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**A PRACTICAL SAMPLING AND EXTRACTION SYSTEM
FOR THE QUANTITATIVE ANALYSIS
OF SUB ng/l OF ORGANOCHLORINE CONTAMINANTS
IN FILTERED WATER AND SUSPENDED SOLIDS**

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• Environment Canada

EXECUTIVE SUMMARY

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This report describes a technical advance which will help make ultratrace analyses of organic compounds more easily accomplished. There are no political consequences to this report.

RÉSUMÉ ADMINISTRATIF

SYSTÈME PRATIQUE DE PRÉLÈVEMENT ET D'EXTRACTION POUR LE DOSAGE DE POLLUANTS ORGANOCHLORÉS PRÉSENTS EN CONCENTRATIONS INFÉRIEURES AU ng/L DANS L'EAU FILTRÉE ET DANS LES SOLIDES EN SUSPENSION

Le rapport décrit une méthode perfectionnée qui facilite le dosage de composés organiques présents à l'état d'ultratraces. Ce rapport n'a aucune répercussion sur le plan politique.

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RÉSUMÉ

On décrit une méthode et l'appareillage nécessaire pour prélever, filtrer, puis extraire des échantillons de 20 L d'eau et de solides en suspension, au moyen d'un matériel robuste, peu coûteux et facile à trouver. Le prélèvement, la filtration et l'extraction des deux phases peuvent s'accomplir en moins d'une heure. On donne le taux de récupération de certains polluants organochlorés représentatifs ajoutés à de l'eau "exempte de composés organiques" et à de l'eau du lac Ontario en concentrations analogues à celles qui sont observées dans l'environnement.

ABSTRACT

An apparatus and procedure is described for the collection, filtration and subsequent extraction of 20% water and suspended solid samples using readily available, inexpensive and sturdy equipment. Water collection, filtration and extraction of both phases can be accomplished in less than one hour. Recoveries of selected representative organochlorine contaminants spiked into 'organic free' water and Lake Ontario water at environmentally realistic levels are presented.

INTRODUCTION

Numerous government agencies and private contracting laboratories in Canada and the United States are deeply involved in the complex task of analysing water samples in the Laurentian Great Lakes watershed for a large and growing list of man-made organic contaminants. The purposes of these analyses are numerous and include loading estimates and studies on the fate and effects of specific contaminants.

Although analytical techniques have become extremely sensitive and sophisticated in recent years, there still exists a requirement for a practical large volume water sampling and extraction system. Such a system is needed, when contaminants are present at low or sub ng/l concentrations, in order to make meaningful loading estimates or quantitative assessment of the fate and effects of the contaminants on the aquatic ecosystem.

At the present time a number of different sampling and extraction techniques are in use by the various laboratories which makes the intercomparison of data sets from different laboratories difficult and sometimes impossible. The techniques range from the simple but inadequate extraction in a 4 l solvent bottle to the combined use of a continuous flow centrifuge for suspended solids with the 200 l APLE (McCrea and Fischer, 1984) solvent extraction system. The later technique is extremely sensitive but very time consuming and

bulky. Other systems with attractive features are sometimes complex and not widely available at the present time.

EQUIPMENT AND MATERIALS

20 l (5 U.S. gallons) stainless steel pressure containers used to collect and store samples. Spartanburg Challenger VI, Spartanburg Steel Products Inc.

20 l stainless steel pressure container used as extraction reservoir. Millipore Cat. #XX6700P20. Millipore Corp.

142 mm stainless steel pressure filter holder. Millipore Cat. #YY3014236. Millipore Corp.

142 mm diameter binder-free glass fibre filters, 0.3 μ m nominal pore size. Gelman Cat. #61635. Gelman Sciences Inc.

Prepurified grade nitrogen, two-stage pressure reducing valve and 1/4" OD polyethylene tubing to pressurize the containers. Any convenient supplier.

Stainless steel quick disconnect hose connections for the pressure containers. Available with the pressure containers.

Variable speed laboratory bench stirrer, speed controller and impeller. Fisher Dyna-Mix. Fisher Scientific.

Corrugated teflon flexible hose for transfer of water and extract. Penntube CT flex #400. Dixon Industries Corp.

Syphon tube: 1/4" O.D. teflon and flexible 'tygon' type tubing. Readily available from numerous sources.

Solvents: Dichloromethane (DCM), 2,2,5-trimethylpentane and n-hexane. All distilled in glass pesticide grade Caledon Laboratories Ltd.

1 l glass bottles narrow neck with teflon lined screw caps. 50 ml glass culture tubes with teflon lined screw caps for water and suspended solids extracts. Any supplier.

Anhydrous Na_2SO_4 . J.T. Baker Chemical Co. Ltd. Various laboratory glassware.

PREPARATION OF EQUIPMENT

Two kinds of 20 l pressure containers are used. The sampling and storage containers are inexpensive stainless steel

beverage pressure tanks and are modified by removal of all the internal pressure shut-off seals and replacing the dip tube seals with teflon replacements. The internal seals of the stainless steel pressure hose connectors are likewise removed. This avoids rubber water contact and possible contamination of the sample.

The sample volume is most easily adjusted and measured by inserting a snug fitting short piece of teflon tube in the storage tank inlet tube. A syphon attached to this will automatically reduce the water level to the height of the bottom of the inlet tube. This adjusted volume was found to be $18.057 \text{ g} \pm 0.48\%$ on a sample of five storage tanks.

The extraction container is a 20 g Millipore stainless steel pressure tank chosen because it is equipped with two extra NPT threaded ports on the top surface. A 15 cm long by 1.25 cm diameter metal rod may thus be threaded at one end and installed in one of the ports as a support stand for the stirrer motor. The other spare port is plugged.

Transfer hoses for both water and DCM extract are teflon and have appropriate stainless steel connectors to mate with the corresponding connectors on the filter holder and pressure tanks.

Nitrogen for pressurizing the containers is most conveniently supplied through 1/4" OD polyethylene tubing with a toggle shut off valve installed near the pressure container connector.

The stirrer is set up to clamp onto the support rod described above with a laboratory clamp such that it can easily be removed and replaced. The stirrer shaft should reach near the water-DCM interface and the impeller should have large blades with a steep pitch so that a medium stirring speed will mix the tank contents thoroughly without producing a persistent emulsion in samples with high levels of natural organic compounds. A 2 l polyethylene graduate provides a convenient receptacle for the stirrer while not in use in the extractor.

METHOD

Fill the storage tank to overflowing and then adjust the volume precisely with a syphon as previously described. The amount syphoned off is approximately 1l and may be used to determine the concentration of suspended solids. Filter into the extraction container at 15 psi through a 0.3 μ m glass fibre filter (binder free) which has been previously heated to 350-400°C.

Suspended Solids

Fold the damp filter in half, roll into a tube and place in a 50 ml screw capped culture tube. Add 20 ml DCM. Cap and store at least 24 hours. Break-up filter with a spatula and pour DCM extract

into a fritted glass filter tube containing 2-5 cm anhydrous Na_2SO_4 . Aspirate under water pump vacuum into a 250 ml RB flask. Add a further 20 ml DCM to the culture tube, cap and shake. Add the DCM to the Na_2SO_4 and aspirate as before. Repeat this procedure twice more and add a final 20 ml DCM directly to the Na_2SO_4 . To the 100 ml combined and dried extract add 5 ml 2,2,5-trimethylpentane as a keeper. The extract is ready for further concentration, cleanup and analysis.

Filtrate

Add 600 ml of DCM and stir for ten minutes at a speed sufficient to ensure thorough mixing of the contents. Remove the stirrer and allow to settle 2-5 minutes depending on emulsion forming potential of sample. Transfer DCM extract to a 1 l screw capped glass bottle using 1-2 psi nitrogen pressure. Decant excess water from glass bottle back into the extraction container. Repeat this procedure twice more using 100 ml DCM each time. After the final transfer, the excess water may be conveniently left in the 1 l bottle until the extract is further concentrated, cleaned up and analysed. This part of the procedure may vary to suit the analysts requirements.

Sample Concentration and Cleanup

In this study the following procedure was used. The combined DCM extract was dried by passing through a 5 cm bed of anhydrous Na_2SO_4 and 5 ml of 2,2,5-trimethylpentane was added as a keeper. Both filtrate and suspended solid extracts were evaporated to approximately 2 ml on a rotovapor at 25°C. The concentrated extracts were allowed to flow by gravity through pasteur pipet mini-columns containing 2.5 cm 44% H_2SO_4 on silica gel topped with 0.5 cm anhydrous Na_2SO_4 . The extracts were eluted from the columns with 2x2 ml of n hexane. The combined eluant was collected in a 10 ml Kuderna Danish tube and concentrated to a final volume of 1 ml under a stream of dry nitrogen on an N-Evap concentrator at 25°C. The 1 ml extract was analysed for the spiked organochlorine contaminants by electron capture gas chromatography using capillary columns.

RESULTS AND DISCUSSION

Selected organochlorine contaminants dissolved in acetone were spiked, in duplicate, into 'organic free' water and Lake Ontario water to test recovery efficiency.

The 'organic free' water was prepared by passing laboratory distilled water through an XAD-4 resin column. Lake Ontario water was collected at 1 m depth from the 1 mile marker buoy off Hamilton, Ontario and found to have 1.9 mg/l suspended solids.

100 µl of the spike solution was added to 17.3 g 'organic free' water, stirred five minutes, allowed to stand 30 minutes and extracted as previously described. Recoveries are shown in Table 1 and range from 81 to 132% with a mean value of 102%.

17.3 g Lake Ontario water was spiked with 100 µl of the contaminant solution. The resulting solution was stirred for 16 hours to allow the contaminants to equilibrate between the liquid and solid phases. Filtration and extraction were performed as previously described. Lake Ontario water (17.3 g) was also extracted unspiked to determine blank values.

Recoveries of contaminants from Lake Ontario water and suspended solids are shown in Table 2. The compounds are listed in order of gas chromatographic elution which is also approximately the order of decreasing solubility in water. This trend is clearly reflected in recoveries from the suspended solids, where 3-54% of the higher substituted PCB's and octachlorostyrene was observed while the chlorobenzenes and chlorotoluenes were found almost exclusively in solution.

Total recoveries were good with a mean total recovery of 86%. A noticeably lower total recovery for the penta to octachlorobiphenyls and mirex suggests some lack of recovery from the suspended solids since these compounds were efficiently recovered from 'organic free' water with no suspended solids.

REFERENCES

McCrea, R.C. and Fishcer, J.D. 1984. Evaluation of an aqueous phase liquid-liquid extractor (APLE) for the determination of organochlorine contaminants. IWD Environment Canada Report, 18 pp.

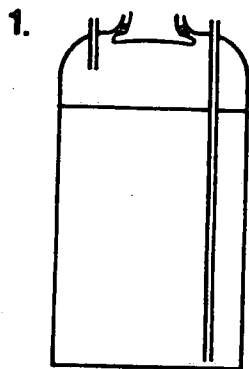
TABLE 1. Recovery of spiked organochlorine contaminants from 'organic free' water

Compound	Amount Spiked ng/l	% Recovery		Mean % Recovery
		Spike 1	Spike 2	
1,2,4-trichlorobenzene	0.83	88	95	92
1,2,3-trichlorobenzene	0.42	110	121	116
2,4,5-trichlorotoluene	0.94	104	87	96
2,3,6-trichlorotoluene	0.93	93	97	95
1,2,4,5-tetrachlorobenzene	0.59	113	106	110
1,2,3,4-tetrachlorobenzene	0.24	120	107	114
Pentachlorobenzene	0.12	100	98	99
Pentachlorotoluene	0.18	112	107	110
Hexachlorobenzene	0.14	99	89	94
2,2',5-trichlorobiphenyl	0.79	83	88	86
2,2',5,5'-tetrachlorobiphenyl	0.52	109	112	111
2,2',3,3'-tetrachlorobiphenyl	0.34	128	134	130
Octachlorostyrene	0.14	102	91	97
2,2',4,4',5,5'-pentachlorobiphenyl	0.42	81	94	88
2,2',4,4',5,5'-hexachlorobiphenyl	0.33	93	132	113
Mirex	0.33	87	101	94
2,2',3,3',4,4',5,5'- Octachlorobiphenyl	0.23	85	96	91
Overall mean recovery				102

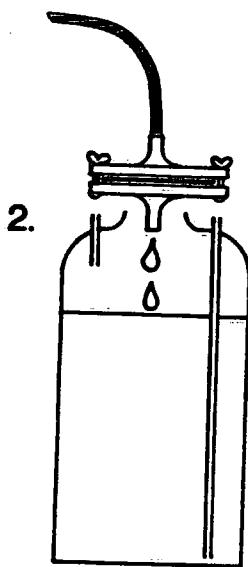
TABLE 2. Recovery of spiked organochlorine contaminants from Lake Ontario water and suspended solids

Compound	Amount Spiked ng/l	% Recovery Filtrate		% Recovery Suspended Solids		Mean Total % Recovery
		Spike 1	Spike 2	Spike 1	Spike 2	
1,2,4-trichlorobenzene	0.83	104	101	ND	ND	103
1,2,3-trichlorobenzene	0.42	117	119	ND	ND	118
2,4,5-trichlorotoluene	0.94	78	92	ND	ND	85
2,3,6-trichlorotoluene	0.93	85	77	ND	ND	81
1,2,4,5-tetrachlorobenzene	0.59	99	94	ND	ND	97
1,2,3,4-tetrachlorobenzene	0.24	91	122	ND	ND	107
Pentachlorobenzene	0.12	68	87	ND	ND	78
Pentachlorotoluene	0.18	105	95	ND	ND	100
Hexachlorobenzene	0.14	88	62	<1	ND	75
2,2',5-trichlorobiphenyl	0.79	65	67	<1	3	68
2,2',5,5'-tetrachlorobiphenyl	0.52	93	81	13	16	102
2,2',3,3'-tetrachlorobiphenyl	0.34	93	80	20	16	105
Octachlorostyrene	0.14	59	70	54	35	109
2,2',4,4',5,5'-pentachlorobiphenyl	0.42	54	35	19	11	60
2,2',4,4',5,5'-hexachlorobiphenyl	0.33	43	34	19	21	59
Mirex	0.33	28	35	23	25	56
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	0.23	36	38	19	23	58
Overall mean recovery						86

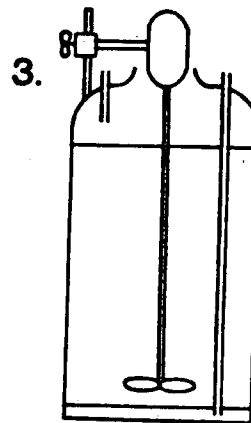
ND = Not Detected



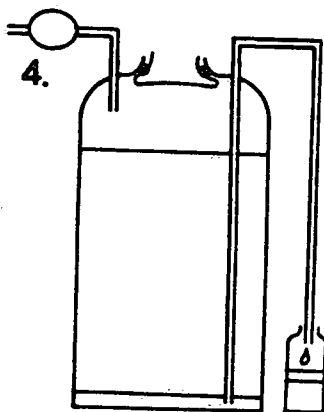
1. Collect water sample.



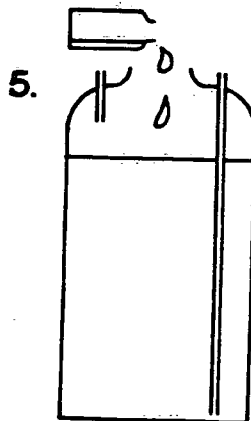
2. Filter water into extraction container.



3. Add DCM. Stir.



4. Allow to settle. Transfer DCM extract to bottle.



5. Decant water from bottle back into extraction container. Repeat steps 3-5.

6.



Store combined DCM extract for further concentration, cleanup and analysis. Place folded GF filter in culture tube with DCM.

Sampling and Extraction Procedure