Mercury Determination: A Hair Raising Experiment

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Abstract

A novel, fast, low-cost portable system for the total analysis of mercury (Hg) in human hair is presented by induction heating-electrothermal vaporization, gold amalgamation, atomic absorption spectrometry (IH-ETV-GA-AAS). Using this innovative technique a detection limit of 1 ng (or 1.5 mg/g based on a 0.6 mg sample) was achieved.

Introduction

Mercury (Hg) has for centuries been a useful metal in a variety of applications. Unfortunately this usefulness is counterbalanced by its neurotoxicological health impact. Hg is introduced in the food chain when anaerobic bacteria at the bottom of the bodies of water convert inorganic Hg into an organic Hg form. Progressively larger and larger life forms consume the former as part of the natural food chain, essentially concentrating the Hg (Skoog, West and Holler 1996). Some aquatic life concentrates Hg by a factor of 100,000 leading to dangerous levels as high as 20 parts per million (ppm) in some potentially commercialized fish intended for human consumption. For these reasons, the American Food and Drug Administration (FDA) has set a legal limit of one ppm and Health Canada an even lower 0.5 ppm limit for fish intended for human consumption. Likewise, these organizations have issued an advisory to women who may become pregnant, pregnant women, nursing mothers, and young children to avoid some types of fish and eat fish and shellfish that are lower in mercury (Health Canada 2004; Rados 2004).

In view of the above, analytical methods play an important role maintaining quality control, minimizing the health impact of Hg. The analysis of human hair has been proven to be reflective of the body's total Hg load (Legrand et al. 2005) and obviously is less intrusive than blood tests (Barbosa et al. 2004). Conventional methods for the determination of Hg in hair include cold-vapour atomic absorption spectrometry (CV-AAS) (Manzoori, Sorouraddin and Haji 1998), cold-vapour atomic fluorescence spectrometry (CV-AFS) and inductively coupled plasma mass spectrometry (ICP-MS) (Gill, Schwartz and Bigras 2002). These methods require about 5 to 10 mg of hair (some 100 strands of hair) and include a lengthy digestion step (which introduces the potential for contamination and loss). To minimize the quantity of hair needed as well as remove the digestion step, direct Hg analyses of human hair strands have been performed by X-ray fluorescence (Toribara and Jackson 1982), particle induced X-ray emission spectroscopy (Valkovic et al. 1973), and laser ablation-inductively coupled mass spectrometry (LA-ICP-MS) (Legrand et al. 2004). These techniques have the advantage of little sample preparation yet are limited by detection limit, expensive instrumentation or difficult calibration. Alternatively, combustion gold amalgamation atomic absorption spectroscopy (C-GA-AAS) has been used for the direct analysis of hair, yet still requires some sample preparation involving the addition of a catalyst (to promote combustion) and modifiers (to absorb combustion by-products) (Cizdziel and Gerstenberger 2004; Legrand et al. 2004). Most recently, induction heating-electrothermal vaporization inductively coupled plasma mass spectrometry (IH-ETV-ICP-MS) was employed for direct analysis of total mercury in a single human hair strand, achieving a detection limit of 20 pg or 30 ng/g (based on a 0.6 mg sample) (Lafleur et al. 2005). The primary disadvantage with this system is its costly and bulky detection system.

Key Terms

Mercury

Human hair

Induction heating electrothermal vaporization

Gold amalgamation

Atomic absorption

We report here an alternative method that is fast, less costly and potentially field portable which combines the simple direct sample vaporization of induction heating-electrothermal vaporization, with a gold amalgamation trap and detection at 253.7 nm by atomic absorption spectrometry (IH-ETV-GA-AAS). This system could be very useful in monitoring Hg exposure in populations at risk such as Native North American fishing populations.

Materials and Methods

Induction heating-electrothermal vaporization (IH-ETV) sample introduction

The IH-ETV sample introduction system has previously been described in detail (Goltz and Salin 1997; Goltz, Skinner and Salin 1998; Rybak and Salin 2001). In previous work, it has been used to vaporize soil slurries (a liquid mixture of water and insoluble matter), cellulose filters and human hair (Rybak and Salin 2001; Salin and Ren 2003; Lafleur et al. 2005). As seen in Figure 1, the IH-ETV consists of a modified "Leco" induction furnace. The samples were placed in commercially available graphite sample cups equipped with boiler caps to prevent the escape of the sample. These graphite cups were placed at the center of the induction coil of the modified furnace which, when turned on, heated the cups without any physical contact and vaporized the sample (in this case hair). The vaporized samples were entrained out of the IH-ETV by an argon (Ar) gas stream through PTFE tubing at a flow rate of 500 mL/min. Furthermore, to eliminate undesirable arcing between the graphite cup and the surrounding quartz chamber (which would char the graphite cup and introduce undesirable particles in the carrier gas stream), water vapour was introduced by the use of a sparger (Ren, Rybak and Salin 2003).

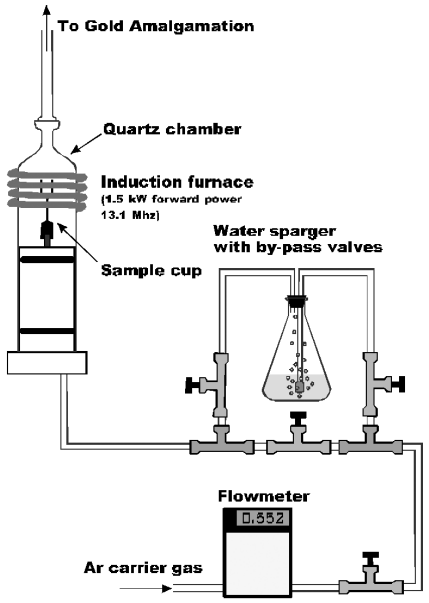

Figure 1. Schematic of the sample introduction Induction Heating-Electrothermal Vaporization (IH-ETV) with water sparged option of argon carrier gas.

The primary advantage of this sample introduction technique was the removal of all sample preparation steps from the assay. This corresponded to a reduction in time and risk of contamination.

The temperature of the graphite cups versus applied voltage was determined by the use of calibrating lacquers and pellets. The applied voltage was varied using a variable transformer. A linear relationship between the applied voltage and the resulting temperature of the graphite cups was observed thus permitting the user to set the desired temperature of vaporization.

Gold Amalgamation Trap (GA)

Gold and Hg have for years been linked by their unique capability to form an amalgam (alloy or mixture of two or more metals) at room temperature. This amalgam is however thermally unstable above approximately 3500C (Aeschliman and Norton 1999).

Based on this information, a gold amalgamation trap for Hg could be designed. Several set-ups have been documented. The source of the gold ranges from gold-sintered silica or gold sintered diatomaceous earth (Takaya and Kohyama 2004), gold-coated sand (Dumarey, Dams and Hoste 1985; Liang and Bloom 1993), gold sponge, to gold sputter-coating on quartz wool (Aeschliman and Norton 1999; Slemr et al. 1979). Heating the traps by means of a tube furnace (Aeschliman and Norton 1999), heating lamps (Takaya and Kohyama 2004) and nichrome heating wire (Liang and Bloom 1993; Slemr et al. 1979) have been documented. A simple yet effective adaptation of these was developed and constructed using powdered gold and nichrome heating wire as seen in Figure 2. Likewise it has been shown that gold traps can reproducibly collect nearly 100% of all types of Hg (organic and inorganic), provided that the sample does not exceed the limit of a given trap, related to the exposed gold surface area (Brosset, and Iverfeldt 1989).

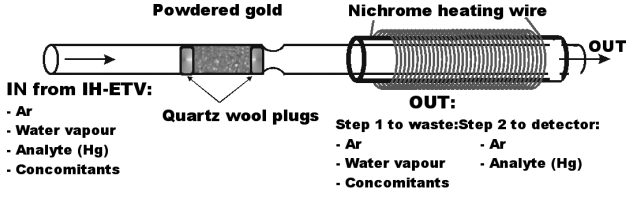

Figure 2. Schematic of the gold amalgamation (GA) trap

The output mixture of the IH-ETV entered the gold trap at one end. At this point the mixture was composed of the inert argon carrier gas, water vapour, the Hg analyte and other concomitants (everything other than the Hg analyte). At room temperature the gold (99.99% purity) theoretically only retained the Hg by the formation of an amalgam. The water vapour and concomitants which were not retained by the gold were swept through the system and were either sent directly to waste or were observed at an early retention time. Meanwhile, the resistance heating nickel-chromium wire was preheated to about 6000C. This high temperature was more than sufficient to rapidly liberate the Hg from the gold (Aeschliman and Norton 1999). Once sufficient time had passed to eliminate the water vapour and other concomitants which would have interfered with the absorption reading, the red-hot resistance heating wire was quickly moved over the gold. Within seconds, the gold trap was heated liberating the Hg from the gold. The Hg (now concentrated) was swept by continuously flowing argon to the detection system. The system was purged between runs to insure that the trap was free of Hg by alternating between blank and sample runs.

Atomic Absorption Spectrometry (AAS)

The detection system used was a simple configuration formerly built in-house. As seen in Figure 3, the atomic absorption spectrometer was comprised of a Hg pen lamp whose UV emission wavelength at 253.7 nm was collimated (light whose rays are parallel) by a quartz lens (Ingle and Crouch 1988). A glass cell equipped with two quartz windows with a 20 cm path length was used. The Hg analyte being carried out of the gold trap by the argon gas passed through this cell where absorption could take place. At the other end, another quartz lens focused the transmitted light onto a 25 mm2 UV-enhanced silicone photodiode equipped with a 254 nm filter. The resulting spectra were recorded on a strip chart and via an A/D converter on computer to facilitate data treatment and analysis. The measured transmittance was subsequently converted to absorption in order to relate the latter to concentration via Beer-Lambert law, (A = ebc).

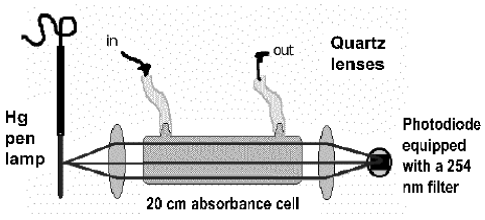

Figure 3. Schematic of the atomic absorption spectrometer (AAS)

Standards, reagents and samples

Standard solutions were prepared by consecutive dilutions of a Hg stock solution, with 1% trace metal grade nitric acid in Milli-Q water (18 MW distilled deionized water). All standards were stored in polypropylene containers (Nalgene) that had been preconditioned with 10 % trace metal grade nitric acid for a period of 24 hours and rinsed with distilled deionized water.

The hair samples came from women living in the village of Brasilia Legal, Brazil. Details of this population and hair collection procedures are described elsewhere (Passos et al. 2003). As part of two other interdisciplinary projects, the mercury concentrations of 12 cm segments of these hair strands were previously determined by CV-AAS (Legrand et al. 2005) and C-GA-AAS (Passos et al. 2003). For this study, hair strands were cut to a 12 cm length from the root end and weighed to the nearest 0.01 mg.

Results and Discussion

Assays were first performed without the gold amalgamation (GA) trap. The liquid Hg standards resulted in a linear calibration plot. However when the standardized hair samples were ran, very large absorbencies were observed as well as a notable baseline drift. These occurrences may be due to the presence of water vapour or other concomitants in the observation cell during the reading, causing erroneous absorbance or scattering. To simultaneously purify, preconcentrate and delay the Hg signal (till the baseline restabilized), the GA trap was introduced.

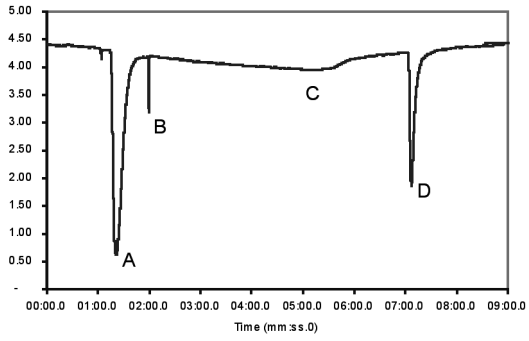

Figure 4. AA) spectrum of a single hair strand (10 pt moving avg) A) Concomitants, B) electronic noise, C) baseline drift, D) Hg analyte

The liquid Hg standards and standardized single hairs were again analyzed. A 10 point boxcar moving average (a smoothing technique) was applied to the acquired spectra. Peak heights were used and the corresponding

absorbencies determined according to Beer's Law. A calibration plot using the liquid Hg standards revealed a linear plot with a detection limit of 1 ng or 1.5 mg/g (based on a 0.6 mg sample hair mass) The spectrum of one of the analyzed hairs can be seen in Figure 4. Of note was the large peak A at 1:00 minute, no doubt due to water vapour and other concomitant. Peak B at 2:00 minutes was due to electronic noise when the IH-ETV switch was depressed. Furthermore, the baseline drifted significantly as before (region C) and consequently was allowed time to stabilize. At the 7 minute mark, the red hot coil was quickly moved over the gold, at which point the Hg was released from the gold and swept by the flowing Ar gas to the detection system and recorded as peak D.

It was thus demonstrated that the gold amalgamation trap successfully retained the Hg. However, the peak height (or peak area) were much larger than expected compared to the liquid standards. Unfortunately there seemed to be other concomitants that were also retained by the gold trap. At this point only speculations to the identity of these concomitants are made, but they were probably organic compounds from the vaporized hair which inherently would scatter the light and absorbed in the approximate region surrounding 254 nm (Ingle and Crouch 1988).

Conclusion

The potential for a low-cost system for the analysis of Hg in human hair by induction heating electrothermal vaporization, gold amalgamation, atomic absorption spectrometry (IH-ETV-GA-AAS) was demonstrated. With its demonstrated characteristics, such as linear temperature control, sample purification and preconcentration, one nanogram detection limit for Hg, and digital acquisition, this system has the potential to be made into a low cost, field portable system capable of monitoring populations at risk due to dietary or work exposure to Hg. The main focus of future work shall be the use of atomic fluorescence spectrometry (AFS) and/or an atomic absorption system with a continuum source background correction system (AAS-BC) to overcome the presence of organic species, to account for scattering and to minimized drift.

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