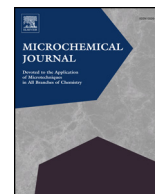




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## Quantification and speciation of mercury in streams and rivers sediment samples from Paracatu, MG, Brazil, using a direct mercury analyzer®



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### ABSTRACT

This paper describes the application of a method for the direct speciation of Hg in sediment samples by thermal desorption using a Direct Mercury Analyzer®. The different thermal behavior of the Hg species allowed direct chemical speciation by DMA. The set of temperature steps was as follows: 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C. Sediment samples presented total Hg concentrations varying over a range of 36 to 1996  $\mu\text{g}\cdot\text{kg}^{-1}$ , with 78% of the samples being over of the TEL (threshold effect level). According to the speciation analysis, a prevalence of oxidized Hg was observed. This method was efficient, simple and adequate for determining the Hg speciation in sediment samples. The great advantage is that the method does not require pretreatment of the samples, and it is applicable to homogeneous solid samples.

### 1. Introduction

Mercury occurs in three oxidation states: the elemental form Hg(0), the less stable mercurous ion Hg(I), and the mercuric ion Hg(II). Elemental mercury can be oxidized and become more toxic when methylation occurs. Organic mercury compounds with short alkyl radicals are among the most dangerous compounds to human life. Intoxication by Hg can affect the human nervous system and harm the brain, heart, kidneys, lungs, and immune system. Mercury toxicity, bioavailability, and mobility in the environment depend strongly on its oxidation state and chemical form. [1–4]

Mercury has been used in the prospecting of gold and silver; the electrolytic production of chlor-alkali; and the manufacturing of plastics, pigments, pesticides, mercury vapor lamps, batteries, and dental products. [4] In Brazil, mercury has been widely used to improve gold extraction from ore, which is the main source of released Hg in the environment. According to the Mineral Annual report by the Brazilian National Department of Mineral Production, in 2013, Brazil had gold reserves of almost 2400 tons, approximately 754 tons (~31%) of which are in Minas Gerais State. [5] The city of Paracatu, also in the state of Minas Gerais, has one of the largest open gold mining in the world. The amount of gold per ton of ore is very small, and therefore, very large masses of ore are exposed to the environment. This type of mining does not use Hg; however, the existence of illegal gold mining is known in

streams and rivers near the mine, which use Hg to improve the extraction efficiency of this precious metal. [6]

Several analytical techniques have been employed for mercury quantification: neutron activation analysis [7–10], inductively coupled plasma mass spectrometry (ICP-MS) [8,11–14], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [15,16], graphite furnace atomic absorption spectrometry (GF-AAS) [17–20], cold vapor atomic absorption spectrometry (CV-AAS) [8,20–25] and atomic fluorescence spectrometry (CV-AFS) [8,20,26–29]; the latter two techniques are the most widely used for measuring total Hg [4]. For Hg determination in solid samples, these techniques, except neutron activation, require prior sample digestion. Generally, all the forms of Hg in the sample are converted to Hg(II) through acid digestion. [4,30,31]

In recent years, the availability of Direct Mercury Analyzers based on thermal decomposition, followed by gold amalgamation and detection by atomic absorption spectrometry (TDAAS), has enabled the determination of total mercury at trace levels in liquid and solid matrices without sample digestion. These instruments allow accurate quantification at very low concentrations in a variety of matrices and do not require any previous sample treatment, in addition to generating minimal waste and reducing the potential for contamination. [7,8,20,23–25,30–43]

For Hg speciation analysis, hyphenated techniques, such as techniques that couple separation techniques (gas chromatography – GC

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[8,44,45], high-performance liquid chromatography – HPLC [8,33,46,47], or capillary electrophoresis – CE [48,49]) and highly sensitive spectroscopic detectors, e.g., inductively coupled plasma mass spectrometry (ICP-MS), are used in most cases [8]. In these cases, selective extraction using a specific solvent to promote analyte extraction is also required. Other techniques, such as sequential chemical extraction [25,37,42,50–54], X-ray absorption analysis [51,52] and thermodesorption coupled to atomic absorption spectrometry (TDAAS) [22–25,28,29,42,43,54–59], can also be employed.

Some studies have used direct Hg analysis to quantify Methyl-Hg (or organic Hg) in solid samples. Chelegão et al. [20] described the evaluation of several parameters for preparing a tuna fish candidate reference material to measure its total Hg and methyl-Hg. They used CV-AAS, DMA and SS-GF AAS for total Hg determination after digestion using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in a high-pressure microwave oven. Methyl-Hg was isolated from the sample using selective extraction with toluene and 6 mol·L<sup>-1</sup> HCl for 15 min at 80 °C, followed by a second extraction with 2% m/v L-cysteine solution. Afterward, methyl-Hg measurements were performed by CV-AAS. Maggi et al. (2009) [36] determined the total Hg and methyl-Hg in Antarctic marine sediment and organisms by direct analysis. For methyl-Hg measurements, sediment samples were shaken with 6 mol·L<sup>-1</sup> HCl for 5 min, while for the biological tissue samples, HBr was used. Toluene was added to the extracts after centrifugation, followed by back-extraction with 1% m/v L-cysteine solution. An aliquot of 200 µL of the final extract was analyzed on a DMA-80 instrument (Milestone). Ruiz-de-Cenzano et al. [41] also employed a method that involves HBr leaching of MeHg, extraction into toluene, and back-extraction into an aqueous L-cysteine solution for the determination of methyl-Hg in fish.

Barst et al. (2013) [39] applied a sample digestion method to fish muscle and liver using 12 M HCl for Hg(II) analysis. Samples in capped tubes were irradiated in a conventional 1100 W microwave oven. After cooling, toluene was added to each sample, the tubes were capped and shaken and then centrifuged. The acidic fraction remaining after toluene extraction of the original digestate was diluted 5-fold with reagent-grade water, and an aliquot was added to a quartz analytical vessel for quantification of ionic Hg with a DMA-80, avoiding a back-extraction step.

Except in the case of direct analysis, a sample preparation step is necessary [8]. Reis et al. [37] developed a thermodesorption speciation method using a LECO instrument (model AMA-254) through variation of the temperature of sample combustion and thereby controlling the release of the different Hg species from the solid matrix. The temperature could not be directly controlled and could be improved by successively increasing the number of active furnaces. After plotting the

number of active furnaces (F) as a function of temperature (T), the equation that best described the data set was determined ( $T(^{\circ}\text{C}) = -0.096F^2 + 5.2F + 71$ ;  $r^2 = 0.9993$ ). Standard materials such as HgCl<sub>2</sub>, Hg-humic acids and HgS, were analyzed using an automatic Hg analyzer being that each material showed a well-resolved peak at specific temperature intervals: 125–225 °C for HgCl<sub>2</sub>, 100–250 °C for Hg-humic acids and 225–325 °C for HgS.

This work proposes a method for the direct analysis of sediment samples aiming for Hg determination and speciation without digestion and/or extraction procedures; only homogenization is indispensable. The sediment samples were collected from streams and rivers of Paracatu, Minas Gerais, Brazil, a city that stands out for its gold extraction and being the largest producing region of Minas Gerais grains. The discovery of gold in the region dates back to the 18th century and was responsible for the acceleration of settlement in the territory. The watercourse where gold was found received the name “Córrego Rico” (Rich Stream), and the area of the deposits was denominated “Morro do Ouro” (Gold Hill). After the decline of gold production, the population began to engage in agricultural activities. In the mid-1980s, there was intense mining activity with the use of mercury indiscriminately and consequent degradation of the area [6,60–63].

## 2. Experimental

### 2.1. Samples

Sediment samples were collected from 9 sites selected in different rivers and streams of Paracatu, Minas Gerais (MG), Brazil, in 2 samplings (Oct/2010 and Nov/2011), as shown in Fig. 1. The most important points of gold mining exploitation were located in Córrego Rico [6], which has its source close to the area of mining in the Morro do Ouro. After draining the city, the stream travels a distance of approximately 60 km and flows into the left bank of the Rio Paracatu [61,63]. Five sampling points were chosen in the Córrego Rico to account for samples near the mining area, in the urban area and outside the city. One point in a tributary of the Córrego Rico and three points in streams out of the mining influence, one of which was in the spring that supplies water to the city, were also chosen. Table S1 presents the geographical coordinates of the collection points.

At every point, sediments were collected next to the margin and in the superficial layer (30 cm deep) using a plastic shovel and bucket, respectively. These samples were stored in plastic flasks and were refrigerated until further use, according to EPA recommendations [64,65]. In the laboratory, the samples were dried at room temperature, manually disaggregated in a mortar and sifted into two fractions

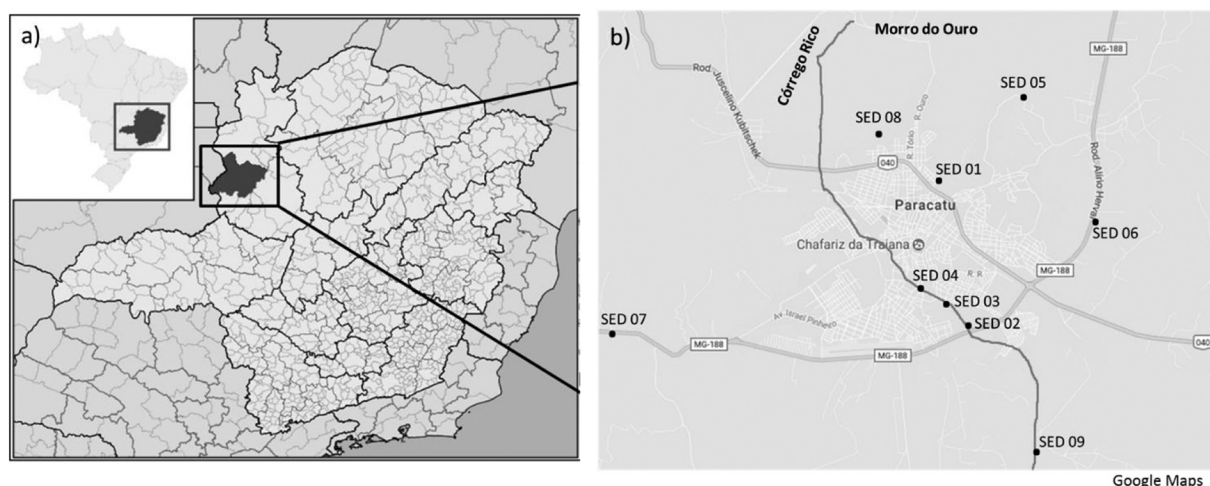


Fig. 1. Paracatu city. a) Location of Paracatu. b) Paracatu sampling points of sediments.

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