

Analysis of Sulfuric Acid Using a Single Set of Operating Conditions with HR-ICP-MS

Julian D. Wills, Torsten Lindemann,
Thermo Fisher Scientific, Bremen,
Germany

Key Words

Mineral Acids, High Purity Samples, Semiconductor,
Sulfuric Acid

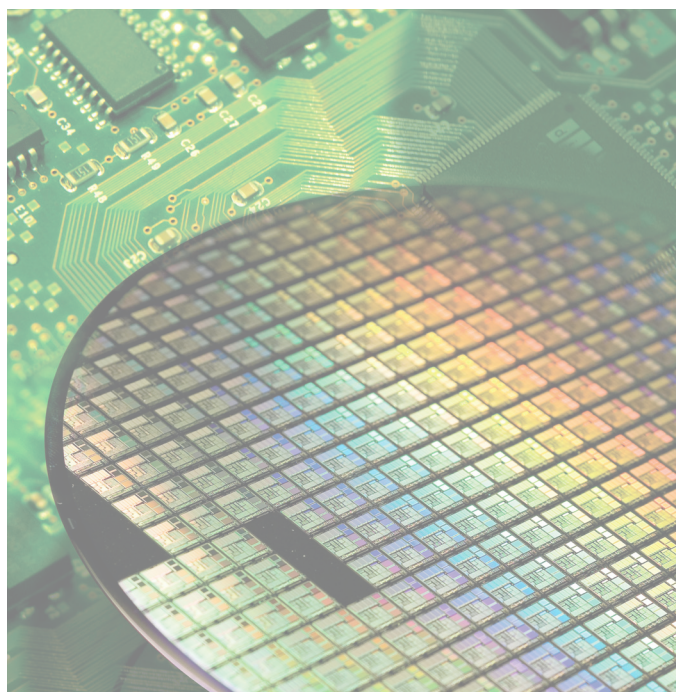
Goal

To demonstrate the ideal suitability of the Thermo Scientific™ ELEMENT 2™ High Resolution (HR) ICP-MS for trace metals analysis in high purity samples, related to the manufacture of semiconductors.

Introduction

With the continual decrease of geometries used in modern IC (integrated circuit) devices, the targeted trace metal content of process chemicals (high purity water, mineral acids, organic solvents etc) used in their production is moving to increasingly lower levels. Concentrated sulfuric acid (H_2SO_4) is used in the semiconductor industry to remove organic substances from the surface of silicon wafers. Since H_2SO_4 comes into contact with wafer surfaces, it is necessary to monitor trace elemental impurities in the acid to prevent any contamination in the wafer production.

High sulfur matrices are problematic in ICP-MS analysis due to the formation of interferences stemming from the matrix. This makes trace analysis of Ti, V, Cr and Zn particularly challenging.



HR-ICP-MS is based on magnetic sector field technology that physically separates the interference from the target analyte due to their small difference in mass. Mass resolution (R) settings of low (LR = 300), medium (MR = 4000) and high (HR = 10000) provide easy, visual method development for interference free analysis, even in the most challenging samples. High mass resolution was used to remove sulfur-based and other interferences for accurate and reliable analysis of ultra trace analytes in high purity grade H_2SO_4 .

ICP-MS Analysis of High Purity H₂SO₄

When developing a multi-elemental HR-ICP-MS method for the analysis of such high purity H₂SO₄ samples, the following problems should be considered:

PROBLEM

Sample preparation used for the lower quality grades is unsuitable for high purity H₂SO₄ due to the extensive sample handling and use of multiple reagents, all of which represent opportunities for contamination.

SOLUTION

Dilute and shoot! Dilute H₂SO₄ 1:10 m/m in high purity water and aspirate the 9.8% H₂SO₄ solution directly.

PROBLEM

1:10 diluted H₂SO₄ is an aggressive and viscous sample matrix and may have to be pumped to the nebulizer. Additionally, one (or more) internal standard(s) should be added to correct for matrix suppression. Both of these steps are possible sources of contamination that should be avoided, if possible.

SOLUTION

A robust, inert, non-contaminating sample introduction system (consisting of a self-aspirating low-flow PFA nebulizer, a Peltier-cooled PFA spray chamber, Pt injector and Pt tipped cones) allows 9.8% concentrations of H₂SO₄ to be aspirated reliably over long periods, without introducing any contamination. By performing an initial standard addition calibration, a matrix-matched calibration is possible and internal standards are not necessary.

PROBLEM

Cold plasma should be used to reduce backgrounds from easily ionizable elements (e.g. Na, K etc.) as well as instrument-derived backgrounds (e.g. Al, Ni and Pt from the sample introduction system and ICP-MS interface).

SOLUTION

The ELEMENT 2 HR-ICP-MS plasma interface provides a clean, non-background contributing sampling, such that typically cold plasma is not required in order to obtain sub pg·g⁻¹ detection limits. A single set of plasma parameters can therefore be used for the analysis of all elements using switching between appropriate resolutions to eliminate interferences (equivalent to switching between cell and non-cell mode with collision/reaction cell ICP-MS). Switching resolution is a process that takes only 1s, significantly faster than collision/reaction cell switching.

PROBLEM

Sulfur generates many of the most troublesome polyatomic interferences in ICP-MS with S-based species severely affecting isotopes of several elements, for example SN on Ti and SO₂ on Zn.

SOLUTION

Use high mass resolution! High resolution Sector Field ICP-MS (HR-ICP-MS) predictably and reliably removes S (and N, Cl, C, P, Ar, Ca etc) based interferences from the isotopes of interest by resolving their small difference in mass. The source of the interference is unimportant, as a single instrument setting (resolution) will remove all interferences independent of the source, whether it comes from the sample matrix or the 'normal' ICP interferences, thus guaranteeing absolute elemental accuracy.

Method

The Thermo Scientific ELEMENT 2 HR-ICP-MS was configured with a completely inert, acid-resistant sample introduction system:

- PFA μ Flow self-aspirating $100 \mu\text{L}\cdot\text{min}^{-1}$ nebulizer
- PFA Scott spray chamber, Peltier-cooled at 0°C
- Platinum injector
- Pt-tipped sample and skimmer cones

By cooling the spray chamber to 0°C (Figure 1), the solvent load in the plasma is reduced, and ionization in complex matrices is improved.

Please note, the Thermo Scientific ELEMENT 2 HR-ICP-MS was not installed in a clean room, but best practices for handling ultra high purity chemicals were followed, including using high purity acids and ultra pure water.

Concentrated H_2SO_4 was diluted 10-fold with ultra-pure water prior to analysis. One clean source of H_2SO_4 was analyzed 10 times to determine the limits of detection (LOD) and background equivalent concentrations (BEC) achievable for this analysis. A second source was analyzed once, then spiked with $5 \text{ pg}\cdot\text{g}^{-1}$ of a multielemental standard and analyzed 5 times to determine recovery.



Figure 1. Peltier-cooled PFA spray chamber for optimum sampling of high concentrations of mineral acids.

Results

All isotopes were measured accurately and efficiently using hot plasma conditions and interferences were removed through the use of the appropriate resolution setting. Sensitivity and selectivity achieved through HR-ICP-MS with a single set of operating conditions is detailed below.

Sensitivity

The Thermo Scientific ELEMENT 2 HR-ICP-MS, with a sensitivity of over $> 2 \text{ Mcps} / \text{ng}\cdot\text{g}^{-1}$ for a mid mass element and off peak noise of $< 0.2 \text{ cps}$ irrespective of mass, can reliably measure $\text{sub pg}\cdot\text{g}^{-1}$ concentrations in any semiconductor process chemical.

Figure 2 shows the standard addition curve obtained for ^{39}K in high resolution ($R=10000$) in $9.8\% \text{ m/m H}_2\text{SO}_4$ with calibration points at $1, 5$ and $10 \text{ pg}\cdot\text{g}^{-1}$. With over 2000 cps for $10 \text{ pg}\cdot\text{g}^{-1}$ of ^{39}K in such a complex matrix, a value of $300 \text{ fg}\cdot\text{g}^{-1}$ for K was returned for this sample – equivalent to $3 \text{ pg}\cdot\text{g}^{-1}$ in the undiluted sample, well below the SEMI Tier C maximum of $10 \text{ pg}\cdot\text{g}^{-1}$.

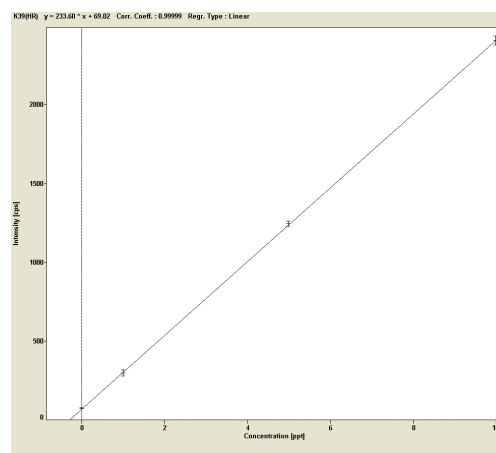


Figure 2. Calibration curve for ^{39}K (hot plasma, $R = 10000$) in $9.8\% \text{ m/m H}_2\text{SO}_4$ with calibration points at $1, 5$ and $10 \text{ pg}\cdot\text{g}^{-1}$.

Selectivity

The 'background' series of Ar based polyatomic interferences are well characterized and can be effectively reduced with collision/reaction cell based ICP-MS.

However, for any complicated sample with high concentrations of matrix elements, only Sector Field ICP-MS with its high mass resolution can predictably and reliably guarantee interference free analysis. For example, the S-based interferences stemming from the H_2SO_4 matrix on Ti and Zn, can easily be removed through the use of the appropriate mass resolution setting.

Medium resolution is able to separate the SN and SNH interferences on Ti at m/z 47 (Figure 3). High resolution is used to separate all the interferences that occur on the isotopes of Zn, an analyte which is difficult to accurately analyze in this matrix by other techniques. Figure 4a shows the mass spectra around the 64, 66, 67 and 68 isotopes of Zn ($R = 10000$) in 9.8% m/m H_2SO_4 spiked with $100 \text{ pg}\cdot\text{g}^{-1}$ of Zn, with Figure 4b spectra rescaled to show the baseline separation of Zn at each respective mass.

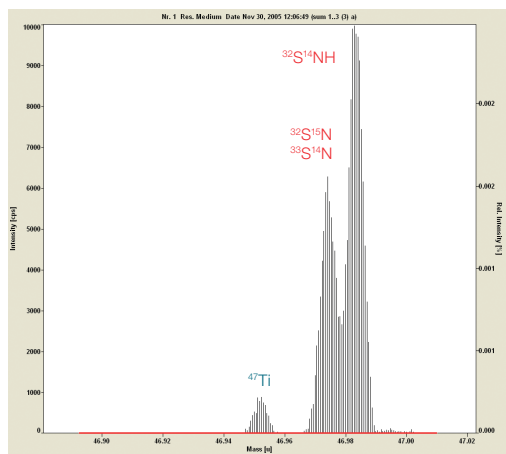


Figure 3. Mass spectrum in medium resolution ($R = 4000$) showing the ^{47}Ti isotope separated from the S based interferences in 9.8% H_2SO_4 .

The LOD and BEC calculated from 10 replicate analyses of 10% H_2SO_4 are shown for 21 elements in Table 1.

Background Equivalent Concentrations (BEC) for all 21 elements measured in 9.8% m/m H_2SO_4 are below $10 \text{ pg}\cdot\text{g}^{-1}$ and therefore meet the SEMI Tier C guideline of $100 \text{ pg}\cdot\text{g}^{-1}$ in concentrated H_2SO_4 . Of these, only 8 are above $1 \text{ pg}\cdot\text{g}^{-1}$.

The same 21 elements were spiked into another source of H_2SO_4 at $5 \text{ pg}\cdot\text{g}^{-1}$ and the recovery determined from 5 replicate measurements of the spiked sample.

For an analysis method to be accepted by SEMI, results of spike recovery experiments should agree to within 75 – 125% of the spiked value. The spike concentration for the recovery experiment should be at 50% of the specified concentration. Therefore for the analysis of SEMI Tier C H_2SO_4 (with guideline maximum concentrations of $100 \text{ pg}\cdot\text{g}^{-1}$ in the concentrated acid), the spike recovery should be made with concentrations of $5 \text{ pg}\cdot\text{g}^{-1}$ (taking into account the 10 fold dilution).

That data shows that spike recovery lies between 86 - 105% for all 21 elements, demonstrating very good analytical performance for this extremely low spike in this challenging sample.

Precisions for five replicate analyses of a $5 \text{ pg}\cdot\text{g}^{-1}$ spiked H_2SO_4 sample are all less than 10% RSD.

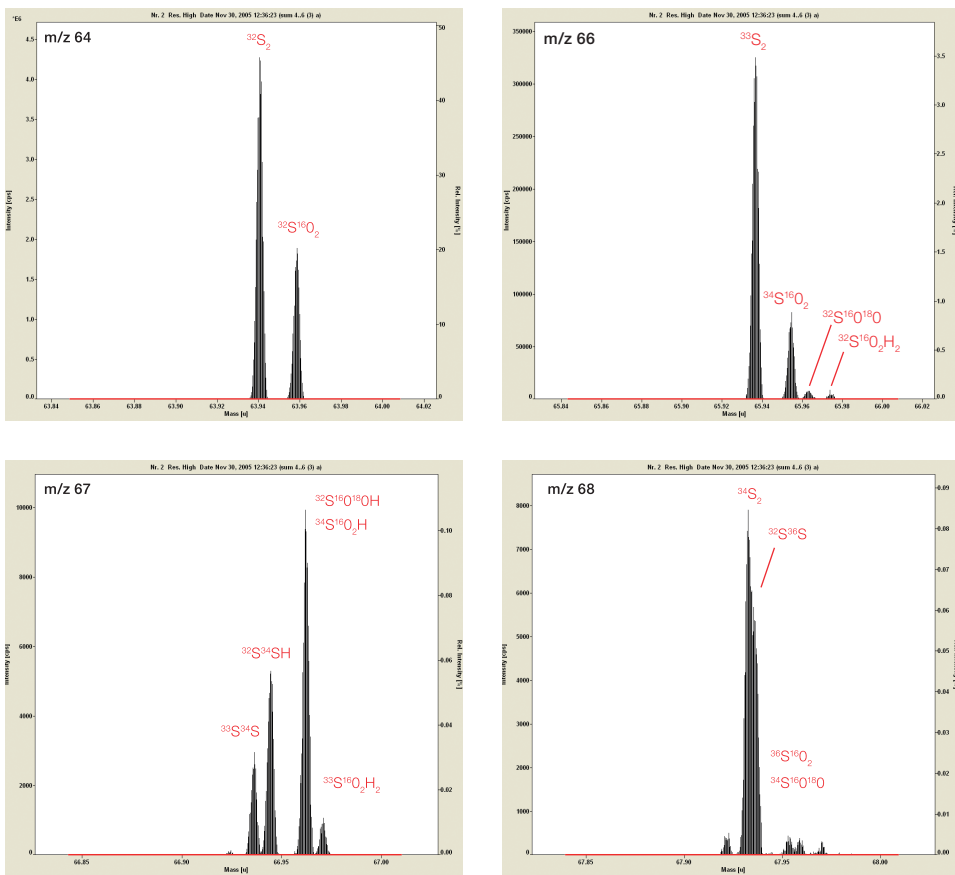


Figure 4a. High resolution ($R = 10000$) spectra of the Zn isotopes with the sensitivity scaled on the largest interference at each mass to show the variety in source and amount of interference that has to be removed at each of the Zn isotopes in 9.8% m/m H_2SO_4 .

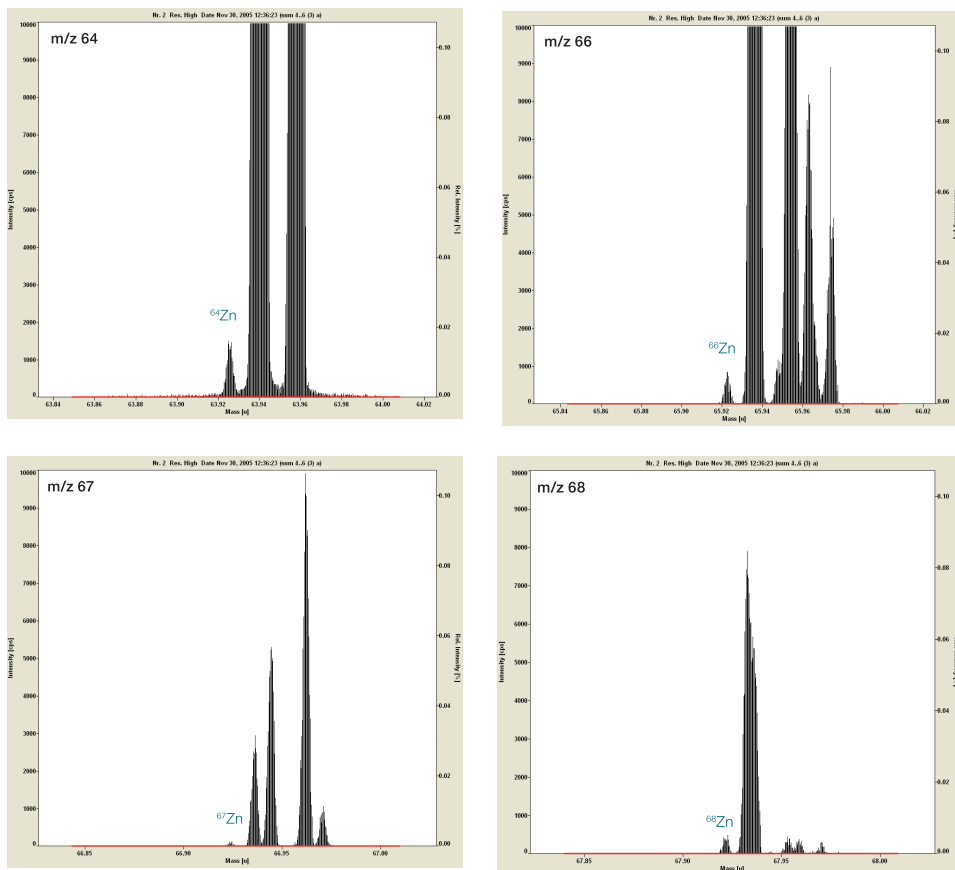


Figure 4b. The same spectra as in Figure 4a but with a fixed sensitivity scale in order to show the effective separation of $100 \text{ pg}\cdot\text{g}^{-1}$ of Zn separated from all interferences in 9.8% m/m H_2SO_4 at each isotope.

Table 1. Summary of results for the analysis of semiconductor Tier C grade 9.8% m/m H₂SO₄ using the Thermo Scientific ELEMENT 2.

All isotopes were measured using hot plasma conditions and interferences were removed through the use of the appropriate resolution setting. All concentration values are reported in units of pg·g⁻¹ in the 9.8% m/m H₂SO₄.

| | ⁷ Li (LR) | ¹¹ B (LR) | ²³ Na (LR) | ²⁴ Mg (MR) | ²⁷ Al (MR) | ³⁹ K (HR) | ⁴⁴ Ca (MR) | ⁴⁸ Ti (MR) | ⁵¹ V (MR) | ⁵² Cr (MR) | ⁵⁵ Mn (MR) | ⁵⁶ Fe (MR) | ⁵⁸ Ni (MR) | ⁶³ Cu (MR) | ⁶⁶ Zn (HR) | ⁷⁵ As (HR) | ¹¹¹ Cd (LR) | ¹¹⁸ Sn (LR) | ¹²¹ Sb (LR) | ¹³⁸ Ba (LR) | ²⁰⁸ Pb (LR) |
|--------------------------------|----------------------|----------------------|-----------------------|-----------------------|-----------------------|----------------------|-----------------------|-----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| LoD | 0.3 | 1.1 | 0.3 | 0.1 | 1.6 | 0.04 | 0.9 | 0.8 | 0.05 | 1.5 | 0.1 | 0.4 | 0.4 | 0.3 | 2.4 | 0.4 | 0.1 | 0.3 | 0.08 | 0.03 | 0.05 |
| BEC | 0.3 | 5.9 | 3.7 | 0.5 | 4.2 | 0.4 | 2.9 | 1.2 | 0.2 | 1.4 | 0.1 | 4.0 | 0.9 | 0.6 | 3.9 | 0.3 | 0.03 | 0.8 | 0.08 | 0.04 | 0.08 |
| Unspiked | 0.3 | 5.1 | <LoD | 0.6 | 5.6 | 0.5 | 2.6 | 1.4 | 0.2 | 0.8 | 0.1 | 3.3 | 0.7 | 1.2 | 13.4 | 0.5 | <LoD | 1.3 | 0.1 | 0.5 | 0.1 |
| 5 pg g ⁻¹ Spike # 1 | 5.0 | 8.9 | 5.0 | 5.9 | 9.6 | 5.5 | 7.6 | 6.5 | 5.1 | 6.2 | 4.9 | 6.6 | 5.7 | 6.4 | 19.8 | 4.9 | 4.5 | 5.8 | 4.9 | 5.3 | 5.0 |
| 5 pg g ⁻¹ Spike # 2 | 5.1 | 9.2 | 5.1 | 6.0 | 9.8 | 5.4 | 8.0 | 6.2 | 5.0 | 5.8 | 5.3 | 7.5 | 5.9 | 6.8 | 17.1 | 5.4 | 5.2 | 6.0 | 5.2 | 5.8 | 5.2 |
| 5 pg g ⁻¹ Spike # 3 | 5.6 | 10.2 | 5.0 | 5.4 | 9.7 | 5.4 | 8.3 | 6.5 | 4.7 | 5.7 | 4.8 | 7.7 | 5.9 | 6.5 | 19.1 | 5.6 | 4.9 | 6.0 | 5.3 | 6.2 | 5.7 |
| 5 pg g ⁻¹ Spike # 4 | 5.5 | 10.0 | 5.1 | 5.5 | 10.2 | 5.6 | 8.5 | 7.2 | 4.7 | 5.8 | 5.2 | 7.7 | 6.3 | 6.2 | 21.1 | 6.2 | 4.8 | 5.6 | 5.4 | 5.9 | 5.5 |
| 5 pg g ⁻¹ Spike # 5 | 5.2 | 10.1 | 5.1 | 5.6 | 10.6 | 5.5 | 7.6 | 6.6 | 5.1 | 5.8 | 5.1 | 8.3 | 5.7 | 6.4 | 17.8 | 5.6 | 4.9 | 5.9 | 5.5 | 5.5 | 5.3 |
| Average | 5.3 | 9.7 | 5.1 | 5.7 | 10.0 | 5.5 | 8.0 | 6.6 | 4.9 | 5.8 | 5.1 | 7.6 | 5.9 | 6.5 | 19.0 | 5.5 | 4.9 | 5.9 | 5.3 | 5.7 | 5.3 |
| %RSD | 4.3 | 6.0 | 1.0 | 4.4 | 4.2 | 1.5 | 4.9 | 5.8 | 4.4 | 3.9 | 3.9 | 7.8 | 5.8 | 3.3 | 8.4 | 8.2 | 5.0 | 2.6 | 4.8 | 5.6 | 5.4 |
| %Recovery | 100 | 91 | 99 | 102 | 87 | 99 | 103 | 103 | 95 | 101 | 99 | 86 | 104 | 106 | 112 | 102 | 97 | 92 | 104 | 105 | 105 |

Conclusions

The Thermo Scientific ELEMENT 2 HR-ICP-MS has been shown to provide the sensitivity, selectivity and stability to meet SEMI guidelines for the multi-elemental ICP-MS analysis of H₂SO₄ to SEMI Tier C levels using a single set of plasma parameters. For elements such as Ti and Zn, only high mass resolution provides the accuracy and precision of data required in the analysis of such a difficult sample matrix.

The Thermo Scientific ELEMENT 2 HR-ICP-MS system is tailored for the short turnaround times demanded by today's semiconductor laboratory:

- Direct elemental analysis of almost every element in the periodic table including phosphorous and sulfur in organic solvents, inorganic chemicals, silanes, and VPD samples
- Less than 0.1 pg·g⁻¹ detection limits for a majority of elements

- No sample preparation other than dilution
- Robust technology to serve as a 24/7 production control tool



Find out more at thermofisher.com/HR-ICP-MS

ThermoFisher
SCIENTIFIC