Introduction
The determination of multiple trace elements in high-matrix samples has always been a difficult analytical challenge. ICP-optical emission spectroscopy (OES) has excellent matrix tolerance and multielement capability, but lacks sensitivity and can suffer from complex spectral interferences. ICP-MS has unsurpassed sensitivity and fewer interferences, but dissolved solids levels must be limited to about 0.1% or less.

Agilent has pioneered many innovations to improve robustness, including an optimized, low-flow sample introduction system, wide-diameter (2.5-mm) torch injector, and a digitally driven 27 MHz RF generator. Combined, these innovations have given the Agilent 7500 with Octopole Reaction System (ORS) the best high-matrix performance of any ICP-MS as indicated by CeO⁺/Ce⁺ ratios of around 1% compared with more typical 2% to 3% for other instruments. However, even with these innovations, total dissolved solids (TDS) must still be limited in order to achieve optimum, stable performance. Typically, this means sample dilution with its associated disadvantages, including increased detection limits, the possibility of sample contamination, additional prep time, and increased waste volume.

To avoid the drawbacks of conventional dilution, Agilent has developed a new technique for the handling of high-matrix samples: “aerosol dilution”. By combining the already excellent robustness of the 7500 ORS ICP-MS with aerosol dilution, the new High Matrix Introduction (HMI) accessory enables the 7500 ORS to analyze 1% TDS (or higher, depending on the matrix) samples directly, eliminating the dilution step and its associated drawbacks. Plasma robustness is significantly improved over conventional ICP-MS (down to 0.2% CeO⁺/Ce⁺), which greatly reduces matrix suppression, making the analysis of high-matrix samples with ICP-MS more reliable and accurate than ever before.
How HMI Works

The 7500 ORS/HMI combines the inherent robustness of the 7500 ORS ICP-MS with online aerosol dilution to reduce the matrix and solvent concentration at the ICP interface in real time without conventional dilution. In doing so, it achieves the advantages of dilution without introducing most of the disadvantages. Matrix suppression is nearly eliminated and CeO⁺/Ce⁺ is reduced to the lowest levels ever achieved. The HMI hardware consists of a modified torch assembly, including a dilution gas line inserted between the spray chamber and torch (Figure 1). Nebulizer gas flow is reduced, reducing the amount of sample aerosol, and a dilution gas is added to maintain the total carrier gas flow into the torch. The sample solution aspirated can be 1% or higher TDS, but since the aerosol production is greatly decreased, the plasma is not overloaded by the extra sample matrix. The benefit of aerosol dilution over conventional dilution is that the water or other solvent is also “diluted,” resulting in a significantly hotter and more robust plasma. This increased robustness is key to improving the ability of ICP-MS to run very high and variable matrix samples routinely and accurately.

Sample Results

Figure 2 shows the relative signal generated for a 10-ppb multielement spike in undiluted NASS-5 seawater standard compared to the signal obtained from the same spike in 1% HNO₃. The 7500cx ORS ICP-MS was optimized at different levels of plasma robustness: 2% CeO⁺/Ce⁺ (representing the typical performance of a non-Agilent system), 1% CeO⁺/Ce⁺ (typical 7500cx performance), and 0.2% CeO⁺/Ce⁺ (HMI used). As can be seen, at 2% CeO⁺/Ce⁺, huge signal loss (suppression) in the NASS-5 seawater matrix is observed, with 50% suppression for Sc and Ba, increasing to 85% suppression (only 15% signal remaining) for Zn (higher ionization potential element). The more robust plasma of the 7500cx handles the matrix much better but still shows 50% to 65% suppression for all analytes. With the HMI, however, suppression is almost eliminated, the worst case being In (only 15% signal loss).

![Signal Suppression in Undiluted NASS-5](image-url)

**Figure 2.** Relative signal suppression of a 10-ppb multielement spike into undiluted NASS-5 seawater under three different levels of plasma robustness as measured by CeO⁺/Ce⁺ levels: 2% (typical for ICP-MS), 1% (typical for 7500cx), and 0.2% (typical for HMI).
Note that no internal standard correction was applied to any of the data in Figure 2. This means that, with HMI, undiluted seawater can be run against a 1% HNO₃ calibration with acceptable recoveries, something no other ICP-MS can claim. The presence of high levels of easily ionized elements (in this case approximately 3% TDS – mostly NaCl) has little effect on the Zn signal, demonstrating the improved robustness of the plasma with HMI.

A further example of improved robustness with HMI is illustrated in Figure 3. This plot shows the signal recovery for several elements measured in a series of solutions containing increasing concentrations of Zn, from 0 ppm up to 1% (10,000 ppm) Zn. The trace element signals are shown relative to the 0 ppm Zn matrix. Despite the lack of any internal standard correction, less than 20% suppression is observed, even in the 1% Zn matrix. In addition, all elements are closely grouped – there is no mass-dependence to the suppression effect. Note that the Zn concentration was ramped from 0 to 10,000 ppm twice and the recovery plots are consistent for both sample sets. Minimal suppression and minimal mass-dependent sensitivity change means that the HMI can measure sample matrices ranging from 0% to 1% metal (in this case Zn), using a single aqueous calibration. When internal standardization is used, much less correction is needed, which increases accuracy and makes it easier to choose suitable internal standards. Productivity is increased since there is no need for close matrix matching.

Matrix buildup on the interface cones and lenses results in poor long-term stability, requiring frequent maintenance and retuning. The HMI kit, by significantly reducing buildup, increases the long-term stability and minimizes maintenance and retuning. Figure 4 shows the normalized internal standard recoveries for five internal standards measured in both H₂ and He mode over a 150-sample sequence of a 1% Cu in 10% nitric acid solution.

![Image of Figure 4]
The Benefit of Lower Oxide Levels

The CeO+/Ce⁺ level is almost universally used as an indicator of plasma robustness, but a low oxide level also has a direct analytical benefit: reduced interferences. Figure 5 shows the effect of MoO interference on Cd on a standard 7500cx and a 7500cx equipped with the HMI kit. While the 7500cx already has a low CeO+/Ce⁺ of 1%, reducing the CeO+/Ce⁺ to 0.2% with HMI significantly improves the accuracy of Cd in the presence of Mo. With 2 ppm Mo present, the observed value for a 1-ppb Cd standard is close to 5 ppb under normal 7500cx conditions. With HMI, 1 ppb Cd can be accurately measured in matrices containing at least 2 ppm Mo. In geological applications, a reduced CeO+/Ce⁺ level improves the quantification of mid- and high-mass rare earth elements (REE), as the interference from BaO⁺ and low-mass REE oxides is reduced significantly.
Simple to Use

In practice, the HMI is extremely simple to set up and operate. Sophisticated software algorithms automate tuning and optimization: the user simply selects the level of plasma robustness required and the ChemStation software automatically loads all the appropriate settings. Once the HMI is fitted, the 7500 ORS ICP-MS can still be operated in standard mode for lower matrix samples, and normal and HMI mode conditions can be switched automatically within a single sequence; there is no need to disconnect any gas lines. Since HMI is a dilution technique, sensitivity is reduced accordingly. However, improved plasma robustness permits lower dilution factors than typically used. In addition, eliminating the inaccuracies and contamination associated with conventional dilution of samples and prep blanks leads to superior overall accuracy and improved detection limits.

Applications of HMI

The virtual elimination of matrix-related signal suppression is a very important step forward for ICP-MS: it means that matrix matching to correct for ionization suppression is no longer necessary. Accuracy when measuring variable, unknown matrix samples is greatly improved, and internal standard selection is simplified. The HMI can handle traditional ICP-OES matrices in many cases, often even using the high-matrix sample digests prepared for OES analysis, thereby eliminating extra sample prep workup. And since the plasma is more robust, sample matrix decomposition is more efficient, which means less routine maintenance on the interface and ion lenses. Applications for HMI include:

- Impurities in high-purity metals
- Soil digests (ICP-OES prep)
- Direct analysis of undiluted seawater
- Restriction of the use of certain Hazardous Substances (RoHS) samples
- Landfill leachates toxicity characteristic leaching procedure (TCLP) prep
- Geological digestions and fusions
- High TDS groundwaters
- Foods samples
- Pharmaceutical matrices
- HPLC-ICP-MS applications that require a high salt buffer

Further Information

Application data acquired using the Agilent 7500cx ICP-MS fitted with the HMI accessory is available from the Agilent Literature Library at: www.agilent.com/chem/icpms.

Figure 6.  HMI control panel. Robust (no aerosol dilution) or Ultra Robust (with three levels of aerosol dilution) can be selected.