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## Pushing the Limits of What's Possible by ICP-MS

**Ed McCurdy, Agilent Technologies, Inc.**

Certain elements, including As, Se, Fe, K, and Ca, are more difficult than others to measure at low levels by ICP-MS. Such analytes may suffer intense spectral interferences or be poorly ionized leading to low sensitivity. Instrument developments such as cool plasma and collision reaction cells have improved performance, but some elements – Si, P, S, Cl – remained “difficult” until the advent of triple quadrupole ICP-MS. MS/MS methods have transformed the analysis of these difficult elements, leading to the rapid development of new applications.

Fluorine is even more challenging for ICP-MS, as the high ionization energy of F (first IP of 17.423 eV) means that almost no positive ions are formed. But even F can be measured by ICP-MS/MS, using an indirect method reported by workers at the University of Aberdeen.



**Figure 1.** Unique configuration of the Agilent 8900 Triple Quadrupole ICP-MS.

# Identification of Perfluoro Alkyl Substances (PFASs) in Spiked River Water Samples

T. N. Nxumalo, A. Akhdhar, A. Raab, E. M. Krupp, J. Feldmann, TESLA, University of Aberdeen, Scotland, UK

## Introduction

Poly- and per-fluorinated alkylated substances (PFAS) are synthetic chemicals used in consumer products, fire suppressant foams, and certain industrial processes. PFASs are used in nonstick coatings, fabric protectors, and food packaging. In common with other halogenated organic compounds such as PCBs and PBDEs, PFASs are long lived and can accumulate in the environment and biological systems. Therefore, the level of PFASs is of interest in samples such as food and drinking water.

Of all the elements analyzed by ICP-MS, fluorine is the most difficult due to its ionization potential of 17.423 eV, which is higher than that of Ar (15.76 eV). However, using chemistry in the ICP plasma, a metal-fluorine cation can be created, allowing fluorine to be detected indirectly (1).  $\text{BaF}^+$ , formed by combining  $\text{F}^-$  with  $\text{Ba}^{2+}$  in the plasma, was found to be the most intense cation formed (2).

ICP-QQQ with  $\text{O}_2$  reaction cell gas was used to resolve the interference from  $\text{Ba}(^{18}\text{OH})^+$ , which is also formed in the plasma and has the same mass as  $\text{BaF}^+$ . Fluorine detection limits of around 0.05 mg/L were obtained using an Agilent 8800 ICP-QQQ as a fluorine-specific detector for RP-HPLC. The method allowed the separation and quantification of PFASs at low ppb level in freshwater (3).

## Experimental

### Workflow

- Duplicate 250 mL river water samples were spiked with 500  $\mu\text{L}$  of a mix of five perfluorinated acids in methanol (MeOH) at four different concentrations. The acids studied were perfluorohexanoic acid (PFHxA); perfluorooctanoic acid (PFOA); perfluorohexanesulfonic acid (PFHxS); perfluorodecanoic acid (PFDA); and perfluorooctanesulfonic acid (PFOS).

- The samples were extracted with a weak anion exchange (WAX) cartridge using a method adopted from Taniyasu and co-workers (4).
- The extracts were dried under  $\text{N}_2$  at 40 °C and reconstituted with 500  $\mu\text{L}$  methanol.
- The samples were centrifuged before analysis.

### Instrumentation

An Agilent 1290 LC system fitted with an ACE Excel 1.7 C 18-amide column was used for the separation of the analytes (see Table 1). After separation, analytes were simultaneously detected using an Agilent 8800 Triple Quadrupole ICP-MS/MS and a Thermo electrospray ionization mass spectrometer (ESI-MS), operating in negative ion mode. Eluent from the HPLC was split, so that 0.4 mL/min went to the ICP-MS/MS and 0.1 mL/min to the ESI-MS.

**Table 1.** RP-HPLC parameters used for the separation of PFASs.

<b>Buffer A</b>	2 mM ammonium acetate, 0.1% formic acid in $\text{H}_2\text{O}$ /acetonitrile (90:10 v/v)
<b>Buffer B</b>	2 mM ammonium acetate, 0.1% formic acid in $\text{H}_2\text{O}$ /acetonitrile (10:90 v/v)
<b>Flow rate</b>	0.5 mL/min
<b>Volume</b>	20 $\mu\text{L}$
<b>Temp.</b>	40 °C
<b>Gradient</b>	0 to 0.5 min: 25% B, 0.5 to 5 min: 50% B, 5 to 10 min: 70% B, 10 to 27 min: 70% B

To promote the formation of  $\text{BaF}^+$ , standards or samples were mixed with 50 ppm Ba online via a T-connector using a mixing ratio of 1:1.5. Fluorine was detected as  $\text{BaF}^+$  using the 8800 ICP-MS/MS, which was tuned for maximum sensitivity at  $m/z$  157 ( $^{138}\text{Ba}^{19}\text{F}^+$ ). Mass 48 was also monitored for the determination of sulfur ( $^{32}\text{S}^{16}\text{O}^+$ ).

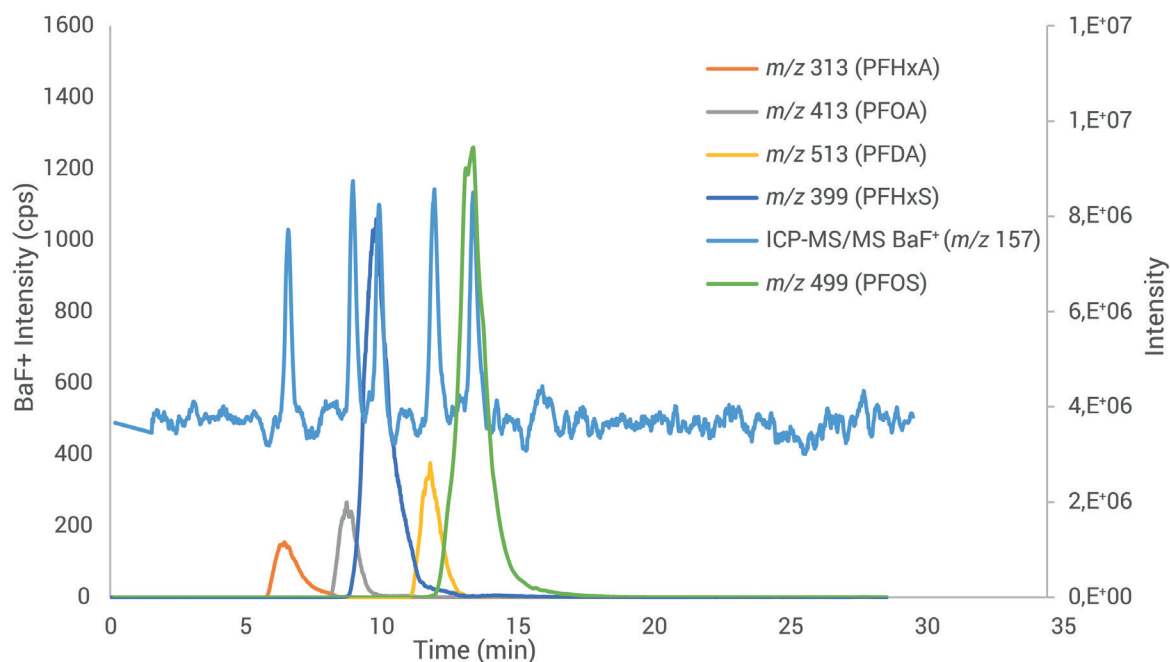


Figure 1. Extracted ESI-MS single ion chromatograms for perfluorinated acids overlaid with the ICP-MS/MS chromatogram of BaF<sup>+</sup> (*m/z* 157).

## Results and discussion

The ICP-MS/MS chromatogram for BaF<sup>+</sup> at a spike level of about 7 mg/L (before extraction) indicated the retention time (RT) of the separated PFASs (Figure 1). The individual PFASs were identified by RT match compared to the extracted single ion chromatograms of the monoisotopic masses of each PFAS from the ESI-MS data. Molecular formulas were determined by ESI-MS with a mass accuracy of < 5 ppm. Monitoring SO<sup>+</sup> by ICP-MS/MS confirmed the identification of the sulfonated perfluorinated compounds PFHxS and PFOS (Figure 2).

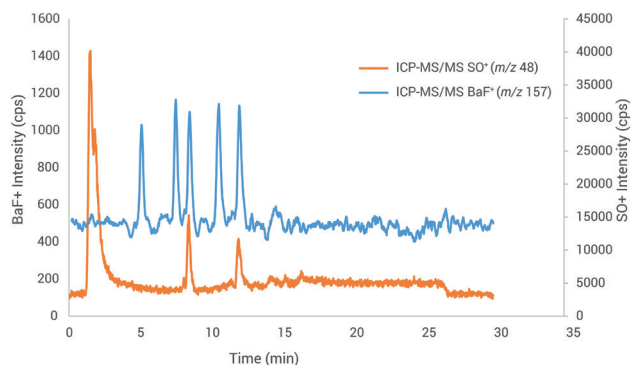


Figure 2. Overlay of ICP-MS/MS chromatograms for BaF<sup>+</sup> (*m/z* 157) and SO<sup>+</sup> (*m/z* 48).

## References

1. N.L.A. Jamari, J.F. Dohmann, A. Raab, E.M. Krupp, J. Feldmann, Novel non-target analysis of fluorine compounds using ICPMS/MS and HPLC-ICPMS/MS, *J. Anal. Atom. Spectrom.*, **2017**, 32, 942–950
2. N.L.A. Jamari, A. Behrens, A. Raab, E.M. Krupp, J. Feldmann, Plasma processes to detect fluorine with ICP-MS as M-F<sup>+</sup>: an argument for building a negative mode ICPMS/MS. *J. Anal. Atom. Spectrom.*, **2018**, 33, 1304-1309
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4. S. Taniyasu *et al.*, Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota, *J. Chromatog. A*, **2005**, 1093, 89–97

## Find out more

See the Agilent case study of the Trace Element Speciation Laboratory at the University of Aberdeen: Tracing the Effects of Trace Elements, [5994-0979EN](#)

# Interference-Free Analysis of Phosphorus in Organic Solvents using ICP-QQQ

Katsuo Mizobuchi and Kazuhiro Sakai, Agilent Technologies, Inc.

## Introduction

Phosphorus ( $^{31}\text{P}$ ) is one of the most difficult elements to analyze at low concentrations by conventional quadrupole ICP-MS (ICP-QMS). This is because of spectral interferences from polyatomic ions such as  $\text{NO}^+$  ( $^{15}\text{N}^{16}\text{O}^+$ ,  $^{14}\text{N}^{17}\text{O}^+$ ) and  $^{14}\text{N}^{16}\text{OH}^+$  at  $m/z$  31. In samples with a high carbon content, such as organic solvents, additional carbon-based polyatomic ions can be formed. These interferences include  $^{13}\text{C}^{18}\text{O}^+$  and  $\text{COH}^+$  ( $^{12}\text{C}^{18}\text{OH}^+$ ,  $^{13}\text{C}^{17}\text{OH}^+$ ) which overlap  $\text{P}^+$  at  $m/z$  31.

Phosphorus is an important element in a range of sample-types and applications including semiconductor chemicals, solar energy, pharmaceutical, petrochemical, life science, and advanced research projects.

In this study, an Agilent 8900 ICP-QQQ operating in MS/MS mode was used to investigate mechanisms to reduce the background equivalent concentration (BEC) for P in isopropyl alcohol (IPA). Two different reaction modes were studied:

- Oxygen mass-shift mode, where the oxide product ion  $\text{PO}^+$  is measured at  $m/z$  47.
- Hydrogen mode, where hydride product ions (mainly  $\text{PH}_3^+$  and  $\text{PH}_4^+$  at  $m/z$  34 and 35 respectively) are produced from reactions with  $\text{H}_2$  cell gas.

## Experimental

**Reagents and samples:** Electronic Grade IPA and a SPEX water-based phosphorus assurance standard (PLP9-3Y) were used.

### Instrumentation

An Agilent 8900 (#200 Semiconductor configuration) ICP-QQQ was used with a 1.5 mm id quartz torch, quartz spray chamber, and PFA nebulizer (MFN 100). Samples were self-aspirated at a flow rate of 0.17 mL/min.

The operating conditions used are shown in Table 1.

**Table 1.** ICP-QQQ operating conditions.

Parameter	Value
RF power (W)	1500
Sampling depth (mm)	18
Carrier gas flow rate (L/min)	0.7
Make up gas flow rate (L/min)	0.55
Option gas (20% $\text{O}_2$ in Ar) flow rate (L/min)	0.25

## Results and discussion

First, oxygen cell gas was investigated under different cell conditions. The BEC for P was measured as a function of octopole bias with various cell gas flow rates to find the optimum cell conditions.

Conditions that give a low collision energy are preferred, as lower collision energy is expected to suppress in-cell reactions. For example, the reaction  $^{13}\text{C}^{18}\text{O}^+ + \text{O}_2 \rightarrow ^{13}\text{C}^{18}\text{O}^{16}\text{O}^+ + \text{O}$  would form interfering ions that would overlap  $^{31}\text{P}^{16}\text{O}^+$  at  $m/z$  47.

To achieve low collision energy, a relatively high (less negative) octopole bias of  $-5$  V was used with a mix of cell gases comprising 0.075 mL/min oxygen and 12 mL/min helium.

At these relative flow rates of He and  $\text{O}_2$  (12/0.075), the density of helium atoms in the cell is 160 times greater than that of oxygen. As a result, most of the ions entering the cell collide with helium before they collide with oxygen. Helium therefore works as a buffer gas, reducing the kinetic energy of the ions before they react with the  $\text{O}_2$  cell gas. Under these optimized  $\text{O}_2/\text{He}$  cell mode conditions, a minimum BEC for P of 0.027 ppb (27 ppt) was obtained, as shown in Table 2 (1).

**Table 2.** BECs and sensitivity for  $^{31}\text{P}$  in IPA by 8900 ICP-QQQ operating with different cell gas conditions.

	Q1→Q2 (m/z)	O <sub>2</sub> (mL/min)	He (mL/min)	H <sub>2</sub> (mL/min)	Octopole Bias (V)	Axial Acceleration (V)	BEC (ppb)	DL (ppb)	Sensitivity (cps/ppb)
O <sub>2</sub>	31→47	0.45	0	0	0	0	0.082	0.009	9150
O <sub>2</sub> +He	31→47	0.075	12	0	-5	+1.5	0.027	0.006	6660
H <sub>2</sub>	31→34	0	0	10	-30	0	0.038	0.017	1220
H <sub>2</sub>	31→35	0	0	10	-30	0	0.008	0.007	1150
He	31→31	0	5	0	-18	0	800	11.339	56

Second, hydrogen mode (P detection as  $\text{PH}_3^+$  and  $\text{PH}_4^+$ ) was investigated. Based on the reaction enthalpies,  $\Delta H_r$ , the probable reaction series (2) that produces  $\text{PH}_3^+$  and  $\text{PH}_4^+$  is:

$\text{P}^+ + \text{H}_2 \rightarrow \text{PH}^+ + \text{H}$  ( $\Delta H_r = +1.13$  eV; endothermic);

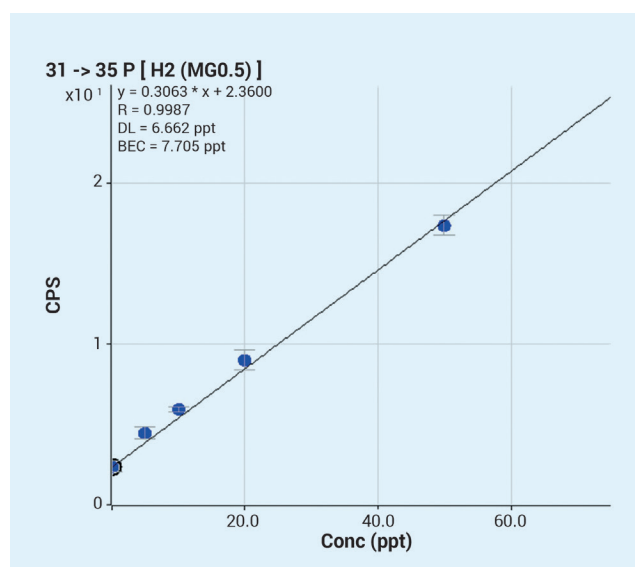
$\text{PH}^+ + \text{H}_2 \rightarrow \text{PH}_3^+$  ( $\Delta H_r < -2.69$  eV; association reaction);

$\text{PH}_3^+ + \text{H}_2 \rightarrow \text{PH}_4^+ + \text{H}$  ( $\Delta H_r = +0.05$  eV; negligibly endothermic).

To promote the first of these reactions, which is endothermic, an octopole bias of  $-30$  V was used to provide cell conditions with high collision energy.

The lowest BEC obtained for  $^{31}\text{P}$  in IPA in  $\text{H}_2$  cell gas was lower than the best achieved using  $\text{O}_2/\text{He}$  cell gas, as shown in Table 2. The BEC achieved for P with  $\text{H}_2$  mode ( $\text{P}^+ \rightarrow \text{PH}_4^+$ ) was 0.008 ppb (7.7 ppt), as illustrated in Figure 1. This BEC is around 3 times lower than the value of 0.027 ppb (27 ppt) obtained with  $\text{O}_2/\text{He}$  mode ( $\text{P}^+ \rightarrow \text{PO}^+$ ). However, the sensitivity obtained using  $\text{O}_2/\text{He}$  mode was about 6 times higher than in  $\text{H}_2$  mode.

The phosphorus BEC achieved using the optimized 8900 ICP-MS/MS  $\text{H}_2$  reaction method was five orders of magnitude lower than the BEC obtained in He collision mode. The analytical sensitivity (cps/ppb) in the  $\text{H}_2$  and  $\text{O}_2/\text{He}$  cell gas modes was also much higher than the sensitivity observed with He mode.



**Figure 1.** Calibration for P in IPA using  $\text{H}_2$  cell gas on the 8900 ICP-QQQ, showing a BEC of 7.7 ppt.

## References

1. K. Mizobuchi, N. Yamada and M. Yukinari, The Japan Society for Analytical Chemistry, 2017 66<sup>th</sup> Nenkai, G4002
2. Journal of Physical and Chemical Reference Data, Vol 17,1988 Supplement No.1, Gas-Phase Ion and Neutral Thermochemistry



# Agilent Japan Welcomes 100 Delegates to the Fifth Event for ICP-QQQ Users in the Semiconductor Industry

Masahiko Endo, Agilent Technologies, Inc.

## Introduction

Agilent Japan's ICP-MS team has nurtured a close relationship with the semiconductor industry over many decades. By working closely together, both parties have benefited from numerous developments in ICP-MS instrumentation, software, and applications (1). The requirement for very low detection limits in the semiconductor industry was among the key drivers for development of the first triple quadrupole ICP-MS. The Agilent 8800 was launched in 2012, followed by the Agilent 8900 in 2016. The Agilent ICP-QQQ provides higher sensitivity, lower background, and better control of interferences than conventional single quadrupole ICP-MS. ICP-QQQ has improved performance for many semicon-related applications, allowing users to achieve accurate analysis at ultralow concentrations. As a result, many semiconductor manufacturers and chemical suppliers have invested in the technique. To support the growing user community within the industry, Agilent recently hosted its fifth ICP-QQQ meeting for semiconductor users.

## A full program at the fifth ICP-QQQ user event



The day's events included presentations by an invited speaker from industry and Agilent applications chemists.

The latest ICP-QQQ event took place on July 24, 2019 at Agilent's Hachioji site in Tokyo, Japan. Due to space limitations, numbers were restricted to 100 customers.



Jones Hsu, an assistant manager in the quality control department of the inorganics business unit at BASF Taiwan, gave an invited talk. The title of his presentation was "Trends in Taiwan Semiconductor Analysis: A New Era of More Stable Data and Lower Concentration". He explained how "ppq" level analysis is now required within the industry. He showed how he and his team are using the 8900 ICP-QQQ fitted with an SPS 4 autosampler to analyze ppq level contaminants in samples such as sulfuric acid. The lab also uses the 8900 to quickly scan for particle contamination on silicon wafers.

Dr Hsu's analytical facility achieves the best data, with the lowest BECs and excellent stability, by analyzing each chemical on a dedicated ICP-QQQ instrument.

Agilent's Katsuo Mizobuchi, senior ICP-MS application chemist, explained how to optimize ICP-QQQ to measure  $^{31}\text{P}$  in organic matrices. And Agilent's Yoshinori Shimamura spoke about single particle analysis in semiconductor applications, which many delegates agreed is an important topic. The feedback from one attendee was: "I am reconvinced that the analysis of single particles in high purity solvents is very important and that we need to prepare to do the analysis."

## Reference

1. Measuring Inorganic Impurities in Semiconductor Manufacturing, [5991-9495EN](#)

# Academics Meet in Poland to Discuss Developments in Metallomics

Sayuri Otaki and Yolande Abdelnour, Agilent Technologies, Inc.

Around 275 delegates met at the 7<sup>th</sup> International Symposium on Metallomics in Warsaw, Poland from June 30 to July 3, 2019 to discuss developments in metallomics. Since the first conference, which was held in Nagoya, Japan in 2007, the biennial meeting continues to attract representatives from the world's leading academic research groups. Each conference aims to further the understanding of the role and interactions of metal ions and their chemical structures in biological systems (7). At this year's event, metallodrug development remained a key area of research, with a range of studies being presented using various measurement devices and analytical methods.

## Analysis of the poster presentations

Of the 157 posters presented across the three poster sessions, ICP-MS was used in 64 (40%). Agilent ICP-MS instrumentation was cited in 24 (38%) of the ICP-MS posters, with an even split between single-quadrupole ICP-MS and triple quadrupole ICP-QQQ.

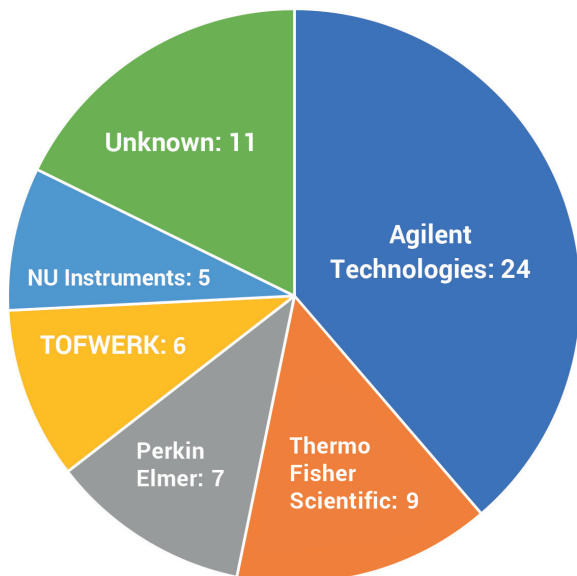


Figure 1. Manufacturer of ICP-MS instrumentation cited in 64 metallomics posters.

Several posters discussed bio-imaging using laser ablation (LA)-ICP-MS. Other hyphenated techniques, such as LC-ICP-MS, were also widely represented in the ICP-MS posters. Emerging fields of study include single cell-ICP-MS and single particle-ICP-MS analysis.

## Multi-element single cell analysis

Agilent's ICP-MS Product Specialist, Yolande Abdelnour presented a paper entitled "Multi-element determination in populations of single cells by Agilent 8900 ICP-QQQ". For the work presented, the 8900 was fitted with a quartz torch with 1.0 mm internal diameter injector and standard nickel cones. A Single-Cell Sample Introduction System for ICP-MS (Glass Expansion) was used for the introduction of intact cells to the ICP-MS. An MVX-7100 Micro-Volume Workstation (Teledyne Cetac) was used to control the low sample flow rate to the ICP-MS.

Agilent ICP-MS MassHunter software provides all the relevant information for the single cell application, and the "Rapid Multi-Element Nanoparticle Analysis" option can measure up to 16 elements in the same batch.

Multiple elements including Mg, Zn, P, S, and Fe in yeast cells were measured using the scICP-QQQ method, as shown in Figure 2.

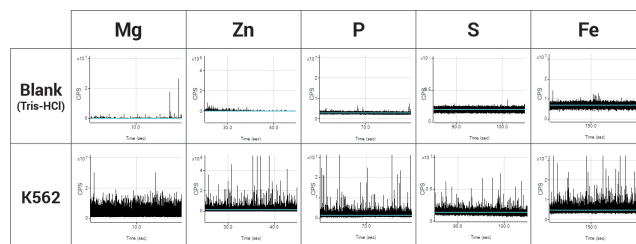


Figure 2. Time scan data showing multiple elements in yeast cells.

## Reference

1. Conference website: <http://metallomics2019.pl/>

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## Your opportunity to meet with Agilent at the WPC 2020

Are you attending the 2020 Winter Conference on Plasma Spectrochemistry, January 12-18, 2020, Tucson, Arizona, USA?

Meet the Agilent team at one or more of the events to be held during the conference:

- Short course: Software Bootcamps, Sunday January 12, 2020
- Lunch seminar: Advances in ICP-OES, Monday January 13, 2020
- Lunch seminar: Understanding all the Qs in ICP-QQQ, Tuesday January 14, 2020
- Lunch seminar: Recent advances in SQ-ICP-MS, Wednesday January 15, 2020
- Customer evening event: Wednesday January 15, 2020
- Lunchtime ICP-QQQ User Meetings for customers who currently own an Agilent Triple Quadrupole ICP-MS, Thursday January 16, 2020

Look out for further communications from Agilent closer to the conference with details on how to book a place at the Agilent events.

Conference website details: [http://icpinformation.org/Winter\\_Conference.html](http://icpinformation.org/Winter_Conference.html)

## Executive summary of recent ICP-QQQ webinar



**Title:** How ICP-MS/MS Improves Data Quality in Everyday Analytical Challenges and for Emerging Contaminants

**Publisher:** Spectroscopy. [Download here](#)

**On-demand webinar:** [Register here](#)

## Latest Agilent ICP-MS publications

- **Application note:** Solving Doubly Charged Ion Interferences using an Agilent 8900 ICP-QQQ, [5994-1155EN](#)
- **Application note:** Routine Elemental Analysis of Dietary Supplements using an Agilent 8900 ICP-QQQ, [5994-1156EN](#)
- **Application note:** Analysis of Nanoparticles in Organic Reagents by Agilent 8900 ICP-QQQ in spICP-MS Mode, [5994-1306EN](#)
- **Brochure (updated):** Fast-Track your Metals Analysis with Solution-Ready ICP-MS: Agilent 7800 Quadrupole ICP-MS, [5991-5874EN](#)
- **Flyer:** Agilent ICP Go Software: Elemental analysis made easy, [5994-0213EN](#)
- **Case study:** Tracing the Effects of Trace Elements: Agilent aids research into environmental processes, [5994-0979EN](#)

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