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# Applications of ion chromatography with electrospray mass spectrometric detection to the determination of environmental contaminants in water

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**Abstract**

Ion chromatography (IC) is widely used for the compliance monitoring of common inorganic anions in drinking water. However, there has recently been considerable interest in the development of IC methods to meet regulatory requirements for analytes other than common inorganic anions, including disinfection byproduct anions, perchlorate, and haloacetic acids. Many of these new methods require the use of large injection volumes, high capacity columns and analyte specific detection schemes, such as inductively coupled plasma mass spectrometry or postcolumn reaction with UV–Vis detection, in order to meet current regulatory objectives. Electrospray ionization mass spectrometry (ESI-MS) is a detection technique that is particularly suitable for the analysis of permanently ionized or polar, ionizable compounds. The combination of IC with MS detection is emerging as an important tool for the analysis of ionic compounds in drinking water, as it provides increased specificity and sensitivity compared to conductivity detection. This paper reports on the application of IC–ESI-MS for the confirmation and quantitation of environmentally significant contaminants, i.e. compounds with adverse health effects which are either regulated or being considered for regulation, such as bromate, perchlorate, haloacetic acids, and selenium species, in various water samples. 

*Keywords:* Water analysis; Perchlorate; Bromate; Inorganic anions; Haloacetic acids; Organic acids; Selenium

## 1. Introduction

Ion chromatography (IC) has been approved for the analysis of common inorganic anions in environmental waters since the mid-1980s, as described in US Environmental Protection Agency (EPA) Method 300.0 [1]. More recently, there has been considerable interest in the development of IC methods for analytes other than common anions, e.g. disinfection byproduct anions, perchlorate, and haloacetic acids. A number of new regulatory methods based on IC have been published over the last decade, including EPA Methods 300.1, 314.0, 317.0, 321.8 and International Organization for Standardization (ISO) Method 15601 [2]. These new methods tend to be more complex than Method 300.0, i.e. use higher capacity columns, larger injection volumes, or measurement techniques other than conductivity detection, in order to achieve the sensitivity or selectivity required for current, and future, regulatory objectives.

The combination of IC with mass spectrometry (MS) detection has gained importance for selected

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applications, in part due to the need for determining newly regulated environmental contaminants with high sensitivity, and also because of recent developments in interfaces for the combination of liquid chromatography and MS detection [3–5]. A number of combinations of IC with MS-based detection approaches have been reported, including IC coupled with inductively coupled plasma mass spectrometry (ICP-MS) [6–10], particle beam MS [11], atmospheric pressure ionization (API) operated in either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) modes [12–15], and even electrospray tandem mass spectrometry (MS–MS) [16,17]. The details on the various combinations of IC with MS detection and the range of analytes that can be determined using these techniques were recently reviewed by Buchberger [18]. In general, MS with ICP ionization serves as an element specific detector, while mass spectrometers with API interfaces tend to provide information on the molecular ion or adducts, although some fragmentation can occur through collision induced dissociation (CID).

The use of IC with both suppressed conductivity and ESI-MS detection provides a very versatile analytical system for the identification and quantitation of environmentally significant inorganic contaminants. The addition of an MS detector to the IC system provides high detection specificity, allowing confirmation and quantification of unresolved analytes. In addition, the use of continuously regenerated suppressors adds ruggedness and can enhance the sensitivity of MS detection by minimizing ionization interferences. This paper explores the feasibility of using IC–MS for the determination of environmentally significant contaminants in a number of applications where positive analyte identification and low detection limits are required.

## 2. Experimental

### *2.1. Instrumentation*

#### *2.1.1. Ion chromatography–mass spectrometry system*

A Dionex (Sunnyvale, CA, USA) DX-500 microbore ion chromatography system was used for this work. The system consisted of a GP40 gradient pump, LC20 chromatography compartment and ED40 electrochemical detector. Dionex IonPac AS9-HC and AS16 analytical columns (250×2 mm I.D.) and their respective guard columns, IonPac AG9-HC and AG16 (50×2 mm I.D.), were used for all separations. A Dionex ASRS-ULTRA (2-mm format) operated in the external water mode was used to perform chemical suppression.

A Finnigan (ThermoFinnigan, Manchester, UK) AQA single-stage quadrupole mass spectrometer was coupled directly to the effluent side of the conductivity cell using 50 cm of 0.010 in. I.D. peak tubing connected through a grounded stainless steel union to minimize feedback to the conductivity detector (1 in.=2.54 cm). Nitrogen was supplied to the ESI source at about 600 l/h from a liquid nitrogen dewar (Praxair, Danbury, CT, USA). A Dionex RP-1 postcolumn pump with pulse damper was added to the system for delivering solvent as required. A Dionex Chromeleon-MS Workstation was used for both IC and MS system control, data collection and processing.

### *2.2. Reagents and procedures*

All solutions were prepared from ACS reagent-grade chemicals in 18 MΩ water, obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Anion stock solutions (1000 mg/l) were prepared from analytical reagent grade sodium salts (EM Science, Gibbstown, NJ, USA), except for sodium perchlorate, which was obtained from Aldrich (Milwaukee, WI, USA). Stock standard solutions were stored at 4 °C and working standards were prepared fresh daily. The nine haloacetic acids, monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), dichlorobromoacetic acid (DCBAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA), were obtained as a mixture in methyl *tert*.-butyl ether (MTBE) from Supelco (Bellefonte, PA, USA). An aqueous stock standard solution was prepared by adding an aliquot of the MTBE solution to water, shaking, and blowing off the MTBE layer with a gentle stream of air.

Sodium hydroxide, 50% (w/w) aqueous solution, obtained from Fisher Scientific (Pittsburgh, PA, USA) was used for preparation of hydroxide eluents. Commercially available (Dionex) 0.5 *M* sodium carbonate concentrate was used for preparation of carbonate eluents. Drinking water and wastewater samples were filtered through 0.45 μm Acrodisc syringe filters (Gelman, Ann Arbor, MI, USA) prior to injection.

## 3. Results and discussions

### *3.1. IC–MS system configuration*

ESI-MS is a powerful detection technique, particularly for permanent cations, anions, and polar ionizable compounds, i.e. the analytes typically determined using ion chromatography. Because electrospray is a ''soft'' ionization technique, it yields mostly molecular mass information [3]. With recent advances in source design which allow the use of typical liquid chromatography flow-rates [5], ESI-MS can conveniently be coupled with IC. From the MS detection viewpoint, separating analytes from major matrix constituents using chromatography reduces MS signal suppression from high levels of competing ionic species. Reducing the eluent conductance with a suppressor, as is the case in IC with suppressed conductivity detection, is also of significant benefit when using MS detection. The analytes are delivered to the MS detector in a low ionic strength, non-corrosive eluent stream, essentially eliminating the need for cleaning of the source [12] and also minimizing background spectral interferences. The use of suppressors has been shown to permit lower MS detection limits for the same analytes compared to analysis performed using non-suppressed conductivity detection [19].

The Finnigan AQA single-stage quadrupole mass spectrometer used in this work has a practical mass range of 60–1600 *m/z*, which is suited for the detection of most low-molecular-mass ionic species typically analyzed by IC. The MS detector utilizes an orthogonal-design source which helps to eliminate noise from neutral compounds and extends the dynamic range of the detector. The atmospheric pressure interface can be operated in either ESI or APCI modes, and handles liquid flow-rates from 0.2 to 2 ml/min without the need for flow-splitting. Although operation of the ESI-MS system at flow-rates typical for conventional bore (4 mm I.D.) ion chromatography columns is possible, the use of narrow bore columns (2 mm I.D.) is generally preferred [5]. Thus, all of the work presented here was performed with 2 mm I.D. columns.

The temperature of the Finnigan AQA ESI probe can be adjusted to allow optimization of the electrospray process and MS signal response for a given set of analytes and eluent conditions. Some control of the degree of analyte fragmentation is provided through the adjustment of the collision induced dissociation voltage. The mass spectrometer was coupled to the IC through a grounded stainless steel union to minimize baseline noise in the conductivity detector.

### *3.2. Determination of perchlorate in wastewater*

Ammonium perchlorate, a widely used ingredient in solid rocket propellants, has been found in drinking water wells in regions of the USA where aerospace material, munitions and fireworks were developed, tested, or manufactured. To date, perchlorate has been found in ground and surface waters in California, Nevada, Utah, Texas, New York, Maryland, Arkansas and West Virginia [20]. Perchlorate interferes with the function of the thyroid gland and its presence in drinking water poses a considerable health risk, even at trace levels. Perchlorate contamination of public drinking water wells is a serious problem in California and the Department of Health Services (DHS) has adopted an action level for perchlorate in drinking water of 4 μg/l [21].

Ion chromatography is emerging as the most viable means for the routine quantification of trace level perchlorate, although this anion has also been determined by electrospray ionization mass spectrometry after ion-pair extraction and by electrospray ionization with tandem mass spectrometry [22,23]. However, since the latter two approaches employed sample introduction by flow injection (FI) rather than a chromatographic separation of the analyte from other sample constituents, the method of standard addition had to be applied to quantitate per-

chlorate in different water matrices, thus significantly increasing the time required for each individual analysis. In one case, a groundwater sample resulted in a signal suppression of more than 90% [23]. This strong dependence on the sample matrix means that detection limits, and consequently reporting limits, have to be carefully evaluated for each sample. These drawbacks of the FI–ESI-MS approach clearly advocate the use of a chromatographic separation to isolate the analyte from other sample constituents prior to quantitation by ESI-MS.

EPA Method 314.0 is approved for monitoring of perchlorate in drinking water, as required by the recent changes in the Unregulated Contaminant Monitoring Rule [24]. This IC method uses a large loop injection onto an IonPac AS16 column, isocratic elution with a hydroxide eluent, and suppressed conductivity detection [25]. Although this method is capable of detecting perchlorate in reagent water at concentrations below 1 μg/l, the presence of high concentrations of matrix ions (e.g. chloride or sulfate) can make the detection of low μg/l levels of perchlorate difficult, if not impossible, in complex samples such as wastewaters.

Fig. 1a shows a chromatogram of an attempt to determine perchlorate in a reclaimed municipal wastewater using IC with suppressed conductivity detection. Although there were several small peaks near the retention time of the target analyte, none of those peaks matched the retention time of perchlorate exactly. Using ESI-MS as a more selective detection technique, perchlorate could easily be detected and quantitated, at a level of 2.6 μg/l, as illustrated in Fig. 1b.

The two mass chromatograms in Fig. 1b were obtained by selected ion monitoring at two different $m/z$ values, 99 for $^{35}ClO_4^-$ and 101 for $^{37}ClO_4^-$. The areas for the perchlorate peak in the two chromatograms are different, reflecting the natural abundance ratio of the two chlorine isotopes $^{35}Cl$ and $^{37}Cl$ of about 3:1. Therefore, the ESI-MS analysis provides additional confirmation that the detected solute contains chlorine. Because the mass spectral background and noise at $m/z$ 101 are lower than at $m/z$ 99, both signals are equally suitable for the quantification of perchlorate. Method detection limits (MDLs) using MS detection were derived by calculating the standard deviation of the results of seven replicate

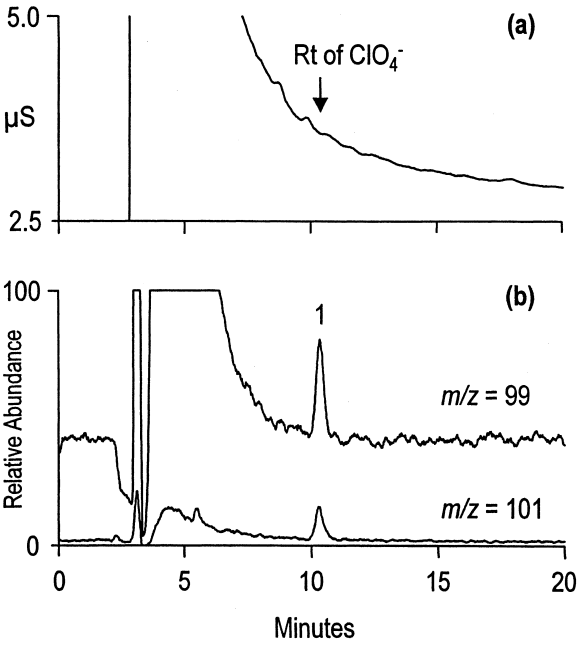


Fig. 1. Determination of perchlorate in reclaimed wastewater using IC–MS. Conditions: guard column, IonPac AG16 (2 mm I.D.); analytical column, IonPac AS16 (2 mm I.D.); eluent, 65 m*M* sodium hydroxide; flow-rate, 0.3 ml/min; injection volume, 250 μl; detection, (a) suppressed conductivity with ASRS-ULTRA operated at 300 mA in external water mode, (b) negative ESI-MS, ESI probe at 300 °C and −2.5 kV, source CID voltage at 10 V, selected ion monitoring at $m/z$ 99 and 101, 15-point boxcar smoothing; peak, 1=perchlorate (2.6 μg/l).

analyses of a low-level standard, as described in Method 314.0 protocol [25]. Using the results of seven replicate injections of a 1.0 μg/l standard, a method detection limit of about 0.3 μg/l in reagent water was calculated for both signals, as shown in Table 1.

### *3.3. Bromate in drinking water*

Bromate, formed as a disinfection byproduct (DBP) from the ozonation of source water containing bromide, has been classified as a group 2B probable human carcinogen, even at trace levels [26]. The Stage 1 Disinfectant/Disinfection Byproduct (D/DBP) Rule published by the EPA specifies maximum contaminant levels (MCLs) for a number of DBPs, including an MCL for bromate of 10 μg/l and an MCL for chlorite of 1000 μg/l in finished

Table 1
Method detection limits for perchlorate and bromate in reagent water using IC–MS

| Anion | Injected concentration (μg/l) | Peak area RSD (%) | Calculated MDL (μg/l)[a] |
|---|---|---|---|
| Perchlorate (*m/z* 99) | 1.00 | 9.5 | 0.36 |
| Perchlorate (*m/z* 101) | 1.00 | 10.9 | 0.42 |
| Perchlorate (*m/z* 99+101) | 1.00 | 6.6 | 0.26 |
| Bromate (*m/z* 127) | 1.28 | 11.8 | 0.46 |
| Bromate (*m/z* 129) | 1.28 | 32.7 | 1.25 |
| Bromate (*m/z* 127+129) | 1.28 | 11.0 | 0.42 |

[a] MDL=SD $t_{s,99}$ where $t_{s,99}$=3.14 for $n$=7.

drinking water [26]. EPA Method 300.1, which uses an IonPac AS9-HC column and suppressed conductivity detection, is the only analytical method currently approved for the analysis of bromate [27]. Both EPA Methods 300.1 and 300.0 are approved for the analysis of chlorite and bromide [2].

The EPA is convening a second stage of the D/DBP Rule to further reduce the risks from disinfection byproducts. Method 317.0 is a new IC method that uses an IonPac AS9-HC column and suppressed conductivity detection, followed by post-column addition of *o*-dianisidine to enhance visible absorbance detection of the bromate ion [28]. It is anticipated that EPA Method 317.0 will be promulgated for regulatory use when the Stage 2 D/DBP rule is published [2]. In addition, both electrospray MS–MS and ICP-MS have been employed as detection techniques for the ion chromatographic analysis of bromate. The use of IC with electrospray MS–MS detection resulted in a limit of quantitation for bromate of approximately 0.1 μg/l after appropriate sample pretreatment followed by solid-phase extraction and elution with a water–methanol ammonium nitrate eluent [16,17]. Ion chromatography coupled with ICP-MS detection required less sample pretreatment in order to achieve an MDL of 0.8 μg/l for bromate. However, the separation conditions had to be carefully chosen as brominated haloacetic acids could interfere with the analysis [9,29]. It has also been reported recently that API-MS coupled with suppressed IC could achieve a detection limit of 0.5 μg/l for bromate, although sample pretreatment was required to remove matrix anions prior to drinking water analysis [19].

The use of IC with dual suppressed conductivity and ESI-MS detection can provide similar performance to Method 317.0 for the simultaneous determination of inorganic anions and trace bromate. Fig. 2 shows chromatograms obtained from the direct injection of a drinking water sample containing 22

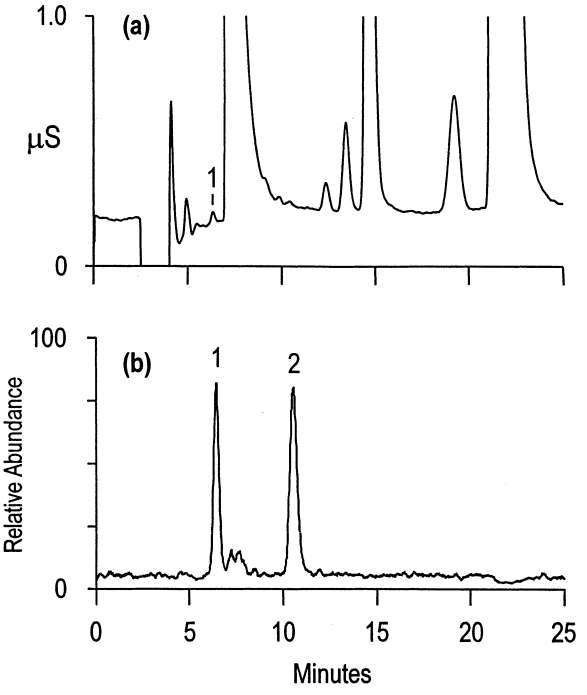


Fig. 2. Determination of bromate in drinking water using IC–MS. Conditions: guard column, IonPac AG9-HC (2 mm I.D.); analytical column, IonPac AS9-HC; eluent, 9.0 m*M* sodium carbonate; flow-rate, 0.25 ml/min; injection volume, 50 μl; detection, (a) suppressed conductivity with ASRS-ULTRA operated at 100 mA in external water mode, (b) negative ESI-MS, ESI probe at 275 °C and −2.5 kV, source CID voltage at 10 V, selected ion monitoring at *m/z*=127, 15-point boxcar smoothing; sample, drinking water; peaks: 1=bromate (22 μg/l); 2=dichloroacetic acid (not quantitated).

μg/l of bromate using a 2 mm I.D. IonPac AS9-HC column, a carbonate eluent and suppressed conductivity (a) and ESI-MS (b) detection. The common inorganic anions can be determined using suppressed conductivity, while bromate can be observed in both traces, although it is determined with more specificity and sensitivity with the MS detector. It should be noted that dichloroacetic acid, an environmentally significant DBP, is detected at the same mass ($m/z$ 127) as bromate, yet this solute is not detected using conductivity detection at this level. Using the results of seven replicate injections of a 1.28 μg/l standard, a bromate MDL of 0.5 μg/l was calculated for $m/z$ 127 (Table 1).

### *3.4. Haloacetic acids in drinking water*

Chlorine and bromine substituted acetic acids, also known as ''haloacetic acids'' (HAAs), are common drinking water disinfection byproducts. Due to their potential adverse human health effects, the levels of these compounds in finished drinking water must be monitored. The Stage 1 D/DBP Rule specifies an MCL of 60 μg/l for the sum of five specific HAAs [30]. The analytical methods presently accepted by the EPA for the determination of HAAs, e.g. Method 552.2, are based on gas chromatography with electron capture detection. In order to be amenable to GC analysis, the haloacetic acids must be extracted from water then derivatized to their methyl esters [31]. The extraction and derivatization steps are time consuming and make such methods susceptible to analyte loss and contamination.

Analysis of water samples for haloacetic acids by IC with conductivity detection is very difficult due to the need to separate all of the target analytes from mg/l levels of common anions present in drinking water, such as chloride, bromide, nitrate, and sulfate. The D/DBP regulations require the determination of HAAs at low μg/l levels, yet even with sample pretreatment and preconcentration, the use of conventional IC is not sufficiently selective to permit compliance monitoring of HAAs.

Haloacetic acids in water have been determined using liquid–liquid extraction into MTBE, followed by addition of perfluoroheptanoic acid and FI–ESI-MS detection of 'association complexes' of perfluoroheptanoic acid and HAAs [32]. Although MDLs below 1 μg/l were reported for all nine HAAs, the application of the method to different water samples required the use of standard addition techniques for quantification. As discussed in the section on perchlorate, the omission of a chromatographic separation of the analytes from the sample matrix prior to ESI-MS detection does not result in a significant reduction in total analysis time. Another approach to the determination of HAAs made use of high-field asymmetric waveform ion mobility spectrometry MS [33]. While detection limits for six HAAs ranging from 5 to 40 μg/l could be achieved with this technique, the instrumentation used is not commercially available.

Off-line extraction of HAAs into MTBE with analyte preconcentration was coupled with reversed-phase liquid chromatography and ESI-MS detection by Hashimoto and Otsuki [34]. Although complete separation of all nine HAAs was not achieved, the reported detection limits ranged from 0.003 to 0.070 μg/l, largely due to the high preconcentration factor of 2000 resulting from the extraction process. The nine HAAs have also been determined using ion-pairing liquid chromatography coupled with ESI-MS detection. The use of a large volume (500 μl) injection, reversed-phase separation with volatile ion-pairing reagents plus post-separation addition of propan-2-ol resulted in sub-μg/l detection limits for the nine HAAs [35].

Preliminary work in our laboratory using on-line sample preconcentration prior to an anion-exchange separation with gradient elution and ESI-MS detection has shown that all of the nine haloacetic acids can be separated and detected selectively at low μg/l levels, as shown in Fig. 3. The post-separation addition of an organic solvent, i.e. methanol, was found to increase MS detection sensitivity, as previously reported by others [35]. Using method programming of the source voltage, sensitivity could be optimized for each of the HAAs. This is important for minimizing the formation of undesirable fragments or adducts that can reduce sensitivity. The haloacetic acids could be detected as their pseudomolecular ions $[M–H]^-$ or as the decarboxylated species $[M–H–COO]^-$. With continuous aspiration at higher HAA concentrations (e.g. 1–100 μ$M$), dimer ions $[2M–H]^-$ were also observed. The relative distribution of the different species is mostly

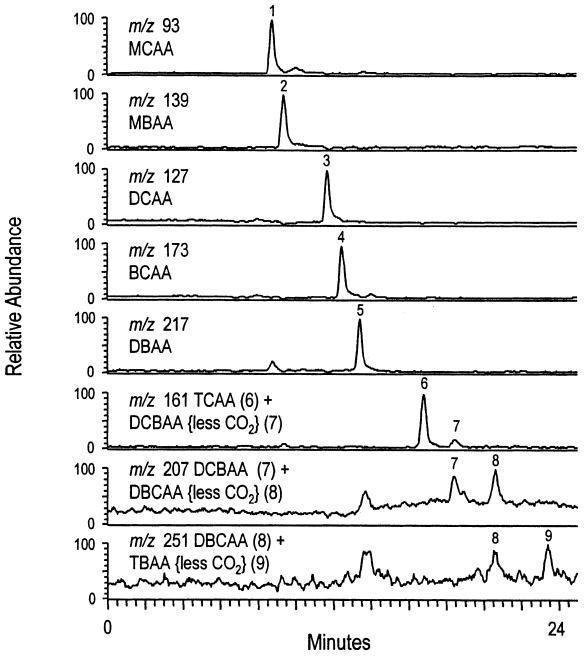


Fig. 3. Determination of haloacetic acids using IC–MS. Conditions as for Fig. 1, except: eluent, 5–70 m*M* sodium hydroxide gradient; flow-rate, 0.25 ml/min; detection, negative ESI-MS, ESI probe at 275 °C and −2.5 kV, source CID voltage at 10 to 20 V, selected ion monitoring as indicated, 15-point boxcar smoothing; sample, 5 ml preconcentrated on an IonPac TAC-LP1 column; post column solvent addition, 90% (v/v) aqueous methanol at 0.25 ml/min; peaks: 1=MCAA (3 μg/l); 2=MBAA (2 μg/l); 3=DCAA (3 μg/l); 4=BCAA (2 μg/l); 5=DBAA (1 μg/l); 6=TCAA (1 μg/l); 7=DCBAA (2 μg/l); 8=DBCAA (2 μg/l); 9=TBAA (1 μg/l).

controlled by the ESI probe temperature and by the source CID voltage used. In general, decarboxylation is favored for the more heavily substituted haloacetic acids, as shown in the mass spectra in Fig. 4, which were collected using continuous sample aspiration and multi channel analysis (MCA) acquisition over a 2 min time period.

Compared to the pseudo-molecular ion, the signal for the decarboxylated ion is clearly lower for dibromochloroacetic acid (a) than for tribromoacetic acid (b). As the loss of $CO_2$ results in a mass difference of 44 Da, which is the same as the mass difference between $^{35}Cl$ and $^{79}Br$ (and $^{37}Cl$ and $^{81}Br$), several of the haloacetic acids are detected at more than one of the $m/z$ values selectively monitored, e.g. peak 8 (dibromochloroacetic acid) at $m/z$ 207 and 251, as shown in Fig. 3. The preconcentration of a 5 ml sample volume allows detection limits in the range of 0.2–1.0 μg/l for the nine haloacetic acids. Furthermore, it should be noted that for the Stage 2 D/DBP rule, quantitation of only six of the nine HAAs is required, which does not include the three HAAs for which the lowest sensitivity was observed, i.e. DCBAA, DBCAA, and TBAA.

### *3.5. Selenium speciation by IC–MS*

The toxicity of selenium depends upon its chemical form, hence methods of analysis which can determine the various inorganic and organoselenium species are of particular current interest [36]. ICP-MS has often been used as a sensitive element-specific detection technique for the ion chromatographic analysis of selenium containing compounds [10,36–38]. However, the use of ICP-MS can only confirm the presence of selenium itself; the identity of individual species must be inferred from the coincidence of retention times with those of known standards. Liquid chromatography coupled with ICP-MS has also been used to aid in the collection of selenium containing fractions in human urine samples prior to species identification using ESI-MS–MS detection [39].

The main selenium species of concern in environmental samples are selenite and selenate, which are typically present at low levels along with high concentrations of sulfate [36]. The determination of selenate in the presence of high levels of sulfate by IC is generally difficult as the retention times of those species are similar on most anion-exchange columns. In addition, common approaches to reducing the level of sulfate prior to analysis, e.g. treatment with barium-form cation-exchange cartridges, are not applicable due to the chemical similarity of sulfate and selenate. Fig. 5a shows the chromatogram obtained for a standard in reagent water containing 50 μg/l each of selenite and selenate in the presence of 1000 mg/l of sulfate analyzed using an IonPac AS9-HC column and conductivity detection. Despite using a high-capacity column, selenate is barely detected on the tailing end of the very large sulfate peak. Fig. 5b shows the result of the same analysis using ESI-MS detection in selected ion mode. For each selenium species, the masses corresponding to

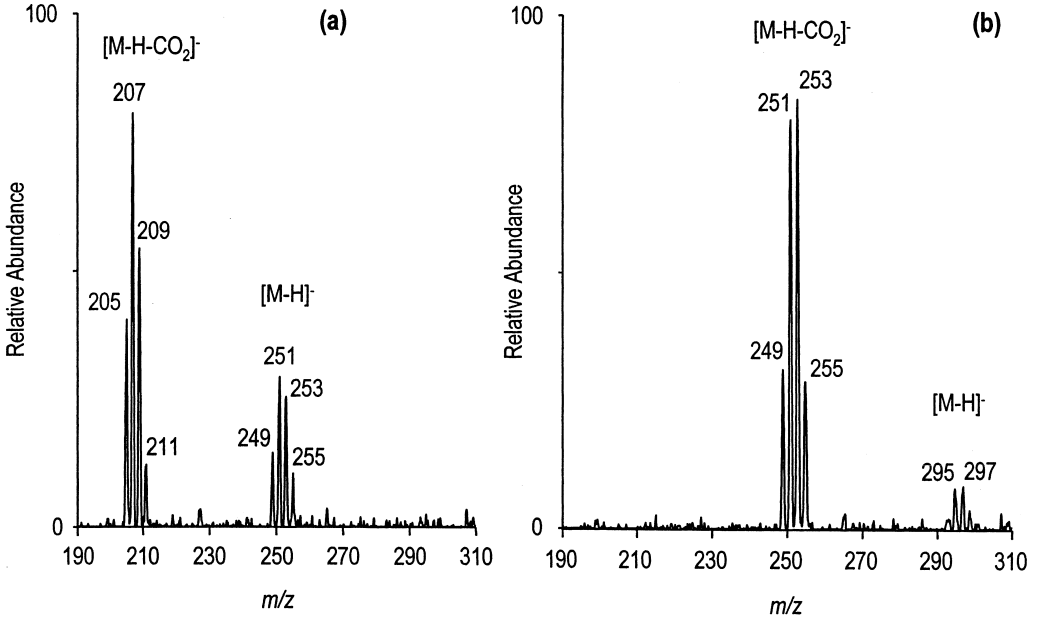


Fig. 4. Mass spectra of dibromochloroacetic acid (a) and tribromoacetic acid (b). Conditions: sample introduction, continuous aspiration at 0.3 ml/min; detection, negative ESI-MS, ESI probe at 300 °C and −2.5 kV, source CID voltage at 20 V, MCA mode for 2 min; solutes, 1 $\mu M$ each.

the five most abundant selenium isotopes were monitored. The masses with the highest signal-to-noise ratio for each species were added together for the traces shown, representing $H^{78}SeO_3^-$ and $H^{80}SeO_3^-$ for selenite and $H^{76}SeO_4^-$ and $H^{78}SeO_4^-$ for selenate. As illustrated by Fig. 5b, the ESI-MS detection of the selenium species is very specific and does not suffer from interference by sulfate.

It is noteworthy that simple inorganic anions which can be multiply charged in solution (e.g. selenite and selenate) are typically observed as singly charged anions in ESI-MS. This charge reduction is presumably due to the fact that multiple charges very close to a central atom (in this case Se) would create a very high local field strength which is not stable under ESI conditions. When the charge centers are separated by several atoms, multiply charged ions are indeed detected in ESI-MS. For example, the authors have observed doubly charged anions for citric and isocitric acids, aconitic acid, and 1,2-benzenedisulfonic acid using the Finnigan AQA.

As illustrated by Fig. 5b, the ESI-MS detection of the selenium species is very specific and does not suffer from interference by sulfate. Since selenium has six stable isotopes, the selenium species have very distinctive isotope patterns, making it relatively easy to locate unknown compounds which contain selenium in a chromatogram. The mass spectral peaks corresponding to the five most abundant selenium isotopes in selenite and selenate ($^{76}Se$, $^{77}Se$, $^{78}Se$, $^{80}Se$, and $^{82}Se$) were monitored and their measured relative intensities, determined using the conditions shown in Fig. 5b, were compared to the calculated intensities obtained from the Chromeleon-MS software. The results for selenite and selenate, shown in Table 2, demonstrate good agreement between actual and calculated abundances for the five major isotopomers for each solute. It should also be noted that selenocyanate, $SeCN^-$, a selenium species found in refinery process waters [37,38], could also be detected with high sensitivity and selectivity by ESI-MS (base ion at $m/z$ 106). The IC conditions were similar to those described previously for use with ICP-MS detection [36].

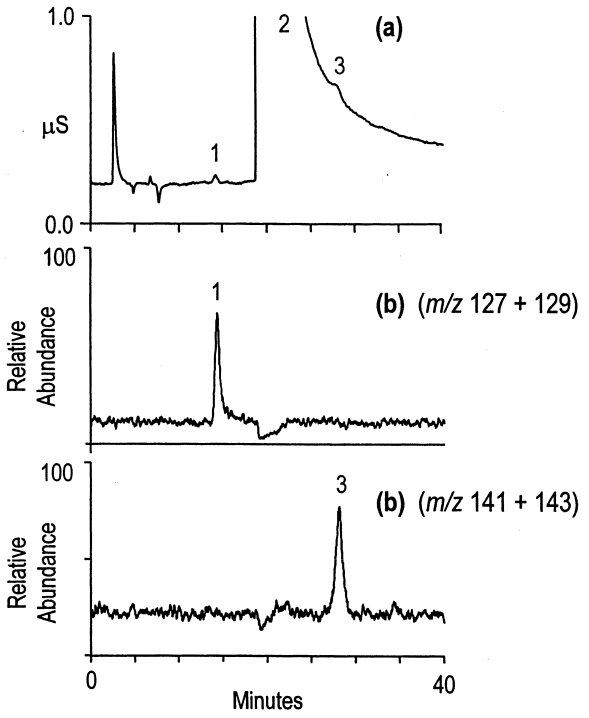


Fig. 5. Selenium speciation using IC–MS. Conditions as for Fig. 2, except: injection volume, 25 μl; selected ion monitoring, $m/z$=125–147; peaks: 1=selenite (50 μg/l); 2=sulfate (1000 mg/l); 3=selenate (50 μg/l).

## 4. Conclusions

The feasibility of using ESI-MS as a versatile, selective, and sensitive detection technique for ion chromatography has been demonstrated for a number of environmentally significant contaminants. Mass spectrometry detection can be coupled with IC using standard separation conditions appropriate for 2-mm I.D. ion-exchange columns, while the use of continuously regenerated suppressors enhances the sensitivity of MS detection by minimizing ionization interferences. The sensitivity of ESI-MS detection is comparable to (or greater than) conductivity detection, with some MDLs in the sub-μg/l range. The additional capabilities of MS detection provide high detection specificity, allowing analyte confirmation and quantification of unresolved solutes. Future work will focus on more quantitative aspects of IC–MS, i.e. analyte recovery studies from spiked samples, in addition to improving the sensitivity of the HAA analysis to permit direct injection determination of these solutes in drinking water.

Table 2
Distribution of mass spectral peaks for selenite and selenate

| Anion | Relative intensity (actual) | Relative intensity (calculated) |
|---|---|---|
| Selenite ($m/z$ 125) | 18.1 | 17.5 |
| Selenite ($m/z$ 126) | 15.3 | 15.2 |
| Selenite ($m/z$ 127) | 47.3 | 47.6 |
| Selenite ($m/z$ 129) | 100.0 | 100.0 |
| Selenite ($m/z$ 131) | 19.5 | 19.0 |
| Selenate ($m/z$ 141) | 18.1 | 19.0 |
| Selenate ($m/z$ 142) | 15.3 | 15.1 |
| Selenate ($m/z$ 143) | 47.3 | 47.6 |
| Selenate ($m/z$ 145) | 100.0 | 100.0 |
| Selenate ($m/z$ 147) | 19.6 | 19.0 |

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