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Direct detection of trace haloacetates in drinking water using microbore ion chromatography
Improved detector sensitivity using a hydroxide gradient and a monolithic ion-exchange type suppressor

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Abstract

A highly sensitive gradient microbore ion chromatographic method was developed with electrolytically generated hydroxide eluents for the determination of low μg/L levels of chloroacetate, bromoacetate, trifluoroacetate, dichloroacetate, chlorodifluoroacetate, dibromoacetate, trichloroacetate, bromodichloroacetate and dibromochloroacetate disinfectant by-products formed as a result of chlorination of drinking waters. The possibility of using a packed bed Dionex Atlas suppressor with a hydroxide gradient at microbore flow rates was investigated in order to reduce baseline noise levels. The Atlas suppressor displayed a very significant reduction in noise levels compared to the standard alternative ASRS Ultra suppressor, reducing noise by a factor of 15–20 in some cases, allowing trace haloacetic acids (HAs) to be seen with the direct injection of 100 μL of treated water, with prior chloride and sulfate removal. To lower detection limits even further, a solid phase extraction was employed to preconcentrate HAs, resulting in detection limits of between 0.09 and 21.5 μg/L. The method was applied to the determination of HAs in environmental samples and standard addition curves for three drinking water samples were carried out for both direct injection and preconcentration methods. R^2 values in both cases were ≥0.98. Combined content for US Environmental Protection Agency regulated HAs in the three drinking water samples from Dublin City University; New Ross, Co. Wexford and Drogheda, Co. Louth were 46.5, 58.3 and 12.6 μg/L, respectively.
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1. Introduction

Disinfectant by-products (DBPs) in treated drinking waters are of significant concern, as the presence of certain DBPs represents a potential health hazard to humans. Initial concerns arose upon the discovery of such hazards associated with the formation of trihalomethanes (THMs) in the early 1970s. Since then, the second most abundant class of DBP, the haloacetic acids (HAs), have received increased attention, with improvements in analytical technology highlighting their presence, albeit at ultra-trace levels, in most chlorinated waters. Research over the past few years has clearly linked the formation of HAs, for the most part, to the chlorination of natural organic matter (NOM) containing water as part of its treatment process, as well as inorganic bromide found in ground and surface waters [1–5].

In the European context only trihalomethanes are currently covered by legislation and are limited within the European Union to a maximum of 150 μg/L for total THMs until further review in 2008 when this value is to be reduced to 100 μg/L. However, in the USA the US Enviromental Protection Agency (EPA) has stated that the presence

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of HAs also requires legislation, and a combined maximum contaminant level (MCL) of 60 μg/L for the five most commonly occurring HAs, namely, chloroacetate, bromoacetate, dichloroacetate, dibromoacetate and trichloroacetate, has been proposed. Within this regulation, dichloroacetate should never be present and trichloroacetate concentrations should not amount to more than 30 μg/L.

Currently the bulk of routine analyses for both THMs and HAs are carried out by gas chromatography with electron capture or mass spectrometric detection (EPA Methods 552 and 552.2) [6,7]. These methods have become the standard EPA Methods for HA analyses and although extremely time-consuming derivatisation/extraction procedures are required, the methods are both reliable and exhibit excellent detection limits. Two reviews have been compiled recently detailing the various analytical approaches taken for the determination of DBPs, one focusing on all DBPs [8] and the second looking at HAs in isolation [9]. Both of the above articles review liquid chromatographic techniques for HA determinations and highlight the fact that until recently, despite obvious advantages, the technique of ion chromatography (IC) has received only limited attention. Given that the pK_a of all the HAs of interest are lower than 2.8, they exist as anions in treated drinking waters and therefore direct analysis of haloacetates is possible by IC, thereby eliminating complex derivatisation procedures.

Some recent studies into the use of IC include that carried out by Sarzanini et al., who developed and compared ion-pair chromatography and anion-exchange chromatography methods [10]. Although some reasonable separations were obtained, detection limits were higher than those obtainable with the standard GC method and complete resolution and quantitation of all five of the EPA regulated HA species in drinking water samples was not possible. Nair et al. [11] developed a similar anion-exchange method using a carbonate–hydrogencarbonate eluent and reported similar detection limits to Sarzanini. Although both of these anion-exchange methods were more sensitive than other ion-pair or ion-exclusion methods investigated, they still exhibited limited selectivity and detection limits close to the proposed MCL of 60 μg/L, highlighting the need for improved methods with more sensitive detection. Large volume injection has been used a means to reduce detection limits by Liu et al., who used 500 μL sample volumes with standard bore Dionex AS9HC and AS16 columns [13,14]. Lui et al. also combined high volume injection with a microwave evaporative preconcentration technique with almost 100% recovery for all HAs. Detection limits were reported in the sub μg/L range and the technique offered excellent separation from matrix anions in drinking water supplies after cleanup with chloride removal cartridges. In a recent paper by Liu et al., levels of HAs and other oxyhalide DBPs, such as chlorate and bromate were determined in bottled drinking water [15]. Again, the detection limits were in the sub-μg/L range. It has also been reported that sample volumes of up to 900 μL have been used with limit of detections (LODs) of 0.089–0.118 μg/L in an ion-pair chromatography method [12].

Improvements in HA detection limits have recently been reported through the use of the new Dionex AEES Atlas suppressor with carbonate/bicarbonate eluents [13]. The suppressor itself, which has a suppression bed composed of an ion-exchange monolith and flow distribution disks, has been specifically designed for use with carbonate/bicarbonate eluents, and is of too low a capacity to be used with hydroxide eluents run with standard bore IC (suppression capacity up to 25 mN at 1.0 mL/min compared to 200 mN at 1.0 mL/min for the ASRS Ultra suppressor (Dionex)). However, the work detailed in this paper outlines the possibility of using the Atlas suppressor with electrolytically generated hydroxide eluents for a microbore IC method. The large reduction seen in baseline noise resulting from this combination results in a large reduction in detection limits compared to those obtained using the ASRS Ultra suppressor. Samples of treated water were collected and the possibility of direct microbore IC analysis without preconcentration was investigated. Additionally, to reduce detection limits to sub-μg/L concentrations, samples were also preconcentrated 25-fold using a hyper-crosslinked polystyrene–divinylbenzene (PS–DVB) sorbent [10,16,17] and analysed using the above method.

2. Experimental

2.1. Instrumentation

For chromatographic separations, a Dionex DX500 ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with a GP50 gradient pump, EG40 eluent generation system equipped with a continuously regenerating anion trap column (CRATC), LC25 chromatography oven operated at 40 °C and a CD20 electrical conductivity detector was used. Suppression was carried out with either a 2 mm Dionex ASRS Ultra suppressor (at 50 mA) or a 4 mm AEES Atlas electrolytic suppressor (at 19 mA), in the auto-recycle mode. Current was supplied to the Atlas suppressor with a Dionex SC20 suppressor controller. Injection was carried out using a 100 μL sample loop. The analytical column used was a Dionex IonPac AS16 (250 mm × 2 mm) and all tubing was microbore polyether ether ketone (PEEK). Optimum ion chromatography conditions were 2.5 mM KOH for 10 min, then ramped linearly to 20 mM for 5 min and kept at 20 mM KOH for a further 20 min (eluent flow rate = 0.3 mL/min). Post-acquisition re-equilibration time was 10 min. For instrument control and data acquisition, a Dell Optiplex GX1 personal computer was used with Peak Net 6.0 software installed. Where preconcentration was required, a Gilson Minipuls 3 peristaltic pump (Gilson, Middleton, WI, USA) was employed and fitted with Anachem 0.63 mm poly(vinyl chloride) (PVC) peristaltic tubing (Anachem, Luton, UK). Preconcentration was carried out using Merck LiChrolut EN solid-phase extraction

(SPE) cartridges (Merck, Darmstadt, Germany) at a flow rate of 2 mL/min. For chloride and sulfate removal, Alltech Maxi-Clean IC-Ba, IC-Ag and IC-H cleanup cartridges were used (Alltech Associates, Deerfield, IL, USA).

2.2. Chemicals

All reagents used were of analytical reagent grade purity. Sodium chloroacetate (98%), bromoacetic acid (99%+), sodium trifluoroacetate (98%), sodium dichloroacetate (98%), chlorodifluoroacetic acid (98%), dibromoacetic acid (97%), trichloroacetic acid (99%+), bromodichloroacetic acid (neat) and dibromochloroacetic acid (neat) were all ordered from Aldrich (Milwaukee, WI, USA) along with all inorganic anions and carboxylates prepared from their respective sodium salts. Stock HA solutions were prepared to a concentration of 10 mM and stored in the refrigerator for a maximum of 2 weeks at 4 °C in the dark. Stock inorganic anion and carboxylate standards were prepared to a concentration of 1000 mg/L. All working standards were freshly prepared daily using diluent water from a Milli-Q purification system (Millipore, Bedford, MA, USA) with a specific resistance of 18.3 MΩ cm. Sulfuric acid used for acidification of preconcentration samples and standards was 99% purity and also ordered from Aldrich along with analytical-grade potassium hydrogenphthalate (with ortho isomer) for use as an internal standard. This standard was initially prepared to a concentration of 10 mM and was prepared along with the stock HA solutions. Drinking water samples (50 mL) for HA determinations were collected from the Dublin City University laboratory water supply, as well as two others from New Ross, Co. Wexford, and Drogheda, Co. Louth.

2.3. Sample collection and treatment

Samples of drinking water were collected from domestic taps by allowing the tap to run for approximately 3 min. The sample bottle (1000 mL) was then rinsed three times with drinking water before sampling. Samples were immediately chilled in a refrigerator at 4 °C and kept in the dark to minimise degradation of HAs. Samples were kept in a refrigerator until analysis or transportation to the laboratory. During transportation, sample bottles were stored in an insulated container containing an ice pack for analysis on the same day. All the samples collected and analysed in this work originated from chlorinated sources. In all, one sample from three locations was taken in this way and all samples were analysed the following day. In the USEPA Method 552.2, ammonium chloride is added to water samples to ensure the conversion of free chlorine to combined chlorine [2]. However, it was feared that the addition of such levels of chloride and subsequent IC separation might have caused overloading of the anion-exchange column, even after cleanup with SPE chloride removal cartridges. Fresh working standards were prepared daily from the stock solutions outlined in Section 2.2 for analytical performance determinations and made to the mark with Milli-Q water. All solutions pertaining to a particular sample HA determination were prepared from that sample of drinking water. When fortifications were made a volume of the stock standard was transferred to a 50-mL volumetric flask and made to the mark with sample. The dilution factor was then taken into account. This dilution factor was small with the largest standard addition spike concentration of 10 μM corresponding to a dilution factor of 1/1000. The phthalate internal standard was used as a retention time marker and to assess the separation of phthalate from trichloroacetate and added to the samples at a concentration of 1 μM, which corresponded to a 1/10,000 dilution of sample and as a result was negligible (5 μL phthalate in 50 mL of sample).

Volumes of 50 mL of sample were acidified to <pH 0.3 by addition of a 4.5 mL aliquot of concentrated sulfuric acid. LiChrolut EN SPE cartridges were preconditioned with 3 mL MeOH, followed by 3 mL 200 mM sulfuric acid. Samples were loaded onto the solid phase extraction cartridge at a flow rate of 2 mL/min. After preconcentration, the cartridge was washed with 1 mL of Milli-Q water and eluted finally with 2 mL of 10 mM NaOH. This solution was then passed through a series of Alltech Maxi Clean cartridges at a flow rate of 1 mL/min, which were preconditioned with 10 mL Milli-Q water prior to the cleaning step. This series consisted of two IC-Ba, one IC-Ag and one IC-H cartridge. The first 1 mL of the eluate was discarded and the remaining solution was passed through a 0.45 μm filter prior to injection onto the IC.

3. Results and discussion

3.1. Separation of HAs

For the purpose of HA determinations, a high capacity ion exchange column was necessary to separate trace HAs from commonly occurring inorganic anions such as chloride, sulfate and nitrate, present in large excess. Early attempts using a Dionex AS11HC (250 mm × 2 mm) column were unsuccessful in separating bromoacetate, chlorodifluoroacetate and dibromoacetate from these anions with adequate resolution, so the IonPac AS16 was employed in an effort to improve this. The microbore AS16 is a high capacity hydroxide selective column (42.5 μeq./column) and requires a hydroxide eluent gradient to separate and elute HAs in a convenient run time. Resolution was optimum using 2.5 mM KOH as the starter concentration. Chloroacetate and bromoacetate are very hydrophilic and are eluted first at 9.30 and 10.70 min. The later eluting trichloroacetate, bromodichloroacetate and dibromochloroacetate required 20 mM KOH for elution and all nine HAs could be eluted in a 35-min runtime using the gradient program detailed in Section 2.1. It was noticed from the optimisation of the anion-exchange method that oven temperature played a major role in separating the inorganic anions from HAs. The effect of elevated temperature allowed

complete separation of all but one of the HAs from additional matrix inorganic anions when the AS16 column was employed. Unfortunately, bromoacetate coeluted with chloride at near LOD concentrations, but could be seen as a shoulder on the chloride peak at higher concentrations. All HAs displayed an increase in retention time with an increase in temperature. Nitrate retention increased at a much slower rate than the HAs and at the optimum temperature was resolved from trifluoroacetate and dichloroacetate. Sulfate was dramatically affected by temperature and increased in retention time by approximately 3 min with an increase in temperature of 22 °C. Chloroacetate when run at 45 °C was completely resolved from chloride, but nitrate coeluted with trifluoroacetate. Therefore, the final optimum temperature used in all experiments here was 40 °C. Furthermore, there was no interference from other naturally occurring anions like bromide and oxalate in the final optimised method. Oxalate coeluted with the sulfate peak and bromide coeluted with nitrate. Both had little or no resolution between their adjacent inorganic anions. Where preconcentrated samples were separated, there was no observable preconcentration of bromide and thus was not retained on the solid phase extraction cartridge. Any preconcentrated oxalate coeluted with large sulfate peak and was not observed.

3.2. Improvements in sensitivity with Atlas suppressor

Initially, separations were carried out using a Dionex ASRS Ultra (2 mm) operated at 50 mA, but limits of detection were not low enough to allow direct determination of HAs in drinking water supplies and required 25-fold preconcentration using a solid phase extraction technique (detailed in Section 3.3). The Atlas suppressor was considered, even though it was designed for carbonate eluents, due to the low overall capacity of the hydroxide eluents used at microbore flow rates (0.3 mL/min). Upon investigation, it was found that the Atlas suppressor offered far superior suppression capabilities to that of the ASRS Ultra under these eluent conditions. A standard solution in Milli-Q water of each of the HAs (concentration 2 μM for all HAs along with trace levels of fluoride, formate, chloride, chlorite, nitrate, carbonate, sulfate and phthalate, was run with both suppressors and the noise levels were compared. Upon inspection of the standard chromatograms, the noise levels at the beginning of the gradient run were 15–20 times less when the Atlas suppressor was employed, and approximately 5–10 times less at the higher 20 mM hydroxide concentration at the end of the run. Typical chromatograms using each suppressor are overlaid and are shown in Fig. 1a, together with expanded sections (Fig. 1b) of the baseline noise to illustrate clearly the improvements obtained (the overlaid chromatogram in Fig. 1a obtained using the Ultra suppressor has been offset by +1 μS for clarity). As a result of these improvements, an assessment of limits of detection was carried out. To do this, a standard of the nine HAs was prepared in Milli-Q water to a concentration of 10 μM and serial dilutions were carried out until a

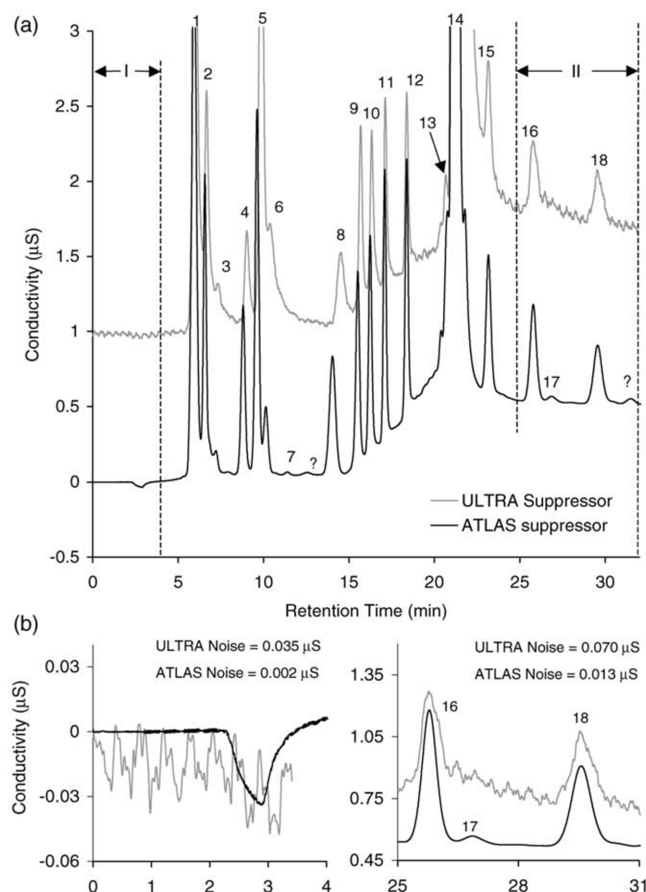

Fig. 1. Comparisons of HA separations with both Atlas and ASRS Ultra suppressors. (a) Elution order: 1 = fluoride, 2 = formate, 3 = chlorite, 4 = chloroacetate, 5 = chloride, 6 = bromoacetate, 7 = nitrite, 8 = trifluoroacetate, 9 = nitrate, 10 = dichloroacetate, 11 = chlorodifluoroacetate, 12 = dibromoacetate, 13 = carbonate, 14 = sulfate, 15 = thiosulfate, 16 = trichloroacetate, 17 = bromodichloroacetate, 18 = dibromochloroacetate, [HA] = 2 μM. (b) Enlargement of regions I and II. Other conditions: 2.5 mM KOH for 10 min, then ramped linearly to 20 mM for 5 min and kept at 20 mM KOH for a further 20 min (eluent flow rate = 0.3 mL/min).

signal-to-noise ratio of just above 3:1 was achieved for each HA. Limits of detection for the chromatographic method are listed in Table 1 and show that once the Atlas suppressor was used, detection limits improved and in some cases, up to 45 times lower (chloroacetate) than when the ASRS Ultra suppressor was used.

3.3. Sample pretreatment

Despite these significant improvements in detection limits, to obtain sub-μg/L detection limits (if required) it was necessary to apply developed preconcentration and sample cleanup techniques, or increase the loop size to 500 μL, as carried out by Liu et al. [13–15]. However, as this was a microbore IC method the use of large injection volumes was not investigated due to overloading of the microbore column with the excess matrix inorganic anions. Therefore, trace determinations were carried out using a 25-fold SPE preconcentration

Table 1
Analytical performance data for KOH gradient IC method for HAs and LODs with Atlas and ASRS Ultra suppressors and overall method LOD including preconcentration

	$ClCH_2COO^-$	$BrCH_2COO^-$	CF_3COO^-	Cl_2CHCOO^-	ClF_2CHCOO^-	Br_2CHCOO^-	CCl_3COO^-	$BrCl_2COO^-$	$Br_2ClCCOO^-$
Average t_r (min)	9.2	10.6	14.8	16.5	17.2	18.5	23.3	25.9	29.7
Average peak height (µS)	3.5	1.4	4.7	5.9	6.2	6.2	3.5	3.4	2.1
Average peak area (µS min)	1.2	0.5	1.4	1.4	1.4	1.5	1.5	1.3	1.2
Repeatability (% R.S.D.)[a]									
Retention time	0.6	0.6	0.3	0.2	0.1	0.1	0.1	0.2	0.3
Peak area	1.9	4.9	4.3	1.3	2.3	2.7	3.2	4.4	3.3
Peak height	3.0	3.0	2.2	1.4	2.0	1.7	2.1	3.4	2.2
Linearity[b]									
R^2	0.999	0.987	0.983	0.994	0.995	0.998	0.998	0.995	0.992
Slope	0.267	0.120	0.370	0.604	0.661	0.606	0.315	0.120	0.067
Intercept	0.622	−0.280	−0.717	−1.232	−1.178	−0.649	0.122	−0.065	−0.054
Detection limits (µg/L)[c]									
AEES Ultra	65.1	N/A	79.1	5.6	77.4	129.6	521.6	442.8	379.1
AEES Atlas	1.4	5.4	2.9	8.2	7.3	12.5	16.3	42.6	73.5
With SPE and Atlas	0.1	0.3	0.7	0.4	0.3	0.8	1.1	4.0	21.5

N/A: not calculated due to residual chloride interference. Standard errors above the 15-µM calibration standard concentration were all less than 10% R.S.D. and all lower calibration standard concentration errors were less than 20% for triplicate injections.

[a] Data based upon 20 repeat injections of a 10 µM HA standard.

[b] Calibration standard concentrations: 5, 10, 15, 25, 40, 50 and 75 µM ($n = 7$). Each standard injected in triplicate. Linearity based on peak height.

[c] Based upon 3× baseline noise (measured from 0.0 to 2.2 min for 2.5 mM KOH and 25–32 min for 20 mM KOH eluents), 100 µL injection volume.

technique outlined in Section 2.3. As part of the above clean-up, two IC-Ba cartridges in series were used and were successful in removing approximately 90% of all the residual sulfate (used for acidification) in the eluate. Only one IC-Ag and one IC-H Maxi Clean cartridge was required for chloride removal and this was successful in removing approximately 98% of total chloride from drinking water samples. Percent recovery data for both LiChrolut EN and the Maxi Clean cartridge series are listed in Table 2, with eight out of nine percent recoveries for the Maxi Clean cartridges ranging between 93% and 103%. Bromoacetate percent recovery with these cartridges was slightly less at 84%. This was possibly due to the coelution with residual chloride making integration of peak heights more inaccurate rather than a slight specificity of the cleanup cartridges for bromoacetate. Trifluoroacetate displayed very poor recoveries from the preconcentration procedure at 17%. Trifluoroacetate has a very low pK_a value at pH 0.3 and may not be significantly protonated at the method pH and suggests a reason for its poor recovery. It was thought that if lower pH values were used

Table 2
Recovery and precision data for preconcentration of HAs on LiChrolut EN SPE cartridges

HA	Standard concentration (µM)	Standard pH[a]	Preconcentrated volume[b] (mL)	Eluent volume (10 mM NaOH)[c] (mL)	Average recovery (%) ($n = 6$)[d]	R.S.D. (%) ($n = 6$)[d]	Percent recovery of Maxi Clean cartridge series ($n = 3$)[e]
$ClCH_2COO^-$	5	0.3	50	2.0	65	15.3	98
Cl_2CHCOO^-	5	0.3	50	2.0	84	12.9	103
CCl_3COO^-	10	0.3	50	2.0	58	11.8	98
$BrCH_2COO^-$	5	0.3	50	2.0	63	16.3	84
Br_2CHCOO^-	0.2	0.3	50	2.0	66	18.0	100
$BrCl_2COO^-$	0.2	0.3	50	2.0	30	4.6	96
$Br_2ClCCOO^-$	0.2	0.3	50	2.0	13	7.8	93
ClF_2CHCOO^-	10	0.3	50	2.0	87	13.9	100
CF_3COO^-	5	0.3	50	2.0	17	29.2	94

[a] Adjusted using sulfuric acid.

[b] Loaded at 2.0 mL/min.

[c] Following 1.0 mL wash using Milli-Q water.

[d] Each repeat preconcentration carried out using fresh SPE cartridges.

[e] Carried out on three separate cartridge series of IC-Ba, IC-Ba, IC-Ag, IC-H preconditioned with 10 mL Milli-Q water prior to use.

the sorbent would have become unstable. Furthermore, dibromochloroacetate and bromodichloroacetate showed very poor percent recoveries at 13% and 30%, respectively. The use of a larger elution volume from the SPE cartridges (from 2 mL to 4 mL NaOH) could be used to improve recovery data percent, but this led to a more dilute sample extract and in fact did not improve overall detection limits.

3.4. Analysis of drinking water samples

3.4.1. HAs in drinking water without using preconcentration procedure

In an attempt to observe HAs directly (no preconcentration stage) a sample of drinking water was collected from our laboratory water supply in Dublin City University, Dublin, Ireland and kept in the refrigerator at 4 °C in the dark and analysed within 48 h. It was expected from our optimisation procedure that excess chloride present in the sample would interfere significantly with weakly retained chloroacetate and bromoacetate and, furthermore, sulfate was also expected to interfere with trace dibromoacetate and trichloroacetate. In order to minimise this, approximately 20 mL aliquots of this sample were collected and passed through cleanup IC-Ba, IC-Ag and IC-H cartridges at a flow rate of 1 mL/min using the calibrated peristaltic pump. Prior to the cleanup step, cartridges were preconditioned with approximately 10 mL of Milli-Q water. After removal of excess chloride and sulfate and following filtering, 100 μL of the resulting solution was injected onto the IC using the optimum chromatographic conditions. Upon examination of the chromatograms, trace levels of chloroacetate, chlorodifluoroacetate and dibromoacetate were observed (see Fig. 2b). For quantification purposes, a standard addition curve was carried out by preparing HAs in the pre-treated water sample over a concentration range of 0.5–10 μM. The resulting standard addition curves yielded concentrations of 3.0 μg/L chloroacetate and 43.5 μg/L dibromoacetate. Levels of chlorodifluoroacetate were below detection limit and so could not be quantified accurately. All correlation coefficients were above 0.99 and demonstrated excellent linearity.

A second sample of drinking water was collected from New Ross, Co. Wexford, Ireland and a similar experiment was carried out. In this case, HA levels were much higher and could be directly quantified without the use of preconcentration. Trace levels of chloroacetate, chlorodifluoroacetate, dibromoacetate, trichloroacetate and bromodichloroacetate were observed (see Fig. 2a). Similarly, a standard addition curve was constructed over a concentration range of 0.2–1.0 μM of each of the HAs and concentrations of each of the HAs found is listed in Table 3. Some of the HA peaks observed had signal-to-noise ratios of less than 3:1 and so were not quantified, although dibromoacetate was quantified at a concentration of 22.1 μg/L and trichloroacetate was quantified at a concentration of 17.7 μg/L. It should be noted that nitrate caused significant interference at the level present in the sample when using direct injection and completely

Table 3
HAs observed in three chlorinated drinking water supplies

Sample name	HAs observed (μg/L)									
	$ClCH_2COO^-$	$BrCH_2COO^-$	CF_3COO^-	Cl_2CHCOO^-	ClF_2CHCOO^-	Br_2CHCOO^-	CCl_3COO^-	$BrCl_2COO^-$	$Br_2ClCCOO^-$	Total HAs
New Ross, Co. Wexford, Ireland[a]	<LOD	–	<LOD	–	<LOD	22.1	17.7	<LOD	<LOD	39.8
Dublin City University, Co. Dublin, Ireland[a]	3.0	–	–	–	1.0	43.5	–	–	–	47.5
New Ross, Co. Wexford, Ireland[b]	4.3	–	–	24.5	2.7	–	29.5	<LOD	–	61.0
Drogheda, Co. Louth, Ireland[b]	1.0	–	1.0	7.8	1.1	–	3.8	–	–	14.7

<LOD: peaks observed less than LOD value (calculated as signal-to-noise ratio of 3:1).
[a] Values calculated by standard addition without preconcentration.
[b] Values calculated by standard addition with preconcentration.

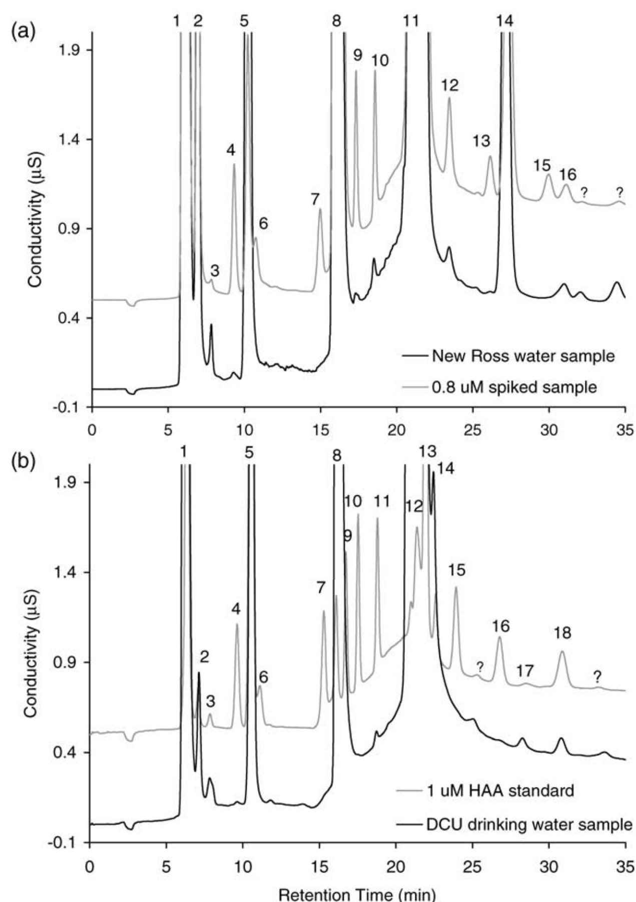

Fig. 2. (a) Non-preconcentrated sample of New Ross drinking water supply passed through chloride and sulfate removal cartridges and run on IC with overlay of 0.8 µM HA spiked water sample. Elution order: 1 = fluoride, 2 = formate, 3 = chlorite, 4 = chloroacetate, 5 = chloride, 6 = bromoacetate, 7 = trifluoroacetate, 8 = nitrate, 9 = chlorodifluoroacetate, 10 = dibromoacetate, 11 = sulfate, 12 = TCAA, 13 = bromodichloroacetate, 14 = phthalate (internal standard), 15 = dibromochloroacetate, 16 = phosphate. Other conditions are as in Fig. 1. (b) Non-preconcentrated Dublin City University drinking water sample passed through chloride and sulfate removal cartridges and run on IC overlaid with 1 µM standard solution prepared in Milli-Q water. Elution order: 1 = fluoride, 2 = formate, 3 = chlorite, 4 = chloroacetate, 5 = chloride, 6 = bromoacetate, 7 = trifluoroacetate, 8 = nitrate, 9 = DCAA, 10 = chlorodifluoroacetate, 11 = dibromoacetate, 12 = carbonate, 13 = sulfate, 14 = thiosulfate, 15 = TCAA, 16 = bromodichloroacetate, 17 = phthalate, 18 = dibromochloroacetate. Other conditions are as in Fig. 1.

masked any dichloroacetate that was present in the drinking water supply. In order for this method to be successful for drinking water quality control, dichloroacetate needed to be resolved from nitrate, as regulations stipulate that dichloroacetate should never be present in domestic drinking water supplies.

3.4.2. Preconcentration and HA determination in drinking water supplies

In order to accurately determine HA concentrations, including dichloroacetate, preconcentration was carried out on two drinking water samples. These water samples were preconcentrated and pretreated as outlined in Section 3.3 above and extracts subsequently injected onto the IC (100 µL). The first sample was once again the drinking water from New Ross, Co. Wexford, Ireland and the second was a sample taken from Drogheda, Co. Louth, Ireland. As was seen previously, levels of chloroacetate, chlorodifluoroacetate, dibromoacetate, trichloroacetate and bromodichloroacetate were observed in the New Ross water supply. Furthermore, due to the fact that nitrate was not retained on the LiChrolut EN cartridge during preconcentration, the nitrate peak observed was significantly reduced allowing quantification of the dichloroacetate peak, which was present in both preconcentrated water samples. As before, a standard addition curve was constructed over a concentration range of 0.0, 0.2, 0.4, 0.6 and 0.8 µM of each of the HAs. Each of the spiked sample solutions were adjusted to 0.3 pH units and preconcentrated in the usual manner. Peak heights for each of the HAs were plotted and resulting HA concentrations calculated. For the EPA regulated haloacetic acids, the New Ross

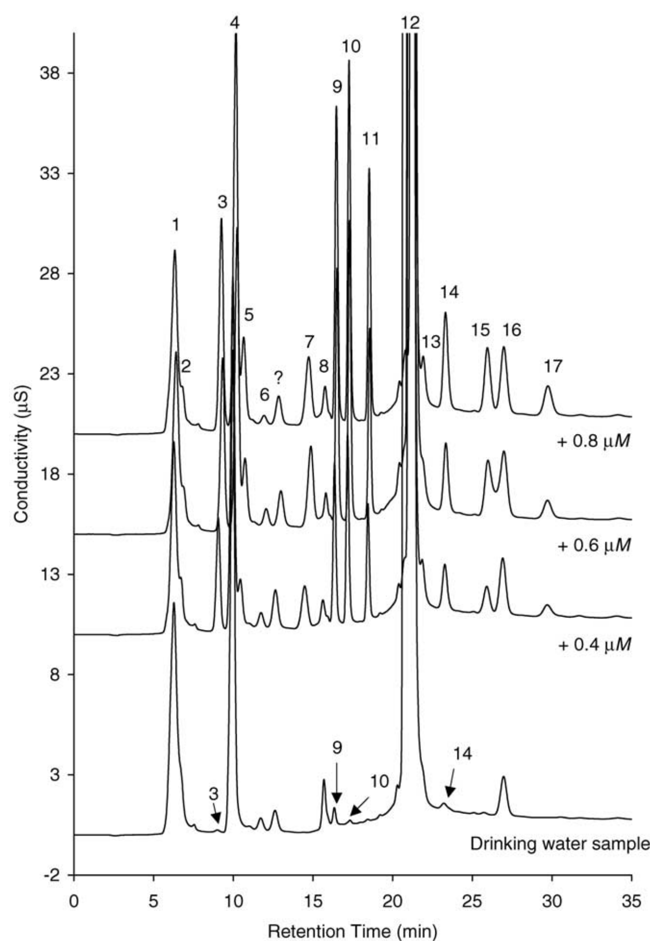

Fig. 3. Standard addition of HAs in drinking water from Drogheda, Co. Louth, Ireland. Sample and spiked samples preconcentrated 25-fold using SPE (LiChrolut EN). Elution order: 1 = fluoride, 2 = formate, 3 = chloroacetate, 4 = chloride, 5 = bromoacetate, 6 = nitrite, 7 = trifluoroacetate, 8 = nitrate, 9 = DCAA, 10 = chlorodifluoroacetate, 11 = dibromoacetate, 12 = sulfate, 13 = thiosulfate, 14 = trichloroacetate, 15 = bromodichloroacetate, 16 = phthalate (internal standard), 17 = dibromochloroacetate. Concentration range = 0–0.8 µM HA.

water sample contained 58.3 μg/L of the five regulated HAs in total, which lies just under the EPA maximum contamination limit. Excluding dichloroacetate, the total concentration of these five HAs was 33.8 μg/L. Upon examination of the standard addition data obtained for the New Ross sample analysed without preconcentration, the total HA5 concentration (without dichloroacetate), shows excellent agreement with this value at 39.8 μg/L. The second water sample from Drogheda Co. Louth, Ireland was analysed in the same way by means of 25-fold preconcentration. Again, levels of chloroacetate, trifluoroacetate, dichloroacetate, chlorodifluoroacetate and trichloroacetate were observed. The only regulated HAs with peak heights greater than LOD level were chloroacetate, dichloroacetate and trichloroacetate and summed to a total of 12.6 μg/L chlorodifluoroacetate and trifluoroacetate were also observed and the total of all HA was quantified at 14.7 μg/L. All standard addition curves displayed linearity (Fig. 3) with correlation coefficients above 0.98. Once more, all these figures can be found in Table 3.

4. Conclusions

By using the Atlas suppressor with hydroxide eluents at low flow rates, significantly lower detection limits for nine HA species were obtained than with the ASRS Ultra suppressor. Limits of detection without preconcentration were between 1.4 and 73.5 μg/L for a microbore IC method with only 100 μL injection volume. With solid phase extraction this was further reduced to a concentration range of 0.09–21.5 μg/L for the HA9. When preconcentration was employed, a reduction in residual nitrate allowed identification and quantification of dichloroacetate. The developed method is indeed simple, practical and a viable alternative to conventional gas chromatographic techniques.

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