



Suitable extraction of soils and sediments for mercury species and determination combined with the cold vapor generation atomic absorption spectrometry technique



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ABSTRACT

This work reports a fast and efficient procedure for mercury species extraction using Universol® as extractor reagent in soil and sediment samples combined with the cold vapor generation atomic absorption spectrometry (CV AAS) technique. Hg_{total} was determined after oxidation CH_3Hg^+ to Hg^{2+} with $KMnO_4$ and reduction Hg^{2+} to Hg^0 with $NaBH_4$. To ensure specificity and sensitivity in the Hg^{2+} determination, L-cysteine was added before the reduction with $SnCl_2$ to form complex with organic mercury species. Recovery values of between 98 and 102% were obtained for Hg_{total} , and 96–100% for Hg^{2+} . The relative standard deviations were lower than 2.7%. The detection limits were 0.07 and 0.08 $mg\ kg^{-1}$ for Hg_{total} and Hg^{2+} , respectively. The use of Universol® reagent combined with the CV AAS technique proved to be a simple and efficient procedure for the determination of Hg_{total} and Hg^{2+} in soil and sediment samples without interconversion of species allowing chemical speciation studies.

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1. Introduction

Soil pollution by toxic metals has been reported worldwide for decades. Due to this type of contamination, soils can be considered as a source of risk to human health and environmental quality, since they act as a filter or a dispersion agent for contaminants which can be introduced into water bodies and/or the food chain [1].

Metals such as mercury originating from natural sources are sometimes present in soils in small quantities. However, this amount can increase significantly due to anthropogenic activities, such as improper disposal of industrial, agricultural, domestic, commercial and hospital wastes, which release these contaminants into the soil, causing environmental degradation by altering the physical, chemical and biological characteristics of the area [2].

Soils have a high capacity to trap and store mercury due to its strong interaction with the soil constituents, especially organic compounds. This is more pronounced in clay soils, where the metal tends to remain stored for long periods [3].

Since mercury can be transformed into even more toxic organic forms in soils through the processes of oxidation and sorption, the analysis of soil samples to determine the amount of total mercury does not provide a conclusive evaluation regarding potential impacts on human

health and the environment [4]. Thus, the details of the screening of chemistry species in soils need to be understood since they are important for monitoring the environmental impact in a particular area over time [5].

To ensure that the levels of metals resulting from the improper disposal of municipal waste minimize potential problems for soil organisms, plants, animals and humans, government agencies such as the United States Environmental Protection Agency [6] and Council of European Communities [7] have established regulations governing the maximum levels of metals in soils.

In this context, considering the high toxicity of mercury, efficient sample preparation methods are required to quantify the mercury species in environmental and clinic waste samples. Alkaline reagents, such as tetramethylammonium hydroxide (TMAH), have been used for the rapid preparation of biological tissue samples prior to mercury speciation analysis [8–13]. The alkaline digestion of biological materials with TMAH offers a rapid and simple approach, which is a distinct advantage over conventional preparation techniques.

The successful use of alkaline reagents has encouraged the discovery of new reagents to improve the efficiency and sensitivity of the analysis of complex matrices, such as soil samples, which are composed of organic (including decomposing organisms) and inorganic constituents.

In this study, the use of an alkaline reagent, named Universol® (pH \approx 14), in association with cold vapor generation coupled to atomic absorption spectrometry, was used to extraction soil and sediment

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samples. A patent application for this reagent has been filed at the National Intellectual Property Institute (01400003467).

2. Experimental

2.1. Instrumentation

The measurements of mercury were carried by CV AAS. A Varian (Victoria, Australia) SpectrAA-220 flame atomic absorption spectrophotometer equipped with a continuous flow Varian VGA 77 vapor generation accessory was used. The VGA system consists of a three-channel peristaltic pump equipped with Tygon and polyethylene tubes that carry the sample through a reaction coil where it is acidified and mixed with a suitable reductant. The mercury vapor formed is transferred to an absorption cell for determination by the spectrometer [14]. The mercury hollow cathode lamp (Varian) was operated at 4.0 mA, the wavelength was set to 253.7 nm and the spectral band pass to 0.5 nm.

2.2. Reagents, samples and reference material

All chemical reagents were of analytical grade. The water was deionized in a Milli-Q system (Gehaka, São Paulo, SP, Brazil). Working solutions of Hg^{2+} were prepared by appropriate dilution of a 1000 mg L^{-1} Hg^{2+} stock standard solution (Merck, Darmstadt, Germany) in deionized water. The stock solution of CH_3Hg^+ (100 mg L^{-1}) was prepared by dissolving the CH_3HgCl salt, with a purity of 99.9% (Fluka, Steinheim, Germany) in methanol (Vetec, Rio de Janeiro, Brazil) and storing the solution in a dark glass bottle at 4 °C. Working solutions of CH_3Hg^+ were prepared by appropriate dilution of the stock solution in deionized water. The NaBH_4 (Merck) solutions were prepared in the range of 0.1–0.6% (w/v) in 0.5% (w/v) NaOH (Vetec, Rio de Janeiro, Brazil). Solutions of HCl were obtained by appropriate dilution of concentrated HCl of 36.5–38.0% purity (Vetec). The $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ solutions in 20% HCl (v/v) were prepared from the corresponding salt purchased from Merck (Darmstadt, Germany). An oxidizing agent solution was prepared by dissolving KMnO_4 (Merck, Darmstadt, Germany). The excess of KMnO_4 was reduced through the addition of a $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (Vetec, Rio de Janeiro, Brazil). L-cysteine chlorohydrate (99%) was obtained from Merck (Darmstadt, Germany). The interference study was carried out by dissolving appropriate amounts of the following compounds: Fe^{3+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Zn^{2+} (Carlo Erba, Val de Reuil, France). Nitrogen with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the carrier gas. Antifoam A (Sigma Aldrich, Missouri, US) was used as an anti-foaming agent. A mixture of reagents called Universol® 40% (v/v), with a patent application filed at the National Intellectual Property Institute (number 01400003467), was used in the extraction of the soil samples and a certified material. Universol® is a mixture of alkaline reagents (pH \approx 14). European Reference Material ERM CC580 (estuarine sediment), obtained from the Institute for

Table 1
Optimized CV AAS parameters.

Parameter	Studied interval	Optimum condition
<i>Reduction of Hg^{2+} with SnCl_2</i>		
SnCl_2 concentration (% w/v)	0.25–10.0	0.75
SnCl_2 flow rate (mL min^{-1})	0.5–2.0	1.0
Water flow rate (mL min^{-1})	0.5–2.0	0.75
Sample flow rate (mL min^{-1})	1.0–13.0	9.0
<i>Reduction of Hg^{2+} and CH_3Hg^+ with NaBH_4 in alkaline medium</i>		
KMnO_4 concentration (% w/v)	0.0–0.5	0.1
NaBH_4 concentration (% w/v)	0.1–2.0	1.0
HCl concentration (mol L^{-1})	0.5–7.0	3.0
NaBH_4 flow rate (mL min^{-1})	0.5–2.0	2.0
HCl flow rate (mL min^{-1})	0.5–3.0	1.0
Sample flow rate (mL min^{-1})	1.0–13.0	7.0

Table 2

Experimental conditions for the procedure to extract mercury from soil and ERM CC580 samples.

Variable parameter	Studied interval	Optimum condition
Volume of Universol® (μL)	100–1000	500 (ERM) 1000 (soil)
Antifoam concentration (% v/v)	0.1–1.5	0.5
Soil mass (mg)	50.0–500.0	500.0
ERMCC580 mass (mg)	10.0–250.0	150.0
L-cysteine concentration (% w/v)	0.1–1.0	1.0
Extraction time (min)	0.0–60.0	30.0
Temperature (°C)	30.0–70.0	60.0

Reference Materials and Measurements (IRMM) (Geel, Belgium), was used to evaluate the accuracy of the method and to optimize some variables. Soil samples collected from a solid waste disposal site (Romaria, Minas Gerais, Brazil) were kept under refrigeration in PTFE bottles until analysis. Plastic and glass containers were washed with tap water and a diluted detergent. They were then immersed in a 10% v/v HNO_3 solution for 48 h, rinsed thoroughly with deionized water and dried at room temperature.

2.3. Mercury cold vapor generation

The mercury determination by selective reduction was investigated using two different reducing agents: NaBH_4 and SnCl_2 . In order to ensure that the Hg^{2+} and CH_3Hg^+ species were efficiently transformed into mercury vapor, firstly, the parameters of the CV AAS system (concentration and flow rate of the reducing agents and the carrier solutions, sample flow rate and KMnO_4 concentration) were optimized, followed by a study on the extraction procedure.

2.4. Extraction procedure

In polypropylene tubes (50 mL), 10–150 mg of the certified material (ERM CC580) sample was weighed separately and mixed with 250 μL of the L-cysteine solution (0.1–2% m/v) and 100–1000 μL of the Universol® solution (40% v/v). The tubes were placed into the thermostatic bath and heated at 60 °C for 30 min to extraction of the samples.

Table 3

Interference effect of some ions in the recovery of Hg_{total} and Hg^{2+} in soil samples using the proposed method.

Interferent	Interferent: Hg	Recovery (%) Hg_{total} ($\text{CH}_3\text{Hg}^+ + \text{Hg}^{2+}$)	Recovery (%) Hg^{2+}
Fe^{3+}	1:10	93 \pm 0.6	92 \pm 2.0
	1:100	94 \pm 1.3	95 \pm 0.3
	1:1000	96 \pm 0.3	93 \pm 0.8
	1:10,000	92 \pm 1.6	93 \pm 0.7
Cu^{2+}	1:10	109 \pm 0.3	109 \pm 0.1
	1:100	99 \pm 0.4	107 \pm 0.1
	1:1000	109 \pm 0.3	107 \pm 0.3
	1:10,000	107 \pm 0.2	106 \pm 0.3
Cr^{3+}	1:10	101 \pm 0.9	106 \pm 2.0
	1:100	102 \pm 2.4	104 \pm 0.4
	1:1000	105 \pm 0.7	98 \pm 1.0
	1:10,000	95 \pm 0.4	95 \pm 0.1
Ni^{2+}	1:10	103 \pm 0.3	102 \pm 1.6
	1:100	101 \pm 0.2	100 \pm 0.8
	1:1000	97 \pm 0.3	100 \pm 2.0
	1:10,000	98 \pm 0.3	99 \pm 1.3
Zn^{2+}	1:10	102 \pm 0.3	106 \pm 3.2
	1:100	106 \pm 0.5	107 \pm 0.1
	1:1000	99 \pm 0.4	97 \pm 0.1
	1:10,000	100 \pm 0.1	97 \pm 0.5

Experimental conditions: 500.0 mg of soil, 1000 μL of 40% (v/v) Universol®, NaBH_4 : 1.0% w/v, HCl: 3.0 mol L^{-1} , KMnO_4 : 0.1% w/v, Antifoam: 0.5% (v/v), SnCl_2 : 0.75% (w/v), L-cysteine: 1.0% (w/v), 60 °C and 30.0 min.

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