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Analytical Methods for Speciation of Mercury in Gas Condensates

Critical Assessment and Recommendations

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Résumé — Méthodes analytiques pour la spéciation du mercure dans les condensats de gaz : évaluation critique et conseils — La présence de multiples formes du mercure dans les condensats de gaz peut poser de graves problèmes de corrosion d'installations ou d'empoisonnement de catalyseurs. Afin de comprendre et d'optimiser le procédé de démercuration, il est nécessaire de connaître la concentration des différentes espèces présentes. Cet article de synthèse sur les méthodes analytiques de spéciation du mercure dans les condensats de gaz présente les avantages et les inconvénients de ces méthodes. Une attention particulière est donnée à la chromatographie en phase gazeuse couplée à une détection spécifique, présentée ici comme la meilleure technique pour l'analyse du mercure en spéciation dans des échantillons organiques. Cet article abordera les problèmes liés à la justesse des données disponibles, à la stabilité des composés du mercure dans les solutions organiques, ainsi qu'à la formation possible d'artefacts et à l'inexistence de matériel de référence.

Mots-clés : mercure, condensats de gaz, spéciation, chromatographie en phase gazeuse.

Abstract — Analytical Methods for Speciation of Mercury in Gas Condensates: Critical Assessment and Recommendations — The wide range of mercury species present in gas condensates can cause major problems such as corrosion of installations and reduced catalyst life. The understanding of speciation of this element is required to predict and improve the efficiency of mercury removal technologies. This review paper presents the state-of-the-art of the analytical methods available for the analysis of mercury speciation in gas condensates, highlighting the advantages and drawbacks. Particular attention is given to gas chromatography with mercury specific detection as the most promising tool for mercury speciation analysis in hydrocarbon-rich samples. Questions regarding accuracy of the data available are raised in view of the limited stability of mercury species in organic solutions, possibility of artefacts formation and unavailability of reference materials.

Keywords: mercury, gas condensates, speciation, gas chromatography.

INTRODUCTION

The diversification of the feedstock supply in the petroleum industry resulting from the need to optimize the profitability of refining and of petrochemical operations has resulted in a serious increase in catalyst poisoning cases and operating problems such as corrosion of aluminium alloys in steam cracker cold boxes (Sarrazin *et al.*, 1993). The origin of these problems was identified as due to the presence of mercury in gas condensates. Therefore its removal from natural gas liquid condensates is important to reduce the risk factor of corrosion and due to environmental concerns about mercury.

Two ways are envisageable to resolve the problem of mercury: erection of guard beds downstream the steam cracker which resolves partially the problems as part of these impurities are trapped in the steam cracker equipment. While installing guard beds protecting the cold box could appear as a cheaper solution than pre-treatment, it would solve only a small part of all the problems associated with natural gas condensates.

The other solution is an upstream treatment: as mercury tends to distribute throughout all the major cuts in an olefin unit, the best or preferred location for mercury removal in olefin plants is the feedstock before it enters the plant. This upstream treatment leads to a higher investment but resolves definitely the contamination. Several companies have chosen to propose the pre-treatment solution among which *IFP* which is able to propose an industrially proven solution which eliminates all the risk associated with steam-cracker effluents pollution for different types of feedstocks including unclear feedstocks: the *Ram* (removal arsenic mercury) process (Sarrazin *et al.*, 1993; Didillon *et al.*, 2000).

Mercury in gas condensates occurs in a very wide concentration range (10-3000 ppb) (Sarrazin *et al.*, 1993). The prerequisite of risk assessment is the accurate measurement of its concentration, 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 distribution of mercury in crude petroleum and gas condensates is well known, the forms of mercury compounds present are uncertain (Wilhelm and Bloom, 2000). 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 (Wilhelm and Bloom, 2000; Frech *et al.*, 1996).

The determination of mercury speciation (distribution, according to the IUPAC definition (Templeton *et al.*, 2000), amongst defined chemical species in a system in feedstock supply and refinery products is essential to understand the mechanisms of the interaction of mercury with equipment, catalysts and mercury removal systems, and to evaluate the potential hazards to maintenance workers. This should allow the prevention of the above mentioned technical problems and

allow a better optimization of the elimination of mercury from petroleum and its products.

The determination of mercury speciation in gas condensates (and in condensate fractions) is difficult because of the wide range of boiling points (b.p.) exhibited by the different species that may be present, the complexity of the condensate matrix and the similarity of its physicochemical properties to those of an important class of mercury compounds (dialkyl mercury), and the reactivity of some species with each other and with matrix components, the latter leading to the poor stability of the system.

Originally, mercury speciation in gas condensates was operationally defined and approached by sequential extractions followed by the determination of the total mercury in the subsequent fractions (Frech *et al.*, 1996; Furuta *et al.*, 1990). 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 (Snell *et al.*, 1996; Tao *et al.*, 1998; Shafawi *et al.*, 1999a; Bouyssiére *et al.*, 2000).

The objective of this review is to evaluate critically the state-of-the-art of analytical procedures available for speciation analysis of mercury in gas condensates with a highlight on hyphenated techniques.

1 OCCURRENCE AND CHEMISTRY OF MERCURY COMPOUNDS IN GAS CONDENSATE SAMPLES

In contrast to natural gas that contains principally mercury in metallic form (Hg°), a variety of mercury species can be encountered in gas condensates. The presence and proportions of these species are highly dependent upon the source, the stage of production, the sampling technique used, storage of the sample and age of the sample. Most frequently, classifications are made on the basis of physical (particulate bound and dissolved mercury), or chemical (inorganic and organic mercury) properties. The majority of Hg in gas condensates seems to be associated with the particulate fraction (Bloom, 2000). Most of dissolved mercury (> 60%) is contained in the naphtha fractions (36°-170°C) (Sarrazin *et al.*, 1993).

Inorganic mercury may be present in condensates in metallic (elemental, Hg°) or oxidized forms. The latter may be insoluble or dispersed as colloid (HgS , Hg_2Cl_2) or soluble (*e.g.* HgCl_2). Organic compounds contain mercury at the +2 oxidation state. They include organometallic compounds (with a Hg-C covalent bond) which can be fully alkylated (dialkyl mercury species) or partly alkylated (monoalkyl mercury species), and coordination complexes in which Hg^{2+} is coordinated by organic ligands, *e.g.* tetraphenylporphyrin.

Elemental mercury (Hg°) has a boiling point of 357°C and is soluble to a certain degree in organic solvents. Saturated solutions of hexane, heptane, octane, dodecane and paraffin oil contain 1.23, 1.15, 1.59 and $4.2 \mu\text{g g}^{-1}$ of mercury at ambient temperature, the figures varying as a function of temperature. Elemental mercury readily adsorbs on metallic surfaces (container wall) and solid suspended particles and may diffuse through polyethylene. Hg° is known to oxidize in hydrocarbon samples exposed to air and to react with Hg (II) compounds to produce the insoluble Hg_2Cl_2 . Owing to the high volatility and the low solubility, the elemental mercury may occur in gas condensates in the range of 10% or less of the total Hg .

The soluble inorganic, oxidized mercury is usually referred to as HgCl_2 (b.p. 276°C) which is an order of magnitude more soluble than Hg° in gas condensates. It partitions to saturated aqueous solutions of alkali metal salts such as NaCl or KCl . Since hydroxy-, oxychloride and weak Hg (II) complexes with other ligands will partition as well, the attribution of all the soluble mercury to HgCl_2 is rather speculative. Tao *et al.* (1998) observed by GC-ICP MS (gas chromatography-inductively coupled plasma mass spectrometry) of a gas condensates sample a broad peak at the retention time corresponding to HgCl_2 .

The insoluble mercury occurs mostly as HgS , which sublimates at 584°C and forms a colloidal suspension in gas condensates. Particulate Hg was found to reside in a relatively narrow particle size range, 1-10 μm and can be readily removed by filtration. The particulate fraction may also contain Hg_2Cl_2 (melting point m.p. 400°C) produced by reaction of Hg° and Hg (II) in the condensates during storage.

Dialkyl mercury compounds include a range of species with different boiling points: Me_2Hg 96°C , Et_2Hg 159°C , $i\text{Pr}_2\text{Hg}$ 170°C , Pr_2Hg 190°C , and Bu_2Hg 206°C (Sarrazin *et al.*, 1993). Mixed alkyl species, such as *e.g.* MeEtHg exist, but their physicochemical properties are poorly known. The highest boiling point species potentially present seems to be Ph_2Hg (m.p. 121°C). Despite their volatility, dialkyl mercury compounds are unlikely to be stripped by inert gases from the condensate sample because of their virtual miscibility with the condensate sample.

Because of the similar physicochemical properties of the above species gas chromatography (GC) needs imperatively to be used to achieve their separation. Operationally defined procedures will produce information only on total dialkyl mercury. It is interesting to note that the published concentrations of dialkyl mercury obtained by non-species specific procedures are typically higher than those obtained by GC with mercury specific detection.

Some organomercury species can be polar and partition to saturated alkali metal salt solutions, especially in the presence of a complexing agent, such as, *e.g.* cysteine. MeHgCl (b.p. 170°C) is the most widely referred to of these species but, again, unambiguous evidence of its occurrence

by GC techniques is relatively scarce. Sub-ng traces of monomethyl mercury were observed (Bloom, 2000). The presence of polar species (organomercury halide and inorganic) salts is associated with the presence of water (moisture) or with particulate matter (which is capable of adsorbing mercury species). Dialkyl species can be converted to monoalkyl chlorides by reaction with conc. HCl .

Very little is known on mercury coordination complexes in which an Hg atom would be coordinated by sulfur or nitrogen ligands. Organic sulfide, thiol, thiophene or mercaptan species have been postulated to exist but no evidence of their presence has yet been produced (Wilhelm and Bloom, 2000). Another category of coordination complexes is porphyrin complexes which were found in crude petroleum and shale oils (Ebdon *et al.*, 1994). Furuta *et al.* (1990) found that the mercury complex with tetraphenylporphyrin behaved like inorganic dissolved mercury when condensate sample was equilibrated with an aqueous solution of NaCl , *i.e.* it partitioned to the aqueous phase due to the replacement of the porphyrin ligand by chloride.

2 OPERATIONALLY DEFINED DETERMINATION OF SPECIATION OF MERCURY COMPOUNDS

To our knowledge, the first procedure for mercury speciation in gas condensates was developed by Furuta *et al.* (1990). It was based on sequential extraction. First, Hg° was separated from a sample by purging it with helium; under the purge conditions neither mono- nor dimethyl mercury was extracted into gas phase. Then, ionic Hg (II), MeHgCl , and Hg -porphyrin complexes were extracted into an NaCl (or cysteine) solution. Upon acidification with HCl , MeHgCl was reextracted into benzene. The remaining mercury was considered to be dialkyl mercury.

An operationally defined extraction protocol for the qualitative detection of mercury species in gas condensates was proposed by Frech *et al.* (1996). In this procedure total inorganic mercury (referred to as the sum of Hg^{2+} and Hg°) was converted by Grignard reaction to Bu_2Hg . Note that in another work (Snell *et al.*, 1998) the same authors observed that Hg° did not react with the Grignard reagent and underwent butylation. Ionic Hg (Hg^{2+}) was extracted from gas condensates into an equal volume of water. Extraction with a cysteine solution allowed the extraction of the sum Hg° , Hg^{2+} and monoalkyl mercury. The mercury remaining in the condensates after extraction with cysteine solution was considered to be dialkyl mercury.

Another comprehensive procedure for the analysis of operationally defined speciation of mercury in gas condensates was developed by Bloom (2000). The procedure provides independent data on:

- total mercury (SnCl_2 reducible Hg present in a condensate sample upon oxidation of the latter with BrCl solution);

- total dissolved mercury (vacuum filtered through a 0.8 μm filter);
- ionic and weakly complexed Hg (II) (extractable with saturated KCl solution from 0.8 μm filtered samples);
- total volatile Hg (purgable and adsorbable on a gold-coated sand trap);
- monomethyl mercury (determined in the third fraction by GC-CF AFS—gas chromatography-cryofocusing absorption fluorescence spectroscopy—after ethylation with NaBEt_4) (Bloom, 1989).

Operationally defined speciation procedures suffer from a risk of inaccuracies because large quantities of one species could give rise to a false positive signal for another. This problem was found to be particularly acute in samples containing high levels of Hg° . Also, in some cases several species are determined as one. Finally, no unambiguous identification of the species extracted is available. Therefore, molecule specific protocols employing chromatography with mercury specific detection have been employed.

3 DETERMINATION OF MERCURY SPECIATION IN GAS CONDENSATES BY GC WITH ELEMENT SPECIFIC DETECTION

The volatility and reasonable thermal stability of mercury compounds, both inorganic and organic, make GC the preferred separation technique. GC features the advantage of the ease of coupling with mercury specific and extremely sensitive (sub-pg level) detectors, as reviewed elsewhere (Lobinski and Adams, 1997). In the case of gas condensates analysis the most pronounced difficulty, except the need for derivatization of more polar species, is due to the complexity of matrix and coelution of large amounts of hydrocarbons with the target species.

3.1 Chromatographic Conditions

3.1.1 Injector Conditions

The inlet temperature and the injection speed clearly play a role in GC determination of organomercury species but no agreement on the optimum conditions apparently exists.

Injector Temperature and Speed

Degradation of certain dialkyl mercury species, especially Et_2Hg as a function of injection temperature, accompanied by the formation of Hg° , was noticed (Shafawi *et al.*, 1999a). It was totally eliminated at temperatures as low as 125°C (Shafawi *et al.*, 1999a). These results are in contradiction to those obtained by Tao *et al.* (1998) who observed only a slight degradation of Et_2Hg and Bu_2Hg at temperatures exceeding 225°C with good results still obtained at 280°C. No degradation at temperatures up to 280°C was observed by Bouyssiere *et al.* (2000). Injection temperature above 300°C

was recommended for HgCl_2 due to its slow vaporization in the inlet (Tao *et al.*, 1998).

Injection Speed

Slow injection above 225°C resulted in a ghost peak between the Hg° and HgCl_2 peaks tentatively attributed to the formation of mercury amalgam with stainless steel needle or to retention of HgCl_2 in the syringe (Tao *et al.*, 1998).

Injection Mode

Pulsed splitless injection and on-column injection modes were compared for the comprehensive separation of Hg° , dialkyl mercury species, and monoalkyl mercury and Hg^{2+} bromides (Tao *et al.*, 1998). None of these injection modes were judged to be fully satisfactory and they should be considered as complementary. Whereas chromatograms for monoalkyl mercury and dialkyl mercury species were similar for both injection modes, different behaviors for Hg° and HgCl_2 were observed. Hg° and HgCl_2 (derivatized to bromide) coeluted in the void as a sharp signal in the pulsed splitless mode. The on-column injection mode offered an advantage of the separation of Hg° from HgCl_2 . The latter compound, however, suffered from the considerable peak broadening making its determination impractical.

3.1.2 Separation Conditions

Non-Polar Columns

Non-polar columns allow sharp peaks to be obtained for Hg° and dialkyl mercury species regardless of the injection mode (Tao *et al.*, 1998; Bouyssiere *et al.*, 2000). Satisfactory resolution of dialkyl mercury species was achieved using non-polar columns but of other mercury species only MeHgCl could be eluted—*nota bene*: at the same retention time as Et_2Hg (Bouyssiere *et al.*, 2000). Broad peaks for HgCl_2 and monoalkyl mercury species, even in the on-column mode (Tao *et al.*, 1998). Conversion of the ionic species to fully alkylated compounds is therefore required.

Even if organomercury species can be separated from each other, the complexity of the gas condensate matrix makes them coelute with hydrocarbon species. The resolution can be enhanced by using a column designed for volatile compounds (DB-624) held at 30°C (Snell *et al.*, 1996). Even with such a column, however, complete separation of Me_2Hg from hydrocarbons was still not achieved. The use of low column temperature results in broad peaks and raises the detection limits because of the increased difficulty in resolving mercury peaks from the noise.

Polar Columns

A polar column allowed the elution of EtHgCl and PhHgCl but the retention times were considerable (30–40 min) and resulted in peak tailing. Also, the problems of coelution with hydrocarbons were not eliminated (Tao *et al.*, 1998). Bromides were found to be less strongly retained than chlorides (Tao *et al.*, 1998).

3.2 Detection Conditions

The most popular analytical techniques for the mercury determination include cold vapor atomic absorption spectrometry (CV AAS) (Clevenger *et al.*, 1997) and atomic fluorescence spectrometry (CV AFS) (Bloom, 2000; Clevenger *et al.*, 1997) because of their pg to sub-pg absolute detection limits and wide availability of relatively low-cost equipment. The pre-requisite of the successful use of these techniques is the conversion of mercury in the chromatographic effluent into elemental mercury vapor (Hg^0) which is achieved by harsh oxidation (by BrCl (Bloom, 2000) or $\text{K}_2\text{Cr}_2\text{O}_7$ (Schickling and Broekaert, 1995) or by pyrolysis (Shafawi *et al.*, 1999b)). For these reasons, plasma source (microwave induced and inductively coupled) detectors that offer similar detection limits but do not require mercury to be pre-converted to Hg^0 have been by far more popular as detectors of mercury in GC effluents of gas condensates.

3.2.1 Atomic Absorption and Fluorescence Techniques

Although CV AAS and CV AFS are considered to be mercury specific GC detectors, hydrocarbons eluting from a GC column, or degradation products of derivatization reagents, can readily produce peaks that may be misinterpreted as mercury compounds. Numerous peaks, apparently not from Hg, were observed by GC-CV AAS of gas condensate samples when measurements were carried out using the most sensitive mercury line (185 nm) (Emteborg *et al.*, 1999). Efficient background correction is essential but may be insufficient because of the continually changing amount of hydrocarbons leaving the GC column. Verification of the origin of signals by measurements of peak ratios obtained using two different lines is recommended.

Ghost signals can also be readily generated with hydrocarbons in AFS, especially if pyrolysis happens to be incomplete. AFS was proposed as a convenient method for the total mercury in gas condensates. The determination was carried out by direct vaporization of a sample at 400°C and the adsorption of mercury species by a gold-coated silica trap at 200°C. The release of Hg was achieved by heating the trap at 900°C (Shafawi *et al.*, 1999b). In a modification of this method, developed to obtain information on speciation of mercury, the GC effluent was introduced into an AFS *via* a pyrolysis unit. Complete conversion after pyrolysis was claimed (Shafawi *et al.*, 1999a). The absolute detection limits were 2.5-7 pg for 1 μl injections. Several dialkyl species were identified in the condensates analyzed. However, the quantification carried out at the detection limits, the unusually high (up to 100% of the total mercury) proportions of alkyl mercury species found, and the fact that no alkyl mercury species were found in some of the samples run in parallel by GC-ICP MS (Bouyssiere *et al.*, 2000) induce doubts about the validity of the coupling.

3.2.2 Atomic Emission Spectrometry (AES)

A microwave induced plasma (MIP) has been the most widely used excitation source of GC effluents (Lobinski and Adams, 1997). MIP AES is capable of detecting sub-pg amounts of mercury and can be readily coupled to capillary GC, indeed a commercial instrument exists (Sullivan and Quimby, 1990; Quimby and Sullivan, 1990). However, in the case of gas condensates, the detection limits for mercury species are elevated for direct measurement of the column eluate because of the large quantities of carbon compounds entering the plasma in the same time as the analytes. Indeed, carbon compounds not only give rise to emission that spectrally interferes with the signal from mercury but can also reduce the excitation capability of an MIP which has limited thermal energy.

The interference due to the hydrocarbon emission over a broad wavelength range with the mercury emission line (253.652 nm) results in an unstable background that needs to be corrected. Background correction is made by subtracting the proportion of the carbon emission signal from that measured on the mercury line. In order to obtain an accurate measurement two conditions must be fulfilled. Firstly, the emission from carbon (247.857 nm) must be measured simultaneously with the mercury line. Secondly, the two emission signals should be proportional, in the absence of mercury, throughout the chromatogram. Since the amount of carbon reaching the plasma constantly changes, a disproportional response is usually obtained.

Another problem to be resolved is an overload of plasma leading to the quenching of its excitation energy. This is observed in the chromatogram as a dip both in carbon and in mercury emission intensity. Even with accurate background correction analytical errors will appear; in the worst case the plasma will be extinguished. This problem is difficult to solve. A plasma can tolerate larger amounts of carbon compounds at increased microwave powers but the signal-to-noise ratio of the detector response is reduced. It is therefore essential to limit the coelution of mercury species with hydrocarbon compounds present in the condensate. This can be readily achieved by split injection or by injecting dilute gas condensates solutions, at the expense however of the detection limits. An alternative is venting light hydrocarbons off the plasma but information on Hg^0 and methyl mercury will then be lost. Detection limits after 30-fold dilution with toluene were reported to be 2.3 $\mu\text{g l}^{-1}$ for Bu_2Hg and 3.1 $\mu\text{g l}^{-1}$ for MeBuHg (Snell *et al.*, 1996).

An elegant way for the alleviation of matrix effects was proposed by Snell *et al.* (1996). The method was based on heartcutting Hg peaks by the post-column collection of the eluting Hg compound on an amalgamation trap. Mercury compounds collected on-line within a specific time window were converted to Hg^0 that formed an amalgam with the trap material. The latter was usually an Au-Pt alloy owing to its

superior trapping properties in the presence of hydrocarbons in comparison with pure gold. Heating of the trap released Hg° that was transported to the plasma by a stream of helium. The technique turned out to be particularly attractive for the determination of Hg species, such as *e.g.* Me_2Hg , that coelute with a major condensate component, such as *e.g.* toluene. By removing the source of the carbon background emission, the trap allowed injection of untreated condensate sample and the determination of Me_2Hg down to $0.24 \mu\text{g l}^{-1}$ and butylated species to $0.56 \mu\text{g l}^{-1}$.

The use of a more robust inductively coupled plasma (ICP) for excitation for emission spectrometry is tempting. Kato *et al.* (1992) reported a GC-ICP AES coupling with an axially viewed plasma to offer a detection limit of 3 pg Hg. No applications of GC-ICP AES for hydrocarbon-rich samples have been, to our knowledge, reported.

3.2.3 Inductively Coupled Plasma Mass Spectrometry (ICP MS)

ICP MS is the most sensitive detection technique for mercury in gas chromatographic effluents. Absolute detection limits down to the low fg levels can readily be achieved (Tao *et al.*, 1998; Bouyssiere *et al.*, 2000; Prange and Jantzen, 1995; Wasik *et al.*, 1998). An ICP is more robust than an MIP and tolerates higher load of organic compounds. In terms of petroleum matrices ICP MS has been successfully used as GC detector of organolead in fuel (Kim *et al.*, 1992), metalloporphyrin in shale oil (Ebdon *et al.*, 1994; Pretorius *et al.*, 1993) and organomercury in gas condensates (Tao *et al.*, 1998; Bouyssiere *et al.*, 2000).

The major consideration in Hg detection by ICP MS in GC effluents of complex organic samples such as gas condensates is the risk of coelution of a mercury compound with hydrocarbons. However, because of the robustness of the plasma and the different measurement principle these problems are much less pronounced than in the case of MIP AES.

The signal from xenon, added after the column to the GC carrier gas was demonstrated to be suitable for the optimization of ICP MS parameters for various mercury species provided that they do not coelute with a major condensate hydrocarbon component (Tao *et al.*, 1998). The xenon signal intensity is also a valuable parameter for monitoring the plasma stability. The quenching of plasma energy due to the coelution of hydrocarbons is seen as a dip in the xenon intensity (Bouyssiere *et al.*, 2000). The addition of oxygen to the plasma not only prevents the carbon buildup on the cones but also limits the loss in signal intensity due to hydrocarbons entering the plasma (Bouyssiere *et al.*, 2000).

Whereas overload of plasma leads to the signal suppression because of the reduced plasma ionization efficiency, small quantities of coeluting hydrocarbons (that are difficult to monitor) may lead to signal enhancement

(Tao *et al.*, 1998; Bouyssiere *et al.*, 2000). This is clearly seen on standard addition curves which show slopes greater than calibration curves obtained for standard solutions (Bouyssiere *et al.*, 2000). The mechanism of this enhancement is probably due to the energy transfer from C^+ to Hg in the plasma (Tao *et al.*, 1998), as was also shown elsewhere for the As signal in the presence of methanol (Larsen and Sturup, 1994).

To date, the GC-ICP MS coupling has been the only one to produce species specific information on the whole range of dialkyl species in some gas condensates samples at the $\mu\text{g l}^{-1}$ and sub- $\mu\text{g l}^{-1}$ levels (Tao *et al.*, 1998).

4 DETERMINATION OF MERCURY SPECIATION BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) COUPLED WITH ELEMENT SPECIFIC DETECTION

The use of HPLC suffers from the poorer separation efficiency than in the case of GC and the lack of sensitive interfaces with atomic spectrometry. However, the potential advantage of avoiding the derivatization step has spurred attempts to use this technique to examine ionic, inorganic and monoalkyl(aryl) mercury species in gas condensates (Schickling and Broekaert, 1995; Zettlitzer *et al.*, 1997).

HgCl_2 , MeHgCl , PhHgAc and Ph_2Hg were separated by reversed-phase HPLC using gradient elution with acetonitrile mobile phase containing bromide (Schickling and Broekaert, 1995). Prior to determination, the organic ligands and the matrix were destroyed by oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ followed by reduction of mercury to Hg° for cold vapor generation (Schickling and Broekaert, 1995). The detection limits were in the range 8-14 $\mu\text{g l}^{-1}$ (as Hg). Only a 30-s broad (half-width) peak at the retention time corresponding to Hg^{2+} could possibly be attributed to mercury. Baseline instability and ghost peaks were attributed to the overcompensation of the D_2 -background correction. When injecting a gas condensate serious instabilities of the working pressure in the HPLC column were observed.

A similar approach was used by Zettlitzer *et al.* (1997) to examine monoalkyl mercury in German gas condensates.

5 SAMPLE PREPARATION

Prior to injection on a chromatographic column a gas condensate sample should be, at least, filtered to remove particles that could block the syringe or the column. Dilution may be required to reduce the sample viscosity. Other sample preparation operations often carried out aim at the alleviation of the matrix effect (extraction techniques), or at the improvement of thermal stability, volatilization or retention properties of mercury species (derivatization).

5.1 Filtration and Dilution

Since gas condensates may contain particulate matter that is capable of sorbing mercury, filtration is advisable to obtain homogenous samples and to minimize inhomogeneity as a source of variation of analytical results. The presence of H₂S may precipitate HgS that has a low solubility.

Dissolved mercury is referred to a sample obtained by vacuum filtration through a 0.8 µm nitrocellulose membrane filter (Bloom, 2000). Multiple filtrations or dilution with hexane may be necessary to obtain a successful filtration and a sufficient filtrate volume. Up to 30% of Hg⁰ was found to be lost during vacuum filtration (Bloom, 2000). For this reason, in cases where volatile Hg⁰ exceeded 5% of the total mercury, independent determinations of Hg⁰ in filtered and unfiltered samples were necessary in order to obtain a correction factor. Losses of alkyl mercury during filtration were judged insignificant because of the excellent solubility of these species in the gas condensates matrix, in contrast to Hg⁰ (Bloom, 2000).

Dilution of the condensate may sometimes be required to reduce its viscosity or to assure a reasonably stable background for mercury signals. Benzene, toluene and xylene are universal solvents but some condensates can be dissolved in hexane, iso-octane or iso-propanol, which may be useful in some cases.

5.2 Techniques to Reduce Matrix Effect

The similarity of the physicochemical properties of analyte species, especially dialkyl mercury compounds, and of the condensate matrix renders the separation of the matrix prior to chromatography a difficult task. Some techniques are available for the ionic species as discussed above in the section on operational procedures.

Solid-phase microextraction (SPME) was used for Me₂Hg but the detection limit was an order of magnitude poorer because the analyte mass collected was small compared with liquid sample injection (Snell *et al.*, 1996). Me₂Hg is normally quickly adsorbed on poly(dimethylsiloxane) film from the headspace above a sample. The main problem when using SPME for gas condensates analysis is that large amounts of various hydrocarbon compounds are also adsorbed on the fiber. When released, they disturb the plasma and cause background instability. Hydrocarbon compounds can remain on the fiber film after desorption resulting in memory effects.

5.3 Derivatization

The poor thermal stability of ionic mercury species requires them to be converted to more stable compounds prior to GC analysis. Two types of derivatization techniques were employed:

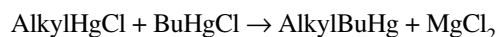
- alkylation using the Grignard reaction leading to dialkyl mercury species;

- halogenation with bromide leading to thermally stable and volatile alkyl mercury and Hg (II) bromides.

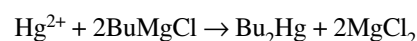
Gas condensate is a complex matrix that may cause interference with the derivatization reaction or with the stability of the derivatized sample.

5.3.1 Derivatization Using the Grignard Reaction

The derivatization of mercury and organomercury compounds with Grignard reagent was introduced 10 years ago by the group of Frech (Bulska *et al.*, 1991) in order to facilitate chromatographic separation of both methyl mercury and inorganic mercury in the same chromatographic run. The reactions:



and:



are carried out in an organic phase under water-free conditions. They can be performed in open glass vessels in a conventional fume hood and can be carried out directly on natural gas condensates.

During a Grignard reaction particular attention should be paid to:

- *choice of Grignard reagent.* It should assure the quantitative alkylation of inorganic or monoalkyl mercury compounds. The quantitative reaction takes place for ethylation, propylation and butylation but not for pentylation or hexylation (Emteborg *et al.*, 1999). Preference has been given to butylation since, on one hand, the natural occurrence of butyl derivatives of mercury in gas condensates is smaller than that of methyl, ethyl or propyl (Tao *et al.*, 1998), and on the other hand, butylation results in relatively low boiling mercury species that coelute with heavier carbon compounds which are less abundant in gas condensates samples;
- *duration and temperature of the Grignard reaction.* For samples containing inorganic mercury species it is important to limit both the reaction time and temperature as demetallation of Me₂Hg and MeHg⁺ may occur under harsher conditions. Replacement of indigenous methyl groups with butyl groups was demonstrated on prolonged contact of samples containing MeHg⁺ and Me₂Hg with BuMgCl. The degree of methyl replacement appeared to be proportional to the reaction time (Emteborg *et al.*, 1999). Therefore the originally recommended 20-min reaction time (Bulska *et al.*, 1991) was reduced to 5 min and the need for placing the reaction tube in ice was emphasized (Snell *et al.*, 1996);
- *order of operations.* Sample should be reacted with the Grignard reagent before dilution with toluene to reduce the concentration of reaction by-products in the derivatized solution. They may coelute with the mercury compounds leading to spectral interferences, especially when background correction is insufficient.

5.3.2 Derivatization Using Halogenation

Bromide is known to counteract the ionic character of the mercury compounds (Tao *et al.*, 1998; Wu, 1991). The addition of KBr was found to lead to an increase of the retention times and peak intensity in HPLC (Schickling and Broekaert, 1995). Also in GC, the derivatization of methyl mercury by reaction with HBr (Mizuishi *et al.*, 1997) or KI (Kato *et al.*, 1992; Barshick *et al.*, 1999; Lansens *et al.*, 1990) is well established prior to chromatography of mercury compounds on polar columns. The bromides formed were further stabilized by adding HBr to the carrier gas.

Free halogens are known to react rapidly with organic mercury species causing dealkylation of di- and monoalkyl species present in gas condensates. Emteborg *et al.* (1999) found that bromide (and iodide) at concentration of the order 1 ppm in a gas condensate induced dealkylation. The halogens can also be retained in a capillary column and react with subsequently injected samples. The complete removal of these halides from the column was advised to avoid the degradation of dialkyl mercury species (Emteborg *et al.*, 1999).

6 ACCURACY

6.1 Mercury Standards

An elemental mercury (Hg°) standard is prepared by equilibrating (by shaking) a droplet of mercury in heptane (Emteborg *et al.*, 1999) or iso-octane (Tao *et al.*, 1998) for 24 h in a gas tight vessel to produce a saturated solution. The exact concentration of mercury is determined by the solvent and the temperature of the solution and is 1-10 ppm. In order to prevent oxidation of metallic mercury (tarnishing the droplet) the purification of the solvent from potential oxidising agents by shaking it with active carbon and filtration, followed by bubbling with mercury-free argon for 6 h is recommended.

Several mercury compounds: mono- and dialkyl mercury and inorganic species are commercially available in reasonably good purity. Stock solutions are prepared in toluene, but in the case of monoalkyl species the dissolution of the compound in a small amount of propanol is advised prior to dilution with toluene.

The mixed dialkyl mercury species can be prepared by reacting a monoalkyl species with an appropriate Grignard reagent. It is recommended to verify the chromatographic purity of standards prepared in this way and to determine the total mercury concentration in their solutions.

Tetraphenylporphyrinato mercury complex (insoluble in water) was prepared by reaction of HgCl_2 with tetraphenylporphyrin in dimethylformamide (DMF) and extraction of the complex formed into chloroform (Furuta *et al.*, 1990).

All stock standard solutions should be stored in darkness at 4°C in glass containers. Working standard solutions were prepared daily. It is recommended to use a mercury-free condensate sample for dilutions of standards.

6.2 Stability of Mercury Compounds in Gas Condensate Sampling and Storage

Sampling of gas condensates for mercury speciation analysis is a critical step of the analytical procedure and is potentially a source of considerable errors. Significant losses of mercury and changes in its speciation may occur by reaction of species with atmosphere and sample container material, and by reactions between the species themselves and between the species and other gas condensates constituents. Therefore, a condensate sample should be taken directly from the feed liquid previous to contact with air and water. Analysis should be carried out on site, or, if not possible, the sample should be transferred into a glass- or Teflon-lined container without a headspace and the time between sampling and analysis should be reduced to minimum.

6.2.1 Losses during Storage—Choice of Container

Adsorption and/or reactions with the container wall are the principal pathways of the loss of mercury and changes in its speciation. Stability during storage was investigated in detail by Bloom (2000). Metal and polyethylene (PE) containers were found unsuitable for the collection and storage of Hg in petroleum due to either loss of Hg, or species interconversion. The glass and Teflon containers were the most appropriate materials for most of the species. Hg (II) was lost ($t_{1/2} = 3$ d), probably by sorption, from glass containers whereas Hg° was lost ($t_{1/2} = 30$ d) from Teflon containers. Me_2Hg and Hg° were lost from plastic containers by diffusion through the container walls (Bloom, 2000). Hg (II) was rapidly lost from all the containers except those made of Al that converted it (reversibly) to Hg° . This problem was particularly acute for the two most common mercury species: Hg (II) and Hg° .

The most stable standard solution is that of HgCl_2 stored in glass. The rate of species losses depends on the volume/surface ratio, minor changes in the chemical composition and physical properties of the container material and possible impurities of the solvent.

6.2.2 Species Interconversion

Chemical reactions between HgCl_2 and Ph_2Hg and between MeHgCl and Ph_2Hg take place (Schickling and Broekaert, 1995). Another important reaction leading to analytical errors is the formation of Hg (I) compounds from the dissolved Hg° and HgCl_2 . Both Hg° and HgCl_2 , if present alone in standard solutions, are relatively stable, with half-lives of 10 d and few

months, respectively (Snell *et al.*, 1998). However, when both Hg° and HgCl_2 are present their concentration rapidly decreases with time as a result of the Hg_2^{2+} precipitation. The latter forms a colloidal material which is not soluble in organic solvents at detectable concentrations. The compound can be maintained in solution by ultrasonic treatment and can be butylated with a Grignard reagent to the thermally stable Bu_2Hg_2 compound (Snell *et al.*, 1998). Note that monoalkyl mercury species are stable, in contrast to HgCl_2 , even in the presence of Hg° (Snell *et al.*, 1998).

6.3 Identification and Quantification

As discussed above, the risk of artefact signals is significant in the case of gas condensates analysis even with mercury specific detectors such as AAS or AFS. Therefore it is recommended to verify the behavior of a mercury-free gas condensate having the hydrocarbon composition as close as possible to the analyzed sample. The acquisition of a chromatogram with an independent detector is recommended. It should be noted that this source of error cannot be corrected by the method of standard additions.

The method of standard addition is a useful tool to confirm the identity of peaks present and to correct for the signal suppression/enhancement errors. The recovery tests are essential since there exist no certified reference materials for mercury species in gas condensates. Calibration with species solutions containing a single species is recommended to avoid errors stemming from conversion reactions.

CONCLUSIONS

The determination of mercury speciation in gas condensates remains a difficult task despite the increasing number of analytical procedures developed. The combination of gas chromatography that guarantees the separation of mercury species in gas condensates from each other with a robust, sensitive and mercury specific detector, such as ICP MS, seems to be the most suitable tool for the analysis of speciation of dialkyl mercury compounds, Hg° and, after derivatization, monoalkyl mercury species and weakly complexed Hg^{2+} . The latter and Hg° seem to be the most abundant mercury in gas condensates, organomercury compounds accounting for less than a few percent of the total mercury. The information on the forms and the stability of Hg^{2+} coordination complexes present in gas condensates is missing because of the absence of suitable methodology. The coupling of capillary zone electrophoresis with ICP MS detection should allow an insight into speciation of Hg^{2+} in gas condensates. 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 metal species in complex

samples. Another urgent and important issue to be addressed is the reliability of sampling and an agreement on a normalized sampling procedure that would allow the comparison of results obtained by different research groups for gas condensates samples of different origins.

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