

Plasma Robustness and Matrix Tolerance

Agilent ICP-MS technology brief

Leading commercial laboratories choose Agilent ICP-MS instruments because they provide superior plasma robustness

To fully decompose the sample matrix, dissociate matrix-based polyatomic interferences, and ionize the analyte atoms, Agilent ICP-MS systems use as standard:

- An efficient, low-flow concentric nebulizer to reduce sample loading
- A Scott-type double-pass spray chamber for most effective droplet filtering
- Peltier-cooling of the spray chamber as standard, giving better removal of excess water vapor
- Low carrier gas flow rate for higher plasma central channel temperature
- A plasma torch with a wide—2.5 mm internal diameter injector as standard, to lower aerosol density
- A 27 MHz RF generator for highest ionization efficiency—critical to achieve high sensitivity for poorly ionized elements

With Agilent's robust—low CeO/Ce—plasma, you benefit from higher sensitivity, lower polyatomic interferences, less matrix deposition on the interface, so reduced drift and maintenance.

Why plasma robustness matters

A robust, high-temperature plasma decomposes the sample matrix better, giving lower interferences and less matrix deposition on the interface cones. A higher plasma temperature also gives higher sensitivity and lower detection limits, particularly for poorly ionized elements like Be, As, Se, Cd, and Hg.

The robustness of an ICP-MS instrument is measured using the CeO⁺ to Ce⁺ ratio. This ratio shows how effectively the plasma breaks apart the strongly bound Ce-O molecule. Agilent ICP-MS systems operate at around 1.0 to 1.5% CeO/Ce, as standard—2x lower than comparable non-Agilent instruments. Low CeO/Ce equals high robustness, which translates into better matrix tolerance, higher analyte sensitivity, lower levels of interference, less drift, and reduced maintenance.

Plasma robustness doesn't happen by accident. Agilent ICP-MS instruments are designed to give very high ion transmission through the interface, ion extraction, and ion focusing. As a result, users can optimize the plasma for robustness, while still delivering industry-leading sensitivity and detection limits. And for low-matrix samples you can tune for extremely high, GHz sensitivity!



Figure 1. The plasma of an ICP-MS must have enough energy to dry the aerosol droplets, decompose and dissociate the matrix, and then atomize and ionize the analyte elements.



Plasma temperature and analyte ionization

The plasma must dry the aerosol droplets and decompose the matrix, and still retain enough energy to atomize and ionize the analyte elements. Plasma generator and load coil design, sample introduction configuration, and tuning settings have a major impact on the effective temperature in the central channel of the plasma. Agilent ICP-MS systems are designed and optimized to give the highest performance in all these aspects.

ICP-MS measures ions, not atoms. The degree of ionization of an element determines its sensitivity, so it is critical that the plasma has enough energy to form ions effectively. Ionization depends on the element's ionization potential (IP), which is a measure of the energy required to remove one electron from the atom. For ICP-MS analytes, IPs range from 3.89 electronvolts (eV) for Cs, up to 12.97 eV for Cl. The plasma is formed from argon, which has a first IP of 15.76, so most elements are fully or substantially ionized.

A change in plasma temperature affects the ionization of elements with a high first IP more than elements with a low first IP, as illustrated in Figure 2. An easily ionized element such as Ba is almost 100% ionized regardless of the plasma temperature. By contrast Cd is >80% ionized at a plasma temperature of 7800 K, decreasing to <40% ionization at a plasma temperature of 6800 K.

A poorly designed or optimized plasma—or an application where excessive sample matrix loading overloads the plasma—can dramatically reduce sensitivity for critical trace elements.



Figure 2. Degree of ionization for elements at various plasma temperatures. For poorly ionized elements, a small change in plasma temperature has a major impact on ionization and therefore sensitivity.

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Impact of plasma temperature on ionization of key trace elements.

The elements can be classified according to their first IP, as shown in Table 1. Many of the most important trace elements, including Be, As, Se, Cd, and Hg, have IPs above 8 eV, meaning they are more difficult to ionize and sensitivity is lower.

Table 1. Elements grouped by first ionization potential.

IP range (eV)	Element
<6	Li, Na, Al, K, Ga, Rb, Sr, In, Cs, Ba, some REE
6 to 8	Mg, most Transition Elements, Ge, Y, Zr, Nb, Mo, Ru, Rh, Ag, Sn, some REE, Hf, Ta, W, Re, Tl, Pb, Bi, Th, U
8 to 11	Be, B, Si, P, S, Zn, As, Se, Pd, Cd, Sb, Te, I, Os, Ir, Pt, Au, Hg
>11	C, N, O, F, Cl, Br

Figure 2 shows that sensitivity for these elements is dramatically lower with a poorly designed or optimized plasma, which is problematic as these are elements where the lowest DLs are needed.

Conclusion

Labs choose ICP-MS for its high sensitivity and low detection limits. However, the real-world performance of an ICP-MS is highly dependent on the effectiveness of the plasma.

Agilent ICP-MS systems use an optimized plasma design and operating conditions that consistently achieve the highest level of robustness. As well as improving matrix tolerance, this approach increases ionization, providing the lowest possible detection limits. The greatest improvement in DLs is achieved for the poorly ionized trace elements.

Agilent ICP-MS systems are designed with the goal of delivering higher analyte sensitivity, lower levels of interferences, less drift, and reduced maintenance.

