Determination of bromate and bromoacetic acids in water by ion chromatography-inductively coupled plasma mass spectrometry

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A new method for the simultaneous determination of bromate and six bromoacetic acids in water was developed by online coupling anion-exchange chromatography separation to element-specific inductively coupled plasma mass spectrometry (ICP-MS) detection. Factors affecting the chromatographic and ICP-MS performances were systematically investigated. The separation was achieved on a Dionex IonPac® AS11-HC column (4.0  \times 250 \text{ mm}) by elution with 100 mM ammonium nitrate. The detection limits (3\( \sigma \)) of the analytes were 0.13–0.36 \( \mu \text{g L}^{-1} \) based on a 500-\( \mu \text{L} \) sample injection. The possible masking of bromochloroacetic acid by the relatively high level of bromide in the chromatogram was avoided by sample pretreatment with Dionex OnGuard® Ag and H cartridges. The sample matrix did not show significant influence on the analysis. The method has been applied to analysis of various waters with good precisions and spiked recoveries of 80.8–113.8%.

Introduction

During the disinfection process of natural water by means of chlorination or ozonization for the production of drinking water, several brominated disinfection by-products (DBPs), such as bromate and bromoacetic acids (BAAs), have been identified as being possibly formed, especially in case of high levels of bromide existing in raw water.\(^1\) Bromate has been regarded as a Group 2B carcinogen to human health, and its maximum contamination level (MCL) was set at 10 \( \mu \text{g L}^{-1} \) in 1998 by the United States Environmental Protection Agency (EPA). BAAs include monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCAA) and bromodichloroacetic acid (BDCAA). Because of their potential harmful effects on human health, MBAA and DBAA (and sometimes BCAA) in drinking water are regulated as the components of haloacetic acids (HAAs) by EPA, and all the 6 BAAs are encouraged to be simultaneously determined together with mono-, di- and trichloroacetic acid under the EPA Information Collection Rule. Stimulated by the strict control of bromate and BAAs at \( \mu \text{g L}^{-1} \) levels, much more attention has been paid to establishing highly sensitive, selective and automatic methods for them in recent years. For bromate determination, successful methods were mainly based on ion chromatography (IC),\(^2,3\) utilizing high-capacity columns, post-column chemical derivatization, or coupling with specific and sensitive inductively coupled plasma mass spectrometry (ICP-MS) detection,\(^4,5\) and the limits of detection (LODs) obtained were approximately in the range of 0.1–3.5 \( \mu \text{g L}^{-1} \). More recently, Elwaer et al.\(^6\) coupled a flow injection system instead of IC with ICP-MS for the determination of bromate, which allowed a LOD of 0.13 \( \mu \text{g L}^{-1} \) bromate. For BAAs monitoring, there were several analytical techniques used: gas chromatography with electron capture detection (GC-ECD)\(^7,8\) or mass spectrometry detection (GC-MS),\(^9,10\) capillary electrophoresis (CE);\(^11,12\) liquid chromatography (LC),\(^13–15\) and electrospray ionization mass spectrometry (ESI-MS).\(^16,17\) The LODs of GC-ECD methods were not more than 1 \( \mu \text{g L}^{-1} \), but extraction and esterification and preconcentration procedures were essential and somewhat longer analytical periods were expected. Furthermore, side reactions have been shown to occur when diazomethane was used for the methylation of BAAs, especially in white light.\(^18,19\) Only coupled with appropriate sample pretreatment can CE methods meet the practical sensitivity requirements. The methods based on IC with conductivity detection (IC-CD) were poor in sensitivity and suffered from serious matrix interference. Recently, ESI-MS coupled with LC could achieve a LOD less than 70 \( \mu \text{g L}^{-1} \), but the low LOD was often severely compromised by an intense background that obscured ions of trace analytes in solution.\(^20\)

In this study, an IC-ICP-MS method was developed for the determination of bromate and BAAs in water. It required neither tedious liquid–liquid extraction nor chemical derivatization and was almost free from the matrix interference. Based on a 500-\(\mu\text{L}\) injection, the LODs (3\( \sigma \)) for the 7 analytes were in the range of 0.13–0.36 \( \mu \text{g L}^{-1} \). The sample pretreatment with Dionex OnGuard® Ag (containing styrene-based sulfonic acid resin in silver form) and H cartridges\(^21,22\) resulted in substantial reduction of bromide at concentrations of 2–4 orders of magnitude higher than those of BCAA as well as high levels of chloride in the sample matrix. The elimination of bromide was aimed to avoid its possible masking on its neighboring effluent component BCAA in the chromatogram.

Experimental

Instrumentation

The Agilent 1100 Series LC module (Waldbronn, Germany) used in this study consisted of an isocratic pump, a handheld control module and a Rheodyne Series 7725s manual injection valve. The LC separation column chosen after a preliminary study was IonPac® AS11-HC (4.0 \( \times \) 250 mm) from Dionex (Sunnyvale, CA, USA). It was used with its corresponding guard column (AG11-HC).

An Agilent 7500a quadrupole ICP-MS (Yokogawa Analytical System, Kyoto, Japan), which served as an element-specific detector here, was equipped with a dual pass spray chamber (Scott type, water-cooled to 2 °C), a Meinhard quartz concentric nebulizer, a standard quartz torch (concentric tube
of 2.5 mm id), a nickel sampler cone and a nickel skimmer cone. The optimized parameters were as follows: rf power, 1390 W; plasma gas, 15 L min\(^{-1}\) Ar; auxiliary gas, 0.9 L min\(^{-1}\) Ar; carrier gas, 1.23 L min\(^{-1}\) Ar; make-up gas, zero; sample depth, 6.0 mm; detector mode, pulse; monitoring isotope, \(^{79}\)Br. The natural sample flow rate of the nebulizer was 75 \mu L min\(^{-1}\) when a carrier gas flowed at 1.23 L min\(^{-1}\). The outlet of AS11-HC column was directly connected to the nebulizer via a piece of PFA tubing, meanwhile the LC and ICP-MS were connected electronically. The data acquisition and analysis were performed by the Agilent ICP-MS ChemStation software with Plasma Chromatographic option.

**Chemicals and materials**

Neat BAAs (obtained from Supelco except TBAA from Sigma) were used to prepare the individual standard solutions. Bromate and bromide standards were product of AccuStandard (New Haven, CT, USA). Ammonium nitrate (Merck), aqueous ammonia (ca. 25%, Riedel-de Haën), methanol (J. T. Baker), acetonitrile (J. T. Baker), 2-propanol (Merck) and other chemicals involved were of analytical reagent grade or better. High-purity water with a specific resistance of 18.2 M\(\Omega\) cm was used throughout for all sample and solution preparations as well as dilutions. OnGuard\textsuperscript{6} Ag cartridges (1 ml) and H cartridges (1 ml) from Dionex were preconditioned and used according to the supplier’s manuals.\textsuperscript{26} A membrane disc filter of 0.45 \mu m pore size (Whatman, Clifton, NJ, USA) was used to remove insoluble particles in samples prior to treatment with cartridges.

**Procedure**

A portion of filtered water sample (ca. 15 mL) was passed through Ag and H cartridges in tandem at ca. 2 mL min\(^{-1}\). The aliquot of the treated sample was injected into IC via a 500-\mu L loop. The analytes were eluted from AS11-HC column by 100 mM NH\(_4\)NO\(_3\) at 1.0 mL min\(^{-1}\), and the chromatographic signal was detected at \(m/z = 79\) by the ICP-MS in time resolved analysis mode at 100 ms per scan under the optimized conditions described above.

**Results and discussion**

**Separation mode consideration**

The LC separation of BAAs (or widely, HAA) has been achieved in three different modes of ion-pair, ion-exclusion and anion-exchange. On the other hand, almost all the separations of bromate from other inorganic anions have been accomplished by anion-exchange chromatography.\textsuperscript{2,3} Therefore, anion-exchange mode was chosen here for the separation of bromate and BAAs from the sample matrix and one another. According to their \(pK_a\) values, they were completely dissociated and existed as anions at pH > 4 but perhaps had different chromatographic behaviors. The choice of the anion-exchange mode was also partially due to the facts that in ion-pair chromatography not all these species formed ion-pair complexes with the same ion-pairing reagent and the use of higher contents of organic solvent eluent required special introduction devices and Pt interface with ICP-MS.

**Separation column**

Three anion-exchange columns (Agilent G3154A, Dionex IonPac AS9-HC and AS11-HC) were examined for their separation efficiency. The Agilent G3154A column (4.6 × 150 mm) was packed with chemically bonded anion exchange resin, in which hydrophilic polymethacrylate served as the basic resin. The packing materials in AS9-HC and AS11-HC columns (both 4.0 × 250 mm) were latex-agglomerated poly(ethylvinylbenzene) resin crosslinked with 55% divinylbenzene, but their latex layers were different in crosslinking degree and core size.\textsuperscript{26} On the basis of preliminary experimental results, NH\(_4\)NO\(_3\) solution of 100 mM was used as the mobile phase at 1.0 mL min\(^{-1}\) to examine the column efficiency for the separation of the target analytes together with bromide in reagent water. The G3154A column just gave 5 peaks at 2.55, 2.89, 3.38, 6.65, 8.27 min, respectively, in the range of 0–50 min. The use of the AS9-HC column did not give complete separation of all the bromine species under the conditions applied. For example, bromate–MBAA and bromide–BCAA were not resolved. However, when the concentration of NH\(_4\)NO\(_3\) decreased to 20 mM, the overlapping of bromate–MBAA and bromide–BCAA peaks became smaller but their quantitative resolutions were still impossible. Significantly improved separation of the target 8 bromine species was observed on AS11-HC column (Fig. 1). Such a different separation efficiency between AS9-HC and AS11-HC could be due to their difference in column packing composition. Meanwhile, AS11-HC column has a high capacity of 290 \mu eq\textsubscript{v} which allowed the separation of various anions at the mg L\(^{-1}\) level without overloading and peak broadening even in high ionic strength matrices.

**Choice of the eluent**

For LC-ICP-MS, metal-free eluent is most desirable. Ammonium-containing compounds would be easily converted to volatile compounds during the passage through the high temperature region of the plasma and would be one of the best candidates for mobile phase components. The experimental results showed that NH\(_4\)NO\(_3\) solution of 100 mM was the most suitable mobile phase for the elution and detection of the target bromine species, which ensured that the isotropic elution was completed within 48 min and the peak resolution between bromate and MBBAA (the two most difficult to resolve species due to their close \(pK_a\) values) was better than 98%. It could be noted that faster elution and better peak resolutions and shapes for BDCAA, BDCAA and TBAA could be expected if a concentration gradient elution system was applied and the NH\(_4\)NO\(_3\) concentration was increased at the time when the 5 earlier peaks had appeared. However, gradient elution of the analytes was not performed in this study because of a shortage of the essential accessories at this time.

Some electrolytes and organic solvents possibly present in samples or eluents were examined for their effects on the ICP-MS detection of analytes (directly aspirated from the autosampler to the concentric nebulizer, rather than eluted from the LC column). Lower than 0.2 M aqueous NH\(_3\), NH\(_4\)NO\(_3\), NH\(_4\)(CO\(_3\))\(_2\), NH\(_4\)Ac, NH\(_4\)Cl, HNO\(_3\) or acetic acid did not show significant effects on the blank intensity and net signals of the analytes. However, organic solvents, such as

![Fig. 1 Chromatogram of a mixture of bromine species on AS11-HC column with 100 mM NH\(_4\)NO\(_3\) elution at 1.0 mL min\(^{-1}\)](image)
acetonitrile, methanol and 2-propanol, significantly suppressed both the net signals of bromine-containing species and the blank intensity. The magnitudes of organic solvent effects were different, depending on the solvent polarity, and in an order of acetonitrile > 2-propanol > methanol. In the case of normal ICP-MS configuration, if there was any organic solvent present in 100 mM NH4NO3, the peak heights and areas for all bromine species became smaller. The decrease varied in the order acetonitrile > 2-propanol > methanol (all at 2%, v/v). Meanwhile, the use of organic solvents had some or little impact on the elution speed, depending on their hydrophobicity. Therefore, organic solvent was not recommended for use.

Effect of mobile phase flow rate
The retention time (tR), peak area and peak width (W½, width at half height, was used here) for every analyte became shorter or smaller with increasing flow rate of the eluent. The resolution (R) for every two adjacent Gaussian peaks could be calculated as

\[ R = \frac{1.18(t_{R1} - t_{R2})}{W_{1} + W_{2}} \]

Among all the 8 species, the R between bromate and MBAA is the smallest. It was decreased from 1.540 to 1.256 when 100 mM NH4NO3 flow rate increased from 0.5 to 1.6 mL min \(^{-1}\). Meanwhile, all the peaks were good in peak symmetry, and the tailing factor for MBAA, one with relatively poorer shape, was from 1.87 to 1.27. Based on the results of the effects of the flow rate on retention times, peak widths, peak resolutions and peak areas of all the Br species, and the requirement for separation efficiency, quantification sensitivity and short analytical period, a flow rate of 1.0 mL min \(^{-1}\) was employed. At this flow rate, a complete separation of all the 8 species was obtained in 48 min.

Effect of sample injection volume
The retention time for each analyte became slightly longer as the sample injection volume (S) increased from 10 to 2000 μL, and the peak area versus S was linear. For analysis of sample without preconcentration, a volume of 500 μL can meet the normal sensitivity requirement with the ICP-MS detection.

Effect of high levels of bromide
Bromide was actually present at a much higher level than any target analyte in raw water and finished water. It gave a much larger peak in the chromatogram, which was in turn likely to overlap or mask its neighboring peaks, especially the subsequent peak for BCAA, although the difference in retention time of BCAA and bromide was 1.8 min. When a mixture of the analytes (at 20 μg L \(^{-1}\) for bromate, BCAA and DBAA, and 40 μg L \(^{-1}\) for the other 4 species) and bromide at different levels up to 1.22 mg L \(^{-1}\) was injected into the column, the recoveries of all target analytes were in the range of 93.2–107.2% while the peak retentions remained constant. It should be noted that the real concentrations of BCAA and other analytes could be much lower than the level tested above, and in this case, the tailing of bromide peak could affect the judgement on the presence of BCAA. Therefore, it was necessary to reduce the bromide level in the sample before the sample injection.

For this purpose, a Dionex OnGuard®Ag cartridge, which contains styrene-based sulfonic acid resin in silver format, can be used together with a cation exchange resin-based H cartridge. Such a combination of Ag and H cartridges has been designed to reduce chloride in the sample matrix for bromate determination by IC-CD.26,27 Meanwhile, cations (primarily metal ions) in the sample matrix and silver leached from the Ag cartridge were significantly reduced by H cartridge. When a portion of sample was passed through the Ag-H cartridges in tandem, bromide was absorbed as a precipitate of silver salt along with chloride, while all 7 analytes were found to be unretained with recoveries of 97.1–100.4% by ICP-MS. For bromide at 75 mg L \(^{-1}\) in 5.0 mL sample, the pretreatment left bromide of 55 μg L \(^{-1}\) in the treated effluent. Such a pretreatment allowed the easy identification of BCAA as well as other analytes.

Analytical characteristics of the method
The calibrations for all 8 analytes were established by injecting mixed standards at different levels and eluting and detecting the corresponding analytes under the optimized conditions. All the calibration graphs were linear at least up to 200 μg L \(^{-1}\) for each analyte in peak area mode. Their LODs (3σ) were estimated to be (in μg L \(^{-1}\)): bromate, 0.22; MBAA, 0.16; BCAA, 0.20; DBAA, 0.23; BDCAA, 0.27; DBCAA, 0.34; TBAA, 0.36. LODs of BAAs obtained by this IC-ICP-MS method were much lower than those obtained by CE17 and IC18–20 methods, and comparable with those by GC-ECD14,15 and LC-ESI-MS.23 For bromate, the proposed method was one of the more sensitive methods reported so far.17–21 Bromide quantification is also feasible by this method (without pretreatment) with a LOD of 0.13 μg L \(^{-1}\).

Possible overloading of the IC column could be dominated by major concentrations of chloride, sulfate, nitrate, carbonate, etc., although they were not monitored here. However, the overloading should not occur for typical water samples when 100 mM NH4NO3 was used as the eluent and a high capacity separation column was employed. Furthermore, chloride and some other anions can be substantially removed together with bromide by Ag–H cartridge treatment. Bromide up to 75 mg L \(^{-1}\) did not significantly affect the analytical characteristics of the target analytes. Metal ions in the sample matrix were also partially trapped by H cartridge. For example, the presence of Na\(^{+}\), Mg\(^{2+}\), Ca\(^{2+}\), K\(^{+}\), (10 mg L \(^{-1}\) each) and Al\(^{3+}\), Fe\(^{3+}\), Ba\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\), Br\(^{-}\), Si\(^{4+}\) (2.0 mg L \(^{-1}\) each) in the sample did not affect the determination of analytes. The combination of high capacity column, ICP-MS and the Ag-H cartridge treatment therefore guaranteed the good selectivity of this method.

Sample analysis and spike recovery
Several types of water samples collected from different waterworks were analyzed by the described method. Meanwhile the recoveries of several samples at different spiked levels were evaluated. As shown in Table 1, bromate was the dominant brominated DBP in tap water, and only BCAA and DBAA were at detectable levels among all BAAs. Membrane filtered water contained 6 brominated DBPs at detectable levels. Plant raw, feed and product waters had much lower levels of brominated DBPs, some of them even undetectable. BCAA was unexpectedly found in raw and plant feed waters at sub-μg L \(^{-1}\) levels and the reason was not clear. On the other hand, when the same samples of raw water, plant feed and plant product water were analyzed by GC-MS for BAAs and by IC-CD for bromate, the results for these samples were just reported as: MBAA < 5, BCAA < 5, DBAA < 5, BDCAA < 5, DBCAA < 50, TBAA < 100 and bromate <10 μg L \(^{-1}\). Meanwhile, the spiked recoveries of each analyte in various types of waters were found to be in the range of 80.8–113.8%.

Conclusions
The results obtained in this study demonstrate the feasibility of the developed isocratic IC-ICP-MS method for the determinations of bromate and BAAs at trace and even ultra-trace levels in water samples without any further sample preconcentration.
Table 1  Analytical results and spiked recoveries of brominated DBPs in water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration/µg L⁻¹ and spiked recovery (%)²</th>
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<tbody>
<tr>
<td>Spiked tap water 1⁰</td>
<td>Spiked/µg L⁻¹: 5.0 (108.4±7.0) (89.9±3.8)</td>
</tr>
<tr>
<td>Spiked tap water 2⁰</td>
<td>7.09±0.12 &lt;0.16</td>
</tr>
<tr>
<td>Raw water²</td>
<td>0.22±0.07 &lt;0.23</td>
</tr>
<tr>
<td>Spiked raw water³</td>
<td>5.0 (101.2±3.6) (84.2±5.7)</td>
</tr>
<tr>
<td>Plant feed water</td>
<td>0.30 (mg L⁻¹)</td>
</tr>
<tr>
<td>Spiked plant feed water</td>
<td>7.5 (107.8±5.6) (80.8±4.9)</td>
</tr>
<tr>
<td>Plant membrane filtered water</td>
<td>7.55±0.41 0.52±0.10 5.17±0.23 3.65±0.16 1.27±0.05 0.61±0.05 &lt;0.36</td>
</tr>
<tr>
<td>Spiked plant membrane filtered water²</td>
<td>2.0 (96.7±4.8) (108.7±5.3)</td>
</tr>
<tr>
<td>Spiked plant product water</td>
<td>0.54±0.05 &lt;0.16</td>
</tr>
<tr>
<td>Spiked plant product water²</td>
<td>10.0 (107.6±3.4) (90.0±4.4)</td>
</tr>
</tbody>
</table>

Table 1 indicates the concentrations and recoveries of brominated DBPs in water samples. The data are presented as mean ± standard deviation from triplicate measurements. Concentrations are given in µg L⁻¹, and recoveries are expressed as a percentage of spiked recovery. The table includes results from spiked tap water, raw water, plant feed water, and other water samples. The recoveries range from 0.22% to 109.5%, demonstrating the effectiveness of the spiked recovery method. The table also highlights the use of various analytical methods for the detection and quantification of DBPs, including chromatography and spectrophotometry. The references cited at the end of the table provide further details on the methodologies and validation of the analytical procedures.

References