Agilent ICP-MS Journal

Agilent
Trusted Answers

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Celebrating a Quarter of a Century of the ICP-MS Journal

In September 1998, the ICP-MS team at Hewlett Packard, now Agilent, published the first issue of "The Hot Source", a new journal for users of the HP 4500 ICP-MS. 25 years on, the Agilent ICP-MS Journal continues to be published quarterly, keeping users informed about the latest Agilent developments and industry and applications news.

The Agilent ICP-MS Journal provides a mix of technical content, news about Agilent ICP-MS products, consumables, and support, and articles on a range of novel and established applications. Issue 94 includes reports from research groups that detect nano scale particles and measure elements that would have been considered impossible to run on ICP-MS when the Hot Source was first published.

We would like to thank all the Agilent ICP-MS users and specialists who have offered their technical expertise, contributed an article, or provided data. We wouldn't have a Journal without you!

Figure 1. A selection of cover images from 25 years of the Agilent ICP-MS Journal.

LA-ICP-MS/MS for *In-Situ* Analysis of Fluorine Distribution in Geological and Biological Materials

David Clases, Raquel Gonzalez de Vega, Jörg Feldmann, University of Graz, Austria, and John Parnell, University of Aberdeen, UK

Elements that ICP-MS can (and can't) measure

ICP-MS is generally accepted as being able to detect all naturally occurring elements (and many radiogenic isotopes) except H, He, N, O, F, Ne, and Ar, the plasma support gas. Of these "not measurable" elements, H (mass 1 u) and He (4 u) are below the mass range of commercial quadrupole mass spectrometers. N and O cannot be measured due to high backgrounds from the H_2O/HNO_3 and N_2/O_2 in the air that surrounds the plasma.

N and O also have high 1st ionization potentials (IPs), which means it takes a lot of energy to remove the first electron to convert the element's atoms to positive ions. The relationship between 1st IP and ionization is shown in Figure 1. Ar has a 1st IP of 15.76 electronvolts (eV), which defines the plasma ionization environment. N and O have 1st IPs of 14.53 and 13.61 eV, respectively, which are close to the 1st IP of Ar so the degree of ionization – and therefore the sensitivity – is low. Other elements with very high 1st IPs (above 11 eV) include C, Br, and Cl, all of which are considered "difficult" for ICP-MS.

Fluorine (F) and neon (Ne) have 1st IPs of 17.423 and 21.565 eV, respectively, both higher than Ar, so these elements do not form a significant number of ions in the plasma. F is therefore one of a very small group of elements that have historically been considered impossible to measure using ICP-MS.

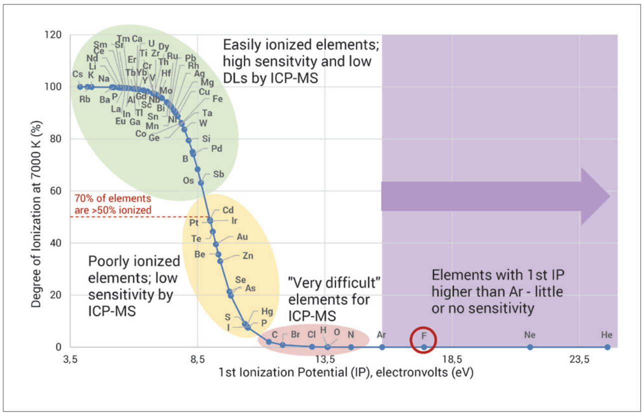

Figure 1. Plot showing degree of ionization against 1st ionization potential at a plasma temperature of 7000 K. Fluorine (F) is highlighted.

Fluorine analysis by ICP-MS

For many years, researchers have sought to develop ICP-MS methods to analyze F at trace levels. The interest arises because existing techniques for F analysis such as ion chromatography (IC) and ion selective electrode (ISE) are either not sensitive enough or have insufficient selectivity. Target applications include analysis of fluorinated organic compounds such as poly- and per-fluoro alkyl substances (PFAS) in environmental and food samples. PFASs are synthetic chemicals used in consumer products – for example non-stick coatings, fabric protectors, and food packaging – as well as in fire suppressants and certain industrial processes. In common with other halogenated organic compounds such as PCBs and PBDEs, PFASs are long lived and can accumulate in biological systems. The levels of PFASs are therefore of interest in samples such as food and drinking water, as well as industrial waste streams.

An early attempt to measure F by ICP-MS investigated the possibility of complexing F with Al to form AlF^{2+} in solution. The Al species were then separated by HPLC and the AlF^{2+} was determined by measuring Al by ICP-MS (*1*). However, this approach converts all the forms of F to AlF^{2+}, and therefore it cannot be used for F speciation. A method that relies on complexing the F in solution is also not applicable to *in situ* measurement, such as bio- or geo-imaging using laser ablation ICP-MS (LA-ICP-MS).

With the development of triple quadrupole ICP-MS in 2012, an alternative approach became possible, where the F is combined with a metal to form $M\text{-}F^+$ ions in the plasma, rather than in solution. Barium (Ba) was identified as the most suitable metal for the reaction, forming the product ion $^{138}Ba^{19}F^+$ (*2*). The method uses MS/MS with O_2 reaction cell gas to resolve the $^{138}Ba^{18}OH^+$ overlap on BaF^+ at mass 157. The $BaOH^+$ ions react with the O_2 cell gas, so the interference is removed. This approach was used for quantification of PFAS at ppb levels in waters, following separation by HPLC. The ICP-MS/MS BaF^+ method enabled element-specific determination of PFAS compounds that could not be detected by ESI-MS (*3*).

In-situ measurement of F by LA-ICP-MS/MS

As well as trace F measurement and speciation of fluorinated organic compounds, there is also a great deal of interest in how F and its compounds are distributed and partitioned in natural systems, such as biological tissue and geological materials. The current state-of-the-art for elemental distribution and imaging applications is LA-ICP-MS. An Agilent 8900 ICP-MS/MS was coupled to an Analyte G2 193 nm Excimer laser (Teledyne Cetac) to assess the distribution of F in geological samples and tooth sections (*4*). To enable BaF^+ ions to be formed in the plasma, the standard LA-ICP-MS setup was modified with a T-connector before the torch to add a Ba solution aerosol to the LA carrier gas. The F signal response was calibrated by ablating spiked gelatin standards.

The different ablation characteristics of gelatin and the samples of interest mean the F concentration results cannot be considered quantitative. But many imaging applications are concerned with distribution, so relative levels are of more interest than absolute concentrations.

The LA-ICP-MS/MS method was used to measure the distribution of F (as BaF^+), Cu, and Zn in a section of a wisdom tooth, as shown in Figure 2. The level and distribution of F in teeth is of interest as an indication of exposure via food and drinking water, and to check the effectiveness of F-supplementation as part of public health programs. F is easily incorporated into teeth as F^- is exchanged with hydroxide in the hydroxyapatite mineral that dental enamel is composed of. In the image in Figure 2, it is apparent that F is relatively high in the enamel surface, but also in the pulp cavity. Cu and Zn were associated with the pulp cavity and, particularly in the case of Cu, with the amalgam filling.

Conclusion

LA-ICP-MS/MS with online formation of BaF^+ in the plasma offers a novel approach to assessing the distribution of F in biological and geological materials. The method allows F distribution to be determined *in-situ* at low- or sub-µg/g (ppm) levels in solid samples.

References

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2. Feasibility Study of Fluorine Detection by ICP-QQQ, pp 222–224, in Handbook of ICP-QQQ Applications, Agilent publication 5991-2802EN
3. Jamari, N.L.A., Dohmann, J.F., Raab, A., Krupp, E.M., and Feldmann, J., *J. Anal. Atom. Spectrom.*, **2017**, 32, 942
4. Clases, D., Gonzalez de Vega, R., Parnell, J., and Feldmann, J., *J. Anal. At. Spectrom.*, **2023**, 38, 1661

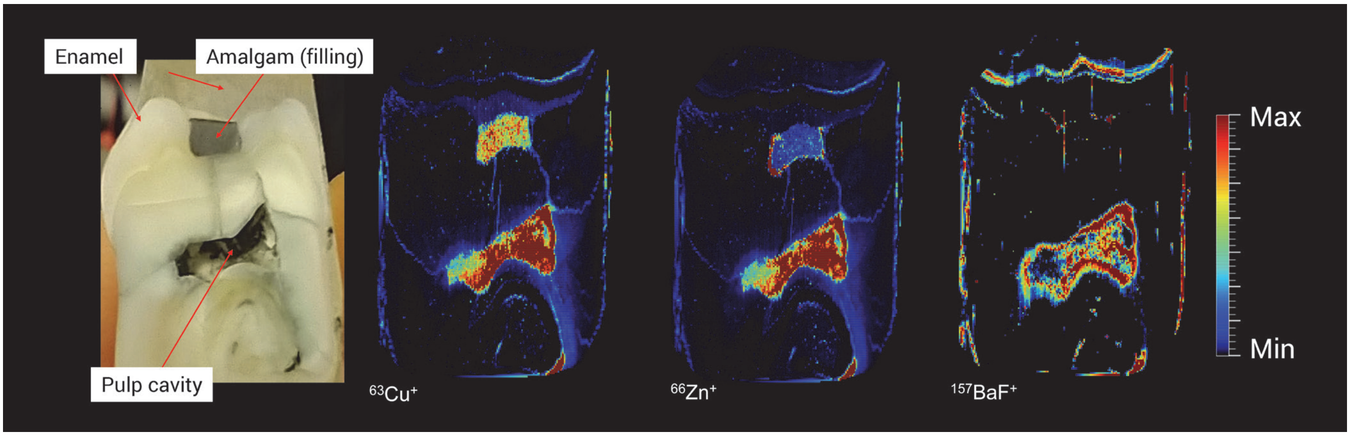

Figure 2. Section of a wisdom tooth showing distribution of Cu, Zn, and F (as BaF^+) measured using LA-ICP-MS/MS.

Microplastics by ICP-MS. Key Factors for Successful Analysis of Sub-Micron Particles in Ultrapure Water

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Carbon analysis by ICP-MS

As mentioned in the previous article on fluorine imaging, there are a small number of elements that have not previously been considered suitable for trace level analysis using ICP-MS. Among these elements, carbon (C) is considered one of the most difficult.

Carbon has a first ionization potential (1st IP) of 11.266 eV, so is only about 2% ionized at a plasma temperature of 7000 K, meaning only 1 in 50 of the carbon atoms are converted to C^+ ions. As a result, the ICP-MS sensitivity for C is ~50x lower than it would be for a fully ionized element. A second major problem for C analysis is that the background signal is high with ICP-MS, due to dissolved carbon in the reagents and from CO_2 and CO in the air that surrounds the plasma (*1*).

Applications that require low level C analysis, such as monitoring polymer particle contamination of high-purity reagents, require careful optimization of the ICP-MS system to control contamination and ensure good signal-to-noise for C. In this work, an Agilent 8900 ICP-QQQ (Semiconductor configuration) was used to measure C in ultrapure water (UPW). The 8900 was operated with a N_2 flushed Agilent SPS 4 autosampler to reduce potential contamination. Figure 1 shows the C calibration at µg/L (ppb) levels. The background equivalent concentration (BEC) was 8.892 ppb, confirming the effectiveness of the steps taken to reduce C contamination.

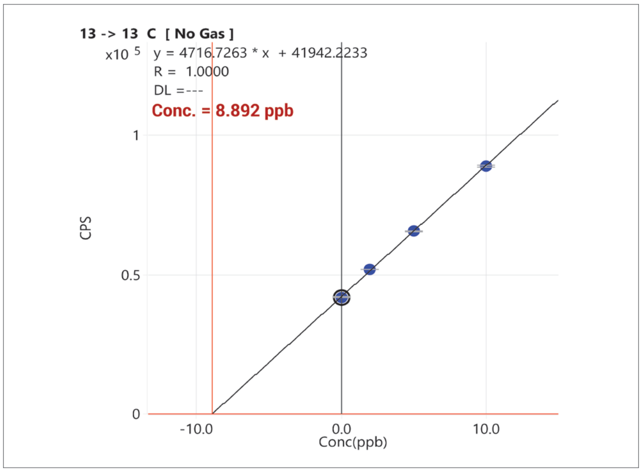

Figure 1. Calibration at single-ppb level for dissolved (ionic) C in UPW.

Researchers often measure C at its minor isotope ^{13}C (1.07% abundance) to help avoid the high background at the major isotope, ^{12}C (98.93% abundance) (*2, 3*). But measuring the minor isotope does not improve the signal-to-noise if the background is due to carbon, so controlling contamination is essential. For this work on the analysis of sub-micron polymer particles, ^{12}C was measured.

Polymer particles by single particle (sp)ICP-MS

Samples of UPW – unspiked and spiked with either 5 ppb ionic C or 5 ppb 400 nm C particles – were measured in single particle (sp) mode on the 8900 ICP-QQQ. Latex polymer particles were obtained from Agilent.

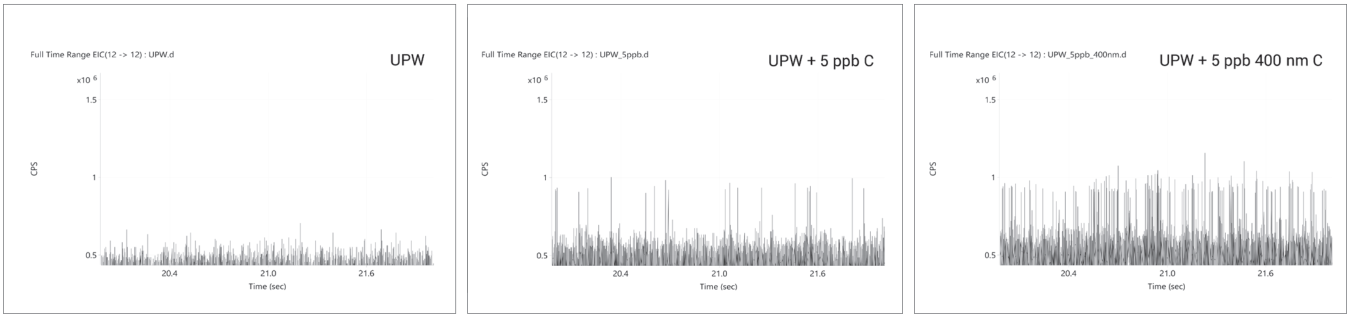

Figure 2. TRA plots of ^{12}C signal in UPW (left), UPW spiked with 5 ppb ionic C (middle), and UPW spiked with 5 ppb of 400 nm polymer particles (right).

The 8900 was operated in MS/MS mode with both Q1 and Q2 set to *m/z* 12. Data was acquired using fast time resolved analysis (TRA) with a dwell time of 100 µs. The high elemental background signal for ^{12}C meant the detector switched automatically between pulse count and analog mode as the signal was collected for each TRA measurement. A dwell time of 100 µs is used in both detector modes on Agilent ICP-MS systems and there is no settling time required between measurements, as the mass does not change for each element's acquisition.

Figure 2 shows a representative section (lasting approximately 2 s) from each of the time plots for the blank UPW, UPW spiked with 5 ppb ionic C, and UPW spiked with 5 ppb of 400 nm C particles. The difference in measured signals between the three samples is clear, confirming the effective control of the ^{12}C background in the UPW and the high analyte sensitivity for the spikes.

Determination of polymer particle size distribution

Despite the steps taken to optimize the sample introduction system and plasma conditions, the elemental background signal for ^{12}C was still high relative to the signal for individual polymer particles. The single particle analysis module of Agilent ICP-MS MassHunter software supports manual adjustment of the background threshold, which aids discrimination of small particles above a high intensity ionic background.

Figure 3 shows the signal distribution and particle size distribution for the UPW sample spiked with 5 ppb 400 nm C, processed using the ICP-MS MassHunter single particle analysis software. The 400 nm polymer particles were clearly separated from the background signal, with a median particle size of 374 nm and a particle size threshold at approximately 300 nm.

Conclusion

Careful attention to sample introduction and optimized plasma conditions for C ionization enabled detection of sub-micron polymer particles at single ppb levels in UPW.

Controlling contamination from polymer particles as well as metallic particles is an emerging requirement in the semiconductor industry. As manufacturers develop integrated circuits with smaller features to support the latest generation of high speed and mobile chips, controlling contamination becomes ever more critical.

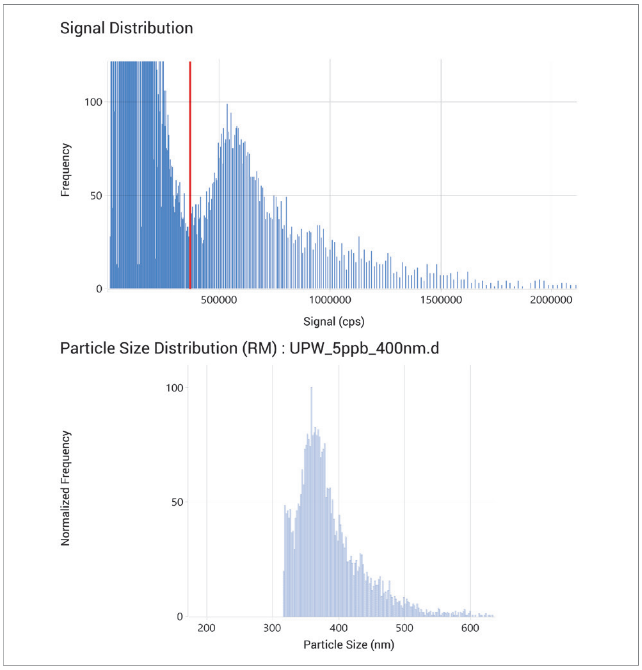

Figure 3. Signal distribution (top) and particle size distribution (bottom) for 5 ppb of 400 nm carbon particles in UPW. Median size, 374 nm.

The Agilent 8900 ICP-MS/MS provides exceptionally high ion transmission, low random background, and effective control of spectral overlaps to enable ultratrace level analysis as required by semiconductor suppliers and manufacturers. The use of single particle analysis mode to detect and characterize organic and metallic particle contamination adds another capability for analysts leading the development of the next generation of chips.

References

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2. Gonzalez de Vega, R., Goyen, S., Lockwood, T. E., Doble, P. A.,. Camp, E. F., Clases, D., *Anal. Chim. Acta*, **2021**, 1174, 338737
3. Particle Size Analysis of Polystyrene Microplastics by Single Particle (sp)ICP-MS, Agilent publication 5994-4897EN

Analysis of Silica and Iron Oxide Nanoparticles in Semiconductor Process Chemicals Using ICP-MS/MS

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ICP-MS for process chemical analysis

Semiconductor manufacturers and suppliers have relied on ICP-MS since the technique was first commercialized in the 1980s. With its combination of wide elemental coverage, fast analysis, and extremely low detection limits (DLs), ICP-MS quickly became the standard method for analyzing trace element contaminants in the process chemicals used in integrated circuit (IC) fabrication.

In the past 30 years, semiconductor chips have become an essential part of almost every aspect of modern life. Industry innovations have delivered chips with smaller size, faster processing speed, and lower power requirements. Each generation of chips has higher transistor density and smaller device dimensions, which necessitates the use of higher purity materials and process chemicals. Agilent works closely with leading semiconductor manufacturers to ensure ICP-MS performance has continued to improve to meet the industry's evolving analytical requirements (*1*).

ICP-QQQ in semiconductor manufacturing

In 2012, Agilent launched the Agilent 8800, the world's first triple quadrupole ICP-MS (ICP-QQQ). The tandem (MS/MS) mass spectrometer configuration transformed the analysis of high purity chemicals. The 8800 and later 8900 provide high sensitivity, low background, and enable the reliable use of reactive cell gases to resolve difficult spectral overlaps. ICP-MS/MS dramatically improves the DLs for critical analytes including S, P, Si, and Fe, which suffer intense interferences when measured using single quadrupole ICP-MS.

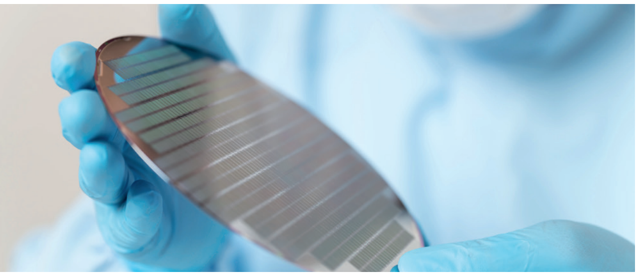


Figure 1. Manufacturing yield and device performance of modern IC chips depend on controlling dissolved and particulate contamination.

While dissolved elemental contaminants have historically been the primary focus for the semiconductor industry, there is growing awareness of the importance of nano-scale particulate contamination. Nanoparticles (NPs) can affect critical fabrication processes, leading to spot defects, compromising the integrity of the circuit, and reducing yield. The Agilent 8900 ICP-MS/MS allows manufacturers to fully characterize process chemicals by measuring particulate contaminants as well as dissolved element content.

Particles of interest include silica (SiO_2) and iron (Fe) as they may indicate contamination from the Si wafer substrate or stainless-steel process equipment, respectively. Table 1 shows the preferred analytical masses for Si and Fe, together with the main spectral overlaps that form in aqueous and organic chemicals.

Table 1. Main spectral overlaps that affect ICP-MS analysis of Si and Fe.

		Main Spectral Overlaps	
Element	**Mass**	**Aqueous**	**Organic**
Si	28	$^{14}N_2^+$	$^{12}C^{16}O^+$
Fe	56	$^{40}Ar^{16}O^+$	$^{12}C_2{}^{16}O_2^+$

SiO_2 NPs in process chemicals

Silica NPs were measured in ultrapure water (UPW), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and isopropyl alcohol (IPA) (*2*). These chemicals come into direct contact with the wafer surface during chip fabrication and can therefore contribute particulate contamination. Examples of the signal distribution plots for SiO_2 particles in 5x diluted concentrated HCl and 100x diluted concentrated H_2SO_4 are shown in Figure 2.

The plots in Figure 2 show the signal distribution in the blank and spiked acids, demonstrating that the 8900 ICP-MS/MS was easily able to detect 50 nm SiO_2 NPs spiked at 20 ng/L (ppt) in the diluted acids.

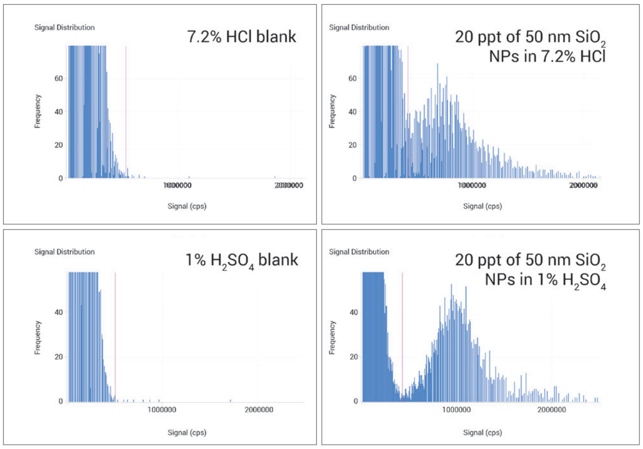


Figure 2. Signal distribution in blank and SiO_2 NP spiked HCl and H_2SO_4.

Iron NPs in semiconductor solvents

Iron NPs were spiked into four organic solvents that are widely used in semiconductor manufacturing (*3*). IPA is used extensively for cleaning and drying wafers, Propylene Glycol Methyl Ether (PGME) and Propylene Glycol Methyl Ether Acetate (PGMEA) are used as solvents for diluting photoresist, and n-Butyl Acetate (nBA) is used as a developer for n-type photoresist. In organic solvents, a C_2O_2 polyatomic ion overlaps Fe at *m/z* 56, but ICP-MS/MS with O_2 cell gas resolves the C_2O_2 and ArO overlaps so 15 nm Fe_3O_4 NPs can be accurately determined at 1 ppt in solvents (Figure 3).

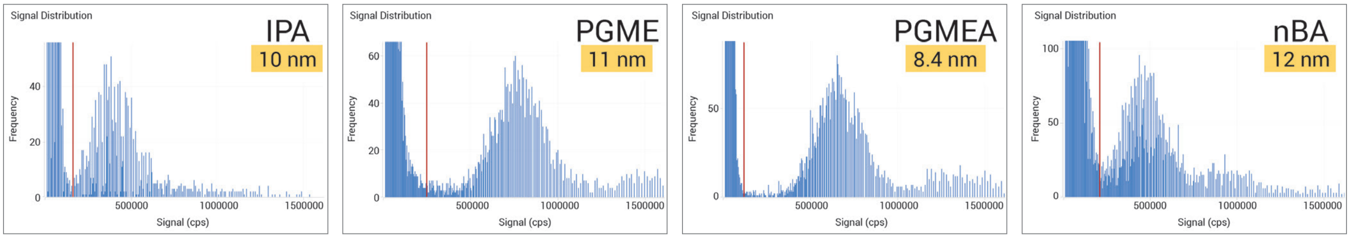
Conclusion

Agilent's ICP-MS/MS instruments have transformed trace element analysis in semiconductor labs, delivering much lower detection limits for dissolved contaminants, and extending analyte coverage to include previously difficult elements such as Si, S, and P. The Agilent 8900 ICP-MS/MS also provides semiconductor labs with a proven technique for routine particle size characterization in critical process chemicals, including high-purity solvents.

References

1. Measuring Inorganic Impurities in Semiconductor Manufacturing, Agilent publication 5991-9495EN
2. Analysis of 50 nm Silica Nanoparticles in Semiconductor Process Chemicals by spICP-MS/MS, Agilent publication 5994-5866EN
3. Analysis of 15 nm Iron Nanoparticles in Organic Solvents by spICP-MS, Agilent publication 5994-1747EN

Signal distribution and NP threshold for 15 nm Fe_3O_4 NPs spiked at 1 ppt in semiconductor solvents



Particle size distribution (15 nm highlighted)

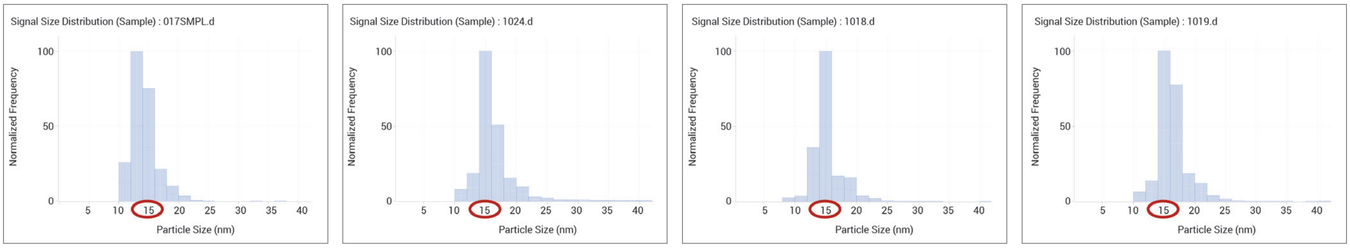
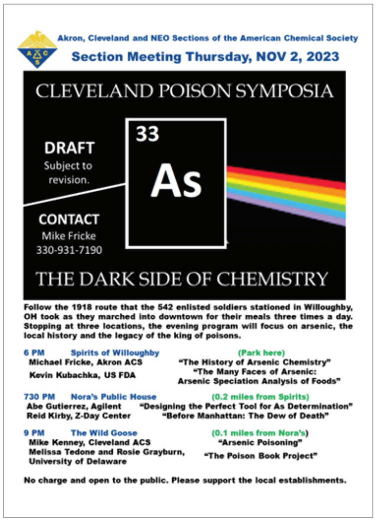


Figure 3. Signal distribution (top) and particle size distribution (bottom) for 15 nm Fe_3O_4 NPs spiked at 1 ng/L (ppt) in four organic solvents used in the semiconductor industry. The iron NPs were detected and accurately quantified at 1 ppt in all the solvents, which were run undiluted.

American Chemical Society “Themed Walking Symposium” on the history of arsenic as a poison



Akron, Cleveland and NEO Sections of the American Chemical Society

Section Meeting Thursday, NOV 2, 2023

CLEVELAND POISON SYMPOSIA

DRAFT
Subject to revision.

CONTACT
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330-931-7190

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As

THE DARK SIDE OF CHEMISTRY

Follow the 1918 route that the 542 enlisted soldiers stationed in Willoughby, OH took as they marched into downtown for their meals three times a day. Stopping at three locations, the evening program will focus on arsenic, the local history and the legacy of the king of poisons.

6 PM Spirits of Willoughby (Park here)
Michael Fricke, Akron ACS “The History of Arsenic Chemistry”
Kevin Kubachka, US FDA “The Many Faces of Arsenic: Arsenic Speciation Analysis of Foods”

730 PM Nora’s Public House (0.2 miles from Spirits)
Abe Gutierrez, Agilent “Designing the Perfect Tool for As Determination”
Reid Kirby, Z-Day Center “Before Manhattan: The Dew of Death”

9 PM The Wild Goose (0.1 miles from Nora’s)
Mike Kenney, Cleveland ACS “Arsenic Poisoning”
Melissa Tedone and Rosie Grayburn, University of Delaware “The Poison Book Project”

No charge and open to the public. Please support the local establishments.

On November 2nd, 2023, the Akron, Cleveland, and Northeastern Ohio Sections of the American Chemical Society (ACS) held an evening symposium taking in three locations in the town of Willoughby, Ohio. The symposium featured a series of talks by leading experts on arsenic (As) and its long history of use as a poison.

Willoughby was a well-chosen location for the symposium. In the summer of 1918, a site just outside the town was set up to manufacture lewisite, an As-based poison gas. The gas was discovered by accident in 1903 by a PhD candidate, Julius Arthur Nieuwland, who was studying the reaction of acetylene with $AsCl_3$ at the Catholic University of America in Washington, D.C. Lewisite is named after Winford Lee Lewis, who is credited with perfecting its synthesis in April 1918 at the Chemical Warfare Service unit at the Catholic University.

The Willoughby lewisite production plant became known as “The Mousetrap” because, to keep their work secret, the 542 enlisted soldiers who worked there were not allowed to leave the site, except to march into town for their meals.

The First World War ended before the lewisite produced at the Willoughby plant could be shipped to the battlefields of Europe. But the legacy of the plant’s operation and its place in the story of arsenic’s use as a poison can still be found in the region.

Latest Agilent ICP-MS publications

- **Spectroscopy tutorial article** by Ed McCurdy and Peter Riles, Spectroscopy The Resource Issue, 38, 8, 2023, Non-Specific Calibration Combined with Helium Collision Mode for Elemental Screening (spectroscopyonline.com)
- **Spectroscopy tutorial article** by William M. Geiger, Ed McCurdy, Mark Kelinske, Spectroscopy, 38, S9, 2023, GC-ICP-MS for Process and Quality Control in Semiconductor Manufacturing (spectroscopyonline.com)
- **Application note:** Direct Analysis of Metallic Impurities in SiC and GaN Wafers by LA-GED-MSAG-ICP-MS/MS, 5994-6670EN
- **Case study:** Indian Institute of Science. Climate and Environmental Research Enabled by Ability to Measure Metals at Parts-per-Trillion Concentrations, 5994-6479EN

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