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Review

Using ion chromatography to monitor haloacetic acids in drinking water: a review of current technologies

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Abstract

A review of the application of ion chromatography to the determination of haloacetic acids in drinking water is given. As it requires no sample derivatisation, ion chromatography in its various modes, such as ion-exchange, ion-interaction and ion-exclusion chromatography, is increasingly being investigated as a simpler alternative to gas chromatographic methods for the determination of polar disinfection by-products (DBPs) in drinking waters. Detection limits quoted for the regulated haloacetic acids (HAA5), are commonly in the mid to low μg/L range, however, in most cases analyte preconcentration is still necessary for detection at concentrations commonly found in actual drinking water samples. The coupling of ion chromatography to electrospray mass spectrometry provides a potential future direction, with improved sensitivity and selectivity compared to conductivity based detection, however associated cost and complexity for routine analysis is currently relatively high.

Keywords: Reviews; Water analysis; Haloacetic acids

Contents

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1. Introduction

Certain disinfectant by-products (DBPs) in drinking waters have long been causing concern due to potential harmful effects from long term exposure. Initial fears were aroused with the discovery of the health hazards associated with the consumption of trihalomethanes (THMs) in the early 1970s. These compounds were subsequently studied in detail, whilst the presence of other DBPs, such as the haloacetic acids (HAAs), was somewhat ignored. Recently however, potential health risks to humans from long term exposure to particular HAAs has led to increased efforts to monitor and reduce their concentration in drinking waters. Analytical methods for the determination of DBPs in drinking water have been predominantly gas chromatography based, with increasing use of mass spectrometry detection. Two reviews have been compiled recently detailing the various analytical approaches taken for the determination of DBPs, one focusing on all DBPs [1] and the second looking at HAAs in isolation [2]. However, in each of the above reviews liquid chromatographic methods of analysis, and in particular ion chromatography (IC), have received only limited attention. Given that the HAAs exist as anions in the actual treated drinking waters, IC would seem to hold much potential for this particular analytical challenge and a number of workers have begun to develop these potential methods. Therefore, this review details the work published to-date utilising IC in its various modes to determine, either qualitatively or quantitatively, HAAs in drinking water.

1.1. Factors affecting the formation of HAAs

Before discussing analysis of drinking water for HAAs it is important to be clear on how HAAs are formed in the first place and to be clear which chemical species are included within the group term HAA. To clarify the latter point, the species of interest within this review are listed in Table 1, together with their chemical formula and pK_a values where available. The pK_a values of the acids shown range from ~0.7 to 2.8, which means the acids only exist in protonated form under strongly acidic conditions, which has important implications for extraction and preconcentration techniques, as discussed later. For the purposes of this review methods specifically developed for the determination of fluorinated HAAs have not been included as currently there exists no regulations on the levels of these species in drinking waters and their source has not been directly related to drinking water disinfection procedures.

1.2. Chlorination

Chlorination is currently the most widespread method for disinfection and has been in use since the early 20th century. Its application is both simple and relatively inexpensive, and chlorine acts as an effective disinfectant against a wide range of bacteria, viruses and other pathogenic organisms. Moreover, chlorination results in adequate residual chlorine post-treatment to preserve waters from potential microbial growth during distribution. Since the discovery of potentially hazardous DBPs, measures have been taken to try to reduce the levels of DBP formation in chlorinated waters. Such measures include a reduction in the chlorine dosage, the repositioning of the chlorine addition in the treatment process, the use of alternature chemical sources of chlorine and a more comprehensive removal of NOM prior to chlorination.

Research over the past few years has linked the formation of HAAs, for the most part, to the chlorination of water as part of its treatment process, as well as inorganic bromide found in ground and surface waters [3–7]. Natural organic matter (NOM) in water is known to undergo oxidation by the halogen containing disinfectant species to form a wide variety of DBPs, including HAAs. A major cause for concern lies in the fact that only approximately 40% of these DBPs have been classified (see Fig. 1) [1]. In the European context, only THMs are currently covered by legislation and are limited within the European Union to a maximum of 150 μg/L for the total THMs, until further review in 2008. The USEPA has imposed a maximum contamination limit (MCL) for total THMs of 80 μg/L. This is to be assessed and reduced to 40 μg/L in the coming years [8]. For HAAs, it is proposed that the MCL for the five commonly occurring acids (HAA5), namely, monochloro-, monobromo-, dichloro-, dibromo- and trichloro-acetic acids, should not exceed 60 μg/L in total. Again, this is to be lowered in the coming years to 30 μg/L. Within this regulation, dichloro-acetic acid (DCAA) should never be present, and trichloro-acetic acid (TCAA) concentrations should not amount to more than 30 μg/L.

1.3. pH

There is an inverse relationship between the formation of HAAs and an increase in pH. Many halogenated organics hydrolyse at high pH values and total organic halide (TOX)

Table 1
Haloacetic acids (HAAs) and known pK_a values

Haloacetic acid	Abbreviation	Chemical formula	pK_a [ref.]	Boiling point
Monochloro-acetic acid	MCAA	$ClCH_2CO_2H$	2.86 [36]	187.8
Dichloro-acetic acid	DCAA	Cl_2CHCO_2H	1.25 [34] 1.29 [36] 1.30 [23]	194
Trichloro-acetic acid	TCAA	Cl_3CCO_2H	0.63 [34] 0.65 [36] 0.7 [23]	197.5
Monobromo-acetic acid	MBAA	$BrCH_2CO_2H$	2.87 [23] 2.86 [22] 2.7 [36]	208
Dibromo-acetic acid	DBAA	Br_2CHCO_2H	–	195
Tribromo-acetic acid	TBAA	Br_3CCO_2H	0.66 [36]	245
Bromochloro-acetic acid	BCAA	$BrClCHCO_2H$	–	103.5
Dibromochloro-acetic acid	DBCAA	Br_2ClCCO_2H	–	–
Dichlorobromo-acetic acid	DCBAA	Cl_2BrCCO_2H	–	–

concentrations have been reported to be halved at pH 12 compared with TOX at pH 7 over a period of 72 h and at 20 °C [9]. However, as pH decreases the formation of THMs decreases to a lower concentration than existing HAAs according to Pourmoghaddas and Stevens [10]. Thus, the variance in pH results in a trade-off between THM and HAA concentrations [11]. These studies carried out by Pourmoghaddas and Stevens displayed the effect of pH over 6, 48 and 168 h over three pH values of 5, 7 and 9.4.

1.4. Contact time

As one would expect as the contact time increases so does the formation of most DBPs. However, this is not the case for all halogenated DBPs. For example following formation, haloacetonitriles and haloketones decay relatively rapidly due to the presence of residual chlorine [4,12].

1.5. Temperature and season

Due to the kinetics of the formation process, the increase in temperature during the summer months can cause an increase in the level of DBPs in water. In addition to this, during summer months there exists a larger level of NOM and an increased rate of microbial growth. To combat these seasonal effects higher concentrations of chlorine can sometimes be added during treatment [12,13]. The combination of these factors often results in substantially higher levels of DBPs during this period.

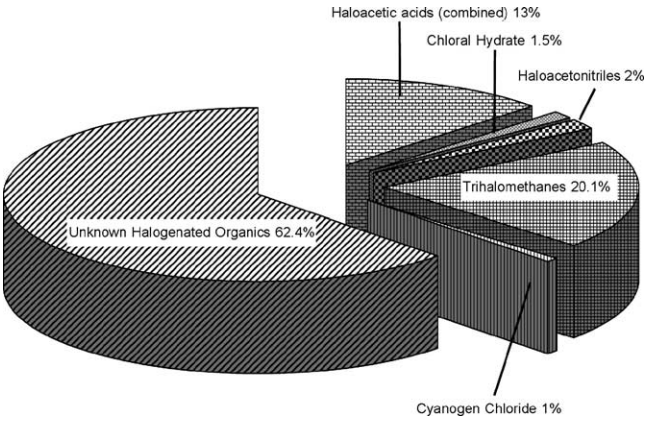

Fig. 1. Relative proportions of halogenated DBPs resulting from drinking water chlorination [1].

Experiments have been carried out by Dojlido et al. [14] to investigate if boiling of post-treatment water samples spiked with HAAs would cause them to decompose. Their findings concluded that boiling for as little as 10 min did have an effect and reduced HAAs by up to 72% for TCAA and 31% for MBAA. However, unfortunately boiling was later found to decompose the HAAs to their corresponding THMs [15]. This effect also has obvious important implications for the choice of preconcentration procedures used prior to analysis, as discussed later.

1.6. Concentration of chlorine and bromide

An increase in dose of chlorine causes an increase in the level of HAAs as opposed to THMs. Moreover, the amount of trichlorinated organics is greater than that of the di- and monochlorinated species with this increase. The quantity of chlorinated organics is greater than that of the brominated category. As stated earlier, an increase in chlorine dose does limit some species of DBPs by hydrolysis due to residual chlorine. ClO_2 has been used as an alternative method for chlorination and shows that with an increased concentration of ClO_2 there is a reduction in the formation probabilities of THMs and HAAs, with little effect from variances in pH [16].

In water treatment systems hypobromous acid is formed due to reaction of bromide and chlorine [17]. Hypobromous acid reacts roughly 25 times faster than hypochlorous acid and forms DBPs with NOM. The HOBr/HOCl ratio plays an important role in the formation of THMs and HAAs. The

bromide ion shifts the distribution of DBPs to the more brominated form.

2. Preconcentration methods for HAAs

In order to analyse trace levels of HAAs in drinking and potable waters by most current methods, including IC, it is necessary to employ a preconcentration step and therefore the preconcentration of HAAs is also briefly reviewed here. A number of preconcentration techniques have been investigated for the HAAs and current USEPA method 552 incorporates solvent extraction using MTBE and an acidified sample solution. Method 552.2 also uses MTBE solvent extraction but includes a back extraction procedure into sodium hydrogen carbonate solution following a derivatisation step. Both these extraction methods were developed with analysis using GC in mind.

Some efforts have been made to modify solvent extraction methods for improved compatibility with IC. Lopez-Avila et al. [18] modified a micro-extraction procedure specified within Standard Method 6233B of the American Public Health Association. The modified procedure was based upon the extraction of aqueous samples (acidified to pH < 0.5 and amended with copper sulphate pentahydrate and sodium sulfate) with MTBE, and subsequent back extraction into reagent water.

However, this modified procedure gave highly variable percent recoveries from spiked drinking water samples, particularly recoveries for spikes within the low μg/L range (<30% in several cases). In addition, the whole extraction procedure was rather complex and convoluted, including long periods of mixing and centrifugation, totally well over 1 hr preparation time per sample. In more recent work by Liu and Mou [19,20], a microwave evaporation preconcentration method was developed. From initial observations of this work recoveries appear excellent at >90% for MCAA, DCAA and TCAA. However, upon closer inspection it becomes clear that these data were obtained for spiked samples at relatively high concentrations, up to 0.2 mg/L, approximately 100 times greater than the spikes used by Lopez-Avila et al. to calculate their recovery data [18]. In addition, this method resulted in no reduction in the concentration of residual inorganic anions, meaning high chloride, nitrate and sulphate levels caused problems in the subsequent separation step. The degradation of certain HAAs at high temperatures suggested by Dojlido et al. [14] was said to be overcome through adjustment of the sample to >pH 10, although the exact reasons for this are unclear. Without such adjustment recoveries for DCAA and TCAA at pH 8 were as low as 30–40%.

2.1. Solid phase extraction

Solid phase extraction (SPE) has continuously gained in popularity since commercially available silica-based chemically bonded phases appeared somewhere around the mid 1970s. These silica-based sorbents have dominated SPE and have proven very successful. More recently polymeric phases have gained in popularity due to their greater compatibility to highly acidic or basic solutions. For reasons of cost, practicality, safety and the inability to be used 'on-line', traditional solvent extraction methods are, were possible, being replaced with SPE. An obvious example of this is the USEPA method 552.1, which replaces solvent extraction with SPE using anion-exchange phases for the extraction and preconcentration of HAAs.

2.2. Problems with SPE

There are several fundamental problems associated with SPE as a preconcentration technique, a number of which are particularly pertinent to the extraction and preconcentration of HAAs from drinking water. Firstly, SPE in most instances can be regarded as at best a 'semi-selective' technique. This means sample matrix will always affect analyte recoveries to some extent, as components of the sample will have some degree of affinity, however small, for the stationary phase used. For example, using ion-exchange resins will see matrix ions competing for stationary phase sites and when using reversed-phase substrates neutral species within the sample will also compete for retention. Secondly, by its very nature SPE is capacity dependant. Cartridges used will have a finite capacity for analytes under specific sample conditions. Invariably this means recoveries vary with sample load volume, analyte concentration and also sample load rate (details of which are often missing from papers discussing sample preparation using SPE). Finally, there exists the problem of analyte recovery. It is clear that the higher the affinity of the analyte for a particular stationary phase, the more difficult it will be to obtain quantitative recovery of that analyte from that phase. Further to the above, there exist the physical problems associated with SPE such as contamination, blocking, channelling and dissolution.

The first of the above fundamental problems is ideally illustrated by USEPA method 552.1, which by using anion-exchange based SPE sees the sample matrix play a role in analyte recoveries, as relatively high concentrations of matrix anions, such as chloride, nitrate and sulphate, competing for ion-exchange sites within the stationary phase.

2.3. Comparison of stationary phases

Martinez et al. carried out a study on four commercially available SPE cartridges for the extraction and preconcentration of HAAs [21]. The four sorbents investigated were a strong quaternary ammonium anion-exchanger (LC-SAX), a highly cross-linked polymer of polystyrene–divinylbenzene (PS–DVB) (LiChrolut EN), a graphitised carbon black (Envi-Carb) and a macroporous poly(divinylbenzene-co-*N*-vinylpyrrolidone) copolymer (Oasis HLB). With the latter three phases samples were adjusted to pH 0.5 to ensure HAAs were extracted in protonated form. The work proved to be a

Table 2
Variation in recovery data for HAAs on LiChrolut EN SPE cartridges

HAA	Sample matrix	Sample pH[a]	HAA concentration (mg/L)	Sample volume (mL)	Number of replicates (*n*)	% Recovery (±R.S.D.%)	Ref.
MCAA	Standard	0.5	0.2	25	4	91 (<12)	[21]
MCAA	Ground water	1.8	0.3	50	4	26 (3)	[22]
MCAA	Ground water	1.8	0.03	50	4	35 (8)	[22]
MBAA	Standard	0.5	0.2	25	4	65 (<12)	[21]
MBAA	Ground water	1.8	0.2	50	4	42 (6)	[22]
MBAA	Ground water	1.8	0.02	50	4	51 (9)	[22]
MBAA	Tap water	1.0	0.05	100	3	80.3 (8.4)	[23]
DCAA	Standard	0.5	0.2	25	4	104 (<12)	[21]
DCAA	Ground water	1.8	0.3	50	4	55 (5)	[22]
DCAA	Ground water	1.8	0.03	50	4	45 (12)	[22]
DCAA	Tap water	1.0	0.05	100	3	83.7 (13)	[23]
DBAA	Standard	0.5	0.2	25	4	85 (<12)	[21]
DBAA	Ground water	1.8	0.1	50	4	56 (7)	[22]
DBAA	Ground water	1.8	0.01	50	4	48 (9)	[22]
DBAA	Tap water	1.0	0.05	100	3	73.1 (13)	[23]
TCAA	Standard	0.5	0.2	25	4	101 (<12)	[21]
TCAA	Ground water	1.8	0.1	50	4	75 (5)	[22]
TCAA	Ground water	1.8	0.01	50	4	69 (8)	[22]
TCAA	Tap water	1.0	0.05	100	3	81.8 (11)	[23]
TBAA	Ground water	1.8	1.0	50	4	33 (2)	[22]
TBAA	Ground water	1.8	0.1	50	4	39 (8)	[22]
TBAA	Tap water	1.0	0.05	100	3	77.7 (3)	[23]

[a] Adjusted using sulphuric acid.

useful comparison of these phases but unfortunately was carried out on simple standard solutions and not actual drinking water samples, limiting its applicability. The study showed that the hyper-cross-linked PS–DVB phase (LiChrolut EN), resulted in the highest percent recoveries, between 91 and 104% for MCAA, DCAA and TCAA, and 64 and 84% for MBAA and DBAA, respectively (25 mL sample volume). Increasing sample volume further saw substantial reductions in these recovery data.

The above LiChrolut EN phase has also been applied to HAA extraction in two similar studies carried out by Loos and Barceló [22] and Sarzanini et al. [23]. The variability in the recovery data reported for HAAs in these three studies is summarised below in Table 2. It is clear from Table 2 that substantial differences in recovery data can be obtained dependent upon the exact conditions used.

Sarzanini et al. [23] also briefly investigated peconcentration of HAAs on activated carbon. However, under the conditions used, recoveries were poor and evidence was presented of incomplete elution of DBAA, TCAA and TBAA using MeOH.

2.4. Interference elimination

As mentioned briefly above, the use of various preconcentration methods for HAAs often produces a concentrated sample that contains a high concentration of matrix anions, which may interfere with the determination of target HAAs in the following IC analysis. This may be a result of these anions being present in high concentrations in the original sample and they have not been eliminated during the preconcentration procedure, or they may result from a sample pre-treatment step such as sample acidification. With drinking water samples, these matrix anions are generally chloride and sulphate (and to a lesser extent nitrate). The reduction/removal of these anions from the concentrated sample can be achieved using treatment with cation-exchange SPE cartridges in the Ag form, for the selective removal of chloride [23,29], or in the Ba form, for the removal of excess sulphate. However, it is recommended that following the use of a Ag cartridge clean-up step, a cation-exchange SPE cartridge in the acid form (H^+) be used to remove any Ag ions which may have bled from the Ag SPE cartridge into the sample extract, and which could form precipitates in the sample solution and eventually foul the analytical column.

3. Application of IC to the determination of HAAs

Due to the fact that HAAs exist as anions in drinking waters, IC is an obvious choice for their separation and detection, as apart from the aforementioned preconcentration steps, it requires no additional sample pre-treatment. For this review we define IC to include all modes of LC that utilise a charged stationary phase (permanent or dynamic) for the separation of ionic analytes.

It is possible to separate and detect HAAs by various forms of IC, and this review will detail work involving

ion-exchange chromatography, ion-interaction chromatography and ion-exclusion chromatography. Definitions and descriptions of the retention mechanisms for each of these modes of IC is beyond the scope of this review but each are clearly described elsewhere by Haddad and Jackson [24]. Detection with each of the above is generally either based on direct UV–vis absorbance or suppressed conductivity. More recently electrospray ionisation mass spectrometry (ESI-MS) and inductively coupled plasma mass spectrometry (ICP-MS) have been successfully applied to the detection of HAAs following IC separation and these will be dealt with separately.

3.1. Ion-interaction chromatography

Certain HAAs show retention on reversed-phase columns without the use of an ion-interaction reagent (IIR) [25]. However, to obtain acceptable resolution of each HAA and common matrix anions, the use of a suitable IIR is essential. Early work in this area was carried out by Vichot and Furton [26], who developed an ion-interaction method coupled with indirect UV detection. More recently, Sarzanini et al. [23] developed and compared two ion-interaction methods for the separation of HAAs. The first method involved the use of tetrabutlyammonium chloride (TTACl) as the ion-interaction reagent used within a MeOH/water mobile phase. The second method developed used cetyltrimethylammonium chloride (CTACl) as the IIR, this time within a MeCN/water mobile phase. Both methods used a 25 cm ODS column and direct UV absorbance at 210 nm. With the CTACl method, the concentration of the IIR required was < 10 times that of the TTACl method, due to a much higher degree of hydrophobicity of the IIR. Both methods, under optimal conditions were able to separate MBAA, DCAA, DBAA and TCAA in under 20 min (MCAA not shown). However, when the above HAAs were spiked into tap water (at high levels of between 25 and 30 mg/L), NO_3^- interfered with MBAA and overall detector sensitivity was poor. Making the methods on their own unsuitable for real sample analysis.

Takino et al. [27] investigated the use of a number of volatile aliphatic amines as IIRs for the separation of HAAs. The volatile nature of the IIR was necessary to allow ESI-MS be used for detection, as discussed below. The IIRs investigated were dimethylbutylamine (DMBA), dibutylamine (DBA) and tributylamine (TBA). Gradient elution methods were developed by Takino et al. for each of the above IIRs, with the mobile phase containing 5 mM of IIR and increasing from 10 to 50% MeCN over 20 min. The separations were carried out on a 15 cm microbore ODS column, with the DBAA method resulting in the baseline separation of all nine HAAs in under 14 min. In a more recent study Loos and Barceló [22] used triethylamine (TEA) as an IIR, again at 5 mM concentration, with a MeCN gradient of 15–50% over 12 min. On a standard 250 mm × 4 mm ODS column only partial separation of the HAAs was achieved using this method, although the use of ESI-MS detection in single ion monitoring (SIM) mode allowed the quantification of individual HAAs.

3.2. Ion-exchange chromatography

Nair et al. [28] were amongst the first to highlight the potential of IC, using anion-exchange in combination with suppressed conductivity detection for the monitoring of HAAs in drinking water. Although detection limits using a $Na_2CO_3/NaHCO_3$ eluent were less than those obtainable using the standard GC-ECD method, reasonable separations were possible. However, in this work MCAA and MBAA were found to co-elute and TBAA was not shown.

A much more complex (and much more sensitive) IC based method was developed later by Lopez-Avila et al. [18]. This method combined a multi-step solvent micro-extraction procedure (mentioned earlier), an on-line anion concentrator column, upon which the total extract from the micro-extraction was loaded, and a 12 stage gradient elution program over 60 min. The method employed a 25 cm microbore Dionex AS11 separator column with a NaOH eluent and suppression using a 2 mm anion self-regenerating suppressor module (ASRS, Dionex). Perhaps not surprisingly, the multi-step gradient resulted in impressive resolution of the nine HAAs and common anions and detection limits for the nine HAAs, based upon 60 mL sample volumes, were in between 0.05 and 1.1 μg/L.

Sarzanini et al. [23] evaluated and compared two anion-exchange columns and various eluents for the isocratic separation of HAAs and common anions, specifically Dionex AS9 and AS11 columns with NaOH or $Na_2CO_3/NaHCO_3$ eluents. Using both of the above eluents in turn, Sarzanini et al. found resolution of MBAA and Cl^- and DCAA and NO_3^- was poor with the AS11 column. With the AS9 column resolution of the above species was somewhat improved. Using a 0.3 mM carbonate/bicarbonate (3:1) eluent the separation of five HAAs, Cl^- and NO_3^- in spiked (500 μg/L each) and preconcentrated (10-fold) tap water was shown (SO_4^{2-} peak not included in chromatogram shown).

Most recently Liu and Mou [29] has attempted to improve detection limits of a suppressed anion-exchange method ($Na_2CO_3/NaHCO_3$ gradient) through the use of a high capacity column (AS9-HC) and the direct injection of up to 500 μL of sample. In standard solutions detection limits for all nine HAAs were in the range 0.4–32 μg/L. In the analysis of real samples, matrix anions caused problems with the quantification of several HAAs and the samples required a clean-up stage using On-Guard Ag cartridges to lower chloride, bromide and phosphate levels prior to sample analysis. This study showed the results from the analysis of several treated water samples, within which traces of DCAA, BCAA, DBAA and TCAA could be identified.

3.3. Ion-exclusion chromatography

Ion-exclusion chromatography has long since been a popular choice for the separation of weak hydrophilic carboxylic acids. Stationary phases of highly sulphonated PS-DVB in the H^+ form are commonly used with dilute solutions of

sulphuric acid and hydrochloric acid as eluents. Such conditions often result in peak tailing for hydrophobic carboxylic acids, but hydrophilic acid peak shapes are relatively sharp [30,31]. However, the use of strong acid eluents reduces the sensitivity of conductimetric detection for weak acid analytes, including HAAs.

In an attempt to solve this problem Tanaka et al. proposed a novel method called vacancy ion-exclusion chromatography [32,33] and applied it to the separation and detection of HAAs [34]. Vacancy ion-exclusion uses a solution of the analyte anions or the sample itself as the actual mobile phase. Injections of pure water result in 'vacancy' peaks at retention times matching those of the acids contained within the mobile phase solution or sample. Although the exact retention mechanism for this vacancy ion chromatographic method is not completely explained within these papers, the actual separations achieved (for standard solutions) were impressive. However, it was not clear how such a technique could be applied to real samples and so more work is required for this technique to be practical.

4. IC-ESI-MS

The development of ESI-MS has meant an alternative sensitive and selective method of detecting HAAs is now available. The simplicity of ion chromatography as a separation step for the HAAs (requiring no sample derivatization), combined with the selectivity and sensitivity of ESI-MS detection potentially makes IC-MS an ideal approach to the determination of trace HAAs in drinking water. For IC-ESI-MS work, low flow rates must be used, with eluents consisting of only volatile species. Therefore, conventional standard bore IC columns cannot be used due to excessive band broadening. Microbore IC columns are now available from most IC manufacturers and can be run at flow rates of less than 0.30 mL/min, which approximately corresponds to the maximum flow rate for ESI-MS before sensitivity is compromised.

As mentioned above, ion-interaction chromatography has been used with ESI-MS by a number of groups and has shown some promising results. Takino et al. work with DMBA, DBA and TBA as IIRs [27] showed that an increase in chain length offered longer retention but also more importantly reduced contamination of the mass spectrometer and hence proposed TBA as an ideal IIR for this type of detection. Loos et al., supported this hypothesis and suggested the use of the TEA as the IIR [22]. Using negative ESI mode and a mobile phase flow rate of 0.5 mL/min (detailed above), optimised detector conditions for the HAAs were as follows; drying gas flow — 11 L/min; drying gas temp — 350 °C; Nebuliser pressure — 55 p.s.i.; vaporiser temperature — 400 °C; capillary potential — 5000 V; fragmentation potential — 40 V. Haloacetates are observed in ESI-MS under the above conditions as their pseudo molecular ions $[M - H]^-$, their decarboxylated form $[M - COOH]^-$ and in a dimer form $[2M - H]^-$. A list of *m*/*z* values for these ions is shown in Table 3.

Table 3
Observed/measured ions (*m*/*z*) from HAAs using ESI-MS

Haloacetic acid	$[M - H]^-$	$[M - COOH]^-$	$[2M - H]^-$
MCAA	**93**		187
DCAA	**127**, 129		257
TCAA	163	**117**	
MBAA	**137**, 139		277
DBAA	**217**	173	435
TBAA	295	**251**, **253**	
BCAA	**173**		345
DBCAA	251	**207**	
DCBAA	207	**163**	

Dominant species observed shown in bold.

Roehl et al. [35] proposed a method using anion-exchange chromatography (Dionex AS162 mm i.d. column) with a gradient of 5–70 mM NaOH at a flow rate of 0.25 mL/min with eluent suppression. Eluent suppression results in the conversion of the hydroxide eluent to pure water prior to introduction into the MS interface. It is important to note that HAAs are non-volatile organic compounds. After suppression, the eluate comprises of a very dilute solution of HAAs in water. This solution does not allow complete volatilisation of the analyte ions at the electrospray nozzle and results in a poor signal from the MS. To overcome this problem a secondary pump is required that delivers a volatile organic solvent such as methanol through a T-junction before the MS that acts to improve sample volatilisation and subsequent sensitivity. Post separation introduction of an organic solvent was also shown to improve sensitivity by Takino et al. [27]. The chromatograms obtained by Roehl et al. for low level HAA standard solutions, after on-line preconcentration, using the above method are shown as Fig. 2.

5. IC-ICP-MS

In the very latest application of IC to the determination of HAAs, Liu et al. [37] have utilised ICP-MS as a highly sensitive and selective detection system. The study used suppressed IC with a hydrophilic anion-exchange column and a steep gradient of NaOH (flow rate = 1 mL/min), coupled on-line with the ICP-MS. The detector was used to selectively monitor ^{35}ClO ions for chlorinated HAAs and ^{79}Br for brominated species (dominant ions formed within the plasma). Detection limits between 16 and 24 μg/L for the chlorinated acids and 0.3 and 1 μg/L for the brominated acids were quoted based upon an injection volume of 150 μL. For application to actual drinking water samples reduction of chloride was required and carried out using On-Guard Ag cartridges prior to injection.

Table 4 summarises how the above IC-ESI-MS and IC-ICP-MS based methods compare with the other IC methods discussed within this review. The table shows the type of separation method, eluent conditions, mode of detection and detection limits with preconcentration details if used.

Table 4
Ion chromatographic methods for HAAs, separation and detection conditions and detection limits

Separation mode (column)	Eluent	Detection mode	Detection limits (conditions)	Ref.
Anion-exchange (IonPac AS11)	NaOH gradient	Suppressed conductivity	0.45–1.10 μg/L (60 mL preconcentrated to 6 mL by microextraction, followed by 5 mL injection onto anion trap column IonPac TAC-LP)	[18]
Anion-exchange (IonPac AS9HC)	Na_2CO_3 isocratic	Suppressed conductivity	0.06–0.85 μg/L (10-fold preconcented using microwave evaporation, 500 μL injection volume)	[20]
Anion-exchange (IonPac AS9)	Na_2CO_3/$NaHCO_3$ isocratic	Suppressed conductivity	25–207 μg/L (100 μL injection volume)	[23]
Anion-exchange (Alltech Universal Anion 300)	Na_2CO_3/$NaHCO_3$ isocratic	Suppressed conductivity	8–80 μg/L (100 μL injection volume)	[28]
Anion-exchange (IonPac AS16)	NaOH gradient	Eluent suppression/ICP-MS	0.34–24 μg/L (150 μL injection volume)	[37]
Ion-interaction (LiChrospher 100 RP-18)	50% MeOH, 50 mM TBACl, pH 5.0	UV absorbance at 210 nm	1.5–30 mg/L (100 μL injection volume)	[23]
Ion-interaction (LiChrospher RP-18)	MeCN gradient, 5 mM TEA, 5 mM acetic acid	ESI-MS	0.2–1.6 μg/L (166-fold enrichment by SPE)	[22]
Ion-interaction (Inertsil ODS3)	MeCN gradient, 5 mM DBA	ESI-MS	0.02–0.12 μg/L (500 μL injection volume)	[27]
Vacancy ion-exclusion (TSKgel OApak-A)	500 μM DCAA, MCAA and TCAA, pH 3.17, 1% butanol	Conductivity	0.15–3.4 μM (500 μL injection volume)	[34]

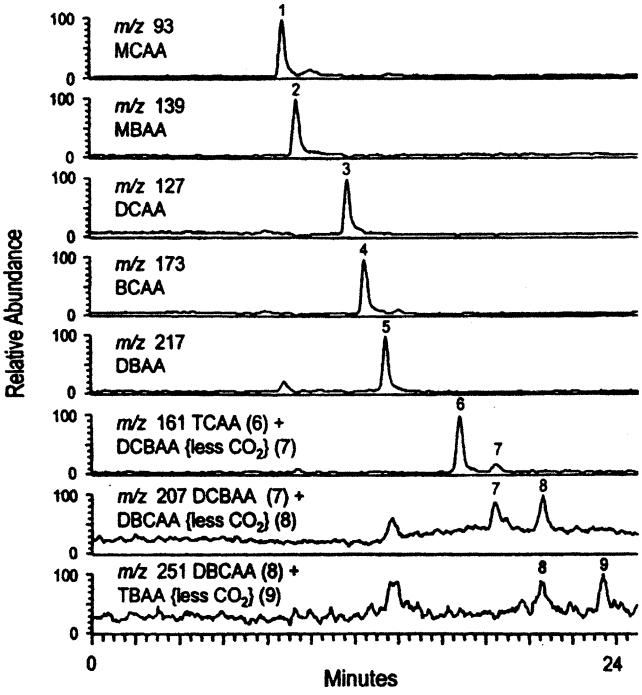

Fig. 2. Ion chromatograms of HAAs obtained using suppressed IC coupled with ESI-MS detection. Analyte concentrations between 1 and 3 μg/L. Reproduced with permission from Roehl et al. [35].

6. Conclusions

From compiling this review a number of trends have become clear. It has been shown in almost every case that currently most IC methods developed require some form of sample preconcentration, combined in many cases with removal/reduction of matrix anions. So far the results obtained show this aspect of the work to be lacking, with recovery data being highly irreproducible. The use of automation and on-line technologies to carryout such sample pre-treatment may provide some progress in this area, although there has been few attempts made in this area to-date. The use of ESI-MS detection appears to be a very promising development. However, there are still only a few papers investigating this approach. With the large number of variables affecting sensitivity with ESI-MS and the incompatibility of ESI-MS with many common IC eluents, it is clear much more work in this area is still required.

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