Agilent ICP-MS Journal

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A Decade of Triple Quadrupole ICP-MS, Learning Resources, and Laser Tuning Tips

This issue of the Agilent ICP-MS Journal features expert users' tuning tips to optimize laser ablation ICP-MS, plus an introduction to the Agilent ICP-MS learning resources available through the Agilent University Online Learning Paths.

We also introduce some upcoming activities and resources related to the 10th anniversary of the launch of the world's first triple quadrupole ICP-MS, the Agilent 8800, at the 2012 Winter Conference in Tucson, Arizona. Dozens of application notes and hundreds of peer-reviewed journal articles highlight the breadth of applications and industries that have benefited from the improved performance of ICP-QQQ.

A separate article explains the principles of operation of the tandem MS (MS/MS) modes that allow demanding applications to be addressed using ICP-QQQ.

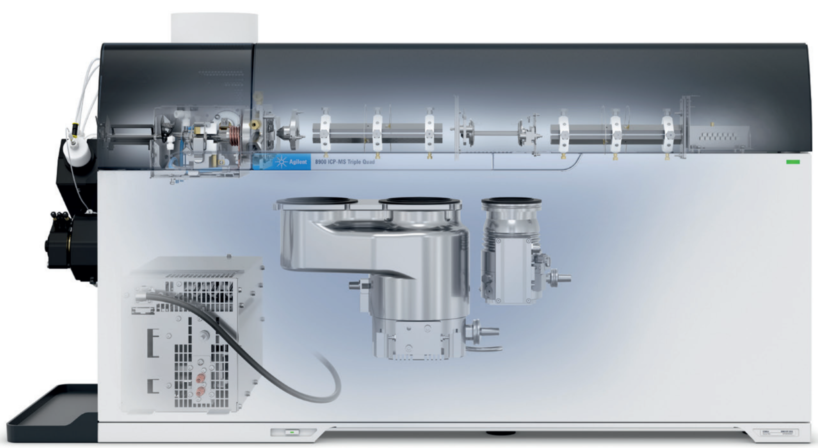

Figure 1. The tandem MS (MS/MS) configuration of the Agilent 8900 ICP-QQQ.

Tips and Tricks for Optimizing Tuning Conditions for Laser Ablation ICP-MS (LA-ICP-MS)

Contribution from Bundoora Research Centre, Rio Tinto; University of Tasmania (CODES); Adelaide Microscopy Unit, Adelaide University; Queensland University of Technology; and Macquarie University, Australia

Optimizing performance for LA-ICP-MS

ICP-MS systems are typically optimized for a balance between high sensitivity and good matrix tolerance. For liquid sample analysis, sensitivity is monitored using several elements in a tune solution, and matrix tolerance is measured using the plasma robustness (CeO^+/Ce^+) ratio. Ce is used for this check because it has a strong metal oxide bond. A low CeO/Ce ratio shows that the plasma has the high energy needed to dissociate CeO.

Sensitivity and plasma robustness are also important for LA-ICP-MS, even though plasma temperature should be higher due to the absence of any solvent. LA-ICP-MS optimization is typically performed using NIST "61x" Trace Elements in Glass Standard Reference Materials (SRMs). The SRMs comprise a series of glass beads doped with 61 elements at concentrations from ~450 ppm in NIST 610, ~40 ppm in NIST 612, down to sub-ppm levels in NIST 616. NIST 610 and 612 are commonly used for tuning and calibration in LA-ICP-MS laboratories.

NIST 610 and 612 contain many elements suitable for sensitivity optimization, but the SRMs include all the rare earth elements (REE). Therefore, the CeO ion (mass 156) that is used to monitor the oxide ratio in solution mode cannot be used for LA-ICP-MS, due to the overlap from ^{156}Gd (and ^{156}Dy). For LA-ICP-MS, the ThO^+/Th^+ ratio is usually used to monitor plasma robustness. Air will build up in the gas lines of a system that is left vented for some time, so the ThO^+/Th^+ ratio is often high when the system is first started. This effect is reduced by purging the gases through the system.

Figure 1. LA tuning lines in NIST 612 Glass. Image courtesy of Maxwell Morrisette, CODES Analytical Laboratories, University of Tasmania, Australia.

LA-ICP-MS users also check the ratio of U/Th as it is a useful indicator of plasma operation. The NIST glasses contain Th and U at almost equal concentrations, e.g., NIST 612 has certified values of 37.79 ±0.08 mg/kg (ppm) for Th and 37.38 ±0.08 mg/kg for U. Both elements are almost 100% abundant at their primary isotopes, Th-232 (100%) and U-238 (99.27%), and both have a low first ionization potential (IP), so are almost 100% ionized. Therefore, the ratio of the U/Th signals should be 1.

Table 1. Properties of thorium and uranium.

Element	Mass	First IP	Melting Point (°C)	Dissociation Energy of Oxide Bond (eV)
Thorium	232	6.31	1750	9
Uranium	238	6.19	1132	7.8

If the U/Th ratio in NIST 61x measured by LA-ICP-MS deviates significantly from 1, it usually indicates that the gas flow through the torch is not well optimized. The carrier gas flow includes the helium flow through the ablation chamber plus the argon make up flow added after the chamber. If the sum of these flows is too high, the difference in ionization and oxide bond dissociation energy between U and Th will lead to a U/Th ratio >1. A higher gas flow reduces the effective temperature of the plasma, so Th is less well ionized relative to U, and more of the Th remains as the undissociated oxide ion. Tune by reducing the carrier gas flow to give a U/Th ratio of 1.

Note: U is more volatile than Th, so the relative signals of U and Th will be affected by the laser conditions as well as plasma conditions.

Reflections on a Decade of Triple Quadrupole ICP-MS: Technology Transformed. Performance Redefined

Ed McCurdy, Agilent Technologies, Inc.

Background to the development of ICP-QQQ

Single quadrupole ICP-MS is an immensely powerful technique, offering fast, multi-element analysis with low detection limits and wide dynamic range. The most significant limitations of the technique for routine applications – matrix tolerance and spectral overlaps – had been largely overcome by 2010. By then, aerosol dilution technology was allowing samples containing % levels of dissolved solids to be run routinely, while helium (He) mode collision/reaction cell (CRC) addressed common polyatomic ions, improving accuracy.

But, even with an effective He cell mode, some spectral interferences could affect performance in demanding applications. Problematic interferences included intense backgrounds from polyatomic ions, isobaric overlaps, doubly charged ion interferences, and peak tail overlaps.

Some of these interferences could theoretically be addressed using reactive cell gases in the CRC of a single quadrupole ICP-MS. But such instruments do not provide complete control of the reaction chemistry. To realize the full potential of CRC methods with reactive cell gases, a new configuration of ICP-MS was needed.

Impact of Agilent ICP-QQQ launch in 2012

The Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) was launched at the 2012 Winter Conference on Plasma Spectrochemistry in Tucson, Arizona. The 8800 was well received, being honored with several prestigious industry awards. These included: IBO 2012 Product of the Show; ACCSI Outstanding New Scientific Instrument Product of 2012; SelectScience Best New Spectroscopy Product of 2012; and R&D 100 2013 Analytical Instruments award.

The new instrument also attracted enormous interest from ICP-MS users and the wider analytical community, with its potential to improve performance in demanding applications quickly becoming apparent. Published methods quickly followed, with the first edition of the Agilent Handbook of ICP-QQQ Applications being produced in 2013. Regular updates have followed, with the 5th Edition due for release later in 2022.

Figure 1. Handbook of ICP-QQQ Applications, 5th Edition, due for publication in 2022.

User publications also soon started to appear and, since 2017, Agilent has maintained an online bibliography of publications that used an Agilent 8800 or 8900 ICP-QQQ.

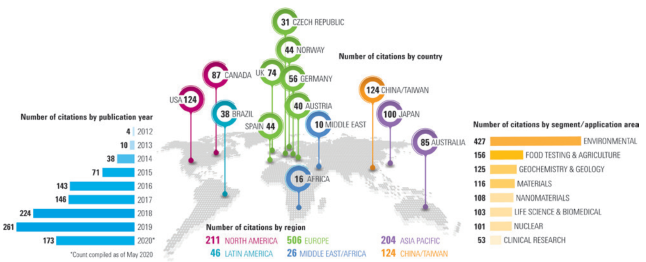

Figure 2. Interactive, online Agilent ICP-QQQ bibliography.

The scope of these publications is impressive, covering a wide range of industries and sample types. Many papers focus on applications involving "difficult" analytes such as Si, P, and S in research areas such as life science, clinical research, and pharmaceuticals. But ICP-QQQ is also used for semiconductor, materials, geochemistry, nuclear, food, and environmental analysis, among many others. The updated ICP-QQQ bibliography – due for release in 2022 – now contains more than 1700 citations.

MS/MS Operation with ICP-QQQ: Redefining ICP-MS Reaction Mode Performance Since 2012

Ed McCurdy and Glenn Woods, Agilent Technologies, Inc.

Principles of tandem mass spectrometry

Tandem mass spectrometry – or MS/MS – is a well-known and widely used technique in organic mass spectrometry, where it is used to study the structure of organic molecules. Various MS/MS configurations exist, of which triple quadrupole MS (QQQ, or TQ) is the most relevant to ICP-MS. In organic-QQQ MS, the first analyzer quadrupole, Q1, selects the mass of the precursor ion of interest, which passes through to a collision cell for fragmentation. The resulting fragments are then selected by a second mass analyzer, Q2, (or Q3, if a quadrupole is also used in the cell) and passed to the detector.

ICP-MS measures elemental ions, so the analyte ions are not fragmented. Instead, the cell of an ICP-MS/MS is typically filled with a reactive gas, and the aim of the analysis is to separate the precursor ions from any spectral overlaps.

The principle of ICP-MS/MS is based on the differences in the reactivity of the precursor (analyte) ions and any on-mass interfering ions, so different reaction gases are used for different applications.

ICP-MS/MS modes of operation

Figure 1 shows the modes of operation of ICP-MS/MS:

1. **On-mass measurement:** The analyte precursor ion does not react with the cell gas and so remains at its original mass. Interfering ions that overlap the analyte mass do react and so are neutralized or moved.
2. **Mass-shift measurement:** The analyte precursor ions do react and so move to a new product ion mass. Interfering ions do not react and so remain at their original mass. Q2 is set to the analyte product ion mass, so the original overlap is avoided.

MS/MS on-mass measurement removes the interference.

MS/MS mass-shift measurement avoids the interference.

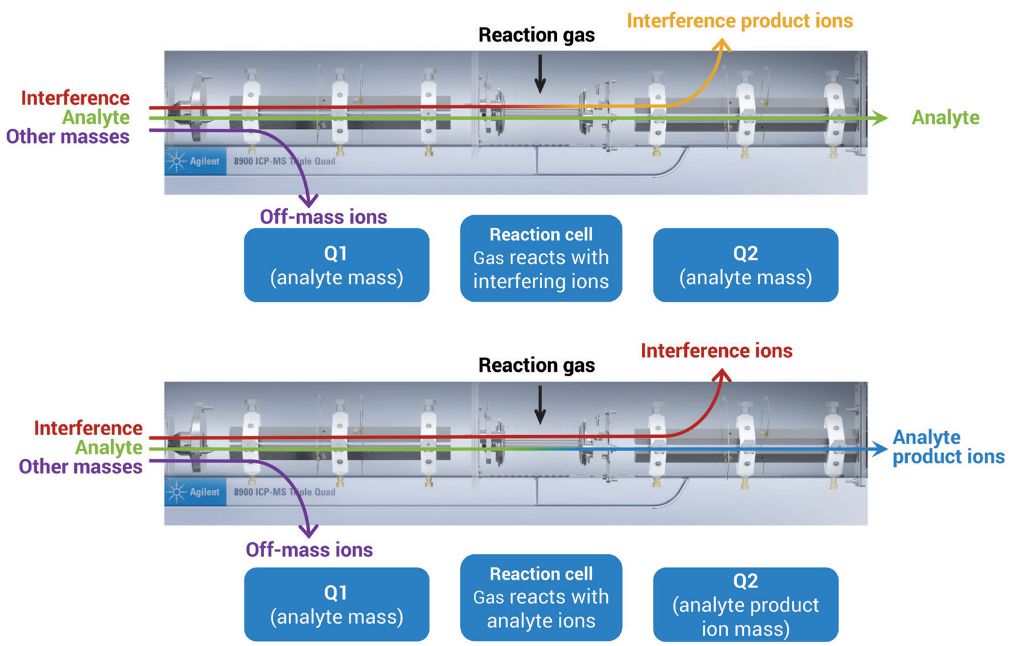

Figure 1. ICP-MS/MS modes of operation. **Top: On-mass measurement**. The analyte is unreactive and remains at its original mass. Interfering ions react and are neutralized or moved to a different mass. Q2 is set to the original analyte mass, so the interference product ions are rejected. **Bottom: Mass-shift measurement**. Analyte ions are reactive and form reaction product ions at a different mass, avoiding the original on-mass overlap.

Reactive cell gases can be used with single quadrupole or bandpass ICP-MS. But, without a Q1 mass filter, off-mass ions can enter the cell, leading to unpredictable reaction chemistry that can create new product ion overlaps. ICP-MS/MS uses double mass selection to control the reaction cell processes, providing reliable and consistent reaction mode results, even in complex, varied samples.

Any ICP-MS requires good underlying performance – a robust plasma, high sensitivity across the mass range, and good control of polyatomic interferences with helium collision mode. But MS/MS enables analysts to reliably use reactive cell gases, which opens up new possibilities for ICP-MS. MS/MS reaction gas methods can remove intense polyatomic interferences, improving detection limits for many analytes, including elements such as Si, P, and S that were previously difficult for ICP-MS. ICP-MS/MS can also address other types of spectral overlaps, such as isobaric overlaps, doubly charged ion overlaps, and peak tail overlaps, all of which are difficult to deal with using conventional ICP-MS.

ICP-MS/MS performance illustrations

An example of an MS/MS on-mass measurement is shown in Figure 2. The method uses NH_3 reaction gas to resolve the Hg-204 isobaric overlap on Pb-204, allowing the minor Pb isotope to be measured free from overlap. The Pb-204 isotope is required for some Pb isotope ratio measurements in geochronology. Resolving isobaric overlaps is extremely useful for ICP-MS users, enabling many novel applications in geochemistry, nuclear science, and environmental monitoring.

Figure 3 shows an MS/MS mass-shift method, where sulfur was measured at low concentration using O_2 cell gas. The O_2 reaction gas converts the S^+ analyte ions to SO^+ product ions ($^{32}S^+ \rightarrow {}^{32}S^{16}O^+$), so the major isotope of S is measured at *m/z* 48. With MS/MS, the existing ions at mass 48 ($^{48}Ca^+$, $^{48}Ti^+$, $^{36}Ar^{12}C^+$, etc.) are rejected by Q1, so cannot overlap the SO^+ product ions.

Conclusion

The development of triple quadrupole ICP-MS 10 years ago dramatically extended the capabilities of ICP-MS. Agilent ICP-MS/MS methods have led to many new and exciting application possibilities for ICP-MS users.

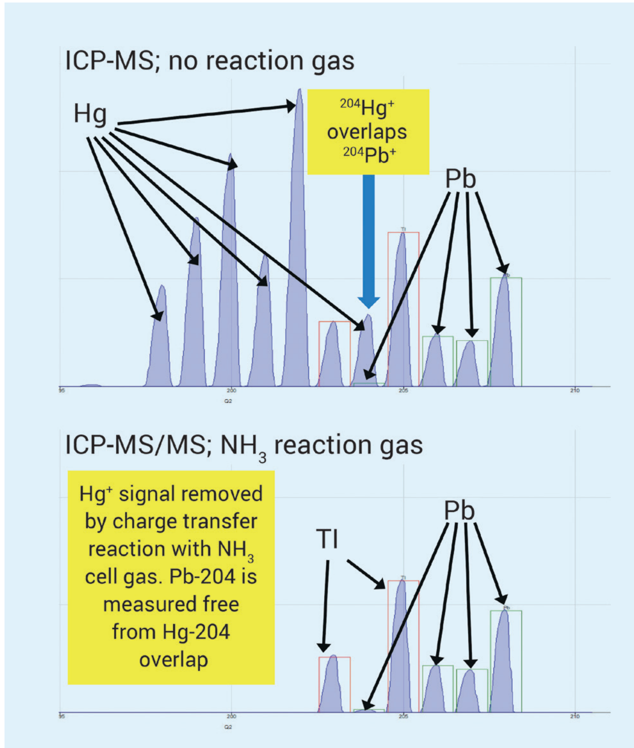

Figure 2. Top: Single quadrupole ICP-MS. Pb-204 is overlapped by Hg-204. **Bottom: ICP-MS/MS**. the Hg signal is neutralized by charge transfer reaction with NH_3 cell gas. Pb-204 is measured on-mass.

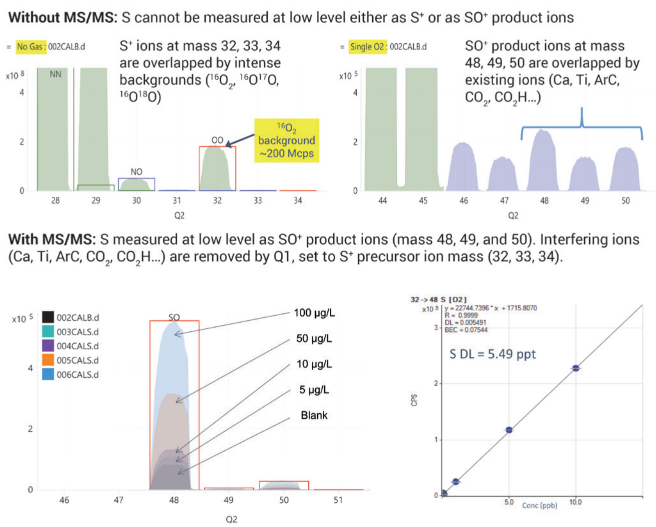

Figure 3. Top: Single quadrupole ICP-MS. S analysis is difficult due to intense backgrounds. O_2 reaction mode does not work well due to existing ions at the SO^+ product ion masses. **Bottom: ICP-MS/MS**. O_2 reaction gas is used successfully for low-level S analysis.

Further information

Handbook of ICP-QQQ Applications using the Agilent 8800 and 8900, Agilent publication, 5991-2802EN

Agilent ICP-MS and ICP-QQQ Online Learning Paths at Agilent University

Alan Lynch and Jandee Kahl, Agilent Technologies, Inc.

Self-paced online learning for Agilent ICP-MS

Do you want to learn how to use the full power of your Agilent ICP-MS system? Discover complete self-paced, online Learning Paths for Agilent ICP-MS systems at Agilent University for single quadrupole (7800, 7850, 7900) and triple quadrupole (8800, 8900) instruments. Course content is appropriate for beginners to intermediate level analysts who either use versions of ICP-MS MassHunter up to 4.6, or the later version 5.1.

Learning Paths for single and triple quadruple ICP-MS systems structure your online learning, presenting key information in logical, sequential steps. Modules include an introduction to the basic principles of ICP-MS, an explanation of the function of each part of the instrument, and worked examples of typical software operations.

Understand Batch creation, optimization, data processing and review, as well as maintenance and troubleshooting. You can maximize your learning retention by viewing the self-paced courses while seated in front of your instrument. Increase your lab productivity by mastering your analytical software and using advanced features to improve sample throughput.

For anyone who wants greater control over their learning environment, self-paced online courses provide the most flexible and convenient training option. The average time to complete a single eLearning module is 20 minutes and most courses include a knowledge check to allow you to confirm your understanding. Each course can be viewed in its entirety immediately after purchase, or over multiple days to best fit your schedule. Consider working with your manager to design a course of study that best meets the future needs of your lab while demonstrating your willingness to expand your ICP-MS knowledge and advance your career.

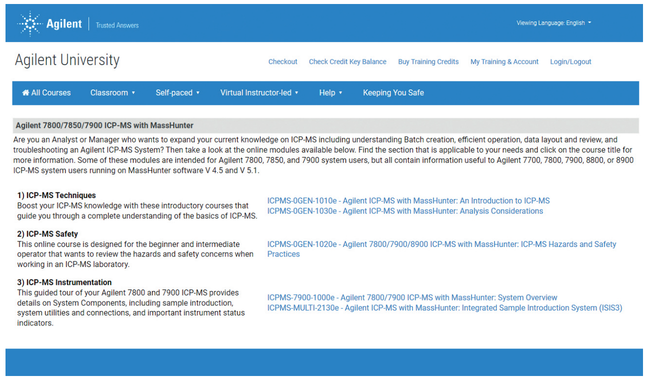

Figure 1. Agilent University self-paced learning modules for single quadrupole ICP-MS.

Register with Agilent University to access courses

Users will need to purchase Training Credits to access most courses. You can purchase course credits individually or save money with an Agilent University ePass that allows unlimited access to content for all product lines. Agilent University ePasses are available in 3-month (600 Training Credits) and 1-year (1200 Training Credits) options. Use the Training Credits Convertor to estimate the cost of credits based on your location. Learning modules are best viewed on a laptop, desktop, or tablet screen. Mobile devices are not recommended. Check out the Self-paced Participant Guide for help with registering and viewing courses.

Note: even if you already have an account for Agilent.com, you will need to create a separate account for Agilent University to register for training courses.

Access and register for the Agilent ICP-MS learning paths by following the links:

Agilent 7800/7850/7900 ICP-MS with MassHunter

Agilent 8800/8900 Triple Quadrupole ICP-MS with MassHunter

Agilent Cool Clear: Protect Your ICP-MS Cooling Circuit With A Specially Formulated Coolant Fluid

Gareth Pearson, Agilent Technologies, Inc.

Importance of using the right fluid in your mass spectrometer's cooling circuit

To ensure optimum instrument performance and to avoid unplanned downtime, you should use a purpose-blended coolant in your spectrometer's chiller or heat exchanger. Off-the-shelf coolant, tap water, and de-ionized water do not contain the corrosion inhibitors and other chemicals needed for optimum cooling circuit performance. Without the right blend of corrosion-inhibiting chemicals at the right levels, corrosion can occur, and deposits can build up in the cooling water circuit. These deposits may reduce cooling efficiency or even cause blockages, leading to unplanned downtime.

Figure 1. Agilent Cool Clear coolant fluid, part number 5799-0037. The pack includes 2 gallons of coolant, containing a corrosion inhibitor combined with high purity water and clarifier for the protection of your spectrometer's cooling circuit.

Comparison of coolants

Agilent Cool Clear was compared to a non-approved coolant that did not contain any corrosion inhibitor. Figure 2 (left) shows the cooling water manifold of an Agilent ICP-MS after two months using the non-Agilent coolant. Cu and Zn corrosion products were identified in the cooling water and deposits can be seen on the internal surfaces of the manifold. Figure 2, right, shows the manifold after 3.5 months use with Agilent Cool Clear. No signs of corrosion are visible on the internal surfaces of the cooling water manifold, confirming the superior protection provided by Cool Clear.

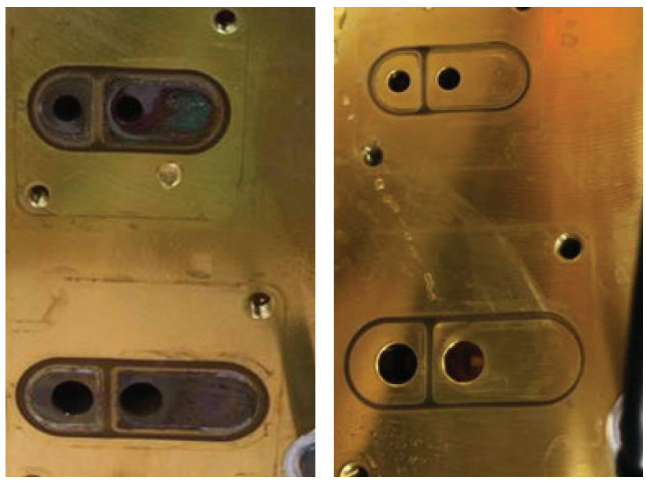

Figure 2. ICP-MS cooling water manifold after several months of operation using different types of fluid in the cooling circuit. Left: after two months use with non-approved coolant. Right: after 3.5 months operation using Agilent Cool Clear.

Annual replacement of the ICP-MS coolant is recommended. An Agilent service engineer replaces the coolant as part of the instrument preventative maintenance service.

Learn more: Agilent Technical Note, 5994-4576EN

Are you maximizing the potential of your ICP-MS? Watch this on-demand webinar for some useful tips and tricks from Agilent ICP-MS specialists

SeparationScience
PREMIER LEARNING FOR ANALYTICAL SCIENTISTS

Knowing How to Make ICP-MS Easier

Having the right information at the right time can help you improve the productivity of your lab. Based on feedback from users, Agilent has developed intuitive and powerful software, a range of Easy-fit supplies, and complete analytical workflows that simplify the running of an Agilent ICP-MS.

During the 1-hour webinar, Agilent specialists share information designed to make your ICP-MS applications easier to run and your instrument easier to maintain.

- Learn how Agilent Easy-fit supplies can simplify your workflow.
- Discover selection tools that help you to optimize your ICP-MS configuration for your sample-types.
- Better understand ICP-MS MassHunter software functions.
- Learn about software tools and time-saving tips that simplify ICP-MS workflows.

Presenters: Gareth Pearson, ICP-MS Supplies Product Manager; Glenn Woods, ICP-MS MassHunter Product Manager; and James Dellis, R&D Applications Chemist for Supplies Product Development

Link to the recorded webinar hosted by SeparationScience:
Knowing How to Make ICP-MS Easier (sepscience.com)

Latest Agilent ICP-MS publications

- **Application note:** ICP-MS Analysis of Trace and Major Elements in Drinking Water According to US EPA Method 200.8, 5994-4744EN
- **Application note:** Authenticating Geographical Origin of Tea Using ICP-MS and Agilent Mass Profiler Professional Software, 5994-4583EN
- **Application note:** Analysis of Undiluted Seawater using ICP-MS with Ultra High Matrix Introduction (UHMI) and Discrete Sampling (DS), 5994-4467EN
- **Application note:** Evaluation of the Elemental Content of a Single Cell using Fast Time-Resolved Analysis (TRA) ICP-MS, 5994-4460EN
- **Application note:** Analysis of Platinum Group Elements (PGEs), Silver, and Gold in Roadside Dust using Triple Quadrupole ICP-MS, 5991-6768EN
- **Technical brief:** The ICP-MS Vacuum Interface, 5994-4695EN
- **Technical brief** *(updated)***:** Agilent I-AS Clean Autosampler, 5988-2992EN

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