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Article

A low-cost device for sample introduction and determination of mercury by Cold Vapour Atomic Absorption Spectrometry – application for irrigation water and paddy soil

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Mercury (Hg) is a global pollutant that is released into the environment from geological and anthropogenic sources and its compounds are highly mobile and toxic at trace level. A simple method based on cold vapour atomic absorption spectrometry (CV AAS) for the determination of total mercury in irrigation waters and extractable mercury in paddy soil was validated, using a low-cost sample introduction device. The validated method presented a linear range from 0.2 to 2.0 µg L^{-1}; detection limits were 0.03 µg L^{-1} and 0.012 mg kg^{-1} (dry basis) for irrigation water and paddy soil respectively. Trueness was evaluated using spiked samples; the mean recovery was 101% (n=8) and 99.4% (n=6) for irrigation water and paddy soil respectively. Precision, expressed as relative standard deviation (RSD), was 9.6% (n=10) and 24% (n=8) for irrigation water and paddy soil respectively. These figures of merit were adequate for the determination of total Hg levels in irrigation waters and extractable Hg in paddy soils established by the regulations. To assess analytical performance several samples from the Eastern zone of Uruguay were analysed. Sample preparation consisted of an acid digestion using an economical pressurized reactor. Hg levels in waters and paddy soils were all below the maximum allowed and therefore were apt for agricultural use. These results are very important not only locally but also for the world since Uruguay is currently among the eight-largest paddy rice and milled rice exporter in the world. This method can be an alternative instead of the more expensive techniques mostly not available in developing countries and very easy to implement in environmental laboratories.

Keywords: Cold vapour atomic absorption spectrometry, paddy soil, water, mercury, low cost sample introduction device.

INTRODUCTION

The toxicity of mercury (Hg) is well known, affecting the environment (water, soil, air and biota), therefore, the scientific community has devoted efforts and research for the study of the damage that Hg causes to the environment in general. Historical and contemporary evidence suggests that Hg atmospheric levels increased between two and five times since the development of the industrial era. Due to its physicochemical properties, including high mobility and long period of residence in the atmosphere and the fact that the contamination of aquatic food chains is widespread geographically, Hg is considered as a global problem and a matter of concern [1, 2]. If waters and their sediments become contaminated from sources such as atmospheric deposition and discharges from industrial, municipal, or agricultural operations, toxic substances could concentrate in seafood and wildlife [3]. In 1992, under the Clean Water Act (CWA) the United States Environmental Protection Agency (USEPA) provided criterion concentrations for Hg as a priority toxic pollutant [4].

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The presence of Hg in aquatic systems is a matter of concern since it can participate in processes of bioaccumulation and biomagnification in the food chain. So many countries established the maximum admitted levels of total Hg as a parameter for the determination of the water quality [5-7].

In contaminated waters, such as industrial wastewaters, or water bodies near gold mines, Hg concentrations can reach the μg L^{-1} range [8]. For drinking water the maximum level of inorganic Hg recommended by the USEPA in accordance with the Safe Drinking Water Act (SDWA), is 0.002 mg L^{-1} [4]. The World Health Organization (WHO) established the maximum in 0.006 mg L^{-1} [8, 9]. In Uruguay, governmental authorities manage the water resources and provide drinking water to the population of the country. To prevent environmental contamination, water control is managed by local regulation. According to this regulation the maximum Hg concentration admitted is 0.001 mg L^{-1} [10].

The environmental mobility and toxicity of Hg in soils depend on its species. Soluble inorganic Hg species are more easily transported by natural processes and serve as the substrate for methylation process. These extractable organomercury species and extractable inorganic species constitute the majority of potentially toxic Hg in soils. The "non-mobile" Hg species such as mercury sulfide are chemically stable in the soil for longer geologic time periods and thus are less toxic [11].

In addition to Hg that can be found naturally, an anthropogenic source contributing to the soil contamination exists since a wide variety of organic mercurials have been used in the past as disinfectants and pesticides. Primarily fungicides, insecticides and herbicides were used in agriculture as preservatives. Some of these agrochemicals include organomercurials such as phenylmercuric acetate, phenylmercuric nitrate, nitromersol, thimerosol, mercurochrome and mercurobutol [12]. Currently none of them is registered in the USEPA, but because of its persistence in soil and environment, mercurial pesticides have been classified as permanent (half-alive more than 20 years) and hence monitoring them is relevant even though they are no longer applied [12]. According the Canadian Council of Ministers of the Environment the maximum amount of inorganic Hg in soils for agricultural use is 6.6 mg kg^{-1} [13].

In Uruguay surveillance of the quality of the water for agricultural use and of paddy soils is important not only for public health reasons but for economical reasons as well. According to the Food and Agricultural Organization for the United Nations (FAO) Uruguay is one of the top ten rice-exporting countries in the world. All major suppliers of rice belong to Asia but there are also a few countries, particularly Argentina, Uruguay, United States and Egypt, that consolidated themselves as reliable rice exporters [14]. Rice is planted once a year, mostly in the coastal plains (Eastern Zone), in the valley of Uruguay River, and in areas located along the border with Brazil and Argentina (Northern Zone).

Analytical determinations at trace levels of total Hg in environmental samples can be carried out by several techniques. The analyses must be reliable and fast, thus causing constant pressure on analytical laboratories which must fulfil an increasingly demand. This has triggered research for alternative rapid, simple and economical methods for the determination of contaminants at trace levels. Expensive techniques sometimes are not available mainly in developing countries.

The most popular detection technique for the determination of Hg in several matrices is cold vapour atomic absorption spectrometry (CVAAS) [15-19]. This technique also presents some important advantages, including the separation of the analyte from the matrix, which reduces the number of interferences that may occur. Some variations for the cold vapour method are commonly used, such as cold vapour atomic fluorescence spectrometry (CAFS) [19-21] and cold vapour inductively coupled plasma-optical emission spectrometry (CV-ICP-OES) [19, 22] all of them have also been successfully used for Hg determination. These techniques require the use of a commercial module for sample introduction, typically flow injection manifolds. For this module, the estimate cost is USD 7.000 to USD 10.000. More recently, highly sensitive and selective detection methods include instrumental techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS) [20, 23], total reflection X-ray fluorescence (TXRF) [20, 24], and thermal desorption/atomic absorption technique [20, 25-26] have been used for mercury determination in environmental samples.

The aim of this work is to present a simple low-cost system for sample introduction and subsequent determination of Hg by CVAAS using an atomic absorption spectrometer. The system coupled to the spectrometer consists of a glass separation funnel and a piece of a commercial midget impinger, both devices commercially available for less than USD 300. The performance of the proposed system was evaluated in terms of figures of merit and once validated it was applied to environmental samples analysis. In addition, the sample preparation of soils was carried out using a low-cost pressurized reactor.

MATERIALS AND METHODS

Reagents

All chemicals were of analytical reagent grade and all the solutions were prepared with ultrapure water of 18.2 MΩ cm resistivity (ASTM Type I). All glassware was soaked overnight in 10% (v/v) HNO_3 before use. All reagents were with low content of Hg checked by blank analysis.

An Hg 1000 mg L^{-1} commercial standard solution (Merck) for atomic absorption spectrometry was used. The reducing agent was stannous chloride (20% w/v $SnCl_2.2H_2O$). Nitrogen (dried and purified by a combined Drierite/molecular sieve trap) was used as carrier gas.

Acid digestion was made with a mixture of sulfuric acid (H_2SO_4) - nitric acid (HNO_3) (1 + 1 v/v), potassium permanganate solution ($KMnO_4$) 5% (w/v) and potassium persulfate solution ($K_2S_2O_8$) 5% (w/v). The subsequent treatment was carried out with hydroxylamine hydrochloride solution ($NH_2OH.HCl$) 12% (w/v).

For validation, a standard reference material (SRM) Inorganics in Marine Sediment was analysed (NIST 2702). The certified value for total Hg was 0.4474 ± 0.0069 mg kg^{-1}.

Calibration solutions

The commercial stock solution of 1000 mg L^{-1} was diluted to prepare an initial intermediate standard solution (10 mg L^{-1}) and from this, a second standard intermediate solution of 100 µg L^{-1}. Calibration solutions in the range of 0.1 - 2.0 µg L^{-1} were prepared daily by stepwise dilutions from the second intermediate standard solution. Ultrapure water was used for all dilutions.

To evaluate possible matrix interferences, standard additions were made at two levels of concentration spiking water and paddy soils so that the final concentration of Hg in the reactor was 1.0 and 1.8 µg L^{-1}.

Method

The analytical strategy for total Hg determination is based on a sample treatment that ensures that the metal is in its highest oxidation state (Hg^{2+}) in inorganic form and a subsequent reduction to elemental Hg^0 using a suitable reducing agent ($SnCl_2$). The reduction step takes place in a reactor (separation funnel in this method) and an inert gas as N_2 (or Ar) carries the Hg^0 vapour formed in the reduction process from the reactor to the measuring system. This process will be detailed bellow for the proposed assembly.

After generation of Hg^0 vapour, the inert gas transports it to a closed measuring cell with quartz windows. Detection takes place using a hollow cathode lamp or electrodeless discharge (EDL) and measurements are carried out at 253.65 nm.

Samples

For evaluation of the analytical performance of this system, several samples of irrigation water and paddy soil were collected and analysed. The sampling plan was carried out following the International Organization for Standardization (ISO 5667-1:1980, ISO 5667-2:1991 and ISO 5667-3:2003) recommendations [30-33]. Nine sampling points in rivers and lagoons were selected on the East part of Uruguay (East zone in Figure 1); these are water sources used to irrigate rice crops.

Figure 1. Regions of rice crops in Uruguay.

From each location, the samples were taken in duplicate and were conserved in glass bottles (pH was adjusted to pH< 2 with HNO_3) and stored at 4 °C during transportation. Twenty soil samples were collected from the three zones destined in Uruguay for rice crops (Figure 1). The sampling plan was done according to the recommendations of the USEPA standard operation procedure for soil sampling [34].

For each location, the sample was obtained by inserting a trowel (maximum depth: 15 cm) in 20 points within a surface of 1000 m^2 to conform a bulk sample of approximately 1 kg. The bulk sample was placed inside a polyethylene zip-closed bag and transported to the laboratory. Before analysis, samples were dried in an oven at 70 °C (for maximum 48 hours) and sieved through a sieve DIN Nº 12 (106 µm).

Sample preparation

For irrigation water, sample preparation was done according the standard methods for total Hg determination in environmental waters (USEPA 245.1 and 7470a) [27, 28]. Acid digestion was carried in a Kjeldahl digestion unit (VELP Scientifica) using glass tubes. 30 mL of each sample was heated for 1 hour at 80 °C with 1 mL of a mixture of HNO_3:H_2SO_4 (1:1 v/v), 0.5 mL of $K_2S_2O_8$ 5% (w/v) and five drops of $KMnO_4$ 5% (w/v) solution. After digestion, the solution was let to cool until it reached room temperature, then 2 drops of $NH_2OH.HCl$ 12% (w/v) were added and was agitated until the colour disappeared and then completed to a volume of 40 mL with ultrapure water. Reagent blanks were also run.

For paddy soil, sample preparation was adapted from the USEPA 3200 Method [29] as follows: 0.2 g of paddy soil was accurately weighed in a 30 mL screw-capped Teflon® PFA vessel (Savillex, Minnetonka, MN, USA) and 7 mL of concentrated HNO_3 and 1 mL of ultrapure water were added. The vessel was placed in a pressurized reactor (a domestic stainless steel pressure cooker with a capacity of up to 6 vessels) and heated in a hot plate for 1 hour. After cooling, the suspension obtained was centrifuged for 3 minutes at 3000 rpm and the supernatant was used for the analytical determinations after completed to a final volume of 40 mL with ultrapure water. Reagent blanks were measured alongside the samples.

Instrumentation

All measurements were taken with a Perkin Elmer model AAnalyst 200® atomic absorption spectrometer coupled to a PC with the software WinLab 32 AA®, fitted with a 15 cm absorption cell with quartz windows. The operating conditions were continuous data acquisition mode (MHS); slit width 2.7 nm; integration time: 58 s; analytical signal: peak area; electrodeless discharge lamp (EDL) for Hg (Perkin Elmer®); intensity = 220 mA and λ = 253.65 nm.

The reactor, consisting of a separation funnel (borosilicate 3.3 glass, 125 mL) commonly used for liquid-liquid separations with a PTFE stopcock in the lower part that allows the removal of the solution after each determination.

A commercial glass (borosilicate 3.3, Pyrex®) midget impinger, with fritted nozzle, was placed inside the separation funnel; the two pieces of glass were fitted together using a 20/40 ground joint. A complete impinger (commercially available as midget impinger for a 25 mL glass tube) costs approximately USD

150. The carrier gas (N_2) passes through the porous glass membrane (pore size: 200 μm) located at the end and at the thinnest part of the reactor, into the solution. This allows both the input of the carrier gas and the released the vapour (Hg^0) to move towards the detection system (Figure 1).

Figure 2 describes the complete system. This design permits the bubbling of the carrier gas into the reactor and therefore an efficient transportation of the analyte towards the detection system. Before the absorption cell, a tube containing silica gel was placed to prevent the passage of moisture to the detection system. The system was completed with silicone tubes and at the end of the absorption cell a flask with a $KMnO_4$ solution (5% m/v) acts as a trap for the Hg vapour generated in the reactor thus avoiding contamination of the laboratory environment.

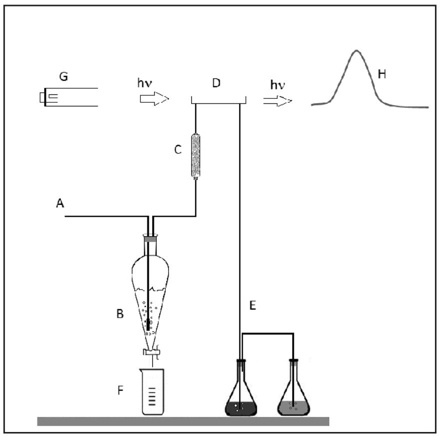

Figure 2. Scheme of the complete device used for Hg determination coupled to CVAAS.
A: N_2 inlet (1 L min^{-1}); B: separation funnel with a piece that ends with a porous glass membrane; C: desiccant; D: absorption cell; E: trap for Hg vapour (the flask on the left side containing $KMnO_4$, and the other one containing water to close the system); F: Waste; G: Hg lamp; H: transient signal.

The general procedure for the proposed system is the following: after sample preparation, the final volume was in all cases 40 mL completed with ultrapure water. Place the sample (previously digested) or standard in the reactor (separation funnel) and then add 2 mL of the reducing agent ($SnCl_2$ 20% w/v), and cover the reactor immediately.

Record the instrumental signal (peak area). After the measurement time (30 s for this system), discard the solution by opening the stopcock. Wash the reactor by placing ultrapure water in the separation funnel and discard by opening the stopcock at least 2 times. After this sequence, the system is ready for a new determination. Ultrapure water volume depends on the volume of the sample; in previous assays, it was demonstrated that for proper operation total volume in the reactor must not be less than 35 mL and not exceed 45 mL due to the geometry of the system.

RESULTS AND DISCUSSION

Sample introduction system

The use of a separation funnel with an impinger piece as a reactor coupled with the CVAAS detection system was successful in terms of analytical performance being a low-cost alternative to the expensive flow injection manifolds. The piriform separation funnel (reactor) was chosen due to its particular design since it has several advantages.

Inside the reactor, the redox reactions that occur are: $Hg^{2+} + 2e^- \rightarrow Hg^0$ and $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ the reaction is instantaneous. Elemental Hg is poorly soluble in water, but it can be detected when Hg is in the vapour state, so it is necessary to promote mass transfer from the liquid phase to the vapour phase. The angular design of the reactor allows less dead volume compared to a cylindrical one, enabling all Hg that is in the vapour state to migrate immediately into the carrier gas stream (N_2). The entry of nitrogen as microbubbles generated by the porous glass membrane (pore size: 200 μm) favours two important aspects in the system: the generation of a vortex which acts as a mixer and simultaneously the exposure surface mass transfer is enhanced by the spherical shape thereof.

A constant flow rate of 60 mL min^{-1} ensures vigorous mixing and the pore size of the membrane ensures adequate mass transfer of Hg in the liquid phase to the gas phase, to reach the absorption cell quantitatively, generating a transient signal (Figure 3). The time required for each determination is about 3 minutes, whereby the sampling frequency can be estimated at 20 samples/hour. This frequency is similar for FIAS commercial systems.

The amount of the reducing agent ($SnCl_2$) in large excess was to ensure good reaction rate. Once the sample was added, the reactor was immediately closed allowing the passage of nitrogen. The curved shape at the top of the reactor also improves the breaking of the bubbles and decreases the possibility of generating a dead volume. Another advantage of this reactor is that is very easy to empty it using the PTFE stopcock of the bottom, facilitating its cleaning and reloading. The commercial flow analysers have very serious problems with carry over effects and tubing must be often removed because of cross contamination. This assembly did not present this inconvenient.

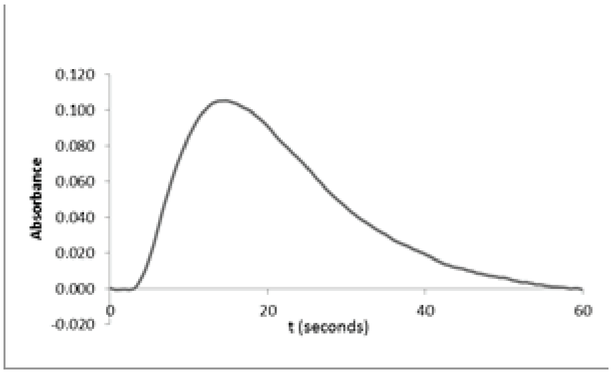

Figure 3. Transient signal obtained for Hg determination.

Figures of merit and method validation

The figures of merit were obtained according the recommendations of the Eurachem Guide: The Fitness for Purpose of Analytical Methods [35]. For the evaluation of linearity, blank and 10 standard solutions in the range 0.2 - 1.8 µg L^{-1} were measured and the results (peak areas) were plotted versus concentration. Linearity in this range was confirmed by visual inspection of the plot (R^2= 0.999) and analysis of residuals.

Detection (DL, 3*s*) and quantification (QL, 10*s*) limits were estimated by measuring (n=10) the dispersion of the blank signal and referring the measurements to the calibration curve. Blank signals were approximately 2.0% of the value of the signal (peak area) of the highest standard used for the calibration curve.

Slopes of external calibration curves and standard addition curves were determined for water and paddy soil. The slope values were 0.5502 L μg^{-1} for external calibration (n>30), 0.5628 L μg^{-1} for water samples (n=9) and 0.5670 L μg^{-1} for paddy soils (n=20). These results show no significant differences between slopes so no evidence of multiplicative interferences was found for either irrigation water or paddy soils (differences lower than 5% between slopes).

To establish the trueness of the method, nine irrigation waters and twenty paddy soils were analysed. The trueness of the method was verified for both kinds of samples by a spike/recovery approach at two levels (40 and 70 ng Hg). Recoveries obtained from these analyses are shown in Table I.

In addition, a standard reference material (SRM) Inorganics in Marine Sediment (NIST 2702) was analysed. Mean Hg concentration was 0.425 ± 0.053 mg kg^{-1} (n=15), this corresponds a recovery of 95% compared with the certified value.

Precision as relative standard deviation (RSD (%)) was estimated by both instrumental and analytical repetition. Table I summarizes the main figures of merit obtained for the validation.

Table I. Figures of merit

Parameter	Results	
	Irrigation water	Paddy soil
Detection Limit (DL) (n = 10)	0.03 µg L^{-1}	0.012 mg kg^{-1} (dry basis)
Quantification Limit (QL) (n = 10)	0.10 µg L^{-1}	0.039 mg kg^{-1} (dry basis)
Linearity (µg L^{-1})	0.2 – 2.0	
R^2	> 0.997	
Precision (Instrumental) RSD (%)	6.1 (n=15)	
Intermediate Precision RSD (%)	9.6 (n=10)	24 (n=8)
Trueness (% R)	101.0 (n=8)	99.4 (n=6)

These figures of merit were adequate for the intended purpose since the quantification limit allows the methodology to be useful for water and soil surveillance and monitoring without a pre-concentration step or flow injection manifolds for sample introduction.

Almeida et al. postulate an alternative sample preparation method for the determination of extractable Hg in soils and sediments using CVAAS. The authors report a detection limit of 0.07 mg kg^{-1} using a flow injection manifold for sample introduction and our method provides a lower LD for paddy soils (0.012 mg kg^{-1}) considering the above-mentioned advantages and the fit for purpose [37].

Precision was good, considering that is a manual method and it is in accordance with Horwitz theory about variability at trace levels (coefficients of variation less than 45%) [36]. Trueness resulted suitable, thus the method can be considered accurate (truthful and precise).

Real sample analysis

For irrigation waters samples the concentration of total Hg was below the DL for eight of them, only one was < QL (0.10 µg L^{-1}). All irrigation waters analyzed were suitable for agricultural use (< 0.2 µg L^{-1}).

Table II shows the results of extractable Hg levels for paddy soil samples. All of them comply with the requirements established by the Canadian Council of Ministers of the Environment (< 6.6 mg kg^{-1}).

USEPA 3200 standard method recommends a microwave assisted treatment for soils. An analytical microwave oven is an expensive instrument not always available in routine analysis laboratories. The use of a pressurized reactor as an alternative was successful in this work thus reducing the cost of analysis.

Table II. Mercury levels in paddy soils.

Sample	mg kg^{-1} (dry basis)	Sample	mg kg^{-1} (dry basis)
1	0.070 ± 0.003	11	< 0.039
2	0.094 ± 0.023	12	0.046 ± 0.002
3	0.066 ± 0.002	13	< 0.039
4	0.063 ± 0.001	14	0.041 ± 0.002
5	< 0.039	15	< 0.039
6	0.070 ± 0.003	16	0.039 ± 0.004
7	0.155 ± 0.028	17	0.066 ± 0.002
8	0.092 ± 0.002	18	0.063 ± 0.001
9	< 0.039	19	0.113 ± 0.014
10	0.051 ± 0.001	20	0.112 ± 0.002

Values expressed as mean ± dispersion between duplicates (QL = 0.039 mg kg^{-1})

CONCLUSIONS

An economic analytical tool for sample introduction and subsequent determination of total Hg in irrigation waters and extractable Hg in paddy soil coupled to the CV-AAS technique was developed and validated. This design can be postulated as a simple low-cost alternative to the commercial flow injection manifolds for sample introduction for total Hg determination in these samples. This method has proven to be an alternative to more expensive techniques such as CV-AFS not frequently available in developing countries and presented advantages compared with commercial flow systems used for sample introduction. Figures of merit were adequate for monitoring purposes according the regulations. Hg levels in all the analysed samples were far below the maximum admitted values.

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Disclosure Statement

The authors declare that there is no conflict of interest regarding the publication of this article.

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