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Ultra-Trace Determination of Non-metallic Elements in Dilute Nitric Acid Using NexION 5000 ICP-MS

Abstract

Nitric acid is widely used throughout the semiconductor and electronics industry. Various purity grades are required, depending on the application and the intended use. Ultrapure or semiconductor-grade ammonia (HNO_3) is used for the wet-etching of silicon and various heavy metals. It is also often blended with other materials to form polishing agents which are used on the metal components of board interconnections. For these reasons, the semiconductor industry has required ever-lower detection of a broad range of impurities, including non-metallic elements, in nitric acid solutions in order to meet manufacturing requirements. Due to the presence of complex spectral interferences resulting from plasma gases and the sample matrix, the low-ppt quantification of non-metallic elements – such as arsenic (As), bromine (Br), chlorine (Cl), iodine (I), phosphorus (P), sulfur (S), selenium (Se) and silicon (Si) – found in dilute nitric acid can be challenging using conventional ICP-MS.

This issue is easily addressed by using an ICP-MS system that not only mass filters the ions before they enter the collision-reaction cell but also controls the reaction in the cell, a feature only available in quadrupole cells. This ensures that there are no side reactions with reaction byproducts, allowing predictable and repeatable interference removal to be achieved, regardless of the sample matrix. The result of using this type of instrumentation in the analysis of non-metallic elements is often outstanding BECs and DLs.

In this application brief, the NexION® 5000 multi-quadrupole ICP-MS was used to determine the detection limits (DLs) and background equivalent concentrations (BECs) of non-metallic impurities in a dilute nitric acid solution. The analysis was performed using a single analytical method and either hot or cold plasma conditions, depending upon the analyte.

Experimental

Sample Preparation

Ultrapure water (UPW 18.27 ΩM.cm⁻¹) was used to prepare all calibration standards and sample dilutions. For the analysis of Si, further purification was carried out using a special PFA distillation device. Electronic-grade 70% nitric acid (EP-S HNO₃, Duksan Co., Ansan City, Korea) was double-purified using either a PFA (for Si) or a quartz (for all other analytes) purifier. To evaluate the presence of transition metal impurities, the purified nitric acid was concentrated 100-fold through evaporation. After concentration, the acid residual was slightly diluted with UPW before ICP-MS analysis. The concentrations of all target elements in this pre-concentrated acid solution were found to be less than 5 ppt.

All the calibration standards were prepared by gravimetric dilution of PerkinElmer's single-element standard solutions (see the *Consumables Used* table on page 5) using a 0.7% HNO₃ solution in 60 mL polyethylene containers. These containers were pre-screened for cleanliness after going through an extensive acid cleaning procedure. A five-point calibration scheme was used for the quantification of all elements, which consists of four calibration standards and one blank solution, as shown in Table 1.

Table 1. Concentrations of Calibration Standards.

Analyte	Calibration Concentrations (ppt)
Si	100, 200, 500, 1000
Br and I	50, 100, 200, 500
Cl	250, 1000, 2000, 5000
P, S, Se	10, 20, 40, 100
As	2.5, 5, 10, 20

Instrumentation

All analyses were performed using the NexION 5000 multi-quadrupole ICP-MS (PerkinElmer, Shelton, Connecticut, USA), which was developed with the requirements of semiconductor testing facilities in mind. This ICP-MS comes standard with the highest quality materials, such as a SiIQ spraychamber, PFA-ST3 nebulizer and platinum cones as is required for this application market. Conditions and hardware used for this analysis are shown in Table 2.

Table 2. NexION 5000 ICP-MS Instrument Conditions.

Parameter	Value
Nebulizer	PFA ST3 Nebulizer (self-aspirating)
Sample Probe	Self-Aspirating Probe 80 cm length 0.25 mm i.d.
Spray Chamber	SiIQ Cyclonic Spray Chamber
RF Power	Hot Plasma 1600 W
Cold Plasma	1000 W
Torch and Injector	One-piece Quartz Torch with 1.5 mm i.d. Injector
Plasma Gas Flow	15 L.min ⁻¹
Auxiliary Gas Flow	0.8 L.min ⁻¹
Nebulizer Flow	0.92-1.15 L.min ⁻¹
Analyzer Mode	MS/MS, Mass Shift, and Single Quad
Scan Mode	Peak Hopping
Sweeps	30
Dwell Time	100 ms
Readings	1
Replicates	3
Cell Mode	Reaction and Standard
Cell Gas	H ₂ and O ₂

Silicon, bromine and iodine are easily adsorbed onto the sample introduction system and ICP-MS interface and are not easily removed. As such, these components were cleaned with ultrapure water for an extended period of time before the analyses took place.

Due to the high ionization potential of these non-metallic elements, analyses of P, S, Cl, As, Se, Br, and I were performed using hot plasma conditions with an RF power of 1600 W. In order to minimize the generation of plasma-based interferences, cold plasma conditions (RF power: 1000 W) were used for the analysis of Si.

Although the interferences on P, Si and S (Table 3) are effectively managed in the production of ultrapure water, this is more challenging to control in the production of nitric acid, where the acid matrix itself is the largest source of spectral interferences.

Table 3. Ionization Potential, Relative Ionization Efficiency (%) and Interferences in MS/MS mode.

Element	m/z	Ionization Potential (eV)	Ionization Efficiency* (%)	Interferences in HNO ₃
Si	28	8.15	85	¹⁴ N ₂ ⁺ , ¹² C ¹⁶ O ⁺
P	31	10.49	33	¹⁴ N ¹⁷ O ⁺ , ¹⁴ N ¹⁶ OH ⁺ , ¹² C ¹⁶ OH ₃ ⁺ , ¹² C ¹⁸ OH ⁺
S	32	10.36	14	¹⁶ O ₂ ⁺ , ¹⁴ N ¹⁸ O ⁺ , ¹⁴ N ¹⁶ OH ₂ ⁺
Cl	35	12.97	1	¹⁶ O ¹⁸ OH ⁺ , ³⁴ SH ⁺
As	75	9.79	52	⁴⁰ Ar ³⁵ Cl ⁺ , ³⁶ Ar ³⁸ ArH ⁺ , ¹² C ¹⁶ OH ₃ ⁺ , ¹² C ³¹ P ¹⁶ O ₂ ⁺
Br	79	11.81	5	⁴⁰ Ar ³⁸ ArH ⁺ , ³¹ P ¹⁶ O ₃ ⁺
Se	80	9.75	33	⁴⁰ Ar ₂ ⁺ , ³² S ¹⁶ O ₃ ⁺
I	127	10.45	29	

* Ionization efficiency measured in Ar plasma may vary depending on the measurement conditions.

In order to eliminate spectral interferences on P, S, Se, and As, these analytes are often reacted with O₂ to form PO⁺, SO⁺, SeO⁺ and AsO⁺ respectively via exothermic mass-shifted reactions (Table 4). Since quadrupole-based Universal Cell Technology (UCT) works on frequency and not amplitude modulation, the Universal Cell is able to control the reaction and ensures that undesired endothermic reactions do not proceed, as this can produce potentially unwanted products that could later interfere with the analyte. Moreover, the dynamic bandpass tuning capability of UCT eliminates precursor species of other unwanted exothermic reactions by making them unstable in the cell, ensuring that these reactions do not proceed.

While Si exothermically combines with O₂ to form a stable SiO⁺ ion, polyatomic interferences from N₂⁺ and CO⁺ also easily react with O₂ and shift masses along with the analyte of interest. As such, O₂ is not regarded as being an efficient reaction gas for the analysis of Si, so H₂ is often used as a reaction gas for this analyte. In this example, exothermic reactions hydrogenate N₂⁺ and CO⁺, while the hydrogenation of Si proceeds through a slow endothermic reaction (Table 4). The difference in reactivity between the analyte ion and the polyatomic species with hydrogen is significant, resulting in the easy separation of Si from N₂⁺ and CO⁺ by shifting the polyatomic interferences instead of the analyte.

While Cl can also produce ClH⁺ ions via an exothermic reaction with H₂, the ClH⁺ ions undergo a chain reaction and eventually form H₂Cl⁺ (Table 4). By applying a low RPq to the cell (RPq 0.25, Table 5), this reaction is allowed to proceed unhindered.

Table 5. Analytes and Analytical Conditions.

Element	Isotope Selection (Q1/Q3)	Cell Mode	Cell Gas	Flow Rate (mL/min)	RPq
Si	28 / 28	MS/MS	H ₂	1.8	0.25
P	31 / 47	Mass Shift	O ₂	1.3	0.25
S	32 / 48	Mass Shift	O ₂	1.6	0.25
Cl	35 / 37	Mass Shift	H ₂	1.5	0.25
Se	80 / 96	Mass Shift	O ₂	1.6	0.25
As	75 / 91	Mass Shift	O ₂	1.6	0.25
Br	79	Single Quad (Q3)	None		0.25
I	127 / 127	MS/MS	None		0.25

The analysis took place using the reaction gases summarized in Table 4. Conditions were selected to control the aforementioned spectral interferences, allowing for the accurate quantitation of the analytes. All elements were characterized using a single analytical method where P, S, Si, Cl, As and Se were all measured in Reaction mode and Br and I were measured in Standard mode.

An NM-H₂ Plus Hydrogen Generator (PerkinElmer, Shelton, Connecticut, USA) was used to meet the delivery rate and purity requirements of the ICP-MS application (99.99995%) without the need to store hydrogen gas cylinders. For the analysis of P, S, Se, and As, oxygen was used (99.9999%, UP grade, Daesung Industry, Guroo, Seoul, Korea).

Table 4. Enthalpy of Reaction.

Analyte	Reaction	ΔHr (eV)
P	P ⁺ + O ₂ → PO ⁺ + O	-3.17
S	S ⁺ + O ₂ → SO ⁺ + O	-0.34
Se	Se ⁺ + O ₂ → SeO ⁺ + O	-0.71
As	As ⁺ + O ₂ → AsO ⁺ + O	-1.21
Si ⁺	Si ⁺ + H ₂ → SiH ⁺ + H	1.30
N ₂ ⁺	N ₂ ⁺ + H ₂ → N ₂ H ⁺ + H	-0.60
CO ⁺	CO ⁺ + H ₂ → COH ⁺ + H	-1.63
Cl ⁺	Cl ⁺ + H ₂ → ClH ⁺ + H	-0.17
ClH ⁺	ClH ⁺ + H ₂ → H ₂ Cl ⁺ + H	-0.39

Results and Discussion

Correlation coefficients of > 0.9995 were achieved for all calibration curves, confirming the linearity of calibration for these non-metal elements.

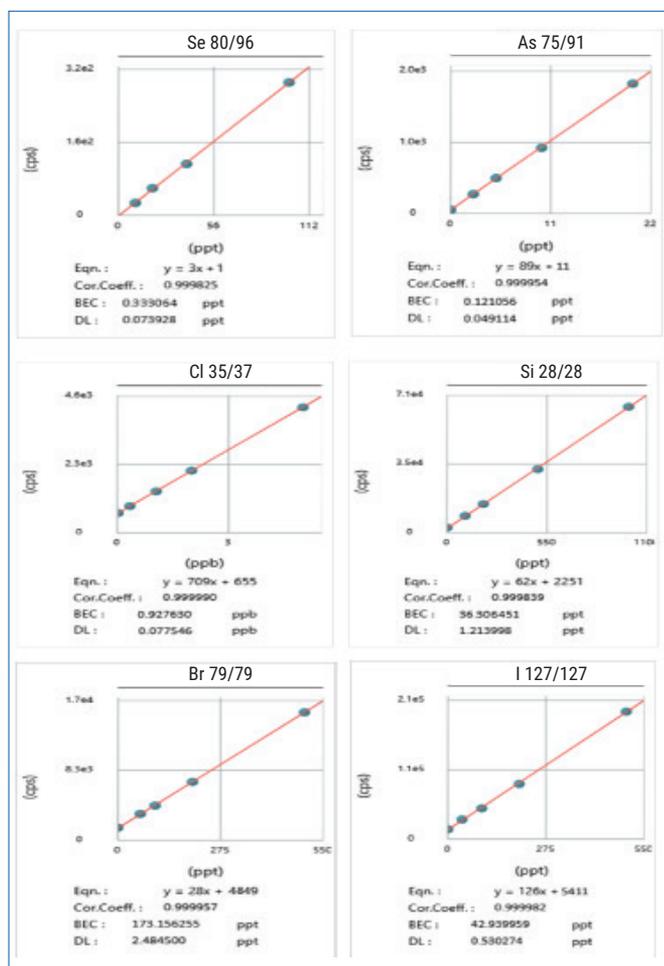


Figure 1. Calibration curve of all the elements created in a 0.7% nitric acid matrix.

From these calibration results, the obtained BECs and DLs were determined and are shown in Figure 2. The results show that the detection limits of Si and S in 0.7% HNO_3 were around 1 ppt (ng/L); P, Se, As, and I were 1 ppt; Cl was at 0.1 ppb; while Br detection limit was < 3 ppt and is to date the lowest known reported value for this sample matrix and other low-matrix samples (e.g. ultrapure water, hydrogen peroxide, dilute HNO_3 and HCl). All transition metal contaminants in 0.7% HNO_3 were found to be less than 5 ppt (ng/L) which correlated with the findings from the pre-concentration step.

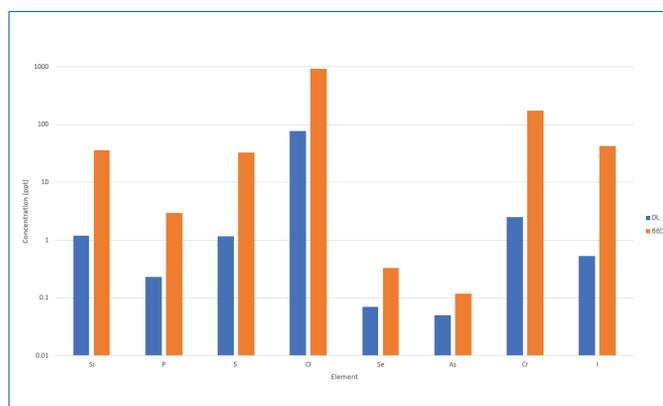


Figure 2. BECs and DLs of elements in 0.7% HNO_3 .

Conclusions

Owing to the unique multi-quadrupole functionality of the NexION 5000 ICP-MS, outstanding BECs and DLs for non-metals in a 0.7% nitric acid solution were achieved. The mixed-mode method utilizing both hot and cold plasma conditions took place using a single analytical method. Here, the plasma conditions were rapidly switched without the need to create additional methods or repeat the analysis under different plasma conditions, saving on the time of analysis and simplifying the analytical run. Although nitric acid introduces additional spectral interferences through the elevation of the nitrogen background and background contamination from organic and inorganic impurities, the NexION 5000 ICP-MS rapidly removed these interferences. This allows the NexION 5000 system to achieve the lowest known reported BECs and DLs for these elements under hot plasma (P, S, Cl, As, Se, Br, and I) and cold plasma (Si) conditions. Consequently, the findings from this study indicate that the NexION 5000 ICP-MS can meet and exceed the needs of the semiconductor industry for this application.

Consumables Used

Component	Description	Part Number
Nebulizer	PFA ST3 MicroFlow	N8152378
Sample Probe	Self-Aspirating Probe 80 cm length 0.25 mm i.d.	N8152512
Spray Chamber	SilQ Cyclonic Spray Chamber	N8152424
Torch	One-Piece Quartz Torch, 1.5 mm i.d. Injector – Double Blue Mark	N8152427
Cones	Platinum Sampler	N8161140
	Platinum Skimmer	N8161041
	Hyper-Skimmer with OmniRing Assembly	N8160120
Single-Element Standards	Selenium, 1000 ppm, 125 mL	N9303752
	Arsenic, 1000 ppm, 125 mL	N9303727
	Silicon, 1000 ppm, 125 mL	N9303799
	Phosphorus, 1000 ppm, 125 mL	N9303788
	Sulfur, 1000 ppm, 125 mL	N9303796
	Bromide, 1000 ppm, 125 mL	TruQ MS Custom Standard
	Chloride, 1000 ppm, 125 mL	TruQ MS Custom Standard
Iodide, 1000 ppm, 125 mL	TruQ MS Custom Standard	