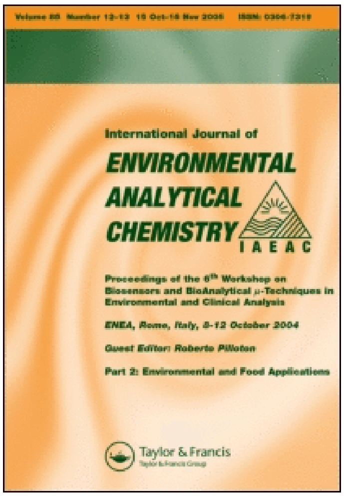

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Potentiometric Determination of Organohalides in Natural Water Using Tenax Adsorption and Combustion

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The method described in this paper involves adsorption of organohalides from natural water samples on porous polymer Tenax GC followed by thermal desorption at 400°C and oxidative combustion to hydrogen halides. The halides are captured in water solution containing formaldehyde and sulfamic acid and measured either by direct potentiometry with high sensitive chloride ion selective electrode or by potentiometric titration with Hg^{2+} titrant solution. The efficiencies of the adsorption, combustion and detection as well as elimination of interferences are presented. Analysis time after adsorption is rapid (2 min) and procedures are simple, making the technique suitable for routine application.

KEY WORDS Organohalides, water, adsorption, combustion, detection.

INTRODUCTION

Halogenated organocompounds are of considerable interest in the environmental field research because they are suspected to cause adverse health problems.[1,2] Their presence and origin are well documented.[3-9] Current methods of analysis identify groups of organohalides such as volatile[9,10] and non-polar compounds. Recently the analysis for total organohalides as a group parameter has been recognized as an indicator of water quality because it includes in the measurement the amount of potentially harmful compounds.[12,13] The first step in the analysis for trace organohalides in water is their separation and preconcentration. Several methods have been reported using the adsorption of organic compounds onto ground, granular activated carbon.[14-16] Another method is the mini-column method employing Amberlite XAD resin as the sorbent.[13] Solvent extraction has also been suggested for the separation and preconcentration step.[17] The efficiencies of liquid-liquid extraction, carbon and XAD resin have been evaluated by Janarden *et al.*[18-19] and by Chriswell *et al.*.[20] The extraction of trace amounts of organic compounds from water has been reviewed by Dressler.[21] Published data seem to favour the extraction with porous organic polymers over the other techniques.

The second step involved in the method is the desorption of the compounds from the sorbent. This can be performed either with a liquid or by heating. Liquid desorption with a number of elements has been applied mostly in combination with chromatographic detection of organic compounds.[22] In desorption, the compounds are released by the action of heat and these are transported by the carrier gas into the converter and/or detector. The desorption temperature must be high enough to allow all compounds of interest to be transferred into the gaseous phase. The maximal desorption temperature is determined by the thermal stability of the sorbent. Tenax GC porous polymer was found to be stable up to 400°C whereas Amberlite XAD-2 only was acceptable to 275°C.[22] The drawback of activated carbon is that due to the high desorption temperature some inorganic halides are detected and the column cartridges have to be treated by a nitrate wash to displace inorganic chloride. Since freshly ground activated carbon contains some halogens that are not removable, a blank determination is necessary.[23]

The third step of the total organohalides analysis is their conversion into a measurable form. The pyrolytic conversion of organohalides to simple halides has been reviewed by Debal and Levy.[24] Further development resulted in a relatively standard procedure in which the sample is vapourized in the stream of an inert carrier gas and is joined by oxygen in a combustion zone held over 800°C. The resulting gases are swept into a detecting system.

The last step is the detection of the halides. Generally, potentiometric or coulometric techniques in different variations have been applied. Kriggsman *et al.*[27] have described a semi-automatic argentometric preselected end-potential titration monitored by an Ag_2S ion-selective electrode. Potman and Sahmen[28] modified this method by using Hg^{2+} as titrant. A microcoulometric method based on argentometry has been described.[12, 25]

Based on the above information, Tenax GC resin as the sorbent, thermal desorption in the carrier gas stream, combination in an oxygen rich atmosphere and direct potentiometric detection were selected, tested and optimized.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade. The stock solutions, prepared by weight, were standardized by appropriate standard analytical methods. The water used in this study was distilled from a potassium permanganate-sodium hydroxide solution and passed through a column packed with Tenax GC in order to remove residual trace organics. Absorption solution contained 1 ml of formaldehyde (38 %) and 0.1 g of sulfamic acid in 100 ml of water and was made fresh each day.

Apparatus

Resin cartridges made of quartz with quartz fibre filter plugs on both ends were packed with Tenax GC 35/60 mesh (Enka, N.V., Holland) and heated to 400°C in the stream of CO_2 gas for 20 min to remove possible contaminants. Model studies were performed using gravity flow from a 10 l reservoir. Stock solutions of model compounds were prepared in acetone and diluted with water so that the aqueous solutions contained 100 μg/l of chloride or bromide. At the end of the sampling period the cartridge was connected to the CO_2 line for 30 min to remove trapped water. A Dohrman MO S-200 pyrolysis furnace with three independently heated zones was used for the oxidative combustion. The furnace was equipped with a quartz combustion tube connected to a water-cooled absorption vessel. Figure 1 shows a scheme of the apparatus used for desorption and combustion. The water-cooled absorption vessel shown in Figure 2 was equipped with a combination high sensitive chloride ion-selective electrode.[29] The gases from the combustion tube were absorbed in 5 ml of the absorption solution. The electrode exhibited practical

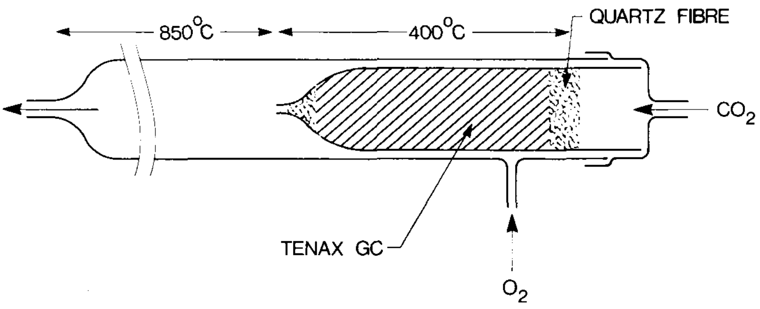

FIGURE 1 Pyrolytic tubes with resin cartridge used for adsorption, thermal desorption and combustion.

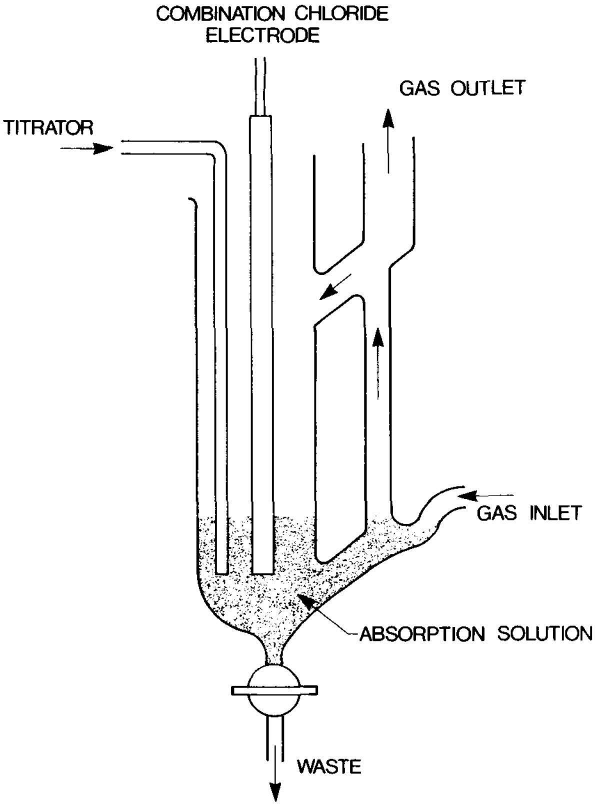

FIGURE 2 Absorption vessel used for absorption of the combustion products and measurement of halides.

detection limit of 20 ppb Cl^- in the absorbing solution. The detection limit of the system for samples depends on the volume of the sample passed through the Tenax cartridge. Assuming a 1000 ml sample and 5.0 ml volume of the absorbing solution, the detection limit in the sample is 0.1 ppb Cl^-. A Radiometer PHM64 pH meter in conjunction with TTT60 titrate, ABU12 autoburette and REA160 recording system was used for direct potentiometric measurement as well as for preselected end-point and stepped end-point titration[30] of halide ions.

Procedure

The water sample is passed through the resin cartridge at the rate of 10 ml/min. After the desired volume of sample is eluted, most of the residual water is removed in the stream of CO_2 (30 min) and the cartridge is inserted into the desorption inlet zone of the furnace heated to 400°C. Released and vapourized organics are swept by a continuous stream of CO_2 (100 ml/min) into a combustion zone held at 850°C where they are combusted in an oxygen enriched atmosphere (100 ml/min). The gases then flow into the absorption vessel where the halides are captured and determined. After the potential of the chloride-ion electrode reaches a stable reading, the concentration of halide ions is determined by comparing with a previously prepared calibration graph. Alternatively, a preselected end-point titration system automatically balances the changes of potential by adding the Hg^{2+} titrant solution and the concentration of halides is calculated from the volume of added solution.

RESULTS AND DISCUSSION

Performance of the Detection System

Two versions of the detection of halide ion were selected and tested. Both employed a highly sensitive chloride ion electrode operated either in a direct potentiometry mode or in a preselected end-point potentiometric titration mode, using Hg^{2+} titrant solution. The performances of the systems were tested by measuring known concentrations of Cl^- ion directly in the absorption vessel.For practical purposes, the chloride ion electrode exhibited a detection limit of 20 ppb of Cl^- in the absorption solution. The precision expressed as relative standard deviation was better than 5%. The detection limit of the mercurimetric titration with 1×10^{-4} M $Hg(NO_3)_2$ solution was 80 ppb of Cl^- in 5 ml and the relative standard deviation was 4%. The advantage of direct potentiometry is sensitivity and simplicity of the instrumentation. The disadvantage is that the volume of the absorption solution must be accurately measured and replaced for each measurement and the electrode requires frequent recalibration. Furthermore, the electrode did not perform reproducibly in the solutions containing lower than 10:1 ratio of Cl^- to Br^- ion. The titration method is less sensitive but more precise. Several determinations can be made in the same absorption solution and its volume is not important. There is no calibration involved and mutual interference of chloride and bromide is negligible. The attempts to determine low levels of bromide and chloride in admixture by consecutive stepped end-point titration were not successful.

Efficiency of the Oxidative Combustion

In order to test the efficiency of the oxidative combustion of organohalide compounds to measurable halide ions, the acetone solutions of several model compounds were slowly injected into the 400°C zone of the furnace and the produced halide ions were titrated in the absorption vessel. Preliminary experiments showed that the recovery of chloroform was not affected by the temperature of the combustion zone varying from 800 to 1000°C nor by varying the flow rate of CO_2 (50 to 200 ml/min) and O_2 (50 to 100 ml/min). Therefore, all experiments were conducted under the following conditions: 400°C temperature of the inlet zone; 850°C temperature of the combustion zone; 100 ml/min CO_2 flow rate and 100 ml/min O_2 flow rate. Results of recovery and precision are presented in Table I.

TABLE I
Efficiency of the oxidative combustion

Compound	Cl(Br) Taken (μg)	Mean ($n=5$) Cl(Br) Found (μg)	S_r (%)
Carbontetrachloride	1.2	1.0	5
	12.0	11.0	2
Trichloromethane	1.7	1.4	4
	17.0	16.0	2
Chloroacetone	0.9	0.7	8
	9.0	9.0	5
Chlorobenzene	1.4	1.3	6
	14.0	12.0	3
Trichlorobenzene	1.5	1.3	3
	15.0	14.0	2
Pentachlorophenol	1.8	1.5	5
	18.0	15.0	4
DDT	0.8	0.6	10
	8.0	6.0	6
Atrazine	1.2	1.1	8
	12.0	10.0	5
Aldrin	1.3	1.1	5
	13.0	12.0	3
Trichloroacetic acid	0.6	0.6	10
	6.0	5.0	6
Tribromomethane	1.6	1.4	4
	16.0	15.0	2
Bromobenzene	1.7	1.5	6
	17.0	15.0	5
Bromophenol	1.1	1.0	9
	11.0	9.0	5
Tribromophenol	1.1	1.0	7
	11.0	9.0	4
Bromobenzoic acid	0.7	0.5	11
	7.0	5.0	7

Efficiency of Adsorption and Desorption

The efficiency of adsorption and thermal desorption (total efficiency) was established by analyzing the synthetic samples of water containing known amounts of organohalides. Recoveries of ten model compounds as shown in Table II averaged 80% at 1.0 ppb levels of chlorine or bromine in the sample. Relative standard deviations were in the range of 5% at 1.0 ppb levels.

TABLE II
Efficiency of the determination

Compound	Cl(Br) Taken (μg)	Mean ($n=5$) Cl(Br) Found (μg)	S_r (%)
Carbontetrachloride	1.4	1.2	6
Trichloromethane	1.3	1.1	5
Chlorobenzene	1.4	1.1	4
Trichloroacetate	0.6	0.4	8
Pentachlorophenol	1.8	1.4	6
DDT	1.6	1.3	5
Aldrin	2.6	2.2	3
Bromobenzene	1.7	1.6	5
Bromophenol	2.2	2.0	4
Bromobenzoate	3.5	3.3	3

Interferences

The oxidative combustion of organosulfur and organonitrogen compounds produces ionic species (SO_3^{2-}, S^{2-}, NO_x, CN^-) which interfere with the response of the chloride electrode as well as the mercurimetric titration. To eliminate these interferences the absorption solution contains formaldehyde (1 ml of 38% solution) and 0.1 g of sulfamic acid in 100 ml of water.[31] This solution, besides eliminating the interferences from sulfur and nitrogen, adjusts the pH and total ionic strength required for optimal performance of the electrode. Table III shows the results of the determination of carbontetrachloride in the presence of sulfur (carbondisulfide) and nitrogen (cyclohexylamine). No significant interference was observed.

One of the problems in organohalide analysis is to ensure that inorganic halides do not interfere. Data on the determination of carbontetrachloride in the presence of inorganic chloride as presented in Table IV show insignificant interference. Free chlorine present in disinfected water interferes and has to be reduced prior to the analysis.

TABLE III
Influence of nitrogen and sulfur on chlorine determination

S Taken (μg)	N Taken (μg)	Cl Taken (μg)	Cl Found (μg)	Recovery (%)
		1.2	1.0	83
		12.0	11.0	92
1.4	1.7		0.1	
14.0	17.0		0.1	
1.4	1.7	1.2	1.1	92
14.0	17.0	1.2	1.3	108
1.4	1.7	12.0	12.5	104
14.0	17.0	12.0	12.9	108

TABLE IV
Determination of carbontetrachloride in presence of inorganic chloride

Inorganic Cl Taken (μg)	Organic Cl Taken (μg)	Organic Cl Found (μg)	Recovery (%)
	1.2	1.0	83
	12.0	11.0	92
0.4	1.2	1.1	92
3.5	1.2	1.0	83
35.4	1.2	1.2	100
354.0	1.2	1.3	108
0.4	12.0	11.0	92
3.5	12.0	13.0	108
35.4	12.0	13.0	108
354.0	12.0	13.2	110

Five, three-litre Lake Ontario water samples were taken for analysis by the proposed method. The samples were divided into three, one-litre aliquots. The first aliquots was analyzed for organohalides without any treatment, whereas aliquots two and three were spiked with a known amount of trichloromethane prior to the analysis. Results are summarized in table V.

TABLE V
Determination of organochlorine in lake-water

Sample No.	Cl Taken (μg/l)	Cl Found (μg/l)	Recovery (%)
1	0.0	68.0	—
	13.0	75.0	93
	130.0	187.0	94
2	0.0	27.0	—
	13.0	35.0	88
	26.0	48.0	91
3	0.0	41.0	—
	13.0	50.0	93
	65.0	91.0	86
4	0.0	52.0	—
	26.0	61.0	78
	130.0	159.0	87
5	0.0	91.0	—
	52.0	129.0	90
	130.0	191.0	86

CONCLUSION

Analytical procedures involved are simple and rapid. The required instrumentation is relatively inexpensive and easy to operate. Sulfun and nitrogen interferences are eliminated. The sensitivity, recovery and precision compare well with other techniques. The described method is suitable for routine analysis of Tenax adsorbable organohalides in natural water. Proper selection of the sample volume allows the application of the method over wide range of concentration

Sommaire

La faible concentration d'organo-halogénures prévue dans les études environnementales nécessite la création de méthodes analytiques permettant la détection de ces composés jusqu'aux niveaux inférieurs aux parties par milliard. La méthode décrite dans la présente étude a recours à l'absorption des organo-halogénures par un polymère poreux de marque Tenax GC, suivie de désorption thermique à 400° et de conversion pyrolitique en halogénures d'hydrogène. Les halogénures sont captés dans une solution aqueuse contenant du formaldéhyde et de l'acide sulfamique. Ils sont ensuite doses, soit par potentiometrie directe comportant une électrode fortement sensible aux ions chlore, soit par titrage potentiométrique en utilisant une solution titrée au moyen de Hg^{2+}. On présente dans cette étude l'efficacité de l'absorption, de la combustion et de la détection ainsi que l'élimination des interférences. Le temps d'analyse est rapide (2 min.) et les méthodes sont simples. Il s'ensuit que cette technique se prête bien aux applications courantes.

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