Performance comparison between furnace atomisation plasma emission spectrometry and microwave induced plasma-atomic emission spectrometry for the determination of mercury species in gas chromatography effluents

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Wolfgang Frech,[a] James P. Snell[a] and Ralph E. Sturgeon[b]

[a] *Department of Analytical Chemistry, Umeå University, S-901 87 Umeå, Sweden*
[b] *Institute for National Measurement Standards, National Research Council of Canada, Ottawa, ON, Canada K1A 0R6*

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A Beenakker microwave-induced plasma (MIP) and a furnace atomization plasma excitation spectrometry (FAPES) source were compared with respect to performance capabilities for the analysis of derivatised mercury species when coupled with high resolution GC for sample introduction. Natural gas condensate was used as a test material. Emission was monitored at the 253.6 nm mercury line. For standard solutions, comparable LODs were estimated for dimethyl-, methylbutyl- and dibutylmercury for both sources that were between 0.5 and 4.1 pg. In diluted condensate (5%) detection limits were between 1.5 and 4.7 pg. However, measurement of dimethylmercury was not possible with the MIP as the plasma was extinguished due to solvent vapour overload. Precision of replicate measurement of dimethyl-, methylbutyl- and dibutylmercury was better than 2% RSD for 2.5 μl injections to the FAPES at concentrations well above the LOD. The linear range spans 3 decades in both sources. Molecular emission from NO bands gives rise to background in both sources. In the FAPES source, hydrocarbon effluents reduce NO concentrations giving rise to background fluctuations, whereas in the MIP background fluctuations arise mainly from quenching of the plasma.

Introduction

Low power helium microwave-induced plasmas (MIPs) have been extensively used as excitation sources for gaseous effluents from gas chromatography (GC) and supercritical fluid chromatography (SFE) eluates. The popularity of these plasmas can, for the large part, be ascribed to their low capital and operating costs and their high electron and excitation temperatures, in the range of 20 000 and 3500 K, respectively, resulting in good atomic emission spectroscopy (AES) sensitivities for both metals and non-metals.[1] However, these sources are also characterised by little tolerance towards introduction of sample compounds because kinetic gas temperatures are relatively low, in the region of 1300–2100 K.[1] Moreover, the resonance structure of the discharge can be easily disturbed when the plasma is loaded by matrix species, resulting in decreased analyte emission. For these reasons, low power helium plasmas are preferentially used as detectors for gaseous and/or dry aerosol samples.

The Beenakker cavity[2] allows stable operation of a plasma at atmospheric pressure and in addition, axial viewing of the plasma provides, for most elements, detection limits at the pg s^{-1} level with a dynamic range of up to five orders of magnitude.[3] However, tolerance towards plasma loading remains critical. For example, in the presence of as little as a few 100 ppm (v/v) molecular gases, the sensitivity decreases significantly[4] such that there is a risk of obtaining interference effects even with gaseous sample introduction.

Several new designs of atmospheric pressure MIP sources have therefore been proposed, primarily with the intention of addressing inter-element effects. For example, Jin *et al.*[5] developed a microwave plasma torch (MPT) characterised by a rotationally symmetric plasma having lowest densities along a central axis through which the sample is introduced. With this plasma configuration, little disturbance by sample constituents is observed as interaction with resonant discharge regions is small. Recently, the MPT has been further optimised.[6]

A comparative study of the MPT, Beenakker and surfatron cavities for AES was performed by Camuna-Aguilar *et al.*[7] For C and Cl, similar detection limits, in the lower ng ml^{-1} range, were estimated with these three sources with a helium plasma. The MPT was, as expected, least affected by organic sample constituents and provided best correlation between experimental and theoretical element ratios for hydrocarbon species. When Hg^0 was determined, detection limits that differed by 50-fold were found amongst the three cavities, the most sensitive being the surfatron, the least the MPT (detection limit 0.5 ng Hg^{2+} ml^{-1}).[8] The surfatron was, on the other hand, most prone to de-tuning of the discharge by sample concomitants.

Another recently developed source is that used for furnace atomisation plasma emission spectrometry (FAPES). This is a capacitively coupled radiofrequency plasma formed between a graphite tube and a central electrode. It can be sustained at atmospheric pressure and combines the advantages of the graphite atomiser with those of the capacitively coupled plasma,[9,10] *i.e.*, the atomiser allows *in-situ* sample pretreatment which facilitates thermal decomposition of sample constituents. At the same time, high plasma excitation temperatures (3500 K) give rise to excellent atomic and molecular emission sensitivities. Several physical properties of the FAPES have so far been characterised, wherein it was concluded that typical FAPES temperatures and electron densities in this helium plasma are similar to those in a helium-MIP.[11] The spatial distribution and intensity of atomic and molecular

emission in FAPES is dependent on the matrix and plasma working conditions.[12] In line with these findings, it was observed that analytical performance strongly suffers from interference effects if the analyte is present in the plasma together with matrix species.[13] However, the graphite furnace facilitates minimisation of interference effects, permitting platform atomisation and removal of matrix species by sample pre-treatment in the presence of modifiers.[13] Unfortunately, this concept is not compatible with on-line coupling of the source to chromatographic systems.

On-line coupling of the FAPES has so far only been tested in connection with a vapour generation system for the determination of mercury species[14] using an unheated furnace, as the analyte was completely separated from the matrix during an ethylation step.

The analytical possibilities of on-line GC-FAPES coupling have yet to be investigated. The concept of such a system should provide inherent advantages because the capacitively coupled FAPES offers high sensitivities, is expected to be relatively stable and less prone to interference effects than Beenakker or surfatron sources due to the presence of the resistively heated furnace.

The aim of this work, therefore, has been to compare the analytical performance of capillary GC coupled to an MIP sustained in a Beenakker cavity[15] with results from a similarly coupled FAPES source for the determination of mercury species. For this purpose, natural gas condensates as well as hexane concentrates of derivatised mercury species extracted from such samples were used. The two sources were evaluated with respect to detection limits, working range, precision at optimum concentrations and susceptibility to changes in background intensity or plasma suppression from co-eluting hydrocarbon species. Chromatographically separated species included dimethyl-, methylbutyl- and dibutylmercury.

Experimental

Instrumentation

GC- MIP-AES. Mercury species were selectively determined by GC-MIP-AES by the methods given in ref. 15. A Varian 3300 gas chromatograph was fitted with a DB-1 column (15 m, 0.53 mm id, J&W Scientific, Rancho Cordova, CA, USA). An on-column injector was used and a temporally controlled, pneumatically actuated valve (Valco Instruments Co. Inc., Houston, TX, USA) was connected to the column end. The valve passes column eluate beyond a specific retention time through a heated interface to the plasma. An atmospheric pressure helium plasma was generated in a Beenakker TM_{010} cavity fitted with an aluminium oxide mini MIP torch (AHF Injenieurbüro, Tübingen, Germany). Flow rates are 30–35 ml min^{-1} for plasma gas and 75–80 ml min^{-1} for the concentric flow of shielding gas. The microwave generator (AHF Injenieurbüro) applies 150 W at 2450 MHz. Axial emission from both the Hg 253.652 nm and C 247.857 nm lines is monitored simultaneously by a 0.75 m Rowland circle polychromator (Applied Chromatography Systems, Luton, UK).

For measurement of wavelength spectra, the GC column was replaced by two 20 cm lengths of deactivated fused silica capillary (0.32 mm id, J&W Scientific) connected to the GC injector and switching valve. The other ends of each capillary were passed through a Teflon coated septum into a 2 ml glass tube. Decane vapour from the headspace of the tube was introduced to the plasma, with temperature control of the tube by equilibration with the GC oven. A fibre optic cable was mounted axially to the MIP torch and transmitted light was focused onto the entrance slit of a Varian AA6 Czerny–Turner spectrometer. The photomultiplier tube was set to 650 V and the light intensity was optimised by adjusting the slit, which gave a band pass between 0.2 and 0.5 nm. The signal from the 100 mV maximum deflection output from the spectrometer's control unit was passed to a computer with an AD converter board and spectra were collected with Varian Star software.

GC-FAPES. The FAPES source, rf power supply and matchbox have been described earlier.[16] Pyrolytic graphite coated electrographite tubes having no sample introduction hole (Ringsdorff Werke, Bonn, Germany) were used. The right-hand quartz window was removed and the internal purge gas (plasma gas) was admitted to the furnace only from the left side. Argon was used as the external sheath gas at a flow of 1 l min^{-1}. With the exception of the interface between the GC and the FAPES source, the same GC system and operating parameters described above were used. The GC effluents were transported to the FAPES source *via* a 35 cm length of 0.25 mm id fused silica tubing originating from the actuator valve. This line was housed within a 6 mm id thermostated copper tube, maintained at 180 °C using heater tape. Effluents were directly transported to a modified nickel centre electrode assembly, as described earlier.[14] A Swagelock 'T' union, fitted to the transfer line, was used to admit an auxiliary flow of helium gas concentric with the fused silica line, maintained at 120 ml min^{-1} with a mass flow controller. The auxiliary helium was pre-heated to the column temperature by prior passage through a 5 m length of dummy column located within the GC oven. This arrangement reduced the residence time of the analyte within the heated side arm of the interface, thereby minimising condensation of analyte species within the Macor side arm[14] because the latter could not be maintained at 180 °C, otherwise the RF cable would overheat.

Typically, a 50 W forward power plasma was sustained in the FAPES source using only the column effluent and auxiliary plasma gas and the furnace was maintained at a constant temperature of 700 °C.

Mercury emission was monitored at 253.6 nm using a 0.5 m Czerny–Turner monochromator with spectral bandwidth set to 0.3 nm. The bandwidth was empirically optimised for the highest signal to noise ratio. The wavelength was centred with a mercury hollow cathode lamp. No background correction system was available. Samples were fed from the PMT across a load resistor to a model 417 Keithley picoammeter (Keithley Instruments, Cleveland, OH, USA) and then to an analogue-to-digital (A/D) board. The picoammeter permitted suppression of the background such that the full range of the A/D converter could be utilised.

Reagents

Stock solutions of mercury species were prepared in analytical-reagent grade toluene or hexane by dissolution of their salts and stored in darkness at 4 °C. 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). Working standards were freshly prepared by dilution in the appropriate solvent. A sample of natural gas condensate, low in mercury content (<1 μg l^{-1}), was obtained from Statoil, Kårstö, Norway.

Sample preparation for gas chromatography

Samples of 1 ml volume were placed in 10 ml glass centrifuge tubes and derivatised with 0.4 ml of 2 M butylmagnesium chloride in THF (Aldrich, Steinheim, Germany) for 5 min in an ice–water bath with occasional shaking. Subsequently, 0.4 ml of 0.6 M hydrochloric acid was added to quench the reaction, the mixture was centrifuged for 3 min at 5400 rpm and the organic phase removed. For the purpose of this study,

Table 1 Chromatographic conditions for FAPES and Beenakker MIP systems

Chromatograph	Varian 3300 or 3400 GC (Varian, Palo Alto, CA, USA)
Column	J&W DB-1 (15 m, 0.53 mm id, 1.5 μm phase) (J&W Scientific, Rancho Cordova, CA, USA)
He carrier gas pressure	8 psi (corresponds to 8 ml min^{-1} at 50 °C)
Initial temperature/hold time	50 °C/2 min
Heating ramp	50 °C min^{-1}
Final temperature/hold time	180 °C/1 min

condensate blanks are derivatised samples of the diluted condensate because the level of mercury species in this sample is well below the detection limits achievable.

Chromatography and detection

Sample volumes of 0.5 to 2.5 μl organic extracts were directly injected onto the head of the column and subjected to the chromatographic conditions summarised in Table 1. With the MIP, signals were translated through an AD converter board to Varian Star Workstation v.4.02 software, which permits determination of signal peak height and area. With the FAPES, signals were acquired directly from the PMT and processed with use of in-house software having a time resolution of 25 ms to permit determination of both peak height and area.

Results and discussion

Speciation of mercury often relies on derivatisation and chromatographic techniques to effect separation from the host matrix. Although ethylation with sodium tetraethylborate is convenient and often used for aqueous samples, it is not applicable to organic systems and may be prone to interferences.[17] Derivatisation with Grignard reagents, while being very efficient for organic samples, does not permit a simultaneous separation of the derivatised mercury species from the matrix. As a consequence, when coupled to capillary GC for separation, volatile co-eluting matrix species may be present and give rise to perturbations in the efficiency of power coupling to MIP sources.[1] Additionally, spectroscopic interferences from carbon containing moieties can occur rendering quantitation of mercury peaks difficult at low concentrations.[15] Further, it is possible that use of Grignard reagents may lead to the formation of additional volatile organic compounds that co-elute with the same retention characteristics as methylmercury.[18]

There is thus a need for more robust He plasma sources which can be easily coupled to GC columns; FAPES potentially meets this requirement. Analysis of natural gas condensates for mercury species presents a suitable test sample for performance evaluation. Determinations are particularly difficult because high detection power is needed for μg l^{-1} concentrations of many species in addition to robustness to accept various types of hydrocarbon species with minimum perturbation. Since the derivatisation and GC characteristics of such samples have already been optimised and described,[15] this permits controlled introduction of mercury species into either a Beenakker MIP or the FAPES source with the consequence that any notable differences in performance stem primarily from the source.

Optimisation of FAPES

The GC-Beenakker cavity-spectrometer system used in this study has been earlier optimised for mercury speciation in a wide variety of samples.[15,18,19] FAPES, on the other hand, has never been interfaced to a high performance GC and, as such, requires optimisation of a number of parameters, *viz.* forward power and sheath gas flow and furnace temperature for best signal to noise ratio. Injection of 10 μl volumes of helium saturated with metallic mercury (at room temperature) through the GC injection port (held at room temperature) and a short length of deactivated fused silica column was used to establish an optimum forward power as well as helium plasma and argon sheath gas flow rates. A forward power of 50 W was selected for operation as lower power resulted in decreased sensitivity whereas higher power enhanced sensitivity at the expense of increased noise. An external argon sheath gas was preferable to helium as the latter reduced sensitivity nearly three-fold. This is likely due to enhanced diffusion of ambient atmosphere into the discharge when helium is used, as the observation window on the furnace had been removed to enhance transmission of analyte radiation as well as eliminating an optical surface which carbon would otherwise occlude. Carbon deposition was found to arise from the decomposition of hydrocarbons co-eluting with the sample. During these optimisation experiments, the temperature of the furnace was arbitrarily maintained at 700 °C in an effort to minimise adsorption of mercury onto the graphite tube wall.

Introduction of derivatised samples (methylbutyl- and dibutylmercury species) through the analytical column (using conditions given in Table 1) was used to optimise the auxiliary and plasma gas flow rates as well as tube temperature. Chromatograms were obtained for these species at a tube temperature of 800 °C in the absence and presence of 120 ml min^{-1} auxiliary gas flow. The chromatographic effluent (20 ml min^{-1}) was either fed through the centre electrode into a 250 ml min^{-1} helium plasma gas used to sustain the plasma, or was supported by an auxiliary gas flow of 120 ml min^{-1} with no helium plasma gas, the former being sufficient to sustain the plasma. The auxiliary gas was found to give a flat baseline, enhance sensitivity and equalise the response from both species. The ratio of methylbutylmercury : dibutylmercury species integrated intensity is 0.57 ± 0.03 in the absence of the auxiliary gas whereas a ratio of 0.94 ± 0.07 was obtained with this gas flow. It is likely that the auxiliary gas flow enhances transport efficiency through the cooler regions of the interface, thereby eliminating potential deposition of species (causing lower sensitivity) as well as peak broadening for dibutylmercury. The elevated baseline arises from broadband emission from the (0,2) γ-NO band, which is known to be present in this source.[16]

The effect of tube temperature on the response was investigated in the range from ambient to 900 °C. Sustained heating at temperatures above 900 °C was not attempted due to noticeable heating of the rf-connector and cable. Above 500 °C, little further change in performance was evident beyond that discussed in connection with Fig. 1, which illustrates the effect of tube temperature on response at 254 nm for the injection of 2.5 μl of hexane containing 1% decane and 20 μg l^{-1} each of methylbutyl- and dibutylmercury. The furnace was at room temperature for curve (a) and maintained at 600 °C for curve (b). It is clear that sensitivity for methylbutyl- and dibutylmercury is substantially enhanced (9- and 7.5-fold, respectively) at the higher temperature. Baseline stability is also improved. The dip in each chromatogram is a consequence of decane quenching the (0,2) γ-NO band intensity. The implications of this will be discussed later in connection with the corresponding results obtained with the MIP. With the tube temperature at 600 °C, the baseline intensity is enhanced by about 10% and the disturbance caused by the decane is reduced. This is consistent with an overall increased excitation efficiency, as is also seen for the mercury species. Reduction of NO partial pressure in the furnace likely occurs as the competition for oxygen between carbon and nitrogen favours CO formation as the furnace temperature

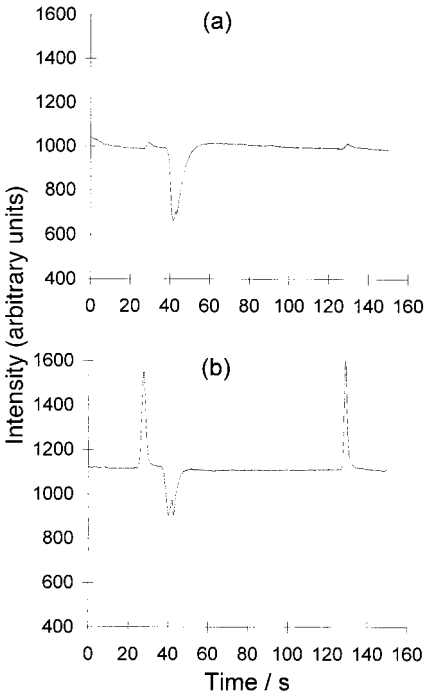

Fig. 1 Effect of furnace temperature on FAPES signals for $CH_3HgC_4H_9$ and C_4H_9Hg with the graphite furnace at (a) room temperature and (b) 600 °C.

increases.[20] The decrease in the intensity of the dip during elution of decane into a 600 °C furnace may be a consequence of increased pyrolysis of the decane with consequent emission from resulting carbon containing moieties. Further elaboration of this point will be made later in connection with discussion of the background arising in the MIP.

In light of the above, optimum conditions for the detection of mercury species were concluded to be a furnace temperature of 600 °C, an external argon sheath gas, an auxiliary helium gas flow of 120 ml min^{-1} and no additional plasma gas.

Spectral background and interference effects

At the 254 nm mercury line, an elevation of the spectral background arises from the presence of nearby intense molecular bands due to excitation of the γ-NO spectrum in the FAPES source.[16] A further increase in this background occurs with the removal of the right hand end window, presumably due to enhanced diffusion of ambient atmosphere into the discharge. As the furnace is heated to 600 °C, reduction of the NO partial pressure occurs, as noted earlier. The introduction of hydrocarbons generally also leads to reduction of background emission intensity. Decane was selected as a model hydrocarbon to study this effect since it elutes in a region between methylbutyl- and dibutylmercury. Fig. 2 shows the effect of introduction of 2.5 μl volumes of increasing concentrations (0.25–4%) of decane in hexane into the FAPES source at a furnace temperature of 600 °C. At low concentrations, suppression of NO intensity occurs during elution of the decane, possibly as a result of reaction between NO and decomposition products of the decane. At higher concentration, an enhancement in the background occurs during this event, possibly due to emission from molecular carbon containing species such as C_2N_2.[22] As these reactions are competitive processes, there will be some concentration of hydrocarbon beyond which a suppression will become an enhancement, provided the excitation capabilities of the plasma are not exceeded. The effect of these competitive processes is also

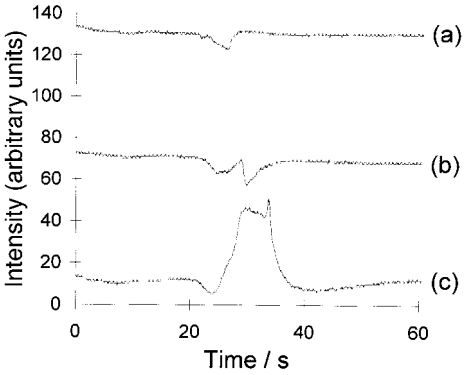

Fig. 2 Interference effect of decane on FAPES emission at 254 nm. FAPES signals given by 2.5 μl injections of (a) 0.25, (b) 1.0 and (c) 4.0% (v/v) of decane in hexane. Trace offset by (a) 20; (b) −40 and (c) −100 intensity.

evident during a dynamic run, wherein small dips on both the leading and trailing edges of the emission transients are evident.

A similar situation arises with the Beenakker MIP in that NO emission is also present at 254 nm. Fig. 3 presents a spectral scan from 200–400 nm that shows molecular band heads corresponding to the γ-NO system, confirming the identity of this species.

Fig. 4 (a) and (b) illustrate the effect of introduction of increasing amounts of several hydrocarbons, including decane in a hexane solution into the MIP. At low concentration, no significant disturbance in the baseline is evident in the mercury channel and the elution peaks for the hydrocarbons are well behaved. At ten-fold higher concentration, dips in the intensity at the mercury emission line temporally coincide with elution peaks for carbon. Noteworthy, however, is the suppression of the emission signal at the C(I) line over the central portion of its elution peak, indicative of suppression of the excitation capacity of the MIP or a reduction in background intensity from the NO-γ band. Although difficult to see in Fig. 3, the C(I) line is overlapped by about 10 pm by the NO-γ band with a head at 247.87 nm.[22] The relative amount of carbon introduced into the plasma for each hydrocarbon increases with the molecular weight of the species and this is reflected in the extent of suppression of the C(I) line at the centre of the elution peak. As with FAPES, dips in emission intensity at the mercury emission line in the presence of hydrocarbon species [otherwise evident in Fig. 4(b)] are associated with a reduction of NO emission intensity and coincide with suppression of the excitation capacity of the plasma, which is evident from the increase in microwave power reflected by the plasma.

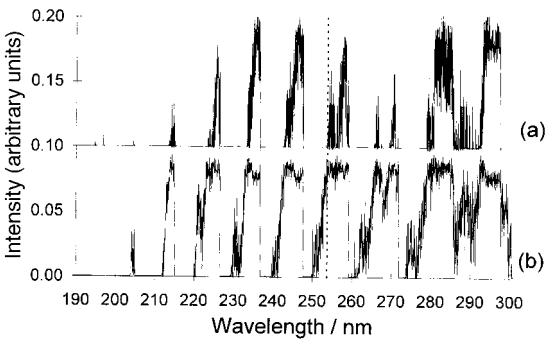

Fig. 3 Emission spectra from the Beenakker MIP with (a) 8 ml min^{-1} He saturated with decane at 55 °C and (b) 8 ml min^{-1} pure He introduced to the plasma gas. Spectrum (a) offset by 0.1 intensity. A dotted line is superimposed at 253.6 nm to mark the Hg measurement wavelength.

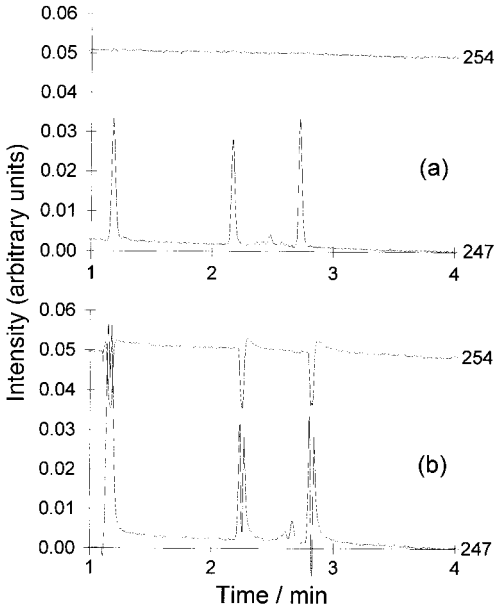

Fig. 4 Interference effect of decane on MIP emission at 254 nm. MIP signals given by 2.0 µl injections of (a) 0.01 and (b) 0.1% (v/v) 2,2,4-trimethylpentane, nonane and decane in hexane. Traces at 254 nm (a) offset by 0.05 intensity.

Further increases in the hydrocarbon loading eventually result in the extinction of the plasma.

Figures of merit

Limits of detection (LOD), based on a 3 s criterion for replicate peak area intensity measurements obtained from solutions containing concentrations within an order of magnitude of the LOD for both sources, are summarised in Table 2. This approach was used as it will yield more conservative numbers which reflect variabilities introduced by sample injection as well as emission response variations in the source when sample is present. On the introduction of 0.5 pg of methylbutyl- and dibutylmercury into the FAPES source, responses from each species can be clearly discerned above the baseline noise despite the fact that both are present below the estimated limit of detection. Essentially similar LODs arise with both sources, although FAPES is biased somewhat lower. In light of the fact that a low resolution spectrometer was used for FAPES measurements, in contrast to the higher performance offered by the optical system used for the MIP, even greater disparity in the values should accrue if the FAPES sources had been evaluated with the higher resolution optical system.[21]

To estimate the improvement in signal to noise ratio achieved using the Rowland circle spectrometer, the spectrometers' optical characteristics were compared. Assuming that noise introduced by the spectrometer was limited to the shot noise on the photomultiplier tube, a value, proportional to the signal to noise ratio was calculated from the equation $(H.D_{\theta}.A/F)^{-1/2}$, where H = slit height, D_{θ} = reciprocal dispersion (rad nm^{-1}), A = effective grating area (equal to the grating area multiplied by the cosine of the blaze angle) and F = the focal length.[23,24] Using manufacturers' data for the two systems, the signal to noise ratio was estimated to be 2.1 times higher for the Rowland circle spectrometer.

Table 2 Detection limits (pg) for Hg species in hexane

Species	FAPES[a]	Beenakker MIP
$(CH_3)_2Hg$	0.5[b]	2.1[c]
$CH_3HgC_4H_9$	0.9[d]	4.1[c]
$(C_4H_9)_2Hg$	1.7[d]	4.1[c]

[a]A lower resolution spectrometer was used with the FAPES, which deteriorated detection limits for this system. [b]0.5 µl injection volume. [c]2.5 µl injection volume. [d]2.0 µl injection volume.

Table 3 Precision comparison[a]

Species	FAPES	Beenakker MIP
$(CH_3)_2Hg$	4.7[b]	2.2[c]
$CH_3HgC_4H_9$	1.8[d]	1.5[c]
$(C_4H_9)_2Hg$	1.9[d]	2.1[c]

[a]Percentage relative standard deviation, based on injected volumes of 100 µg l^{-1} Hg in 5% (v/v) natural gas condensate in hexane. [b]0.5 µl injection volume. [c]2.5 µl injection volume. [d]2.0 µl injection volume.

Table 3 summarises precision, expressed as % relative standard deviation (RSD), of replicate injections at concentrations 50–100 times above the LODs. Data for the dimethylmercury were obtained using standard solutions in hexane or a spiked 5% (v/v) natural gas condensate in hexane. Data for methylbutyl- and dibutylmercury are derived from injections of clean hexane containing the derivatised species. It is clear that, in the presence of a real sample matrix, the precision is degraded due to baseline instabilities arising from co-eluting hydrocarbons. Despite this, such sample matrices can be accommodated with the FAPES source whereas their presence causes complete extinction of the Beenakker MIP. In general, precision of measurement with the Beenakker MIP is not significantly different from the corresponding data reported for FAPES.

Calibration curves for methylbutyl- and dibutylmercury were prepared from a single derivatised spiked solution of hexane from which serial dilution permitted access to lower concentrations. In this manner, potential errors which might arise with variable derivatisation efficiencies are avoided for more reliable results. Sample volumes of 2.5 µl were injected. Standards for dimethylmercury originated from simple dilution of a stock solution with hexane. Smaller sample volumes were used with this species in an effort to limit the amount of hexane placed on the column, as it has a similar retention time to that of dimethylmercury. For FAPES, 0.5 µl volumes could be tolerated whereas the MIP would extinguish with sample volumes greater than 0.2 µl, even with venting of the solvent. Fig. 5 reports the slopes of the calibration curves at each calibration mass for each species. Linear ranges for both sources are similar and extend from the LOD to approximately 1 ng (three orders of magnitude). With the FAPES source, slopes increased with increasing mass beyond 1 ng. Some evidence of this is also present with the Beenakker MIP.

The enhanced sensitivities observed with higher mass can not arise as a result of increased transport efficiency of these species to the sources, as the inflection point for a given source occurs at a common mass for all species. Additionally, all calibration curves were prepared by injection of the various standards in random order in an effort to minimise the effect of any drift in response as well as any changes in transport efficiency related to saturation of potential adsorption sites within the interface. Ionisation can also be eliminated as a candidate for this curvature because the degree of ionisation of mercury in this plasma is too small to result in such an effect (<1%).[21] The reason for this curvature is apparently related to the source, but is unknown at this time.

Sample analysis

A sample of natural gas condensate (NGC) was selected for study. The approximate composition of the condensate is: pentanes, 5%; *n*-hexane, 65%; toluene, 3.5%; benzene, 1.5%; other aromatic compounds, 5.5%, and other C_4 to C_{25} aliphatic

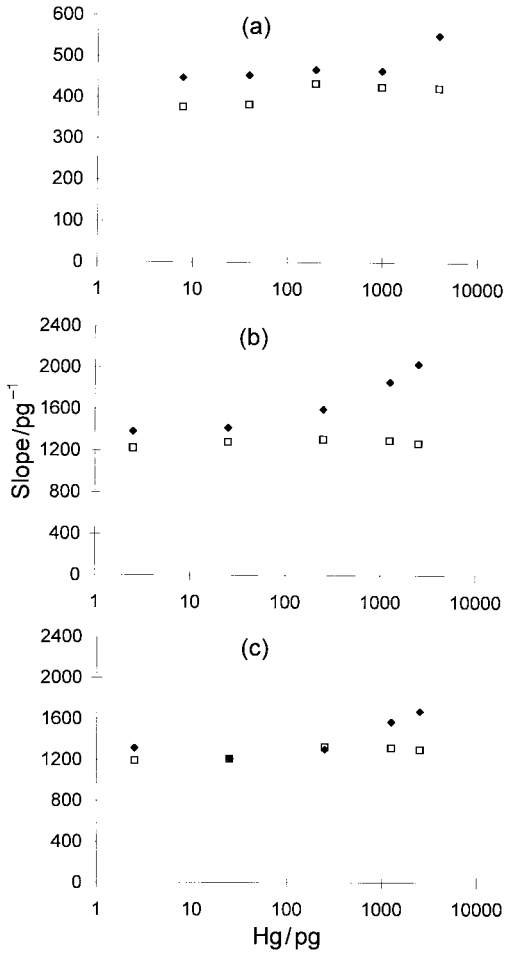

Fig. 5 Calibration curve slopes measured (peak area intensity *versus* pg Hg injected) for different masses of (a) $(CH_3)_2Hg$, (b) $CH_3HgC_4H_9$ and (c) $(C_4H_9)_2Hg$. FAPES results are plotted as diamonds, MIP as open squares.

and aromatic hydrocarbons, 20%. Direct sample introduction is precluded due to the large number of hydrocarbon species which are present. These result in complex spectra, loading of the column with low volatility hydrocarbon fractions that tend to slowly bleed through the system altering responses and retention times as well as introducing drift into the baseline. For this study, samples were therefore diluted between 10- and 20-fold prior to analysis.

Samples for dimethylmercury were examined separately for two reasons. Due to its high volatility, the peak appears immediately after the elution tail of the hexane solvent, requiring that sample volumes of 0.5 µl or less be injected. Secondly, derivatisation of this species must be avoided to prevent decomposition and transalkylation in the presence of the Grignard reagent. Derivatisation of a 500 µg l^{-1} standard of dimethylmercury in hexane produces artefact signals for both methylbutyl- and dibutylmercury. Although this problem has been highlighted earlier,[15] wherein it was suggested that short derivatisation times (5 min) would make this problem negligible, the 4 min reaction time used here shows that 5–10% of the dimethylmercury is transformed. A more significant interconversion (50%) was observed when a 500 µg l^{-1} sample of phenylmercury was derivatised. The reactivity of the Grignard reagent might be a significant factor responsible for this. This problem requires further study.

Chromatograms were obtained for samples spiked with dimethylmercury in hexane containing 10 and 5% NGC in hexane. A stable, flat baseline is obtained in pure hexane after the initial disturbance from the solvent plug. In the presence of condensate, baseline disturbances arise as a consequence of co-eluting volatile hydrocarbons originating from the NGC. These disturbances degrade the LOD for dimethylmercury (see for example, Table 4).

Table 4 Detection limits for Hg species in natural gas condensate[a]

Species	FAPES	Beenakker MIP
$(CH_3)_2Hg$	7.1[b]	Measurement not possible
$CH_3HgC_4H_9$	3.4[c,d]	3.1[e]
$(C_4H_9)_2Hg$	7.8[c,d]	2.3[e]

[a]Injected after 1 + 19 dilution in hexane. [b]0.5 µl injection volume. [c]2.5 µl injection volume. [d]Values based on 3*s* of the baseline measured over 12 s. [e]2.0 µl injection volume.

Sample volumes as small as 0.1 µl of such NGC containing solutions can not be accommodated by the Beenakker MIP source, as the plasma is extinguished. Quantitation of dimethylmercury at such concentrations in NGC with the MIP requires either a headspace analysis using SPME techniques (LOD 20 µg l^{-1}) or high temperature combustion of the GC effluent followed by amalgamation of mercury with subsequent desorption into the plasma (LOD 0.25 and 0.56 µg l^{-1} for dimethylmercury and dibutylmercury, respectively).[15]

Recoveries of dimethylmercury spikes from solutions of 10% (v/v) NGC in hexane were determined with the FAPES at concentrations between 25 and 200 µg l^{-1}. A mean recovery of 70 ± 1% (4 different concentrations) was obtained. The recovery increased to 90 ± 2% in 5% (v/v) NGC. The source of this interference (reduced recovery) is unknown. Quantitation is feasible either by use of the method of additions or by application of the (constant) recovery factor.

FAPES chromatograms were recorded for methylbutyl- and dibutylmercury in a 4.1% (v/v) NGC in hexane spiked at a concentration of 3.9 ng ml^{-1} for each species. The peak area of methylbutylmercury is not significantly affected by the NGC matrix compared to pure hexane, whereas that for dibutylmercury results in an apparent recovery greater than 100%. In the presence of NGC, the lower volatility of the dibutylmercury causes it to elute with a less volatile fraction of hydrocarbon species, altering its transport efficiency through the interface. It is believed that this is an instrumental artefact, introduced by the experimental conditions, since the interface could not be maintained at a temperature sufficient to prevent condensation of NGC matrix species. A response hysteresis occurs, in that the intensities for dibutylmercury in hexane are different when run before or after an NGC sample has been processed.

Table 4 summarises calculated limits of detection for the three mercury species in the NGC sample (5% v/v NGC in hexane) for both the FAPES and MIP sources. LODs for methylbutyl- and dibutylmercury are based on 2.5 µl injection volumes of condensate blanks. Those for dimethylmercury are based on replicate measurements of 0.5 µl injection volumes of a 12 µg l^{-1} spiked sample, for reasons discussed earlier. Baseline measurements for methylbutyl- and dibutylmercury were used in order to permit a direct comparison of data reported earlier with the MIP.[15] No measurements could be obtained for dimethylmercury using the MIP, for reasons discussed earlier. An identical LOD is obtained for methylbutylmercury whereas that for dibutylmercury is degraded by a factor of 3 for the FAPES relative to the MIP. This is likely a consequence of the problems experienced with the interface. Use of a higher resolution spectrometer with the FAPES source should serve to improve these LODs.[21]

Conclusions

With the systems used, comparable LODs can be achieved for methylbutyl- and dibutylmercury with real samples. Had a

higher resolution optical system been used with the FAPES, better LODs would accrue. Measurements of dimethylmercury in NGC are impossible to achieve with the Beenakker MIP due to lack of robustness of this plasma towards loading with hydrocarbon solvents. Although baseline disturbances are present with both sources during sample elution, it is significant that in FAPES these occur as a result of changes in background emission from NO, whereas in the MIP, these are due to suppression of the excitation capability of the plasma. With FAPES, this problem may be ameliorated with use of a suitable background correction system, whereas there is little that can be done to solve this problem with the MIP.

Several of the problems noted in this study could be attributed to the non-optimal interface used with the FAPES system. This highlights the importance of evaluating experimental systems with real samples, as none of these problems were evident when processing synthetic solutions. Clearly, FAPES should be a useful source for GC effluent detection, particularly in view of the additional flexibility arising from heating of the furnace.

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