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Technical Overview and Performance Capability of the Agilent 7900s ICP-MS for Semiconductor Applications

Introduction

Agilent ICP-MS systems are widely used for accurate low-level analysis of trace contaminants across a wide range of high-purity chemicals used in the semiconductor industry.

The first commercial ICP-MS to offer reliable, routine cool plasma operation was the Agilent 4500, launched in 1994. This instrument enabled low-level analysis of previously problematic elements Na, K, Ca, and Fe, allowing semiconductor laboratories to expand their capabilities in metals analysis from GFAAS to ICP-MS. Building on the success of the 4500, Agilent introduced further innovations in the 7500s, 7500cs, and 7700s models, providing more sensitivity, stability, and matrix tolerance.

Working closely with semiconductor manufacturers and suppliers, Agilent has continually developed ICP-MS solutions to meet the needs of the industry. As well as further developing cool plasma, Agilent also introduced the Octopole Reaction System (ORS) on the 7500cs, providing a complementary approach to controlling interferences. ORS uses a unique, octopole-based collision/reaction cell (CRC) to attenuate spectral overlaps using both collision and reaction modes.

Other key innovations include the off-axis Omega ion lens, which provides high ion transmission and low backgrounds, ensuring low detection limits. Operational aspects are also addressed using innovative materials and manufacturing processes to ensure Agilent benchtop ICP-MS systems offers a high level of cleanroom compatibility. This focus on continually improving performance for high purity chemicals analysis, has led to Agilent becoming an ICP-MS vendor of choice for large semiconductor manufacturers and their supply chain.

Design goals of the Agilent 7900s ICP-MS

The Agilent 7900 ICP-MS was designed for ease of use and practicality, while further improving sensitivity, detection limits, and interference-removal capability.

The 7900s model (option #200) is configured specifically for semiconductor applications, incorporating a PFA nebulizer, Pt interface, and high transmission "s-type" ion lens.

The 7900s advances ICP-MS performance for routine semiconductor applications by combining high sensitivity, matrix tolerance, interference removal, and stability in a single reliable and easy to use system. The 7900s is ideal for semiconductor applications that require excellent detection limits, but do not need the advanced capabilities of the Agilent 8900 triple quadrupole ICP-MS (ICP-QQQ).

Agilent ICP-MS MassHunter software features include comprehensive autotuning routines, predefined preset methods for ultrapure reagents, and simple calibration using method of standard additions (MSA). After acquisition of the MSA calibration, it is automatically converted to an external calibration for analysis of subsequent samples.

IntelliQuant is an easy to use data analysis function for ICP-MS MassHunter, providing insight into the overall sample composition, even for elements not selected for quantification. IntelliQuant enables even novice users to confidently identify contaminants for process chemical monitoring and failure analysis.

The 7900s uses a robust, frequency matching RF generator for improved performance in volatile organic solvents, and a fourth-generation ORS⁴ collision/reaction cell with ultrafast cell gas switching.

An Orthogonal Detector System (ODS) with high-speed data acquisition supports advanced applications such as nanoparticle measurement in high purity reagents.

To meet the needs of semiconductor laboratories, the 7900s features a small bench-top cabinet with easy access for routine maintenance, and low utility (heat extraction) requirements for cleanroom installation.

Basic performance of the 7900s

The 7900s interface and ion lens configuration delivers high ion transmission and low background. This translates into improved detection limits (DLs) and background equivalent concentrations (BECs) compared to competitive systems and previous Agilent models. Figure 1 shows typical DLs and BECs for the 7900s in a matrix of 1% HNO_3.

Most elements have DLs around 0.1 ng/L (ppt) or below. Elements marked with a * were measured using cool plasma conditions. Cool plasma is the semiconductor industry's standard approach to reduce several intense background signals in high purity chemicals.

Agilent developed the first ICP-MS capable of routine operation under cool plasma conditions (the 4500 Series), which used the proprietary ShieldTorch system to control the
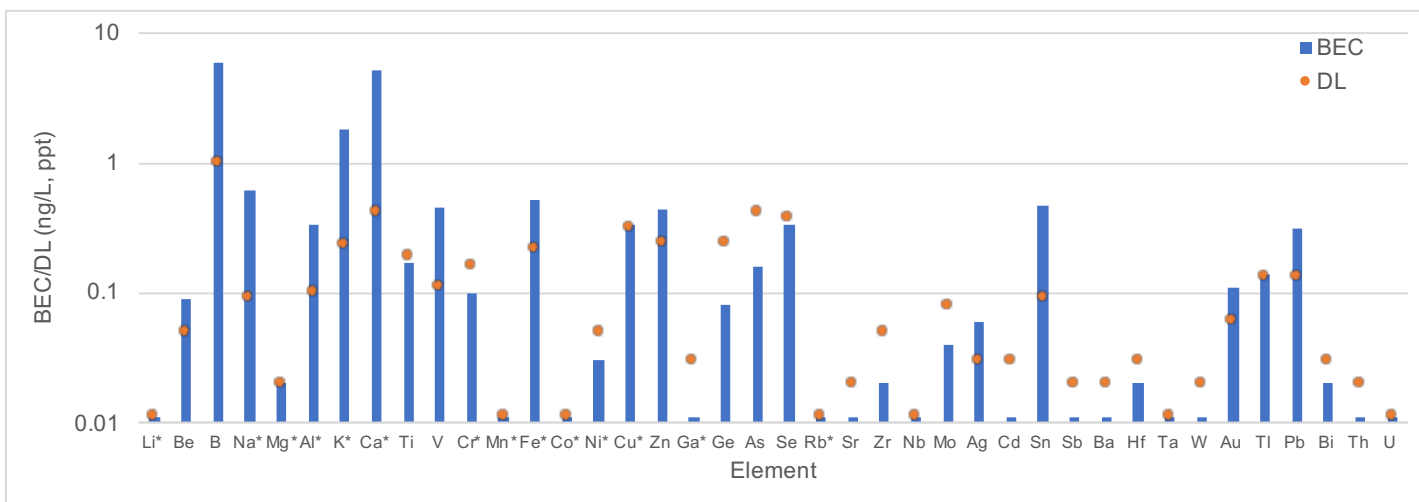

Figure 1. Typical Agilent 7900s background equivalent concentrations (BEC) and detection limits (DL) in 1% HNO_3 (ng/L, ppt).

plasma offset potential. Cool plasma led to the acceptance and widespread use of ICP-MS in the semiconductor industry, as it enabled manufacturers to measure the previously difficult elements Na, K, Ca, and Fe.

In each subsequent generation of Agilent ICP-MS instrument, cool plasma has been refined, allowing analysts to use the most effective interference removal techniques. The 7900s provides a further enhanced cool plasma operation, with improved robustness and stability due to the use of a new frequency matching RF generator.

Improved interference removal in He cell mode

Collision/reaction cells (CRCs) offer another way to control spectral interferences in ICP-MS. Agilent CRCs with helium (He) cell gas selectively attenuate polyatomic ion overlaps in complex sample matrices using kinetic energy discrimination (KED).

The unique ORS[4] cell used in the 7900s has longer rods than previous versions, combined with a smaller internal diameter, higher RF frequency, and higher cell gas pressure. As a result, higher collision energies are achieved and higher KED bias voltages can be used, giving better rejection of polyatomic interferences. More effective removal of background (plasma-based) polyatomic ions by the Agilent ORS[4] cell provides lower DL and BEC for many elements.

This capability is illustrated in Figure 2, which shows a calibration for P in 1% HNO_3, measured in ORS[4] enhanced He mode. The improved discrimination between the NO^+/NOH^+ polyatomic ions and the P^+ ions improves the BEC and DL by 10x to 50x compared to the lower energy He mode available on other instruments.
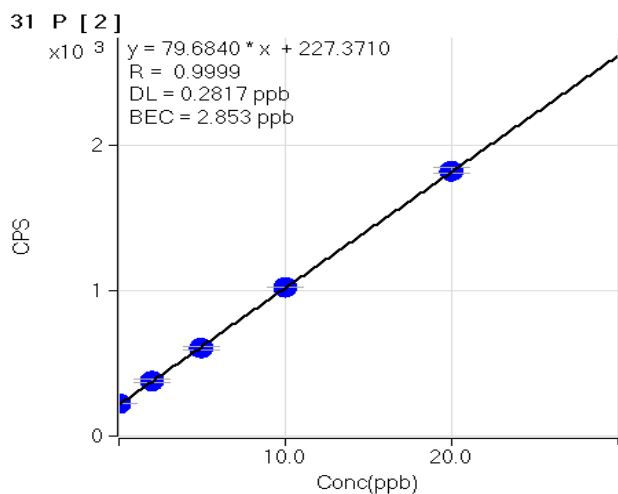
31 P [2]

$$y = 79.6840 * x + 227.3710$$
$$R = 0.9999$$
$$DL = 0.2817 \text{ ppb}$$
$$BEC = 2.853 \text{ ppb}$$

Figure 2. Calibration for ^{31}P in 1% HNO_3 in enhanced He mode.

The higher collision energy of ORS[4] also means that some weakly-bound polyatomic ions such as ArO^+ (dissociation energy 0.6 eV), $ArAr^+$ (1.3 eV), and $ArCl^+$ (2.2 eV) are removed by collision induced dissociation (CID).

Application of reactive cell gases

The 7900s ORS[4] includes a He cell gas line as standard, while up to two further gas lines can be added. These optional cell gas lines allow reaction gases such as H_2, O_2, and NH_3 to be used to reduce DLs and BECs for specific interfered elements. In the BEC and DL data shown in Figure 1, the optimum results for elements such as K, Ca, Fe, and Se were obtained with H_2 cell gas.

The effectiveness of H_2 reaction gas is illustrated in Figure 3 for Si. H_2 cell gas removes the N_2^+ interference at m/z 28, so Si can be measured directly at its major isotope of [28]Si. The high cell gas density and collision energy of ORS[4] on the 7900s increases H_2 mode reaction efficiency and delivers lower DLs for Si.
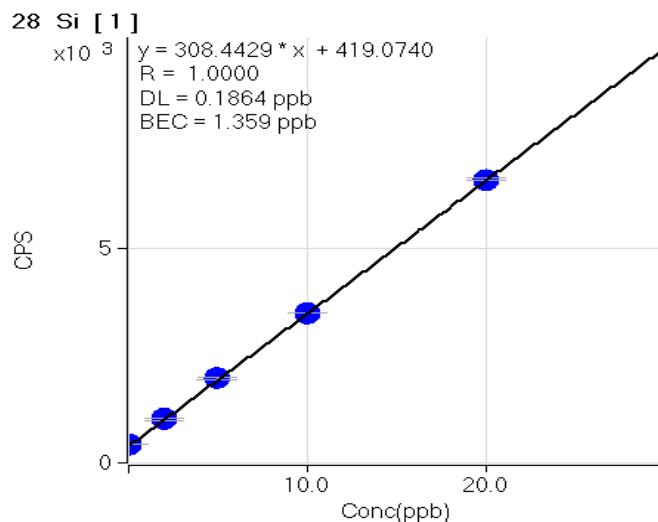
28 Si [1]

$$y = 308.4429 * x + 419.0740$$
$$R = 1.0000$$
$$DL = 0.1864 \text{ ppb}$$
$$BEC = 1.359 \text{ ppb}$$

Figure 3. Calibration for [28]Si in 1% HNO_3 in H_2 reaction mode.

Note that the water used to prepare the calibrations shown in Figures 2 and 3 was normal laboratory DI water and was not further purified. Elements such as P and Si might be expected to be present at significant levels in such water, so blank contamination would have contributed to the BEC.

The high performance of H_2 reaction mode on the 7900s reduces the need for other reactive cell gases such as NH_3. NH_3 provides efficient removal of certain interferences and is often used with Agilent triple quadrupole ICP-MS/MS systems. However, on conventional ICP-MS, NH_3 forms many new product ions in the cell. These product ions can cause further interferences, making NH_3 unsuitable for the analysis of most variable or complex matrices.

However, in semiconductor applications, NH_3 can be used to address some well-defined interferences. One example is the analysis of trace V in concentrated (20%) HCl. The only useful isotope of V at m/z 51 is overlapped by an intense ClO interference. ClO^+ is not very reactive with H_2, so H_2 cell mode does not reduce the interference sufficiently for the lowest V DL to be achieved in the highest purity HCl.
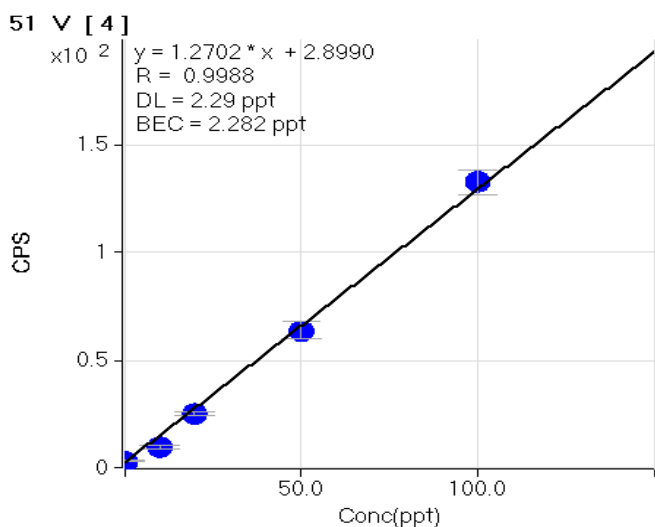

51 V [4]

$$y = 1.2702 * x + 2.8990$$
$$R = 0.9988$$
$$DL = 2.29 \text{ ppt}$$
$$BEC = 2.282 \text{ ppt}$$

Figure 4. Calibration for ^{51}V in 20% HCl in NH_3 reaction mode.

As shown in Figure 4, NH_3 mode effectively removes the ClO interference in undiluted 20% HCl, providing a BEC and DL of only 2.3 ppt for V.

When multiple cell gas modes are used within a method, the ORS[4] switches rapidly between modes during a single visit to each sample vial. Multi-mode acquision minimizes the potential for sample contamination, as well as increasing sample throughput and reducing the volume of sample required.

Switching modes within each run does not compromise stability, as the cell (and plasma) conditions rapidly adjust to each change of settings. Figures 5 and 6, show the long-term (nine hours) stability of several elements measured

in dilute HNO_3 under He mode and cool plasma conditions respectively. All acquisition modes were collected during one visit to the sample vial. Sample data acquisition was performed once every 35 minutes. Signal drift was within ±5% over the nine hour run, and the RSD was <3% for all analytes.
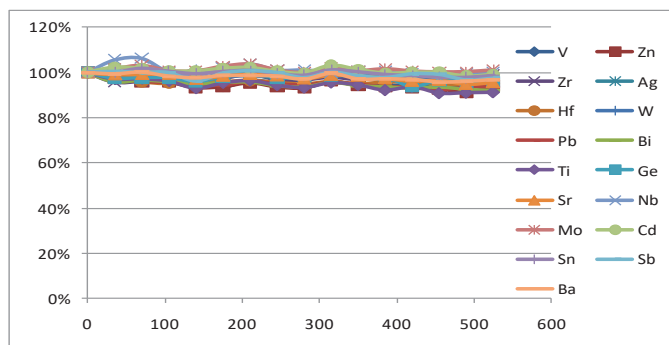

Figure 5. Long-term stability (9 hours) of 100 ppt spike in 1% HNO_3 for elements measured in He cell gas mode.
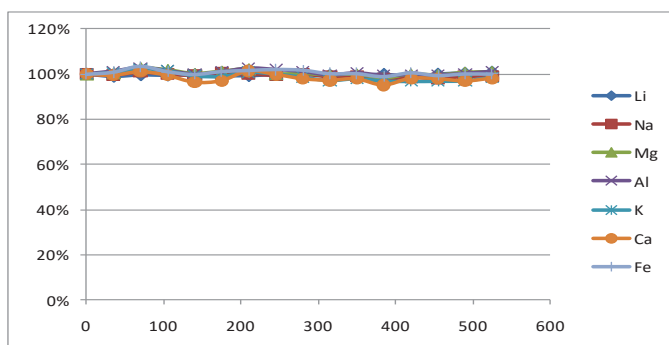

Figure 6. Long-term stability (9 hours) of 100 ppt spike in 1% HNO_3 for elements measured using cool plasma.
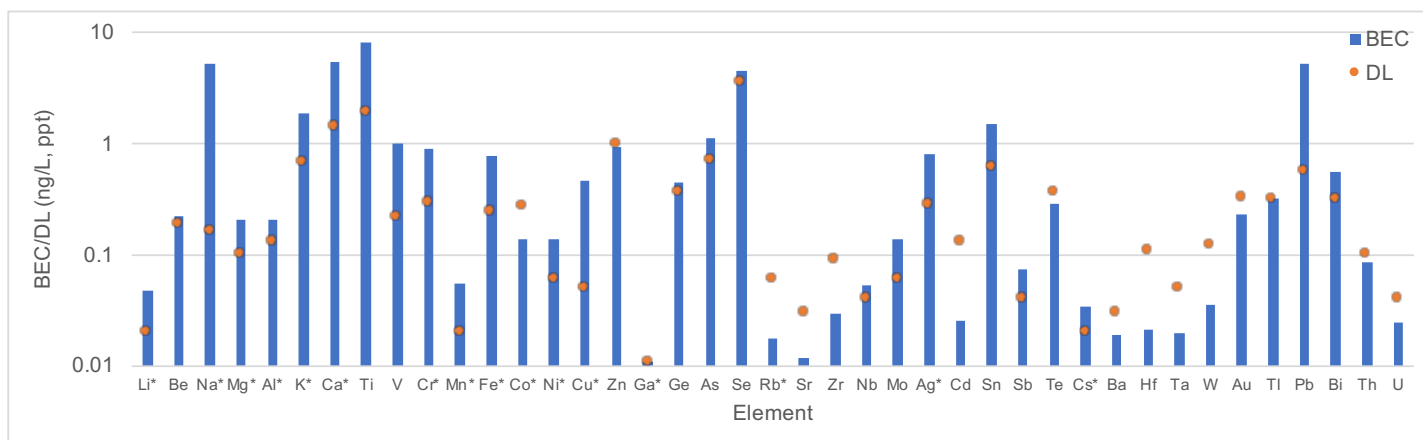
Figure 7. Typical Agilent 7900s background equivalent concentrations (BEC) and detection limits (DL) in undiluted IPA (ng/L, ppt).

Improved analysis of organic solvents

The 7900s incorporates a robust, solid state, frequency matching ICP RF generator. This design responds more quickly to any change of impedance in the plasma, compared to a conventional fixed frequency generator. In practice, the design makes it easier to switch between plasma conditions (for example hot and cool plasma) and sample types (for example more or less volatile solvents) during routine analysis. Organic solvents commonly used in the semiconductor industry (such as isopropyl alcohol (IPA), methanol, PGMEA, NMP, and ethyl lactate) can be introduced without destabilizing the plasma.

IPA is the most important organic solvent in the semiconductor industry. The solvent is frequently used to clean silicon wafers and must be analyzed to check for trace element contaminants. When used for the analysis of most organic solvents (including IPA), the 7900s is fitted with an optional organics torch with a 1.5 mm internal diameter (ID) injector. A torch with a 1.0 mm ID injector is also available, allowing the direct analysis of the most volatile solvents, such as acetone.

Figure 7 illustrates the single-ppt and sub-ppt BECs and DLs achieved for the analysis of multiple elements in undiluted IPA. All elements were measured with a BEC and DL <10 ppt, and most were around 0.1 ppt or below. For high purity Grade 4 IPA, SEMI standard C41-0705 specifies a maximum contaminant level of 100 ppt for each element. The 7900s easily achieves the DL requirements for high purity IPA used in semiconductor fabrication, as specifed in the SEMI standard.

The elements Be, Ti, V, Zn, Ge, As, Se, Sr, Zr, Nb, Mo, Cd, Sn, Sb, Te, Ba, Hf, Ta, W, Au, Tl, Pb, Bi, Th, and U were measured in undiluted IPA using normal hot plasma conditions (with no gas, He, or H_2 cell gas).

Figure 8 shows the excellent raw count rate stability for a 100 ppt spike of several elements in undiluted IPA, measured continuously over 4 hours. Total signal variation was <5% RSD.
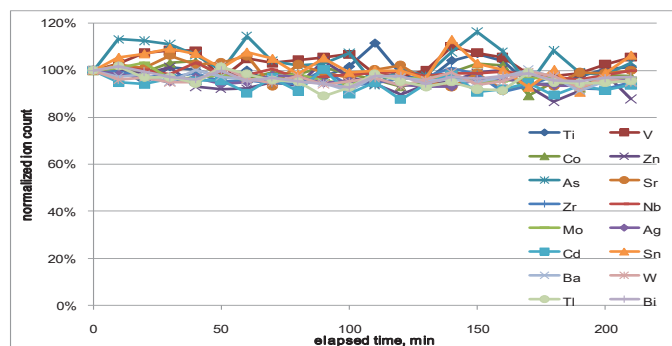

Figure 8. 4 hours stability of 100 ppt spike in IPA (He mode).

The high volatility of IPA (boiling point 82.4 °C) could make it difficult to maintain plasma stability, particularly when switching between cool and hot plasma conditions within each sample analysis. The 7900s solves this issue using a robust frequency matching plasma RF generator and effective grounding of the plasma using the ShieldTorch system. This combination means that cool plasma conditions can be used routinely for the analysis of organic solvents on the 7900s, as shown in the long-term stability data in Figure 9.
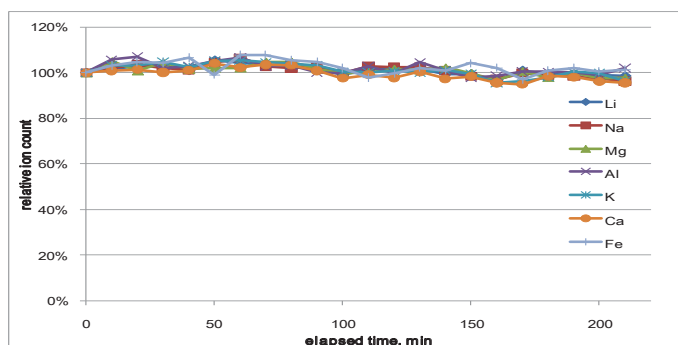
Figure 9. 4 hours stability of 100 ppt spike in IPA (cool plasma).

The elements in Figure 9 were measured in cool plasma, while the corresponding elements shown in Figure 8 were measured using normal hot plasma conditions. The plasma conditions were switched automatically between cool plasma and hot plasma for each sample in the analytical sequence, illustrating the stability, robustness, and matrix tolerance of the 7900s ICP-MS RF generator.

The basic performance illustrations in this publication indicate the detection limit, stability, and interference removal capability of the 7900s. Agilent ICP-MS systems are in routine use in semiconductor laboratories worldwide, performing critical analysis of trace contaminants in a wide range of process chemicals. Typical semiconductor sample types routinely analyzed using Agilent ICP-MS systems include:

- Ultrapure water (UPW)
- Concentrated H_2O_2
- Dilute HNO_3 (1% w/w)
- Concentrated HNO_3 (68% w/w)
- Concentrated HF (38% w/w)
- Concentrated HCl (20% w/w)
- 10x diluted H_2SO_4 (9.8% w/w)
- Tetramethylammonium hydroxide TMAH (6.25% w/w)
- Concentrated ammonium hydroxide (20% w/w)

- Isopropyl alcohol IPA (100%)
- N-methyl-2-pyrrolidone NMP (100%)
- Native and thermally oxidized Si wafer VPD solutions (30 ppm/2000 ppm Si)

Recommended 7900s configurations and tuning conditions are available for all these chemicals. Some sample types listed may require optional sample introduction systems, such as a PFA nebulizer and spray chamber and inert torch for the analysis of concentrated HF.

Conclusion

In addition to reduced cleanroom setup and operating costs due to its small size and low service requirements, the Agilent 7900s provides higher sensitivity and lower BECs/DLs than comparable systems. In addition to the industry standard ShieldTorch system for cool plasma, the 7900s includes the proprietary ORS[4] collision/reaction cell. The ORS[4] can be fitted with up to 3 cell gas lines (helium plus up to two reaction gases), allowing total flexibility in operating modes to control interferences. The ORS[4] cell improves performance for several critical elements by enhancing the efficiency of collision and reaction modes, and increasing collision induced dissociation. These developments allow several elements—such as P— to be determined at lower concentrations than previously possible.

The robust RF generator of the 7900s increases tolerance of high matrix levels and volatile organic solvents, enabling the routine analysis of many process chemicals. Improved matrix tolerance and stability applies to both conventional hot plasma analysis and cool plasma operation.

Details regarding recommended configurations and operating conditions for the analysis of a range of common semiconductor chemicals are provided in the tuning guide that is available for the 7900s instrument.

For more information

For more information about Agilent ICP-MS products and services, visit www.agilent.com/chem/icpms

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