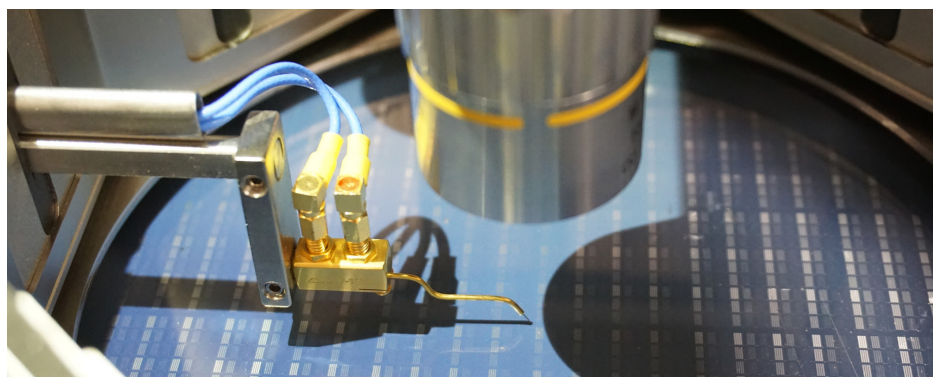


Automated Analysis of Ultratrace Elemental Impurities in Isopropyl Alcohol

Online calibration using the IAS Automated Standard Addition System (ASAS)



Authors

Kazuhiro Sakai and Katsuo Mizobuchi
Agilent Technologies, Japan

Riro Kobayashi
IAS Inc, Japan

Introduction

Contamination control is critical in the semiconductor industry. Inorganic impurities are of particular concern, as they affect the electrical properties of the insulating and conducting layers from which semiconductor devices are made. Trace element contamination during wafer fabrication can therefore reduce the manufacturing yield and operational reliability of semiconductor devices. To minimize contamination, process chemicals must be monitored for ultratrace (ng/L; ppt) levels of elemental impurities.

Isopropyl alcohol (IPA) is an important organic solvent used in semiconductor manufacturing to remove organic and metallic residues and impurities from the surface of silicon wafers. Since IPA comes into direct contact with the wafer surface, the concentration of trace metals present in the solvent should be extremely low. For high purity Grade 4 IPA, SEMI standard C41-0705 specifies a maximum contaminant level of 100 ppt for each element (1). Delivering accurate analysis at these low concentrations requires a highly sensitive analytical instrument, together with a suitable clean laboratory environment, and advanced sample handling skills. Modern ICP-MS systems include predefined settings and auto-optimization routines

to simplify operation. But the sample preparation, sample processing, and calibration steps still require a highly skilled analyst. Automating these steps would simplify the method, reducing the level of skill required for analysts to reliably perform the analysis.

Agilent ICP-MS systems can be integrated with various automated sample introduction systems, depending on a laboratory's requirements. Systems are available that automate a range of sample handling steps such as dilution, acidification, spiking, and calibration. One of the simplest, easiest-to-use and most cost-effective systems for automating semiconductor sample handling is the Automated Standard Addition System (ASAS) from IAS Inc. The ASAS can automatically add online spikes to generate a method of standard additions (MSA) or external calibration curve. In addition to simplifying the analysis, the automated sample introduction system decreases manual sample handling, reducing errors, and lowering the potential for sample contamination.

In this study, trace element impurities in IPA were quantified by online MSA using an IAS ASAS (Tokyo, Japan) and Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ). The method allows the accurate and reliable quantification of ultratrace level impurities in IPA without requiring a highly skilled analyst.

Experimental

Reagents and samples

High purity IPA was prepared for analysis by distilling electronic-grade IPA in the lab. The IPA samples were introduced into the ICP-QQQ undiluted, to minimize the risk of contamination and to achieve the lowest possible detection limits (DLs).

A 1 µg/L (ppb) mixed multi-element standard solution was used to create the MSA calibration spikes. The working standard solution was prepared by diluting a 10 ppm mixed multi-element standard (SPEX CertiPrep, Metuchen, NJ, US) with distilled IPA. To stabilize the spiked elements, nitric acid (68% ultrapure HNO₃) was added to the IPA samples at a final acid concentration of 1%.

The 1 ppb working standard solution was placed into a clean sample bottle and connected to the standard line of the ASAS. All MSA calibration (spike) solutions required for the analysis were automatically prepared and added online by the ASAS. Spike concentrations of 0, 5, 10, 20, and 50 ppt were added to the IPA sample. The sample preparation and analysis steps were performed in a Class 10,000 clean-room.

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ instrument was used. The instrument was fitted with a glass concentric nebulizer (G1820-65138) self-aspirating with PFA sample tubing (G1820-65478; 0.3 mm id, 1.6 mm od).

A Peltier-cooled quartz spray chamber, quartz torch, platinum-tipped sampling and skimmer cones, and s-lens were used.

When organic solvents are analyzed, carbon in the sample aerosol can be deposited on the sampling cone, causing instability and signal drift. To prevent carbon deposition during the analysis of solvents such as IPA, oxygen is added to the carrier gas to oxidize the carbon in the plasma. Volatile organic solvents also cause a very high solvent vapor pressure in the spray chamber, leading to plasma instability. To reduce solvent vapor pressure and ensure reliable plasma ignition and operation, the spray chamber temperature is reduced to below zero degrees. In this work, the spray chamber was cooled to -5 °C using the Peltier device that is standard on all Agilent ICP-MS systems. For stable operation of the plasma, a torch with a narrow (1.5 mm) injector replaced the standard 2.5 mm injector torch.

Combining cool plasma with collision/reaction cell (CRC) operation has been shown to be a powerful mode for interference removal in ICP-MS (2). These conditions can also be used for the analysis of organic solvent samples, but such samples require more plasma energy to decompose the organic matrix. The analyst must balance reducing the plasma temperature enough to control the ionization of interfering species, while maintaining sufficient energy to decompose the matrix. With Agilent ICP-MS systems, the ShieldTorch System provides effective reduction of the plasma potential, so ionization of polyatomic ions is minimized, even at higher forward power. "Cool plasma" conditions provide better robustness and matrix tolerance on Agilent ICP-MS systems than on systems that do not have such effective control of plasma potential.

Furthermore, all Agilent ICP-MS systems have two separate gas controls contributing to the total "carrier" gas flow passing through the central, injector tube. The nebulizer gas flow (the flow that passes through the nebulizer and aspirates the sample) is adjusted to give optimum sample aspiration. The make-up gas flow is then optimized to control the total carrier gas flow that transports the sample aerosol through the central channel of the plasma. This total carrier flow, combined with the plasma power and sampling depth, determines the "coolness" of the plasma conditions.

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits for each analyte. Laboratories measuring ultratrace levels of contaminant metals often use a multitune method, where several tuning steps are applied sequentially during the measurement of each solution. This approach allows the tuning conditions to be optimized for the removal of different

types of interferences, while maintaining sensitivity for each analyte. In this work, several reaction cell gases (He, H₂, O₂, and NH₃) were used for the analytes being measured.

Instrument tuning conditions are shown in Table 1 and other acquisition parameters are shown in Table 2.

Table 1. Agilent 8900 ICP-QQQ operating conditions.

| | H ₂ (cool plasma*) | NH ₃ (cool plasma*) | O ₂ He | H ₂ | He | No gas |
|---|-------------------------------|--------------------------------|-------------------|----------------|-----|--------|
| Scan type | MS/MS | | | | | |
| RF power (W) | 1500 | | | | | |
| Sampling depth (mm) | 18.0 | | | | | |
| Nebulizer gas flow rate (L/min) | 0.70 | | | | | |
| 20% O ₂ Ar balance gas flow rate (L/min) | 0.30 (30%)** | | | | | |
| Spray chamber temp (°C) | -5.0 | | | | | |
| Make-up gas flow rate (L/min) | 0.80 | 0.70 | 0.50 | | | |
| Extract 1 (V) | -100 | | | | | |
| Extract 2 (V) | -10.0 | | | | | |
| Omega bias (V) | -70.0 | | | | | |
| Omega lens (V) | 4.0 | | | | | |
| Q1 entrance (V) | -50.0 | | | | | |
| He cell gas flow rate (mL/min) | - | 1.0 | 12.0 | - | 5.0 | - |
| H ₂ cell gas flow rate (mL/min) | 5.0 | - | - | 10.0 | - | - |
| NH ₃ cell gas flow rate (mL/min)*** | - | 2 (20%)** | - | - | - | - |
| O ₂ cell gas flow rate (mL/min) | - | - | 0.075 (5%)** | - | - | - |
| OctP bias (V) | -18 | -5 | -3 | -30 | -20 | -10 |
| Axial acceleration (V) | 1.0 | | | 0 | | |
| Energy discrimination (V) | 0 | -10 | | | 3 | |

Table 2. Acquisition parameters.

| Parameter | Setting |
|----------------------|------------------------------------|
| Q2 peak pattern | 1 point |
| Replicates | 3 (spiked samples) |
| | 10 (unspiked sample) |
| Sweeps/replicate | 10 |
| Integration time (s) | 1 (all elements except phosphorus) |
| | 10 (phosphorus) |

* Optimum cool plasma conditions were achieved by adjusting the make-up gas flow while maintaining a high forward power setting.

** Values in parentheses are % of the maximum flow of the gas controller, as displayed in the tuning pane of ICP-MS MassHunter.

*** 10% NH₃ balanced with 90% He

Automated Standard Addition System (ASAS)

The IAS ASAS is an automated online sample processing device. It uses a precise, microflow syringe pump to add specific volumes of spike solutions or diluent to the sample flow as it passes to the ICP-MS nebulizer. The small footprint of the ASAS allows it to be easily positioned between the autosampler and ICP-MS, as shown in Figure 1. This arrangement is beneficial in the small workspace typically available in semiconductor clean-rooms. Once connected in line, the ASAS can be used to automatically generate a calibration curve using either external standards or MSA.

MSA calibrations have the advantage of exact matrix matching, since the calibration is created in the actual sample matrix. However, conventional manual MSA spiking is often regarded as complicated and time-consuming. With automatic spike additions using ASAS, the complexity is eliminated. Also, the Agilent ICP-MS MassHunter software allows an MSA calibration in one sample to be automatically converted to an external calibration. This function allows other samples of the same type to be run against the MSA calibration, without requiring the subsequent samples to be spiked individually. With these two improvements, MSA can be as fast and easy to run as conventional external calibration.

Spike recoveries are typically carried out as a routine performance check during semiconductor chemical analysis. This can be automated to simplify and speed up the analysis. The ASAS microvolume syringe pump adds the spike to the continuously flowing sample stream, so the risk of sample contamination and errors is minimized.

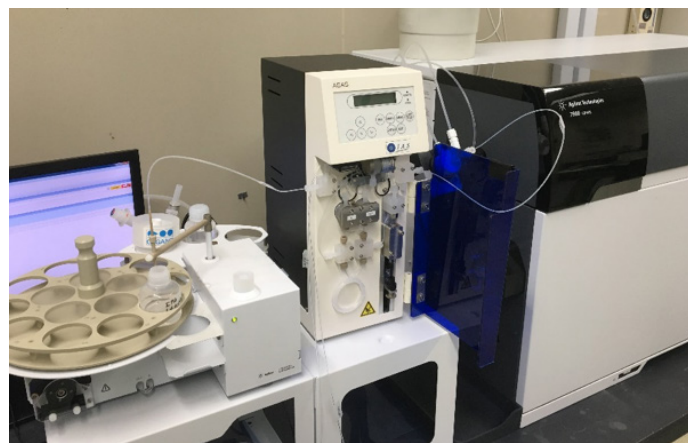
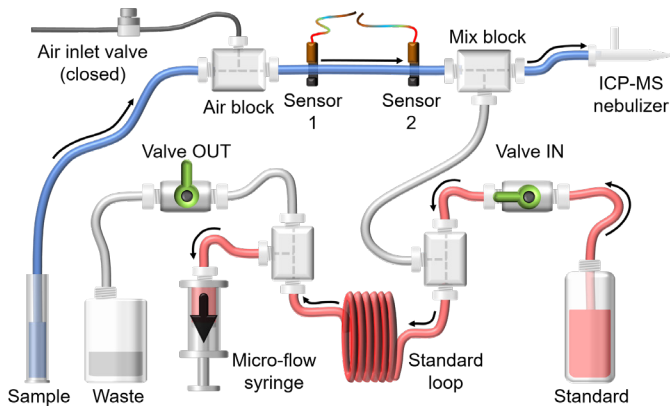


Figure 1. An Agilent ICP-MS fitted with an IAS ASAS automated standard addition system and the Agilent I-AS integrated autosampler.

ASAS operation consists of the following four steps:

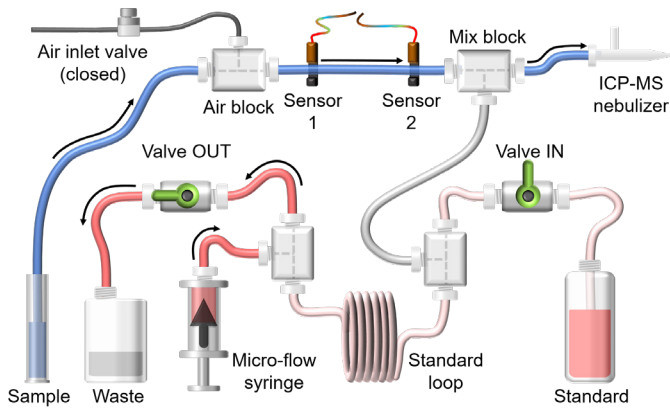
Step 1: Loop is filled with the standard solution.

“Valve IN” in the standard line opens and the syringe pump activates. This loads the standard solution along a dedicated uptake line from the standard bottle to the loop.



Step 2: Excess standard solution is pumped to waste.

“Valve OUT” in the standard line opens, “Valve IN” closes, and the syringe pump discharges, pumping the remaining standard solution to the waste bottle—bypassing the loop.

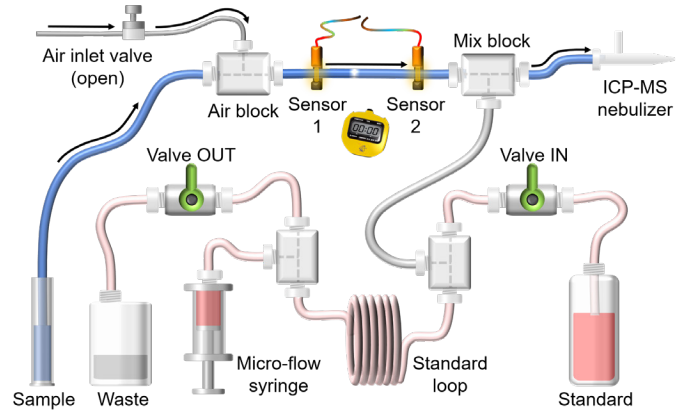


Step 3: Sample flow rate is measured to allow calculation of MSA spike volumes.

To minimize the potential for contamination from peristaltic pump tubing, high-purity samples are usually introduced using self aspiration. This means that the flow rate varies, depending on the sample viscosity and tubing length. To allow the MSA spike additions to be calculated accurately, the ASAS system first measures the sample flow rate, as follows:

- When the autosampler probe moves to the sample vial, it triggers measurement of the sample uptake rate.
- An air bubble is introduced via the “Air inlet valve”.

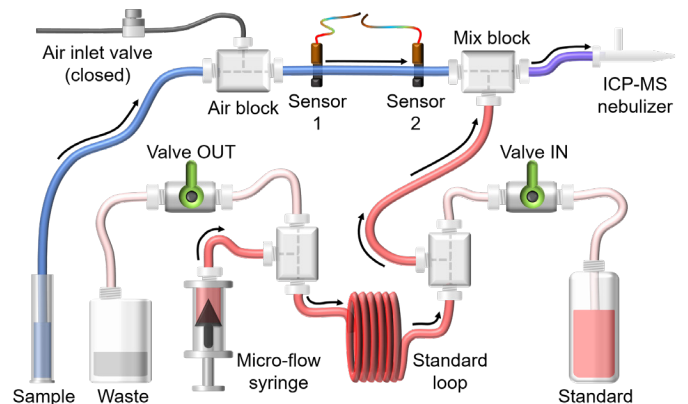
- Optical fiber sensors measure the elapsed time between the air bubble passing Sensor 1 and Sensor 2. The elapsed time is inversely proportional to the sample flow rate, allowing the actual solution flow rate to be calculated.



Step 4: MSA spikes are added automatically.

The syringe pump delivers the standard solution from the loop into the sample line via the “Mix Block”. The standard solution flow rate needed to give each of the required MSA spike levels is calculated automatically, as explained later in the worked example.

The MSA spike solution is mixed with the sample online and the spiked sample is passed to the ICP-MS nebulizer.



Worked example: Addition of a 50 ppt MSA spike to a sample flowing at 200 µL/min.

- A 1 ppb spike standard is prepared and placed in a sample bottle connected to the Standard line of the ASAS.
- The microflow syringe loads the spike standard into the ASAS loop via the dedicated uptake line.
- The autosampler moves to the next sample vial.

- The ASAS measures the sample uptake line flow rate (as previously outlined in Step 3). In this example, we will use a nominal flow rate of 200 $\mu\text{L}/\text{min}$.
- Based on the measured sample flow rate, the ASAS software calculates the flow rate of the 1 ppb stock standard required to give a 50 ppt spike concentration. In this case, to achieve a spike level of 50 ppt in the sample flow of 200 $\mu\text{L}/\text{min}$, the standard would need to be introduced at a flow rate of 10.0 $\mu\text{L}/\text{min}$ (20x dilution of the 1 ppb standard).
- The standard in the loop is added to the sample via the “Mix Block” at the calculated flow rate. The mixed, spiked sample then passes to the ICP-MS for analysis.

The ASAS can accurately add the standard solution at any flow rate between 0.10 and 99.99 $\mu\text{L}/\text{min}$. However, to avoid over diluting the sample, the recommended standard flow rate is between 1.00 and 10.00 $\mu\text{L}/\text{min}$. This assumes a typical nebulizer self-aspiration flow rate of 200 $\mu\text{L}/\text{min}$.

The volume of the ASAS microflow syringe is about 800 μL , and the loop volume is 700 μL . When the volume of the standard solution remaining in the syringe falls below a set value, the syringe is automatically refilled. This happens after the current set of standard additions has completed.

If the total volume of standard solution required for the spike additions exceeds the loop volume, the syringe automatically refills the loop to ensure continuous operation.

Integrating the ASAS with the Agilent 8900 ICP-QQQ offers the following advantages for ultratrace elemental analysis of semiconductor samples:

- Compatibility with the Agilent I-AS autosampler and self-aspirating nebulizers
- Compact, easy-to-use, online system
- Automated creation of MSA or external calibrations
- Automated spike addition for spike recovery studies
- The ASAS can also be installed as part of the IAS Continuous Chemical Samples Inspection (CSI) system. This system provides online monitoring of multiple streams, baths, and containers of semiconductor process chemicals.

Results and Discussion

DLs and BECs

In total, 47 elements—including all 22 elements specified in SEMI standard C41-0705—were measured using the 8900 ICP-QQQ. The instrument was operated in multiple tune modes, which were switched automatically during a single visit to each sample vial. Data for each of the modes was combined automatically into a single report for each sample. Detection Limits (DLs) and Background Equivalent Concentrations (BECs) in undiluted IPA are given in Table 3. The DLs were calculated from 3 x the standard deviation (SD) of 10 replicate measurements of the blank (unspiked) IPA sample. The DLs and BECs for all SEMI required elements (shown in bold) were all well below the grade 4 requirements of 100 ppt; many were below 0.1 ppt. These results illustrate how the 8900 ICP-QQQ provides performance that ensures compliance with higher chemical purities that will be required for semiconductor manufacturing in the future. DLs and BECs for Hf and Re could not be calculated, as the measured background signal was zero counts per second in all replicates of the blank IPA. The BEC for Cu reported using the normal, preferred isotope of Cu-63 was unexpectedly high, at 6.4 ppt. This result was compared to the BEC measured using the secondary isotope, ^{65}Cu , and the two measured concentrations were in agreement. This suggests the high BEC observed using ^{63}Cu was due to trace Cu contamination in the IPA sample rather than any interference on ^{63}Cu .

The ASAS was used to perform an automatic spike recovery test. Ten separate IPA solutions were spiked at 20 ppt and measured against an external calibration that was created automatically by converting the MSA calibration. The spike recovery accuracy and repeatability (%RSD) results are also shown in Table 3. Excellent spike recoveries of between 91–108% were achieved for all elements at the 20 ppt level, and RSDs ($n=10$) were between 1.6 and 8.9%. The results show the excellent reproducibility of the ASAS spike additions, as well as the good stability of the 8900 ICP-QQQ when aspirating organic solvents. This demonstrates the suitability of the ASAS-ICP-QQQ method for the routine analysis of ppt-level contaminant elements in IPA.

Table 3. DLs, BECs, and spike recoveries in IPA. Analytes shown in bold are SEMI grade 4 elements.

| Analyte | Q1 | Q2 | Tune mode | DL (ng/L) | BEC (ng/L) | 20 ng/L Recovery (%) | 20 ng/L n=10 RSD (%) | SEMI standard C41-0705 Grade 4 (ng/L) |
|-----------|-----|-----|-------------------|-----------|------------|----------------------|----------------------|---------------------------------------|
| Li | 7 | 7 | *H ₂ | 0.010 | 0.040 | 99 | 2.4 | <100 |
| Be | 9 | 9 | No gas | 0.023 | 0.005 | 99 | 2.4 | |
| B | 11 | 11 | No gas | 1.2 | 12 | 96 | 8.0 | <100 |
| Na | 23 | 23 | *NH ₃ | 0.060 | 0.97 | 109 | 5.7 | <100 |
| Mg | 24 | 24 | *NH ₃ | 0.020 | 0.082 | 102 | 2.7 | <100 |
| Al | 27 | 27 | *NH ₃ | 0.042 | 0.16 | 100 | 2.8 | <100 |
| P | 31 | 47 | O ₂ He | 2.6 | 43 | 99 | 7.9 | <16,000** |
| K | 39 | 39 | *NH ₃ | 0.64 | 1.1 | 107 | 4.9 | <100 |
| Ca | 40 | 40 | *NH ₃ | 0.19 | 0.62 | 108 | 4.7 | <100 |
| Ti | 48 | 64 | O ₂ He | 0.23 | 1.3 | 99 | 2.4 | <100 |
| V | 51 | 67 | O ₂ He | 0.020 | 0.030 | 99 | 2.3 | <100 |
| Cr | 52 | 52 | *NH ₃ | 0.16 | 0.48 | 92 | 1.7 | <100 |
| Mn | 55 | 55 | *NH ₃ | 0.030 | 0.030 | 102 | 2.4 | <100 |
| Fe | 56 | 56 | *NH ₃ | 0.16 | 0.72 | 101 | 2.5 | <100 |
| Co | 59 | 59 | He | 0.020 | 0.020 | 99 | 2.1 | |
| Ni | 60 | 60 | He | 0.43 | 0.80 | 101 | 2.0 | <100 |
| Cu | 63 | 63 | O ₂ He | 0.38 | 6.4 | 97 | 2.3 | <100 |
| Zn | 64 | 64 | He | 0.71 | 0.72 | 98 | 6.9 | <100 |
| Ga | 71 | 71 | O ₂ He | 0.013 | 0.005 | 100 | 2.8 | |
| Ge | 74 | 74 | He | 0.30 | 0.070 | 96 | 8.1 | |
| As | 75 | 91 | O ₂ He | 0.41 | 0.26 | 108 | 2.7 | <100 |
| Rb | 85 | 85 | H ₂ | 0.17 | 0.59 | 101 | 2.4 | |
| Sr | 88 | 88 | O ₂ He | 0.005 | 0.002 | 98 | 2.4 | |
| Zr | 90 | 106 | O ₂ He | 0.030 | 0.020 | 99 | 2.7 | |
| Nb | 93 | 93 | H ₂ | 0.14 | 0.41 | 102 | 4.0 | |
| Mo | 98 | 130 | O ₂ He | 0.17 | 0.11 | 103 | 4.1 | |
| Ru | 101 | 101 | He | 0.080 | 0.03 | 99 | 2.9 | |
| Rh | 103 | 103 | O ₂ He | 0.070 | 0.18 | 99 | 2.1 | |
| Pd | 105 | 105 | O ₂ He | 0.070 | 0.040 | 100 | 2.5 | |
| Ag | 107 | 107 | O ₂ He | 0.014 | 0.006 | 97 | 2.6 | |
| Cd | 111 | 111 | O ₂ He | 0.035 | 0.004 | 98 | 4.0 | <100 |
| In | 115 | 115 | O ₂ He | 0.012 | 0.008 | 99 | 1.8 | |
| Sn | 118 | 118 | O ₂ He | 0.058 | 0.034 | 100 | 4.9 | <100 |
| Sb | 121 | 121 | O ₂ He | 0.056 | 0.009 | 103 | 2.3 | <100 |
| Te | 125 | 125 | O ₂ He | 0.78 | 0.29 | 97 | 8.9 | |
| Cs | 133 | 133 | *H ₂ | 0.060 | 0.022 | 96 | 4.2 | |
| Ba | 138 | 138 | O ₂ He | 0.009 | 0.004 | 99 | 2.4 | <100 |
| Hf | 178 | 178 | He | 0.000 | 0.000 | 105 | 5.1 | |
| W | 182 | 214 | O ₂ He | 0.21 | 0.049 | 97 | 5.7 | |
| Re | 185 | 185 | O ₂ He | 0.000 | 0.000 | 96 | 3.0 | |

Table continues.

Table continued.

| Analyte | Q1 | Q2 | Tune mode | DL (ng/L) | BEC (ng/L) | 20 ng/L Recovery (%) | 20 ng/L n=10 RSD (%) | SEMI standard C41-0705 Grade 4 (ng/L) |
|-----------|-----|-----|-------------------|-----------|------------|----------------------|----------------------|---------------------------------------|
| Ir | 193 | 193 | No gas | 0.060 | 0.006 | 101 | 6.7 | |
| Pt | 195 | 195 | O ₂ He | 0.51 | 0.45 | 100 | 3.0 | |
| Tl | 205 | 205 | O ₂ He | 0.018 | 0.008 | 99 | 2.1 | |
| Pb | 208 | 208 | O ₂ He | 0.047 | 0.042 | 100 | 2.7 | <100 |
| Bi | 209 | 209 | O ₂ He | 0.021 | 0.004 | 98 | 1.6 | |
| Th | 232 | 248 | O ₂ He | 0.11 | 0.022 | 97 | 4.6 | |
| U | 238 | 254 | O ₂ He | 0.18 | 0.048 | 91 | 6.6 | |

Resolving polyatomic interferences on Mg, Al, and Cr

In this work, high-power cool plasma conditions were combined with reaction cell gases to provide the most effective control of intense background and matrix-based interferences. Cool plasma conditions were obtained by adjusting the make-up gas flow, while maintaining plasma energy with normal "hot plasma" RF power of 1500 W. These plasma conditions ensured sufficient plasma robustness to allow long-term analysis of the organic matrix, while providing effective control of carbon-based interferences on analytes such as Mg, Al, and Cr (Table 4).

Table 4. Main interferences arising from organic solvent matrix.

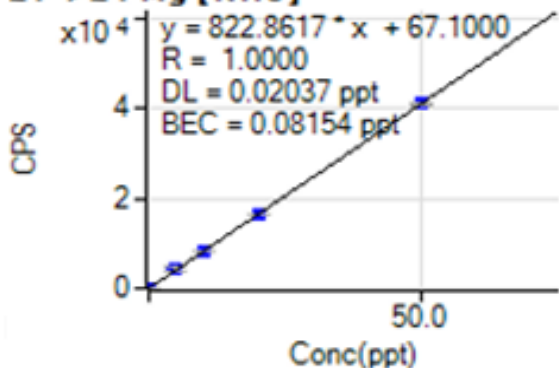
| Analyte | Interferences | DL (ng/L) | BEC (ng/L) |
|------------------|---|-----------|------------|
| ²⁴ Mg | ¹² C ₂ ⁺ | 0.020 | 0.082 |
| ²⁷ Al | ¹² C ¹⁵ N ⁺ , ¹³ C ¹⁴ N ⁺ , ¹² C ¹⁴ N ¹ H ⁺ | 0.042 | 0.16 |
| ³¹ P | ¹⁵ N ¹⁶ O ⁺ , ¹⁴ N ¹⁷ O ⁺ , ¹³ C ¹⁸ O ⁺ | 2.6 | 43 |
| ⁵² Cr | ⁴⁰ Ar ¹² C ⁺ | 0.16 | 0.48 |

The major isotope of magnesium, ²⁴Mg⁺, suffers an intense polyatomic interference from ¹²C₂⁺ in organic samples. Cool plasma conditions can suppress the ionization of C₂, and CRC mode can also be employed successfully to resolve the interference. In this work, the lowest DLs for Mg were achieved using a combination of high-power cool plasma conditions and on-mass measurement in MS/MS mode with NH₃ cell gas. The calibration curve for ²⁴Mg shows that the ¹²C₂⁺ interference was removed successfully, achieving a BEC less than 0.1 ng/L (ppt), and a detection limit of 0.020 ppt (Figure 2).

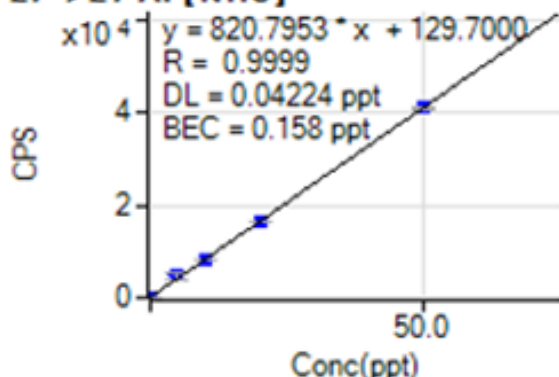
* High-power cool plasma conditions: the temperature of the plasma was adjusted by changing the make-up gas flow rate.

** < 16,000 ppt is the concentration limit for elemental P that is equivalent to the SEMI specified limit of 50 ppb (50,000 ppt) for PO₄.

24->24 Mg [NH3]



27->27 Al [NH3]



52->52 Cr [NH3]

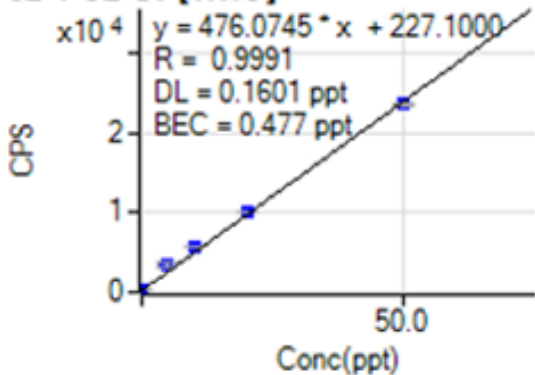


Figure 2. MSA calibration curves for ^{24}Mg , ^{27}Al , and ^{52}Cr .

The same approach was effective for the determination of other elements that suffer carbon-based polyatomic interference in organic solvents, such as ^{27}Al and ^{52}Cr . The calibrations shown in Figure 2 demonstrate that the interferences from $^{12}\text{C}^{15}\text{N}^+$, $^{13}\text{C}^{14}\text{N}^+$, $^{12}\text{C}^{14}\text{NH}^+$ on $^{27}\text{Al}^+$ and $^{40}\text{Ar}^{12}\text{C}^+$ on $^{52}\text{Cr}^+$ were minimized using high-power cool plasma conditions and NH_3 cell gas. These conditions gave BECs and DLs of 0.16 and 0.042 ppt for Al, and 0.48 and 0.16 ppt for Cr, respectively (Table 4).

P determination

SEMI Standard C41-0705 specifies the maximum concentration of phosphate allowed in high purity IPA, with a limit of 50 $\mu\text{g/L}$ (ppb) or 50,000 ppt. This limit equates to an elemental concentration of about 16,000 ppt for phosphorus (P).

The analysis of P in IPA needs an ORS cell mode that can resolve P from the normal plasma background polyatomic ions formed from N and O – $^{14}\text{N}^{16}\text{O}^+\text{H}^+$, $^{15}\text{N}^{16}\text{O}^+$, and $^{14}\text{N}^{17}\text{O}^+$. In addition, potential carbon-based interferences that overlap P^+ at m/z 31 must also be resolved. MS/MS mass shift operation with oxygen reaction cell gas has been shown to be suitable for the analysis of P. Using this method, the P^+ ions react with O_2 cell gas to form a reaction product ion PO^+ at m/z 47, mass-shifted away from the original on-mass interferences.

A previous study (3) demonstrated that a relatively high octopole bias (-3 V) with a mix of cell gases comprising 0.075 mL/min oxygen plus 12 mL/min helium could be used successfully for low-level analysis of P. The relative cell gas flow rates mean that the density of helium atoms in the cell is 160 (12/0.075) times greater than that of oxygen. Most of the ions entering the cell will therefore collide multiple times with helium atoms before they collide (and react) with an oxygen atom. Helium works as a buffer gas, reducing the kinetic energy of the ions before they react with the O_2 cell gas. This low collision energy should reduce the in-cell formation of certain unwanted reaction product ions, for example, $^{13}\text{C}^{18}\text{O}^+ + \text{O}_2 \rightarrow ^{13}\text{C}^{18}\text{O}^{16}\text{O}^+ + \text{O}$. Suppressing these reactions reduces the formation of interfering product ions that could overlap the analyte product ion $^{31}\text{P}^{16}\text{O}^+$ at m/z 47. Using these mixed cell gas conditions, a minimum BEC for P of 27 ppt in IPA was reported (3).

31->47 P [O2He]

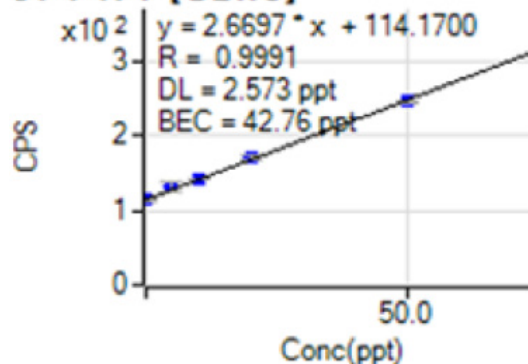


Figure 3. MSA calibration curve for ^{31}P .

The measurement conditions for P described in reference 3 were also used in this study. The calibration curve in Figure 3 shows good linearity from 5 to 50 ppt for P. The BEC was 43 ng/L (ppt) and the DL was 2.6 ppt (Table 3). Given the much higher typical contaminant levels for P compared to the other trace metals, it would be reasonable to calibrate P at a higher concentration level than the other elements. This modification could easily be applied to the ASAS methodology described here, if a higher P concentration was added to the working stock standard solution. The ASAS would then prepare and inject the online MSA spikes from the mixed standard, including the higher P spike levels. The upper limit for P defined in SEMI Grade 4 purity chemicals is also much higher than for the other trace elements. The relatively high BEC of 43 ppt is still several orders of magnitude lower than the 16,000 ppt concentration limit specified for P.

Conclusions

By automating the processes of sample preparation and standard spiking, the IAS ASAS automated-MSA system simplifies the elemental analysis of semiconductor process chemicals using the Agilent 8900 ICP-QQQ. The multi-element standard is prepared and connected to the ASAS, and the samples are loaded into the I-AS autosampler. The ASAS system then automatically performs all required steps, including online MSA spike additions and introduction of the sample to the ICP-QQQ.

Eliminating manual sample handling steps during ultratrace analysis lowers the risk of contamination. Limiting the handling of reagents and samples also reduces the likelihood of errors arising during the experimental procedure. Automating

calibration and spike addition leads to increased consistency and higher confidence in the quality of the results.

The Agilent 8900 ICP-QQQ was operated using optimized plasma conditions and MS/MS mode to measure 47 elements in IPA. BECs at sub-ppt to ppt levels were acquired for all analytes – including all the elements specified in SEMI C41-0705. The results easily meet the current SEMI grade 4 specifications for all elements, including P, in IPA.

The excellent spike recovery and repeatability results for all elements at the 20 ppt level show the suitability of the automated ASAS method for the routine analysis of semiconductor process chemicals. The long-term robustness of this method is enhanced by using high-power cool plasma conditions. These conditions provide superior matrix decomposition and improved analyte ionization in the presence of the organic solvent matrix.

References

1. SEMI C41-0705, Specifications and Guidelines for 2-Propanol, 2005.
2. J. Takahashi and K. Mizobuchi, Asia Pacific Winter Conference on Plasma Spectroscopy 2008.
3. K. Mizobuchi, N. Yamada and M. Yukinari, The Japan Society for Analytical Chemistry, 66th Nenkai, 2017.

www.agilent.com/chem/8900icp-ms

DE23358049

This information is subject to change without notice.

© Agilent Technologies, Inc. 2022
Printed in the USA, June 7, 2022
5994-0273EN