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Short Communication

Critical evaluation of distillation procedure for the determination of methylmercury in soil samples

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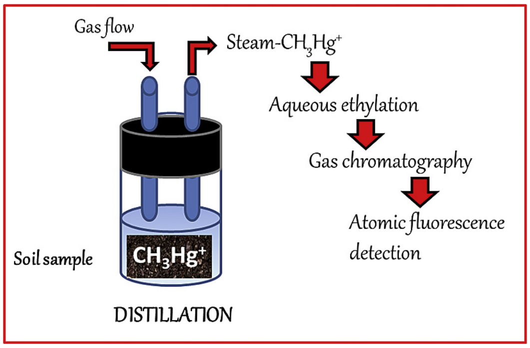
HIGHLIGHTS

- The influence of soil properties on methylmercury recovery by distillation procedure was evaluated.
- Optimal conditions for methylmercury extraction followed by GC-AFS reached similar results with isotopic dilution analysis.
- The optimized and validated methodology was satisfactory applied to real soil samples collected from Chilean territory.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, the efficiency of distillation process for extracting monomethylmercury (MMHg) from soil samples was studied and optimized using an experimental design methodology. The influence of soil composition on MMHg extraction was evaluated by testing of four soil samples with different geochemical characteristics. Optimization suggested that the acid concentration and the duration of the distillation process were most significant and the most favorable conditions, established as a compromise for the studied soils, were determined to be a 70 min distillation using an 0.2 M acid. Corresponding limits of detection (LOD) and quantification (LOQ) were 0.21 and 0.7 pg absolute, respectively. The optimized methodology was applied with satisfactory results to soil samples and was compared to a reference methodology based on isotopic dilution analysis followed by gas chromatography-inductively coupled plasma mass spectrometry (IDA-GC-ICP-MS). Using the optimized conditions, recoveries ranged from 82 to 98%, which is an increase of 9–34% relative to the previously used standard operating procedure. Finally, the validated methodology was applied to quantify MMHg in soils collected from different sites impacted by coal fired power plants in the north-central zone of Chile, measuring MMHg concentrations ranging from 0.091 to 2.8 ng g^{-1}. These data are to the best of our knowledge the first MMHg measurements reported for Chile.

1. Introduction

The environmental impact of mercury and its toxicity are known

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to be related to its chemical form, in which it is present in the environment (Guangliang Liu et al., 2012). Monomethylmercury (MMHg) is the most toxic mercury species and considerably more harmful than elemental mercury or mercuric mercury and its inorganic salts. MMHg is a toxin that exhibits systematic and delayed action on various organ systems, resulting in an alteration of their functions, with the nervous system being the most affected (Dorea, 2008; Mineshi Sakamoto et al., 2012). Multiple studies have reported that this compound is efficiently adsorbed from the gastrointestinal tract and is able to crosses the blood-brain and placenta barrier. In the central nervous system, MMHg can cause irreversible damage (Harada, 1995; Wolfe et al., 1998).

In the environment, MMHg is the product of biotic and abiotic methylation in different environmental matrices including soil and sediment (Qian et al., 2000; Selin, 2009). In this context, environmental factors such as pH, redox potential or organic matter can promote its formation. Furthermore, mercury species in soils are strongly bound to the organic matter, which play an important role in the transport and transformation of mercury in this environment (Fernandez-Martinez et al., 2005; Jagtap and Maher, 2015). Due to its mobility in soils, MMHg is also a risk for groundwater and has the possibility of being absorbed by the existing vegetal biota (Li et al., 2010).

Many analytical techniques have been used for the determination of MMHg in environmental samples. Due to its high sensitivity and selectivity, atomic fluorescence spectroscopy (AFS) and inductively coupled plasma-mass spectrometry (ICP-MS) are most frequently used. Nevertheless, because of the high acquisition cost and maintenance cost of ICP-MS, AFS coupled to liquid (LC) or gas chromatography (GC) has become the most widely reported technique in speciation studies (Ramalhosa et al., 2001; Gao et al., 2012). Prior to analysis, it is necessary to separate MMHg from the sample to avoid matrix interference during sample processing. Especially derivatization steps required for GC analysis are prone to matrix suppression. Distillation methods are widely used to extract MMHg from complex matrices (Cai et al., 1997; Pietila et al., 2014). This methodology is based on a simple atmospheric pressure distillation and does not require complex reagents to obtain reliable results. It generates very little waste and has been demonstrated to be an effective and environmentally friendly analytical procedure. Moreover, distillation has proven to have a high efficiency (high recovery rates) compared with other extraction techniques. Besides, the Environmental Protection Agency (EPA, USA) has endorsed the use of distillation for MMHg determination in aqueous matrices (Method 1630, 1998). However, the use of distillation may result in the formation of an MMHg artifact, which can create a bias in samples containing high amounts of inorganic Hg (Hintelmann, 1999; Han et al., 2003). Notwithstanding these potential complication, it was also reported that the artifact MMHg formed is negligible for quantitative purposes in environmental samples having less than 2 $\mu g\ g^{-1}$ of total Hg (Liang et al., 2004). Method validation for MMHg analysis of soils samples is further complicated by the absence of certified reference materials, which are not commercially available for soils.

Soils are a notoriously complex matrix, often creating additional challenges for the isolation of any analyte. To improve consistency and quantitative recoveries, several modifications have been added to the methodology originally proposed for soil sample analysis (Westöö, 1966). Nevertheless, recovery yields below 76% are still being observed in some situations, probably due to matrix effects (Jagtap and Maher, 2015).

These low recoveries are likely due to incomplete distillation of MMHg from the soils samples, which requires a) the release of MMHg from the solid matrix by adding an acid solution and temperature and b) the distillation of CH_3HgCl that formed in the acid solution (Horvat et al., 1993a; Bowles and Apte, 1998). Since an excess amount of KCl is typically used to ensure a quantitative formation of the chloride, the distillation process itself should not be affected by the matrix. Hence, it is more likely that leaching is the critical step in this analytical technique. It is therefore critical that the interactions CH_3Hg^+ with the matrix are weakened to achieve quantitative extraction (Bollen and Biester, 2011; Cappuyns, 2012). In soils, all mercury species are deemed to strongly interact with organic matter, with humic and fulvic acids being mainly responsible for the metal retention (Yudovich and Ketris, 2005). AS well, the clay that is present in soils also has a large capacity to adsorb mercury species (Gabriel and Williamson, 2004; Yudovich and Ketris, 2005). Finally, factors such as pH and cation exchange capacity (CEC) of the soils could affect the mobility and the extractability of metals in soils. Some studies report that the ability of CH_3Hg^+ to bind to humic or fulvic matter can be modified for pH (Xu and Allard, 1991) and the chemical form of MMHg may depend on pH. For example at low pH (2–5), CH_3HgCl is expected to dominate over CH_3HgOH, whereas at higher pH, the hydroxide is the principal form compared to chloride or the free cation, which is usually present only in negligible quantities in environmental matrices. (Gabriel and Williamson, 2004). For this reason, optimization of acid and temperature or the addition of complexing anions have been recommended in the literature to overcome the various interactions of MMHg in soil matrices, regardless of whether the soil is organic, clay or sandy (Horvat et al., 1993b; Gabriel and Williamson, 2004; Issaro et al., 2009).

In view of the differences in the physical and chemical properties of the selected soils, it is essential to identify the significant variables involved in the distillation process with the subsequent optimization of the distillation procedure for each type of soil. In this work, we propose to optimize the extraction of MMHg from soil samples by distillation followed by GC-AFS. To evaluate potential matrix effects, a collection of four natural soil samples of different chemical characteristic was used for developing the method. The figures of merit were estimated and the accuracy of the final procedure was assessed by (i) analyzing certified reference materials and (ii) comparing results obtained by external calibration using AFS detection with those acquired by isotopic dilution analysis (IDA-GC-ICP-MS). Finally, the optimized method was applied to a series of real soil samples to demonstrate its applicability.

2. Experimental

2.1. Instrumentation and materials

The concentration of MMHg was determined by capillary gas chromatography coupled to atomic fluorescence spectroscopy (GC-AFS). The instrument used was Tekran 2700 Gas Chromatograph (Tekran® Instruments Corporation, Toronto, Canada) equipped with an AFS detector system. Chromatographic separation of mercury compounds was performed on a capillary GC column (DB-1, 15 m × 0.53 mm ID) using argon as the carrier gas at a flow rate of 15 $mL\ min^{-1}$.

A ThermoFisher (Bremen, Germany) XSeries 2 ICP-MS was used for ICP-MS analysis. The samples were introduced into the plasma with a borosilicate glass conical nebulizer (1 $mL\ min^{-1}$, AHF, Tubingen, Germany) via a conical spray chamber with impact bead (AHF). The ions of masses m/z 199, 200, and 201 were monitored in peak transient mode.

All glassware and plastic materials used in this study were rinsed with deionized water, decontaminated overnight in 20% (v/v) nitric acid solution and then rinsed again with deionized water.