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Simultaneous determination of trace oxyhalides and haloacetic acids using suppressed ion chromatography-electrospray mass spectrometry

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Abstract

A new analytical procedure for the simultaneous determination of trace oxyhalides and haloacetic acids (HAs) in drinking water and aqueous soil extracts is described. The method uses micro-bore ion chromatography (IC) coupled with suppressed conductivity (SC) and electrospray ionization mass spectrometric detection (ESI-MS). The IC–SC–ESI-MS system included a secondary flow of 100% MeOH, which was added to the column eluate (post-suppressor) and resulted in a significant increase in sensitivity for all analytes. All ESI-MS parameters were optimized for HA analysis and sensitivity quantitatively compared to suppressed conductivity. Full analytical performance characteristics for the developed method are presented for monochloro-, monobromo-, dichloro-, dibromo-, trichloro-, bromochloro, chlorodifluoro-, trifluoro-, dichlorobromo- and dibromochloroacetic acid, as well as the oxyhalides iodate, bromate, chlorate and perchlorate. In the case of the HAs, an optimised 25-fold SPE preconcentration method meant all analytes could be readily detected well below the USEPA 60 μg/L regulatory limit using conductivity and/or ESI-MS. The IC–ESI-MS method was applied to the determination of oxyhalides and HAs in both soil extracts and drinking water samples. Soil samples were extracted using ultra pure water with subsequent determination of perchlorate at 1.68 μg/g of soil. A drinking water sample containing HAs was preconcentrated using LiChrolut EN solid phase extraction cartridges with subsequent sulphate and chloride removal. Total HAs were determined at 13 μg/L.

Keywords: Ion chromatography; Electrospray ionization mass spectrometry; Haloacetic acids; Oxyhalides; Drinking water; Soil extracts

1. Introduction

Electrospray ionization mass spectrometry (ESI-MS) has increased in popularity in the past number of years either with direct infusion [1,2] or employing a separation step [3–5] for the determination of small polar organic and inorganic species in various sample matrices. This interest has arisen due to its distinct advantages over alternative non-specific modes of detection, such as unknown peak and target ion mass identification.

For many years there has been concern with the presence of halogenated compounds in domestic drinking water arising from disinfection of supplies with ozone or chlorine [6–9]. These so-called disinfection by-products (DBPs) take many forms, are usually present at ultra-trace concentrations, and according to Weinberg, to-date only 40% of all DBPs associated with chlorination have been classified [10]. Therefore, to effectively monitor and identify the presence of these complex range of species, there is a clear requirement for improved analytical techniques, capable not only of efficient separation of target species and matrix components, but also to offer, where required, more selective detection and structural elucidation. Of the DBPs that have been classified, the haloacetic acids (HAs) are one of the groups of species that are already subject to regulation. Therefore, reliable and sensitive methods for their identification are required. The determination of (HAs) by ion chromatography (IC) shows definite promise as a reliable and less time consuming alternative to the current USEPA recommended methods (Standard Methods 552–552.2), which involve solvent extraction and derivatization with diazomethane and subsequent gas chromatographic analysis [11–13]. For example, there have been a number of recent papers detailing improvements in IC and sample pretreatment/preconcentration methods, allowing levels of HAs to be determined in drinking water samples, in some cases below the 1 μg/L level [14,15]. More recently, the direct detection of

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HAs in drinking water matrices has been shown by Barron and Paull, based upon a method showing increased sensitivity with suppressed conductivity (SC) detection, involving little or no sample pretreatment [16]. However, in the majority of the above studies the range of HAs investigated are limited in many cases to those currently subject to regulation in drinking water. For example, many separation-based methods do not include several important fluorinated species. Chlorofluorocarbons (CFCs), traditionally used as refrigerants, and hydrofluorocarbons (HFCs), used as aerosol replacement products, are thought to undergo photodegradation to yield halogenated species such as mono-, di- and trifluoroacetate (TFA) as well as heterogeneously halogenated species like chlorodifluoroacetate (CDFA) [17,18]. In fact, degradation of HFCs by naturally occurring atmospheric hydroxyl radicals accounts for the main source of TFA with over 40% of HFC 134a (CF_3CH_2F) being converted to TFA in the troposphere [18]. The presence of these species in environmental samples and water sources is therefore of considerable interest. There is currently no regulation method for the determination of TFA or CDFA in environmental matrices. However, Wang et al. have applied IC with UV detection to the analysis of fluoroacetates in soil [19]. Although detection limits were not sufficient for sub-μg/L determinations, the method offered acceptable resolution from mg/L concentrations of other inorganic anions and used a very simple extraction technique using only ultra pure water.

Along with the HAs, many papers have investigated oxyhalide formation and presence through drinking water ozonation [20–23]. In particular bromate has been a main target analyte, due to potential health risk to humans [24], although interest in chlorate and chlorite also exists. The preferred technique for bromate is IC, generally coupled with post-column reaction detection of the resultant tribromide ion species [25]. This method is very sensitive with detection limits in the sub-μg/L range. A further oxyhalide of particular current interest in environmental and drinking waters [26,27], and other matrices such as soils [28], animal tissues [29] and vegetation [30], is perchlorate. Although not associated with drinking water disinfection, perchlorate is a known endocrine disruptor inhibiting iodine uptake by the thyroid gland. As a very polarizable anion, ultra-trace perchlorate determination in complex matrices by suppressed IC can be problematic due to its strong retention on conventional high capacity columns. As a result, more methods employing perchlorate-specific modes of detection like ESI-MS are being developed [27,31–33].

As both oxyhalides of interest and the HAs are present as anions in drinking water samples, potential exists for their simultaneous determination using IC. However, due to frequent coelution with each other and the mg/L matrix components of the sample, combined with their low concentration and the non-specific nature of suppressed conductivity or UV detection, a single routine and reliable method is a significant challenge. Suppressed IC with hydroxide eluents is very suitable for coupling with ESI-MS and the aqueous IC eluate causes no background spectral interference or contamination, and non-volatile buffers are not involved [34]. In general the problems associated with analyte volatility in aqueous solutions, as well as common flow rates used within standard bore IC, has been overcome with post-column addition of organic solvents and accurate pre-ESI-MS flow splitters [35]. The ability to monitor single ions using extracted ion chromatograms (EICs) with ESI-MS allows for detection of a specific mass or range of masses corresponding to analytes of interest, in some cases simplifying the problem of complete chromatographic resolution, as well as certain background interferences to a limited degree.

In this study, the possibility for the simultaneous determination of ultra-trace HAs and oxyhalides is demonstrated. Utilising ESI-MS in conjunction with suppressed conductivity detection the possibility for routine analysis of these compounds by IC as a simultaneous and higher throughput alternative to individual standard methods is proposed. The described simultaneous use of both suppressed IC and ESI-MS provides a new powerful combination the quantitative identification of these important species in relatively complex sample matrices. The developed method was applied to determinations in both soil extracts and drinking water.

2. Experimental

2.1. Instrumentation

All separations were carried out using a Dionex DX-500 ion chromatograph (Dionex, Sunnyvale, CA, USA) comprising of a GP50 gradient pump, LC25 column oven (adjustable to 1 °C increments over a 35–45 °C temperature range) and a CD20 conductivity detector. Dionex IonPac AG16 guard (2 mm × 50 mm) and AS16 (2 mm × 250 mm) analytical columns were used for all separations and all tubing was micro-bore polyether ether ketone (PEEK). The injection volume for all work was 100 μL and eluent flow rate was 0.30 mL/min. For suppressed conductivity detection, a Dionex AEES Atlas suppressor was used and operated at 19 mA with a Dionex SC20 suppressor controller in the external water mode. Conductivity acquisitions were carried out using a Dell DX1 personal computer with Dionex Peak Net Version 6.0 installed. For mass spectrometry, a Bruker Daltonics Esquire∼LC (Bremen, Germany) electrospray octopole ion trap was employed, complete with Bruker Daltonics NT 4.0 software. Optimized parameters for ESI-MS are listed in Table 1. For removal of carbonate from the hydroxide eluent, a Dionex continuously regenerated anion trap column (CR-ATC) was employed. Both the Atlas and CR-ATC were configured to a secondary Waters 501 HPLC pump (Millipore-Waters, Milford, MA, USA), which continuously supplied regenerative Milli-Q water at a flow rate of 0.30 mL/min. For direct infusion-MS, a Cole Parmer 74900 series threaded screw syringe type pump was filled with sample and infused at 250 μL/h. For IC–SC–ESI-MS, the suppressed IC eluate was coupled to the electrospray via a T-junction supplied with a 0.12 mL/min flow of 100% MeOH before entering the electrospray needle. The pump used for MeOH supply was a Hewlett-Packard HP1100 micro-bore pump (Hewlett-Packard, Palto Alto, CA, USA). Sample preconcentration with subsequent sulphate and chloride removal used Merck LiChrolut EN (Merck, Darmstadt,

Table 1
Optimized ESI-MS Parameters for HAs

Parameter	Optimised value
Capillary (V)	4413
End plate offset (V)	−892
Skim 1 (V)	−17
Capillary exit offset (V)	−50
Octopole (V)	−1.5
Octopole Δ (V)	−1.4
Trap drive	38.8
Skim 2 (V)	−5.7
Octopole RF (Vpp)	55.5
Lens 1	5.2
Lens 2	54.7
N_2 drying gas flow (L/min)	8
Dry gas temp (°C)	300
Nebulizer pressure (psi)	55

Germany) solid phase extraction cartridges followed by Alltech MaxiClean IC-Ba, IC-Ag and IC-H cleanup cartridges (Alltech Associates, Deerfield, IL, USA), as detailed in an earlier study [37].

2.2. Reagents

Analytical grade monochloroacetic acid (MCA), monobromoacetic acid (MBA), dichloroacetic acid (DCA), dibromoacetic acid (DBA), trichloroacetic acid (TCA), trifluoroacetic acid (TFA), chlorodifluoroacetic acid (CDFA), bromochloroacetic acid (BCA) dichlorobromoacetic acid (DCBA) and chlorodibromoacetic acid (CDBA), as well as the potassium salts of iodate, bromate, chlorite, chlorate, perchlorate, fluoride, chloride, and sulphate and the sodium salt of nitrate were obtained from Sigma–Aldrich (Gillingham, UK). All oxyhalides and HAs were prepared to a stock concentration of 10 mM and stored in a refrigerator at 4 °C until required for use for working standards. All eluents were prepared from a 50% solution of sodium hydroxide in water purchased from Sigma–Aldrich. All eluents and standards were prepared using diluent water from a Millipore water purification system (Millipore, Bedford, MA, USA) with a specific resistance of 18.3 MΩ cm. Eluents were passed through a 0.25 μm filter, followed by 15 min sonication prior to use. Methanol used for volatilisation was of MS grade and ordered from Romil (Cambridge, UK).

2.3. Optimized IC conditions, sample collection and pretreatment

For the simultaneous separation of sample inorganic anions, oxyhalides and HAs, the optimized IC method employed a dual temperature and hydroxide eluent concentration gradient as described in previous work [36]. Hydroxide concentration was set at 1 mM for the first 20 min then ramped to 4 mM hydroxide over a 20-min period, then to 20 mM over 5 min. This hydroxide concentration was then maintained for a further 26 min. The initial temperature for the separation of early eluting anions was 30 °C. At 20 min the temperature was set at 45 °C and then returned to 30 °C at 30 min. Equilibration time was 16 min between successive runs.

Drinking water samples were collected in a 1000 mL sample container, which was rinsed in triplicate with sample before collection. Samples were immediately transferred to a refrigerator at 4 °C and analysed on the same day. The preconcentration and cleanup procedure is described in detail elsewhere [37]. In addition to drinking waters, a sample of soil was taken from a sampling site within Co. Meath, Ireland. This sample was then transferred to a crucible and dried in an oven at 37 °C for 24 h. The dried soil was then transferred to a mortar and grinded to a fine powder with a pestle. A mass of 2.0 g of dried soil was weighed out and placed in a conical Erlenmeyer flask. Exactly 20 mL of Milli-Q water was added to the flask and the Erlenmeyer flask was left for 3 h on an automatic shaker. The resulting solution in the Erlenmeyer flask was allowed to stand for half an hour and then filtered using 0.45 μm vacuum filters and transferred to a vial. Fortifications were made by preparing the desired concentration of all analytes in 20 mL of Milli-Q water solution used for extraction.

2.4. Removal of interferences

It should be noted that μg/L range detection with both ESI-MS and suppressed conductivity detection modes suffered significant interference from mg/L concentrations of inorganic anions in these highly complex sample matrices. Thus, adequate sample pretreatment to remove this interference was necessary for successful method development and validation. As such, both chloride and sulphate were selectively removed from all samples after preconcentration/extraction using Alltech MaxiClean cartridges in the barium, silver and acid form (Alltech Associates, Deerfield, IL, USA). In the optimized preconcentration method for drinking water samples, an inherent 'self-cleaning' effect was observed, removing nitrate along with any other strong acid anion contaminants in the matrix. This allowed complete IC resolution and sensitive detection of most HAs and all oxyhalides, with interferences only affecting MBA and TCA determinations with suppressed conductivity measurements. All analytes could be observed readily after this pretreatment with ESI-MS in the single ion monitoring mode.

It should also be noted that an EG40 was not utilized here for eluent generation as in previous works [16,36,37]. It was found that a substantial background peak was observed at *m/z* 183 in the total ion chromatogram (TIC) with the EG40 installed and this significantly affected sensitivity of the MS even in single ion monitoring mode for most analytes, suggesting some form of analyte suppression. This interference was later identified as styrene sulphonate, which leached into generated hydroxide eluents and arose from disintegration of the membranes used within the KOH cartridge. Once manually prepared eluents were employed, this interference was removed and sensitivity enhanced.

3. Results and discussion

3.1. IC of HAs and oxyhalides

For the simultaneous separation of sample inorganic anions, oxyhalides and HAs, the optimized IC method employed a dual temperature and hydroxide eluent concentration gradient, modified from that described in previous work [36]. There is a clear advantage to be had from using a hydroxide eluent when coupling suppressed IC with ESI-MS detection, namely the elimination of background buffers within the eluate entering the MS. However, manipulating separation selectivity using purely hydroxide eluents can prove problematic with complex mixtures. Here, temperature has been shown to be of significant use in improving resolution of closely eluting and overlapping peaks. The combined dual gradient method resulted in acceptable resolution of 19 significant species even with a relatively large sample injection volume for a micro-bore column (100 μL), at a high standard concentration of 20 μM for all analytes (Fig. 1).

For conductivity detection, the suppressor used was the Dionex Atlas suppressor, typically used with carbonate/bicarbonate eluents. The low capacity suppressor can be used very successfully with hydroxide eluents with a microbore system at the eluent flow rates used here. It is also worthy of note, that for robust day to day use, the suppressor used must be able to withstand additional backpressures arising from the ESI interface, and without using addition of pressure regulating devices, this requirement favours packed bed and monolithic bed suppressors over membrane based systems. The analytical performance data for the dual gradient suppressed IC method are discussed in detail in Section 3.4.

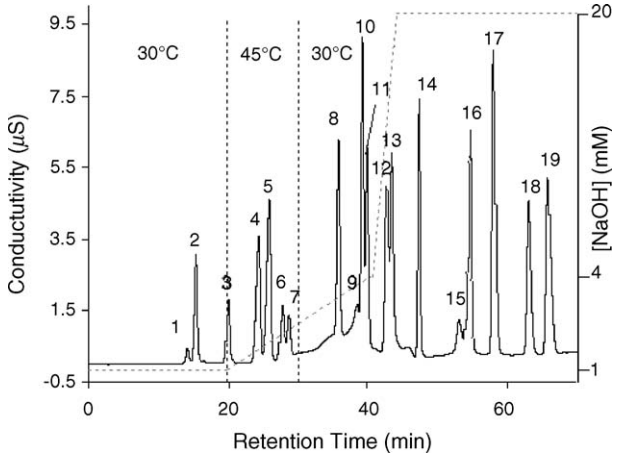

Fig. 1. Optimized IC method for use with conductivity and ESI-MS detection using temperature program from 30 to 45 °C at 20 min for a duration of 10 min. Suppressor and current: Dionex AEES Atlas in external water mode at 19 mA. Column: Ion Pac AG16 (2 mm × 50 mm) and AS16 (2 mm × 250 mm). Also included is the hydroxide gradient profile (highlighted in grey). Oven: Dionex LC25. Elution order: 1 = acetate, 2 = iodate, 3 = chlorite, 4 = MCA, 5 = bromate, 6 = chloride, 7 = MBA, 8 = TFA, 9 = nitrate/bromide, 10 = chlorate, 11 = DCA, 12 = CDFA, 13 = BCA, 14 = DBA, 15 = carbonate, 16 = TCA, 17 = DCBA, 18 = CDBA, 19 = perchlorate. Concentrations of HAs and oxyhalides = 20 μM. Acetate, chloride and carbonate concentrations unknown and appeared as impurities in Milli-Q water.

3.2. Optimization of ESI-MS parameters by direct infusion and coupling IC to ESI-MS

Optimization of ESI-MS parameters was first carried out by directly infusing a solution of each HA in MeOH:water. Three distinct ion types were observed for each HA; their pseudo molecular ion $[M-H]^-$; their decarboxylated fragment ion $[M–COOH]^-$ and a dimerised form $[2M-H]^-$. These ion types were reported previously by Roehl et al. [34]. The MS–MS facility on this ion trap detector was not utilized, as all analyte molecules were of low molecular mass and simple molecular structure and fragment or pseudo molecular ions were easily distinguished from their isotopic patterns.

Although not specifically included in this optimization study for simplicity, it was observed that signal intensity for the oxyhalide species of interest remained acceptable under the above conditions. Obviously, for chlorine and bromine containing species, signals corresponding to their natural isotopic ratios were observed. All final conditions are listed in Table 1 (however, it should be noted that these optimized parameters here are strongly dependent on the type of MS instrument and may vary significantly to those of another manufacturer or model).

Coupling the suppressed IC to the ESI chamber was carried out via a T-junction prior to the electrospray needle and was supplied with a constant counter-flow of 100% MeOH. Methanol, acetonitrile and propan-2-ol were studied as suitable solvents due to their high volatilization and desolvation ability. Some confusion has recently arisen on the use of post-column solvent addition. Previous studies have shown a definite enhancement of MS sensitivity for low molecular weight organic acids [34,38], but in a recent study by Mascolo et al., this approach did not result in any significant improvement in sensitivity using methanol as the volatilizing solvent and that a higher dry gas temperature may have had a similar effect [39]. In this study, an increase in dry gas temperature did not boost sensitivity in any significant manner when IC–MS was carried out without post-column solvent addition. It was found here that sensitivity for nearly all analytes increased to a maximum with an additional secondary MeOH flow of 0.12 mL/min with a significant reduction in sensitivity for all analytes was observed beyond a total flow rate of 0.42 mL/min. Little or no improvement was observed with either acetonitrile or propan-2-ol.

Taking the above maximum flow into account, the effect of % MeOH in the total flow was investigated. It was found that increasing % MeOH markedly increased peak intensities for most analytes with up to a three-fold increase in sensitivity (for $[DCA–H]^-$) towards 100% MeOH secondary flow. Enhancements in sensitivity with this volatilizing solvent can be found in Fig. 2, which shows the log of the peak intensity for 15 observed ions against (A) increasing flow and % MeOH and (B) increasing % MeOH.

3.3. Trends in observed ion types for each HA

Using the optimum ESI-MS parameters listed in Table 1, the relative abundance of each individual HA ion displayed some interesting trends. Table 2 shows the percentage relative intensi-

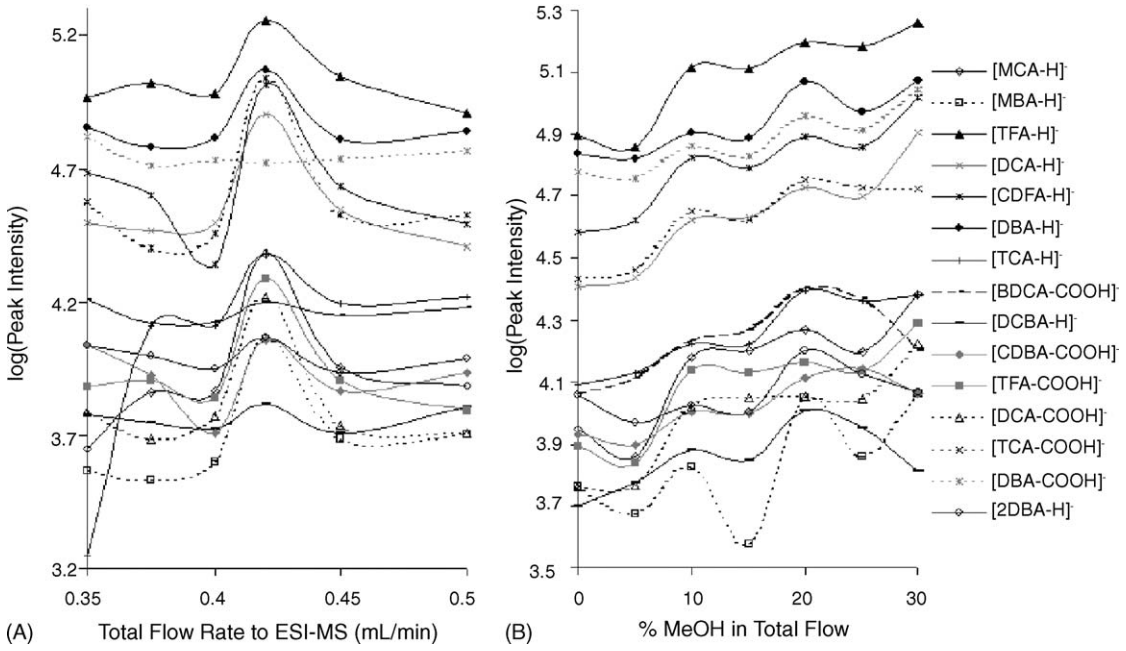

Fig. 2. (A) Effect of secondary 100% MeOH flow on peak intensity for nine HAs. (B) Effect of % MeOH in total 0.42 mL/min flow rate.

ties of each ion observed to the base peak for each HA. From the mass spectral data, it was clear that not only did the degree of halogenation play an important role in which fragment was most stable, but also the type of halogen substituted. Put simply, TFA showed most stability as the pseudo molecular ion. Chlorinated species displayed high stability for the MCA pseudo molecular ion, with an increase in abundance of the decarboxylated ion seen with DCA, and a further increase for TCA. Similarly with the brominated species, the decarboxylated ion emerged as the dominant form with DBA. The appearance of a dominant $[M–COOH]^-$ ion suggested that both the substituted halogen as well as the degree of halogenation played a significant role in its stability as a base peak.

Likewise, trends were apparent with the appearance of dimerised species. There was increased dimer stability associated with a higher degree of bromination, followed by chlorination and fluorination, respectively. Where a species contained two heterogeneous halogens, the larger halogen(s) contributed most to dimer stability. For instance, the intensity of the dimer ions for CDBA, DCBA and TCA are of the order CDBA > DCBA ≫ TCA. The presence of a bromine atom significantly contributed to the dimer ion stability, even though all three were trihalogenated species.

Table 2
Relative Intensities of ion fragments for nine HAs

HA	$[M-H]^-$	$[M–COOH]^-$	$[2M-H]^-$
MCA	100	–	–
MBA	100	–	–
TFA	100	10	3
DCA	100	20	3
CDFA	100	10	11
DBA	90	100	14
TCA	–	100	9
DCBA	–	100	15
CDBA	–	100	16

3.4. Analytical performance characteristics

Accurate and precise determinations of trace HAs and target oxyhalides in the approximately 0.1–100 μg/L range were required for this method to be suited to routine monitoring of HAs and oxyhalides, particularly in drinking water samples, and other environmental matrices of interest. The complete analytical performance characteristics for the dual gradient IC method (temperature and hydroxide) were determined using both suppressed conductivity detection and ESI-MS and results are presented in Table 3. For linearity studies using the conductivity detector, a series of standards ($n = 5$) from 0.05 to 0.5 μM of oxyhalides and HAs were prepared and run on the IC using the optimized dual gradient IC method. All analytes displayed excellent linearity with correlation coefficients >0.99 with the exception of MBA and TCA which co-eluted with trace sulphate and chloride at low levels. As ESI-MS was found to be less sensitive, linearity was studied over the range 5–30 μM ($n = 5$). The extracted ion chromatograms for each ion were examined for linearity. As expected, the most abundant forms of each ion described in Section 3.2 displayed the best linearity. At least one fragment ion from each analyte displayed acceptable linearity, with the exception of CDFA, DCBA and TCA, falling just short of the $R^2 \geq 0.98$ limit.

In a similar manner, limits of detection were determined using both detectors. Data was collected from direct injection of analyte standards, and also following an off-line 25-fold sample preconcentration procedure, previously optimized and detailed elsewhere [37]. Method detection limits were calculated from a low level standard with analyte concentrations corresponding to signal-to-noise ratios approaching 3:1 for all analytes with both

Table 3
Analytical performance data for dual gradient IC method with suppressed conductivity and ESI-MS detectors

Analyte	Linearity (R^2)		Retention time reproducibility	Peak height reproducibility	Peak intensity reproducibility	LOD				
	IC-conductivity (50–500 nM, $n=5$)	IC–ESI-MS (5–30 μM, $n=5$)	(min)/[%R.S.D.] ($n=30$, 2 μM standard)	IC-conductivity (%R.S.D., $n=10$, 2 μM standard)	IC–ESI-MS (%R.S.D., $n=6$, 20 μM standard)	IC-conductivity (direct injection) (μg/L)[a]	IC–ESI-MS (direct injection) (μg/L)[a]	IC-conductivity (with SPE) (μg/L)[a]	IC–ESI-MS (with SPE) (μg/L)[a]	USEPA Standard Method(s) (μg/L)
$[MCA–H]^-$	0.9996	0.9937	25.3 [1.67%]	3.1	9	0.5	313	0.03	19	0.052[b]
$[MBA–H]^-$	n.c.	0.9921	29.5 [1.25%]	9.2	10	n.c.	1440	n.c.	91	0.0075[b]
$[MBA–COOH]^-$	–	0.9879	–	–	–	–	–	–	–	–
$[TFA–H]^-$	0.9982	0.9887	37.2 [1.14%]	2.4	7	1.2	19	0.28	5	–
$[DCA–H]^-$	0.9913	0.9935	41.5 [0.99%]	1.4	10	0.5	–	0.02		0.015[b]
$[DCA–COOH]^-$	–	0.9958	–	–	9	–	40	–	2	–
$[BCA–H]^-$	0.9986	0.9924	–	–	8	2.1	174	n.c.	n.c.	0.14[b]
$[BCA–COOH]^-$	–	0.9975	–	–	5	–	–	–	–	–
$[CDFA–H]^-$	0.9962	0.9745	44.4 [0.94%]	1.8	9	1.7	567	0.08	26	–
$[DBA–H]^-$	0.9984	0.9868	48.9 [0.95%]	3.7	13	2.3	–	0.14	–	0.015[b]
$[DBA–COOH]^-$	–	0.9967	–	–	9	–	44	–	44	–
$[DCBA–H]^-$	0.9996	–	60.1 [0.72%]	1.9	–	2.5	–	0.33	–	0.091[b]
$[DCBA–COOH]^-$	–	0.9666	–	–	9	–	244	–	33	–
$[CDBA–H]^-$	0.9992	–	65.6 [0.62%]	2.5	–	8	–	2.46	–	0.468[b]
$[CDBA–COOH]^-$	–	0.9907	–	–	5	–	448	–	138	–
$[TCA–H]^-$	n.c.	–	56.4 [0.77%]	n.c.	–	2.4	–	0.17	–	0.085[b]
$[TCA–COOH]^-$	–	0.9779	–	–	13	–	74	–	5	–
IO_3^-	0.9966	0.9854	15.7 [2.93%]	2.5	7	1.4	22	–	–	–
BrO_3^-	0.9994	0.989	26.6 [1.59%]	4.1	12	0.6	39	–	–	1.4[c] 1.2[d] 0.17[e]
ClO_3^-	0.9986	0.9939	40.7 [1.07%]	2	9	0.6	9	–	–	1.3[c] 2.6[d]
ClO_4^-	0.9997	0.9932	68.1 [0.66%]	2.5	8	0.96	10	–	–	–

n.c., non calculable due to interference from sulphate/chloride at low analyte levels for MBA/TCA or no SPE % recovery data available for BCA.

[a] LOD calculated by serially diluting a standard in Milli-Q water to a point where signal-to-noise ratio reached 3:1.

[b] Viewed as HA-ester after extraction/derivitisation with diazomethane and GC-ECD, USEPA Method 552 or 552.2 [15,17].

[c] Viewed using suppressed ion chromatography, 50 μL loop injection, USEPA Method 300.1 with a Dionex AS9 column [39].

[d] Viewed using suppressed ion chromatography, 225 μL loop injection USEPA Method 326.0 [40].

[e] Viewed as tribromide ion after post-column reaction with ammonium molybdate, sulphuric acid and potassium iodide, Method 326.0 [40].

detectors. As can be observed from Table 3, ESI-MS did not offer similar detection sensitivities to that of suppressed conductivity detection. The higher sensitivity of the suppressed conductivity detector, compared to the mass spectrometric detection for these analytes was considered unusual at first in comparison to other works, but is obviously highly dependent upon the type and operating conditions of the mass analyser used, and here also reflects the lower LODs found possible through the use of the Dionex AEES Atlas suppressor, allowing direct detection in the sub-μg/L range [16]. For the HAs, direct detection limits using ESI-MS ranged from 0.019 to 1.44 mg/L, with oxyhalides showing better responses ranging from 9 to 39 μg/L, even though MS parameters were optimized for HAs. Concentrations of 10 μg/L perchlorate could be observed with direct injection (EICs at *m/z* 99 and 101) and bromate at 39 μg/L (EICs at *m/z* 127 and 129). Considering the potential toxicity of both of these compounds at trace levels, the combination of both the analyte specific ESI-MS response and the sensitivity of the conductivity detection are clearly advantageous in reducing the number of false positive identifications.

For conductivity under direct injection conditions, a concentration range of 0.5–8 μg/L could easily be observed for all analytes, including oxyhalides, with the detection limits for the regulated HAs below 2.4 μg/L.

When applying the SPE extraction and preconcentration procedure, detection limits for the HAs using both detectors were reduced considerably. Most oxyhalides were not preconcentrated using the developed SPE method and so detection limits were unaffected. For the combined SPE–IC–SC method detection limits ranged from 0.02 to 2.46 μg/L. For SPE–IC–SC–ESI-MS these were between 2 and 138 μg/L. The reproducibility data and % recovery for each analyte HA using the SPE method are detailed elsewhere [37].

Also included within Table 3 for comparison are the method detection limits for various standard USEPA Methods for determination of oxyhalides and HAs [12,13,40,41]. In particular (and most pertinent to analysis of Irish drinking water) is the standard method for analysis of HAs by liquid–liquid extraction-derivatization and gas chromatography with electron capture detection (GC-ECD), Method 552 series. As can be observed, when the SPE preconcentration procedure was used in conjunction with the developed IC method, excellent detection limits were obtained, in many cases similar to those of the current USEPA Method(s), and in the case of MCA, below the standard method. However, considering the extremely time consuming nature of the USEPA Method 552 series, and the much larger preconcentration factor involved in the prescribed solvent extraction procedure, this IC method offered a very competitive alternative in terms of sample preparation and analysis time as well as overall cost. However, a minor drawback with the IC method was the inadequate resolution of MBA and TCA from mg/L concentrations of chloride and sulphate in suppressed conductivity measurements. This could be further improved by adding an extra IC-Ag cartridge to the cleanup procedure, but the effect of this on overall percent recoveries was not examined here.

Retention time reproducibility studies using a similar dual gradient elution program have been described previously [36] and showed that over a 45-h period, retention data did not vary considerably and was well within reproducibility limits. In fact, despite a total run time of over 60 min, the dual gradient method showed retention time reproducibility of <2% for 12 out of the 13 ions, over 30 repeat runs. In repeat peak height (conductivity) and peak intensity (ESI-MS) studies, %R.S.D.s for $n = 6$ replicate injections displayed variance of ≤13% using ESI-MS for all analytes, compared to ≤4.1% for conductivity detection. From this and the above analytical data it is clear that the suppressed conductivity data is more quantitative, however the ESI-MS is useful for additional qualitative identification, and hence the two detectors in combination provide a powerful solution to the analysis of real samples.

3.5. Application to HA and oxyhalide determination in complex matrices

3.5.1. Drinking waters

Samples of laboratory drinking water (1 L) were analysed using the optimized method for both HA and oxyhalide content. A sample was divided into two aliquots, one of which was pretreated as outlined in Section 2.3 (preconcentration and sample cleanup), the other was simply subjected to sample cleanup using the Alltech MaxiClean cartridge series. Both sample aliquots were subsequently analysed using the developed method. The resultant ion chromatograms both from suppressed conductivity and ESI-MS illustrated clearly the wealth of information the developed method can provide on trace level contaminants in treated water supplies. The ion chromatogram obtained for the drinking water sample preconcentrated 25-fold and determined with suppressed conductivity detection yielded peaks corresponding to the retention times of eight HAs (MCA, MBA, TFA, DCA, CDFA, DBA, DCBA and CDBA) and chlorate, with further indications of peaks corresponding to the retention times of BCA and perchlorate also present at much lower levels.

From analysis of the TIC and subsequently EICs (see Fig. 3), very distinct peaks corresponding to the *m/z* of DCA ($[DCA–H]^-$ at *m/z* 127, $[Cl^{37}Cl^{35}CHCOO]^-$ at *m/z* 129) CDFA ($[CDFA–H]^-$ at *m/z* 129), DBA ($[DBA–COOH]^-$ at *m/z* 175 ($Br^{81}Br^{81}$), and at *m/z* 173 ($Br^{79}Br^{81}$)), CDBA ($[CDBA–H]^-$ at *m/z* 207) and chlorate were observed. A very small peak for perchlorate was also observed in the conductivity trace and co-eluted slightly with a preconcentrated component of the sample. This possible perchlorate peak was present within the ESI-MS chromatograms at *m/z* 99 and 101, and well resolved from the isotopic forms of hydrogen sulphate present from the preconcentration procedure. The strong retention and therefore possible preconcentration of perchlorate on polymeric hyper-crosslinked materials, similar in structure to the SPE cartridges used here, has been shown previously by Penner and Nesterenko [42] and so may explain the appearance of this peak in the preconcentrated water sample. Peaks possibly corresponding to DCBA and MBA were also observed with ESI-MS, but were below the detection limit (signal-to-noise ratio of 3:1) and could not be absolutely confirmed.

To determine the levels of HAs in this drinking water sample, a semi-quantitative standard addition (by peak height using sup-

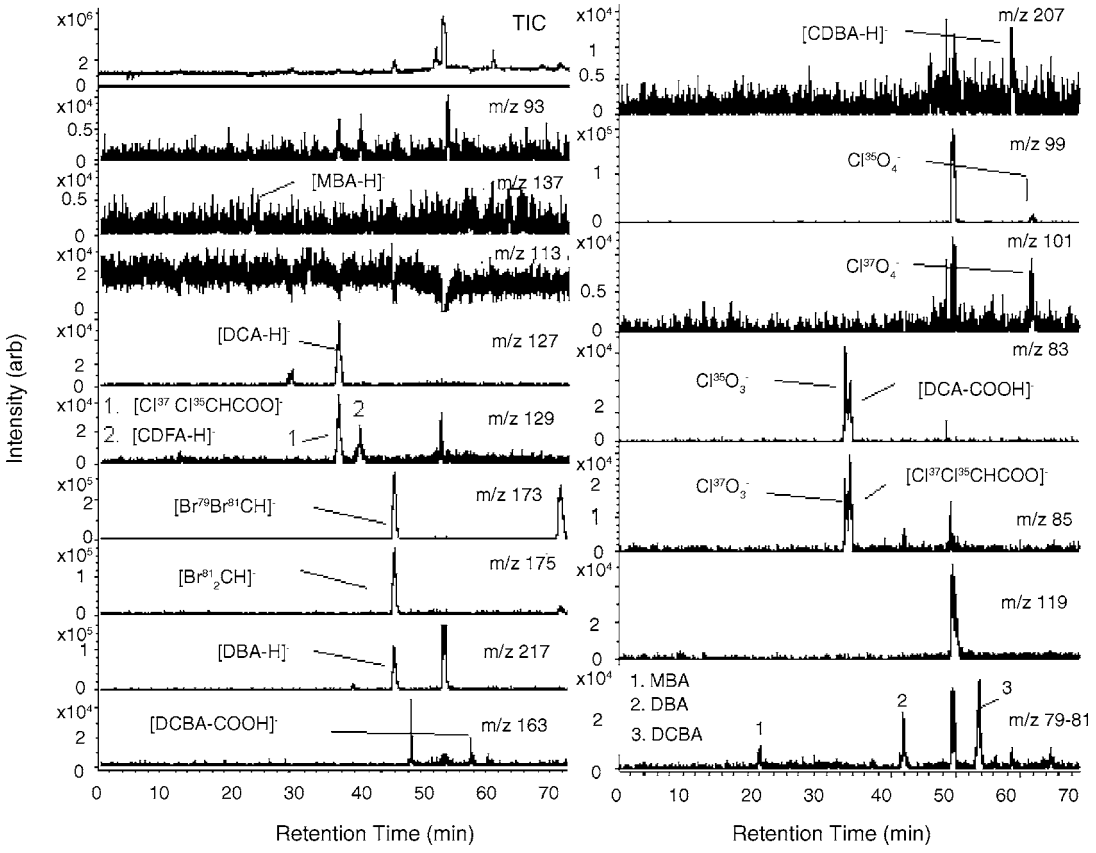

Fig. 3. Extracted ion chromatograms for laboratory drinking water preconcentrated 25-fold showing presence of DCA, CDFA, DBA, chlorate, perchlorate, CDBA and possibly some DCBA and MBA.

pressed conductivity detection) was carried out by spiking two 50 mL aliquots of sample with 1 and 2 μM of each analyte and preconcentrating in the usual manner. The oxyhalides were not quantified, as they did not preconcentrate sufficiently to allow standard addition. The sum total of all HAs in the drinking water sample was 13 μg/L and was well within the specified limit of 60 μg/L, even for analytes not included in the USEPA Stage I Disinfectants and Disinfectant By-products Rule. The levels of each observed HA are listed in Table 4.

3.5.2. Soil extracts

The application of dual gradient suppressed IC-conductivity–ESI-MS to the analysis of soil extracts was considered, as such samples obviously provided a suitably challenging and complex matrix likely to contain trace HAs and oxyhalides. As discussed in Section 1, presence of fluorinated and chlorofluorinated acetic acids is most likely in soil samples. However, possible sources of chlorinated or brominated acetic acids in such matrices are not discussed widely in current literature and were included here for completion. Surprisingly, when a neat aqueous soil extract was run on the IC and the resulting chromatograms obtained by conductivity detection were examined, peaks corresponding to the retention times of BCA, DBA, DCBA, CDBA and perchlorate were observed at various concentrations. Particularly evident were the peaks corresponding to the retention times of DCA and

Table 4
Semi-quantitative standard addition of HAs in laboratory water supply

HA	% Recovery and standard deviation of SPE method[a]	Concentration in original water sample (nM)	Concentration in original water sample (μg/L)
MCA	65 ± 10	6	0.53 ± 0.05
MBA	63 ± 28	6	0.78 ± 0.22
DCA	84 ± 10	7	0.92 ± 0.09
CDFA	87 ± 15	6	0.74 ± 0.11
TFA	17 ± 23	3	0.34 ± 0.08
DBA	66 ± 18	8	1.84 ± 0.33
DCBA	13 ± 4.6	31	6.39 ± 0.29
CDBA	30 ± 7.8	5	1.29 ± 0.10
Total [HA]	–	–	12.8 ± 1.27

[a] Percent recoveries taken from [37] with the addition of DCBA and CDBA.

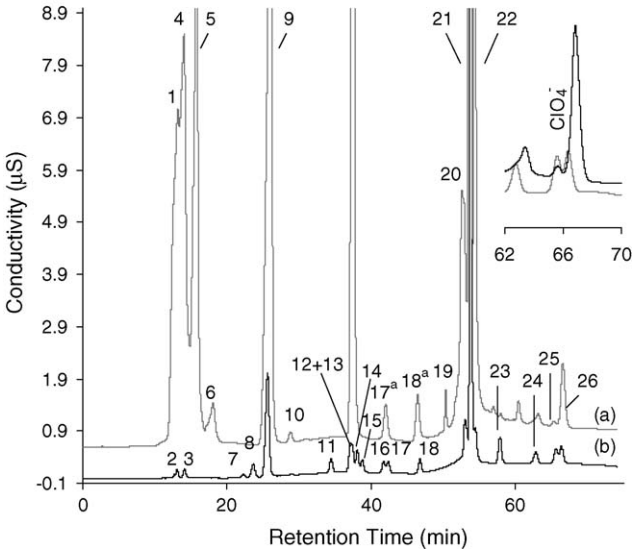

Fig. 4. Overlay of neat soil sample extract (a) and 1 μM standard (b) conductivity traces and their corresponding *m/z* values in parenthesis. Elution order: 1 = unknown (*m/z* = 191), 2 = fluoride, 3 = iodate, 4 = unknown (*m/z* = 89, 201), 5 = unknown (*m/z* = 101), 6 = unknown (*m/z* = 317), 7 = MCA, 8 = bromate, 9 = chloride, 10 = nitrite, 11 = TFA, 12 = nitrate, 13 = bromide, 14 = chlorate, 15 = DCA, 16 = CDFA, 17 = BCA, 17[a] = unknown (*m/z* = 203), 18 = DBA, 18[a] = unknown (*m/z* = 121), 19 = unknown (*m/z* = 87), 20 = carbonate, 21 = sulphate, 22 = unknown (*m/z* = 89), 23 = CDBA, 24 = CDBA, 25 = perchlorate, 26 = phosphate. Inset: enhancement of perchlorate peak.

DBA, which indicated these HAs were present at ≥0.5 mg/L (Fig. 4).

This neat extract was also simultaneously detected using ESI-MS. From the resultant total ion chromatogram, individual masses were extracted for any peak observed. No signals were obtained for any of the deprotonated, decarboxylated or dimerised ions for either DBA or BCA and so directly contradicted the conductivity trace. Both peaks corresponded to *m/z* 203 and 121, respectively, and obviously did not correlate with any analyte mass. If these were indeed the suspected HAs, they would have been observed quite readily with ESI-MS at this level. This observation highlighted the advantage of the combined detection modes in clearly being able to identify false positive peaks in this instance. However, the ESI-MS was not sufficiently sensitive to confirm the presence of DCBA or CDBA, therefore the only detectable extracted analyte mass for the target HAs and oxyhalides in the sample was *m/z* 99, corresponding to the retention time and mass of perchlorate. Confirmation of the presence of this oxyhalide was again carried out by extracting the $Cl^{37}O_4^-$ peak at *m/z* 101, which was indeed present at an expected ratio of 3:1. Other solute *m/z* ratios, including perchlorate observed in this soil sample are shown in Fig. 5.

Following identification of perchlorate, a short standard addition quantification with ESI-MS was carried out by spiking the soil sample as before with 0, 2, 5, 9 and 17 μM of perchlorate and plotting peak intensity versus perchlorate concentration. The concentration of perchlorate determined in the

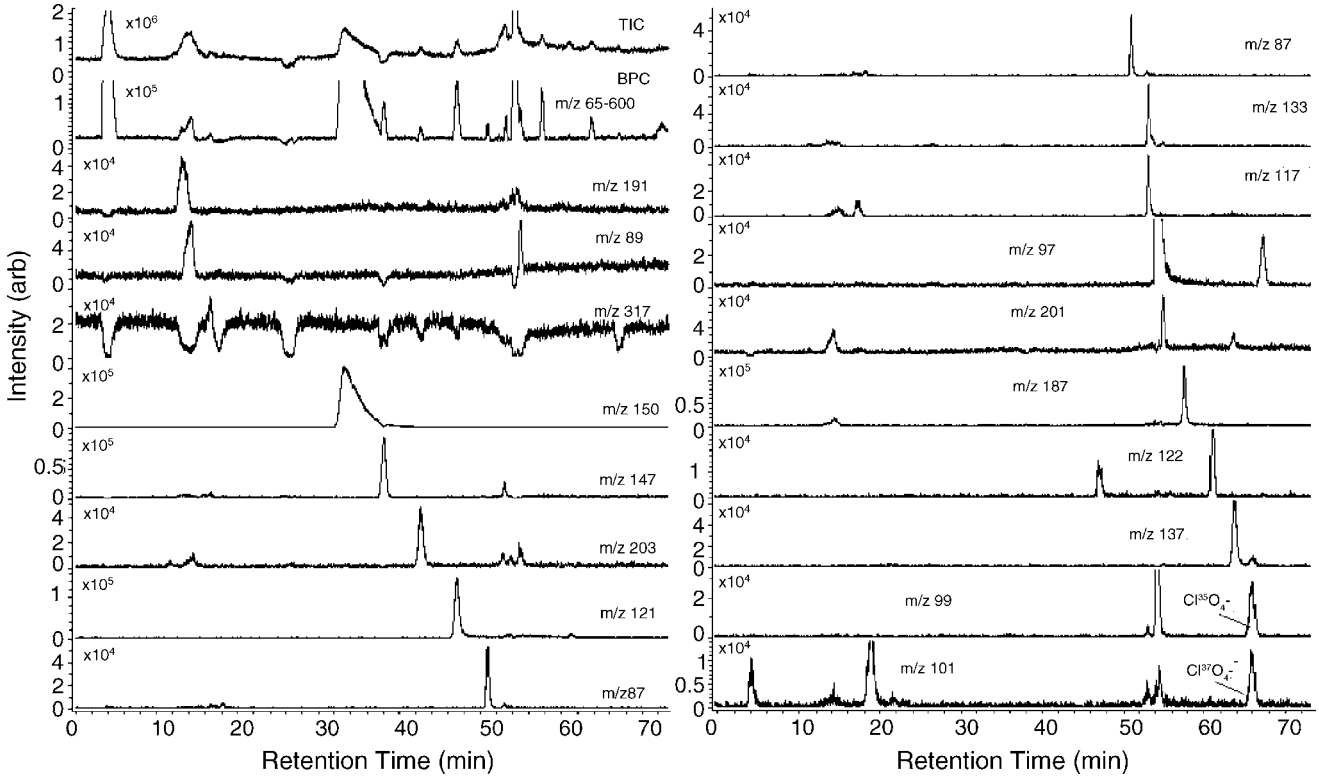

Fig. 5. Overlays of all extracted ion chromatograms (EICs) for each unknown peak in the soil extract sample (including perchlorate at *m/z* 99 and 101). Also included is the total ion chromatogram (TIC) and the base peak chromatogram (BPC) from *m/z* 65–500.

soil sample extract was 1.7 ± 0.8 μM, 168 ± 79 μg/L and hence 1.68 ± 0.79 μg/g in the original soil sample.

4. Conclusions

The advantages of combining IC with suppressed conductivity and ESI-MS to the determination of oxyhalides and HAs has been shown. The developed method displayed linearity with both detectors, although conductivity detection showed superior correlation coefficients. Detection studies showed that conductivity detection still offered the highest sensitivity in contrast to ESI-MS. Reproducibility of the combined temperature and hydroxide gradient showed excellent %R.S.D.s for retention time. With respect to peak height, conductivity detection showed excellent peak reproducibility for $n = 10$ replicate runs. Application of the method to two very different sample types was shown, with a number of HAs and oxyhalides present in the drinking water sample (HAs at 13 μg/L concentration in total) and perchlorate clearly present in soil samples. The IC method indeed offers itself to the monitoring of HAs and oxyhalides in drinking water and when coupled to MS, and significantly reduces the level of false positive results.

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