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Speciation analysis for mercury in gas condensates by capillary gas chromatography with inductively coupled plasma mass spectrometric detection

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Abstract

A method allowing species-selective determination of atomic mercury, non-polar dialkylated mercury compounds, polar monoalkylated species and inorganic mercury complexes in natural gas condensates was developed. Inductively coupled plasma mass spectrometry was employed as a detection method for capillary gas chromatography and compared with microwave induced plasma atomic emission detection for the analysis of hydrocarbon-rich matrices. The method was based on two consecutive injections allowing comprehensive speciation analysis. First a sample aliquot was diluted with toluene and analysed for Hg⁰ and individual dialkylmercury compounds. Then, another aliquot was butylated with a Grignard reagent for the species specific determination of Hg(II) and monoalkylated mercury species. The detection limits were down to 0.08 pg level.

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1. Introduction

The need to optimize the profitability of refining operations in petroleum industry has resulted in diversification of feedstock supply and in the increased use of natural gas condensates. The latter, however, contain mercury (10–3000 ng ml⁻¹) that is blamed for the poisoning of catalysts and corrosion of aluminum alloys in steam cracker cold boxes [1]. The prerequisite of risk assessment is the accurate measurement of the concentration of mercury, its distribution among the various distillation fractions (e.g., naphtha, kerosene, diesel oil and the residue) and

its distribution among various chemical forms. Whereas the boiling point distribution of mercury in crude petroleum and gas condensates is well known, the forms of mercury compounds present are uncertain [2]. Evidence is growing that mercury in gas condensates is present in a variety of physical and chemical species that feature different solubility, volatility, toxicity and chemical reactivity [2–4].

The determination of mercury speciation (distribution, according to the IUPAC definition, amongst defined chemical species in a system [5]) in feedstock supply and refinery products is essential to understand the mechanisms of the interaction of mercury with equipment, catalysts and mercury removal systems, to evaluate its hazards to maintenance workers, and to improve the technologies for

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the elimination of mercury from petroleum and its products.

The determination of mercury speciation in gas condensate (and in condensate fractions) is difficult because of the complexity of the condensate matrix, the similarity of its physicochemical properties to those of an important class of mercury compounds (dialkylmercury), and the reactivity of some species with each other and with matrix components leading to the poor stability of the system. Originally, mercury speciation in gas condensate was operationally defined and approached by sequential extractions followed by the determination of the total mercury in the subsequent fractions [3,6]. The poor selectivity of these methods and the impossibility of the unambiguous confirmation of the identity of species present is spurring the development of truly species selective methods based on the coupling of chromatography with mercury specific detection, as indicated in recent reviews [1,3,7].

A straightforward use of the most popular techniques for the total mercury determination, such as cold vapour atomic absorption (AAS) or fluorescence (AFS) spectrometry, as on-line gas chromatography (GC) detectors raises several problems. Not only has the post-column conversion of mercury to Hg^0 to be immediate, complete, and independent of the initial speciation, but also matrix components eluting from the column, even when efficiently combusted, may generate ghost peaks [8]. More success was reported with the microwave induced plasma (MIP) atomic emission spectrometry (AES) detection [9]. However, several problems such as plasma quenching and difficulties with efficient background correction in view of the continually changing amount of hydrocarbons leaving the GC column required post-column purification of the mercury compounds of interest prior to detection [9].

Many of the above problems can be eliminated by the use of a more robust plasma, such as an inductively coupled plasma (ICP) and detection of mercury atomic ions. ICP mass spectrometry (MS) is rapidly gaining popularity as an element specific detector in GC [10], especially since the availability of a commercial interface [11]. Its major advantages, such as high tolerance to complex matrices and the low-femtogram-level detection limits, are of particular value in petrochemical analysis including

determination of metalloporphyrins in shale [12,13], speciation of organolead in fuel [14] or speciation of mercury and arsenic [15,16].

Speciation of mercury in gas condensates poses several problems on the level of chromatography. Non-polar columns allow sharp peaks to be obtained for Hg^0 and dialkylmercury, but not for other species such as monoalkylmercury and Hg(II) , the latter being apparently the most abundant species in gas condensates [16]. The use of polar columns required the pre-treatment with HBr and chromatographing of HgBr_2 with a loss of factor 10 in terms of detection limits. This research aims at the development of a method for comprehensive and sensitive mercury speciation in gas condensates. For this purpose an approach based on the consecutive injection of non-derivatized (for Hg^0 and dialkylmercury species) and derivatized gas condensate sample (for polar mercury species) was optimized.

2. Experimental

2.1. Apparatus

GC–MIP–AES experiments were carried out with a HP Model 6890 gas chromatograph (Hewlett-Packard, Wilmington, DE, USA) equipped with a HP Model G2350A atomic emission detector. Injection were made by means of a HP 6890 series automatic sampler. Data were handled using a HP Model D3398A ChemStation.

The GC–ICP–MS setup consisted of a HP Model 5890 Series II Plus gas chromatograph (Agilent, Wilmington, DE, USA) equipped with a split–splitless injection port with electronic pressure control and an ICP–MS instrument—HP Model 4500 Plus ICP–MS system (Agilent, Japan). Injections were made in the splitless mode, using a HP 6890 series automatic sampler. The chromatographic data were handled using specific software (Agilent) developed for the ICP system. The GC–ICP–MS interface was described in detail elsewhere [17]. In brief, a deactivated fused-silica 1.5 m×0.32 mm I.D. capillary tube was threaded through a 1-m flexible heated transfer line and further through a 10-cm rigid

transfer line up to the end of the central channel of the ICP-MS torch. The transfer line was efficiently heated up to 250 °C on the full length. The makeup argon gas was supplemented with xenon by adding the latter as a 100 µg ml⁻¹ solution in argon gas at 5 ml min⁻¹ (Air Liquide, France). The makeup gas was preheated by passing through a 1-m 1/16 in. coil inside the chromatographic oven (1 in.=2.54 cm).

2.2. Standards

Metallic mercury (Hg⁰), dimethylmercury (Me₂Hg) and Grignard reagents (MeMgCl, PrMgCl and BuMgCl) were purchased from Strem (Bisschein, France) Mercury(II) chloride (HgCl₂) and methylmercury chloride (MeHgCl) were obtained from Sigma–Aldrich (Saint Quentin Fallavier, France). Stock solutions of HgCl₂, MeHgCl and Et₂Hg (1000 µg ml⁻¹) were prepared in toluene. A 10 µg ml⁻¹ dilution was obtained daily. Further dilutions were performed just before an analysis.

Retention time standards of Me₂Hg, MeEtHg, MePrHg, and MeBuHg were prepared by Grignard methylation, ethylation, propylation and butylation of MeHgCl, respectively. Standards of Pr₂Hg and Bu₂Hg were obtained by Grignard propylation and butylation of HgCl₂, respectively. The Grignard reaction was carried out by mixing 2 ml of 500 ng ml⁻¹ solution of MeHgCl or HgCl₂ with 200 µl of a relevant Grignard reagent. After occasional shaking 10% of 0.5 M H₂SO₄ was added, the transparent organic phase was recovered, dried over anhydrous Na₂SO₄ and used as a retention time standard. The standards were prepared on the day of use.

Stock standard solutions of elemental mercury in hexane, isooctane and toluene were prepared by shaking a drop of mercury (ca. 0.3–0.5 g) in 10 ml of the corresponding solvent in a sealed glass vial for 2 days. The exact concentrations of the standard solutions were determined by high-resolution ICP-MS in standard conditions. The concentrations of Hg⁰ in the saturated solutions in hexane, isooctane and toluene were 2.1, 2.7 and 9.7 µg g⁻¹, respectively. The dilutions were carried out with the relevant solvent as required.

The standards were stored in glass vials at 4 °C.

Table 1

Average composition of the gas condensate samples analyzed (mass fraction according to the boiling point)

% of Mass	Temperature (°C)
Initial point	80
0–10	190
10–20	256
20–30	295
30–40	325
40–50	361
50–60	400
60–70	440
70–80	492
80–90	563
90–100	660

2.3. Samples

Gas condensates having the average composition shown in Table 1 came from Thailand. Some of gas condensates analysed contained notable amounts of suspended solids that might either be mercury compounds or contain adsorbed mercury compounds. The analysis of condensates with suspended solids is difficult because the inhomogeneous distribution in the sampled solution, blocking the nebulizer (in the case of ICP-MS analysis), or of the injection syringe, and accumulation in the GC injection liner (in the case of GC–ICP-MS analyses). The amount of suspended mercury was evaluated by filtration using an 0.8 µm filter. Alternatively, the particulate matter was removed by ultracentrifugation.

2.4. Glassware

Glassware was cleaned first with acetone, then with a common detergent (RBS) for 30 min, thoroughly rinsed with water and soaked for 24 h in 10% HNO₃ solution. Finally, glassware was rinsed with water and dried.

2.5. Analytical procedure

ICP-MS conditions were optimized daily using the continual signal of the ¹²⁶Xe isotope. This signal served (1) to tune the MS spectrometer, (2) to adjust the position of the transfer line (fused-silica capillary) in the torch, and (3) to optimize ICP operating parameters such as the xyz position, radiofrequency

(RF) power, RF matching voltage, lens voltages, and auxiliary, plasma and carrier gas flow-rates. These parameters were optimized daily with the objective to reach the maximum sensitivity for the ^{126}Xe isotope. Dwell time was optimized, for each group of organometallic compounds, in a way that intensity data for at least 10 points could be acquired for the narrowest peak in the chromatogram. Oxygen was added to the auxiliary argon gas at 12 ml min^{-1} in order to minimize the carbon deposition (due to the organic solvent injected on the chromatographic column) on the ICP cones.

GC–ICP–MS conditions are summarized in Table 2. Gas condensate samples were analysed within less than 1 week after receipt. An aliquot of 1 ml of gas condensate sample was weighed and diluted with toluene 1:4 or 1:9. A 1-ml aliquot of the diluted solution was placed in an autosampler vial and analysed by GC–ICP–MS. Another aliquot (2 ml) was placed in a 20-ml glass vial and mixed with 200 μl of 2 M butylmagnesium chloride in tetrahydrofuran. After occasional shaking for 5 min to complete the butylation, a 10-ml volume of 0.5 M sulfuric acid was added to destroy the excess of the Grignard reagent. After vigorous shaking, the phases were separated by centrifugation and the organic supernatant was placed in an autosampler vial and analysed by GC–ICP–MS under the conditions summarized in Table 1. For the total mercury determi-

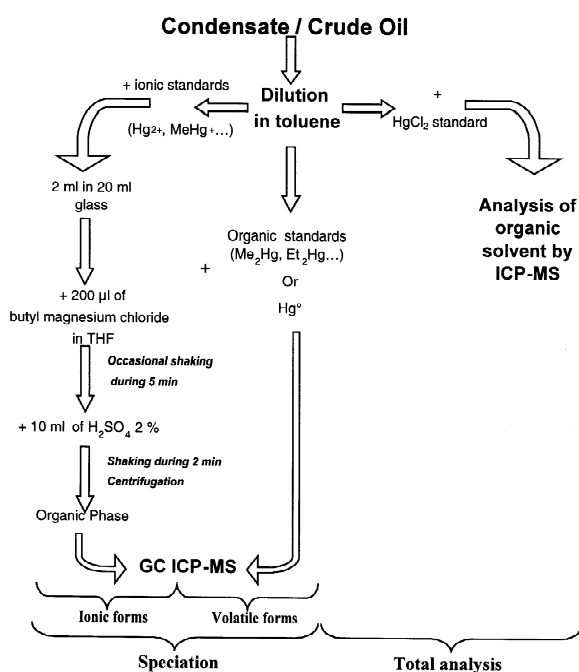


Fig. 1. Principle of the analytical method for the characterization of the Hg speciation in gas condensates.

nation an aliquot of condensate was diluted with 2-propanol and analysed by high-resolution ICP–MS. The principle of the analytical method is shown in Fig. 1.

Table 2
GC–ICP–MS operating conditions

Chromatographic column	HP-5 (30 m×0.32 mm, 0.25 μm)
Injection	Splitless, purge time 1 min
Injection temperature	150 °C
Injection volume	1 μl
Carrier gas (flow-rate)	Helium (2 ml min $^{-1}$)
Oven temperature programme	60 °C (1 min) to 280 °C at 50 °C min $^{-1}$
Transferline temperature	250 °C
ICP–MS detection conditions	
ICP–MS	Agilent 7500
Plasma gas (flow-rate)	Argon at 15 l min $^{-1}$
Auxiliary gas	1% (v/v) O $_2$ in Ar (1 l min $^{-1}$)
Makeup gas	Xe (1000 $\mu\text{g ml}^{-1}$ in Ar) 5 ml min $^{-1}$ in Ar 0.75 l min $^{-1}$
Isotopes monitored	^{199}Hg , ^{200}Hg , ^{202}Hg , ^{126}Xe
Forward power	1250 W
Sampling depth	6 cm

3. Results and discussion

3.1. GC–ICP–MS of organomercury species

The separation of Hg^0 and dialkylmercury species is shown in Fig. 2. The peaks are symmetrical except Hg^0 that slightly tails and dimethylmercury that gives a broader peak. The tailing of the Hg^0 peak may be explained by the high reactivity of Hg^0 and formation of amalgam with the stainless steel needle of the syringe [16]. Regarding Me_2Hg a similar tailing was attributed to the column overloading by the solvent. It seems unlikely since similar shape was

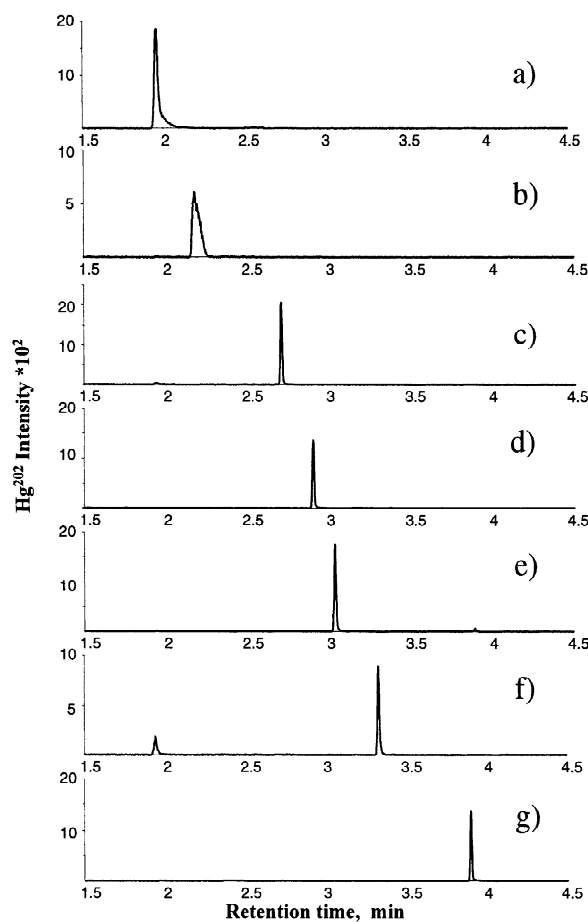


Fig. 2. GC–ICP–MS chromatograms of Hg^0 and organomercury standards. (a) Hg^0 , (b) Me_2Hg , (c) MePrHg , (d) Et_2Hg , (e) MeBuHg , (f) Pr_2Hg , (g) Bu_2Hg . Ca. 50 μg each.

observed regardless of the solvent (hexane, iso-octane, toluene) and was not affected by reducing the initial temperature of the oven.

The retention times (t_R) of the standards injected are linearly correlated with the boiling points (b.p.s) of the dialkylmercury compounds by the equation $\text{b.p.} = 68t_R - 49$ ($r^2 = 0.96$) and with the numbers of carbon atoms (n_C) by the equation $n_C = 3.5t_R - 5.7$ ($r^2 = 0.99$). These correlations prove, on one hand, that the synthesis of the retention time standards lead to the expected compounds and, on the other hand, allow the identification of unknown mercury species if detected in the chromatograms of real samples.

3.2. Effect of the gas condensate matrix in GC–MIP–AES

The analysis of undiluted gas condensate samples is impossible with the MIP atomic emission detector available. Indeed, when the Hg -254 line is monitored the noise of the baseline does not allow the recognition of mercury peaks, the discharge tube becomes rapidly dirty despite the addition of oxygen and for most of condensate samples the plasma is extinguished.

The choice of the solvent for the dilution in GC–MIP–AES is critical because it needs to be vented off the plasma prior to elution of the first analyte. Hexane was chosen because of its low boiling temperature and the possibility to be separated prior to elution of MeEtHg (and higher boiling compounds). Note that Me_2Hg cannot be separated from the solvent regardless of the latter and is co-vented off the plasma. The same applies to Hg^0 that is apparently not retained by the column.

Even when a sample is diluted 1:9, organic components affect the plasma stability and produce strong negative peaks (Fig. 3a). A spike of Bu_2Hg (Fig. 3b) indicated detection limits higher than 20 ng ml^{-1} that is by far too high for any practical significance of the method.

This type of problem was also identified by Snell et al. [9] and solved for Me_2Hg by diverting the corresponding fraction of the GC effluent to an amalgamation trap to remove the carbon interference followed by the determination of mercury released from the trap. Our investigations focused on the

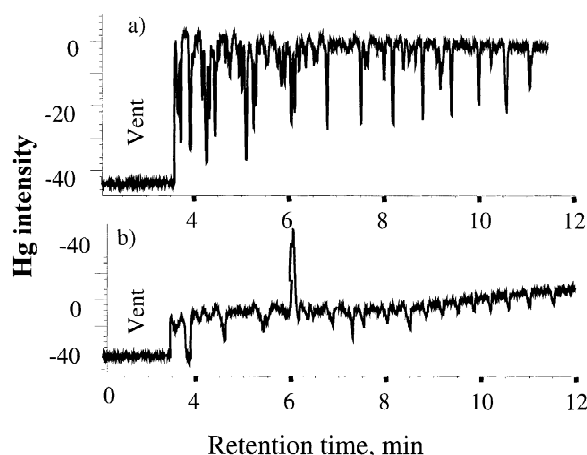


Fig. 3. Effect of the gas condensate matrix in GC–MIP–AES analysis. (a) Blank (mercury-free condensate); (b) blank condensate spiked with 100 ng ml^{-1} of Bu_2Hg .

replacing of MIP–AES by ICP–MS featuring a more robust plasma and lower detection limits.

3.3. Effect of the gas condensate matrix in GC–ICP–MS

The higher power of ICP–MS allows the injection of a gas condensate sample without extinguishing the plasma. Fig. 4 shows the baseline on the mercury channel when different solvents are injected. As can be seen the baseline is stable except a dip corresponding to the elution of the sample dilution solvent. The latter may be indispensable in some cases to lower the viscosity of some condensates, or to avoid the contamination of the injector and of the column.

The dilution solvent should be chosen in a way that no compound of interest be eluted at the time the solvent band reaches the plasma. The width of the dip can be reduced (but not eliminated) by the addition of oxygen to the plasma, the latter also preventing the deposition of carbon on the cones.

Of the solvents investigated only the elution of toluene did not overlap with any of the standards investigated.

3.4. Quantification of dialkylmercury compounds

Table 3 shows calibration curves in the range of

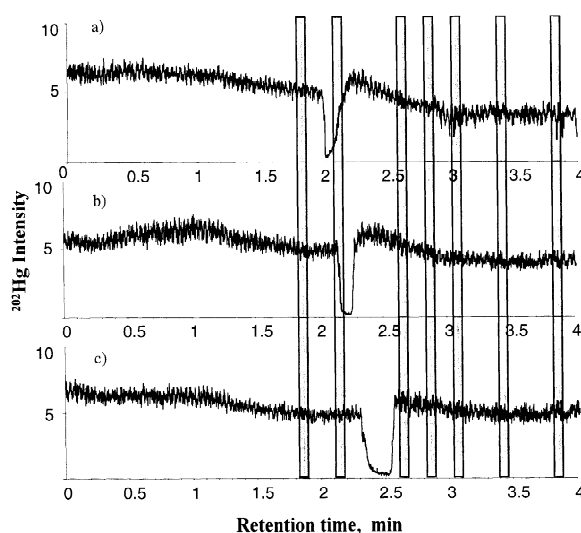


Fig. 4. Effect of the dilution solvent on the plasma stability in GC–ICP–MS. (a) Hexane, (b) isooctane, (c) toluene. The position of the eluted Hg^0 and dialkylmercury standards was shaded in the chromatograms (cf. Fig. 2 for the elution order).

$0.1\text{--}50 \text{ ng ml}^{-1}$. As can be seen that the curves can be considered as linear. The slopes vary depending on the compound and the organic matrix analysed. The slopes are similar for Me_2Hg , MeBuHg and Bu_2Hg and twice as low as in the case of Et_2Hg . The reason may be the loss of mercury during the derivatization reaction (and ca. 50%) recovery. In order to compensate for possibly low recoveries for ionic organomercury species the method of standard additions should be used for their quantification.

A noteworthy effect is the dependence of the slope of the calibration curve on the composition of the injected organic solution. For instance, the intensity of the Et_2Hg peak is 30% higher in toluene than in isooctane or hexane. Also, when a condensate sample is diluted, the effect of toluene to enhance the response factor for Et_2Hg is clearly seen. Me_2Hg gives the highest response in hexane.

The origin of these variations in intensity is the changing amount of carbon arriving at the plasma modifying the ionization conditions. The power of plasma decreases with the arrival of carbon because of the very high ionization potential of the latter (11.26 eV). On the other hand the carbon rich plasma may improve the ionization of mercury. This can explain the different response factors as a function of

Table 3
Effect of the organic matrix on the slope and linearity of the calibration curve for the different dialkylmercury compounds

	Me ₂ Hg		Et ₂ Hg		MeBuHg		Bu ₂ Hg	
	Slope	R ²	Slope	R ²	Slope	R ²	Slope	R ²
Hexane	93.2±2.2	0.996	153.9±1.9	0.999	87.9±1.9	0.996	69.5±1.1	0.998
Isooctane	76.6±3.2	0.987	156.9±2.1	0.998	83.8±2.1	0.995	67.3±2.1	0.995
Toluene	81.2±5.7	0.960	205.8±7.2	0.992	74.2±1.4	0.997	67.2±1.5	0.996
Condensate diluted* 1:1	82.9±1.3	0.998	149.3±2.7	0.998	72.3±1.9	0.994	61.0±0.1	0.999
Condensate diluted* 1:9	84.5±2.3	0.995	159.9±5.7	0.990	72.2±0.9	0.999	63.8±0.7	0.999
Condensate diluted* 1:99	84.9±6.0	0.960	190.6±10.6	0.980	73.0±1.8	0.995	66.6±1.3	0.997

*Toluene was used for the dilution.

an actual concentration of carbon in the plasma at a given moment.

Indeed, the smallest difference is observed for Bu₂Hg that is the highest boiling mercury species investigated and elutes long after the solvent band or most of hydrocarbons from a gas condensate samples have passed. Not also that a reason for the highest Me₂Hg response in hexane may be the solvent effect. Indeed in the case of other solvents Me₂Hg elutes before and not after the solvent peak.

The practical conclusion is the need for the use of the method of standard additions for the accurate quantification of alkylmercury species in gas condensate samples.

Based on the Et₂Hg the detection limit is in the range 81–112 fg depending on the solvent.

3.5. Quantification of atomic mercury (Hg⁰)

Gas chromatography offers the possibility of the separation of Hg⁰ that is not retained on the column. Calibration curves are linear but their slope depends on the solvent for the same nominal amount of mercury (Table 4). The highest response factor is obtained for mercury dissolved in isooctane. The response factors for hexane and toluene solutions are twice lower. The detection limit for the determi-

Table 4
Effect of the organic solvent on the slope of the GC–ICP–MS calibration curve for Hg⁰

	Slope	R ²
Hexane	135.3±3.1	0.997
Isooctane	196.0±4.6	0.996
Toluene	116.4±2.4	0.997

nation of Hg⁰ in gas condensate by GC–ICP–MS is 150 fg.

3.6. Optimisation of the derivatization conditions

The Grignard derivatization has been found a convenient method for the conversion of ionic or partly alkylated mercury species into dialkylated compounds [8,18,19]. In this work the preference was given to butyl magnesium chloride (BuMgCl) because, on one hand, the probability for the natural occurrence of butyl derivatives of mercury is smaller than that of methyl, ethyl or propyl, and, on the other hand, butyl derivatives are less volatile and elute from the GC column after the bulk of the hydrocarbons (cf. Fig. 2a). The optimisation of the butylation reaction included the verification that no conversion of the already present Hg⁰ and dialkylmercury will not react with the Grignard reagent and that the derivatization yield will be reproducible.

Table 5 shows results of the derivatization reaction carried out on dialkylmercury species spiked on a toluene solution. It can be seen that the peak intensity is not affected. Neither the formation of any other mercury species was observed. The derivatiza-

Table 5
Effect of the derivatization with butylmagnesium chloride on stability of dialkylmercury species in organic solution

	Concentration (ng ml ⁻¹)	
	Before derivation	After derivation
Me ₂ Hg	20	20.7±1.2
MePrHg	25	25.5±0.9
Et ₂ Hg	172	173.3±12.6
MeBuHg	25	27.1±5.4
Pr ₂ Hg	25	25.1±0.5

Table 6
Effect of the derivatization with butylmagnesium chloride on the stability of Hg⁰ solution in toluene

	Concentration (ng ml ⁻¹)				
	0	50	100	150	200
Initial Hg ⁰ concentration	0	50	100	150	200
Hg ⁰ concentration after derivatization	0	23.8±0.6	49.1±1.3	84.2±2.2	97.9±2.6
Hg ²⁺ concentration after derivatization	0	1.2±0.1	1.6±0.1	2.6±0.1	4.4±0.1
% of the Hg ⁰ derivatization	–	2.2	1.6	1.7	2.2

tion of an Hg⁰ standard, spiked on the toluene matrix is shown in Table 6. It shows that a small amount of Bu₂Hg is produced from Hg⁰ that corresponds to ca. 1–2% of Hg⁰ undergoing butylation. A correction for this amount may be needed if a sample contains a significant amount of Hg⁰. Also, Hg⁰ is lost, possibly by evaporation during the derivatization. This phenomenon does not affect the analytical result because Hg⁰ is determined from a sample aliquot that is not derivatized.

3.7. Speciation of mercury in gas condensates

The detection limits of the method developed are summarised in Table 7.

Fig. 5 shows typical gas chromatograms obtained during the analysis of gas condensates. The direct injection of the condensate allows the determination of Hg⁰ and dialkylmercury species (if present). The simultaneous monitoring of the ¹²⁶Xe isotope allows the detection of the plasma instability due to the elution of the solvent band. For sensitivity variation correction as well as for matrix-induced variation correction an internal standard is necessary. In order to be effective the latter should have the same retention time as the analyte species which makes the

Table 7
Detection limits of the method developed

Species	Detection limit, µg l ⁻¹ (1 µl injected)
Hg ⁰	0.98
Me ₂ Hg	1.32
MePrHg	0.16
Et ₂ Hg	0.08
MeBuHg	0.14
Pr ₂ Hg	0.20
Bu ₂ Hg	0.11

use of stable isotope enriched mercury species for this purpose recommended.

The derivatization of the gas condensate (Fig. 5b) leads to the occurrence of a Bu₂Hg peak proportional to the amount of Hg(II). The zoom shows that the initial part of the chromatogram is unaffected (except some loss of intensity of the Hg⁰ peak, discussed above). The problem of reagent blank is negligible. The derivatization of pure solvents and mercury free gas condensates did not lead to detectable peaks.

Table 8 shows the results of the gas condensate analyses. Metallic mercury and non covalently bound Hg(II) are the only species detected and account for over 90% of mercury.

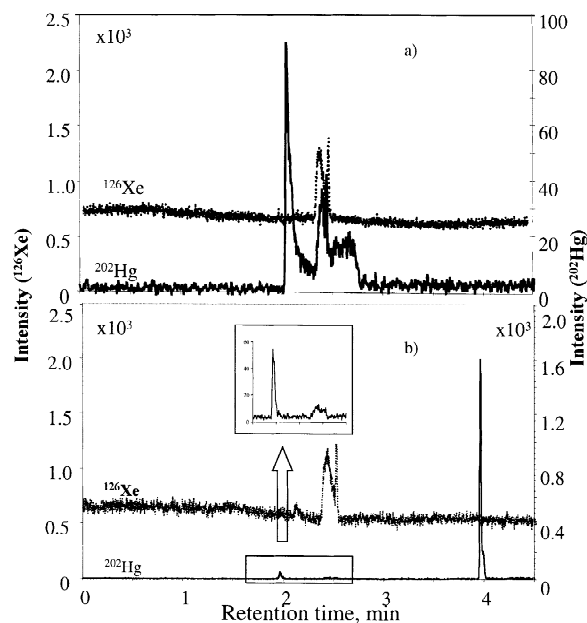


Fig. 5. Speciation of mercury in a gas condensate. (a) Underivatized condensate sample: ²⁰²Hg and ¹²⁶Xe chromatograms. (b) Condensate sample derivatized by butylation with BuMgCl: ²⁰²Hg and ¹²⁶Xe chromatograms.

Table 8
Results for the determination of mercury species in gas condensate

Condensate	Concentration (ng ml ⁻¹)		
	Hg ²⁺	Hg ⁰	Total
1	681.7±14.5	71.4±16.6	600
2	13.2±3.1	2.8±1.4	15
3	408.6±1.4	13.5±4.8	500
4	651.2±26.4	299.5±26.4	950
5	75.4±7	29.7±13.1	146
6	280.1±20.7	40.7±6.1	370
7	255.6±14.2	22.9±3.4	370
8	871±6.7	100.4±18.7	950
9	10.3	<D.L.	13
10	5.7	<D.L.	9

4. Conclusions

ICP-MS appears to be the detection method of choice for the gas chromatographic analysis of complex hydrocarbon matrices for metal species. The complexity of the mercury speciation favours a dual approach in which non polar species are detected followed the direct injection of a gas condensate sample on a gas chromatographic column whereas polar ones are detected in parallel in a Grignard derivatized sample aliquot. Hg⁰ and Hg(II) are the major mercury species detected accounting for over 90% of mercury in gas condensates. It is therefore likely that dialkylmercury detected in natural gas are unstable during the condensation processes and are converted to Hg²⁺.

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