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Stability and reactions of mercury species in organic solution†

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The stability over time of elemental mercury, methylmercury and inorganic mercury species was evaluated in heptane, toluene and mixed hydrocarbon solutions. Elemental mercury and inorganic mercury(II) were determined using a specific extraction method followed by ICP-MS or CVAAS. Methylmercury and mercury(II) were determined by GC–MIP-AES after derivatisation with Grignard reagent. The results show that significant losses of mercury species from solution can occur by two pathways: by adsorption on the container wall and by reactions forming mercury(I) compounds. For the latter pathway, rapid losses of dissolved elemental mercury and mercury(II) chloride species occur when both are present in solution. For heptane solutions containing $HgCl_2$, 80% of the $HgCl_2$ remains after 13 d in a pure standard compared with 11% in a standard containing Hg^0. Mercury(I) compounds form a colloidal material, which is not soluble in these organic solvents at a detectable concentration. Mercury(I) compounds were butylated with Grignard reagent to form the organic mercury(I) compound $(C_4H_9)_2Hg_2$ that was measured specifically by GC–MIP-AES and GC–MS. This new compound was stable and appeared to precipitate from solution.

Keywords: *Mercury species; mercury(I) compounds; hydrocarbon solutions; species stability*

Mercury is present in both produced and processed natural gas and hydrocarbon liquids and must be monitored to satisfy environmental concerns and to ensure the safe transport and efficient processing of these products. In addition to its poisoning of industrial catalysts, elemental mercury damages aluminium alloy heat exchangers and pipelines by corrosion[1] and presents a health risk to engineers upon inspection and maintenance of mercury-contaminated equipment. It is known that mercury may be present in natural gas as metallic mercury or oxidised organic and inorganic species.[2] The different chemical and physical properties of the species must be considered in the evaluation of potential health effects and in the design of systems to remove mercury from natural gas. The properties of a species also have implications both for its stability in a sample and its eventual determination.

As there is currently a lack of knowledge on the stability of mercury species in liquid hydrocarbons, there is an uncertainty in the reliability of sampling procedures, in particular sample storage. In addition, there is a need from industry for hydrocarbon reference materials containing trace levels of mercury species to control the accuracy of the determination of total mercury or individual mercury species in complex samples. For the preparation of such a reference material, it is essential that the stabilities of mercury species and possible mechanisms of their loss from organic solution are known.

Previously, experiments were conducted to elucidate the forms and reactions of inorganic mercury species in organic solvents at ppm concentrations.[3–5] These experiments demonstrated that metallic and oxidised mercury species may react rapidly with each other or halogens and that stable Hg_2^{2+} species may even be formed. These reactions were also found to occur at trace concentrations in aqueous solution.[6,7] Therefore, when preparing reference standards for mercury species, possible interactions between the species must be considered.

In this work, the stabilities of elemental mercury, mercury(II) chloride, methylmercury chloride and dimethylmercury were determined in hydrocarbon solution. Species loss from solution is shown and the mechanisms of their loss are described. The formation of an organic mercury(I) species, $(C_4H_9)_2Hg_2$, is also demonstrated.

Experimental

Chemicals were of analytical-reagent grade unless indicated otherwise.

Preparation of organic standard solutions containing mercury species

Standard solutions for stability tests were prepared in calibrated flasks and transferred to acid-washed 100 ml brown glass bottles with Teflon-lined screw-caps (Schott, Duran, Germany).

Elemental mercury standard solutions were prepared from a saturated solution of Hg^0 in heptane (distilled in glass, Burdick and Jackson, Muskegon, MI, USA) at room temperature (between 21 and 23 °C). The solution was prepared by a method based on that of Spencer and Voight.[8] Mercury-free argon was bubbled through the solvent for 6 h, Hg^0 was added and the mixture was shaken for 24 h. Some batches of heptane were found to tarnish the surface of the mercury droplet, suggesting oxidation. This heptane was purified by shaking with active carbon and filtration before use. The temperature of the solution was measured before dilution and used to calculate the Hg^0 concentration, using the equation below, according to Spencer and Voight.[8] As an example, at 22 °C the concentration of Hg^0 in heptane is 1.072 mg l^{-1}.

$$C = M_{\mathrm{r(Hg)}}\left[\frac{\rho_{\mathrm{(heptane)}}}{M_{\mathrm{r(heptane)}}}\right]\times 10^{A\log(T)+B}$$

where C is concentration (g l^{-1}), M_r is molecular mass (200.59 and 100.21 g mol^{-1}), $\rho_{\mathrm{(heptane)}}$ = density (683.76 g l^{-1}), T = temperature (K) and A and B are experimentally determined coefficients (A = 17.462, B = -49.232).

Stock standard solutions of mercury species were prepared in toluene from their salts and stored in darkness at 4 °C. The solutions prepared were 222.0 mg l^{-1} $HgCl_2$ (> 99%, Riedel-de

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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) (all concentrations are as Hg). Suspensions of Hg_2Cl_2 were prepared by the addition of about 100 mg of the solid to 50 ml of 2,2,4-trimethylpentane (Merck) as described by Kreevoy and Werwerka.[4] The solvent was decanted off to remove $HgCl_2$, which is soluble and present as an impurity, then another 50 ml of fresh solvent were added.

Synthetic condensate standard solutions were prepared in 2 l calibrated flasks and a blank solution was prepared in a 1 l calibrated flask. The standards contained 30% 2,2,4-trimethylpentane (Merck), 20% heptane (distilled in glass, Burdick and Jackson), 20% nonane (anhydrous +99%, Aldrich, Milwaukee, WI, USA), 15% decane (technical +95%, Merck) and 15% toluene. Components were added by volume and standards and blanks were made up to volume with 2,2,4-trimethylpentane. Mercury species were added to two standards in the following concentrations. Standard 1 contained 147 μg l^{-1} Hg^0, 147 μg l^{-1} $HgCl_2$, 36.8 μg l^{-1} CH_3HgCl and 36.8 μg l^{-1} $(CH_3)_2Hg$ and standard 2 contained 147 μg l^{-1} $HgCl_2$ and 36.8 μg l^{-1} $(CH_3)_2Hg$. The standards were stored in brown glass bottles with ground-glass stoppers at room temperature.

Sample preparation for gas chromatography

Samples of 1 ml were placed in 10 ml glass centrifuge tubes and derivatised with 0.4 ml of 2 M butylmagnesium chloride in tetrahydrofuran (Aldrich Chemie) 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 was removed. Samples to be analysed for mercury(I) compounds were placed in an ultrasound bath (Bandelin, Berlin, Germany) with an applied power of 320 W at 35 kHz for 30 min before aliquots were taken for derivatisation.

GC–MIP-AES

Mercury species were selectively determined by GC–MIP-AES by the methods described previously.[9] A Varian (Palo Alto, CA, USA) 3300 gas chromatograph was fitted with a DB-624 column (30 m × 0.53 mm id, 3 μm stationary phase, J & W Scientific, Rancho Cordova, CA, USA) with helium as carrier gas at 11 psi, which corresponds to a flow rate of about 8 ml min^{-1} at 50 °C. An on-column injector was used and a temporally controlled, pneumatically actuated valve (Valco Instruments, Houston, TX, USA) was connected to the column end. The valve passed column eluate of 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 were 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) applied 150 W at 2450 MHz. Emission was monitored axially by a 0.75 m Rowland circle polychromator (Applied Chromatography Systems, Luton, UK) at the Hg 253.652 nm and C 247.857 nm lines. $(CH_3)_2Hg$ and the butylated derivative of CH_3HgCl both co-eluted with masses of toluene and nonane, respectively, which the plasma cannot tolerate. For the determination of these compounds, an in-line amalgamation trap (described previously[9]) was placed between the chromatograph and the plasma. Briefly, the trap consisted of a quartz tube with a heated zone at about 900 °C and a zone at ambient temperature containing a bundle of wire, an alloy of gold (85% m/m) and platinum (15%) (Rasmussen, Hamar, Norway). The column eluate at the retention time corresponding to the species of interest was passed to the trap with a flow of oxygen. The eluate was combusted and mercury species were collected on the wire. For determination, the wire was heated to about 500 °C and mercury vapour was carried to the plasma on a flow of helium.

For long-term stability tests, three derivatives were prepared for each sample and three replicate measurements were made for a species. A freshly prepared CH_3HgCl standard is used for calibration.

GC–MS

A Fisons Instruments (Loughborough, UK) MD800 mass spectrometer was coupled to a Fisons 8000 Series gas chromatograph fitted with a J & W DB-5 column (60 m × 0.32 mm id, 0.25 μm stationary phase) and an autosampler. The eluate was ionised by a tungsten filament operated at 70 V. Mass spectra were recorded between *m/z* 100 and 600, and individual mass channels were recorded at *m/z* 202, 316 and 514.

Determination of total mercury in organic solvents by ICP-MS

A Perkin-Elmer Elan 6000 (Perkin-Elmer SCIEX, Thornhill, ON, Canada), equipped with an MCN-100 micro-concentric nebuliser (CETAC Technologies, Omaha, NE, USA) was used. Before analysis, all samples and standards were diluted 20-fold with propanol (Merck). Samples were introduced into the ICP at flow rates of typically 120 mg min^{-1} for 30 s. Between each sample the system was flushed for 1 min with Milli-Q purified water (Millipore, Sundbyberg, Sweden) containing 0.1% HNO_3 (distilled in-house) and 0.1% HCl (distilled). An auxiliary oxygen gas flow of 25 ml min^{-1} was added to the nebuliser gas. Mercury was determined at 202 u using an rf power of 1400 W. For calibration, freshly prepared $HgCl_2$ standard solutions in propanol were analysed. A standard solution was analysed before and after each sample to compensate for drift in sensitivity. Three replicates were taken of each sample.

CVAAS

A conventional, batch-wise procedure was used to free mercury from aqueous solutions. The reducing agent was 10% $SnCl_2$ (J. T. Baker, Deventer, The Netherlands) in 3% H_2SO_4 (Merck) and 0.5 ml was added to a 20 ml reaction vessel followed by 0.5 ml of sample or standard solution. A gas inlet was opened and argon purged through the solution for 2 min to free and transport Hg^0 to a bundle of gold–platinum wire in a quartz tube. A trap containing K_2CO_3 (Merck, heat treated at 500 °C to remove mercury) and granular $MgClO_4$ was placed between the reaction vessel and the gold-platinum to remove acid vapours and moisture. Mercury was vaporised by resistively heating a coil of wire around the tube to about 600 °C with temperature control provided by a CAL Controls (Hitchin, UK) Model 3200 power switching unit with an NiCr–Ni thermocouple. Mercury was detected by CVAAS at the 254 nm line using a flow injection mercury system (FIMS, Bodenseewerk Perkin-Elmer, Überlingen, Germany).

Extraction of mercury species from synthetic condensates and from heptane and heptane–toluene mixture

Samples were centrifuged at 5400 rpm for 5 min to remove solids before extraction. To extract Hg^{2+} species selectively, a sample of 2 ml was mixed with an equal amount of 1 M NaCl, 0.25 M ascorbic acid and 0.1 M HCl in water. After shaking for 15 min, the aqueous phase was removed. The extraction was repeated and the aqueous phases were combined. Hg^0 was then extracted from the remaining organic phase into 2 ml of 5 M HNO_3–1 M NaCl with shaking for 15 min. The extraction efficiencies of Hg^{2+} and Hg^0 were both > 97%, with an RSD of 10% for the extraction process and determination by CVAAS. Mercury in the extracts was determined by CVAAS and comparison with freshly prepared $HgCl_2$ standards of the appropriate blank extraction solution. From an aliquot of sample, one extraction was made for each species. Two replicate measurements were made of each extract.

The instrumentation for stability tests was recalibrated with freshly prepared standards at every measurement occasion to ensure that drift would not affect the reported results. For ICP-MS and CVAAS, Hg^0 standards were analysed by comparison with $HgCl_2$ standards and gave concentration values in accordance with those predicted by the equation given above.[8] The sensitivity of the MIP-AES detector varies by about 20% with torch conditions and plasma tuning over weeks of use whereas the CVAAS sensitivity varies by < 10%.

Results

Stability of the synthetic condensate standards

$HgCl_2$ was determined in the synthetic condensate standards by GC–MIP-AES immediately after preparation, and after 5 and 7 months of storage (Fig. 1). CH_3HgCl was determined immediately after preparation and after 5 months. $(CH_3)_2Hg$ and Hg^0 could not be separated under the conditions used and were not determined. After 5 months the concentration of CH_3HgCl in standard 1 was unchanged. However, the $HgCl_2$ concentration in both standards decreased considerably over 7 months. The decrease was much larger in standard 1, which also contained Hg^0, from 147 to 34 $\mu g\ l^{-1}$ compared with 126 $\mu g\ l^{-1}$ for standard 2.

Because of the difference in the rate of loss of $HgCl_2$ from solution between the two standards, the mechanism of loss was further evaluated by monitoring one-component hydrocarbon solutions containing only $HgCl_2$ or a mixture of $HgCl_2$ and Hg^0.

Stability of total mercury in organic solutions containing Hg^0

Hg^0 standards with a calculated concentration of 226 $\mu g\ l^{-1}$ were prepared in pure heptane and a 1 + 4 mixture of heptane and toluene. The total dissolved Hg content of the samples was measured over the following 9 d by ICP-MS. The Hg content of the solutions diminished to about half of the original value over this period (Fig. 2).

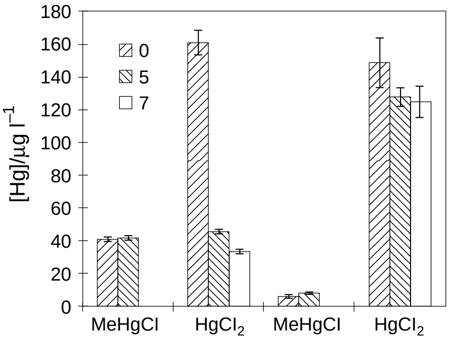

Fig. 1 $HgCl_2$ and CH_3HgCl concentrations in synthetic condensates. Mercury concentrations determined by GC–MIP-AES 0, 5 and 7 months after preparation of the synthetic condensates. The mean concentration of three derivatives is shown; error bars represent 1 s.

Stability of Hg^0 *and* $HgCl_2$ *in organic solutions in glass and HDPE containers*

Solutions of 229 $\mu g\ l^{-1}$ Hg^0 or 200 $\mu g\ l^{-1}$ $HgCl_2$ in heptane were transferred into brown glass and high-density polyethene (HDPE) bottles. $HgCl_2$ and Hg^0 were specifically extracted from the samples 4 and 13 d later and were determined by CVAAS (Fig. 3). The concentration of Hg^0 decreased more rapidly than that of $HgCl_2$ and both species were lost at a higher rate in HDPE bottles.

Solutions containing 229 $\mu g\ l^{-1}$ Hg^0 and 200 $\mu g\ l^{-1}$ $HgCl_2$ were prepared in heptane in brown glass and HDPE bottles. $HgCl_2$ was extracted from the solutions and determined by CVAAS (Fig. 3). In the presence of Hg^0, $HgCl_2$ was lost at a much higher rate from both types of bottle.

Chromatograms of samples containing Hg_2Cl_2

A sample of Hg_2Cl_2 colloid in 2,2,4-trimethylpentane was prepared by the method described above and derivatised with Grignard reagent. Samples of a solution containing 229 mg l^{-1} Hg^0 and 200 mg l^{-1} $HgCl_2$ in heptane prepared in a glass bottle were derivatised 3 weeks after the preparation of the solution. One sample was taken from the container before and one after treatment with ultrasound.

GC–MIP-AES gave chromatograms for the samples shown in Fig. 4. All have a peak at 9.4 min, corresponding to $(C_4H_9)_2Hg$, whereas the colloidal and ultrasound-treated samples show an additional peak at 12 min. This suggests the

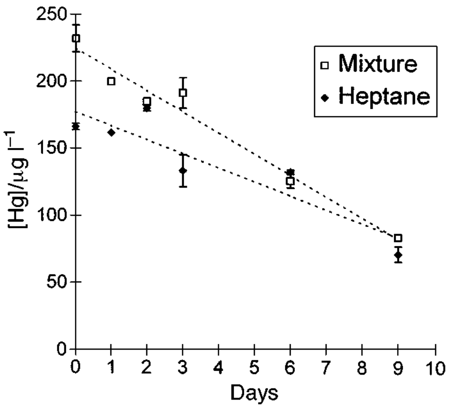

Fig. 2 Concentration of total Hg over time in organic solutions with added Hg^0. The mean concentration of three replicate measurements is given; error bars represent 1 s.

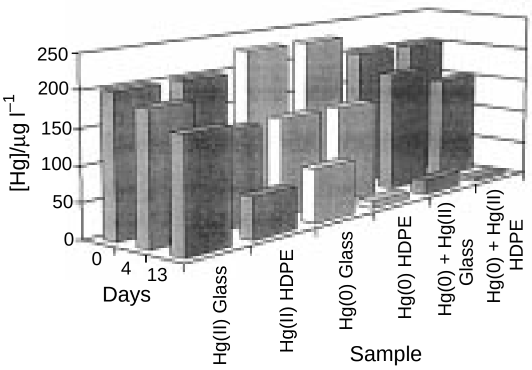

Fig. 3 Concentrations of Hg^0 (light bars) and $HgCl_2$ (dark bars) in heptane over time.

presence of an insoluble Hg species in the mixture, re-suspended by ultrasound.

To gather compositional information on the species present, a sample of the colloid suspension was derivatised and a full mass scan chromatogram was produced by GC–MS. A signal was given at 10.5 min from an aggregate of two mercury species. The leading edge of the signal gave a mass spectrum consistent with $(C_4H_9)_2Hg$ and its fragmentation products (Fig. 5). The central part of the signal gave additional ions in the mass spectrum with the most abundant masses at *m/z* 516 and 518. This mass spectrum is consistent with the isotope ratios of two mercury atoms and two butyl groups, and gave the same fragmentation products as $(C_4H_9)_2Hg$.

The chromatogram was reproduced by recording specific masses to enhance sensitivity (Fig. 6). Although the two Hg species appear to co-elute, there is a difference in retention time, with the maximum signal of the mass corresponding to $(C_4H_9)_2Hg$ appearing moments earlier. A higher resolution was obtained using the column and temperature programme of the GC–MIP-AES instrument.

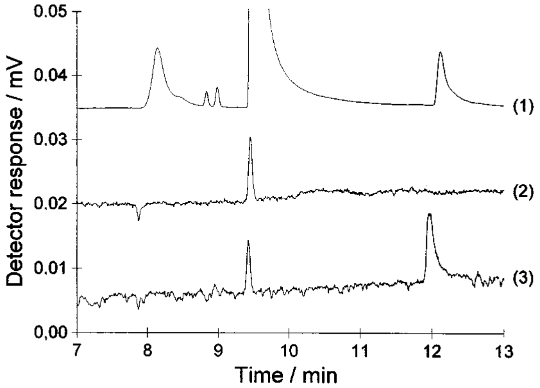

Fig. 4 GC–MIP-AES traces. Chromatograms given by derivatives of Hg_2Cl_2 colloid in 2,2,4-trimethylpentane (1) and a 229 μg l^{-1} Hg^0 + 200 μg l^{-1} $HgCl_2$ standard in heptane with samples taken before (2) and after (3) ultrasound treatment of the container. The chromatogram from the colloid is attenuated 10 ×.

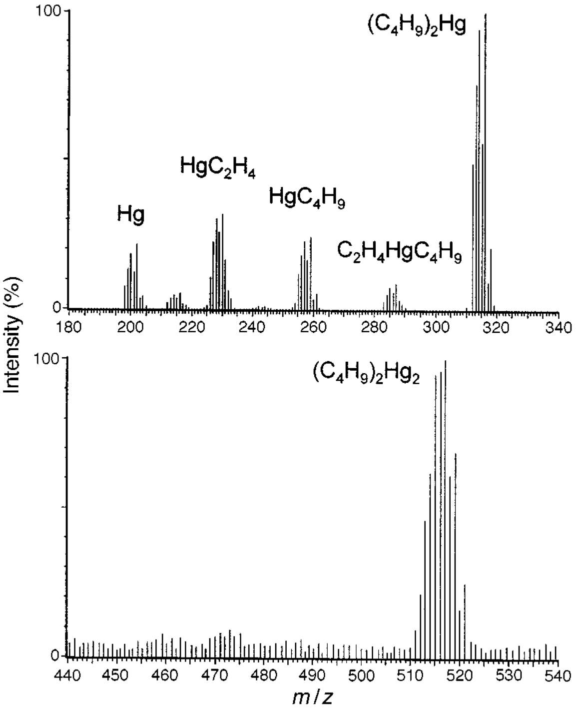

Fig. 5 Mass spectra of Hg_2Cl_2 and $HgCl_2$ derivatives. Mass range from *m/z* 350 to 600 is expanded 200 ×.

Discussion

Previously, a method for the determination of Hg species in organic solution was developed.[9] Grignard reagent is added to replace the polar ligands of a mercury species with butyl groups, to assist GC separation. Hg^0 does not react significantly with Grignard reagent under the conditions for derivatisation, and would not be determined by GC–MIP-AES. However, CH_3HgCl and $HgCl_2$ react rapidly with Grignard reagent to form the corresponding butyl derivatives.

It was found that standards containing only Hg^0 rapidly lost mercury, the total concentration being reduced to about half after 10 d (Fig. 2). The rate of loss of Hg^0 is greater than that of $HgCl_2$ from a comparable standard, *e.g.*, after storage in glass for 13 d, 34% of added Hg^0 and 80% of the $HgCl_2$ remain (Fig. 3).

As can be seen in Fig. 1, in the synthetic condensate standard used for long-term stability tests containing Hg^0 and $HgCl_2$, the $HgCl_2$ dissolved decreases to 23% of the original concentration over 7 months. In the corresponding standard without Hg^0, the concentration of $HgCl_2$ is considerably more stable, falling to 86%. This difference in the rate of species loss was also observed with the heptane standards in short-term experiments with solutions containing $HgCl_2$ alone or with an approximately equal concentration of Hg^0 (Fig. 3). The greatest rate of loss of $HgCl_2$ in a glass bottled standard, where only 11% was left after 13 d, was found in standards containing both species.

By using sample containers of different materials, which are expected to interact to different extents with the Hg species present, the rates of loss of both Hg^0 and $HgCl_2$ showed a large surface dependence (Fig. 3). With HDPE, 4% Hg^0 and 30% $HgCl_2$ remained after 13 d. However, when species were combined, losses of $HgCl_2$ were the largest, independent of the container material used.

It is clear that the most stable standard is that of $HgCl_2$ in glass, however, it should be noted that the exact rate of species loss from solution may also depend on the volume/surface area ratio, minor changes in the chemical composition and physical properties of the container material and possible impurities in the solvent.

Significant losses of Hg from organic solution can therefore occur by two pathways. There is no doubt that the container material can affect species loss. However, the highest rates of loss noted for $HgCl_2$ in the presence of Hg^0 are due to the formation of Hg_2Cl_2. This species is relatively insoluble in organic solvents and forms colloids that precipitate and adsorb on the container walls. This compound could be suspended in the solvent by ultrasound treatment of the container and detected after derivatisation by GC–MIP-AES.

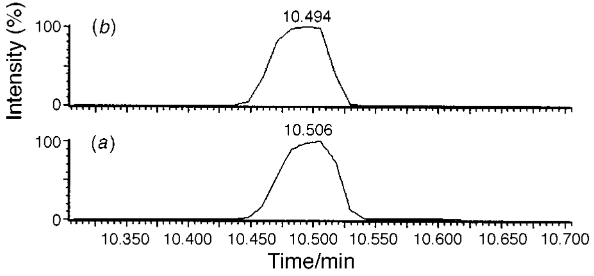

Fig. 6 Chromatograms of Hg_2Cl_2 and $HgCl_2$ derivatives obtained by GC–MS with selective ion monitoring at *m/z* (*a*) 202, (*b*) 316 and (*c*) 514.

In contrast to $HgCl_2$, CH_3HgCl is stable even in the presence of Hg^0. This may be explained by the predicted instability of methylated mercury(I) compounds compared with mercury(I) halides reported previously.[10,11]

From the GC–MIP-AES and GC–MS results, it is concluded that the Hg_2Cl_2 colloid reacts directly with Grignard reagent to form a compound not previously described, which has a different GC retention time to other mercury species. We postulate that the compound is $(C_4H_9)_2Hg_2$, as GC–MS shows a multiplet signal [Fig. 5 (bottom)] corresponding to the isotope ratios of two Hg atoms combined with two butyl groups. The molecule is presumably linear with an Hg–Hg bond at the centre. The fragmentation pattern of $(C_4H_9)_2Hg_2$ gave signals only at masses common to those from the fragmentation of $(C_4H_9)_2Hg$, which is expected as the Hg–Hg bond is of relatively low strength. This new compound appeared to be stable and precipitated virtually completely from solution when concentrated colloidal suspensions of Hg_2Cl_2 were derivatised.

Conclusions

Hg speciation analyses in hydrocarbon solutions may be hindered by the formation of $Hg_2{}^{2+}$ not available for specific determination because of its precipitation. As a consequence of the formation of $Hg_2{}^{2+}$, the concentration of Hg^0 and Hg^{2+} species will change with time when both are present. Therefore, the production of a stable pure hydrocarbon reference material, useful for comparative measurements, containing both Hg^0 and Hg^{2+} might only be possible after the addition of a reagent to inhibit reactions that lead to the formation of $Hg_2{}^{2+}$. Real condensate samples should be analysed as soon as possible after collection but may contain $Hg_2{}^{2+}$ precipitates, which could lead to the erroneous determination of total Hg. Ultrasonic treatment of the sample container prior to the determination of total Hg is likely to increase the recovery.

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