Agilent ICP-MS Journal

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Ed McCurdy, ICP-MS Product Marketing, Agilent UK

The first issue of Agilent's ICP-MS Journal was published in September 1998, under the Hewlett-Packard Company brand. There have been many developments in ICP-MS technology since then, together with changes in the markets, regulations, and applications that the technique addresses. Over the years, we've reported on many of the key innovations and applications in this exciting field. As the number of Agilent ICP-MS users continues to grow, our mission is to continue to keep you informed of key trends in the field of plasma spectrochemistry.

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Analysis of Total Arsenic and Volatile As Compounds in Gas and Liquefied Gas Samples by GC-ICP-MS

Laura Freije-Carrelo[1], Mariella Moldovan[1], J. Ignacio García Alonso[1], Thuy Diep Thanh VO[2], Jorge Ruiz Encinar[1]
[1]University of Oviedo, Oviedo, Spain; [2]Borealis Polyolefine GmbH, Linz, Austria

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 is one of the most prevalent elemental impurities in such sample-types and its presence in monomer gases such as ethylene and propylene affects the properties of the polymers produced from these gases. Volatile forms of As are also highly active catalyst poisons, so the element must be carefully monitored and controlled in the petrochemical and polymer industries. Importantly, the toxicity of As depends on the chemical species, with arsine being the most toxic form. Reliable analytical methods are required for both total and speciation analysis of arsenic compounds in gaseous samples.

This study presents a novel GC-ICP-MS method to simultaneously perform arsenic speciation analysis and total elemental As determination in one measurement.

Experimental

Gas standards and samples: An arsine (AsH_3) standard in N_2 (Linde AG, Germany) was used for quantification purposes. Liquefied butane pressurized under N_2 and doped with arsine (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 i.d.) was used. The GC was coupled to an Agilent 7900 ICP-MS using Agilent's 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. Details of the novel GC-ICP-MS configuration and operating conditions can be seen in References 1 and 2.

Table 1. Optimized GC and ICP-MS parameters.

GC parameters		
Column flow (mL/min)	3	
Transfer line flow (mL/min)	5	
Oven gradient	40 to 250ºC in 5 min 2 min at 250ºC	
Injection mode	Split	
Split ratio	1:6	
GC-ICP-MS interface temp (ºC)	250	
ICP-MS parameters		
Cell gas modes	No gas	He
RF power (W)	1600	
Sampling depth (mm)	8	
Dilution gas (L/min)	0.3-0.4	
Nitrogen flow (mL/min)	10	
Extraction Lens 1 (V)	0	

Results and Discussion

An arsine in nitrogen standard was used for the optimization of the system operating conditions. Chromatograms of a 68 ppb (v/v) arsine standard in nitrogen and a N_2 blank are shown in Figure 1. The N_2 blank chromatogram is shown on a y-axis scale that is approximately two orders of magnitude lower than the scale used for the arsine sample. As can be seen, the first peak in the arsine standard chromatogram appears at 0.2 min, corresponding to the total arsenic eluted from the inert transfer line (column bypass flow). A second peak is observed at 3.8 min corresponding to the speciation analysis (arsine eluted from the column). The chromatograms demonstrate that total and speciation analysis can be performed simultaneously within the same injection.

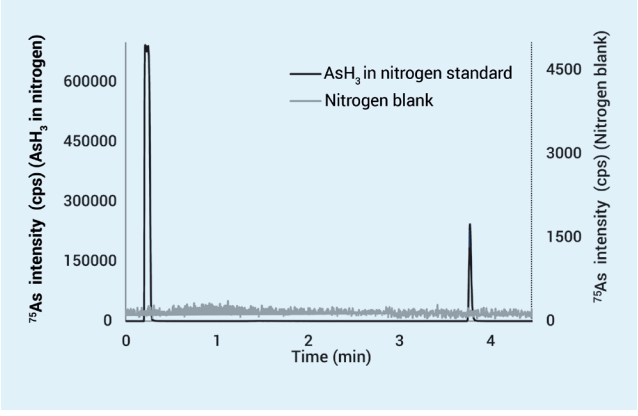


Figure 1. Chromatogram of arsine in nitrogen (68 ppb, v/v). (Reprinted with permission from Laura Freije-Carrelo et al, Anal. Chem., 2017, 89 (11), pp 5719–5724. Copyright 2017 American Chemical Society).

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 arsine or if other As species are present in the sample. Integration of peak areas for the "total As" and arsine in each point of a calibration curve from 0.2 to 68 ppb (n = 13) showed a mean recovery for the arsine peak of 89 ± 11 % of the total As in the standard. This indicates 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. Moreover, the arsenic 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.

Calibration: Calibration curves were generated for "total As" and speciation (AsH_3) analysis based on AsH_3 standard levels from 0.2 ppb to 68 ppb, as shown in Figure 2. The method showed very 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 analyses 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.

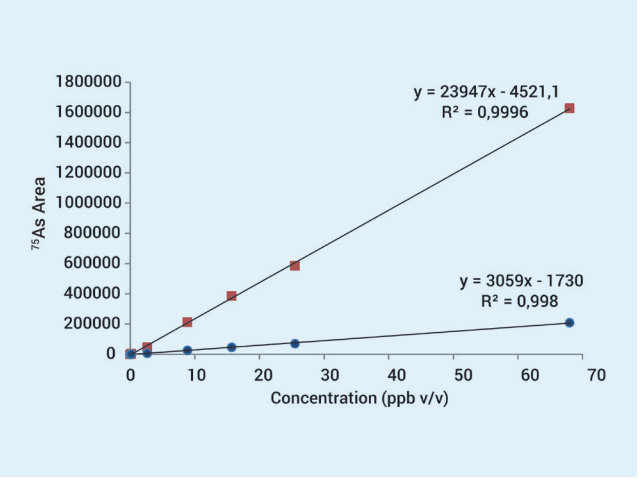


Figure 2. Calibration curves for "total As" (red points) and arsine (blue points) using arsine standards.

Synthetic sample analysis: Liquefied butane doped with a non-certified level of arsine was analyzed as a synthetic sample. He cell mode was used for analysis of the samples to minimize the occurrence of polyatomic interferences. The vaporization chamber was set at 120 ºC and connected on-line with the gas dilutor for vaporization of the sample. A chromatogram of this sample diluted 1:7 in Ar is shown in Figure 3. Results obtained for total and speciation analysis are given in Table 2.

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

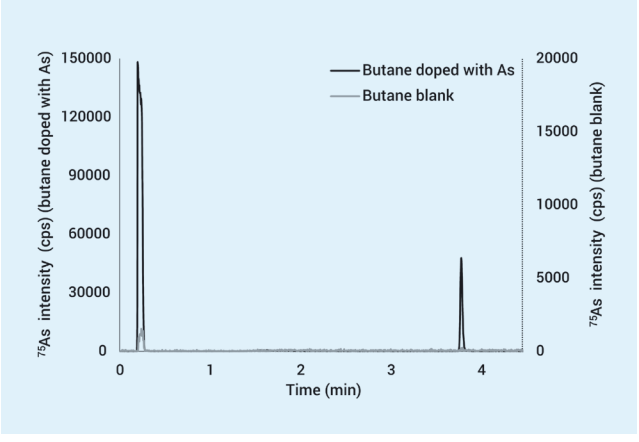


Figure 3. As chromatograms of doped liquefied butane and butane blank diluted 1:7.

Actual sample analysis: A real propylene sample containing both gas and liquefied phases was analyzed. The vaporization chamber was set at 120 ºC and connected on-line with the gas dilutor for vaporization of the liquid phase of the sample. For the gas phase analysis, the sample was introduced directly into the gas dilutor. Quantitative results are given in Table 2. The results demonstrate that the method could also be used to assess the partition of total As and its species between gas and liquid phases of liquefied gas samples.

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

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

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 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 new method is fast (5 min per injection), making it convenient for implementation in industrial laboratories, where rapid determination of contaminants is required to support acceptance or rejection of a stock gas.

References and More Information

1. Laura Freije-Carrelo et al., Instrumental Setup for Simultaneous Total and Speciation Analysis of Volatile Arsenic Compounds in Gas and Liquefied Gas Samples, *Anal. Chem.* **2017**, 89, 5719−5724
2. Agilent publication, 2017, 5991-8799EN

Interference-Free Measurement of Trace Mercury in Tungsten-Rich Cosmetic Samples using ICP-QQQ

Xiang-cheng Zeng[1], Ke Wang[2], Xin-mei Wang[2], Juan-e Song[1], and Donna Hsu[1]
[1]Agilent Technologies Co. Ltd, China. [2]Shanghai Institute for Food and Drug Control, China

Introduction

Many mercury (Hg) compounds are toxic, causing symptoms ranging from skin irritation, headaches, and tremors, through to nervous system damage and renal failure. Because Hg compounds are easily absorbed through the skin, their use in cosmetics is controlled. For example, the US Food and Drug Administration (FDA) does not allow Hg in cosmetics, except under specific conditions where there are no other safe and effective preservatives available [1].

Increasingly, however, Hg has been found in cosmetic products such as skin creams, soap, and lotions sold as "anti-aging" or "skin lightening".

Analysis of Hg by ICP-MS: Hg is a challenging element to determine at low levels by ICP-MS. It has a high first ionization potential (10.44 eV), so is relatively poorly ionized in the plasma, leading to low sensitivity. Also, Hg has seven naturally occurring isotopes, each with relatively low % abundance, further reducing sensitivity. Despite these difficulties, ICP-MS can still be used successfully to perform trace-level analysis of Hg. However, some cosmetics contain large amounts of tungsten (W). This leads to polyatomic interferences from WO^+ and WOH^+ that affect all the Hg isotopes, making Hg measurement even more challenging. For example, the most abundant Hg isotopes, ^{200}Hg and ^{202}Hg, suffer overlaps from $^{184}W^{16}O^+$ and $^{186}W^{16}O^+$, respectively. Conventional single quadrupole ICP-MS (ICP-QMS) fitted with a collision/reaction cell (CRC) is unable to resolve the WO^+ and WOH^+ interferences sufficiently to allow the accurate determination of Hg at trace levels.

In this study, the superior interference removal capability of triple quadrupole ICP-MS (ICP-QQQ) in MS/MS mode with O_2 cell gas was used for on-mass detection of Hg in a tungsten matrix. $^{200}Hg^+$ and WO^+ ions at *m/z* 200 enter the CRC. WO^+ reacts with O_2 cell gas to form WO_2^+ and WO_3^+, shifting to higher masses. Hg^+ does not react and so remains at *m/z* 200. Q2 is set to 200 u, allowing $^{200}Hg^+$ ions to pass to the detector free of interference. In MS/MS, reaction chemistry is controlled and consistent because only the target analyte mass enters the CRC. This capability offers a much more predictable and reliable approach to resolving interferences on a wide range of elements.

Experimental

Standards and samples: Mercury standards were prepared in 0.5 % high purity hydrochloric acid (TAMA-Pure-AA-100, Kanagawa, Japan).

A tungsten-rich cosmetic sample was bought from a local store in Shanghai. The liquid sample was weighed to the nearest 0.100 g, and then diluted 100-fold with Milli-Q de-ionized water acidified with 0.5 % HCl. The sample was shaken for a couple of minutes to ensure it was fully homogenized.

Instrumentation: An Agilent 8900 Standard configuration ICP-QQQ was used. The standard sample introduction system was used, comprising a glass concentric nebulizer, quartz double-pass spray chamber, 2.5 mm injector quartz torch, and Ni interface cones. The ICP-QQQ was operated in no gas mode, with He cell gas, and with O_2 cell gas in both single quad (SQ) and MS/MS modes.

Results and Discussion

Multiple isotope analysis study: To demonstrate the ability of MS/MS to resolve interferences on multiple isotopes, a scan spectrum comparison was made. The mass range of the Hg isotopes was acquired for a simple Hg standard and a solution containing the same concentration of Hg spiked into a high W matrix. The overlaid spectra are shown in Figure 1, confirming that the measured isotopic abundances match the natural Hg isotope pattern despite the presence of the high W matrix in the second sample.

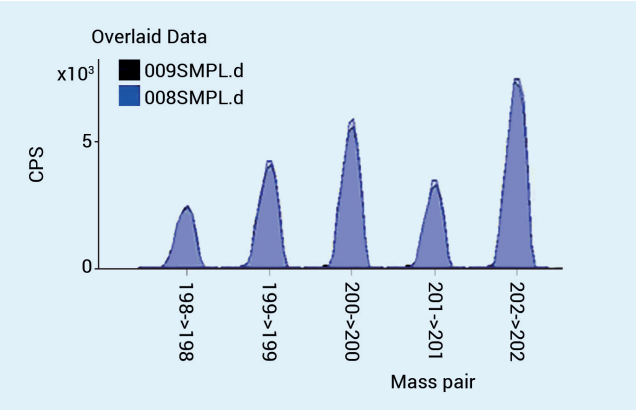


Figure 1. Hg isotopes with and without a W matrix, confirming the complete removal of W-based interferences by ICP-QQQ with MS/MS.

Hg in tungsten-rich samples: Hg was measured in a tungsten-rich cosmetic sample using the four different cell gas modes. The five most abundant isotopes of Hg (198, 199, 200, 201, and 202) were used for quantitation, giving five independently calibrated results for Hg. This approach, which is included in several regulated methods across the environmental, food and pharmaceutical industries, is analogous to the use of "qualifier ions" in organic mass spectrometry. The results are shown in Table 1.

Table 1. Hg concentration measured in 100x diluted tungsten-rich cosmetic sample, quantitated independently using five isotopes (µg/L).

	198	199	200	201	202
No gas	2670	872	1364	47.7	987
He	1732	577	907	24.6	665
O_2 Single Quad	7.72	2.49	3.99	0.028	2.88
O_2 MS/MS	0.021	0.018	0.024	0.015	0.017

Matrix-based interferences affect different isotopes of an analyte to different degrees, so giving different errors in quantitative results. Comparing the elemental concentrations calculated from different isotopes of an element is a useful approach to identify whether the reported concentration was affected by any interferences. The Hg concentrations measured in MS/MS mode with O_2 (around 0.02 µg/L for all five isotopes) are much lower and more consistent than the results measured using the other cell gas modes. The good agreement between the results obtained for the five isotopes shows that O_2 in MS/MS mode can simultaneously remove polyatomic interferences from all five Hg isotopes. The results obtained using O_2 cell gas in single-quad mode suggest that the WO^+ and WOH^+ interferences on ^{201}Hg could be reduced effectively (reported concentration of 0.028 µg/L). However, the other four Hg isotopes gave variable results in this mode, indicating that MS/MS is essential for full control of the reaction chemistry.

Spike recovery test: A spike recovery test was performed with a 30 ppt spike of Hg being added to the diluted sample. Recovery was 104%, confirming the interference removal capability and matrix tolerance of the method.

Conclusions

The 8900 ICP-QQQ operating in MS/MS mode with O_2 cell gas is highly effective for the removal of tungsten oxide/hydroxide polyatomic interferences on the five major Hg isotopes.

- Using an MS/MS on-mass method with O_2 reaction cell gas, Hg was measured accurately and consistently at trace levels in the presence of W.
- Compared to conventional single quadrupole ICP-MS, ICP-MS/MS reduced interferences by more than two orders of magnitude.
- The 8900 ICP-MS/MS method easily meets the requirements of trace level Hg analysis in tungsten-rich cosmetic samples.

References

1. Federal Food, Drug, and Cosmetic Act (FD&C Act), accessed December 2017, https://www.fda.gov/Cosmetics/GuidanceRegulation/LawsRegulations/ucm2005209.htm
2. N. Sugiyama and G. Woods, Agilent publication, 2012, 5991-0892EN.
3. J. Song, X. Zeng, D. Yan and W. Wu, Agilent publication, 2015, 5991-5400EN.
4. L. Balcaen, E. Bolea-Fernandez, M. Resano, F. Vanhaecke, *Anal. Chim. Acta*, **2015**, 894, 7–19.

Japan Hosts Another Successful Asia-Pacific Winter Plasma Conference

Sayuri Otaki, Global Marketing Manager – ICP-MS, Agilent Technologies International Japan

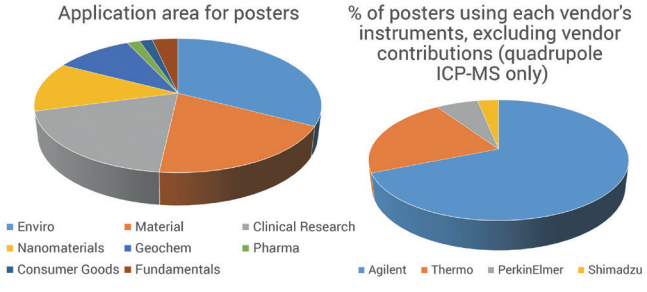
Introduction

The first Asia-Pacific Winter Conference on Plasma Spectrochemistry (APWC) was held in Thailand in 2005. Since then, the event has also been held in Japan, China, and Korea. The APWC returned to Japan in November 2017, where more than 210 attendees from around the world gathered in the historic coastal city of Matsue for the seventh APWC.

The major topics discussed at the conference reflect the wider trends in the developments of plasma spectrochemistry. These topics – including single nanoparticle and single cell analysis, laser ablation, isotope ratio and isotope dilution, and speciation – were covered in the general sessions and the five plenary lectures delivered by leading international researchers Gary Hieftje. Ryszard Lobinski, Jörg Feldmann, Marcel Burger, and Frank Vanhaecke.

Poster Review

A review of the 90 poster presentations showed that more than 25% of the posters related to environmental applications. Materials analysis and clinical/life science research is also a large and growing segment for ICP-MS. The review also showed that Agilent ICP-MS and ICP-QQQ systems were used in more than half of the posters.



Agilent's Contribution - A Team Effort

Agilent's ICP-MS product line is based in Tokyo – a short flight away from Matsue. Given the proximity, Agilent was well represented at the conference with an experienced team in attendance from Japan, plus field representatives from other Asian countries.

Hot Topic: Single Nanoparticle (SNP) Analysis

Agilent's luncheon seminar on Single Nanoparticle (SNP) analysis attracted over 100 attendees, highlighting the wide interest in SNP analysis from researchers and industry.

Why MS/MS? Explaining the unique benefits

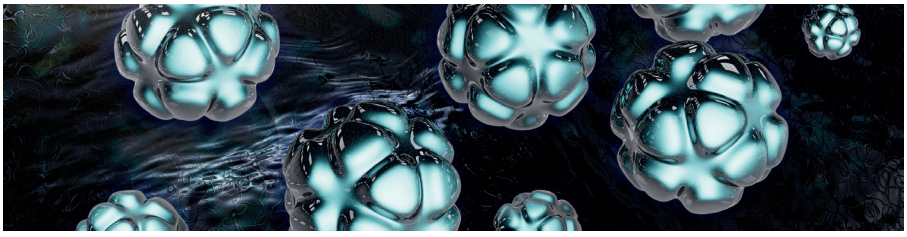
In an oral presentation, Senior Agilent Applications Chemist, Michiko Yamanaka, presented a technical and performance comparison of MS/MS vs Bandpass MS. The talk illustrated how MS/MS gives improved control of reaction chemistry.

Agilent's Michiko Yamanaka presenting at the APWC.

Details of the next APWC will be available soon.

On-Demand Webinars

The application of ICP-MS for the characterization of single nanoparticles in biological and environmental water samples



This webinar discusses the use of single-particle (sp-) ICP-MS as an emerging analytical technique for the measurement of nanoparticles. Includes sample preparation, method optimization, and data interpretation.

Presenter: Arturo Keller, Professor of Biogeochemistry, University of California, Santa Barbara, USA

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How does ICP-MS improve productivity and profitability in the environmental laboratory?

This presentation examines practical ways to configure ICP-MS for the analysis of the wide variety of matrices typically encountered during routine operation at an environmental testing laboratory. Techniques for ensuring calibration stability and effective control of interferences are discussed.

Presenter: Richard Burrows, Corporate Technical Director, TestAmerica, USA

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Agilent ICP-MS Publications

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- **Application note:** Simultaneous Total and Speciation Analysis of Volatile Arsenic Compounds in Gas and Liquefied Gas Samples using GC-ICP-MS, 5991-8799EN
- **Application note:** Direct Analysis of Trace Metal Impurities in High Purity Nitric Acid using ICP-QQQ, 5991-8798EN
- **Application note:** Multielement Analysis and Selenium Speciation in Cattle and Fish Feed using LC-ICP-QQQ, 5991-9015EN
- **Application note:** Absolute Quantification of Proteins in Snake Venom Using capLC-ICP-QQQ and Online Isotope Dilution Analysis, 5991-9016EN

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