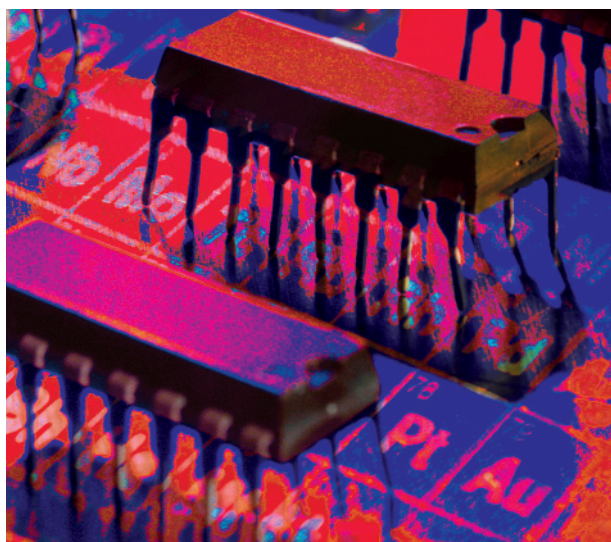


The Benefits of Dynamic Reaction Cell ICP-MS Technology to Determine Ultratrace Metal Contamination Levels in High-Purity Phosphoric and Sulfuric Acid

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This study investigates the applicability of a quadrupole-based ICP-MS fitted with a dynamic reaction cell (DRC) to analyze high-purity phosphoric and sulfuric acid used in the semiconductor industry. It compares the DRC approach with traditional ICP-MS background reduction techniques to compensate for phosphorus- and sulfur-based interferences and presents data that suggests that the DRC technology can reach the next generation of semiconductor purity levels for these chemicals.



The drive for more-compact integrated circuits and smaller electronic devices has put very stringent demands on suppliers of high-purity chemicals used in the semiconductor manufacturing process. To reduce defects and increase yield, lower trace element contamination levels are being required in all process chemicals, especially as initiatives like the International Technology Roadmap for Semiconductors (ITRS) (1) are setting the course for the next generation of semiconductor devices. Of particular significance are contamination issues associated with high-purity acids, because their aggressive dissolution properties make them prone to acquire metal from other sources. In addition, they are often used in large quantities with other chemicals to dissolve metals from the surface of silicon wafers, to build a layer of silicon dioxide on top of the silicon substrate, or as an etchant. For these reasons, trace element purity levels in

concentrated mineral acids must be monitored very closely.

Two of the most important acids used in the manufacture of semiconductor devices are phosphoric and sulfuric acids. Even though trace element purity levels are not as strict as for acids such as hydrofluoric and hydrochloric, they are still low enough to present problems for the analytical techniques being used. The major difficulties are related to their extremely high acid concentration — ~85% w/v for phosphoric acid and ~98% w/v for sulfuric acid — which produces corrosion problems and very high specific gravity — 1.70 g/mL for phosphoric acid and 1.83 g/mL for sulfuric acid — which in turn produces sample viscosity effects. In addition, when inductively coupled plasma–mass spectrometry (ICP-MS) is required to analyze the highest purity acids, the phosphate and sulfate matrices generate a significant number of plasma-based ionic species, which interfere with many of the analyte elements.

Phosphoric Acid

The Semiconductor Equipment and Materials International (SEMI) Standards organization has realized the implication of the difficulties associated with the analysis of both these acids. For example, in its *Book of SEMI Standards (BOSS)* (2), SEMI has approved the use of ICP-MS for the determination of 23 elements in Grade 3 phosphoric acid (3). However, SEMI states that, to meet the method quality control and data quality objectives of 75–125% spike recovery at 50% of the maximum limit of impurity, 5.00 g of sample must be weighed and diluted to 10 mL with deionized water. In other words, this is the maximum dilution that

can be made to meet the spike recovery reporting requirements. SEMI states that the concentration in the specification should be reported in weight/weight (w/w) units. Table I shows the trace metal limits for Grade 3 phosphoric acid, together with the concentrations of each element at 50% of the impurity level after sample preparation — based on 5 g of sample diluted to 10 mL with deionized water. It can be seen that the concentration of trace metals being presented to the instrument is approximately five times less than the Grade 3 purity level. For some of the more difficult elements such as iron, potassium, calcium, copper, and zinc, these levels are not much higher than their realistic detection limit in phosphoric acid. In fact, a study by Aleksejczyk and Gibilisco using SEMI methodology showed that detection limits (DL) for these elements were only 5–15 times lower than Grade 3 levels (4). The predominant reason for such poor detection capability in this study was the effects of major spectral interferences produced by a combination of ions from the phosphoric acid matrix and the argon gas on analyte background signals. Therefore, to avoid these interferences, the most sensitive isotopes of some elements could not be used for quantitation. The study also suggested that because of the extremely harsh phosphoric acid matrix, conditioning of the interface cones and ion optics was crucial to maintaining good long-term signal stability.

Sulfuric Acid

Sulfuric acid is even more of a problem. Grade 3 does not yet exist as a specified standard. The lowest purity levels in the SEMI BOSS are Tier B and Tier C Guidelines, which are set at a maximum of 1 ppb and 100 ppt, respectively, for a similar group of elements to phosphoric acid (5). However, neither of these guidelines has become a standard, because no methodology is available showing 75–125% spike recovery at 50% of 1 ppb and 100 ppt purity levels. In fact, the book states that, until standardized test methods are published, methodology shall be agreed on between user and producer. The highest grade of sulfuric acid listed in BOSS is

Table I. SEMI Grade 3 phosphoric acid maximum trace metal purity levels.

| Element | Grade 3 Level (ppb) | Final Concentration (ppb) After Sample Preparation (w/w) |
|-----------|---------------------|--|
| Aluminum | 50 | 10.4 |
| Antimony | 1000 | 207.3 |
| Arsenic | 50 | 10.4 |
| Barium | 50 | 10.4 |
| Boron | 50 | 10.4 |
| Cadmium | 50 | 10.4 |
| Calcium | 150 | 31.1 |
| Chromium | 50 | 10.4 |
| Cobalt | 50 | 10.4 |
| Copper | 50 | 10.4 |
| Gold | 50 | 10.4 |
| Iron | 100 | 20.7 |
| Lead | 50 | 10.4 |
| Lithium | 10 | 2.1 |
| Magnesium | 50 | 10.4 |
| Manganese | 50 | 10.4 |
| Nickel | 50 | 10.4 |
| Potassium | 150 | 31.1 |
| Silicon | 50 | 10.4 |
| Sodium | 250 | 51.8 |
| Strontium | 10 | 2.1 |
| Titanium | 50 | 10.4 |
| Zinc | 50 | 10.4 |

Grade 2, which is set at 10 ppb for the majority of elements (5). However, the book states that for the determination of chromium, cobalt, lithium, manganese, nickel, titanium, vanadium, and zinc, the sulfuric acid must be evaporated off and made up to volume with 1% nitric acid. The reason is that in ICP-MS, the high concentration of sulfur ions can potentially produce severe spectral overlaps that interfere with the isotopes of these elements. Even though the remainder of the elements can be determined by a 1:15 dilution of the acid, it states that sodium, potassium, calcium, and iron must be determined by graphite furnace atomic absorption (GFAA). In addition, it says that for boron and tantalum, the standards for calibration must be matrix-matched with equal amounts of sulfuric acid certified to have both elements below 1 µg/mL. There is no question that if this complicated and time-consuming procedure is required for 10 ppb levels, it will be even more difficult to get down to 1 ppb and 100 ppt purity levels.

Spectral Interferences

It is therefore clear that the ultratrace analysis of phosphoric and sulfuric acid by traditional ICP-MS is very difficult, because of the very high concentration of matrix ions, combined with their aggressive corrosion properties. Unfortunately, the extremely low quantitation levels do not permit larger dilutions, so when analyzing these acids, ICP-MS is always going to struggle with matrix suppression, matrix and plasma-induced spectral interferences, and corrosion of instrumental components. Of these three problem areas, by far the two more difficult to overcome, as indicated by the SEMI methodology, are the matrix effects and the formation of polyatomic spectral interferences. These interferences are formed between the matrix ions (phosphorus, sulfur, oxygen, and hydrogen) or through a combination of the matrix ions with ions from the argon plasma, which have the potential to overlap with analyte isotopes. Table II shows some of the major polyatomic spectral interferences in phosphoric and sulfuric acid.

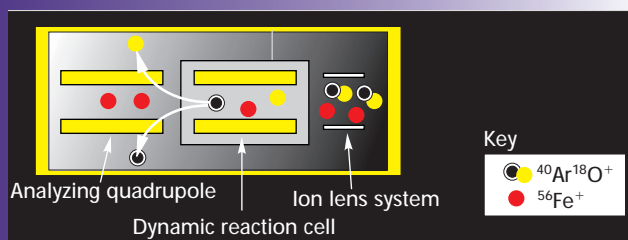


Figure 1. Diagram of the dynamic reaction cell showing the analysis of ^{56}Fe in the presence of $^{40}\text{Ar}^{16}\text{O}$.

Cool Plasma Technology

A number of approaches have been used to reduce these kinds of interferences using quadrupole-based instrumentation. The first major breakthrough came in

the mid-1990s with the commercialization of the cool or cold plasma approach. This technology, reported in the literature in the late 1980s, uses a low-temperature plasma to minimize the formation of some of the troublesome argon-based, polyatomic ions generated in the plasma (6). Under normal plasma conditions (typically 1200 W of rf power and 1.0 L/min of nebulizer gas flow), argon ions combine with matrix and solvent-based ions to generate polyatomic species that spectrally interfere with many analyte ions. By using cool plasma conditions (500–800 W of rf power and 1.5–1.8 L/min nebulizer gas flow), the ionization conditions in the plasma are changed and many of these polyatomic interferences cannot be formed. The result is that detection limits are improved for critical semiconductor elements such as iron, potassium, and calcium (7).

One of the disadvantages of the cool plasma approach is that because the ionization temperature is so low, matrix-derived oxide and hydroxide molecular ions are easily formed; these ions have the potential to spectrally interfere with many analytes. Also, it is expected that chemical matrices with a higher boiling point will not decompose readily in a cool plasma, as it provides much less energy than a normal plasma. In addition to the detection capability for the other elements being severely compromised by the sample matrix, nondecomposed acids can cause corrosion problems on the interface and mass spectrometer vacuum system. Finally, a significant disadvantage of the cool plasma approach is that, to obtain the best performance for a full suite of elements, a multielement analysis often necessitates the use of two sets of operating conditions — one run for the cool plasma elements and another for normal plasma elements. This results in much longer analysis times and also higher sample consumption.

Collision Cell Technology

The next major development to reduce spectral interferences was collision cell technology, which was commercially introduced in the mid- to late-1990s in an attempt to reduce polyatomic spectral interferences and improve the performance of quadrupole ICP-MS (8). Colli-

sion cell technology employs a multipole (typically a hexapole or octapole) housed within a cell placed just before the analyzer quadrupole. It uses a collision gas — typically hydrogen or helium — to stimulate ion–molecule collisions that convert the polyatomic spectral interference to a noninterfering species. The analyte ions then emerge from the collision cell and are directed toward the quadrupole analyzer for normal mass separation. Although this technology initially showed great promise, it struggled to reduce background levels low enough to improve detection limits over the cool plasma approach for problematic elements such as iron, potassium, and calcium (9). In addition, it appeared to offer no benefit to eliminate matrix-induced polyatomic interferences such as SO and PO. For that reason, it was not viewed as being significantly better than traditional quadrupole instrumentation for semiconductor-type samples.

Table II. Some of the major polyatomic spectral interferences seen in phosphoric and sulfuric acid.

| Analyte Isotope | Spectral Interference in H ₃ PO ₄ | Spectral Interference in H ₂ SO ₄ |
|------------------|---|--|
| ³⁹ K | ³⁸ ArH | ³⁸ ArH |
| ⁴⁰ Ca | ⁴⁰ Ar | ⁴⁰ Ar |
| ⁴⁸ Ti | ³¹ P ¹⁶ O ¹⁶ H | ³² S ¹⁶ O |
| ⁵¹ V | — | ³⁴ S ¹⁶ OH |
| ⁵² Cr | — | ³⁴ S ¹⁸ O |
| ⁵⁶ Fe | ⁴⁰ Ar ¹⁶ O | ⁴⁰ Ar ¹⁶ O |
| ⁶³ Cu | ³¹ P ¹⁶ O ¹⁶ O | — |
| ⁶⁴ Zn | ³¹ P ¹⁶ O ¹⁶ OH | ³² S ³² S, ³² S ¹⁶ O ¹⁶ O |
| ⁷¹ Ga | ⁴⁰ Ar ³¹ P | — |
| ⁷² Ge | — | ⁴⁰ Ar ³² S |

The Dynamic Reaction Cell

The need for ICP-MS to provide good detection limits for semiconductor-related elements led to the development of dynamic reaction cell (DRC) technology (10). Similar in appearance to the collision cell, the DRC is a pressurized multipole positioned immediately before the analyzer quadrupole. However, in DRC technology, a mass-

filtering quadrupole is used instead of a hexapole or octapole ion guide. A reactive gas such as ammonia is bled into the cell, which causes ion molecule chemistry to take place. By a number of different mechanisms, the gaseous molecules react with the interfering ions to convert them into species that will not interfere with the analyte. The analyte mass then emerges from the DRC free

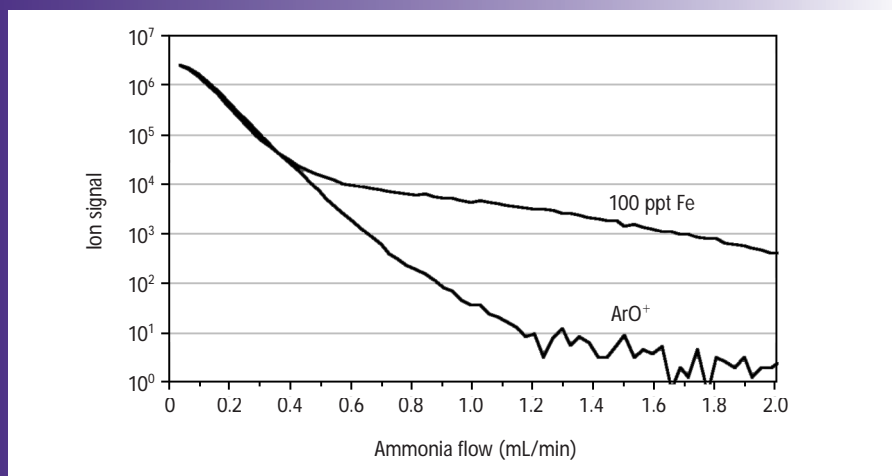


Figure 2. Plots of the $^{40}\text{Ar}^{16}\text{O}$ background intensity compared with a plot of 100 ppt ^{56}Fe as the flow of ammonia reaction gas is increased.

of its interference and steered into the analyzer quadrupole for conventional mass separation. The advantage of using a quadrupole in the reaction cell is that the stability regions are much better defined than with a hexapole or octapole. This allows precise control of the chemistry that takes place within

the cell. Therefore with careful optimization of the quadrupole electrical fields, unwanted side reactions, which could potentially lead to new interferences, are prevented by establishing clear high- and low-mass boundaries inside the DRC. In this filtering process, known as *chemical resolution*, every

time an analyte and interfering ions enter the DRC, the bandpass of the quadrupole can be optimized for that specific problem and then changed on-the-fly for the next analyte (11).

This process of ion-molecule chemistry is exemplified in Figure 1, which shows one of the most common interferences in ICP-MS — the polyatomic interference of $^{40}\text{Ar}^{16}\text{O}$ on the determination of ^{56}Fe . In this example, the reaction gas (ammonia) is bled into the DRC, which contains analyte ions (^{56}Fe) and the interference ($^{40}\text{Ar}^{16}\text{O}$). The ammonia gas reacts with the $^{40}\text{Ar}^{16}\text{O}$ to form new species that will not interfere with ^{56}Fe . However, there is very little reaction between the ammonia gas and the ^{56}Fe . With the optimum flow of reaction gas, the chemical cleansing process is so thorough that the background from the $^{40}\text{Ar}^{16}\text{O}$ is virtually eliminated.

Figure 2 shows a plot of the $^{40}\text{Ar}^{16}\text{O}$ background intensity, compared with 100 ppt of ^{56}Fe as the flow of ammonia

Figure 3 (right). Comparison between (a) DRC and (b) standard mode calibration curves for the determination of ^{52}Cr in sulfuric acid.

reaction gas is increased. It can be clearly seen that under the optimum gas flow conditions, the $^{40}\text{Ar}^{16}\text{O}$ intensity has been reduced by five to six orders of magnitude to less than 10 cps, which translates into a detection limit of less than 0.2 ppt for ^{56}Fe .

The DRC approach shows similar background reduction performance for other common polyatomic spectral interferences, including ^{40}Ar on the determination of ^{40}Ca and $^{38}\text{Ar}^1\text{H}$ on the determination of ^{39}K . Detection limits for both these elements are better than 0.3 ppt. The added benefit of the DRC is that it uses a robust, high-temperature plasma. This means that, unlike the cool-plasma approach, elements with a high first ionization potential can be determined with no sacrifice in sensitivity. By using the optimum reaction gas, many of the other problematic in-

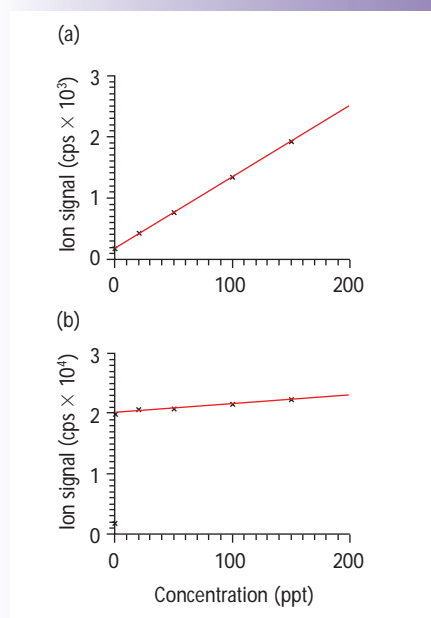


Figure 4 (right). Calibration curves for (a) $\text{Zn}(\text{NH}_3)_3$ ion at m/z 115, (b) ^{115}In , and (c) ^{120}Sn . By using the $\text{Zn}(\text{NH}_3)_3$ ion at 115, the normal $^{32}\text{S}^{32}\text{S}$ and $^{32}\text{S}^{16}\text{O}^{16}\text{O}$ interferences on zinc at mass 64 are no longer a problem.

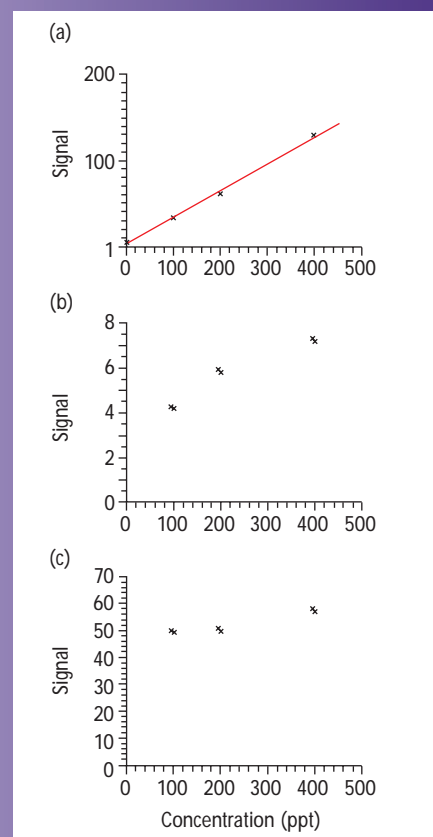


Table III. Detection limits (DL) and background equivalent concentrations (BEC) in deionized water achieved with the DRC ICP-MS, generated in multielement mode using one-second integration time*.

| Element | DL (ppt) | BEC (ppt) |
|---------|----------|-----------|
| As | 0.48 | 1.6 |
| B | 1.93 | 1.50 |
| Na | 0.14 | 0.22 |
| Mg | 0.08 | 0.18 |
| Al | 0.05 | 0.09 |
| K | 0.27 | 2.60 |
| Ca | 0.10 | 0.10 |
| Ti | 0.92 | 1.70 |
| V | 0.12 | 0.04 |
| Cr | 0.12 | 0.12 |
| Mn | 0.17 | 0.54 |
| Fe | 0.12 | 0.40 |
| Ni | 0.10 | 0.20 |
| Co | 0.04 | 0.04 |
| Cu | 0.05 | 0.10 |
| Zn | 0.45 | 1.20 |
| Sn | 0.12 | 0.88 |
| Sb | 0.08 | 0.08 |
| Ba | 0.06 | 0.04 |
| Pb | 0.07 | 0.09 |

* The data for the elements in red were obtained using ammonia reaction gas, while the elements in black were obtained in standard mode.

interferences, such as $^{40}\text{Ar}^{40}\text{Ar}$ on ^{80}Se , $^{40}\text{Ar}^{35}\text{Cl}$ on ^{75}As , and $^{40}\text{Ar}^{12}\text{C}$ on ^{52}Cr , are relatively straightforward to overcome.

Table III represents aqueous multi-element detection limits (DL) and background equivalent concentrations (BEC) in parts per trillion achieved with the DRC for a group of elements considered most important by the semiconductor industry. It should be noted that the background equivalent concentration is defined as the apparent concentration for the background signal based on the sensitivity of the element at a specified mass. The lower the BEC value, the more easily a signal generated by an element can be discerned from the background. Many analysts in the semiconductor industry believe BEC is a more accurate indicator than DL of the performance of an ICP-MS system. It's worth emphasizing that the

Table IV. Detection limits, background equivalent concentrations, and 50-ppt spike recoveries for a selected group of elements in 10% sulfuric acid*.

| Element | Mass | BEC (ppt) | DL (ppt) | 50 ppt spike recovery (%) |
|-------------------------------------|------|-----------|----------|---------------------------|
| B | 11 | 25 | 24 | 106 |
| Na | 23 | 3.5 | 1.5 | 101 |
| Mg | 24 | 1.6 | 0.8 | 104 |
| Al | 27 | 2.4 | 2.3 | 103 |
| K | 39 | 51 | 5.7 | 100 |
| Ca | 40 | 5.5 | 3.0 | 100 |
| TiNH(NH ₃) ₃ | 114 | 4.4 | 3.4 | 92 |
| V | 51 | 1.6 | 0.7 | 99 |
| Cr | 52 | 5.2 | 2 | 91 |
| Mn | 55 | 11 | 2.3 | 99 |
| Fe | 56 | 22 | 7.4 | 102 |
| Co | 59 | 2.2 | 0.74 | 100 |
| Ni | 60 | 26 | 7.5 | 104 |
| Cu | 63 | 24 | 1.9 | 98 |
| Zn(NH ₃) ₃ | 115 | 14 | 16 | 98 |
| Ge | 74 | 1.5 | 2.3 | 99 |
| As | 75 | 12 | 2.2 | 98 |
| Sn | 120 | 3.9 | 1.5 | 99 |
| Sb | 121 | 0.40 | 0.2 | 99 |
| Au | 197 | 0.70 | 0.67 | 98 |
| Pb | 208 | 0.93 | 0.70 | 100 |

* The data for the elements in red were obtained using ammonia reaction gas, while the elements in black were obtained in standard mode.

Table V. Detection limits, background equivalent concentrations, and 50-ppt spike recoveries for a selected group of elements in 1% phosphoric acid*.

| Element | Mass | BEC (ppt) | DL (ppt) | 50 ppt spike recovery (%) |
|---------|------|-----------|----------|---------------------------|
| B | 11 | 180 | 10 | 91 |
| Na | 23 | 51 | 14 | 109 |
| Mg | 24 | 24 | 6.4 | 105 |
| Al | 27 | 33 | 3.1 | 103 |
| K | 39 | 44 | 4.5 | 97 |
| Ca | 40 | 57 | 5.5 | 124 |
| V | 51 | 28 | 2.9 | 98 |
| Cr | 52 | 100 | 8.0 | 99 |
| Mn | 55 | 28 | 1.6 | 103 |
| Fe | 56 | 130 | 12 | 114 |
| Co | 59 | 15 | 2.4 | 101 |
| Ni | 60 | 490 | 14 | 114 |
| Cu | 63 | 60 | 1.4 | 109 |
| Zn | 64 | 72 | 11 | 84 |
| As | 75 | 34 | 5 | 107 |
| Mo | 95 | 190 | 17 | 106 |
| Sn | 120 | 9.2 | 5.6 | 103 |
| Pb | 208 | 20 | 0.8 | 100 |

* The data for the elements in red were obtained using ammonia reaction gas, while the elements in black were obtained in standard mode.

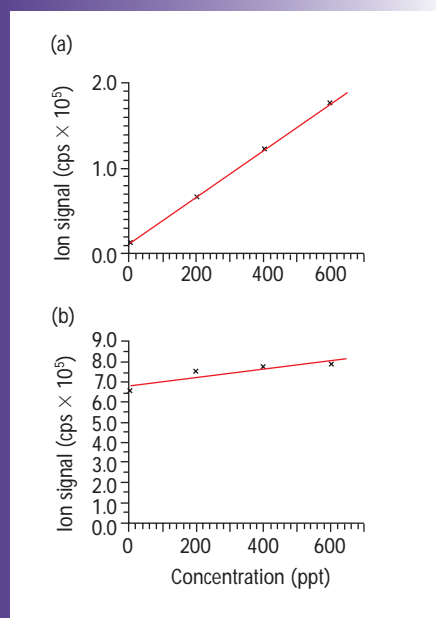


Figure 5. Comparison between (a) DRC and (b) standard mode calibration curves for the determination of ^{65}Cu in phosphoric acid.

DRC can be used without reaction gas for the determination of elements that don't suffer from polyatomic spectral interferences. These elements are shown in black in Table III.

DRC Technology Applied to Semiconductor Chemicals

DRC technology has already been successfully applied to the analysis of high-purity nitric acid (12), hydrochloric acid (12), and hydrogen peroxide (13). The work in this study will focus on the capability of the DRC to analyze high-purity sulfuric and phosphoric acid, with the emphasis on the elimination of sulfur- and phosphorus-based polyatomic species. All the data presented were generated on an ELAN DRC II (PerkinElmer Instruments, Shelton, CT) using a PFA-100 microconcentric nebulizer and a PFA spray chamber (Elemental Scientific, Omaha, NE).

Analysis of Sulfuric Acid

Let us first take a look at sulfuric acid. The aim of this work was to use a simple dilution of the sample to avoid the complex sample preparation and lengthy matrix elimination steps outlined in the SEMI BOSS. As mentioned previously, the major concern in this matrix is the extremely high concentra-

tion of sulfur. Sulfur makes the determination of elements such as ^{48}Ti , ^{51}V , ^{52}Cr , and ^{64}Zn virtually impossible by traditional ICP-MS because of the many sulfur-based polyatomic spectral interferences, including $^{32}\text{S}^{16}\text{O}$, $^{34}\text{S}^{16}\text{OH}$, $^{34}\text{S}^{18}\text{O}$, and $^{32}\text{S}^{32}\text{S}$. A cool-plasma approach cannot be used because the temperature is too low to ionize the high-ionization-potential elements. Even with dilution, the high sulfuric acid content will cause severe matrix suppression on the analyte masses with a cool plasma (13).

Using DRC technology, however, the sulfuric acid matrix has very little effect on the determination of these elements. The harmful sulfur-based spectral interferences can be significantly reduced by careful selection and optimization of the reaction cell's chemical resolution parameters. In addition, a high-temperature plasma can be used, so the ionization conditions are suited for the full suite of elements in the sulfuric acid matrix. The elimination of one of the major spectral interferences — $^{34}\text{S}^{18}\text{O}$ on the determination of ^{52}Cr — in sulfuric acid, using the DRC is seen in Figure 3. Figure 3 shows two calibration curves (0–200 ppt) generated for the determination of ^{52}Cr in 10% sulfuric acid. Plot (a) on the top is in the DRC

mode using 0.6 mL/min of ammonia gas in the reaction cell, while plot (b) on the bottom is in the standard ICP-MS mode. It clearly shows that in the standard mode, the polyatomic ion $^{34}\text{S}^{18}\text{O}$ has elevated the background at mass 52 to more than 20,000 cps, making the determination of ultratrace levels of chromium extremely difficult, whereas removal of the $^{34}\text{S}^{18}\text{O}$ using the DRC reduces the background level at mass 52 to about 100 cps.

Other difficult elements in sulfuric acid include zinc and titanium. Normally, zinc can be determined in the standard mode using one of the zinc isotopes at 64, 66, 67, 68, or 70 amu. However, in samples with high sulfur content, its detection limit is severely compromised because of the spectral background produced by sulfur-based polyatomic ions, making the most sensitive isotopes impractical to use. For that reason, advantage is taken of the unique capability of the DRC process to form a brand new molecular ion complex between the zinc and the ammonia gas. By optimizing the cell parameters, ^{64}Zn and $^{14}\text{NH}_3$ can be made to react to generate the $\text{Zn}(\text{NH}_3)_3$ ion at mass 115, which is then used for quantitation. Figure 4a shows a 0–400 ppt calibration curve for $\text{Zn}(\text{NH}_3)_3$ at

Table VI. Comparison of analyte sensitivity in 1% nitric acid to sensitivities in 10% sulfuric acid and 1% phosphoric acid using hot-plasma conditions (1600 W)*.

| Element/mass (amu) | 10% H_2SO_4 Ratio to 1% HNO_3 | 1% H_3PO_4 Ratio to 1% HNO_3 |
|--------------------|---|--|
| B (11) | 114 | 89 |
| Na (23) | 86 | 93 |
| Mg (24) | 122 | 103 |
| Al (27) | 90 | 96 |
| K (39) | 110 | 97 |
| Ca (40) | 105 | 103 |
| Cr (52) | 106 | 89 |
| Fe (56) | 90 | 80 |
| Ni (60) | 97 | 85 |
| Cu (63) | 99 | 82 |
| Zn (64) | 112 | — |
| Sn (120) | 118 | 105 |
| Ba (138) | 118 | 111 |
| Ta (181) | 91 | 77 |
| Pb (208) | 84 | 107 |

* The data for the elements in red were obtained using ammonia reaction gas, and the elements in black were obtained in standard mode.

m/z 115. By using mass 115, the normal $^{32}\text{S}^{32}\text{S}$, or $^{32}\text{S}^{16}\text{O}^{16}\text{O}$ interferences on zinc at mass 64 are no longer a problem. However, the ^{113}In calibration data in Figure 4b indicate that there could be a very small contribution from ^{115}In , so caution should be taken if there is a significant amount of indium in the sample. On the other hand, there appears to be no contribution from ^{115}Sn on the zinc signal, as demonstrated by the ^{120}Sn calibration data (Figure 4c).

Similarly, titanium has five isotopes at 46, 47, 48, 49, and 50 amu, which all have significant spectral interferences from sulfur-based polyatomic ions. For this reason, to achieve the lowest detection limits, advantage is taken of the DRC's ability to form the $\text{TiNH}(\text{NH}_3)_3$ ion at mass 114, which is then used for quantitation.

DL, BEC, and 50-ppt spike recoveries for a selected group of elements in a 1:10 dilution (w/w) of 99% sulfuric acid are shown in Table IV. The BEC and spike recoveries are calculated using the method

of standard additions. It is worth emphasizing that 50 ppt represents 50% of Tier B Guidelines for sulfuric acid (1 ppb), based on a 1:10 dilution. It can be seen that all the recoveries easily meet the SEMI specification of 75–125%.

Analysis of Phosphoric Acid

Let's now turn our attention to phosphoric acid. Once again, the aim was to carry out the analysis using a simple dilution of the sample. Because high concentrations of phosphoric acid can have a deleterious effect on instrument components, it was felt that it would be more advantageous to have a much larger dilution than the sample preparation of 5 g/10 mL specified in SEMI Grade 3. The major concern in phosphoric acid is the extremely high concentration of phosphorus, which makes the determination of copper and zinc at their most abundant isotopes very difficult, because of the polyatomic spectral interferences, $^{31}\text{P}^{16}\text{O}_2$ and $^{31}\text{P}^{16}\text{O}_2\text{H}$ at masses 63 and 64, respectively. Unfortunately, for the same

reasons as sulfuric acid, cool-plasma technology does not offer any significant benefits to reduce these interferences.

Using DRC technology, however, the phosphorus-based spectral interferences can be significantly reduced by careful selection and optimization of the DRC parameters. The elimination of one of the major spectral interferences in 1% phosphoric acid is seen in Figure 5. Figure 5 shows two calibration curves (0–600 ppt) generated for the determination of ^{63}Cu . The top plot (Figure 5a) is in the DRC mode using 0.3 mL/min of ammonia gas in the reaction cell, while the bottom plot (Figure 5b) is in the standard ICP-MS mode. It clearly shows that in the standard mode, the polyatomic ion $^{31}\text{P}^{16}\text{O}_2$ has elevated the background at mass 63 to more than 700,000 cps, making the determination of ultralow levels of copper extremely difficult. When the $^{31}\text{P}^{16}\text{O}_2$ is removed using the chemical resolution of the DRC, the background at mass 63 is reduced to about 1000 cps.

A similar improvement of three orders of magnitude is also seen for the reduction of the $^{31}\text{P}^{16}\text{O}^{16}\text{OH}$ interference on the ^{64}Zn isotope. This background reduction capability results in detection limits of approximately 1 ppt for Cu and Zn in 1% phosphoric acid.

Detection limits, BEC, and 50-ppt spike recoveries for the complete suite of elements in 1% phosphoric acid are shown in Table V (BECs and spike recoveries are calculated using the method of standard additions). There is a wide specification range of 10–1000 ppb for the 23 elements in SEMI Grade 3 phosphoric acid, as indicated in Table I. A spike of 50 ppt was chosen because it represents the final concentration at 50% of the lowest specification (10 ppb), based on a 1% (w/w) solution of phosphoric acid. It can be seen that all the recoveries meet the SEMI specification of 75–125%.

For the analysis of both phosphoric and sulfuric acid, one set of hot plasma conditions was used for the full suite of elements. The result is that matrix sup-

pression is kept to an absolute minimum because of the high ionization temperature. This is confirmed by the data in Table VI, which compares analyte sensitivities in 10% sulfuric acid and 1% phosphoric acid to those in 1% nitric acid, using hot-plasma conditions (1600 W). For the vast majority of the elements, the ratios of the signals are very close to 100%, suggesting very little matrix suppression. This kind of matrix performance indicates that many chemical or acid matrices could be analyzed using simple aqueous–nitric acid calibration standards.

Conclusion

Both high-purity sulfuric and phosphoric acid have proven to be very difficult samples to analyze by conventional ICP-MS because of corrosion problems, signal suppression, and spectral overlaps associated with the matrix. As indicated by SEMI methodology, the sulfuric acid matrix has to be removed to determine many of the elements, while

other elements have to be determined by GFAA. In the case of phosphoric acid, the specification levels necessitate a 1:2 dilution (w/w), which degrades instrumental components and also affects long-term signal stability.

This study has clearly shown that DRC technology dramatically reduces the formation of harmful polyatomic spectral interferences produced by the high concentration of sulfur and phosphorus in the sample. The result is that a full suite of elements can be determined in both sulfuric acid at the Tier B Guideline level and phosphoric acid at the Grade 3 Standard level, with a simple dilution of the sample. The added benefit of this technology is that a robust, high-temperature plasma is used for all the analytes. The result is that matrix suppression is kept to an absolute minimum, which offers the exciting potential of using simple aqueous–nitric acid standards to analyze a wide variety of complex sample matrices.

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