

Ultratrace measurement of calcium in ultrapure water using the Agilent 8800 Triple Quadrupole ICP-MS

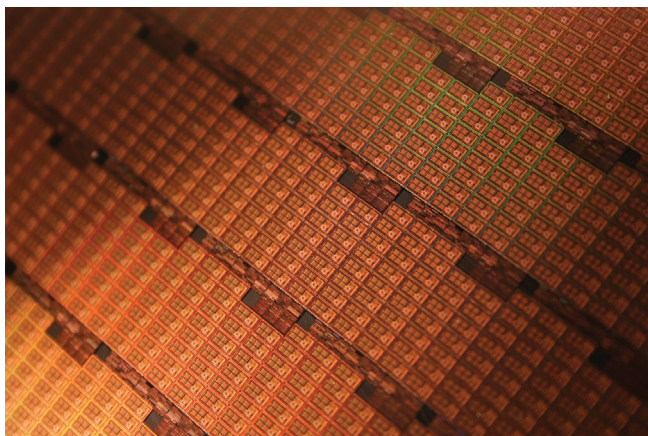
Application note

Semiconductor

Authors

Albert Lee, Vincent Yang, Jones Hsu, Eva Wu and Ronan Shih
BASF Taiwan Ltd., Taipei, Taiwan

Katsuo Mizobuchi
Agilent Technologies, Tokyo, Japan



Introduction

In the semiconductor industry, the control of metal impurities in the process chemicals used in the manufacture of semiconductor devices is critical to achieve the required product performance and yield. As device performance is continually increasing, the required impurity control becomes ever more stringent. For example, metal content of the ultra pure water (UPW) used in the manufacturing process must be at the sub-ppt level. ICP-MS is the standard technique used for the trace metals analysis of semiconductor chemicals and devices. The most common instrument and measurement technique used in the semiconductor industry is single quadrupole ICP-MS (ICP-QMS) with cool plasma. The cool plasma technique [1], developed in the mid 1990's, enables the quantification of key contaminant elements at the single ppt level. Collision and reaction cell ICP-QMS, developed from 2000 onwards, enabled the direct analysis of more complex semiconductor matrices, but did not improve on the detection limits or background



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equivalent concentration (BEC) of cool plasma. To achieve measurement at the sub-ppt level, reduction of the BEC is required.

The Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) provides new reaction cell technology that enables a BEC of 100 ppq for Ca. This application note describes the theory and operation of the Agilent 8800 ICP-QQQ to achieve the sub-ppt measurement of Ca in UPW.

Experimental

Instrumentation

A standard Agilent 8800 Triple Quadrupole ICP-MS mainframe (option #200 semiconductor version) was used. The sample introduction system features a quartz torch and spray chamber, and a concentric PFA nebulizer (which was operated in self-aspiration mode). Platinum interface cones were also used. Cool plasma conditions were used throughout and plasma parameters are shown in Table 1.

Table 1. Agilent 8800 ICP-QQQ operating parameters

Parameter	Value
RF (W)	600
Carrier gas (L/min)	0.7
Make up gas (L/min)	1
Sampling depth (mm)	18

As can be seen in Figure 1, compared to conventional ICP-QMS, the 8800 features an additional quadrupole mass filter (Q1), situated in front of the Octopole Reaction System (ORS³) cell and quadrupole mass filter (now called Q2). The Agilent 8800 ICP-QQQ can be operated in two scan modes: single quad mode and MS/MS mode. Single quad mode emulates ICP-QMS: Q1 is fixed and operates simply as an ion guide.

MS/MS mode is unique to ICP-QQQ: Q1 operates as a 1 amu window mass filter, selecting the ions that enter the cell. Because plasma ions are eliminated from the cell by Q1, ion transmission through the cell is greatly increased. When a reaction gas is added, reaction efficiency is also greatly enhanced, enabling the use of lower reaction gas flow rates which also increases ion transmission and, therefore, sensitivity.

Calibration standards

A Ca standard was prepared in UPW acidified with 0.1% high purity HNO₃. This was used to make 50 ppt and 100 ppt additions to a UPW blank acidified with 0.1% high purity HNO₃.

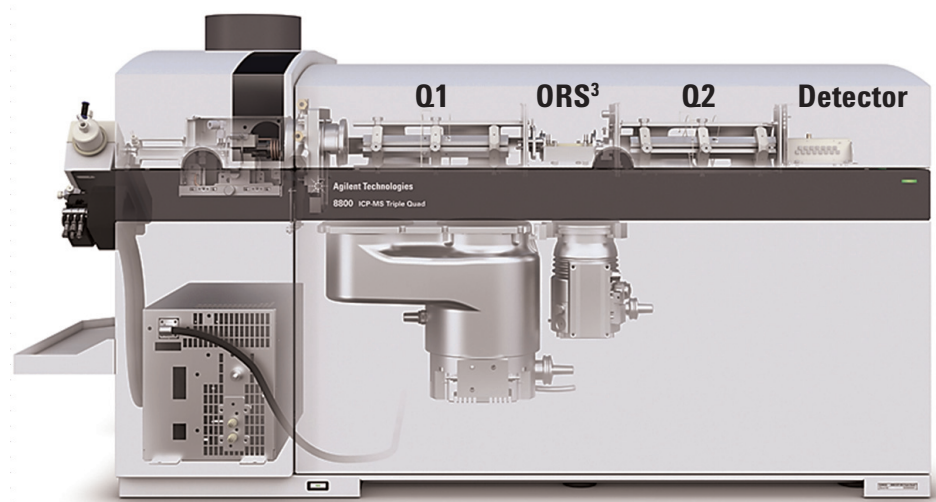


Figure 1. Cutaway diagram of the Agilent 8800 ICP-QQQ

Results

The sample was acidified to be 0.1% HNO₃. Figure 2 shows the BECs obtained for Ca using method of standard additions (MSA), using three different operating conditions: single quad mode with no cell gas, MS/MS mode with no cell gas, and finally MS/MS mode with an H₂ cell gas flow of 1 mL/min. The first operating condition emulates the Agilent 7700 ICP-QMS operated in cool plasma mode. The obtained BEC of 6.8 ppt is similar to that routinely achieved with the Agilent 7700.

Using MS/MS mode (without cell gas) improved the BEC to 1.4 ppt. MS/MS mode with H₂ at 1 mL/min in the cell further improved the BEC down to 0.041 ppt (41 ppq). The obtained MSA plot is shown in Figure 3. The Agilent 8800 achieved a BEC for Ca in UPW two orders of magnitude lower than the BEC obtained using conventional ICP-QMS.

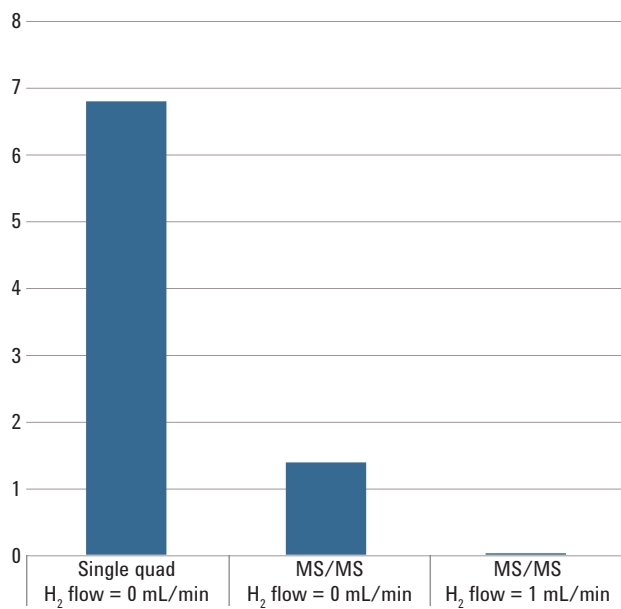
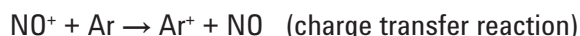


Figure 2. BECs for Ca obtained using single quad mode with no cell gas [6.8 ppt], MS/MS mode with no cell gas [1.4 ppt], and MS/MS mode with an H₂ cell gas flow of 1 mL/min [0.041 ppt].

Discussion

Figure 4 shows the spectrum obtained from UPW using cool plasma mode and single quad mode (no cell gas).

As can be seen, Ar⁺ is suppressed under the low temperature plasma conditions and two intense peaks are observed at $m/z = 19$ and 30 . These are (H₂O)H⁺ and NO⁺, respectively. With single quad mode, all ions formed in the plasma including these two intense ions pass through to the cell. Even with no cell gas, an unexpected reaction occurs in the cell which causes a new interference at $m/z = 40$. The likely reaction occurring in the cell is:



which increases the BEC for Ca by several ppt. Although the ionization potential (IP) of NO (IP = 9.26 eV) is lower than that of Ar (IP = 15.7 eV), a metastable ion, NO⁺ exists close to the ionization potential of Ar [2]. So it is reasonable to assume that the charge transfer reaction shown occurs in the cell. With the MS/MS mode, Q1 rejects all non-target ions such as NO⁺ and (H₂O)H⁺, preventing unwanted reactions from occurring in the cell, which lowers the BEC. The addition of H₂ in the cell also removes any residual ⁴⁰Ar⁺ that is formed even under cool plasma conditions.

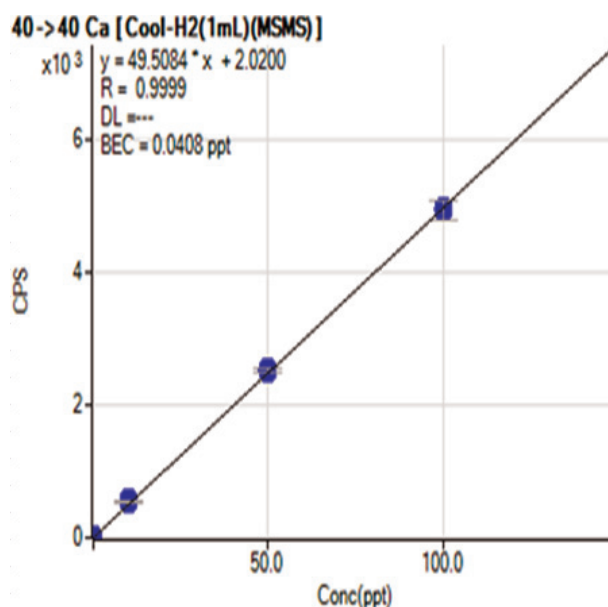


Figure 3. MSA calibration plot for Ca using MS/MS mode with H₂ cell gas at 1 mL/min.

Conclusions

The plasma derived polyatomic ion NO^+ , which is formed in cool plasma mode, can generate small amounts of Ar^+ in the cell by charge transfer reaction, which interferes with Ca at $m/z = 40$. The Agilent 8800 ICP-QQQ operated in MS/MS mode, which is unique to ICP-QQQ, stops plasma derived ions from entering the cell, preventing unwanted reactions from occurring. This enabled the Agilent 8800 Triple Quadrupole ICP-MS to achieve a BEC of 41 ppq for Ca in UPW.

References

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2. R. Marx, Y.M. Yang, G. Mauclaire, M. Heninger, and S. Fenistein, Radioactive lifetimes and reactivity of metastable $\text{NO}^+(\text{a}^3\Sigma^+, \nu)$ and $\text{O}_2^+(\text{a}^4 \text{II}, \nu)$, *J.Chem. Phys.*, Vol. 95, No. 4, 2259-2264, 1991

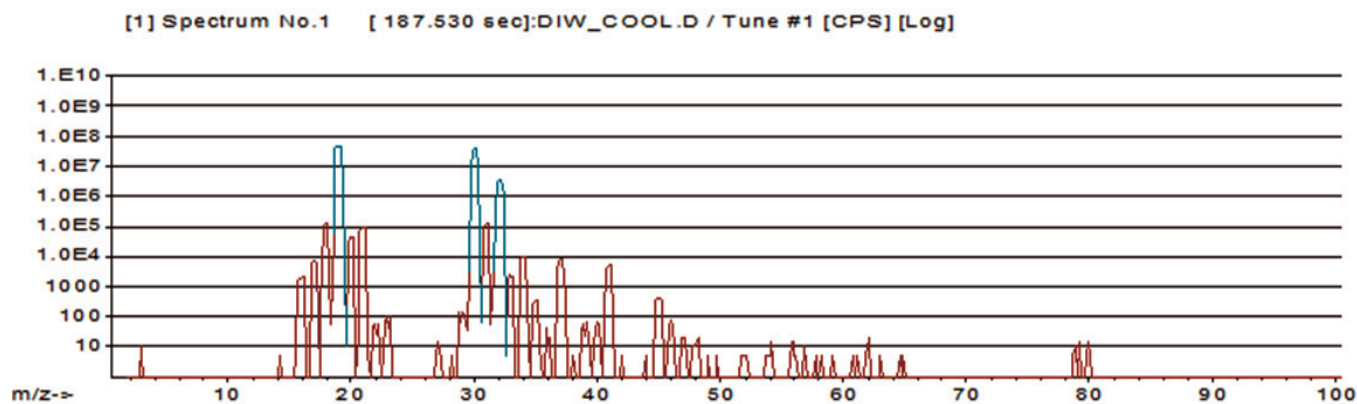


Figure 4. Spectrum of UPW acquired using cool plasma mode and single quad mode (no cell gas)

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