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New design of cold finger for sample preparation in open system: Determination of Hg in biological samples by CV-AAS

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ABSTRACT

This paper presents studies involving the determination of Hg in biological samples by cold vapor atomic absorption spectrometry (CV-AAS) using a simple and inexpensive system for sample digestion. The system consists of a glass tube that is closed with a small glass tube filled with cold water, which is called cold finger, and helps the recirculation of the acids within the bigger tube. The use of cold finger avoided the loss of analyte and the excessive evaporation of the acids during the heating. Thus, lower amount of acid was required, decreasing the risk of contamination. Studies of temperature of the digester block were performed with aqueous standard solutions in an interval between 80 and 120 °C. No significant loss of analyte was observed when compared with the open system. Certified reference materials (CRMs) were used to evaluate the accuracy of the proposed methodology. For this process, samples were digested with HNO_3 for 2 h in a digester block between 90 and 120 °C, using the open system with the cold finger. The use of the cold finger system was efficient with similar results to those expected for CRMs for mercury (Hg) concentrations. For the open system, loss of analyte was observed when the digestion temperature was increased. The limit of detection (LOD) was 0.08 μg L^{-1}. The digestion procedure using cold finger in an open system is useful, at boiling point solution temperature, safe and simple for Hg determination in biological samples. Moreover, it can be used as an alternative to microwave-assisted digestion.

1. Introduction

Mercury (Hg) is a global pollutant which requires a great attention due to its bioaccumulation properties and reactivity. It is highly toxic even in low concentrations, and its dispersion in the environment is due to natural emissions or anthropogenic activities. The main indirect source of human contamination of Hg is through the consumption of fish products (fish, crustaceans, etc.). Thus, the need for the development and validation of analytical methodologies for the determination and control of this toxic metal in food samples is evident [1,2].

Among the analytical techniques used for the determination of Hg, cold vapor atomic absorption spectrometry (CV-AAS) is widely applied since it is a low cost technique [3,4]. Using this technique, mercury species are typically mineralized to Hg^{2+} through acid attack and then reduced to the elemental form (Hg^0) by reaction with $SnCl_2$ or $NaBH_4$ [5,6]. However, organomercury species are not reduced to metallic Hg with $SnCl_2$ nor completely with $NaBH_4$. Thus, the organic matter in the sample must be sufficiently oxidized to liberate mercury species from the sample matrix for the inorganic form (Hg^{2+}) [7].

Due to the need to convert mercury species into its most appropriate form for CV-AAS, special attention is focused on the sample preparation step. Generally, the sample preparation involves heating the sample in the presence of different combinations of mineral acids such as nitric, hydrochloric, sulfuric and perchloric acids and also other oxidizing agents such as hydrogen peroxide. However, this step becomes critical due to the high volatility of Hg or incomplete digestion of the sample [8,9]. Consequently, the wet digestion at high temperatures using open systems is not feasible due to possible losses of analyte and/or to the evaporation of the solvent [10]. An alternative to the sample digestion for the determination of volatile elements is the use of closed systems mainly assisted by microwave because the risk of analyte losses by evaporation and contamination is minimized [11–15].

The use of cold finger system for a complete digestion of the samples in an open system with conventional heating is still little explored. Although the applicability of this technique has been demonstrated in earlier works [16,17], recent papers have showed it as a promising alternative to more sophisticated methods of sample

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preparation with accurate and precise results for the determination of volatile elements and trace elements [18–21].

Silva et al. [18] performed studies on the presence of Hg, Zn, Fe and Mn in sediment samples, after these were submitted to the digestion process at 70 °C for 1 h in a thermal-kinetic reactor cold finger. Recently, Jesus et al. [20] conducted studies for the determination of Pb in vegetable foods. However, the authors only reported the use of a cold finger system, without giving further details of the design or studies showing its effectiveness.

Based on the above considerations, this paper presents a new technique for the digestion of biological samples using an open system at high temperature for the determination of Hg. For this proposes, a cold finger was developed and inserted in a digestion vessel for sample preparation using an open system with conventional heating.

2. Experimental

2.1. Instrumentation

All measurements were conducted using an AA-6300 atomic absorption spectrometer (Shimadzu, Japan) equipped with deuterium arc background correction and a mercury hollow cathode lamp source (Hamamatsu photonics K.K., Japan). The spectrometer was operated under the following conditions: wavelength, 253.7 nm; spectral band pass, 0.7 nm; and lamp current, 4 mA. A quartz tube atomizer (QTA) of 14.7 cm length and 2.4 mm diameter was mounted in the flame compartment of the spectrometer positioned in the optical path and maintained at room temperature. The steady-state absorbance measurements were made in a continuous graphic mode. Argon, with a purity of 99.996% (Linde, São Paulo, Brazil), was used as the carrier gas.

A hydride generator HVG-1 (Shimadzu, Japan) was coupled to the spectrometer, and the vapor generator system was manually operated. A 0.5% m/v $SnCl_2$ in 3.0% v/v HCl was used as reducing agent. The reducing agent, carrier solution (4.0% v/v HCl), and samples were injected using a continuous flow mode. A 70 mL min^{-1} flow of Ar purge gas was introduced into a gas–liquid separator merging with the effluent from the confluence point and transporting the volatile species directly to the QTA. Fig. 1 schematically illustrates the system used in this work.

For the sample acid digestion, a heated digester block was used (MA-4025 model, Marconi, Piracicaba, SP, Brazil). In each digester tube a cold finger was introduced to avoid losses by volatilization of Hg and reagents, as shown in Fig. 2. The system consists of a glass tube closed with a small glass tube and filled with cold water in order to help the recirculation of the acids within the bigger tube. A Shimadzu TOC-5000 total organic carbon analyzer (Shimadzu GmbH Europe, Duisburg, Germany) was used for the determination of the residual organic carbon content.

2.2. Reagents and samples

Analytical reagent grade materials were used for all experiments. All solutions were prepared using high-purity water with a resistivity of 18.3 MΩ cm and were obtained from a Direct-Q 3 Water Purification System (Millipore Corporation, Bedford, MA, USA). A standard stock solution (1000 mg L^{-1}) of inorganic mercury was prepared from Tritisol® (Merck, Darmstadt, Germany). Standard stock solutions (1000 mg L^{-1}) of methylmercury (CH_3HgCl) and ethylmercury (CH_3CH_2HgCl) were prepared dissolving methylmercury chloride (Fluka Analytical, Steinheim, Germany) and ethylmercury chloride (Analytical Supelco, Bellefonte, USA) in bidistilled alcohol, respectively. The nitric acid (Vetec, RJ, Brazil) and hydrochloric acid (Synth, SP, Brazil) were purified by doubly subboiling distillation in a quartz system MA-075 (Marconi, model MA-075, Piracicaba, SP, Brazil). Tin chloride (Sigma-Aldrich, Steinheim, Germany) was used as a reducing agent. Plastic and glass containers were washed with tap water and with a diluted Extran solution followed by immersion in 10% v/v HNO_3 for at least 48 h and a thorough rinse with ultrapure water prior to use.

Certified reference materials (CRMs) from the National Research Council Canada were used to evaluate the accuracy of the proposed system: DOLT-4 (dogfish liver), DORM-3 (dogfish muscle) and TORT-2 (lobster hepatopancreas).

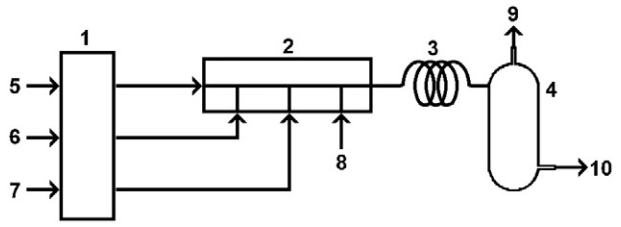

Fig. 1. Schematic diagram of cold vapor system. 1: Peristaltic pump; 2: confluence points; 3: reaction coil; 4: gas–liquid separator; 5: sample; 6: HCl (3.0% v/v); 7: $SnCl_2$ (0.5% m/v); 8: argon inlet; 9: to QTA for AAS; 10: outlet to waste.

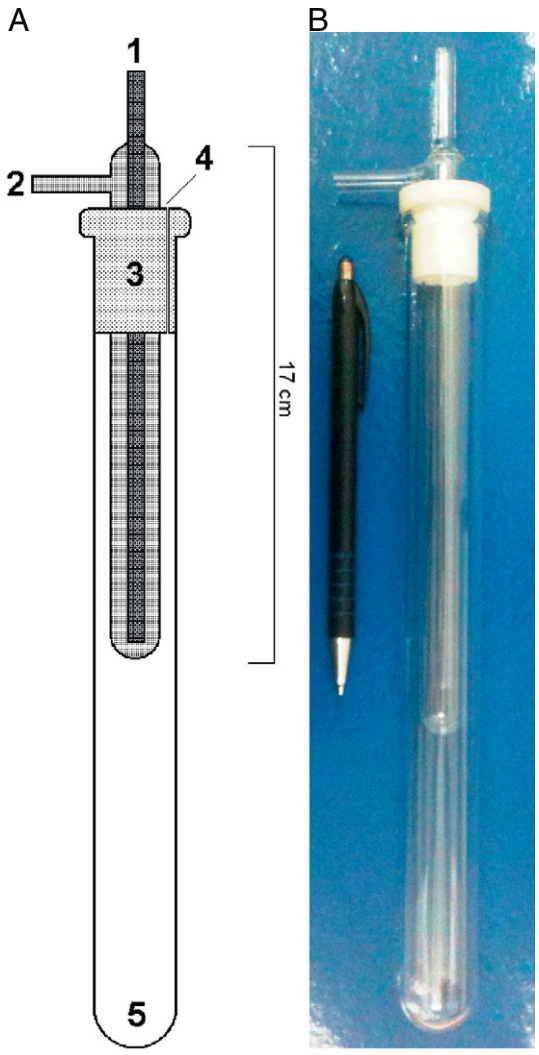

Fig. 2. A) Schematic diagram of cold finger coupled to glass digester tube. 1: Water inlet; 2: water outlet; 3: end cap of PTFE; 4: outlet to gas; 5: reaction flask. B) Picture of cold finger system.

2.3. Sample preparation procedures

Biological samples were treated by acid digestion using a digester block (open system) with or without the use of the cold finger