JAAS

TECHNICAL NOTE

View Article Online
View Journal

Cite this: DOI: 10.1039/c5ja00087d

Direct mercury analysis in environmental solids by ICP-MS with on-line sample ashing and mercury pre-concentration using a direct mercury analyzer

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A commercially available direct mercury analyzer (DMA) based on sample combustion, pre-concentration by amalgamation with gold, and atomic absorption spectrophotometry (AAS) was coupled to a sector field inductively coupled plasma mass spectrometer (ICP-MS). The combined system (DMA-ICP-MS) was optimized and evaluated for the determination of mercury in environmental samples using both external calibration and isotope dilution for quantitation. The method was validated using certified reference materials, including sediment, leaves, and fish-muscle tissue. The limit of detection was ~0.37 pg, about two orders of magnitude lower than the DMA system alone. Precision was generally <7% relative standard deviation, and total analysis time per sample was <8 min. The DMA-ICP-MS system has several advantages over both the DMA alone and conventional cold-vapor AAS for the determination of mercury, including increased sensitivity, lower detection limits, decreased potential for sample contamination, and applicability to Hg stable isotope tracer studies.

Received 14th March 2015
Accepted 14th April 2015

DOI: 10.1039/c5ja00087d

www.rsc.org/jaas

Introduction

Mercury (Hg) is a persistent, mobile, and highly toxic environmental pollutant that is routinely measured in environmental and toxicological studies and biomonitoring programs.[1–3] Direct mercury analyzers (DMAs) are commonly used for determining total-Hg in a variety of sample matrices. These instruments integrate sample combustion, matrix removal and Hg pre-concentration *via* amalgamation with gold, and atomic absorption spectrophotometry. They are popular because they increase analytical throughput, reduce waste generation and the potential for sample contamination, and have relatively low operating and capital costs. However, atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) based methods are unable to distinguish individual isotopes, and thus are not suitable for quantitation using isotope dilution or for isotope tracing studies.

Isotope dilution mass spectrometry (IDMS) is an accurate method to quantify elements that have more than one isotope, and it has long been used for the determination of Hg in environmental samples.[4] In IDMS, a sample is mixed with an isotopic standard enriched in one of the minor isotopes of the analyte element, and, after equilibration, mass spectrometry is used to measure the altered isotope ratios. The resulting isotopic compositions, along with the mass of the sample and spike, are used to calculate the concentration of the element in the sample. Mercury stable isotopes have also been used as tracers to investigate Hg transformations in the environment, and for more than a decade, these studies have yielded significant new insight into the processes controlling Hg speciation and bioavailability.[5]

Coupling a DMA to an inductively coupled plasma mass spectrometer (ICP-MS) offers several potential advantages over both the DMA alone and conventional cold vapor (CV)-AAS or CV-AFS for the determination of Hg, including: (1) increased sensitivity and lower detection limits, (2) efficient (*ca.* 100%) Hg introduction compared to conventional liquid nebulization, (3) simple interface design and operation, (4) improved accuracy though use of isotope dilution, (5) increased speed and throughput of analyses, and (6) the possibility of direct analysis of solid samples as part of Hg stable isotope tracer studies of environmental processes.

Because there are no reports in the literature specifically evaluating a DMA-ICP-MS coupled system, the aim of the current study was to: (1) develop a simple procedure to couple the DMA with an ICP-MS, (2) optimize the combined system, (3) evaluate common analytical figures-of-merit using both external calibration and IDMS, and (4) apply the method to environmental and biological sample matrices.

Materials and methods

Standards and reference materials

^{201}Hg (93.08%) enriched stable isotope was obtained from Oak Ridge National Laboratory as HgO. The oxide was dissolved in 10% high-purity (Optima grade) HNO_3 and diluted. A single element natural isotopic abundance Hg standard obtained

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from Spex Certiprep (Metuchen, NJ, USA) was used to optimize the ICP-MS prior to analysis, and to calculate the concentration of the enriched stable isotope spike using reverse-IDMS. For the latter, approx. 1.05 g of the natural isotopic abundant Hg (concentration 493.9 ng g^{-1}) was accurately weighed and added to 0.25 g of the 415 ng g^{-1} spike, and the mixture diluted to ~50.00 g in 10% HNO_3. The concentration of the ^{201}Hg spike was determined by reverse IDMS using the same equations for IDMS.[6]

DORM-3 (dogfish muscle), NIST 2709 (sediment), and NIST 1547 (peach leaves) was used as reference materials. DORM-3 was obtained from the National Research Council of Canada (Ottawa), and the other reference materials were from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Ultrapure water (>18 MΩ cm^{-1}) was obtained from a Barnstead Nanopure Diamond system.

Direct mercury analyzer

A DMA-80 (Milestone Inc., Shelton, CT) was used throughout this study. DMAs and their applications in environmental and biological studies have been described elsewhere.[7–9] Briefly, samples were weighed in nickel or quartz boats and placed in an autosampler which sequentially inserts them into the DMA's combustion tube where they were heated to ~650 °C with oxygen as a carrier gas. Gaseous combustion products were carried through a heated catalyst, where Hg species are converted to elemental Hg vapor (Hg^0), and where halogens and other species which can interfere with the analysis are trapped. Mercury vapor and other decomposition products were carried to a glass tube gold-coated sand where Hg^0 is selectively trapped. Later, the trap is rapidly heated to release Hg^0 vapor into a single beam spectrophotometer. Mercury concentration is calculated based on the absorbance measured at 253.7 nm and the weight of the sample. In the current study, operating times for drying, combustion, and post-combustion flushing periods were 60, 180, and 45 s, respectively, for a total analysis time of <5 min per sample. DMA instrumental settings are given in Table 1.

Table 1 DMA-ICP-MS instrumental settings

DMA parameters	
Gas flow	200 mL min^{-1}
Drying	200 °C for 60 s
Decomposition	650 °C for 180 s
Purge 1	60 s
Amalgamator heat	~850 °C for 12 s
Purge 2	45 s
Plasma parameters	
Cool gas flow	16 L min^{-1}
Aux. gas flow	1.03 L min^{-1}
Sample gas flow	1.05 L min^{-1}
RF power	1280 W
ICP-MS data acquisition parameters	
Isotopes	^{201}Hg, ^{202}Hg
Resolution	Low
Mass window	5%
Points per peak	100

ICP-MS

A sector field-ICP-MS (Element-XR, Thermo Scientific) was used to measure Hg isotopes. The ICP-MS was optimized prior to analysis using a Hg tuning solution (Spex Certiprep; Metuchen, NJ, USA) introduced using a microflow concentric nebulizer and a peltier-cooled cyclonic spray chamber (PC^3; Elemental Scientific, Omaha, NE, USA). Argon from the DMA was introduced downstream of the PC^3 just prior to the torch using a T-junction (Fig. 1). This setup allows for easy instrument tuning and, if desired, introduction of solutions for measuring mass discrimination. When tuning the ICP-MS, argon from the DMA was kept on. When running samples on the DMA-ICP-MS, the optimized nebulizer gas flow was kept on but the uptake line from the solution was removed.

ICP-MS instrumental settings are given in Table 1. Mercury isotopes (^{201}Hg and ^{202}Hg) were monitored in low resolution mode. A higher resolution setting was not necessary because interferences are not present as the Hg is isolated from the matrix *via* the amalgamation step. The mass window was set to 5% with 100 points per peak, yielding 5 data points (averaged per pass) across the middle portion of the flat-topped peak. Fast electric scanning (123 runs per pass) was used with an integration time of 10 ms, resulting in a data point for each isotope every 0.86 s over a total acquisition time of 1.72 min.

DMA combination with ICP-MS: interface and operation

A schematic of the DMA-ICP-MS interface showing the operation of the system during a typical analytical run is shown in Fig. 1. Instrumental settings for both the DMA and the ICP-MS are given in Table 1. Valves "upstream" and "downstream" of the DMA were used to direct gases compatible with DMA and ICP-MS. The operation of the valves and triggering of the ICP-MS was done manually; however, this could certainly be automated by researchers or instrument manufacturers. To interface the DMA with the ICP-MS, a 3.175 mm (OD) teflon tube was inserted directly into the outlet of the DMA analysis cell making a tight seal without any further manipulation. The other end of the tube was connected to a 4-port stainless steel valve (Valco Inc., Houston, TX, USA). The entire length of the tube was wrapped in silicone rubber-encapsulated heat tape (Thermolyne-Barnstead) to prevent condensation in the line. The "downstream" valve was used to direct gases leaving the DMA either to vent or to the ICP-MS *via* another 3.175 mm (OD) Teflon tube.

At the start of a run and during the sample drying and decomposition (sample ashing and Hg pre-concentration) phase of the analysis, the upstream valve was positioned to deliver O_2 to the DMA, while the downstream valve was positioned to direct combustion products to vent. The valves were switched at the conclusion of the decomposition phase (during the start of purge 1 phase, before the amalgamator is heated) to change the carrier gas from O_2 to argon and to change from vent to the ICP-MS. Doing this early in this stage allows the system

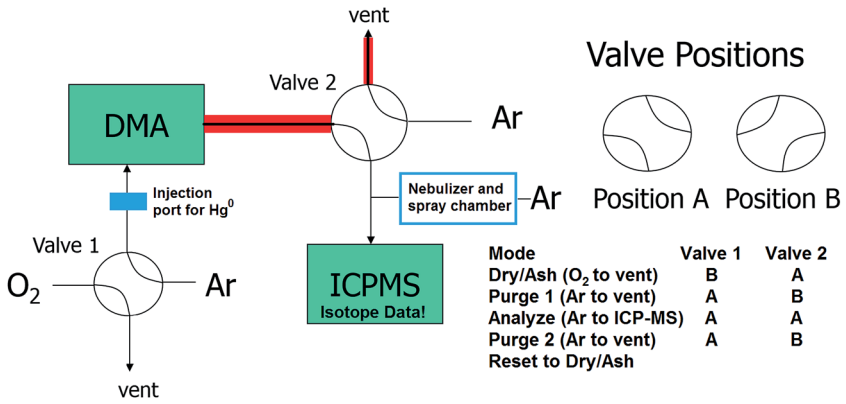

Fig. 1 Schematic of the DMA-ICP-MS interface shown in ICP-MS analysis mode (left) and operation of the valves during a typical run (right).

time to stabilize. Next, data acquisition was initiated for the ICP-MS about 10 s before the amalgamator was heated to drive off Hg. This analytical scheme allows Hg (free of combustion products) to be carried to the plasma in argon.

DMA-ICP-MS (external calibration)

For external calibration, a single isotope (^{202}Hg) was monitored in low resolution mode and peak areas were used for quantitation. The system was calibrated using a temperature-controlled Hg-vapor calibration unit (Tekran 2505) and standard solutions. For calibration in the low range, a gas-tight syringe (Hamilton Company) was used to deliver approximately 50, 100, 150, 200, 250, 300 and 350 pg of Hg to the DMA *via* an injection port that was outfitted to the carrier gas stream just prior to entering the combustion chamber (Fig. 1). For calibration at higher levels, a standard solution was weighed into quartz boats using an analytical balance with 0.1 mg readability, and the boats delivered to the DMA. The standard solutions were prepared from a 10 000 mg L^{-1} stock solution (SPEX CertiPrep) and delivered approximately 1.5, 4.0 and 10 ng of Hg to the DMA. The weights of the solutions introduced to the DMA ranged from about 20 to 50 mg.

DMA-ICP-MS (isotope dilution quantitation)

For isotope dilution measurements (single spike method), a ^{201}Hg enriched isotope standard solution (described above) was used. The samples were accurately weighed in a combustion boat using the same balance described above. The spike solution was then added directly on the sample and the mixture was re-weighed. Spikes were added to deliver ~4.65 ng ^{201}Hg for NIST 2709 and DORM-3, and 0.11 ng for NIST 1547. The boats were delivered to the DMA and the DMA run as described before. ^{201}Hg and ^{202}Hg were monitored by the ICP-MS in low resolution mode and peak areas were used to determine the Hg

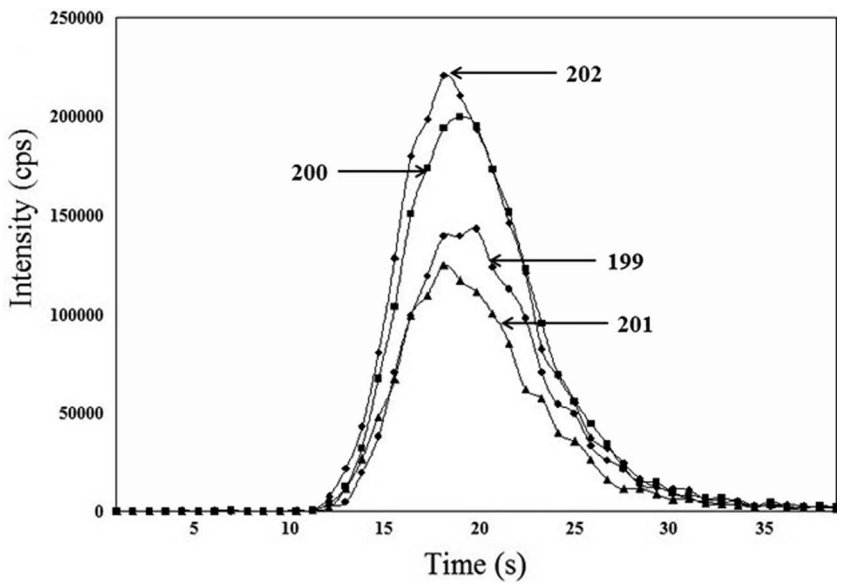

Fig. 2 Typical intensity *vs.* time chromatogram generated by the DMA-ICP-MS. At ~10 s in the figure the DMA gold trap is heated releasing Hg to the ICP-MS. Numbers in the figure represent four of the stable isotopes of Hg that were monitored.

isotope ratio in the sample. The ratio, together with the mass of the sample and spike, was used to quantify total-Hg in certified reference materials and lake sediment using standard isotope dilution calculations.[4,6]

Results and discussion

For conventional IDMS of solution digests, an intimate mix of the isotope spike with the sample is critical to achieve accurate data. This is not as important for samples that are subject to thermal decomposition as long as all the Hg is quantitatively transferred and measured. Moreover, because Hg isotopes will fractionate as they desorb from a heated gold trap (lighter isotopes preferentially desorbing first), it is important that the entire area of the peak be used in the calculations so that the data captures accurate isotope ratios.[10] A typical intensity *versus* time chromatogram generated by the DMA-ICP-MS is shown in Fig. 2. There is very little time delay (<2 s) from when the DMA amalgamator is heated to when the ICP-MS Hg signal rises.

Limit of detection, accuracy, and precision

For the DMA-alone, the limit of detection (LOD, 3σ criteria) was 13 pg based on eight blank measurements (empty sample boats) and the slope of the calibration curve in the low concentration range (gas phase standard injections). Using the same approach the LOD for the DMA-ICP-MS was 0.37 pg, nearly two orders of magnitude lower than the DMA alone. The DMA-ICP-MS LOD corresponds to 1.2 pg g^{-1} for 250 mg of sediment (a typical weight for sediment in a DMA boat) or 5.0 pg g^{-1} for 60 mg of biological tissue (typical weight for fish tissue in a DMA boat). Thus, the DMA-ICP-MS method is capable of ultra-trace level analyses. Moreover, there was virtually no carryover between samples for sample weights that deliver less about 40 ng of Hg. Nevertheless, because Hg can adsorb on Teflon surfaces, carryover should be monitored, particularly following samples containing relatively high levels of Hg.

The method was validated using a variety of certified reference materials, including sediment (NIST 2709), leaves (NIST 1547), and fish tissue (DORM 3). Recoveries for these certified reference materials were within the certified range (Table 2). Following U.S. Environmental Protection Agency Method 7473, the DMA alone yielded recoveries ranging from 100–103% of certified values, indicating that the DMA was operating properly. The corresponding DMA-ICP-MS data was also in good agreement with certified values: ±8% for external calibration and slightly better accuracy (±2%) for isotope dilution measurements.

For external calibration of the DMA-ICP-MS, precision was <7% relative standard deviation (RSD) (Table 2). For IDMS quantitation, the precision was <4% RSD for both DORM-3 ($n = 9$) and NIST 2709 ($n = 5$), but higher for NIST 1547 leaves (11% RSD), which had the lowest Hg levels of the three (31 ± 7 ng g^{-1}). Uncertainty in the results can stem from the relatively small weights used for either the spike solutions or the sample, where a small difference in weight can have a big impact on results. We kept the absolute amounts of Hg to <40 ng (~0.5–40 ng) to minimize carryover and prevent overloading the DMA with Hg. Thus, sample weights for NIST 2709 soil (1400 ± 80 ng g^{-1}), DORM-3 (382 ± 60 ng g^{-1}) and NIST 1547 (31 ± 7 ng g^{-1}) were ~25 mg, ~125 mg, and ~200 mg, respectively. Also, whereas the DMA itself and the transfer line from the DMA to the downstream valve was heated to prevent condensation, we still wanted to keep the volume of liquid (mass of spike) to a minimum (spike levels were 20–50 mg). Using weights lower than these for the sample and spike are likely to increase uncertainty in the analytical results.

We are currently using the DMA-ICP-MS method to determine total-Hg in sediments from an old-growth cypress wetland at Sky Lake, an oxbow lake in the Mississippi Delta alluvial flood

Table 3 Total-Hg in sediment from Sky Lake determined by DMA-ICP-MS using IDMS

Sample	Date	T-Hg (ng g^{-1}) ($n = 3$)	RSD (%)
Wetland	11/30/2014	88.7 ± 4.4	5.0
Wetland		91.9 ± 6.4	6.9
Open water		35.5 ± 3.2	9.0
Wetland	1/25/2015	147 ± 4	2.8
Wetland		119 ± 15	12.6
Open water		110 ± 5	5.0
Open water		106 ± 8	7.7

Table 2 Total-Hg (ng g^{-1}) in reference materials determined by thermal decomposition, amalgamation, atomic absorption spectrometry (method 7473) and by the DMA-ICP-MS using external calibration or isotope dilution mass spectrometry[a]

			Observed								
			Method 7473			External calibration			IDMS		
Matrix	Reference material	Certified	Conc.	RSD (%)	Recovery (%)	Conc.	RSD (%)	Recovery (%)	Conc.	RSD (%)	Recovery (%)
Sediment	NIST 2709	1400 ± 80	1396 ± 23	1.6	100	1510 ± 80	5.3	108	1416 ± 24	1.7	101
Leaves	NIST 1547	31 ± 7	32 ± 2	5.2	103	29 ± 2	6.9	94	31 ± 4	11	100
Fish-muscle	DORM-3	382 ± 60	387 ± 23	5.9	101	420 ± 15	3.6	107	373 ± 12	3.3	98

[a] $n = 5$, except for DORM-3 where $n = 9$.

plain, as part of a stable isotope tracer study examining Hg methylation/demethylation rates. So far, the RSD has been <13% (2.8–12.6%), based on seven different sediment samples run in triplicate and ranging in concentration from 35–147 ng g^{-1} (Table 3).

Conclusions

A direct mercury analyzer was coupled with an ICP-MS for the direct determination of Hg in environmental and biological samples. The approach eliminates the need for acid-digestion of samples and allows for isotope ratio measurements. Compared to both the DMA alone and conventional CV-AAS, the combined system was shown to lower detection limits, increase sensitivity, and provide accurate quantification by the isotope dilution method. Anticipated environmental applications of the method include evaluating Hg burdens in suspended sediments, non-lethal fish-Hg determinations using milligram quantities of tissue, exposure studies using temporally-resolved hair analysis, and environmental process studies using Hg stable isotope tracers.

Acknowledgements

We thank Dr Edward Heithmar and Ms Charlita Rosal (U.S. Environmental Protection Agency) who, along with the corresponding author, presented the analytical approach behind the present work at Winter Conference on Plasma Spectrochemistry in 2002. We also thank Oscar "Beau" Black, Kristen Dickerson, Ruiqi Feng, and Jingjing Chen for help with various aspects of the project. The ICP-MS used in this study was obtained through a U.S. National Science Foundation grant (Award #0923080).

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