



Trace level analysis of sulfur, phosphorus, silicon and chlorine in NMP using the Agilent 8800 Triple Quadrupole ICP-MS

Application note

Semiconductor

Author

Naoki Sugiyama

Agilent Technologies, Tokyo, Japan



Introduction

N-Methyl-2-Pyrrolidone (NMP), which has the chemical formula C_5H_9NO , is a stable, water-soluble organic solvent that is widely used in the pharmaceutical, petrochemical, polymer science and especially semiconductor industries. Electronic grade NMP is used by semiconductor manufacturers as a wafer cleaner and photoresist stripper and as such the solvent comes into direct contact with wafer surfaces. This requires NMP with the lowest possible trace metal (and non-metal) contaminant levels. ICP-MS is the technique of choice for the measurement of trace metal impurities in semiconductor process chemicals. It is a challenge, however for ICP-MS to measure non-metallic impurities such as sulfur, phosphorus, silicon, and chlorine in NMP. The low ionization efficiency of these elements greatly reduces analyte signal, while the elevated background signal (measured as background equivalent concentration, BEC) due to N-, O-, and C-based polyatomic ions formed from the NMP matrix makes low-level analysis even more difficult.



Agilent Technologies

The high sensitivity and interference removal power of triple quadrupole ICP-MS makes it uniquely suited to the challenge of this application. This note describes the performance of the Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ), operated in MS/MS mode, for the measurement of S, P, Si and Cl in NMP.

Application considerations

As stated above, this application is challenging because the analytes are poorly ionized and/or severely interfered by polyatomic species derived from the NMP matrix. As shown in Table 1, BECs measured using non-cell ICP-MS are in the ppm range. S, P and Cl are poorly ionized (Cl is less than 1% ionized), while Si (BEC >100 ppm), suffers overlaps from intense N_2 and CO peaks. While conventional quadrupole ICP-MS (ICP-QMS) with reaction cell can reduce these interferences to some extent, BECs remain in the high ppb–low ppm range and prevent measurement at the levels required by the semiconductor industry.

Table 1. ICP-QMS BECs obtained (without reaction cell) for selected analytes in NMP

| Element | m/z | Ionization potential (eV) | Ionization ratio (%) | BEC without cell (ppm) | Interference |
|---------|-------|---------------------------|----------------------|------------------------|---------------------------------|
| Si | 28 | 8.152 | 87.9 | >100 | $^{14}N_2^+$, $^{12}C^{16}O^+$ |
| P | 31 | 10.487 | 28.8 | 0.39 | $^{14}N^{16}OH^+$, COH_3^+ |
| S | 32 | 10.360 | 11.5 | 9.5 | $^{16}O_2^+$, NOH_2^+ |
| Cl | 35 | 12.967 | 0.46 | 0.26 | $^{16}O^{18}OH^+$ |

Experimental

Reagents and sample preparation

Semiconductor grade NMP was obtained from Kanto Chemical Co. (Kusaka-shi, Japan). After further purification by sub-boiling distillation at 120 °C, the NMP was acidified by adding high purity HNO_3 (Tamapure 100 grade, TAMA Chemicals Co., Kawasaki-shi, Japan) to a concentration of 1% w/w. The acidified NMP was analyzed directly (without further pre-treatment or dilution) for S, P, Si and Cl using the method of standard addition (MSA). Single element standards for S, P and Si were obtained from Kanto Chemical Co., and the Cl standard was prepared from NaCl (Wako Pure Chemicals Industries Ltd., Osaka, Japan).

Instrumentation

An Agilent 8800 Triple Quadrupole ICP-MS equipped with the semiconductor configuration (Pt interface cones and high transmission ion lens) was used throughout. The standard 2.5 mm injector quartz ICP torch was replaced with the organics torch (G3280-80080), which has an injector I.D. of 1.5 mm, to reduce plasma loading by the organic matrix. A C-flow 200 PFA nebulizer (G3285-80000) was used in self-aspiration mode with a carrier gas (CRGS) flow rate of 0.50 L/min. An optional gas flow of 20% O_2 in Ar was added to the carrier gas to prevent carbon built up on the interface cones.

The plasma and cell parameters were then optimized for best performance for the application.

Plasma tuning conditions - optimization

Figure 1 shows the Co signals obtained for a 1 ppb Co spike in water and NMP, both acidified to 1% HNO_3 . The Co signal is plotted as a function of the make-up gas (MUGS) flow rate.

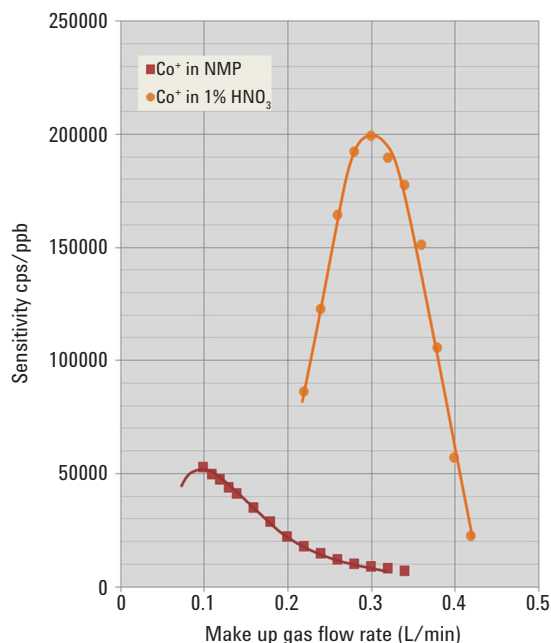


Figure 1. 1 ppb Co signal in 1% HNO_3 and acidified NMP as a function of MUGS flow rate

The optimum MUGS flow rate for NMP analysis is 0.20 L/min lower than that for 1% HNO₃, and Co sensitivity in NMP is about four times lower than in 1% HNO₃. The heavy organic matrix absorbs plasma energy, which reduces its ionizing power. Table 2 summarizes the plasma conditions selected for NMP analysis.

Table 2. Plasma conditions for NMP analysis

| Parameter | Unit | Tuning value |
|---------------------------|-------|--------------------------|
| RF | W | 1550 |
| Sampling depth | mm | 8.0 |
| Carrier gas flow | L/min | 0.50 |
| Make up gas flow | L/min | 0.10 |
| Option gas flow | L/min | 0.12 (12% of full scale) |
| Spray chamber temperature | °C | 0 |

Cell tuning conditions - optimization

Both hydrogen (H₂) and oxygen (O₂) were used as reaction gases in the Octopole Reaction System (ORS³). Unless otherwise noted, MS/MS mode was used, where the first quadrupole (Q1), which is located before the collision/reaction cell, is operated as a mass filter, passing only a single *m/z* to the cell. Table 3 summarizes the cell tuning parameters (gas flow rate and voltages) used. "On-mass" denotes measurements were made directly on the analyte mass. "Mass-shift" denotes that measurements were made using the mass-shift method, where the analyte is reacted with a reaction gas in the cell to form a product ion, shifting it away from an interference and allowing it to be measured at a different (interference-free) mass.

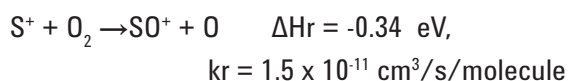
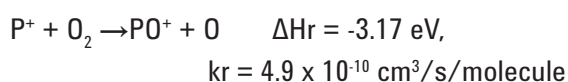
Table 3. Cell tuning parameters

| Parameter | Unit | O ₂ reaction cell | | H ₂ reaction cell | |
|------------------|--------|------------------------------|------------|------------------------------|------------|
| | | On-mass | Mass-shift | On-mass | Mass-shift |
| Measurement mode | - | On-mass | Mass-shift | On-mass | Mass-shift |
| Cell gas | - | O ₂ | | H ₂ | |
| Gas flow rate | mL/min | 0.30 | | 4.0 | |
| OctpBias | V | -14 | | -10 | |
| OctpRF | V | 180 | | | |
| KED | V | -5 | -5 | 0 | -5 |

Results and Discussion

P and S in NMP

The mass-shift method using O₂ worked well for P and S measurement in NMP. The reactions of P and S with O₂ are exothermic, indicated by the negative value for ΔH, as shown below [1]; therefore P⁺ and S⁺ are efficiently [2] converted to their oxide ions, PO⁺ and SO⁺. P and S can be measured as the product ions, avoiding the original spectroscopic interferences on their elemental masses, *m/z* 31 and *m/z* 32.



Figures 2 and 3 show calibration plots obtained using the O₂ mass-shift method for the measurement of P and S in NMP. To demonstrate the effectiveness of MS/MS, which is unique to ICP-QQQ, two acquisition modes, Single Quad (SQ) and MS/MS were applied. In SQ mode, Q1 acts simply as an ion guide, emulating conventional single quadrupole ICP-MS (ICP-QMS). In MS/MS mode, Q1 is fixed at the analyte mass (*m/z* 31 for P and *m/z* 32 for S). Only analyte ions and on-mass interferences (those having the same mass as the analyte) are able to pass through to the cell.

Figure 2 shows calibration plots for P and S in SQ mode, while Figure 3 shows plots for P and S in MS/MS mode. As can be seen, MS/MS gave much lower BECs for both P and S than were achieved with SQ mode. MS/MS mode, with the O₂ mass-shift method, achieved BECs of 0.55 ppb and 5.5 ppb for P and S in NMP, respectively.

The MS/MS mode BECs were one order of magnitude lower than SQ mode for P and two orders of magnitude lower for S. The improvement in MS/MS mode is more

significant for S because a plasma-derived ion, ArC⁺, overlaps SO⁺ at m/z 48 in SQ mode. In MS/MS mode, Q1 rejects ArC⁺ before it can enter the cell, so the interference on SO⁺ is eliminated. This demonstrates the unique capability which ICP-QQQ with MS/MS has to realize the full potential of reaction chemistry. The low BECs and linear calibration plots achieved in MS/MS scan mode also proves that the matrix-derived interferences do not react with O₂, allowing the analytes to be separated from the interferences.

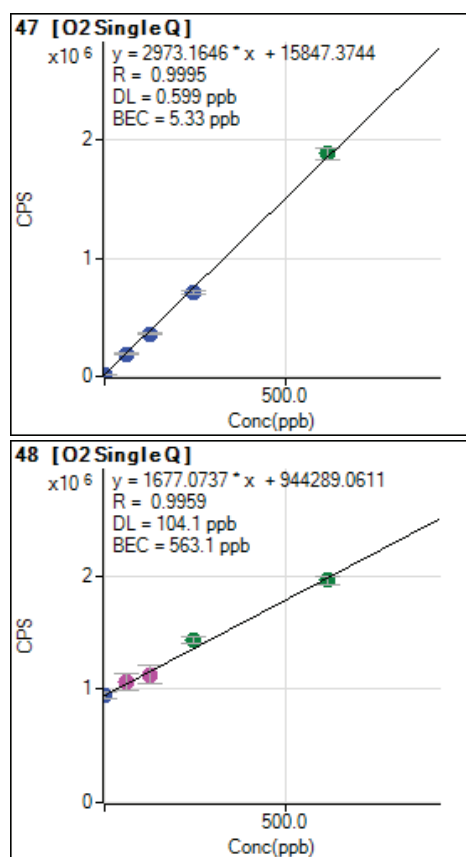


Figure 2. Calibration curve of O₂ mass-shift method for P (top) and S (bottom) in NMP with single quad scan, emulating conventional ICP-QMS

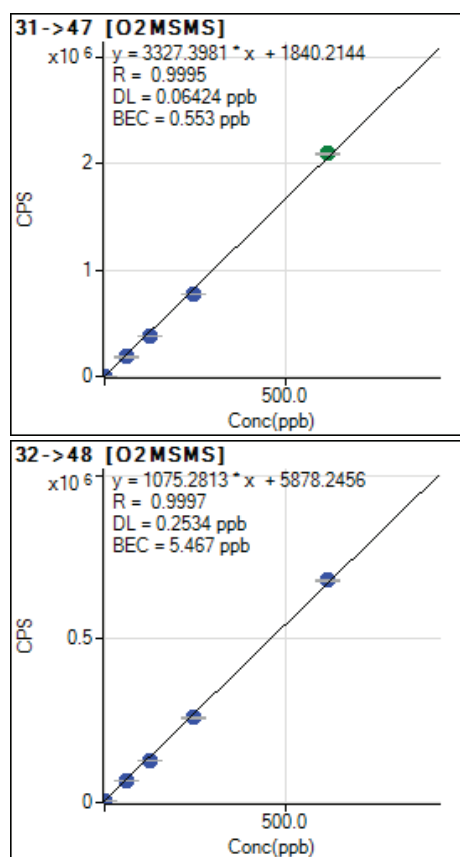
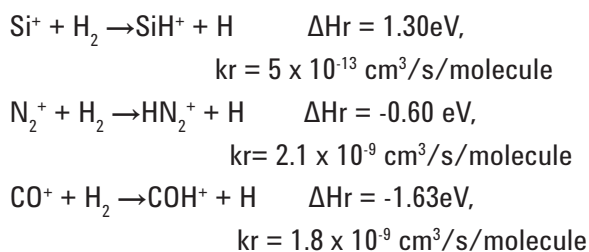


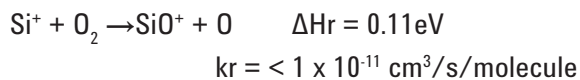
Figure 3. Calibration curve of O₂ mass-shift for P (top) and S (bottom) in NMP with MS/MS scan

Si in NMP

H₂ and O₂ cell gases were both applied to the measurement of Si in NMP. The reaction kinetics for Si and its major interferences with H₂ cell gas are shown below. The reaction rate data suggests that Si does not react with H₂ cell gas (endothermic reaction indicated by the positive value for ΔH), and so could be measured in NMP using the direct, on-mass method. While the reaction of Si⁺ with H₂ is endothermic, the reactions of the major interfering ions on Si at mass 28 (N₂⁺ and CO⁺) are exothermic, and these interferences are therefore neutralized or reacted away.



Oxygen cell gas was also tested. As shown below, the reaction of Si⁺ with O₂ to form SiO⁺ is endothermic. However, collisional processes in the cell provide additional energy which promotes the reaction, enabling the O₂ mass-shift method to be applied.



Unfortunately a major interference on Si at *m/z* 28 (CO⁺) also reacts with O₂, so the BEC achieved using the O₂ mass-shift method to measure Si as SiO⁺ (Q1=28, Q2=44) was not satisfactory. Fortunately, another Si reaction product ion (SiO₂⁺) also forms and this can be measured at *m/z* 60 (Q1 = 28, Q2 = 60) giving better results, as shown in Figure 4.

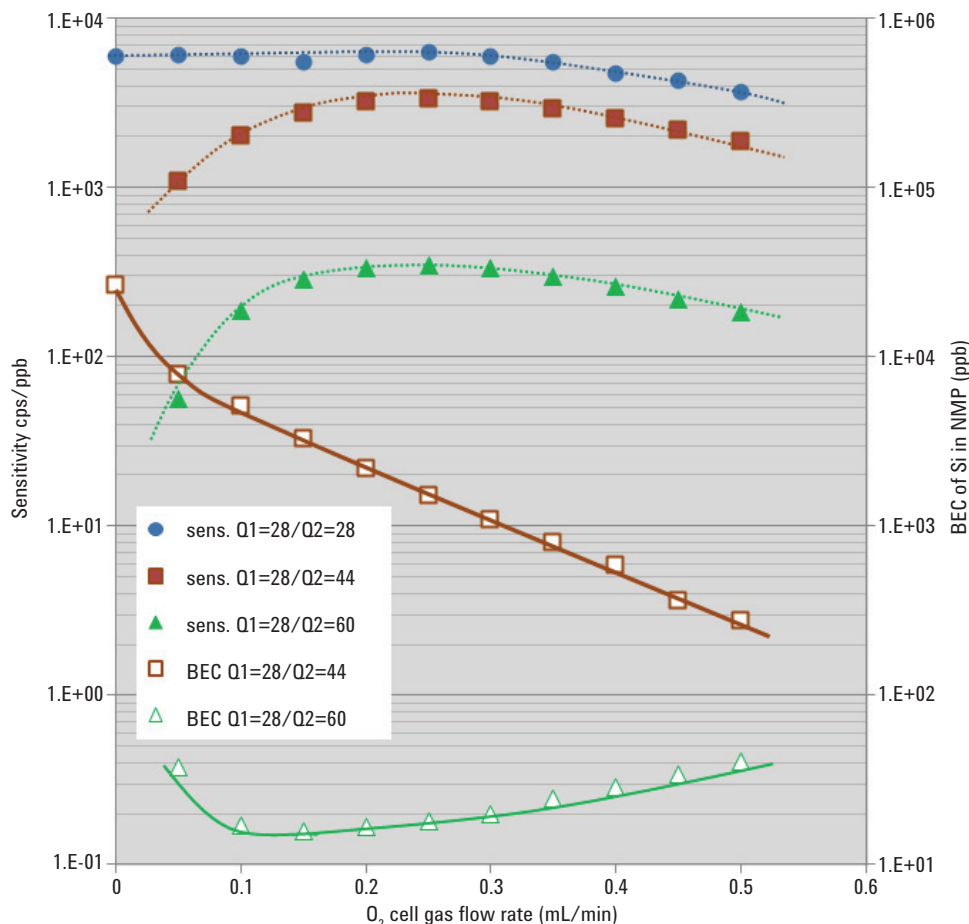


Figure 4. BECs of Si in NMP obtained using product ions SiO⁺ and SiO₂⁺, as a function of O₂ cell gas flow rate

The results obtained are shown in Figure 5 (top). The H₂ on-mass method achieved a BEC of 15.8 ppb for Si in NMP. Using the O₂ mass-shift method to measure SiO₂⁺ gave a BEC of 11.9 ppb (Figure 5, bottom) for Si in NMP.

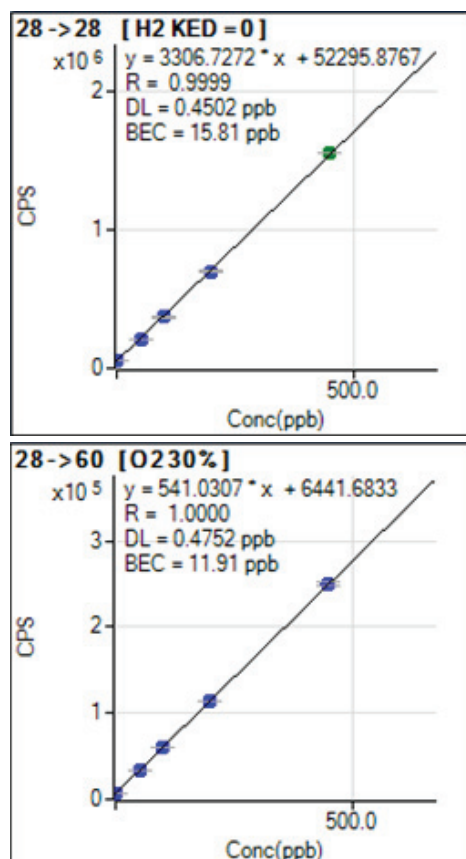
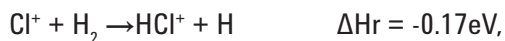


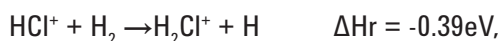
Figure 5. Calibration plots for Si in NMP. Top: H₂ on-mass method (Q1=Q2=28). Bottom: O₂ mass-shift method (Q1=28, Q2=60)

Cl in NMP

Cl⁺ reacts with H₂ exothermically to form HCl⁺ as shown below. HCl⁺ continues to react via a chain reaction to form H₂Cl⁺. Preliminary tests showed the reaction is more efficient than the reaction with O₂ to form ClO⁺, so the H₂ mass-shift method (Q1=35, Q2=37) was applied to the measurement of Cl in NMP.



$$k_r = 9.2 \times 10^{-10} \text{ cm}^3/\text{s}/\text{molecule}$$



$$k_r = 1.3 \times 10^{-9} \text{ cm}^3/\text{s}/\text{molecule}$$

Figure 6 (top) shows calibration plots obtained for Cl in NMP using the H₂ mass-shift method. The plot obtained using the O₂ mass-shift method (Figure 6, bottom) is also shown for comparison. A slightly better BEC of 34.2 ppb was achieved for Cl in NMP using the H₂ mass-shift method.

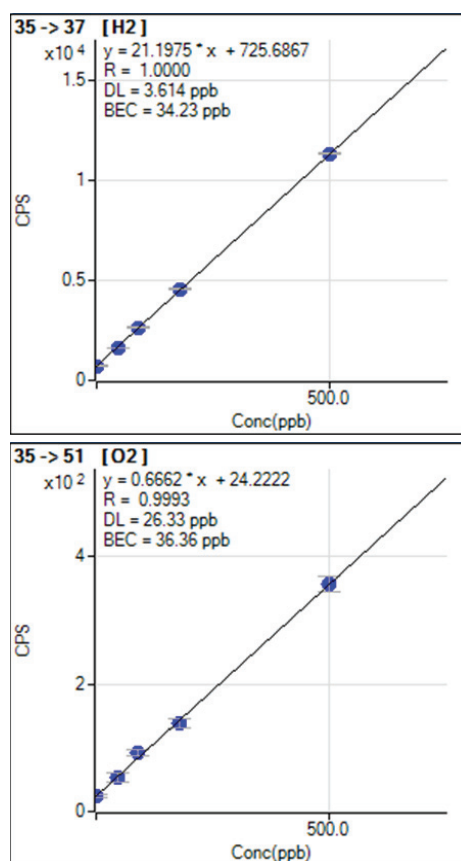


Figure 6. Calibration plots for Cl in NMP. Top: H₂ mass-shift method (Q1=35, Q2=37). Bottom: O₂ mass-shift method (Q1=35, Q2=51)

Table 4 summarizes the BECs achieved for each analyte by the various approaches. Only the lowest BEC achieved for each analyte is shown. In every case, the mass-shift method proved to be superior to on-mass measurement, and O₂ cell gas was used for all analytes except Cl. Detection limits for all analytes except Cl were in the mid to low ppt range. The limiting factor for Cl is its very low degree of ionization; nevertheless, low ppb detection limits were obtained. For routine analysis, an automated method can be set to measure all analytes with a single visit to the sample vial.

Table 4. Summary of BECs and DLs in NMP

| Element | Method | Q1 | Q2 | Product ion | BEC ppb | DL ppb |
|---------|---------------------------|----|----|-------------------------------|---------|--------|
| P | O ₂ mass-shift | 31 | 47 | PO ⁺ | 0.55 | 0.06 |
| S | O ₂ mass-shift | 32 | 48 | SO ⁺ | 5.47 | 0.25 |
| Si | O ₂ mass-shift | 28 | 60 | SiO ₂ ⁺ | 11.9 | 0.48 |
| Cl | H ₂ mass-shift | 35 | 37 | ClH ₂ ⁺ | 34.2 | 3.61 |

Conclusions

S, P, Si and Cl are all challenging elements for quadrupole ICP-MS. The measurement of these elements becomes even more difficult in organic matrices such as NMP. However the Agilent 8800 Triple Quad ICP-MS, using the mass-shift method with the unique MS/MS mode, was able to achieve low BECs for all analytes, demonstrating the flexibility and capability of ICP-QQQ in solving the most difficult challenges in ICP-MS.

References

1. Agilent 8800 Triple Quadrupole ICP-MS: Understanding oxygen reaction mode in ICP-MS/MS, Agilent publication 5991-1708EN.
2. Gas phase ion-molecule reaction rate constants through 1986, Yasumasa Ikezo, Shingo Matsuoka, Masahiro Takebe and Albert Viggiano, Maruzen Company Ltd.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2013

Published April 19, 2013

Publication number: 5991-2303EN



Agilent Technologies