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Novel Uses for Agilent ICP-MS in a Changing World

Agilent ICP-MS users and commercial partners are continuing to develop interesting and innovative new research and routine applications. In this issue of the Agilent ICP-MS Journal, we present a new approach for direct solids analysis using a combination of laser ablation ICP-MS and laser induced breakdown spectroscopy (LIBS).

We also introduce a new method for monitoring trace levels of Rare Earth Elements (REE) in natural waters. The REEs are among a group of technology critical elements (TCEs) that are increasingly used in novel products and industrial processes. Use and disposal of these elements leads to the need for new techniques to monitor their levels at extremely low levels in environmental samples.

Finally, we explain a fundamental aspect of ICP-MS — the impact of plasma robustness on performance.

Figure 1. Agilent 8900 ICP-QQQ with ICP-MS MassHunter monitor displaying laser image from Applied Spectra Inc.

Tandem Laser Ablation and Laser Induced Breakdown Spectroscopy Extends the Capabilities of LA-ICP-MS

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New developments in direct sampling of solids

Laser ablation (LA)-ICP-MS is widely used for the direct analysis and quantification of the elemental composition of solid samples, eliminating the need to dissolve the sample. LA-ICP-MS is a highly sensitive multi-element technique with a wide analytical dynamic range from ppt to ppm-level in the solid. Combining LA with the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) further enhances performance. ICP-QQQ offers higher sensitivity, lower backgrounds, and MS/MS operation for more effective control of interferences than single quadrupole ICP-MS. As a result, LA-ICP-QQQ using the Agilent 8900 has led to advances in the analysis of industrial materials, geological samples, and in life science applications.

Innovations in laser sampling technology are expanding the capabilities of LA-ICP-MS and LA-ICP-QQQ even further. Applied Spectra Inc has combined Laser Ablation and Laser Induced Breakdown Spectroscopy (LIBS) into a single analyzer, the J200 Tandem Laser Ablation system. This system can be coupled to any Agilent single or triple quadrupole ICP-MS system.

Laser ablation removes or "ablates" material from the sample surface through the interaction of the sample material with a pulsed, high energy, focused laser beam. The high energy density of the laser pulse causes ionization of the gas (usually helium) above the sample surface, forming a plasma. This plasma ablates particles from the sample surface, as well as vaporizing and ionizing the elemental content. As the plasma expands and cools, condensation of the ablated material occurs, and the particles and vapor created are transported to the ICP-MS for analysis.

Optical emission data is also generated from the plasma that is formed at the sample surface. The laser induced plasma contains information for all elements present in the sample, including major elements and non-metals

that are difficult to analyze by ICP-MS. In conventional laser ablation systems, this spectral information is wasted, but LA-LIBS-ICP-MS combines the analytical capabilities of LA-ICP-MS and LIBS, enabling the measurement of more elements in a sample.
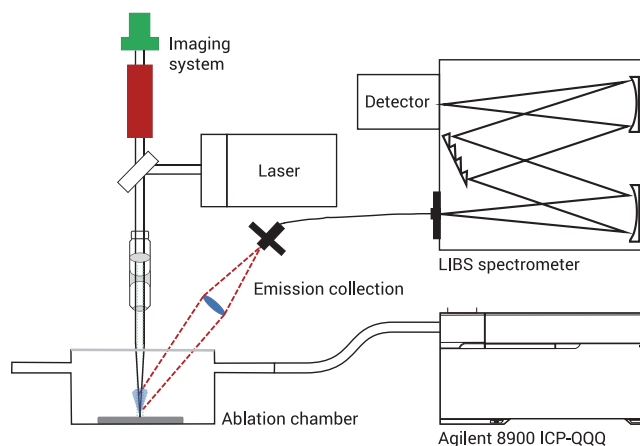

Figure 1. Schematic of J200 LA-LIBS system connected to the Agilent 8900 ICP-QQQ.

Using specially designed collection optics and spectrometer timing controls, the LIBS measures the optical emission spectra from individual laser pulses, in parallel with collection of the ICP-MS mass spectra. Since the laser induced plasma has a higher ionization energy than an ICP, elements such as F can be analyzed by LIBS, as well as C, H, O, and N, which cannot be measured using ICP-MS.

The schematic of the LA-LIBS system in Figure 1 shows the collection of LIBS spectra from the ablation site and the transport of particles to the ICP-MS.

Flexible operation modes of tandem LA

The J200 tandem LA system can be used for LA analyses only, in tandem (both LA and LIBS) mode, and, if the ICP-MS is in use, as a LIBS-only analyzer.

Figure 2 shows a 3D map of a meteorite sample collected using just the LIBS spectral information. Each layer in the depth direction represents spectral information for an individual laser pulse. The ability to collect information from each pulse without transport effects makes LIBS especially suitable for the measurement of elements that vaporize easily (such as C or even Na). The LIBS analysis can provide additional element results, confirmatory measurement, or even correction for the ICP-MS data.
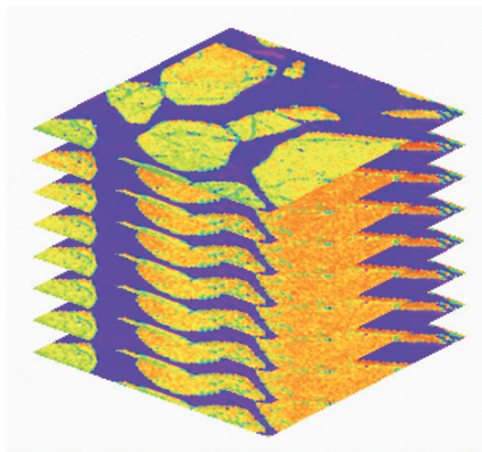

Figure 2. 3D LIBS magnesium data for a pallasite meteorite, which is an iron-nickel and olivine (Mg rich silicate mineral) material.

Applications of LA-LIBS-ICP-QQQ

Using the 8900 ICP-QQQ installed in the Applied Spectra Applications and Demonstration Lab in West Sacramento, we have begun to investigate the capabilities of LA-LIBS-ICP-QQQ. Early applications that have benefitted from this combination include:

- Low concentration measurement of P in a Ni alloy. The $^{62}Ni^{++}$ interference on $^{31}P^+$ was removed using the 8900 in MS/MS mode.

- Determination of Sc in a Zr matrix. The $^{90}Zr^{++}$ interference on $^{45}Sc^+$ was removed using the 8900 in MS/MS mode.

- The simultaneous analysis of F by LIBS and trace element data by ICP-MS in the mineral apatite (Ca phosphate mineral that makes up teeth, bones, and natural minerals).

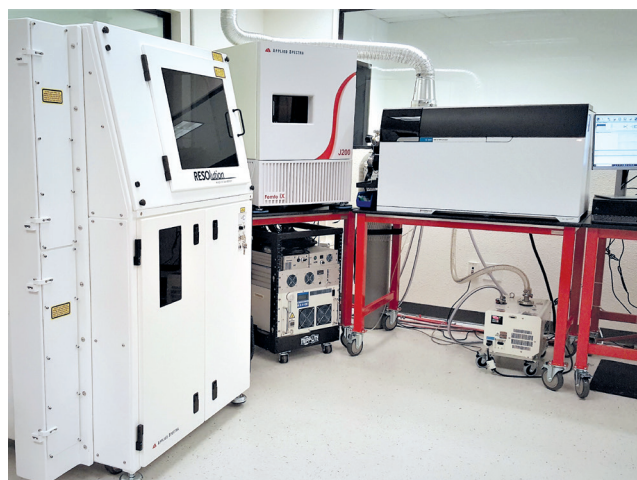More in-depth information about each of these applications will be available soon.

Figure 3. The Applied Spectra Applications Lab showing, from left to right, the RESOlution SE 193 nm LA system, the J200 iX femtosecond Tandem LA-LIBS system, and the Agilent 8900 ICP-QQQ.

A full range of LA systems

In addition to the tandem LA-LIBS system, the LA instrument range from Applied Spectra includes 193 to 1064 nm nanosecond lasers, as well as femtosecond lasers (in multiple wavelengths). All LA systems are compatible with LIBS and all can be connected to an Agilent ICP-MS or ICP-QQQ system. The combination of LIBS and LA-ICP-MS offers complementary detection of the whole periodic table, including elements not normally measured using ICP-MS, such as C, H, O, N, F, and Cl.

Combining LA-LIBS with ICP-QQQ provides higher sensitivity and lower detection limits than conventional single quadrupole ICP-MS. This combination has already been used successfully for the analysis of a range of biological, geological, and industrial materials. For all these applications, LIBS extends the elemental coverage of LA-ICP-MS, providing a valuable and unique data set.

More information

https://appliedspectra.com/

Determination of Emerging Pollutants in River Water using ICP-QQQ in MS/MS Mass-Shift Mode

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Assessing the impact of industrial uses on the level of Rare Earth Elements in the environment

Rare Earth Elements (REEs), also known as lanthanides, occur naturally at ultralow concentrations in surface waters. However, REEs are increasingly used in industrial processes and advanced materials such as catalysts, magnets, and television and smartphone screens. This increasing use has led to concern about the impact of anthropogenic sources of REEs in the environment. More evidence is required to understand the effects of REEs in the environment, and regulations may be introduced to limit their disposal into water courses.

Determination of REEs in waste and natural waters is challenging for conventional single quadrupole ICP-MS. The natural background concentration of the REEs is often below the detection limit of ICP-QMS. Also, the analysis may be hindered by spectral interferences such as BaO^+ on Eu^+, BaH^+ on La^+, and overlaps from low mass REE-oxide ions on high mass REEs.

A chelating resin can be used to preconcentrate the REEs and separate them from Ba, which is usually present at much higher concentration. But this approach must be optimized for each sample matrix, requiring time, skill, and resources that may not be available in routine labs.

In this work, an Agilent 8900 ICP-QQQ was used for the direct analysis of ultratrace REEs in river water.

Experimental

REE analysis using ICP-MS/MS with O-atom addition

The Agilent 8900 tandem mass spectrometer (MS/MS) uses Q1 (before the cell) to control the ions that can enter the cell and react. This ensures that the product ions formed from each analyte can be identified unequivocally, even if matrix elements are present at adjacent masses.

MS/MS mass-shift using O-atom transfer with O_2 or N_2O reaction gas can resolve Ba-based and light REE-oxide interferences on the REEs. The reaction of REE^+ with N_2O ($REE^+ + N_2O \rightarrow REEO^+ + N_2$) is exothermic for all REEs. Sensitivity with N_2O was comparable to or better than with O_2 (*1*), so N_2O reaction gas was used for this work.

Instrumentation

An Agilent 8900 ICP-QQQ (Advanced Applications model #100) was used in this study. The instrument was fitted with the standard quartz double-pass spray chamber, quartz torch with 2.5 mm id injector, and Ni interface cones. Sample delivery was via a peristaltic pump and optional, small dead volume PFA microflow nebulizer (G3139-65100).

The samples were clean, natural waters, so 'low-matrix' preset plasma conditions were selected in the Agilent ICP-MS MassHunter software. The preset plasma setting automatically optimizes the plasma conditions for the routine analysis of samples with total dissolved solids < 0.1%. Main operating conditions are shown in Table 1.

Table 1. ICP-QQQ operating conditions.

Parameter	Value
RF Power (W)	1500
Sampling Depth (mm)	8.0
Nebulizer Gas Flow Rate (L/min)	1.05
Make up Gas Flow Rate (L/min)	0.0
N_2O Cell Gas Flow Rate (% of full scale)	20
Axial Acceleration (V)	1.0

Method detection limits (MDLs)

MDLs for the REEs were calculated from three times the standard deviation of nine replicate measurements of a low-level standard (0.3 ppt each REE in 1% HNO_3). The results are summarized in Table 2.

All the MDLs were sub ppt levels, confirming the suitability of the 8900 ICP-MS/MS method for the determination of REEs at background levels in natural environmental waters.

Table 2. REE MDLs calculated from 3 x SD of a 0.3 ppt standard (n = 9).

Element	Q1 /Q2	MDL (ppt)	Element	Q1 /Q2	MDL (ppt)
Sc	45/61	0.127	Gd	157/173	0.078
Y	89/105	0.053	Tb	159/175	0.059
La	139/155	0.062	Dy	163/179	0.073
Ce	140/156	0.061	Ho	165/181	0.100
Pr	141/157	0.057	Er	166/182	0.092
Nd	146/162	0.066	Tm	169/185	0.079
Sm	147/163	0.096	Yb	172/188	0.096
Eu	153/169	0.082	Lu	175/191	0.052

Results and discussion

River water samples were collected at four locations on the Tama River, Japan. Two of the sampling points were at wastewater treatment plant (WWTP) discharge points. Three samples were collected from each sampling point, then filtered through a 0.45 μm filter, and acidified to 1% HNO_3.

Each water sample was analyzed in triplicate using the 8900 ICP-QQQ, and the average REE concentration for each site is shown in Figure 1 (top). The REEs are a chemically similar group of elements, so tend to behave consistently. However, in most natural materials, the REEs alternate between high and low concentrations, giving a saw-tooth profile which makes it difficult to see anomalies. For this reason, geochemists often normalize REE data by dividing the concentration of each REE measured in the sample by that element's value in a reference material. In this case, the reference material used was Post-Archean Australian Shale (PAAS) (2), as shown in Figure 1 (bottom).

Apart from gadolinium (Gd), the normalized REE results for waters from different points on the river gave consistent, smooth profiles, despite the low concentrations. Gd was consistent with the other REEs in the river water collected at the upstream location (Mitake). But there was a spike in the Gd concentration in the samples taken at the other three sites. The results indicate contamination by Gd compounds, which were not removed by WWTP and so were discharged into the river. A possible source is widely used Gd-based magnetic resonance imaging (MRI) contrast agents.
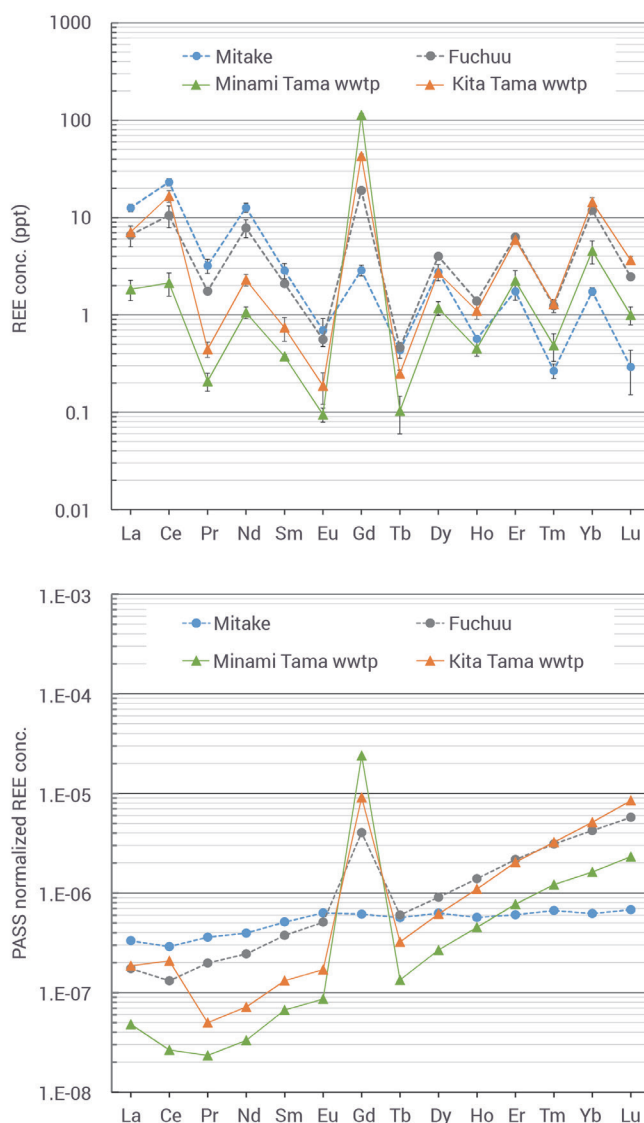

Figure 1. Concentrations of REEs in Tama River water samples by ICP-QQQ. Top: Average of three samples from each site with error bars showing two times the SD. Bottom: Same REE results normalized to PAAS values.

References

1. Naoki Sugiyama, Agilent publication, 5994-1785EN
2. W.B Nance and S.R Taylor, Rare earth element patterns and crustal evolution—I. Australian post-Archean sedimentary rocks, *Geochimica et Cosmochimica Acta*, Vol. 40, issue 12, **1976**, 1539-1551

Understanding Plasma Robustness and Its Importance For ICP-MS Analytical Performance

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Plasma robustness and why it matters

For most typical ICP-MS applications, the critical performance characteristics can be summarized as:

1. Can the instrument handle my samples?

2. Will it achieve the detection limits I need?

3. Can it resolve any spectral interferences?

These three inter-related aspects can be referred to as the "three pillars of successful ICP-MS analysis".

The first of these pillars – the ability of an ICP-MS to handle typical sample types – is mainly determined by how well the plasma decomposes the sample matrix. This is often referred to as plasma "robustness" and is usually monitored using the CeO/Ce ratio. The oxide ratio shows the plasma's ability to break apart the strongly-bound Ce-O molecule, which represents decomposition of the sample matrix as well as other molecular ions.

Agilent ICP-MS systems typically operate with an oxide ratio of around 1.0%, while other ICP-MS systems may run with levels of 2% or even 3% CeO/Ce. But many users don't realize how a small change in the oxide ratio can have a big effect on analytical performance. In this article we explain how optimizing for plasma robustness – low CeO/Ce – is beneficial in many ICP-MS laboratories.

The ICP ion source – a key part of any ICP-MS

The plasma of an ICP-MS does an amazing job. The gas carrying the aerosol droplets from the spray chamber is set to about 1 liter per minute, so the droplets pass through the plasma in a few milliseconds. In this time, the plasma must dry, decompose, dissociate, atomize, and ionize the sample, as illustrated in Figure 1.

The torch injectors used in commercial ICP-MS systems are typically between 1.5 and 2.5 mm internal diameter (ID). The difference this makes to the linear gas velocity through the central channel is summarized in Table 1.
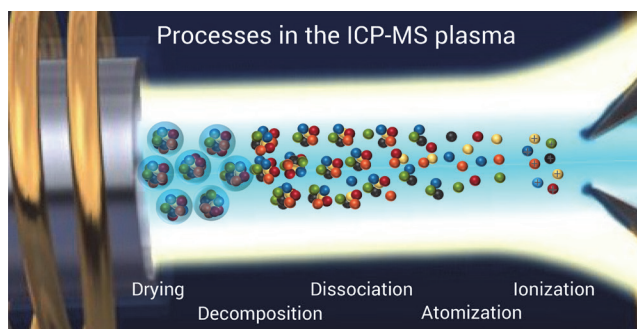

Figure 1. Schematic of processes in the plasma of an ICP-MS.

The cross-sectional area of the torch injector increases as the square of the internal diameter, so a small change in injector diameter has a large effect on gas velocity. For example, decreasing the torch ID 20% from 2.5 to 2.0 mm increases the gas velocity by >55% from 3.4 to 5.3 m/s.

Table 1. Linear gas velocity for different ICP torch injector diameters and carrier gas flows. Excludes special torches used for applications such as volatile organic solvents or single nanoparticle analysis.

Carrier Gas Flow (L/min)	Torch Injector ID (mm)	Linear Gas Velocity (m/s)
1	2.5	3.395
1	2	5.305
1	1.8	6.550
1	1.5	9.431
0.9	2.5	3.056
1.1	2.5	3.735

As the carrier gas emerges from the injector tube of the torch, it punches through the center of the plasma. A lower carrier gas velocity causes a smaller cooled zone at the back of the plasma, which increases the distance (and time) that droplets spend in the hottest part of the plasma. This increases the effective plasma temperature, leading to better matrix decomposition, lower levels of residual molecular (polyatomic) ions, and higher ionization. Higher ionization means better sensitivity.

As well as reducing cooling at the back of the plasma, a wider torch injector also reduces the density of the

aerosol. Aerosol density can be further reduced by using a low flow nebulizer and a double-pass spray chamber, which removes more of the large aerosol droplets.

Aerosol density is important for ICP-MS performance because each aerosol droplet absorbs energy as it evaporates, cooling the region around it. If the droplets are close together, they cool each other, compromising the processes illustrated in Figure 1.

Extending ICP-MS matrix tolerance to % levels

Agilent ICP-MS systems are routinely operated at a low CeO/Ce ratio of around 1% − 2 or 3 times lower than is typical for non-Agilent ICP-MS systems. This ensures that most normal sample types can easily be tolerated for routine, long-term analysis. However, some applications require the analysis of samples that contain much higher levels of total dissolved solids (TDS), up to several %.

Percent level TDS samples can be analyzed routinely on Agilent ICP-MS systems by using high matrix introduction (HMI/uHMI) technology. HMI adds automated and fully calibrated aerosol dilution capability, using an additional argon gas flow to dilute the aerosol before it reaches the torch. HMI further improves plasma robustness, minimizing matrix suppression and giving consistent high ionization of poorly-ionized elements. This is illustrated in Figure 2 for Cd recovery in a range of salt matrices.
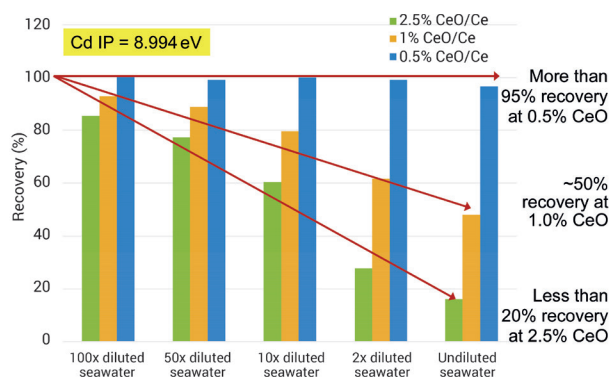

Figure 2. Comparison of Cd recovery in variable saline matrix samples at different CeO/Ce ratios. Agilent HMI (0.5% CeO/Ce) eliminates suppression, giving consistent Cd recovery in all matrix levels.

As well as reducing matrix suppression, a robust, low CeO/Ce plasma also increases analyte ionization (which equates to sensitivity).

Ionization efficiency in the ICP-MS plasma

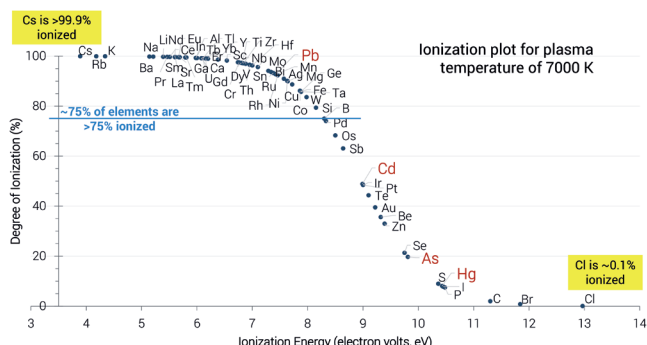The effect of plasma temperature on ionization of key trace elements is illustrated in Figures 3 and 4.

Figure 3. Degree of ionization plotted against 1st ionization energy in electron volts (eV) for all elements. As, Cd, Hg, and Pb are highlighted.

Figure 3 shows the degree of ionization plotted against 1st ionization energy (or ionization potential, IP) for all elements. The 1st IP is the amount of energy needed to remove the first electron to ionize a neutral atom.
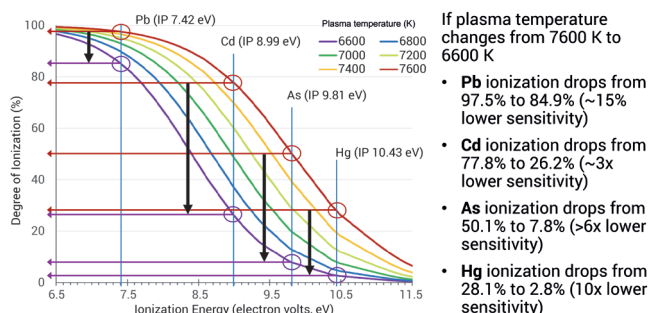
Figure 4. Impact of a small change in plasma temperature on ionization and therefore sensitivity for As, Cd, Hg, and Pb.

Figure 4 shows the central part of the plot in Figure 3 (from 6.5 eV to 11.5 eV) plotted as a simple line for plasma temperatures between 6600 and 7600 K. The effect of plasma temperature on ionization is illustrated for four critical ICP-MS analytes, As, Cd, Hg, and Pb (1st IPs between 7.43 and 10.43 eV). The decrease in ionization of all four elements at lower plasma temperatures is indicated by the black arrows.

High and consistent ionization is critical for successful ICP-MS analysis. A robust plasma ensures the highest sensitivity while minimizing matrix suppression.

Newly updated! Agilent ICP-QQQ Bibliography

The world's first commercial triple quadrupole ICP-MS, the Agilent 8800, was launched in 2012. Since then, we have been maintaining an interactive online bibliography of journal articles and publications where Agilent ICP-QQQ instruments were used. The latest update of the Agilent ICP-QQQ bibliography is now available online, with more than 500 new publications since the last update in May 2018. The increasing use of Agilent ICP-QQQ instruments is illustrated by the fact that more articles have been published in the last two years than in the previous six years.

Around the globe and across industries...
Agilent ICP-QQQ technology has been cited in over one thousand respected papers

Number of citations by country

- 31 CZECH REPUBLIC
- 44 NORWAY
- 87 CANADA
- UK 74
- 56 GERMANY
- USA 124
- 38 BRAZIL
- 40 AUSTRIA
- SPAIN 44
- 10 MIDDLE EAST
- 124 CHINA/TAIWAN
- 100 JAPAN
- 85 AUSTRALIA
- 16 AFRICA

Number of citations by publication year

Citations	Year
4	2012
10	2013
38	2014
71	2015
143	2016
146	2017
224	2018
261	2019
173	2020*

*Count compiled as of May 2020

Number of citations by segment/application area

Citations	Segment
427	ENVIRONMENTAL
156	FOOD TESTING & AGRICULTURE
125	GEOCHEMISTRY & GEOLOGY
116	MATERIALS
108	NANOMATERIALS
103	LIFE SCIENCE & BIOMEDICAL
101	NUCLEAR
53	CLINICAL RESEARCH

Number of citations by region

- 211 NORTH AMERICA
- 506 EUROPE
- 204 ASIA PACIFIC
- 46 LATIN AMERICA
- 26 MIDDLE EAST/AFRICA
- 124 CHINA/TAIWAN

The bibliography page Agilent ICP-QQQ Bibliography lists the reference, title, author(s), institution, and country for each publication – plus a link to the abstract or full paper if available online. Papers are organized by industry segment/application area, and the lead author address indicates that Agilent ICP-QQQ instruments are helping scientists solve problems in laboratories all around the world.

Latest Agilent ICP-MS publications

- **Brochure (updated):** Agilent 7900 ICP-MS: Raise Your Expectations with the Next Generation of ICP-MS, 5991-3719EN
- **Brochure (updated):** Agilent 8900 Triple Quadrupole ICP-MS: Leave Interferences Behind With MS/MS, 5991-6900EN
- **Application note:** Measurement of ^{87}Sr/^{86}Sr Isotope Ratios in Rocks by ICP-QQQ in Mass-Shift Mode: The direct Agilent 8900 ICP-QQQ method removes need for chromatographic separation of ^{87}Sr and ^{87}Rb, 5994-2019EN
- **Application note (updated):** Performance of the Agilent 7900 ICP-MS with UHMI for High Salt Matrix Analysis: Extending the matrix tolerance of ICP-MS to percent levels of total dissolved solids, 5991-4257EN
- **Application brief:** Analysis of Trace Elements in Palm Oil using ICP-MS: Future proof the quality control of vegetable oils with an Agilent 7800 ICP-MS, 5994-1953EN
- **Flyer:** Agilent ICP-MS IntelliQuant Software: For greater sample insight and confidence in results, 5994-1677EN
- **Flyer (updated):** Simplify Testing of Elemental Impurities in Pharmaceuticals with Agilent's Certified Reference Materials Kit: ICH Q3D/USP <233> Elemental Impurities Kits, 5991-8177EN

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