopyridine	238.0	1202.7
1-Chlorodecane	Chlorinated hydrocarbon	223.4	1255.7
2-Methylnaphthalene	Polyaromatic hydrocarbon	241.0	1264.3
Biphenyl	Hydrocarbon	255.9	1344.6
1-Chlorododecane	Chlorinated hydrocarbon	260.0	1431.9
Diacetone-L-sorbose	Sugar derivative	—	1570.7
Anthracene	Polyaromatic hydrocarbon	340.0	1742.6
Dioctylphthalate	Phthalate	384.0	2501.8

TABLE III

LOWER BOILING ORGANICS SELECTED FOR EVALUATION OF FC-113

GC conditions: the same as Table II except the temperature program was isothermal at 50°C for 8 min then 3°C/min to 150°C and 35°C/min to 275°C, then 10 min at 275°C.

Compound	Functional group	Boiling point (°C)	Kovats index
Toluene	Aromatic hydrocarbon	110.6	765.6
Ethyl butyrate	Ester	121.0	787.6
Ethyl benzene	Aromatic hydrocarbon	136.2	844.0
Cyclohexanone	Ketone	155.6	857.1
Anisole	Ether	155.0	893.3
1,4-Dichlorobenzene	Aromatic chloro-hydrocarbon	174.0	987.3
2-Ethylhexanol	Alcohol	185.0	1014.4
Acetophenone	Ketone	202.6	1031.6
Tolunitrile	Aromatic nitrile	205.0	1050.4
Isophorone	Ketone	214.0	1087.8
2,4-Dichlorophenol	Phenol	210.0	1144.0
Naphthalene	Polyaromatic hydrocarbon	218.0	1160.2
Benzothiazole	Heterocyclic thiazole	231.0	1190.2
Quinoline	Benzopyridine	238.0	1205.1
1-Chlorodecane	Chlorinated hydrocarbon	223.4	1255.3
2-Methylnaphthalene	Polyaromatic hydrocarbon	241.0	1271.4
Biphenyl	Hydrocarbon	255.9	1368.2
Ethyl cinnamate	Aromatic ester	271.0	1459.0
Diacetone-L-sorbose	Sugar	—	1534.1
Tributyl phosphate	Phosphate ester	289.0	1552.0

C_{11}, C_{13} and C_{15} hydrocarbons). The sample was stored at 0°C until analysis. Triplicate samples of both FC-113 and methylene chloride were completed and analyzed by capillary GC chromatography. Quantitation was done using standard curves vs. internal standards.

(4) A 10-l sample of distilled water was extracted by both methylene chloride and freon FC-113 using two modified CLLEs to test the efficiency of a distillation apparatus. The flow was adjusted to a rate of 2 l/h. The extracts were concentrated in the EVACS chamber to approximately 10 ml. Further concentration to 0.5 ml was completed in the EVACS chamber using nitrogen stripping at 1 ml/min flow-rate. Each concentration stack was rinsed with 1 ml of solvent and added to each sample. It was observed that less time was needed for the final concentration and stripping steps of the freon extracts. Sample vials were kept at 0°C until the GC and GC–MS analysis.

(5) A finished chlorinated drinking water sample was extracted using both methylene chloride and FC-113 in the same way. The sampling run was terminated after 45 l of water were extracted by both methylene chloride and FC-113. The samples were concentrated down to 0.5 ml by a stand alone EVACS[16] and analyzed by capillary GC and GC–MS. The concentration factor of the detected organic compounds in the original water sample is 10^5.

RESULTS AND DISCUSSION

Solvent blanks showed FC-113, to have no contaminants at 200-fold concentration, and when used to extract chlorinated Milli-Q water no byproducts were observed. FC-113 would not be expected to have better extraction efficiency than methylene chloride because of its lower polarity shown by its solubility parameter (7.3 *vs.* 9.6 for methylene chloride). The azeotropic mixture of FC-113 and methylene chloride has a solubility parameter of 8.4. Spinning band distillation (30 plates) failed to separate the cyclohexene preservative from the azeotrope[3]. The formation of cyclohexene artifacts when extracting chlorinated water with the azeotrope remained unsolved. Therefore, the azeotropic mixture of FC-113 and methylene chloride cannot be used for the extraction. Methanol, acetone, acetonitrile and ethyl alcohol form azeotropes with FC-113 but they are miscible with water and this can affect the partitioning of organics between the water sample and the solvent. Another approach to improve the extraction efficiency is to saturate the water sample with salt (salting out). This is easily done for the analysis of small sample volumes. It is more difficult for large volumes of water samples (50–100 l) which are needed to extract detectable amounts of the trace organics for instrumental analysis or for any biological testing.

Table IV represents the partitioning characteristics (*E*- and *p*-values) of methylene chloride and FC-113. The extraction method described by Suffet and Faust[17] was used in this study. Some of the compounds tested showed lower *E*- and *p*-values for FC-113 than those of methylene chloride. The only compound that is dramatically lower with FC-113 was diacetone-L-sorbose which is a very polar sugar derivative.

The comparative recoveries of methylene chloride and FC-113 for the organic compounds listed in Table III are shown in Table V. Table VI represents the statistical

TABLE IV

PARTITIONING CHARACTERISTICS OF CH_2Cl_2 AND FC-113

E-Value = fraction extracted at an equilibrated water-to-solvent ratio of 10:1. *p*-Value = fraction extracted at an equilibrated water-to-solvent ratio of 1:1. Method of calculation: Suffet and Faust[17]. Number of determinations = 4. GC conditions are the same as Table II.

Compound	*E-Value*		*p-Value*	
	CH_2Cl_2	FC-113	CH_2Cl_2	FC-113
Acetophenone*	0.92 ± 0.01	0.82 ± 0.04	0.99	0.98
Isophorone*	0.93 ± 0.01	0.75 ± 0.03	0.99	0.97
2,4-Dichlorophenol*	0.79 ± 0.02	0.56 ± 0.03	0.97	0.93
Quinoline	0.88 ± 0.01	0.70 ± 0.02	0.99	0.96
1-Chlorodecane	0.94 ± 0.01	0.73 ± 0.09	0.99	0.96
2-Methylnaphthalene	0.95 ± 0.01	1.11 ± 0.08	0.99	1.01
Biphenyl	0.93 ± 0.02	0.94 ± 0.04	0.99	0.99
Ethyl cinnamate	0.92 ± 0.00	1.01 ± 0.04	0.99	0.98
Diacetone-L-sorbose	0.57 ± 0.01	0.03 ± 0.00	0.93	0.28
Dioctylphthalate*	0.84 ± 0.01	0.89 ± 0.13	0.98	0.99

* U.S. EPA Priority Pollutant[19].

TABLE V

COMPARATIVE RECOVERIES OF CH$_2$Cl$_2$ AND FC-113

From 1 l water to 1 ml solvent. GC conditions are the same as Table III.

Compound	Concentration in water ($\mu g/l$)	Recovery $\pm$ standard deviation (%)	
		CH$_2$Cl$_2$	FC-113
Toluene	19	53 $\pm$ 7	37 $\pm$ 3
Ethyl butyrate	17	80 $\pm$ 3	80 $\pm$ 11
Ethyl benzene	20	54 $\pm$ 9	39 $\pm$ 7
Cyclohexanone	17	70 $\pm$ 1	23 $\pm$ 3
Anisole	17	74 $\pm$ 5	69 $\pm$ 4
1,4-Dichlorobenzene	16	66 $\pm$ 8	61 $\pm$ 6
2-Ethylhexanol	8	46 $\pm$ 5	53 $\pm$ 3
Acetophenone	9	61 $\pm$ 2	56 $\pm$ 4
Tolunitrile	8	61 $\pm$ 1	77 $\pm$ 5
Isophorone	17	79 $\pm$ 0	61 $\pm$ 3
Naphthalene	16	64 $\pm$ 4	77 $\pm$ 2
Benzothiazole	1	N.D.	58 $\pm$ 6
1-Chlorodecane	20	14 $\pm$ 1	14 $\pm$ 1
2-Methylnaphthalene	16	60 $\pm$ 3	78 $\pm$ 1
Biphenyl	10	65 $\pm$ 2	89 $\pm$ 2
Ethyl cinnamate	14	N.D.	100 $\pm$ 6
Diacetone-L-sorbose	7	51 $\pm$ 2	N.D.
Tributyl phosphate	26	100 $\pm$ 4	97 $\pm$ 10

TABLE VI

ANALYSIS OF VARIANCE (ANOVA) OF EXTRACTION RECOVERY DATA OF CH$_2$Cl$_2$ AND FC-113

From 1 l water to 1 ml solvent. Extraction efficiencies of freon, FC-113 and methylene chloride are equivalent. The theoretical Student $t_{0.975}$ value is 2.4469.

Compound	$t_{0.975}$	ANOVA
Toluene	4.202	Reject — freon lower
Ethyl butyrate	0.00	Accept — equivalent
Ethyl benzene	2.731	Reject — freon lower
Cyclohexanone	29.725	Reject — freon lower
Anisole	1.562	Accept — equivalent
1,4-Dichlorobenzene	1.00	Accept — equivalent
2-Ethylhexanol	2.401	Accept — equivalent
Acetophenone	2.236	Accept — equivalent
Toluonitrile	6.276	Reject — freon higher
Isophorone	12.00	Reject — freon lower
Naphthalene	5.814	Reject — freon higher
1-Chlorodecane	0.00	Accept — equivalent
2-Methylnaphthalene	11.358	Reject — freon higher
Biphenyl	16.971	Reject — freon higher
Tributyl phosphate	0.557	Accept — equivalent

significance of the ANOVA (analysis of variance) comparison using the Student-t test. Tables V and VI indicate that the CLLE efficiency of 1 l of Milli-Q water by FC-113 is comparable to methylene chloride when 1–30 ng/l of organics are extracted and concentrated 1000 fold. Seven compounds: ethyl butyrate, anisole, 1,4-dichlorobenzene, 2-ethylhexanol, acetophenone, 1-chlorodecane and tributyl phosphate gave statistically similar recoveries for both solvents. Of the rest, eleven compounds of the mixture FC-113 showed higher extraction efficiency when using FC-113 for seven compounds while four compounds were better extracted by methylene chloride. For unexplained reasons benzothiazole and ethyl cinnamate were not detected in the methylene chloride extracts but gave recoveries of 58 ± 6 and $100 \pm 6\%$, respectively, with FC-113. However, previous analysis with methylene chloride could detect ethyl cinnamate[14]. Only diacetone-L-sorbose was not detected in the FC-113 extracts and gave $51 \pm 2\%$ recovery with methylene chloride.

Table VII shows the compounds identified by GC–MS in the four distilled and drinking water sample extracts. These samples are: (1) $2 \cdot 10^4$-fold concentration of 10 l of distilled water extracted by FC-113 (Fig. 5a); (2) $2 \cdot 10^4$-fold concentration of 10 l of distilled water extracted by methylene chloride (Fig. 5b); (3) 10^5-fold concentration of 45 l of finished water sample extracted by FC-113 (Fig. 6a); (4) 10^5-fold concentration of 45 l of finished water sample extracted by methylene chloride (Fig. 6b).

Fig. 7 shows computer reconstructed chromatograms of the four extracts to demonstrate the difference between FC-113 and methylene chloride. Peak-by-peak comparison of both distilled and finished water extracts (excluding the cyclohexene peaks) indicate that FC-113 is as efficient as methylene chloride for extracting organic compounds from aqueous samples. Methylene chloride was expected to be more efficient than FC-113 because of its higher solubility parameter, δ (9.6 vs. 7.3 for FC-113). At present, there is no explanation of why the FC-113's efficiency is equivalent to that of the methylene chloride.

Of particular interest is the area on the chromatograms between Kovats indices 600 and 1300 (Fig. 7) which contains very large peaks only in the methylene chloride samples. These large peaks are air oxidation or oxidation and chlorination byproducts of cyclohexene, the preservative in methylene chloride, which result from the reaction with residual chlorine in the finished drinking water[3]. In the methylene chloride distilled water extract the large peaks affected the resolution of other chromatographic peaks present in the sample between retention time (t_R) 30.02 and 35.22 min (Fig. 5) which corresponds to a Kovats index of 1000–1200 (Fig. 7). In the chlorinated water extract the larger number of peaks are both oxidation and chlorination cyclohexene byproducts. These peaks are located at t_R 11.31–38.39 (Fig. 6) which corresponds to a Kovats index of 600–1300 (Fig. 7). Peaks observed in the FC-113 extracts in that region (Kovats index 600–1300) could not be observed by GC or GC–MS in the methylene chloride samples because they are masked by the cyclohexene artifacts.

Table VII lists the compounds identified in the four samples. There are mainly three groups of impurities:

(a) Cyclohexene artifacts which originate from the oxidation and chlorination reactions occurring between methylene chloride and cyclohexene, the preservative in the solvent. In presence of the free chlorine residual used as a disinfectant in the finished water, the number and concentration of the cyclohexene derivatives was dramatically greater than those in the distilled water extracts[3];
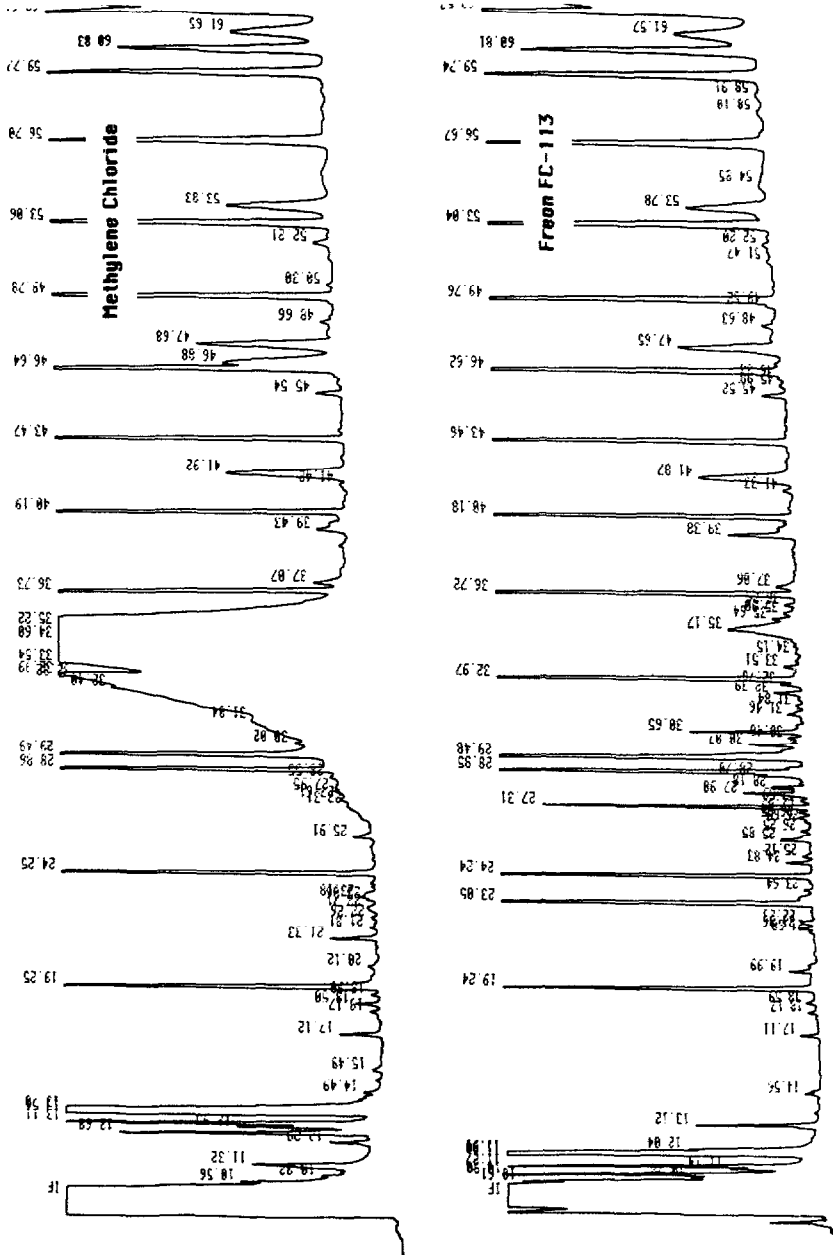
Fig. 5. Chromatograms of distilled water extracts.

TABLE VII

GC–MS COMPOUND IDENTIFICATION

GC and GC–MS conditions: Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and a capillary DB-1, 30 m × 0.25 mm I.D. column. Sample sizes of 1.0 μl were injected on column at 50°C. The temperature programme was isothermal at 50°C for 8 min, 5°C/min to 275°C final temperature, then isothermal at 275°C for 10 min. The GC–MS apparatus was a Hewlett-Packard 5970 MSD. The mass range for the MS was 40–400 a.m.u. using a scan rate of 500 a.m.u./s. EM multiplier voltage was 1800 V and the transfer line temperature was 280°C.

Compound	Distilled water		Finished water	
	FC-113	CH$_2$Cl$_2$	FC-113	CH$_2$Cl$_2$
Cyclohexene related compounds				
Cyclohexene		X		X
Chlorocyclohexene				2
Cyclohexen-1-one				X
Dichlorocyclohexane		X		3
Chlorocyclohexanol		X		2
Chlorocyclohexanone				X
Bromocyclohexanol				X
Haloform related compounds				
Bromoform*			X	X
Dibromochloromethane*				X
1,1,1-Trichloroacetone			X	X
Other compounds				
Benzaldehyde	X		X	
Benzothiazole	X	X		
Tetrachloroethylene*				X
C$_3$-benzene isomer			2	X
C$_4$-benzene isomer				X
Trichloromethylbenzene			X	
Methyl phenyl hexanone			X	
Tolunitrile or phenylacetonitrile			X	X
Naphthalene*			X	X
Methyl naphthalene			2	X
Biphenyl			X	
Dichlorobiphenyl*	X			
Ethyl cinnamate			X	
Dihydroactinidiolide			X	X
Tributyl phosphate			X	
C$_{12}$ Fatty acid		X		
C$_{14}$ Fatty acid	X	X		
C$_{16}$ Fatty acid	X	X		X
C$_{18}$ Fatty acid				X
Diethyl phthalate*	X	X	X	
Dibutyl phthalate*	X	X	X	X
Dioctyl phthalate*	X	X		

* Represent EPA priority pollutant[19]. GC–MS analysis was not confirmed by standards. Numbers represent isomers.

(b) Phthalates, which are used in all types of plastic products and may originate from laboratory contamination;
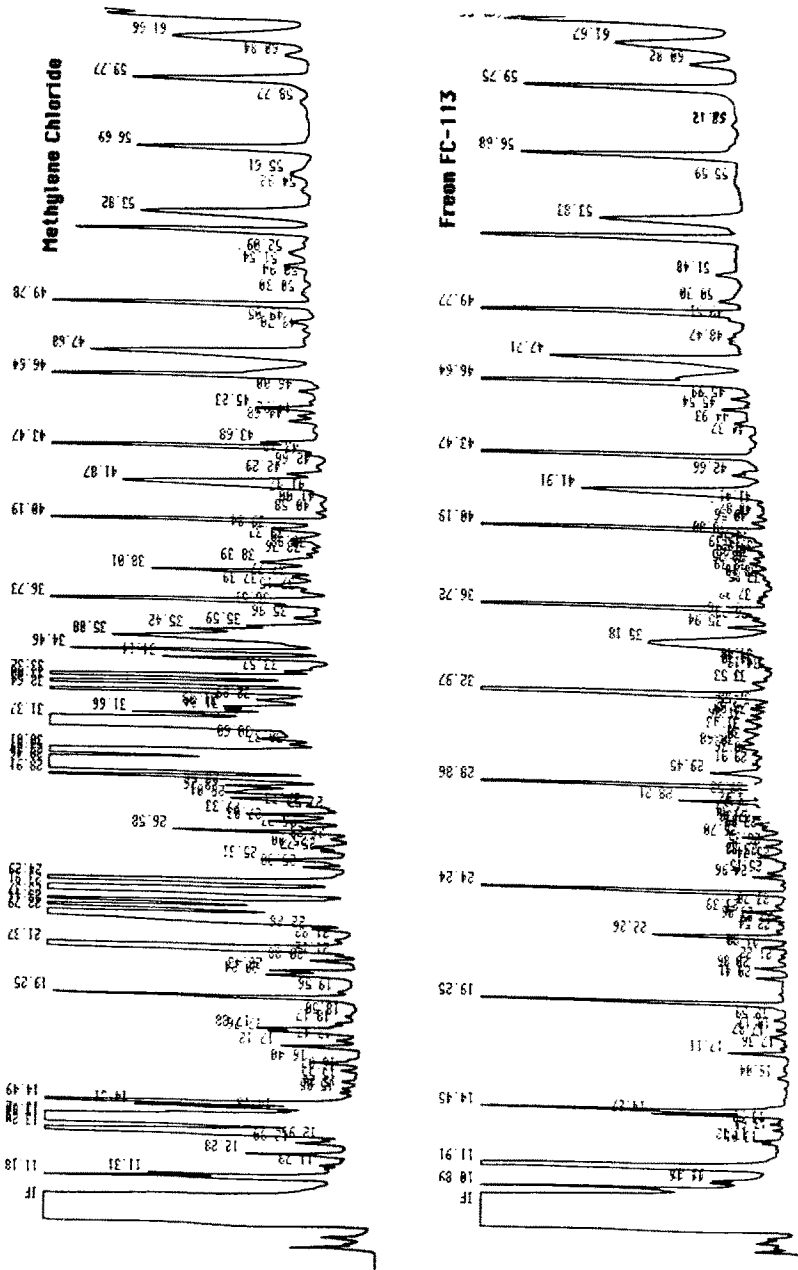
(c) Long chain fatty acids.
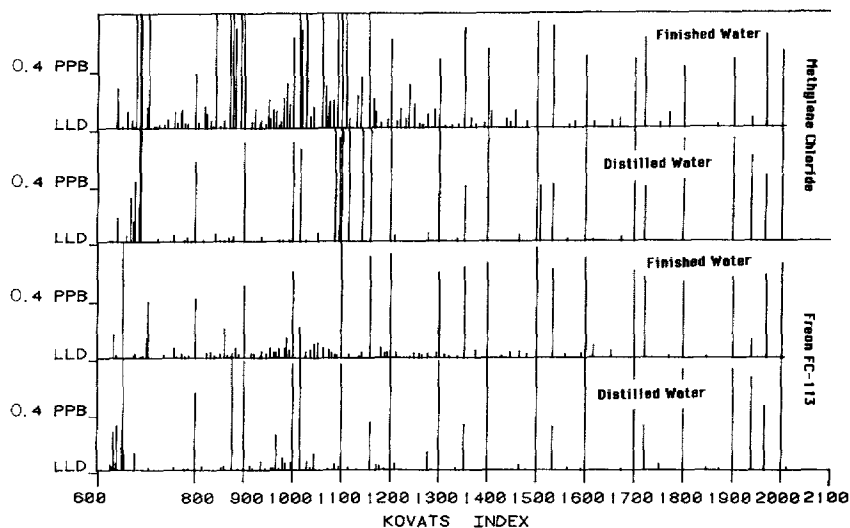
Fig. 6. Chromatograms of finished water extracts.

Fig. 7. Computer reconstructed chromatograms of the four extracts. ppb = parts per billion = μg/l (the American billion is 10^9). LLD = Lower limit of detection.

In addition to these impurities, other compound classes of organics were found to be present which originate from the water samples. These included:

(a) Haloforms originating from the reaction between chlorine and natural humic or industrial organic compounds. Trichloroacetone is an important intermediate in the haloform reaction[18] and has been observed in many extracts of chlorinated drinking water samples. Bromoform and chlorodibromomethane are specified as priority pollutants[19];

(b) Aromatic compounds (alkyl benzenes, naphthalene, methyl naphthalene and biphenyl). These compounds are commonly found in crude oil distillates such as gasoline and general organic solvents. Naphthalene is specified as a priority pollutant[19];

(c) Tetrachloroethylene is a degreasing agent and is considered a priority pollutant[19];

(d) Ethyl cinnamate is an ester used as fixative for perfumes and in glass prisms and lenses. Tributyl phosphate is used as plasticizer for cellulose esters, lacquers, plastics and vinyl resins;

(e) The remaining compounds represent a variety of aldehydes, esters, ketones, etc. The hazard of these chemicals at trace levels is unknown.

CONCLUSION

The comparative study of freon FC-113 and methylene chloride proved that FC-113 can be used to extract non-polar organic compounds (*e.g.*, EPA method 625 compounds) from chlorinated drinking water samples. The use of FC-113 is safer, takes less time for evaporation and eliminates the cyclohexene problem associated with the methylene chloride extracts. Identification of more compounds in the FC-113 extracts which were masked by the cyclohexene derivatives in the methylene chloride extracts shows that FC-113 can be an alternative to methylene chloride.

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