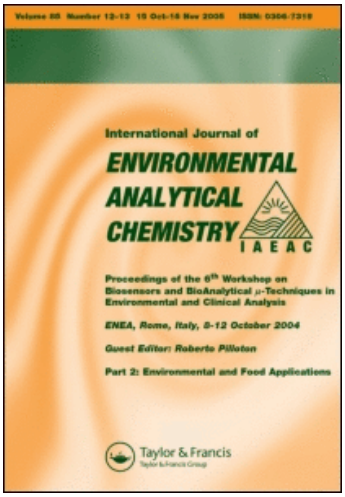

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The Determination of Polycyclic Aromatic Hydrocarbons at the ng/L Level in Ottawa Tap Water

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The Determination of Polycyclic Aromatic Hydrocarbons at the ng/L Level in Ottawa Tap Water

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Samples of Ottawa drinking water, collected in January and February 1978 were analysed by Gas Chromatography/Mass Spectrometry (GC/MS) for fifty polycyclic aromatic hydrocarbons (PAH) and five oxygenated polycyclic aromatic hydrocarbons (O-PAH), following extraction of the organic species using Amberlite XAD-2 macroreticular resin. In the January sample, thirty PAHs, ranging in concentration from 0.05 to 14 ng/L with a mean value of 3.8 ng/L and a total weight of 114 ng/L and four O-PAHs, ranging in concentration from 0.10 to 1.8 ng/L with a mean value of 0.91 ng/L and a total weight of 3.7 ng/L, were detected. In the February sample, thirty-six PAHs, ranging in concentration from 0.05 to 8.1 ng/L with a mean value of 1.4 ng/L and a total weight of 50.4 ng/L and five O-PAHs, ranging in concentration from 0.20 to 2.4 ng/L with a mean value of 1.0 ng/L and a total weight of 5.2 ng/L, were detected. Twenty-eight PAHs and four O-PAHs were common to the two samples. The use of Amberlite XAD-2 macroreticular resin to extract PAHs from drinking water is shown to be effective, although the recovery of individual PAHs from artificially loaded XAD-2 resin varied from 57 to 100%.

KEY WORDS: Drinking water, polycyclic aromatic hydrocarbons, XAD-2 macroreticular resin.

INTRODUCTION

The past few years have witnessed a dramatic increase in the number and variety of anthropogenic organic contaminants detectable at low levels (*ca* ng/L) in potable water.[1,2,3,4,5,6] Potable water treatment procedures are largely inefficient for the removal of organic contaminants and, in fact, may introduce additional organic compounds through the interaction of added chemicals with the organic species present in the raw water

supply, (e.g. trihalomethanes[7]) or by the slow release of accumulated contaminants from saturated activated charcoal beds[8] into the treated water.

Because of the low concentration of most organic pollutants, large volumes (*ca* 200 L) of potable water must be analysed in order to detect the organic contaminants with modern techniques such as Gas Chromatography/Mass Spectrometry (GC/MS). A wide range of techniques including solvent extraction,[9,10] polyurethane foam,[5,12,13] or macroreticular resins[14,15,16,17] have been developed to provide concentrated solutions of the organic contaminants suitable for analysis by GC/MS. Among these techniques, macroreticular resins, particularly the Amberlite XAD series, have been used effectively to concentrate a variety of organic contaminants in drinking water.[2,3,6,15,18,19]

As a first step in the assessment of the scope and the magnitude of the anthropogenic contamination of Canadian drinking water supplies, we have undertaken studies to evaluate the use of Amberlite XAD-2 resin for the analysis of organic contaminants in potable water. We have previously reported our studies on organochlorinated pesticides[18] and organophosphates[19] and report here on polycyclic aromatic hydrocarbons in Ottawa drinking water.

EXPERIMENTAL

Solvents and chemicals

All solvents were of "distilled in glass quality and were re-distilled in an all glass system. All compounds in the standard solutions were obtained from commercial sources and were used as received.

Sample preparation

Sample preparation has been reported in detail elsewhere[19] and is briefly summarised here. Sampling cartridges, containing *ca* 15 g Amberlite XAD-2 (Rohm and Haas, Philadelphia U.S.A.) macroreticular resin that had been previously cleaned by the method of McNeil *et al.*,[2] were rinsed with 250 mL acetone and washed with at least 1 L of purified water. The cartridges were attached to a potable water tap in our laboratory and the flow of water was controlled at *ca* 70 mL/min. When the required volume (*ca* 300 L) of water had been passed through the cartridge, the cartridge was disconnected from the tap and as much water as possible was removed from the cartridge by careful draining followed by the application of vacuum from a water aspirator. The XAD-2 resin was eluted

with 300 mL of 15:85, v/v acetone hexane solution at a flow rate of *ca* 5 mL/min. The organic layer was dried by passage through a drying column containing anhydrous sodium sulfate over a glass wool plug. Both the sodium sulfate and the glass wool plug were cleaned by successive washings with methylene chloride, acetone and hexane prior to use. The dried solution was concentrated to a volume of *ca* 3 mL using a rotary evaporator, then quantitatively transferred with acetone to a graduated vial and was further concentrated, using a gentle stream of dry nitrogen gas, to a final volume of 1 mL.

Sample analysis

A 10 uL aliquot of the concentrated extract was injected into a Finnigan 4000 GC/MS coupled to a 6110 data system. Of the three GC columns that were used (3% OV-101, 3% OV-17 and 3% OV-225) the 3% OV-17 provided the best separation of the detectable PAHs and was used throughout this study. A 1.8 m × 2 mm i.d. glass column, packed with 3% OV-17 on 80/100 mesh Chromosorb 750, was operated at an initial temperature of 100°C for 1 min and was programmed to a final temperature of 225°C at a rate of 3°/min and held at that temperature for the remainder of the analysis. The flow of helium carrier gas was set at 20 mL/min and the injection port temperature set at 200°C. The glass jet separator and the ion source temperatures were set at 260°C and 250°C, respectively. Data acquisition was under the control of the Finnigan 6110 data system. The mass range, 35 to 400 amu, was scanned at a rate of 2.1 s/scan and the mass spectra (*ca* 1000) stored on magnetic disk for subsequent analysis.

Recovery study

Two XAD-2 macroreticular resin cartridges were connected in series such that the effluent from the first cartridge passed through the second. In one experiment, the preparation of the control blank, this system was connected to a potable water tap in our laboratory and subjected to a flow of water at a rate of 70 mL/min until a total of 100 L of water had been collected. In the second experiment, a 0.5 mL aliquot of a solution of PAH standards in acetone containing from 1.3 to 3.3 ug/mL of thirty-two selected PAHs detected in Ottawa drinking water was injected onto the head of the second cartridge and forced onto the resin bed by a stream of purified nitrogen gas. This level of artificial loading of the XAD-2 resin is the equivalent of a mean concentration of *ca* 10 ng/L in the original

drinking water sample. The sampling system was then connected to a potable water tap in our laboratory and subjected to a flow of water at a rate of 70 mL/min until a total of 100 L of water had been collected. In both experiments the second cartridge was then treated as described above prior to analysis by GC/MS.

RESULTS AND DISCUSSION

Initially, a concentrated extract of Ottawa tap water was analysed qualitatively by GC/MS to determine which low molecular weight PAHs might be present. Based on the interpretation of the mass spectra obtained, a number of PAHs were tentatively identified. To confirm identification a solution was prepared containing fifty PAHs and five O-PAHs, which were selected on the basis of tentative identification and commercial availability. Using this solution to establish retention times, mass spectral characteristics and optimum GC conditions to provide the maximum resolution of the compounds involved, Ottawa potable water was screened for these fifty-five compounds.

To test the effectiveness of our method of analysis for PAHs in drinking water, a control blank was prepared and analysed and a recovery study of thirty-two selected PAHs from XAD-2 resin was conducted.

None of the fifty-five compounds contained in the standard solution was detected in the concentrated extract from the control blank (Experimental). This indicates that the XAD-2 resin is effective for the removal of these compounds from drinking water and that none of the reference compounds originate from the pre-cleaned[2] XAD-2 resin. However, when the amounts of PAH loaded and recovered are compared (Table I), an average recovery of 0.84 is observed, with recoveries ranging from 0.57 to 1 of the loaded material. The weighted average recovery was 0.88 of loaded material. The fate of the unrecovered material has not been established, although, based on the results of the control blank, it is not likely that these materials were carried away by the effluent water.

Two separate Ottawa drinking water samples, collected in January and February 1978, were analysed in order to obtain some indication of whether the results are representative of the general background level of anthropogenic contamination during the test time period or of intermittent contamination events. Aliquots of the reference standard solution (fifty PAHs and five O-PAHs) and the concentrated extracts from XAD-2 resin were analysed consecutively by GC/MS under identical operating conditions. As is evident from Figure 1, a representative gas chromatogram of the drinking water, XAD-2 resin extract concentrate, as reconstructed from the total ion current, contained a multitude of poorly

TABLE I

The recovery of selected polycyclic aromatic hydrocarbons from Amberlite XAD-2 macroreticular resin

Compound	Amount Loaded (ng)	Fraction recovered
Naphthalene	625	0.57
2-Methylnaphthalene	1200	0.88
1-Methylnaphthalene	625	0.71
2-Ethylnaphthalene 2,6-Dimethylnaphthalene	>2300	>0.86
Biphenyl	775	0.66
1,3-Dimethylnaphthalene	975	0.81
2,3-Dimethylnaphthalene 1,4-Dimethylnaphthalene	>2250	>0.82
4-Phenyltoluene	600	0.85
Diphenylmethane 3-Phenyltoluene	>2075	>0.76
Acenaphthene	625	0.60
Bibenzyl	975	0.65
1,1-Diphenylethylene	1625	0.98
cis Stilbene	575	1.0
2,3,5-Trimethylnaphthalene	700	0.75
3,3′-Dimethylbiphenyl	1625	1.0
Fluorene	750	0.89
4,4′-Dimethylbiphenyl	700	0.90
trans Stilbene 9,10-Dihydrophenanthrene	>1075	>0.84
Phenanthrene Anthracene	>1700	>1.0
Triphenylmethane	800	0.87
Fluoranthene	650	1.0
Pyrene	725	1.0
1,2-Benzfluorene 2,3-Benzfluorene	>1550	>0.99
Triphenylene Benz(a)anthracene Chrysene	>1650	>1.0
Average	1110	0.84

defined peaks. Complete mass spectra, free of extraneous ions, could rarely be obtained from such data despite the background subtraction routine possible with the data system and, hence, individual components of the concentrate could not be identified in this fashion. Compound identification was achieved from mass chromatograms (Figure 2) which were

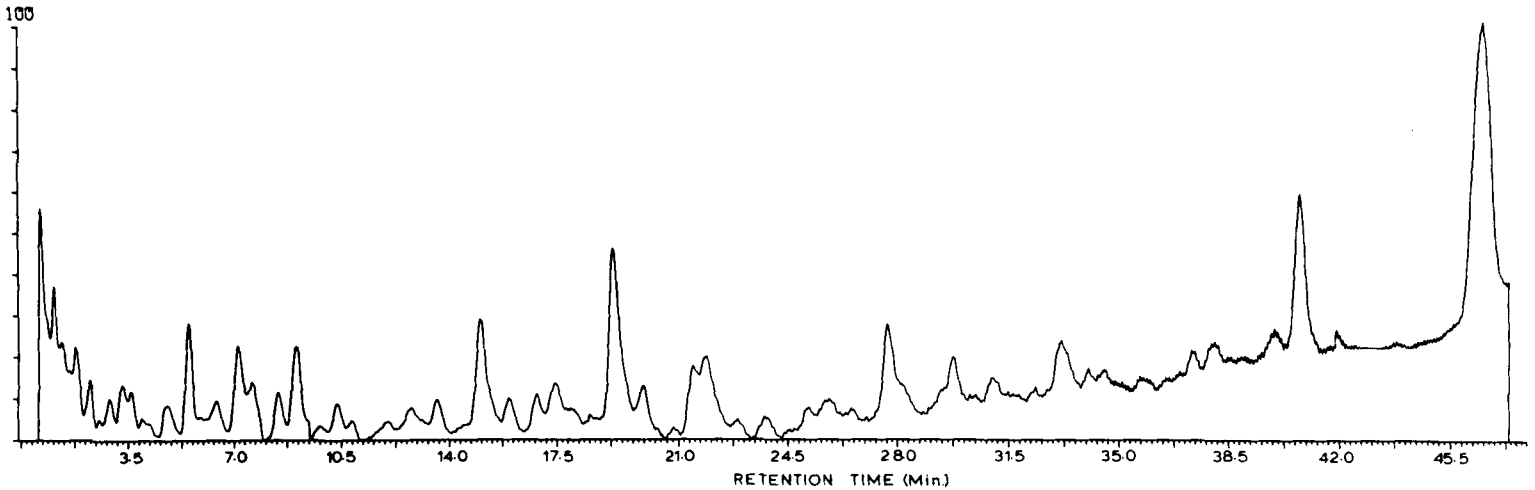

FIGURE 1 Reconstructed gas chromatogram (total ion current) from Ottawa drinking water Amberlite XAD-2 resin extract.

reconstructed from selected ion currents rather than the total ion current. Mass chromatograms for selected ions that were characteristic of the compound of interest were obtained by searching the accumulated data for the ion of interest and recording the abundance of this ion as a function of retention time. As an example, the mass chromatograms of three ions—m/e 128, m/e 142, and m/e 154—are superimposed in Figure 2. The location of the peaks corresponding to the compounds of interest are indicated by asterisks in each chromatogram. For m/e 128 the asterisked peak corresponds to the molecular ion of naphthalene, for m/e 142 to the

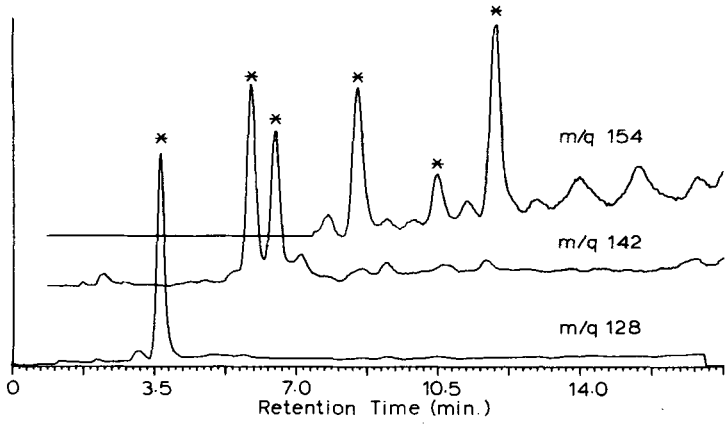

FIGURE 2 Reconstructed mass chromatograms for ions m/e 128, m/e 142 and m/e 154 from Ottawa drinking water Amberlite XAD-2 resin extract.

molecular ions of 2-methylnaphthalene and 1-methylnaphthalene, respectively, in order of increasing retention time and for m/e 154 to the molecular ions of biphenyl, 2-vinylnaphthalene and acenaphthene, respectively, in order of increasing retention times. The retention times for each standard were established by analysis of the reference standard solution and the data from the XAD-2 resin extracts were then searched for the ion of interest within the appropriate time region. In all instances the molecular ion and the next most abundant ion were selected as the characteristic ions which are listed in Tables II and III.

A compound was considered identified if the two ions characteristic of the compound of interest were found to elute from the column within the retention time window (± 0.1 min) of the reference standard and to be in the relative abundance ratio ($\pm 20\%$) observed in the mass spectrum of the pure compound. For most, but not all, compounds screened unique identification was possible. In some instances however, co-eluting isomers yielding similar mass spectra could not be resolved sufficiently to allow

TABLE II

Polycyclic aromatic hydrocarbons detected in Ottawa drinking water sampled in January (2) and February (1) 1978.

Compound	Ions monitored		Rel. ret. time[a]	Concentration (ng/L) 1	2
Naphthalene	128	102	1.00	6.8	4.8
2-Methylnaphthalene	142	141	1.59	2.4	4.6
1-Methylnaphthalene	142	141	1.75	1.0	2.0
Azulene	128	102	1.90	n.d.	n.d.
2-Ethylnapthalene	156	141	2.26	>0.70	2.1
2,6-Dimethylnaphthalene	156	141	2.32		
Biphenyl	154	153	2.30	0.70	1.1
1,3-Dimethylnaphthalene	156	141	2.51	1.9	1.1
2-Vinylnaphthalene	154	153	2.68	n.d.	n.d.
2,3-Dimethylnaphthalene	156	141	2.69	>0.68	14
1,4-Dimethylnaphthalene	156	141	2.69		
3-Phenyltoluene	168	167	2.74	0.20	1.5
Diphenylmethane	168	91	2.88	1.4	2.8
4-Phenyltoluene	168	167	2.94	0.20	3.7
Acenaphthylene	152	151	3.00	0.05	n.d.
Acenaphthene	154	153	3.25	0.20	1.8
Bibenzyl	182	91	3.41	1.9	1.5
1,1-Diphenylethylene	180	179	3.48	>7.4	n.d.
cis Stilbene	180	179	3.59		
2,2-Diphenylpropane	196	181	3.62	n.d.	n.d.
2,3,5-Trimethylnaphthalene	170	155	3.71	0.65	5.2
3,3'-Dimethylbiphenyl	182	167	4.03	0.31	5.2
Fluorene	166	165	4.15	0.15	2.2
4,4'-Dimethylbiphenyl	182	167	4.18	0.57	7.0
4-Vinylbiphenyl	180	178	4.56	n.d.	n.d.
Diphenylacetylene	178	89	4.90	0.05	n.d.
9,10-Dihydroanthracene	180	179	5.03	0.66	n.d.
trans Stilbene	180	179	5.20	>0.47	9.2
9,10-Dihydrophenanthrene	180	179	5.29		
10,11-Dihydro-5H-dibenzo (a,d)cycloheptane	194	179	6.03	0.40	n.d.
Phenanthrene	178	89	6.08	>0.52	2.2
Anthracene	178	89	6.14		
1-Phenylnaphthalene	204	203	6.77	n.d.	n.d.
1-Methylphenanthrene	192	191	7.06	n.d.	11
2-Methylanthracene	192	191	7.25	0.51	0.70
9-Methylanthracene	192	191	7.59	n.d.	0.70
9-Vinylanthracene	204	203	7.82	n.d.	n.d.
Triphenylmethane	244	167	8.04	n.d.	n.d.
Fluoranthene	202	101	8.41	0.55	1.9
Pyrene	202	101	8.90	0.53	1.7
9,10-Dimethylanthracene	206	191	8.99	0.19	n.d.
Triphenylethylene	256	178	9.25	0.08	n.d.
p-Terphenyl	230	115	9.44	n.d.	n.d.
1,2-Benzfluorene	216	108	9.64	n.d.	n.d.
2,3-Benzfluorene	216	108	9.73	n.d.	n.d.
Benzylbiphenyl	244	167	9.75	n.d.	n.d.
1,1'-Binaphthyl	254	126	10.95	n.d.	n.d.
Triphenylene	228	114	11.5		
Benz(a)anthracene	228	114	11.6	>8.1	3.3
Chrysene	228	114	11.8		

TABLE III

Oxygenated polycyclic aromatic hydrocarbons detected in Ottawa drinking water sampled in January (2) and February (1) 1978.

Compound	Ions monitored		Rel. ret. time[a]	Concentration (ng/L) 1	2
Xanthene	182	181	4.83	0.20	0.10
9-Fluorenone	180	152	5.93	0.90	1.5
Perinaphthenone	180	152	7.70	0.28	0.15
Anthrone	194	165	7.90	1.4	n.d.
Anthraquinone	208	180	8.11	2.4	1.8
Naphthalene	128	102	1.00		

[a]Retention times are relative to the retention time of naphthalene (3.81 min).

unequivocal identification. Such co-eluting isomers are grouped together in Table II and are indicated by > beside the concentration value which is the sum of the contributions from all co-eluting isomers. Furthermore, it needs to be emphasized that, because of the large number of compounds contained in the field sample extract, it was not possible to entirely eliminate from all the ion peaks of interest, contributions from possible interfering species. This was particularly true for methyl substituted PAHs for which numerous positional isomers may elute within a narrow time window. In many cases only a small number of the possible positional isomers were available commercially and could be included in our reference standard. Hence, unequivocal identification of positional isomers was often not possible.

Quantitative estimations of the detectable PAHs and O-PAHs in Ottawa drinking water were obtained by comparison of the areas of the two characteristic ion peaks (Tables II and III) in the mass chromatograms of the reference standard and the field sample, respectively. The average of the concentrations for the two ions is presented in Tables II (PAHs) and III (O-PAHs) for the two water samples analysed. No corrections were made for incomplete recovery. Of the fifty PAHs in our standard, thirty eight are detected in at least one of the two drinking water samples tested. In sample 1 (February 1978) thirty-six PAHs (Table II), ranging in concentration from 0.05 to 8.1 ng/L and in sample 2 (January 1978) thirty PAHs (Table II), ranging in concentration from 0.05 to 14 ng/L, were detected. Twenty-eight PAHs and four O-PAHs were detected in both samples analysed. The lower concentration of 0.05 ng/L represents the lower limit of detection of this method of analysis. There is appreciable variation in the concentrations of most of the PAHs detected

(pH 7), were added. The solution was stirred at room temperature and 1 ml aliquots were removed at timed intervals and titrated with ferrous ammonium sulfate.

Preparation of standard chlorine dioxide-chlorine mixtures

Pure chlorine dioxide solution was diluted with water to give an approximate concentration of 0.7 mg ml. The concentration of the solution was then determined spectrophotometrically.[10]

The chlorine solution was prepared by adding chlorine gas to water and its concentration was determined by titration with ferrous ammonium sulfate.[6]

The chlorine dioxide-chlorine solutions were prepared by adding aliquots of the chlorine solution, equivalent to 0.1, 0.2 and 0.3 mg, to 5, 10 and 20 ml portions of the chlorine dioxide solution. The concentrations of chlorine and chlorine dioxide were then determined by differential titration with ferrous ammonium sulfate using either glycine or oxalic acid.

RESULTS AND DISCUSSION

A direct spectrophotometric determination of chlorine dioxide in the presence of chlorine, using acid chrome violet K (ACVK) has been reported[10] and the accuracy of the technique has been verified using electron spin resonance spectrometry.[11] There is no method, however, for direct quantitation of chlorine in the presence of chlorine dioxide. Instead the amount of chlorine is determined by differential titration. Husband *et al.*[3] used differential iodometric titration (Eqs. 1–3).

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \quad (1)$$

$$2ClO_2 + 2I^- \rightarrow 2ClO_2^- + I_2 \quad (2)$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O \quad (3)$$

Titration at neutral pH with thiosulfate gives a titre (titre A) representing chlorine and one-fifth of the chlorine dioxide value (Eqs. 1–2). The solution is then acidified and the titration continued to give a second titre (titre B, Eq. 3). If titre B is equal to four times titre A, then there is no chlorine present in the solution. Husband *et al.* reported that ca. 1% chlorine relative to chlorine dioxide could be detected by this method. However, in our hands the method was not found to be satisfactory. Although the acid titre was found to be equal to four times the neutral titre, indicating the absence of chlorine, the absolute value obtained for

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