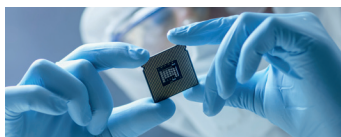


October 2020, Issue 82



Page 1

Agilent ICP-MS Methods for a Range of Contaminants

Pages 2-3

GC-ICP-QQQ Method to Measure Trace Contaminants in Arsenic Gas Used for III-V Compound Semiconductors

Pages 4-5

HPLC-ICP-MS Supports Newly Approved US FDA Limit for Inorganic Arsenic in All Types of Infant Rice Cereals

Page 6

Agilent Japan Welcomes Semiconductor Users for Live Webinar to Introduce Recent Solutions Using ICP-QQQ

Page 7

Executive Summary Articles for Webinar Series on Improving Data Quality in ICP Methods

Page 8

Spectroscopy Article on ICP-MS/MS for Analysis of Sulfur and S Isotope Ratios; Latest Agilent ICP-MS Publications

Agilent ICP-MS Methods for a Range of Contaminants

ICP-MS is used to accurately determine contaminants across a range of different industries and sample types. In this issue of the Journal, we illustrate this with a range of very different ICP-MS applications.

An article from Consci, Ltd in the US describes a new GC-ICP-QQQ method to measure trace hydride gas contaminants in arsine (AsH_3), a precursor used in manufacturing gallium arsenide and other semiconductors.

Agilent Japan recently hosted an online webinar series for ICP-QQQ users in the semiconductor industry. Topics covered included trace chlorine analysis in organic solvents, and analysis of iron nanoparticles down to 15 nm diameter and ppq concentrations.

Finally, monitoring contaminants in food is discussed in an article updating the status of an FDA method using HPLC coupled to ICP-MS for inorganic arsenic analysis in infant rice cereals.



Figure 1. Agilent 7900 ICP-MS coupled to an Agilent 1260 HPLC: one example of the integrated speciation systems available from Agilent.

GC-ICP-QQQ Method to Measure Trace Contaminants in Arsine Gas Used for III-V Compound Semiconductors

William M. Geiger¹, Blake McElmurry¹, Jesus Anguiano¹, Mark Kelinske². ¹Consci, Ltd., Pasadena, Texas, USA, ²Agilent Technologies Inc.

Beyond silicon semiconductors

Modern electronics are mostly based on silicon semiconductors, but some devices require alternative materials with different properties. One example is III-V compound semiconductors, which consist of elements from groups III and V of the periodic table. These compounds usually contain Al, Ga, or In (from Group III) combined with N, P, As, or Sb (from Group V). Among the most widely used III-V compounds are gallium arsenide (GaAs), aluminum gallium arsenide (AlGaAs), and indium gallium arsenide nitride (InGaAsN), all of which are manufactured using arsine gas (AsH_3) as a precursor.

The appeal of III-V compounds is that they have much higher “carrier mobility” than silicon, which means charge can pass more freely through the crystal lattice. This property enables higher performance and greater chip density with lower power consumption and less heat generation; critical factors in microelectronics. As a result, III-V compound semiconductors are increasingly used in devices such as high electron mobility transistors (HEMT) and field effect transistors (FET).

Another benefit of III-V compound semiconductors is that, unlike Si semiconductors, they can emit light, which is fundamental to the large and growing field of optoelectronics. Light emitting diodes (LED) are widely used in lighting, monitors, displays, consumer electronics, illuminated switches, and infrared remote controls. Other III-V compound semiconductor devices include vertical-cavity surface-emitting lasers (VCSEL), which improve the efficiency of fiberoptic communications.

The properties of an optoelectronic device are controlled by the composition of the semiconductor. For example, the wavelength of light emitted by an LED is determined

* The band gap is the difference between the highest energy level of “bound” electrons and the lowest energy level of “mobile” electrons. An electron moving between these states emits light of a characteristic wavelength.



Figure 1. LEDs can be manufactured with a wide range of different wavelengths depending on the semiconductor material and dopants.

by the “band gap” (or energy gap)* of the semiconductor material used. Ternary (three element) or quaternary (four element) mixtures of III-V compounds are used to manufacture LEDs with band gaps that emit different wavelengths, from infrared, through visible wavelengths, to ultraviolet. The reverse process, where photon energy (light) is converted to electron mobility, is the principle that underpins photovoltaic (PV) electricity generation.

Mixed materials and deliberately added dopant elements are used to control the electrical and optical properties of the semiconductor device. But unwanted contaminants also affect the material's properties, for example by changing the energy gap of the semiconductor material, altering carrier mobility, or reducing breakdown voltage.

Contamination from n-type (negative) dopant elements – such as Si, P, S, and Ge – affects the performance and reliability of devices made from III-V compound semiconductors. Therefore, it is critical to determine the level of silane (SiH_4), phosphine (PH_3), hydrogen sulfide (H_2S), and germane (GeH_4) impurities in the arsine precursor. Analysis of stibine (SbH_3), hydrogen selenide (H_2Se), and stannane (SnH_4) is also sometimes required.

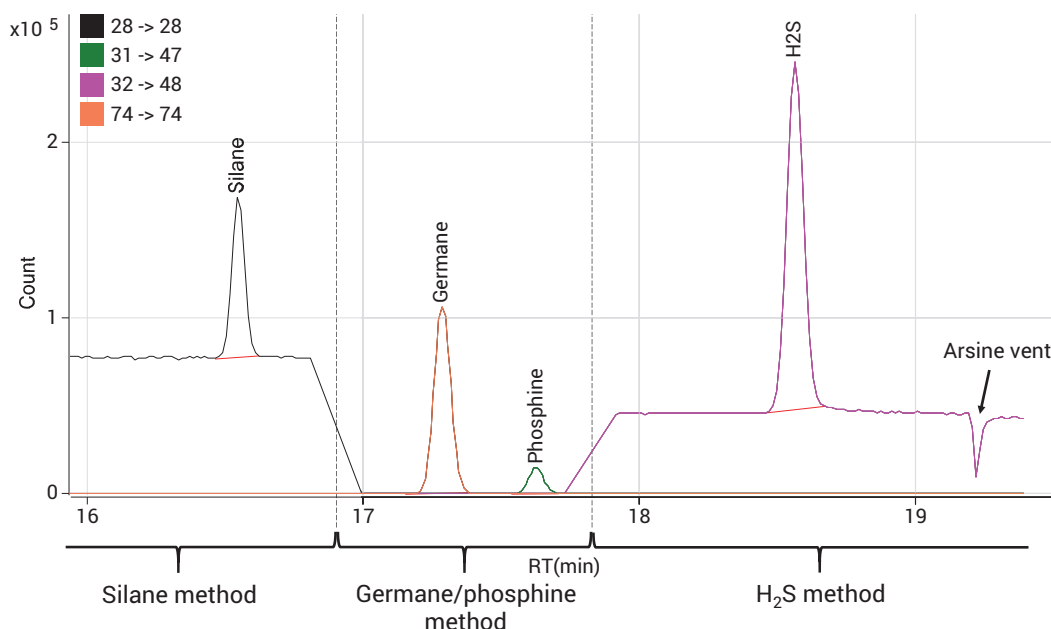


Figure 2. Overlaid chromatograms for critical contaminants in arsine gas, measured in one run using GC-ICP-QQQ with a multi tune time program.

Germanium contamination is of particular concern, so GeH_4 impurities must be measured at or below single digit ppb levels in arsine. Gas chromatography (GC) coupled to ICP-MS is currently the only technique capable of measuring GeH_4 at sub-ppb levels in arsine.

Experimental

An Agilent 7890B GC coupled to an Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used for the separation and detection of impurities in arsine. The Agilent GC-ICP-MS interface was modified using a high flow Deans switch. This change allowed the arsine to be vented at its elution time, preventing the matrix from entering the ICP-MS torch. For GC-ICP-QQQ operating and acquisition conditions, see the application note (7).

Results and discussion

Figure 2 shows an overlaid chromatogram acquired for a standard containing SiH_4 , PH_3 , H_2S , and GeH_4 at 24 ppb (by volume) in arsine. The method settings and acquisition parameters were switched automatically during the run, ensuring that each compound was measured under optimum conditions. The detection limits achieved using the optimized multi tune method are shown in Table 1.

Table 1. GC-ICP-QQQ detection limits for SiH_4 , GeH_4 , PH_3 , and H_2S in arsine.

	Retention Time (s)	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
SiH_4	992	308146	140	0.51
GeH_4	1037	438374	8000	0.01
PH_3	1057	60451	4700	0.02
H_2S	1112	883099	490	0.15

Conclusion

GC-ICP-QQQ was used to separate and measure SiH_4 , PH_3 , H_2S , and GeH_4 in arsine at sub ppbv levels, using a single GC column and a single injection.

The best detection limits for all compounds were achieved by operating the 8900 ICP-QQQ in MS/MS mode with H_2 and O_2 cell gases. The multi tune method allowed us to maximize signal averaging, and therefore achieve low DLs for all contaminant compounds using a single injection.

More information

1. W. M. Geiger *et al.* Agilent publication, [5994-2213EN](#)

Warning: Hydride gases such as arsine are hazardous and toxic. Ensure all appropriate safety procedures are followed.

HPLC-ICP-MS Supports Newly Approved US FDA Limit for Inorganic Arsenic in All Types of Infant Rice Cereals

Jenny Nelson^{1,2}, ¹University of California, Davis, USA, ²Agilent Technologies, Inc.

Guidance for manufacturers of infant rice products

In August 2020, the US Food and Drug Administration (FDA) finalized their guidance for industry on inorganic arsenic (iAs) in rice cereals for infants (1). The new "action level" limit of 100 µg/kg (ppb) iAs was originally issued in April 2016, giving industry plenty of time to prepare. The limit is based on assessment of the risk of iAs to the health of infants, while taking into consideration the levels achievable by industry working to current Good Manufacturing Practices (cGMP).

Arsenic in rice

Arsenic is known to be toxic and carcinogenic to humans even at low levels of exposure (1). Although As can occur naturally in the environment, it can also be present as the result of human activity. Sources of environmental contamination include mining, ore smelting and refining, wood preservative, and pesticides.

Rice plants are especially efficient at accumulating arsenic from their environment because the flooded fields in which they are grown make it easier to take up arsenic compounds. Infants and children are at greater risk of As exposure from rice because, relative to body weight, they consume more food than adults do. Also, infants' diets tend to be less varied.

Focus on inorganic arsenic

The toxicity of As is affected by its chemical form and oxidation state. Inorganic As species, arsenite (As III) and arsenate (As V), are more toxic than the methylated organic species, such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). As(III) is the most toxic species. The aim of the FDA's action level for iAs in rice cereals is to help reduce infants' dietary exposure to the most toxic forms of As.

Total As and speciation measurements

The FDA recommends that food manufacturers analyze all rice-based infant cereals for total As content. Samples that contain more than 100 ppb total As should then be further analyzed for inorganic As to assess compliance with the iAs action limit. The FDA's Elemental Analysis Manual (EAM): Section 4.11 (2) recommends the use of HPLC-ICP-MS to determine iAs – as the sum of As(III) and As(V) – in infant rice cereals.

The method can also be used by food manufacturers to test ingredients for total As and iAs. Ingredients found to contain iAs could be replaced, ensuring that final products are safe for consumption. Infant rice cereal products with >100 ppb iAs may be considered adulterated under section 402(a)(1) of the Food, Drug, and Cosmetic Act, making them liable to investigation (1).

Proven Agilent HPLC-ICP-MS methods

Agilent has been providing robust and reliable solutions for the measurement of iAs in foods and beverages for many years – including collaborating with many leading external research groups. The FDA's new action limit and ongoing public concern about food contamination, is expected to increase demand for routine monitoring of iAs in foods.

Agilent ICP-MS and ICP-QQQ instruments link seamlessly with Agilent HPLC systems through optimized interfaces and integrated software control. The coupled system is set up and operated from the ICP-MS MassHunter software, giving simple, automated analysis.

In one study using an Agilent HPLC-ICP-MS system, the EAM 4.11 method was applied to the determination of four As species – including As(III) and As(V) – in 31 infant rice cereals (3, 4). The four species were separated using isocratic anion exchange HPLC, and the chromatographic peaks were detected using ICP-MS, as shown in Figure 1.

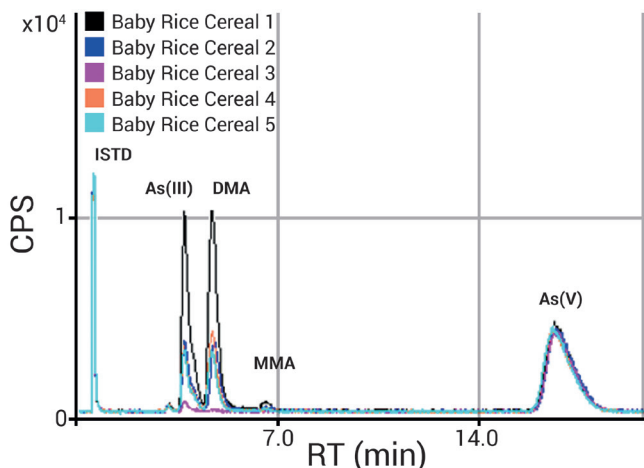


Figure 1. Overlay of As chromatograms in five rice cereals measured using an Agilent HPLC-ICP-MS system (4).

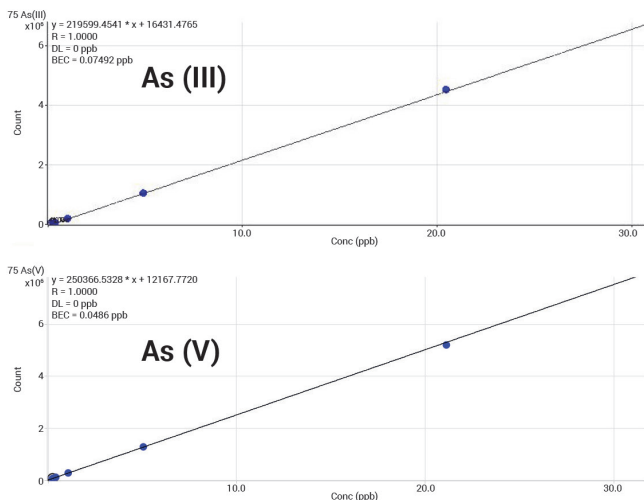


Figure 2. Calibration curves for As(III) and As(V) by HPLC-ICP-MS.

The good sensitivity (LODs and LOQs) and precision (%RSD) of the HPLC-ICP-MS method enabled all arsenic species to be detected at low levels.

In another study, a fast screening method for the determination of iAs in baby rice cereal was developed using an Agilent HPLC-ICP-MS system (5, 6). The faster separation was achieved by oxidizing As(III) to As(V) with H₂O₂ during sample preparation. Total iAs (sum of As(III) and As(V)) was then quantified as As(V). A full speciation analysis was completed in under two minutes, which is 10x faster than the EAM 4.11 method. The fast HPLC-ICP-MS method delivered lower LODs and LOQs compared to the EAM 4.11 method. The results in Table 2 show that two of the samples measured contained iAs above the new 100 ppb FDA action level.

Table 1. Quantitative results in µg/kg (ppb) for As species in six infant rice market basket samples measured in duplicate by HPLC-ICP-MS (6).

Baby Rice Cereal Sample	DMA	MMA Conc. (ppb)	iAs	FDA Action Limit for iAs
A_1	11.4	ND	63.3	Pass
A_2	11.2	ND	62.3	
B_1	12.5	ND	53.6	Pass
B_2	14.9	ND	56.4	
C_1	33.9	ND	106.4	Fail
C_2	36.0	ND	113.5	
D_1	15.4	ND	102.6	Fail
D_2	15.1	ND	103.6	
E_1	41.9	2.2	87.9	Pass
E_2	39.0	2.3	82.1	
F_1	46.4	8.7	89.4	Pass
F_2	46.7	9.0	90.4	

ND = not detected

Conclusion

The Agilent HPLC-ICP-MS methods provide labs with a routine capability to monitor iAs in rice and rice-based infant cereals, as well as enabling food producers to meet regulatory requirements.

References

1. US FDA, [Guidance for Industry: Action Level for Inorganic Arsenic in Rice Cereals for Infants](#), accessed Sept. 2020
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3. R. Juskelis, W. Li, J. Nelson, J. C. Cappozzo, *J. Agric. Food Chem.* **2013**, 61, 45, 10670–10676
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5. P. J. Gray, C. K. Tanabe, S. E. Ebeler, J. Nelson, *J. Anal. At. Spectrom.*, **2017**, 32, 1031-1034
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Agilent Japan Welcomes Semiconductor Users for Live Webinar to Introduce Recent Solutions Using ICP-QQQ

Masahiko Endo, Agilent Technologies, Inc.

Introduction

Even in these unusual times, Agilent continues to maintain a close working relationship with industry experts from leading semiconductor manufacturers and suppliers. Following the success of previous live seminars (see meeting report in Agilent ICP-MS Journal issue 78 (7)), Agilent Japan recently hosted a Live Online Webinar for semiconductor users.

The 2020 meeting was held over two days in September and October and focused on new applications and methods for triple quadrupole ICP-MS in the semiconductor industry.



A full program at the ICP-QQQ user event

The 2020 Agilent ICP-QQQ semiconductor seminar sessions were scheduled over two days:

Day 1

- Online ICP-MS analysis for Semiconductor Manufacturing Process (guest presenter from IAS Inc.)
- Fe nanoparticle analysis by single particle ICP-MS

Day 2

- The reaction mechanism and analysis tips for chlorine analysis in organic solvents by ICP-QQQ
- Agilent semiconductor solutions in Atomic Spectroscopy and Chromatography

Agilent invited Katsu Kawabata, President of IAS Inc, as a guest speaker. Katsu talked about integrated VPD analysis of Si wafers and introduced an online sampling system for automated standard addition ICP-MS analysis of trace metal impurities in semiconductor process chemicals. Katsu also presented IAS solutions for semiconductor gas analysis and for analyzing nanoparticles in semiconductor chemicals.

Agilent ICP-MS application chemist specialist Yoshinori Shimamura also spoke about single particle analysis in semiconductor applications, a topic of great interest to semiconductor customers. The control of metal impurities in chemical solutions used in semiconductor manufacturing processes is becoming stricter year by year, with increasing need for metal nanoparticle measurement. Iron is one of the most important contaminant elements, and Yoshinori presented an ICP-QQQ method that enables detection of Fe_3O_4 particles as small as 15 nm, at ppq concentrations, an analysis not previously possible by ICP-MS.

Katsuo Mizobuchi, senior ICP-MS applications chemist at Agilent Japan, explained the principles and optimization of ICP-QQQ to measure Cl in organic matrices. Chlorine analysis in organic solvents was previously very difficult by ICP-MS, but ICP-MS/MS enables this analysis at low levels.

Agilent's Kazuhiko Miyashita, Atomic Product Specialist, introduced the range of Agilent Atomic Spectroscopy and Chromatography Solutions for the Semiconductor industry. He spoke about applications for a wide range of inorganic analyzers, from atomic absorption to ICP-OES and ICP-MS (2), as well as semiconductor-related analyses using Agilent GC/MS and LC TOF systems.

References

1. Agilent ICP-MS Journal issue 78, 2019, Agilent publication [5994-1490EN](#)
2. Measuring Inorganic Impurities in Semiconductor Manufacturing, [5991-9495EN](#)

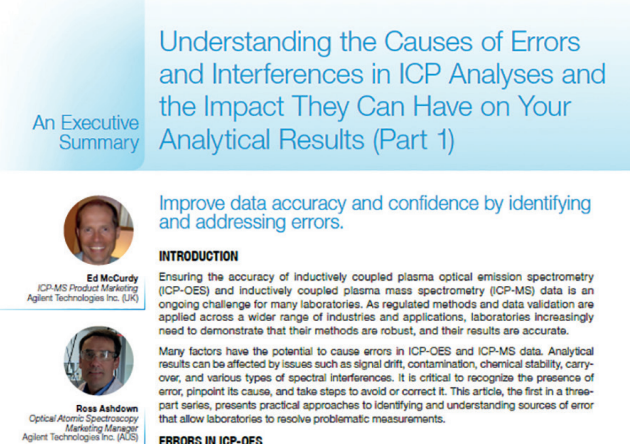
Executive Summary Articles for Recent Webinar Series on Improving Data Quality in ICP Methods

Ed McCurdy and Ross Ashdown, Agilent Technologies, Inc.

Agilent would like to thank everyone who attended the live broadcasts or watched on-demand our recent webinars on How to Improve Your ICP Data Quality. The number of attendees was unprecedented and there was a very high level of engagement in the Q&A sessions. As we were unable to answer all questions live, we are producing a follow-up Q&A summary to distribute to all attendees.

Read the articles

Spectroscopy has now produced a set of free, open-access Executive Summary articles covering the main subject areas at each of the webinars. The content includes:



An Executive Summary

Understanding the Causes of Errors and Interferences in ICP Analyses and the Impact They Can Have on Your Analytical Results (Part 1)

Improve data accuracy and confidence by identifying and addressing errors.

INTRODUCTION

Ensuring the accuracy of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) data is an ongoing challenge for many laboratories. As regulated methods and data validation are applied across a wider range of industries and applications, laboratories increasingly need to demonstrate that their methods are robust, and their results are accurate.

Many factors have the potential to cause errors in ICP-OES and ICP-MS data. Analytical results can be affected by issues such as signal drift, contamination, chemical stability, carry-over, and various types of spectral interferences. It is critical to recognize the presence of error, pinpoint its cause, and take steps to avoid or correct it. This article, the first in a three-part series, presents practical approaches to identifying and understanding sources of error that allow laboratories to resolve problematic measurements.

ERRORS IN ICP-OES

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Optical Atomic Spectroscopy
Marketing Manager
Agilent Technologies Inc. (AUS)

Event 1. The summary article for the first webinar discusses common causes of errors and interferences in ICP-OES and ICP-MS methods. The article describes how to identify and address errors from sample preparation, through to suppression and spectral overlaps.

Among other insights, we describe how using background correction approaches can contribute to improved data quality in ICP-OES. We also show how HCI can be used to stabilize several common ICP-MS analytes, including Ag and Hg. Another useful tip is how to monitor internal standard signals to help identify matrix suppression.

Event 2. The summary article for the second webinar discusses how ICP instrument configuration, optimization and novel software tools can be used to identify and address the causes of many errors. Regulated and routine methods often include quality control (QC) checks that flag known errors. But these approaches don't always work when sample types in routine analysis differ from the CRMs and standard solutions used during method development.

New Agilent Smart Tools – such as IntelliQuant and Neb Alert – provide operational and sample insights to ensure the accuracy of results, even in unusual and variable samples. We explain the importance of optimizing the ICP-MS plasma for robustness, and show how to control polyatomic interferences using helium collision/reaction cell mode illustrated using real analytical examples.

Event 3. The final article of the series shows how extending ICP methods into novel application areas and sample types can lead to new and unfamiliar errors and interferences. IntelliQuant Screening can help users identify and correct for unexpected matrix components in a mixed sample batch.

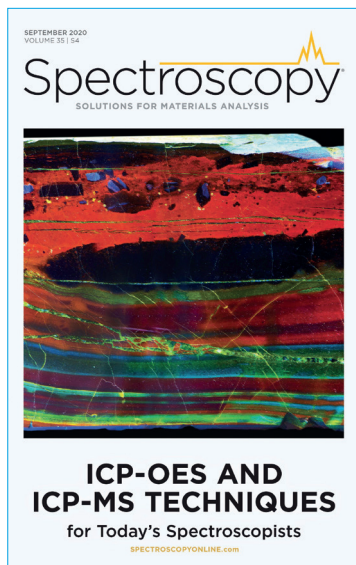
ICP-MS methods for new sample types can benefit from the use of qualifier isotopes to verify results. A novel half-mass correction approach addresses doubly charged ion interferences on As and Se. And triple quadrupole ICP-MS extends the range of ICP-MS by enabling the analysis of more complex samples and previously difficult elements such as sulfur, chlorine and fluorine. We also show how the improved abundance sensitivity of ICP-MS/MS allows trace analysis of elements with adjacent-mass overlaps.

Access the recorded webcasts

All three parts of the original webinar series are available to view on demand at this link:

[Errors and interferences in ICP methods webinar series](#)

Spectroscopy article on S analysis using ICP-MS/MS



The latest Spectroscopy special issue on “ICP-OES and ICP-MS Techniques for Today’s Spectroscopists” was published in September 2020. This issue includes a paper on “Accurate, Low-Level Sulfur Analysis by ICP-MS Using MS/MS with Oxygen Reaction Cell Gas”, written by Agilent ICP-MS specialists Ed McCurdy, Glenn Woods, Bastian Georg, and Naoki Sugiyama.

The article discusses the need for accurate low-level analysis of sulfur in a range of applications and why it is a difficult element to measure by single quadrupole ICP-MS. The authors explain how ICP-MS/MS can be used to determine sulfur accurately at lower levels than was previously possible by ICP-MS.

The method uses oxygen reaction gas to form SO^+ product ions, with MS/MS ensuring the $^{32}\text{S}^{16}\text{O}^+$ product ions are measured free from interference from other elements (such as ^{31}P). The application of MS/MS to isotope ratio analysis is also explored. Example data shows how the mass filter before the cell must operate with a 1 u mass window to prevent inter-isotope overlaps from the other isotopes of S. For example, the potential product ion overlap from $^{32}\text{S}^{18}\text{O}^+$ on $^{34}\text{S}^{16}\text{O}^+$ is avoided by using MS/MS to exclude the ^{32}S ions from the cell when ^{34}S is measured.

Access the online paper here: <https://www.spectroscopyonline.com/view/accurate-low-level-sulfur-analysis-by-icp-ms-using-ms-ms-with-oxygen-reaction-cell-gas>

Or download the full Special Issue pdf here: <https://cdn.sanity.io/files/0vv8moc6/spectroscopy/cebdb01a7c434e23e03df6b00fd1ce73e0db6ab6.pdf>

Latest Agilent ICP-MS publications

- **Application note:** Characterization of Rare Earth Elements used for Radiolabeling Applications by ICP-QQQ: Analysis of gadolinium (III) oxide and terbium using ICP-MS/MS with oxygen cell gas, [5994-2389EN](#)
- **Application note:** Determination of Trace Impurities in Electronic Grade Arsenic by GC-ICP-QQQ: Sub-ppb detection limits for hydride gas contaminants using a single column, single injection volume, and multi-tune method, [5994-2213EN](#)

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