

Direct injection ion chromatography for the control of chlorinated drinking water: simultaneous estimation of nine haloacetic acids and quantitation of bromate, chlorite and chlorate along with the major inorganic anions

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ABSTRACT

Most methods for the analysis of haloacetic acids published in recent years are based on ion chromatography with direct injection, employing a gradient elution with potassium hydroxide (KOH). This work reports the exploration of an alternative eluent, a buffer of sodium carbonate/sodium hydrogen carbonate, aimed at the simultaneous analysis of nine haloacetic acids along with bromate, chlorite and chlorate. The alternative of both a less alkaline eluent and a lower temperature of operation may prevent the partial decomposition of some of the haloacetic acids during the analytical process, especially the more vulnerable brominated ones. Gradient elution at temperature of 7 °C yielded the best results, with an acceptable separation of 17 analytes (which includes the major natural inorganic anions) and a good linearity. Precision ranges from 0.3 to 23.4 (% V.C.), and detection limits are within units of $\mu\text{g L}^{-1}$, except for tribromoacetic acid – somewhat high in comparison with those of the official methods. Nonetheless, with the basic instrumentation setup herein described, this method may be suitable for monitoring when the drinking water treatments are to be optimized. This is especially interesting for small communities or for developing/developed countries in which regulations on disinfection by-products others than trihalomethanes are being addressed.

Key words | bromate, chlorate, chlorite, direct injection ion chromatography, disinfection by-products, haloacetic acids analysis

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INTRODUCTION

The need to optimize drinking water treatment to attenuate the formation of disinfection by-products and the increasing implementation of a legal standard for haloacetic acids (HAAs), particularly in developed countries, has promoted the search for suitable and reliable analytical methods. For years, the method of choice has been based on gas chromatography (GC) coupled with electron capture or mass spectrometry (MSD) detectors. The EPA method 552.2 (Munch *et al.* 1995) and the Standard Method 6251B (Eaton *et al.* 1998) have been extensively applied for the

five regulated HAAs in the USA, but the more recent 552.3 Method (Domino *et al.* 2004) outperforms both. All three methods need extraction and derivatization owing to the non-volatility of these analytes, and this is why liquid chromatography (LC) methods have been searched and tested more recently. Due to the strong acidity of HAAs, methods on ion-exchange chromatography (IC) have been tested for almost two decades. However, there was a need to concentrate the samples because of the low sensitivity of the conductivity detectors (Lopez-Avila *et al.* 1999;

Sarzanini *et al.* 1999; Magnuson & Kelty 2000; Liu & Mou 2003; Paull & Barron 2004; Barron & Paull 2006; Sun & Gu 2007) with the collateral result of too high concentration of the common inorganic anions – generally chloride, sulphate and, to a lesser extent, nitrate – for most water samples, and a need for clean-up in many cases. Direct injection was attempted, but this was limited to water samples with low contents of inorganic anions and, in any case, this resulted in low sensitivity for some of the species (Nair *et al.* 1994; Liu & Mou 2003; Bruzzoniti *et al.* 2008). It was deemed inappropriate for analysing all nine HAAs (Mathew *et al.* 2009; Shia & Adams 2009). In 2009, the EPA method 557 was issued (Zaffiro *et al.* 2009): a direct injection IC method with electrospray ionization and tandem-mass spectrometry (IC-ESI-MS/MS). The method employs generated potassium hydroxide (KOH) as eluent, internal standard quantification with four isotopically enriched ^{13}C -HAAs, and an operation temperature of 15°C . So far, it is the most potent method based on IC.

Gradient elution in hydroxide-selective columns has been extensively applied, more recently with alkaline hydroxides generated electrolytically. In contrast, elution with a buffer solution of sodium carbonate and sodium hydrogen carbonate is very uncommon, but historically it was one of the first to be employed (Nair *et al.* 1994; Sarzanini *et al.* 1999) with a more recent application (Mathew *et al.* 2009) in gradient mode. The goal of the present work was to search for a simultaneous method for the analysis of nine HAAs along with bromate, chlorite and chlorate, all of them anionic disinfection by-products. The use of a less alkaline eluent, based on $\text{CO}_3^{2-}/\text{HCO}_3^-$, was expected to prevent the partial decomposition of some of the HAAs during the analytical process – especially the more vulnerable brominated ones (Heller-Grossman *et al.* 1993; Slingsby *et al.* 2008; Lifongo *et al.* 2010). In addition, this method would allow the major common inorganic anions naturally present in water to be quantitated in the same run, so that a total of 19 analytes could be monitored.

A demand for more accessible methodology for these analytes is expected during the next years, especially for the HAAs. In 2003 the European Commission organized a stakeholders' consultation to explore a revision of the Drinking Water Directive 98/83/EC, to revise the current list of chemical parameters (Hulsmann 2009). Technical consultants proposed that chlorite, chlorate and haloacetic acids be included. EUREAU (2008)

issued a position paper conditionally accepting chlorite and HAAs, but affirming that the difficulty involved in analysing HAAs is a serious drawback. The proposed bill was due to be submitted to the European Parliament in 2010, but this stage has been postponed *sine die*. Years ago, the USA, Canada, Japan and Holland introduced a legal limit, although only for five HAAs.

METHODS

Apparatus and reagents

Ion chromatograph was from Metrohm, mod. 850 Professional IC, provided with two high-pressure pumps, column temperature control between $+5$ and $+80^\circ\text{C}$ ($<0.05^\circ\text{C}$ stability) and digital conductivity detector after the sequential chemical suppression device and MagICNetTM 2.3 software. An Agilent MSD trap XCT mass spectrometer with an ESI source was also used. Two columns connected in series: Metrosep A Supp 1 HS + Metrosep A Supp 5 (250/4 mm). ACS grade reagents Na_2CO_3 , NaHCO_3 and H_2SO_4 were from Panreac and ultrapure water was from Millipore Direct-QTM3. The solid standards for analysis were: monochloroacetic acid (MCA), monobromoacetic acid (MBA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), dibromoacetic acid (DBA), chlorobromoacetic acid (CBA), chlorodibromoacetic acid (CDBA), dichlorobromoacetic acid (DCBA) and tribromoacetic acid (TBA) from Sigma-Aldrich; solid NaClO_3 (ACS $>99\%$) was from Sigma-Aldrich; solid NaClO_2 ($>80\%$) and NaBrO_3 ($>99\%$) were from Fluka, and solid KBr (ACS grade) was from Panreac. The mixture of 1.0 mg L^{-1} of each of the anions, F^- , Cl^- , NO_2^- , NO_3^- , HPO_4^- , SO_4^- , was also supplied by Sigma-Aldrich. All nine solutions of HAAs were diluted to 1 mg L^{-1} and kept refrigerated at $<4^\circ\text{C}$ for no longer than 3 days. Individual and multicomponent solutions of all the standards were prepared and assayed for identification and calibration, using peak areas.

Analytical method developed

The following conditions for analysis were established.

Eluent A: ultrapure water; eluent B: $16.0\text{ mM Na}_2\text{CO}_3$ and 5.0 mM NaHCO_3

Chemical suppressors: ultrapure water and 100 mM H_2SO_4

Working pressure: 12.5–13.5 Mpa, the limit set at 14.5 Mpa

Flow: 0.7 mL min^{-1}

Loop injection: $100 \mu\text{L}$

Column temperature: 7°C

Conductivity detector: measurements from $<0.00001 \mu\text{S cm}^{-1}$

Gradient program of the eluent:

min	A (%)	B (%)
0	90	10
20	90	10
40	10	90
60	10	90
66	90	10
70	90	10

Figure 1 shows a chromatogram obtained with these conditions.

The MSD parameters were as follows: N_2 flow was used for electrospray at 11 L min^{-1} , a pressure of 55 psi and a temperature of 350°C . 3.5 KV was used for ionization with a skimmer at -15 V and the capillary exit at -50 V . The

negative mode was used for ionization. For the detection of the HAAs, the following masses were recorded:

Min	Mass 1	Mass 2	Mass 3
0–15	93–95	137–139	
15–32.5	127–129	173–175	217–219
32.5–40	117–119		
40–48	163–165		
48–59	207–209		
59–70	251–253		

Each HAA was confirmed with two signals corresponding to the isotopic envelope. In the case of MCA, MBA, DCA, DBA and CBA, the ions corresponded to the deprotonation process, while the rest of the HAAs underwent in-source decarboxylation and that was the reason for the low mass signals.

Application to disinfected waters

Samples of municipal drinking waters from eight cities in the region of Castile and Leon (January 2012) were assayed. To quench the reaction of free chlorine with the residual

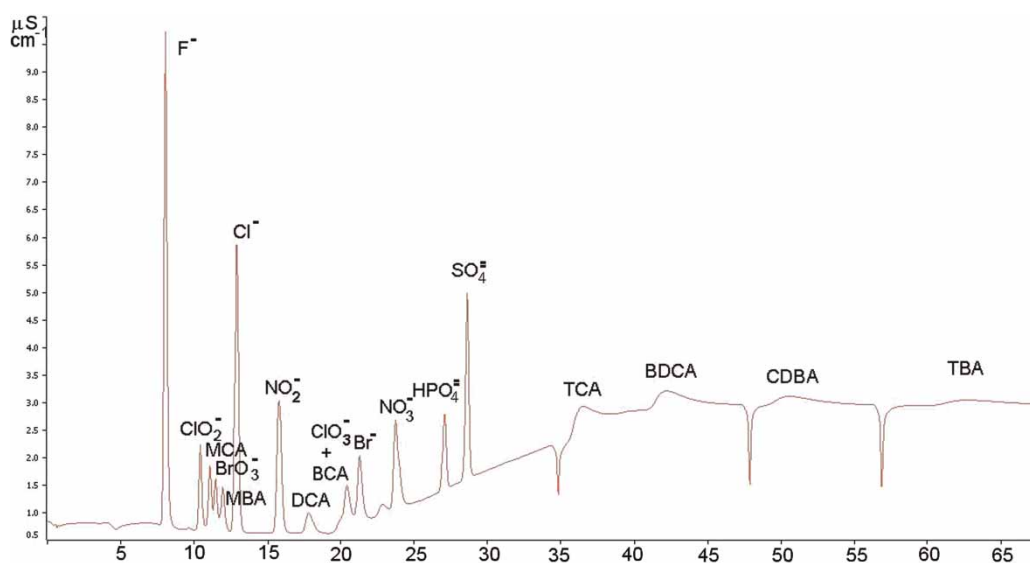


Figure 1 | Chromatogram of a multicomponent dissolution of the 19 standards (1 mg L^{-1} , apart from 5 mg L^{-1} for the trihaloacetic acids), once optimized, as recorded by the conductivity detector.

natural organic matter of water, about 0.1 mg of solid $(\text{NH}_4)_2\text{CO}_3$ was placed in 120 mL amber vials before filling them with the water samples.

RESULTS AND DISCUSSION

Given that a number of drinking waters may be very rich in chloride and sulphate, a high-capacity column was chosen. The following variables were studied: flow rate, concentration and mode of the eluent (isocratic or gradient), column temperature, and quantitation either by conductivity or MSD.

Optimization of separation

Since the elution time was expected to be rather long, a first trial would be to perform the runs at temperatures higher than room temperature in order to accelerate the elution of the most strongly retained analytes. This option may be successfully applied in reverse-phase high performance liquid chromatography (HPLC), but regarding IC the behaviour is less predictable and even less so when the sample to be analysed is simultaneously composed of inorganic, organic and varyingly charged ions (Barron *et al.* 2005). Because of the contradictory results normally obtained, few authors have employed temperature gradients in ion-exchange separations. Nonetheless, Barron *et al.* (2005) studied this phenomenon and controlled the separation of the anionic disinfection by-products by programming temperatures higher than room temperature.

A constant temperature of 45 °C was set, after which elution in isocratic mode was carried out with 3.2 mM Na_2CO_3 + 1.0 mM NaHCO_3 at 0.7 mL min^{-1} . The individual injection of 20 μL of DCA or TCA (1.0 mg L^{-1}) yielded three peaks: acetate, chloride and either DCA or TCA, respectively. This indicated a partial decomposition of both analytes, probably more pronounced because of their long retention time, during which they were exposed to this temperature. However, when MBA was injected it did not seem to be affected since it yielded a single peak in the same trial – perhaps because its retention time was much shorter. Following this, a temperature of 25 °C was explored, with flows of 0.7 and 0.8 mL min^{-1} ; the aim of the latter flow was to speed up elution and reduce the time of

exposure to this temperature. All nine HAAs were eluted without any apparent decomposition, this time DCA and TCA yielding a single peak, although again very wide (at the conductivity detector), but very clear (at the mass spectrometer detector), and also with a very long retention time. A multicomponent injection of the nine HAAs (1.0 mg L^{-1}) provided complete resolution for all, but another multicomponent injection, this time with the nine HAAs (0.5 mg L^{-1}) + ten inorganic anions (0.5 mg L^{-1}) revealed coelution of $\text{MBA} + \text{Cl}^-$, $\text{MCA} + \text{BrO}_3^-$ and $\text{BCA} + \text{ClO}_3^- + \text{Br}^-$. On returning to a flow rate of 0.7 mL min^{-1} , this only resolved the latter coelution for bromide.

The instability of the HAAs via either decarboxylation or hydrolysis at high pH and temperature values has been documented for chlorinated waters both in laboratory (Heller-Grossman *et al.* 1993; Lifongo *et al.* 2010) and simulated distribution systems (Zhang *et al.* 2000; Zhang & Minear 2002). Although a different and complicated behaviour can be noted for each of the nine HAAs, in general, temperatures above 15 °C lead to their decomposition, with special intensity in the case of the brominated compounds. Degradation mechanisms may occur predominantly via decarboxylation for high temperatures, while via hydrolysis for high pH values. Regarding stability during the analytical process, immediately before the approval of EPA method 557, Slingby *et al.* (2008) performed a study at different temperatures. High instability was found above 15 °C, especially for some of the brominated species ($\text{DBA} > \text{CDBA} > \text{MBA}$, although much less for TBA), so that a temperature of 15 °C was chosen as a compromise. In contrast, no information is available regarding the few methods published for HAAs based on elution with $\text{CO}_3^{2-}/\text{HCO}_3^-$, and hence little information is known about their stability as a function of temperature during the analytical process. Thus, different temperatures for the elution were studied as follows. We tried to solve the above coelutions and reduce the long retention times of the four trihaloacetics, with their wide peaks. At minute 25 we programmed a gradient concentration of the eluent of up to five-fold the initial concentration of 1.6 mM Na_2CO_3 + 0.5 mM NaHCO_3 , with a flow rate of either 0.7 or 0.8 mL min^{-1} . Figure 2 shows the chromatograms recorded at temperatures of 35, 25, 15, 10 and 7 °C. A better resolution is perceivable as temperature lowers, but the coelution of $\text{BCA} + \text{ClO}_3^-$ could not be resolved. It may also be observed that inorganic anions can become advanced or delayed,

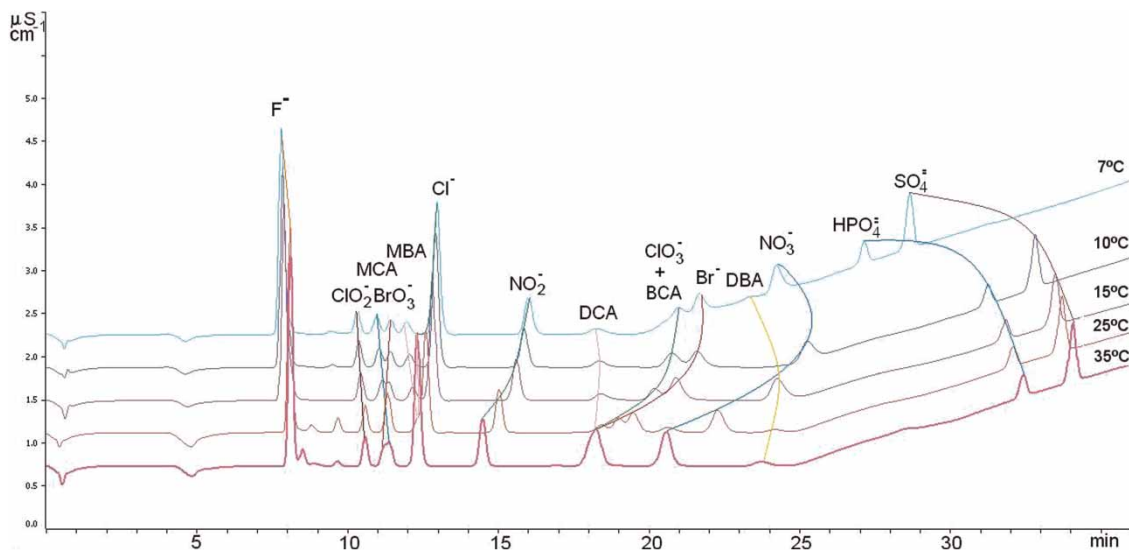


Figure 2 | Chromatograms of a multicomponent dissolution of 19 standards (0.5 mg L^{-1}), at the indicated temperatures and flow rate of 0.7 mL min^{-1} . Elution of trihaloacetic acids is not shown. A gradient concentration of the eluent was programmed at minute 25 of up to five-fold the initial concentration of $1.6 \text{ mM Na}_2\text{CO}_3 + 0.5 \text{ mM NaHCO}_3$.

depending on the temperature, without a definite pattern, as pointed out by Barron *et al.* (2005). A temperature of 7°C was selected, with the eluent gradient beginning at minute 20, returning to the initial conditions at minute 66 for the next run. Figure 1 shows that the peaks of the trihaloacetic acids kept their wide shape, which impeded their quantitation by conductimetry. Thus, MSD remains as the only option. Quantitation of BCA is made then by subtracting the value of ClO_3^- (conductimetry) from the whole peak area (MSD).

Most recently, published methods based on IC use gradient elution with KOH. As indicated above, this involves high pH values, ranging from 10.1 to 12.8. This may result in a partial decomposition of some of the HAAs through hydrolysis. No in-depth study specifically addressing the extent of this phenomenon for the analytical process appears to have been published. Nevertheless, the use of a less alkaline eluent, such as that based on $\text{CO}_3^{2-}/\text{HCO}_3^-$, which operates at pH 10.25, will prevent it. In addition, no special care will be taken to prevent the formation of carbonate, as is the case for the sodium or potassium hydroxide dissolutions and, likewise, there will be no need for an electrolyte generator.

Performance of the method

Since performance of this apparatus is well known for the common inorganic anions through commercial information

on applications, this study was restricted to the HAAs and bromate, chlorite and chlorate anions, except for linearity.

Linearity

Five multicomponent solutions with standards of the 19 analytes were prepared in $1.6 \text{ mM Na}_2\text{CO}_3 + 0.5 \text{ mM NaHCO}_3$. Triplicate injections were made in order to obtain five-point calibration curves (Table 1). From the beginning, the aim was to quantitate all analytes with the conductivity detector. At the concentrations of points 3 to 5, all the analytes could be quantitated with either of the detectors; but at those of points 1 and 2, only BrO_3^- , ClO_2^- , ClO_3^- (this needed subtraction of BCA), MCA, MBA, DCA, BDCA and CDBA. In addition, at the concentrations of point 1, the mass spectrometer detector was only able to quantitate MCA, MBA, DCA, BCA and DBA. Eventually, it was decided that the quantitation of inorganic anions be performed using conductimetry and that of the HAAs by MSD.

Detection limits

These were determined in a natural matrix only for the disinfection by-products, that is, HAAs and bromate, chlorite and chlorate. The method by Glaser *et al.* (1981)

Table 1 | Concentrations of 19 analytes to build the calibration curve

	Point 1	Point 2	Point 3	Point 4	Point 5
mg L ⁻¹					
Fluoride	0.1	0.2	1.0	2.0	10.0
Chlorite	0.005	0.02	0.1	1.0	10.0
Bromate	0.002	0.01	0.1	0.2	1.0
Chloride	2.5	5.0	25.0	50.0	150.0
Nitrite	0.1	0.2	1.0	2.0	10.0
Chlorate	0.005	0.02	0.1	1.0	10.0
Bromide	0.1	0.2	1.0	2.0	10.0
Nitrate	0.1	0.2	1.0	2.0	10.0
HPO ₄ ²⁻	1.0	2.0	10.0	20.0	100.0
Sulphate	5.0	10.0	50.0	100.0	500.0
µg L ⁻¹					
MCA	5.0	10.0	20.0	50.0	100.0
MBA	5.0	10.0	20.0	50.0	100.0
DCA	5.0	10.0	20.0	50.0	100.0
BCA	5.0	10.0	20.0	50.0	100.0
DBA	5.0	10.0	20.0	50.0	100.0
TCA	5.0	10.0	50.0	100.0	500.0
BDCA	5.0	10.0	50.0	100.0	500.0
CDBA	5.0	10.0	50.0	100.0	500.0
TBA	5.0	10.0	50.0	100.0	500.0

was applied, which performs seven injections of a multi-component mixture of analytes in concentrations between two- and five-fold the estimated LOD. A commercial mineral water of moderate hardness (25.6 °HF) and mineralization (515 µS cm⁻¹ conductivity) was used to test for a natural matrix effect, and the following standards were added to it at concentrations of five-fold the estimated limit of detection (LOD): 5 µg L⁻¹ of BrO₃⁻, MCA, MBA, DCA and BCA; 10 µg L⁻¹ of ClO₂⁻, ClO₃⁻ and DBA; 50 µg l⁻¹ of TCA, BDCA and CDBA; and 100 µg L⁻¹ of TBA. According to Glaser's method, the following formula was applied:

$$\text{LOD} = 3.707 \times \text{SD}$$

SD being the standard deviation of the seven results, and 3.707 being 'Student's *t*-test value' for six degrees of freedom and 99% of probability. The values are summarized in Table 2.

Table 2 | Regression coefficients of calibration curves and values of retention time, limit of detection and precision

	t _R (min)	r	LOD (µg L ⁻¹)	Precision ^a V.C. (%)
MCA	10.7	0.9980	5.0	17.0–19.0
MBA	11.0	0.9782	5.10	13.1–21.4
DCA	18.5	0.9987	3.35	3.0–13.4
BCA	19.1	0.9951	5.32	3.9–9.9
DBA	22.08	0.9836	5.28	5.4–12.2
TCA	38.12	0.9959	8.16	3.1–6.4
BDCA	42.0	0.9769	9.27	2.0–23.1
CDBA	50.11	0.9998	5.75	2.3–4.0
TBA	63.21	0.9987	14.0	3.0–6.0
Fluoride	8.36	0.9975		
Chlorite	10.01	0.9998	2.21	0.3–20.0
Bromate	11.60	0.9974	1.10	3.8–6.7
Chloride	12.71	0.9997		
Nitrite	16.56	0.9999		
Chlorate	19.61	0.9949	1.30	3.5–8.8
Bromide	21.18	0.9982		
Nitrate	23.59	0.9998		
Phosphate	26.28	1.0000		
Sulphate	29.24	0.9999		

^aAs variation coefficient, at two levels of concentration (higher–lower).

Precision

This was studied in the same matrix at two levels of concentration: 5 and 10 µg L⁻¹ for MCA, MBA, DCA and BCA; 5 and 20 µg L⁻¹ for DBA; 10 and 50 µg L⁻¹ for TCA, BDCA and CDBA; 20 and 100 µg L⁻¹ for TBA; 5 and 50 µg L⁻¹ for BrO₃⁻, 10 and 500 µg L⁻¹ for ClO₂⁻ and ClO₃⁻. Each of the two multicomponent solutions was injected seven times. Table 2 shows the values expressed as variation coefficients.

Application to disinfected waters

Replicates of municipal drinking waters from eight cities in the region of Castile and Leon (January 2012) were analysed. Enormous differences can be identified (Table 3) between the individual values, to a greater extent higher for the less chlorinated species, particularly for the MCA. The total HAA contents are of greater than or equal to the

Table 3 | Application of method to municipal drinking waters from eight cities in the region of Castile and Leon (January 2012)

City ($\mu\text{g L}^{-1}$)	MCA	MBA	DCA	BCA	DBA	TCA	BDCA	CDBA	TBA	Total HAAs	Bromate	Chlorite	Chlorate
Avila	102.3	<6.0	35.1	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 137.4	10	204	287
Burgos	105.2	<6.0	7.1	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 112.3	19	107	429
Leon	<5.0	<6.0	4.7	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 4.7	12	283	328
Palencia	48.4	<6.0	<3.35	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 48.4	11	279	279
Salamanca	<5.0	52.4	32.2	<6.0	7.8	<8.16	<9.27	<5.75	<14.0	≥ 92.4	23	70	270
Soria	<5.0	<6.0	112.1	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 112.1	10	108	909
Valladolid	89.3	34.2	7.6	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 131.1	10	186	313
Zamora	114.2	84.7	<3.35	<6.0	<5.28	<8.16	<9.27	<5.75	<14.0	≥ 198.8	21	146	596

sum of the quantifiable values. It is worth noting the high values measured for most of the cities, so that only two out of eight municipal waters showed (at least) quantifiable values below $60 \mu\text{g L}^{-1}$, the USA's legal limit. This could be accounted for by the low temperature of the waters in this month, since at low temperatures the HAA values tend to be higher than those for trihalomethanes (THMs) (Zhang & Minear 2002; Bayless & Andrews 2008). An equation was obtained for this phenomenon in a former study for these same cities, so that for water temperatures below 11.1°C the HAA concentrations were higher than those of THMs (Garcia-Villanova *et al.* 2010a). At higher temperatures THM levels rose while those for HAAs decreased. This is attributable in part to the chemical and/or microbial decomposition (decarboxylation) of HAAs into THMs, one of the mechanisms that contribute to the higher THM formation in the summer.

Regarding the concentrations of bromate, rather high figures were found, all of them reaching the legal limit of $10 \mu\text{g L}^{-1}$ or doubling it. This was also explained in a former study (Garcia-Villanova *et al.* 2010b) by the high contents of bromate generally found in the commercial hypochlorite reagents employed for the disinfection of drinking waters in Castile and Leon.

CONCLUSIONS

- Good linearity was observed in general – for three of the HAAs it can be described as acceptable.
- The detection limits for the HAAs are somewhat high in comparison with those reported for the official methods

based either on GC (EPA methods 552.2, 552.3 and the Standard Method 6251B) or on IC-ESI-MS/MS (EPA method 557). The last World Health Organization (WHO) guidelines for drinking water (2011) are of 200, 50 and $20 \mu\text{g L}^{-1}$ for TCA, DCA and MCA, respectively. Our procedure allows us to ascertain the conformity/non-conformity with the WHO's recommendations. The legal limits established for the sum of five HAAs in Canada and the USA are, respectively, 80 and $60 \mu\text{g L}^{-1}$. In our study, the sum of the LOD for these five HAAs was $34.89 \mu\text{g L}^{-1}$; hence, it only enables determination of whether the values in water are or are not within the legal limits of these regulations.

- Since the extent to which reactions of decarboxylation or hydrolysis may proceed are not yet completely known and, besides, they may fluctuate during the analytical process, working conditions involving both lower temperatures and pH values are desirable. A more in-depth study addressing their stability should be carried out.
- Nevertheless, in order to promote extensive control of these disinfection by-products by any community, we started from a very basic instrumental setup, particularly regarding the MS detector. Additional options should be tested to improve performance, particularly the use of a triple quadrupole ESI-MSD.
- A study on the addition of acetonitrile or (even better) methanol solvent in order to enhance volatility of the analytical stream before it enters this interface is also advisable. In all probability, all this would improve the sensitivity by one order of magnitude or more. Furthermore, during the experimental part of this work, a new

column with a higher capacity for resolution was developed, namely *Metrosep A Supp 7* (250/4 mm). This could resolve the overlapping peaks of BCA + ClO₃⁻, but it requires further testing.

- Since the instrumentation used for this study is becoming more and more common in waterworks laboratories, this procedure can help in monitoring for the self-control and optimization of drinking water treatments, aimed at attenuating the formation of disinfection by-products. This is especially interesting for communities or countries in which regulations concerning disinfection by-products other than THMs are being implemented.
- Quite high values were found for the concentrations of HAAs and bromate in most of the eight municipal drinking waters of Castile and Leon analysed (January 2012). In addition, enormous differences were found for the individual values of each HAA, to a greater extent higher for the less chlorinated species.

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