# Analysis of Organic Solvent Samples by Automatic Standard Addition Method using ASAS-ICP-MS/MS

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APWC 2017
Matsue
K-03

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## Introduction

- Elemental analysis of process chemicals at ultra-trace levels (ng/L; ppt) is a vital application to ensure the yield and operational reliability of semiconductor devices.
- Isopropyl alcohol (IPA) is used to remove organic and metallic residues and impurities from the surface of silicon wafers.
- Since IPA comes into direct contact with the wafer surface, it is necessary to control the concentration of trace metals present in the organic solvent.
- SEMI standard C41-0705 specifies a maximum contaminant level of less than 100 ppt for each element in high purity grade 4 IPA [1].
- Advanced analytical skills are required for the application.

In this study, impurities in IPA were quantified by Method of Standard Addition (MSA) using an Automatic Standard Addition System (ASAS) (IAS Inc. Japan) and triple quadrupole ICP-MS (ICP-MS/MS).

The method allows the quantification of ultra-trace level impurities in IPA regardless of the skill level of the analyst.

## Experimental

### Reagents and samples

- Sample: distilled IPA (Electronic Grade).
- Standard stock solution for MSA: a 1 µg/L (ppb) mixed multi-element standard solution was prepared by diluting a 10 ppm mixed multi-element standard solution :XSTC-7, XSTC-8 and XSTC-331(SPEX CertiPrep, NJ, US) with distilled IPA. Nitric acid (68% ultrapure $HNO_3$ (TAMAPURE-AA-10) ) was added to 1% to stabilize the spiked elements in the IPA sample.
- The stock solution was loaded on the ASAS.
- All target concentration solutions required for the analysis were automatically prepared by the ASAS.
- All preparation and analysis steps were performed in a Class 10,000 clean room.

### Instrumentation

- Standard Agilent 8900 Semiconductor configuration ICP-MS/MS instrument with s-lens equipped with:
  - A glass coaxial nebulizer.
  - Peltier cooled quartz spray chamber
  - Quartz torch (1.5 mm id)
  - Platinum-tipped sampling and skimmer cones

Tuning conditions are shown in Table 1, other acquisition parameters are shown in Table 2. A photo of the ASAS fitted to the ICP-MS/MS is shown in Figure 1.

Table 1. ICP-MS/MS operating conditions.

| | $H_2$ (MG0.8) | $NH_3$ | No gas | $H_2$ (MG0.5) | He | $O_2$ He |
|---|---|---|---|---|---|---|
| Scan type | MS/MS | | | | | |
| RF power (W) | 1500 | | | | | |
| Sampling depth (mm) | 18 | | | | | |
| Carrier gas flow rate (L/min) | 0.70 | | | | | |
| 20% $O_2$ Ar balance gas flow rate (L/min) | 0.30 (30 % of full scale) | | | | | |
| Spray chamber temp (°C) | -5 | | | | | |
| Makeup gas (MG) flow rate (L/min) | 0.80 | 0.70 | 0.50 | | | |
| He gas flow rate (mL/min) | - | 1 | - | - | 5 | 12 |
| $H_2$ gas flow rate (mL/min) | 5 | - | - | 10 | - | - |
| $NH_3$ gas flow rate (mL/min) | - | 2.0 (20%) | - | - | - | - |
| $O_2$ gas flow rate (mL/min) | - | - | - | - | - | 0.075 (5%) |
| OctP bias (V) | -18 | -5 | -10 | -30 | -20 | -3 |
| Axial acceleration (V) | 1 | | 0 | | | 1 |
| Energy discrimination (V) | 0 | -10 | 3 | -10 | 3 | -10 |

Table 2. Acquisition parameters.

| Parameter | Setting |
|---|---|
| Q2 peak pattern | 1 point |
| Replicates | 3 (spiked solution) |
| | 10 (unspiked solution) |
| Sweeps/replicate | 10 |
| Integration time | Phosphorus: 10 sec, all other elements: 1 sec |

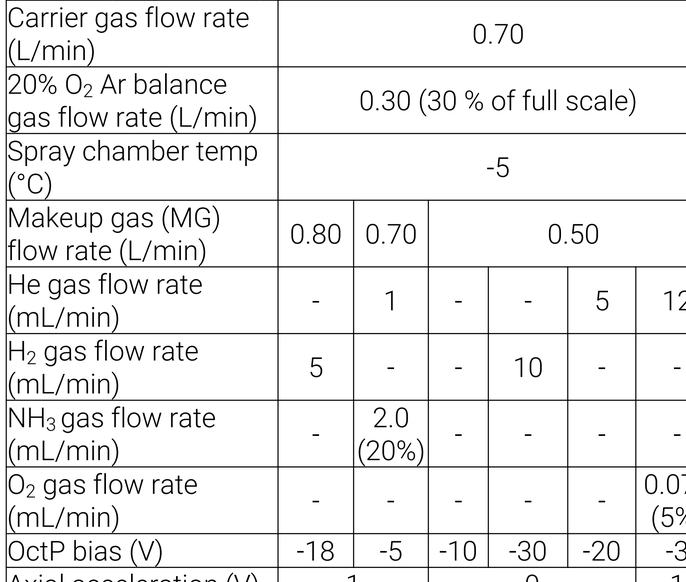


Figure 1. ASAS-ICP-MS/MS.

## Experimental

### Automated Standard Addition System (ASAS)

The operation of the IAS Automated Standard Addition System (ASAS) is described in the working example and in Figure 2.

**Working example: How to add a 50 ppt spike to the sample?**

- Prepare a 1 ppb standard stock solution for MSA.
- When the autosampler probe moves to one of the vials, it triggers the automatic measurement of the sample uptake rate using two flow sensors.
- An air bubble is introduced from the valve labeled “Air Valve”.
- Optical fiber sensors then measure the time it takes for the air bubble to pass from Sensor 1 to Sensor 2. (The flow rate will be approximately 200 µL/min in self-aspiration mode).
- The ASAS software automatically calculates the flow rate of the 1 ppb stock standard required to achieve the 50 ppt spike level.
- The standard will be introduced to the sample via the “Mix Block” at the calculated flow rate by the syringe pump.

In this example, introducing a 1 ppb stock standard solution at 10.0 µL/min would equate to spiking the sample at the 50 ppt concentration level.

- The syringe pump delivers the standard solution from the loop into the sample line via the “Mix Block”. The appropriate flow rate is calculated automatically, as explained in the working example. The MSA solution is then introduced into the plasma of the ICP-MS using a nebulizer operating in self-aspiration mode.

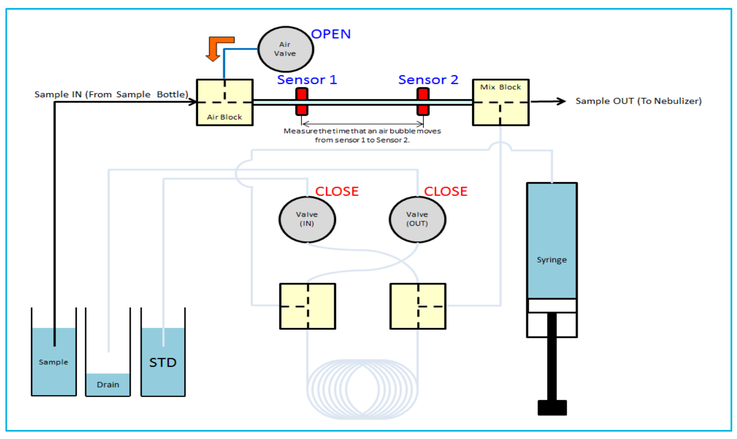


Figure 2. Operation of the ASAS.

## Results and Discussion

### DLs and BECs

- 48 elements were measured in IPA using the 8900 operating in multiple tune modes.
- Quantitative results and DLs for SEMI and non-SEMI specified elements are shown in Table 4.
- Each detection limit was calculated as 3-sigma of 10 replicate measurements of a blank IPA sample.

### Mg, Al, and Cr determination

Combining cool plasma with CRC technology is a powerful mode for interference removal [2].

In this study, a more robust warm plasma was used and a small amount of oxygen gas was mixed with argon gas to decompose the carbon matrix thus avoiding carbon deposition on the interface cones.

Because the major isotope of $^{24}Mg^+$ suffers an interference from $^{12}Cr^{12}C$ in organic samples, Mg was determined using a warm plasma with $NH_3$ cell gas.

- The calibration curve for $^{24}Mg$ shows that $^{12}C^{12}C^+$ interference was removed successfully.
- BEC for Mg: 0.082 ng/L (ppt).
- DL for Mg: 0.020 ppt (Table 3).

The same approach was effective for the determination of other interfered elements such as $^{27}Al$ and $^{52}Cr$.

### P determination

In this study, the same measurement conditions proposed by Mizobuchi et al were used for P ($He+O_2$ mode) [4].

- The calibration curve in Figure 3 shows good linearity from 5 to 50 ppt for P.
- BEC for P: 43 ng/L (ppt).
- DL for P: 2.6 ppt (Table 3).

Table 3. Main interferences in organic solvents.

| Analyte | Interferences | DL (ng/L) | BEC (ng/L) |
|---|---|---|---|
| $^{24}Mg$ | $^{12}Cr^{12}C^+$ | 0.020 | 0.082 |
| $^{27}Al$ | $^{12}C^{15}N^+$, $^{13}C^{14}N^+$, $^{12}C^{14}N^1H^+$ [3] | 0.042 | 0.16 |
| $^{52}Cr$ | $^{40}Ar^{12}C^+$ | 0.16 | 0.48 |
| $^{31}P$ | $^{15}N^{16}O^+$, $^{14}N^{17}O^+$, $^{13}C^{18}O^+$ | 2.6 | 43 |

## Results and Discussion

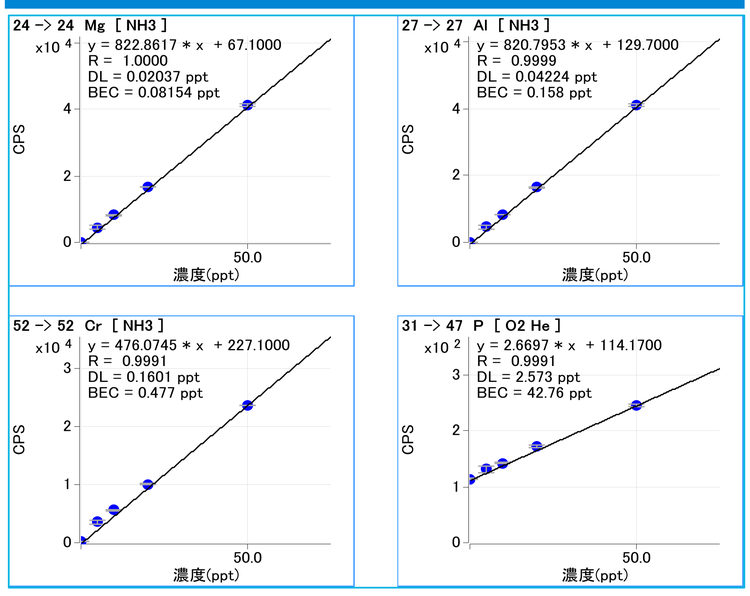


Figure 3. MSA calibration curves for $^{24}Mg$, $^{27}Al$, $^{52}Cr$, $^{31}P$.

Table 4. DLs and BECs 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(%) |
|---|---|---|---|---|---|---|
| Li | 7 | 7 | $H_2$ (MG0.8) | 0.010 | 0.040 | 99 |
| Be | 9 | 9 | No gas | 0.023 | 0.005 | 99 |
| B | 11 | 11 | No gas | 1.2 | 12 | 96 |
| Na | 23 | 23 | $NH_3$ | 0.060 | 0.97 | 109 |
| Mg | 24 | 24 | $NH_3$ | 0.020 | 0.082 | 102 |
| Al | 27 | 27 | $NH_3$ | 0.042 | 0.16 | 100 |
| P | 31 | 47 | $O_2$ He | 2.6 | 43 | 99 |
| K | 39 | 39 | $NH_3$ | 1.6 | 2.7 | 107 |
| Ca | 40 | 40 | $NH_3$ | 0.19 | 0.62 | 108 |
| Ti | 48 | 64 | $O_2$ He | 0.23 | 1.3 | 99 |
| V | 51 | 67 | $O_2$ He | 0.020 | 0.030 | 99 |
| Cr | 52 | 52 | $NH_3$ | 0.16 | 0.48 | 92 |
| Mn | 55 | 55 | $NH_3$ | 0.030 | 0.030 | 102 |
| Fe | 56 | 56 | $NH_3$ | 0.16 | 1.1 | 101 |
| Co | 59 | 59 | He | 0.020 | 0.020 | 99 |
| Ni | 60 | 60 | He | 0.43 | 0.80 | 101 |
| Cu | 63 | 63 | $O_2$ He | 0.38 | 6.4 | 97 |
| Zn | 64 | 64 | He | 0.71 | 0.72 | 98 |
| Ga | 71 | 71 | $O_2$ He | 0.013 | 0.005 | 100 |
| Ge | 74 | 74 | He | 0.30 | 0.070 | 96 |
| As | 75 | 91 | $O_2$ He | 0.41 | 0.26 | 108 |
| Sr | 88 | 88 | $O_2$ He | 0.005 | 0.002 | 98 |
| Zr | 90 | 106 | $O_2$ He | 0.030 | 0.020 | 99 |
| Nb | 93 | 93 | $H_2$ (MG0.5) | 0.14 | 0.41 | 102 |
| Mo | 98 | 130 | $O_2$ He | 0.17 | 0.11 | 103 |
| Ru | 101 | 101 | He | 0.080 | 0.03 | 99 |
| Rh | 103 | 103 | $O_2$ He | 0.070 | 0.18 | 99 |
| Pd | 105 | 105 | $O_2$ He | 0.070 | 0.040 | 100 |
| Ag | 107 | 107 | $O_2$ He | 0.014 | 0.006 | 97 |
| Cd | 111 | 111 | $O_2$ He | 0.035 | 0.004 | 98 |
| In | 115 | 115 | $O_2$ He | 0.012 | 0.008 | 99 |
| Sn | 118 | 118 | $O_2$ He | 0.058 | 0.034 | 100 |
| Sb | 121 | 121 | $O_2$ He | 0.056 | 0.009 | 103 |
| Te | 125 | 125 | $O_2$ He | 0.78 | 0.29 | 97 |
| Cs | 133 | 133 | $H_2$ (MG0.8) | 0.060 | 0.022 | 96 |
| Ba | 138 | 138 | $O_2$ He | 0.009 | 0.004 | 99 |
| Hf | 178 | 178 | He | 0.000 | 0.000 | 105 |
| Ta | 181 | 213 | $O_2$ He | 0.033 | 0.009 | 96 |
| W | 182 | 214 | $O_2$ He | 0.21 | 0.049 | 97 |
| Re | 185 | 185 | $O_2$ He | 0.000 | 0.000 | 96 |
| Ir | 193 | 193 | No gas | 0.060 | 0.006 | 101 |
| Pt | 195 | 195 | $O_2$ He | 0.51 | 0.45 | 100 |
| Au | 197 | 197 | $O_2$ He | 0.063 | 0.007 | 110 |
| Tl | 205 | 205 | $O_2$ He | 0.029 | 0.015 | 99 |
| Pb | 208 | 208 | $O_2$ He | 0.047 | 0.042 | 100 |
| Bi | 209 | 209 | $O_2$ He | 0.021 | 0.004 | 98 |
| Th | 232 | 248 | $O_2$ He | 0.11 | 0.022 | 97 |
| U | 238 | 254 | $O_2$ He | 0.18 | 0.048 | 91 |

## Conclusions

- By providing a high degree of automation, the Agilent 8900 ICPMS/MS fitted with IAS’s ASAS auto-MSA system simplifies the elemental analysis of semiconductor process chemicals.
- Eliminating manual tasks 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, leading to an increased confidence in the data quality.
- The elements specified in SEMI C41-0705, including P were measured at sub-ppt to ppt levels in IPA. The results exceed current SEMI specifications for IPA.

## 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, 2014 74th Touronkai, E1009
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