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Species specific isotope dilution calibration for determination of mercury species by gas chromatography coupled to inductively coupled plasma- or furnace atomisation plasma ionisation-mass spectrometry

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Standard solutions of $(CH_3)_2Hg$, CH_3HgCl and $HgCl_2$ were prepared in toluene from isotopically enriched mercury. Methods for synthesising $(CH_3)_2Hg$ and CH_3HgCl, from $HgCl_2$, were developed with reaction yields of 95.2% and 92.7%, respectively, without noticeable loss of isotope. Isotopically enriched species standards were then used for species specific isotope dilution calibration and method assurance tests for mercury species determination. An interface was built to couple a gas chromatograph (GC) to an inductively coupled plasma mass spectrometer (ICP-MS) that resulted in rapid and efficient transfer of organic mercury compounds eluted from natural gas condensates. Oxygen, introduced to the plasma auxiliary gas, reduced matrix interferences and improved sensitivity by a factor of two. The GC-ICP-MS method with species specific isotope dilution calibration gave recovery values of 97.7 ± 2.0, 104.1 ± 0.7 and 106.6 ± 2.1% for $(CH_3)_2Hg$, CH_3HgCl and $HgCl_2$, respectively, in natural gas condensate compared to a standard solution of the species in toluene. Detection limits of the three species, calculated from 3*s* of the peak areas derived from 20 pg of the species (as Hg) in solution, were 8, 2 and 3 pg. Furnace atomisation plasma ionisation mass spectrometry (FAPIMS) was also evaluated as a detector with the GC methodology. When the plasma was operated with optimised conditions for the generation of elemental ions, recoveries were 100.0 ± 2.9, 98.3 ± 1.5 and 97.5 ± 1.2% for $(CH_3)_2Hg$, CH_3HgCl and $HgCl_2$ in a 10% condensate solution, and a detection limit of 33 pg was obtained for methylmercury. A plasma was also generated and sustained with reduced rf power and graphite furnace temperature so that molecular ions and fragments were produced and detected by the same spectrometer, which demonstrated the potential of FAPIMS as a sensitive elemental detector additionally capable of providing molecular mass spectra for the identification of species eluted from a GC column.

Introduction

Speciation techniques often involve coupled apparatus that requires rigorous testing for method assurance. When using separation methods for speciation that, for example, make use of chromatography, matrix interference on detection can vary between sample components and analyte species. For analytical techniques that make use of mass spectrometric (MS) detectors, the use of stable, enriched, elemental isotopes for calibration has greatly improved the precision and accuracy of determination.[1–3] The use of enriched isotopes, with MS detectors, should also benefit speciation methodology.[4–6] However, for these methods, it is essential that the added spike of enriched isotope and the indigenous element species for determination are present in the same chemical form. Isotope dilution calibration also provides an important diagnostic tool for the development of new analytical methods in that isotopes can be used as tracers. This is exemplified by the work of Hintelmann and Evans,[7] who used isotope enriched methylmercury chloride as a tracer to check for species specific recoveries and the occurrence of transalkylation reactions during the determination of methyl- and inorganic mercury in a number of certified reference materials. Isotopically enriched species should represent the state-of-the-art for specific accurate and precise instrumental calibration. Not only are they useful for routine determination, speeding analysis, but they also greatly assist in the testing and diagnostics of new analytical methods and techniques.

Techniques for mercury species determination often rely on species identification by chromatographic retention time, as this allows the use of sensitive and selective element specific detectors, including inductively coupled plasma-mass spectrometry (ICP-MS) and microwave induced plasma atomic emission spectrometry (MIP-AES). However, these detectors cannot verify the identity of the eluted species or be used to identify unknown signals. Electrospray ionisation mass spectrometry (ES-MS) was used to successfully identify inorganic and organometallic mercury species (for reviews see refs. 8 and 9). However, an ES-MS method has not yet been developed for the identification and quantitation of mercury at trace levels, and might also face a number of challenges. In particular, variation in the conductivity of samples in organic solutions could lead to difficulty in forming a stable electrospray, and the possibility of accurate quantitation would be further reduced by matrix effects and non-linearity of the analyte mass–detector response relationship. Positive identification with the possibility of quantification may be achieved with a reference technique such as gas chromatography (GC) coupled to electron impact mass spectrometry (EI-MS)[10] or glow discharge mass spectrometry (GD-MS). Ideally, a source that may be conveniently and rapidly switched between providing sensitive elemental detection and molecular information for

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Table 1 Supplier's recommended atom fraction composition of the enriched mercury aliquot and mass fractions determined by ICP-MS. Precision for the determined values is represented by the standard deviation of measurements, as mass fractions (of the total)

Mass	196	198	199	200	201	202	204
Certified fraction	0.0040	0.9600	0.0017	0.0300	0.0025	0.0015	<0.0005
Determined ICP-MS fraction	0.0024	0.9582	0.0012	0.0333	0.0026	0.0018	0.0004
Precision/1*s*	0.0001	0.0191	0.0001	0.0010	0.0001	0.0002	<0.0001

identification could be applied.[11–14] Furnace atomisation plasma ionisation mass spectrometry (FAPIMS) has the potential to be operated as a robust elemental ion source and as a softer generator of molecular ions.[15] The thermal temperature of the source and the rf power applied to the plasma may be varied to produce conditions suitable for the production of the desired ions.[15]

The importance of species specific mercury species determination in natural gas condensate, amongst other petroleum products, was discussed in a 1999 review by Wilhelm and Bloom.[16] The different chemical and physical properties of the species can affect the efficiency of methods for the removal of mercury from hydrocarbon products, depending on their species content. Unremoved mercury may reduce the lifetime of catalysts, heat exchangers and other aluminium plant for product processing and transport, and there is an additional concern that the toxicity of mercury species could present a health risk to engineers.

The organic matrix associated with a natural gas condensate allows for the dissolution of several mercury species, such as elemental mercury and dimethylmercury, in much greater concentrations than may be present in aqueous samples.[10] Consequently, methods were developed for the determination of a number of different organic mercury species in condensates.[17–21] To use isotope dilution calibration for mercury speciation methods for this matrix, it is therefore essential that a number of different mercury species are used. Ideally, these should be produced by synthetic routes that yield high fractions of the desired compounds with minimal loss of the enriched isotope.

In this article we report the use of enriched ^{198}Hg for the preparation of dimethylmercury, methylmercury chloride and mercuric chloride standards, which were used for both the development of new GC-ICP-MS methodology for the determination of mercury species in natural gas condensates and other organic samples, and testing of GC-FAPIMS for atomic and molecular ion mass spectrometry. Optimal conditions for sensitive measurements by GC-ICP-MS were determined, including the development of a simple heated interface, with the aim of providing efficient transfer of volatilised organometallic species. FAPIMS was evaluated for analytical performance in the elemental mode by measurement of the recovery of analyte species and a detection limit for methylmercury, and by the acquisition of molecular spectra.

Experimental

Preparation of enriched isotope species standards

A 15 mg mass of enriched metallic mercury was obtained with the isotopic composition, in atom fractions, given in Table 1.

Table 2 Compositions of isotopically enriched mercury species stock solutions in mg l^{-1} as Hg

	Species		
Standard name	$(CH_3)_2Hg$	CH_3HgCl	$HgCl_2$
$(CH_3)_2Hg$	590.3	27.1	1.3
CH_3HgCl	3.3	500.8	38.3
$HgCl_2$	<DL	2.4	930.0

The mercury was dissolved in 0.2 ml of nitric acid (in-house distilled, Heraeus quartz still, Germany) in a borosilicate glass tube and the acid was evaporated to near dryness, whereupon 0.2 ml of concentrated hydrochloric acid (in-house distilled) was added, and again heated until dryness. Toluene, added by weight to give about 10 ml, rapidly dissolved the resulting powder. This solution was taken as the ^{198}Hg enriched mercuric chloride stock.

A dimethylmercury stock solution was prepared by reacting 4 ml of the enriched $HgCl_2$ stock with 1.6 ml of a 2.4 M methylmagnesium chloride solution in tetrahydrofuran (Merck, Darmstadt, Germany). The solution was cooled on ice prior to mixing and was then raised to, and held at, room temperature (22 °C) for 7 h. The solution was again cooled on ice, reacted with 1.6 ml of 0.6 M hydrochloric acid (distilled in Milli-Q purified water), centrifuged and the organic phase was retained and weighed.

Methylmercury chloride was prepared by an un-symmetrisation reaction between the mercuric chloride and dimethylmercury stock solutions.[22] Half of the mass of the dimethylmercury stock was mixed with 2 ml of the mercuric chloride stock, to give an approximately equimolar mixture of the compounds, in an open borosilicate tube fitted with a Liebig condenser. The tube was placed in a heating block at 100 °C and the solution was refluxed for 6 h.

The species concentrations of the isotope enriched stock solutions were determined by comparison with natural isotope ratio standards by GC-ICP-MS and are given in Table 2. All samples were derivatised with Grignard reagent by a previously described method.[10]

Standard calibration and methods

Mercury species stock solutions of natural isotope composition were prepared in toluene (distilled in glass grade, Burdick & Jackson, Muskeyon, MI, USA) by dissolution of their salts. The solutions made were 222.0 mg l^{-1} $HgCl_2$ (>99%, p.a., Riedel de Haën, Seelze, Germany), 201.2 mg l^{-1} CH_3HgCl (>95%, Merck, Darmstadt, Germany) and 997.5 mg l^{-1} $(CH_3)_2Hg$ (>95%, Aldrich Chemie, Steinheim, Germany). For FAPIMS tests, additional stock solutions of 1113 mg l^{-1} CH_3HgCl and 1056 mg l^{-1} $HgCl_2$ (both Reagent Grade, Alfa Aesar, Canada) were prepared. Solutions of the individual mercury species in organic solvents were previously shown to be stable over the period of use.[10]

Isotope dilution calibration

Integrated signal peaks were taken for all determinations with time windows assigned visually. For recovery tests, signals were integrated with baselines subtracted that were set by averaging 2 groups of 7 points at the start and end of the window. Isotope dilution calibration calculations were made using equation 1,[23] where C_x and C_s are the mercury concentrations of the original sample and the added isotope spike, R_m is the measured ratio of $^{198}Hg^+ : {}^{202}Hg^+$ for the spiked sample, A_x and B_x are the atom fractions of ^{198}Hg and ^{202}Hg in the unspiked sample and A_s and B_s are the corresponding atom fractions in the enriched isotope standard.

$$C_x = \left(\frac{C_s 198}{200.59}\right)\left(\frac{A_s - R_m B_s}{R_m B_x - A_x}\right) \quad (1)$$

The standards' isotope fractions used for calibration calculation were determined by introduction of aqueous standards of natural and isotope enriched mercury into the ICP-MS. By this method possible mass bias of the instrument would be automatically corrected.[24] The mass fractions, for $^{198}Hg^+$ and $^{202}Hg^+$, were determined with relative standard deviations of 0.16 and 0.58% for the natural standard and 1.91 and 0.02% for the enriched.

GC-ICP-MS

A Varian 3300 gas chromatograph (Varian, Palo Alto, CA, USA) was fitted with an on-column injector liner (Varian) and a 15 m capillary column (0.53 mm id, 1.5 μm BP-1, Supelco, Frölunda, Sweden). The injector was held at 180 °C and the GC oven was temperature programmed: initiated at 80 °C for 1 min, followed by a ramp to 180 °C at 40 °C min^{-1} and held for 0.5 min. The column was connected to a 0.32 mm id deactivated fused silica capillary (Supelco) that was fed through a heated interface to the plasma. The interface, shown in Fig. 1, directed the capillary through a 0.75 mm id Teflon tube together with a 0.2 mm diameter NiCr wire with a resistance of 2.4 Ω m^{-1}. An in-house built power supply provided 18 V ac that resistively heated the NiCr wire to 180 ± 10 °C. A standard PerkinElmer (Norwalk, Connecticut, NY, USA) adapter tube was drilled out to 6 mm id to within 2 mm of the ceramic insert, and a 4 mm id piece of Teflon tube was fitted. The transfer line was held in place on the adapter tube by an in-house constructed T-connection. This also allowed the supply of the instrument's nebuliser gas as well as holding the electrical connections. Inside the injector, the transfer capillary extended about 2 mm from the transfer tube, which terminated inside the ceramic tube about 2 mm from the opening. In the rf field, the NiCr wire was kept perpendicular to the field to avoid conduction of rf energy.[25] From the interface to the GC, the NiCr wire was coiled around the transfer tube, as well as passing inside it, and the assembly was covered with a woven sleeve of heat resistant fibre. The transport lines and interfaces of both ion sources were designed to keep a constant temperature over their length.[25] Teflon tubes proved to have sufficient heat tolerance to the temperatures below 200 °C that were used and provided the interfaces with some mechanical flexibility. The NiCr wire would reach operating temperature within a few seconds, and maintain it with no more than 2 °C fluctuation.

A PerkinElmer ELAN 6000 ICP-MS was operated with rf power of 1200 W and nebuliser gas flow of 0.7 l min^{-1} Ar. An additional corrugated ¼-in Teflon tube (PerkinElmer) was connected *via* a Teflon Swagelok ¼-in three-way union to the auxiliary gas inlet of the torch, and provided a regulated supply of oxygen gas. A standard ceramic injector tube and standard gas flow rates were used with the GC interface so that plasma conditions would not require sensitive flow and position re-

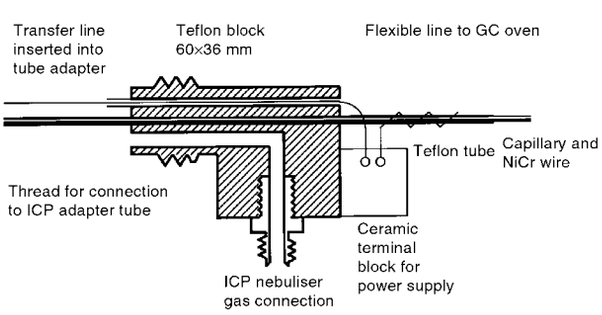

Fig. 1 T-connector of the GC-ICP interface.

optimisation. The ELAN data collection software was triggered by closure of a switch on the injector of the GC. Data were collected by peak hopping with $^{198}Hg^+$ and $^{202}Hg^+$ monitored with a dwell time of 25 ms and sufficient readings to record the complete chromatograms. Data files were extracted with GRAMS32 v.5.0 (Galactic Industries, Salem, NH, USA) for evaluation by Microsoft Excel v.7.0.

GC-FAPIMS

The basic FAPIMS source and interface has been described in an earlier publication[13] and only changes to the configuration are given here. The GC for the FAPIMS source was a Varian 3400 fitted with an on-column injector liner (Varian), a 15 m capillary column (0.32 mm id, 1.5 μm DB®-1, J&W Scientific, Rancho Cordova, CA, USA) and a polyimide lined, pneumatically switched six port valve (1/32-in ports, Valco Instruments Co. Inc., Houston, TX, USA) that was switched to pass either column eluate or pure helium gas flow (make up gas). A deactivated fused silica transfer capillary (0.25 mm id, Chromatographic Specialties Inc.) led from the valve through a similar transfer line to that of the GC-ICP interface, with temperature control by the use of a variable transformer as power supply. The GC-ICP-MS column temperature program was used with the addition of programmed valve timing to vent the toluene solvent. Within the FAPIMS workhead, the original 1 mm diameter graphite rod electrode and mount was replaced by a system analogous to that previously described[14,15] where the transfer capillary was passed directly into the base of a hollow, perforated nickel rf electrode. Purge gas, introduced well upstream of the mouth of the transfer capillary, flowed concurrently with effluent gas inside the transfer capillary and ensured that eluent from the capillary was flushed efficiently from the inside of the nickel rf electrode to the plasma. The electrode terminated 1 mm from the end of an integrated contact cuvette (ICC) tube that faced the MS sampling interface with 3 mm separation. The entire source is enclosed in a workhead fabricated from a copper block and fitted with ports for furnace power, purge gas and water cooling (shown in Fig. 1 of ref. 13). The ICC furnace was heated (300 to 650 °C) by a PerkinElmer HGA-500 power supply and temperatures quoted were those read from the power supply, which may deviate from the true temperature of the ICC. RF power (10–100 W) was supplied to the electrode from a Model RF10L 40 MHz generator and AM-5 matchbox (RF Power Products, Voorhees, NJ, USA). The workhead was mounted on the interface with three 1-in micrometer heads, which permitted translation in three dimensions. For all measurements described here, the furnace was positioned so that the sampling orifice was on-line, about 1 mm below the central axis of the furnace (about 2 mm above the bottom tube wall). This location typically provided optimum signal intensity. The temperature of the capillary within the FAPIMS source was regulated together with the temperature of the workhead by adjusting the flow of cooling water when current was applied to the graphite furnace. The workhead was typically operated with a surface temperature of 70 °C. This temperature appeared to be sufficient for the species measured here as compared with earlier results from a similar system;[19] dibutylmercury peaks did not show tailing.

A research prototype of a PerkinElmer SCIEX ELAN 6000 was used for all FAPIMS measurements. The general operation and vacuum requirements have been described previously.[14] For the experiments described here, sampling plate diameters of 0.25 mm id or 0.50 mm id, with a sampler–skimmer (0.88 mm id) separation of 5.0 mm were used. Both sampler and skimmer cones sit on MACOR ceramic mounts, electrically isolated from the instrument ground. Voltages are applied to the sampler and skimmer cones by external dc power supplies (Hewlett-Packard, Models 6516A and E3612A,

respectively) and can be optimised for maximum signal intensity for each element. Because the FAPIMS source is low power (10–100 W) and the graphite furnace is operated at low relative temperatures for steady-state data collection, the interface was not water-cooled. Gas flows supplied to the workhead were calibrated using a bubble flow meter. For all measurements, the source was held slightly above atmospheric pressure to reduce the diffusion of atmospheric gases into the source, which might quench the plasma.

For recovery and detection limit data collection, the same scan conditions were used as cited for GC-ICP-MS measurements. Spectral scan data were acquired from sampling of headspace effluents generated by a continuous flow of gas through a vial containing CH_3HgCl (Alfa Aesar). Dwell times of 100 ms were typically used. Data files were exported from the ELAN signal graphics program by in-house software for evaluation by Microsoft Excel.

Results and discussion

Synthesis of isotopically enriched mercury species standards

The principal consideration for preparation of the isotopically enriched mercury species standards was to efficiently convert metallic mercury to a single chemical form with minimum loss. The species concentrations, determined by GC-ICP-MS, are shown in Table 2. Conversion of $HgCl_2$ to $(CH_3)_2Hg$ and CH_3HgCl proceeded with 95.2 and 92.7% efficiencies to give standards with acceptable species purity when compared to the natural isotope ratio standards used (see Experimental). As determination is made with mixed isotope enriched species standards, species purity is not of practical importance as long as the added concentrations of each species are known precisely.

Traditional synthetic routes for the preparation of di-organomercurials often make use of Grignard reagents.[22] The reaction of methylmagnesium chloride with an inorganic mercury salt produces almost only dimethylmercury, with a less than 5% yield of monomethylmercury. The reaction was easily controlled and could be performed without unusual safety precautions. The amount of natural mercury in the Grignard reagent was less than the detection limit of 8 $\mu g\ l^{-1}$. Monomethylmercury was produced by reaction of dimethylmercury with an equimolar concentration of the inorganic form. Here, it was necessary to use toluene as the solvent, as it does not form ligands to inorganic mercury salts,[22] and to heat the mixture to speed equilibration. Preliminary tests with natural mercury indicated that the reaction between the species may be concentration dependent as it occurred very slowly at concentrations of 10 $mg\ l^{-1}$ (of each species) and has not been observed in solutions at trace ($<1\ mg\ l^{-1}$) concentrations.[10]

The atom fractions taken for isotope dilution calculations were those determined by ICP-MS analysis of the aqueous solution. The ICP-MS determined isotopic fractions were all within 0.3% of the values certified for the enriched standard, as shown in Table 1, and the isotopic fractions of a natural mercury standard were within 0.3% of literature values.[26] Reagents used in the preparation of the enriched isotope species showed no detectable mercury concentration by GC-ICP-MS.

Although the ^{198}Hg for standard preparation was enriched to 96%, less than 1% was present as ^{202}Hg, which was also used to measure the ratio. Consequently, significant alterations in isotope ratios were obtained for spiked samples, which would theoretically improve the precision of determination over the use of a less highly enriched isotope spike.

Table 3 GC-ICP-MS and GC-FAPIMS performance. Recoveries of natural isotope ratio mercury species in natural gas condensate (GC-ICP-MS) and 10% (v/v) condensate in toluene (GC-FAPIMS), determined by isotope dilution calibration (ID) and standard addition calibration (SA). For GC-ICP-MS measurements, standards contained about 20 $\mu g\ l^{-1}$ of each species with a spike concentration between 16 and 20 $\mu g\ l^{-1}$ of the appropriate species. For GC-FAPIMS, standards and spike concentrations were about 1 mg^{-1}

	Calibration	$(CH_3)_2Hg$	CH_3HgCl	$HgCl_2$
GC-ICP-MS	ID	97.7 ± 2.0	104.1 ± 0.7	106.6 ± 2.1
Recovery (%), $n=4$	SA	105.5 ± 14.5	88.1 ± 17.4	93.3 ± 13.5
GC-FAPIMS	ID	100.0 ± 2.9	98.3 ± 1.5	97.5 ± 1.2
Recovery (%), $n=3$	SA	85.6 ± 54.2	104.6 ± 10.0	99.8 ± 8.5

GC-ICP-MS optimisation

As stated in the Experimental section, modifications to the ICP-MS were kept to a minimum so that torch gas flows and position optimisations could be simplified. An oxygen flow of 10 $ml\ min^{-1}$ was introduced to the auxiliary gas supply on the ICP torch, however, to prevent carbon deposition. Platinum sampler and skimmer cones were used as a precaution against erosion by oxygen, which might occur with nickel cones, and no carbon was deposited. The addition of oxygen increased signals for mercury by about 40%, while increasing the flow to 20 $ml\ min^{-1}$ diminished the signal to its original value. A possible explanation for the observed increase in sensitivity may be the "thermal pinch effect",[27] wherein the introduction of a molecular gas to an ICP absorbs rf energy that causes the plasma to contract. The plasma is sustained by this contraction if a sufficient plasma density can be maintained. In this case, the efficiencies of ionization and transport to the mass spectrometer may be increased as the analyte is exposed to a more confined and denser plasma.

GC-ICP-MS analytical performance

The GC-ICP-MS and GC-FAPIMS instrument performance was evaluated by measuring sensitivity, detection limits and precision. Matrix tolerance was assessed by measuring the response from dimethylmercury, methylmercury chloride and mercuric chloride added to natural gas condensate, relative to that from standards of the species in toluene. Table 3 shows the recovery of mercury species in condensate, expressed as a percentage. The values given for calibration by standard addition are a comparison of $^{198}Hg^+$ signals from toluene and condensate samples with natural mercury content determined by the addition of a spike. These show that the species were approximately completely recovered in condensate; however, the average precision of the determined values is poor, at 15%. Using species specific isotope dilution, the recoveries are closer to 100% for all species and have greatly improved precision, at about 2%, over the values determined by standard addition. Typical chromatograms are shown in Fig. 2.

The detection limits for the species, given in Table 4, are similar to comparable techniques reported in the literature.[19–21,28,29] However, the isotope dilution GC-ICP-MS method may provide a further improvement in sensitivity as dilution of samples can be avoided, given the method's tolerance to higher masses of matrix. It should also be possible to determine elemental mercury using this chromatographic method, although this was not attempted because it is unlikely that a stable solution could be produced.[10,17]

FAPIMS analytical performance

The design of the FAPIMS ion source and mass spectrometer interface for elemental detection were described previously.[14] The essential procedural difference between FAPIMS and ICP-MS systems was the inclusion of a timed solvent venting event. A venting valve was found to be necessary as the introduction of a solvent plug, 9 mg of toluene, to the plasma resulted in severe plasma attenuation and deposition of carbon on the

Table 4 ICP-MS method detection limits for mercury species in pg, as Hg. Detection limits were calculated as 3*s* of the $^{198}Hg^+$: $^{202}Hg^+$ ratios and as 3*s* of the $^{202}Hg^+$ integrated signals for 10 replicate measurements of 19.95 pg $(CH_3)_2Hg$, 20.21 pg CH_3HgCl or 22.20 pg $HgCl_2$ (all as Hg, with the latter two species as their butyl derivatives)

	$(CH_3)_2Hg$	CH_3HgCl	$HgCl_2$
Isotope ratio	4	2	3
$^{202}Hg^+$ signal area	8	2	3

central perforated electrode within the furnace. It is suspected that the carbon deposits reduced sensitivity over time. For dimethylmercury, which eluted from the GC close in time to the toluene solvent, valve timing could be set to reject the majority of the toluene. However, despite careful optimisation of valve timing, sensitivity decreased gradually to 50% of the original value over 10 sample injections (on the occasion of recovery values measurement).

The influence of the matrix is also apparent from the recovery values determined by standard addition and given in Table 3. The fraction of dimethylmercury recovered when using a 10% (v/v) condensate solution, compared to pure toluene, was estimated using a spike of enriched isotope dimethylmercury. Recoveries were calculated by the method of isotope dilution calibration described in the Experimental section, and by standard addition, with the $^{198}Hg^+$ ion monitored for spiked and unspiked samples. Each sample or spike was measured three times in series. A significant drift in signal intensity was evident to such an extent that the calibration was not useful. Results from standard addition returned a precision of 54% (1*s*), as measurement conditions deviated between sample and standard. In contrast, for species specific isotope dilution, a considerably more accurate and precise recovery value of $100 \pm 2.9\%$ was obtained from data taken on the same measurement occasion. For monomethyl- and inorganic mercury, derivatised to their respective butyl-forms, matrix induced interferences were less severe as solvent and lighter components eluted before the mercury species. Recovery values show similarly high precision and accuracy with the results for species specific isotope dilution within 1*s* of 100%.

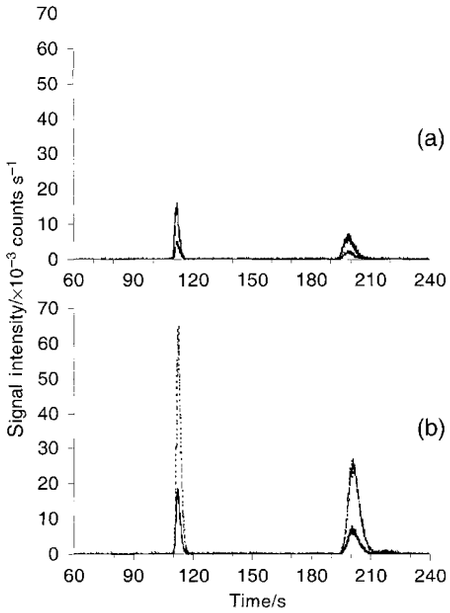

Fig. 2 Chromatogram (a) is given by a natural gas condensate spiked with 20.2 μg l^{-1} of CH_3HgCl and 22.2 μg l^{-1} $HgCl_2$, (b) is the spiked condensate with addition of 16.8 μg l^{-1} isotopically enriched $CH_3{}^{198}HgCl_2$ and 18.2 μg l^{-1} $^{198}HgCl_2$. Broken lines are the $^{198}Hg^+$ signal, solid lines are $^{202}Hg^+$.

A detection limit for methylmercury determination with this system was estimated to be 33 pg by measuring 10 replicate signals obtained with 1 μl injections of a 111.3 μg l^{-1} $CH_3HgC_4H_9$ solution, based on 3*s* of the integrated peak. A similar detection limit may be expected for the butyl derivative of inorganic mercury, whereas that for dimethylmercury may be compromised by a drift in sensitivity, as discussed previously in this section. The GC-FAPIMS system used here, therefore, possesses limits of detection higher than other element specific detectors, such as MIP-AES, ICP-MS or CVAAS, applied for mercury speciation. However, the detection limit is significantly better than those achievable with techniques that permit monitoring of molecular ions. It is likely that this system could be further optimised to improve the sensitivity of elemental measurement. The ion optics of the current spectrometer are designed to sample an ion beam from an ICP, which has a much higher thermal temperature and lower gas density.

Molecular species identification with GC-FAPIMS

Perhaps the most attractive feature of the FAPIMS source is its potential to generate and detect intact molecular ions. By coupling FAPIMS with GC, the speciation capability of the source can be extended, providing a degree of information competitive with GC-EI-MS systems. The key to generating this data is the careful selection of source temperature and plasma power. An example of the effect that these parameters have on the nature of the ions detected is illustrated in Fig. 3. Under low power and low temperature conditions [Fig. 3(a)] the molecular $Hg(CH_3)^+$ ion predominates. At higher furnace temperatures but similar plasma power [Fig. 3(b)] the molecular ion $[Hg(CH_3)^+]$ undergoes significant decomposition within the furnace. As such, the dominant ion in the region shown is the atomic $^{202}Hg^+$, and although there is still evidence for the molecular ion $[Hg(CH_3)^+]$, significant overlap exists on a nominal mass basis with the elemental adduct ion $[Hg(H_2O)^+]$. Similarly, both the higher power and higher gas temperature generated using a 20 W plasma promote the

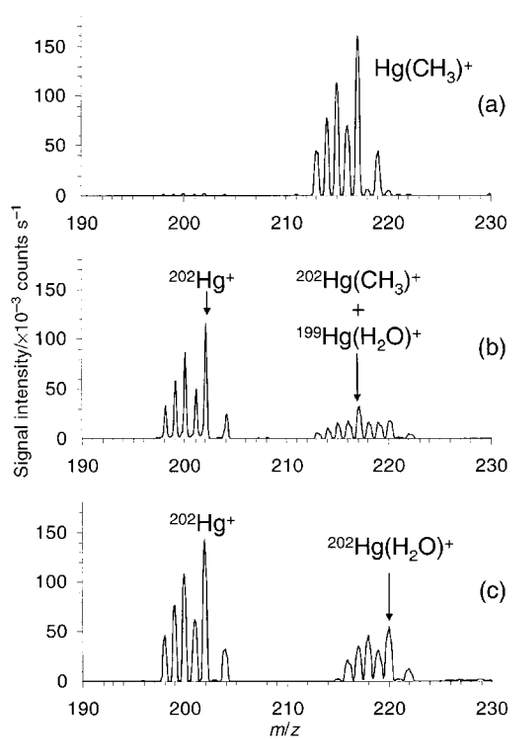

Fig. 3 Molecular mass spectra obtained by FAPIMS operated with different conditions for ion generation, with continuous introduction of methylmercury chloride vapour in helium. Trace (a) was obtained with 10 W rf power and a furnace temperature of 300 °C, trace (b) with 10 W rf at 650 °C and trace (c) 20 W rf at 300 °C.

decomposition of the molecular ion in the furnace, generating a spectrum dominated by atomic and atomic-adduct ions, as illustrated in Fig. 3(c).

The results shown in Fig. 3 clearly demonstrate that, with the careful selection of operating conditions, molecular ion information and therefore direct speciation information can be obtained. Unfortunately, the mass spectrometer used for these experiments is incapable of generating the total ion chromatograms (TICs) routinely employed in GC-MS applications for the identification of molecular ions over a selected mass range. In addition, its limited mass range ($\sim$250 m/z) precludes the identification of larger molecular ions such as dibutylmercury. Further, even though ions can be detected at the upper mass range, poor resolution and mass calibration make identification of multi-isotopic ions a complicated task with the current instrument, especially when spectral interferences exist. At this stage, it is only possible to establish proof of principle. For this source (or any other low power molecular ion source) to truly reach its potential, coupling to a mass spectrometer having good transmission over a mass range to at least 500 is required, including fast scanning software normally associated with modern benchtop GC-MS instruments.

Conclusions

Dimethylmercury, methylmercury chloride and mercuric chloride standards can be efficiently synthesised from isotopically enriched mercury metal. Their production was simple and efficient with no waste of expensive isotope. Standards were of sufficient purity for implementation of species specific isotope dilution calibration and were also useful in the evaluation of new speciation techniques. In future, isotopically enriched species standards could be applied to the development of techniques for total measurement of elements forming volatile species. A reliable and precise GC-ICP-MS method was developed having low detection limits and improved matrix tolerance compared with other speciation approaches for samples with organic matrices, requiring only the T-connection and an oxygen supply to set up. A new detector for mercury speciation, FAPIMS, demonstrated potential for sensitive atomic measurement, together with molecular measurement useful for the identification of new compounds.

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References

1 K. G. Heumann, L. Rottmann and J. Vogl, *J. Anal. At. Spectrom.*, 1994, **9**, 1351.
2 J. P. Snell, E. Björn and W. Frech, *J. Anal. At. Spectrom.*, 2000, **15**, 397.
3 J. Diemer and K. G. Heumann, *Fresenius J. Anal. Chem.*, 2000, **368**, 103.
4 K. G. Heumann, S. M. Gallus, G. Rädlinger and J. Vogl, *Spectrochim. Acta, Part B*, 1998, **53**, 273.
5 S. M. Gallus and K. G. Heumann, *J. Anal. At. Spectrom.*, 1996, **11**, 887.
6 H. Emteborg, E. Björklund, F. Ödman, L. Karlsson, L. Mathiasson, W. Frech and D. C. Baxter, *Analyst*, 1996, **121**, 19.
7 H. Hintelmann and R. D. Evans, *Fresenius J. Anal. Chem.*, 1997, **358**, 378.
8 I. I. Stewart, *Spectrochim. Acta, Part B*, 1999, **54**, 1649.
9 W. Henderson, B. K. Nicholson and L. J. McCaffrey, *Tetrahedron*, 1998, **17**, 4291.
10 J. Snell, J. Qian, M. Johansson, K. Smit and W. Frech, *Analyst*, 1998, **123**, 905.
11 B. Rosenkranz, G. O'Connor and E. Hywel Evans, *J. Anal. At. Spectrom.*, 2000, **15**, 7.
12 M. W. Borer and G. M. Hieftje, *Spectrochim. Acta, Part B*, 1991, **14**, 463.
13 I. I. Stewart, R. Guevremont and R. E. Sturgeon, *Anal. Chem.*, 1999, **71**, 5146.
14 M. S. Jiminez and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 1997, **12**, 597.
15 R. Guevremont and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2000, **15**, 37.
16 S. M. Wilhelm and N. Bloom, *Fuel Processing Technology*, 2000, **63**, 1.
17 N. S. Bloom, *Fresenius J. Anal. Chem.*, 2000, **366**, 438.
18 H. Tao, T. Murakami, M. Tominaga and A. Miyazaki, *J. Anal. At. Spectrom.*, 1998, **13**, 1085.
19 W. Frech, J. P. Snell and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 1998, **13**, 1347.
20 A. Shafawi, L. Ebdon, M. Foulkes, P. Stockwell and W. Corns, *Anal. Chim. Acta*, 2000, **415**, 21.
21 J. P. Snell, W. Frech and Y. Thomassen, *Analyst*, 1996, **121**, 1055.
22 J. L. Wardell, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, UK, 1982, vol. 2, ch. 17, pp. 892–894.
23 J. D. Fassett and P. J. Paulsen, *Anal. Chem.*, 1989, **61**, 643A.
24 H. P. Longerich, *At. Spectrosc.*, 1989, **10**, 112.
25 J. Poehlman, B. W. Pack and G. M. Hieftje, *Int. Lab.*, 1999, **29**, 26.
26 *CRC Handbook of Chemistry and Physics, 71st Edition*, CRC Press, Cleveland, OH, USA, 1990–1991.
27 A. Montaser and D. W. Golightly, *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, VCH, Cambridge, UK, 2nd edn., 1992, pp. 882–883.
28 N. G. Orellana Velado, R. Pereiro and A. Sanz-Medel, *J. Anal. At. Spectrom.*, 1998, **13**, 905.
29 H. Emteborg, H. W. Sinemus, B. Radziuk, D. C. Baxter and W. Frech, *Spectrochim. Acta, Part B.*, 1996, **51**, 829.