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

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Abstract

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

Keywords: Petroleum production waters; Mercury; Photochemical vapor generation; Inductively coupled plasma optical emission spectrometry

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4 57 **1. Introduction**
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11 60 Brazil), production water (PW) is the water produced together with petroleum [1]. It
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13 61 comprises a mixture of endogenous (formation) water (naturally present in geological
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15 62 reservoirs) and injected water (water introduced into the reservoir to enhance
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17 63 petroleum yield).¹ It is hazardous due its complex composition and, sometimes, its
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19 64 volume exceeds that of oil/gas production by five-fold.²⁻³ Production water is
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21 65 considered a wastewater with a natural chemical composition reflecting the geological
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23 66 characteristics of the reservoir of origin.²⁻³ This may include toxic substances, such as
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25 67 aromatic fractions of oil (BTEX and polycyclic aromatic hydrocarbons), organic acids,
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27 68 phenols and alkylated phenols. Additionally, toxic elements (arsenic, lead, mercury,
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29 69 among others) and radionuclides can be present⁴ in a matrix of high salinity and
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31 70 temperature differing significantly from that of seawater.⁵ Added chemicals, such as
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33 71 corrosion inhibitors, scale inhibitors, biocides, oxygen scavengers, emulsion-breakers
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35 72 or deoilers, antifoam agents, viscosifiers, hydrate inhibitors and cleaners may also be
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37 73 present.⁶ All such compounds influence the composition of PW and its physico-
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39 74 chemical properties. Clearly, due to the environmental risk associated with it, and
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41 75 considering the fact that a fraction of treated PW usually enters the ocean, there is
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43 76 interest in developing analytical methods to characterize such waste to enable
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45 77 monitoring its characteristics before it is discharged.
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57 78 Toxic inorganic species (trace metals and semi-metals) in PW are an
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59 79 environmental and health concern because of the risk of their bioaccumulation. To
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80 date, only a few metallic contaminants (i.e., Pb, V, Cr and Mn) have been determined

in PW in attempts to regulate the control of this effluent.⁶⁻¹⁰ Although mercury has a high toxicity and tendency to bioaccumulate in marine animals and ultimately enter the human food chain, no reports of its determination in PW are available. Moreover, most mercury released into the marine environment is in the inorganic form and may undergo biogeochemical transformations, such as bacterial methylation, converting it into the more toxic form of methylmercury (CH_3Hg^+).¹¹⁻¹³

Several analytical techniques have been employed for the determination of mercury at trace concentrations. The most popular is, undoubtedly, cold vapor generation (CVG) using chemical reducing agents such as NaBH_4 ,¹⁴⁻¹⁵ stannous chloride,¹⁶ sodium cyanotrihydroborate (III)¹⁷ and sodium/potassium tetrahydroborate (THB)¹⁸ or by electrolytic reduction.¹⁹ CVG is usually coupled with various detection platforms, such as atomic absorption (CVG-AAS),^{14-15,19} atomic fluorescence (CVG-AFS)¹⁸ or inductively coupled plasmas (CVG-ICP-MS and CVG-ICP-OES).^{16,18} These techniques are sometimes operated with flow injection (FIA) systems^{15,20} to increase the degree of automation and enhance productivity. Despite their high detection power, alternative approaches to reduction based on photochemical reactions are currently being pursued. Exposure of samples to UV radiation in the presence of low molecular weight (LMW) organic compounds, such as formic, acetic and propionic acids,²¹ generates electron donors such as $\cdot\text{H}$ and $\cdot\text{CO}$ radicals which are capable of reducing metal ions to various vapor species.²¹⁻²²

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

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105 focuses on the development and optimization of a UV-photochemical generation
106 approach to the determination of inorganic mercury in samples of high salinity artificial
107 PW samples (APW) and authentic PW obtained from Brazilian offshore petroleum
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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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.

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16 134 A Gilson Miniplus 2 peristaltic pump (Gilson, Middleton, WI, USA), fitted with
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18 135 1.42 mm i.d. Tygon® tubing, was used to deliver samples (and standard solutions) to
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21 136 the photoreactor. A second such pump, fitted with 2.79 mm id Tygon® tubing, was
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24 137 employed to extract waste from GLS I. All connections and tees were constructed from
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26 138 low pressure flangeless fittings (Upchurch Scientific Inc., Oak Harbor, WA, USA).

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29 139 Polyethylene vessels and sampling tubes (Fisher Scientific Canada, Ottawa, ON,
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31 140 CA) of different volumes, used in all steps of the procedure, were pre-cleaned in order
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34 141 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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41 144 Salinity measurements were performed with a model S/Mill-E hand-held
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44 145 refractometer furnished by Atago (Saitama, Japan).

46 47 146 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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56 150 prepared using high-purity deionized water (DIW) of 18.2 MΩ-cm resistivity produced
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59 151 in the laboratory using a commercial deionization system (Barnstead/Thermolyne,
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152 Dubuque, IA, USA). A 1,000 µg mL⁻¹ 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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18 159 **2.3. Preparation of artificial PW samples and collection of real field samples**
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23 161 Artificial PW samples (APW) served for method development (due to a limited
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26 162 supply of authentic PW samples) and to check instrument robustness. Optimization of
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28 163 the methodology was undertaken using spiked solutions of DIW containing varying
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31 164 contents of potential individual interferents and LMW. APW samples were prepared by
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33 165 dissolving inorganic salts and organic reagents (KCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$;
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35 166 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; NaHCO_3 ; Na_2SO_4 ; NaCl; NaBr; CH_3COONa ; phenol)
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38 167 in deionized water in accordance with the information given in Table 1. The salinity of
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41 168 each APW sample is presented in Table 1 as well.

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43 169 Authentic PW samples, supplied by Petrobras, were collected from Brazilian
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46 170 offshore petroleum platforms and stored in pre-cleaned polyethylene containers. They
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49 171 were acidified to pH 1.8 with high purity nitric acid to ensure stability of mercury.
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53 173 **2.4. General analytical procedure**
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58 175 ICP-OES operating parameters, reagent concentrations and physical parameters
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60 176 of the system were all optimized. Spectrometer parameters are summarized in Table 2.

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

Preparation and manipulation of all samples was conducted in a class-10 environment within a clean laboratory. PW samples were first passed through a disposable syringe filter (pore diameter $0.45 \mu\text{m}$) to remove oil and suspended particulate material. Both artificial and real samples were diluted ten-fold prior to analysis to minimize the impact of the sample matrix.

2.5. Sample analysis

Before each measurement, samples were diluted 10-fold with DIW and sufficient formic acid then added to yield a concentration of 1.62 mol L^{-1} . In practice, 25 mL of sample were mixed with 18.75 mL formic acid and approximately 200 mL DIW then added. This solution was transferred to a precleaned 250-mL volumetric flask and a 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 volume was made to the mark by addition of DIW and the sample was pumped into the photoreactor at a flow rate of 1.57 mL min^{-1} for the measurement of Hg signals.

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.
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207 **3. Results and discussion**

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209 Optimization studies were based on earlier work by Vieira *et al.*,²⁴ Grinberg and
210 Sturgeon²⁵ and Zheng *et al.*,²⁶ 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.²⁷ The effect of

their concentration was investigated in the range 0 – 2.71, 0 – 1.66 and 0 – 1.35 mol L⁻¹ for formic, acetic and propionic acid, respectively. The time of exposure to UV light was maintained constant at 100 s and all tests were performed at an added spike concentration of 10 µg L⁻¹ inorganic mercury.

From Figure 2, it is evident that response increased with concentration of LMW acid up to 1.62 mol L⁻¹ for formic acid while maximum signals were observed at 1.66 and 1.01 mol L⁻¹ for acetic and propionic acids, respectively. At higher concentrations, the signals remained practically constant, indicating that no additional photochemical reduction of inorganic Hg could be achieved. These results are in accord with those of others,²⁸⁻²⁹ who demonstrated that the generation efficiency in such media is higher than in the presence of other organic molecules, such as aldehydes and ketones. Additionally, these short chain acids provide a more favorable photoreduction environment than methylation and ethylation processes.³⁰

Propionic acid resulted in the formation of a large amount of foam in the GLS, inducing some instability in the plasma. Foam production could be associated with the release of CO₂ and formation of CH₃Hg⁺, as showed by Yin *et al.*²⁸ Thus, no further studies were performed using this acid. For subsequent work, a formic acid concentration of 1.63 mol L⁻¹ and an acetic acid concentration of 1.66 mol L⁻¹ were used.

3.2. Influence of irradiation time

PVG is enhanced in the presence of most organic acids because of their strong absorption in the deep UV.³⁰ Although the mechanism of PVG of mercury is not

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

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

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

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269 **3.3. Influence of sample pH**

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The effect of sample pH was examined over the range 0.5 to 8.0 in the presence of both LMW organic acids. It is noteworthy that the original pH of a 10 µg L⁻¹ solution

of inorganic mercury in both 1.63 mol L⁻¹ formic and 1.66 mol L⁻¹ acetic acid was 2.5. The pH of such solutions was adjusted to the desired value using dilute solutions of either NH₄OH or H₂SO₄. Results are presented in Fig. 3.

Maximum response was achieved at pH 1.5 and 2 for formic and acetic acid, respectively. At high pH, signals decreased, possibly due to ·OH radicals preventing reduction of Hg(II) or competing via oxidation reactions.³¹ Yin et al.²⁸ reported that methylation and ethylation processes were most favorable when the pH was 4.0 in acetic acid solutions. This may explain the decrease in signal response over this pH region. At low pH, re-oxidation of the Hg⁰ may rapidly occur in the solution due to the presence of OH and H₂O₂ species likely generated by the UV irradiation.^{28,32}

3.4 Interferences

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

3.4.1. Influence of chloride ion

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

3.4.2. Evaluation of potential interferences from organic constituents

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

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

Phenol has been reported to be in the range of 0.004–1.20 mg L⁻¹ in PW samples of varying origin.^{2,34,39-40} The effect of toluene was examined in the range 0 – 0.63% in accordance with the findings in ref 40. Ethanol and methanol were also tested due to their possible presence in produced water samples although no reports of their concentrations are known.

The concentration of phenol was varied from 0 – 15 mg L⁻¹ as it is known to be an efficient quencher of photochemical reactions. Thus, although this concentration range is notably higher than that reported in real PW samples, it serves as a worst case test of the impact of high amounts of generic organic species on the proposed methodology. In the formic acid medium, Hg signals decreased continuously with increasing phenol concentration. At a concentration of 15 mg L⁻¹ phenol, response was suppressed 30%. Akbal and Onar⁴¹ and Roig *et al.*⁴² have demonstrated that phenol photolyses on exposure to UV light, even under low pH conditions, yielding intermediate species which may impair the PVG efficiency of mercury. This was also evident from this study; when phenol was added to the sample after the UV photochemical generation, by continuous on-line addition through a T connection, no effect was observed, even at a concentration of 15 mg L⁻¹. No significant variation (\pm 15%) was observed in the presence of either toluene, in the range 0 – 0.63% (0 – 5.80 mol L⁻¹), ethanol 0 – 3% (0 – 13.8 mol L⁻¹) or methanol 0-10% (0 – 32 mol L⁻¹).

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3.4.3. Evaluation of possible interferences from inorganic species

Three separate groups of inorganic species were evaluated for their effect on PVG response: (i) metal and semi-metal ions such as Zn(II), Ni(II), Fe(III), Pb(II), As(III), Cr(III), Se(IV), Sb(II) and Cu(II); (ii) alkali metals and alkaline earth ions such as Ba(II), K(I), Mg(II), Sr(II) and Ca(II) and (iii) NO₃⁻, which is usually added to samples as nitric acid to ensure preservation. The concentration ranges tested were based on earlier studies that examined the presence of these species in PW samples^{2,4-5,33-39} and are summarized in Table 3. This evaluation was only performed in formic acid media because, as noted earlier, use of acetic acid to induce PVG of inorganic mercury in highly saline media was not viable.

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

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

3.4. Effect of nitrate

Interference from NO_3^- on PVG processes has been well documented.^{30,43} Guo *et al.*⁴⁴, reported that the presence of nitrate ions altered the yield of volatile species of selenium and modified the nature of the generated product. Sturgeon and Grinberg³⁰ 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 mol L^{-1} acetic acid medium, probably because of its ability to participate in a number of radical scavenging reactions. In this study, the influence of nitrate ion was evaluated over the range $0 - 0.14 \text{ mol L}^{-1}$ in solutions of 1.62 mol L^{-1} formic acid spiked with $10 \mu\text{g L}^{-1} \text{Hg(II)}$. Response decreased approximately 15% at the highest concentration of nitrate added. This effect was less pronounced than reported in earlier studies using an acetic acid medium³⁰, and was independent of the form in which it was added to the solution (as sodium nitrate or nitric acid).

4. Analytical figures of merit and method application

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

Figures of merit obtained herein were compared with those reported for conventional CVG based on use of SnCl_2 as the reductant.⁴⁵ A 20-fold improvement in the LOD is obtained when using the PVG methodology compared to conventional CVG with ICP-OES detection.

APW samples, having salinities ranging from 55-150‰ (Table 1), were used to evaluate the recovery of a $10 \mu\text{g L}^{-1}$ spike of Hg(II) using the proposed methodology. Standard additions was used following a 10-fold dilution of the APW medium with DIW such that the impact of salinity would be minimized. Table 5 compares the slopes of such standard additions curves with those generated using external calibration curves prepared in a matrix-free DIW sample. It should be noted that the concentration of inorganic ions present in samples APW-1, APW-2 and APW-3 were significantly higher than samples APW-4 and APW-5. On the other hand, phenol was present in samples APW-4 and APW-5. Slopes of the standard additions curves are similar for the various APW samples tested, independent of their salinity. However, they are slight higher than that for the external calibration curve, indicating that matrix interferences are present and that reliable quantitation cannot be based on the latter approach. This is consistent with the enhanced response noted earlier and due to elevated levels of sodium chloride.

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

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

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

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

5. Conclusions

The method proposed for the determination of inorganic mercury in PW samples by PVG-ICP-OES is conveniently accomplished in a medium of 1.62 mol L^{-1} formic acid at pH 1.5 using a 30 s exposure to UV radiation under continuous-flow conditions. A 10-fold dilution of samples alleviates potential interferences but still requires the method of additions for quantitation due to the enhancement effect of NaCl on Hg response. Calibration can also be performed using a matrix matching strategy employing artificial PW (APW) for preparation of standards, particularly when small volumes of test samples are available. Spike recoveries in the range 79-124% were obtained using this approach.

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438 This method provides a lower procedural LOD ($1.2 \mu\text{g L}^{-1}$) than conventional
439 CVG methodology employing AAS detection ($4.1 \mu\text{g L}^{-1}$) wherein Hg(II) is reduced with
440 SnCl_2 .
441 Although there is no specific law in Brazil that requires the determination of Hg
442 in PW samples, resolution 393/2007 from CONAMA (Conselho Nacional do Meio
443 Ambiente, Brazil) requires oil companies in Brazil to undertake monitoring surveys for
444 metal concentrations in PW prior to its disposal into the ocean. The PVG-ICP-OES
445 methodology developed here can be readily employed to evaluate the concentration
446 of inorganic Hg in high salinity PW samples.

447
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Table 1. Composition of artificial production waters (APW) employed in recovery experiments.

Substance	Concentration (mg L ⁻¹)				
	APW-1	APW-2	APW-3	APW-4	APW-5
KCl	500	100	610	100	610
MgCl ₂ .6H ₂ O	660	320	390	320	390
CaCl ₂ .2H ₂ O	5600	840	2800	840	2800
BaCl ₂ .2H ₂ O	190	70	230	70	230
SrCl ₂ .6H ₂ O	400	200	400	200	400
FeCl ₃ .6H ₂ O	30	-	-	-	-
NaHCO ₃	-	440	950	440	950
Na ₂ SO ₄	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 ⁻¹)	0.35 (acetic acid)
	0.45 (formic acid)
Plasma Ar gas flow rate (L min ⁻¹)	15
GLS argon flow rate (mL min ⁻¹)	100
Sample flow rate (mL min ⁻¹)	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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Table 3. Range of concentration of possible interferents.

Interferent	Range of concentration tested	Tolerable concentration ^a
Phenol	0–15 mg L ⁻¹	10 mg L ⁻¹
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 ⁻¹	>75 mg L ⁻¹
Ca(II) ^b	0–1250 mg L ⁻¹	500 mg L ⁻¹
Ni(II) and Sb(III) ^b	0–100 µg L ⁻¹	5 µg L ⁻¹
Cu(II), Pb(II), and Zn(II)	0–100 µg L ⁻¹	>100 µg L ⁻¹
Fe(III)	0–100 µg L ⁻¹	5 µg L ⁻¹
As(III) ^b	0–100 µg L ⁻¹	15 µg L ⁻¹
Se(IV) ^c	0–100 µg L ⁻¹	15 µg L ⁻¹
Cr(III)	0–100 µg L ⁻¹	25 µg L ⁻¹
NO ₃ ⁻	0–0.14 mol L ⁻¹	0.14 mol L ⁻¹

^a Tolerable concentration before which 15% deviation of response occurs. Experiments were performed with individual aqueous solutions containing interferent and Hg(II).

^b Enhancement of inorganic Hg signal.

^c Suppression of inorganic Hg signal.

590 **Table 4.** Figures of merit for optimized methodology.

Parameter	Value
Typical calibration equation ($\mu\text{g L}^{-1}$) ^a	$I = 212.3 [\text{Hg}] - 351.8$
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^b
Procedural limit of quantification ($\mu\text{g L}^{-1}$)	4.0^b
Precision (%)	9.5

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

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 µg ⁻¹) ^b	R ²
External calibration ^c	DIW ^a	--	189 ± 13	0.9963
Analyte additions ^c	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

^a In the presence of 1.62 mol L⁻¹ formic acid

^b Expressed as slope ± standard error. Based on 3 point-standard addition

^c Constructed by addition of Hg(II) in the range of 10-50 µg L⁻¹.in the presence of 1.62 mol L⁻¹ 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 ^a	Hg added ($\mu\text{g L}^{-1}$)	Hg found ^b ($\mu\text{g L}^{-1}$)	Recovery (%)
APW-1 (16‰)	10.0	7.8 ± 0.1	78 ± 1
APW-2 (15‰)	10.0	9.6 ± 0.1	96 ± 1
APW-3 (5.5‰)	10.0	8.6 ± 0.1	86 ± 1
APW-4 (9‰)	10.0	9.2 ± 0.2	92 ± 2
APW-5 (15‰)	10.0	11.3 ± 0.1	113 ± 1

^a Values in parentheses are the salinities of each APW sample.

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

^a Results obtained using method of additions for calibration. Mean ± 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 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). (♦) 1.63 mol L^{-1} formic acid; (■) 1.66 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 mL min^{-1} sample flow rate (75 s UV irradiation) in 1.63 mol L^{-1} formic acid and 1.66 mol L^{-1} acetic acid. Error bars represent standard deviation of three measurements.

FIGURE 1

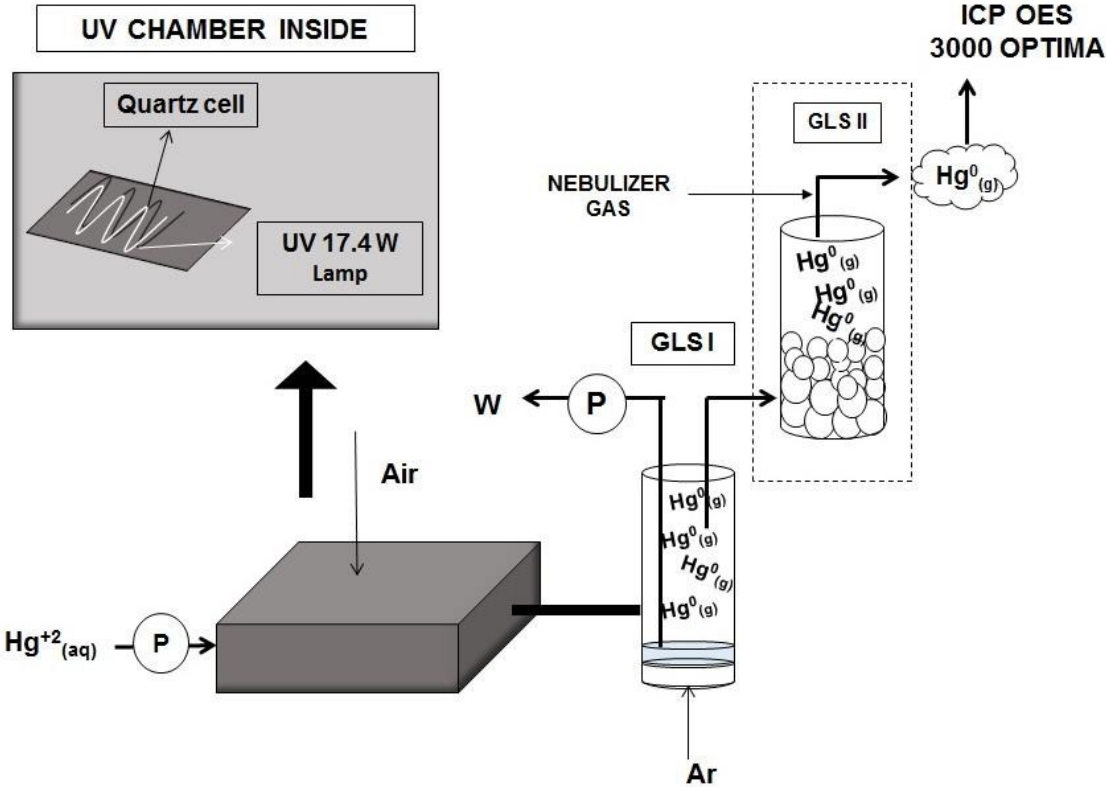


FIGURE 2

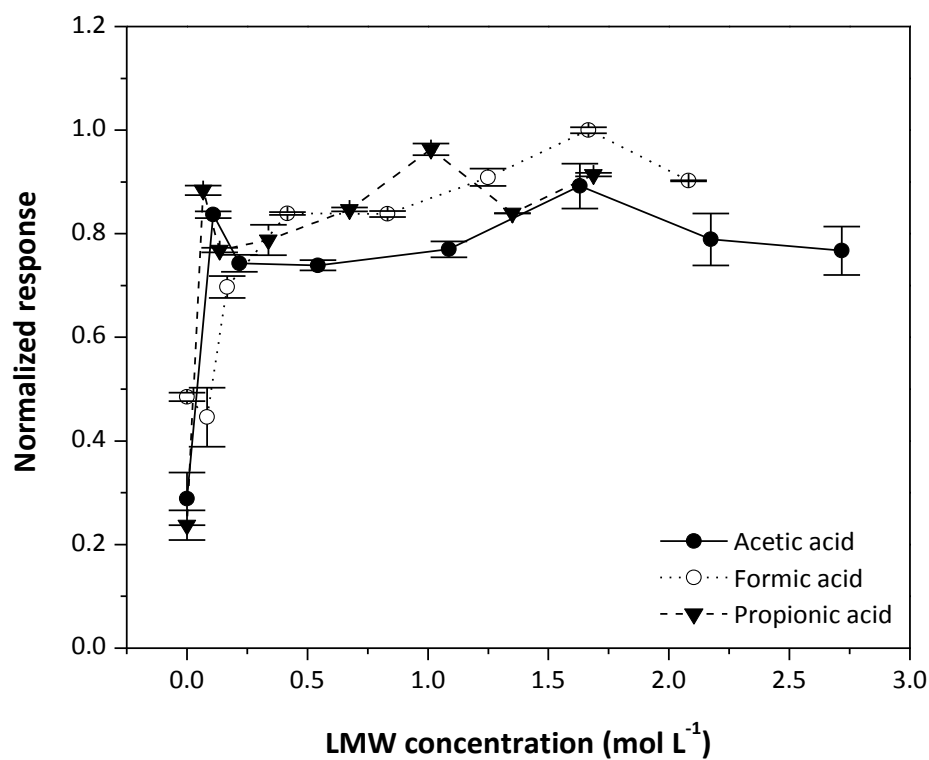


FIGURE 3

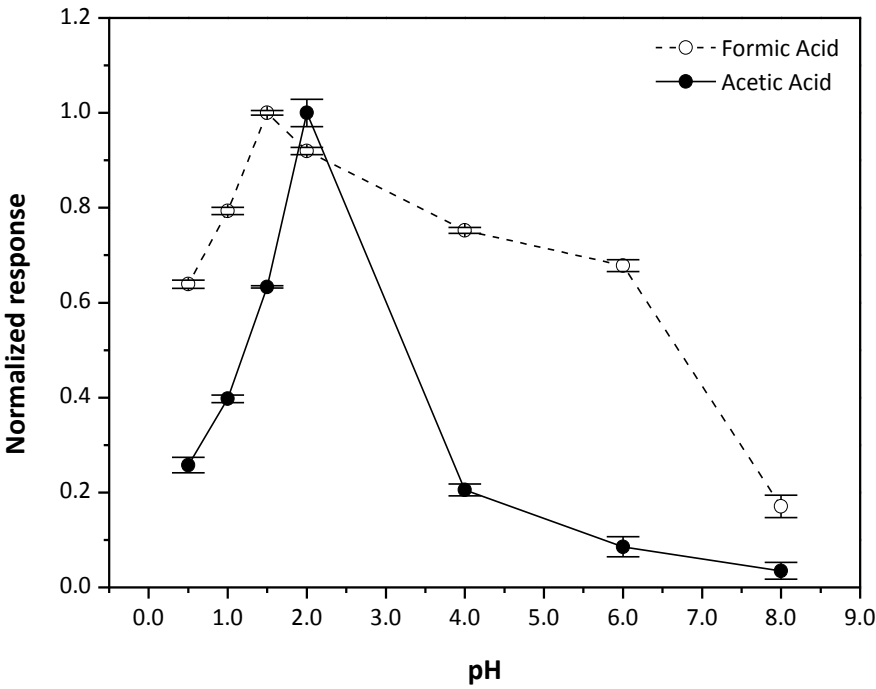


FIGURE 4

