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### **Determination of inorganic mercury in petroleum production water by inductively coupled plasma optical emission spectrometry following photochemical vapor generation**

Francisco, Barbara Bruna Alves; Rocha, Anderson Araujo; Grinberg, Patricia; Sturgeon, Ralph E.; Cassella, Ricardo Jorgensen

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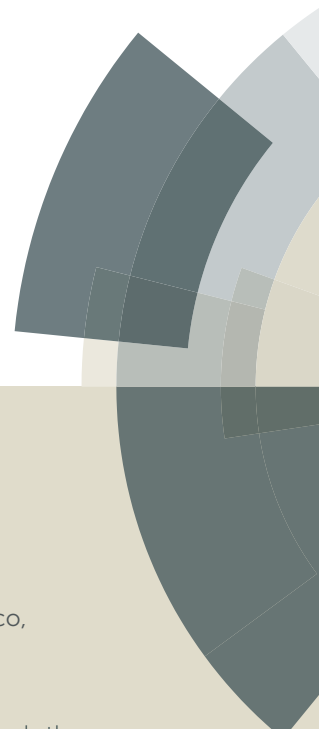
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**DETERMINATION OF INORGANIC MERCURY IN PETROLEUM PRODUCTION WATER BY  
INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY FOLLOWING  
PHOTOCHEMICAL VAPOR GENERATION**

Barbara Bruna A. Francisco<sup>ab</sup>, Anderson A. Rocha<sup>b</sup>, Patricia Grinberg<sup>a</sup>, Ralph E. Sturgeon<sup>a</sup> and Ricardo J. Cassella<sup>b\*</sup>

<sup>a</sup> Measurement Science and Standards, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9.

<sup>b</sup> Departamento de Química Analítica, Universidade Federal Fluminense, Outeiro de São João Batista, s/n, Centro, Niterói, RJ, Brazil 24020-150.

\* Corresponding author  
Email address: cassella@vm.uff.br  
Tel.: + 55 21 26292344  
Fax: + 55 21 26292143

33 **Abstract**View Article Online  
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35 A photochemical vapor generation system coupled to an inductively coupled plasma  
36 optical emission spectrometer (ICP-OES) was used for the determination of inorganic  
37 mercury in high salinity water arising from offshore petroleum exploration platforms,  
38 i.e., production water (PW). The system comprised a 17 W UV grid lamp for  
39 photogeneration along with two gas/liquid separators functioning in tandem to  
40 minimize aerosol transport into the plasma. Analytical conditions, including type and  
41 concentration of low molecular weight organic acid, UV exposure time and solution pH  
42 were optimized. Continuous-flow processing of a sample containing 1.63 mol L<sup>-1</sup> formic  
43 acid at pH 1.5 for a UV irradiation time of 30 s permitted Hg(II) to be determined based  
44 on the method of additions. Procedural limits of detection and quantification of 1.2  
45 and 4.0 µg L<sup>-1</sup>, respectively, were achieved. In the absence of a suitable Certified  
46 Reference Material with which to validate methodology, recoveries of 10 - 40 µg L<sup>-1</sup>  
47 Hg(II) spikes added to real samples were examined and ranged from 79 to 121%.

48

49 **Keywords:** Petroleum production waters; Mercury; Photochemical vapor generation;

50 Inductively coupled plasma optical emission spectrometry

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## 1. Introduction

58

59 According to the Brazilian National Council of the Environment (CONAMA,  
60 Brazil), production water (PW) is the water produced together with petroleum [1]. It  
61 comprises a mixture of endogenous (formation) water (naturally present in geological  
62 reservoirs) and injected water (water introduced into the reservoir to enhance  
63 petroleum yield).<sup>1</sup> It is hazardous due its complex composition and, sometimes, its  
64 volume exceeds that of oil/gas production by five-fold.<sup>2-3</sup> Production water is  
65 considered a wastewater with a natural chemical composition reflecting the geological  
66 characteristics of the reservoir of origin.<sup>2-3</sup> This may include toxic substances, such as  
67 aromatic fractions of oil (BTEX and polycyclic aromatic hydrocarbons), organic acids,  
68 phenols and alkylated phenols. Additionally, toxic elements (arsenic, lead, mercury,  
69 among others) and radionuclides can be present<sup>4</sup> in a matrix of high salinity and  
70 temperature differing significantly from that of seawater.<sup>5</sup> Added chemicals, such as  
71 corrosion inhibitors, scale inhibitors, biocides, oxygen scavengers, emulsion-breakers  
72 or deoilers, antifoam agents, viscosifiers, hydrate inhibitors and cleaners may also be  
73 present.<sup>6</sup> All such compounds influence the composition of PW and its physico-  
74 chemical properties. Clearly, due to the environmental risk associated with it, and  
75 considering the fact that a fraction of treated PW usually enters the ocean, there is  
76 interest in developing analytical methods to characterize such waste to enable  
77 monitoring its characteristics before it is discharged.

78 Toxic inorganic species (trace metals and semi-metals) in PW are an  
79 environmental and health concern because of the risk of their bioaccumulation. To  
80 date, only a few metallic contaminants (i.e., Pb, V, Cr and Mn) have been determined

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81 in PW in attempts to regulate the control of this effluent.<sup>6-10</sup> Although mercury has a  
82 high toxicity and tendency to bioaccumulate in marine animals and ultimately enter  
83 the human food chain, no reports of its determination in PW are available. Moreover,  
84 most mercury released into the marine environment is in the inorganic form and may  
85 undergo biogeochemical transformations, such as bacterial methylation, converting it  
86 into the more toxic form of methylmercury ( $\text{CH}_3\text{Hg}^+$ ).<sup>11-13</sup>

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87 Several analytical techniques have been employed for the determination of  
88 mercury at trace concentrations. The most popular is, undoubtedly, cold vapor  
89 generation (CVG) using chemical reducing agents such as  $\text{NaBH}_4$ ,<sup>14-15</sup> stannous  
90 chloride,<sup>16</sup> sodium cyanotrihydroborate (III)<sup>17</sup> and sodium/potassium tetrahydroborate  
91 (THB)<sup>18</sup> or by electrolytic reduction.<sup>19</sup> CVG is usually coupled with various detection  
92 platforms, such as atomic absorption (CVG-AAS),<sup>14-15,19</sup> atomic fluorescence (CVG-  
93 AFS)<sup>18</sup> or inductively coupled plasmas (CVG-ICP-MS and CVG-ICP-OES).<sup>16,18</sup> These  
94 techniques are sometimes operated with flow injection (FIA) systems<sup>15,20</sup> to increase  
95 the degree of automation and enhance productivity. Despite their high detection  
96 power, alternative approaches to reduction based on photochemical reactions are  
97 currently being pursued. Exposure of samples to UV radiation in the presence of low  
98 molecular weight (LMW) organic compounds, such as formic, acetic and propionic  
99 acids,<sup>21</sup> generates electron donors such as  $\cdot\text{H}$  and  $\cdot\text{CO}$  radicals which are capable of  
100 reducing metal ions to various vapor species.<sup>21-22</sup>

101 Photochemical vapor generation (PVG) possess several advantages over  
102 traditional CVG techniques, including greener chemistry, simplicity, low-cost and  
103 enhanced freedom from possible interferences.<sup>23</sup> These characteristics make PVG  
104 attractive for the determination of inorganic mercury in PW samples. The present work

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3 105 focuses on the development and optimization of a UV-photochemical generation  
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6 106 approach to the determination of inorganic mercury in samples of high salinity artificial  
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8 107 PW samples (APW) and authentic PW obtained from Brazilian offshore petroleum  
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10 108 exploration platforms.  
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## 110 2. Experimental

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### 112 2.1. Instrumentation

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114 A Perkin-Elmer 3000 Optima ICP-OES (Thornhill, Ontario, CA) was interfaced to  
115 a home-made PVG system. The experimental setup consisted of a UV photoreactor  
116 and two gas-liquid separators. The former comprised a 17 W low pressure UV mercury  
117 grid lamp (Analamp, Claremont, CA) over which was placed a quartz tube (25 cm x 2.5  
118 mm i.d. x 3.5 mm o.d.; 5 mL internal volume), shaped to conform to the discharge  
119 lamp geometry, to permit irradiation of the sample. The lamp was enclosed in a metal  
120 chamber flushed with nitrogen to prevent ozone formation and cooled with the help of  
121 a fan to avoid overheating.

122 One gas-liquid separator (GLS I) was placed immediately at the output of the  
123 photoreactor. A carrier flow of argon was introduced at the bottom of the GLS and  
124 passed through a sintered glass frit which supported the irradiated liquid sample. A  
125 second gas-liquid separator (GLS II), filled with glass beads of varying sizes, was placed  
126 in tandem to the first and simply served to reduce residual aerosol carryover to the  
127 plasma. This arrangement was particularly beneficial when organic constituents were  
128 added to the system to study the impact of interferences on the analysis of real

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3 129 samples. A 70 cm length of PTFE (4.0 mm i.d) tubing connected the outlet of GLS I (or  
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5  
6 130 GLS II, depending on the experiment) to the base of the quartz torch. A T connector  
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8 131 was placed after GLS II to introduce an Ar carrier gas (*via* the instrument nebulizer gas  
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11 132 stream) into the system and transport the elemental mercury vapor to the ICP-OES  
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13 133 torch. A schematic diagram of the setup is presented in Fig. 1.

14 134 A Gilson Miniplus 2 peristaltic pump (Gilson, Middleton, WI, USA), fitted with  
15  
16 135 1.42 mm i.d. Tygon® tubing, was used to deliver samples (and standard solutions) to  
17  
18 136 the photoreactor. A second such pump, fitted with 2.79 mm id Tygon® tubing, was  
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21 137 employed to extract waste from GLS I. All connections and tees were constructed from  
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24 138 low pressure flangeless fittings (Upchurch Scientific Inc., Oak Harbor, WA, USA).

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27 139 Polyethylene vessels and sampling tubes (Fisher Scientific Canada, Ottawa, ON,  
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30 140 CA) of different volumes, used in all steps of the procedure, were pre-cleaned in order  
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33 141 to reduce contamination. These were kept overnight in a solution of 5% v/v nitric acid,  
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36 142 rinsed several times with high-purity deionized water and dried in a class-10 clean  
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39 143 hood before use.

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42 144 Salinity measurements were performed with a model S/Mill-E hand-held  
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45 145 refractometer furnished by Atago (Saitama, Japan).

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## 48 49 147 **2.2. Reagents, solutions and materials**

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54 149 Analytical-grade reagents were used in all experiments. All solutions were  
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57 150 prepared using high-purity deionized water (DIW) of 18.2 MΩ-cm resistivity produced  
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60 151 in the laboratory using a commercial deionization system (Barnstead/Thermolyne,  
152 Dubuque, IA, USA). A 1,000 µg mL<sup>-1</sup> solution of inorganic mercury, purchased from SCP



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3 153 Science (Quebec, CA), served as the primary calibration standard. Formic, glacial acetic  
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6 154 and propionic acids were sourced from Fisher Chemicals (Fair Lawn, NJ, USA). Nitric  
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8 155 acid was purified in-house prior to use by sub-boiling distillation of analytical grade  
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11 156 feedstock using a quartz still. All solutions were prepared in a class-10 environment  
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13 157 within a clean laboratory.  
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### 159 **2.3. Preparation of artificial PW samples and collection of real field samples**

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161 Artificial PW samples (APW) served for method development (due to a limited  
162 supply of authentic PW samples) and to check instrument robustness. Optimization of  
163 the methodology was undertaken using spiked solutions of DIW containing varying  
164 contents of potential individual interferents and LMW. APW samples were prepared by  
165 dissolving inorganic salts and organic reagents (KCl,  $MgCl_2 \cdot 6H_2O$ ;  $CaCl_2 \cdot 2H_2O$ ;  
166  $BaCl_2 \cdot 2H_2O$ ;  $SrCl_2 \cdot 6H_2O$ ;  $FeCl_3 \cdot 6H_2O$ ;  $NaHCO_3$ ;  $Na_2SO_4$ ; NaCl; NaBr;  $CH_3COONa$ ; phenol)  
167 in deionized water in accordance with the information given in Table 1. The salinity of  
168 each APW sample is presented in Table 1 as well.

169 Authentic PW samples, supplied by Petrobras, were collected from Brazilian  
170 offshore petroleum platforms and stored in pre-cleaned polyethylene containers. They  
171 were acidified to pH 1.8 with high purity nitric acid to ensure stability of mercury.

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### 173 **2.4. General analytical procedure**

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175 ICP-OES operating parameters, reagent concentrations and physical parameters  
176 of the system were all optimized. Spectrometer parameters are summarized in Table 2.

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3 177 The optimized method was applied to the determination of mercury in  
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6 178 authentic PW and spiked APW samples. For all optimization studies, a working solution  
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8 179 containing  $10 \mu\text{g L}^{-1}$  inorganic mercury together with an appropriate concentration of  
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11 180 LMW was employed. Samples and test solutions were pumped through the  
12  
13 181 photoreactor and subsequently to GLS I and GLS II from which the mercury vapor was  
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16 182 directed to the ICP-OES.

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18 183 Preparation and manipulation of all samples was conducted in a class-10  
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20 184 environment within a clean laboratory. PW samples were first passed through a  
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22 185 disposable syringe filter (pore diameter  $0.45 \mu\text{m}$ ) to remove oil and suspended  
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24 186 particulate material. Both artificial and real samples were diluted ten-fold prior to  
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26 187 analysis to minimize the impact of the sample matrix.  
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### 33 189 **2.5. Sample analysis**

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37 191 Before each measurement, samples were diluted 10-fold with DIW and sufficient  
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39 192 formic acid then added to yield a concentration of  $1.62 \text{ mol L}^{-1}$ . In practice, 25 mL of  
40  
41 193 sample were mixed with 18.75 mL formic acid and approximately 200 mL DIW then  
42  
43 194 added. This solution was transferred to a precleaned 250-mL volumetric flask and a  
44  
45 195 sufficient volume of  $6 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  solution added to yield a pH of 1.5. The final  
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47 196 volume was made to the mark by addition of DIW and the sample was pumped into  
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49 197 the photoreactor at a flow rate of  $1.57 \text{ mL min}^{-1}$  for the measurement of Hg signals.  
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## 201 2.5. Safety considerations

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203 The full range of volatile species generated during PVG is unknown and should  
204 be considered toxic. Inhalation and contact with skin and eyes should be avoided and,  
205 consequently, all work should be performed under well-ventilated conditions.

206

## 207 3. Results and discussion

208

209 Optimization studies were based on earlier work by Vieira *et al.*,<sup>24</sup> Grinberg and  
210 Sturgeon<sup>25</sup> and Zheng *et al.*,<sup>26</sup> which detailed the initial selection of low molecular  
211 weight (LMW) organic acids and their concentrations, irradiation time and the  
212 evaluation of the efficiency of PVG. As noted earlier, all test solutions used for  
213 optimization comprised high purity DIW to which the individual components of  
214 interest were added and subsequently examined for response in order to  
215 systematically isolate the impact of each variable. After optimization, the methodology  
216 was first applied to spiked APW samples to determine spike recoveries and robustness  
217 before subsequent analysis of real PW samples.

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### 219 3.1. Selection of low molecular weight organic acid and its concentration

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221 Formic, acetic and propionic acids were tested for their relative efficiency for  
222 photochemical vapor generation. Sufficient speed of reduction (likely due to radical  
223 generation through photolysis of the LMW) is obtained only when an adequate  
224 concentration of the organic acid is present in the reaction medium.<sup>27</sup> The effect of

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3 225 their concentration was investigated in the range 0 – 2.71, 0 – 1.66 and 0 – 1.35 mol L<sup>-1</sup>  
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6 226 for formic, acetic and propionic acid, respectively. The time of exposure to UV light  
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8 227 was maintained constant at 100 s and all tests were performed at an added spike  
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10 228 concentration of 10 µg L<sup>-1</sup> inorganic mercury.

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13 229 From Figure 2, it is evident that response increased with concentration of LMW  
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15 230 acid up to 1.62 mol L<sup>-1</sup> for formic acid while maximum signals were observed at 1.66  
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17 231 and 1.01 mol L<sup>-1</sup> for acetic and propionic acids, respectively. At higher concentrations,  
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19 232 the signals remained practically constant, indicating that no additional photochemical  
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21 233 reduction of inorganic Hg could be achieved. These results are in accord with those of  
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23 234 others,<sup>28-29</sup> who demonstrated that the generation efficiency in such media is higher  
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25 235 than in the presence of other organic molecules, such as aldehydes and ketones.  
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27 236 Additionally, these short chain acids provide a more favorable photoreduction  
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29 237 environment than methylation and ethylation processes.<sup>30</sup>

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31 238 Propionic acid resulted in the formation of a large amount of foam in the GLS,  
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33 239 inducing some instability in the plasma. Foam production could be associated with the  
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35 240 release of CO<sub>2</sub> and formation of CH<sub>3</sub>Hg<sup>+</sup>, as showed by Yin *et al.*<sup>28</sup> Thus, no further  
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37 241 studies were performed using this acid. For subsequent work, a formic acid  
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39 242 concentration of 1.63 mol L<sup>-1</sup> and an acetic acid concentration of 1.66 mol L<sup>-1</sup> were  
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41 243 used.

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### 43 245 **3.2. Influence of irradiation time**

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46 247 PVG is enhanced in the presence of most organic acids because of their strong  
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48 248 absorption in the deep UV.<sup>30</sup> Although the mechanism of PVG of mercury is not

249 entirely clear, the general concept is that absorption of UV radiation by LMW acid  
250 medium induces radical formation, promoting reduction of mercury.<sup>26,30</sup> Irradiation  
251 time plays an important role in this process because the formation of radicals is  
252 enhanced with an increase in the amount of energy (through photon absorption)  
253 delivered to the system.

254 When test solutions containing 1.62 mol L<sup>-1</sup> formic acid or 1.66 mol L<sup>-1</sup> acetic  
255 acid were delivered to the photoreactor with the UV lamp off, response was  
256 indistinguishable from instrumental noise, highlighting the need for UV irradiation to  
257 achieve vapor generation. Test solutions were then pumped to the reactor with the  
258 lamp on and the irradiation time was varied from 30 to 180 s. For formic acid,  
259 maximum response was achieved using an irradiation time of 30 s. Longer irradiation  
260 times decreased signal intensity until no signal above background noise occurred when  
261 the irradiation time reached 130 s. This may have been a consequence of the longer  
262 residence times of reduced mercury in the acidic medium giving rise to re-oxidation; it  
263 appears to be a common phenomenon in such PVG systems.<sup>24-26</sup>

264 When acetic acid was used for photogeneration, the kinetics of the process was  
265 noticeably different, requiring a 60s irradiation before any product was detected.  
266 Maximum response was achieved with a 90 s irradiation time, after which it  
267 continuously decreased with longer times in the same manner as with formic acid.

### 269 3.3. Influence of sample pH

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271 The effect of sample pH was examined over the range 0.5 to 8.0 in the presence  
272 of both LMW organic acids. It is noteworthy that the original pH of a 10 µg L<sup>-1</sup> solution

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3 273 of inorganic mercury in both 1.63 mol L<sup>-1</sup> formic and 1.66 mol L<sup>-1</sup> acetic acid was 2.5,  
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273 of inorganic mercury in both 1.63 mol L<sup>-1</sup> formic and 1.66 mol L<sup>-1</sup> acetic acid was 2.5,  
274 The pH of such solutions was adjusted to the desired value using dilute solutions of  
275 either NH<sub>4</sub>OH or H<sub>2</sub>SO<sub>4</sub>. Results are presented in Fig. 3.

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276 Maximum response was achieved at pH 1.5 and 2 for formic and acetic acid,  
277 respectively. At high pH, signals decreased, possibly due to ·OH radicals preventing  
278 reduction of Hg(II) or competing via oxidation reactions.<sup>31</sup> Yin et al.<sup>28</sup> reported that  
279 methylation and ethylation processes were most favorable when the pH was 4.0 in  
280 acetic acid solutions. This may explain the decrease in signal response over this pH  
281 region. At low pH, re-oxidation of the Hg<sup>0</sup> may rapidly occur in the solution due to the  
282 presence of OH and H<sub>2</sub>O<sub>2</sub> species likely generated by the UV irradiation.<sup>28,32</sup>

### 284 3.4 Interferences

285  
286 The effect of the sample matrix may be significant due to its complex nature as  
287 it contains a large variety of organic and inorganic substances that may interfere with  
288 the PVG process. The interference study comprised investigations along three avenues:  
289 (i) evaluation of the influence of chloride ion (the main constituent); (ii) evaluation of  
290 possible organic interferences using phenol, toluene, ethanol and methanol as model  
291 compounds, and (iii) evaluation of the influence of additional inorganic species  
292 (selected cations and anions known to be present in such samples).<sup>2,4-5,33-39</sup>

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### 297 **3.4.1. Influence of chloride ion**

298

299 Sodium chloride is the principal inorganic component of PW samples and is  
300 present at concentrations higher than that in seawater; sample salinity ranges up to  
301 267‰. As chloride ion forms stable complexes with Hg(II), its effect on response was  
302 studied in the range 0 to 80 g L<sup>-1</sup>. Results obtained in both formic and acetic acid media  
303 are depicted in Fig. 4. In formic acid, signal intensity increased with increasing Cl<sup>-</sup>  
304 concentration up to 60 g L<sup>-1</sup>, beyond which response slightly decreased. The impact of  
305 chloride is thus minimal in terms of complexation reactions removing Hg(II) from the  
306 vapor generation process; enhanced signals may be a consequence of increased  
307 efficiency of the gas/liquid phase separation process due to the rising ionic strength of  
308 the medium (i.e., salting out effect). On the other hand, in acetic acid, signals were  
309 close to instrumental noise even when the salt was present at concentrations as low as  
310 5 g L<sup>-1</sup>. Although an interesting observation, the reason for such signal suppression in  
311 acetic acid was not further investigated and is beyond the scope of this study. Based  
312 on these results, use of acetic acid for PVG of inorganic mercury in real samples of PW  
313 was not further investigated.

314

### 315 **3.4.2. Evaluation of potential interferences from organic constituents**

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317 The presence of organic substances in PW samples is very common, since the  
318 formation water, which is mixed with the injected water to yield production water, is  
319 in contact with the oil in the reservoir. In order to evaluate the influence of organic  
320 compounds on PVG of inorganic mercury, phenol, toluene, ethanol and methanol were

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3 321 used as model compounds. Results are presented in Table 3. In this study tolerable  
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6 322 concentration was defined as the maximum concentration of interferent at which a  
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8 323 15% deviation of the response occurs.

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11 324 Phenol has been reported to be in the range of 0.004–1.20 mg L<sup>-1</sup> in PW  
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13 325 samples of varying origin.<sup>2,34,39-40</sup> The effect of toluene was examined in the range 0 –  
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15 326 0.63% in accordance with the findings in ref 40. Ethanol and methanol were also tested  
16  
17 327 due to their possible presence in produced water samples although no reports of their  
18  
19 328 concentrations are known.

20  
21  
22 329 The concentration of phenol was varied from 0 – 15 mg L<sup>-1</sup> as it is known to be  
23  
24 330 an efficient quencher of photochemical reactions. Thus, although this concentration  
25  
26 331 range is notably higher than that reported in real PW samples, it serves as a worst case  
27  
28 332 test of the impact of high amounts of generic organic species on the proposed  
29  
30 333 methodology. In the formic acid medium, Hg signals decreased continuously with  
31  
32 334 increasing phenol concentration. At a concentration of 15 mg L<sup>-1</sup> phenol, response was  
33  
34 335 suppressed 30%. Akbal and Onar<sup>41</sup> and Roig *et al.*<sup>42</sup> have demonstrated that phenol  
35  
36 336 photolyses on exposure to UV light, even under low pH conditions, yielding  
37  
38 337 intermediate species which may impair the PVG efficiency of mercury. This was also  
39  
40 338 evident from this study; when phenol was added to the sample after the UV  
41  
42 339 photochemical generation, by continuous on-line addition through a T connection, no  
43  
44 340 effect was observed, even at a concentration of 15 mg L<sup>-1</sup>. No significant variation ( $\pm$   
45  
46 341 15%) was observed in the presence of either toluene, in the range 0 – 0.63% (0 – 5.80  
47  
48 342 mol L<sup>-1</sup>), ethanol 0 – 3% (0 - 13.8 mol L<sup>-1</sup>) or methanol 0-10% (0 – 32 mol L<sup>-1</sup>).

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50 344



### 3.4.3. Evaluation of possible interferences from inorganic species

346

347 Three separate groups of inorganic species were evaluated for their effect on  
348 PVG response: (i) metal and semi-metal ions such as Zn(II), Ni(II), Fe(III), Pb(II), As(III),  
349 Cr(III), Se(IV), Sb(II) and Cu(II); (ii) alkali metals and alkaline earth ions such as Ba(II),  
350 K(I), Mg(II), Sr(II) and Ca(II) and (iii)  $\text{NO}_3^-$ , which is usually added to samples as nitric  
351 acid to ensure preservation. The concentration ranges tested were based on earlier  
352 studies that examined the presence of these species in PW samples<sup>2,4-5,33-39</sup> and are  
353 summarized in Table 3. This evaluation was only performed in formic acid media  
354 because, as noted earlier, use of acetic acid to induce PVG of inorganic mercury in  
355 highly saline media was not viable.

356 No significant interference was observed in the presence of K(I), Ba(II), Sr(II),  
357 Mg(II), Cu(II), Pb(II) and Zn (II) over the concentration ranges studied, whereas the  
358 presence of Ca(II), Ni(II), Sb(III), As(III), Se(IV), Fe(III) and Cr(III) was significant.  
359 Maximum tolerable concentrations for each tested interferent are summarized in  
360 Table 3.

361 No inferences could be made regarding the mechanism of these interferences,  
362 suffice to state that more work needs to be done to address this but that, at the  
363 concentration levels likely to be encountered in (10-fold diluted) PW samples, their  
364 presence can be tolerated. An additional important aspect to be considered is the very  
365 high concentration of NaCl present in such samples, which makes the effect of this  
366 component predominant over all other interferents present at lower-concentrations.

367

368

### 369 3.4. Effect of nitrate

370

371 Interference from  $\text{NO}_3^-$  on PVG processes has been well documented.<sup>30,43</sup> Guo *et al.*<sup>44</sup>,  
372 reported that the presence of nitrate ions altered the yield of volatile species of  
373 selenium and modified the nature of the generated product. Sturgeon and Grinberg<sup>30</sup>  
374 noted that  $0.7 \text{ mol L}^{-1} \text{NO}_3^-$  (as nitric acid) caused total inhibition of PVG of Hg in a  $0.83$   
375  $\text{mol L}^{-1}$  acetic acid medium, probably because of its ability to participate in a number of  
376 radical scavenging reactions. In this study, the influence of nitrate ion was evaluated  
377 over the range  $0 - 0.14 \text{ mol L}^{-1}$  in solutions of  $1.62 \text{ mol L}^{-1}$  formic acid spiked with  $10 \mu\text{g}$   
378  $\text{L}^{-1}$  Hg(II). Response decreased approximately 15% at the highest concentration of  
379 nitrate added. This effect was less pronounced than reported in earlier studies using  
380 an acetic acid medium<sup>30</sup>, and was independent of the form in which it was added to  
381 the solution (as sodium nitrate or nitric acid).

382

### 383 4. Analytical figures of merit and method application

384

385 Analytical figures of merit, derived under optimum conditions in the presence  
386 of formic acid, are summarized in Table 4. The limit of detection (LOD) was based on a  
387  $3s$  criterion, where  $s$  is the standard deviation of the results for 10 repetitive  
388 measurements of the processed blank. The limit of quantification (LOQ) was based on  
389  $10s$ . The precision of the proposed procedure was calculated from the relative  
390 standard deviation of the mean of the linear slopes of ten analytical curves  
391 constructed over ten different days.

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3 392 Figures of merit obtained herein were compared with those reported for  
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6 393 conventional CVG based on use of  $\text{SnCl}_2$  as the reductant.<sup>45</sup> A 20-fold improvement in  
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8 394 the LOD is obtained when using the PVG methodology compared to conventional CVG  
9  
10  
11 395 with ICP-OES detection.

12  
13 396 APW samples, having salinities ranging from 55-150‰ (Table 1), were used to  
14  
15 397 evaluate the recovery of a  $10 \mu\text{g L}^{-1}$  spike of Hg(II) using the proposed methodology.  
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18 398 Standard additions was used following a 10-fold dilution of the APW medium with DIW  
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21 399 such that the impact of salinity would be minimized. Table 5 compares the slopes of  
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23  
24 400 such standard additions curves with those generated using external calibration curves  
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26 401 prepared in a matrix-free DIW sample. It should be noted that the concentration of  
27  
28 402 inorganic ions present in samples APW-1, APW-2 and APW-3 were significantly higher  
29  
30  
31 403 than samples APW-4 and APW-5. On the other hand, phenol was present in samples  
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34 404 APW-4 and APW-5. Slopes of the standard additions curves are similar for the various  
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36 405 APW samples tested, independent of their salinity. However, they are slight higher  
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38 406 than that for the external calibration curve, indicating that matrix interferences are  
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41 407 present and that reliable quantitation cannot be based on the latter approach. This is  
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44 408 consistent with the enhanced response noted earlier and due to elevated levels of  
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46 409 sodium chloride.

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49 410 Results for spike recoveries, shown in Table 6, range from 78 to 113%,  
50  
51 411 confirming that the methodology can be satisfactorily used to determine inorganic Hg  
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54 412 in highly saline media.

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56 413 Results for real samples of PW (similarly diluted 10-fold with DIW before  
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58 414 analysis) were quantitated against matrix matched calibration standards. For this  
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60 415 purpose, spikes were added to artificial PW (APW) solutions containing  $1.62 \text{ mol L}^{-1}$

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3 416 formic acid. Results are summarized in Table 7. Replicate determinations (n=3) on four  
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6 417 spiked PW samples show precision on the order of 1-4% RSD in the concentration  
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8 418 range of 8-10  $\mu\text{g L}^{-1}$ . Recovery tests were also performed to evaluate the accuracy of  
9  
10 419 the method whereby Hg(II) was added to 10-fold diluted PW at three levels  
11  
12 420 (approximately 10, 25 and 40  $\mu\text{g L}^{-1}$ ). Recoveries ranging from 79 to 121% were  
13  
14 421 achieved. The salinity of the real samples was higher than that of the APW samples,  
15  
16 422 reaching values up to 267%.

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18 423 It is clear that artificial PW (APW) samples can be used to prepare “external”  
19  
20 424 matrix-matched calibration curves for the analysis of real PW to permit monitoring of  
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22 425 Hg(II) in these highly saline effluents prior to their discharge into natural water bodies.  
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24 426

## 25 427 **5. Conclusions**

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27 428  
28 429 The method proposed for the determination of inorganic mercury in PW  
29  
30 430 samples by PVG-ICP-OES is conveniently accomplished in a medium of 1.62 mol L<sup>-1</sup>  
31  
32 431 formic acid at pH 1.5 using a 30 s exposure to UV radiation under continuous-flow  
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34 432 conditions. A 10-fold dilution of samples alleviates potential interferences but still  
35  
36 433 requires the method of additions for quantitation due to the enhancement effect of  
37  
38 434 NaCl on Hg response. Calibration can also be performed using a matrix matching  
39  
40 435 strategy employing artificial PW (APW) for preparation of standards, particularly when  
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42 436 small volumes of test samples are available. Spike recoveries in the range 79-124%  
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44 437 were obtained using this approach.  
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3 438 This method provides a lower procedural LOD ( $1.2 \mu\text{g L}^{-1}$ ) than conventional  
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6 439 CVG methodology employing AAS detection ( $4.1 \mu\text{g L}^{-1}$ ) wherein Hg(II) is reduced with  
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8 440  $\text{SnCl}_2$ .

9  
10 441 Although there is no specific law in Brazil that requires the determination of Hg  
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12 442 in PW samples, resolution 393/2007 from CONAMA (Conselho Nacional do Meio  
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14 443 Ambiente, Brazil) requires oil companies in Brazil to undertake monitoring surveys for  
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16 444 metal concentrations in PW prior to its disposal into the ocean. The PVG-ICP-OES  
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18 445 methodology developed here can be readily employed to evaluate the concentration  
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20 446 of inorganic Hg in high salinity PW samples.  
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460 authentic PW samples.  
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574 **Table 1.** Composition of artificial production waters (APW) employed in recovery  
575 experiments.

Substance	Concentration (mg L <sup>-1</sup> )				
	APW-1	APW-2	APW-3	APW-4	APW-5
KCl	500	100	610	100	610
MgCl <sub>2</sub> .6H <sub>2</sub> O	660	320	390	320	390
CaCl <sub>2</sub> .2H <sub>2</sub> O	5600	840	2800	840	2800
BaCl <sub>2</sub> .2H <sub>2</sub> O	190	70	230	70	230
SrCl <sub>2</sub> .6H <sub>2</sub> O	400	200	400	200	400
FeCl <sub>3</sub> .6H <sub>2</sub> O	30	-	-	-	-
NaHCO <sub>3</sub>	-	440	950	440	950
Na <sub>2</sub> SO <sub>4</sub>	70	-	170	-	170
NaCl	91000	30000	53000	30000	53000
NaBr	150	80	-	80	-
Sodium acetate	29	-	-	-	-
Phenol	-	-	-	7	10
Salinity (‰)	150	55	90	55	90

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578 **Table 2.** Experimental parameters for PVG-ICP-OES.

System parameters	Optimized Conditions
Transfer gas flow rate (L min <sup>-1</sup> )	0.35 (acetic acid) 0.45 (formic acid)
Plasma Ar gas flow rate (L min <sup>-1</sup> )	15
GLS argon flow rate (mL min <sup>-1</sup> )	100
Sample flow rate (mL min <sup>-1</sup> )	3
RF power (W)	1300
Wavelength (nm)	253.652
Signal processing	Peak area
ICP OES view	Radial
Viewing height (mm)	15.0
Integration time (s)	100
Read time (s)	100

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581 **Table 3.** Range of concentration of possible interferents.

Interferent	Range of concentration tested	Tolerable concentration <sup>a</sup>
Phenol	0–15 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>
toluene	0–0.63	>0.063%
ethanol	0–3%	>3%
methanol	0–32 mol/L	>10%
K(I), Ba(II), Sr(II) and Mg(II)	0–75 mg L <sup>-1</sup>	>75 mg L <sup>-1</sup>
Ca(II) <sup>b</sup>	0–1250 mg L <sup>-1</sup>	500 mg L <sup>-1</sup>
Ni(II) and Sb(III) <sup>b</sup>	0–100 µg L <sup>-1</sup>	5 µg L <sup>-1</sup>
Cu(II), Pb(II), and Zn(II)	0–100 µg L <sup>-1</sup>	>100 µg L <sup>-1</sup>
Fe(III)	0–100 µg L <sup>-1</sup>	5 µg L <sup>-1</sup>
As(III) <sup>b</sup>	0–100 µg L <sup>-1</sup>	15 µg L <sup>-1</sup>
Se(IV) <sup>c</sup>	0–100 µg L <sup>-1</sup>	15 µg L <sup>-1</sup>
Cr(III)	0–100 µg L <sup>-1</sup>	25 µg L <sup>-1</sup>
NO <sub>3</sub> <sup>-</sup>	0–0.14 mol L <sup>-1</sup>	0.14 mol L <sup>-1</sup>

582 <sup>a</sup> Tolerable concentration before which 15% deviation of response occurs. Experiments were performed  
 583 with individual aqueous solutions containing interferent and Hg(II).

584 <sup>b</sup> Enhancement of inorganic Hg signal.

585 <sup>c</sup> Suppression of inorganic Hg signal.

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589

590 **Table 4.** Figures of merit for optimized methodology.View Article Online  
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Parameter	Value
Typical calibration equation ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	$I = 212.3 [\text{Hg}] - 351.8$
$R^2$	0.9927
Linear range ( $\mu\text{g L}^{-1}$ )	up to 50
Procedural limit of detection ( $\mu\text{g L}^{-1}$ )	1.2 <sup>b</sup>
Procedural limit of quantification ( $\mu\text{g L}^{-1}$ )	4.0 <sup>b</sup>
Precision (%)	9.5

591 <sup>a</sup> Calibration performed in the range of 5 - 50  $\mu\text{g L}^{-1}$ .592 <sup>b</sup> LOD and LOQ were corrected for the 10-fold dilution of the sample and thus refer to the neat sample.

593

**Table 5.** Comparison of slopes of calibration curves and analyte addition curves prepared from spiked APW samples.

Method	Sample	Salinity (‰)	Slope of the curve ( $L \mu g^{-1}$ ) <sup>b</sup>	R <sup>2</sup>
External calibration <sup>c</sup>	DIW <sup>a</sup>	--	189 ± 13	0.9963
Analyte additions <sup>c</sup>	APW-1	150	210 ± 14	0.9938
	APW-2	55	221 ± 11	0.9987
	APW-3	90	228 ± 18	0.9924
	APW-4	55	229 ± 15	0.9995
	APW-5	90	220 ± 15	0.9946

<sup>a</sup> In the presence of 1.62 mol L<sup>-1</sup> formic acid

<sup>b</sup> Expressed as slope ± standard error. Based on 3 point-standard addition

<sup>c</sup> Constructed by addition of Hg(II) in the range of 10-50  $\mu g L^{-1}$ . in the presence of 1.62 mol L<sup>-1</sup> formic acid. Based on 5 point calibration curve.

**Table 6.** Recovery of a 10  $\mu\text{g L}^{-1}$  spike of Hg(II) from APW samples based on quantitation by the method of additions.

Sample <sup>a</sup>	Hg added ( $\mu\text{g L}^{-1}$ )	Hg found <sup>b</sup> ( $\mu\text{g L}^{-1}$ )	Recovery (%)
APW-1 (16‰)	10.0	7.8 $\pm$ 0.1	78 $\pm$ 1
APW-2 (15‰)	10.0	9.6 $\pm$ 0.1	96 $\pm$ 1
APW-3 (5.5‰)	10.0	8.6 $\pm$ 0.1	86 $\pm$ 1
APW-4 (9‰)	10.0	9.2 $\pm$ 0.2	92 $\pm$ 2
APW-5 (15‰)	10.0	11.3 $\pm$ 0.1	113 $\pm$ 1

<sup>a</sup> Values in parentheses are the salinities of each APW sample.

<sup>b</sup> Expressed as mean  $\pm$  standard deviation (n = 3).



**Table 7.** Results for the determination of inorganic mercury in samples of produced waters and spike recoveries.

Sample (Salinity,‰)	Hg added ( $\mu\text{g L}^{-1}$ )	Hg found <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	Spike Recovery (%)
<b>PW-1</b> <b>(267‰)</b>	0	< 1.2	--
	9.32	10.1 $\pm$ 0.1	108 $\pm$ 1
	25.09	28.6 $\pm$ 0.3	114 $\pm$ 1
	38.19	40.2 $\pm$ 2.0	105 $\pm$ 5
<b>PW-2</b> <b>(239‰)</b>	0	< 1.2	--
	9.31	9.38 $\pm$ 0.14	101 $\pm$ 2
	25.25	29.9 $\pm$ 0.2	118 $\pm$ 1
	38.92	47.4 $\pm$ 0.4	121 $\pm$ 1
<b>PW-3</b> <b>(237‰)</b>	0	< 1.2	--
	10.20	8.10 $\pm$ 0.32	79.4 $\pm$ 3.1
	23.79	27.2 $\pm$ 0.5	114 $\pm$ 2
	34.75	43.3 $\pm$ 0.3	124 $\pm$ 1
<b>PW-4</b> <b>(78 ‰)</b>	0	< 1.2	--
	8.0	7.42 $\pm$ 0.15	92.8 $\pm$ 1.6
	18.19	16.6 $\pm$ 0.2	91.2 $\pm$ 1.1
	25.75	26.3 $\pm$ 0.1	102 $\pm$ 0.4

<sup>a</sup> Results obtained using method of additions for calibration. Mean  $\pm$  standard deviation (n = 3) reported.

## Figures and Captions

**Figure 1.** Schematic of the experimental system for the determination of inorganic mercury in production waters by photochemical vapor generation coupled to ICP-OES.

**Figure 2.** Effect of LMW acid concentration on response from  $10 \mu\text{g L}^{-1}$  Hg(II). Sample flow rate was  $3 \text{ mL min}^{-1}$ . Error bars represent standard deviation of three measurements.

**Figure 3.** Effect of sample pH on response in continuous-flow mode of a solution containing  $10 \mu\text{g L}^{-1}$  Hg(II). ( $\blacklozenge$ )  $1.63 \text{ mol L}^{-1}$  formic acid; ( $\blacksquare$ )  $1.66 \text{ mol L}^{-1}$  acetic acid. Error bars represent standard deviation of three measurements.

**Figure 4.** Effect of chloride concentration on PVG response from a solution containing  $10 \mu\text{g L}^{-1}$  Hg(II) using continuous-flow mode with  $3 \text{ mL min}^{-1}$  sample flow rate (75 s UV irradiation) in  $1.63 \text{ mol L}^{-1}$  formic acid and  $1.66 \text{ mol L}^{-1}$  acetic acid. Error bars represent standard deviation of three measurements.

FIGURE 1

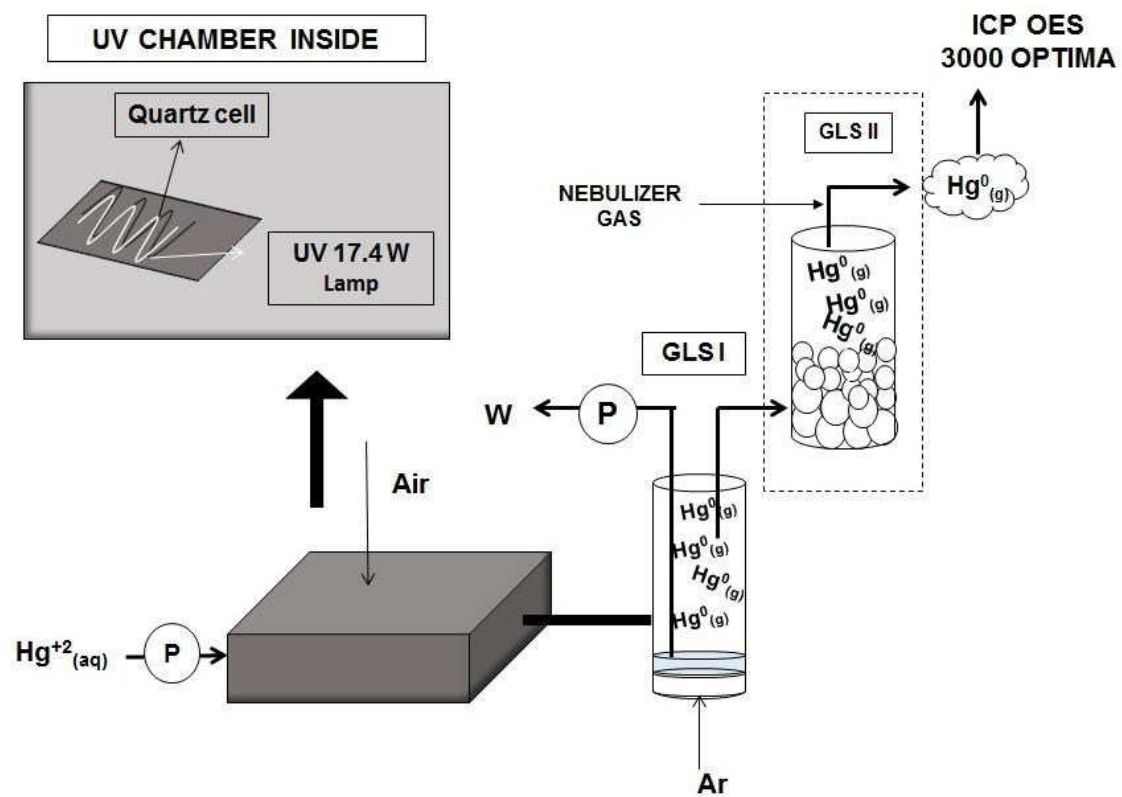


FIGURE 2

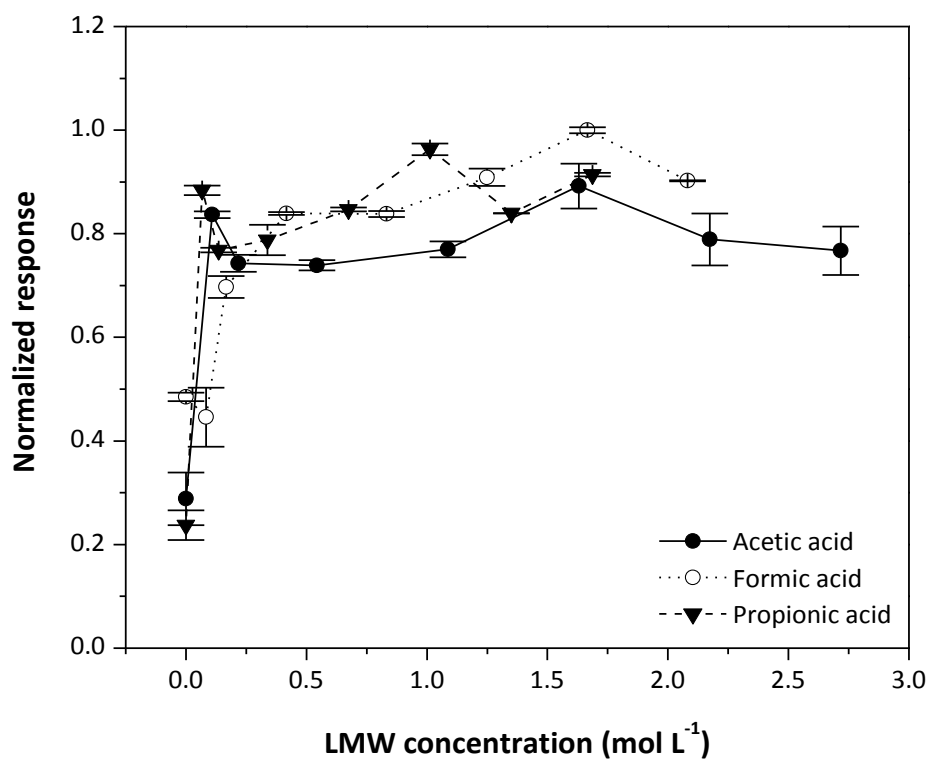


FIGURE 3

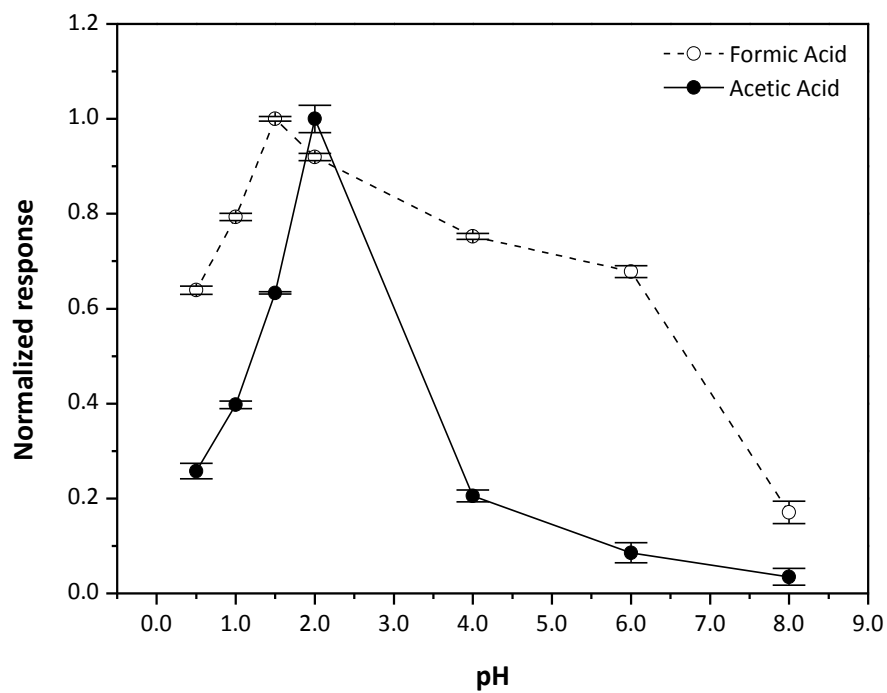


FIGURE 4

