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Determination of bromide in complex matrices by pre-column derivatization linked to solid-phase extraction and high-performance liquid chromatography

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Abstract

Bromide has been determined (i) in the presence of a large excess of chloride and other ions to evaluate its level in sea water, concentrated hydrochloric acid and salts, (ii) after selective mineralization of aliphatic bromo-compounds to measure total bromide residues of fumigants such as 1,2-dibromoethane in water and (iii) to assess bromate levels in water after removal of any free bromide, and reduction of bromate to bromide. The method involves a pre-column derivatization of bromide to 4-bromoacetanilide by reaction with 2-iodosobenzoic acid and acetanilide, sample clean-up by solid-phase extraction using C_{18} cartridges and high-performance liquid chromatography. The method is simple and precise and has a limit of detection of 1 μg/l bromide.

Keywords: Derivatization, LC; Solid-phase extraction; Bromide

1. Introduction

On the occurrence of elevated amounts in environmental samples, bromide represents a dangerous hazard to public health [1,2], and it is necessary to have an accurate method for the determination of bromide in natural matrices. Elevated dietary levels of bromide exert changes on the status of the thyroid gland, with eventual substitution of iodide by bromide during the biosynthesis of thyroid hormones [3,4]. Bromide occurs in varying amounts in some fresh water streams due to industrial discharges or in well and ground water supplies in coastal areas as a result of sea water intrusion. The concentration of bromide in sea water is typically 60–70 mg/l, which is about 300 times lower than the chloride concentration [5]. During oxidative disinfection of drinking water with ozone or chlorine, bromide is oxidized to bromate [6,7], which is a suspected carcinogen [8]. Thus, because of their different levels of toxicity, it would also be interesting to determine bromate when present together with bromide. Various aliphatic bromo-compounds, such as methyl bromide, 1,2-dibromoethane and 1,2-dibromo-3-chloropropane, are used as fumigants. Because these pesticides are also suspected carcinogens, their maximum contaminant levels in drinking water supplies are established at very low levels, such as 0.05 μg/l for 1,2-dibromoethane [9]. These bromo-organics can alkylate nitrogenous compounds and leave bromide residues. The concentration of bromide and residues of aliphatic bromo-

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compounds in water is an indicator of the degree of treatment, and this makes their analysis important.

Besides sea water, other kinds of samples where bromide is present with large amounts of chloride are in concentrated hydrochloric acid and in brine. Hydrochloric acid plays a vital role in the electronics industry as it is used for various processes such as etching and surface cleaning of semiconductors. The purity of the hydrochloric acid employed in the wafer cleaning operations has a direct impact on the yield and reliability of devices. It is known that bromide impurity adheres to the wafer's surface, and cannot be removed by heating even up to 1000°C, resulting into device reliability problems [10]. For this reason, the levels of trace impurities, including bromide, in the electronic grade hydrochloric acid must be monitored. Such samples can have up to 5 mg/l bromide, which is about 100 000 times lower than the chloride concentration. In the chemical industry, bromine can be recovered from bromide contained in deep-well brines through oxidation of bromide to bromine with chlorine, followed by removal of the bromine from brine by steam distillation. The residual bromide concentration in the spent brine is therefore an important parameter in process-control monitoring and for pollution control. In a spent-brine solution, the total salt concentration can be as high as 240 g/l; the concentration of chloride can reach 150 g/l and that of bromide can reach up to 5 g/l.

Determination of low μg/l to mg/l levels of bromide in samples as above has traditionally been a difficult analytical problem. A wide variety of methods based on different principles are available for the determination of bromide. Spectrophotometric procedures involve oxidation to bromine, but the latter is converted, in order to measure it more accurately, into either tri-iodide by reaction with iodide [11], or to eosin [12] and bromophenol blue [13–15] by reaction with fluorescein and phenol red, respectively. There is a positive interference from high concentrations of chloride and a negative interference by ammonium ion [13]. Another nitrogen-containing compound, hydroxylamine, is reducing in character and interferes by consuming chloramine T [16]. Recently, a method has been developed involving pre-treatment with permanganate and hydrogen peroxide for the destruction of hydroxylamine prior to adding reagents [17]. In yet another oxidimetric method, bromide is oxidized to bromine in a flow reactor packed with chloramine T; the optical absorption of bromine is used for quantification [18]. The method is not applicable to μg/l levels of bromide.

Ion chromatography has been used for the determination of trace anions, including bromide, with conductivity detection [19,20]. However, the column is overloaded when the chloride concentration is very large, and nitrate, which is often present as a 100-fold excess in environmental samples, interferes by eluting very near to bromide. Ion chromatography with electrochemical detection has been preferred at times [21]. A post-column reaction detector is developed based on the reaction of bromide or iodide, chloramine T and 4,4′-bis(dimethylamino)diphenylmethane, resulting into a blue dye formation which is measured spectrophotometrically [22]. In this method also, large concentrations of chloride can affect the chromatographic separation.

Derivatization to 2-bromoethanol, by ethylene oxide and GC with electron capture detection [23], or to phenylmercuric bromide, by phenylboronic acid–mercuric nitrate and capillary GC with flame ionization or microwave-induced plasma atomic emission detection, have been used [24]. In HPLC, halides are derivatized by the use of phenylboronic acid–mercuric nitrate, and the phenylmercury(II) halides that are formed are extracted into chloroform and chromatographed. Improved separations and quantitative recoveries are obtained with the use of 4-bromophenylboronic acid (detection at 230 nm) [25]. However, these methods may not be suitable for the analysis of samples, e.g., sea water, concentrated hydrochloric acid and salts, in which one halide is in a very large excess over others. Difficulties have been reported due to closely eluting chloride in the ion chromatographic determination of bromate [6,7]. The use of a silver-form cation-exchange resin was found to be effective in reducing the chloride concentration in the injected sample, and for determining bromate at the μg/l level. Ion chromatography also finds application in the determination of bromine in organic compounds after their oxygen-flask combustion to liberate bromide [26].

The application of reversed-phase HPLC to the

analysis of inorganic anions involving their pre-column derivatization reaction and sensitive UV or fluorimetric detection is a powerful means of analysis, though it is, as yet, a relatively unexplored field [27]. Previously, we have used acetanilide and 2-iodosobenzoic acid as derivatizing reagents in a pre-column reaction, when bromide was converted to 4-bromoacetanilide and subjected to HPLC [28]. Difficulties were encountered due to the high acidity and ionic concentration in the injection sample leading to poor column performance and low sensitivity when this method was applied to concentrated hydrochloric acid and salts containing low levels of bromide. We also applied this technique to the determination of total bromine in organic compounds, utilizing mineralization by oxygen-flask combustion [29]. Since the aim of this work was to analyze bromine bound to aliphatic compounds, the model fumigant being 1,2-dibromoethane, the search was for a mineralization procedure that could exclude bromine attached to aromatic compounds. Thus, in conjunction with our principle derivatization technique for bromide, suitable methodologies have been worked out in this study to meet the above analytical requirements as well as to determine bromate in the presence of bromide.

2. Experimental

2.1. Apparatus

The HPLC instrumentation used consisted of a Shimadzu LC-5A reciprocating pump, a Rheodyne 7010 loop injector, a Shimadzu SPD-2A variable wavelength UV detector (8 μl flow-through cell) and a Shimadzu C-R2AX integrator fitted with a printer-plotter. The analytical column was 25 cm×4.6 mm I.D. ODS-1 (5 μm particle size, Anachem). A refillable guard column (2 cm×2 mm) was home packed with pellicular C_{18} (particle size 25–40 μm, Alltech, Deerfield, IL, USA). Solid-phase extraction cartridges (2.8 ml) containing 500 mg of C_{18} sorbent were obtained from Alltech.

The mobile phase was 65:35 (v/v) methanol–water, the solvent flow-rate was 1 ml/min and the eluent was monitored at 240 nm.

2.2. Reagents and standards

2-Iodosobenzoic acid was synthesized as reported earlier [28]. Acetanilide and 4-bromoacetanilide were purified by repeated recrystallization using standard methods [30].

The mixed derivatizing reagents were prepared by dissolving (in a standard flask) 150 mg of 2-iodosobenzoic acid and 100 mg of acetanilide in 100 ml of methanol, which was pre-mixed with 1 ml of concentrated sulphuric acid and cooled to room temperature. The mixture was filtered through a 0.45-μm membrane filter.

The stock solution of bromide contained 223.1 mg of potassium bromide (AnalaR, BDH, Poole, UK) in 100 ml of water in a standard flask, and 5 ml of this solution was diluted to volume with water in a 250-ml standard flask. The diluted solution contained 30 μg/ml bromide.

An accurately weighed amount (391.4 mg) of potassium bromate (AnalaR) was dissolved in 100 ml of water in a standard flask, and a 2.5-ml volume of this solution was diluted to 250 ml. The diluted solution contained 30 μg/ml bromate.

The above 30 μg/ml analyte solutions were sequentially diluted to give less concentrated standards of bromide and bromate.

A stock solution of 1,2-dibromoethane (ethylene dibromide, Aldrich, Milwaukee, WI, USA), 30 μg/ml, was prepared in ethanol, and used for preparing test solutions of lower concentrations by dilution with water.

A freshly cut piece of sodium was washed with methanol–benzene (1:1, v/v) and dried between folds of filter paper. Approximately 2.3 g of the sodium were suspended in anhydrous methanol for dissolution and finally diluted to 100 ml with methanol to give about 1 *M* sodium methoxide reagent.

2.3. Samples

Commercially available samples of concentrated hydrochloric acid, and salt samples of sodium chloride, potassium chloride, potassium perchlorate, sodium sulphate, sodium acetate, potassium nitrate and ammonium chloride were used to determine their bromide impurity. Sea water was collected from the Arabian Sea and the Indian Ocean.

2.4. Determination of bromide in standard solutions

A 5-ml volume of a standard solution containing 1–30 μg of bromide was mixed with 500 μl of mixed reagents, shaken for 1 min, and added to the C_{18} cartridge, which had been activated previously with 2 ml of methanol, conditioned with 2 ml of water and allowed to flow under a gentle suction. The cartridge was washed twice with 1 ml of water and the retained analyte was eluted with 2 ml of methanol. The eluent was dried under air and redissolved in 2 ml of the mobile phase. A 10-μl aliquot was injected onto the HPLC column.

2.5. Determination of bromide in sea water, concentrated hydrochloric acid or salts

Accurately weighed amounts of the salt were dissolved in water, and known volumes of sea water or concentrated hydrochloric acid were diluted with water. The sample solutions were filtered through a 0.45-μm membrane filter. Suitable aliquots of this solution were derivatized, subjected to solid-phase extraction and HPLC, as described in Section 2.4.

2.6. Determination of total bromine bound to aliphatic compounds

The water sample was filtered through a 0.45-μm membrane filter. A standard flask (100 ml) was filled up to the calibration mark with aqueous sample, mixed with 2 ml of hexane, capped with a PTFE stopper and shaken well to extract the bromo-compound. After phase separation, 1 ml of hexane layer (upper), settled in the neck of the standard flask, was carefully pipetted (without sucking in any of the aqueous phase), placed in a 10-ml round-bottomed flask fitted with a 15-cm water condenser, mixed with 3 ml of methanol, 1 ml of sodium methoxide and gently refluxed over a water bath for 10 min. The condenser was removed and heating continued for 2–3 min until all of the hexane had evaporated. The contents were cooled, acidified with 2 ml of 1 *M* sulphuric acid, quantitatively transferred to a beaker and subjected to pre-column derivatization and solid-phase extraction as described in Section 2.4.

2.7. Determination of bromate in the presence of bromide

A 1-ml volume of mixed reagents was diluted to 2 ml with water, mixed slowly, with constant stirring, with a known volume (5 ml) of a filtered (0.45μm membrane filter) aqueous sample, and subjected to solid-phase extraction using a C_{18} cartridge that has previously been activated with methanol and water. The eluents were collected, treated with 500 μl of 0.05 *M* ascorbic acid, shaken well for 1 min, then combined with 500 μl of 10% (v/v) hydrogen peroxide and again shaken for 1 min. This was followed by pre-column derivatization and solid-phase extraction as described in Section 2.4.

3. Results and discussion

3.1. Selection of the oxidizing agent

Many oxidizing agents such as permanganate [11], peroxymonosulphate [13] and chloramine T [14,15] have been employed for bromine formation. These oxidants have drawbacks of either undergoing side-reactions with the halogen scavengers, which are organic compounds, or forming bromate, which itself does not respond to bromination of organic compounds in a typical pre-column derivatization reaction, as used in this work. The selectivity of 2-iodosobenzoic acid as an oxidizing agent has already been demonstrated [31–35]. Its redox potential at 25°C was found to be 1.21 V at pH 1, 1.08 V at pH 2, 0.53 V at pH 4 and 0.48 V at pH 7 [33]. The redox potential for the system $Br_2+2e=2Br^-$ being 1.07 V [36].

3.2. Selection of the bromine scavenger

The purpose of this reagent is to utilize bromine produced in the oxidation step in forming a bromo-organic compound that is easily separable from its precursor and any organic impurity present in the injection sample, and that can be easily detected. Substituted aromatic amines and phenols, which respond to bromination quickly and have only one available *ortho* or *para* position active for electrophilic nuclear bromination, were studied in order

to avoid formation of more than one isomer of the bromo-compound and hence the chromatographic peak. A relatively large breakthrough volume of the bromo-derivative during solid-phase extraction was another consideration so that increased sensitivity could be achieved by a better enrichment ratio. Polar compounds such as phenols were not used as possible bromine scavengers, since for reversed-phase sorbents the breakthrough volume is a function of the hydrophobicity of the solute [37,38]. Aromatic amines tend to undergo oxidation either with the oxidizing agent used or with the bromine formed in the reaction, mostly due to the high electron density at the nitrogen. Deactivation of the amino group by an electron-withdrawing substituent, such as an acetyl group, without affecting its *ortho–para* directive influence, was a natural solution to the problem. In this respect, acetanilide was found to be the most suitable bromine scavenger. The bromination reaction of acetanilide is almost instantaneous; although the reagent has two *ortho* and one *para* positions available for electrophilic reaction, the *ortho* substitution is greatly impeded by the large size of the acetylamino group. When acetanilide is present in excess over the liberated bromine, no *ortho* isomer was formed.

3.3. Selection of mineralization reagent for aliphatic bromo-compounds

The oxygen-flask combustion method for the mineralization of a variety of organic halogen compounds has been tested earlier [26,29] and was found to yield a total of bromine. Since the aim in this work was to evaluate bromine present in commonly used fumigants that are aliphatic in nature, a mineralization method was sought to distinguish them from other classes of halogen compounds. The nucleophilic substitution reaction of alkyl halides appeared to be promising. Thus, on treatment with one of the reagents such as sodium hydroxide, a tertiary amine (triethylamine) and sodium methoxide, the reaction products of alkyl halides are bromide ion along with a substitution or dehydrohalogenation product. Sodium methoxide was selected due to its rapid nucleophilic reactions [39]. Sodium methoxide is specific in its reaction with alkyl bromides, and other classes of compounds such as bromo-aromatics do not produce bromide, also, sodium methoxide is soluble in pentane and hexane [40].

3.4. Selection of reagent for bromate reduction

Bromate can be reduced to bromine or bromide by many reducing agents. The reactions usually occur with different velocities in weak-to-strongly acidic media. Reaction of bromate with hydrazine, hydroxylamine and ascorbic acid occurs in moderately to weakly acidic media. Ascorbic acid appeared to be the reducing agent of choice, since its reaction with bromate is rapid, it can provide the acidity necessary for the reaction, and the remaining ascorbic acid after bromate reduction can be easily removed by reaction with hydrogen peroxide. Hydrogen peroxide does not interfere with the bromide derivatization chemistry.

3.5. Chemistry of derivatization

The determination of bromide is based on a sequence of pre-column reactions, which are oxidation with 2-iodosobenzoic acid to produce bromine in acidic medium and the electrophilic substitution reaction of bromine with acetanilide to form 4-bromoacetanilide.

The bromide liberated in the substitution reaction is again oxidized by 2-iodosobenzoic acid, and this sequence of oxidation and substitution reactions continues until all of the bromide is covalently bound.

For its determination in aqueous samples, alkyl bromide (the model fumigant taken being 1,2-dibromoethane) is extracted with hexane, and the hexane extract is treated with sodium methoxide for mineralization. The liberated bromide is subjected to pre-column derivatization as described above.

Bromate itself does not undergo derivatization under the present set of reactions. Its reactions with halides in acidic medium are slow and proceed under the catalysis of ammonium molybdate [41,42]. Thus, in weakly acidic medium, in the presence of an excess of 2-iodosobenzoic acid, any bromide present is preferentially oxidized by 2-iodosobenzoic acid and derivatized as 4-bromoacetanilide. The eluents after solid-phase extraction contain unchanged bro-

mate, which is then reduced with ascorbic acid to bromide and derivatized to evaluate the bromate.

3.6. Optimization and validation of the derivatization reaction

The reaction of bromide with 2-iodosobenzoic acid in acid medium is very fast, and the liberated bromine also reacts instantaneously with acetanilide. Therefore, shaking of the reaction mixture for 1 min was optimal for completion of the reaction. The amount of derivatizing agents does not play a critical role, provided that sufficient acetanilide is added to scavenge all the bromine liberated, and that there is sufficient 2-iodosobenzoic acid to oxidize the bromide and any reducing agent also present in the sample solution. Large excesses of derivatizing agent neither cause side reactions nor affect chromatography, since both acetanilide and 2-iodosobenzoic acid have low capacity factors, and are also significantly lost during clean-up by solid-phase extraction. The chromatographic peak for 4-bromoacetanilide was confirmed by comparison of its retention time with that of the authentic substance under the same chromatographic conditions, and confirmation of the identity of the derivative formed was done by comparison of its UV and IR spectra with that of 4-bromoacetanilide when the agreement was excellent. The ratio of peak area of equal molar masses of bromide (after derivatization) and of authentic 4-bromoacetanilide was 0.998 (R.S.D.= 2.1%). This confirmed the quantitative nature of the derivatization reaction.

3.7. Chromatographic conditions

HPLC separation was conducted on a C_{18} column with a mobile phase of 65:35 (v/v) methanol–water when base line separation of the peak of interest was obtained with a mobile phase flow-rate of 1 ml/min. The eluent was monitored at 240 nm, since most anilides absorb strongly at this wavelength [43]. A typical chromatogram obtained for bromide in pure solutions is given in Fig. 1.

3.8. Calibration graph and detection limits

The limit of detection [44] was found to be 1 μg/l bromide with a standard deviation of 3.2%. A

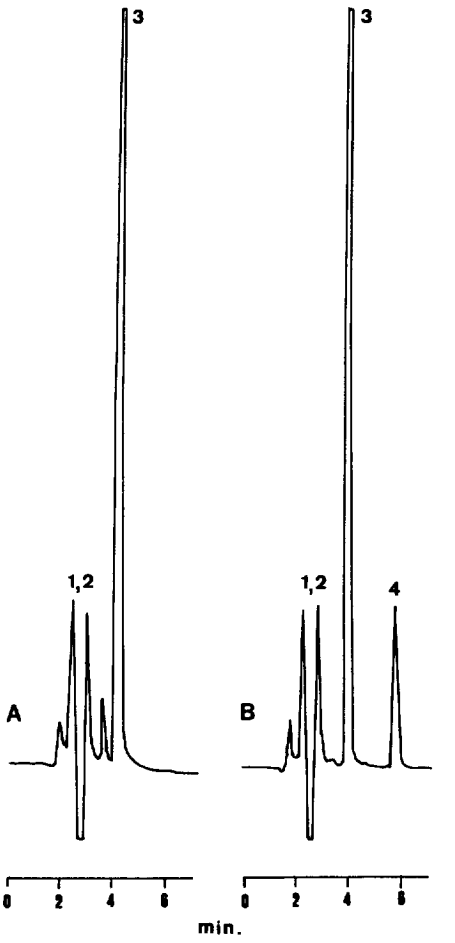

Fig. 1. Chromatograms of (A) a reagent blank and (B) pre-column derivatized 5 μg/ml bromide in a pure solution without using solid-phase extraction. Peaks: 1,2=2-iodo- and 2-iodosobenzoic acid; 3=acetanilide and 4=4-bromoacetanilide. Column: C_{18}, 25 cm×4.6 mm I.D.; particle size, 5 μm; detection wavelength, 240 nm, A f.s., 0.16; mobile-phase, methanol–water (65:35, v/v); flow-rate, 1 ml/min.

comparison of diverse methods for bromide determination is given in Table 1.

A rectilinear calibration graph was obtained between the amount of analyte (measured as 4-bromoacetanilide) and its peak area from the detection limit to the 6 mg/l bromide level. At a detector sensitivity of 0.16 AUFS, the slope was 609 AU l/mg bromide (2.8% R.S.D.), intercept −8.8 AU (4.6% R.S.D.) and the correlation coefficient was 0.9998 (n=8).

A linear calibration graph was obtained for bromate over the range 6 μg/l to 10 mg/l (limit of detection 2.5 μg/l, 5.2% R.S.D.), and for 1,2-di-

Table 1
Comparison of diverse methods for bromide determination

Method	Detection	LD[a]	ULD[a]	Reference
Spectrophotometry:				
Oxidation to bromate	355 nm	56 μg/l	1.2 mg/l	[41]
Bromophenol blue formation	590 nm	?[b]	5 mg/l	[13]
Bromophenol blue formation	590 nm	90 μg/l	10 mg/l	[15]
Bromophenol blue formation	590 nm	?	2.4 mg/l	[17]
Oxidation to bromine	390 nm	?	5 g/l	[18]
Ion Chromatography:				
Vydac 302-IC anion-exchange column	600 nm	15 ng	160 ng	[22]
Zipax SAX column	200 nm	10 ng	5 μg	[46]
Vydac-302	190 nm	1 ng/ml	100 ng/ml	[47]
Aminopropylsilica column	214 nm	1 ng	50 ng	[48]
Anion-exchange	conductivity	20 ng	?	[49]
AS4A ion-exchange column	conductivity	40 μg/l	1.5 μg/ml	[19]
AS4A ion-exchange column	conductivity	10 μg/l	5 mg/l	[20]
AS4A ion-exchange column	electrochemical	1 μg/l	100 μg/l	[21]
AS4A ion-exchange column	conductivity	11.2 μg/l	40 mg/l	[50]
Reversed-phase HPLC:				
Ion-pair on C_{18} column	electrochemical	1 mg/kg	100 mg/kg	[51]
C_{18} column	240 nm	1 μg/l	6 mg/l	Present work
Gas Chromatography:				
Capillary carbowax column	electron capture	20 μg/l	16 mg/l	[23]
Capillary DB 5 methyl–phenyl silicone	atomic emission	2.9 ng	?	[24]

[a] LD=Limit of detection; ULD=Upper limit of detection.
[b] The '?' appears where data are not mentioned in the original literature.

bromoethane over the range 0.3 to 300 μg/l (limit of detection 0.08 μg/l, 6.8% R.S.D.).

3.9. Validation of the analytical procedure

The proposed method was applied to the determination of bromide standards in the presence of known amounts of chloride and other ions. Results are given in Table 2. For precision studies, six aliquots of the same standard were separately derivatized and one injection of each was chromatographed. Over the entire range tested, the average recovery was 99% with a R.S.D. of 1.3%.

3.10. Interferences

Interference by a number of ions was studied by spiking 20 mg/l bromide with known amounts of foreign materials and analyzing the solutions by the present method. Amounts which did not change the results by more than 2% were set as the tolerance limit. Chloride, nitrate, phosphate, perchlorate, sul-

Table 2
HPLC determination of bromide after pre-column derivatization to 4-bromoacetanilide

Bromide taken (μg/100 ml)	Recovery (%) (n=6)	R.S.D. (%)
6.00	99	2.3
60.0	102	1.1
90.0[a]	99	1.0
120.0[b]	103	0.8
150.0	101	0.8
180.0[c]	102	0.7
240.0[d]	98	1.0
270.0	98	1.2
300.0[e]	99	1.5
330.0	98	1.6
360.0[f]	99	2.1

[a] The standard mixed with 500 μg of sodium dihydrogen phosphate.
[b] The standard mixed with 1000 μg of potassium chloride.
[c] The standard mixed with 2000 μg of sodium nitrate.
[d] The standard mixed with 10 μg of potassium iodide.
[e] The standard mixed with 100 μg of lead nitrate.
[f] The standard mixed with 100 μg of mercuric chloride.

phate, hydrogen carbonate, ammonium, calcium, magnesium, zinc, cadmium and cobalt could be avoided when present as up to a 1000-fold excess over bromide. Iron(III), copper(II), lead and mercury(II) were masked by ethylenediaminetetraacetic acid (EDTA, disodium salt) and were tolerated at up to a 100-fold excess. Reducing ions could react either with 2-iodosobenzoic acid or with the bromine liberated in the oxidation step, leading to excessive consumption of the oxidant and incomplete derivatization. Increasing the amount of 2-iodosobenzoic acid for derivatization circumvents this error. Up to a 10-fold excess of 2-iodosobenzoic acid to that recommended in the present work does not affect the quality of the chromatograms obtained, since the acid elutes near the void volume of the column. Up to equal amounts (to bromide) of reducing ions that could be tolerated include iron(II), sulphide, thiosulphate, sulphite, thiocyanate, nitrite, iodide, hydroxylamine and manganese(II). Iodate can be tolerated up to a 10-fold excess over bromide.

Any organic matter that also undergoes bromination, such as phenol and aniline, interfered severely and should be removed by solid-phase extraction using C_{18} cartridges before pre-column derivatization.

3.11. Application to spiked or real samples

The present method has been used to determine bromide in sea water, concentrated hydrochloric acid and in various salts. The chromatograms obtained

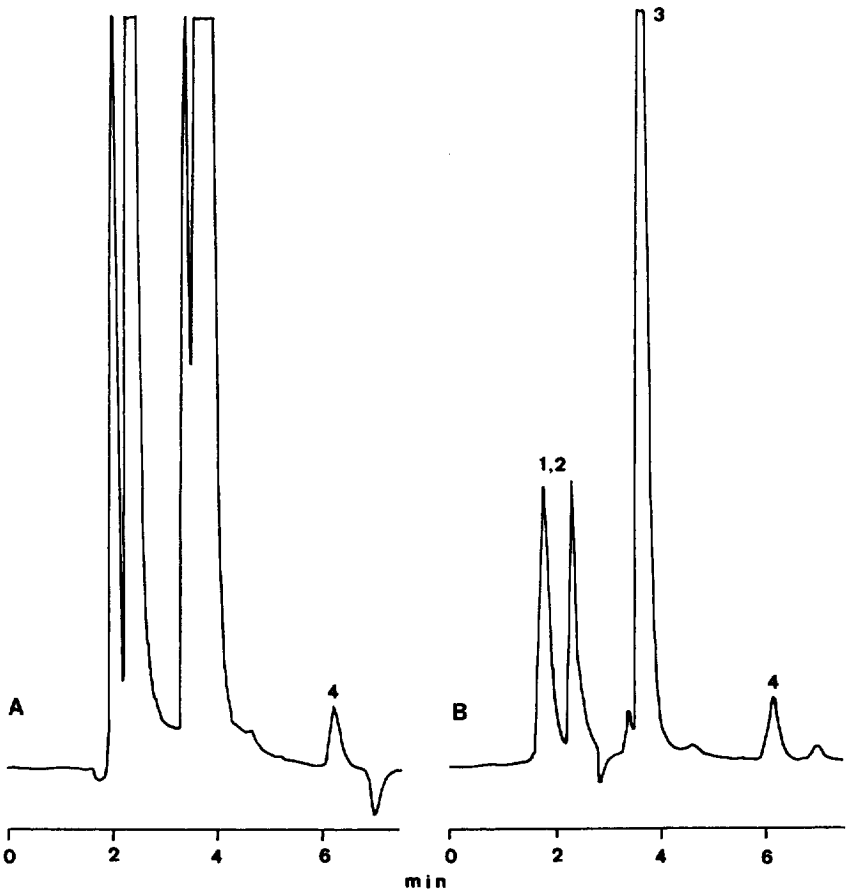

Fig. 2. Chromatograms obtained for the determination of 0.5 μg/ml bromide in hydrochloric acid, (A) without using solid-phase extraction and (B) using solid-phase extraction for sample clean-up. Chromatographic conditions and peaks assignments as in Fig. 1.

Table 3
Determination of bromide in sea water, concentrated hydrochloric acid and in salts

Sample	Bromide found (mg/100 g[a])	Recovery (%) of 1 mg Br/100 g of spikes[b]	R.S.D. (%)
Sea water	19.5	101	1.1
Sea water	21.2	103	1.5
Concentrated HCl	2.6	104	1.8
Concentrated HCl	0.0	102	1.5
Concentrated HCl	1.0	102	1.1
Concentrated HCl	0.14	106	1.6
Potassium chloride	38.0	99	1.0
Sodium sulphate	6.4	106	1.5
Table salt	38.5	103	1.0
Table salt	23.2	102	0.8
Table salt	11.5	104	1.3
Sodium acetate	0.0	100	1.1
Ammonium chloride	5.0	110	1.8
Potassium perchlorate	9.5	109	1.5
Potassium nitrate	0.0	98	1.4

[a] The results are the average of three determinations.
[b] The results are the average of five determinations.

both with and without the use of solid-phase extraction for sample clean-up are given in Fig. 2. The applicability of the present method to such samples was ascertained by determining their native bromide level, and then by the standard addition method. The results are given in Table 3, where the average recovery of spikes was 103% with a R.S.D. of 1.3%. Water samples were spiked separately with known amounts of 1,2-dibromoethane and bromate, and the bromide content was determined after mineralization with sodium methoxide and reduction with ascorbic acid. Samples containing 1,2-dibromoethane were also mixed with bromide and bromo-aromatics and were found not to vitiate the results, since bromide was separated during extraction of the analyte with hexane, and bromo-aromatics were not mineralized. The average recovery for 1,2-dibromoethane was 103% with an overall R.S.D. of 5.1% (Table 4). Bromate samples were also mixed with bromide and the interference of bromide was avoided by its derivatization and removal by solid-phase extraction before bromate reduction. The average recovery for bromate was 98% with an overall R.S.D. of 4.5% (Table 5).

Table 4
Determination of total fumigant bromide (TFB) residue after mineralization with sodium methoxide (model compound tested being 1,2-dibromoethane)

Sample	TFB added (μg/l)	TFB found (μg/l)	n	R.S.D. (%)
Drinking water[a]	0.33	0.38	6	6.8
	2	2.21	5	5.1
	6[b]	5.74	5	4.7
	10[c]	9.53	6	4.2
Surface water[a]	0.40	0.36	7	6.6
	2	2.18	5	6.0
	6[d]	6.41	5	4.4
	10	10.56	6	4.1
	14[e]	13.35	5	4.5

[a] The total fumigant bromide (TFB) residue in the sample was below the detection limit.
[b] Sample mixed with 5 μg/l bromobenzene and 5 μg/l bromide.
[c] Sample mixed with 10 μg/l 1,4-dibromobenzene.
[d] Sample mixed with 5 μg/l 4-bromophenol.
[e] Sample mixed with 15 μg/l 1,3,5-tribromobenzene and 15 μg/l bromide.

4. Conclusions

Determination of bromide by derivatization to 4-bromoacetanilide enables the use of reversed-phase HPLC as an alternative technique to ion chromatography for this ion, and avoids many interferences due to the presence of large amounts of other ions which are stubborn in the rival method. Substances that

Table 5
Determination of bromate after reduction to bromide

Sample	Bromate added (μg/l)	Bromate found (μg/l)	n	R.S.D. (%)
Drinking water[a]	6[b]	5.69	6	4.8
	8	7.82	6	5.1
	10[c]	10.36	5	4.2
Deionized water[a]	6[b]	5.65	7	5.2
	8	8.20	7	4.0
	10[c]	9.72	6	3.5

[a] The bromate in the sample was below the detection limit.
[b] Sample also contains 10 μg/l bromide.
[c] Sample also contains 30 μg/l bromide.

yield bromide after mineralization, reduction (as demonstrated in this work) and by ion-exchange chromatography can also be determined by this method. Yet another application quantitates analytes that can oxidize bromide to bromine, which is then scavenged and determined as 4-bromoacetanilide [45]. It would be interesting to work out an on-line SPE–LC technique for this determination which is liable to yield better detection limits for the analyte since the whole extract is introduced on to the column.

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