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# Arsenic Analysis in the Petroleum Industry: A Review

Aurore Mere, Maxime Enrico, Honggang Zhou, Emmanuel Tessier, and Brice Bouyssiere\*

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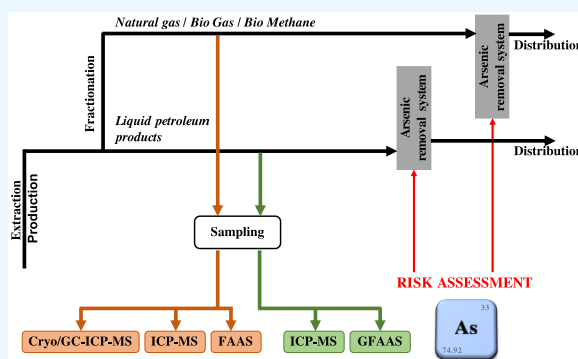
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**ABSTRACT:** The presence of arsenic in natural gas and liquid hydrocarbons is of great concern for oil companies. In addition to health risks due to its toxicity as well as environmental issues, arsenic is responsible for irreversible poisoning of catalysts and clogging of pipes via the accumulation of As-containing precipitates. To address these problems and to better design treatment units, robust methods for the analysis of arsenic and its compounds in oil streams are required. In addition, the use of feedstocks as a novel source of energy is becoming increasingly important. Most biomasses used as feedstocks are contaminated with arsenic. To avoid problems related to the presence of this element, it is therefore also necessary to have reliable methods for the analysis of arsenic and its compounds in these new fluids. This review outlines the sampling techniques, sample preparation methods, and arsenic analysis techniques developed during recent decades and commonly used in the oil industry and in the new feedstock energy domain.



## 1. INTRODUCTION

Arsenic (As) is the 20th most abundant element in the Earth's crust and is generally found in its inorganic form in soils, rocks and water<sup>1</sup> at concentrations of several mg/kg.<sup>2</sup> As is also present in biota, especially marine organisms, and in crude oil.<sup>3</sup> Marine organisms have the ability to bioaccumulate arsenic, with concentrations reaching up to 2 g kg<sup>-1</sup> dry weight.<sup>4</sup> Long-term decomposition of marine organisms gives rise to oil with the persistence of As in the oil matrix,<sup>2</sup> with a suspected role of alkylation/dealkylation reactions in the solubilization of As.<sup>2,5</sup>

The presence of arsenic in petroleum fluids is the source of various problems for oil companies. First, As represents a health and safety risk for personnel in contact with these fluids. Arsenic might be responsible for skin lesions, respiratory diseases, and cardiovascular diseases and can cause several long-term cancer developments.<sup>6–8</sup> Another issue relates to the environmental impact of arsenic released to the atmosphere by natural gas burning.<sup>9</sup> From an industrial point of view, there are two major problems related to the occurrence of As. First, the precipitation of As-containing particles leads to the clogging of pipes and valves. This phenomenon was first observed in 1987 after the blockage of pipes at a US gas distribution company. Delgado-Morales et al.<sup>5</sup> suggested that the formation of these solid deposits occurred in the presence of a metallic substrate and were formed from arsenic and H<sub>2</sub>S. Irgolic et al.<sup>2</sup> identified volatile alkylarsines as the source of these residues. The second major concern relates to catalyst poisoning during steam cracking and natural gas processing. Small amounts of As

might cause severe and irreversible damage to catalysts, representing high financial costs.<sup>9,10</sup>

The total concentration range of arsenic in natural gas was determined to be 0.01–63 μg dm<sup>-3</sup>.<sup>2</sup> It was later demonstrated that different organic and inorganic forms of As are present,<sup>11,12</sup> with a dominance of trimethylarsine (TMA, (CH<sub>3</sub>)<sub>3</sub>As), triethylarsine ((C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>As), triphenylarsine ((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>As), and arsine (AsH<sub>3</sub>).<sup>4,9,13,14</sup> TMA is the most abundant volatile As species in natural gas (55–80% of the total As in natural gas).<sup>5</sup> The dominance of TMA is thought to be related to its higher stability over time compared to that of other As compounds.<sup>4</sup>

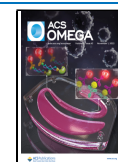
Few articles mention the total amount of As in crude oil; only Olsen et al.<sup>15</sup> and Stigter et al.<sup>16</sup> were able to identify a concentration range from <10 to 26.2 μg kg<sup>-1</sup> of As in real crude oil samples. The main forms of arsenic in these matrices are TMA, which is predominant, dimethylated arsenic ((CH<sub>3</sub>)<sub>2</sub>As), and monomethylated arsenic ((CH<sub>3</sub>)As).<sup>3</sup>

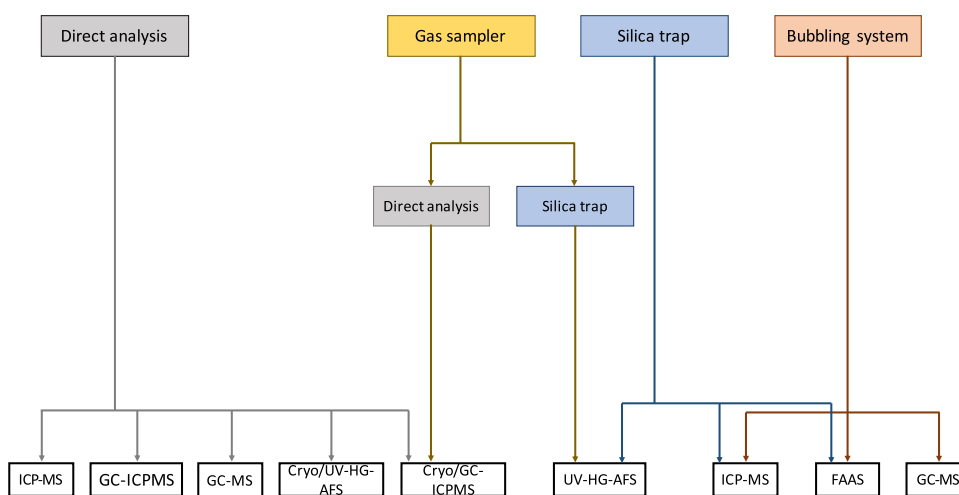
Arsenic removal systems can be set up by oil companies. The development of these units is based on the total arsenic concentration and, if possible, on the speciation of arsenic in the oil fluids. Therefore, before they are set up, it is essential to determine the arsenic content of natural gas and liquid

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**Figure 1.** Diagram of arsenic analysis in natural gas.

hydrocarbons. This methodology will also be of great importance in the field of new energy feedstocks because As can be present in biogas (and thus biomethane)<sup>17</sup> and in bio-oil during the hydroliquefaction (HTL) of biomass such as swine manure, which may contain high levels of arsenic.<sup>18</sup>

## 2. SAMPLING AND ANALYSIS OF As IN NATURAL GAS

**2.1. Sampling.** **2.1.1. As-Selective Sorption.** **2.1.1.1. Bubbling Systems.** This sampling technique consists of bubbling natural gas in one bubbler<sup>2</sup> or several bubblers<sup>4,9,14,19</sup> connected in series containing a trapping solution. Several trapping solutions can be used for this technique, but they must be able to oxidize volatile arsenicals for their pentavalent oxidizing species, such as oxidizing organic arsenic to the arsenate ion ( $\text{AsO}_4^{3-}$ ).<sup>4</sup>

Concentrated nitric acid ( $\text{HNO}_3$ ) can be used as a trapping solution.<sup>2,14,19</sup> However, it has been shown that a 2% aqueous silver nitrate ( $\text{AgNO}_3$ ) solution provides better TMA trapping efficiency than a concentrated nitric acid solution.<sup>4,14</sup> Despite this, it has been shown that the arsenic trapping efficiency in a 2%  $\text{AgNO}_3$  solution is only 70%. These results were obtained by comparing the amount of TMA found in a natural gas sample after bubbling in this solution and analyzing it directly by cryotrapping/gas chromatography–inductively coupled plasma–mass spectrometry (Cryo/GC–ICP–MS). This loss of efficiency can be explained by the potential absorption of arsenic on the walls of the bubblers.<sup>9</sup>

Furthermore, if the natural gas contains a high concentration of  $\text{H}_2\text{S}$ , a black solid is formed in the 2%  $\text{AgNO}_3$  solution, which inhibits the analysis of this solution.<sup>14</sup>

**2.1.1.2. Traps.** This sampling technique involves passing a natural gas stream through a tube containing a solid sorbent. This technique allows for large volumes of gas to be sampled.<sup>20</sup> The sorbent used is silica gel impregnated with 1%<sup>21</sup> or 2%<sup>9</sup>  $\text{AgNO}_3$ . When the gas stream is passed through the trap, the arsenic retained within it is desorbed with concentrated  $\text{HNO}_3$ . The eluate is then analyzed by UV irradiation–hydride generation–atomic fluorescence spectrometry (UV–HG–AFS), by ICP–MS, or by flame atomic absorption spectrometry (FAAS) (see section 3.2.2 after sampling). Uroic et al.<sup>21</sup> obtained a TMA absorption efficiency of 99.8% with this type of trap. However, Krupp et al.<sup>9</sup> obtained a TMA absorption efficiency of only 70% with this type of trap. This absorption

efficiency was obtained by comparing the amount of TMA found in a natural gas sample after trapping on a silver nitrate impregnated silica gel trap and by direct analysis of the sample by Cryo/GC–ICP–MS. This result is considered to be due to incomplete absorption inside the trap due to the very low polarity of TMA or incomplete desorption of TMA during its extraction from the trap with nitric acid.<sup>9</sup>

**2.1.2. Gas Samplers: Cylinders and Inert Plastic Bags (Tedlar Bags).** Natural gas sampling can be conducted using pressurized cylinders or Tedlar bags. Arsenic analysis in natural gas sampled with these two types of samplers can be determined directly by Cryo/GC–ICP–MS.<sup>9</sup> Arsenic can also be determined by releasing some or all of the sampled gas into a silicon trap impregnated with  $\text{AgNO}_3$ , where the eluate (see section 2.1.1.2) from this tube is then analyzed by UV–HG–AFS (see Figure 1).<sup>21</sup>

Pressurized cylinders can be used to sample gases at high pressures directly on the production system or in the well under initial pressure.<sup>2</sup> Although natural gas sampling with pressurized cylinders is a fast and easy-to-handle method, arsenic depletion has been observed in natural gas samples stored in steel cylinders.<sup>45</sup> To overcome this problem, a special coating (Silcosteel or Sulfinert) has been designed to create an inert internal surface in these cylinders to limit the interactions between arsenic and the cylinder walls.

Inert plastic bags (Tedlar bags) can also be used to sample natural gas.<sup>22</sup> However, unlike cylinders, natural gas must be depressurized to be sampled in Tedlar bags. It has been shown that, within 24 h, there is no significant loss in the various volatile arsenic species contained in these bags. However, it has been shown that, over time, there is adsorption of arsenic compounds to the inner surface of the Tedlar bags, which suggests that arsenic analysis should be carried out no later than 24 h after sampling.<sup>20</sup>

**2.2. Analysis.** **2.2.1. Direct Analysis.** Total arsenic and its species in natural gas can be analyzed directly without a sample preparation and preconcentration step. Freije-Carrelo et al.<sup>23</sup> developed a GC–ICP–MS method that allows for the simultaneous analysis of total arsenic and its speciation in natural gas. To perform this simultaneous analysis, two gas injection valves were interconnected. The first valve directs the gas sample into the analytical column (GC column) for arsenic speciation analysis. The second valve allows for the same gas sample to be directed into a transfer line directly connected to

the GC–ICP–MS interface to analyze the total arsenic by continuous flow injection analysis (FIA). The detection limits obtained with this technique are very low, i.e., 2 ppt for total analysis and 12 ppt for speciation, and matrix effects are negligible.<sup>23</sup>

Arsenic species in natural gas can also be analyzed directly using the cryotrapping technique. This technique is widely used in the research laboratory, but there have been no publications mentioning its direct use in the field. This technique does not require any sample preparation beforehand. This method consists of trapping gas samples in a capillary column,<sup>2</sup> a GC column,<sup>22</sup> or a glass tube filled with a chromatographic packing.<sup>24</sup> This trapping is carried out cryogenically using liquid hydrogen,<sup>9</sup> liquid nitrogen,<sup>20</sup> or an acetone/liquid nitrogen mixture.<sup>25</sup> The arsenic species contained in the gas samples are then thermally desorbed from these columns/tubes using temperature ramps reaching a maximum temperature of 160–290 °C. The carrier gas used is helium.

Arsenic species can be analyzed using different techniques/detectors and can first be separated by GC. After separation, As species can be analyzed by MS. The detection limit obtained with this technique is 0.5 ng dm<sup>-3</sup>.<sup>2</sup> After this separation by GC, the As species can also be analyzed by ICP–MS. Detection limits are generally on the order of a few ng m<sup>-3</sup> but can vary depending on the amount of gas analyzed.<sup>9,20,21,22,24</sup> Arsenic species in the analyzed gases can also be directly analyzed by ICP–MS without a GC separation phase.<sup>25</sup>

The cryotrapping technique coupled with ICP–MS is an extremely sensitive and reproducible method, and when coupled with GC–ICP–MS, the speciation of arsenic in natural gas can be analyzed. Furthermore, the trapping efficiency of cryotrapping is 100% compared to that obtained with bubbling solutions and traps.<sup>9</sup> However, the technique is very expensive and cannot be used directly in the field.

Uroic et al.<sup>21</sup> developed a cryotrapping/UV–HG–AFS method, which is a promising technique for direct field use for the measurement of arsenic compounds in natural gas. The cryotrapping and coupling technique was equivalent to that used by Cryo/GC–ICP–MS described in this same publication. The only difference is that the detector used was an AFS and that a precursor hydride generation step was performed. A detection limit of 1 μg m<sup>-3</sup> for 20 L of natural gas was obtained. Despite the lack of sensitivity and precision of this technique compared to Cryo/GC–ICP–MS, it is inexpensive and can be used to carry out preliminary measurements directly in the field before moving on to more precise analyses.

**2.2.2. Analysis after Preconcentration.** The bubbling solutions (see section 2.1.1.1) obtained after bubbling the gas sample can be analyzed by ICP–MS to obtain the total arsenic concentration.<sup>4,14,19</sup> ICP–MS is a very sensitive and selective analytical method for the analysis of total arsenic in bubbling/trapping solutions.<sup>4</sup> The detection limit found in the trapping solution and with this type of detector (analysis with reaction cell) is 0.09 ppb.<sup>14</sup> To analyze the total arsenic in the trapping solutions, As species can also be mineralized (addition of nitric acid and concentrated hydrogen peroxide) by microwave assistance to transform all arsenic compounds into arsenate and then analyzed by FAAS (see Figure 1). The detection limit obtained with this analytical method was 5.0 μg L<sup>-1</sup>.<sup>9</sup> Irgolic et al.<sup>2</sup> were able to determine the total arsenic in their trapping solutions by mineralizing these solutions with sulfuric acid. These authors were also able to perform speciation by directly

analyzing these trapping solutions by GC–MS after hydride generation without going through the mineralization step.<sup>2</sup>

The eluate obtained after desorption of arsenic retained on the surface of silica traps can be analyzed by FAAS or ICP–MS with a collision cell (to eliminate ArCl<sup>-</sup> interference) for the determination of total arsenic.<sup>9</sup> Total arsenic can also be determined from the eluate by UV–HG–AFS. UV photo-oxidation converts organic arsenic compounds to inorganic arsenic, and the addition of sodium borohydride to the eluate reduces all inorganic arsenic compounds to arsine. The detection limit obtained with the UV–HG–AFS technique is 1 μg m<sup>-3</sup> for 20 L of sampled gas.<sup>21</sup>

### 3. SAMPLING AND ANALYSIS OF As IN HYDROCARBON LIQUIDS

**3.1. Sample Preparation.** **3.1.1. Microemulsions.** The microemulsion technique consists of stabilizing a liquid hydrocarbon sample in the form of a microemulsion before analysis. There are two types of microemulsions: those prepared with surfactants and those prepared without detergents.

Detergent-free microemulsions involve creating a homogeneous solution using three components. This solution is usually composed of the sample, propan-1-ol, and HNO<sub>3</sub>.<sup>1026</sup> Water can also be added to this solution.<sup>27</sup> The volumetric ratios of these components vary depending on the sample analyzed. However, it was found that, when the volume of the sample was greater than 10% of the final volume of the solution, the solution was not homogeneous.<sup>27</sup> It has been shown that there is no loss of arsenic from detergent-free microemulsions over time.<sup>26</sup> Despite this, arsenic recoveries in detergent-free microemulsions are 2.5% lower than those obtained in surfactant microemulsions.<sup>27</sup>

Surfactant microemulsions consist of mixing the sample with Triton X-100. The concentration and amount of surfactant added vary from author to author.<sup>27,28,29</sup> When the sample volume is greater than 20%, the solution obtained with Triton X-100 is biphasic even after immediate stirring after its addition.<sup>27</sup> Microemulsions prepared with Triton X-100 are stable for at least 2 h.<sup>28</sup> The recovery rates of arsenic in microemulsions are 86% with the addition of 2.5% Triton X-100<sup>29</sup> and close to 100% with the addition of 4% Triton X-100.<sup>27</sup>

Both of these microemulsion techniques do not require any further sample pretreatment, are rapid techniques, and allow for the accurate determination of arsenic in liquid hydrocarbons.<sup>27,28</sup> Finally, these preparations reduce background noise and make the signal more stable during analysis.<sup>29</sup>

**3.1.2. Extraction, Mineralization, and Digestion.** Liquid hydrocarbons can be mineralized to analyze the arsenic contained in them. This step destroys the matrix and therefore limits interference with the matrix during the analysis. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), HNO<sub>3</sub>, or hydrogen chloride (HCl) can be used, as well as water, to carry out this mineralization.<sup>33031</sup> A potassium permanganate (KMnO<sub>4</sub>) solution can be added to facilitate mineralization.<sup>31</sup> Iodine can also be added to the solution to increase the water solubility of the arsenic compounds.<sup>30</sup>

The arsenic compounds can also be extracted from the matrix without destroying the matrix. In crude oil samples, a liquid–liquid extraction of arsenic compounds can be performed with HNO<sub>3</sub>.<sup>26</sup> In naphthas, a liquid–liquid extraction of arsenic compounds can be performed with a solution of sodium hypochlorite (NaOCl), H<sub>2</sub>SO<sub>4</sub>, and water followed by digestion of the obtained aqueous solution (ASTM UOP946-96, n.d.).

**Table 1. Summary of Sample Preparation Methods Used for Arsenic Concentration Analysis with Their Detection Limits (MDLs)**

ref	sample type	sample processing	analysis	MDL
Microemulsions				
27	gasoline and kerosene	detergent-free microemulsion (propan-1-ol + HNO <sub>3</sub> + water) and surfactant emulsion (Triton X-100 (in HNO <sub>3</sub> ))	ETAAS	2 μg L <sup>-1</sup>
10	naphtha, gasoline, and petroleum condensate	detergent-free microemulsion (propan-1-ol + HNO <sub>3</sub> )	GFAAS	1.9 μg L <sup>-1</sup>
26	diesel and naphtha	detergent-free microemulsion (propan-1-ol + HNO <sub>3</sub> )	GFAAS	diesel: 1.8 μg L <sup>-1</sup> naphtha: 1.5 μg L <sup>-1</sup>
40	naphtha	surfactant emulsion (Triton X-100 (in HNO <sub>3</sub> ))	ETAAS	2.7 μg L <sup>-1</sup>
29	naphtha	surfactant emulsion (Triton X-100 (in water))	ICP-MS	0.1 μg L <sup>-1</sup>
Extraction, Mineralization, and Digestion				
30	gasoline	iodine/HNO <sub>3</sub> mineralization	ETAAS	5.6 μg L <sup>-1</sup>
34	naphtha	chemical extraction and HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub> digestion	HG-AAS	
26	gasoline	HNO <sub>3</sub> extraction	GFAAS	1.2 μg L <sup>-1</sup>
32	oil	extraction in solid surface	DDP	0.016 ppm
31	diesel	chemical mineralization	GFAAS	
3	refined hydrocarbons, residual fuel oil and crude oil	HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> mineralization	HG + analysis helium-DC plasma	absolute MDL 1.0–0.1 ng
33	butter	combustion in an oxygen bomb, extraction in solid surface and HCl digestion	HG-AAS	5 ppb
16	crude oil cargos	HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> digestion	HG-AAS	10 μg kg <sup>-1</sup>
Dilution and Direct Injection				
13	gas condensate	direct injection	GC-ICP-MS	absolute MDL 0.05 pg
36	crude oil	dilution in xylene	ICP-MS FI-HG-ICPMS	0.04 μg kg <sup>-1</sup> 0.002 μg kg <sup>-1</sup>
38	crude oil	direct injection	GFAAS	5.1 μg kg <sup>-1</sup>
15	condensate and naphtha	dilution in xylene	ICP-MS	0.2 ng g <sup>-1</sup>
39	naphtha and condensate	direct injection	ETAAS	naphtha: 0.56 μg L <sup>-1</sup> condensate: 1.33 μg L <sup>-1</sup>

Arsenic in paraffin or petroleum can be extracted on a solid surface using a microcrystalline naphthalene or cetyltrimethylammonium bromide adsorbent. The detection limit obtained with this solid surface extraction is 0.016 ppm.<sup>32</sup> Arsenic can be extracted on a solid surface using a Chelex 100 column, but the sample must first be burnt in an oxygen bomb.<sup>33</sup>

Liquid hydrocarbons can also be digested to destroy the matrix and analyzed for arsenic. This digestion is usually an acid digestion, where concentrated H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, or HCl is added to the samples to achieve this digestion.<sup>16,32,33,34</sup> Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be added to the acid solution to promote digestion of the matrix.<sup>16</sup>

Brandão et al.<sup>26</sup> determined the concentrations of As found in different liquid hydrocarbon samples by analyzing them with the microemulsion technique developed by them, the mineralization technique developed by Aneva and Iancheva,<sup>30</sup> the technique EPA SW-846 Test Method 30301,<sup>31</sup> and the technique ASTM UOP946-96.<sup>34</sup> The arsenic concentrations found in these samples using these four sample preparation techniques are equivalent, showing their accuracy.<sup>26</sup> Despite this, arsenic remains one of the most volatile elements, which makes it difficult to analyze quantitatively, especially when it undergoes sample preparation or matrix destruction.<sup>35</sup> Moreover, the analysis of arsenic in aqueous medium (after mineralization) could be challenging when there is residual carbon in the solutions,<sup>51,52</sup> as the presence of carbon in the plasma can change the ionization efficiency of As and thus its

response.<sup>13,52</sup> Recently, the LGC (Laboratory of the Government Chemist) recommended adding 5% of MeOH on the mineralized solution in order to saturate the plasma in carbon and to avoid the increase of carbon during mineralization.

**3.1.3. Dilution and Direct Injection.** Liquid hydrocarbons can be directly analyzed without sample preparation, which saves analysis time<sup>36</sup> and minimizes sample handling.<sup>37</sup>

Samples can be either diluted in xylene<sup>15,36</sup> or toluene<sup>13</sup> or injected directly into the analytical instrument.<sup>37–39</sup> It has been shown that the dilution of liquid hydrocarbons in organic solvents increases sensitivity when these samples are analyzed by ICP-MS.<sup>36</sup> However, the difference in volatility of arsenic species such as TMA and TPA (commonly used as standards) may influence the results of ICP-MS analysis as the response, due to a possible fractionation in the spray chamber link to their volatility, could be significantly different. In addition, due to the high viscosity of liquid hydrocarbons, especially fuel oil,<sup>3</sup> the dilution factor must be relatively high, making it even more difficult to analyze arsenic, which is at trace levels in this type of sample.<sup>15</sup>

Direct injection of samples without a dilution step can significantly improve the sensitivity of the method if multiple injections are used.<sup>39</sup> If direct injections are carried out to analyze liquid hydrocarbons by graphite furnace atomic absorption spectrometry (GFAAS), a chemical modifier must be added to the sample (see section 3.2.1) to ensure that the pyrolysis temperature is sufficiently high to efficiently destroy

the matrix in the furnace and, above all, that this high pyrolysis temperature does not result in arsenic losses.<sup>26</sup>

The dilution of liquid hydrocarbon samples followed by their analysis can make it possible to analyze the speciation of the arsenic contained in them, particularly by capillary GC–ICP–MS (see section 3.2.2).<sup>13</sup>

**3.2. Analytical Methods. 3.2.1. Analysis by GFAAS.** Liquid hydrocarbon samples that have undergone sample preparation, such as microemulsions, extraction, or digestion (see section 2.1), can be analyzed by GFAAS, also known as electrothermal atomic adsorption (ETAAS). This analytical technique allows for direct analysis of these samples without the need for sample preparation.<sup>10,37,39</sup> Atomic absorption spectrometry is one of the most widely used techniques for analyzing liquid hydrocarbons, but arsenic remains a difficult element to analyze by this technique in complex matrices.<sup>27</sup> When it is coupled with a graphite furnace, this technique provides good sensitivity for arsenic analysis in complex matrices and is a relatively affordable technique compared to ICP–MS.<sup>26,37</sup> This technique consists of introducing the sample into a graphite furnace so that it is first pyrolyzed and then atomized. The arsenic is then analyzed by AAS. Temperatures and atomization times vary from 2100 to 2600 °C and from 2 to 10 s, respectively; the carrier and purge gas used is usually argon.<sup>10,26–28,30,31,37,39</sup>

To apply such high pyrolysis and atomization temperatures without loss of arsenic, a chemical modifier must be injected into the furnace during the GFAAS analysis.<sup>39</sup> The most widely used chemical modifier, also known as the “conventional” or “universal” modifier, is Pb/MgNO<sub>3</sub>.<sup>26,27,31,37</sup> Triton X-100 can be added to this chemical modifier to improve the analytical signal during analysis.<sup>10,36</sup> Other chemical modifiers can be used, such as Ni(NO<sub>3</sub>)<sub>2</sub><sup>1,26,30</sup> and La<sub>2</sub>O<sub>3</sub>.<sup>39</sup> The latter provides a better detection limit for arsenic analysis in naphthas of 0.56 μg L<sup>-1</sup> than the detection limit obtained with palladium, rhodium, tungsten, silver, and mixed palladium and magnesium modifiers.<sup>39</sup> So-called “permanent” modifiers such as ruthenium<sup>27</sup> and iridium<sup>28</sup> can also be used. The iridium permanent modifier has been shown to improve the sensitivity of the analysis compared to the “conventional” chemical modifier of Pb/MgNO<sub>3</sub>.<sup>28</sup>

The detection limits obtained for arsenic analysis by GFAAS are between 0.5 μg·L<sup>-1</sup> and 5.6 μg·L<sup>-1</sup>.<sup>10,26–28,30,31,37–39</sup> They are presented in Table 1.

**3.2.2. Analysis by ICP–MS.** Microemulsions and diluted liquid hydrocarbons (see section 2.1) can also be analyzed by ICP–MS. This technique is very sensitive and allows for the analysis of complex matrices with minimum sample preparation but remains very expensive.<sup>26</sup>

To introduce the sample into the instrument, Olsen et al.<sup>15</sup> used a Meinhardt–Scott chamber and obtained good analytical precision and a detection limit of 0.2 ng g<sup>-1</sup> for arsenic. de Albuquerque et al.<sup>36</sup> used a concentric micronebulizer coupled to a refrigerated cyclonic spray chamber and obtained a detection limit of 0.04 μg kg<sup>-1</sup>. The carrier and nebulizer gas used is generally argon.<sup>13,15,29,36</sup> To avoid carbon deposition problems and to ensure plasma stability, O<sub>2</sub> should be used as an auxiliary gas in the analysis of liquid hydrocarbons by ICP–MS.<sup>29,36</sup>

Arsenic can also be analyzed by FI–HG–ICP–MS.<sup>36</sup> After acid digestion of the sample, HCl is added to the digestate to convert As(V) to As(III). The solution is then mixed with NaBH<sub>4</sub>, and the hydrides are separated in a liquid–gas separator and introduced directly into the ICP–MS instrument. The

detection limit obtained with this technique is very low, i.e., 0.002 μg kg<sup>-1</sup>, but the generation of hydrides lengthens the analysis time compared to analysis by ICP–MS alone.<sup>36</sup>

Speciation of arsenic in liquid hydrocarbons, especially in gas condensates, can be carried out using ICP–MS coupled with capillary GC.<sup>13</sup> The absolute detection limit obtained with this technique is 0.05 pg, but this technique makes it difficult to identify certain peaks of arsenical compounds that interfere with other peaks of other compounds present in the analyzed samples.<sup>13</sup>

**3.2.3. Analysis by Other Methods.** Arsenic in liquid hydrocarbon samples can be analyzed by atomic absorption spectrometry after hydride generation (HG–AAS). Generally, prior to hydride generation, reagents such as ammonia–water and HCl,<sup>33</sup> ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) (ASTM UOP946-96, n.d.), and mixture of hydrochloric acid + hydroxylammonium chloride + potassium iodide as well as ascorbic acid<sup>16</sup> are added to the sample to adjust the pH. To generate the hydrides, NaBH<sub>4</sub><sup>33</sup> alone or a solution of NaBH<sub>4</sub> and sodium hydroxide (NaOH)<sup>16,34</sup> are added to the sample as reducing agents. Generally, HCl is added throughout the analysis, and the measured wavelength for arsenic is 193.7 nm.<sup>33,34</sup> The detection limit obtained for arsenic analysis by HG–AAS is approximately 10 ppb (see Table 1).

After extraction on a solid surface, arsenic in oil can be analyzed by differential pulse chromatography (DPP).<sup>32</sup> HCl–pyridine–NaCl is often used as the supporting electrolyte. This method is simple, fast, and selective and has a detection limit of 0.016 ppm.<sup>32</sup>

After mineralization, arsenic compounds in crude oil can be analyzed by helium-DC plasma after hydride generation.<sup>3</sup> A buffer of oxalic acid was added to the ore to adjust the pH to identify and quantify the arsenic compounds in the samples. With this buffer, arsine, arsenate, methyl arsenate, dimethyl arsenate, and trimethyl arsenate compounds were observed in the crude oil samples.<sup>3</sup>

## 4. SAMPLING AND ANALYSIS OF As IN THE NEW ENERGY FEEDSTOCK DOMAIN

Arsenic is present in many biomasses, including plants,<sup>41,42,43</sup> paper,<sup>44</sup> pig manure,<sup>18</sup> sludge,<sup>45</sup> and wood.<sup>46</sup> The byproducts resulting from this biomass are bio-oils as well as biogas and can be obtained notably by pyrolysis<sup>41,42,43,45,46</sup> or by coliquefaction.<sup>18</sup> These byproducts formed from these As-contaminated biomasses thus remain contaminated with this element.

To determine the total As concentration in bio-oils, they must first undergo digestion. This digestion process is usually performed by adding HNO<sub>3</sub> and HCl to the bio-oil samples.<sup>18,42–43,44,46</sup> Digestion can also be performed by adding HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub><sup>41</sup> or by adding HNO<sub>3</sub>, HF and HClO<sub>4</sub>.<sup>45</sup> Digestion of bio-oil samples can be promoted by performing microwave-assisted digestion after the addition of reagents.<sup>18,42,43,46</sup> Arsenic in these digestates is usually analyzed by ICP–MS.<sup>41–45</sup> Arsenic can also be analyzed in digestate by ICP–optical emission spectroscopy (OES),<sup>46</sup> with a detection limit of 25 mg/kg.<sup>18</sup> The total As concentrations found in bio-oils are in the mg kg<sup>-1</sup> range.<sup>41,43–45</sup>

To analyze total As as well as its speciation in biogas, there are different sampling and analytical methods. Biogas can bubble in HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> solutions contained in three bubblers in series. The total arsenic trapped in these bubbler solutions was then analyzed by ICP–MS.<sup>47,48</sup> Arsenic in biogas can also be trapped by passing a biogas stream through a silica trap impregnated with

1% AgNO<sub>3</sub>.<sup>49</sup> The arsenic retained within the trap is desorbed with boiling concentrated HNO<sub>3</sub>. The eluate was then analyzed by UV–HG–AFS to determine total arsenic. Arsenic speciation can be determined from the eluate of this tube by adding concentrated H<sub>2</sub>O<sub>2</sub> and analyzing this solution by HPLC–ICP–MS.<sup>49</sup> With this analytical technique, Mestrot et al.<sup>50</sup> was able to quantify TMA, dimethylarsine, and arsine in biogas samples. Finally, biogas can be sampled in Tedlar bags, and the speciation of arsenic contained in it can be directly determined by Cryo/GC–ICP–MS after transferring the biogas contained in the Tedlar bag to a Cryo-Catcher column.<sup>17</sup>

## 5. CONCLUSION

Various sampling techniques, sample preparation methods, pretreatment methods, and analytical methods for As concentration determination in the petroleum industry have been described in this review. However, most articles have focused on laboratory methods, but potential artifacts related to on-site sampling/analysis have not been comprehensively discussed. Determining arsenic compounds in gaseous and petroleum effluents is difficult due to the possibility of contamination, loss by adsorption, or the occurrence of chemical reactions related to changes in temperature, pressure, and redox conditions. In the petroleum industry, the difficulty is not in obtaining samples, performing analyses, or even detecting arsenic with a sufficiently low detection limit but in preparing the sampling campaign while anticipating the validation of the results by identifying and eliminating all possible artifacts related to the on-site environment. With the increasing development of new energy feedstocks, most of which contain arsenic, the determination of arsenic in biogas and bio-oil has become important. The proper consideration of potential artifacts related to the sampling and analysis of these fluids should be predominant to validate the concentration of arsenic found in these new fluids. Therefore, additional work is still needed to identify artifacts and avoid them by using appropriate sampling/analysis methods.

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