

Ultra trace measurement of potassium and other elements in ultrapure water using the Agilent 8800 ICP-QQQ in cool plasma reaction cell mode

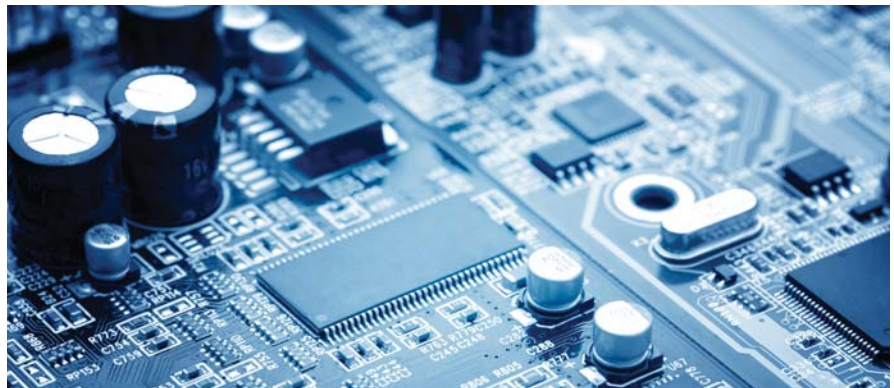
Application note

Semiconductor

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Introduction

The drive to downsize semiconductor components is relentless, as the industry responds to the market demands for more compact devices, faster operational speeds, lower power consumption and lower cost. The trend for ever smaller and higher density device architecture requires that higher purity chemicals and materials are used in the semiconductor manufacturing process, since any impurities present in the process chemicals may contaminate surfaces and directly affect the performance and yield of the final product. Consequently, semiconductor applications have always required the highest performance, cutting edge technology, and specific, clean sampling techniques to keep pace with evolving analytical demands.

Since its inception, ICP-MS has been of interest for the elemental impurity analysis of chemicals and materials used by semiconductor industries; however, some analytical challenges remain unsolved. The development of collision/reaction cells (CRC) for quadrupole ICP-MS (ICP-QMS) addressed some of the analytical difficulties by allowing specific interferences to be



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removed by chemical reaction in the CRC. However, these ICP-QMS reaction mode methods are unable to achieve the extremely low limits of detection now required by the industry.

Cool plasma is an ICP-MS mode of analysis that was developed more than 20 years ago for the determination of difficult, interfered elements such as Na, Mg, Al, K, Ca and Fe at trace levels [1]. The concentrations of K, Ca and Fe are strictly controlled in semiconductor device manufacturing processes and chemicals, but they are difficult elements to determine by ICP-MS due to argide interferences e.g. ArH^+ on $^{39}\text{K}^+$, Ar^+ on $^{40}\text{Ca}^+$ and ArO^+ on $^{56}\text{Fe}^+$. Cool plasma employs a lower temperature plasma that has sufficient energy to ionize the analytes but not the argide interferences, thereby allowing the analyst to measure the interfered elements at trace (ppt) levels, free from the interfering ions. The low temperature plasma also prevents the re-ionization of Easily Ionized Elements (EIEs) such as Li and Na that may be deposited on the interface of the ICP-MS. Even after the introduction of a high concentration of EIEs, cool plasma ensures a low background level of these elements is maintained.

Agilent ICP-MS systems (the 7900 ICP-MS and 8800 Triple Quadrupole ICP-MS (ICP-QQQ)) are available in two configurations; the standard configuration is for general applications while the "s" configuration (option #200) is optimized for semiconductor applications. The "s" configuration includes a specially designed "s-lens" to support cool plasma performance, which remains the semiconductor industry standard technique for a number of high-purity chemical applications. Both the 7900 ICP-MS and the 8800 ICP-QQQ instruments also support CRC operation, giving total flexibility for method optimization for the extremely high performance capability required in the semiconductor industry.

This note describes how the Agilent 8800 ICP-QQQ provides improved cool plasma performance combined with unique MS/MS mode reaction cell methodology to achieve a Background Equivalent Concentration (BEC) of 30 ppq for K in ultrapure water (UPW) and BECs at the ppq level for all the other elements studied: Li, Na, Mg, Al, Ca, Cr, Mn, Fe, Ni and Cu.

Experimental

A semiconductor configuration Agilent 8800 Triple Quadrupole ICP-MS was used. The sample introduction system features a quartz torch with a 2.5 mm i.d. injector, quartz spray chamber, and a PFA concentric nebulizer. The semiconductor configuration also includes platinum interface cones, which were fitted for the analysis. The sample was self-aspirated at about 180 $\mu\text{L}/\text{min}$ using a carrier gas flow rate of 0.7 L/min. An Agilent I-AS autosampler was used, with a flowing rinse port kit (Organo Corp., Tokyo, Japan) fitted in one of the I-AS rinse port positions. The rinse port kit continuously supplies fresh UPW for the probe rinse during analysis; this eliminates the possibility of the buildup of trace contamination that may occur in a static (non-flowing) rinse container.



Figure 1. Photograph of the Organo flowing rinse port kit fitted to the Agilent I-AS autosampler

High purity HNO_3 (TAMAPURE-AA-10, TAMA Chemicals Co. Ltd. Kanagawa, Japan) was used to acidify the blanks and samples. Standard solutions were prepared by serial dilution from a SPEX 331 mixed standard (SPEX CertiPrep, NJ, USA).

Cool plasma conditions were used throughout, and the plasma parameters are shown in Table 1. A low-temperature plasma dramatically reduces the formation of argide-interferences e.g., Ar^+ , ArH^+ and ArO^+ . To establish cool plasma conditions, the total injector gas flow rate (carrier gas flow rate + make up gas flow rate) is increased, the RF forward power is decreased, and a longer sample depth (SD) is used. With the low temperature plasma conditions of cool plasma, hard extraction (significantly negative voltage applied to extraction lens 1) is recommended.

The 8800 ICP-QQQ has a tandem MS configuration which enables operation in MS/MS mode (where both quadrupoles are operated as unit mass filters). MS/MS mode ensures that the reaction chemistry in the CRC is controlled and predictable, as only the target analyte ion and direct, on-mass interferences are passed to the cell. This ensures that the reactions are consistent even when using a highly reactive cell gas such as ammonia. In this study, a cell gas of 10% NH₃ in He (99.99%) was used, introduced using the 8800 ICP-QQQ's third cell gas line. The performance was compared for cool plasma mode (with no cell gas), and cool plasma with NH₃ MS/MS reaction mode.

Table 1. Agilent 8800 ICP-QQQ operating parameters

Tuning parameters	Unit	Cool plasma	Cool plasma + NH ₃ reaction
RF power (RF)	W		600
Sample depth (SD)	mm		18
Carrier gas flow rate (CRGS)	L/min		0.7
Make up gas flow rate (MUGS)	L/min		0.8
Scan mode	-		MS/MS
Extraction lens 1 (Ex1)	V		-100
Extraction lens 2 (Ex2)	V		-12
Omega bias	V		-70
Omega lens	V		6.7
OctpBias	V	-20	-10
KED	V	15	-10
Cell gas	-	NA	10% NH ₃ in He
Cell gas flow rate	mL/min	NA	1

Results and discussion

Investigation of the background signal at m/z 39 under cool plasma conditions

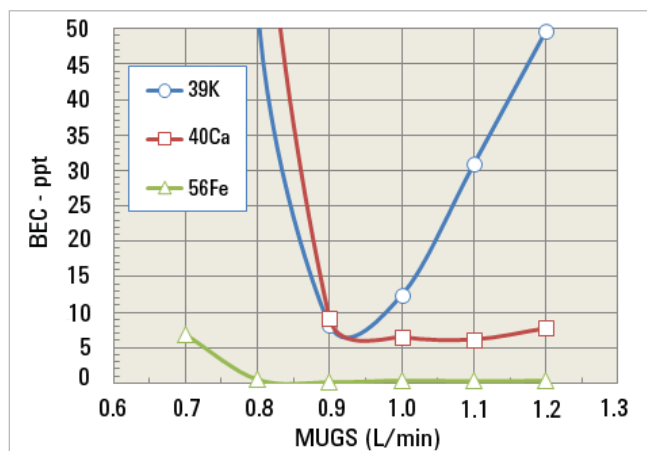


Figure 2: BEC of K, Ca and Fe as a function of makeup gas (MUGS) flow rate

Figure 2 shows the BEC of ³⁹K, ⁴⁰Ca and ⁵⁶Fe in UPW as a function of makeup gas (MUGS) flow rate. As shown, an increase in MUGS (cooler plasma conditions) results in a decrease of the BEC for each element. This indicates a reduction in the production (ionization) of the argide ions that overlap each of the analyte ion masses. However, above a MUGS flow rate of 0.9 L/min, the BEC of ³⁹K starts to increase again. This indicates that, apart from the ionization of ArH⁺, there is another factor that also affects the background signal at m/z 39. The first factor is the decreasing formation of ³⁸ArH⁺ with higher MUGS flow rate (lower plasma temperature). Second, we suspect the presence of a water cluster ion, H₃O(H₂O)⁺, which is likely to form under low temperature plasma conditions. To test this hypothesis, we monitored two signal ratios; R1 (signal at m/z 37 to signal at m/z 39) and R2 (signal at m/z 41 to signal at m/z 39). If the background signal at m/z 39 is mainly due to ArH⁺, R2 should match the ratio of the Ar 40/38 isotope abundance (⁴⁰ArH⁺/³⁸ArH⁺) = 1581. If the signal at m/z 39 is mainly due to the water cluster ion, R1 should match the ratio of the abundance of the water cluster ions consisting of the different oxygen isotopes, ¹⁶O and ¹⁸O (99.5/0.409 = 243), as shown in Table 2.

Table 2. Abundance of water cluster ions

Water cluster ion	Mass number	Abundance %
(H ₃ ¹⁶ O ⁺)(H ₂ ¹⁶ O)	37	99.5
(H ₃ ¹⁶ O ⁺)(H ₂ ¹⁸ O) or (H ₃ ¹⁸ O ⁺)(H ₂ ¹⁶ O)	39	0.409

Figure 3 is a plot of the signal ratios R1 and R2 as a function of MUGS. It shows that R2 is close to 1581 when the MUGS flow is low, indicating that the signal at *m/z* 39 is dominated by ArH⁺ at low MUGS flow. However, when the MUGS flow is high (> 1 L/min), R1 approaches 243, indicating that the signal at *m/z* 39 is dominated by the water cluster ion at high MUGS flow. This result confirms the background at *m/z* 39 is due to the combination of two interfering ions, ArH⁺ and the water cluster ion. The findings suggest that it may not be possible to completely remove the background signal at *m/z* 39 simply through applying cool plasma conditions, as there is no plasma temperature where both interferences on ³⁹K⁺ are at a minimum level.

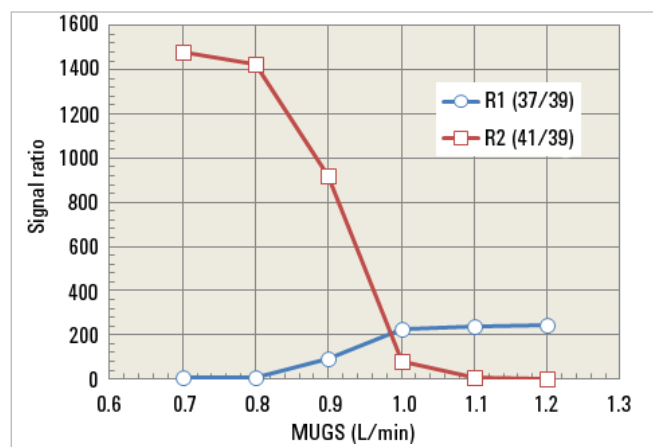
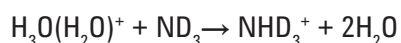


Figure 3. Signal ratio of R1 and R2 as a function of MUGS

Cool plasma/NH₃ reaction cell mode for K analysis

The water cluster ion is known to react with deuterated ammonia (ND₃) via the fast proton transfer reaction shown below [2].



It is reasonable to assume that the water cluster ion reaction with NH₃ would proceed at a similar rate to the reaction with ND₃, offering a NH₃ reaction cell method to remove the water cluster ion.

Ammonia reaction gas mode under cool plasma conditions was used to determine K in UPW. The BEC was measured at 30 ppq. A comparative study carried out using a 7500cs ICP-QMS in cool plasma/NH₃ reaction mode achieved a BEC of 500 ppt for K [3]. We attribute the improvement of BEC achieved with the 8800 to the MS/MS reaction capability of the ICP-QQQ technique. In ICP-QMS, all ions formed in the plasma enter the reaction cell and react with NH₃ and product ions that are formed in the cell. These reactions lead to the formation of new product ions at *m/z* 39. In contrast, MS/MS prevents any unwanted precursor ions from entering the cell thus minimizing the formation of undesired product ions.

Multi-element analysis using cool plasma/NH₃ MS/MS reaction mode

The new cool plasma method with MS/MS and NH₃ reaction mode was applied to the multi-element analysis of UPW. As can be seen from the results in Table 3, BECs < 0.05 ppt (ng/L) or 50 ppq were achieved for all elements except Ca, Fe and Ni, all of which had BECs < 150 ppq.

Table 3. DL and BEC of elements in UPW determined using ICP-QQQ in cool plasma/NH₃ reaction mode

Mass/Element	Sensitivity, cps/ppq	DL, ppt	BEC, ppt
7 Li	6.2	0.000	0.000
23 Na	94.0	0.014	0.035
24 Mg	44.0	0.010	0.005
27 Al	42.7	0.010	0.002
39 K	96.8	0.000	0.030
40 Ca	42.5	0.035	0.091
52 Cr	36.5	0.029	0.037
55 Mn	64.5	0.020	0.011
56 Fe	42.2	0.488	0.134
60 Ni	13.4	0.270	0.101
65 Cu	15.5	0.014	0.029

Conclusion

The Agilent 8800 ICP-QQQ was used to confirm the presence of a water cluster ion, $\text{H}_3\text{O}(\text{H}_2\text{O})^+$, which contributes to the background signal for K at m/z 39 under cool plasma conditions. This water cluster ion was removed successfully using NH_3 cell gas in MS/MS mode. The 8800 ICP-QQQ BEC for ^{39}K was more than a factor of 10 lower than that achieved using a conventional quadrupole ICP-MS. This demonstrates the benefit of MS/MS reaction mode, which stops any non-target, plasma-derived ions from entering the cell, and thereby prevents the creation of potentially interfering cell-formed product ions. This enabled the Agilent 8800 ICP-QQQ to achieve a BEC of 30 ppq for K in UPW and a BEC < 150 ppq for all other elements, including Ca, Fe and Ni.

References

1. K. Sakata and K Kawabata, *Spectrochim. Acta*, 1994, 49B, 1027.
2. Vincent G. Anicich, *An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics*, 2003 (p369), JPL Publication 03-19, NASA.
3. Junichi Takahashi et al., Use of collision reaction cell under cool plasma condition in ICP-MS, Asia Pacific Winter Plasma Conference 2008 (O-10).

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