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Optimizing ICP-MS Methods and Performance

This issue of the Agilent ICP-MS Journal marks almost 23 years since the first issue of “The Hot Source” was published in September 1998. In that first issue, we celebrated having shipped 500 HP 4500 ICP-MS instruments (in June 1998), a remarkable achievement just four years after launching the first HP/Agilent ICP-MS available worldwide.

Since then, Agilent ICP-MS systems have developed beyond recognition, setting new standards for inorganic analysis with innovations including the world’s first helium mode collision/reaction cell and the world’s first ICP-MS/MS. But our core aim remains focused on providing instruments, methods, consumables, and support to enable researchers and analysts to consistently achieve accurate, reliable results in their varied sample types.

In this issue, we present articles on a new method for ultratrace level analysis, the link between hardware development and improved ICP-MS performance, and new resources for ordering consumables.



Figure 1. Agilent 8900 ICP-MS/MS. Unmatched performance for trace element analysis.

Analysis of Impurities in Ultrapure Water (UPW) Using Agilent 8900 ICP-QQQ with Hot Plasma and m-Lens

Kazuhiro Sakai and Yoshinori Shimamura, Agilent Technologies, Inc.

Introduction

The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ or ICP-MS/MS) has rapidly become established as the technique of choice for the analysis of high purity process chemicals used in the semiconductor industry. The 8900 meets the industry's need for trace and ultratrace element analysis due to its high sensitivity, low background, and interference removal capabilities.

The 8900 has the flexibility to operate in several modes to give optimum performance across different applications. For example, semiconductor labs often use cool plasma conditions to achieve the lowest background equivalent concentrations (BECs) and detection limits (DLs) for interfered and easily ionized elements (EIEs). Cool plasma reduces EIE backgrounds and suppresses the formation of intense argon-based interferences such as Ar^+ , ArH^+ , and ArO^+ , allowing low-level analysis of ^{40}Ca , ^{39}K , and ^{56}Fe , respectively.

Cool plasma gives excellent results in low matrix samples, such as UPW, H_2O_2 , HNO_3 , and HCl (1). However, high matrix samples, such as silicon and metal digests, are difficult to run using cool plasma due to the higher level of matrix suppression. More robust, hot plasma conditions are preferred for such sample types.

In a recent study, an 8900 fitted with the optional m-lens was used to determine 38 elements in two digested silicon samples prepared at 10 and 100 ppm Si (2). The m-lens and the skimmer cone that it is paired with have an optimized geometry that minimizes EIE backgrounds when using normal, hot plasma conditions. Using m-lens, the 8900 was able to measure all required elements at ppt levels in the Si matrix without using cool plasma.

The 8900 with m-lens can also be used to analyze semiconductor elements in low matrix samples – such as UPW – using only normal, hot plasma conditions.

Industry requirements

ASTM International and Semiconductor Equipment and Materials International (SEMI) publish standards regarding the specifications for semiconductor reagents. The standards for UPW (ASTM D5127-13 (2018) and SEMI F63-0521 (2021)) require a technique such as ICP-QQQ that can determine most elements with a BEC of < 1 ppt (50 ppt for B) and a DL < 0.5 ppt (15 ppt for B).

Experimental

Instrumentation

The 8900 Semiconductor Configuration ICP-QQQ with standard PFA-100 microflow nebulizer (200 $\mu\text{L}/\text{min}$), quartz spray chamber, quartz torch with 2.5 mm injector, and Pt sampling cone was used for the analysis. The 8900 was fitted with the optional m-lens (part number G3666-67500) and Pt-tipped, Ni-based skimmer cone for m-lens (part number G3666-67501).

In this study, three cell modes were used (Table 1). All elements were measured using normal, hot plasma conditions (CeO/Ce ratio $< 2\%$).

Table 1. ICP-QQQ operating parameters.

	No Gas	$\text{NH}_3 + \text{H}_2$	O_2
RF Power (W)		1600	
Sampling Depth (mm)		8.0	
Nebulizer Gas (L/min)		0.70	
Makeup gas (L/min)		0.48	
He Flow Rate (mL/min)	0	1	0
H_2 Flow Rate (mL/min)	0	2	0
* NH_3 Flow Rate (mL/min)	0	2.0 (20%)	0
O_2 Flow Rate (mL/min)	0	0	0.45 (30%)

*Mix of 10% NH_3 in 90% He

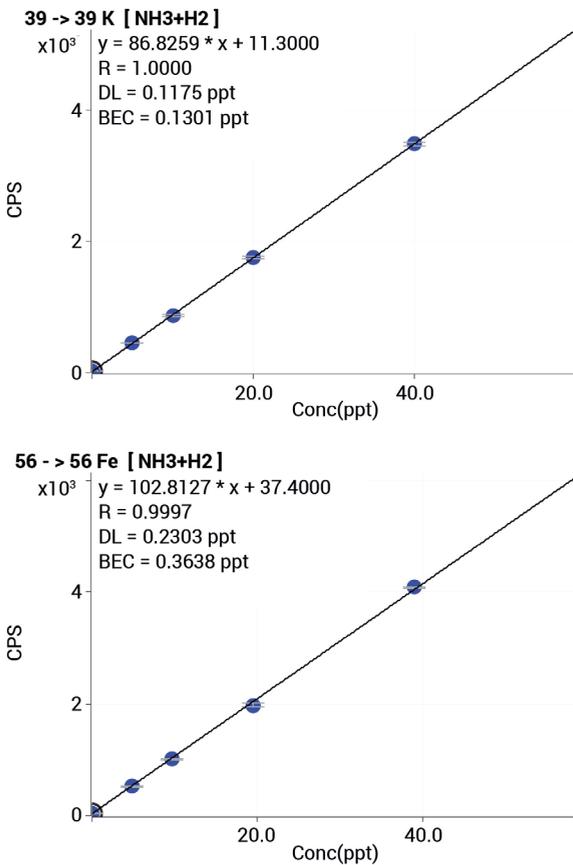


Figure 1. Representative MSA calibration plots for K and Fe.

Sample preparation and calibration

A UPW sample was acidified to 0.1% with high purity 68% HNO₃. The 8900 ICP-QQQ was calibrated using the method of standard addition (MSA), as is typical for the analysis of high-purity semiconductor samples. A mixed multi-element standard (SPEX CertiPrep, NJ, US) was prepared and spiked into the UPW to give standard additions at 5, 10, 20, and 40 ppt. No background subtraction or blank correction was performed. Example calibrations for K and Fe are shown in Figure 1.

DLs and BECs

BECs below 0.5 ppt and DLs below 0.3 ppt were obtained for all 26 SEMI specified elements apart from B (1.11 and 1.18 ppt, respectively), easily meeting the limits specified for UPW by ASTM and SEMI. The results (Figure 2) show the suitability of the 8900 ICP-QQQ using hot plasma and m-lens for the analysis of ultratrace contaminants in high purity semiconductor process chemicals.

References

1. Determination of Ultratrace Elements in High Purity Hydrogen Peroxide by ICP-QQQ, [5991-7701EN](#)
2. Analysis of Ultratrace Impurities in High Silicon Matrix Samples by ICP-QQQ [5994-2890EN](#)

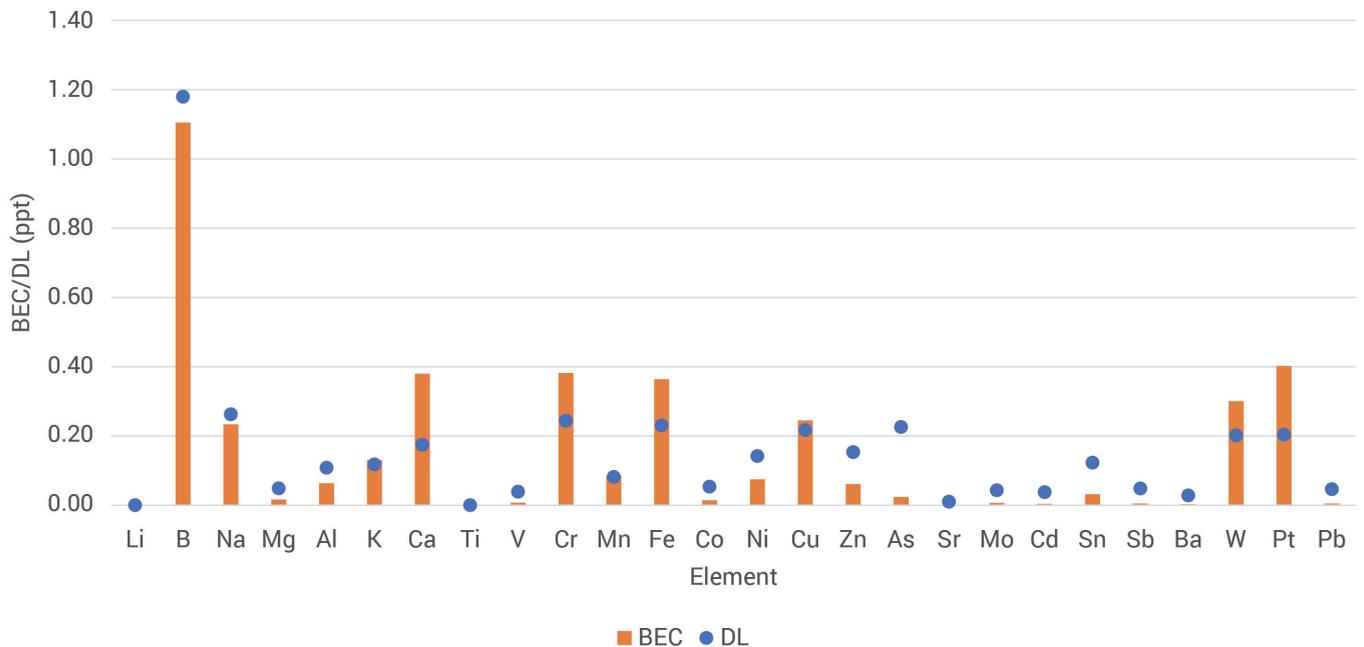


Figure 2. BECs and DLs for SEMI specified elements in UPW measured using the 8900 ICP-QQQ with hot plasma conditions.

Space Charge in ICP-MS. What Causes It and What Does It Mean for Your Analysis?

Ed McCurdy, Agilent Technologies, Inc.

Space charge in ICP-MS

“Space charge” is a term most ICP-MS users have probably heard of, but many may not be aware what causes space charge and the implications for their analysis. Space charge is a fundamental property of ion beams. In ICP-MS, space charge is caused by the charge imbalance that occurs after ions are extracted from the plasma and passed into the high vacuum region.

A plasma is a substantially ionized gas in which the number of positively charged ions is more-or-less balanced by the number of free electrons, giving an overall potential close to neutral. An ICP-MS plasma consists mainly of ions from the Ar support gas and – in normal, aqueous solution analysis – N, O, H, and C from the surrounding air and the sample solution. Further ions come from elements in the sample and other chemicals used to prepare or stabilize the solution.

The composition of the ion beam remains largely unchanged after it is extracted into the interface region via the sampling cone. But, behind the skimmer cone, the pressure drops further, the beam density decreases, and the charged particles become more mobile. Electrons are much lighter and more mobile than ions and are repelled by the (usually) negative lens voltages, so the electrons quickly diffuse radially out of the ion beam.

This process, illustrated in Figure 1, is called “charge separation”, where the loss of the electrons leaves the ion beam with an overall positive charge. The positively charged ions that remain try to repel each other, leading to beam dispersion, defocusing, and loss of transmission. The ion lenses of an ICP-MS system are typically designed to control this beam dispersion, to maintain high ion transmission, and therefore good sensitivity. How well the beam dispersion is controlled depends on the vacuum pressure, the geometry of the skimmer cone and ion lens, and the voltages applied to them.

Maintaining high ion transmission and sensitivity is critical for overall ICP-MS performance, but space charge doesn’t affect all ions equally. An ion’s kinetic energy (KE) is proportional to its mass, so light ions (with lower KE) are more easily deflected and dispersed than heavier (higher KE) ions. This means that the light (low mass) ions tend to migrate to the outer edges of the ion beam, leaving fewer near the central axis, as shown in Figure 2.

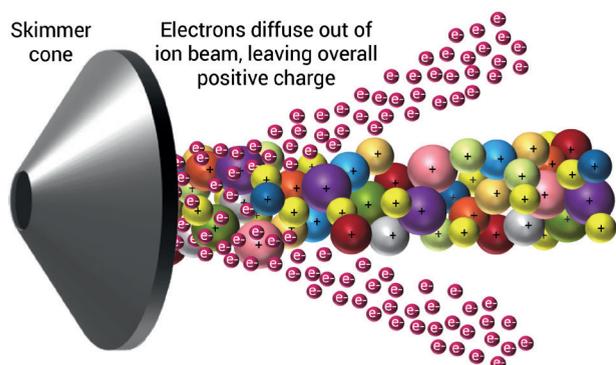


Figure 1. The process of charge separation occurs after the ion beam passes through the skimmer cone into the high vacuum region.

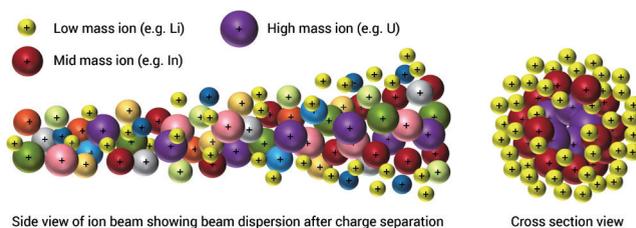


Figure 2. Space charge causes mass dependent ion beam dispersion, leading to defocusing and lower transmission of light ions.

Mass dependent defocusing due to space charge is one of the main reasons a typical ICP-MS mass/response curve has lower sensitivity for low mass elements than for mid and high mass elements. This is despite the fact that elemental concentrations measured by ICP-MS are usually calculated on a wt/vol or wt/wt basis. On this basis, the number of ions per unit of concentration should be much higher for a low mass element than a high mass element.

For example, 1 ng of Li (atomic weight 6.941) contains about 34 times as many atoms as 1 ng of U (atomic weight 238). If ion transmission was equal for all masses, Li should give 34 times as many counts per ppb as U. This is illustrated in Figure 3 (top), which shows the number of atoms per ng for all elements. Normally an ICP-MS mass response curve is a totally different shape (inset, in red), as a high proportion of low mass ions are lost due to space charge.

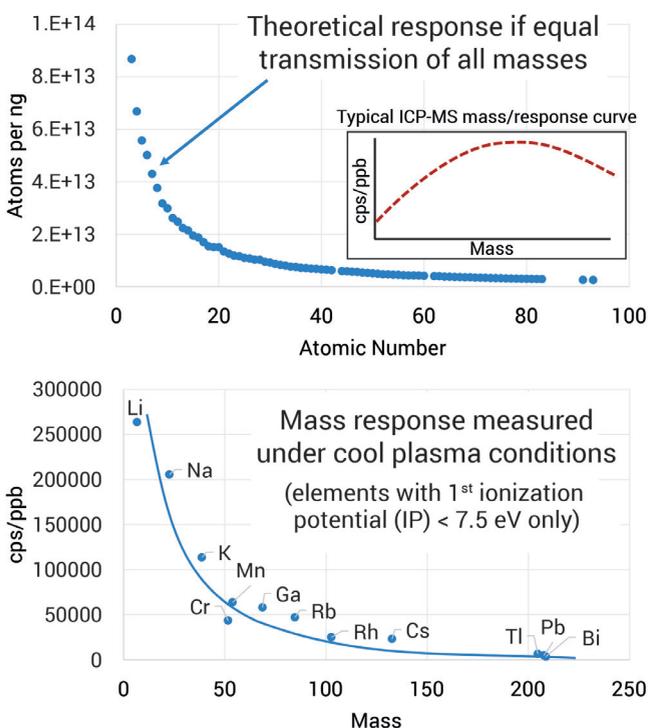


Figure 3. Top: number of atoms per ng for all elements. Bottom: measured mass/response (cps/ppb, corrected for isotopic abundance) for easily ionized elements (1st IP <7.5 eV) in cool plasma conditions.

Interestingly, under cool plasma conditions, considering only easily ionized elements, the mass response curve (Figure 3, bottom) does closely match the theoretical response for equal transmission of all masses. This is because cooler plasma conditions provide less energy for ionization, affecting poorly ionized elements to a greater degree. These elements include the “gas and solvent” elements (Ar, N, O, H, and C) and the molecular species formed from them (N₂, O₂, NO, ArH, ArO, Ar₂, etc.). The absence of these ions in the ion beam extracted from a cool plasma means that the beam contains far fewer ions overall, so space charge effects are almost eliminated.

Cool plasma is not suitable for all ICP-MS applications, as the lower energy plasma has poorer matrix tolerance and gives less ionization for high 1st IP analytes. But cool plasma remains useful for semiconductor applications where the high sensitivity and low backgrounds allow trace analysis in low matrix samples such as UPW.

Everything is connected

Optimizing the geometry of the ICP-MS skimmer cone and ion lens gives higher ion transmission and less mass bias. This enables the plasma and interface to be further optimized for higher performance, as shown in Figure 4.

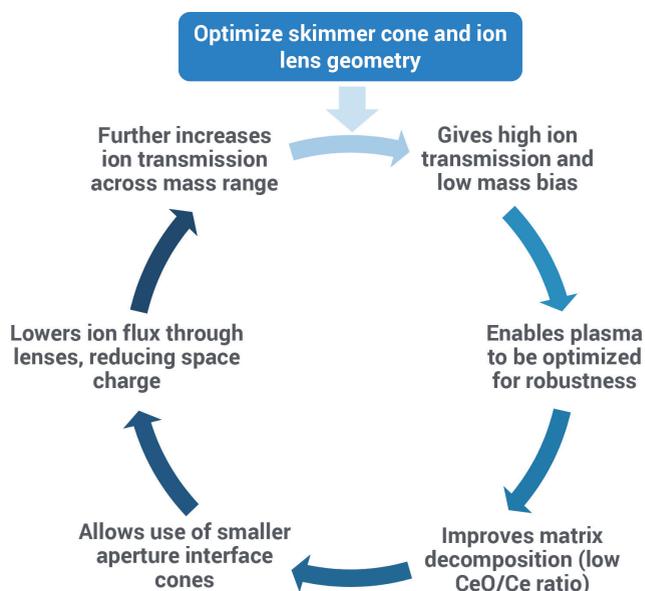


Figure 4. Optimized skimmer cone and ion lens geometry of Agilent ICP-MS enables system to be developed for higher overall performance.

Conclusion

In ICP-MS, space charge occurs when the positively charged ions repel each other in the ion beam, with light ions being deflected more. Space charge effects are influenced by the geometry and operating conditions of the skimmer cone and ion lens. On Agilent ICP-MS systems, an optimized design controls space charge, increasing ion transmission and reducing mass bias, so providing much lower DLs for light elements.

Mass bias is lower with cool plasma. This suggests that space charge is primarily due to the gas and solvent ions present in the normal (hot plasma) ion beam, rather than being caused by high levels of sample matrix ions.

Consumables Update: Workflow Ordering Guide for Water Analysis; New Easy-fit Peristaltic Pump Tubing

Gareth Pearson, Agilent Technologies, Inc.

Consumable workflow ordering guide for EPA 200.8, EPA 6020A, and ISO 17294-2



This new guide introduces the complete Agilent ICP-MS workflow solution for regulated water and waste analysis, simplifying the process of identifying and ordering relevant consumables and supplies.

Publication number:
5994-3274EN

This 8-page guide includes information on regulations, instrument solutions, hardware options, typical tuning conditions, and method information for water and waste analysis, plus links to relevant references.

The guide includes links to all the supplies and standards that you will need to conduct your analysis using an Agilent 7850 or 7900 ICP-MS. To speed up ordering, simply click the MyList links to give direct access to your customized consumables lists on the Agilent web store.

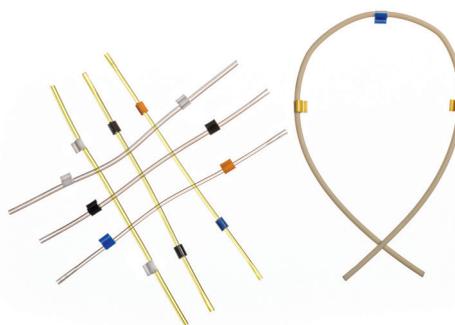
Optimized Easy-fit peristaltic pump tubing

Easy-fit peristaltic pump tubing is pre-cut to the optimum length, eliminating the need to trim, providing improved ease of use and greater productivity. In qualifying the easy-fit peristaltic pump tubing range, we verified:

- Low leachable metals and fast wash out to prevent contamination and reduce carryover.
- Secure tab adhesion, even for tubing that has been pre-soaked in nitric acid cleaning solution.
- Stable flow rate for better long-term signal stability over the lifetime of the tube.
- Fast recovery from compression, ensuring signals stabilize faster when changing pump speeds.

- Easy and secure insertion of sample uptake tube, due to accurately cut and flared ends.

The tubing range has been extended to include PVC solvent flexible (known as Solvaflex) options that are resistant to commonly used organic solvents.



Part Number Product Description

5005-0020	Sample uptake, aqueous, acid, or alkaline matrix [Std for 7xx0 and 8x00]. Clear PVC, 2-stop, white/white tabs, 1.02 mm ID, 1 pack of 12 pcs.
5005-0021	Online Internal standard (ISTD) uptake with aqueous solutions [Std for 7xx0 and 8x00]. Flared-end clear PVC, 2-stop, blue/orange tabs, 0.25 mm ID, 1 pack of 12 pcs.
5005-0022	Spray chamber drain [Std for 7xx0 and 8x00]. Beige thermoplastic elastomer, 3-stop, yellow/blue tabs, 1.52 mm ID, 1 pack of 12 pcs.
5005-0023	High matrix uptake, aqueous, recommended for online sample dilution 1:1 with ISTD Flared-end clear PVC, 2-stop, black/black tabs, 0.76 mm ID, 1 pack of 12 pcs.
5005-0025	Sample uptake with organic solvent matrix. Yellow PVC solvent flexible, 2-stop, white/white tabs, 1.02 mm ID, 1 pack of 12 pcs.
5005-0026	High matrix uptake, organic, recommended for online organic solvent sample dilution 1:1 with ISTD Flared-end yellow PVC solvent flexible, 2-stop, black/black tabs, 0.76 mm ID, 1 pack of 12 pcs.
5005-0027	Online Internal standard (ISTD) uptake with organic solvent matrix Flared-end yellow PVC solvent flexible, 2-stop, blue/orange tabs, 0.25 mm ID, 1 pack of 12 pcs.
5042-4799	Sample uptake with samples in Xylene matrix. Black, fluoro-elastomer polymer, 3-stop, yellow/blue tabs, 1.52 mm ID, 1 pack of 12 pcs.
G1820-65217	High purity sample uptake, recommended for trace analysis when not using self-aspirating nebulizer Silicone, 3-stop, white/white tabs, 1.02 mm ID, 1 pack of 12 pcs.

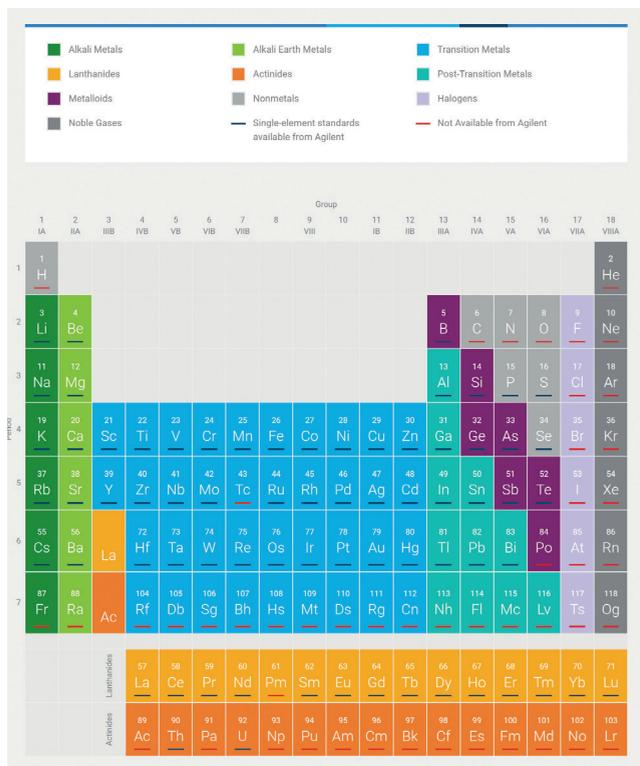
[Learn more here.](#)

Explore Our New Interactive Periodic Table for Ordering Single Element Standards and Other Supplies

Gareth Pearson, Agilent Technologies, Inc.

Simple, intuitive interface gives easy access to check and order spectroscopy standards

To ensure the accuracy and consistency of ICP-MS analyses, Agilent offers a comprehensive portfolio of single-element and multi-element reference materials for calibration and quality control. Following the 2019 150th anniversary of Dmitri Mendeleev’s creation of the first periodic table of elements, Agilent has launched a new periodic table ordering page. The interactive page will help you find and order high quality ISO 17025 and 17034 accredited chemical standards and certified reference materials.



Explore the table at:

<https://explore.agilent.com/periodic-table-standards>

Information behind the element symbol

Clicking on an element symbol in the table opens a page of information relevant to atomic spectroscopy for that element, including the recommended mass number for ICP-MS analysis. There are also useful tips on storage, stability, and matrix compatibility, as well as links to Agilent standards that contain the element of interest.

33 74.92
As
9.79 616
18.59 616

Arsenic

Atomic weight: 74.9216

Chemical form in solution: H₃AsO₄ and HAsO₂

Isotope abundance: 75 (100%)*

* Highlighted isotope is the recommended mass number for ICP-MS analysis

Oxidation states: +5/+3/mix, -3

✕

Storage conditions

Store at room temperature (15° to 30°C)

Stability

2-100 ppb levels—stable for months alone or mixed with other elements at equivalent levels—in 1% HNO₃/LDPE container. 1-10,000 ppm solutions chemically stable for years in 1-5% HNO₃/LDPE container.

Matrix compatibility

- Aqueous/HNO₃
- H₂O at pH 7
- H₂SO₄
- H₃PO₄ (not commonly used due to attacking containers)

Single element inorganic standards

AA | MP-AES Standards at 1,000 ug/mL+

MP-AES | ICP-OES Standards at 10,000 ug/mL+

ICP-OES | ICP-MS Standards at 1,000 ug/mL+

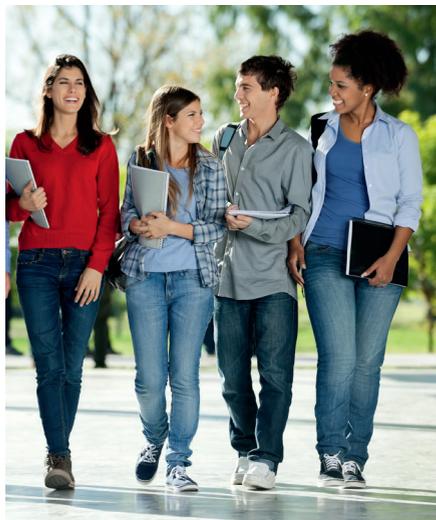
ICP-OES | ICP-MS Standards at 10 and 100 ug/mL+

Single element lamps +

Concerns About Heavy Metals in Baby Foods

An investigative committee in the U.S. House of Representatives issued a [report](#) in February 2021 showing that many baby foods sold in US supermarkets contained unacceptably high concentrations of As, Cd, Pb, and Hg. These findings led to the development of the [Baby Food Safety Act 2021](#). The Act proposes new maximum levels of inorganic As, Cd, Pb, and Hg permitted in baby foods sold in the US, impacting imports of raw materials and final products into the US. Learn more in Agilent application note, [5994-3713EN](#)

Agilent Academia Insights Newsletter



The Agilent ICP-MS team enjoy close links with many university and research institutes around the world. If you work in this field or are interested in developments in this area, why not sign up to receive the Agilent Academia Insights newsletter? On the registration page, you can choose to receive targeted information relevant to your research or instrumentation interests. You will receive a copy of the newsletter into your inbox four times a year.

[Register for the Agilent Academia Insights newsletter here](#)

Latest Agilent ICP-MS publications

- **Spectroscopy executive summary:** Use of Microwave Digestion and ICP Methods for Elemental Analysis of Food Samples, [download](#)
- **Applications compendium:** ICP-QQQ Applications in Geochemistry, Mineral Analysis, and Nuclear Science, [5994-3155EN](#)
- **Application note:** Fast and Accurate Speciation of Mercury in Milk and Honey Food Products by HPLC-ICP-MS: Method compliant with FSSAI regulations using an Agilent 7850 ICP-MS with HPLC, [5994-3628EN](#)
- **Application note:** Analysis of Inorganic Arsenic, Cadmium, Lead, and Mercury in Baby Foods by ICP-MS: Addressing new action limits in US Baby Food Safety Act 2021 using an Agilent 7850 ICP-MS and HPLC-ICP-MS, [5994-3713EN](#)
- **Application note (updated):** Fast, Accurate Analysis of 28 Elements in Water using ISO Method 17294-2 for ICP-MS, [5994-2804EN](#)
- **Application note (updated):** Routine Analysis of Fortified Foods using Single Quadrupole ICP-MS, [5994-0842EN](#)
- **Application note (updated):** Ultra-Trace ICP-MS Analysis of Metals in Mineral Reference Materials, [5991-6406EN](#)
- **Application note (updated):** Using Heteroatoms as “Natural Labels” in the Quantitative Analysis of Active Pharmaceutical Ingredients by HPLC-ICP-MS, [5991-5445EN](#)
- **Technical flyer:** ICP-MS Ion Lens Design, [5994-3527EN](#)
- **Technical flyer:** Controlling Cell-Formed Product Ions in ICP-QQQ, [5994-3548EN](#)

This information is subject to change without notice.