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DETERMINATION OF CHLORINATED PESTICIDES IN POTABLE WATER

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SUMMARY

A procedure is described for monitoring organochlorine pesticides in potable water. Material adsorbed from water on to Amberlite XAD-2 macroreticular resin was eluted with *n*-hexane and the concentrated eluate was analyzed without further treatment.

Electron capture (^{63}Ni) gas chromatography utilizing a column of 4% QF-1 and 2% SE-30 on 80–100 mesh HP Chromosorb W at 180° permitted identification of organochlorine pesticides and indicated the presence of phthalates. Confirmatory qualitative and quantitative analyses were done by specific ion-monitoring mass spectrometry. Levels determined in Ottawa drinking water were 17 ppt α-BHC, 1.3 ppt lindane, 0.7 ppt aldrin, and less than 0.05 ppt for each of heptachlor, heptachlor epoxide, dieldrin, endrin, chlordane, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDT, and *p,p'*-DDE.

INTRODUCTION

The ubiquity of chlorinated pesticides and polychlorinated biphenyls (PCBs) and the consequential environmental hazards has created much interest. Although their occurrence in finished waters has been confirmed[1,2], the levels detected vary widely[1–5] and are dependent upon location, time of analysis, and method of analysis. Nevertheless, tentative standards for drinking water, based on toxicological considerations, have been established (Table I).

A variety of analytical procedures capable of measuring low levels of chlorinated organic compounds in water is documented. These include the use of activated

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TABLE I

COMPARISON OF DRINKING WATER STANDARDS

Pesticide	*Maximum permissible level (mg/l)* *		
	*Canada, NH & W. 1968*** *(ref. 6)*	*U.S. E.P.A.*	
		1972 (ref. 7)	*1975 (ref. 8)*
Aldrin	0.017	0.001	0.001
Chlordane	0.003	0.003	0.003
DDT	0.042	0.05	0.05
Dieldrin	0.017	0.001	0.001
Endrin	0.001	0.0005	0.0002
Heptachlor	0.018	0.0001	0.0001
Heptachlor epoxide	0.018	0.0001	0.0001
Lindane	0.056	0.005	0.004

* Equivalent to parts per million.

** Tentative standard for raw as well as treated water.

carbon[9,10], solvent extraction[11,12], reversed-phase liquid–liquid partition[3], reverse osmosis[4], polyurethane foams[13], support-coated silicones[5], and volatile stripping[14,15], and are discussed elsewhere[1,4]. Recently the use of porous polymer resins has found considerable success in the analysis of aqueous samples[16,17]. A low-polarity styrene–divinyl benzene copolymer (Amberlite XAD-2; Rohm & Haas, Philadelphia, Pa., U.S.A.) with a high sorptive capacity has been widely used[17]. The method[17] has been demonstrated to be accurate and reliable for the analysis of a large number of compounds, including chlorinated pesticides, occurring in water.

The present work was initiated in order to evaluate the use of macroreticular resins in the development of analytical methodology for Canadian drinking water. Organochlorine pesticides have been detected in numerous natural[1,3,5] and finished[2–5] water supplies, thus presenting a possible health hazard to the population. With this in mind, these investigations were focussed on the determination of chlorinated pesticide levels in Ottawa drinking water.

EXPERIMENTAL

Preliminary studies were conducted to determine a suitable method for the isolation of organochlorine pesticides from tap water. Liquid–liquid extraction[18] using *n*-hexane and cyclohexane, and extraction using 30 g XAD-2 and XAD-4 columns followed by elution with *n*-hexane (see below) was applied to four 100-l tap water samples. Comparison of the concentrated extracts by means of electron-capture gas chromatography (GC–ECD) indicated that cyclohexane and XAD-2 afford optimum pesticide recovery and minimum background. Recent advances with macroreticular resins[17] prompted the use of XAD-2 for further work.

All glassware was triply rinsed with distilled water, acetone, and hexane in turn and was oven-dried at 130° after each solvent wash. Residue-free (distilled in glass, Caledon Labs., Georgetown, Canada) solvents were used throughout. PTFE tubing, stopcocks, and liners were used where indicated due to the inert nature and versatility of the material.

Preparation of XAD-2 column

The column employed consisted of a 50 cm × 1.8 cm I.D. glass tube equipped with a removable PTFE stopcock and a 500-ml reservoir with a 24/40 $ joint. Amberlite XAD-2 resin (30 g, Rohm and Haas) was slurried in distilled water, and the fines were decanted; this procedure was repeated twice. A silanized glass wool plug was placed in the bottom of the column, and the aqueous slurry of XAD-2 was poured into the column and allowed to settle and drain until a 2-cm layer of water covered the resin. Another silanized glass wool plug was secured atop the resin and a modified clean-up procedure[19] as follows was applied. The column was eluted with distilled water (250 ml), *n*-hexane (250 ml), acetone (250 ml), and again with *n*-hexane (250 ml). Concentration of the final *n*-hexane eluate to 2 ml using a rotary evaporator was followed by GC–ECD (see below) of a 1-μl sample. Column elution with 250-ml portions of *n*-hexane was continued until a clean GC tracing of the concentrates was obtained.

Tap water extraction

The column reservoir was connected to a laboratory water tap by means of glass and PTFE tubing. Provision was made for overflow of water from the reservoir. The influent water, sampled during January, 1975, had a pH in the range 8.4–8.6 and was adjusted to a temperature of 20 ± 2° by control of cold and warm water taps.

A measured volume (100, 200, or 300 l) of tap water was passed through the column at a flow-rate of 15–20 ml/min. The column was allowed to drain until the water level reached the upper glass wool plug and was then eluted with 250 ml *n*-hexane at a rate of 15 ml/min. The *n*-hexane eluate, collected in a 500-ml, 24/40 $ jointed round bottom glass flask, was reduced to 5 ml by means of a Büchi rotary evaporator. A 50-ml, 24/40 $ jointed glass flask connected at the bottom to a 3-ml, calibrated, tapered tube[2] was used to further reduce the combined concentrate and three *n*-hexane rinses to a volume of 0.3 ml. The tightly glass-stoppered flask was stored at 4° until 1 h prior to analysis.

Gas chromatographic analysis

A Hewlett-Packard Model 5710 A gas chromatograph, equipped with a ^{63}Ni electron capture detector and a coiled glass column, 1.8 m × 3.5 mm I.D., packed with a mixture of 4% QF-1 and 2% SE-30 on 80–100 mesh HP Chromosorb W was used throughout the procedure.

Columns packed with 3% OV-17 on 80–100 mesh HP Chromosorb W, and a mixture of 3% QF-1 and 2% SE-30 on 80–100 mesh HP Chromosorb W, gave slightly inferior separation and were utilized as a confirmatory procedure. High-purity argon–methane (95:5) was used as the carrier gas at a flow-rate of 55 ml/min. The injector, oven, and detector temperatures were kept at 200°, 180°, and 300°, respectively. One microliter of standard and extract solutions were injected on to the columns.

Standard solutions were prepared by dissolving selected organochlorine pesticides and phthalates in *n*-hexane. All standards were analyzed individually, on an additive basis, and as a composite mixture in order to determine possible effects on retention time and for peak identification (Fig. 1, Table II). A negligible shift in relative retention time was noted upon comparison of results obtained with the composite mixture and the individual components.

TABLE II

GC–ECD IDENTIFICATION OF SOME ORGANOCHLORINE PESTICIDES IN OTTAWA TAP WATER

XAD-2 extract peak No.	*Retention time relative to aldrin*		*Standard compounds*
	XAD-2 extract	*Standards mixture**	
1	0.13	0.11	chlordane
2	0.18	0.18	chlordane
3	0.23**		
4	0.28	0.31	chlordane
5	0.35	0.35	α-BHC
6	0.40**		
7	0.43	0.44	lindane
8	0.57**		
9	0.64	0.61	chlordane
10	0.74	0.72	dieldrin
11	0.84	0.80	heptachlor
12	0.94**		
13	1.00	1.00	aldrin
14	1.02	1.02	chlordane
15	1.22	1.22	chlordane
16	1.33	1.34	heptachlor epoxide
17	1.41**		
18	1.63	1.62	chlordane
19	1.77	1.77	chlordane
20	1.93	1.89	chlordane
21	2.04	2.05	endrin + *p,p'*-DDE
22	2.21**		
23	2.68**		
24	2.87	2.92	*o,p'*-DDT
25	3.16**		
26	3.51**		
27	3.75	3.77	*p,p'*-DDD
28	4.14**		
29	6.40**		
30	7.78**		
31	9.09**		
32	10.50	10.50	di(2-ethylhexyl) phthalate

* Only peaks which closely match those in XAD-2 extracts are listed.
** Comparison with Arochlor 1254 suggests that these may represent PCBs.

Since the interference of PCBs on pesticide analyses has been noted[20], a standard solution containing 0.3 ng/μl of each component and an excess (5.0 ng/μl) of Arochlor 1254 was analyzed. Retention time and peak height of the other components were unaffected by the preponderance of Arochlor 1254. Initially the Armour–Burke PCB separation procedure[21] was successfully applied to a tap water extract and a composite standards mixture. However, use of this technique was discontinued since it was found that analyses of untreated samples, using the reported conditions, gave better overall results.

Comparison of results obtained from analyses of standards, tap water extracts, and tap water extracts spiked with small quantities of aldrin confirmed the occurence of organochlorine pesticides and phthalates in Ottawa tap water (Table II, Figs. 1 and 2).

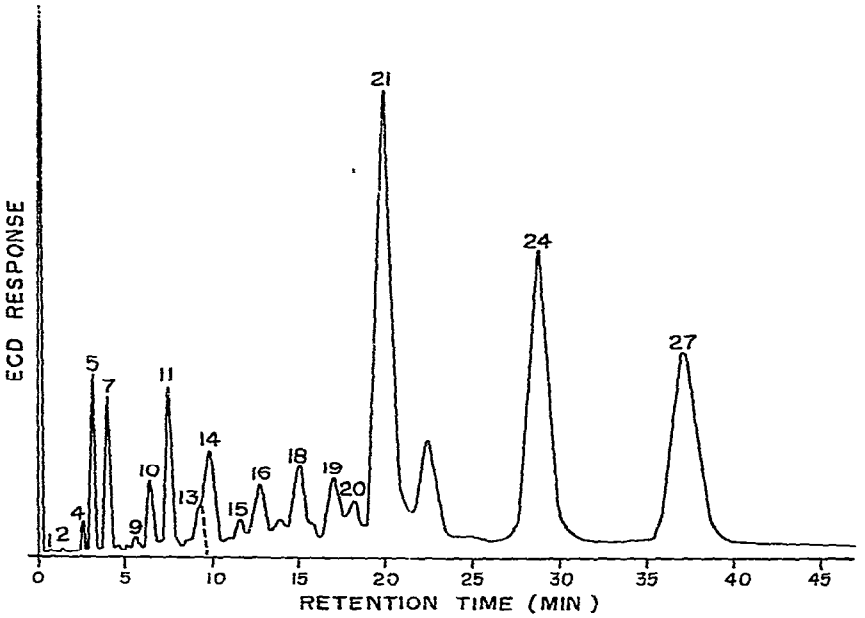

Fig. 1. Electron capture gas chromatogram of standard pesticide mixture (0.3 ng of each component). For peak numbering, see Table II. The operating parameters for the gas chromatograph are described in the text.

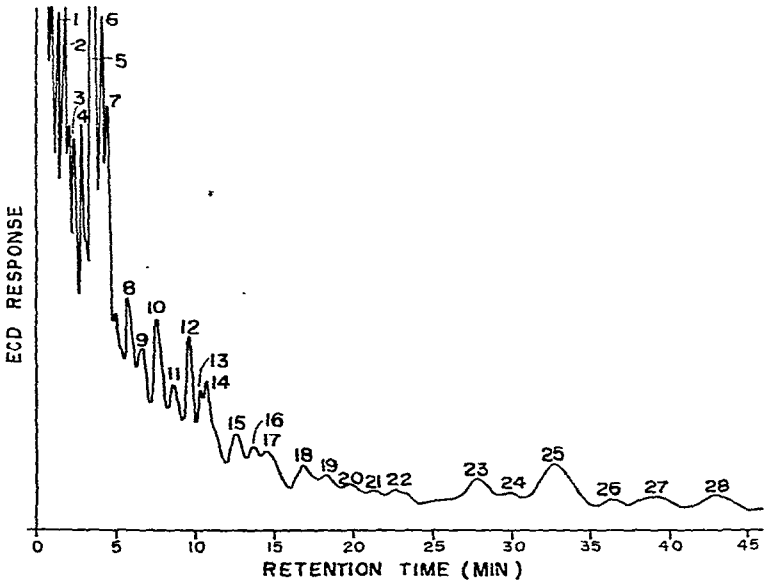

Fig. 2. Electron capture gas chromatogram of XAD-2 extract (from 200 l of Ottawa tap water). For peak numbering, see Table II. The operating parameters for the gas chromatograph are described in the text.

Gas chromatographic–mass spectrometric analysis

Qualitative and quantitative analyses of standards and tap water extracts were performed on a Varian Model 1440 gas chromatograph interfaced to a Varian MAT 311A high-resolution mass spectrometer with Watson-Biemann separator.

The GC conditions were: columns, 4% QF-1 and 2% SE-30 on 80–100 mesh HP Chromosorb W in a coiled glass column, 1.8 m × 3.5 mm I.D.; column temperature isothermal, 180–240°, depending on samples; injector temperature, 275°; interface temperature, 275°; carrier gas, helium at a flow-rate of 30 ml/min.

The mass spectrometric (MS) conditions were: source temperature, 250°; emmission, 3 mA; accelerating voltage, 3 kV; S.E.M. voltage, 2 kV; electron energy, 70 eV; resolution, $M/\Delta M = 5000$ (10% valley).

The instrument was operated in the specific ion-monitoring mode with perfluorokerosene as the reference compound. Masses to be monitored were set on the peak matching unit and were checked regularly against the reference peak. Comparison of peak heights with those of standards analyzed under identical conditions allowed calculation of quantitative data (Table IV).

Recovery studies

Although studies on the retention of organics in water by macroreticular resins vary in methodology[16,17,22,23], they generally indicate high retention efficiency. A procedure was developed to confirm the recovery efficiency of the present analytical scheme.

Two XAD-2 columns, identical to the type used for tap water extraction, were connected in tandem by means of a short piece of PTFE tubing and 24/40 $\overline{\$}$ jointed

TABLE III

PER CENT RECOVERY EFFICIENCY FOR XAD-2 TAP WATER EXTRACTION DETERMINED BY GG–MS

Compound	*1 µl standard solution**		*1 µl XAD-2 eluate*** *peak height (cm)*	*Per cent recovery*
	Weight injected (ng)	*Peak height (cm)*		
α-BHC	13	16.3	12.2	75
Lindane	1.0	1.3	1.0	77
Heptachlor	1.0	11.4	8.5	75
Heptachlor epoxide	1.0	3.7	2.7	73
o,p'-DDD	0.5	24.0	17.0	71
o,p'-DDT	0.5	5.3	4.9	92
p,p'-DDT	0.5	1.8	1.8	100
p,p'-DDE	0.5	12.8	9.4	73
Aldrin	1.0	5.1	4.1	80
Chlordane	0.5	14.5	13.4	92
Dieldrin	1.0	10.3	9.0	87
Endrin	1.0	10.9	9.2	84
Dibutyl phthalate	30	22.5	23.5	104
Di(2-ethylhexyl) phthalate	100	16.3	21.0	129

* 0.3 ml of this solution on an XAD-2 column was washed with 100 l of XAD-2 treated tap water and the components were eluted with 250 ml *n*-hexane which was concentrated to give 0.3 ml of XAD-2 eluate (see text).

glass connecting tube. The apparatus was connected to a laboratory water tap as previously indicated and 100 l of tap water were passed through at a flow-rate of 15–20 ml/min. Both columns were allowed to drain and were eluted separately with 250 ml *n*-hexane. The eluates were concentrated to 0.3 ml in the usual manner. GC–MS spectrometric analysis of the eluate from the upper column indicated the presence of organochlorine pesticides and phthalates, while no such materials were detected in the lower column eluate blank.

Per cent recovery determinations with this apparatus were preceded by reapplication of the column clean-up procedure and flushing with tap water (500 ml) to remove residual *n*-hexane. A 0.3-ml aliquot of standards in *n*-hexane solution (Table III) was added to the lower column reservoir, which contained 450 ml of tap water treated by passage through the upper column. The water level was drained to within 2 cm of the glass wool plug, 400 ml of treated water were added to the reservoir, the apparatus was assembled, and 100 l of tap water were passed through the system. The columns were drained, eluted with 250 ml *n*-hexane, and the eluates were concentrated to 0.3 ml.

Comparison of the lower column eluate and the solution containing standards in *n*-hexane by means of GS–MS allowed calculation of per cent recovery data (Table III).

TABLE IV

GC–MS ANALYSIS OF OTTAWA TAP WATER XAD-2 EXTRACT

Compound	*Ion mass monitored**	*Column temperature (°C)*	*Retention time (min)*	*Concentration detected in Ottawa tap water*** (ppt)*
α-BHC	218.9116 180.9379	180	2.0	17
Lindane	218.9116	180	2.4	1.3
Aldrin	66.0469 363.8728	180	4.7	0.70
Heptachlor	271.8102	180	3.8	⩽0.013
Heptachlor epoxide	271.8102	180	5.9	⩽0.044
Dieldrin	379.8678 271.8102 344.8988	180	6.7	⩽0.0095
Endrin	344.8988	200	5.3	⩽0.013
o,p'-DDD	235.0081	200	4.7	⩽0.0012
o,p'-DDT	235.0081	200	6.0	⩽0.0001
p,p'-DDD + *p,p'*-DDT***	235.0081	200	7.4	⩽0.0005
p,p'-DDE	317.9351	200	4.5	⩽0.016
Chlordane	372.8260	200	3.5	0.0053
Dibutyl phthalate	149.0239	200	2.5	29
Di(2-ethylhexyl) phthalate	149.0239	240	3.5	78

* Data obtained from ref. 27.

** Quantitative data obtained by comparison of GC–MS analyses of standards and tap water extracts were adjusted by per cent recovery values (Table III).

*** Both *p,p'*-DDD and *p,p'*-DDT had identical retention times and both gave strong peaks at *m/e* 235. They can be distinguished by their different molecular ions, but since none could be detected distinction was unnecessary.

RESULTS AND DISCUSSION

The use of XAD-2 resin for isolation and recovery of a variety of organic compounds from water and for development as a standardized analytical procedure has been explored[17]. The present study has confirmed the utility of the method for determining selected organochlorine pesticides in drinking water.

Measured volumes of tap water were extracted by passage through 30 g XAD-2 columns. The modified XAD-2 column clean-up usually resulted in clean blanks after only one series of *n*-hexane, acetone, *n*-hexane washes. This rapid and efficient method obviated the use of long sequential solvent extraction methods[17]. Use of the appropriate GC column (4% QF-1 and 2% SE-30 on HP Chromosorb W) allowed direct injection and analysis of the concentrated *n*-hexane eluate from the XAD-2 column. Under the specified conditions, good resolution and retention time reproducibility as well as suppressed PCB response and interference were achieved.

Major GC peaks with retention times greater than 0.1 (relative to aldrin) were identified (Table II). Confirmatory analysis and quantitation was achieved by means of specific ion-monitoring GC–MS (Table IV). Material from at least 200 l of tap water was required for quantitative analysis. The sensitivity of the method is achieved, in part, by efficient extraction (see Table III) and effective concentration of the sample extract from 300–0.3 ml, *i.e.*, a factor of 10^6. Analytical sensitivity is largely limited by operational parameters as well as nature of the sample. Use of a Varian Model 1440 gas chromatograph interfaced to a Varian MAT 311A high-resolution mass spectrometer operated in the specific ion-monitoring mode gave sensitivity in the order of nanograms for most of the chlorinated pesticides. The overall limit of detection under the experimental conditions is approximately 0.01 ppt* for the compounds studied. This limit could be extended by the application of aids such as time-averaging computer.

A procedure utilizing XAD-2 treated tap water was designed for the determination of per cent recovery for the analytical scheme. The aim of the design was to duplicate the experimental conditions as closely as possible, without introduction of unknown quantities of the materials under study. Determination of blanks for the clean-up column and the analytical column (see above) indicated, as anticipated, the presence of materials in the former column while no material was detected in the latter column. Per cent recoveries, ranging from 71–100% for organochlorine pesticides were found (Table III). These values are consistent with those found by other workers[16,17]. Values exceeding 100% for the phthalates are probably due to contamination resulting from the ubiquity of phthalates.

The possible presence of taste- and odour-producing or toxic organic contaminants, even in low concentration, in drinking water is of concern to the consumer. Concentrations of organochlorine pesticides detected in Ottawa tap water (Table IV) are expressed in terms of 17 ppt or less. These correspond to values found elsewhere[3] and are well below published maximum permissible levels for drinking water (Table I). They also correspond to levels determined by *n*-hexane liquid–liquid extraction[24] and are somewhat lower than those found in Ottawa River water[25]. The results (Table IV) show very low levels of DDT and its analogues, compounds whose

* Throughout this article, the American trillion (10^{-12}) is meant.

occurrence in the environment has resulted in many investigations and controversies. Also, the preponderance of α-BHC as compared to the isomeric but more toxic γ-BHC (lindane) and the other identified pesticides should be noted. Similar results have been observed elsewhere in surface water[26].

The use of XAD-2 macroreticular resin in the determination of low levels of organochlorine pesticides in water is a useful technique. Its potential for development into a standard procedure is clearly indicated.

Qualitative and quantitative analysis of other organic components in treated water is being pursued. Application of temperature programming (70–180°) to the analytical method provides a means to resolve the more volatile substances in the extracts. Recent studies indicate the occurrence of many such substances in Ottawa drinking water in low concentration.

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