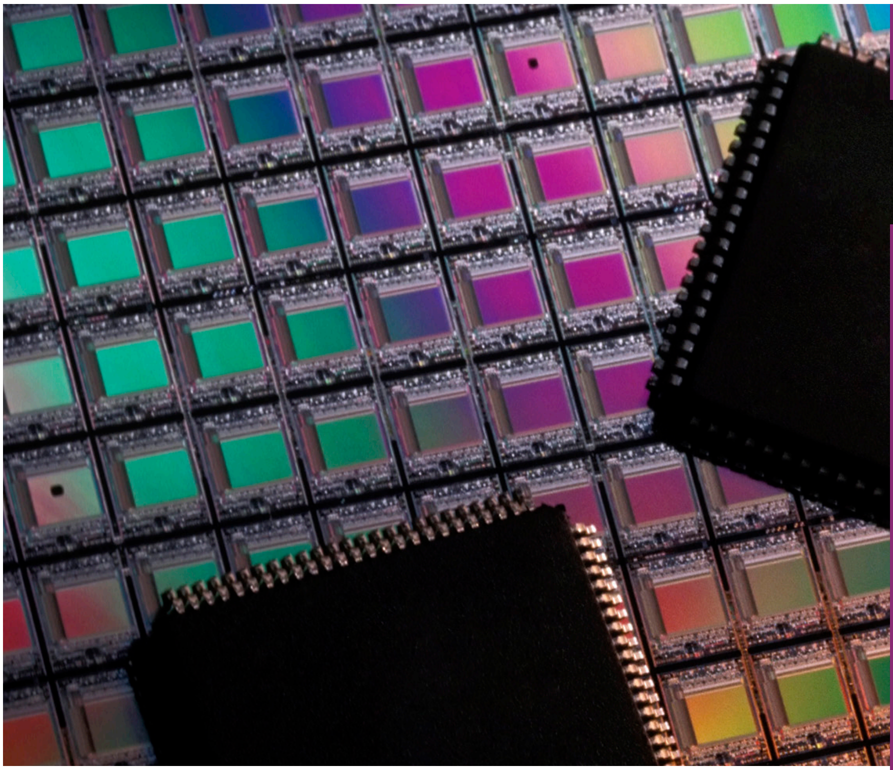

APPLICATION BRIEF

ICP - Mass Spectrometry

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Rapid Ultra-Trace Analysis of Impurities in Ultrapure Water using the NexION 5000 ICP-MS

Introduction

Since ultrapure water (UPW) is used throughout the semiconductor industry in a variety of applications, impurities need to be controlled as this will have a direct impact on the quality and overall yield of semiconductor products.[1] ICP-MS is often used to quantify sub-ppt concentrations of impurities due to its ability to provide the accurate quantification of elements at low concentrations. With the ubiquitous use of UPW in semiconductor device fabrication, many of these laboratories require methods which are able to deliver sub-ppt detection limits within a relatively short period of time in order to achieve a fast response to impurities in UPW.

In order to meet these needs, it is necessary to address interferences, as these can impact the ability to detect at ultra-low concentrations, and to reduce sample-to-sample run times. Interferences in ICP-MS are often most significant in the form of polyatomic interferences and can be effectively dealt with through the use of collision/reaction gases in a collision/reaction cell. Reaction gases are far more effective at removing argon-based interferences than collision gases, since this type of interference often exceeds four orders of magnitude when compared to the analyte signal. Reaction gases are therefore able to decrease the interference to background levels which are deemed to be acceptable by the semiconductor industry. Although pure, highly reactive gases often offer the most complete interference removal, there are some countries where the use of such gases is restricted in the laboratory due to regional safety regulations. As a result, less reactive gases, such as O_2 or H_2, are typically used in this setting. Since H_2 has a high-flammability potential, many laboratories prefer to use hydrogen generators for its production. These devices deliver high purity H_2 gas on demand.

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Although interferences can be somewhat effectively dealt with by using these kinds of reaction gases, other ions which are not at the mass of interest can also be permitted into the cell. For this reason, the placement of an additional analyzer quadrupole before the cell makes a huge difference. Here, any ions which could compete with the reaction or with the by-product of the reaction are filtered from the ion beam, ensuring that only on-mass ions enter the cell for interference removal. This type of control further lowers the background equivalent concentrations (BECs) and detection limits (DLs) for the analyte of interest.

Since it is important to be able to detect the lowest possible level of impurities in UPW, cold plasma (i.e. low RF power[2]) can be used to support the elimination of argon-based spectral interferences. This mode of operation lowers the energy within the plasma, reducing the formation of argon ions and thereby limits the formation of interferences arising from plasma gases. Moreover, since it is often necessary for these labs to provide an answer relatively quickly, the use of an ICP-MS with a fully-digital RF generator, which can rapidly switch between hot and cold plasma, is additionally beneficial.

This work describes a method for the determination of the DLs and BECs of impurities in ultrapure water using PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS. The analysis was performed in Multi-Quad mode using hydrogen as a reaction gas under cold plasma conditions. In the developed method, a single reaction gas and single set of plasma conditions were used to achieve sub-ppt DLs and BECs while significantly reducing the time required for analysis.

Experimental Conditions

Sample Preparation

Ultrapure water (18.27 MΩ.cm^{-1}) was used to prepare all blanks and standard solutions. Calibration standards with concentrations of 5, 10, 20 and 40 ppt were prepared in UPW from a 1 ppb intermediate stock. The intermediate stock solution was prepared from a multi-element certified stock solution (10 ppm, Multi-Element Calibration Standard 3, PerkinElmer Inc., Shelton, Connecticut, USA).

Instrumentation

All analyses were performed using the NexION 5000 Multi-Quadrupole ICP-MS (PerkinElmer Inc., Shelton, Connecticut, USA) with the conditions shown in Table 1. This multi-quadrupole ICP-MS has the ability to control the mass range entering the high-vacuum region of the ion optics via the Quadrupole Ion Deflector (Q0), allowing for a cleaner overall system. The ions are then mass-separated in the first Transmission Analyzer Quadrupole (Q1) where only the nominal mass of interest is allowed to proceed to the Universal Cell (Q2). Here, the analyte ion and interference undergo a controlled reaction in the cell. In the cell, reaction by-products are ejected before they have a chance to react and form new interferences. Thereafter, the analyte mass is selected in the second Transmission Analyzer Quadrupole (Q3) for detection. An NM-H_2 Plus Hydrogen Generator (PerkinElmer Inc., Shelton, Connecticut, USA) was used to meet the delivery rate, and with a purity of 99.9999%, exceeds the needs of H_2 for ICP-MS applications. Cold Plasma mode was used for all analyses since this was found to significantly improve the BECs for many of the analytes.

Table 1. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Nebulizer	PFA (Self-Aspirating), 0.25 mm ID Capillary
Spray Chamber	SilQ Cyclonic (Standard)
RF Power	550 W
Injector	1.5 mm ID
Plasma Gas Flow	15 L.min^{-1}
Auxiliary Gas Flow	1.2 mL.min^{-1}
Nebulizer Flow	0.97 mL.min^{-1}
Analyzer Mode	MS/MS
Scan Mode	Peak Hopping
Sweeps	30
Dwell Time	50 ms
Readings	1
Replicates	3
Cell Mode	Reaction
Cell Gas	H_2

As shown in Table 2, Reaction mode was used for certain analytes typically required by the semiconductor industry in order to eliminate interferences from Si, C, O and Ar. Reaction mode with a low gas flow rate (0.1 mL.min^{-1}) was also used for analytes which are relatively free from interferences – namely lithium, beryllium and sodium – in order to shorten the analytical run time since fast analysis was of particular focus. Higher gas flows were applied to $^{39}K^+$, $^{40}Ca^+$ and $^{56}Fe^+$ to eliminate the argon-based polyatomic interferences at these masses in the form of ArH^+, Ar^+, and ArO^+ respectively, and the RPq increased in accordance with what was empirically determined to be the most appropriate value. All analyses took place in MS/MS Multi-Quad mode.[1]

Results and Discussion

Calibration curves (Figure 1) were plotted and were found to have correlation coefficients (r2) ≥0.999 (n=4 + blank) showing that the calibrations were adequately linear for all analytes, even under cold plasma conditions.

Table 2. Analytes and Analytical Conditions.

Element	Isotope Selection (Q1/Q3)	Cell Mode	Gas Flow (mL.min^{-1})	RPq
Li	7/7	Reaction	0.1	0.5
Be	9/9	Reaction	0.1	0.5
Na	23/23	Reaction	0.1	0.25
Mg	24/24	Reaction	0.6	0.4
Al	27/27	Reaction	0.6	0.4
K	39/39	Reaction	1.5	0.6
Ca	40/40	Reaction	1.5	0.8
Cr	52/52	Reaction	1.1	0.8
Mn	55/55	Reaction	0.6	0.65
Fe	56/56	Reaction	1.5	0.45
Ni	58/58	Reaction	0.6	0.4
Co	59/59	Reaction	0.6	0.65
Cu	63/63	Reaction	0.6	0.65
Zn	64/64	Reaction	0.6	0.4

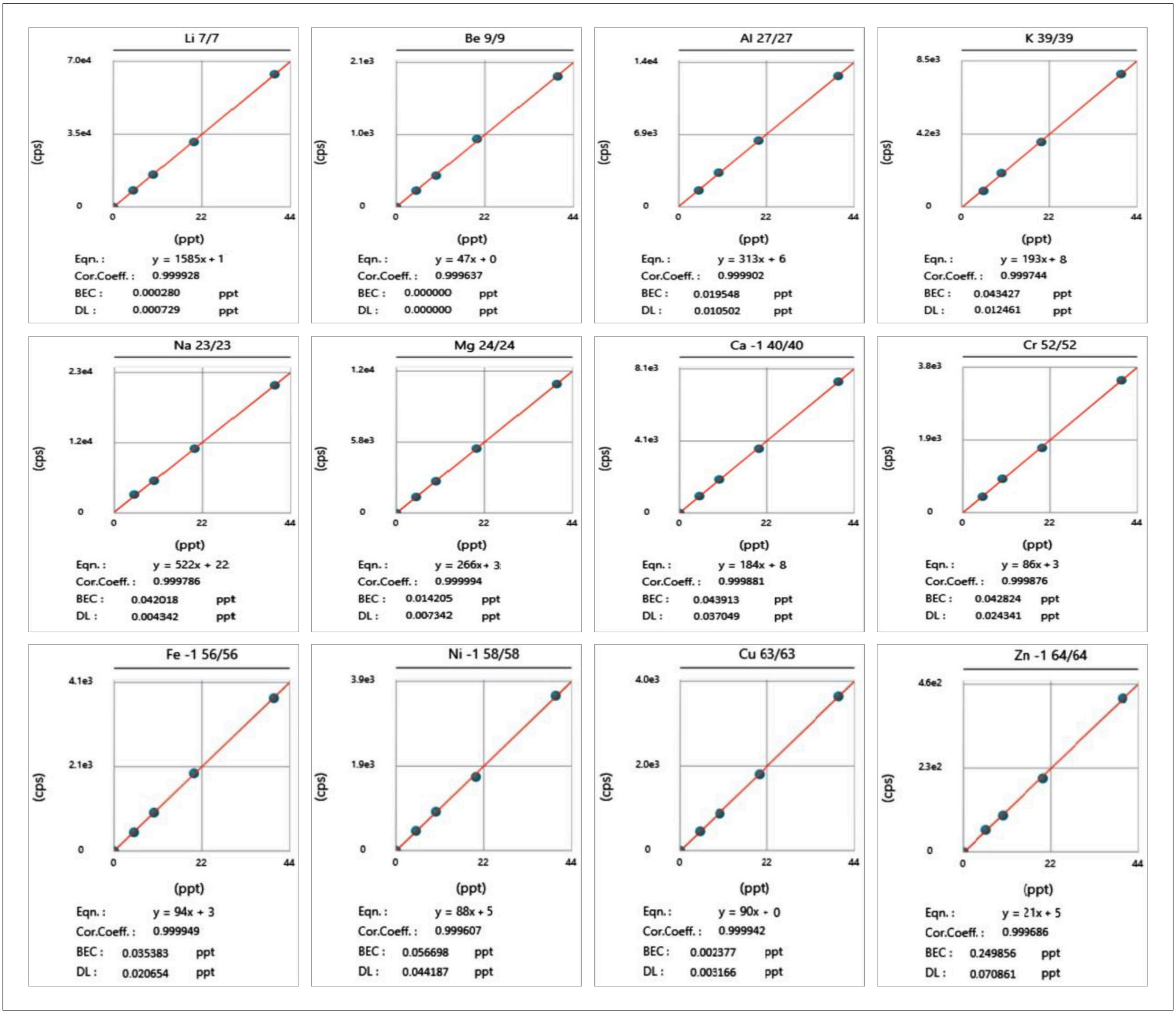

Figure 1. Calibration curves of analytes in Cold Plasma mode using H_2 as a reaction gas.

In this application brief, DLs and BECs were determined using UPW, and were calculated using the traditional 3σ method often used to determine these. As can be seen in Figure 2, sub-ppt DLs and BECs were obtained for all analytes evaluated using a single reaction gas and set of plasma conditions, where the analysis time for each sample was 116 sec. Despite the presence of large polyatomic interferences – ArH^+, Ar^+, and ArO^+ on $^{39}K^+$, $^{40}Ca^+$, and $^{56}Fe^+$ respectively – and the lower effectiveness of hydrogen as a reaction gas when compared to NH_3, these elements can be easily quantified at parts per quadrillion (ppq) concentrations in Cold Plasma mode, as shown in Figure 2. Moreover, elements (Li, Be, Na, etc.) that have few interferences and were subjected to the hydrogen reaction gas remain relatively unaffected at lower gas flows and still deliver outstanding BECs (Figure 2) with good linearity over a wide concentration range while maintaining high sensitivity (Figure 1).

Conclusion

This application brief demonstrates the ability of the NexION 5000 Multi-Quadrupole ICP-MS to deliver outstanding DLs and BECs for Li, Be, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Co, Cu and Zn, allowing for the accurate quantification of these elements at the ppq level. The reaction gas generated with a NM-H_2 Plus Hydrogen Generator was found to deliver the level of purity required by this semiconductor application, without posing any of the potential safety hazards associated with having hydrogen gas cylinders in the lab. The use of this gas and a single plasma mode (Cold Plasma) allowed for analysis times as short as 116 seconds per sample to be achieved, supporting the rapid response needs for UPW analysis in semiconductor laboratories.

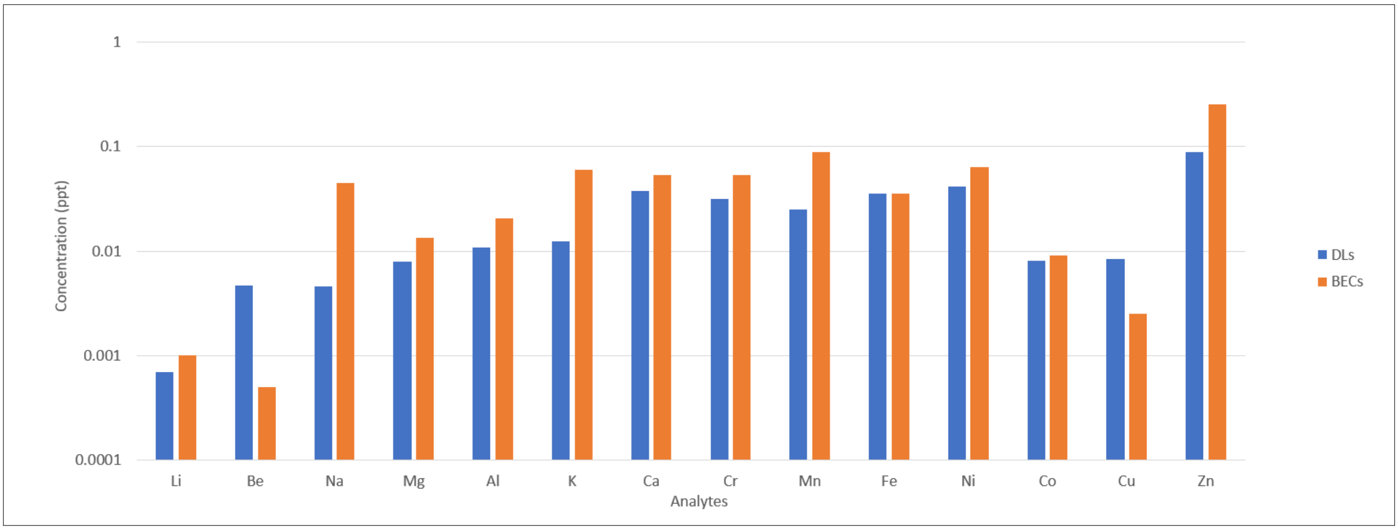

Figure 2. Detection limits and background equivalent concentrations in ultrapure water, where concentrations are shown in ppt.

Consumables Used

Component Description	Part Number
Platinum Sampler Cone	W1033614
Platinum Skimmer Cone	N8161041
Multi-Element Calibration Stock Solution 3	N9300233
1.5 mm Fixed Injector Torch	N8152427

References

1. Pruszkowski E., 2020, Characterization of Ultrapure Water using NexION 5000 ICP-MS, PerkinElmer App Note.
2. Thomas R., 2004, Practical Guide to ICP-MS, Marcel Dekker Inc. New York ISBN: 0-8247-5319-4

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