



Investigation of the Grignard reaction and experimental conditions for the determination of inorganic mercury and methylmercury in crude oils by GC–ICP–MS



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HIGHLIGHTS

- Mercury species in crude oils were determined by a modified Bouysiere's method.
- The Grignard reaction conditions and instrumental parameters were optimized.
- The determination of the analytes can be performed using different Grignard reagents.
- The dialkylmercury species can be determined using Bu₂Hg calibration solutions.

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ABSTRACT

A method proposed by Bouysiere et al. [3] for mercury speciation in gas condensates by GC–ICP–MS was investigated for the determination of Hg²⁺ (as inorganic mercury) and MeHg⁺ in crude oil samples. The Grignard reaction conditions and instrumental parameters were optimized. The original volume (0.5 mL) of the Grignard reagent was duplicated, and a sample/toluene ratio of 1:19 was used to avoid the total consumption and/or destruction of the Grignard reagent by the components of the oil matrices. Furthermore, the split injection mode was applied. When BuMgCl was used for the derivatization reaction, a limit of detection of 0.03 μg L⁻¹ Hg²⁺ was obtained. Precision was always better than 12%. Quantitative recoveries (80–117%) of Hg²⁺ (as MeBuHg and Bu₂Hg) were obtained for the determination of MeHg⁺ and inorganic mercury in spiked samples, respectively. Besides BuMgCl, other Grignard reagents such as MeMgCl, EtMgCl and PrMgCl can be used for the determination of Hg²⁺ as inorganic mercury and MeHg⁺. Moreover, mercury species such as Me₂Hg, MeEtHg, Et₂Hg, Pr₂Hg and MePrHg can be determined by direct injection into the GC–ICP–MS using Bu₂Hg standard solutions for external calibration.

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1. Introduction

Mercury naturally occurs in crude oil and natural gas and its concentration is highly dependent on geological location. Mercury concentration ranges of 0.1–20,000 ng g⁻¹ [1] and of 10–3000 ng g⁻¹ [2] have been found in crude oils and gas condensates, respectively.

Various mercury species are present in crude oils [1] and gas condensates [2,3]. In crude oils, the identified mercury species include elemental mercury (Hg⁰), dialkylmercury compounds, colloidal mercuric sulfide, complexed ionic mercury species [1,4],

asphaltene mercury [1] and alkylatable Hg²⁺ [4]. In gas condensates, inorganic mercury can be present as Hg⁰ or oxidized forms. The organic mercury compounds are also present as fully (dialkyl) or partly (monoalkyl) alkylated species as well as coordination complexes [2].

Mercury has a direct negative impact on the petroleum industry [4–8]. The determination of the mercury species in feedstock supply and refinery products is essential to understand the mechanisms of the interaction of these species with catalysts, to evaluate their hazardous effects to the workers and to improve the technologies for the elimination of mercury from crude oil and related products [3].

In 1996 and 1998, Snell et al. [9,10] used a microwave induced plasma atomic emission spectrometer (MIP–AES) coupled to a GC

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(GC-MIP-AES) for the determination of diethylmercury (DiEtHg), methylmercury (MeHg⁺) and inorganic mercury (Hg²⁺) in gas condensates. However, the large amount of carbon compounds present in these matrices might cause spectral interferences and also overload the plasma discharge. Thus, a post-column amalgamation trap was used for the purification of the derivatized mercury compounds, prior to their detection. Although the plasma could tolerate large amounts of carbon compounds with the increase of the microwave power, the signal-to-noise ratio of the detector was significantly degraded. In 1998, Tao et al. [11] substituted the MIP-AES for an inductively coupled plasma mass spectrometer, which was coupled to the GC (GC-ICP-MS) since the plasma of the ICP-MS was more robust than that of the MIP-AES [2]. Since then, GC-ICP-MS has been applied for the determination of various mercury species (e.g. inorganic mercury and MeHg⁺) in different hydrocarbon-rich matrices such as gas condensate [3,11], naphtha and crude oil [11]. Moreover, the GC technique has been coupled to a cold vapor atomic fluorescence spectrometer (CV AFS) for the determination of inorganic mercury (Hg²⁺) and MeHg⁺ in gas condensate and crude oil samples [4] and inorganic mercury (Hg²⁺) in synthetic condensate standard solutions [10].

In 2000, Bouyssiere et al. [2] reviewed the methods for mercury speciation in gas condensates, and mentioned that the gas chromatography (GC) coupled to a specific technique for mercury detection would be the most promising tool for mercury speciation in these matrices.

The GC separation of inorganic mercury (Hg²⁺) and MeHg⁺ in hydrocarbon-rich samples, followed by quantification with ICP-MS, has been performed by using non-polar [3,9,10] and polar (pre-treated with HBr) [11] capillary columns. The use of non-polar columns requires derivatization pre-reactions for the conversion of Hg²⁺ and MeHg⁺ into suitable species for the chromatographic separation [2,3].

The derivatization procedures for the determination of Hg²⁺ and MeHg⁺ in gas condensates have been based on alkylation with Grignard reagents such as methylmagnesium chloride (MeMgCl), propylmagnesium chloride (PrMgCl) and butylmagnesium chloride (BuMgCl) [3,9,10,12]. In crude oil samples, the Grignard reactions have not been used for the derivatization of Hg²⁺ and MeHg⁺. Only ethylation with sodium tetraethylborate (NaBEt₄) in aqueous extracts has been reported for the determination of MeHg⁺ in crude oils and also in condensates [4].

Butylation has been the most used Grignard reaction for the determination of Hg²⁺ and MeHg⁺ in gas condensates [3,9,10] since the natural occurrence of butyl derivatives of mercury in these matrices is less frequent than that of methyl, ethyl or propyl. Furthermore, butylation results in relatively low boiling mercury species that co-elute with heavier carbon compounds, which are less abundant in gas condensate samples [2].

The time required for the complete reaction of the mercury species with butylmagnesium chloride (BuMgCl) depends on the volume and freshness of the Grignard reagent as well as on the sample constituents, for example, the amount of moisture which consumes the Grignard reagent [12]. Besides the reaction time, the temperature and the order of addition of the sample diluent (e.g. toluene) for the Grignard reaction are important parameters which influence the reaction yield [9]. Snell et al. [9] observed that the addition of BuMgCl before diluting with toluene led to a lower concentration of the reaction by-products in the derivatized solution than those found when BuMgCl was added after diluting with toluene for the determination of Hg²⁺ and MeHg⁺ in gas condensate samples by GC-MIP-AES, using post-column mercury species amalgamation. Moreover, the authors concluded that the reaction time (5 min and 20 min were tested) and temperature (ice bath at 4 °C and room temperature were tested) should be limited, since the de-methylation of Me₂Hg and MeHg⁺ might occur under harsher

conditions. In 1999, Emtborg et al. [12] identified the conversion of MeBuHg into Bu₂Hg when MeBuHg was left to stand at room temperature for long times up to 60 min, without any quenching of the reaction. The MeBuHg compound was formed from the reaction of MeHg⁺ in toluene with BuMgCl at 0 °C (ice/water bath) for 5 min. The degree of methyl group replacement appeared to be proportional to the reaction time.

In 2002, Bouyssiere et al. [3] developed a method for mercury speciation in gas condensates by GC-ICP-MS. Elemental mercury and organomercury species were directly determined whereas the polar species (Hg²⁺ and MeHg⁺) were derivatized using BuMgCl. The order of addition of the diluent (toluene) and the derivatization reaction temperature were different from the recommendations given by Snell et al. [9], described above. The sample dilution with toluene (1:4 or 1:9) was carried out before adding of BuMgCl, and the Grignard reaction was performed at room temperature. The reaction time was 5 min, with occasional shaking. The splitless injection mode was used. The authors tested different dialkylmercury compounds for the preparation of the calibration curves. The results revealed that the slopes obtained for Bu₂Hg (prepared from the butylation of Hg²⁺) and MeBuHg (prepared from the butylation of MeHg⁺) were approximately twice lower than those found for Et₂Hg (prepared from a stock solution in toluene). The explanation given by the authors was the probable loss of mercury during the derivatization reaction. Another observed effect was the variation of the slopes for the different organic matrices. The origin of the variations in the emission signal intensity was probably due to the change of the amount of carbon arriving in the plasma, consequently modifying the ionization conditions. Because of that, the authors recommended the use of the standard addition method for the quantification of these species in order to compensate the low recoveries (ca. 50%) due to the mercury loss and matrix effect.

In this work, a method proposed by Bouyssiere et al. [3] for mercury speciation in gas condensate samples will be investigated for the determination of Hg²⁺ and MeHg⁺ in crude oils, which are much more complex matrices. Different Grignard reaction conditions (derivatization reaction time, the amount and type of the Grignard reagent and ratio of the sample dilution with toluene) and instrumental parameters (transfer line and plasma injector temperatures as well as sample injection mode into GC) will be tested. The accuracy will be demonstrated by the analysis of spiked samples since certified concentrations of the analytes in crude oils were not commercially available.

2. Experimental

2.1. Equipment

An Agilent gas chromatograph Model 6890 (Waldbronn, Germany) was used for the separation of the mercury species. An Agilent ICP-MS Model 7500ce (Hyogo, Japan) with an octapole reaction system was coupled to the gas chromatograph via a commercially available interface from Agilent for the quantification of the mercury isotopes. Peak areas were used to quantify the mercury isotopes. The GC-ICP-MS operating conditions (Table 1) were optimized using a 5.0 µg L⁻¹ Hg²⁺ (as diphenylmercury) standard solution in toluene. Splitless and split (ratios of 1:2, 1:5 and 1:10) injection modes were tested. Although the mercury signal intensity for the split injection was lower than that obtained for the splitless mode, the signal-to-noise ratio was higher and, therefore, the split injection mode (1:10) was selected. Transfer line and plasma injector temperatures of 150, 200, 250, 280 and 300 °C were tested. The highest mercury signal and the lowest relative standard deviation were obtained at 280 °C. Therefore, both the transfer line and the plasma injector were operated at this temperature.

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