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1 **Development of an automated system for the analysis of inorganic chloramines in**
2 **swimming pools via multi-syringe chromatography and photometric detection with ABTS**

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6

7 **Abstract**

8 Inorganic chloramines are disinfection by-products resulting from the unwanted reaction
9 between chlorine used as disinfectant in swimming pools and nitrogenous compounds brought
10 by bathers. This parameter (total chloramines or combined chlorine) is currently measured on
11 site by a colorimetric method that does not allow to measure only inorganic chloramines. In this
12 paper, a multi-syringe chromatography system combined with a post column derivatization is
13 applied for the first time for the specific detection of the three individual inorganic chloramines
14 (monochloramine, dichloramine and trichloramine). These latter ones are separated using a
15 low-pressure monolithic C18 column, and separately detected after a post-column reaction with
16 the chromogenic reagent ABTS (2,2'-azino-bis-(3-ethyl-benzothiazoline)-6-sulfonic acid-
17 diammonium salt). Development of two ABTS reagents provides discrimination of chlorine
18 and monochloramine that are not separated on the column. Optimization of the experimental
19 conditions enables determination of inorganic chloramines with very good detection limits
20 (around 10 $\mu\text{g eq.Cl}_2 \text{ L}^{-1}$) without interferences from other chlorinated compounds such as
21 organic chloramines or free available chlorine. The validation of the whole procedure has been
22 successfully applied to real swimming pools samples.

23 **Keywords:** Multi-syringe chromatography; inorganic chloramines; free chlorine; post-column
24 reaction; swimming pools.

25

26 **1. Introduction**

27 Among disinfection by-products commonly found in swimming pools, inorganic chloramines
28 are the most often encountered at the highest concentrations, with monochloramine (MCA,
29 NH_2Cl) mainly found in water (up to $1180 \mu\text{g L}^{-1}$), followed by trichloramine (TCA, NCl_3) (up
30 to $800 \mu\text{g L}^{-1}$) and dichloramine (DCA, NHCl_2) (up to $650 \mu\text{g L}^{-1}$) [1]. Inorganic chloramines
31 are a group of three chemical substances in aqueous solution formed by reactions between
32 chlorine at oxidation state (+I), ammonia and amino acids coming from urea and sweat brought
33 by bathers (such as uric acid, urea, creatinine, L-arginine, L-histidine, glycine) [2].

34 These chloramines are present in various types of waters where chlorine is used as disinfectant
35 or for biofouling control (drinking waters, swimming pools waters, wastewaters, industrial
36 chlorinated effluents) [1, 3-6]. In particular for swimming pools, respiratory issues, such as
37 asthma, wheeze, cough and lower respiratory tract infections, have been correlated with
38 swimming pool attendance, which is likely due to chlorinated volatile DBPs, such as
39 chloramines and especially TCA [7-9]. TCA is also assumed to cause skin and eye irritations
40 [10]. MCA and DCA have not been yet assumed to be toxic but their roles as precursors of the
41 potent carcinogen N-nitrosodimethylamine (NDMA) have been emphasized by several authors
42 [11-13]. Consequently, reliable, rapid and sensitive methods are required to monitor pool water
43 quality and to assess their mitigation strategies.

44 Many methods have been proposed for the determination and quantification of chloramines and
45 have been reviewed by Kinani et al. [14]. The most commonly used are based on the redox
46 reaction using N, N-diethyl-p-phenylenediamine (DPD) as the reducing agent with colorimetric

47 or amperometric detection. The colorimetric method uses the red coloration produced by the
48 reaction between DPD, free chlorine and inorganic chloramines (after addition of iodide) with
49 a spectrophotometric measurement at 510 nm, whereas the titrimetric method employs
50 ammonium sulfate with ferrous ion as the final reagent of the colored solution produced by
51 DPD reaction. These methods are simple and sensitive (quantification limits (LOQ) are around
52 30 $\mu\text{g eq. Cl}_2 \text{ L}^{-1}$), but they suffer from a lack of selectivity. Indeed, organic chloramines may
53 interfere with inorganic chloramines as they react in the same way in the presence of the iodide
54 ions, leading to an overestimation of the real amount of inorganic chloramines in samples with
55 large amounts of organic nitrogen [15]. Another colorimetric method using a derivatization
56 reaction has been developed to differentiate inorganic monochloramine from organic
57 chloramines using phenol type reagent as color reagent [16]. The derivatized product can be
58 measured spectrophotometrically at a wavelength of 655 nm. However, this method suffers
59 from a low sensitivity (LOQ > 270 $\mu\text{g eq. Cl}_2 \text{ L}^{-1}$) and from the ability to detect only
60 monochloramine.

61 To overcome these issues and to allow individual determination of the three chloramines,
62 chromatographic separation using high performance liquid chromatography (HPLC) has been
63 proposed. Separations of chloramines are generally performed using reversed-phase HPLC on
64 a C_{18} -phase column. Direct spectrophotometric detection is possible at specific wavelength for
65 each chloramine (MCA at 240 nm, DCA at 210 or 280 nm and TCA at 220 nm) [17,18].
66 However, quantification limits of this detection method are generally very high (LOQ >200 μg
67 $\text{eq. Cl}_2 \text{ L}^{-1}$), and selectivity is also very low as many other co-eluting compounds can interfere
68 in the wavelength range below 250-300 nm. Direct amperometric detection with a working
69 glassy carbon electrode is also proposed with a better sensitivity (quantification limits 2-13
70 times lower than those obtained by spectrophotometric detection), but interference from oxygen
71 seriously hampers application of this method [19]. Chemical derivatization generally provides

72 low sensitivity, except when LC-MS/MS is used with a pre-column derivatization of MCA.
73 This method is very sensitive and specific for MCA, but drawbacks are the high cost and
74 complexity of the detection method, and the inability to measure DCA and TCA [20]. The most
75 efficient derivatization method for inorganic chloramines to date is the post-column
76 derivatization with potassium iodide and photometric or electrochemical detection of triiodide
77 ions formed [21]. Although the sensitivity of this method is quite high (LOQ around 30 $\mu\text{g eq. Cl}_2 \text{ L}^{-1}$),
78 the post-column reaction is non-specific to inorganic chloramines (potassium iodide
79 can react with many other compounds).

80 The aim of this study was to develop a low-cost automated analyzer for the individual
81 quantification of MCA, DCA and TCA. So far, the only on-line automated analytical tool for
82 determination of these three inorganic chloramines is membrane-introduction mass
83 spectrometry (MIMS), which uses a semi permeable membrane coupled to a mass spectrometer
84 [15]. This analytical tool is very specific for inorganic chloramines, but lacks of sensitivity
85 (LOQ =60-300 $\mu\text{g eq. Cl}_2 \text{ L}^{-1}$), remains costly and requires qualified personnel to handle with
86 MS interpretations. Our aim was thus to propose an alternative analytical method based on the
87 simplicity and versatility of flow injection techniques coupled to liquid chromatography
88 separation for the determination of individual inorganic chloramines.

89 A multi-syringe chromatography (MSC) system using monolithic column is thus developed to
90 obtain a low-pressure automated portable system with relatively low-cost and simple
91 components, able to be used as an on-line system. In order to achieve better sensitivity and
92 specificity than direct spectrophotometric detection, a new post-column reaction for all
93 inorganic chloramines is proposed using 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic
94 acid) diammonium salt (ABTS), an indicator already used by Solterman et al. [22] for the
95 detection of trichloramine. Optimizations of this post-column reaction and of the

96 chromatographic separation of chloramines are presented, and the developed method applied
97 on real swimming pool samples.

98

99 **2. Material and methods**

100 2.1. Reagents and solutions

101 All chemicals were of analytical reagent grade and used without further purification. Ultrapure
102 water purified with a Milli-Q system (Millipore, USA, resistivity >18 MΩ cm) was used for the
103 preparations of the whole solutions. Sodium hypochlorite solutions were prepared by dilution
104 of a commercially available NaOCl solution (4.00-4.99% active chlorine, Sigma-Aldrich,
105 France) and standardized by iodometric titration. Ammonium stock standard solution (2 g L⁻¹)
106 was prepared from ammonium chloride (Alfa Aesar, Germany). Solutions of ABTS (2,2'-azino-
107 bis-(3-ethyl-benzothiazoline)-6-sulfonic acid-diammonium salt, Sigma-Aldrich) were prepared
108 by dissolving appropriate amount in water. Acetonitrile (MeCN) (HPLC-Gradient phase,
109 Sigma-Aldrich) was used as the organic mobile phase. Formic acid (Fisher chemical, France),
110 sulfuric acid (Fisher chemical), hydrochloric acid (Sigma-Aldrich) and sodium hydroxide
111 (Sigma-Aldrich) were used for pH adjustments.

112

113 2.2. Inorganic chloramines standard solutions

114 Inorganic chloramines are unstable and sensitive to light, so they had to be prepared daily and
115 stored in amber glass or polytetrafluoroethylene bottles at +4 °C and kept out of direct light.
116 Inorganic chloramines solutions prepared were standardized by using DPD/FAS titrimetric
117 method.

118 MCA standard solution was prepared by slowly adding 5 mL of sodium hypochlorite solution
119 ($6 \text{ mmol Cl}_2 \text{ L}^{-1}$) to 5 mL of ammonium chloride solution (12 mmol L^{-1}) whose pH was prior
120 adjusted at 9 with 0.1 M NaOH (ammonia to chlorine molar ratio was 2:1). Final pH was
121 between 10.5 and 11. The reaction vial was then covered with aluminum foil and stored at +4
122 °C for 60 min before use.

123 DCA standard solution was prepared by acidification of the MCA solution with 0.1 M formic
124 acid to reach a pH value between 3.5 and 4. This solution was then stirred at room temperature
125 for 2 h while pH was monitored and readjusted as necessary, and then left for 4 h at +4 °C
126 before use.

127 TCA standard solution was prepared by addition of 5 mL of a $6 \text{ mmol Cl}_2 \text{ L}^{-1}$ sodium
128 hypochlorite solution (whose pH was previously adjusted below 3 with 0.5 M H_2SO_4) to 5 mL
129 of a 1.9 mmol L^{-1} ammonium chloride solution (ammonia to chlorine molar ratio was 1:3.15).
130 Final pH was between 2.3 and 2.5. The reaction vial was then covered with aluminum foil and
131 stored at +4 °C for 45 min before use.

132 A solution of MCA and DCA was prepared by additions of 5 mL of a $6 \text{ mmol Cl}_2 \text{ L}^{-1}$ sodium
133 hypochlorite solution (whose pH was previously adjusted to 6 with 0.1 M formic acid) to 5 mL
134 of a 6 mmol L^{-1} ammonium chloride solution (ammonia to chlorine molar ratio was 1:1). Final
135 pH was between 5.2 and 5.8. The vial was then covered with aluminum foil and stored at +4
136 °C for 45 min before use.

137 For the study on inorganic bromamines, monobromamine (NH_2Br), dibromamine (NHBr_2) and
138 tribromamine (NBr_3) were prepared as described by Galal-Gorchev and Morris [23] and by Lei
139 et al. [24], while bromochloramine (NHBrCl) was prepared following Allard et al.'s method
140 [25].

141

142 2.3 HPLC separation of inorganic chloramines with direct UV detection

143 Inorganic chloramines separation has been first optimized by using a HPLC system consisting
144 of an L-2130 pump, an L-2400 UV detector, and an L-2200 autosampler (Hitachi Elite
145 LaChrom system, Tokyo, Japan). HPLC separations were performed on a RP-18 Onyx™
146 monolithic column (25 mm x 4.6 mm, Merck, Germany). Detection was performed at 245 nm
147 for MCA, 295 nm for DCA (210 nm for mixtures of MCA + DCA) and 220 nm for TCA. The
148 column temperature was fixed at 25 °C, the flow rate was set at 0.5 mL min⁻¹, and the injected
149 sample volume was 20 µL.

150

151 2.4. Reaction of inorganic chloramines with ABTS

152 The reaction between free chlorine or inorganic chloramines with ABTS was studied using a
153 Jasco V-670 spectrophotometer operating with the Spectra Manager software. The solutions
154 were analyzed in a 10 mm light path quartz cell.

155 Solutions of ABTS were stored at 4 °C and were stable for at least 2 months. Solution A was
156 prepared by dissolving 13.6 mg of ABTS in 100 mL 0.4 M HCl ([ABTS] = 0.25 mM). Solution
157 B was prepared by dissolving 13.6 mg of ABTS in 100 mL of 5 mM phosphate buffer at pH 3.
158 For the kinetic measurements in quartz cells, 1 mL of sample and 2 mL of the appropriate ABTS
159 solution were added and mixed in the cell, and absorbance was measured every 5 s at 405 nm.

160

161 2.5. MSC instrumentation and software

162

163 The device used is described in Fig.1. It included a multisyringe burette (BU-4-S, Crison
164 Instruments, Spain) equipped with four syringes (Hamilton, Switzerland). Three syringes were
165 used: S1 (5 mL; mobile phase: MeCN/H₂O: 20/80), S2 (2.5 mL; ABTS solution A) and S3 (2.5

166 mL; ABTS solution B). Standard solenoid valves on the head of S1 were replaced by a two-
167 way connector made of Delrin® (Sciware System SL, Spain) in order to resist organic solvents.
168 This connector linked S1 with a new solenoid valve (V1, Takasago, Japan) which was situated
169 outside the syringe module and allowed a maximum operating pressure of 6 bars. V2 and V3
170 were standard solenoid valves. The manifold was built up with a 0.8 mm internal diameter
171 poly(tetrafluoroethylene) (PTFE) tubing. S1 was connected to one port of a 6-port injection
172 valve module (Crison Instruments) equipped with a 20 µL loop. The three other ports of the
173 injection valve were connected to the sample vial, the monolithic column and waste. The
174 injection loop was filled with the sample thanks to a solenoid micro-pump (MP1) (Bio-Chem,
175 USA). The indicated stroke volume for the micro-pumps was 20 µL. MP1 and V1 were
176 computer-controlled by means of a MCFIA/MPFS system (Sciware System SL) having eight
177 digital 12V output channels.

178 The separation of chloramines was performed on an Onyx™ monolithic C18 column (25 mm
179 x 4.6 mm, Merck, Germany) at room temperature, using a mixture of acetonitrile and water as
180 mobile phase (MeCN/H₂O: 20/80).

181 A PEEK (polyether ether ketone) T-mixer equipped with a PAT frit (PEEK Alloyed with
182 Teflon, Interchim, France) was used to mix the eluent from the column with the ABTS solution
183 during the post-column derivatization. A 100 µL PTFE tubing (0.5 mm internal diameter) was
184 used to connect the T-mixer to the flow cell to ensure enough time to complete reaction between
185 chloramines and ABTS.

186 The detection system was composed of an ultra violet-visible light source (DH-2000 Deuterium
187 Tungsten Halogen Light sources; wavelength range 215-2000 nm; Ocean Optics, USA), a FIA-
188 ZSMA PEEK flow cell (50 mm pathlength, 130 µL internal volume, Ocean Optics) and of a
189 USB 2000 miniature fiber-optic spectrometer detector (detector range: 200 - 1100 nm, Ocean

190 Optics) connected to a computer via an USB interface. The analytical wavelength was set at
 191 405 nm. Two FC-UV600-2 optical fibers (Ocean Optics) were used to guide the light from the
 192 source through the flow cell and further to the spectrophotometric detector. System control,
 193 data acquisition and processing were performed using the software package Autoanalysis 5.0
 194 (Sciware System SL).

195

196 2.6. MSC procedure

197 The optimized protocol used for the MSC system is presented in Table 1 and summarized as
 198 follows:

199 A first cycle (separation/derivatization) was run with ABTS (solution B) to measure only free
 200 chlorine. After injection of the sample in the loop (Load position, step 1), chromatographic
 201 separation was performed by switching the valve to “Inject” position (step 4) and by dispensing
 202 the mobile phase (step 6), while absorbance measurement was carried out at 405 nm. After
 203 reloading of the syringes (step 8), a second cycle was run with ABTS (solution A) to measure
 204 inorganic chloramines (step 9-13).

205 **Table 1** Analytical procedure for Multi-syringe chromatography analysis of free chlorine with
 206 ABTS solution B and inorganic chloramines with ABTS solution A.

207

Step	V1	V2	V3	Injection Valve	Mode	Volume (ml)	Flow rate (mL min ⁻¹) ^a	MP1 (μL)
1	OFF	OFF	OFF	LOAD	-	-	-	500
2	Get dark spectrum continuous							
3	Get blank spectrum continuous							

4	OFF	OFF	OFF	INJECT	-	-	-	-
5	Start MEASUREMENT				-	-	-	-
6	ON	OFF	ON	INJECT	Dispense	5	0.30	-
7	STOP MEASUREMENT				-	-	-	-
8	OFF	OFF	OFF	INJECT	Pick up	5	5	-
9	OFF	OFF	OFF	LOAD	-	-	-	500
10	OFF	OFF	OFF	INJECT	-	-	-	-
11	Start MEASUREMENT							
12	ON	ON	OFF	INJECT	Dispense	5	0.30	-
13	STOP MEASUREMENT							
14	OFF	OFF	OFF	INJECT	Pick up	5	5	-

208 a. Flow rate of S1; Flow rates of S2 and S3 are half that of S1 because of half volumes of S2 and S3 compared to S1.

209 2.7. Swimming pools samples

210 Samples were collected in five indoor swimming pools located in the Aix-Marseille Provence
211 Metropolis. These five pools were supplied with public water works and were continuously
212 disinfected with bleach at a set point concentration of 1 mg L⁻¹ Cl₂ (expressed as free chlorine).
213 Water samples were taken at a depth of 30 cm, stored at 4 °C and analyzed at the laboratory as
214 quick as possible (delay < 1 hour). The sampling took place at peak times with the objective of
215 having a maximum bather load (free swims or classes).

216

217 3. Results and discussion.

218 3.1. Inorganic chloramines standard solutions

219 DPD/FAS titrimetric standardization of chloramines standard solutions was used to provide
220 conversion percentages of chlorine and ammonia into chloramines. In the conditions described

221 in section 2.2, 98 % conversion of free chlorine to monochloramine was achieved within 60
222 minutes, and 95 % of monochloramine was also converted to dichloramine after acidification
223 of the monochloramine solution and completion of the reaction for 6 h.

224 Regarding the trichloramine solutions, different preparation methods were tested as described
225 in the literature [15,22,26]. Chlorine to ammonia molar ratio is usually 3:1 or 3.15:1 with acidic
226 pH between 2.3 and 2.8 but proposed ageing times vary considerably, from 1 h to 1 week. The
227 DPD/FAS determination of the solutions prepared in these various conditions in our laboratory
228 showed that there was always free chlorine and dichloramine in the trichloramine standard
229 solutions, even at very high chlorine to ammonium molar ratio (10:1) as was described by some
230 authors [22].

231 Preparation of trichloramine solutions (according to the protocol described in section 2) and
232 kinetic measurements of chloramines using DPD/FAS titration over 28 h ageing showed that
233 both dichloramine and trichloramine were present immediately after the beginning of the
234 experiment. After 45 min, concentration of trichloramine became stable for 6 h, followed by a
235 slow decrease in trichloramine concentration as well as an increase in dichloramine
236 concentration. Conversion yields of trichloramine were usually around 10 % (based on initial
237 ammonia concentration) after 45 min. This preparation method and ageing time has been chosen
238 for this study in order to reduce the daily preparation time of trichloramine standards.

239 3.2. Inorganic chloramines separation with direct detection

240

241 Optimization of the separation of inorganic chloramines was first studied using HPLC with
242 direct UV detection (on standard solutions with high concentrations of chloramines) as
243 preliminary experiments. Various mobile phases were tested in order to study the separation of
244 inorganic chloramines by HPLC using a monolithic column, which has never been documented

245 before in the literature (only with traditional particle-packed columns). Results in Table 2 show
 246 retention times of the three chloramines and resolution between MCA and DCA whose peaks
 247 were the lower-separated ones. The best compromise between TCA retention time (which
 248 corresponds to the total analysis time for three chloramines) and MCA-DCA resolution was a
 249 mobile phase made of 20 % acetonitrile, leading to short overall retention times and good
 250 separation of the whole chloramines. Representative chromatograms for the separation of the
 251 inorganic chloramines with this mobile phase are depicted in Figure S1 in the supplementary
 252 materials section. Addition of buffers (acidic or neutral) did not improve separation and was
 253 not selected for the rest of the study as it could displace equilibrium between chloramines during
 254 the column separation. Methanol was also tested as the organic solvent of the mobile phase, but
 255 results were not as good as with acetonitrile and it generated higher pressure in the system,
 256 which is not recommended for low-pressure MSC systems. Irrespective of the conditions tested,
 257 chlorine and MCA have not been able to be separated.

258 The same experimental conditions (monolithic column, mobile phase made of 20% MeCN,
 259 eluent flow rate of 0.5 mL min⁻¹) have then been applied to the MSC system coupled to a UV
 260 detector (without post-column reaction). Retention times and resolution of chromatographic
 261 peaks were close to those obtained with the HPLC system, giving proper pressures around 3
 262 bars. MCA and chlorine also co-eluted with this MSC system.

263 **Table 2** Retention times of inorganic chloramines for different mobile phase using HPLC with
 264 a C18 monolithic column (flow rate was 0.5 mL.min⁻¹).

Mobile phase	Retention time (min)			MCA-DCA resolution
	MCA	DCA	TCA	
H ₂ O	1.11	1.89	>30	2.61
Acetonitrile 10% - H ₂ O 90%	1.10	1.86	8.84	2.52

Acetonitrile 20% - H ₂ O 80%	1.09	1.68	6.17	2.29
Acetonitrile 25% - H ₂ O 75%	1.07	1.60	5.02	2.15
Acetonitrile 30% - H ₂ O 70%	1.04	1.53	4.30	1.81
Acetonitrile 40% - H ₂ O 60%	1.01	1.30	2.90	0.91
Acetonitrile 25% - Phosphate buffer pH 7 75%	1.08	1.60	5.02	2.17
Acetonitrile 25% - Acetate buffer pH 4.5 75%	1.07	1.58	5.01	2.11
Methanol 25%- H ₂ O 75%	1.02	1.50	6.34	1.97

265

266 3.3 Optimization of the post-column reaction with ABTS

267 ABTS was used as a post-column reagent being known to be able to react with halogenated
268 compounds to form the colored ABTS^{o+} radical, detectable and quantifiable at 405 nm ($\epsilon =$
269 $31600 \text{ M}^{-1} \text{ cm}^{-1}$). ABTS has indeed already been used as a colorimetric indicator for
270 trichloramine [22] and for detection of monochloramine after addition of nitrite [26] but has
271 never been studied for the simultaneous/sequential detection of all inorganic chloramines and
272 free chlorine.

273

274 3.3.1. Kinetic measurements by batch experiments

275 The objective of the optimization of the reaction between ABTS and chloramines was first to
276 find experimental conditions that ensured rapid and total reaction of the three inorganic
277 chloramines, in order to be used later as post-column reaction on our MSC system. Chlorine
278 and inorganic chloramines react with ABTS as follows:



283 One must therefore bear in mind that stoichiometry of TCA and DCA reactions are three times
284 and twice that of MCA or hypochlorous acid, respectively. Various experimental conditions
285 were tested (pH, addition of iodide catalyst...) in batch experiments (quartz cell) and all
286 inorganic chloramines (and hypochlorous acid) were found to react quickly and quantitatively
287 with ABTS at pH below 2, without catalyst. Figure 2 displays the kinetics of the $\text{ABTS}^{\circ+}$
288 formation for all studied compounds with ABTS dissolved in 0.4 M HCl. All reactions were
289 complete after 30 s, which was fast enough to be used for post-column reaction. Measured
290 absorbance after reaction of DCA ($10^{-5} \text{ mol L}^{-1}$) with ABTS was twice that of MCA and
291 chlorine ($10^{-5} \text{ mol L}^{-1}$), as expected. Regarding TCA, only mixtures of TCA, DCA and HOCl
292 have been able to be formed, and the absorbance depicted for the reaction with TCA
293 (concentration of TCA at $10^{-5} \text{ mol L}^{-1}$ in the mixture) was calculated by subtracting the
294 absorbance of the expected $\text{ABTS}^{\circ+}$ produced by reaction with DCA and HOCl from the total
295 absorbance (originating from the reaction with the three species).

296 The reaction between ABTS and inorganic chloramine and free chlorine is highly dependent on
297 the reaction pH value, and up to now, discrimination between free chlorine and MCA was not
298 achievable, these two compounds being not separated after the chromatographic step. In our
299 previous experiments, ABTS reacted with all chlorinated compounds at acidic pH and with any
300 of them at neutral or basic pH. However, a fine-tuning of the pH around 3 allowed us to separate
301 MCA and HOCl (Fig. 3). MCA did not react with ABTS at pH 3, whereas HOCl still exhibited
302 quantitative and fast reaction. Differentiation between MCA and HOCl was thus possible by

303 running two experiments: one with ABTS in HCl (ABTS solution A) for free chlorine and
304 inorganic chloramines, and one with ABTS at pH 3 (ABTS solution B) for determination of
305 free chlorine.

306

307 3.3.2. Optimization on the MSC system.

308 The MSC system has then been optimized in terms of the post-column reaction by varying
309 several operational parameters: the ratio between flow rates of mobile phase and ABTS
310 solution, the mobile phase flow rate and the tubing volume /length between the mixer and the
311 detector. As the mobile phase and the ABTS solution were delivered by the same piston pump
312 (by use of a multi-syringe pump in order to simplify the experimental set-up), the only way to
313 change the flow-rates ratio was to change the volume of the syringe of ABTS while keeping
314 that of mobile phase constant (5 mL). Therefore, flow rate ratios of 1, 2 or 5 have been able to
315 be obtained by using 5 mL, 2.5 mL or 1 mL syringes for ABTS. For these experiments, flow
316 rate of mobile phase was set at 0.3 mL min⁻¹, pressure was 2.5 bars, and the volume of the
317 tubing between the mixer and the detector was 100 µL. Table 3 shows that peak areas and
318 resolution between MCA and DCA peaks were better when ABTS flow rate was half that of
319 the mobile phase (which corresponded to the volume ratios used in quartz cells experiments).
320 This ratio was selected for the rest of the study.

321 **Table 3** Influence of the ratio between mobile phase and ABTS solution flow rates on MCA
322 and DCA peaks.

323

Monochloramine	Dichloramine	Resolution
----------------	--------------	------------

Ratio of flow rate	Retention		Retention		
	time (min)	Area of peak	time (min)	Area of peak	
1	2.05	10.1	3.5	7.4	1.5
2	2.8	11.5	4.03	9.6	2.01
5	2.71	10.1	3.7	4.1	0.7

324

325 The mobile phase flow rate and the tubing volume between the mixer and the detector had a
326 direct influence on the post-column reaction time. Volumes from 100 to 300 μL and two flow
327 rates (0.3 mL min^{-1} and 0.5 mL min^{-1}) were tested, and best results (peak areas and resolution)
328 were obtained with a flow rate of 0.3 mL min^{-1} and a tubing volume of $100 \mu\text{L}$ (Table 4).
329 Considering the mobile phase and ABTS solution flow rates (global flow rate of 0.45 mL min^{-1})
330 1), this volume corresponded to a reaction time of 13.3 sec, which seemed sufficient to obtain
331 the best compromise between peak areas and resolution.

332 **Table 4** Influence of the mobile phase flow rate and of the volume of the tubing between the
333 mixer and the detector. Flow rate of ABTS was half that of the mobile phase.

334

Flow rate (mL min^{-1})	Volume of the tubing (μL)	Monochloramine		Dichloramine		Resolution
		Retention time (min)	Area of peak	Retention time (min)	Area of peak	
0.3	100	2.88	11.5	4.03	9.6	2.01
0.5	100	1.8	4.05	2.6	1.57	2.15
0.3	200	3.11	12.4	4.35	10.9	1.57
0.5	200	2.01	7.6	2.66	3.7	1.78

0.3	300	3.36	10.9	4.61	8	1.69
0.5	300	2.08	7.3	2.82	6.7	1.51

335

336

337 3.4. Interferences from organic chloramines and other halogenated compounds

338 DPD-based methods for inorganic chloramines measurements are known to suffer from strong
339 interferences from other chlorinated compounds, especially from organic chloramines which
340 are formed during chlorination of organic amines and amino acids [15]. These interferences
341 result in “false positives” for inorganic chloramines determination (appearing as MCA or DCA)
342 with DPD standard methods, which strongly hinders application of this method to real samples
343 with complex matrix content. To assess interferences from organic chloramines on our MSC
344 system, glycine was selected as a model organic amino compound. This latter one was indeed
345 already demonstrated to be chlorine-reactive forming organic chloramines (N-chloro or N-
346 dichloroglycine) [27].

347 The ability of the MSC system to differentiate inorganic and organic chloramines species was
348 demonstrated as follows : 1 mL of a glycine solution (100 mg L⁻¹ as N) was added to 220 mL
349 of 0.01 M phosphate buffer (pH 7) in a flask, then aliquots of free chlorine stock solution were
350 added so that chlorine/nitrogen mass ratio were from 2 to 16 (chlorine/nitrogen molar ratio from
351 0.4 to 3.2). The concentration of residual chlorine was then determined by the DPD/FAS
352 titration method (Fig. 4a.) and by the MSC system after 30 min (Fig. 4b). As expected, the lack
353 of selectivity of DPD/FAS titration was highlighted, as MCA and DCA were quantified in high
354 quantities while it has already been proven by MIMS measurements (during an experiment
355 performed under the same conditions) that none of them were able to be actually present at low
356 Cl/N mass ratios (<14) [15]. On the opposite, our MSC system only detected free chlorine at

357 high Cl/N mass ratio, which proved that organic chloramines did not interfere with our system.
358 Indeed, organic chloramines generated by the chlorination of glycine did not react with the
359 ABTS solution A (or B), as was demonstrated by a direct test in quartz cell. Therefore, coelution
360 of an organic chloramine with an inorganic chloramine would not cause interference on the
361 determination of MCA, DCA or TCA. The same results were obtained during chlorination of
362 asparagine (data not shown).

363 Interferences from other chlorinated disinfection by-products or chlorine-related compounds
364 were also assessed. N-chlorourea, chloroform, bromoform (trihalomethanes), mono-, di- and
365 tri-chloroacetic acids (haloacetic acids) and cyanuric acid (chlorine stabilizer) showed no
366 analytical response with our system, due to the non-reactivity of these compounds with ABTS.

367 Reactivities of inorganic bromamines were also studied. The results showed that NH_2Br
368 coelutes with NH_2Cl , while NHBr_2 and NHBrCl had the same retention time as NHCl_2 .
369 Nevertheless, NBr_3 has been able to be separated from NCl_3 as their retention times were
370 different (13.9 min for trichloramine and 19.6 min for tribromamine). Further studies are in
371 progress in our laboratory to differentiate inorganic bromamines and chloramines by
372 optimization of the ABTS reagent.

373 3.5. Analytical features

374 The analytical procedure of the MSC system was evaluated under the optimized experimental
375 conditions, with ABTS solution A for HOCl and inorganic chloramines determination, and with
376 ABTS solution B for HOCl only (Table 5). Excellent linear regression coefficients were
377 obtained for all chloramines up to at least $7100 \mu\text{g eq.Cl}_2 \text{ L}^{-1}$ ($100 \mu\text{mol eq.Cl}_2 \text{ L}^{-1}$). The limits
378 of detection (LD) and of quantification (LQ) were estimated using the classical 3s and 10s
379 approaches respectively, *i.e.* calculation of LD and LQ through analysis of the standard
380 deviation of blank measurements ($n=8$). Limits of detection for the inorganic chloramines were

381 all around $10 \mu\text{g eq.Cl}_2 \text{ L}^{-1}$, which was comparable to the DPD titrimetric method and 2 to 10
 382 times better than usual MIMS performances [14]. Limits of detection on our MSC system
 383 without post-column reaction (direct UV detection) were 100 to 500 times lower, proving
 384 efficiency of the ABTS detection. Slope of the linear regression equations of HOCl or inorganic
 385 chloramines were all similar after reaction with ABTS (when concentrations were expressed as
 386 equivalent $\text{Cl}_2 \text{ L}^{-1}$, and considering stoichiometry of equations presented in section 3.1), proving
 387 that chloramines concentrations were not affected by the chromatographic separation using our
 388 experimental conditions (monolithic column for fast separation, mobile phase with water),
 389 contrary to what has been previously described when using traditional HPLC method [17].
 390 Regarding sample throughput, the overall procedure took about 30 min, including the two
 391 cycles with ABTS solution A and B, allowing the analysis of 2 samples/h.

392

393 **Table 5** Analytical features of the MSC system developed

394

Analytical parameter	MCA (or HOCl) ^a	DCA ^a	TCA ^a	HOCl ^b
Limit of detection ($\mu\text{g eq.Cl}_2 \text{ L}^{-1}$)	9.3	9.9	10.0	29.2
Limit of quantification (μg $\text{eq.Cl}_2 \text{ L}^{-1}$)	31.2	33	33.5	97.4
Linear working range($\mu\text{g eq.Cl}_2 \text{ L}^{-1}$)	31-7100	33-7100	34-7100	97-7100
Linear regression equation ^c	$A=0.00116xC+0.23$	$A=0.0113xC+0.25$	$A=0.0124xC+0.06$	$A=0.00926xC+0.061$

R ²	0.997	0.998	0.999	0.986
RSD (%) ^d	4.9	3.8	4.4	3.7
Retention time (min)	3.0	4.05	13.9	3.0
RSD of retention time (%)	1.2	1.8	0.4	1.6

395 *a. with ABTS solution A; b. with ABTS solution B; c. A was the area of the peak, C was the analyte concentration ($\mu\text{g eq.Cl}_2 \text{L}^{-1}$)*
396 *); d. RSD was calculated on a 200 $\mu\text{g Cl}_2 \text{L}^{-1}$ standard, n=6 replicates.*

397

398 3.6. Application to real samples

399 Our multisyringe analytical system was applied to real samples collected in swimming pools of
400 Aix-Marseille Provence Metropolis. We first intended to compare our results with MIMS
401 measurements, which was not available in our laboratory. Samples were sent to another French
402 laboratory equipped with a MIMS for comparison purposes, but quantification for MCA and
403 DCA was unfortunately not possible on real samples, due to interferences from other
404 compounds and between inorganic chloramines. Standard addition method was also not
405 possible for validation, as addition of inorganic chloramines to swimming pool samples resulted
406 in modification of chlorine-inorganic chloramine equilibrium and very large differences
407 between added and measured concentrations in these samples.

408 Therefore, we chose to assess the accuracy of the multisyringe system by comparison of the
409 results obtained with our MSC system and those obtained by the DPD/FAS titrimetric assay
410 (Table 6). While measurements for free chlorine were in good agreement (no difference at the
411 0.05 level using Student's t test), significant differences appeared for inorganic chloramines.
412 MCA was detected by DPD/FAS assay in two samples in low concentrations (2 and 3) but not
413 detected by the MSC procedure. DCA measurements resulted in the largest differences between

414 both methods, with DPD/FAS results always much higher than MSC results. This large
 415 discrepancy has been able to be explained by the inability of the DPD/FAS assay to differentiate
 416 between inorganic and organic chloramines [28], which was further demonstrated in this study
 417 on swimming pool samples. Samples were collected during highly crowded hours (except
 418 sample 1 with no inorganic chloramines detectable by the MSC method), and significant
 419 amounts of organic chloramines or other DPD/FAS interferents could have been expected due
 420 to the reaction of chlorine with organic nitrogenous compounds brought by swimmers. TCA
 421 was not quantified by either methods.

422 Our method could be also applied to other types of waters such as drinking waters, especially
 423 when MCA is used as a secondary disinfectant such as in the USA (where significant
 424 concentrations of MCA and DCA are expected).

425

426 **Table 6** Comparative results between our multisyringe system (MSC) and titrimetric assay
 427 (DPD/FAS) on various swimming pool samples (mg eq.Cl₂ L⁻¹, mean ± standard deviation,
 428 n=2 replicates).

429

	HOCl		MCA		DCA		TCA	
	DPD/FAS	MSC	DPD/FAS	MSC	DPD/FAS	MSC	DPD/FAS	MSC
1	1.52±0.03	1.60±0.09	<LQ	<LQ	0.58±0.00	<LQ	<LQ	<LQ
2	1.50±0.01	1.52±0.04	0.20±0.00	<LQ	1.02±0.02	0.37±0.05	<LQ	<LQ
3	1.7±0.04	1.60±0.11	0.1±0.01	<LQ	0.7±0.03	0.68±0.04	<LQ	<LQ
4	1.2±0.00	1.15±0.06	<LQ	<LQ	0.98±0.02	0.06±0.01	<LQ	<LQ

5	1.1±0.03	1.06±0.02	<LQ	<LQ	0.5±0.01	0.22±0.03	<LQ	<LQ
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430

431 **4. Conclusion**

432 In this study, a MSC system based on a chromatographic separation with a monolithic column
433 and post-column derivatization with ABTS was developed for the analysis of inorganic
434 chloramines in water. Use of a mobile phase containing acetonitrile and water enabled
435 successful separation of the chloramines with good resolution and limited pressure in the flow
436 system, leading only to the coelution of chlorine and monochloramine. Optimization of the
437 ABTS reaction resulted in the preparation of two ABTS reagent: one for the quantification of
438 free chlorine only, and one for the quantification of chlorine and the three inorganic
439 chloramines. Mono-, di- and trichloramine were quantified by the MSC system with detection
440 limits around 10 µg eq.Cl₂ L⁻¹, a large linear working range and a very good repeatability.
441 Rather as DPD-based methods, our method was not affected by the presence of organic
442 chloramines. This method applied and validated on real samples represents a promising and
443 cheaper alternative to MIMS, both in laboratory (use of the same method on a widely available
444 LC-UV equipment is also possible) and on-site analysis of inorganic chloramines.

445

446 **Acknowledgements**

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449

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542

543 **Figure captions**

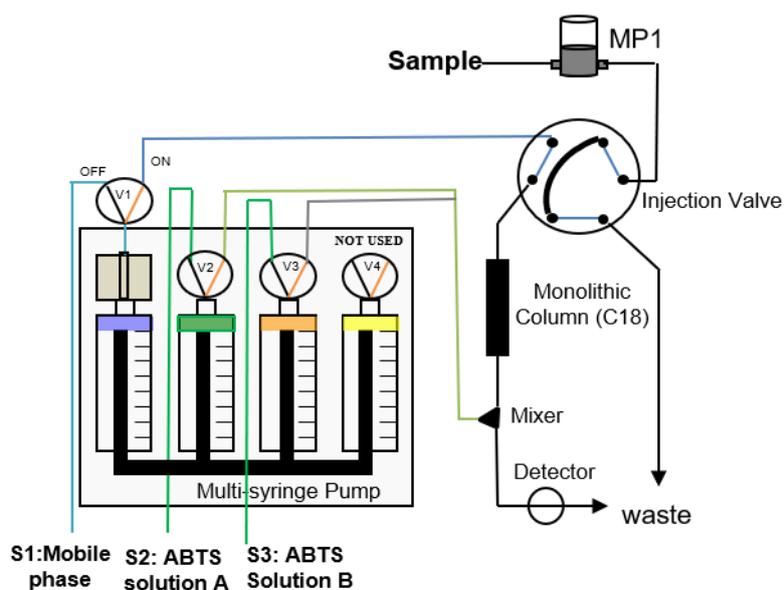
544 *Figure 1- Descriptive scheme of the multi-syringe chromatography manifold for the analysis of*
545 *inorganic chloramines. MP1=Solenoid micro-pump, V1, V2 and V3= solenoid valves.*

546 *Figure 2- Kinetic of the reactions between ABTS solution A (prepared in HCl 0.4M) and free*
547 *chlorine/inorganic chloramines. Protocol: 1 mL sample + 2 mL ABTS solution A. The*
548 *concentration of free chlorine, MCA, DCA and TCA were 10^{-5} mol L⁻¹.*

549 *Figure 3- Kinetic of the reactions between ABTS solution B (prepared in pH 3 buffer) and free*
550 *chlorine or MCA. Protocol: 1 mL sample + 2 mL ABTS solution B. The concentration of free*
551 *chlorine and MCA were 10^{-5} mol L⁻¹.*

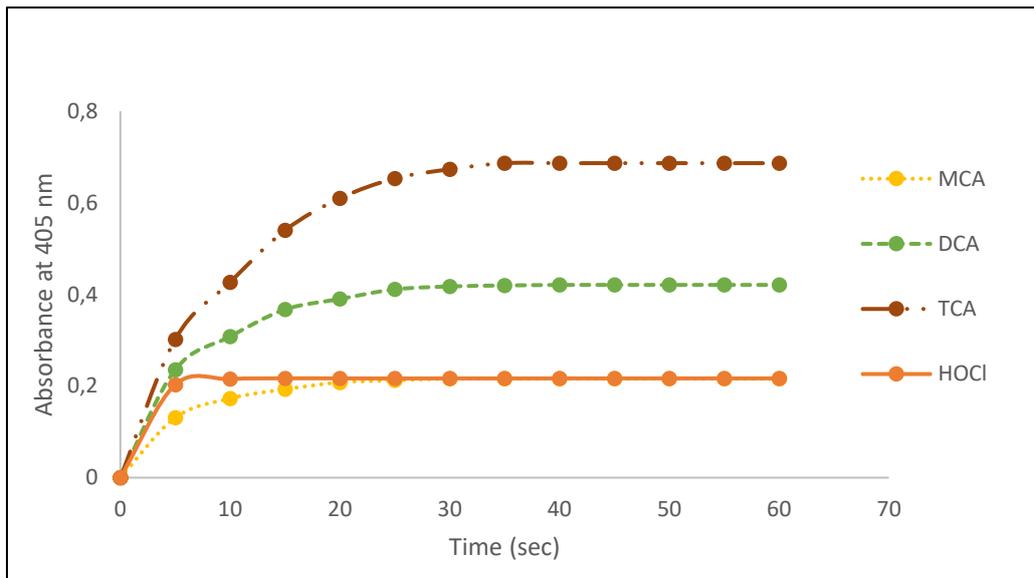
552 *Figure 4- Residual chlorine concentration as function of mass ratio Cl/N after 30 min of*
553 *chlorination of an aqueous solution containing glycine a) measured by DPD/FAS titration, b)*
554 *measured by the MSC system.*

555



556

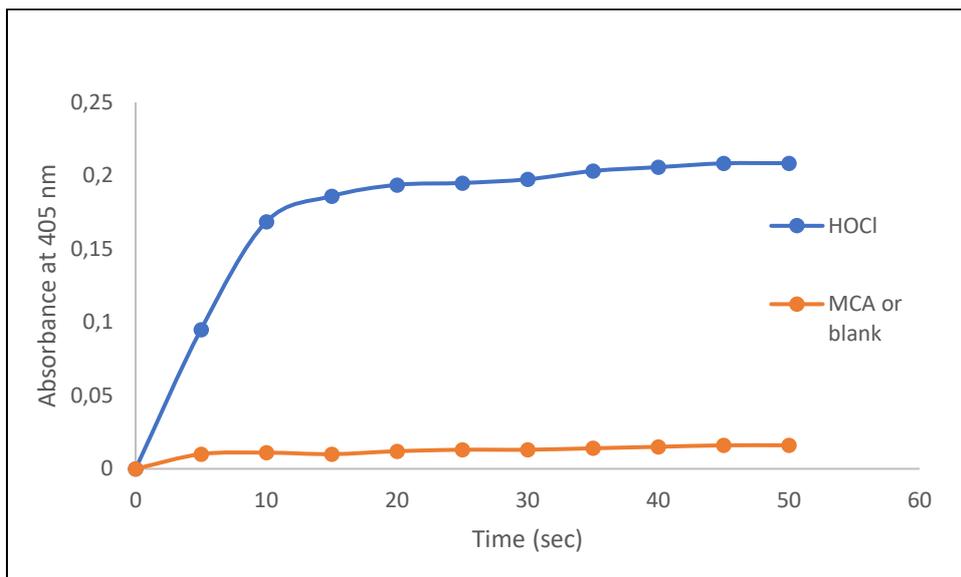
557 *Figure 1.*



558

Figure 2

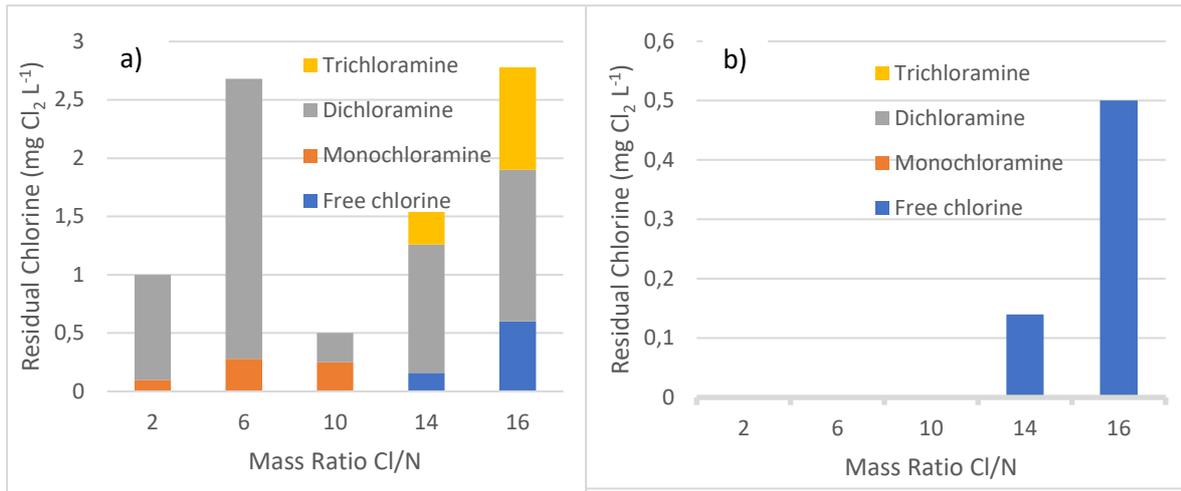
559



560

Figure 3

561



562

563 Figure 4

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565