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New Methods, Software Tools, and Consumables for ICP-MS and ICP-QQQ

In this issue of the Agilent ICP-MS Journal, we highlight two ways that spectral overlaps can be addressed using triple quadrupole and conventional ICP-MS. First, we describe an MS/MS method with H₂ cell gas to resolve polyatomic overlaps from SH⁺ and O₂H⁺ on ³⁵Cl⁺. This enables the determination of Cl at low- and sub-mg/kg levels in crude oil samples. A second article shows a method for correcting doubly-charged interferences on Zn, As, and Se, by measuring the doubly charged ions at half-mass numbers e.g. ¹⁵⁵Gd²⁺ = 77.5.

We also introduce a new version of the ICP Go software interface for simplified routine workflows, and a new nickel-plated, Pt-tipped sampling cone for Agilent ICP-MS systems. Ni-plating increases the resistance of the cone to very aggressive acid matrices, extending the lifetime and reducing routine maintenance.



Figure 1. Agilent 7800 ICP-MS running the ICP Go software interface.

Determination of Chloride in Crude Oils Diluted in *o*-Xylene using an Agilent 8900 ICP-QQQ

Jenny Nelson, UC Davis, California, USA

Effects of chloride in crude oil

To avoid corrosion and fouling during distillation, petroleum producers aim to reduce chlorinated compounds to less than 1 mg/L in crude oil refinery streams (1). ICP-MS is increasingly used in the oil industry, due to the technique's low limits of detection. ASTM D8110–17 specifies ICP-MS for the determination of seven elements in petroleum distillate products (2).

The determination of chloride in oil-based matrices is challenging for conventional single quadrupole ICP-MS. Crude oil and its derivatives may contain sulfur (S), nitrogen (N), and oxygen (O) at variable concentrations, leading to multiple spectral interferences. The ^{35}Cl isotope (75.8% natural abundance) suffers polyatomic interferences from $^{16}\text{O}^{18}\text{O}^1\text{H}^+$ and $^{34}\text{S}^1\text{H}^+$. Also, Cl is extremely poorly ionized because of its high first ionization potential of 12.967 eV, so sensitivity is low.

Collision/reaction cell (CRC) methods with helium cell gas are used successfully to control many common polyatomic interferences in ICP-MS. But He mode cannot reduce the $^{34}\text{S}^1\text{H}^+$ interference sufficiently to allow the accurate determination of Cl at trace levels in samples that contain a high level of S (1). In this work, an Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) with MS/MS mode was used to resolve the interferences on ^{35}Cl .

Measurement of Cl using hydrogen mass-shift mode

Cl^+ reacts exothermically with H_2 cell gas to form ClH^+ , which reacts further with H_2 to form ClH_2^+ (3). This allows the use of a “mass-shift” approach, where the analyte reacts with the cell gas to form a product ion, shifting it away from the original on mass interferences. The method, shown in Figure 1, uses a Q1 set mass of m/z 35 to allow $^{35}\text{Cl}^+$ ions to enter the CRC while excluding any existing ions at m/z 37. The $^{35}\text{Cl}^+$ ions react with H_2 in the cell to form $^{35}\text{Cl}^1\text{H}_2^+$, while the interfering polyatomic ions ($^{16}\text{O}^{18}\text{O}^1\text{H}^+$ and $^{34}\text{S}^1\text{H}^+$) do not react with H_2 . Q2 is set to

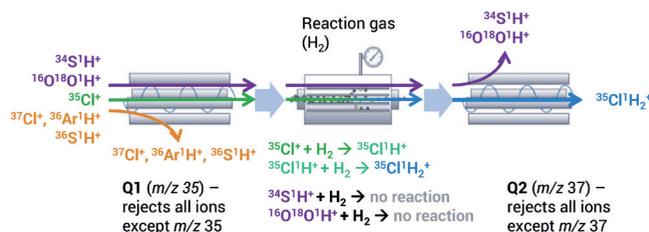


Figure 1. Determination of ^{35}Cl as $^{35}\text{ClH}_2^+$ product ion using ICP-QQQ operating in MS/MS mass-shift mode with H_2 reaction cell gas.

m/z 37, allowing the product ions $^{35}\text{ClH}_2^+$ to pass to the detector, free of interference.

Experimental

Calibration standard and crude oil sample preparation

The calibration standards were prepared by weight from a Cl organic standard (Conostan, Quebec, Canada) diluted in *o*-xylene (Fisher Scientific, NJ, USA). The *o*-xylene diluent included 10% matrix modifier prepared from 8% mineral oil (Fisher Scientific) and 2% dispersant (Chevron Oronite). Scandium (Sc) and yttrium (Y) internal standards (also from Conostan) were added at 0.1 mg/kg.

Direct dilution sample preparation

The composition of the 12 crude oil samples used in this study ranged from 84 to 89 wt.% C, 10 to 14 wt.% H, 0.3 to 2.5 wt.% S, and 400 to 2500 mg/kg N. The samples were diluted 1:5 or 1:10 in *o*-xylene to ensure that the Cl concentrations were within the calibration range. Standard Reference Material (SRM) NIST 1634c Trace Elements in Fuel Oil (NIST, Gaithersburg, MD, USA) was prepared at 1:5 and 1:10 dilution. All samples were shaken for two hours in a mechanical shaker. If any residue was seen on the vial walls, a vortex shaker was used to improve sample solubilization.

The ICP-QQQ instrument was configured for organic solvent analysis by fitting a torch with a 1 mm internal diameter injector, and platinum tipped interface cones.

Solvent resistant pump tubing (0.89 mm i.d., Cole Parmer) and the Agilent organic solvent introduction kit were used. Operating conditions are shown in Table 1.

Table 1. ICP-QQQ operating conditions.

Parameter	Value
RF Power (W)	1500
Nebulizer Gas Flow Rate (L/min)	0.4
Sampling Depth (mm)	8
Spray Chamber Temp (°C)	- 2
Option Gas (Ar 80%, O ₂ 20%) Flow Rate (L/min (MFC setting))	0.35 (35%)
Make up Gas Flow Rate (L/min)	0.1
Nebulizer Pump Speed (rps)	0.1
H ₂ Cell Gas Flow Rate (mL/min)	4.6
Octopole Bias (V)	- 18
Octopole RF (V)	180
Energy Discrimination (V)	0
Integration Time (s)	3

Results and discussion

The calibration plot for ³⁵Cl – measured as ³⁵Cl¹H₂⁺ – in the *o*-xylene diluent (*o*-xylene plus matrix modifier) is shown in Figure 2. The 3σ detection limit (DL), limit of quantification (LOQ), and background equivalent concentration (BEC) for Cl were determined from 10 replicate measurements of the matrix modified blank diluent. The results are shown in Table 2.

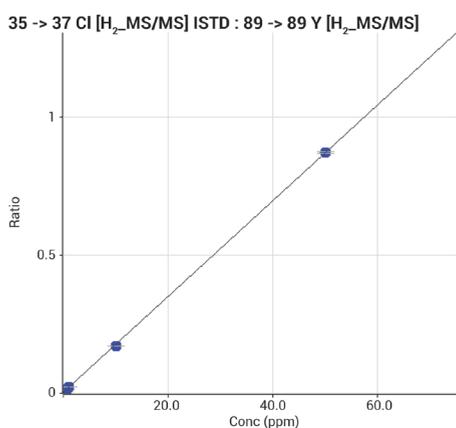


Figure 2. Calibration plot of Cl in *o*-xylene diluent. Units: mg/kg (ppm).

Table 2. DL, LOQ, and BEC of Cl in blank *o*-xylene diluent determined by ICP-QQQ in H₂ mass-shift mode (n = 10).

	DL (mg/kg)	LOQ (mg/kg)	BEC (mg/kg)
Cl	0.01	0.04	0.24

SRM analysis

Chlorine was determined in NIST SRM 1634c Fuel Oil using the 8900 ICP-QQQ operating in H₂ mass-shift mode. The SRM was diluted in *o*-xylene at dilution factors of 5 and 10. Other than carbon and hydrogen, real petroleum samples contain heteroatoms, S, N, and O, and metals such as V and Ni, among others. The sulfur content of NIST 1634c is around 2 wt.%. This SRM is therefore a useful sample to test the capability of the ICP-MS/MS method to resolve the potential ³⁴S¹H⁺ interference on ³⁵Cl.

Cl is not certified in NIST 1634c (5), but the reference (information) value for chlorine is given as 45 mg/kg. As can be seen from the ICP-MS/MS results presented in Table 3, excellent recoveries within ±10% were obtained for Cl, irrespective of the dilution factor.

Table 3. Determination of Cl concentration in NIST 1634c SRM in *o*-xylene diluent using ICP-QQQ.

	Dilution Factor 5		Dilution Factor 10	
	Conc (mg/kg)	*Recovery (%)	Conc (mg/kg)	*Recovery (%)
³⁵ Cl	44.33±1.00	99	48.28±1.89	107

*NIST 1634c reference value for Cl = 45 mg/kg, S = 2 wt%

Quantitative analysis of crude oil samples

Twelve petroleum crude oil samples were analyzed by ICP-QQQ using the method described, and full results are presented in reference 4. Chloride was measured at levels above 1 mg/L in all 12 crude oil samples. The 1 mg/L limit is the potential-corrosion trigger threshold, indicating a risk of corrosion at refining facilities due to the formation of HCl.

References

- Jenny Nelson, Laura Poirier, and Francisco Lopez-Linares, *J. Anal. At. Spectrom.*, **2019**, 34, 1433-1438
- ASTM D8110–17 Standard Test Method for Elemental Analysis of Distillate Products by ICP-MS. ASTM International, West Conshohocken, PA, 2017, www.astm.org/Standards/D8110.htm
- Kazumi Nakano, Agilent publication, [5991 6852EN](#)
- Jenny Nelson, Laura Poirier, and Francisco Lopez-Linares, Agilent publication, [5994-1094EN](#)
- NIST 1634c Certificate of Analysis, https://www-s.nist.gov/srmors/view_cert.cfm?srm=1634c

Correcting Doubly-Charged Ion Interferences Using Half-Mass Mode on the Agilent 7800 and 7900 ICP-MS

Naoki Sugiyama, Tetsuo Kubota, and Ed McCurdy, Agilent Technologies, Inc.

Doubly-charged ion interferences in ICP-MS

ICP-MS measurements can be affected by several types of spectral interferences. The most widely known and significant are polyatomic or molecular ions that overlap the mass of the target analyte ion. Other interferences may be caused by isobaric overlaps, where two elements have an isotope at the same mass, or abundance sensitivity – “peak tail” – overlaps. Finally, doubly-charged ions can cause spectral overlaps on the normal singly-charged ions of certain analytes.

Doubly-charged ions can affect quadrupole ICP-MS measurements because a quadrupole mass spectrometer separates ions based on their mass-to-charge ratio (m/z), rather than their true atomic mass. So, if an atom loses two electrons – giving it a double positive charge (M^{2+}) rather than the usual single positive charge (M^+) – it will appear at half its true mass.

Doubly-charged ions are not a significant problem in most ICP-MS applications, because the level of formation for most elements is low (<<3%). Also, higher mass elements tend to be less abundant than the lower mass elements that would be affected by M^{2+} overlaps. However, M^{2+} overlaps can cause problems for certain combinations of matrix and analyte elements, when:

- The interfering high mass element is present at relatively high concentration.
- The interfering element has a low second ionization energy, i.e. it is relatively easy to remove a second electron from the atom.
- An isotope of a trace analyte must be measured at half the interfering ion's true mass e.g. Zn-66 = $\frac{1}{2}$ Ba-132.

This combination of factors is unusual but can occur for some geological, environmental, and food samples that contain barium and the rare earth elements (REEs) at relatively high levels. These elements have low second ionization energies, and their isotopes occur at twice

the true mass of the critical trace analytes arsenic and selenium, as well as gallium, germanium, and zinc.

Enabling half mass measurement mode

Reaction cell modes using triple quadrupole ICP-MS (ICP-QQQ) can be used to resolve most spectral interferences, including M^{2+} overlaps. For users of conventional (single) quadrupole ICP-MS systems, however, reaction gas modes can prove unreliable, especially when applied to complex and variable sample matrices.



Figure 1. High performance hyperbolic quadrupole used in Agilent ICP-MS systems.

However, users of Agilent 7800 and 7900 ICP-MS systems can use an alternative approach, enabled by the high-performance, high frequency, hyperbolic quadrupole mass analyzers used in these instruments.

This quadrupole maintains high ion transmission at higher resolution settings, so the spectrum can be acquired with peak widths of <0.5 u, much narrower than the normal 0.75 u setting. This allows doubly-charged ions formed from odd-numbered parent ions, such as $^{135}\text{Ba}^{2+}$ at m/z 67.5, to be separated from adjacent singly-charged ions, i.e. m/z 67 and 68. The peaks at half mass must be derived from doubly-charged ions, as all singly-charged ions would appear at whole mass numbers. The known natural isotopic abundances of the interfering element are used to calculate the signal at the masses where the M^{2+} ions from the even-numbered isotopes occur. A correction equation can then subtract the contribution of the M^{2+} ions at the target analyte's mass.

Table 1. BEC and measured concentration of 1 ppb As/Se spike in 1 ppm Nd, Sm, Gd, Dy. Normal mode used no gas, no correction equation. Half mass mode used optimized cell gas and correction equations.

	Normal mode		Half mass mode	
	⁷⁵ As	⁷⁸ Se	⁷⁵ As	⁷⁸ Se
BEC (ppb)	6.13	33.76	0.08	0.04
1 ppb recovery	7.49	37.41	1.07	0.93

Measurement of As and Se in REE matrix

The half mass correction function of ICP-MS MassHunter provides a simple to setup, automated solution to doubly-charged ion overlaps. The Method Wizard is used to create a new method that includes “REE²⁺ Correction”, which automatically applies the half mass measurement mode and the relevant correction equations.

The half mass mode spectrum in Figure 2 shows how As and Se are affected by the presence of the REEs Nd and Gd. The M²⁺ peaks from the odd number isotopes of Nd (¹⁴⁵Nd²⁺ at m/z 72.5) and Gd (¹⁵⁵Gd²⁺ at m/z 77.5) are monitored. These signals are used by the predefined equations to correct the contributions from ¹⁵⁰Nd²⁺ and ¹⁵⁶Gd²⁺ on the target masses of As (75) and Se (78),

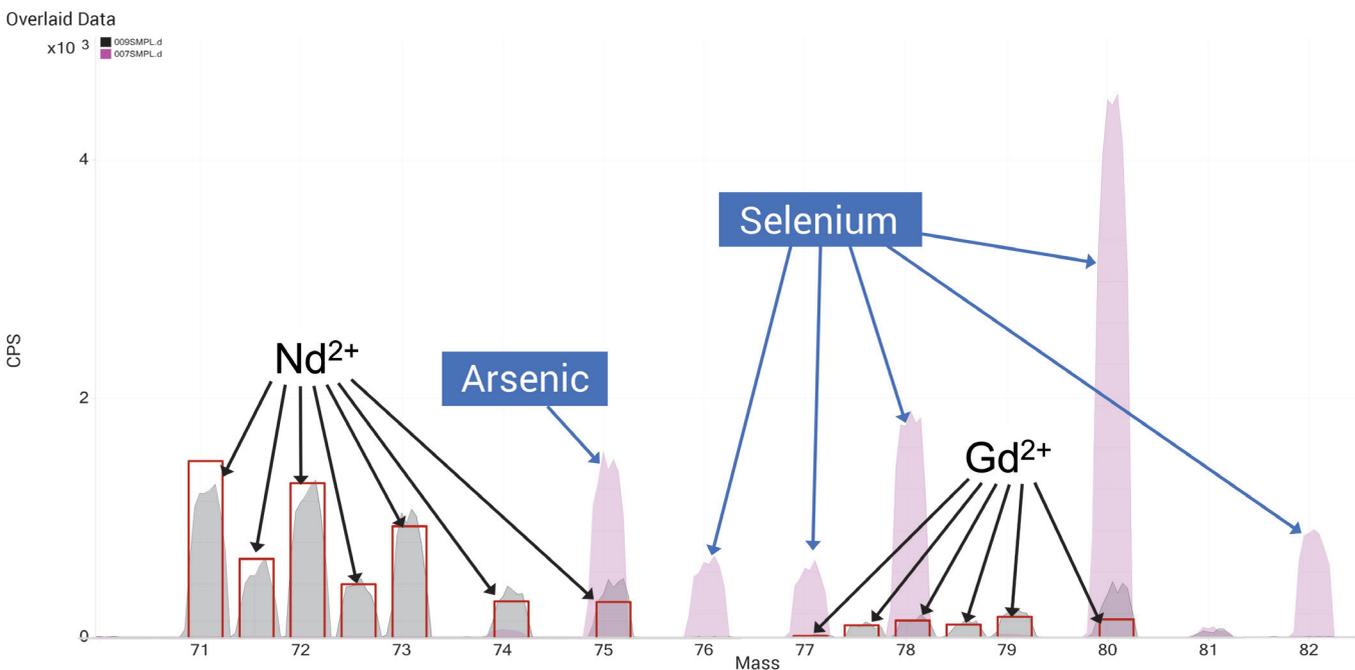


Figure 2. Overlaid narrow peak spectra of 10 ppb As and Se (pink) and 1 ppm Nd and Gd (grey). Note that the apparently interference free Se isotopes at m/z 76 and 77 would be overlapped by M²⁺ ions from ¹⁵²Sm and ¹⁵⁴Sm respectively. For clarity, the REE matrix used for this spectrum contained only Nd and Gd.

respectively. Table 1 shows how the half mass mode, coupled with optimum cell conditions, improved the BEC for As and Se by up to ~3 orders of magnitude. Accurate recovery was also obtained for a 1 ppb As and Se spike in a matrix containing 1 ppm of the REEs Nd, Sm, Gd, and Dy.

Conclusion

The high performance, hyperbolic quadrupole mass filter used in Agilent ICP-MS systems maintains high ion transmission at increased resolution, enabling the use of narrow peak mode. This mode works with equations that use the M²⁺ signals at half masses to correct the contribution from doubly-charged ions on whole mass unit analyte ions.

For users of conventional quadrupole ICP-MS – without the MS/MS mode available on ICP-QQQ – half mass correction offers a simple and automated approach to improve accuracy for several critical interfered analytes.

More information

1. Tetsuo Kubota, Agilent publication, [5994 1435EN](#)

Nickel-Plated Sampling Cones Last Longer and Are Easier to Clean

Gareth Pearson, Agilent Technologies, Inc.

Nickel plating extends cone lifetime

Copper (Cu) is used as the base material for Agilent ICP-MS sampling cones, due to its excellent thermal and electrical properties. However, the Cu base material can corrode when solutions containing strong acids such as hydrochloric acid or aqua regia are run routinely. Corrosion of the Cu base reduces cone lifetime and increases maintenance, as well as degrading analytical performance. Nickel plating the Cu base improves chemical resistance compared to an unplated cone, while maintaining the superior electrical and thermal conductivity provided by the Cu base material.

Ni- and new Pt-tipped, Ni-plated sampling cones

The Agilent nickel-plated sampling cones are available with a Ni tip (part number G3280-67061) and now with a Pt tip (new part number G3280-67142). For high sample matrices and strong acid concentrations, Ni plated cones can significantly increase cone lifetime and reduce the frequency of cleaning.

Putting the new cones to the test

Cu-based sampling cones with a Pt tip are typically used for the analysis of aggressive sample matrices, such as high concentrations of acids. To compare the performance of Pt-tipped sampling cones with and without Ni plating, each was used to analyze 10% aqua regia for 1,090 hours (approximately 45 days of continuous analysis).

Figure 1 shows that the Cu base of the standard Pt-tipped cone was affected by the strong acid. The black coating is copper oxide and the Cu surrounding the tip has been etched and corroded. Figure 2 shows almost no corrosion of the front or back of the Ni-plated, Pt-tipped sampling cone. From the comparison study, the Ni-plated, Pt-tipped cone:

- Lasted more than twice as long when analyzing a 10% aqua regia matrix.
- Required three times less frequent cleaning.

- Was easier to clean: only a simple one-step cleaning routine was required, using sonication in water.

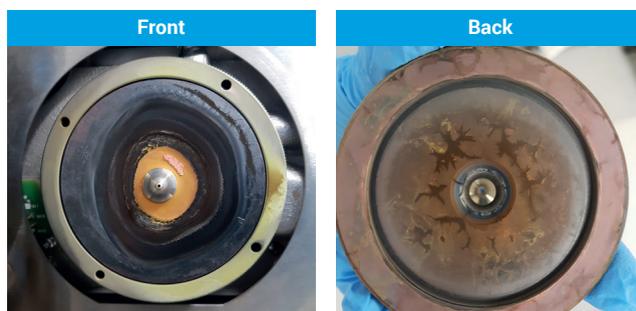


Figure 1. Standard, Cu base (without nickel plating), Pt-tipped sampling cone after 1090 hours running 10% aqua regia.

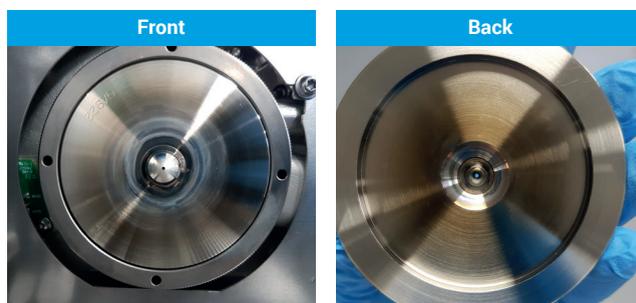


Figure 2. Ni-plated, Pt-tipped sampling cone after 1090 hours running 10% aqua regia.

Compatibility: The Ni-plated sampling cones are suitable for all Agilent 7700/7800/7900 ICP-MS and 8800/8900 triple-quadrupole ICP-MS instruments. An appropriate Ni or Pt-tipped skimmer cone and skimmer base should also be fitted, to suit the ICP-MS model and lens type.

Application: The Ni-plated cones are suitable for analysis of samples prepared in aggressive acid matrices, typical of some environmental, food, and geochemical applications.

Ordering details

Ni-plated ICP-MS sampling cone, [G3280-67061](#)

Ni-plated, Pt-tipped ICP-MS sampling cone, [G3280-67142](#)

Learn more

www.agilent.com/en/promotions/nickel-plated-cones

More Agilent ICP-MS and ICP-QQQ Users Benefit from Agilent ICP Go Software

Glenn Woods, Agilent Technologies, Inc.

Quick and easy ICP-MS sample analysis

To streamline routine sample analysis workflows, Agilent created ICP Go, a simplified, easy to learn, user-friendly software interface to control Agilent ICP-MS systems (7).

ICP Go is browser-based, so it can run on any compatible network-connected device, such as a PC, laptop, tablet, or smartphone. Device independent network connectivity benefits users or lab managers who need to monitor instrument status remotely, or check on the run progress of multiple ICP-MS systems.

ICP Go guides the user through the entire process of running samples using a previously defined batch template. ICP Go is used to control user access, run instrument performance checks, define the sample list, and analyze and report the results.

Availability and compatibility

Revision 1.2 of ICP Go is now available worldwide and supports all compatible Agilent ICP-MS and ICP-QQQ instruments and autosamplers:

- Agilent 7700, 7800, and 7900 ICP-MS
- Agilent 8900 ICP-QQQ
- Agilent SPS 4, ASX 520, and I-AS autosamplers
- Agilent ISIS 3 Integrated Sample Introduction System

ICP Go is also included with Agilent's powerful and comprehensive ICP-MS Analyzer bundles:

- Agilent EPA 200.8 and ISO 17294 Water Analyzers (North America and Western Europe only)
- Agilent Cannabis Analyzer (US and Canada only*)

ICP Go local language support has been extended to include Chinese, as well as English.

Version 1.2 of ICP Go requires ICP-MS MassHunter 4.5 Patch 1, running on Microsoft Windows 10 Professional operating system, 64-bit, version 1803 (or later).

New features for ICP Go revision 1.2

ICP Go has been adopted enthusiastically by routine ICP-MS laboratories, and the new version adds capabilities that further simplify and streamline workflows:

1. More flexible interface for editing currently running batches, for example to add a set of urgent samples or change the order of samples awaiting analysis.
2. Simple backup/restore function for user profiles and batch templates when upgrading or reinstalling.
3. Quick access to internal standard (ISTD) stability plots.



Figure 1. ICP Go screen showing ISTD recovery plot with high and low limits.

ICP Go is installed on the standard ICP-MS MassHunter workstation PC, so all the flexibility and capabilities of the ICP-MS MassHunter software suite are available if required.

More information

1. Agilent ICP Go Software, Agilent publication, [5994-0213EN](#)

* The Agilent ICP-MS Cannabis Analyzer is available in the USA and Canada only. It is intended to be used for cannabis quality control and safety testing in laboratories where such use is permitted under state/country law.

2020 Winter Conference on Plasma Spectrochemistry



The Winter Plasma Conference 2020 was held in Tucson, Arizona, USA from January 12-18. Agilent held a series of well-attended scientific and social events, and presented information on new methods and applications in atomic spectroscopy.

For more details of Agilent posters and talks presented at the conference, visit [Agilent at Winter Plasma Conference 2020](#)

Conference details: http://icpinformation.org/Winter_Conference.html

Date for your diary: The 2021 European Winter Conference on Plasma Spectrochemistry will take place in Ljubljana, Slovenia from 31 January to 5 February 2021.

Event website: www.ewcps2021.ki.si/

Latest Agilent ICP-MS publications

- **Primer (updated):** Handbook of ICP-QQQ Applications using the Agilent 8800 and 8900, [5991-2802EN](#)
- **Technical overview:** Simplifying Correction of Doubly Charged Ion Interferences with Agilent ICP-MS MassHunter. Fast, automated M^{2+} correction routine improves data accuracy for Zn, As, and Se, [5994-1435EN](#)
- **Application note:** Direct Analysis of Zirconium-93 in Nuclear Site Decommissioning Samples by ICP-QQQ. Using MS/MS mass-shift mode to resolve ^{93}Zr from ^{93}Nb without chemical separation, [5994-1532EN](#)
- **Application note:** Analysis of TiO_2 Nanoparticles in Foods and Personal Care Products by Single Particle ICP-QQQ, [5994-1633EN](#)
- **Application note: Fast** Determination of Inorganic Arsenic (iAs) in Food and Animal Feed by HPLC-ICP-MS, [5994-1642EN](#)
- **Application note (updated):** Multi-Element Analysis of Cannabis and Hemp using ICP-MS. Agilent 7800 used to analyze 25 elements in a range of cannabis, hemp, and related products, [5991-8482EN](#)

Agilent products and solutions are intended to be used for cannabis quality control and safety testing in laboratories where such use is permitted under state/country law.

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