

Simultaneous Total and Speciation Analysis of Volatile Arsenic Compounds in Gas and Liquefied Gas Samples using GC-ICP-MS



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Introduction

Volatile metal(loid) elements and compounds are present in many different types of gas and liquefied gas samples, such as natural gas and biogas. Arsenic (As) is one of the most prevalent elemental impurities in such samples, and it is of interest in many industries, including gas exploitation and processing, and polymer manufacturing. In addition to its potential toxicity and effect as an environmental contaminant, As must be carefully monitored and controlled in the petrochemical and polymer industries. Its presence in monomer gases such as ethylene and propylene affects the properties of polymers synthesized from these gases. Volatile forms of As are also highly active catalyst poisons. Importantly, the toxicity of As depends on the chemical species, with arsine being the most toxic form. Reliable analytical methods are required, therefore, for both total and speciation analysis of As compounds in gaseous samples.

Gas chromatography (GC) coupled with a mass spectrometer-based detector provides a powerful solution for As speciation analysis. However, such systems are not always suitable for total As determination in gas samples, because species that do not elute from the column (i.e. associated with particulate matter) cannot be detected.

In this study, a novel GC-ICP-MS method was used that combines As speciation analysis and total elemental As determination in one measurement. The potential of the method for the simultaneous determination of total elemental concentrations and individual species of other elements, such as Hg, in gases is also shown.

Experimental

Gas standards and samples

An arsine (AsH_3) standard in nitrogen (N_2) (Linde AG, Munich) was used for quantification purposes. Liquefied butane pressurized under N_2 and doped with AsH_3 (ISGAS, USA) and a real propylene sample from a cracker plant (Borealis, Sweden) were analyzed.

Instrumentation

An Agilent 7890B GC equipped with two interconnected gas sampling valves and a J&W GS-GasPro column (60 m, 0.32 mm id) was used. The GC was coupled to an Agilent 7900 ICP-MS using an Agilent heated GC-ICP-MS interface (G3158D). A gas dilutor GasMix Aiolos II and a vaporizer chamber (Alytech, France) were used for online dilution of the samples and standards. Optimized GC and ICP-MS parameters are summarized in Table 1.

Table 1. Optimized GC and ICP-MS parameters.

| ICP-MS parameters | | | GC parameters | |
|----------------------------|---------|-----|---|-------|
| Cell gas mode | No gas | He | Column flow (mL/min) | 3 |
| RF power (W) | 1600 | | Transfer line flow (mL/min) | 5 |
| Sampling depth (mm) | 8 | | Oven gradient 40 to 250 °C in 5 min, 2 min at 250 °C | |
| Dilution gas (L/min) | 0.3–0.4 | | | |
| N_2 flow (mL/min) | 10 | | | |
| Extraction 1 lens (V) | 0 | | | |
| Extraction 2 lens (V) | -200 | | Injection mode | Split |
| Omega bias lens (V) | -80 | | Split ratio | 1:6 |
| Omega lens (V) | 10 | | GC-ICP-MS interface temperature (°C) 250 | |
| Cell entrance lens (V) | -30 | -40 | | |
| Cell exit lens (V) | -50 | -60 | | |
| Deflect lens (V) | 10 | 0 | | |
| Plate bias lens (V) | -100 | -60 | | |

New instrumental set-up

A diagram of the GC-ICP-MS configuration is shown in Figure 1. The gas standard, sample, and dilution gas are connected to the dilutor (top right). When a liquefied gas is analyzed, a vaporizer chamber (fixed at 120 °C) is placed between the sample and the gas dilutor inlet so the sample can be vaporized before dilution. When gaseous samples are analyzed, the vaporizer is bypassed and the gas is introduced directly into the dilutor. A 3-way valve allows the dilutor outlet gas flow to be directed to the GC through the gas sampling valves (GSV) 1 and 2 (solid line in the lower part of Figure 1). GSV1 and GSV2 are connected internally, so they are loaded at the same time.

Injection from the two valves can be controlled independently via the ICP-MS MassHunter chromatography method settings, but in this method, both valves were injected at the same time.

When the GSVs are turned to the inject position, the gas volume loaded into GSV1 is injected through the injection port of the GC to the analytical column. Conventional GC separation of the different species is then carried out to separate the individual species as they pass through the GC column to the ICP. Simultaneously, the gas volume loaded into GSV2 is injected into the inert (fused silica deactivated, 5 m, 0.32 mm id) transfer line leading directly to the GC-ICP-MS interface. The transfer line is placed inside the GC oven and heated to the initial temperature of the GC program. The GSV2 gas volume bypasses the GC column and is quickly transferred to the 3-way connector at the column exit. Using this configuration, the gas that was loaded into GSV2 enters the GC-ICP-MS interface and is transferred to the ICP before the dead volume of the GSV1 injection has passed through the GC column. Such direct transfer of the gas volume allows a multi-element Flow Injection Analysis (FIA) to be performed for any ICP-detectable elements present in the gaseous samples. This option allows for fast total analysis and can be used to assess overall recovery of the element from the GC column (i.e. some elemental species might not be eluted from the GC column, for example, when elemental species are adsorbed onto particulate matter).

The ends of both the inert transfer line (for total elemental analysis) and the analytical column (for speciated analysis) are connected to the GC-ICP-MS interface with a two-hole ferrule. At this point, the gas flows are mixed online with the carrier Ar gas flow (previously heated in the pre-heating pipe located inside the GC oven) and transferred through the heated GC interface to the ICP-MS plasma. Using this approach, total and speciation analysis of the elements of interest can be performed simultaneously, on the same sample injection, in a simple, and reproducible way.

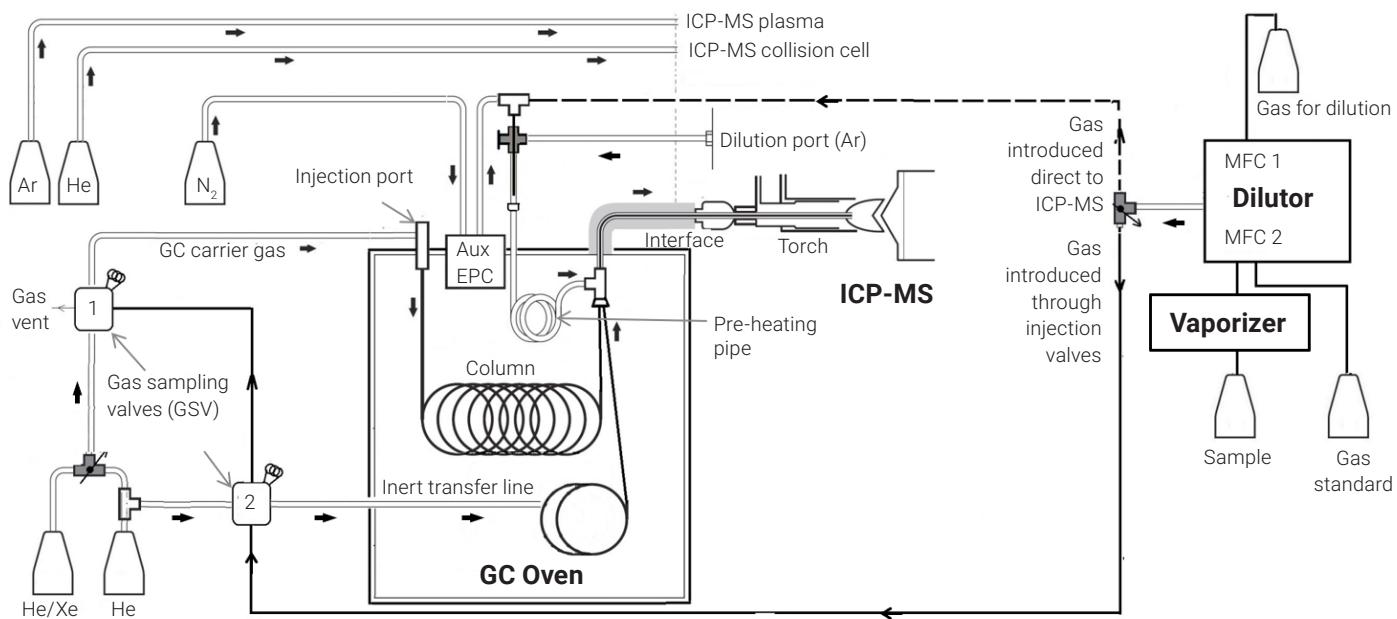


Figure 1. Diagram of the GC-ICP-MS instrumental set-up for simultaneous total and speciation analysis (Reprinted with permission from Laura Freije-Carrelo et al, Anal. Chem., 2017, 89 (11), pp 5719–5724. Copyright 2017 American Chemical Society).

Using the same system configuration, the 3-way valve after the gas dilutor can be used to divert the gas flow directly to the GC-ICP-MS interface (dashed line in upper-right part of Figure 1), bypassing the gas sampling valves and GC column. Using a cross piece, this flow is mixed with the ICP-MS Ar dilution gas before entering the pre-heating pipe. This setup supports:

- Optimization of the ICP-MS operating conditions by allowing monitoring of the continuous signal of the analytes present in the gas standard/sample.
- Analysis using a fast, qualitative screening acquisition to find out whether the sample contains the target elements and if subsequent quantitative analysis is necessary.

Also, a second 3-way valve is installed (lower left part of Figure 1) for selection of the GC carrier gas. The valve allows the carrier gas to be switched from He to a mixture of Xe in He for optimization of the torch position and ICP-MS sensitivity. Finally, an auxiliary electronic pressure control (Aux EPC) controls the addition of a constant pressure of N₂ into the Ar dilution gas flow that is added to the column/bypass flow at the entrance of the GC-ICP-MS interface. Addition of N₂ has been shown to enhance As sensitivity in GC-ICP-MS applications [1].

Results and Discussion

An AsH₃ in N₂ standard was used to optimize the operating conditions of the system. Chromatograms of a 68 ppb (v/v) arsine standard in N₂ and a N₂ blank are shown in Figure 2. The N₂ blank chromatogram is shown on a y-axis scale that is approximately two orders of magnitude lower than the scale used for the AsH₃ sample. As can be seen, the first peak in the arsine standard chromatogram appears at 0.2 min, corresponding to the total As eluted from the inert transfer line (column bypass flow). A second peak is observed at 3.8 min, corresponding to the speciation analysis (AsH₃ eluted from the column). The chromatogram demonstrates that total and speciation analyses can be performed simultaneously within the same injection.

The difference in the peak area observed for total and speciation analysis is due to the split ratio used (1:6) in the GC injector. No adsorption or loss of analyte is expected in the inert transfer line. Therefore, the comparison between the experimentally obtained and the expected theoretical GC inlet split ratio can be used to assess if the total As observed is exclusively in the form of AsH₃ or if other As species are present in the sample. Integration of peak areas for the “total As” and AsH₃ in each point of a calibration curve from 0.2 to 68 ppb (n=13) showed a mean recovery for the AsH₃ peak of 89 ±11 % of the total As in the standard. The results indicate

that, as expected, As is exclusively present as arsine in the standard. Note that an accurate and precise split ratio is assumed for such mass balance calculations. Also, the As peak coelutes with the sample matrix in the total analysis (column bypass) measurement, so sensitivity may not be consistent for both direct and GC conditions. These two facts could explain the significant uncertainty (12% RSD) observed for the calculated recovery.

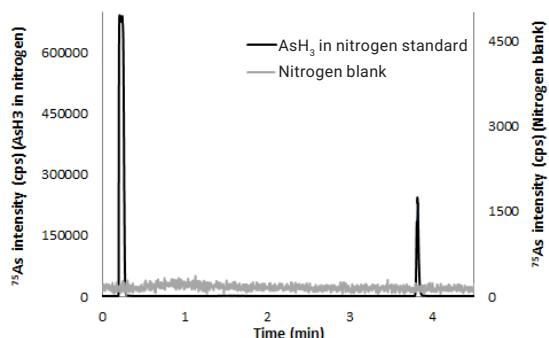


Figure 2. Chromatogram of arsine in nitrogen (68 ppb, v/v). (Reprinted with permission from Laura Freije-Carrelo et al, Anal. Chem., 2017, 89 (11), pp 5719–5724. Copyright 2017 American Chemical Society).

Calibration curves were generated for “total As” and speciation (AsH_3) analysis based on AsH_3 standard levels from 0.2 to 68 ppb, as shown in Figure 3. The method showed good linearity within the tested range of concentration for both total ($r^2=0.9996$) and speciation analysis ($r^2=0.998$). Detection limits of 2 ppt for total As and 12 ppt for AsH_3 by speciation analysis were obtained. To the best of our knowledge, these are the lowest DLs for direct total As and AsH_3 speciation analysis in gaseous samples ever reported in the literature.

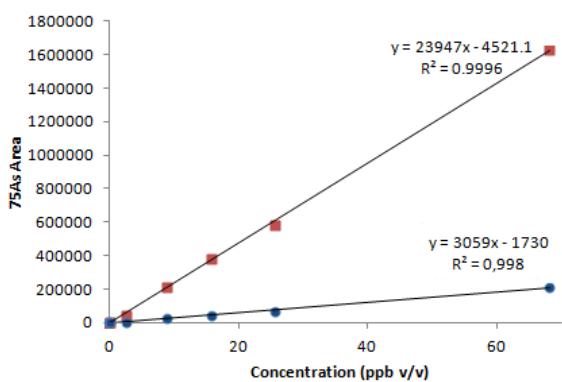


Figure 3. Calibration curves for “total As” (red points) and AsH_3 (blue points) using arsine standards.

Synthetic sample analysis

Liquefied butane doped with a non-certified level of arsine was analyzed as a synthetic sample. Helium mode was used for analysis of the samples to minimize the occurrence of any polyatomic interferences. The vaporization chamber was set at 120 °C and connected online with the gas dilutor to vaporize the sample. A chromatogram of butane diluted 1:7 in Ar is shown in Figure 4.

Results obtained for total and arsine speciation analysis are given in Table 2. The synthetic butane sample was also analyzed by the producer (ISGAS) and an independent lab, with results of 218 and 40 ppb arsine, respectively. The wide range of these results illustrates the difficulty of developing a method for the reliable analysis of gaseous and liquified gas samples. The results obtained in this study are given in Table 2. The measured concentration of ~95 ppb arsine is within the range of concentrations obtained by the other two laboratories, giving confidence in the applicability of the new GC-ICP-MS method.

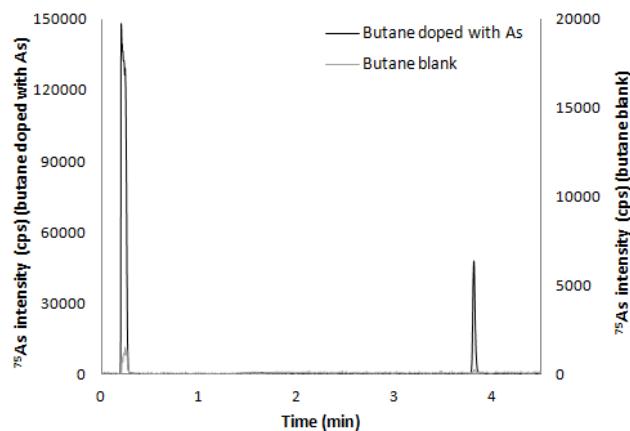


Figure 4. As chromatograms of blank and arsine-doped liquefied butane diluted 1:7. Intensity scale of the butane blank chromatogram is 7.5x lower.

Table 2. Quantitative results (ppb As, v/v) obtained for arsine-doped liquefied butane and propylene samples. Expanded uncertainties (95% confidence level) are given (not including the uncertainty of the arsine in N_2 standard).

| | Liquefied butane | Propylene (gas phase) | Propylene (liquid phase) |
|---------------------|------------------|-----------------------|--------------------------|
| Total analysis | 92 ± 4 | 54 ± 4 | 34 ± 3 |
| Speciation analysis | 95 ± 4 | 53 ± 13 | 31 ± 5 |

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Mercury in butane

The butane sample was also doped with mercury. Hg was measured simultaneously in the same acquisition as As to show the multi-elemental capability of the system. The chromatogram for Hg is shown in Figure 5. As can be seen, signals for both total Hg (first peak) and Hg species (second peak) were clearly detected. However, the peak profile observed for Hg shows much more tailing than the As peak. The peak shape is likely due to unspecific adsorption of Hg species along the valves and devices from the gas cylinder to the ICP. The peak tailing could probably be reduced using a method and conditions optimized for Hg analysis.

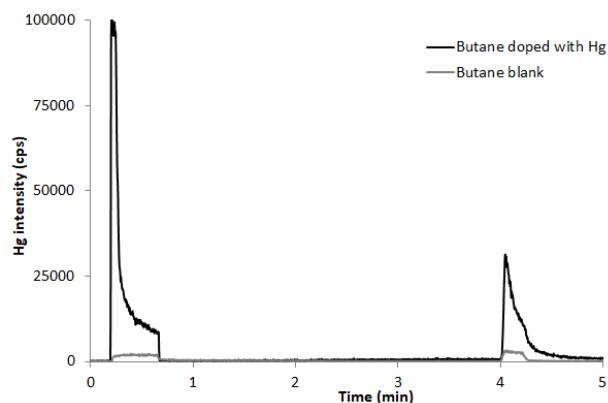


Figure 5. Hg chromatograms of blank and mercury-doped liquefied butane diluted 1:7.

Real sample analysis

Finally, a real propylene sample containing both gas and liquefied phases was analyzed. The vaporization chamber was set at 120 °C and connected online with the gas dilutor for vaporization of the liquid phase of the sample. For the gas phase analysis, the sample was introduced directly to the gas dilutor. Quantitative results are given in Table 2. The results demonstrate that the setup could also be used to assess the partition of total As and its species between gas and liquid phases of liquefied gas samples.

Conclusions

The novel GC-ICP-MS method has been shown to be suitable for the direct, simultaneous quantitative analysis (total and speciation) of ICP-detectable elements such as As and Hg present in gas and liquefied gas samples.

Detection limits in the low ppt levels were obtained for both total As and speciated As analysis without the need for a preconcentration step. The speed of the new GC-ICP-MS method (5 min per injection) makes it convenient for implementation in industrial laboratories. The fast analysis times allow the determination of contaminants to support acceptance or rejection of a stock of gas.

The use of ICP-MS for detection ensures the GC-ICP-MS setup is suitable for simultaneous quantitative analysis (total and speciation) of any ICP-detectable element present in gas and liquefied gas samples.

References

1. Yang Song, Yuhong Chen, Determination of Arsine in Ethylene and Propylene by GC-ICP-MS, Handbook of Hyphenated ICP-MS Applications, 2nd Edition, pp 75–76, Agilent publication 2015, 5990-9473EN.

More Information

This study was originally published in:

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