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Published in:
J A A S

Link to article, DOI:
10.1039/b511803b

Publication date:
2005

Document Version
Publisher's PDF, also known as Version of record

COMMUNICATION

JAAS
www.rsc.org/jaas

Induction heating-electrothermal vaporization for direct mercury analysis of a single human hair strand by inductively coupled plasma mass spectrometry

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Received 18th August 2005, Accepted 21st September 2005
First published as an Advance Article on the web 6th October 2005

DOI: 10.1039/b511803b

It was demonstrated that a single human hair strand can be analyzed for total mercury using an induction heating-electrothermal vaporizer with ICP-MS detection, achieving a detection limit of 20 pg or 30 ng g^{-1} (based on a 0.6 mg sample).

There is a growing concern about mercury from environmental and dietary sources and its effects on human health. For example, populations where fish is a dietary staple may be at risk due to mercury levels present in fish tissue. In many epidemiological studies, hair has been used as a biomarker because the mercury in the bloodstream is incorporated into the hair structure as it grows. Natural mercury concentrations in hair range from 0.3 to 1.0 μg g^{-1} for typical North American populations.[1] Since hair grows at roughly one cm per month, it is possible to track mercury exposure along the length of the hair. Hair samples are also more convenient to collect and store when compared to blood samples.

The most widely used methods of determining mercury in hair involve a digestion protocol followed by detection using either cold-vapor atomic absorption (CV-AAS), cold-vapor fluorescence spectroscopy (CV-AFS), or inductively coupled plasma mass spectrometry (ICP-MS).[2] However, a digestion step is time consuming (typically hours) and may result in sample contamination or analyte loss. These methods also require about 5–10 mg of hair; 100 hair strands may be needed to achieve this amount.

X-ray fluorescence,[3] particle induced X-ray emission spectroscopy,[4] and laser ablation-ICP-MS[5] have been used to directly analyze human hair strands for mercury. While there is little sample preparation required, X-ray fluorescence has relatively high detection limits, particle induced X-ray spectrometry is expensive and LA-ICP-MS often has calibration problems. Recently, commercial mercury analyzers have been used for direct analysis of solid hair samples. These instruments integrate a methodology called combustion-gold amalgamation-atomic absorption spectroscopy (C-G-AAS) that uses sample combustion with a catalyst, mercury collection with gold amalgamation, then detection by CV-AAS. This technique has been successfully applied to the analysis of powdered human hair, horse fur, and single human hair strands.[6,7] However, some sample preparation can still be required, as the addition of modifiers to the hair sample may be needed to absorb combustion by-products.

We report an alternate method using an induction heating-electrothermal vaporizer (IH-ETV) that requires only simple, direct sample vaporization followed by detection. In an IH-ETV, a graphite cup containing the sample is inductively heated at a user-set temperature. The vaporized analyte is transported to a detector (an ICP-MS in our case) by a carrier gas. An advantage of this set-up is the reduction of the risk of contamination due to the non-contact heating environment and the ability to interchange the graphite sample cup. Furthermore, no sample preparation is required. There is also the potential for multi-elemental analysis and excellent detection limits with ICP-MS, the vaporization temperature is easily controlled, and the inexpensive graphite cups can be customized in shape and size to suit a particular sample. In previous work, the IH-ETV has been used to vaporize soil slurries and cellulose filters.[8,9] Our objective in this project is to show that IH-ETV-ICP-MS can be used to rapidly determine mercury in a single hair strand.

The IH-ETV system used in this study, a modified LECO Model 521 induction furnace (LECO, St. Joseph, MI, USA), has been previously described in detail.[10–12] To eliminate the risk of arcing, the glass sample chamber was replaced with one made of quartz and the argon carrier gas was passed through a sparger containing distilled deionized water.[13] Commercially available graphite cups along with boiler caps were used (type S-16 and BC-1, Bay Carbon Inc., Bay City, MI, USA). The vaporized samples were carried in the argon stream to a Perkin-Elmer SCIEX Elan 6000 ICP-MS system (SCIEX, Concord, ON, Canada) through PTFE tubing at a flow rate of 0.5 l min^{-1}. Typical operating values were used for the other parameters of the ICP-MS.

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.[14] For this study, hair strands collected from four individuals were cut to a 12 cm length from the root end and weighed to the nearest 0.01 mg. As part of two other interdisciplinary projects, the mercury concentrations of 12 cm segments of these hair strands were previously determined by CV-AAS and C-GA-AAS.[7,14]

Calibration using the external standards methodology was undertaken with Hg standard solutions and with a hair certified reference material (CRM). Mercury calibration solutions were prepared in a 1% HNO_3 matrix from a 1000 μg g^{-1} Hg stock solution (SCP Science, Baie d'Urfé, QC, Canada) on the same day of analysis. The CRM, BCR 397 (IRMM, Belgium), was composed of powdered human hair. The samples or standards (one coiled hair strand, 10 μl of solution, or up to 1 mg of CRM) were placed inside a graphite cup, then covered with a boiler cap and heated to approximately 800 °C. A boiler

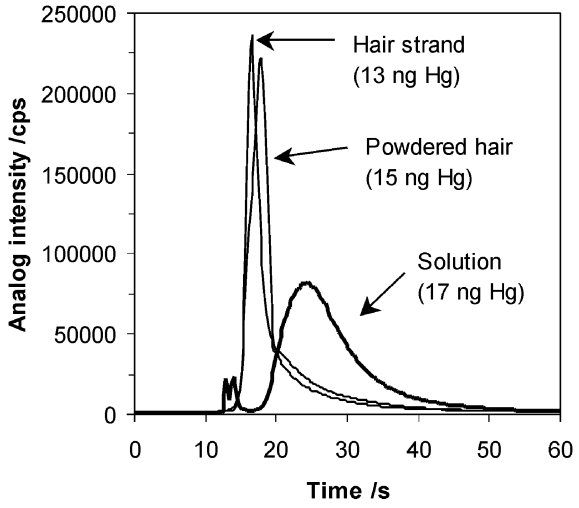

Fig. 1 Transient profiles of ^{202}Hg for various types of samples.

cap is a graphite lid that fits over the sample cup. The cap prevents the unvaporized sample from escaping from the cup when the carrier gas and heating is applied, while a small hole at the top of the cap allows the vaporized sample to exit.

The same graphite cup and boiler cap were used for all samples in a given day, and then changed daily. Blanks (empty graphite cup) were checked routinely. No problems with sample carryover were seen. The ^{197}Au isotope was also monitored as a background signal. Total analysis time for a sample was less than two minutes.

Typical ^{202}Hg transient profiles from a hair strand, powdered hair CRM and a mercury calibration solution with approximately the same peak area are overlaid in Fig. 1. The graphite cup was heated for 40 s (data acquisition started 10 s before the beginning of the heating step). The hair strand and the powdered hair CRM show similar peak shapes, though a minor distinction can be made between the steepness of the leading edges. This is probably due to different heating rates between the hair strand and the powdered hair. The entire hair strand touched the walls of the cup and was vaporized quickly, while some of the powdered hair rested on other hair and was momentarily insulated. The slight differences in peak heights show that height is not useful for accurate quantification. However, the peak areas are the same, indicating that powdered hair is a suitable calibration material for hair strands if peak areas are used.

In contrast to the hair matrices, the transient profile of the mercury solution shows two distinct sets of peaks for ^{202}Hg. Infrared measurements have shown that it takes roughly 10 s after power has been applied to the induction coil for the cup to reach 80% of its final temperature setting. Therefore when the cup was heated, the water in the solution immediately vaporized. The water probably carried some of the mercury, resulting in the small peak at the beginning of the profile, while the rest of the mercury came off as a broad peak afterwards. There may be two possible reasons for the broad peak shape of the solution when compared to the peaks for the hair. First, it was observed that the solution permeated into the graphite cup, and it may have taken longer for it to be released when heated. Second, it may be due to different thermal properties of the forms of mercury present in the samples (organic mercury bound to sulfur in the hair matrices *versus* inorganic mercury in the solution). One last observation can be made about the liquid calibration peak area—it was less than that of the hair strand and the powdered hair for the same amount of mercury. The peaks areas for mercury solutions were consistently low when cups containing mercury solution were not immediately analyzed. Experiments show that the loss of mercury is time-dependent and reheating of the cup at higher temperatures did not result in further mercury release. This indicates that there was some analyte loss, probably due to evaporation. Therefore mercury solutions are unsuitable for external standards calibration of hair strands.

Table 1 Determination of mercury concentrations in hair strands

Sample ID	Hg by CV-AAS/ μg g^{-1}	Mean Hg by IH-ETV-ICP-MS/ μg g^{-1} ± SD[a]	%RSD	%Recovery
BL529	3.9	3.94 ± 0.03	0.8	101
BL565	8.2	10.5 ± 0.3	2	128
BL591	13.8	13.6 ± 0.3	4	99
BL442	13.9	15.51 ± 0.08	0.5	112

[a] $n = 3$, except $n = 2$ for BL529.

An external standards calibration plot was constructed using the peak areas of the transient signals for the blank, and roughly 0.5 mg and 1 mg of the CRM. Using a linear least squares regression, R^2 greater than 0.999 were routinely achieved. In Table 1, the total mercury concentrations determined for the hair strands by external standards using the powdered CRM are compared with an estimate previously determined by CV-AAS using the protocol described by Farant *et al.*[15] When the concentrations of the four hair strand samples (11 total replicates) from IH-ETV-ICP-MS were plotted against the concentrations estimated by CV-AAS, a slope of 1.03 and R^2 of 0.95 were obtained. At less than 4% relative standard deviation (RSD), precision for hair strand analysis was comparable to that of C-G-AAS and CV-AAS methods.[6,15] On average, the percent recovery was 110%.

The detection limit (3σ) achieved by this method was 20 pg of Hg, or the equivalent of 30 ng g^{-1} for a 12 cm strand of hair (0.6 mg, 1 cm of hair = 0.05 mg). This detection limit also means that only 0.4 cm (corresponding to about two weeks of growth) or roughly 0.02 mg of hair is needed to detect a natural mercury level of 1 μg g^{-1}. As a consequence, just one hair strand is sufficient to estimate mercury levels in an individual—much less hair than the 100 strands that may be required for traditional methods with a digestion step.

We have demonstrated that IH-ETV-ICP-MS can easily determine mercury concentrations in a single hair strand, using external standards calibration with powdered hair CRMs. The results were comparable to that of CV-AAS, but were obtained more quickly and required a smaller sample size—making IH-ETV-ICP-MS a possibility for routine hair analysis for mercury. In the future, with the controllable temperature of the IH-ETV and the multi-element capability of the ICP-MS, we hope to determine other elements in human hair.

Acknowledgements

We thank C. Passos and D. Mergler of the Centre d'Etudes des Interactions Biologiques entre la Santé et l'Environnement (CINBIOSE) at l'Université du Québec à Montréal for providing the hair samples. Scholarship support from the Natural Sciences and Engineering Research Council (NSERC) and the Fonds de Recherche sur la Nature et les Technologies (FQRNT) is gratefully acknowledged by JPL.

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