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Method for the fast determination of bromate, nitrate and nitrite by ultra performance liquid chromatography–mass spectrometry and their monitoring in saudi arabian drinking water with chemometric data treatment

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1 Method for the fast determination of bromate, nitrate and nitrite by Ultra Performance Liquid  
2 Chromatography–Mass Spectrometry and their monitoring in Saudi Arabian drinking water with  
3 chemometric data treatment.

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## 28 ABSTRACT

29 A rapid, sensitive and precise method for the determination of bromate ( $\text{BrO}_3^-$ ), nitrate ( $\text{NO}_3^-$ )  
30 and nitrite ( $\text{NO}_2^-$ ) in drinking water was developed with Ultra performance Liquid  
31 Chromatography–Mass Spectrometry (UPLC-ESI/MS). The elution of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$   
32 was attained in less than two minutes in a reverse phase column. Quality parameters of the  
33 method were established; run-to-run and day-to-day precisions were  $<3\%$  when analysing  
34 standards at  $10 \mu\text{g L}^{-1}$ . The limit of detection was  $0.04 \mu\text{g NO}_2^- \text{L}^{-1}$  and  $0.03 \mu\text{g L}^{-1}$  for both  
35  $\text{NO}_3^-$  and  $\text{BrO}_3^-$ . The developed UPLC-ESI/MS method was used to quantify these anions in  
36 metropolitan water from Saudi Arabia (Jeddah, Dammam and Riyadh areas) and commercial  
37 bottled water (from well or unknown source) after mere filtration steps. The quantified levels of  
38  $\text{NO}_3^-$  were not found to pose a risk. In contrast,  $\text{BrO}_3^-$  was found above the maximum  
39 contaminant level established by the US Environmental Protection Agency in 25 and 33% of the  
40 bottled and metropolitan waters, respectively.  $\text{NO}_2^-$  was found at higher concentrations than the  
41 aforementioned limits in 70 and 92% of the bottled and metropolitan water samples,  
42 respectively. Therefore, remediation measures or improvements in the disinfection treatments are  
43 required. The concentrations of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  were mapped with Principal Component  
44 analysis (PCA), which differentiated metropolitan water from bottled water through the  
45 concentrations of  $\text{BrO}_3^-$  and  $\text{NO}_3^-$  mainly. Furthermore, it was possible to discriminate between  
46 well water; blend of well water and desalinated water; and desalinated water. The point or source  
47 (region) was found to not be distinctive.

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51 KEYWORDS: bromate; nitrate; nitrite; UPLC-MS; Saudi Arabia; drinking water

52  
53 INTRODUCTION

54  
55 Water disinfection is an important step to ensure that water can be consumed safely.  
56 Typical disinfection methods to destroy pathogens include treatment with chemical reactive  
57 agents (i.e chlorine, chlorine dioxide, chloramines, ozone, and potassium permanganate) or  
58 physical means (i.e irradiation with UV or nanofiltration) [1]. Side effect of some these  
59 treatments are the generation of disinfection by-products (DBPs) when disinfection agents react  
60 with substance already present naturally in the water to be treated. The risks to health of DBPs is  
61 considered to be low compared to the exposure to pathogens [2]. Despite that non-chemical  
62 disinfection methods would avoid DBPs, small doses of chlorine or mono-chloramine are added  
63 to water to ensure its safety after distribution [2].

64 Bromide, which is a majority element in seawater (i.e 67 mg/L) [3], is present in water  
65 used in the production of metropolitan drinking water in Saudi Arabia. Bromate ( $\text{BrO}_3^-$ ) is a  
66 DBP that can be generated from the ozonation of naturally occurring bromide present in such  
67 source water [2,4]. Therefore, desalinated seawater can lead to high levels of  $\text{BrO}_3^-$  due to  
68 remaining levels of its precursor before the oxidising treatment [5]. In a previous study carried  
69 out by the authors,  $\text{BrO}_3^-$  was found between 8-75  $\mu\text{g L}^{-1}$  in desalinated water [6].  $\text{BrO}_3^-$  was  
70 found to be carcinogenic in animals which revealed the need to control this substance in drinking  
71 water [7]. In 1998, the International Agency of Research Cancer (IARC) listed the  $\text{BrO}_3^-$  in  
72 Group 2B (possibly carcinogenic to humans) [8]. Thereafter, the World Health Organization  
73 (WHO) and US Environmental Protection Agency (EPA) set up provisional guideline value and

74 a maximum contaminant level (MCL), respectively, at  $10 \mu\text{g BrO}_3^- \text{L}^{-1}$  in drinking water [2,4,9]  
75 and the public health goal at “zero” [4].

76 Nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) have a different origin than  $\text{BrO}_3^-$  in drinking water. In  
77 nature, both  $\text{NO}_3^-$  and  $\text{NO}_2^-$  derive from the nitrogen cycle in plants and soils; they originate  
78 from the microbial digestion of nitrogen rich sources such as plant tissues, faeces or nitrogen-  
79 based fertilisers [10-11]. Both  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are highly soluble species that can consequently  
80 leach to surface and ground water [12-14]. This has detrimental effects on biodiversity as well as  
81 on human beings; for instance; it can cause eutrophication [2, 10]; methemoglobinemia disease  
82 in infants [15-18] and they have been associated with increased incidence of cancer [10]. Many  
83 environmental regulatory organizations have set the guidelines for  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in drinking  
84 water. The EPA has set the Maximum Contaminant Level (MCL) for  $\text{NO}_3^-$  at  $10 \text{ mg L}^{-1}$  in  
85 drinking water [4], which coincides with the standard of quality in bottled water set by the  
86 International Bottled Water Association (IBWA) [19]. In contrast the WHO and European  
87 Commission set up the guideline level at  $50 \text{ mg L}^{-1}$  [2, 20]. For  $\text{NO}_2^-$ , the EPA and IBWA has  
88 set the MCL and standard of quality, respectively, at  $1 \text{ mg L}^{-1}$  in drinking water [4,19]; the  
89 current WHO guideline value is  $3 \text{ mg L}^{-1}$  [2] but the limit in Europe is more restrictive:  $0.5 \text{ mg}$   
90  $\text{L}^{-1}$  [20].

91 Monitoring studies are necessary to know the level of exposure to  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$   
92 and identify potential hotspots. Many analytical procedures have been developed to assess the  
93 levels of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in drinking water. Ion chromatography is recognized as the  
94 method with best analytical achievability for the determination of  $\text{BrO}_3^-$  by WHO [2]; ion  
95 chromatography-conductivity detection method has been extensively applied for the analysis of  
96 such types of compounds in water matrices [21-22]. The low running cost of capillary zone

97 electrophoresis and typical high separation efficacy makes it also an attractive technique for the  
98 analyses of anions in drinking water [23]. Improvements in stationary phases that lead to the  
99 development of Ultra Performance Liquid Chromatography (UPLC) implied gains in analysis  
100 throughput and sensitivity compared to earlier methods. UPLC, in combination with the superior  
101 confirmatory capability of mass spectrometry (MS), made UPLC-MS a technique of choice.  
102 Earlier works by our group showed the potential of UPLC-MS for the individual analysis of  
103  $\text{BrO}_3^-$  and  $\text{NO}_3^-$  [6, 24], however ion suppression made not possible the simultaneous analysis  
104 of such similar anions. A method suitable for the fast determination  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  has  
105 been developed in this work. The developed method will be applied to quantify the potential  
106 hazardous species in metropolitan and bottled water samples from the Kingdom of Saudi Arabia.  
107 The levels of the study anions will be examined with Principal Component Analysis (PCA), for  
108 the first time to our knowledge, to establish whether  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  can be used to  
109 identify the type of sample (desalinated water; well water; desalinated and ground water) from  
110 different Saudi regions and possible counterfeit bottled water.

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118 2. Materials and methods

119 2.1 Materials. All solvents and chemicals used in this study were of HPLC or analytical grade,  
120 obtained from Merck (Darmstadt, Germany). Potassium bromate (ACS reagent,  $\geq 99.8\%$ ), and,  
121 sodium nitrate and sodium nitrite of ReagentPlus<sup>®</sup> grade (assay purity  $\geq 99.0\%$ ) were obtained  
122 from Sigma-Aldrich (Steinheim, Germany). Ultrapure water was purified by means of Milli-Q  
123 water purification system (Millipore Corporation, Bedford, USA). Stock standard solutions of  
124  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  at concentration level  $500 \text{ mg L}^{-1}$  were prepared in ultrapure Milli-Q  
125 water and used for further dilutions. Standard mixtures of the nitrate and nitrite were prepared by  
126 weight. Standard solutions and water samples were filtered through a  $0.22 \mu\text{m}$  PTFE syringe  
127 filter (Macherey-Nagel GmbH, Düren, Germany) before being injected into the UPLC system.

128  
129 2.2 Sample preparation and quantitative analysis. Metropolitan water was obtained from  
130 different locations using clear glass bottles (500 mL) supplied by the Saudi Arabian nationalised  
131 company Saline Water Conversion Corporation. Bottled water (non-carbonated), from various  
132 trademarks, was purchased from hypermarket in Riyadh, Saudi Arabia. These bottled water  
133 samples had been treated with ozone. Metropolitan and bottled samples were stored in  
134 refrigerator at  $4^\circ\text{C}$  and analysed within two days to avoid microbial growth. Blank (ultrapure  
135 water) and quality control samples were analysed in each batch to ascertain that contamination of  
136 water samples did not arise and detection sensitivity of the target analytes was stable throughout  
137 the analysis. The quantification was carried out by external calibration in triplicate and the  
138 quantification of the recovery rates was carried out with standard addition method consisting of  
139 samples spiked with  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  at four (50, 200, 400 and 500%) levels in addition to  
140 non-spiked samples (duplicate). Recovery rates were obtained from the slope obtained when

141 plotting the correlation between the added amount of bromate, nitrate and nitrite, and the amount  
142 found.

143

144 2.3 UPLC-ESI/MS analysis. The chromatographic analysis of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  was  
145 carried out using a Waters Acquity® UPLC system (Milford USA) with an Acquity® BEH  $\text{C}_{18}$   
146 column (50 mm  $\times$  2.1 mm i.d., 1.7  $\mu\text{m}$  particle size) (Waters, Milford, USA) column. A pre-  
147 column, VanGuard™ BEH  $\text{C}_{18}$  1.7  $\mu\text{m}$  was used to protect the analytical column during the  
148 analysis. The optimal chromatographic conditions for the analysis of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  was  
149 obtained using isocratic elution mode consisting of 75% methanol in water (v/v) at a flow rate of  
150 200  $\mu\text{L min}^{-1}$ . The temperature of the analysis was controlled in an oven at 25 °C. The sample  
151 injection volume was 5  $\mu\text{L}$ . A column with polar stationary phase Water Acquity® BEH Amide  
152 column (50 mm  $\times$  2.1 mm i.d., 1.7  $\mu\text{m}$  particle size) was also tested.

153 The detection of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  was performed on Quattro Premier™ triple quadrupole  
154 mass spectrometer (Micromass, Milford, USA) with an electrospray ionization source (Z-spray)  
155 coupled with an Acquity® UPLC system. The instrument was operated in negative ionization  
156 mode. The data acquisition in full scan mode (m/z 40-200) was used to select the most abundant  
157 ions from each analyte. Selected Ion Recording (SIR) was applied for their detection with higher  
158 sensitivity. Dwell time was 0.025 s and the total scan cycle was 1 s. Factors affecting the ion  
159 transmission parameters were optimized by infusing a standard mixture of sodium nitrate,  
160 potassium bromate and sodium nitrite solution at 10  $\text{mg L}^{-1}$ . The optimized working parameters  
161 were as follows. Cone voltage: 40; 46; 40; 38 V for m/z 46.2 ( $\text{NO}_3^-$ ), m/z 62.2 ( $\text{NO}_2^-$ ), m/z  
162 129.0 ( $^{81}\text{BrO}_3^-$ ) and m/z 127.0 ( $^{79}\text{BrO}_3^-$ ), respectively. Capillary voltage 3.2 kV; source  
163 temperature, 120°C; desolvation temperature, 300°C; cone gas flow rate, 60  $\text{L h}^{-1}$ ; desolvation



164 gas flow rate, 600 L h<sup>-1</sup>. Nitrogen (99.99% purity), produced with a Peak Scientific nitrogen  
165 generator model NM30LA (Inchinann, United Kingdom), was used as cone gas. Argon (99.99%  
166 purity), obtained from Speciality Gas Centre (Jeddah, Saudi Arabia), was used as collision gas.  
167 The primary vacuum for the mass spectrometer was provided with an Oerlikon rotary pump,  
168 model SOGEVAC SV40 BI (Paris, France). The data acquisition and processing were performed  
169 using MassLynx V4.1 software.

170 Quality parameters of the optimised UPLC-MS method were assessed. Linearity was measured  
171 between 0.1 and 1000 µg·L<sup>-1</sup>; limits of detection (LOD) were established at a signal-to-noise  
172 ratio of 3; Run-to-run precision was estimated from six replicate injections of a mixture of  
173 BrO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> standard at 0.05 µg·mL<sup>-1</sup> in the same day, and day-to-day precision was  
174 measured from six replicate injections of the same standard along three consecutive days.

175

#### 176 2.4 Chemometric analysis.

177 The Unscrambler® X version 10.3 (CAMO Software AS., Norway) was used to build a Principal  
178 Components Analyses (PCA) model from the concentration of BrO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> in  
179 metropolitan and bottled waters. In order to give the same weight to every value (BrO<sub>3</sub><sup>-</sup> was  
180 found at µg·L<sup>-1</sup> level in contrast with the other two analytes, which were present at levels of  
181 mg·L<sup>-1</sup>), BrO<sub>3</sub><sup>-</sup> concentrations were given a weight of 1000 times higher than its quantified  
182 values. Validation of PCA models relied on the leave-one-out cross-validation, in which each  
183 particular sample was predicted by using the remaining samples as standards for building the  
184 calibration model.

185

## 186 3. Results and discussion

187 3.1 Optimisation of UPLC conditions. The separation of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  with reverse  
188 phase columns ( $\text{C}_8$ ,  $\text{C}_{18}$ ) was challenging because the interaction of the 3 anions with the  
189 stationary phase was weak and very similar among them. Their behaviour was dominated by  
190 their net negative charge, which becomes stabilised by solvation in the mobile phase. Higher  
191 level of retention was intended when using Hydrophilic Interaction Chromatography (HILIC)  
192 with amide groups in the stationary phase. Mobile phase compositions, constituted with  
193 methanol/acetonitrile in water at different proportions (0-100%), were tested at flow rate  
194 between 100 and 500  $\mu\text{L min}^{-1}$ . The addition of formic acid (0.1 – 1%) in the mobile phase was  
195 also investigated as a way to shield the charge of the analytes or displace the equilibria towards  
196 nitrous acid (case of  $\text{NO}_2^-$ ) and achieve higher retention for the neutral species. All the  
197 conditions studied lead to very limited or no separation among  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ . The  
198 HILIC column (with mobile phase methanol: water 50:50, v/v) made possible to achieve slightly  
199 higher retention for nitrite and nitrate (retention time 0.80 and 0.82 min, respectively), however  
200 the symmetry factor of the peaks led to limited peak height and sensitivity and for that reason  
201 that column was discarded. In terms of retention and separation in reversed phase  
202 chromatography, the percentage of organic solvent in the mobile phase did not cause a great  
203 effect on the retention of  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .  $\text{BrO}_3^-$  presented the lowest retention of the three and  
204 its signal was affected by the composition of the mobile phase. In a previous work, a mobile  
205 phase of water with 0.1% formic acid in water, at 200  $\mu\text{L min}^{-1}$ , led to a retention time of 0.4  
206 min. Despite that the added acid reduced peak tailing, the peak asymmetry factor for  $\text{BrO}_3^-$   
207 (measured at 10% of the peak height) was 1.1 [6]. In this work, a mobile phase of 75% methanol  
208 in water, in absence of formic acid, led to higher retention (0.7 minute) and improved peak

209 symmetry (tailing factor: 1.0) at  $200 \mu\text{L min}^{-1}$ , being the dead volume 0.1 min at these  
210 conditions. Peak symmetry and separation from the dead volume was poorer with a  $\text{C}_8$  column  
211 when compared to a  $\text{C}_{18}$ . The latter, an Acquity<sup>®</sup> BEH  $\text{C}_{18}$  column with dimension  $50 \text{ mm} \times 2.1$   
212  $\text{mm i.d.}$ ,  $1.7 \mu\text{m}$  particle size, with a mobile phase consisting of methanol/water (75:25, v/v) in  
213 isocratic elution at flow rate  $200 \mu\text{L min}^{-1}$ , was adopted as the optimal conditions which lead to  
214 the chromatogram shown in Figure 1. The chromatographic peaks from the analytes were not  
215 resolved but their co-elution was not found to affect their detection. Acetonitrile was not found  
216 advantageous with respect to the results achieved with methanol. Comparatively, low flow rates,  
217 which favoured ionic evaporation and efficient desolvation in the electrospray ionization source,  
218 were found to be advantageous for the analysis of the anions. At  $200 \mu\text{L min}^{-1}$ , chromatographic  
219 peaks presented peak width that could be defined with a minimum of 15 scan points and analysis  
220 time of just 1 min.

221

222 3.2 Optimisation of the MS conditions and UPLC-MS quality parameters.

223 The electrospray (ESI) ionization conditions related with desolvation, ionic evaporation and  
224 transmission of the analyte ions were investigated: cone voltage (10–100 V), capillary voltage  
225 (2.0–4.5 kV), source temperature (80–150 °C), desolvation temperature (250–450 °C) and  
226 desolvation gas ( $300\text{--}700 \text{ L h}^{-1}$ ). The ESI/MS parameters that offered the best sensitivity are  
227 provided in section 2.1. Temperatures and source gases in the higher range were found to  
228 provide higher sensitivity because these favoured ionic evaporation. However, the high  
229 percentage of organic solvent in the mobile phase (75%) and relative low flow rate prevented  
230 needing extreme settings for optimal sensitivity.

231 The relationship between the concentration of the analytes and their response was assessed across the  
232 range 0.1-1000  $\mu\text{g L}^{-1}$  and was found to be linear; calibration curves with  $r^2 < 0.999$  were obtained  
233 in all cases and t correlation test confirmed the correlation (P 0.05). The working range was  
234 limited to 0.1-100  $\mu\text{g L}^{-1}$  given that the concentrations of the analytes were expected in that  
235 range. Quality parameters obtained under optimal conditions are given in Table 1. The  
236 instrumental limit of detection (S/N=3) for  $\text{NO}_2^-$  was 0.04  $\mu\text{g L}^{-1}$  and for  $\text{NO}_3^-$  and  $\text{BO}_3^-$  was  
237 0.03  $\mu\text{g L}^{-1}$ . Run-to-run and day-to-day precisions were  $< 3\%$  (n = 6) for the three anions when  
238 analyzing a standard mixture solutions at 10  $\mu\text{g L}^{-1}$ . The sensitivity achieved for  $\text{NO}_3^-$  did not  
239 decrease when compared to its individual analysis with UPLC-MS [24]. It improved previous  
240 LC-MS method using reversed phase chromatography where LODs for nitrate and nitrite were 1  
241  $\mu\text{g L}^{-1}$  and 12  $\mu\text{g L}^{-1}$  [25], respectively. The sensitivity of the developed method was, however,  
242 about 10 times poorer than a non-routine method recently developed based on spectroscopic  
243 detection assisted by graphene oxide modified with amino groups and gold nanoparticles [26].  
244 Furthermore, the detection of bromate improved by 10 times previous results with UPLC-MS  
245 [6]. This improvement can be attributed to better ionic evaporation achieved with the higher  
246 proportion of organic solvent in the mobile phase. The sensitivity reached was also superior to  
247 the levels achieved with completely different approaches: ionic chromatography-conductivity  
248 detection; liquid chromatography-inductively coupled plasma/ mass spectrometry detection;  
249 capillary electrophoresis and mass spectrometry detection by 2-25 times [27-29]. An analysis  
250 time of just 1.5 minutes for  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , without need of column preconditioning due  
251 to isocratic conditions, made the optimised method as one the fastest and most sensitive methods  
252 available to the best of our knowledge.

253

254 3.3 Determination of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in bottled and metropolitan samples from Saudi  
255 Arabia.

256 Reporting the concentration of the potentially hazardous anions in drinking water is important to  
257 identify improvements needed in the production of drinking water. A total of 32 samples of  
258 different origin from the Kingdom of Saudi Arabia were analysed by external calibration and  
259 standard addition. High recovery rates (94-99%) were found for the 3 analytes in both  
260 metropolitan and bottled waters (Table 2 and 3), which indicates that ion suppression in the ESI  
261 or losses in the filtration step were marginal. Therefore, external calibration is an appropriate  
262 way to carry out the quantification.

263 In metropolitan water, the concentration range found for  $\text{BrO}_3^-$  was  $5.83\text{-}13.45 \mu\text{g L}^{-1}$ ; for  
264  $\text{NO}_2^-$ ,  $0.83\text{-}1.57 \text{mg L}^{-1}$ ; and for  $\text{NO}_3^-$ ,  $1.65\text{-}4.61 \text{mg L}^{-1}$  (quantification shown in Table 2). The  
265 higher levels of  $\text{BrO}_3^-$  were found in desalinated water which had not been blended with well  
266 water. This is because well water may dilute the species ( $\text{Br}^-$ ) that would subsequently be  
267 oxidised to  $\text{BrO}_3^-$ . In contrast, desalinated water contained among the lowest levels  $\text{NO}_3^-$  and  
268  $\text{NO}_2^-$  compared to well water, which may have received higher level of leachates from the  
269 degradation of nitrogen rich sources.

270 Among the relatively low number of metropolitan water samples analysed and given in Table 2,  
271 33% contained  $\text{BrO}_3^-$  levels above the  $10 \mu\text{g L}^{-1}$  target by the WHO, US EPA and Gulf  
272 standards for metropolitan water in Saudi Arabia (P 0.05) [4,30]. In previous works >70% of a  
273 limited number of samples analysed were higher than the  $10 \mu\text{g L}^{-1}$  [6, 28]. In contrast, the levels  
274 of  $\text{NO}_3^-$  were all below the EPA limit of  $10 \text{mg L}^{-1}$  (P 0.05) [4]. However, 92% of the samples  
275 had  $\text{NO}_2^-$  levels above the EPA MCL for  $\text{NO}_2^-$  ( $1 \text{mg L}^{-1}$ , P 0.05) [4] despite all of them  
276 complying with the Gulf standards ( $3 \text{mg/L NO}_2^-$ )[30].

277 Among the bottled water samples, 25% presented higher  $\text{BrO}_3^-$  concentration than the WHO and  
278 EPA targets (P 0.05) [2,4]; all the samples were below the MCL for  $\text{NO}_3^-$  [4]; and 70% were  
279 above the EPA limit for  $\text{NO}_2^-$  (P 0.05) [4] or entirely over the Gulf standards for bottled water  
280 ( $0.2 \text{ mg L}^{-1}\text{NO}_2^-$ ) [31]. Previous work carried out in Saudi Arabia showed a broad range of  
281 concentration for these compounds: 8% [32]; 17% [6]; and 60 % of the samples had higher  
282  $\text{BrO}_3^-$  [28] than the EPA MCL. The levels of  $\text{NO}_2^-$  detected in this research are about two time  
283 the highest level of nitrite detected ( $0.38 \text{ mg L}^{-1}$ ) in a recent comprehensive study which  
284 monitored 145 wells in Makkah City [33] and also contrasts with the low detection rate of  $\text{NO}_2^-$   
285 in the assessment of 571 European bottled mineral waters (< 8% had levels above  $0.01 \text{ mg L}^{-1}$ )  
286 [34]. Another important difference with these European samples is that whereas 37% of the  
287 samples had  $\text{NO}_3^- > 2.6 \text{ mg L}^{-1}$  [34], only 15% of the samples in our equivalent study (Table 3)  
288 reached such high level. Oxidation conditions prior bottling water and ammonia-related levels  
289 before oxidation can be the origin of such differences. Our data shows that  $\text{NO}_3^-$  is at non  
290 problematic levels; this is in agreement with other recent studies in Saudi Arabia found that all  
291 the samples tested were below the EPA goal [24] while others showed that it is still of concern  
292 since 20% of the samples presented higher  $\text{NO}_3^-$  than the EPA limits [32]. A study where 388  
293 wells of 6 regions of the Kingdom of Saudi Arabia were investigated, much higher  
294 concentrations of nitrate were found: 8% of the wells had  $\text{NO}_3^- > 45 \text{ mg L}^{-1}$  [35]. Our study  
295 shows both  $\text{NO}_2^-$  and  $\text{BrO}_3^-$  are problematic in both metropolitan and bottled water. The levels  
296 of these toxicants in bottled water are especially relevant because this type of water is typically  
297 used to prepare infant formulas. Remediation measures to decrease  $\text{Br}^-$  and nitrogenated  
298 compounds in water sources; optimising the disinfection conditions currently applied and  
299 selecting those (concentration, pH, duration) that would make possible effective disinfection,

300 reducing the formation of  $\text{BrO}_3^-$  and increase the oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  (keeping both  
301 below the regulated levels); or blending types of water to lower the levels of these potential  
302 toxicants are recommendable.

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304 3.4 Mapping bottle and metropolitan waters with PCA model built from  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$   
305 levels in samples from Saudi Arabia.

306 A PCA model was built from the quantified  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  levels in metropolitan and  
307 bottled water samples given in Tables 2 and 3. The data was represented using axis, PC, which  
308 better explain the variation among the data. The scores plot (Figure 2), which classifies the  
309 samples based on the concentration of the anions, revealed patterns that were related with the  
310 sample characteristics. The samples were mainly distributed along PC1 (which explains 77%) of  
311 the variation. Metropolitan water appeared distributed mainly in the first 2 quarters of the plot,  
312 whereas bottled water appeared mainly in the second half of the plot. However, there were some  
313 bottled water samples appearing in the region where metropolitan water predominated. It could  
314 be hypothesised that these bottled samples contained metropolitan water.

315 Figure 3 shows the distribution of the variables (loading plot). When correlating the scores plot  
316 (Figure 2) with the loading plot (Figure 3), it can be observed that  $\text{BrO}_3^-$ , which is located at one  
317 extreme of PC1, was the variable causing the main differentiation among samples along PC1. In  
318 contrast,  $\text{NO}_3^-$  is the variable responsible for the distribution of the samples along PC2.  
319 Therefore metropolitan samples were mainly described by the levels of  $\text{BrO}_3^-$  (which is in  
320 agreement with higher level of this ion in desalinated water. Bottled water (mainly from well  
321 water and thus with input of nitrogenated species from organic matter degradation) appeared  
322 mostly distributed along PC2. A more detailed PC model giving details of the type of water and

323 its origin is shown in Figure 4. Metropolitan water from the same geographical region were not  
324 grouped, however those samples from desalinated water were distinctively separated from  
325 samples containing both desalinated water and well water, and from well water only, along PC1.  
326 Bottled water samples number 12, 13,16 and 20 did not have their origin in their label.  
327 According to our model, these samples could be bottled metropolitan water. The bottled water  
328 samples number 2, 4 and 6 appeared in the interface between metropolitan water and bottled well  
329 water. These appeared labelled as well water, however their levels of  $\text{BrO}_3^-$  ( $>8 \mu\text{g L}^{-1}$ ) were in  
330 the higher range of their type (Table 3). Based on the position of these samples in the PCA  
331 model, it could be hypothesized that these bottled water samples could contain a blend of well  
332 water and desalinated water.

333

#### 334 4. Conclusions

- 335 • The UPLC-ESI/MS method developed for the determination of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ,  
336 with an analysis time of just 1.5 min; high sensitivity 0.03-0.04  $\mu\text{g/L}$ ; high precision  
337 ( $<3\%$ ) and recoveries ( $>94\%$ ) is advantageous for monitoring drinking water.
- 338 • The analysis of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in 20 bottled water samples and in 12  
339 metropolitan water samples from different sites in the Kingdom of Saudi Arabia showed  
340 that the levels of  $\text{BrO}_3^-$  and  $\text{NO}_2^-$  were in many cases above recommended levels.  
341 Specifically,  
342 the concentration of  $\text{BrO}_3^-$  was found higher than the US EPA MCL in 25 and 33% of  
343 the bottled and metropolitan waters, respectively. The levels of  $\text{NO}_2^-$  were higher than  
344 the US EPA MCL in 70 and 92% of the bottled and metropolitan water samples,  
345 respectively, and all samples were below the EPA limits for  $\text{NO}_3^-$ . These results indicate



346 that remediation measures/disinfection conditions need to be further optimised with view  
347 to the DBPs generated.

- 348 • A PCA model using  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations showed capacity to  
349 discriminate between desalinated water; well water; and desalinated water blended with  
350 well water in Saudi Arabia. The level of bromate was the main variable making possible  
351 the distinction among drinking water samples.  $\text{NO}_3^-$  had less influence in mapping the  
352 samples and mainly described the bottled drinking waters. The geographical sampling  
353 site was not useful to classify the metropolitan drinking water samples.

354

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470  
471 Figure captions

472  
473 Figure 1. UPLC-ESI/MS chromatograms and spectra of  $\text{NO}_2^-$ ,  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  in bottled water  
474 (sample n<sup>o</sup> 1 in Table 3). The chromatographic conditions were isocratic (75% methanol in water  
475 (v/v)) at a flow rate of  $200 \mu\text{L min}^{-1}$ ,  $25^\circ\text{C}$ . The column used was an Acquity® BEH  $\text{C}_{18}$  (50 mm  
476  $\times$  2.1 mm i.d., 1.7  $\mu\text{m}$  particle size).

477  
478 Figure 2. PCA scores plot obtained from metropolitan and bottled waters as a function of  $\text{BrO}_3^-$ ,  
479  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations.

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481 Figure 3. PCA loading plot showing the contribution of the variables in the model.

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484 Figure 4. Scores plot showing the distribution of metropolitan and bottled water samples. The  
485 metropolitan water sampling site and type of water (desalinated; well; blend of well and  
486 desalinated water; and unknown (?)) appear indicated in the sample name. The number in  
487 brackets corresponds to the sample number listed in Tables 2 and 3. The region of the plot  
488 comprising metropolitan water samples has been circled. A zoom into closely distributed samples  
489 is provided.

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509 Table 1. Quality parameters obtained with the optimised UPLC-ESI/MS method.

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Analyte	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )	Run-to-run precision (n=6), RSD (%)	Day-to-day precision (n=6), RSD (%)
$\text{NO}_3^-$	0.030	0.092	1.3	2.6
$\text{NO}_2^-$	0.039	0.12	1.5	2.9
$^{81}\text{BrO}_3^-$	0.029	0.092	1.4	2.7
$^{79}\text{BrO}_3^-$	0.040	0.12	1.6	3.1

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519520 Table 2. Concentrations of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $^{81}\text{BrO}_3^-$  in metropolitan water samples and  
521 recoveries (R) obtained in their determination with UPLC-ESI/MS

Metropoli- tan water (samplen <sup>o</sup> )*	Water source	$\text{NO}_2^-$		$\text{NO}_3^-$		$^{81}\text{BrO}_3^-$	
		( $\text{mg L}^{-1}$ ) $\pm$ SD	R (%)	( $\text{mg L}^{-1}$ ) $\pm$ SD	R (%)	( $\mu\text{g L}^{-1}$ ) $\pm$ SD	R (%)
Jeddah (1)	Desalinated + well water	1.37 $\pm$ 0.04	95	4.11 $\pm$ 0.03	95	5.83 $\pm$ 0.03	96
Jeddah (2)	Desalinated + well water	1.41 $\pm$ 0.04	97	4.08 $\pm$ 0.03	97	6.35 $\pm$ 0.02	97
Jeddah (3)	Desalinated water	1.35 $\pm$ 0.04	96	4.35 $\pm$ 0.03	97	9.31 $\pm$ 0.01	97
Jeddah (4)	Desalinated water	0.89 $\pm$ 0.05	95	2.02 $\pm$ 0.04	94	13.45 $\pm$ 0.01	98
Dammam (5)	Desalinated + well water	1.32 $\pm$ 0.04	98	2.41 $\pm$ 0.04	97	8.67 $\pm$ 0.02	98
Dammam (6)	Desalinated + well water	1.49 $\pm$ 0.04	95	4.61 $\pm$ 0.03	97	9.78 $\pm$ 0.01	97



Dammam (7)	Desalinated water	0.97±0.05	95	2.14±0.04	96	12.35±0.01	94
Dammam (8)	Desalinated water	1.29±0.04	94	3.65±0.03	96	7.80±0.02	98
Riyadh (9)	Desalinated + well water	1.57±0.04	98	2.53±0.03	95	8.63± 0.02	96
Riyadh (10)	Desalinated + well water	1.32±0.04	95	2.45±0.03	95	10.76±0.01	95
Riyadh (11)	Desalinated + well water	1.33±0.04	96	2.53±0.03	97	7.98±0.02	98
Riyadh (12)	Desalinated water	0.83±0.05	97	1.65±0.04	96	11.54±0.01	98

522 <sup>a</sup>Treated with hypochlorite disinfectant and obtained from different locations

523 <sup>b</sup> R: Recovery

524 <sup>c</sup> SD = standard deviation (n = 3)

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529 Table 3. Concentrations of NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and <sup>81</sup>BrO<sub>3</sub><sup>-</sup> in bottled water samples and recoveries

530 obtained in their determination with UPLC-ESI/MS

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Bottled water (number)	Water source	NO <sub>2</sub> <sup>-</sup> (mg L <sup>-1</sup> )		NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )		BrO <sub>3</sub> <sup>-</sup> (μg L <sup>-1</sup> )	
		mean± SD	R <sup>b</sup> (%)	mean± SD	R (%)	mean± SD	R (%)
1	Well water	1.59 ±0.04	99	4.89 ±0.03	98	6.79 ± 0.02	99
2	Well water	0.89 ±0.05	98	2.85 ±0.03	97	8.41 ± 0.02	98
3	Well water	1.52 ±0.04	96	3.96 ±0.03	98	4.15 ± 0.03	97

4	Well water	0.56 ±0.05	98	0.97 ± 0.05	99	8.52 ± 0.02	96
5	Well water	0.58 ±0.05	99	4.65 ±0.03	99	2.35 ± 0.04	99
6	Well water	3.46 ±0.02	99	6.54 ±0.02	98	10.16 ± 0.01	98
7	Well water	3.22 ±0.03	98	9.65 ±0.01	96	6.60 ± 0.02	99
8	Well water	1.62 ±0.04	99	5.21 ±0.02	99	3.60 ± 0.03	99
9	Well water	1.36 ±0.04	98	3.45 ±0.03	97	5.59 ± 0.03	99
10	Well water	1.45 ±0.04	98	5.32 ±0.03	99	7.42 ± 0.02	99
11	Well water	1.32 ±0.04	99	3.78 ±0.03	97	3.65 ± 0.03	99
12	– <sup>a</sup>	0.63 ±0.05	98	0.41 ±0.05	99	11.42 ± 0.01	98
13	–	0.72 ± 0.05	99	0.53 ±0.05	98	11.96 ± 0.01	98
14	–	1.43 ±0.04	99	4.22 ±0.03	98	2.82 ± 0.04	98
15	–	2.84 ±0.03	99	7.65 ±0.02	99	4.02 ± 0.03	98
16	–	0.64 ±0.05	98	1.45 ±0.04	99	11.40 ± 0.01	99
17	–	1.42 ±0.04	99	3.52 ±0.03	97	3.41 ± 0.03	99
18	–	1.65 ±0.04	99	2.65 ±0.03	97	4.97 ± 0.03	99
19	–	0.78 ±0.05	97	1.33 ± 0.04	99	3.42 ± 0.03	98
20	–	1.88 ±0.44	99	2.80 ± 0.03	98	10.74 ± 0.01	98

532 <sup>a</sup> Unknown source of water

533 <sup>b</sup> R: Recovery

534 <sup>c</sup> SD = standard deviation (n = 3)

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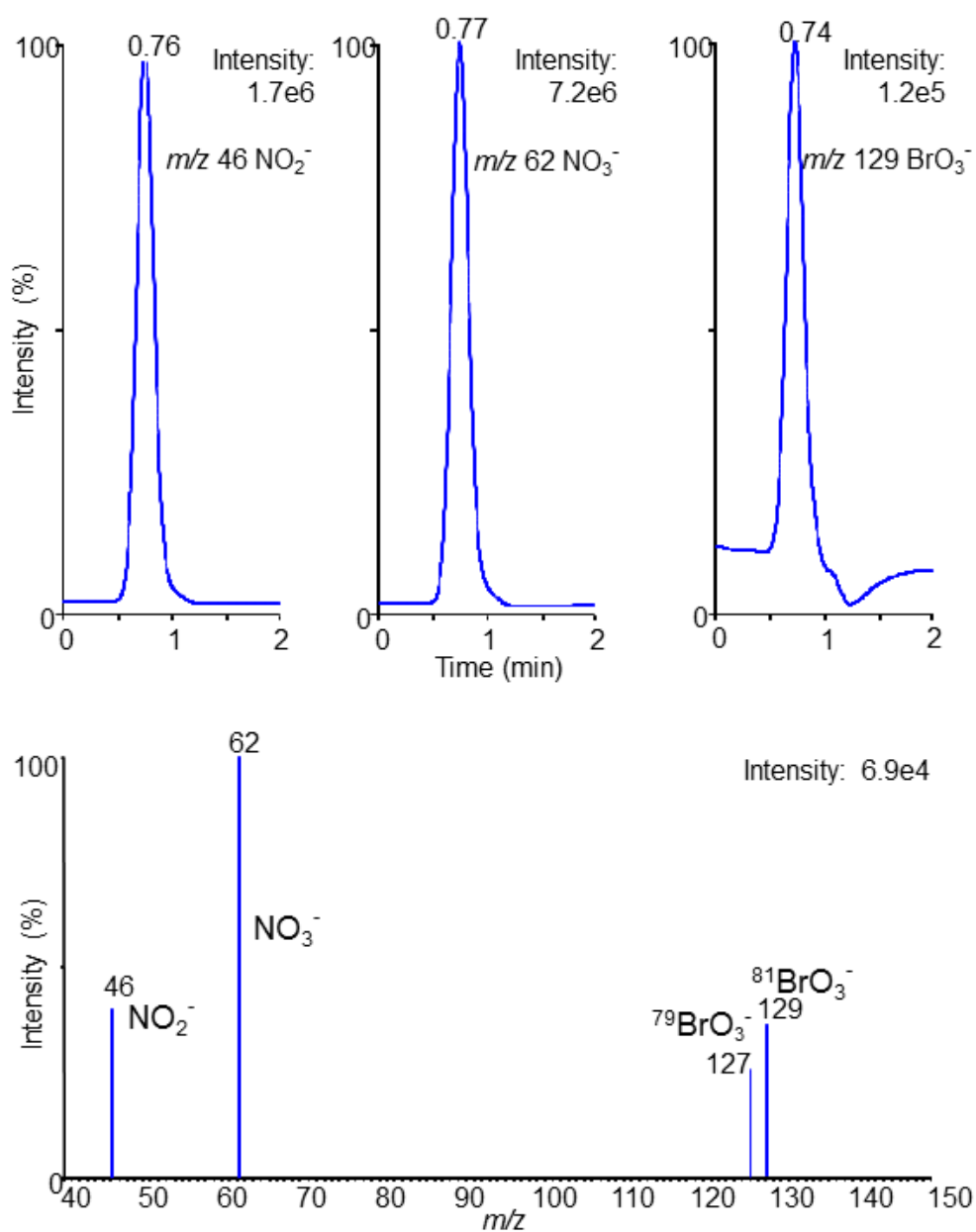
536 HIGHLIGHTS:

- 537 • Analysis of BrO<sub>3</sub><sup>–</sup>, NO<sub>3</sub><sup>–</sup> and NO<sub>2</sub><sup>–</sup> in 1.5 min by UPLC-MS
- 538 • Monitoring of BrO<sub>3</sub><sup>–</sup>, NO<sub>3</sub><sup>–</sup> and NO<sub>2</sub><sup>–</sup> in Saudi Arabia drinking water
- 539 • PCA analysis discriminates among types of metropolitan and bottled water

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**Figure 1.** UPLC-ESI/MS chromatograms and spectra of  $\text{NO}_2^-$ ,  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  in bottled water (sample n°1 in Table 3). The chromatographic conditions were isocratic (75% methanol in water (v/v)) at a flow rate of  $200 \mu\text{L min}^{-1}$ ,  $25^\circ\text{C}$ . The column used was an Acquity® BEH  $\text{C}_{18}$  (50 mm  $\times$  2.1 mm i.d., 1.7  $\mu\text{m}$  particle size).

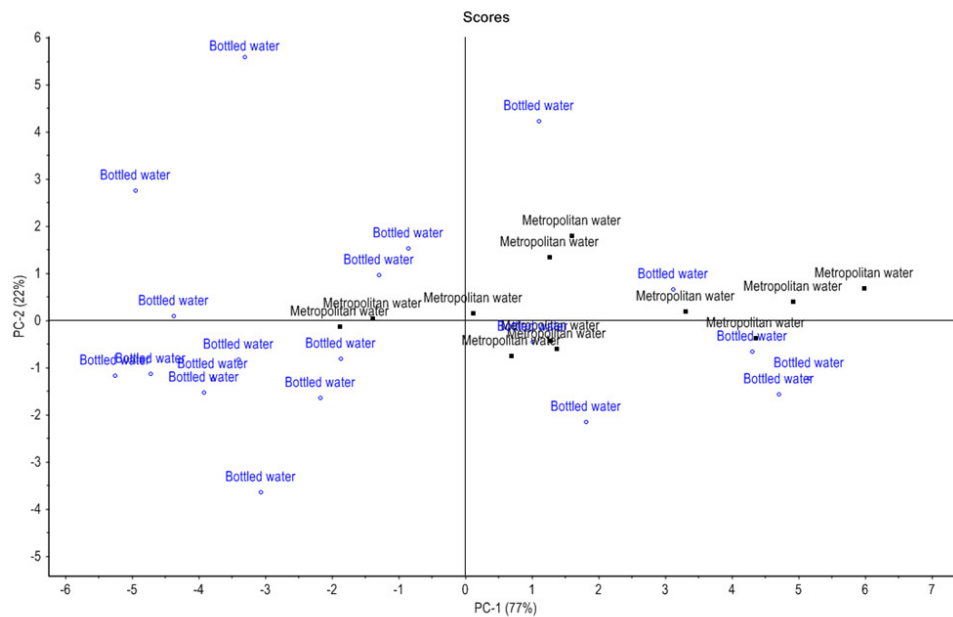


Figure 2. PCA scores plot obtained from metropolitan and bottled waters as a function of  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations.

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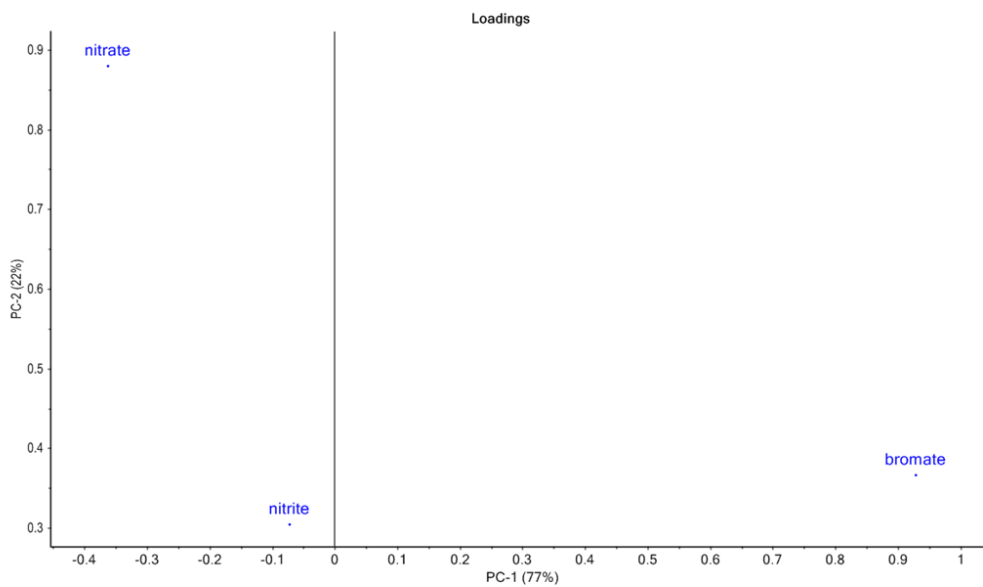


Figure 3. PCA loading plot showing the contribution of the variables in the model

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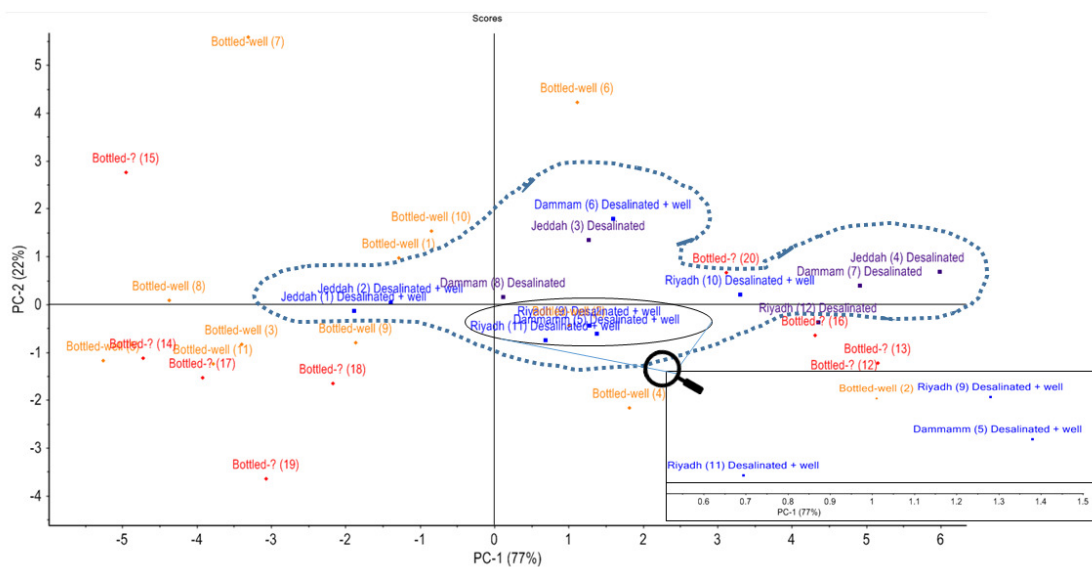


Figure 4. Scores plot showing the distribution of metropolitan and bottled water samples. The metropolitan water sampling site and type of water (desalinated; well; blend of well and desalinated water; and unknown (?)) appear indicated in the sample name. The number in brackets corresponds to the sample number in Tables 2 and 3. The region of the plot comprising metropolitan water samples has been circled. A zoom into closely distributed samples is provided.

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