Agilent ICP-MS Journal

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Trusted Answers

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Optimizing ICP-MS for Routine and Advanced Applications

ICP-MS is an extraordinarily powerful technique, equally at home in routine, high throughput contract analysis laboratories and in research institutes investigating the most unusual and obscure applications. Yet, across this vast array of diverse measurements, there are nearly always certain parameters that, when optimized, make a critical contribution to the success of the analysis.

Issue 92 of the Agilent ICP-MS Journal provides some tips showing how users can improve the chemical stability of some difficult analytes and optimize washout for the analysis of typical acidified samples. A separate article explains some of the critical factors that contribute to the unparalleled success of Agilent ICP-MS systems in laser ablation (LA) ICP-MS applications.

The ever-expanding range of ICP-MS applications is further illustrated by a report on the recent European Winter Conference on Plasma Spectrochemistry. The applications presented at the conference highlight some of the novel uses of Agilent ICP-MS and ICP-QQQ (MS/MS) instruments in leading research institutes.

Figure 1. Agilent 8900 ICP-QQQ provides MS/MS selectivity to address the most demanding ICP-MS applications.

Tips and Tricks to Improve Element Stability and Ensure Effective Washout in ICP-MS Applications

Glenn Woods and Ed McCurdy, Agilent Technologies, Inc.

Requirements for multielement analysis

ICP-MS is a multielement analysis technique and is often used for trace element measurements. This combination can present some challenges as users must ensure that incompatible elements are chemically stabilized in the same solution, while avoiding trace level contamination of samples and standards.

Historically, ICP-MS users were advised to use only HNO_3 to stabilize samples, to avoid the risk of errors due to polyatomic interferences derived from other acids such as HCl, $HClO_4$, or H_2SO_4. However, some elements, such as As, Se, Mo, Sn, Sb, Hg, and Tl, can be unstable or incompletely soluble in nitric acid solutions. This leads to several analytical issues, such as low recovery of Sn from soil extracts, poor stability for Mo and Tl, and poor washout (carryover) and comparatively long stabilization times for Hg, shown in Figure 1. The development of collision/reaction cells (CRC) able to operate effectively in helium (He) mode removed the restriction on acid types, as He mode provided a simple and reliable way to deal with polyatomic ion overlaps including Cl- and S-based interferences (*1*). ICP-MS users were therefore free to use the optimum acid or acids for sample digestion and analyte stabilization.

HCl for sample stabilization

With He mode able to resolve the Cl interferences, ICP-MS users can now routinely add HCl as well as HNO_3 for sample stabilization, addressing many long-standing issues including Hg instability. HCl complexes Hg as $[HgCl_4]^{2-}$, ensuring that backgrounds are controlled, as shown in the ppt level calibration in Figure 2. Hg is a critical element that can now be measured at low levels using ICP-MS, along with other regulated analytes. This enables labs to simplify and streamline their routine analytical workflow, for example by removing the need for a separate, single-element technique for Hg.

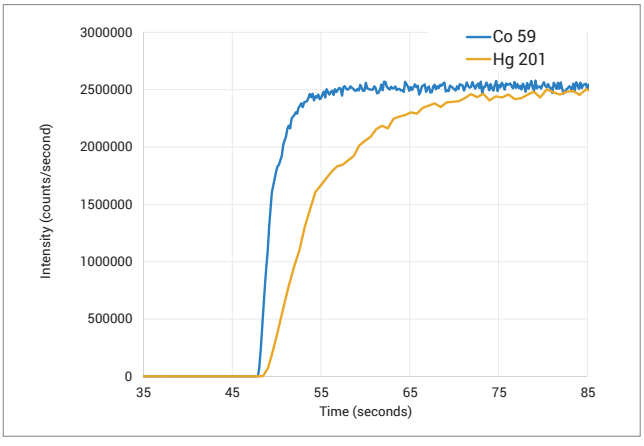

Figure 1. Wash-in signal for Co and Hg, shows slow stabilization for Hg due to chemical instability and adsorption on the sample uptake tubing.

Adding HCl at a concentration of around 0.5% to all solutions (samples, calibration blanks and standards, QCs, etc.) ensures that most common elemental stability issues are resolved. Recoveries are improved, calibration linearity is more reliable, and sample throughput can be increased, as wash-in and washout times are shorter.

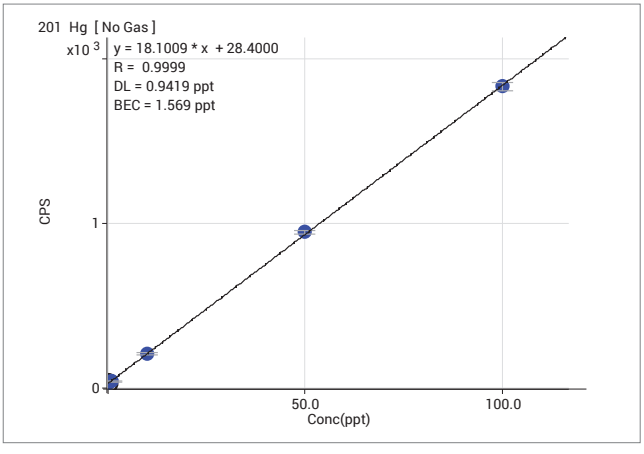

Figure 2. Hg calibration showing low background (BEC 1.6 ppt) and detection limit (0.9 ppt) made possible by HCl stabilization.

It is often assumed that adding HCl to sample solutions will cause chemical instability for some analytes; Ag is often cited as a chloride incompatible element. While it is

true that trace Cl causes Ag to precipitate as insoluble AgCl, an excess of Cl promotes the formation of soluble anionic complexes with the general formula $AgCl_n^{(n-1)-}$. A HCl concentration of 0.5% (in addition to 1–2% HNO_3) is sufficient to stabilize Ag at concentrations up to a few µg/L (ppb). However, the solubility of the complexes depends on the relative amount of Ag^+ and Cl^-, so a higher HCl concentration is required for higher Ag concentrations. The effect of insufficient HCl on the stability of the higher concentration Ag standards is shown by the non-linear calibration in Figure 3.

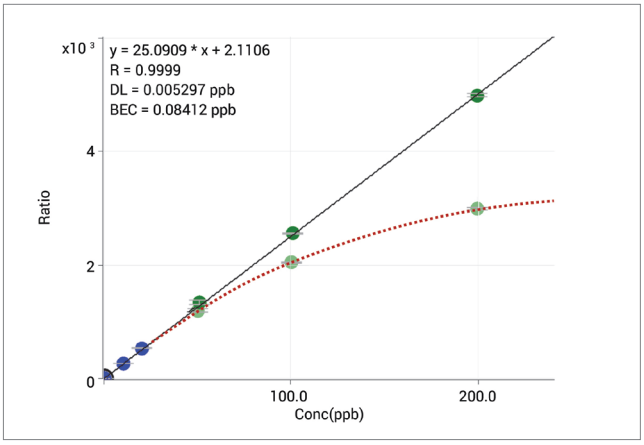

Figure 3. Calibration plot for silver. Red dotted line shows non-linearity due to insufficient HCl to stabilize higher standards. Solid black line shows good linearity for Ag with a higher concentration of HCl.

Optimizing rinse chemistry and protocol

Chemical solubility is also an important consideration for optimizing the process of flushing or rinsing between samples during an analytical sequence. Users who are new to ICP-MS often assume that a simple de-ionized water or dilute HNO_3 rinse is sufficient to avoid carryover of the signals from one sample to the next. But some elements tend to adsorb onto the inner surfaces of the uptake tubing and sample introduction system, leading to raised backgrounds and signal instability. Figure 4 shows a multi-step rinse program with alternating strongly acidic and strongly basic rinse solutions, which dramatically improves the washout of many elements. The "tip wash" in the pumped rinse station removes any sample solution that may remain on the outside of the autosampler probe.

This step avoids contaminating the subsequent rinse solutions. The addition of ethanol and mannitol (for boron) and Au(III)Cl (for Hg) can further improve the removal of these specific analytes. The final rinse step conditions the sample introduction system to the same acid mix as the samples, ensuring rapid equilibration when the next sample is introduced.

Reference

1. McCurdy, E., and Woods, G., *J. Anal. Atom. Spectrom.*, **2004**, 19, 607–615.

Pumped rinse port (tip wash)

A few seconds in slightly basic water (dilute ammonium hydroxide)

Rinse bottle 1

Ammonia, EDTA, surfactant (e.g. Nereid). Optional trace EtOH and mannitol (for boron rinse out)

Rinse bottle 2

5% HNO_3 and 5% HCl – can also add 0.2 ppm Au(III)Cl (for Hg washout)

Rinse bottle 3

Matched to acid mix of samples – e.g. 1% HNO_3 and 0.5% HCl

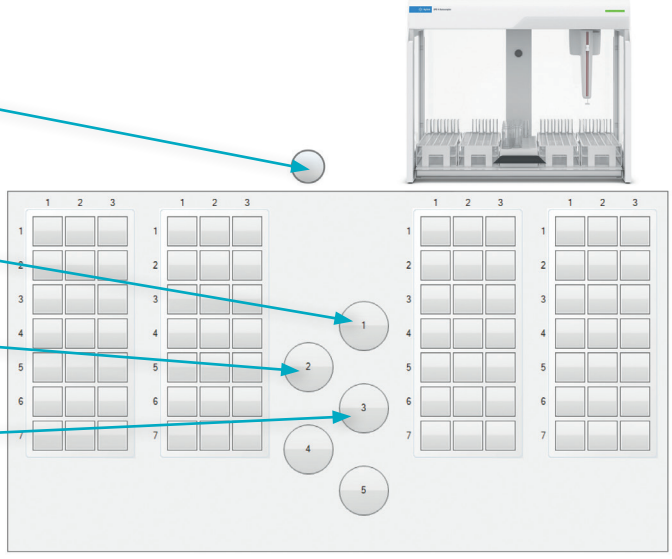

Figure 4. An optimized rinse sequence of alternating acidic and basic rinse solutions improves the washout of difficult, "sticky" elements. The final rinse solution is an acid mix that closely matches the composition of the samples, to ensure the spray chamber is equilibrated for the next sample analysis. The figure shows the rinse bottle layout for the Agilent SPS 4 autosampler. A similar rinse program can be applied to other compatible autosamplers.

Agilent ICP-MS System Suitability for Laser Ablation (LA) ICP-MS Applications

Fred Fryer, Bastian Georg, and Ed McCurdy, Agilent Technologies, Inc.

Laser ablation ICP-MS

ICP-MS is mainly used to analyze liquid samples, but direct analysis of solids and gases is also possible with an appropriate accessory. For solid sample analysis, the most common approach is laser ablation (LA), which has been used since the early days of ICP-MS. In LA-ICP-MS analysis, intense pulses of light (usually UV) are focused on a sample which is held in an enclosed chamber. High quality optics allow the laser beam to be focused to a spot size as small as a few microns (µm) diameter, as shown in Figure 1. The energy in the pulsed light beam creates a micro plasma in the helium carrier gas above the sample surface. This plasma "ablates" the sample, removing material which is carried to the ICP to be decomposed, atomized, and ionized in the same way as for liquid sample droplets.

Critical parameters that affect the laser interaction with the sample surface include the laser wavelength, energy density (known as fluence), pulse duration, and repetition rate, as well as the sample composition and surface morphology. As a result of these variations, a different laser will work best for different sample types, so the optimum laser system will depend on the application.

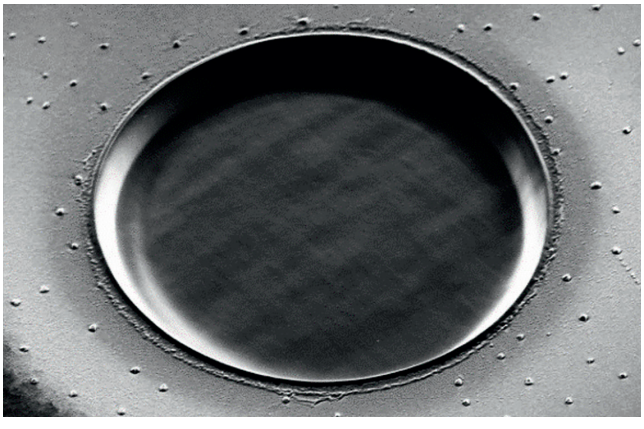

Figure 1. Analyte Excite excimer laser ablation crater (50 µm diameter). Image courtesy of Teledyne Photon Machines.

LA-ICP-MS optimization and acquisition

Under optimum conditions, the ablation will produce a consistent and representative cloud of vapor and fine particles from the sample. Particles should be smaller than ~100 nm to be processed effectively in the plasma.

Higher laser energy or fluence (measured in J/cm^2) removes more sample mass, increasing the signal. But higher fluence also ablates larger particles, which are not fully decomposed in the plasma, leading to high oxides, poor stability, and elemental fractionation. Higher fluence also causes more damage to the sample, so is less suitable for small spot applications such as imaging.

Successful LA-ICP-MS analysis requires an ICP-MS with high sensitivity, low background, good matrix tolerance, effective control of interferences, fast acquisition speed, and wide linear dynamic range – factors that are also critical for liquid sample analysis.

Agilent ICP-MS systems provide exceptionally high signal-to-noise (S/N) in the "dry" plasma (no liquid aerosol) conditions that are characteristic of laser ablation. A high S/N provides two major benefits:

1. The ablation conditions can be optimized for the sample type and analytical goal. There is no need to compromise spot size, fluence, or repetition rate to provide enough signal for the analysis.
2. The ICP-MS conditions can also be optimized for the application. Users don't have to compromise robustness to maximize signal, or to use longer integration times for trace analytes.

Agilent LA ICP-MS users typically optimize the laser conditions to give fluence of around 0.2 to 2.5 J/cm^2 to ensure minimal sample damage and consistent signal from multiple shots at the same site. By contrast, users of non-Agilent LA-ICP-MS systems may need 100 times higher fluence (20 J/cm^2) to give adequate sensitivity.

Similarly, Agilent users typically optimize the ICP-MS for robust plasma conditions with an oxide ratio (ThO^+/Th^+) of ~0.001 (0.1%) or less. Users of non-Agilent ICP-MS systems may have to run with robustness degraded by as much as a factor of five (ThO/Th of 0.5%) to give sufficient sensitivity for trace analysis.

Bulk analysis vs small features and imaging

LA-ICP-MS can be used for bulk analysis, where a large sample area is ablated during each acquisition to determine the overall sample composition. LA-ICP-MS analysis of a bulk sample produces a steady-state signal, shown in Figure 2, similar to liquid analysis. Replicate measurements and external calibrations can be used to quantify elements from major to trace levels (ppm and below) if well-characterized solid standards are available.

LA-ICP-MS is also used for micro-analysis, where small features/inclusions are ablated individually, and for depth profiling and imaging, where time-resolved analysis (TRA) data is collected as the sample is being ablated. For these types of time-based measurements, acquisition speed is an important factor. However, faster acquisitions use shorter dwell times, giving fewer counts for each analyte. So, for multielement analysis of short-lived TRA signals, high ICP-MS sensitivity is even more essential. This is illustrated in Figure 3, which compares the signals

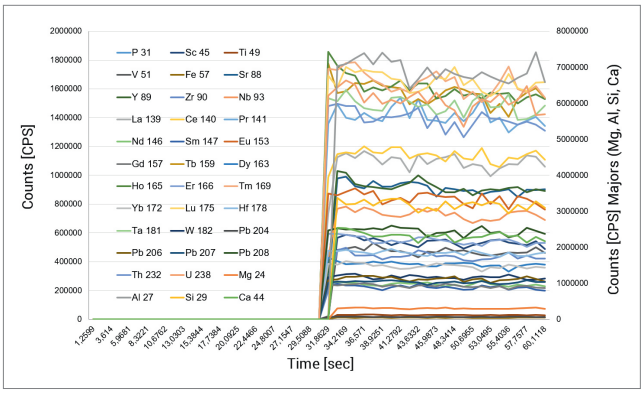

Figure 2. Agilent 7900 signal for 36 masses from line ablation of NIST 610: 30 seconds of gas blank followed by 30 seconds ablation. 193 nm Excimer laser; 40 µm spot, 5 Hz, 2 J/cm^2. Data courtesy of CODES Analytical Laboratories, University of Tasmania, Australia.

for elements specified in ASTM Standard Method E2927-16E1 (from a total of 40 masses measured) using dwell times of 5 and 0.1 ms (*1*). Longer dwell times give better detection limits (DLs) and a smoother signal, while shorter dwell times give better time resolution but lower signal and poorer DLs. Agilent ICP-MS systems enable trace level analytes (such as Au, Figure 3, right, inset) to be measured, even when short integration times are used.

Reference

1. ASTM Standard E2927, **2022**, DOI: 10.1520/E2927-16E01, http://www.astm.org

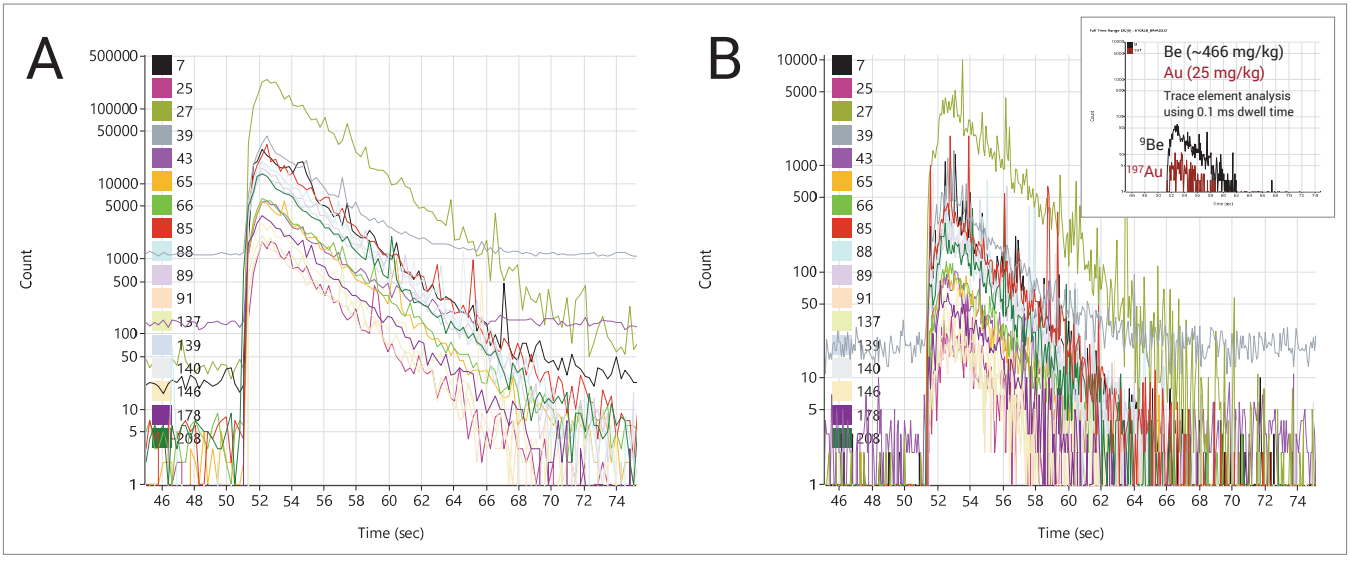

Figure 3. ASTM E2927-16E1 elements measured during a 1 s ablation of NIST 610; 40 masses in total. **(A):** Dwell time of 5 ms per mass gives excellent signal-to-noise and low DLs. **(B):** Dwell time of 0.1 ms per mass gives better time resolution, but poorer DLs. Inset: Very high sensitivity and good control of mass bias means Agilent ICP-MS can measure trace level (Au) and low mass (Be) analytes even with 0.1 ms dwell time.

Highlights from the 2023 European Winter Conference on Plasma Spectrochemistry

Sébastien Sannac, Uwe Noetzel, Fred Fryer, Alain Desprez, Matthias Balski, and Ed McCurdy, Agilent Technologies, Inc.

EWCPS 2023, Ljubljana, Slovenia

At the end of January 2023, almost 550 attendees gathered in the beautiful Slovenian capital, Ljubljana for the 19th European Winter Conference on Plasma Spectrochemistry (EWCPS).

Figure 1. View of Ljubljana city, overlooked by the imposing castle.

The European Winter Conference series started in 1985 and remains the leading forum for the exchange of information on novel instrumentation and applications relating to plasma spectrochemistry. With so many face-to-face events having been scaled back or canceled in recent years, it was wonderful to meet again for a mix of leading scientific contributions and lively social activities in such a warm and friendly location.

Leading themes at this year's conference included applications in disease research, the use of ICP-MS in monitoring and regulating emerging pollutants (including nanomaterials), and high-resolution imaging using laser ablation (LA) ICP-MS. Applications involving isotopic analysis were also well represented, with stable isotope ratio analysis in clinical research becoming more widely reported, along with established applications in geochemistry, geochronology, and nuclear science.

While multi-collector ICP-MS and Thermal Ionization (TIMS) are the gold standard for high precision isotopic analysis, quadrupole ICP-MS remains an essential technique for many applications, particularly where MS/MS enables problematic spectral overlaps to be resolved.

Agilent sponsored research awards

Since 2003, Agilent has been delighted to recognize and support the work of outstanding researchers in Plasma Spectrochemistry by sponsoring scientific awards at the European Winter Conference.

At this year's conference, the European Award for Plasma Spectrochemistry was won by Heidi Goenaga-Infante of LGC, UK and the European Rising Star award was won by Thibaut Van Acker of Ghent University, Belgium. Agilent warmly congratulates both recipients.

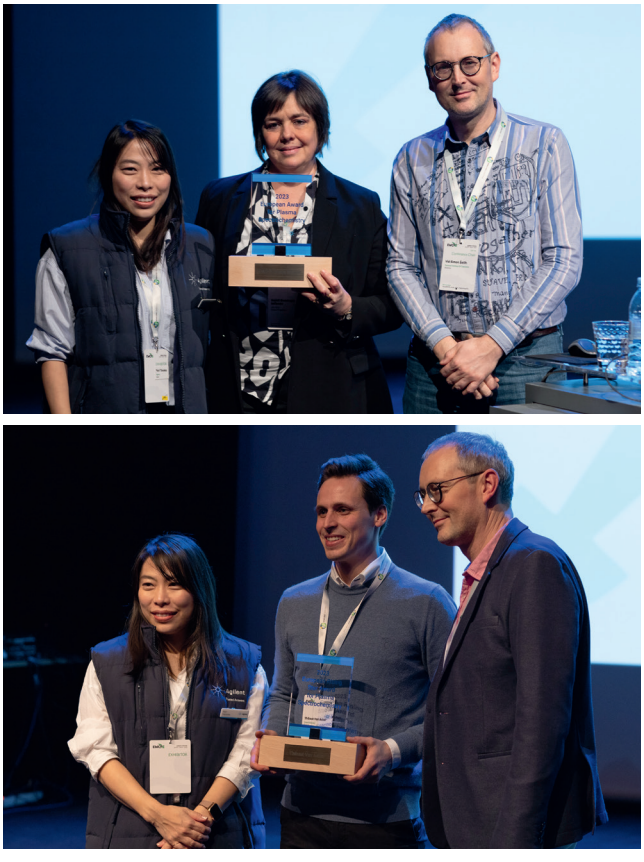

Figure 2. Heidi Goenaga-Infante (top) and Thibaut Van Acker (bottom) receive their awards from Agilent's Yuri Tanaka (left) and Vid Simon Šelih, EWCPS 2023 Conference Chair (right). Photos courtesy of Tine Lisjak, EWCPS 2023.

Agilent scientific posters and lunch seminar

Agilent presented posters on a variety of novel ICP-MS applications from measuring potentially toxic trace elements in alternative proteins to using ICP-MS for quality control of raw materials used in lithium-ion battery manufacturing. See page 8 for further details.

Agilent also hosted a lunch seminar focusing on novel applications that have been enabled by ICP-MS/MS. The seminar marked more than a decade since Agilent launched the first ICP-MS/MS, the Agilent 8800, in 2012.

Figure 3. Lunch seminar cake celebrating more than 10 years since the launch of the first triple quadrupole ICP-MS.

The well-attended seminar included presentations covering a variety of ICP-MS/MS topics:

- Reflections on the first decade of triple quadrupole ICP-MS: Addressing challenging applications with ICP-MS/MS, *presented by Ed McCurdy, Agilent Technologies, UK*
- Speciation analysis of non-metals and metalloids with ICP-QQQ, *presented by Dr. Simone Braeuer, University of Graz, Austria*
- Nuclear ICP-MS applications made possible by MS/MS mode, *presented by Dr Ben Russell, National Physical Laboratory, UK*

Special thanks to our guest speakers Simone and Ben, and particular appreciation to Ben for stepping in at the last minute when the scheduled speaker was unable to attend the conference.

As at previous conferences, we counted the number of posters presented by users of ICP-MS systems supplied by all the different instrument vendors. The count (Figure 4) showed that Agilent ICP-MS are the most widely used systems for research, as well as being well known for their leading role in routine analysis. More than half of the posters that described applications run on quadrupole ICP-MS and MS/MS instruments used Agilent systems.

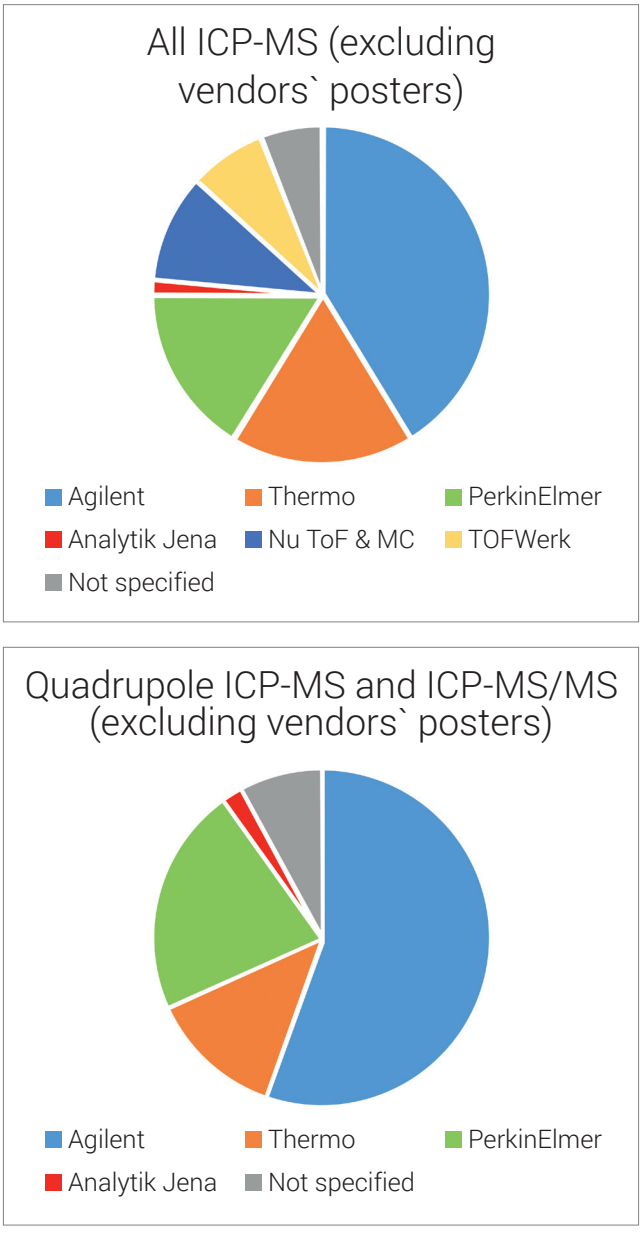

Figure 4. EWCPS 2023 poster counts for all ICP-MS posters (top), and quadrupole ICP-MS only (single quad and MS/MS, bottom). The counts exclude posters presented by instrument vendors.

Agilent scientific posters and lunch seminar from the EWCPS 23

At the recent European Winter Conference on Plasma Spectrochemistry (EWCPS), Agilent scientists presented posters on a range of novel applications. The PDF reprints of the ICP-MS can now be accessed on the conference resources page of Agilent.com. The resources page also includes a link to the video of the Agilent ICP-MS/MS lunch seminar, which was live-streamed during the event.

Selected Agilent 8900 ICP-MS/MS posters:

- Investigation of Microplastic Size and Number Changes During Simulated UV-Degradation Using Single Particle ICP-MS/MS
- Single-Cell and Bulk ICP-MS Investigation of Accumulation Patterns of Pt-based Drugs in Cisplatin-Sensitive and -Resistant Cell Models
- Particle Analysis of Two High Purity Grades of N-Methyl-2-Pyrrolidone (NMP) using Single Particle (sp)ICP-MS/MS Method
- Direct Metal Analysis by New Galvano-Mirror fs-LA-ICP-MS using 100%-Normalization Method with NIST 612 Glass SRM as Calibration Standard

Selected Agilent 7850 ICP-MS posters:

- High Accuracy Standard Addition ICP-MS Analysis of Elemental Impurities in Electrolyte Used for Lithium-Ion Batteries
- Determination of Heavy Metals and Nutrient Elements in Alternative Protein Foods Using ICP-MS
- Authenticating Geographical Origin of Tea from the North East Region of India Using ICP-MS and Agilent Mass Profiler Professional Chemometrics Software

Latest Agilent ICP-MS publications

- **Application note:** Analysis of 50 nm Silica Nanoparticles in Semiconductor Process Chemicals by spICP-MS/MS, 5994-5866EN
- **Application note:** Elemental Analysis of Pure Metals and Alloys by Femtosecond Laser Ablation (LA-)ICP-MS, 5994-5540EN
- **Technical flyer:** ICP-MS MassHunter Software: Intelligent Sequence quality control module, 5994-5865EN
- **Technical flyer** (updated)**:** Nanoparticle Analysis by ICP-MS, 5991-8828EN

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