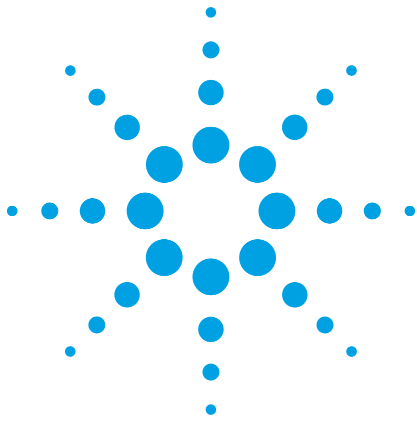

Ultra-low level determination of phosphorus, sulfur, silicon and chlorine using the Agilent 8900 ICP-QQQ

Application note

Semiconductor

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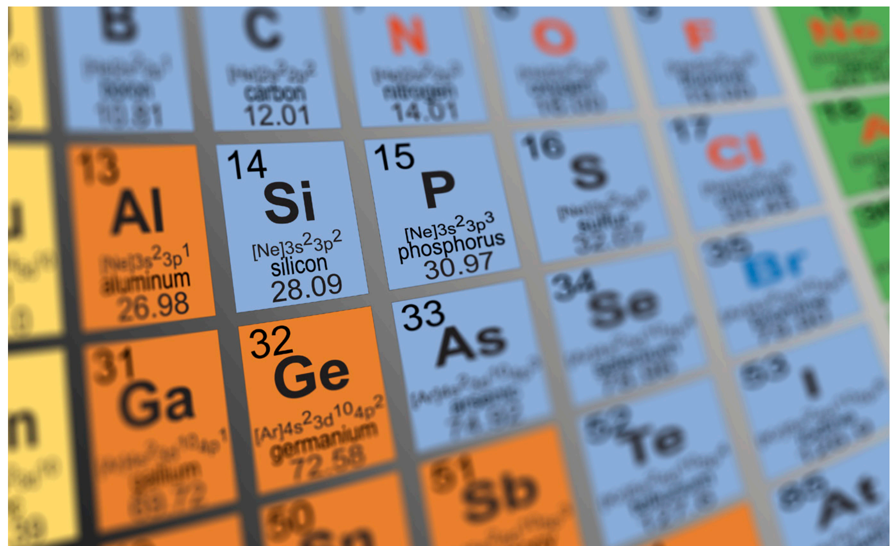

Introduction

Quadrupole ICP-MS (ICP-QMS) is one of the most sensitive and versatile analytical tools used in inorganic analysis. With sensitivity approaching 1,000 million counts per second/part per million (1 G cps/ppm) and background signals typically less than 1 cps, the latest instrumentation achieves detection limits (DL) in the ppq (ng/L) range for most of the elements in the periodic table. Detection limits tend to be lowest for elements at masses higher than 80 amu, while some lower mass elements are more difficult to measure at trace levels due to the presence of spectral overlaps from polyatomic interferences. ICP-QMS can utilize cool plasma and/or collision/reaction cell methods to address the problem of background interferences, with successful results in many applications.

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More recently, the introduction of triple quadrupole ICP-MS (ICP-QQQ) has dramatically improved the reliability and performance of reaction cell methods by allowing a double mass filter (MS/MS) to be applied to control reaction chemistry in the cell. This now allows analysts to resolve interferences on a wide range of elements in a controlled and effective manner [1].

With the introduction of Agilent's second generation ICP-QQQ instrument, the Agilent 8900 Triple Quadrupole ICP-MS, reaction cell operation with MS/MS mode has been further refined. This note describes the performance of the 8900 ICP-QQQ for the analysis of some of the most challenging elements for ICP-MS: phosphorus (P), sulfur (S), silicon (Si), and chlorine (Cl). The first ionization potentials of these elements are relatively high, which reduces the degree of ionization and therefore the analyte signal. Furthermore, the background signals are elevated due to plasma-, solvent- and matrix-based polyatomic ions, making low-level analysis even more difficult. As ICP-MS technology has developed, there has been a growing demand and expectation to measure these difficult elements together with more conventional elements in high purity chemicals and materials. Details of the methods used to control the interferences on the four elements are presented, together with background equivalent concentrations (BECs) and detection limits (DLs) for P, S, Si and Cl in ultra-pure water (UPW), and P, S and Si in the highest grade hydrogen peroxide (H_2O_2).

Experimental

Instrumentation

An Agilent 8900 ICP-QQQ (#200, Semiconductor Configuration) was used for all measurements. The sample introduction system comprised a PFA concentric nebulizer, a quartz spray chamber and torch, and platinum interface cones. The 8900 #200 ICP-QQQ is fitted with a new argon gas flow control system specially designed to minimize sulfur/silicon contamination from the gas line components.

Normal, hot plasma conditions were used throughout. Extraction lens voltages were optimized for maximum sensitivity using an Agilent 1 ppb tuning solution containing Li, Y, Ce and Tl. Operating and tuning parameters are summarized in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating parameters

Parameter	Unit	Value
RF power	W	1500
Sampling depth	mm	8.0
Carrier gas flow rate	L/min	0.70
Makeup gas flow rate	L/min	0.52
Extraction lens 1	V	4.0
Extraction lens 2	V	-210
Omega lens bias	V	-80
Omega lens	V	8.0

Method and cell tuning

Based on previous studies, oxygen (O_2) mass-shift mode was used for the analysis of P and S [2], hydrogen (H_2) on-mass mode was used for Si, and Cl was determined using H_2 mass-shift mode [3]. The reaction processes used for removal of the primary interference on each analyte were as follows:

Sulfur by oxygen mass-shift mode

The intense polyatomic interference from $^{16}O_2^+$ on the primary isotope of S, $^{32}S^+$ at *m/z* 32, is avoided by shifting S^+ away from the interfering O_2^+ ion, using an O-atom addition reaction. S^+ reacts readily with O_2 cell gas to form the product ion SO^+, which can be measured free of interference at M + 16 amu (*m/z* 48 for the primary $^{32}S^{16}O^+$ isotope product ion), as shown in the following equations:

$$^{32}S^+ + O_2 \langle\text{cell gas}\rangle \rightarrow {}^{32}S^{16}O^+ + O$$

$$^{16}O_2^+ + O_2 \langle\text{cell gas}\rangle \rightarrow \text{no reaction}$$

Phosphorus by oxygen mass-shift mode

A similar mass-shift approach is used for the measurement of P as PO^+. The native mass of P (*m/z* 31) suffers an intense background interference from $^{14}N^{16}O^{1}H^+$, $^{15}N^{16}O^+$, and $^{14}N^{17}O^+$. These background polyatomic ions are avoided by reacting P^+ with O_2 cell gas, shifting the P^+ away from the interfering ions, and measuring it as the PO^+ product ion at *m/z* 47:

$$^{31}P^+ + O_2 \langle\text{cell gas}\rangle \rightarrow {}^{31}P^{16}O^+ + O$$

$$NOH^+/NO^+ + O_2 \langle\text{cell gas}\rangle \rightarrow \text{no reaction}$$

Table 2. Cell mode related tuning parameters

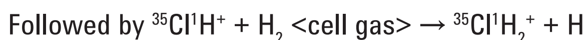
Parameter	Unit	O_2 mass-shift	H_2 on-mass	H_2 mass-shift
Element		^{31}P, ^{32}S	^{28}Si	^{35}Cl
Mass pair	(Q1 → Q2)	(31 → 47), (32 → 48)	(28 → 28)	(35 → 37)
Cell gas		O_2	H_2	
Flow rate	mL/min	0.41	5.0	
OctpBias	V	-3	-18	
KED	V	-8	0	
Axial acceleration	V	1	0	
Cell exit	V	-90	-70	
Deflect	V	8	-6	
Plate bias	V	-60		

Silicon by hydrogen on-mass mode

The analysis of Si uses on-mass measurement with H_2 cell gas, as the primary interferences on the major Si isotope at *m/z* 28, $^{14}N_2^+$ and $^{12}C^{16}O^+$, react readily with H_2, while Si^+ does not react. Thus the N_2^+ and CO^+ interferences can be removed, and $^{28}Si^+$ can be measured free from the interferences at its original mass:

Chlorine by hydrogen mass-shift mode

Cl is a difficult element to analyze at low concentrations using ICP-MS, because it is a common contaminant and is often present in reagents used in the laboratory environment. In addition, its first ionization potential of 12.967 eV is higher than that of any other commonly measured element, meaning that Cl is very poorly ionized, so the sensitivity for Cl^+ is extremely low. A further issue for low-level Cl analysis is the presence of a polyatomic interference from $^{16}O^{18}O^{1}H^+$ on the primary Cl isotope at *m/z* 35. The O_2H^+ overlap can be avoided by measuring Cl as a ClH_2^+ product ion, produced from sequential reaction with H_2 reaction gas:



In all of these methods, the Agilent 8900 ICP-QQQ was operated in MS/MS mode (where both Q1 and Q2 function as mass filters) ensuring that only the target ion or product ion was measured. MS/MS means that potentially overlapping ions are excluded from the collision/reaction cell, so the reaction chemistry is controlled and consistent, even if other matrix elements or analytes are present in the sample. For example, in the case of $^{32}S^{16}O^+$ product ion measured at *m/z* 48, the product ion mass could be overlapped by other ions, such as $^{48}Ca^+$, $^{48}Ti^+$, and $^{36}Ar^{12}C^+$, if these ions were not rejected by Q1. This is the main reason for the improved reaction mode performance of ICP-QQQ compared to ICP-QMS, as ICP-QMS has no mass filter step before the collision/reaction cell.

The ORS^4 collision/reaction cell of the 8900 #200 instrument has the facility to utilize an axial acceleration voltage, which was found to be effective to increase sensitivity in the O_2 mass-shift method used for the determination of P and S. Cell parameters were optimized separately for each mode while aspirating a 1 ppb standard solution of each of the elements. Cell tuning parameters are summarized in Table 2.

Reagents

Standard solutions for P, S and Si were prepared from single element standards purchased from SPEX CertiPrep (NJ, USA), by serial dilution with UPW. The UPW was supplied from ORGANO Corp (Tokyo, Japan). The Cl standard was prepared from high purity HCl purchased from Wako Pure Chemicals Industries Ltd (Osaka, Japan). The highest purity grade H_2O_2,

TAMAPURE-AA-10, was purchased from TAMA Chemicals Co Ltd (Kanagawa, Japan). The calibration standard addition spikes were added directly to the undiluted H_2O_2. A 1% TMAH alkaline rinse was used during the analysis of Cl to maximize the effectiveness of the washout between samples, and prevent any carryover. All pipette tips, vials and bottles were thoroughly cleaned using diluted high purity acids, and rinsed in UPW prior to use.

Results and discussion

To prepare the ICP-QQQ for the analysis, a 1% HNO_3 solution was aspirated overnight to thoroughly clean the sample introduction system. Running the plasma for several hours would also help to remove any contaminants in the Ar gas flow line. P, S and Si were measured together, and Cl was analyzed in a separate batch since it benefited from an alkaline rinse between solutions. Figures 1 and 2 show the calibration curves of the four elements in UPW and P, S and Si in H_2O_2, respectively, measured using the method of standard addition (MSA). The background level of Cl present in the H_2O_2 sample was too high to permit accurate analysis at the spike levels used.

Good linearity at low and sub-ppb levels was observed for all elements measured in both of the sample matrices. The DL for each element was calculated as 3 times the standard deviation of 10 replicates of the blank using an integration time of 1 sec for each element. The results are summarized in Table 3.

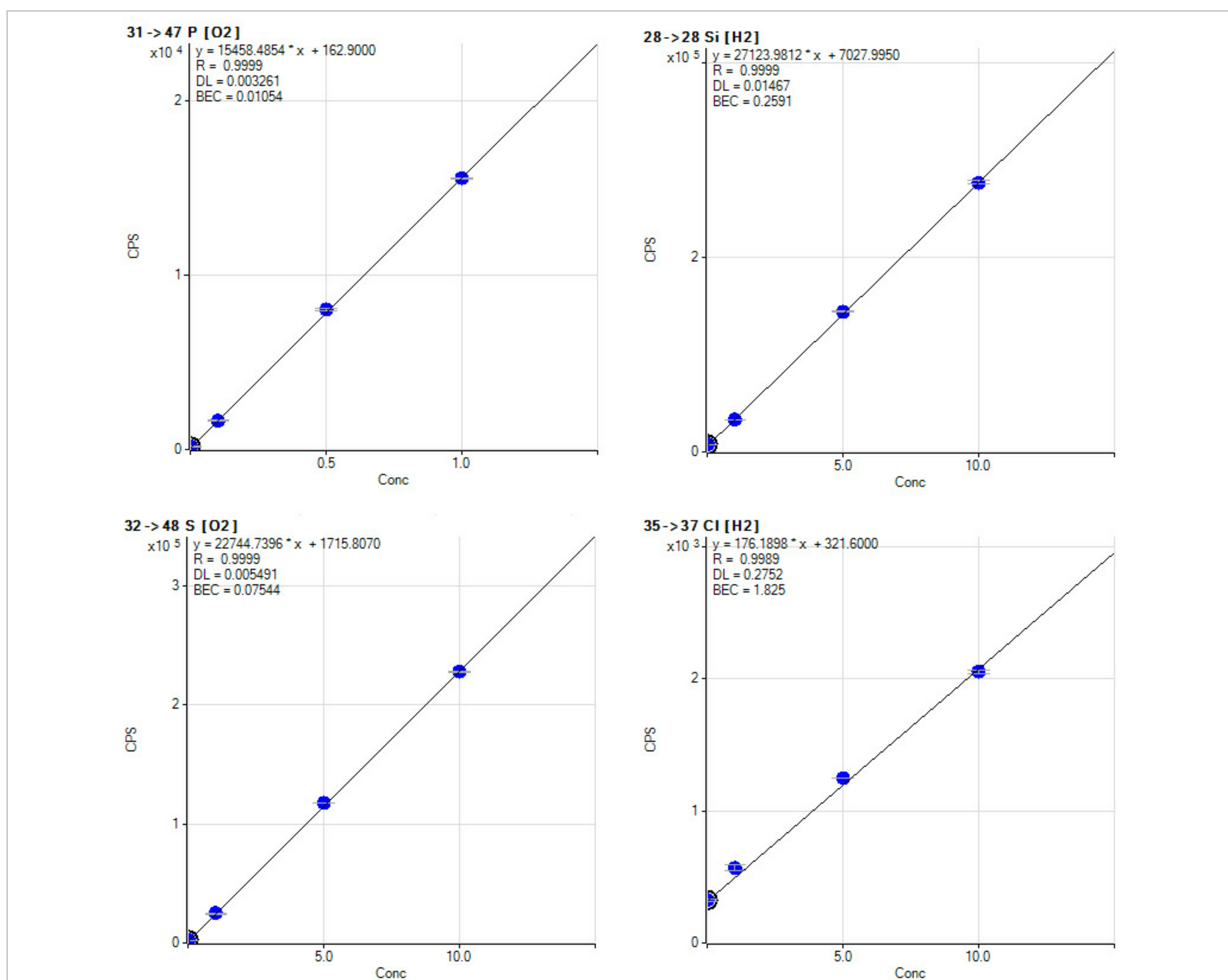


Figure 1. Calibration plots of P, S, Si and Cl in UPW . All values in ug/L (ppb).

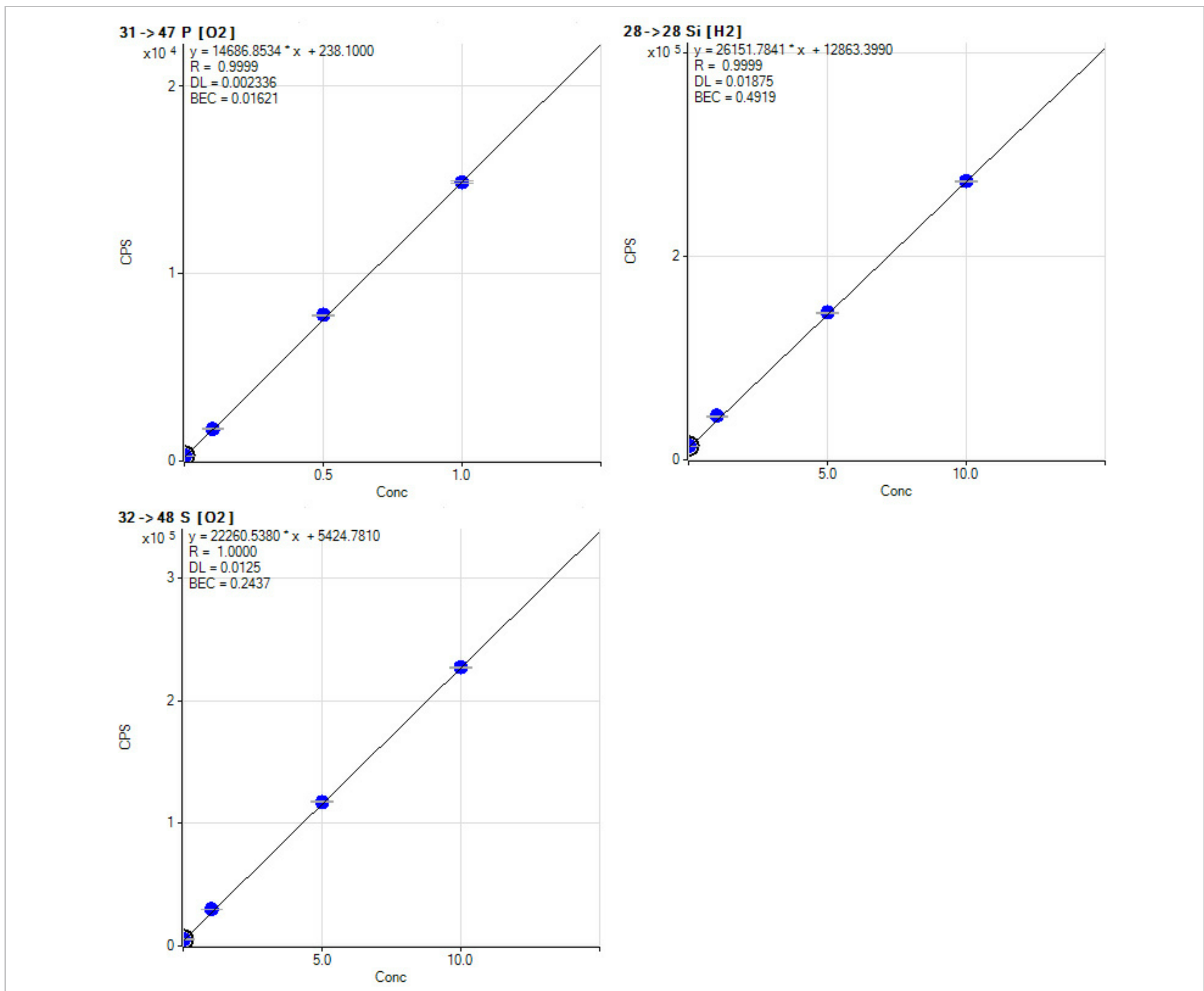


Figure 2. Calibration plots of P, S and Si in H_2O_2

Table 3. BEC and DL of P, S, Si and Cl in UPW and P, S and Si in the highest grade H_2O_2

	P (ppt)		S (ppt)		Si (ppt)		Cl (ppb)	
Element	BEC	DL	BEC	DL	BEC	DL	BEC	DL
UPW	10.5	3.3	75.4	5.5	259	14.7	1.83	0.28
H_2O_2	16.2	2.3	244	12.5	492	18.8		

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode with O_2 and H_2 cell gases successfully eliminated problematic spectral interferences on non-metallic impurities P, S, Si and Cl in UPW and P, S and Si in H_2O_2. The results highlight the advanced performance of the second generation ICP-QQQ for the analysis of challenging elements, by achieving the lowest ever reported BECs for the four elements in UPW.

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