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Headspace In-Tube Microextraction and GC-ICP-MS Determination of Mercury Species in Petroleum Hydrocarbons

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Supporting Information

ABSTRACT: Characterization of mercury contamination in petroleum hydrocarbons (PHs) is necessary in order to assess the risk of corrosion of the processing infrastructure and to assess the level of human exposure to Hg-containing substances. Here we present an accurate and sensitive method for determination of Hg species in PHs by headspace sampling with a possibility of on-line pre-concentration using in-tube extraction (ITEX) combined with gas chromatography−inductively coupled plasma mass spectrometry (GC-ICP-MS) analysis. Mercury species were first extracted from the PHs matrix into an aqueous phase via dithizone chelation and subsequently converted with sodium tetrapropyl borate into volatile derivatives which could be sampled from the headspace prior to GC-ICP-MS analysis. For concentrations in the ng kg^{-1} range, the on-line ITEX method was applied, whereas the μg kg^{-1} range was accessible by static headspace. Quantitation of Hg species was carried out by a double isotope dilution method, with quantitative recoveries of methylmercury (MeHg, average 101 ± 5%) and inorganic mercury (InHg, average 97 ± 7%) by direct headspace injection. Average recoveries of Hg spikes after on-line ITEX pre-concentration were 95 ± 3% for MeHg and 98 ± 8% for InHg. The detection limits for MeHg and InHg were 428 and 46 ng kg^{-1} when measured by static headspace, and 2.4 ng kg^{-1} and 1.7 ng kg^{-1} by on-line ITEX pre-concentration. The accuracy of the pre-concentration method was demonstrated by analysis of a crude oil standard reference material (NIST 2722) certified for InHg.

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INTRODUCTION

Mercury is naturally present in fossil fuels, and although its origin is not fully understood, it is most probable that Hg migrated from the source rock into the reservoirs during formation of the fossil fuels. As the concentration of Hg in the Earth's crust varies significantly among the geographical regions, so does the concentration of Hg in the oil reservoirs with a global range of up to 30 mg kg^{-1}.[1] Elevated concentrations of Hg in crude oil can cause challenges due to Hg's potential to facilitate corrosion within the processing plant infrastructure, with heat exchangers being most often affected. Additionally, Hg is harmful to human health and the environment, and therefore regulatory bodies are enforcing strict limits on allowable levels to reduce it emission. As a result, agreements were put in place to limit extraction of petroleum hydrocarbons (PHs) with Hg concentration above set values or sales of Hg-contaminated PHs are penalized with high price discounts. One of the solutions to maintain the production rate of contaminated wells is to employ mercury removal strategies, which can be highly efficient if they are designed to target specific Hg species present in the stream.

In nature, Hg can be found in several chemical and physical forms, and individual Hg species are broadly categorized into three main groups: (a) *organic species*, dissolved Hg compounds containing at least one organic ligand, e.g., MeHgCl; (b) *inorganic species*, either dissolved mercury salts such as $HgCl_2$ or insoluble salts such as HgS; and (c) *elemental species*, metallic Hg, which can be present in dissolved or particulate form. The dominant species found in the PHs are HgS > Hg^0 > inorganic mercury (InHg), with organic Hg species rarely present and, if so, generally at low sub-μg kg^{-1} levels.[1,2] However, despite the lower abundance of inorganic and organic Hg species, they are the most commonly targeted species due to their reactivity and toxicity.

Several analytical techniques were developed for Hg speciation based on either fractionation of Hg species by their physico-chemical properties (filtration, purge, and extraction) or chromatographic separation by high-performance liquid chromatography (HPLC)[3,4] or gas chromatography (GC).[5−8] Fractionation and/or extraction methods generally involve a number of sample preparation steps as individual Hg species are extracted by various aqueous or organic solvents.[9,10] Such sample preparation is time-consuming and prone to cross-contamination as well as loss of volatile Hg species. Chromatographic separation of Hg species was successfully performed by Schickling and Broekaert,[3] who first destroyed the matrix through $K_2Cr_2O_7$ oxidation and then separated individual Hg species using a HPLC C_{18} column. However, the use of a cold vapor atomic absorption spectrometer as detector resulted in a rather high limit of detection (LOD) of 10 μg kg^{-1} for InHg. Yun et al.[4] compared different extraction methods prior to speciation of Hg on a HPLC C_{18} column with detection by cold vapor atomic fluorescence spectrometry and found that extraction by tetramethylammonium hydroxide yielded the highest recovery efficiency for organic Hg species. Developed method also showed improved LODs for methylmercury (MeHg, 0.05 μg L^{-1}) and ethylmercury (EtHg, 0.07 μg L^{-1}); however, the authors did not perform speciation of inorganic Hg. Gas chromatography (GC) became a popular separation modality

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due to the volatility of PHs and some Hg species. GC was initially coupled with microwave-induced plasma atomic emission spectrometry (MIP-AES), which suffered from spectral interferences[11,12] and so was replaced by inductively coupled plasma mass spectrometry, which offered a robust plasma with superior LODs. The analysis of Hg in PHs using gas chromatography−inductively coupled plasma mass spectrometry (GC-ICP-MS) is performed in two steps. First, the sample is injected directly into the GC-ICP-MS to identify any dialkyl and elemental Hg species; a second portion of sample is then derivatized with Grignard reagent (most often BuMgCl) to alkylate any other Hg species which are not sufficiently volatile for direct GC-ICP-MS detection.[6,8]

Several research groups investigating Grignard alkylation of Hg in organic matrices pointed out significant limitations of this method. It was found that the alkylation efficiency of Grignard reagents is dependent on its freshness and the volume used for derivatization.[11] Exchange of endogenous methyl group by the butyl group from BuMgCl was observed in samples containing MeHg and Me_2Hg species within several minutes upon contact with the Grignard reagent.[11] Such cross-alkylation promoted by the Grignard reagent alters Hg speciation. Additionally, as Grignard reagent is moisture sensitive, varying percentage of water content between samples may lead to sample-dependent alkylation efficiency. To eliminate consumption of the Grignard reagent by matrix constituents, some authors suggested dilution of the samples up to 19 times in organic solvent,[13] with subsequent loss of sensitivity. Furthermore, samples containing high percentages of water, such as emulsions and froth from tailing ponds, will result in violent reaction if Grignard reagent is used. Besides the limitations of the Grignard reagent, the organic matrix of PHs provides its own setbacks when it comes to Hg speciation. Injection of heavy crude oils results in fast deterioration of the GC column due to the irreversible coating of the matrix to the stationary phase. Notably, analysis of organic matrices requires addition of O_2 gas to plasma in order to burn off the excess carbon, and the subsequent increase of plasma temperature requires platinum interface cones for ICP-MS. Such instrument modification ultimately increases the cost of analysis. Apart from dissolved Hg species, PHs very often contain particulate Hg[7] or residual clay and mineral particles which clog the capillary GC column. An organic matrix of PHs also presents a great limitation in the variety of pre-concentration methods that can be used for analysis of ultra-low levels of Hg, as a large number of newly developed pre-concentration techniques focus on Hg species present in aqueous media.[14−18]

Despite these shortcomings, liquid injection of organic matrices after Grignard derivatization has been in use for Hg speciation for the past 3 decades. In this study, we developed a novel method which solves the above-mentioned methodological limitations of the classic Grignard procedure. Our approach employs an aqueous extraction of Hg species from PHs following their alkylation by $NaBPr_4$ and headspace GC-ICP-MS analysis. Such an injection mode results in very clean chromatography and allows on-line pre-concentration by in-tube extraction (ITEX) for improved sensitivity.

■ EXPERIMENTAL SECTION

Equipment. A 5975C GC-MS instrument equipped with Phenomenex (Aschaffenburg, Germany) Zebron ZB-5MS GC column (5% diphenyl, 95% polydimethylsiloxane, 30 m × 0.25 mm × 0.25 μm) and a 7500 ICP-MS instrument from Agilent Technologies (Mississauga, ON, Canada) were used for identification and quantitation of derivatized InHg and MeHg. A commercial heated GC transfer line (Agilent Technologies, Mississauga, ON, Canada) was used to carry the GC gas stream to ICP-MS. Optimization of ICP-MS was carried out by monitoring the signal of 1% xenon in argon sample gas for tuning. Typical operational conditions for GC and ICP-MS are outlined in Table S1 (Supporting Information). Analyte isotopes ^{126}Xe, ^{127}Xe, ^{198}Hg, ^{201}Hg, and ^{202}Hg were monitored by ICP-MS. The ITEX was operated with an automated PAL RSI 85 autosampler (CTC Analytics, Switzerland). Samples were prepared in 20 mL magnetic screw-cap headspace vials with silicone/PTFE septa. A standard trap material, Tenax TA (80/100 mesh, Agilent Technologies, Mississauga, ON, Canada), was used for the dynamic headspace in-tube extraction.

Reagents and Solutions. All chemicals used were of analytical grade. Nitric and hydrochloric acids (Fisher Scientific, Nepean, ON, Canada) were purified in-house by sub-boiling distillation of reagent-grade feedstock in a quartz still. Toluene, dithizone (diphenylthiocarbazone), sodium hydroxide, and sulfuric acid (H_2SO_4) were purchased from Fisher Scientific (Nepean, ON, Canada). *n*-Butylmagnesium chloride (BuMgCl, Grignard reagent) was obtained from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada). High-purity deionized water (DIW) was obtained from a NanoPure mixed-bed ion-exchange system fed with reverse osmosis domestic feedwater (Barnstead/Thermolyne Corp., Dubuque, IA, USA). A 0.01 g mL^{-1} solution of sodium tetrapropylborate was prepared by dissolving $NaBPr_4$ (Synthese Nord GmbH, Rotenburg, Germany) in DIW. Sodium acetate (NaAc) buffer (0.1 M) was prepared by dissolving appropriate amounts of NaAc (ACS grade, Fisher Scientific, Asheville, NC, USA) in water containing acetic acid (trace metal grade, Fisher Scientific, Asheville, NC, USA), and the pH was adjusted with ammonium hydroxide to pH 5.5. Dithizone solution (0.01% w/v) was prepared by dissolving 0.0055 g of dithizone in 50 mL of toluene. Purification of dithizone solution was performed as described elsewhere.[19] Briefly, 50 mL of 0.01% dithizone solution was mixed with 50 mL of 0.1 M NaOH in a separation funnel. Reduced dithizone was collected in the aqueous phase and acidified with a few drops of concentrated HCl (10 M), allowing precipitation of the purified dithizone. Acidified solution was mixed with 50 mL of toluene in a separation funnel to re-dissolve dithizone in toluene. Purified solution was kept in an amber vial and prepared fresh on a regular basis.

Natural-abundance high-purity MeHgCl (>95%) and $HgCl_2$ (99.9999%) were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada) and were used for preparation of stock solutions by dissolving the salt directly in toluene. Working solutions were prepared gravimetrically from stock solutions daily. Internal standard enriched in ^{201}Hg isotope was purchased from Oak Ridge National Laboratory (USA) in metallic form and dissolved in HCl. Working solutions of $In^{201}Hg$ were prepared by sequential dilution of stock solution into methanol, isopropanol, and toluene. $Me^{198}Hg$ isotopically enriched solution in toluene was prepared from NRC CRM EMMS-1,[20] the synthesis of which is described elsewhere.[21] All standards were kept in the freezer at −18 °C when not in use. NIST 2722 standard reference material (SRM) was purchased from the National Institute of Standards and Technology (Gaithersburg, MA, USA).

Sample Preparation and Analysis. All glassware was soaked in 10% (v/v) HNO_3 overnight, rinsed thoroughly with DIW, and dried in an oven at 105 °C prior to use.

Athabasca medium-grade oil sand, provided by InnoTech Alberta (Edmonton, Canada), was used for extraction of bitumen. Bitumen was extracted from 75 g of oil sand following the industry standard Soxhlet Dean−Stark extraction (SDSE) method.[22] The extract solution contained toluene, bitumen, and a small amount of water and solids. This solution was collected from the boiling flask for further characterization and Hg spiking experiments. The water content of the extract solution was 0.73%, determined in triplicate using a Metrohm Karl Fischer titrator (Titrando 836 titrator, Ti 803 stand, and KF Thermoprep oven 832).

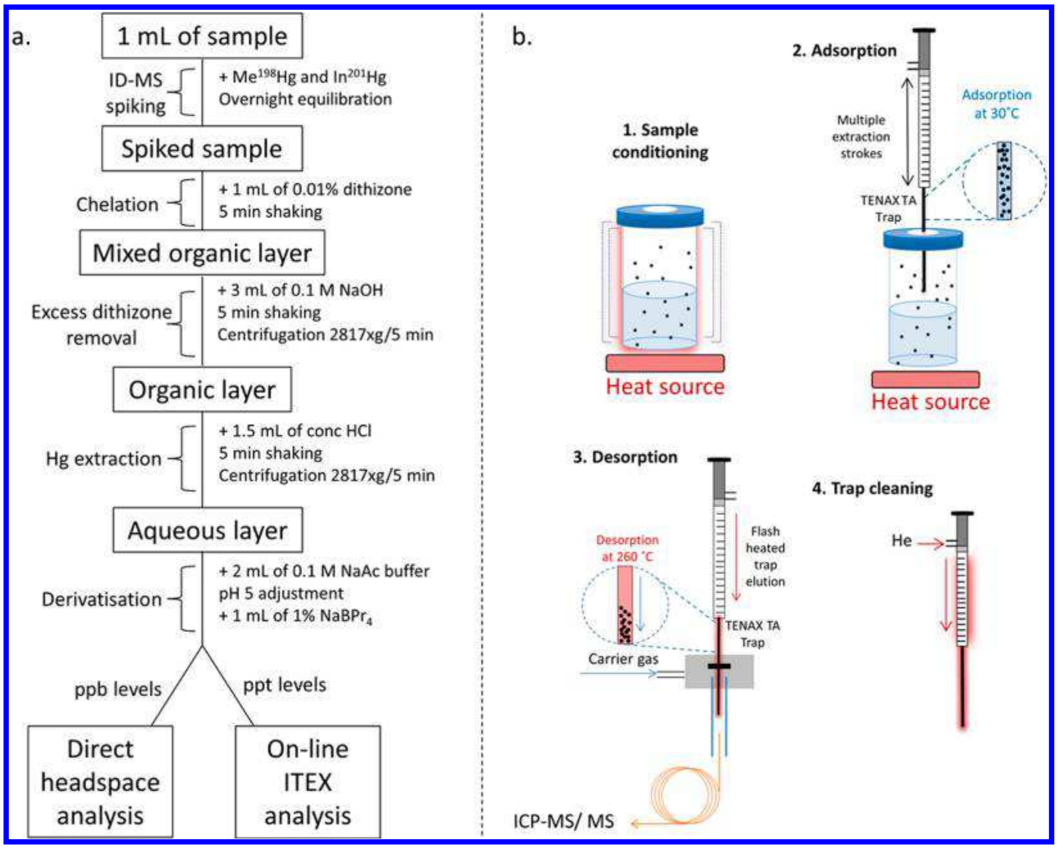

Figure 1. (a) Summary of the analytical method for Hg species extraction from PH matrices. (b) Procedure steps for Hg species analysis using ITEX pre-concentration.

Stock solutions of bitumen spiked with varying concentrations of primary InHg and MeHg standards were mechanically shaken for 60 min, and then enriched Me^{198}Hg and In^{201}Hg internal standards were added. Samples were mechanically shaken for an additional 60 min and left to equilibrate overnight (approximately 16 h). To chelate Hg species, 1 mL of spiked bitumen sample was mixed with 1 mL of 0.01% dithizone solution for 5 min on a mechanical shaker. Afterward, 3 mL of 1 M NaOH was added, and the samples were shaken for an additional 5 min in order to remove excess dithizone. Subsequently, to achieve phase separation, samples were centrifuged for 5 min at 2817*g*, and then the organic phase was collected. Next, 1.5 mL of concentrated HCl was added into the organic phase to promote Hg phase transfer, and the mixture was mechanically shaken for 10 min, followed by 5 min of centrifugation at 2817*g*. Aqueous phase was collected and buffered with 2 mL of 0.1 M acetate buffer, and the pH of the solution was adjusted to 5.5 using 50% (m/v) NaOH. A 1 mL portion of 1% (w/w) $NaBPr_4$ derivatization solution was added into the buffered solution and left to react for 1 h. An overview of Hg extraction and derivatisation can be found in Figure 1a. Prior to static headspace sampling, samples were agitated at 500 rpm in the CTC PAL3 incubator at 75 °C and then injected into GC-ICP-MS.

For determination of MeHg and InHg using the dynamic headspace in-tube extraction, samples were spiked with ng kg^{-1} concentrations of MeHg and InHg. For quantification of the spike recovery, samples were spiked with enriched Me^{198}Hg and In^{201}Hg standards and prepared in the same way as for static headspace analysis. Following 10 min of agitation (500 rpm) at 75 °C, Hg derivatives were extracted by passing the headspace gases through the ITEX sorbent trap by means of a syringe, 40 strokes of 1300 μL/per stroke. The adsorbed analytes were thermally desorbed from the sorbent trap via flash heating to 260 °C and introduced into the GC injector by a 700 μL gas injection. After sample injection, the ITEX trap was heated to 260 °C and flushed for 2 min with a stream of He to eliminate carryover. Additional parameters of ITEX pre-concentration and desorption conditions can be found in Table S1 and graphical representation of Hg pre-concentration using ITEX is shown in Figure 1b.

The collected data were processed by Agilent MassHunter software to yield peak areas and the corresponding ^{202}Hg/^{198}Hg (for MeHg) and ^{202}Hg/^{201}Hg (for InHg) isotope ratios, from which the analyte concentration was calculated.

Liquid injection was also performed to determine the extraction efficiencies of MeHg and InHg by ITEX. For this purpose, 3 mL of 0.1 M NaAc buffer spiked with Hg species was derivatized with 1 mL of 1% (w/w) $NaBPr_4$ and mixed with 1 mL of toluene. After 10 min of manual shaking, the organic layer was transferred to a glass vial for GC-ICP-MS analysis.

Exact concentrations of enriched Me^{198}Hg and In^{201}Hg were determined by reverse isotope dilution by means of Grignard derivatization (BuMgCl).[7] Briefly, 1 mL of enriched standard in toluene was spiked with 1 mL of natural abundance standard in toluene, in a concentration ratio of 1:6, respectively. Standards were left to equilibrate for 30 min, and then 200 μL of BuMgCl was added. Following 5 min of reaction time, 10 mL of 0.2 M H_2SO_4 was added to hydrolyze the excess Grignard reagent. To separate the phases, the mixture was centrifuged for 5 min at 2817*g*, and the organic phase was injected into the GC-ICP-MS.

For all quantification by ID-MS, mass bias was calculated using isotopes ^{126}Xe and ^{127}Xe following a method previously published in the literature.[23,24]

RESULTS AND DISCUSSION

Isotope Dilution Mass Spectrometry. Isotope dilution mass spectrometry (ID-MS) is a well-established quantitation method which has been used for more than 3 decades for trace metals analysis and was discussed in depth in several

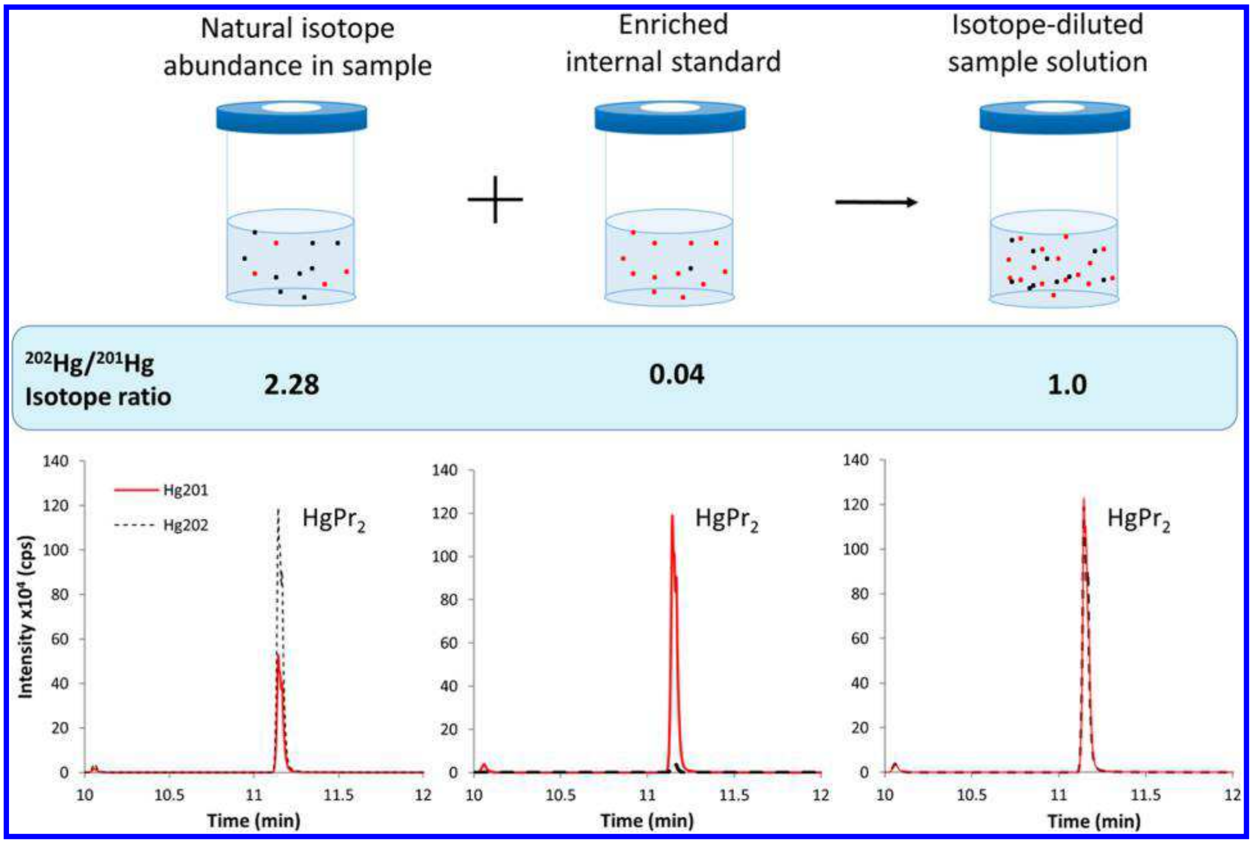

Figure 2. Illustration of the principle of ID-MS for quantitation of InHg by GC-ICP-MS. Sample containing InHg of a natural isotopic abundance is spiked with internal standard enriched in the 201 isotope, and the ratio between isotopes in the resulting mixture is determined by integration of the chromatographic peaks for isotopes 201 and 202.

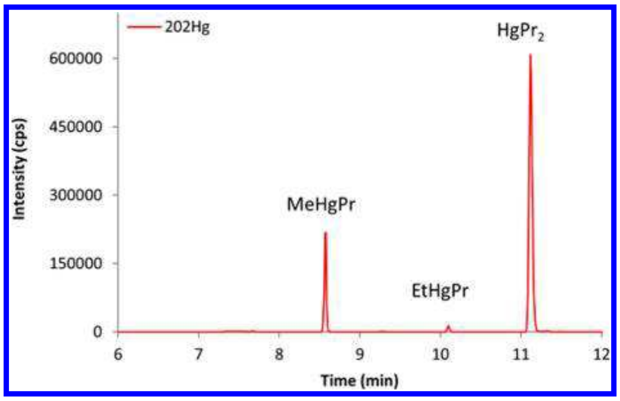

Figure 3. GC-ICP-MS chromatogram of 600 ng kg^{-1} MeHg and InHg extracted from bitumen, derivatized with $NaBPr_4$, and preconcentrated using ITEX trap. Very small quantities of EtHgPr were found due to impurities in the derivatization reagent.

reviews.[23,24] In summary (see Figure 2), quantitation of an analyte in a sample by ID-MS is based on eq 1:[25]

$$w_A = w_B \frac{R_B - Kr_{AB}}{Kr_{AB} - R_A} \frac{m_{B(AB)}}{m_{A(AB)}} \frac{\sum R_A}{\sum R_B} \frac{M_A}{M_B} \qquad (1)$$

where w_A is the mass fraction of analyte in the sample, w_B is the mass fraction of isotopically enriched internal standard, R_A is the natural isotope ratio in the sample (202/201), R_B is the isotope ratio in isotopically enriched internal standard (202/201), K is the mass bias correction factor, r_{AB} is the isotope ratio measured by mass spectrometry in the spiked sample (202/201), $m_{A(AB)}$ is the mass of the sample in the spiked blend, $m_{B(AB)}$ is the mass of the enriched internal standard in the blend, $\sum R_A$ is the sum of all isotope ratios in the sample of the same denominator ($\sum R_A = R_{196/201} + R_{198/201} + R_{199/201} + R_{200/201} + R_{201/201} + R_{202/201} + R_{204/201}$), $\sum R_B$ is the sum of all isotope ratios in the enriched internal standard of the same denominator, M_A is the molar mass of analyte in the sample, and M_B is the molar mass of enriched internal standard.

The only unknown in eq 1 is the isotope ratio (R) in the isotope-diluted sample, which in the case of GC-ICP-MS analysis is calculated from the integrated peak area of the targeted analyte's species. This means that after complete equilibration of the sample with enriched internal standard, any loss of the isotope-diluted sample or the analyte (due to, e.g., volatilization) has no effect on the accuracy of its quantitation. Therefore, homogeneous mixing between sample and enriched internal standard is absolutely crucial and best achieved if the sample is spiked with an identical chemical species of the analyte. In such a scenario, the isotopically enriched internal standard has identical chemical and physical behavior as the naturally present species. Consequently, measurement of the isotope ratio in the isotope-diluted sample eliminates the matrix effect because both isotopes are affected by the matrix in an identical way, meaning that ID-MS is essentially matrix independent. In order to optimize the quantity of the enriched internal standard required for sample spiking, the approximate concentration of the analyte needs to be determined in pre-analysis. To determine an accurate concentration of the enriched internal standard, reversed ID-MS is performed by spiking enriched internal standard with a

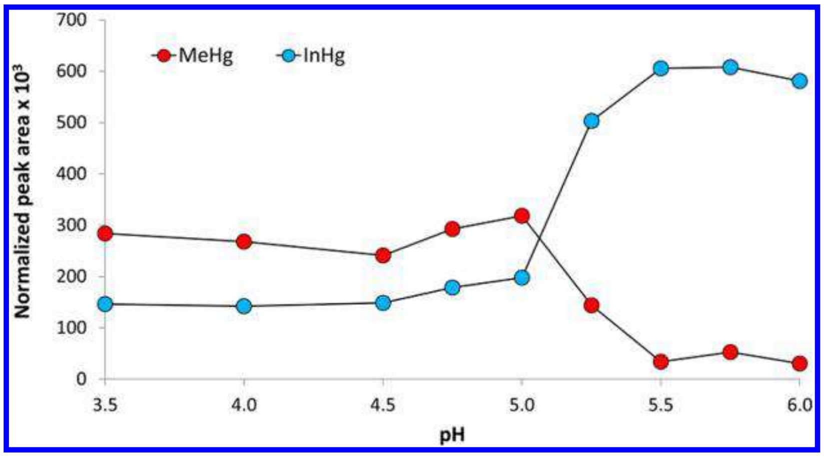

Figure 4. Influence of pH of 0.1 M acetate buffer on derivatization efficiency of selected Hg species. Favorable derivatization condition for organic Hg species were found at pH < 5, whereas InHg species were derivatized more efficiently at pH > 5.

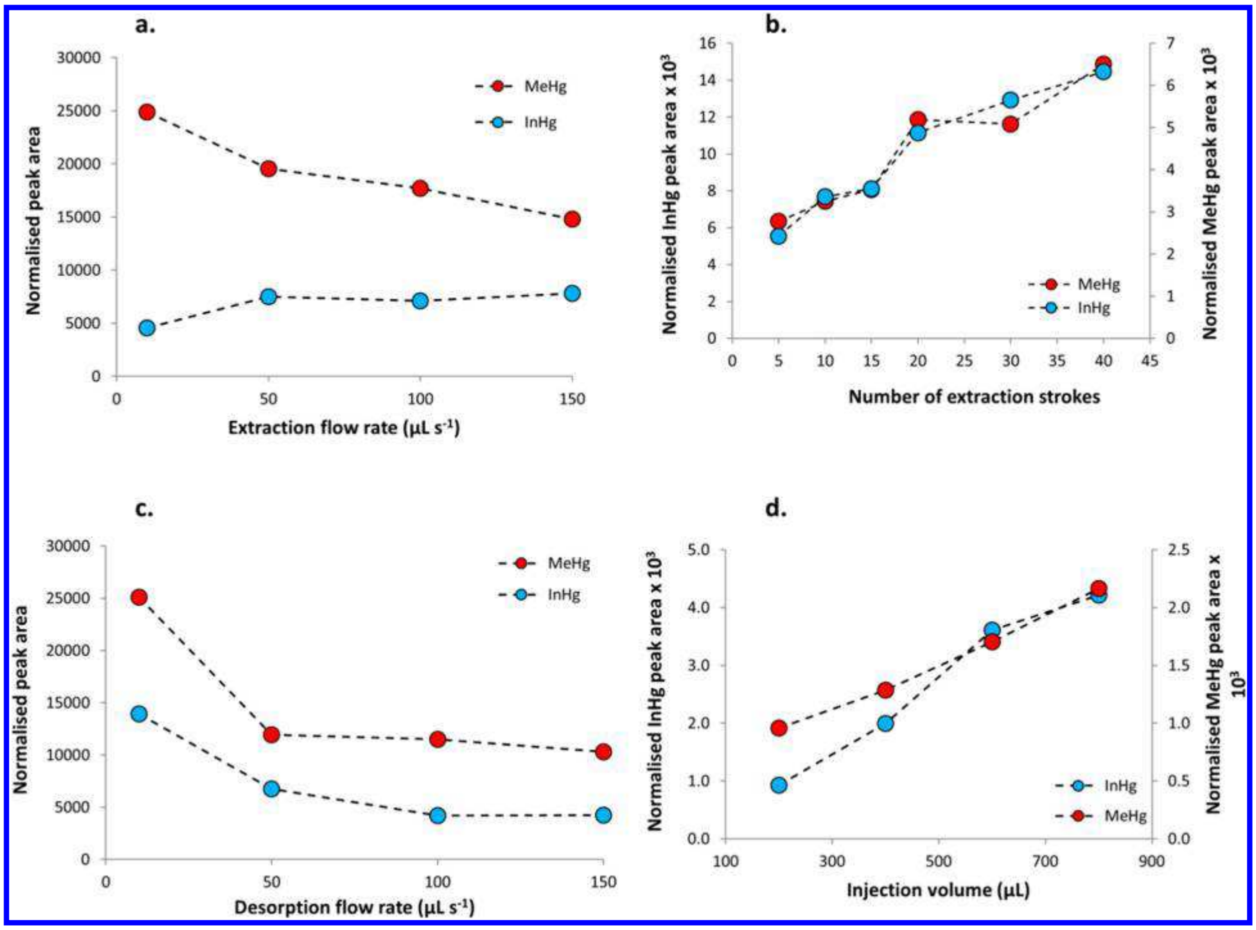

Figure 5. Studied selected parameters of on-line ITEX pre-concentration with focus on maximum extraction and pre-concentration of Hg species. (a) Impact of increasing extraction flow rate on Hg species adsorption on the sorbent. (b) Increase of Hg species pre-concentration with increasing number of extraction strokes. (c) Influence of desorption flow rate on the diffusion of Hg species from the trap to the headspace. (d) Impact of injection volume on the elution of Hg from the trap.

primary standard of natural isotopic composition and solving eq 1 for w_A.

Extraction and Derivatization of MeHg and InHg. To eliminate matrix interference and the undesired impact of the matrix on the analytical instrumentation, it is crucial to separate the analyte from the sample matrix. Extraction of the analyte into the vapor phase, favored by GC analysis, is likely the cleanest and simplest approach to cope with difficult condensed, solid, or multiphase sample matrices. When it comes to organic matrices like PHs, the partial vapor pressure of petroleum constituents is significantly higher than that of the Hg derivatives, and therefore no relative enrichment could be achieved by a simple static headspace sampling approach. Transferring Hg species from the organic phase of PHs to the aqueous phase can solve this issue. Such phase transfer eliminates the complex PHs matrix and unlocks a broad

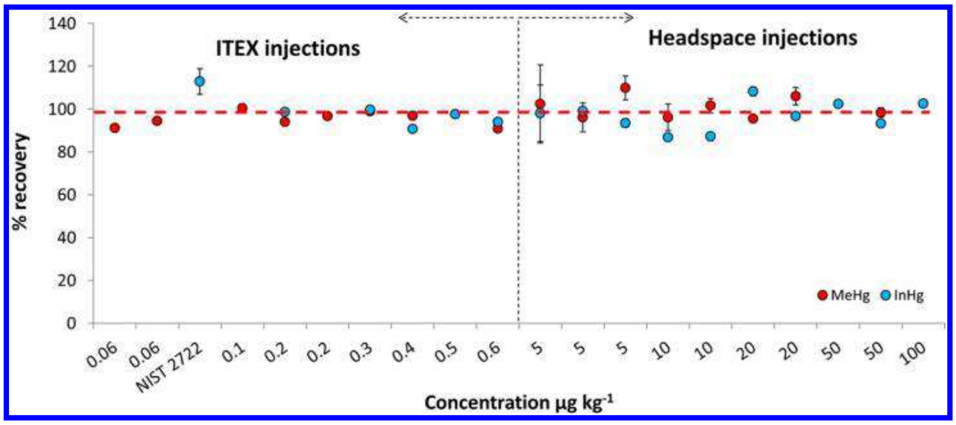

Figure 6. Percentage recoveries of MeHgCl and $HgCl_2$ spiked into the extracted bitumen and analyzed by headspace or ITEX method. NIST 2722 standard reference material contains 129 ng kg^{-1} of InHg. Error bars of spiked bitumen represent RSD of triplicate injection of the sample. The error bar of NIST 2722 sample represents RSD of three individual samples injected three times.

Table 1. Comparison between Certified Reference Concentration of InHg in NIST 2722 SRM and Measured Concentration by ITEX Method with Its Corresponding Percentage of Recovery

SRM ID	certified concentration (ng kg^{-1})	measured concentration(ng kg^{-1})	% recovery
NIST 2722	129 ± 13	146 ± 8	113

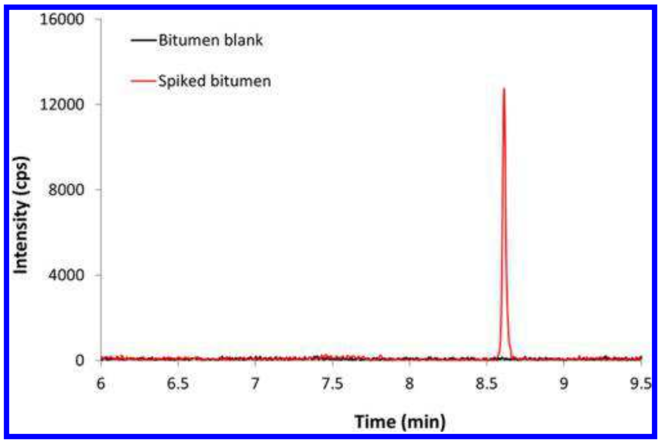

Figure 7. GC-ICP-MS chromatogram of extracted bitumen sample without (black) and with (red) spiked 61.1 ng kg^{-1} of MeHgCl standard with signal-to-noise ratio of 49 clearly distinguished from the background intensities using ITEX pre-concentration.

spectrum of pre-concentration possibilities. To obtain the phase transfer, we adapted the method described by Voegborlo et al.,[19] who used dithizone solution in toluene to extract Hg from the aqueous to the organic phase. The authors used a solution of Na_2S in ethanolic KOH for extraction of Hg to the aqueous phase. However, our results lacked consistency when Na_2S solution was used. Additionally, the required acidification of Na_2S solution results in formation of highly toxic H_2S gas and may lead to formation of HgS particulates, which would alter Hg speciation. Therefore, for extraction of Hg to the aqueous phase, we tested several acidic (concentrated HCl, 2 M HCl, 5% HNO_3, 5% H_2SO_4, 6% KI pH 3) and alkaline solutions (1 M NaCl, 1% L-cysteine in 1 M NaOH). Concentrated HCl provided the best extraction efficiency. Nonetheless, we observed a significant difference in extraction efficiencies between MeHg and InHg (Figure 3).

Upon acidification with concentrated HCl, MeHg-R undergoes ligand exchange to form polar, neutral MeHgCl, which is in equilibrium between aqueous and organic phases. However, due to the hydrophobic methyl group, MeHgCl will partition predominantly into the organic phase. In contrast, InHg forms $Hg(Cl_4)^{2-}$, and therefore it fully transfers from organic to aqueous solution, resulting in significantly better extraction efficiency. Individual constituents of bitumen can interfere with Hg analysis through formation of Hg complexes, hence reducing the extraction efficiency into aqueous media. Formation of Hg−dithizone complexes catalyzed the phase-transfer. In fact, significantly lower concentrations of Hg species were found in HCl when the addition of dithizone was omitted. Interestingly, extraction of MeHgCl from the bitumen

Table 2. Comparison of Reported Limits of Detection for Hg Species in PHs

analytical instrument	analytical method	LOD of Hg species		ref
		InHg	MeHg	
HPLC-CV-AAS	direct analysis	9 mg L^{-1}	9 mg L^{-1}	3
GC-MIP-AES	amalgamation trap	0.56 mg L^{-1}	0.56 mg L^{-1}	12
GC-ICP-MS	direct analysis	520 fg[a]	120 fg[a]	5
GC-ICP-MS	phase transfer	46 ng kg^{-1}	428 ng kg^{-1}	this study
GC-ICP-MS	ITEX trap	1.7 ng kg^{-1}	61.1 ng kg^{-1}	this study
GC-ICP-MS	Grignard method	30 ng L^{-1}	ND[b]	6
GC-ICP-MS	Grignard method	110 ng L^{-1}	ND	13

[a] Absolute concentration. [b] ND = not defined.

matrix using a 1% solution of L-cysteine provided results contradictory to those published in the literature.[10,19] Mixtures of L-cysteine solution with bitumen extract resulted in formation of very thick emulsions which could not be broken by centrifugation at 17000*g* for 40 min, and thus this type of extraction was deemed to be unsuitable. It should be noted that previous use of L-cysteine solution for extraction of MeHgCl from the organic phase was performed either on natural gas condensate samples or laboratory-grade organic solvents. Thus, the matrix composition may have a significant impact on the extraction efficiency. To calculate the method's extraction efficiency, a buffer spiked with 5 μg kg^{-1} of MeHg and InHg was derivatized with $NaBPr_4$, and its headspace was injected to GC-ICP-MS. Peak areas of 5 μg kg^{-1} MeHg and InHg extracted from the bitumen and spiked buffer were used for calculation of extraction efficiencies, which were 5.6% and 16% for MeHg and InHg, respectively.

Following the phase transfer from bitumen into the aqueous solution, Hg species were derivatized using $NaBPr_4$. The derivatization efficiency is species and pH dependent. Although this reagent is generally used at pH 5, it is obvious from Figure 4 that the lower pH provides favorable derivatization conditions for organic Hg, whereas pH > 5 significantly improves the derivatization efficiency of InHg species. For certain applications, the derivatization conditions can be tuned to improve the signal-to-noise ratio for selected Hg species. Additionally, it was observed that $NaBPr_4$ contains small impurities of $NaBEt_nPr_{4-n}$ ($n = 1-4$), as low quantities of EtHgPr were found in all samples and standards analyzed. A similar observation was reported in previously published work.[26]

Optimization of ITEX Pre-concentration Conditions. For the analysis of bitumen samples containing low ng kg^{-1} concentrations of Hg species, the ITEX pre-concentration method was tested. Previously, ITEX showed very good pre-concentration potential for alkylated Hg and Sn species present in water.[26] This method uses a specially designed headspace syringe needle which is packed with selected sorbent, and pre-concentration of analytes takes place during sampling of the headspace. For this purpose, Tenax TA trap was used. This sorbent is made out of a combination of two-thirds Tenax TA material on the bottom part of the tube and one-third Carbosieve S III material on the top. The pre-concentration method consists of four steps: sample conditioning, analyte absorption, analyte desorption, and trap cleaning (Figure 1b). Sample conditioning entails heating and agitation of the sample in order to homogenize and favor headspace partition of the analytes. Organic Hg compounds have high vapor pressure and can be volatilized at room temperature. From our investigation, increasing the conditioning temperature above 50 °C has very limited impact on MeHg extraction; however, the amount of InHg in the headspace doubled when the temperature changed from 40 to 90 °C.

To favor the adsorption of Hg species on the sorbent, the temperature of the trap was set to 30 °C, and the speed of the extraction flow rate was tested. It was observed that, with a slow extraction rate, more MeHg was pre-concentrated on the trap, suggesting that the absorption is flow rate dependent. Notably, InHg adsorption was 40% lower at 10 μL s^{-1} and eventually stabilized with higher extraction rates (Figure 5a). The pre-concentration factor can also be increased with a higher number of repeated extraction strokes (Figure 5b). Because the analytes bind strongly to the sorbent, several consecutive extraction strokes can be performed for each sample. Each time the headspace is extracted from the vial, the equilibria between liquid and vapor phase are disturbed, and more Hg species enter the vapor phase; thus, more extraction strokes increase the signal-to-noise ratio. However, with increasing number of extraction strokes, the analysis time can increase significantly. As a compromise between extraction efficiency and sample throughput, 40 extraction strokes at 50 μL s^{-1} was selected for our work.

During the desorption step, the robotic arm with the trap is moved to the injector of the GC and flash heated to 260 °C within a few seconds. Flash heating of the trap has a great advantage over other pre-concentration methods based on thermal desorption, such as SPME fibers,[27,28] which are generally heated by the GC injector over a prolonged time, such that peak broadening can be observed. To achieve maximum desorption of Hg species from the trap, the desorption flow rate and volume of desorption gas were optimized. We found that a lower desorption flow rate increases the signal-to-noise ratio (Figure 5c), also indicating that the diffusion of analyte from the sorbent to the headspace is flow rate limited, was demonstrated by other researchers.[29,30] Additionally, we observed MeHg peak splitting at desorption flow rates higher than 50 μL s^{-1}. In contrast with data published in the literature,[29,30] we found that increasing the desorption volume significantly improves the elution of Hg derivatives from the trap (Figure 5d); therefore, we selected a desorption volume of 700 μL at a flow rate of 10 μL s^{-1}.

Following the desorption step, the trap was heated to 260 °C and flushed with He for 2 min to elute any residual Hg species in order to prevent carryover between individual injections. To verify the efficiency of the cleaning cycle, an empty vial was repeatedly sampled within the sequence, and no Hg signal was observed during these blank measurements.

Spike Recovery Test Using ID-MS. Bitumen extracted from Athabasca oil sand was spiked with known concentrations of MeHgCl and $HgCl_2$ in toluene to test the effect of the matrix on quantification of Hg compounds. Due to a great matrix diversity of PHs, it is not feasible to prepare matrix-matched standards for external calibration, and several researchers suggested that this method should be avoided.[6,7] Hence, a spike recovery test was performed, and quantitation was attained by ID-MS.

Following a model described by Meija et al.,[31] we performed double isotope dilution using Me^{198}Hg and In^{201}Hg to quantify the recovery of both Hg species simultaneously. To eliminate any bias caused by extraction and/or derivatization efficiency, the samples were spiked with enriched Hg species (enriched internal standard) prior to extraction. In this fashion, if enough time is given to the internal standard and endogenous Hg species to equilibrate, the altered ratio will not be affected by any further sample manipulation. Because the equilibration between the endogenous and enriched Hg species is a crucial step, spiked samples were shaken for 1 h after spiking, although previous studies showed that an equilibration of 15 min is sufficient.[7] The calculated spike recovery of MeHg ranged between 91 and 99% for analysis of spikes in the ng kg^{-1} range analyzed by the ITEX pre-concentration method, and the spike recovery of MeHg in the μg kg^{-1} range analyzed by headspace injection was between 96 and 110% (Figure 4). Similarly, the spike recovery of InHg in the ng kg^{-1} range analyzed by ITEX pre-concentration method was between 91 and 112%, but interestingly the recovery of spikes in the μg kg^{-1} range analyzed by headspace injection showed systematic underestimation between 11 and 21%. Such a systematic effect could be caused by preferential extraction of enriched Hg internal standard that could result from non-homogeneous mixing between enriched and natural spike in the bitumen matrix. To test this hypothesis, bitumen samples spiked with Hg of natural isotopic composition were shaken for 60 min and then spiked with enriched Hg and shaken for another 60 min. Subsequently, the samples were left to stand overnight (approximately 16 h) to achieve complete equilibration and analyzed the following day. The recovery of InHg was found to be in the range of 87−108% (Figure 6). The improved spike recovery suggests that the interactions between individual Hg species and bitumen matrix are not identical; however, with limited knowledge of bitumen matrix composition, the interpretation of these interactions is very challenging, and therefore we recommend overnight equilibration. To test the accuracy of the developed method, NIST 2722 heavy sweet crude oil certified for Hg concentration was analyzed three times over a period of 2 months. As the concentration of Hg in this SRM is in the low ng kg^{-1} range, only the ITEX method could be tested, and it showed satisfactory recovery of an average 113% (Table 1).

Figures of Merit. Limits of detection for static headspace were 428 and 46 ng kg^{-1} for MeHg and InHg spiked into bitumen matrix, respectively, whereas for ITEX methods the LODs were 2.4 ng kg^{-1} for MeHg and 1.7 ng kg^{-1} for InHg. LODs calculations were based on the lowest injected standard as 3 times the S/N ratio, with 61.1 ng kg^{-1} of MeHg providing a ratio of 49, clearly distinguished from the background counts (Figure 7). It should be noted that the methods for calculating the LOD of InHg using the ITEX method was greatly affected by the background concentration of InHg and trace contaminants in the reagents. The method LODs for Hg species achieved by our developed method are comparable to and in many instances better than those obtained by Grignard derivatization or other analytical methods (Table 2).

CONCLUSION

A simple, robust, and versatile method for the speciation of mercury in organic matrices has been developed. To reduce the undesired matrix effect originating from the petroleum hydrocarbon samples, Hg species were extracted and derivatized in aqueous media. This sample treatment allowed headspace analysis and on-line pre-concentration with in-tube extraction. Static headspace injection showed excellent recoveries for MeHg (average 101%) and InHg (average 97%) in spiked bitumen over a $\mu g\ kg^{-1}$ concentration range with LODs of 428 and 46 ng kg^{-1} for MeHg and InHg, respectively. The on-line pre-concentration method based on in-tube extraction was optimized for ultra-trace analysis, giving superior detection limits of 2.4 ng kg^{-1} for MeHg and 1.7 ng kg^{-1} for InHg. To the best of our knowledge, this is the first method which utilizes headspace analysis of Hg species present in organic matrices such as PHs with the possibility of on-line pre-concentration.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b02201.

Table S1, giving typical operational conditions for GC and ICP-MS (PDF)

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Notes

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