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1 **Direct Determination of Trace-Level Haloacetic Acids in Drinking Water by Two-**
2 **Dimensional Ion Chromatography with Suppressed Conductivity**

3

4 Dominique Verrey^{a,b,*}, Mari-Vorgan Louyer^{a,b}, Olivier Thomas^{a,b}, Estelle Baurès^{a,b}

5 ^aEHESP School of Public Health, Sorbonne Paris Cité, 35043 Rennes, France

6 ^bInserm, U1085-IRSET, LERES, 35043 Rennes, France

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9 *Corresponding author. Tel.: +33 2 99 02 29 48 ; fax: +33 2 99 02 29 29.

10 E-mail address: Dominique.Verrey@ehesp.fr (D. Verrey).

11

12 **Abstract**

13 During the treatment process of drinking water, disinfectants (chlorine, ozone, chlorine dioxide)
14 react on water containing organic matter and bromide to produce disinfection by-products at
15 trace levels. Among them, five of the nine existing Halo-Acetic Acids (HAA) are commonly found
16 in drinking water (Monochloroacetic acid MCAA, Dichloroacetic acid DCAA, Monobromoacetic
17 acid MBAA, Dibromoacetic acid DBAA, and Trichloroacetic acid TCAA), including four classified
18 in the 2B IARC group of potential carcinogens (BCAA, DBAA, DCAA, TCAA). With respect to
19 drinking water quality, guidelines are proposed by WHO (2006) and water quality standards are
20 imposed in many countries such as less than 100 µg/L for the sum of the five HAA by US EPA
21 (1998) and Canadian Health Department (2008). For this purpose, two analytical methods are
22 commonly used, GC/MS with derivatization and LC/MS, UV or conductivity. A new method, based
23 on two-dimensional ion chromatography (IC 2D) with suppressed conductivity is proposed. This
24 method presents the main advantage compared to GC or LC methods of offering a quick
25 implementation: direct injection, slight maintenance, lower cost of investment, by leading to
26 good performances (specificity and sensitivity). The use of two different selectivity columns, and
27 the fractionation on the first dimension cancelling interferences, improves the specificity. The
28 sensitivity is enabled by interfacing a preconcentration column between the two different
29 internal diameter columns. The analytical conditions are optimized for the analysis of nine HAA.
30 The performances of the method are evaluated. The optimized method applied to natural water
31 samples demonstrates its ability to quantify HAA at trace levels in drinking water.

32

33 Keywords: ionic chromatography; two dimensions; capillary; haloacetic acids; drinking water

34

35 **1. Introduction**

36 *1.1. Formation, occurrence and regulation of disinfection by-products*

37 During the disinfection step of drinking water treatment process, disinfectants (chlorine, ozone,
38 chlorine dioxide) react on water containing organic matter and bromide to produce disinfection
39 by-products (DBPs). Among the six hundred substances identified, haloacetic acids (HAAs) and
40 trihalomethanes (THM) represent the two major classes and thirty percent on a weight basis
41 [1,2].

42 Among the HAAs, nine bromo and/or chloroacetic acids combinations are
43 possible: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA),

44 monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA),
45 bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), tribromoacetic acid
46 (TBAA).

47 Five of these nine HAA (MCAA, DCAA, TCAA, MBAA, DBAA) were commonly found in drinking
48 water in the US, with a mean concentration of 23 µg/L [3]. In other countries, DCAA and TCAA
49 between 2 µg/L and 12 µg/L were analysed in Canada [4], DCAA (from 0.4 µg/L to 13 µg/L) and
50 TCAA (from 0.6 µg/L to 11 µg/L) in drinking water in China [5], up to 49.5 µg/L for the sum of
51 the five HAA in tap water in Seoul [6], from 0.9 to 87 µg/L for the sum of the nine in Spain [7].
52 Regarding the seasonal influence, the five HAA concentrations were 1.0–38.9 µg/L in winter and
53 0.2–46.7 µg/L in summer, in drinking water of Taiwan, DCAA and TCAA being the two major HAA
54 (around 30% and 26% respectively) [8].

55 In the International Agency for Research on Cancer classification [9], four of the nine HAA are
56 classified in the 2B group as possibly carcinogenic to humans (BCAA [10], DBAA [11], DCAA [12],
57 TCAA [13,14]). World Health Organization (WHO) proposes guidelines for drinking water as a
58 point of departure for national authorities to determine drinking water regulations and standards
59 [15]. WHO has established guidelines for chlorinated HAA (MCAA: 20 µg/L ; DCAA: 50 µg/L ;
60 TCAA: 200 µg/L), but not for brominated HAA. The national authorities approaches are different
61 according to countries. For example, on the sum of the five commonly found HAA, the US EPA has
62 fixed regulation at 60 µg/L in 1998 [16] and Health Canada has fixed recommendation at 80 µg/L
63 in 2008 [17]. In Europe, HAA are not yet standardized despite an increasing demand of sanitary
64 surveys as for example, campaigns in four drinking water systems in France [18].

65

66 *1.2. State of the art of analytical methods*

67 HAA analysis is usually performed by GC or LC techniques (Table 1). The GC methods require two
68 steps of sample preparation, a liquid-liquid extraction (LLE) and an extract concentration
69 [19,20]. To reduce the extraction volume during sample preparation, new techniques have been
70 developed such as the liquid-liquid microextraction [21] and the single-drop microextraction
71 (SDME) [22]. A recent procedure combining liquid-liquid microextraction and headspace
72 (HS) GC may allow reducing the time of sample preparation [23]. In order to get volatile
73 compounds, a derivatization step is carried out before injection of the extract into the gas
74 chromatograph. Two types of detectors are available: (i) the electron capture detector (ECD),
75 specific for halogenated substances, has a good sensitivity but requires training and protection
76 precautions against the radioactive source and (ii) the mass spectrometer (MS) provides better
77 security identification. The main advantage of GC methods is a good sensitivity with limits of
78 detection (LOD) between 0.01 and 1.2 µg/L according to the method and the substance, as
79 shown in Table 1. However the sample preparation steps are heavy to run and time-consuming,
80 which may consider GC analysis of HAA tedious and expensive [19,20].

81 LC methods are divided into two categories: (i) reversed-phase liquid chromatography [24] and
82 (ii) ion chromatography (IC) [25]. Regardless on the technique used, the sample is either injected
83 directly or after a preconcentration step (online or offline) on a solid phase extraction (SPE)
84 cartridge. Direct LC methods can be achieved thanks to an electromembrane extraction (EME)
85 followed by UV detection [26] or a LC/MS/MS technique [27]. Several types of detection are
86 available with IC methods, the most frequent being conductimetry (CD) [25], possibly with
87 preconcentration SPE cartridge for a better sensitivity [28]. The second type of IC detection is
88 MS, often used in tandem [29, 30]. A third type of IC detection is fluorimetry (FL), associated with

89 post-column reaction (PCR) [31]. All LC techniques avoid the tedious steps of sample treatment
90 for GC, with LOD between 0.0007 µg/L and 35.4 µg/L as shown in **Table 1**. The wider range of
91 LOD with regard to GC is explained by the different techniques proposed for separation and
92 detection. With GC or LC, MS detection requires more staff qualification and higher costs of
93 investment and maintenance than the use of specific detectors, but has the advantages of more
94 reliability and specificity. Overall the performances of all methods presented are in compliance
95 with recommendations and regulations for water quality.

96 **Please insert Table 1 here**

97

98 *1.3. Principle of the two-dimensional ion chromatography (IC 2D)*

99 The method proposed hereafter allows to separate the nine HAA using a two-dimensional ion
100 chromatography separation with a conductimetric detection (IC 2D). The interest of the method
101 is the improvement of the sensitivity (thanks to two different diameters of successive columns)
102 and the specificity (different phases). A collection window enables the selection of anions of
103 interest on a column concentrator during the first step (first dimension). Thus, these anions are
104 eluted during the second step (second dimension). The two successive separations on two
105 columns of different diameters (an analytical column and a capillary column) with a
106 concentration step between the two columns, increase the sensitivity by the square of the ratio
107 of the two columns diameters.

108

109 **2. Material and methods**

110 *2.1. Chemicals*

111 All chemicals used to prepare HAA standards solutions were of analytical grade purity and were
112 obtained from Merck (Darmstadt, Germany). Individual haloacetic acids DCAA, BDCAA and BCAA
113 were obtained from Supelco (Bellefonte, PA, USA), MCAA and TCAA from Fluka (Saint-Louis, MO,
114 USA), MBAA, DBAA and TBAA from Dr Ehrenstorfer (Augsburg, Germany) and BCAA from
115 Aldrich (Chicago, IL, USA).

116 Stock solutions of individual HAA were prepared in ultra-pure water (UPW) at a concentration
117 of 1 g/L and stored in the dark at 5 ± 3°C. Working standards were daily fresh prepared at the
118 concentrations range.

119 Stock solutions of 10 inorganic anions (fluoride, chlorite, bromate, chloride, nitrite, bromide,
120 chlorate, nitrate, sulfate, orthophosphate), at 1 g/L, used for interferences study were obtained
121 from Merck (Darmstadt, Germany) and Carlo Erba (Val de Reuil, France).

122 UPW was obtained by a Millipore (Bedford, MA, USA) Rios30 system coupled with a Milli Q
123 Gradient water purification system.

124

125 *2.2. Instrumentation*

126 For this study, a Thermo Scientific Dionex ICS 5000 ion chromatograph (Sunnyvale, CA, USA) was
127 employed. It is composed from several modules: AS-AP Autosampler, Dual Pump (DP) module,
128 Eluent Generator (EG) module and Detector/Chromatography (DC) module. Instrument control,

129 acquisition and data processing were performed using Chromeleon 6 software. The ICS 5000 is
130 configured with two complete chromatographic systems in tandem as shown in **Figure 1**.

131 **Please insert Figure 1 here**

132 The two systems have a few but important differences. Each of both has: i) a gradient pump (P1,
133 P2) for potassium hydroxide (KOH) eluent introduction, produced by an on line automatic eluent
134 generation system (EGC KOH); ii) a continuous regenerating-anion trap column (CR-ATC) for
135 eluent carbonates removal; iii) a chromatographic column (C1, C2) ; iv) an electrolytic
136 suppressor (S1, S2); v) a carbonate removal device trapping sample carbonates (CRD300,
137 CRD200); vi) a conductivity detector (CD1, CD2); vii) a waste (W).

138 The differences are i) the flow rates of the gradient pumps (1 mL/min for P1 and 0.012 mL/min
139 for P2); ii) the characteristics and nature of columns (C1: analytical guard column AG24 [50 × 4
140 mm] + analytical column AS24 [250 × 4 mm] at 10°C; C2: capillary guard column AG26 [50 × 0.4
141 mm] + capillary column AS26 [250 × 0.4 mm] at 15°C); iii) the characteristics of electrolytic
142 suppressors (S1: Anion Self Regenerating Suppressor (ASRS) 300 in external regeneration
143 mode with NaOH 10 mM; S2: Anion Capillary Electrolytic Suppressor (ACES) in recycle
144 regeneration mode); iv) the characteristics of carbonate removal device (CRD 300: external
145 regeneration mode; CRD 200: self-regeneration capillary device).

146 The first system has an injection valve for sample introduction (V). 500 µL of samples are
147 injected thanks to the AS-AP autosampler regulated at 10°C. In order to limit sample volume, the
148 sampler is used in partial loop mode with a 750 µL volume loop.

149 After the separation on the System 1, fractions of interest are automatically collected thanks to a
150 Rheodyne valve (Rohnert Park, CA, USA) and reinjected onto a Thermo Scientific Dionex
151 Monolith Anion Concentrator column 200 IonSwift MAC-200 (capacity 0.24 µeq) before injection
152 in the System 2.

153

154 *2.3. Method*

155 *2.3.1. Optimization method*

156 After the identification of each retention time of the 9 HAAs and the 10 common inorganic
157 anions, in both dimensions, the method optimization was performed in order to separate or
158 eliminate the interferences from the interest compounds. The different steps of this optimization
159 are related to (i) the sample preparation, (ii) the eluent concentration and its gradient, (iii) the
160 temperature of the columns, and (iv) the first dimension collection windows.

161 *Samples preparation*

162 According to standard ISO 23631 [19], the addition of sodium thiosulfate at 10 mg/L allowed to
163 stop residual chlorine action and to eliminate the interference of the chlorite on MBAA.

164 *Eluent concentration and gradient*

165 First chromatographic separation was carried out with the eluent gradient: 3 mM (hold 15 min),
166 first ramp at 0.46 mM/min to 15 mM, second ramp at 500 mM/min to 65 mM (hold 19 min) and
167 third ramp at 7.75 mM/min to 3 mM (hold 3 min to reach an analysis time of 72 min).

168 Second chromatographic separation was carried out with the eluent gradient: 6 mM (hold 50
169 min), first ramp at 500 mM/min to 160 mM (hold 7 min), second ramp at 500 mM/min to 130

170 mM and immediately third ramp at 9.54 mM/min to 6 mM (equilibration time of 2 min to reach
171 an analysis time of 72 min).

172 *Temperature*

173 According to Barron et al. [32], the temperature changes have kinetic and thermodynamic
174 effects in IC. In this study several temperatures from 10 to 30°C were tested.

175 *Collection windows*

176 Three collection windows were determined for respectively mono, di and tri HAAs based on their
177 retention times. This fractionation enabled collecting compound of interest on the
178 preconcentration column.

179

180 *2.3.2. Quantitation method*

181 According to NF EN ISO 10304-1 [33], the resolution factor $R_{1,2}$ between two substances is
182 defined as $R_{2,1} = 2 (t_{R2} - t_{R1}) / (w_2 - w_1)$ (with: $R_{2,1}$ Resolution factor between species 1 and 2, t_R
183 retention time in seconds, w peak width in seconds). Limits of quantification (LOQs) were
184 defined as the lowest concentration for which the relative standard deviation (RSD) of
185 replicate injections is lower than or equal to 20% and the signal-to-noise ratio (S/N) greater than
186 10. LOQs were estimated by analyzing UPW spiked with decreasing amounts of analytes.
187 Quadratic calibration curves were established for each HAA by spiking UPW with five different
188 amounts of HAAs (from the estimated LOQ to 200 µg/L depending on the compound). The
189 determination coefficient was calculated in a quadratic mode. It reflects the deviation of the
190 measured data points from the calibration curve. The LOQ bias was calculated as the difference
191 between the theoretical LOQ and the measured LOQ divided by the theoretical LOQ. The recovery
192 was calculated as the value experimentally obtained from calibration graph divided by the
193 theoretical value. The limit of detection (LOD) was determined as the LOQ divided by 3. The
194 results of the reference GC method and the IC method were tested using the Student t test for
195 paired samples to determine if they were statistically the same or different.

196

197 **3. Results and discussion**

198 *3.1. Chromatographic separation*

199 To optimize the separation of the 9 HAA from each other and from the 10 mineral
200 interferent anions on the two dimensions, the elution gradient was optimized, from 3 and 6 mM of
201 potassium hydroxide to separate the mono and dihaloacetic acids from each other, up to 60
202 mM and more for the 4 trihaloacetic acids.

203 On the first dimension, two factors were taken into account for the optimization of separation.
204 Firstly, the collection windows, defined as the intervals of retention times within which are
205 separated compounds of interest, were adjusted to enable HAAs to go to the preconcentration
206 cartridge while eliminating interfering mineral anions when possible. The intervals of windows
207 were determined for the monohaloacetic acids, dihaloacetic acids and trihaloacetic acids
208 between 20.0 and 27.1 min., 33.5 and 39.8 min., 47.9 and 58.0 min. respectively.

209

210 Secondly, the variation of column temperature from 15 °C to 10°C had an impact on the
211 separation of the two coelution cases concerning bromate/MBAA and nitrite/DBAA. For
212 example, resolutions between bromate and MBAA at 15.0°C, 12.5°C and 10.0°C were determined
213 at 1.1, 1.4 and 1.7 respectively. The better separation was observed on the coelution of
214 bromate/MBAA with 10°C, according to the resolution criterion that the separation between two
215 substances must be greater or equal to 1.3.

216

217 On the second dimension, a coelution was observed for chlorite and MCAA. An addition of
218 sodium thiosulfate, reacting on chlorite ion, led to its elimination. The chromatogram in **Figure**
219 **2** shows the optimized separation on this dimension.

220

Please insert Figure 2 here

221 *3.2. Instrumental performances*

222 For the nine substances, the calibration was made with quadratic model, using a second order
223 equation ($F(x) = C_0 + C_1 \times x + C_2 \times x^2$). The calibration range was validated from the LOQ to 100
224 µg/L, with determination coefficients higher than 0.999 as presented in Table 2.

225

Please insert Table 2 here

226 The second step of performances validation (**Table 3**) was the determination of the limit of
227 quantification (LOQ). The mixtures of the nine HAA in UPW, analyzed at known concentrations
228 were quantified according to calibration functions. LOQ were equal [30] or higher than the ones
229 obtained by other methods such as GC [18,19,21,22] or IC/MS [28,29], and even lower than
230 classical IC [24,27].

231 Spikes of HAA (20 µg/L) in real samples, especially drinking water, enabled to verify the possible
232 matrix impact. The recovery rates presented in **Table 3** were between 88 and 119%, excepted
233 for TCAA (60%), probably because of a problem of optimization (beginning of the substance
234 elution out of the collection window).

235

Please insert Table 3 here

236 *3.3. Application to natural water in treatment process and comparison with GC analysis*

237 One river was sampled four different days and was treated in a drinking water treatment pilot.
238 At the step of disinfection, 4 mg/L chlorine were added during several contact-times (3h, 24h,
239 72h). HAA were analyzed with IC 2D on the twelve chlorinated samples. An available method
240 measuring MCAA, DCAA, TCAA and DBAA with LLE/Derivatization/GC/MS was applied to the
241 samples [34].

242 The analytical results obtained from the two methods are presented in **Table 4**. The t test was
243 used to read the results. For MCAA, TCAA and DBAA, the t test value was inferior to the t test
244 T5% value. It means that the averages of the two methods are not significantly different. For
245 TCAA, the t test value was superior to the t test T5% value. It means that the averages of the two
246 methods are significantly different, with a difference of 2.1 µg/L. Moreover given the fact that
247 trace levels near LOQ are measured, the results were judged acceptable.

248

Please insert Table 4 here

249

250 **4. Conclusion**

251 The method based on IC 2D developed for 9 HAA shows interesting performances in terms of
252 limits of quantification, linearity and accuracy, regarding the need for drinking water quality
253 control for sanitary survey. The practical advantages of the method are demonstrated: fast
254 sample preparation, sensitivity around one microgram per liter and comparable results with a
255 GC method. Starting from these first results, the perspective is, on one hand, to expand this
256 method to other matrices while verifying the absence of specific interferences and, on the other
257 hand, to refine the performance evaluation for each matrix according to analytical standard
258 (e.g. NF T 90-210).

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262

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360 Captions

361 **Table 1:** Existing methods for HAA analysis

362 **Figure 1.** Schematic diagram of the two-dimensional chromatographic system (see explanations
 363 in text)

364 **Figure 2.** Second dimension chromatogram with a mix of 9 HAA at 20 $\mu\text{g/L}$ each

365 **Table 2:** Calibration characteristics

366 **Table 3:** Performances in water

367 **Table 4:** Comparison between GC and IC 2D methods