Expanding the Role of ICP-MS in Environmental Monitoring

Ed McCurdy, ICP-MS Product Marketing, Agilent UK

Determination of trace elements in environmental samples has been one of the main applications of ICP-MS since the earliest days of the technique. As industrialization spreads to new regions, and awareness of the impact of trace metals in the food chain grows, demand for monitoring of trace contaminants increases. In this issue of the ICP-MS Journal, we discuss a major new survey of trace element contamination of agricultural land in China. We also look at the increasing interest in low-level analysis of "technology-critical elements" using ICP-MS. The TCEs include the PGEs, REEs, and other "unusual" elements such as Ga, Ge, In, Nb, Ta, Te, and Tl.

Figure 1. Agilent 8900 ICP-QQQ with Agilent SPS 4 autosampler.

Multi-Element Analysis Method for China Soil Pollution Survey using the Agilent 7800 ICP-MS

Tetsuo Kubota[1] and Dong Yan[2], Agilent Technologies, Japan[1] and Agilent Technologies, China[2]

Introduction

China, in common with many other countries, is committed to improving soil quality, especially for soil that is used for food production. An Action Plan for the Prevention and Control of Soil Pollution was included in China's 13th Five-Year Plan (2016–2020) that was adopted in May 2016. In 2017, a Technical Stipulation of Soil Analysis for China Soil Pollution Survey (1) was established, and China also began a National Soil Pollution Survey. The aim of the survey is to identify which areas of farmland are polluted and to what extent. The results will be used to guide follow-up remediation work.

Soil Survey Requirements

The 2017 Technical Stipulation soil survey method requires the determination of various organic and inorganic pollutants in soil. The method includes around 15 heavy metals and other elements. Recommended analytical techniques are ICP-MS, ICP-OES, Graphite Furnace AAS (GFAAS), or Flame AAS, together with atomic fluorescence (AFS) for As, Hg and, optionally, Sb. Some of the more toxic elements (Cr, As, Cd, Hg, Pb) must be measured. Others, such as, Be, V, Mn, Co, Mo, and Sn may be specified by local authorities, if their analysis is justified based on local pollution sources.

The survey, due to be completed by the end of 2018, requires multiple elements to be determined at low concentrations in very large numbers of varied soil and sediment digests. Given these requirements, the fast, sensitive, multi-element capabilities of ICP-MS make it an ideal analytical technique for the survey.

This study describes the analysis of soil and sediment digests using the Agilent 7800 ICP-MS with SPS 4 autosampler, following preparation by low-pressure microwave digestion.

Experimental

As well as rapid measurement by ICP-MS, fast and efficient sample preparation is also required to make the overall workflow suitable for use in routine environmental labs. An optimized, low-pressure microwave digestion approach was developed by Agilent for the complete digestion of batches of 30 soil and sediment samples.

To demonstrate method performance, five stream sediment CRM samples obtained from NCS, China were digested using a Mars 6 Microwave Digestion System (CEM Corporation, Japan). The CRMs were measured repeatedly, with and without spikes, during a 7-hour sequence. See reference (2) for details. In a separate study, eight soil CRMs were analyzed. This article reports representative results for soil and sediment CRMs.

Instrumentation

All measurements were performed using an Agilent 7800 ICP-MS fitted as standard with HMI, Ni interface cones, and ORS[4] collision cell operating in He mode. An Agilent SPS 4 autosampler was used for introduction of the standards and samples. ICP-MS operating conditions are listed in Table 1. The HMI settings are autotuned as appropriate for the matrix levels of the target sample types. In this case, a dilution factor of 4 was used.

Table 1. 7800 ICP-MS operating conditions

Parameter	No gas mode	He mode
Plasma mode	HMI-4	
RF power (W)	1600	
Nebulizer gas flow (L/min)	0.60	
Dilution gas flow (L/min)	0.35	
Lens tune	Autotune	
Cell gas flow (mL/min)	0.0	4.5
Energy discrimination (V)	5.0	

Shaded parameters are defined in the method and HMI-4 plasma presets; all parameters were automatically optimized during start-up and autotuning.

Results and Discussion

Calibration

Representative calibration curves are shown in Figure 1. For all calibrations, the R value was greater than 0.9999, exceeding the method requirement of 0.999.
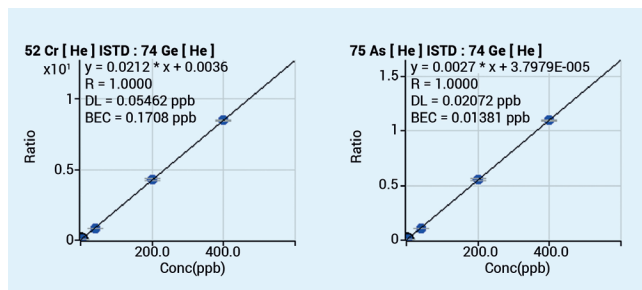

Figure 1. Representative calibration curves for critical, toxic trace elements Cr and As, demonstrating effectiveness of He mode.

Recoveries of QC samples

A mid-range standard was measured as a continuing calibration verification (CCV) QC sample. The CCV was measured automatically after every 20 samples, as stipulated in the method. The method requires that the CCV recovery must be within ±10%; a recovery outside this limit triggers a recalibration. Figure 2 shows that all the elements met the CCV recovery criteria, without the need to recalibrate throughout the 7-hour sequence.
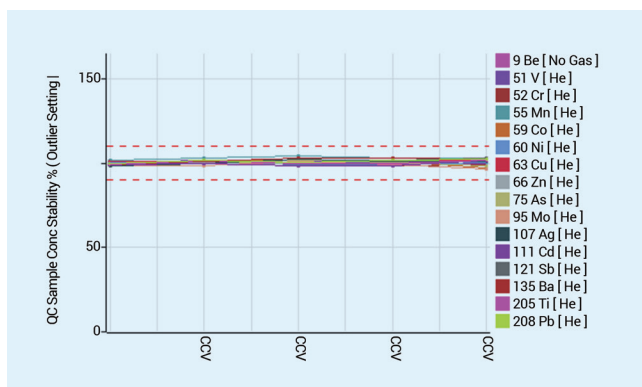

Figure 2. Continuing calibration verification (CCV) recoveries over the course of the sequence. Red lines indicate ± 10% limits.

CRM recoveries

The results in Table 2 show the mean measured concentrations and mean recoveries for a representative sediment and soil CRM. The results for all elements were in good agreement with the certified values. Using closed

vessel digestion, even volatile elements such as As and Sb showed good recoveries.

Conclusions

Reliable routine analysis of the environmental samples targeted in the Technical Stipulation for China Soil method can be carried out quickly and easily using the 7800 ICP-MS with HMI. A rapid, low-pressure microwave digestion approach allowed all specified elements to be measured in one analysis.

Table 2. Mean measured concentrations (n=3) in sediment and soil CRMs as mg/kg in the original CRM (corrected for dilution). Certified values (mg/kg) are included for each CRM, and mean recoveries (%) are shown for all certified elements.

	GBW07307a sediment CRM			GSS-12 soil CRM		
	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Be	1.6 ± 0.4	1.6 ± 0.1	100	2.04	2.04 ± 0.06	100
V	77 ± 9	77 ± 4	100	88	86 ± 4	103
Cr	44 ± 5	43 ± 1	103	59	59 ± 2	100
Mn	896 ± 100	886 ± 25	101	758	774 ± 19	98
Co	14.8 ± 2.1	15.2 ± 0.7	98	12.3	12.6 ± 0.3	98
Ni	23.3 ± 3.6	22.0 ± 0.6	106	34	32 ± 1	106
Cu	23.4 ± 3.6	22.5 ± 1.0	104	27	29 ± 1	93
Zn	844 ± 54	780 ± 19	108	74	78 ± 5	95
As	13.2 ± 1.6	11.3 ± 1.0	117	NA		
Mo	0.82 ± 0.67	0.82 ± 0.05	99	1.02	0.96 ± 0.06	106
Ag	1.24 ± 0.7	1.20 ± 0.08	103	NA		
Cd	6.0 ± 0.4	5.6 ± 0.6	107	0.16	0.15 ± 0.02	106
Sb	2.4 ± 0.8	2.1 ± 0.2	112	1.47	1.17	125
Ba	441 ± 50	437 ± 12	101	444	492 ± 20	90
Tl	0.38 ± 0.58	0.45 ± 0.07	85	0.46	0.51 ± 0.04	90
Pb	609 ± 80	555 ± 19	110	18	19 ± 2	96

References

1. Technical Stipulation of Soil Analysis for China Soil Pollution Survey, 2017, accessed August 2018, Chinese language only: http://www.edcmep.org.cn/ywly_14986/hjfxcs/201709/W020180315331626102260.pdf

2. Agilent application note, 2018, 5994-0309EN

Extending ICP-MS Capability by Resolving Isobaric Spectral Overlaps using MS/MS

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Isobaric Overlaps in ICP-MS

Isobaric interferences – where isotopes of two different elements occur at the same mass – are difficult to address using single quadrupole ICP-MS. Even sector field "high-resolution" ICP-MS cannot separate these overlaps, as the mass difference is far too small. For example, ^{204}Hg and ^{204}Pb both have a nominal mass of 204. Their true masses are 203.97349398 u for ^{204}Hg and 203.9730440 u for ^{204}Pb, so the resolution (M/ΔM) required to separate the isobars is almost 500,000. This is about 50x higher than the best performance available on commercial high-resolution ICP-MS instruments (1).

An alternative approach is to use "chemical resolution", with a collision/reaction cell gas that reacts quickly with one of the isobaric elements and slowly – or not at all – with the other (2). To ensure that only the intended product ions are created, an additional mass selection step (before the collision/reaction cell) is essential. This is achieved using the tandem mass spectrometer (ICP-MS/MS) layout of the Agilent 8900 ICP-QQQ.

Improving the Measurement of Unusual Environmental Contaminants

The novel properties of technology-critical elements such as Ga, Ge, Nb, In, Te, and Ta makes them of interest in high-tech industries. However, their toxicological and environmental impact is not well understood (3).

While these elements can all be measured using ICP-MS, it is not always easy to achieve the low levels required for environmental monitoring. For example, tellurium has a relatively high first ionization potential (IP) of 9.01 eV. This means Te is only about 25% ionized in the ICP, so sensitivity and detection limits are degraded.

Also, the only Te isotope that is free from isobaric overlap is ^{125}Te, so this is the preferred isotope for ICP-MS measurements. But ^{125}Te has an isotopic abundance of only 7.07%, which is almost a factor of five lower than the most abundant Te isotope.

To determine Te at lower levels in environmental samples, it would be beneficial to be able measure the more abundant isotopes, ^{128}Te (31.74%) and ^{130}Te (34.08%). However, both isotopes suffer isobaric overlaps from Xe (a common trace contaminant in high-purity argon gas). In addition, the ^{130}Te isotope is also overlapped by ^{130}Ba, which may be present at mg/kg (ppm) levels in natural environmental samples. An ICP-MS/MS method that removes the Xe and Ba isobaric overlaps would significantly improve the trace determination of Te.

Instrumentation

A standard configuration Agilent 8900 ICP-QQQ was used for all measurements.

A mix of reaction gases was used for optimum removal of the two different interfering ions. NH_3 was added at a flow rate of 2.0 mL/min (Mass Flow Controller setting of 20%); and N_2O was added at a flow rate of 0.45 mL/min (30%); He was added as a buffer gas at 1.0 mL/min. Other operating conditions can be found in the article cited under "More Information".

Resolving Isobaric Overlaps on Tellurium

The mix of N_2O and NH_3 cell gases was used to resolve the isobaric interferences from Xe and Ba on Te at *m/z* 128 and 130. The improvement in trace-level detection of Te due to the removal of the Xe isobaric overlap is illustrated in the calibrations shown in Figure 1. The calibrations cover the concentration range from 1 to 1000 ng/L (ppt), zoomed to show 0 to 200 ppt for clarity.

The two most abundant isotopes of Te, ^{128}Te (left) and ^{130}Te (right) are shown. The upper pair of calibration plots show the calibrations in no gas mode. The y-axis offset is due to the ^{128}Xe and ^{130}Xe contributing to the blank signal, giving background equivalent concentrations (BECs) of 16 ng/L for

^{128}Te and 32 ng/L for ^{130}Te. The difference in the BECs is due to the ~2x higher abundance of ^{130}Xe compared to ^{128}Xe.
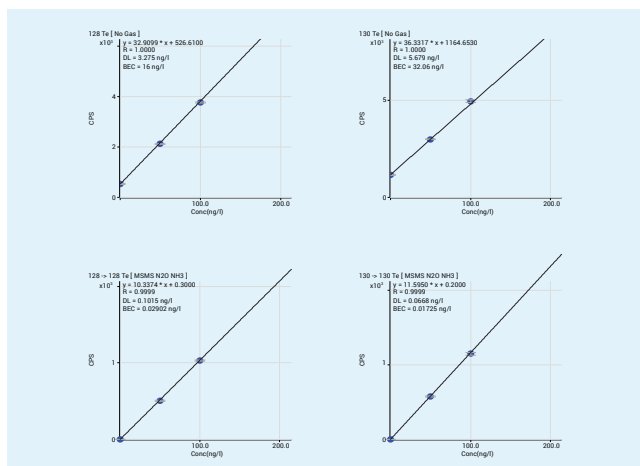

Figure 1. Zoom to show low level calibrations for ^{128}Te (left) and ^{130}Te (right) in no gas mode (top) and MS/MS mode with N_2O/NH_3 cell gas (bottom).

In N_2O/NH_3 cell gas mode (lower pair of plots in Figure 1), the y-axis offset is completely removed (background signals of 0.3 and 0.2 counts per second), leading to BECs of 0.029 ng/L and 0.017 ng/L for ^{128}Te and ^{130}Te, respectively. The Agilent 8900 MS/MS mode with N_2O/NH_3 cell gas reduced the BEC by a factor of more than 500 for ^{128}Te and almost 2000 for ^{130}Te.

Measuring ^{130}Te in Varying Barium Matrix Solutions

The N_2O/NH_3 cell gas method also removes the isobaric overlaps from Ba. The effectiveness of this approach was demonstrated using a series of solutions containing Ba concentrations from 20 to 1000 µg/L (ppb). Each Ba standard was spiked with 500 ng/L (ppt) Te and measured in both no gas mode and N_2O/NH_3 cell gas mode. The measured Te concentrations are shown in the plot in Figure 2, and the recoveries are given in Table 1.

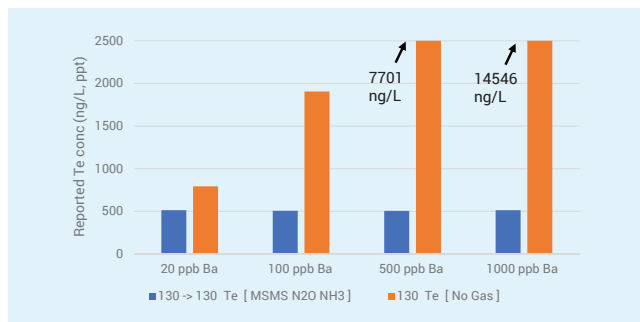**Figure 2.** Reported concentrations for 500 ng/L Te spikes in different Ba matrix levels, measured using N_2O/NH_3 cell gas and no gas mode.

Table 1. Te recovery in Ba matrices. Results obtained using MS/MS mode with N_2O/NH_3 cell gas and no gas mode.

Recovery (%) of 500 ng/L Te spike		
Barium matrix	^{130}Te, N_2O/NH_3	^{130}Te, no gas
20 ppb Ba	103	159
100 ppb Ba	101	381
500 ppb Ba	101	1540
1000 ppb Ba	102	2909

In no gas mode, the Ba matrix gave errors in Te recovery of between 150% for the 20 ppb Ba matrix, up to 2909% (30x too high) in the 1000 ppb Ba matrix. In N_2O/NH_3 mode, the Te recoveries were within +/- 3% for all Ba concentrations, showing the effectiveness of the method to resolve ^{130}Ba.

Conclusions

Direct, isobaric overlaps can be resolved using reactive cell gases and the double mass selection (MS/MS) capabilities of the Agilent 8900 ICP-QQQ.

In this study, isobaric overlaps from both Xe and Ba were chemically resolved from ^{128}Te and ^{130}Te using N_2O and NH_3 cell gases. This allowed Te to be measured using its most abundant isotopes at *m/z* 128 and 130. Compared to no gas mode, the N_2O/NH_3 method reduced the contribution of Xe on ^{130}Te by a factor of almost 2000 and ensured accurate analysis of Te in variable Ba matrices.

Elements such as Te can now be determined accurately using ICP-MS/MS to resolve isobaric overlaps. MS/MS reaction gas methods also allow access to multiple analyte isotopes, enabling isotope ratio and isotope dilution measurements.

References

1. N. Jakubowski, T. Prohaska, L. Rottmann and F. Vanhaecke, *J. Anal. At. Spectrom.*, **2011**, 26, 693−726
2. S. D. Tanner, V. I. Baranov and U Vollkopf, *J. Anal. At. Spectrom.*, **2000**, 15, 1261-1269
3. M. Filiella and I. Rodushkin, *Spectrochim Acta Part B*, **2018**, (141), 80-84

More Information

E. McCurdy, G. Woods, Using Double Mass Selection (MS/MS) and Reaction Cell Gases to Resolve Isobaric Spectral Overlaps in ICP-MS, *Spectroscopy*, **2018**, 33, 9, 26-34.

Pioneer in LA-ICP-MS for Medical Research Wins Prestigious Award for Atomic Spectroscopy

Fred Fryer, Agilent Technologies, Australia

Metals Imaging in Biological Tissues

Each year, *Spectroscopy* magazine works with an independent scientific committee to recognize the work of a young spectroscopist who is making a significant contribution in atomic spectroscopy. The 2019 winner of the "Emerging Leader in Atomic Spectroscopy Award" is Dr Dominic Hare (*1*). Dr Hare is a senior research fellow and the head of the Atomic Pathology Laboratory at the Florey Institute of Neuroscience and Mental Health, located in Melbourne, Australia.

The institute aims to improve quality of life through brain research, and Dr Hare's pioneering work includes applying laser ablation (LA-)ICP-MS to imaging elements in tissue samples. Typically, Dr Hare and his team couple a New Wave laser ablation system to an Agilent ICP-MS or Agilent Triple Quadrupole ICP-MS.

3D Mapping of Metals in the Brain

The development of data analysis software to display the distribution of elements in cross sections of samples has been vital to the success of the LA-ICP-MS imaging methodology (*2, 3*). The data can also be collated using a chemometrics package known within the group as 'Biolite' to create 3D images like the ones shown in Figure 1. Using this pioneering approach, Dr Hare plans to build a standardized map of metal distribution in mice that researchers can refer to when studying metals in diseases such as Parkinson's.

Research into Neurological Diseases

The interaction between iron (present in every brain cell) and dopamine (confined to a select few types of neurons) is fundamental to research into parkinsonian neurodegeneration. The team adds a ytterbium (Yb) tag to the enzyme that makes dopamine. Yb distribution is then measured by LA-ICP-MS to build a spatial map of dopamine throughout the brain. Figure 1 highlights where high levels of both iron and dopamine are present. Vitally, these areas correspond to regions at risk in Parkinson's disease – namely the *pars compacta* of the *substantia nigra* and the olfactory (smell) bulbs. One of the first effects of Parkinson's disease is a loss of sense of smell (*3*).
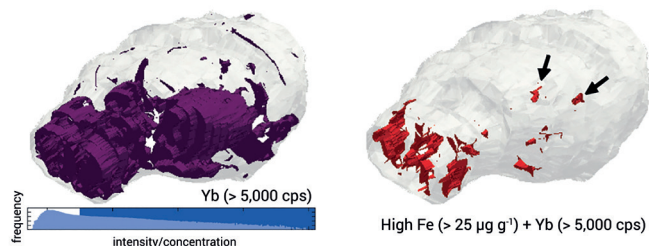

Figure 1. Left: 3D map of Yb (>5000 cps). Right: Brain regions containing high concentrations of both Fe (>25 ug/g) and Yb (>5000 cps).

Multi-Element LA-ICP-MS Methods

The Florey Institute team are developing new methods to investigate the distribution of a wider range of elements in tissues. Dr Hare's work has shown the potential for LA-ICP-MS to be used to investigate the complex interactions between proteins and the metal ions they depend on.

The award will be presented to Dr Hare at the 2019 European Winter Conference on Plasma Spectrochemistry, where he will give a plenary lecture.

More Information and References

1. L. Bush, Spectroscopy Announces the Winner of the 2019 Emerging Leader in Atomic Spectroscopy Award
2. D. Hare et al., Imaging Metals in Brain Tissue by LA-ICP-MS, *J. Vis. Exp.* (119), **2017**
3. Ferrum Blogger: Mapping Metals in the Brain
4. Agilent Aids Research into How Essential Elements Can Become Killers, Agilent website.

On-Demand Education Series Webinars: Learn More About ICP-QQQ From Industry Experts

Abe Gutierrez and Bert Woods, Agilent Technologies Inc., USA

ICP-MS/MS Webinar Series, Part 1: Exploring Four Capabilities That Are Defining the Future of ICP-MS

In Part 1 of this ICP-MS/MS webinar Series, Agilent ICP-MS Specialist Abe Gutierrez provides a brief history of ICP-MS since the 1980s. The introduction focuses on developments that have provided performance improvements to address emerging and developing application needs. Abe explains how improved control of interferences — polyatomic, isobaric, and doubly charged — was needed in many industries and applications. These requirements ultimately led to the development of Agilent's 8800 triple quadrupole ICP-MS in 2012.

Abe goes on to describe four unique capabilities of tandem mass spectrometry (MS/MS) that depend on precise control of ion/molecule reaction chemistry. Using examples run on the Agilent 8900 ICP-QQQ, Abe explains:

- On mass measurement
- Mass-shift measurement
- Precursor ion scan, and
- Product ion scan

With entertaining and informative use of animations to explain collision/reaction cell processes, Abe provides examples of research and routine applications that can now be addressed using ICP-QQQ.

Abe closes with some tips on simple ways to test the interference removal capabilities of ICP-MS instruments.

Watch the webinar at your convenience.

Part 2: How MS/MS Can Improve your ICP-MS Data Quality, Whatever your Application.

In this webcast, Agilent Applications Chemist Bert Woods provides an overview of how ICP-QQQ with MS/MS mode gives improved performance in a wide and expanding range of applications.

Bert illustrates ICP-QQQ performance for unusual, exotic, and difficult elements, showing low-level determination of Te and detection of <50 nm SiO_2 nanoparticles. Using the examples of B in organic solvents and Np in a U matrix, he also discusses how double mass selection improves separation of adjacent peaks. This improvement allows trace analytes to be measured next to major elements.

Bert describes several recent papers where ICP-QQQ was used to resolve isobaric overlaps from natural isotopes on long-lived radionuclides. This is an exciting new possibility in the nuclear and environmental industries and is not practical on other instruments such as single quadrupole or high resolution ICP-MS.

Bert's background in the semiconductor industry enables him to talk knowledgeably about the advantages of MS/MS for ultratrace analysis of process chemicals — a major application of ICP-QQQ.

The webinar discusses new and emerging applications, alongside established ICP-MS methods whose performance is improved dramatically using MS/MS.

Watch the webinar at your convenience.

New! Semiconductor Industry Applications Compendium

The new Agilent Applications Compendium on Measuring Inorganic Impurities in Semiconductor Manufacturing provides a comprehensive resource for scientists wanting to learn about the industry. The publication includes an overview of the role of ICP-MS and ICP-QQQ in the semiconductor industry, along with 23 industry application notes.

Information is included on contamination control, instrument setup for organic solvents and highly corrosive or viscous acids, and automated analysis of silicon wafers and process chemicals.

The 152-page guide is free to download from the Agilent website:
Application note compendium: Measuring Inorganic Impurities in Semiconductor Manufacturing, 5991-9495EN

On-Demand Webinar

Title: This is How you ICP-MS: Mastering the Art of Cone Performance
Presenter: Gareth Pearson, ICP-MS Spectroscopy Supplies Product Manager, Agilent Technologies.
Host: Separation Science

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Conferences and Events

6th FFF-MS Workshop, Nov 22-23, 2018, Koblenz, Germany
European Winter Conference on Plasma Spectrochemistry (EWCPS) February 3-8, 2019, Pau, France

Agilent ICP-MS Publications

- **Application note:** Quantifying Copper Nanoparticles on Edible Plant Leaves using Single-Particle ICP-MS (spICP-MS), 5994-0214EN
- **Application note:** Measuring Multiple Elements in Nanoparticles using spICP-MS in Rapid Multi-Element Nanoparticle Analysis Mode, 5994-0310EN
- **Application note:** Automated Ultratrace Element Analysis of Isopropyl Alcohol with the Agilent 8900 ICP-QQQ, 5994-0273EN
- **Application note:** China Soil Pollution Survey: Determination of Multiple Elements in Sediment and Soil Digests using ICP-MS, 5994-0309EN
- **Application note compendium:** Measuring Inorganic Impurities in Semiconductor Manufacturing, 5991-9495EN

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