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Ultra-trace determination of mercury in water by cold-vapor generation isotope dilution mass spectrometry

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Determination of total Hg at the ppt level in water using cold vapor generation and inductively coupled plasma mass spectrometry for calibration by isotope dilution (ID) with both sector field (SF-ICP-MS) and time-of-flight MS (ICP-TOF-MS) detection is described. Samples were reduced on-line in a flow injection manifold with $SnCl_2$ to generate Hg vapor for both steady-state and transient sample introduction following gold trapping. No significant difference in final Hg concentrations was detected using either approach. Certified reference material ORMS-3 river water (NRCC, Ottawa, Canada) was used for method validation. Mercury concentrations of 12.75 ± 0.24 and 12.34 ± 0.11 pg g^{-1} (mean and one standard deviation, $n = 4$) were obtained using steady-state generation with SF-ICP-MS and ICP-TOF-MS, respectively, in agreement with the certified value of 12.6 ± 1.1 pg g^{-1} (combined uncertainty, $k = 2$). Concentrations of 12.55 ± 0.41 and 12.65 ± 0.30 pg g^{-1} (one standard deviation, $n = 4$) were obtained following gold trapping and SF-ICP-MS and ICP-TOF-MS detection, respectively. Compared with SF-ICP-MS, a 2-fold enhancement in the precision of the measured $^{200}Hg/^{201}Hg$ and $^{202}Hg/^{201}Hg$ ratios in a 100 ppt Hg standard solution was obtained using ICP-TOF-MS. Consequently, improved precisions of 0.87–2.33% RSD in Hg concentrations obtained by steady-state and transient signal acquisition, respectively, in ORMS-3 were obtained using ICP-TOF-MS, compared with 1.88–3.25% RSD obtained with SF-ICP-MS. Method detection limits (LODs, three times standard deviation) of 0.024 and 0.15 pg g^{-1} for Hg using direct CV and following gold trapping, respectively, were obtained using SF-ICP-MS. These were superior to corresponding LODs of 0.30 and 0.87 pg g^{-1} obtained using ICP-TOF-MS as a result of its 15-fold lower sensitivity.

Introduction

Mercury is a well-known hazard with exposure occurring principally through the consumption of water and fish, in which it bioaccumulates.[1] As a result, considerable effort has been devoted to the development of sensitive, accurate and rapid analytical methods for monitoring Hg in biological and environmental samples.

The low pg ml^{-1}concentrations of Hg typically found in natural waters present a significant challenge for its accurate quantitation.[2,3] Over the last decade, numerous methods have been developed for the determination of Hg in natural waters, snow and ice with reported detection limits in the range of 0.13 pg ml^{-1} (ppt) to 14 ng ml^{-1} (ppb).[2–15] Among these techniques, cold-vapor generation atomic absorption spectrometry (CVAAS) is one of the most commonly used owing to its simplicity, high sensitivity and sub-ppt detection power. Cold-vapor generation with/without preconcentration on a gold trap has also been coupled to inductively coupled plasma mass spectrometry (ICP-MS) for determination of Hg at ultratrace levels in waters.[3–5,15] Reported detection limits range from 0.13 to 0.20 ppt. Enhanced performance can be achieved when isotope dilution (ID) calibration is applied, which generally provides for higher accuracy and precision.[16,17] Despite the advantages offered, however, few applications of ID for the determination of Hg in natural waters have been reported[3,5,15] and quadrupole-based instruments (qICP-MS) have always been used.

The precision with which measurements can be made is directly influenced by the quality of the isotope ratio data. In the absence of severe mass bias corrections, matrix or spectral interferences, a limiting precision frequently arises which is determined by the statistical arrival of ions at the detector, for which Poisson counting statistics apply to the intensities of the selected isotopes. Typical qICP-MS machines provide steady-state intensities of some 10^7 counts s^{-1} ppm of analyte and are operated in a peak hopping mode, the duty factor of which for a given isotope is inversely related to the number of isotopes of interest. The precision with which isotope ratios can be measured using sector field ICP-MS (SF-ICP-MS) is generally superior to that achieved by qICP-MS because its flat topped peaks produced in low resolution mode enable a more accurate and precise isotope ratio measurement.[18] Additionally, these machines are capable of significantly increased sensitivity, some 10^9 counts s^{-1} ppm being typical. The speed of current SF-ICP-MS in E-scan mode is competitive with qICP-MS,[18,19] but the number of isotopes that can be simultaneously measured remains limited when transient signal acquisition is required (*e.g.*, vapor generation with gold trapping) if spectral skew is to be avoided. Time-of-flight based ICP-MS[14,20–25] (ICP-TOF-MS) permits generation of a complete mass spectrum from gated packets of ions, simultaneously eliminating correlated noise sources and the spectral skew inherent in scanning spectrometers. This should give rise to improved precision of isotope ratio measurements when multi-isotopic monitoring is performed on transient signals. Unfortunately, these instruments currently suffer from inferior sensitivity, typically 10^6 counts s^{-1} ppm. When tasked with quantitation of ultratrace levels of mercury by ID (10 ppt and lower), an inherent Poisson limited precision in the isotope ratio (assuming an enriched isotopic spike is added such as to result in a 1 : 1 intensity ratio in the selected pair), and hence in the resultant concentration, of 4.5% RSD using a qICP-MS, 0.45% using a SF-ICP-MS and 14% with the ICP-TOF-MS arises, based on

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the above generic instrument sensitivities and assuming a 10 s acquisition time for steady-state sample introduction. These figures of merit can be improved by acquiring data for longer periods of time (assuming no limitation on sample volume) or by increasing the efficiency of sample introduction [using cold vapor (CV) generation[3] or SPME sampling of vapor[14]]. CV generation is particularly attractive as it can be conveniently coupled to a gold amalgamation trap. In this manner, the Poisson limited RSD for ID ratio precision can be improved to 0.63%, 0.06% and 2%, respectively, for the three ICP-MS instruments based on a 50-fold improvement in sensitivity with CV sample introduction. These calculations suggest that current ICP-TOF-MS instrumentation is incapable of achieving the level of precision required for routine analysis of ultratrace concentrations of Hg. It is noteworthy that Evans *et al.*[26] reported on a comparative study of the precision of isotopic ratio measurements for mercury using qICP-MS, SF-ICP-MS, ICP-TOF-MS and multi-collector-ICP-MS. Results obtained with the ICP-TOF-MS system were vastly inferior to those generated by the multi-collector but comparable to the performance of the qICP-MS. The concentration of mercury vapor admitted to each spectrometer was not stated but was sufficient to generate a steady-state signal by heating a sample of Almaden mercury ore. Thus, the relative performance characteristics of the TOF analyzer cannot be assessed from this study when applications relating to ID measurement of ultratrace mercury are contemplated.

The objective of this study was thus to compare the relative performance of SF-ICP-MS and ICP-TOF-MS for the determination of total Hg present at the ppt level in natural water using isotope dilution calibration with cold vapor generation. Both steady-state and transient (following trapping of generated mercury on a gold foil) sample introduction were used. While this study does not provide a generic performance comparison of these two instrument designs for high precision Hg ratio measurements, a relative assessment of their use for the quantitation of ultratrace levels of mercury in real samples by ID is achieved. Reverse isotope dilution was performed to quantify an enriched ^{201}Hg concentration in a spike solution, thereby ensuring the quality of the final results. The method was validated by the determination of Hg in National Research Council Canada ORMS-3 water CRM.

Experimental section

Instrumentation

A ThermoFinnigan Element2 SF-ICP-MS instrument fitted with a plug-in quartz torch with a sapphire injector and a Ag guard electrode (Bremen, Germany) was used. Optimization of the Element2 was performed as recommended by the manufacturer; typical operating conditions are summarized in Table 1. Isotopes of ^{200}Hg, ^{201}Hg and ^{202}Hg were simultaneously monitored. For trapping of the mercury on gold and subsequent transient data acquisition, the dwell time on each isotope was varied, as were the number of channels used to characterize each mass peak so as to provide optimum precision in the Hg ratio measurements. Detector dead time was obtained using the approach of Nelms *et al.*[27] (method 2), wherein the ^{238}U/^{235}U ratio was measured in standard solutions at concentrations of 0.5, 1.0 and 2.5 ng ml^{-1}. A dead time of 18 ± 1 ns (one calculated uncertainty) was derived from a plot of the measured ^{238}U/^{235}U ratios *versus* U concentration at a slope of zero. Mass calibration was only performed once a week as a result of the stability of the instrument.

Analyses were also undertaken on an Optimass 8000 orthogonal acceleration (oa) ICP-TOF-MS instrument (GBC Scientific Equipment Pty. Ltd., Australia). Detailed information on the instrument and its performance characteristics have been reported earlier.[20] Optimization of the Optimass 8000 was performed as recommended by the manufacturer and typical conditions are summarized in Table 2.

Table 1 SF-ICP-MS operating conditions

Rf power	1150 W
Plasma Ar gas flow rate	15.0 l min^{-1}
Auxiliary Ar gas flow rate	1.05 l min^{-1}
Ar carrier gas flow rate	0.69 l min^{-1}
Sampler cone (nickel)	1.1 mm
Skimmer cone (nickel)	0.8 mm
Lens voltage	Focus: −830 V; *x* deflection: −0.95 V; *y* deflection: 1.60 V; shape: 105 V
Resolution	300
Data acquisition	Steady-state: E-scan, 5 runs 70 passes, 5% mass window, 5 ms sample time, 200 samples per peak for direct CV Transient: E-scan, 400 runs, 5% mass window, 5 ms sample time, 200 samples per peak

A PerkinElmer (Norwalk, CT, USA) flow injection mercury system (FIMS) fitted with a gold trap was used for on-line cold vapor generation. The detection system on the FIMS was bypassed and, as shown in Fig. 1, the generated vapor was directed to the ICP torch. Tygon pump tubing was used to deliver sample and reagents: 1.14 mm id for the sample and 0.76 mm id for the reductant. All connections and tees were 0.25–28 low pressure Tefzel flangeless fittings (Upchurch Scientific Inc., Oak Harbor, WA, USA) and 1.58 mm od PTFE tubing (Cole Parmer, Illinois, USA). A gas–liquid separator (10 ml volume, PerkinElmer, part B0507959) ensured efficient stripping of the generated vapor from the liquid phase. An additional subsequent liquid trap ensured that no large liquid droplets nor acid vapor were transported to the ICP torch. Coupling of the FIMS to the mass spectrometers was accomplished by directing generated vapor to the torch through a 0.5 m length of Teflon lined Tygon tubing (0.25″ od). A polypropylene 0.25″ Swagelok T connected the instrument nebulizer gas to the FIMS Ar carrier gas. The two gas flows entered the torch through a ball joint adapter. Following a daily optimization of the spectrometers using liquid sample introduction, the plasma was then extinguished and the spray chamber and nebulizer assembly replaced with the transfer line. Final optimization of the lens voltages and nebulizer gas flow for dry plasma conditions was performed by monitoring

Table 2 ICP-TOF-MS operating conditions

Rf power	1150 W
Plasma Ar gas flow rate	10 l min^{-1}
Auxiliary Ar gas flow rate	1.00 l min^{-1}
Ar carrier gas flow rate	0.60 l min^{-1}
Sampler cone (stainless steel)	1.1 mm
Skimmer cone 1 (stainless steel)	1.0 mm
Skimmer cone 2 (stainless steel)	1.0 mm
Voltage	Skimmer: −950 V; extraction: −1360 V; Z1: −950 V; *Y* mean: −300 V; *Y* deflection: 0 V; *Z* lens mean: −920 V; *Z* lens deflection: 0 V; lens body: −145 V; multiplier gain: 2400 V
Data acquisition	55 s acquisition time for direct CV; 100 spectra collected over 4 s for CV with trapping on gold

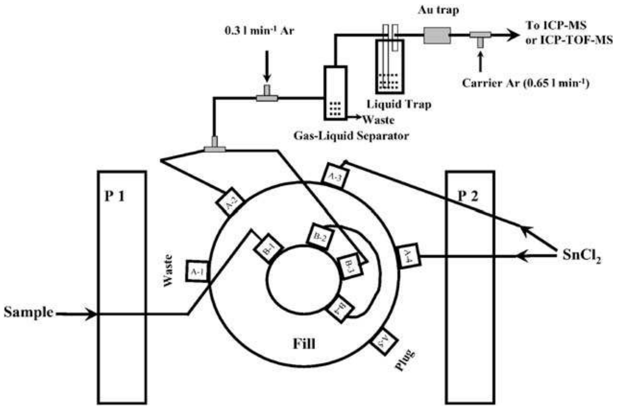

Fig. 1 Schematic diagram of the FIMS/ICP-MS system.

the Hg signal arising from continuous CV generation (bypassing the gold trap) of a 100 ppt Hg standard solution. The nebulizer flow consisted of a combination of the mass spectrometer setting (typically 0.65 l min^{-1}) and the Ar carrier flow from the FIMS (preset to 0.30 l min^{-1}).

Reagents and solutions

Hydrochloric acid was purified in-house by sub-boiling distillation of reagent grade feedstock in a quartz still prior to use. High purity de-ionized water (DIW) was obtained using a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). A 0.5% solution of $SnCl_2$ was prepared by dissolving stannous chloride (Fisher Scientific, Nepean, Canada) in 1% HCl and purging with high purity argon (99.99%, BOC Gases, Mississauga, Ontario, Canada) for at least 2 hours prior to use as the reductant in order to minimize contamination.

"Natural abundance" high purity Hg metal was purchased from Johnson Matthey & Co. Ltd (London, UK). A 1000 µg g^{-1} stock solution was prepared in 5% HCl. A working standard (101 ng g^{-1}) used for ^{201}Hg reverse isotope dilution, was prepared by serial dilution of the stock in 2% HCl.

Enriched ^{201}Hg isotope was purchased from Oak Ridge National Laboratory (USA) as the metal. A 300 µg g^{-1} stock solution was prepared in 5% HCl. A spike solution of 1.9 ng g^{-1} was prepared by serial dilution in 2% HCl. Accurate concentration of the enriched spike was determined by reverse isotope dilution using the gravimetrically prepared natural abundance Hg standard.

The CRM ORMS-3 (Mercury in River Water Reference Material, NRCC, Ottawa, Canada) was used for validation of methodology. This CRM is packaged glass ampoules.

Sample preparation and analysis procedure

Sample preparation was conducted in a class-100 clean room. Freshly spiked samples of ORMS-3 were prepared daily to minimize any possible contamination from the laboratory environment. Each of four replicate vials of ORMS-3 (each containing about 50 g) was opened and 0.100 g of 1.9 ng g^{-1} enriched ^{201}Hg spike was added directly to the vial. Vials were then covered with plastic wrap and vortex shaken prior to analysis. Sample mass was obtained by the difference in weight between the opened vial of ORMS-3 and the dried empty vial after the analysis. A 500 g solution of 2% HCl spiked with the same mass of ^{201}Hg used for ORMS-3 was used to estimate method detection limits.

Four reverse-spike isotope dilution calibration samples were prepared to quantify the concentration of the enriched ^{201}Hg spike. A 1.00 g aliquot of 1.9 ng g^{-1} enriched ^{201}Hg spike solution and 0.100 g of 101 ng g^{-1} natural abundance Hg solution were accurately weighed into a pre-cleaned high density polyethylene bottle and diluted with 50 g of 2% HCl.

Table 3 FIMS program for trapping Hg[a]

Step	Time/s	Pump 1/rpm	Pump 2/rpm	Valve	Cool	Argon	Function
1	15	120	0	Injection	On	On	Pre-fill
2	60	100	100	Fill	Off	On	Load
3	30	0	100	Injection	Off	On	Rinse
4	10	0	0	Injection	Off	On	Heat
5	20	0	0	Injection	On	On	Cooling

[a] A sample volume of 10 ml was processed with each "injection".

For direct CV analysis, both FIMS pumps were operated at 100 rpm to provide for sample and reductant flows of 10 and 4 ml min^{-1}, respectively. The main valve was set to the fill position and an Ar flow of 0.3 l min^{-1} transported the generated Hg vapor through the gas–liquid separator and acid wash trap to the plasma. Following 70 s of sample uptake, data acquisition was initiated and collected for an additional 55 s. Isotopes of ^{200}Hg, ^{201}Hg and ^{202}Hg were simultaneously monitored and ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios were calculated. The Hg concentration was calculated from the average of both ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios. In this way, compensation for mass bias was accomplished without resorting to an external mass bias correction as a result of its opposite influence on these two isotope pairs. This approach has been successfully applied to the determination of butyltins by Rodríguez-González *et al.*[28] using two pairs of Sn ratios with calibration by ID.

The sequence of operating steps for the FIMS amalgamation system is summarized in Table 3. During step 1, the sample tubing leading up to the valve is flushed with new sample solution. In step 2, the valve is switched to the 'fill' position to permit the sample to be mixed on-line with 0.5% $SnCl_2$. The generated vapor is transported in a 0.3 l min^{-1} flow of Ar through a gas–liquid separator and an acid trap and subsequently accumulated on the Pt–Au foil. Following a 60 s sample loading at a flow rate of 10 ml min^{-1}, the valve is switched to the injection position and pump 2 is operated for 30 s to ensure that all Hg^0 was swept through the system to the Pt–Au foil (step 3). Heat is applied to the foil and Hg^0 is released to the ICP for measurement in step 4. Finally, a flow of air is directed at the outer surface of the trap to cool the Pt/Au foil prior to the next run. Runs consisting of 0.5% $SnCl_2$ in 1% HCl were repeated through at least 5 cycles (for cleaning the entire on-line FIMS amalgam system) before processing the real samples. The volume of sample and blank processed was 10 ml. Data acquisition on both spectrometers was manually triggered after an appropriate delay time (80 s) to sample the transient peaks. The acquired data were transferred to an off-line computer for further processing using in-house software to yield peak areas to generate ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios, from which the analyte concentration in the sample was calculated.

Results and discussion

Isotope ratio measurements for Hg

The performance of the SF-ICP-MS and ICP-TOF-MS instruments for measurements of the ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios used for typical ID calibration purposes (*i.e.*, a 1 : 1 ratio of endogenous 202 to spiked 201) were compared. A 100 ppt solution of Hg was used for CV generation to provide both steady-state and transient signals (following trapping on gold).

Table 4 Isotope ratios with SF-ICP-MS and ICP-TOF-MS

	Methods	Measured ratios (one standard deviation $n = 6$)	
		^{200}Hg/^{201}Hg	^{202}Hg/^{201}Hg
SF-ICP-MS	CV[a]	1.7511 ± 0.0066	2.2696 ± 0.0071
	CV with Au trapping[b]	1.750 ± 0.011	2.269 ± 0.012
ICP-TOF-MS	CV[a]	1.7512 ± 0.0031	2.2687 ± 0.0058
	CV with Au trapping[b]	1.7529 ± 0.0070	2.265 ± 0.010

[a] 55 s integration period, 100 ppt standard. [b] 10 ml sample volume, 100 ppt standard.

In contrast to pneumatic sample introduction of the liquid solution, signals derived from CV generation suffered substantially increased noise (±14% RSD) arising from both the reduction and the gas–liquid separation process, as a segmented flow gas stripping arrangement was used. Consequently, the precision of measured Hg ratios based on individual points is also affected. Thus, ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios were calculated based on the summed counts over the full integration (55 s measurement) period. Results are summarized in Table 4.

Although the total integration time was maintained identical for both instruments, acquisition conditions were different for the two MS configurations. Over a 55 s read period, the ICP-TOF-MS summed detector response from 1.76×10^6 ($55 \times 29\,411$) oa pushouts. As the signal intensity was outside the linear range of pulse counting for the TOF, analog detection was used. This provided a typical signal of 3.4×10^5 cps for ^{202}Hg from a 100 ppt Hg standard with continuous CV generation. Cross-calibration of the detector yielded an amplification factor of 35 when changing from pulse counting to analog output, with the result that the equivalent ion count rate (for the purposes of estimating counting statistics) was 9.7×10^3 cps. For the SF-ICP-MS, 5 runs of 70 passes with a 5 ms dwell time on each of 10 channels within a 5% mass defining the isotope peak resulted in a typical signal of 7.0×10^6 cps for ^{202}Hg under these operating conditions. With a 55 s integration time, the total counts recorded for ^{202}Hg was 5.3×10^5 with the TOF and 3.85×10^8 with the SF instrument. Poisson statistics applied to these data provide a count rate limited precision achievable for the ^{202}Hg/^{201}Hg ratio of 0.19% for the TOF and 0.007% with the SF. These values compare well with the experimental precision (Table 4) of 0.26% with the TOF but that for the SF is degraded to 0.31% RSD. Clearly, the compensation for correlated noise, which is high with this sample introduction system, is achieved with the simultaneous measurement capabilities of the TOF, but remains a significant noise component for the SF because of the sequential nature of the data acquisition.

A significant enhancement in the Hg signal (65-fold in peak sensitivity) could be obtained following trapping of all of the mercury generated from a 10 ml sample onto the Pt–Au foil. Desorption transients were similar in shape to those reported by Evans *et al.*[26] and were characterized by a full width at half-maximum of 1s and a base width of 3 s, as is evident from Fig. 2. Mercury isotope ratios derived from transient signals were based on the integrated counts over the full transient. Based on the results of processing 10 ml volumes of the 100 ppt standard, the isotope ratio precisions for ^{202}Hg/^{201}Hg were characterized by a 0.53% RSD with the SF- and 0.44% with the TOF-MS (Table 4). As expected, the resulting precision of the calculated ratios obtained with steady-state CV generation is some 2-fold better than that obtained with transient sample introduction for both detection systems, an observation frequently reported in the literature.[29] It is not possible to compare these data with those reported by Evans *et al.*[26] because the total flux of mercury sampled for transient measurements by these authors was unknown.

Determination of Hg in ORMS-3 using ID with continuous CV generation

The quality of data obtained with ID calibration is largely dependent on the accuracy and precision of the ratio measurements of the selected isotope pairs. An important aspect relating to the accuracy of ratio measurements is the correction undertaken for mass discrimination or mass bias. This can be achieved using an external correction based on the expected ratios divided by the measured ratios from a natural abundance Hg standard having known isotopic composition. Rodríguez-González *et al.*[28] recently reported a new approach to mass bias correction (internal mass bias correction) which obviated the need to run a natural abundance standard. The approach was based on use of the average concentration derived from two pairs of ratios (*e.g.*, ^{118}Sn/^{119}Sn and ^{120}Sn/^{119}Sn in their study) whose mass bias correction effects occurred in opposite directions. The derived average concentration was thus free of mass bias effects. This approach not only saves analysis time, but also reduces the uncertainty associated with such measurements since mass bias correction is eliminated. For this study, both ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios were measured and this internal mass bias correction approach was used for the determination of Hg in ORMS-3 water.

The intensities of the Hg isotopes measured during introduction of only the $SnCl_2$ reductant (sample introduction

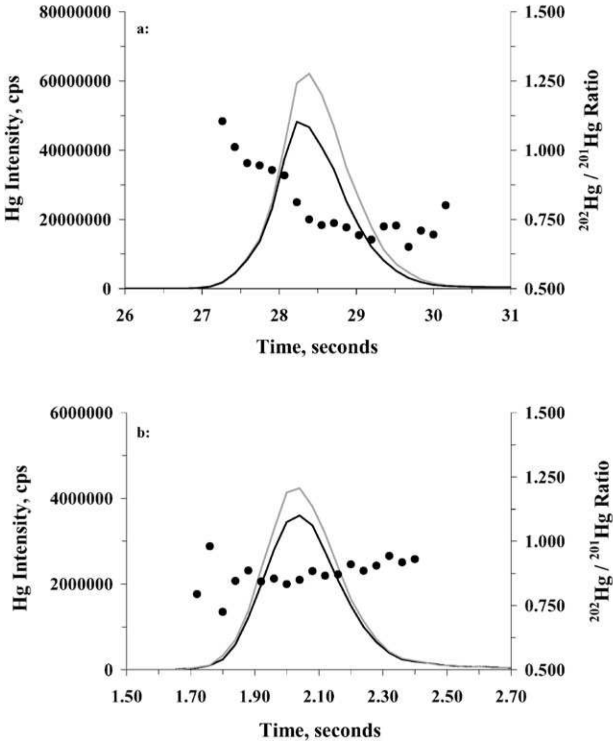

Fig. 2 Chromatograms characterizing a ^{201}Hg spiked ORMS-3 obtained using CV with trapping on Au. (a) SF-ICP-MS detection; (b) ICP-TOF-MS detection. Black trace: ^{202}Hg; grey trace: ^{201}Hg; and closed circles: ^{202}Hg/^{201}Hg ratio.

stopped by pinching the uptake line) served to establish the measurement baseline from which data generated with all spiked ORMS-3 samples were subtracted to yield a blank corrected response. Similarly, the intensities of the Hg isotopes measured in 2% HCl were subtracted from all reverse ID calibration solutions. The following equation was used for quantitation of Hg in ORMS-3 using ID with either SF-ICP-MS or ICP-TOF-MS:

$$C_\mathrm{x} = C_\mathrm{z} \cdot \frac{m_\mathrm{y}}{m_\mathrm{x}} \cdot \frac{m_\mathrm{z}}{m'_\mathrm{y}} \cdot \frac{A_\mathrm{y} - B_\mathrm{y} \cdot R_\mathrm{n}}{B_\mathrm{x} \cdot R_\mathrm{n} - A_\mathrm{x}} \cdot \frac{B_\mathrm{z} \cdot R'_\mathrm{n} - A_\mathrm{z}}{A_\mathrm{y} - B_\mathrm{y} \cdot R'_\mathrm{n}} \cdot \frac{\mathrm{AW_x}}{\mathrm{AW_z}} \qquad (1)$$

where C_x is the analyte concentration in pg g^{-1}; C_z is the concentration of natural abundance Hg standard (pg g^{-1}); m_y is the mass (g) of spike used to prepare the blend solution of sample and spike; m_x is the mass (g) of sample used; m_z is the mass (g) of natural abundance Hg standard used; m'_y is the mass (g) of spike used to prepare the blend solution of spike and natural abundance Hg standard solution; A_y is the abundance of the reference isotope (^{200}Hg or ^{202}Hg) in the spike; B_y is the abundance of the spike isotope (^{201}Hg) in the spike; A_x (or A_z) is the abundance of the reference isotope (^{200}Hg or ^{202}Hg) in the sample (or in the standard); B_x (or B_z) is the abundance of the spike isotope (^{201}Hg) in the sample (or in the standard); R_n is the measured reference/spike isotope ratio in the blend solution of sample and spike; R'_n is the measured reference/spike isotope ratio in the blend solution of spike and natural abundance Hg standard; AW$_\mathrm{x}$ is the analyte atomic weight in the sample and AW$_\mathrm{z}$ is the analyte atomic weight in the natural abundance Hg standard.

A concentration of 12.75 ± 0.24 pg g^{-1} was calculated for Hg (one standard deviation, $n = 4$), based on the average values obtained from the ^{200}Hg/^{201}Hg and ^{202}Hg/^{201}Hg ratios using continuous sample introduction, CV generation and SF-ICP-MS detection. This result is in good agreement with the certified value of 12.6 ± 1.1 pg g^{-1} (combined uncertainty, $k = 2$). Using continuous CV generation with ICP-TOF-MS detection, a concentration of 12.34 ± 0.11 pg g^{-1} (one standard deviation, $n = 4$) was obtained.

The analytical blank for steady-state CV generation was defined by the baseline noise generated by the acidified reductant. Method detection limits (LODs based on three times the standard deviation of the concentration of the blank) for ID-CV-SF-ICP-MS and ICP-TOF-MS techniques were calculated based on eight measurements of a ^{201}Hg spiked sample blank. Values of 0.024 and 0.30 pg g^{-1} were obtained using SF-ICP-MS and ICP-TOF-MS, respectively. The superior LOD obtained with SF-ICP-MS is a direct consequence of its enhanced sensitivity compared with ICP-TOF-MS.

Determination of Hg in ORMS-3 using ID with purge and trap CV generation

Trapping mercury vapor on Au is frequently used to achieve preconcentration in order to improve sensitivity at low concentrations.[4,26] The Pt–Au foil used in these experiments suffered from memory effects in that a carryover signal was generated following trapping of analyte from the sample. This may have been a consequence of the limited heating capabilities of the FIMS system which relies on radiant heat from several IR lamp sources. This problem should be eliminated by use of gold coated sand for trapping,[26] wherein the gold layer is very thin (µm). Five heating cycles of the trap were thus necessary to reduce the signal to background levels following the processing of a 100 ppt standard solution. Consequently, five blank samples were required to be run before the Hg signal returned to the original baseline following the analysis of a 100 ppt standard solution.

As is evident in Fig. 2a, spectral skew arises for the transient signals recorded with the SF-ICP-MS as a consequence of the sequential nature of the data acquisition; measurements made with the ICP-TOF-MS are free from this aberration. As a consequence, ^{202}Hg/^{201}Hg ratios for spiked ORMS-3 calculated at intervals across the transient signals using the SF display a continuous decrease with time (Fig. 2a). This may be due to isotope fractionation during thermal release of Hg from the gold trap, as noted by Evans *et al.*,[26] but data provided by the TOF detection system for the same transient sample introduction do not support this. Fig. 2b illustrates that relatively constant isotope ratios can be obtained across transient signals recorded with the TOF, subject to the limitations of counting statistics. Isotope ratios used for quantitation were thus based solely on the integrated response for each isotope transient, thereby providing optimum precision of measurement.[26]

No significant difference was evident in the ID results for ORMS-3 using either SF- or TOF-MS detection; concentrations of 12.55 ± 0.41 and 12.65 ± 0.30 pg g^{-1} (one standard deviation, $n = 4$) were obtained, respectively. The reproducibility (3.3 and 2.3% RSD) of these results is poorer than that achieved using CV generation with steady-state sample introduction (1.9 and 0.87% RSD).

Method detection limits based on measurement of transient signals were estimated from replicate measurements of the blank (1.4 pg g^{-1}), yielding values of 0.15 and 0.87 pg g^{-1} for Hg by SF- and TOF-MS, respectively. These LODs are inferior to those obtained with direct CV generation due to the inherently lower precision typically characterizing transient signals.[29]

Conclusion

Quantitation of total Hg by CV generation ID at ultra-trace concentrations in water can be achieved using ICP-TOF-MS detection with high precision and accuracy and a LOD of 0.9 pg g^{-1}. Jitaru and Adams[14] reported a detection limit of 0.27 pg ml^{-1} for Hg using solid phase microextraction coupled to GC-ICP-TOF-MS. The often expressed belief that ICP-TOF-MS is incapable of such performance because of its reduced sensitivity relative to even qICP-MS is thus fallacious. Measurement performance is competitive with the more expensive SF-ICP-MS instrumentation if used for such determinations and precision of ratio measurements obeys Poisson statistics. Barbaste *et al.*[30] reported similar performance comparisons for the determination of Pb isotope ratios in wine when ICP-TOF-MS, qICP-MS and multi-collector-ICP-MS machines were used for detection.

References

1 P. J. Craig, *Organometallic Compounds in the Environment: Principles and Reactions*, Longman, Harlow, 1986.
2 J. Allibone, E. Fatemian and P. J. Walker, *J. Anal. At. Spectrom.*, 1999, **14**, 235–239.
3 J. L. Mann, S. E. Long and W. R. Kelly, *J. Anal. At. Spectrom.*, 2003, **18**, 1293–1296.
4 E. Debrah, E. R. Denoyer and J. F. Tyson, *J. Anal. At. Spectrom.*, 1996, **11**, 127–132.
5 S. Willie, *Am. Lab.*, 2002, **34**, 40–43.
6 L. Manganiello, A. Ríos and M. Valcárcel, *Anal. Chem.*, 2002, **74**, 921–925.
7 J. C. A. de Wuilloud, R. G. Wuilloud, M. F. Silva, R. A. Olsina and L. D. Martinez, *Spectrochim. Acta, Part B*, 2002, **57**, 365–374.
8 J. L. Manzoori, M. H. Sorouraddin and A. M. Haji Shabani, *J. Anal. At. Spectrom.*, 1998, **13**, 305–308.
9 J. L. Gómez-Ariza, F. Lorenzo and T. García-Barrera, *J. Chromatogr. A*, 2004, **1056**, 139–144.
10 B. San Vicente de la Riva, J. M. Costa-Fernández, W. J. Jin, R. Pereiro and A. Sanz-Medel, *Anal. Chim. Acta*, 2002, **455**, 179–186.
11 P. F. Schuster, D. P. Krabbenhoft, D. L. Naftz, L. D. Cecil, M. L. Olson, J. F. Dewild, D. D. Susong, J. R. Green and M. L. Abbott, *Environ. Sci. Technol.*, 2002, **36**, 2303–2310.
12 C. F. Boutron, G. M. Vandal, W. F. Fitzgerald and C. P. Ferrari, *Geophys. Res. Lett.*, 1998, **25**, 3315–3318.

13 C. P. Ferrari, A. L. Moreau and C. F. Boutron, *Fresenius' J. Anal. Chem.*, 2000, **366**, 433–437.

14 P. Jitaru and F. C. Adams, *J. Chromatogr. A*, 2004, **1055**, 197–207.

15 R. G. Smith, *Anal. Chem.*, 1993, **65**, 2485–2488.

16 P. De Bièvre in *Isotope Dilution Mass Spectrometry in Trace Element Analysis in Biological Specimens*, eds. R. F. M. Herber and M. Stoeppler, Elsevier, 1994.

17 K. G. Heumann in *Isotope Dilution Mass Spectrometry in Inorganic Mass Spectrometry*, eds. F. Adams, R. Gijbels and R. Van Grieken, John Wiley & Sons, 1988.

18 L. Yang, Z. Mester and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2003, **18**, 1365–1370.

19 ELEMENT2 Thermo Finnigan Application Flash Report No. E15, ThermoFinnigan, November, 2002.

20 R. E. Sturgeon, J. W. Lam and A. Saint, *J. Anal. At. Spectrom.*, 2000, **15**, 607–616.

21 X. Tian, H. Emteborg and F. C. Adams, *J. Anal. At. Spectrom.*, 1999, **14**, 1807–1814.

22 F. Vanhaecke, L. Moens, R. Dams, L. Allen and S. Georgitis, *Anal. Chem.*, 1999, **71**, 3297–3303.

23 H. Emteborg, X. Tian, M. Ostermann, M. Berglund and F. C. Adams, *J. Anal. At. Spectrom.*, 2000, **15**, 239–246.

24 S. N. Willie and R. E. Sturgeon, *Spectrochim. Acta, Part B*, 2001, **56**, 1707–1716.

25 K. Benkhedda, H. Goenaga Infante, E. Ivanova and F. C. Adams, *J. Anal. At. Spectrom.*, 2000, **15**, 1349–1356.

26 R. D. Evans, H. Hintelmann and P. J. Dillon, *J. Anal. At. Spectrom.*, 2001, **16**, 1064–1069.

27 S. M. Nelms, C. R. Quétel, T. Prohaska, J. Vogl and P. D. P. Taylor, *J. Anal. At. Spectrom.*, 2001, **16**, 333–338.

28 P. Rodríguez-González, J. Ruiz Encinar, J. I. García Alonso and A. Sanz-Medel, *J. Anal. At. Spectrom.*, 2002, **17**, 824–830.

29 I. Günther-Leopold, B. Wernli, Z. Kopajtic and D. Günther, *Anal. Bioanal. Chem.*, 2004, **378**, 241–249.

30 M. Barbaste, L. Halicz, A. Galy, B. Medina, H. Emteborg, F. C. Adams and R. Lobinski, *Talanta*, 2001, **54**, 307–317.