Optimizing Performance in a Range of ICP-MS Applications

The past year has seen many changes to the way most of us live and work. While some regions and industries continue to operate under restrictions, others are returning to normal workloads, and many laboratories providing essential services never stopped. The Agilent ICP-MS team thank you for your support during these difficult times.

In this issue of the Agilent ICP-MS Journal, we look at the effect that different sample preparation approaches can have on the trace element levels in foodstuffs. We also report on a new software interface that improves run control and data analysis for laser ablation accessories integrated with ICP-MS MassHunter. Finally, we explain how helium cell gas contributes to the high performance of triple quadrupole ICP-MS, a technique that is often more associated with reactive cell gas methods.
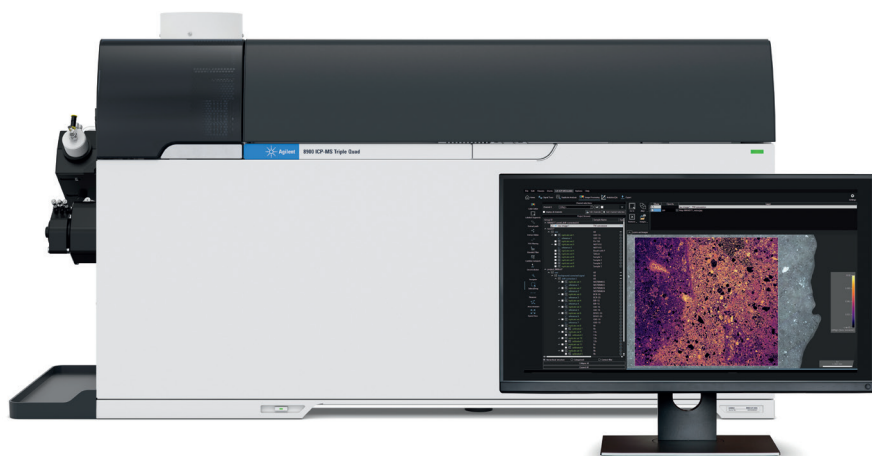

Figure 1. Agilent 8900 shown with HDIP LA-ICP-MS main screen – see article on page 4.

The Effect of Grinding and Rinsing on Trace Element Contamination of Dried Food Samples

Shuofei Dong, Agilent Technologies, Inc.

Food preparation and homogenization procedures

Analysts are keenly aware that good sample preparation is vital for successful analysis, irrespective of the analytical technique being used. An appropriate sample size must be chosen, and thorough homogenization may be required to ensure the analysis is representative of the original material. Analysts must also take care to avoid analyte losses or contamination during sample preparation. Controlling contamination can be particularly problematic when analytes are measured at trace levels using a sensitive technique such as ICP-MS.

Food samples are often ground to a fine powder or blended to a paste for better homogenization and faster digestion. When preparing dry foods such as cereal grains, pulses, nuts, and whole spices, analysts also often rinse the sample with de-ionized water (DIW) to remove surface contamination and dust before grinding and digestion. However, each sample handling step can add (or remove) trace elements, as the sample interacts with reagents, labware, or sample preparation equipment.

Comparing sample preparation strategies

Food analysis labs using organic techniques such as LC/MS or GC/MS do not typically need to consider the potential for trace element contamination during sample preparation. Consequently, analysts may routinely use equipment fitted with stainless steel rotors or blades to grind and homogenize food samples before extraction. A lab that extends its analytical scope to include trace elements may not consider the potential for metal contamination, especially when preparing relatively soft materials such as rice and other cereal grains.

The US Food and Drug Administration (FDA) publishes some general guidance on food preparation and homogenization procedures in the Elemental Analysis Manual (EAM) for Food and Related Products (*1*). More


Figure 1. Dried foodstuffs may typically be ground to a powder before sample digestion.

specifically for ICP-MS, EAM 4.7 states that "elements of interest (e.g. Cr, Ni, Mo, Co, and Fe) may leach from stainless steel and contaminate foods, especially when foods are acidic or tough to grind." Analysts are advised to replace stainless steel grinding components with titanium or tungsten carbide.

In this study, the Agilent 7900 ICP-MS was used to measure 24 elements in rice kernel samples. The samples were prepared using three different approaches prior to acid digestion in a microwave oven:

1. One set of triplicate samples was ground in a rotor mill with stainless steel blades before digestion.

2. A second set of samples was washed three times in DIW before digestion.

3. The final set of samples was digested as received, with no pretreatment.

Instrument operating parameters, the microwave oven program, and other method details will be reported in an upcoming application note.
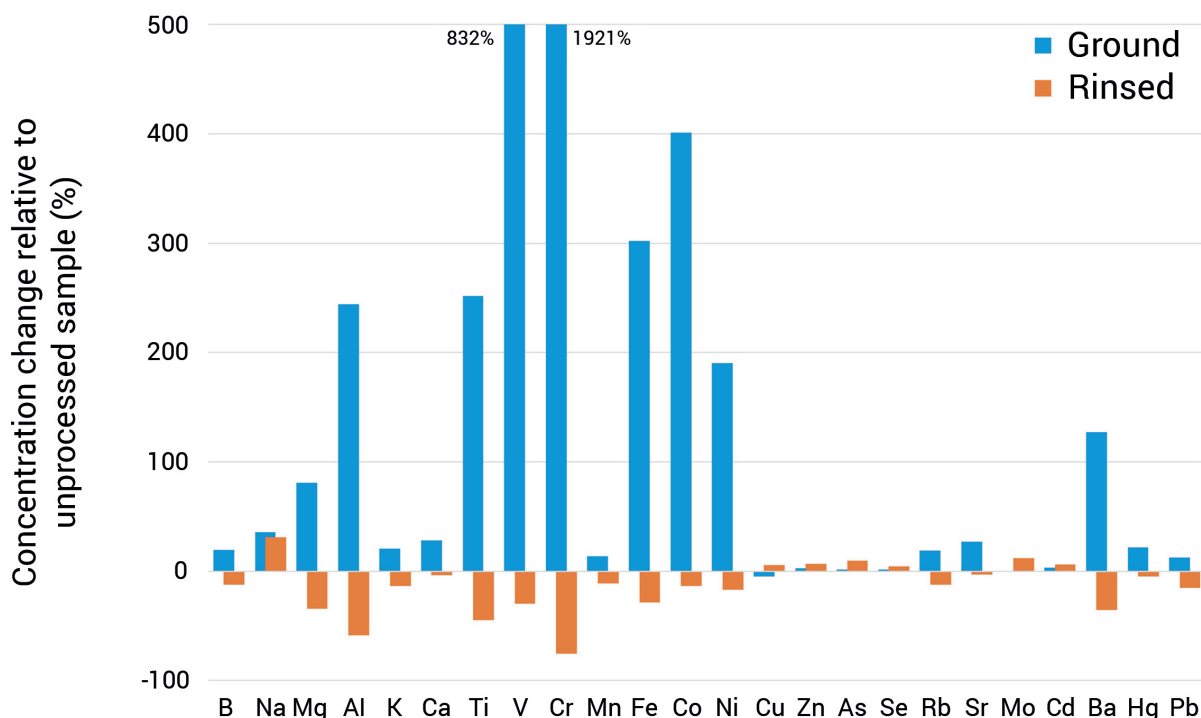
Figure 2. Relative percent change in concentration for 24 elements in rice samples treated by grinding or rinsing before sample digestion. Relative concentration change (n=3) compared to samples that were not processed before digestion.

Figure 2 shows the change in concentration of all elements in sample sets 1 (ground) and 2 (rinsed), as a relative percent change compared to the unprocessed samples (set 3, represented by y = 0). Grinding caused an increase in concentration for all elements apart from Cu, with significant changes being observed for several elements. Grinding had the largest effect on Cr, with a 20x increase in concentration relative to the unprocessed samples. The concentrations of Al, Ti, V, Fe, Co, Ni, and Ba also more than doubled after grinding. Most of these elements are associated with stainless steel.

Compared to grinding of the sample, the changes in elemental concentrations due to rinsing were much less significant. Rinsing slightly decreased the concentration of most elements and marginally increased others. The largest relative changes observed were an approximately 60% decrease in the concentration of Al, and a 75% decrease in the concentration of Cr. These elements were most likely present as trace contaminants on the surface of the rice grains. Surface contamination can arise from metal milling equipment used during the normal processing of rice for food production.

Based on these findings, it is recommended that neither rinsing nor grinding is used prior to digestion of rice samples for ICP-MS analysis. Accurate trace element composition – including any contamination introduced during normal food processing steps – is required for food safety assessment. A complete set of ICP-MS trace element data can also provide the elemental profiles (fingerprints) used for authenticating the region of origin of foodstuffs such as rice.

Reference

1. US FDA, Elemental Analysis Manual (EAM) for Food and Related Products, accessed April 2021, https://www.fda.gov/food/laboratory-methods-food/elemental-analysis-manual-eam-food-and-related-products

HDIP LA-ICP-MS Acquisition and Data Analysis Platform Offers an Alternative to Traditional Software Plug-Ins

Ciprian Stremtan, Stijn Van Malderen, and Damon Green, Teledyne CETAC Technologies, Omaha, NE, USA

Developments in laser ablation ICP-MS

Laser ablation (LA) ICP-MS has progressed greatly in recent years. The laser hardware, especially the sample chamber, has seen improvements in speed (1), flexibility, and reliability. Parallel developments in sample transfer, data acquisition, and calibration have helped make LA-ICP-MS one of the most valuable techniques available to the analyst.

Until recently, integration of data acquisition and analysis software was lagging behind these developments. As labs have taken advantage of the latest hardware to increase sample throughput, increased numbers of samples and larger data volumes have become normal, even in traditional bulk analysis applications. Imaging applications produce even larger data sets.

An integrated software solution that allows operators to optimize and streamline their method setup, data acquisition, and data processing has become a valuable part of LA-ICP-MS workflows. As well as simplifying visualization and interpretation of the data set, such software platforms also help analysts to generate meaningful reports in a timely manner.

The Atomic and Mass Spectrometry (A&MS) Research Unit at Ghent University, led by Prof. Frank Vanhaecke, has decades of experience in LA-ICP-MS. HDIP (HDF-based Image Processing) started as the A&MS group's in-house data reduction software, but continuous development has seen it evolve into a powerful software platform for other Teledyne Cetac LA-ICP-MS users*.

HDIP (Figure 1) can assist an operator at every stage of the analytical process, from designing and optimizing acquisition conditions to performing advanced statistical analysis. Each parameter that has an impact on the data quality is available and can be manually tuned by the operator. Alternatively, the setup, acquisition, and analysis can be fully automated for increased throughput.
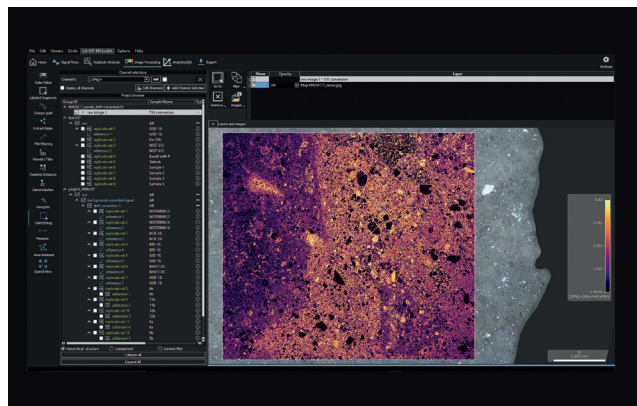

Figure 1. HDIP main acquisition and imaging interface.

An alternative to traditional LA-ICP-MS plug-ins

Software plug-ins have been widely used to connect accessories to ICP-MS systems. For laser ablation, a plug-in often provides the only option for transferring laser scan information to the ICP-MS and for coordinating the acquisition for single or multiple sample scans.

HDIP offers a superior solution for integrating LA with ICP-MS, providing far more advanced capabilities than traditional software plug-ins. The latest generation of laser ablation systems can operate at firing frequencies of 1 kHz, generating baseline-separated single ablation peaks as short as 1 ms duration. The result is drastically increased sample throughput − runs that previously took hours can now be performed in a few minutes.

The trend towards increased throughput and greater data volume has fueled demand for faster and better integrated workflows than can be achieved using traditional laser ablation plug-ins. With HDIP, the ICP-MS data can be matched to the ablation site during or after acquisition. Even if sample by sample triggering was not used, data for individual ablation sites/shots can be extracted from the TRA file and automatically matched to the ablation site using metadata saved in the laser log file.
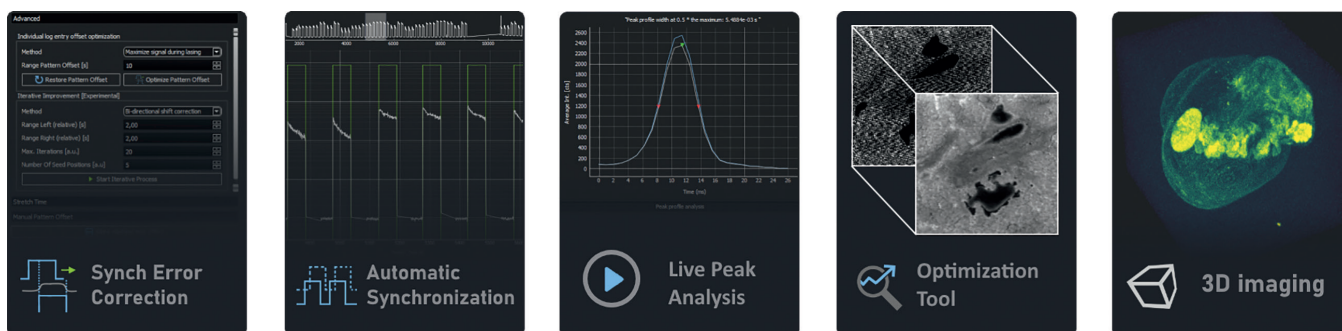
Figure 2. Software images showing the range of features of the HDIP interface.

HDIP uses an advanced algorithm to determine the time difference between the laser shot and the ICP-MS data, allowing automatic synchronization of the laser and the ICP-MS signals (Figure 2). This highly accurate approach reduces overheads, increases throughput, and lowers operating costs. Data transfer errors caused by loss of communication between the laser and the plug-in are avoided, and reliability of the analysis is improved.

More efficient data analysis workflows

Until recently, many LA-ICP-MS labs found data processing extremely slow and laborious, due to the many manual steps involved. Often ICP-MS data files require formatting in a specific spreadsheet layout for export to a separate software package for processing. HDIP enables flexible and more efficient workflows for data analysis and interpretation by offering manual setup or fully automated synchronization, data processing, visualization, and reporting.

HDIP can access the ICP-MS MassHunter method, allowing information such as dwell times per mass to be extracted and used in data analysis calculations. Background subtraction, signal drift correction, and even external calibration can be fully automated, and customized workflows can be created for batch runs.

Optimize method setup

Due to the micro-destructive nature of laser ablation, it is not always possible to analyze the same exact zone twice. This means that for precious samples it is crucial to gather as much usable data as possible during the first run. Even for experienced operators, configuring the measurement parameters correctly can be a challenge. Analysts may struggle with the underlying complexity

of laser ablation and the number of interdependent laser parameters that require optimization. HDIP can calculate the best conditions for a laser ablation study based on a short test measurement, making time-consuming manual optimization steps obsolete.

The optimization tool builds on research carried out at the National Institute of Chemistry in Slovenia (*2, 3*) and can yield the desired elemental image resolution and contrast, irrespective of the sample type. By removing the guesswork from the analysis, the operator can quickly achieve consistent performance over many samples.

The direct integration of HDIP with Agilent ICP-MS MassHunter software means that HDIP can stream and process the live multichannel signals produced by the Agilent ICP-MS system. The live feedback can be used to tune the instrument performance in real time, as the signal response can be analyzed for every individual laser shot. HDIP is both a natural evolution of existing software plug-ins, and an exciting new approach, signaling the potential future capability of integrated LA-ICP-MS.

References

1. S. J. M. Van Malderen, T. Van Acker, F. Vanhaecke, *Anal. Chem.* **2020**, 92, 8, 5756−5764

2. J. T. van Elteren, V. S. Šelih, M. Šala, *J. Anal. At. Spectrom.*, **2019**, 34, 1919-1931

3. S. J. M. Van Malderen et al., 2017, *Spectrochim Acta Part B: At. Spect*, 140, **2018**, 29−34

More information

* HDIP is compatible with Teledyne Cetac lasers running Chromium operating software. To learn more, visit https://la-icpms.com/

Applications of Helium Cell Gas with Kinetic Energy Discrimination in ICP-QQQ

Ed McCurdy, Yan Cheung, and Kazuo Yamanaka, Agilent Technologies, Inc.

Interferences in ICP-MS

Spectral overlaps due to polyatomic ions are the major source of error in most ICP-MS applications. Triple quadrupole ICP-MS (ICP-QQQ) enables more intense polyatomic ion overlaps to be resolved successfully, allowing additional analytes to be measured accurately at lower levels. ICP-QQQ also enables users to resolve isobaric, doubly charged ion, and peak tail overlaps.

Much of the focus for research and method development on ICP-QQQ has rightly been on extending the range of ICP-MS applications. To address this, many novel ICP-QQQ methods use reactive cell gases, with the QQQ's tandem mass spectrometer configuration (MS/MS) being used to control the in-cell reaction chemistry.

However, helium (He) collision mode remains a key tool for the ICP-MS analyst. He mode provides universal attenuation of common polyatomic interferences using kinetic energy discrimination (KED). The KED mechanism works because polyatomic ions are larger than analyte ions at the same mass. The polyatomic ions collide more often with the cell gas — and thereby lose more kinetic energy — than the analyte ions they overlap. The difference in residual energy at the cell exit allows the polyatomic ions to be rejected using a bias voltage.

Extending the scope of He KED

It is often claimed that He collision mode has limited ability to differentiate between polyatomic and atomic (analyte) ions. On some ICP-MS systems, He mode can only remove relatively low intensity interferences, with reaction mode being required for more intense overlaps. However, He mode performance is highly dependent on the design of the ICP-MS and the operating conditions of the collision/reaction cell (CRC). Critical factors are control of the ion energy of ions entering the cell, and a cell design that provides high ion transmission at the high cell gas pressures needed for effective KED.

The optimized He mode of the Agilent 8900 ICP-QQQ can reduce intense polyatomic interferences, such as ArC^+ on $^{52}Cr^+$ in organic solvents, by as much as 6 or 7 orders of magnitude.
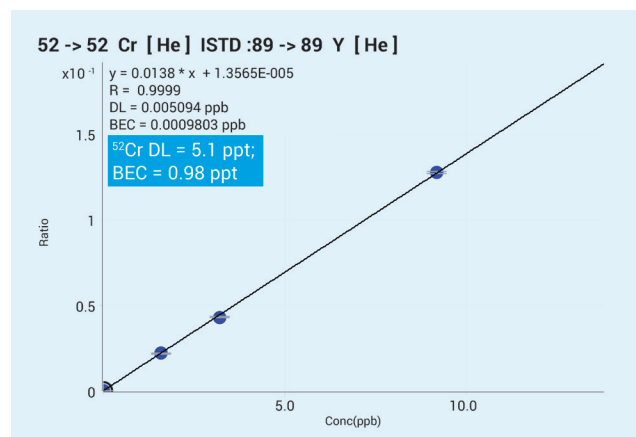
Figure 1. Calibration for ^{52}Cr in 100% xylene, showing effective removal of ArC^+ polyatomic using He cell gas. BEC of 0.98 ppt; DL of 5.1 ppt.

Figure 1 shows a He mode calibration for ^{52}Cr in 100% high-purity xylene, demonstrating a detection limit (DL) of 5 ng/kg (ppt) and a background equivalent concentration (BEC) <1 ng/kg. A higher than normal He cell gas flow rate successfully resolved the intense ArC^+ background signal.

He buffer gas in reaction gas methods

On Agilent ICP-QQQ instruments, He cell gas can also play a valuable role in reaction gas methods. When a highly reactive cell gas such as ammonia (NH_3) is used, reaction product ions may be formed in the cell. This can even occur in ICP-QQQ methods, when the first mass filter — Q1, before the cell — rejects all ions except those at the mass of the analyte of interest.

For example, when analyzing vanadium (V) in high purity HCl, Q1 is set to m/z 51 so the $^{51}V^+$ ions are passed to the cell. The overlapping $^{35}Cl^{16}O^+$ polyatomic ions at m/z 51 also pass through Q1 and enter the cell. The reaction

process used to resolve ClO$^+$ from V$^+$ is that ClO$^+$ reacts with the NH$_3$ cell gas and V$^+$ doesn't (or reacts more slowly). But the reaction of ClO$^+$ with NH$_3$ is a charge transfer reaction, as shown below:

$$ClO^+ + NH_3 \rightarrow ClO + NH_3^+$$
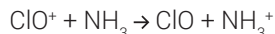
If not controlled, the NH$_3^+$ product ions can go on to react further with the NH$_3$ cell gas, potentially forming new (NH$_3$)$_3^+$ cluster ions at *m/z* 51, as shown below.

$$NH_3^+ + NH_3 \rightarrow (NH_3)_2^+$$

$$\text{Followed by: } (NH_3)_2^+ + NH_3 \rightarrow (NH_3)_3^+$$
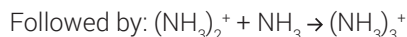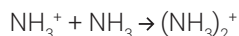
These sequential reactions could occur in the 8900 cell, so operating conditions must be selected to prevent the (NH$_3$)$_3^+$ product ions contributing to the signal at mass 51. Once again, He cell gas provides the solution.

When using highly reactive cell gases such as NH$_3$, the addition of He buffer gas controls the formation of higher mass product ions using two mechanisms. First, cluster ions are weakly bound, so will often dissociate on collision with the He buffer gas. Second, and more significantly, the cell-formed NH$_3^+$ product ions have low kinetic energy, as they are formed from the cell gas, which is essentially stagnant in the pressurized cell. The NH$_3^+$ product ions therefore only have the energy they gain from the reactive collision, which is not enough for them to migrate through the He buffer gas to reach the cell exit. The principle is illustrated in Figure 2 for the example of resolving ClO$^+$ from V$^+$ using NH$_3$ cell gas.
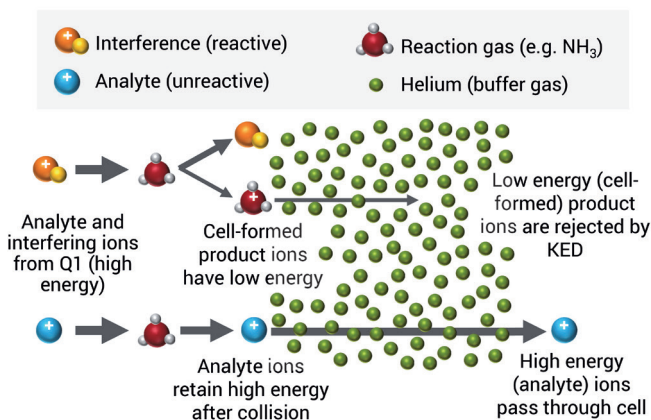
Figure 2. He KED rejects (low energy) cell formed NH$_3^+$ product ions, preventing the formation of potentially overlapping higher mass product ions such as (NH$_3$)$_3^+$ which would overlap V$^+$ at *m/z* 51.

In NH$_3$ mode, the He buffer gas prevents transmission of (low energy) cell-formed reaction product ions by energy discrimination. The process is similar to the removal of reduced-energy polyatomic ions by KED in normal He collision mode.
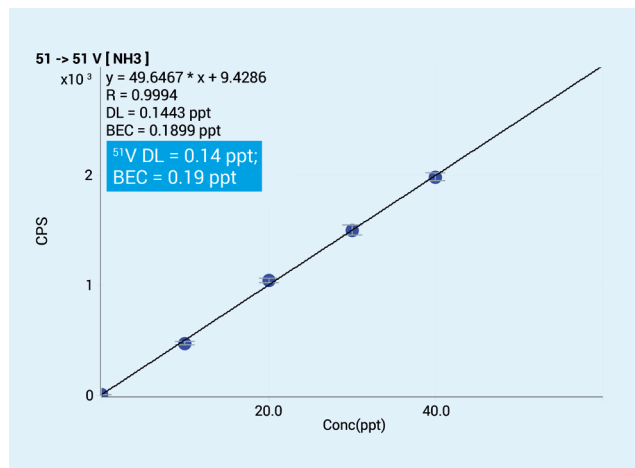
Figure 3. Calibration for ^{51}V in 20% HCl, showing effective removal of ClO$^+$ overlap using NH$_3$/He cell gas. BEC of 0.19 ppt; DL of 0.14 ppt.

Control of cell-formed product ions using He buffer gas is highly efficient, as shown in Figure 3. This shows a low-level calibration for V in high-purity 20% HCl. The removal of the original ClO$^+$ polyatomic overlap and the prevention of the formation of a (NH$_3$)$_3^+$ product ion allows sub-ppt DL and BEC to be achieved for ^{51}V$^+$.

Conclusion

ICP-QQQ is addressing many challenging applications, expanding the range of analytical capabilities far beyond what was possible using single quadrupole ICP-MS. Some of the most dramatic benefits have been in the ability of tandem mass spectrometry (MS/MS) to control reaction chemistry and enable low level analysis of previously difficult analytes.

The Agilent 8900 ICP-QQQ ORS cell also provides a unique level of performance in He collision mode, resolving intense polyatomic overlaps such as ArC on Cr in 100% organic solvents. He buffer gas can also be used to control cell-formed product ions in reaction gas methods. This control provides trace element DLs that meet the most demanding industry requirements for high purity semiconductor process chemicals.

Keep on learning! Download two free ICP-MS e-books
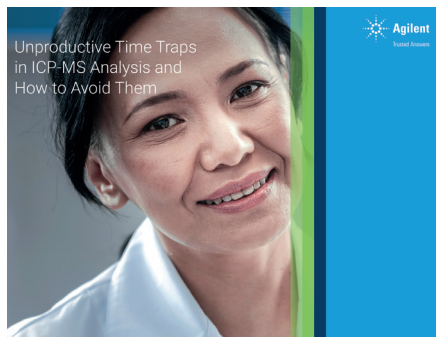
Title: Unproductive Time Traps in ICP-MS Analysis and How to Avoid Them

This new e-book contains practical tips and techniques that will be useful for any lab running an ICP-MS instrument. From ways to control sample contamination through to avoiding over range results, the e-book covers every step of owning, operating, and maintaining an ICP-MS.

Download: https://explore.agilent.com/icp-ms-ebook
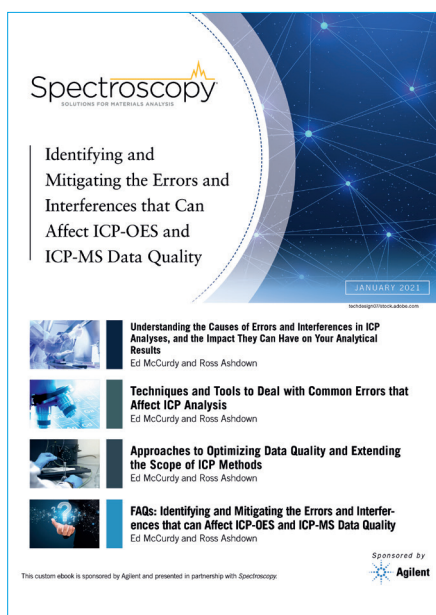
Title: Identifying and Mitigating the Errors and Interferences that Can Affect ICP-OES and ICP-MS Data Quality

Publisher: Spectroscopy

Agilent specialists presented a series of three webinars in 2020 that explored the factors that can degrade data quality in ICP-OES or ICP-MS analysis. This e-book is based on the Q&A sessions that followed each of the webinars.

The e-book summarizes some of the practical approaches that can help users to identify, understand, and mitigate the common sources of error in both techniques. You can also access the on-demand recordings of the webinars from links in the e-book.

Download the ebook: https://www.spectroscopyonline.com/view/identifying-and-mitigating-the-errors-and-interferences-that-can-affect-icp-oes-and-icp-ms-data-quality

Latest Agilent ICP-MS publications

- **Application note:** (updated): Routine Analysis of Fortified Foods using Single Quadrupole ICP-MS, 5994-0842EN

- **Consumables guide:** Recommended ICP-MS consumables to keep your lab online and productive, 5994-3084EN

Agilent

Trusted Answers