Agilent
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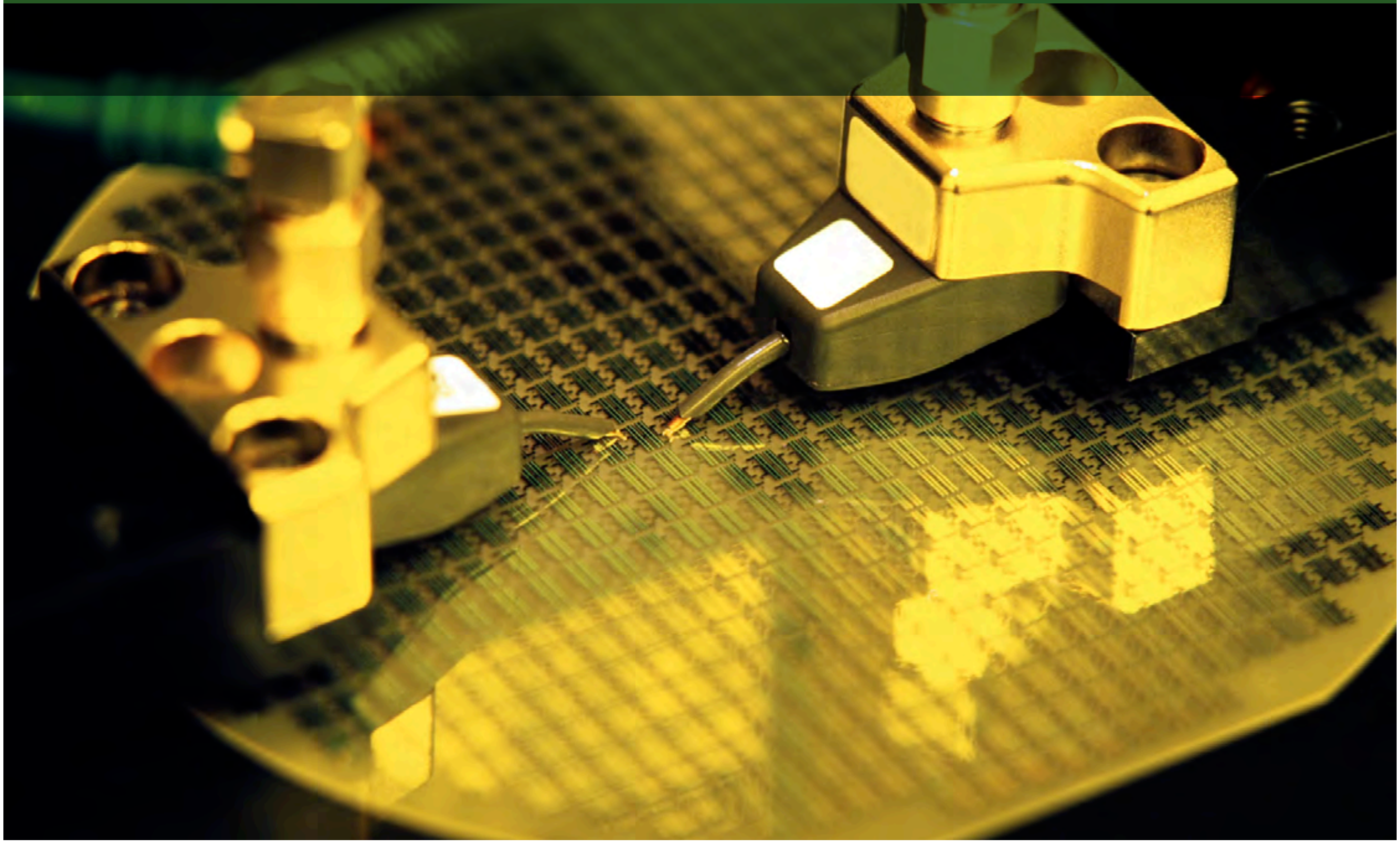
Applications of ICP-MS

Measuring Inorganic Impurities in Semiconductor Manufacturing

Application Compendium



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ICP-MS and ICP-QQQ in the Semiconductor Industry

Today's technological world relies on the integrated circuits (ICs) that are found in devices ranging from manufacturing robots to smart light bulbs, and from mobile telephones to automobiles, aviation and aerospace.

A silicon-based IC device is fabricated from millions of individual transistors (or switches) packed onto a silicon wafer chip. The device is built from patterned layers of oxide, polysilicon, silicon nitride dielectric, and conducting metal interconnects. Layers are connected by "vias" to form a 3D structure that provides the required computing or memory functionality.

During the integrated circuit fabrication process (shown in Figure 1), each conducting or insulating layer is deposited, masked, and etched. This leaves an intricate pattern of features with line widths as small as 10 nanometers (equivalent to about 40 Si atoms). Doped regions are added, depositing or implanting specific atoms to alter the conductivity of the silicon.

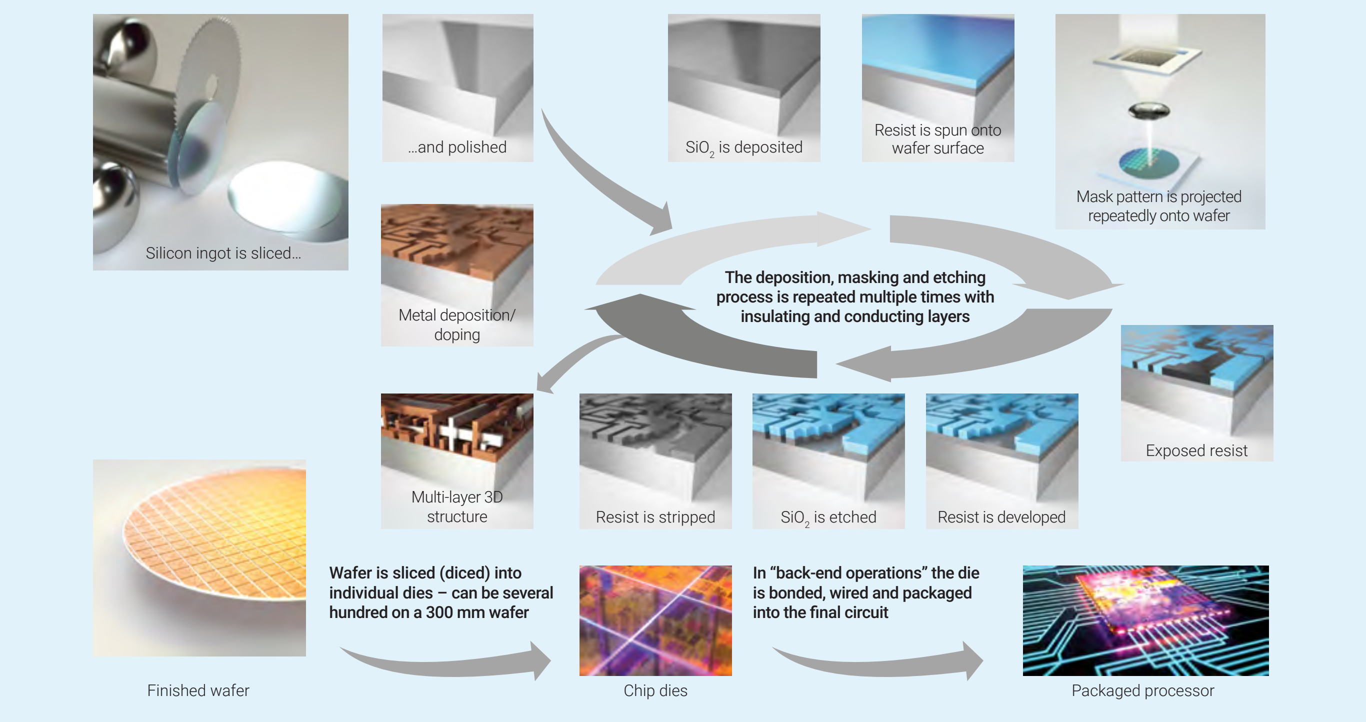

Figure 1. Simplified schematic showing typical steps in silicon wafer fabrication.

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The current “10 nanometer” geometry contains features approximately 1000 times smaller than circuits manufactured in the 1970s. This reduced scale and increased density has required a parallel improvement in the control of contamination. The resultant need for higher-purity chemicals has led to ever-higher demands on the performance of the analytical instruments used to detect metallic impurities, a trend that is likely to continue.

Trace metals in IC device fabrication

Semiconductor device fabrication requires strict control of sources of contamination; industry estimates suggest that contamination accounts for around 50% of yield losses. Metallic contaminants may be introduced via the wafer substrate or the chemicals used during the manufacturing process.

Monitoring and controlling trace element contamination begins with the high-purity wafer substrate. The substrate is usually silicon, but other materials such as silicon carbide, silicon nitride, and gallium arsenide are also used. High-purity electronic-grade silicon must be between 9N and 11N – 99.9999999% to 99.999999999% purity. In terms of contamination, 9N purity means a maximum of one part per billion (ppb) of total impurity elements in the solid Si.

Trace metallic contamination in bulk silicon can be measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after dissolving the Si in hydrofluoric acid. Trace metals in the sliced wafer are measured using a surface analysis technique such as vapor phase decomposition, where the metals are extracted from the Si substrate into a droplet that is then analyzed by ICP-MS.

In addition to the high purity wafer substrate, the purity of chemicals used throughout the wafer fabrication process must be controlled to avoid introducing contaminants. Metallic contaminants are of concern because they can affect the electrical properties of the finished device, for example by reducing dielectric breakdown voltage. As well as contaminants dissolved in process chemicals, insoluble nanoparticles are also monitored throughout the manufacturing process.

ICP-MS in semiconductor manufacturing

When ICP-MS was introduced in the 1980s, it was of great interest to semiconductor manufacturers and chemical suppliers due to its high sensitivity, low detection limits, and multi-element capability. Use of ICP-MS for semiconductor applications increased rapidly in the 1990s, with the development of “cool plasma” on the HP 4500 instrument. Cool plasma allowed Na, K, Ca, and Fe to be determined at trace levels by ICP-MS, so semiconductor manufacturers and chemical suppliers no longer needed graphite furnace AAS to measure these elements.

SEMI specifications

SEMI is a global semiconductor industry association that publishes standards and specifications for process chemicals and gases, among many other things.

Many semiconductor industry manufacturers are currently working with Grade 3 or 4 chemicals (Tier-B or Tier-C specifications, suitable for geometries between 800 and 90 nm). However, with the development of smaller architectures, there is pressure to move to Tier-D and Tier-E chemical specifications. Tier-E requires DLs below 0.1 ppt and accurate spike recovery of target elements at 0.5 ppt. Accurate analysis at these lower levels requires the higher performance of ICP-QQQ.

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ICP-MS manufacturers have continued to improve the technique, a major development being the release of the Agilent 8800 triple quadrupole ICP-MS (ICP-QQQ), in 2012. The 8800 and its successor, the Agilent 8900 ICP-QQQ, provide higher sensitivity, lower backgrounds, and better control of interferences than single quadrupole ICP-MS. This allows a greater number of contaminant elements to be monitored at lower concentrations, including previously difficult elements such as Si, P, S, and Cl.

Silicon and other materials

Metal contamination in the silicon wafer substrate and associated layers and coatings can be monitored using surface metal extraction (SME) , also known as vapor phase decomposition (VPD). In the SME/VPD technique, the surface layer of the wafer (bare Si, or naturally or thermally oxidized SiO_2) is dissolved using HF vapor. The dissolved metals are collected by scanning a droplet of a recovery solution (usually HF and H_2O_2, but sometimes an alternative solution such as HCl/H_2O_2) across the wafer surface. The droplet is then pipetted from the wafer surface and transferred to the ICP-MS for analysis.

Other materials used in chip manufacturing are suitable for analysis using ICP-MS, including metal organic compounds such as trimethyl gallium (TMG), trimethyl aluminum (TMA), dimethyl zinc (DMZ), tetraethoxysilane (TEOS) and trichlorosilane (TCS). Such compounds are precursors used to grow thin metal films or epitaxial crystal layers in metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition. Pure metals such as Al, Cu, Ti, Co, Ni, Ta, W, and Hf are used as sputtering targets for physical vapor deposition (PVD) to create thin metal films on the wafer surface. High-k dielectric materials include chlorides and alcoxides of Zr, Hf, Sr, Ta, and the rare earth elements (REEs). Each of these materials has a limit for acceptable levels of contaminants, requiring analysis using ICP-MS.

Cleaning/etching and process chemicals

During IC fabrication, wafers undergo many processing steps, as illustrated in Figure 1. Chemicals used are in contact with the wafer surface, so control of contamination is critical. Examples of some commonly used chemicals are shown in Table 1.

Among the most critical process chemicals in terms of controlling contamination are ultrapure water (UPW) and the RCA Standard Clean (SC) solutions SC-1 and SC-2. The RCA cleaning procedure removes chemical contaminants and particulate impurities from the wafer surface without damaging the chip. SC-1 (NH_4OH and H_2O_2 in deionized water (DIW)) removes organic residues, films and particles from the wafer surface. SC-2 (HCl and H_2O_2 in DIW) then removes ionic contaminants.

Table 1. Semiconductor process chemicals.

Process	Commonly used chemicals
Cleaning	Pure water, SC-1 (NH_4OH and H_2O_2), SC-2 (HCl and H_2O_2), SPM (sulfuric peroxide mix, a mixture of H_2SO_4 and H_2O_2), DHF (dilute HF), IPA (isopropyl alcohol), methanol
Developing	Photoresist, PGME (propylene glycol monomethyl ether), ethyl lactate, NMP (N-methyl pyrrolidone), TMAH (tetramethyl ammonium hydroxide)
Etching	HF, NH_4F, H_3PO_4, KOH, DMSO (dimethyl sulfoxide), MEA (mono-ethanol amine)
Polishing	CMP (chemical mechanical planarization) slurries, oxalic acid, NH_4OH

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Agilent's Three Decades of ICP-MS Experience Drives Continuous Innovation

Working closely with leading semiconductor manufacturers and chemical suppliers since the late 1980s, Agilent has developed ICP-MS systems and applications that help to address the challenges of this fast-moving industry. From off-axis ion lenses and cool plasma to the unique, high-sensitivity 8900 ICP-QQQ with MS/MS operation, Agilent has been at the forefront of the key ICP-MS innovations critical to the industry.

Agilent innovations

ICP-MS has been used by semiconductor manufacturers and suppliers since its introduction in the 1980s. But evolving industry requirements have led to demands for ever-higher analytical instrument performance. Working closely with the industry, Agilent has introduced many innovations to meet these evolving needs. These innovations address the demanding requirements of the semiconductor industry and are often of benefit for other applications of ICP-MS. The innovations include:

- The very high sensitivity offered by the off-axis ion lens systems of all Agilent systems.
- Cool plasma, available worldwide for the first time on the HP 4500 ICP-MS, eliminated the need for GFAAS in semiconductor applications.
- The small, benchtop design of the HP 4500 made it by far the most suitable system for clean room installations at that time.
- The low-flow, inert sample introduction system, available for all Agilent ICP-MS systems, controls contamination and provides the ability to handle very small sample volumes (such as <500 µL VPD droplets).
- A fully stainless-steel chassis and clean room preparation were introduced with the 7700 ICP-MS.
- Control of reaction chemistry using MS/MS on the 8800 and 8900 ICP-QQQ, which provides unprecedented resolution of interferences.
- A low contamination gas flow path lowers DLs on the 8900 ICP-QQQ Semiconductor (and Advanced Applications) models.
- Agilent's applications expertise in the analysis of high-purity and high performance materials supports semiconductor manufacturers worldwide.

Figure 2. The HP 4500 was the world's first computer controlled benchtop ICP-MS, introduced in 1994.

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Agilent ICP-MS Solutions for the Semiconductor Industry

Agilent's global sales and support organization provides single quadrupole and triple quadrupole ICP-MS systems specifically designed to meet the needs of the semiconductor industry.

Single quadrupole ICP-MS

The Agilent 7900 ICP-MS provides high performance in a compact benchtop single quadrupole instrument. It is a cost-effective solution for measuring trace contamination in process chemicals and lower-purity materials. The 7900 has the performance and flexibility to handle most semiconductor sample types, with options and accessories to allow the analysis of nanoparticles, organic solvents, and highly corrosive acids. It is a workhorse in many semiconductor companies.

Figure 3. The Agilent 7900 single quadrupole ICP-MS is ideal for the routine analysis of process chemicals and materials.

Triple quadrupole ICP-MS

The Agilent 8900 ICP-QQQ is the world's only true triple quadrupole ICP-MS – a tandem mass spectrometer with MS/MS operation that delivers the sensitivity and interference removal required for accurate analysis of the highest purity semiconductor materials.

The 8900 #200 configuration is specifically designed for semiconductor applications, providing high sensitivity, coupled with Agilent's unique Cool Plasma capability. The robust plasma, Pt-tipped interface cones, and optional inert (PFA) sample introduction system allows it to handle even the most difficult semiconductor samples and applications with ease.

Designed to save cleanroom bench space, the 8900 is only 1060 mm wide. Its semiconductor configuration features:

- Four argon gas line mass flow controllers and a fifth gas line for addition of option gases such as O_2/Ar for organics, or He carrier gas for laser ablation.
- Pre-set plasma conditions for consistent setup from day to day and between operators.
- An argon gas flow path designed to minimize background signals for silicon and sulfur, providing guaranteed detection limits of <50 ng/L.
- An optimized interface vacuum design and a new high-transmission "s" type ion lens provide the sensitivity needed for the ultra-trace analysis of high purity semiconductor reagents.
- Methods, tuning, and acquisition templates for all typical semiconductor applications, including the industry-standard cool plasma mode used for low matrix samples such as ultra-pure water (UPW) and hydrogen peroxide.

Figure 4. The Agilent 8900 triple quadrupole ICP-MS semiconductor configuration is designed specifically to meet the current and future needs of the semiconductor industry.

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Automating Analysis of Metal Contaminants in Si Wafers

Agilent ICP-MS systems can be integrated with all leading automated VDP scanners to provide a fully-automated analysis of surface contamination on Si wafers.

Vapor phase decomposition

Metallic contamination of semiconductor devices may be introduced during cleaning, etching oxide growth, and ion implantation processes. Trace contaminants may also remain from the quartzite (sand) used to produce bulk, polycrystalline silicon, and the pure, monocrystalline silicon ingot from which the wafers are sliced. The main contaminant elements in quartzite are iron, aluminum, calcium, and titanium, while other elements may be introduced during the carbothermic processes used to convert quartzite into 98% pure silicon. Gas phase purification and chemical vapor deposition then remove most of the impurities, leaving silica of around 8 9s purity.

Slicing and polishing the wafer can also introduce trace elements, for example from the chemical mechanical planarization (or polishing) slurries. The elements of most concern are the transition metals and alkaline elements, but their distribution in the wafer is not necessarily uniform. Iron can diffuse through the bulk silicon substrate into the surface oxide layer, while titanium impurity levels may vary due to segregation during melting and cooling of the monocrystalline Si ingot.

To ensure that metal contaminants do not adversely affect the IC device, the concentration of trace metals in the wafer surface must be determined. The bare silicon layer on the surface of the wafer quickly oxidizes to SiO_2 when exposed to atmospheric oxygen and water. This naturally oxidized layer is ~0.25 nm (one SiO_2 molecule) thick. If the IC design requires an insulating film, a much thicker oxide layer is formed on the wafer surface by heating the wafer to 900 - 1200 °C in the presence of O_2 or water vapor. This thermally oxidized layer may be up to 100 nm (0.1 µm) thick. For both native and thermally oxidized SiO_2, the trace metals in the oxide layer can be measured at extremely low concentrations using vapor phase decomposition (VPD) coupled with ICP-MS.

Agilent ICP-MS and ICP-QQQ instruments are compatible with all leading VPD systems, including:

- IAS Inc., Japan
- PVA TePla AG, Germany
- NvisANA Co. Ltd, Korea
- NAS GIKEN, Japan

Figure 5. The WCS M300 automated VPD scanner system from NvisANA, Korea.

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Combining ICP-MS and vapor phase decomposition

VPD-ICP-MS is a proven method of measuring trace metal contamination in silicon wafers. The VPD wafer sampling approach has good sensitivity because it concentrates the metals in the oxide layer from a large surface area of the wafer into a single droplet of solution for measurement.

The process (that can be completely automated) involves four steps:

1. The silicon wafer is placed in a VPD chamber, and exposed to HF vapor to dissolve the native oxide or thermally oxidized SiO_2 surface layer.
2. An extraction droplet (typically 250 µL of 2% HF/2% H_2O_2) is placed on the wafer, which is then tilted in a carefully controlled pattern so that the droplet is "scanned" across the wafer surface.
3. As the extraction droplet moves across the wafer surface, it collects the dissolved SiO_2, together with any contaminant metals.
4. The extraction droplet is transferred from the wafer surface to an ICP-MS or ICP-QQQ for analysis.

Advantages of coupling ICP-MS or ICP-QQQ with VPD

VPD can be performed manually, although it takes an experienced operator to get consistent recovery of the dissolved metals in the SiO_2 layer. VPD can also be coupled with a range of elemental analysis techniques to quantify metallic contamination. However, using ICP-MS or ICP-QQQ offers the advantages of high sensitivity and low detection limits for all required analytes, while automating the VPD process ensures consistency and reduces the potential for contamination.

Both the Agilent 7900 and 8900 ICP-MS instruments can be integrated with VPD systems for completely automated analysis of metallic impurities in silicon wafers. Both systems provide the good matrix tolerance required for analysis of thermally oxidized SiO_2, where the SiO_2 matrix concentration can be up to 5000 ppm in the extraction droplet (depending on the thickness of the oxide layer). The 8900 has the added benefit of MS/MS operation, providing the most effective of interference removal of any ICP-MS, and delivering lower detection limits and improved accuracy.

Figure 6. The Munich Metrology Wafer Surface Measurement System (WSMS) manufactured by PVA TePla, integrated with the Agilent 8800 ICP-QQQ.

Figure 7. A fully automated VPD-ICP-MS system Expert PS manufactured by IAS Inc., integrated with Agilent 8800 ICP-QQQ. Image provided courtesy of ST Microelectronics, Crolles, France.

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Setups for Different Sample Types

Handling organic chemicals

Many organic solvents and products are used in semiconductor manufacturing, including IPA (isopropyl alcohol), methanol, TMAH (tetra methyl ammonium hydroxide), NMP (n-methyl pyrrolidone), PGME (propylene glycol monomethyl ether), ethyl lactate, butyl acetate, and photoresist. Some organic chemicals are soluble in water, but often it is preferable to run the samples undiluted, both to minimize the risk of contamination, and to achieve the lowest possible detection limits. ICP-MS is suitable for the direct analysis of both water soluble and non-water-soluble organic samples. Non-water-soluble organics may be run direct, or diluted in a suitable solvent, for example xylene or toluene. Direct analysis of non-water soluble organic samples requires some specific ICP-MS hardware and operating conditions, particularly for the sample introduction and plasma settings.

Solvent resistant sample introduction

Organic solvents may be incompatible with the normal peristaltic pump tubing of the ICP-MS. Self-aspiration nebulization avoids the potential for sample contamination from or damage to the pump tubing, while solvent resistant pump tubing is used for the spray chamber drain. A typical sample introduction setup for the analysis of volatile organic solvents such as IPA and NMP would include:

- Glass or quartz concentric nebulizer
- Quartz spray chamber
- Solvent-resistant drain kit
- Optional “organics” quartz torch with 1.5 mm i.d. injector (a torch with a 1.0 mm i.d. injector is also available, suitable for the most volatile solvents)
- Optional 5th Mass Flow Controller for oxygen addition to the carrier gas
- Pt-tipped sampling and skimmer cones

Control of vapor pressure

The high vapor pressure of some solvents can destabilize or even extinguish the plasma. All Agilent ICP-MS systems are fitted with a Peltier-cooled spray chamber to control solvent vapor pressure. The Agilent ICP RF generator is extremely robust and can easily tolerate the vapor pressure of even the most volatile solvents (such as acetone) at a spray chamber temperature of -5 °C. Some ICP-MS systems require extreme low temperatures (e.g. -20 °C) to tolerate such solvents.

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Removal of carbon

When organic-based samples are analyzed, the high levels of carbon in the sample aerosol can lead to deposition of carbon (soot) on the sampling cone, causing instability and signal drift. To prevent carbon deposition, oxygen is added to the carrier gas to oxidize the carbon in the plasma. Oxygen (as a 20% oxygen in argon mix, for safety) is added using a 5th (option gas) mass flow controller, which is fitted as standard on the Agilent 8900 Semiconductor (and Advanced Applications) ICP-QQQ models and is optional for other systems. When oxygen is added to the plasma, the plasma environment becomes considerably more reactive, so platinum-tipped interface cones should be fitted instead of the standard nickel cones. The Pt-tipped skimmer cone uses a different (brass) skimmer cone base.

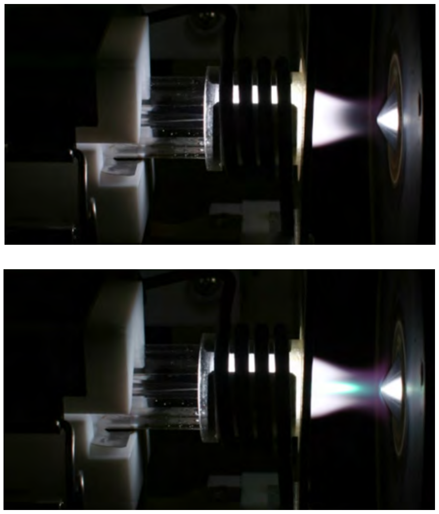

Figure 8. How the ICP-MS plasma looks when aspirating aqueous solutions (top) and organic solvents (bottom).

Optimization of oxygen flow rate

Establishing the appropriate level of oxygen for a particular organic solvent is a simple procedure, as long as the operator has a clear view of the plasma (as provided with the viewing windows fitted to all Agilent ICP-MS systems). An initial flow of oxygen is added to the carrier gas flow (e.g. to give an oxygen level of 5% of the total argon carrier flow) and the organic solvent is aspirated at an appropriate flow rate. The oxygen flow rate is reduced slowly, until a buildup of carbon on the sampling cone is observed. The oxygen flow is then increased until the carbon deposits are decomposed and the green C_2 emission, visible in the central channel of the plasma, stops well before the sample cone orifice. This indicates that the organic matrix is being successfully decomposed.

The difference in the appearance of the plasma when an organic solvent is aspirated is shown in the photographs presented in Figure 8.

The upper photo shows the normal plasma appearance when aspirating aqueous solutions. The lower photo shows the plasma when aspirating an organic matrix (NMP), with insufficient oxygen to fully decompose the carbon. The green (C_2) emission zone extends all the way to the sampling cone tip and would lead to carbon disposition over time. When the O_2 addition is increased, the carbon emission zone retreats from the sampling cone tip. With sufficient (excess) oxygen, the green emission zone disappears completely, and the plasma appears almost the same as when aspirating aqueous solutions. It should be noted, however, that operating with an excess of oxygen addition will lead to shortened cone lifetime.

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Once the optimum oxygen level for each solvent is determined, it can be saved in the acquisition method settings, allowing the correct flow to be set automatically for that sample type in the future. For a given solvent type, sample uptake rate and carrier gas flow rate, the oxygen addition remains constant and does not require routine adjustment. Table 2 shows typical oxygen flow rates and sample introduction configurations used for a range of solvents for which routine methods have been established.

Table 2. Recommended conditions for the analysis of various organic solvents.

Organic solvent	*Sample tubing id (mm)	Torch injector id (mm)	**O_2 flow (% of carrier gas)	**O_2 flow (mL/min)
Ethanol	0.3	1.5	3	35
PGMEA	0.3	1.5	3	35
Ethyl lactate	0.3	1.5	3	35
Kerosene	0.3	1.5	5	60
Methyl isobutyl ketone	0.3	1.5	8	100
Xylene	0.3	1.5	10	120
Toluene	0.3	1.5	12	150
Acetone	0.16	1	5	60

** Assumes a tubing length of 50 to 70 cm.*
*** For safety reasons, O_2 is added as a premixed blend of 20% oxygen in argon, so the flow rate required for the O_2/Ar mixed gas is 5x the amount shown for O_2.*

Sample introduction options for unusual or corrosive samples

Agilent ICP-MS and ICP-QQQ systems can provide accurate trace level analysis of a wide range of chemicals and materials. Most samples can be analyzed using the sample introduction system fitted as standard to the 7900/8900 Semiconductor configurations. However, some sample types are not compatible with the standard sample introduction system, so optional kits and components are available to allow such chemicals to be analyzed successfully.

The standard sample introduction system and interface of the Semiconductor configurations of the Agilent 7900 and 8900 comprise a PFA MicroFlow nebulizer, quartz spray chamber, quartz torch with 2.5 mm i.d. injector, Pt-tipped interface cones, and s-Lens. A summary is shown in Table 3, and full details are provided in publication number 5991-7009EN (Specifications for Agilent 8900 ICP-QQQ Semiconductor configuration) and 5991-3780EN (Specifications for Agilent 7900 ICP-MS Semiconductor configuration).

Table 3. Standard configurations of 7900 ICP-MS and 8900 ICP-QQQ Semiconductor models.

Standard mainframe configuration	Agilent 7900 (#200)
Nebulizer (concentric)	MicroFlow MFN 100 (PFA)
Spray chamber (Scott double-pass)	Quartz
Torch (with ShieldTorch System)	Quartz, 2.5 mm ID injector
Plasma Mass Flow Controllers (Ar)	4
Option gas line**	Option
Cool plasma capability	Supported
Interface cones	Pt (brass skimmer base)
Ion lens	s-Lens
ORS[4] cell gas lines	2 (He & H_2)
3rd cell gas line (low- or high-flow rate options)	Option
EM detector dynamic range	11 orders
EM detector minimum dwell time in TRA mode	0.1 ms (100 µs)

Standard mainframe configuration	Agilent 8900 (#200)
Nebulizer (concentric)	MicroFlow MFN 100 (PFA)
Spray chamber (Scott double-pass)	Quartz
Torch (with ShieldTorch System)	Quartz, 2.5 mm ID injector
Plasma Mass Flow Controllers (Ar)	4 (supporting ultra-trace S and Si)
Option gas**	N/A (included)
Cool plasma capability	Supported
Interface cones	Pt (brass skimmer base)
Ion lens	s-Lens
ORS[4] cell gas lines	4 (He & 2 x high-flow & 1 x low-flow)
3rd/4th cell gas line (low- or high-flow rate options)	N/A (included)
EM detector dynamic range	11 orders
EM detector minimum dwell time in TRA mode	0.1 ms (100 µs)

***For alternative carrier or make-up gases such as 20% O_2/Ar for organics, or He for laser*

Requirements for analysis of several samples types that require special sample introduction hardware are described below.

Figure 9. Inert (HF resistant) O-ring-free PFA sample introduction system.

Hydrofluoric acid

Trace (<0.1%) hydrofluoric acid (HF) can be tolerated for short periods by the standard quartz spray chamber and torch. However, when HF is analyzed as the concentrated acid (typically 38% w/w), or as a component of a wet etching bath or cleaning solution, etching of the quartz will occur. This leads to damaged components and sample contamination. The standard PFA nebulizer is tolerant of high concentrations of HF, but the standard quartz spray chamber, transfer tube, and torch must be replaced with HF-tolerant versions.

A complete PFA inert sample introduction kit (shown in Figure 9) is available, with options for two different torch injector materials (Pt or sapphire). The Pt injector is often prefered for semiconductor applications, but sapphire is lower-cost and does not measurably increase trace element backgrounds. Two different internal diameters – 2.5 mm (standard) or 1.5 mm (used for organic solvents and nanoparticle analysis) – are available for each injector type.

Sulfuric acid

Sulfuric acid (H_2SO_4) is used in semiconductor cleaning processes. Mixed with hydrogen peroxide (H_2O_2) as sulfuric peroxide mix (SPM), it is used for degreasing and to clean organic residues from the wafer surface. Agilent's standard quartz sample introduction system is suitable for the analysis of sulfuric acid. However, concentrated H_2SO_4 has a very high viscosity of 27 centipoise and high specific gravity (1.84) at room temperature. This means that the concentrated acid (98%) is very viscous and does not aspirate or nebulize efficiently. Consequently, H_2SO_4 is diluted 10-fold in ultrapure water for analysis, giving an acid concentration of 9.8%. In addition, the standard Pt-tipped interface cone must be replaced with a Pt-tipped cone with a larger, 18 mm Pt insert*. This is required because the 9.8% H_2SO_4 aerosol forms a gel-like deposit around the tip of the sampling cone, which can etch and corrode the join between the Pt tip and the Cu base of the cone. Using the sampling cone with the larger diameter Pt insert avoids this type of corrosion.

Phosphoric acid

Phosphoric acid (H_3PO_4) has a viscosity – 65 centipoise – that is 2.4 times higher than that of H_2SO_4, and a specific gravity of 1.74 at room temperature. The very high viscosity of H_3PO_4 means that 100 times dilution in ultrapure water is required to allow successful aspiration for ICP-MS analysis. As with H_2SO_4, the Pt-tipped sampling cone with the larger Pt insert is required when analyzing H_3PO_4, to avoid corrosion around the cone tip.

** Agilent part number G3280-67056*

Expanding Capabilities with Accessories and Software

Nanoparticle analysis

To meet evolving requirements for higher integrated circuit (IC) performance and improved device yield, it is essential that contamination is controlled in the wafer substrate and on the surface of the device during fabrication. Given the nanometer scale of device features, currently 10 nm line widths, it is clear there is a critical need to monitor metallic nanoparticles (NPs) as well as dissolved metals in bulk chemicals and wafer processing and cleaning baths.

Iron (Fe) NP contamination is of particular concern because Fe is such a common element in process equipment (for example stainless steel baths and pipes). Determination of Fe NPs in process chemicals and baths is increasingly becoming a priority.

The Agilent 8900 ICP-QQQ provides the highest performance for Fe NP detection in semiconductor applications, with low background, high sensitivity, and effective control of spectral interferences. Fast time resolved analysis (TRA) acquisition enables individual NPs to be detected and characterized, while the dissolved content can also be quantified in the same run. For applications where multiple elements are of interest, Agilent's ICP-MS MassHunter software's Fast Time Program capability supports the acquisition of NP data for up to 16 elements from one visit to the sample.

The Single Nanoparticle Analysis software module available for ICP-MS MassHunter provides the method setup, analysis and data interpretation tools to simplify single NP analysis. Agilent's portfolio of NP solutions also includes support of Field Flow Fractionation (FFF)-ICP-MS for bulk characterization of samples containing multiple sizes and types of nanoparticles.

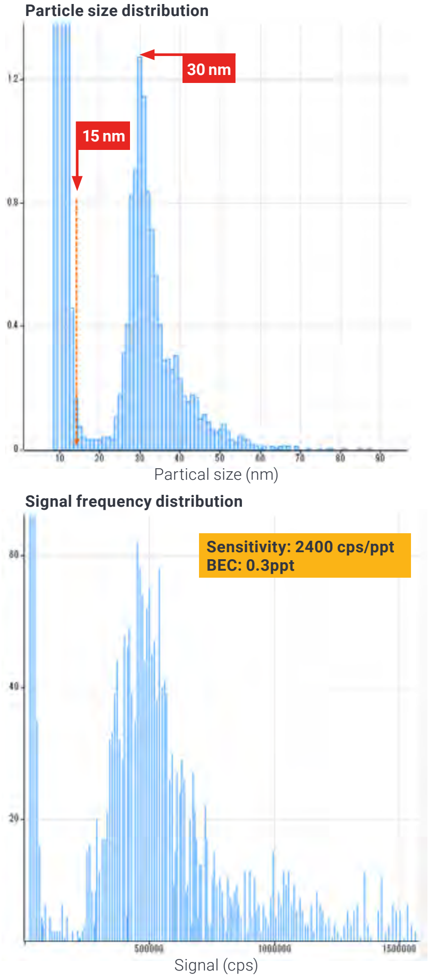

Figure 10. Analysis of Fe nanoparticles (30 nm, 6 ppt) in butyl acetate.

Integrated, contamination-free autosampler

Agilent's I-AS integrated autosampler (shown in Figure 11) is compatible with both the 7900 and the 8900 ICP-MS instruments. It features inert parts for the sample probe and arm, short tubing length to allow self-aspiration, stainless steel and plastic components to minimize cleanroom contamination, and an integrated cover to minimize the risk of sample contamination.

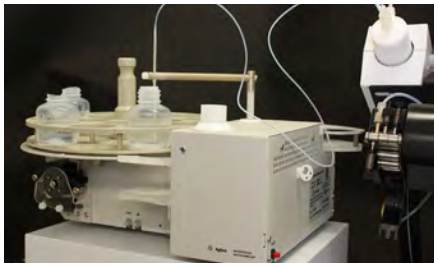

Figure 11. The Agilent I-AS integrated autosampler.

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Online Monitoring of Metal Contaminants in Process Chemicals

Agilent ICP-MS systems can be integrated with automated online semiconductor process chemical monitoring systems from suppliers including IAS Inc., ECI Technology, and ESI.

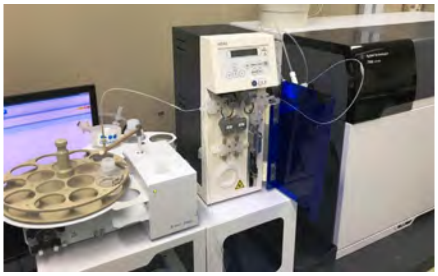

Figure 12. The ASAS automated standard addition device, part of the CSI online monitoring system from IAS Inc., Japan.

Metal impurities in process chemicals are typically monitored at delivery (as part of acceptance criteria), at the central chemical supply, at distribution points, and at the point of use. Real time, online monitoring allows the immediate detection of metal contamination at all stages of the process. This, in turn, allows quick decisions to be made for process control and QA/QC purposes, and rapid assessment of the quality of chemicals awaiting off load from a tanker.

Agilent's ICP-MS and ICP-QQQ systems have been successfully integrated with the CSI (Continuous Chemical Sample Inspection) online monitoring system manufactured by IAS Inc, Japan (Figure 12). The CSI can sample multiple, remote liquid chemical streams, baths, or containers (e.g. tankers or drums).

The sample is delivered to the CSI via a dilution module. The sample flow rate is measured and a micro volume syringe pump then adds standard spikes to automatically generate a method of standard additions (MSA) calibration. MSA spikes are added to the continuously flowing sample, so analysis is very rapid. The system can switch between multiple sample streams, with an appropriate flush time between samples.

Urgent samples – for example from a delivery tanker – can be inserted into the queue and analyzed next. The CSI system integrates with Agilent ICP-MS instruments to provide an online monitoring system suitable for high purity chemicals. The design minimizes the potential for leaks or contamination, and is compatible with either self-aspiration or pumped sample flows.

Figure 13. The ESI scoutDX automated online process monitoring system

The ESI scoutDX* on-line chemical monitoring system (shown in Figure 13) controls up to 20 remote sampling modules. Each module collects a small amount of a chemical or stream and transfers it to the central scoutDX system for ICP-MS analysis. Sample dilution and spiking are performed by a series of syringe pumps and switching valves, which prepare the sample for delivery to the ICP-MS nebulizer.

As well as enabling the rapid identification of trace element contamination, online process chemical analysis systems also reduce human contact with hazardous chemical samples, improving safety and reducing manual handling errors and contamination.

**Described in detail in Agilent ICP-MS Journal issue 69, July 2017.*

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Contamination Control

A clean working area and sample handling techniques are key to successful trace and ultratrace elemental analysis using ICP-MS. Good contamination control at all stages of the analysis has a direct impact on ICP-MS data quality.

Laboratory environment

Agilent ICP-MS instruments can perform low-level analysis of a wide range of high-purity chemicals; but achieving low detection limits also depends on controlling elemental backgrounds. Many semiconductor manufacturers invest in a dedicated cleanroom to accommodate ICP-MS analysis.

Cleanrooms are classified according to the number of ≥0.5 µm particles per cubic foot of laboratory air. Class 1 (ISO3) has up to 1 particle, and Class 10,000 (ISO7) has up to 10,000 particles. Class 1 and Class 10 cleanrooms are expensive to build and maintain, and only retain their rated classification through strict control of working practices. In some labs, the ICP-MS may be installed in a Class 10 enclosure inside a Class 10,000 lab. Sometimes, only the ICP-MS sample introduction area is protected in a clean hood. These enclosures keep the working area clean, while reducing the costs of setting up and maintaining the main lab.

Reagents

Contamination control for high purity reagents is essential for ensuring the integrity of the subsequent analysis. A well-defined protocol for chemical storage and handling is needed to prevent the contamination of reagents in the laboratory.

Inert labware cleaning procedure

A general rule is to clean labware with the same acid/reagent being analyzed. Alternatively, labware can be cleaned using the industry standard cleaning solution (SC2) used to remove ionic contaminants from wafer surfaces. The cleaning method should be appropriate for the level of analysis required.

Instrument cleaning procedure

Before low level (ppt) analysis can be performed on an ICP-QQQ or ICP-MS system, the sample introduction system must be thoroughly cleaned. Multi-step rinsing ensures the backgrounds are minimized.

PTFE sample uptake tubing is recommended for the analysis of high purity samples. Peristaltic pump tubing can contribute trace element contamination, so self-aspiration is usually used for the highest purity reagents.

Common sources of contamination

- Deionized water
- Concentrated acids and reagents
- Flasks and sample vials
- Pipette tips
- ICP-MS sample introduction system
- Lab peripherals and equipment: PCs, printers, chillers, etc…
- Operator’s clothing and personal belongings

ICP-MS Applications

Agilent continuously publishes papers specific to ICP-MS applications in the semiconductor industry. On the following pages are those currently available.

Refer to Agilent's website for later publications or subscribe to the Agilent ICP-MS Journal to stay informed.

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Cleaning/etching

ICP-MS is used to monitor trace contaminants in the chemicals used for cleaning and etching silicon wafers.

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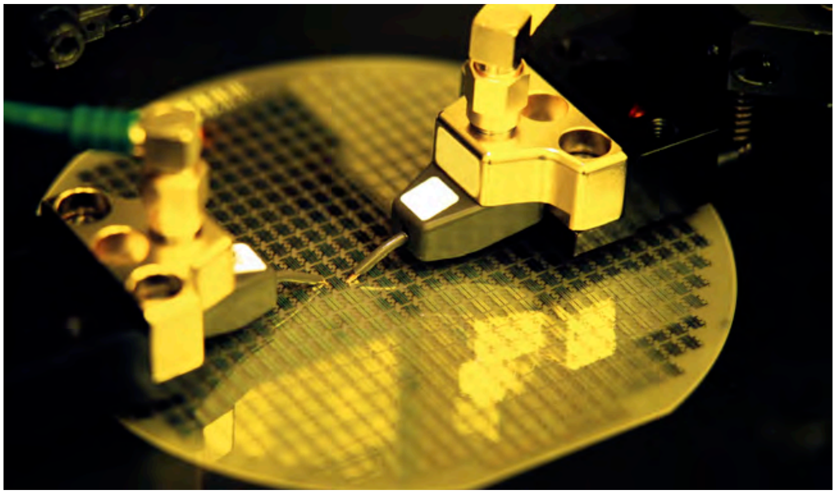
Determination of ultra trace elements in high purity hydrogen peroxide with Agilent 8900 ICP-QQQ

Application note

Semiconductor

Authors

Kazuo Yamanaka
Agilent Technologies, Japan



Introduction

Hydrogen peroxide (H_2O_2) is one of the most important process chemicals used in semiconductor device manufacturing. H_2O_2 is a strong oxidizer that is used for cleaning silicon wafers, removing photoresists, and etching metallic copper on printed circuit boards. As the chemical comes into direct contact with the silicon wafer, it is essential that trace metal contamination is controlled at the lowest possible level, to maintain device performance and production yield.

Semiconductor Equipment and Materials International (SEMI) publishes standards regarding the specifications for semiconductor process chemicals including H_2O_2 (SEMI C30-1110 – Specifications for Hydrogen Peroxide). SEMI Grade 5 is the highest purity level, with maximum contamination levels of 10 ppt for most trace elements. The semiconductor industry standard method for monitoring trace element contaminants is quadrupole ICP-MS (ICP-QMS), but the drive for ever-smaller device architectures and further improvement in device performance has led to demands to monitor a greater number of contaminant elements at lower concentrations. Current industry requirements therefore require analytical methods capable of measuring a wide range of trace elements at single- or sub-ppt level background equivalent concentration (BEC).

SEMI Standard C30-1110 includes specifications for the maximum concentrations of sulfate and phosphate allowed in high purity H_2O_2, with a limit of 30 ppb. This equates to elemental concentrations of sulfur and phosphorus of 10 ppb. These two contaminants are not currently measured by ICP-QMS, but the recent development of triple quadrupole ICP-MS (ICP-QQQ) permits much lower limits of detection for S and P, making it possible to monitor all SEMI elements using a single technique.

This application note presents results for the determination of ppt to sub-ppt level impurities in H_2O_2 using an Agilent 8900 ICP-QQQ. All SEMI specification elements and several additional elements were measured. In addition, compliance with the SEMI specification for sulfate and phosphate was evaluated via the measurement of the S and P elemental concentrations.

The 8900 ICP-QQQ is Agilent's 2nd generation ICP-QQQ, following on from the successful Agilent 8800 ICP-QQQ released in 2012. The 8900 uses a tandem mass spectrometer layout, with two quadrupole mass spectrometers enabling it to operate in MS/MS mode. The 8900 model used in this work features higher sensitivity, a new ORS^4 collision/reaction cell (CRC) with axial acceleration, and a specialized argon gas flow path to provide lower sulfur and silicon backgrounds.

ICP-QQQ offers a more reliable and consistent approach to resolving spectral interferences compared to conventional ICP-QMS, since ICP-QQQ has an additional quadrupole mass filter (Q1) in front of the CRC. In MS/MS mode, Q1 controls the ions that can enter the cell, ensuring that the reaction processes in the cell are consistent, and thereby minimizing the risk of non-target product ions being formed from the matrix elements or other analyte ions. This control of reaction processes not only ensures more consistent results, but also allows the use of highly reactive cell gases, without the risk of creating inter-element product ion overlaps.

In the case of ICP-QMS, non-target ions enter the cell and may pass through it and appear in the spectrum as overlaps on target analyte product ions, or may react with the cell gas to form new interfering product ions. In either case, there is a risk of non-target ions or product ions appearing in the spectrum and causing errors. This risk is reduced or eliminated when ICP-QQQ is used for such applications, making ICP-QQQ suitable for accurate multi-element determinations in complex matrix samples. The ability to use highly selective reaction chemistry also enables more efficient removal of background interferences, so ICP-QQQ also offers superior performance for the analysis of ultra-trace level contaminants in high-purity reagents such as semiconductor grade H_2O_2, as discussed in this note.

Experimental

A standard Agilent 8900 #200 Semiconductor configuration ICP-QQQ instrument was used. The 8900 #200 is fitted with a PFA-100 nebulizer, Peltier cooled quartz spray chamber, quartz torch, platinum-tipped sampling and skimmer cones, and s-lens. The nebulizer was operated in self-aspiration mode to minimize the potential for sample contamination from peristaltic pump tubing.

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits for every analyte. To achieve this, laboratories measuring ultra-trace levels of contaminants can use a multi-tune 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 maximum sensitivity for the analytes. In this work, several reaction cell gases (He, H_2, O_2 and NH_3) were used as appropriate for the large number of analytes being measured. Since H_2O_2 is a low-matrix sample, cool plasma conditions were also applied for the elements where this mode provides the lowest BECs. Tuning parameters are shown in Table 1, and other acquisition parameters are shown in Table 2. Q1 and Q2 settings are shown in Table 3 and Table 4 along with quantification results.

TAMAPURE-AA-10 hydrogen peroxide (35%, Tama Chemicals, Japan) was used as the sample matrix. To stabilize the spiked elements, ultrapure nitric acid (TAMAPURE-AA-10) was added to the H_2O_2 samples at 1 part of 70% HNO_3 to 1000, giving a final acid concentration of 0.07%. As is typical for high-purity semiconductor samples, calibration was by the Method of Standard Additions (MSA). A mixed multi element standard solution (SPEX CertiPrep, NJ, US) was prepared and spiked into the blank H_2O_2 matrix at 10, 20, 30, 40 and 50 ppt to create the standard addition calibration solutions. Sample solutions were prepared just before the analysis.

All sample preparation and analysis was performed in a Class 10,000 clean room.

Table 1. ICP-QQQ tuning parameters.

Tune	Cool-no gas	Cool-NH_3(1)	Cool-NH_3(2)	No gas	H_2	He	O_2(1)	O_2(2)
Acquisition mode	Single Quad	MS/MS						
RF (W)	600			1500				
Carrier gas (L/min)	0.70							
Makeup gas (L/min)	0.90			0.48				
Sampling depth (mm)	18.0			8.0				
Ext 1 (V)	-150.0		-100.0	4.2	4.7	4.2	4.5	3.5
Ext 2 (V)	-18.0	-17.0	-12.0	-250.0				-120.0
Omega bias (V)	-70.0			-140.0				-70
Omega lens (V)	2.0			10.0	8.0	-10.0	10.5	4.0
Q1 entrance (V)	-15.0		-50.0					
NH_3 flow (mL/min)*	-	2.0 (20%)**		-	-	-	-	-
He flow (mL/min)	-	1.0		-	-	5.0	-	-
H_2 flow (mL/min)	-	-	-	-	7.0	-	-	-
O_2 flow (mL/min)	-	-	-	-	-	-	0.3 (30%)**	
Axial acceleration (V)	0.0	1.5		0.0			1.0	
Energy discrimination (V)	15.0	-5.0		5.0	0.0	3.0	-7.0	

*10% NH_3 balanced with 90% He

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

Table 2. Acquisition parameters.

Parameter	Setting
Q2 peak pattern	1 point
Replicates	3 (spiked solution) 10 (unspiked solution)
Sweeps/Replicate	10
Integration time	2 s for all isotopes

Results and discussion

Calibration curves along with the calibration equation, correlation coefficient, detection limit and BEC of several SEMI specification elements are shown in Figure 1. Good linearity was obtained for all SEMI target elements, including P and S, in all of the tune modes used.

Quantitative results and detection limits of the SEMI elements are shown in Table 3. Results of other elements that are not specified in the SEMI standard are shown in Table 4. Each detection limit is calculated as 3-sigma of 10 replicate measurements of a blank H_2O_2 sample. Quantitative results and detection limits are also shown for all of these elements in pure water, for comparison purposes.

Long term stability was evaluated by measuring a H_2O_2 sample spiked at 10 ppt for most elements and 100 ppt for sulfur. Calibration curves were made at the beginning of the sequence and the spiked samples were then run as unknown samples for a total analysis period of 3 h 40 min. The analytical results for the spiked samples are plotted in Figure 2, and the RSDs of the 13 analysis results are shown in Table 3 and Table 4 (Stability Test RSD (%)). Good stability was obtained, with RSDs between 1.0% (for Pb in no gas mode) and 8.1% (for B in no gas mode). The spiked sample results of boron and sulfur slowly increased during the run, possibly due to boron and sulfur contamination from the clean room air and air filtration system.

Table 3. Quantification of trace elements and stability test results for SEMI specification elements in high purity 35% H_2O_2 and pure water

	Q1	Q2	Acquisition mode	Tune	Hydrogen Peroxide			Pure Water	
					Conc. (ppt)	DL (ppt)	Stability Test* RSD (%)	Conc. (ppt)	DL (ppt)
Li		7	Single Quad	Cool	< DL	0.003	4.7	< DL	0.004
B	11	11	MS/MS	No gas	7.7	0.69	8.1	4.6	0.57
Na		23	Single Quad	Cool	0.39	0.031	3.3	0.50	0.069
Mg		24	Single Quad	Cool	0.017	0.017	4.1	< DL	0.012
Al		27	Single Quad	Cool	0.39	0.071	2.9	0.11	0.11
P	31	47	MS/MS	O_2(1)	4.2	0.89	3.3	3.4	0.91
S	32	48	MS/MS	O_2(1)	190	5.1	7.8**	41	3.8
K	39	39	MS/MS	Cool+NH_3(2)	0.21	0.11	2.2	0.20	0.088
Ca	40	40	MS/MS	Cool+NH_3(2)	< DL	0.23	1.9	< DL	0.10
Ti	48	64	MS/MS	O_2(2)	0.097	0.045	2.6	< DL	0.028
V	51	67	MS/MS	O_2(2)	0.067	0.027	2.6	< DL	0.023
Cr	52	52	MS/MS	Cool+NH_3(1)	0.13	0.075	3.5	< DL	0.031
Mn	55	55	MS/MS	Cool+NH_3(1)	< DL	0.012	2.7	< DL	0.004
Fe	56	56	MS/MS	Cool+NH_3(1)	0.13	0.074	3.3	< DL	0.027
Ni	60	60	MS/MS	Cool+NH_3(1)	0.16	0.14	3.7	< DL	0.030
Cu	63	63	MS/MS	Cool+NH_3(1)	< DL	0.048	5.0	0.19	0.18
Zn	64	64	MS/MS	He	0.22	0.14	4.5	0.35	0.17
As	75	91	MS/MS	O_2(2)	< DL	0.087	3.5	< DL	0.081
Cd	114	114	MS/MS	No gas	< DL	0.020	2.3	< DL	0.017
Sn	118	118	MS/MS	No gas	0.088	0.063	2.0	< DL	0.037
Sb	121	121	MS/MS	H_2	< DL	0.015	1.6	< DL	0.022
Ba	138	138	MS/MS	H_2	0.061	0.033	1.2	< DL	0.004
Pb	208	208	MS/MS	No gas	0.081	0.053	1.0	0.056	0.035

SEMI C30-1110 Grade 5, maximum concentration of listed elements: 10 ppt

* Analyte elements were spiked at 10 ppt

** Sulfur was spiked 100 ppt

Table 4. Quantification of trace elements and stability test results for other (non-SEMI specification) elements in high purity 35% H_2O_2 and pure water

	Q1	**Q2**	**Acquisition mode**	**Tune**	**Hydrogen Peroxide**			**Pure Water**	
					Conc. (ppt)	**DL (ppt)**	**Stability Test* RSD (%)**	**Conc. (ppt)**	**DL (ppt)**
Be	9	9	MS/MS	No gas	< DL	0.037	4.7	< DL	0.036
Si**	28	28	MS/MS	H_2	260	25		120	5.9
Sc	45	61	MS/MS	O_2(1)	< DL	0.006	2.4	< DL	0.004
Co	59	59	MS/MS	Cool+NH_3(1)	< DL	0.045	3.6	< DL	0.012
Ga		71	Single Quad	Cool	< DL	0.017	4.1	<DL	0.000
Ge	74	74	MS/MS	He	0.16	0.14	4.4	< DL	0.21
Se	78	78	MS/MS	H_2	< DL	0.26	3.5	< DL	0.15
Rb		85	Single Quad	Cool	< DL	0.012	2.2	< DL	0.008
Sr	88	88	MS/MS	He	< DL	0.015	3.5	< DL	0.006
Zr	90	106	MS/MS	O_2(1)	0.031	0.027	1.3	0.15	0.047
Nb	93	93	MS/MS	He	0.18	0.061	2.8	< DL	0.005
Mo	98	98	MS/MS	He	0.10	0.10	3.4	< DL	0.053
Ru	101	101	MS/MS	He	0.76	0.35	4.2	0.27	0.16
Rh	103	103	MS/MS	O_2(2)	0.29	0.054	1.7	0.066	0.03
Pd	105	105	MS/MS	No gas	0.08	0.052	2.1	0.039	0.037
Ag	107	107	MS/MS	No gas	< DL	0.01	2.2	0.14	0.037
In	115	115	MS/MS	No gas	< DL	0.004	1.8	0.004	0.004
Te	125	125	MS/MS	No gas	< DL	0.16	5.0	< DL	0.19
Cs		133	Single Quad	Cool	< DL	0.014	2.4	< DL	0.016
Hf	178	178	MS/MS	No gas	0.035	0.032	1.6	< DL	0.12
W	182	182	MS/MS	No gas	0.048	0.03	1.9	< DL	0.011
Re	185	185	MS/MS	No gas	< DL	0.049	1.4	< DL	0.011
Ir	193	193	MS/MS	No gas	0.041	0.038	1.6	< DL	0.033
Pt	195	195	MS/MS	H_2	1.7	0.55	2.1	0.85	0.33
Au	197	197	MS/MS	No gas	0.22	0.097	1.5	0.095	0.065
Tl	205	205	MS/MS	No gas	0.017	0.015	1.1	0.03	0.024
Bi	209	209	MS/MS	No gas	< DL	0.008	1.2	< DL	0.007
Th	232	232	MS/MS	No gas	< DL	0.007	1.3	< DL	0.013
U	238	238	MS/MS	No gas	< DL	0.003	1.2	< DL	0.002

* Analyte elements were spiked at 10 ppt

** Si concentration in the mixed spike (10 ppt) was too low for reliable quantification above the blank (260 ppt).

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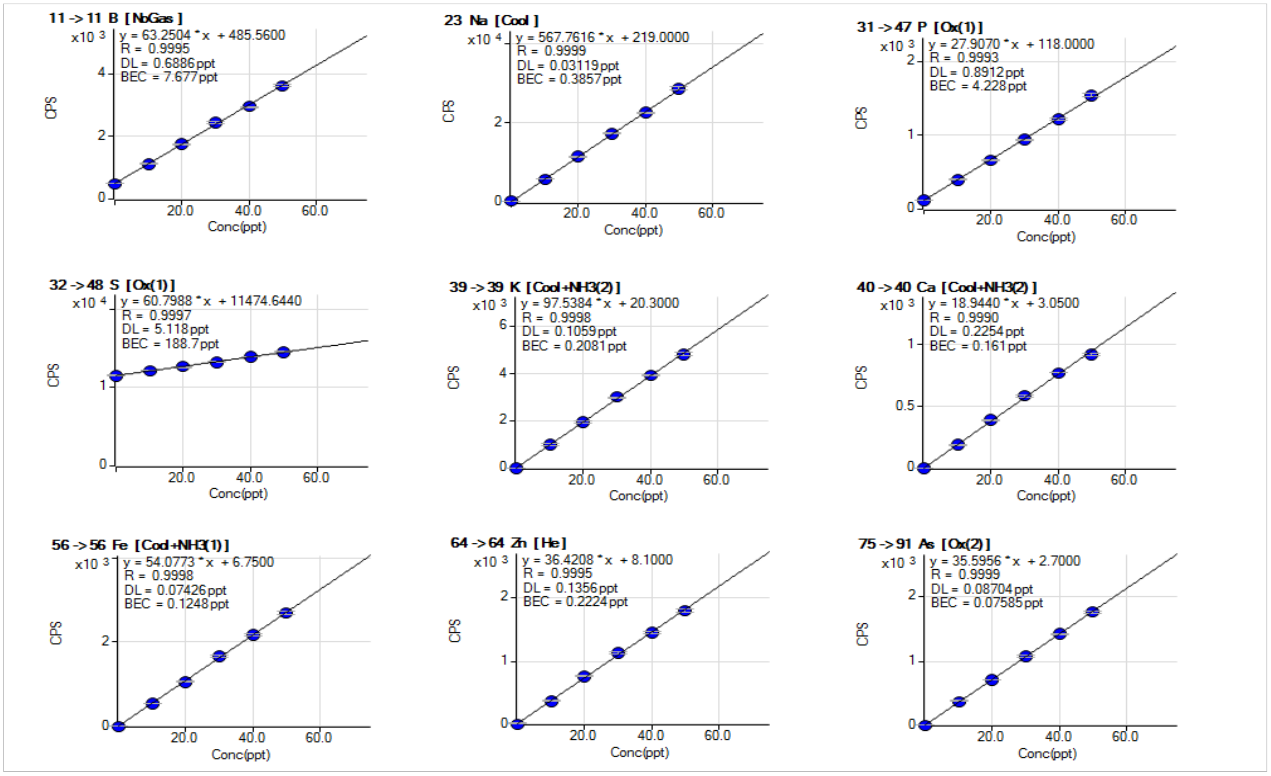

Figure 1. Calibration curves for several SEMI specification elements in high purity 35% H_2O_2

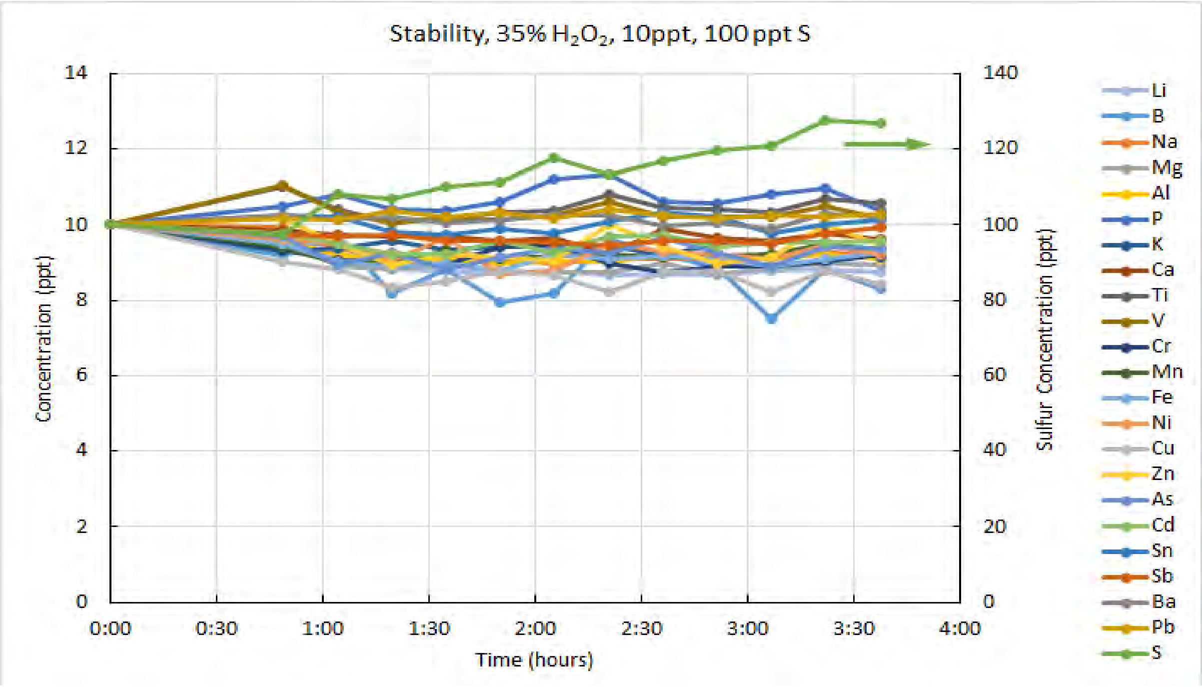

Figure 2. Stability test result of 10 ppt spiked analytes (and 100 ppt sulfur) in high purity 35% H_2O_2. Total analysis time of 3 h 40 min following initial calibration standards. Note: Si concentration in the mixed spike (10 ppt) was too low for reliable quantification above the blank (260 ppt).

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Conclusions

Many elements, including all the elements specified in SEMI C30-1110, together with other trace elements, were measured at sub-ppt to ppt levels in high purity 35% hydrogen peroxide, using the Agilent 8900 ICP-QQQ. Excellent linear calibration curves from 0 ppt to 50 ppt concentration range were obtained. For almost all elements, sub ppt quantitative results were obtained, with the remaining elements having single-ppt detection limits (except Si, 25 ppt). Reproducibility between 1.0 – 8.1 % RSD was obtained at the 10 ppt level (100 ppt for S) for the spiked analytes, for a high purity 35% hydrogen peroxide sample analysis sequence lasting 3 hours 40 minutes. This demonstrates the suitability of the Agilent 8900 Semiconductor configuration ICP-QQQ instrument for routine analysis of the highest-purity semiconductor reagents and process chemicals.

Reference

1.SEMI C30-1110, Specifications for hydrogen peroxide (2010)

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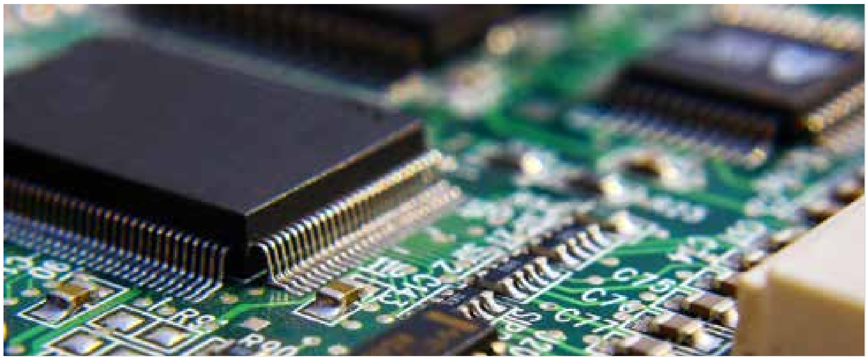
Application Note
Semiconductor

Direct Analysis of Trace Metal Impurities in High Purity Nitric Acid Using ICP-QQQ



Authors

Kazuo Yamanaka and Kazuhiro Sakai

Agilent Technologies, Tokyo, Japan

Introduction

The manufacturing yield of semiconductor devices has always been susceptible to contamination from trace metals. As the industry continues to progress towards devices with smaller features and a higher density of integration, susceptibility to contamination in microfabrication processing presents an increasing challenge. Controlling contamination at these small scales requires ever-higher purity of process chemicals and manufacturing conditions.

The semiconductor device fabrication industry uses well-established cleaning procedures to remove organic and metallic residues and impurities from the surface of silicon wafers. The purity of reagents used during manufacturing processes and the air quality in the fabrication plant are important considerations.

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Nitric acid (HNO_3) plays an important role in the fabrication of semiconductor devices so needs to be of ultrahigh purity. A mix of nitric and hydrofluoric acid is used to etch single crystal silicon and polycrystalline silicon. HNO_3 is also combined with phosphoric acid and acetic acid for wet etching of aluminum. As a reagent, HNO_3 is used in the preparation of other semiconductor materials.

SEMI standard C35-0708 Tier-B protocol for HNO_3 (69.0–70.0 %) specifies contaminant levels of <1 µg/L (ppb) for several elements [1]. The concentration of industrial grade HNO_3 is usually 60–68%, depending on the method of production.

In this study, undiluted HNO_3 was analyzed directly by triple quadrupole ICP-MS (ICP-QQQ). This approach simplified sample preparation and avoided the potential introduction of contaminants during dilution.

Experimental

Samples and standards

Two samples of HNO_3 were used in this study:

- Sample 1: 68 % HNO_3 (high purity-grade)
- Sample 2: 61 % HNO_3 (electronic-grade - lower purity)

No further sample preparation was necessary as all samples were introduced directly into the ICP-QQQ.

Calibration and quantification were done using the method of standard additions (MSA). Standard solutions were prepared by spiking a multi-element standard solution (SPEX CertiPrep, NJ, US) into each HNO_3 sample to give spike levels of 5, 10, 20, 30 and 40 ppt. The density of the nitric acid solution varies with the concentration of the acid, which affects the sample transport, nebulization and droplet evaporation processes in the ICP-MS sample introduction. Therefore, for the most accurate analysis, the acid grade (concentration) used for the spiked MSA calibration solutions should be approximately matched to the acid concentration of the samples. ICP-MS MassHunter allows an MSA calibration to be converted to an external calibration to determine contaminant levels in other nitric acid samples with similar acid concentration. The solutions were prepared just before analysis. All preparation and analyses were performed in a Class 10,000 clean room.

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ instrument was used in this study. The instrument is fitted as standard with a PFA-100 nebulizer, Peltier-cooled quartz spray chamber, quartz torch, platinum-tipped sampling and skimmer cones, and s-lens. The nebulizer was operated in self-aspiration mode to minimize the potential for sample contamination from contact with the peristaltic pump tubing. If large numbers of undiluted HNO_3 samples are run routinely, it is recommended that the large (18 mm) insert Pt cone is fitted. Long-term corrosion of internal ICP-MS components can be minimized by fitting the dry pump option and ball-type interface valve kit.

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits (DLs) for each analyte. To achieve this goal, laboratories measuring ultratrace levels of contaminants can 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, H_2, O_2, and NH_3) and both hot and cool plasma conditions were used as appropriate for the large number of analytes being measured. Tuning conditions are shown in Table 1 and other acquisition parameters are shown in Table 2.

Table 1. ICP-QQQ operating conditions.

	Cool-NH_3	No gas	H_2	He	O_2	O_2-soft
Acquisition mode	MS/MS					
RF power (W)	600	1500				
Sampling depth (mm)	18.0	8.0				
Nebulizer gas (L/min)	0.70					
Makeup gas (L/min)	0.78	0.36				
Extract 1 (V)	-150.0	4.2	4.7	4.2	4.5	3.5
Extract 2 (V)	-17.0	-250.0				-120.0
Omega bias (V)	-70.0	-140.0				-70.0
Omega lens (V)	2.0	10.0	8.0	10.0	10.5	4.0
Q1 entrance (V)	-15.0	-50.0				
He flow (mL/min)	1.0	-	-	5.0	-	-
H_2 flow (mL/min)	-	-	7.0	-	-	-
*NH_3 flow (mL/min)	2.0 (20%)**	-	-	-	-	-
O_2 flow (mL/min)	-	-	-	-	0.45 (30%)**	
Axial acceleration (V)	1.5	0.0			1.0	
Energy discrimination (V)	-5.0	5.0	0.0	3.0	-7.0	

*10% NH_3 balanced with 90% He

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

Table 2. Acquisition parameters.

Parameter	Setting
Q2 peak pattern	1 point
Replicates	3 (spiked solution)
	10 (unspiked solution for DL measurement)
Sweeps/replicate	10
Integration time	2 s for all isotopes

Results and Discussion

DLs and BECs

In total, 49 elements were measured using the 8900 ICP-QQQ operating in multiple tune modes, 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. DLs and Background Equivalent Concentrations (BECs) in undiluted 68% HNO_3 (Sample 1) are given in Table 3. The stability test results are discussed in the ”long-term stability” section of the report.

Table 3. DLs and BECs in high purity 68% HNO_3.

Element	Tune	Q1	Q2	DL ng/L	BEC ng/L	30 ppt Recovery %	Stability test RSD %
Li	Cool-NH_3	7	7	0.061	0.042	93	3.1
Be	No gas	9	9	0.12	0.071	92	3.5
B	No gas	11	11	0.43	3.5	94	6.3
Na	Cool-NH_3	23	23	0.53	2.3	93	3.1
Mg	Cool-NH_3	24	24	0.085	0.049	93	2.0
Al	Cool-NH_3	27	27	0.10	0.16	93	3.6
P	O_2	31	47	8.1	83	95	—**
S	O_2	32	48	2.6	65	93	—**
K	Cool-NH_3	39	39	0.38	0.73	93	2.9
Ca	Cool-NH_3	40	40	0.54	0.38	93	1.2
Sc	O_2	45	61	0.007	0.013	93	0.5
Ti	O_2-soft	48	64	0.039	0.081	93	3.3
V	O_2-soft	51	67	0.041	0.17	93	1.5
Cr	Cool-NH_3	52	52	0.42	0.25	93	3.0
Mn	Cool-NH_3	55	55	0.084	0.014	93	2.5
Fe	Cool-NH_3	56	56	0.75	1.1	92	4.7
Co	Cool-NH_3	59	59	0.21	0.075	93	4.3
Ni	O_2-soft	60	60	0.067	0.38	93	2.0
Cu	Cool-NH_3	63	63	0.12	0.50	94	3.8
Zn	He	64	64	0.52	0.46	93	2.9
Ga	Cool-NH_3	71	71	0 cps	0 cps	92	2.5
Ge	H_2	74	74	0.060	0.10	93	1.4
As	O_2-soft	75	91	0.082	0.081	93	1.8
Se	H2	78	78	0.78	0.41	93	5.5
Rb	Cool-NH_3	85	85	0.089	0.030	93	3.0
Sr	He	88	88	0.014	0.012	93	0.8
Zr	O_2	90	106	0.22	1.0	93	0.4
Nb	He	93	93	0.012	0.014	93	0.8
Mo	He	98	98	0.088	0.10	93	1.0
Ru	He	101	101	0.032	0.034	93	1.2
Pd	No gas	105	105	0.066	0.14	92	1.0
Ag	No gas	107	107	0.029	0.025	93	0.9
Cd	No gas	114	114	0.058	0.046	92	1.4
In	No gas	115	115	0.004	0.004	93	0.6
Sn	No gas	118	118	0.099	0.35	93	0.9
Sb	H_2	121	121	0.056	0.028	93	1.6
Te	H_2	125	125	0.57	0.45	93	5.2
Cs	Cool-NH_3	133	133	0 cps	0 cps	93	2.4
Ba	H_2	138	138	0.014	0.010	93	0.4
Hf	No gas	178	178	0.014	0.005	93	0.9
Ta	He	181	181	0.052	0.065	93	0.5
W	No gas	182	182	0.030	0.022	93	0.7
Ir	No gas	193	193	0.016	0.011	93	0.9
Au	No gas	197	197	0.049	0.068	93	1.7
Tl	No gas	205	205	0.090	0.46*	93	0.6
Pb	No gas	208	208	0.060	0.21	93	0.7
Bi	No gas	209	209	0.018	0.025	93	0.4
Th	No gas	232	232	0.004	0.003	93	0.8
U	No gas	238	238	0.025	0.013	93	0.6

Table continues...

...Table continued

DLs were calculated as 3-sigma of 10 replicate measurements of a blank HNO_3 sample (cps refers counts per second).

**The BEC of Tl was higher than expected, most likely due to residual signal from the ICP-MS tuning solution.*

***P and S concentration in the mixed spike (30 ppt) was too low for reliable quantification above the blank (83 ppt and 65 ppt, respectively).*

Table 4 shows quantitative data for all SEMI specification elements [1] in high purity 68% HNO_3 and electronic-grade 61% HNO_3 determined by MSA. For the greatest accuracy, the two different concentration grades of nitric acid measured in this study were calibrated using separate MSA calibrations. However, if additional samples of similar grade (acid concentration) are measured, the MSA calibration can be easily and automatically converted to an external calibration plot. External calibration allows subsequent samples to be measured without requiring MSA spike additions into each additional sample.

Good linearity was obtained for all SEMI target elements, as shown in the representative calibration curves for B, Na, Al, K, Ca, As, and Pb (Figure 1).

Normally, the concentration in each sample is obtained by multiplying the quantitative value by the dilution factor (usually about 10 times for nitric acid). However, in this study, the quantitative value equals the sample concentration in the original sample, as the acids were measured undiluted. The results given in Table 4 show that all 49 elements studied can be analyzed at significantly lower levels than the <1 ppb maximum limit specified for HNO_3 in SEMI standard C35-0708 Tier-B [1].

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Table 4. Quantitative results for SEMI specification elements [1] in high purity 68% HNO_3 and electronic-grade 61% HNO_3.

Element	High-purity grade 68% HNO_3, ng/L	Electronic grade 61% HNO_3, ng /L	SEMI C35-0708 Tier-B max limit, ng/L
Li	<0.061	0.19	<1000
B	3.5	270	<1000
Na	2.3	130	<1000
Mg	<0.085	11	<1000
Al	0.16	93	<1000
K	0.73	6.5	<1000
Ca	<0.54	50	<1000
Ti	0.081	1.1	<1000
V	0.17	0.24	<1000
Cr	<0.42	70	<1000
Mn	<0.084	3.4	<1000
Fe	1.1	270	<1000
Ni	0.38	28	<1000
Cu	0.50	0.99	<1000
Zn	<0.52	3.8	<1000
As	<0.082	0.25	<1000
Cd	<0.058	0.80	<1000
Sn	0.35	13	<1000
Sb	<0.056	0.11	<1000
Ba	<0.014	0.43	<1000
Pb	0.21	0.31	<1000

Measured values shown as "<" indicate that the measured concentration was below the detection limit.

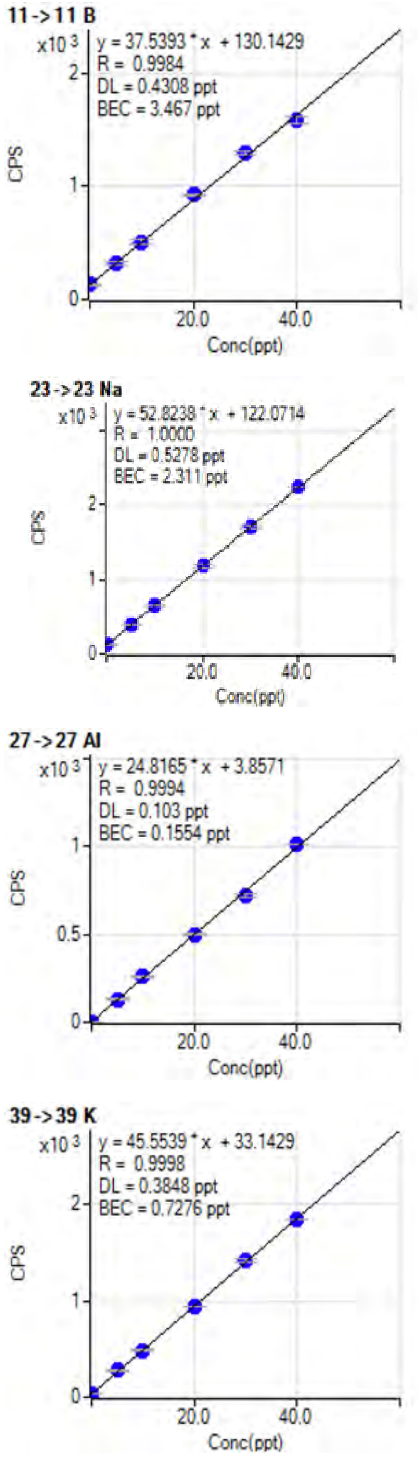

Figure 1. Calibration curves for several SEMI specification elements in high purity 68% HNO_3

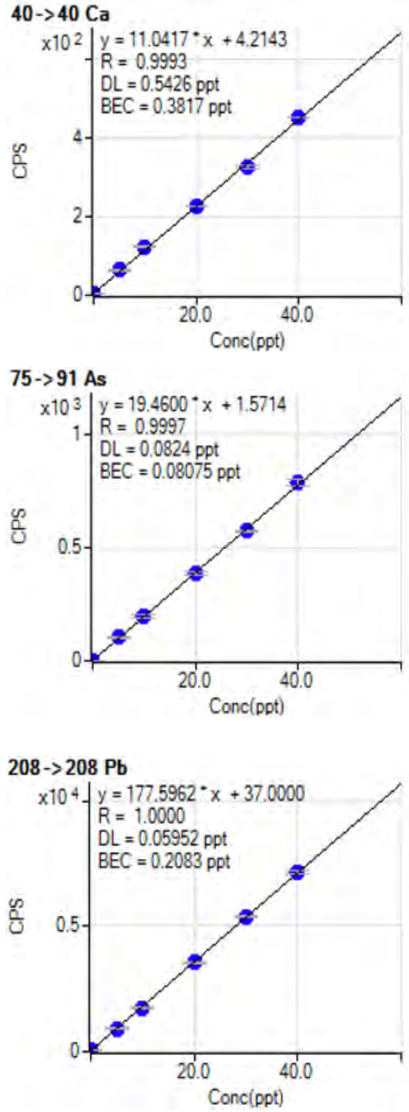

Figure 1. (continued) Calibration curves for several SEMI specification elements in high purity 68% HNO_3.

Long-term stability

Long-term stability was evaluated by measuring a 68% HNO_3 sample spiked at 30 ppt for all elements. Calibration curves were generated at the beginning of the sequence. The spiked samples were then run as unknown samples for a total analysis period of 6.5 hours. The RSDs of the 21 analysis results are shown in Table 3 (stability test RSD (%)). Good stability was maintained throughout the run, with RSDs between 0.4 and 5.5 %. S and P gave less reliable long-term results due to the low concentration of the spike (30 ppt) measured above the relatively high concentration (83 ppt for P; 65 ppt for S) in the unspiked sample.

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode provides the sensitivity, low backgrounds, and unmatched control of interferences required for the analysis of ultratrace elements in high purity nitric acid.

Forty-nine elements were measured at sub-ppt to ppt levels in undiluted high purity 68% HNO_3. Calibrations were linear for all elements between 0–40 ppt. SEMI-specified elements were quantified at the single-figure ppt or sub-ppt level in high purity 68% HNO_3. The reproducibility results for 30 ppt spikes in high purity undiluted 68% HNO_3 were between 0.4–5.5 % RSD for all elements except P and S, in a sequence lasting 6.5 hours.

The results demonstrate the suitability of the Agilent 8900 Semiconductor configuration ICP-QQQ for the routine analysis of the highest-purity semiconductor-grade reagents and process chemicals.

References

1. SEMI C35-0708, Specifications and guidelines for nitric acid (2008).

More Information

For more information on Agilent ICP-MS products and services, visit our website at www.agilent.com/chem/icpms

When analyzing 61–68 % HNO_3 on a routine basis, it is recommended to use the following options:

• G3280-67056	Pt sampling cone (18 mm insert)
• G4915A	Upgrade to dry pump
• G3666-67030	Interface valve kit - ball type valve

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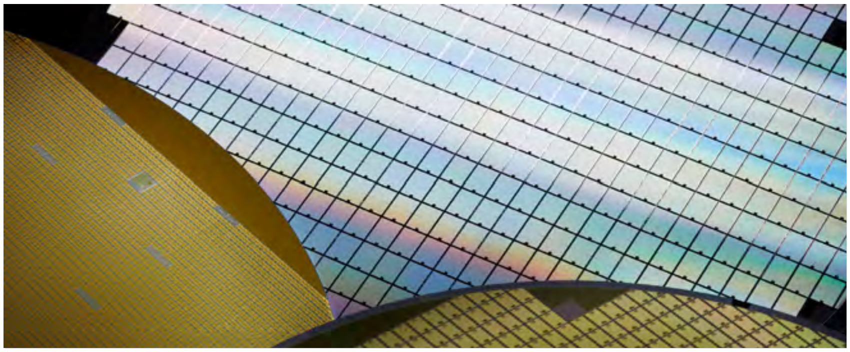
Analysis of Trace Metal Impurities in High Purity Hydrochloric Acid Using ICP-QQQ



Authors

Kazuo Yamanaka and
Kazuhiro Sakai
Agilent Technologies, Japan

Introduction

Hydrochloric acid (HCl) is a component of the standard RCA cleaning process used to remove organic and metallic residues and impurities from the surface of silicon wafers used in semiconductor manufacturing. The cleaning steps are performed before high temperature processing steps such as oxidation and chemical vapor deposition (CVD). RCA Standard Clean 2 (SC-2) removes ionic contaminants from the wafer surface. SC-2 follows SC-1, which removes organic residues and particles. SC-2 consists of HCl combined with hydrogen peroxide (H_2O_2) and de-ionized water (DIW). Since the cleaning solutions are in direct contact with the silicon wafer surface, ultrahigh purity reagents are required for these solutions.

SEMI standard C27-0708 Tier-C protocol for HCl specifies a maximum contaminant level of 100 ppt for each element (HCl 37.0 - 38.0 %) [1]. The concentration of industrial grade HCl is usually 20 or 35%, depending on the method of production. The Cl matrix leads to the formation of several polyatomic ions, which cause significant spectral interferences on some key elements. For example, $H_2{}^{37}Cl^+$ on $^{39}K^+$, $^{35}Cl^{16}O^+$ on $^{51}V^+$, $^{35}Cl^{16}OH^+$ on $^{52}Cr^+$, $^{37}Cl^{16}O^+$ on $^{53}Cr^+$, $^{35}Cl^{37}Cl^+$ on $^{72}Ge^+$, $^{37}Cl_2{}^+$ on $^{74}Ge^+$, and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. As a result of these polyatomic interferences, it has been difficult to determine these elements at the required levels using conventional single quadrupole ICP-MS (ICP-QMS). Even ICP-QMS instruments fitted with a collision/reaction cell (CRC) or bandpass filter can only offer limited reduction of the spectral interferences arising from the Cl matrix. Consequently, some methods for the analysis of high purity HCl by ICP-QMS have recommended sample pretreatment steps to remove the chloride matrix, which can lead to analyte loss and/or sample contamination.

In this study, triple quadrupole ICP-MS (ICP-QQQ) was used to analyze 50 elements in HCl, using MS/MS mode to resolve the polyatomic interferences. All analytes, including the most problematic elements such as K, V, Cr, Ge, and As, could be determined directly in the undiluted HCl with single digit ppt detection limits.

Experimental

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ was used in this study. The instrument was fitted with a PFA-100 nebulizer, Peltier-cooled quartz spray chamber, quartz torch, platinum-tipped sampling and skimmer cones and s-lens.

The nebulizer was operated in self-aspiration mode to minimize the potential for sample contamination from the peristaltic pump tubing. In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits (DLs) for each analyte. To achieve this goal, laboratories measuring ultratrace levels of contaminants can use a multi-tune 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 maximum sensitivity for each analyte. In this work, several reaction cell gases (H_2, O_2, and NH_3) were used as appropriate for the large number of analytes being measured. He was used as a buffer gas in the NH_3 reaction gas modes. Tuning conditions are shown in Table 1 and other acquisition parameters are shown in Table 2.

Table 1. ICP-QQQ operating conditions.

	Cool	Cool-NH_3	No gas	H_2	O_2	NH_3	O_2-soft
Acquisition mode	MS/MS						
RF power (W)	600	1500					
Sampling depth (mm)	18.0	8.0					
Nebulizer gas (L/min)	0.70						
Makeup gas (L/min)	0.90	0.48					
Extract 1 (V)	-150.0		4.2	4.7	4.5		3.5
Extract 2 (V)	-18.0	-17.0	-250.0				-120.0
Omega bias (V)	-70.0	-140.0					-70.0
Omega lens (V)	2.0		10.0	8.0	10.5		4.0
Q1 entrance (V)	-15.0		-50.0				
He flow (mL/min)	-	1.0	-	-	-	1.0	-
H_2 flow (mL/min)	-	-	-	7.0	-	-	-
NH_3 flow (mL/min)	-	2.0 (20%)	-	-	-	2.0 (20%)	-
O_2 flow (mL/min)	-	-	-	-	0.45 (30%)	-	0.45 (30%)
Axial acceleration (V)	0.0	1.5	0.0		1.0	0.2	1.0
Energy discrimination (V)	15.0	-5.0	5.0	0.0	-7.0		

Table 2. Acquisition parameters.

Parameter	Setting
Q2 peak pattern	1 point
Replicates	3 (spiked solution)
	10 (unspiked solution)
Sweeps/replicate	10
Integration time	2 s for all isotopes

Samples and standards

The samples of HCl used in this study included:

- Sample 1: 20% HCl (high purity grade).
- Sample 2: 36% HCl (non-high purity grade).
- Sample 3: 20% HCl (34% high purity grade diluted to 20% with DIW).

No further sample preparation was necessary as all samples were introduced directly into the ICP-QQQ. To run undiluted HCl routinely, it is recommended that the large (18 mm) insert Pt cone is fitted. Long-term corrosion of internal ICP-MS components can be minimized by fitting the dry pump option.

Calibration and quantification were done using the method of standard additions (MSA). Standard solutions were prepared by spiking a multi-element standard solution (SPEX CertiPrep, NJ, US) into each HCl sample type to give spike levels of 10, 20, 30, and 40 ppt. The MSA calibrations were then automatically converted to external calibrations in the ICP-MS MassHunter data analysis table. This conversion allows other samples of the same type (HCl concentration) to be quantified without requiring separate MSA spike additions into each sample. All solutions were prepared just before analysis.

All preparation and analysis was performed in a Class 10,000 clean room.

Results and Discussion

DLs and BECs

In total, 50 elements including all SEMI specification analytes were measured using the 8900 ICP-QQQ operating in multiple tune modes. Data for each mode was combined automatically into a single report for each sample. Detection limits (DLs) and background equivalent concentrations (BECs) in 20% HCl are given in Table 3.

Table 3. DLs and BECs in high purity 20% HCl*.

Element	Cell gas mode	Q1 mass	Q2 mass	DL ng/L	BEC ng/L
Li	Cool-NH$_3$	7	7	0.032	0.016
Be	No gas	9	9	0.022	0.021
B	No gas	11	11	0.55	4.1
Na	Cool-NH$_3$	23	23	0.064	0.15
Mg	Cool-NH$_3$	24	24	0.077	0.056
Al	Cool-NH$_3$	27	27	0.20	0.19
P	O$_2$-soft	31	47	1.1	2.6
K	Cool-NH$_3$	39	39	0.087	0.17
Ca	Cool-NH$_3$	40	40	0.44	0.68
Sc	O$_2$-soft	45	61	0.014	0.012
Ti	O$_2$-soft	48	64	0.051	0.074
V	NH$_3$	51	51	0.11	0.19
Cr	Cool-NH$_3$	52	52	0.18	0.12
Mn	Cool-NH$_3$	55	55	0.016	0.006
Fe	Cool-NH$_3$	56	56	0.24	0.27
Co	Cool-NH$_3$	59	59	0.10	0.038
Ni	Cool-NH$_3$	60	60	0.66	0.26
Cu	Cool-NH$_3$	63	63	0.10	0.12
Zn	NH$_3$	66	66	0.14	0.097
Ga	NH$_3$	71	71	0.015	0.026
Ge	NH$_3$	74	107	0.90	3.0
Ge	NH$_3$	74	107	0.32	0.77
As	O$_2$	75	91	1.4	48
As	O$_2$	75	91	0.73	6.2
Se	H$_2$	78	78	0.44	0.52
Rb	Cool-NH$_3$	85	85	0.041	0.013
Sr	NH$_3$	88	88	0.003	0.001
Y	O$_2$-soft	90	106	0.010	0.006
Zr	O$_2$-soft	93	125	0.012	0.004
Nb	O$_2$	93	125	0.004	0.005
Mo	He	98	98	0.13	0.57
Ru	He	101	101	0.016	0.003
Pd	He	105	105	0.010	0.001
Ag	He	107	107	0.032	0.014
Cd	He	114	114	0.090	0.10
In	He	115	115	0.035	0.021
Sn	He	118	118	0.57	3.3
Sb	He	121	121	0.66	1.5
Te	H$_2$	125	125	0.37	0.31
Cs	NH$_3$	133	133	0.008	0.019
Ba	NH$_3$	138	138	0.005	0.005
Hf	No gas	178	178	0.005	0.004
Ta	He	181	181	0.013	0.010
W	No gas	182	182	0.039	0.062
Re	No gas	185	185	0.12	0.50
Ir	No gas	193	193	0.017	0.012
Au	He	197	197	0.027	0.022
Tl	No gas	205	205	0.007	0.004
Pb	H$_2$	208	208	0.028	0.023
Bi	No gas	209	209	0.024	0.030
Th	No gas	232	232	0.017	0.021
U	No gas	238	238	0.009	0.005

* Shaded rows for Ge and As indicate results measured in Sample 3, due to suspected contamination for these elements in Sample 1.

Quantitative results

Table 4 shows quantitative data for all SEMI specification elements in high purity 20% HCl and non-high purity 36% HCl determined by MSA. The results show that the 8900 ICP-QQQ can measure contaminants in HCl at a much lower level than the 100 ppt maximum limit specified in the SEMI specifications. It is important to note that the concentration specified by SEMI is for 37–38% HCl while the data presented here is for 20 and 36% HCl. Even taking this difference into account, the 8900 ICP-QQQ is clearly able to measure contaminants at levels far lower than current industry requirements for high-purity HCl.

Table 4. Quantitative results for SEMI specification elements in high purity 20% HCl (Sample 1) and non-high purity 36% HCl (Sample 2).

Element	Cell gas mode	Q1	Q2	Sample 1 20% HCl, ng/L	Sample 2 36% HCl, ng/L	DL, ng/L
Li	Cool-NH_3	7	7	<DL	<DL	0.032
B	No gas	11	11	4.1	15	0.55
Na	Cool-NH_3	23	23	0.15	6.4	0.064
Mg	Cool-NH_3	24	24	<DL	6.5	0.077
Al	Cool-NH_3	27	27	<DL	23	0.20
K	Cool-NH_3	39	39	0.17	1.5	0.087
Ca	Cool-NH_3	40	40	0.68	13	0.44
Ti	O_2 soft	48	64	0.074	1.4	0.051
V	NH_3	51	51	0.19	4.6	0.11
Cr	Cool-NH_3	52	52	<DL	0.55	0.18
Mn	Cool-NH_3	55	55	<DL	0.071	0.016
Fe	Cool-NH_3	56	56	0.27	7.6	0.24
Ni	Cool-NH_3	60	60	<DL	<DL	0.66
Cu	Cool-NH_3	63	63	0.12	0.57	0.10
Zn	NH_3	66	66	<DL	1.1	0.14
As	O_2	75	91	48	39	0.73*
Cd	He	114	114	0.10	0.34	0.090
Sn	He	118	118	3.3	2.3	0.57
Sb	He	121	121	1.5	0.95	0.66
Ba	NH_3	138	138	0.005	<DL	0.005
Pb	H_2	208	208	0.023	0.13	0.028

*DL for As measured in Sample 3, due to suspected contamination for this element in Sample 1.

Cr and K determination

Cool plasma is a proven technique used to remove plasma-based interferences. Although it has been largely superseded by CRC methodology, cool plasma remains the most effective analytical mode for some elements in certain matrices. Combining cool plasma with CRC technology has been shown to be a powerful mode for interference removal [2]. Because the major isotope of chromium ($^{52}Cr^+$) suffers an interference from $^{35}Cl^{16}OH^+$ in high purity HCl, Cr was determined using cool plasma with ammonia cell gas. The calibration curve for ^{52}Cr shows that $^{35}Cl^{16}OH^+$ interference was removed successfully, allowing a BEC of 0.12 ng/L (ppt) to be achieved, with a detection limit of 0.18 ppt (Figure 1). The DL and BEC displayed in the ICP-MS MassHunter calibration plots are based on the 10 replicates of the unspiked high-purity 20% HCl sample.

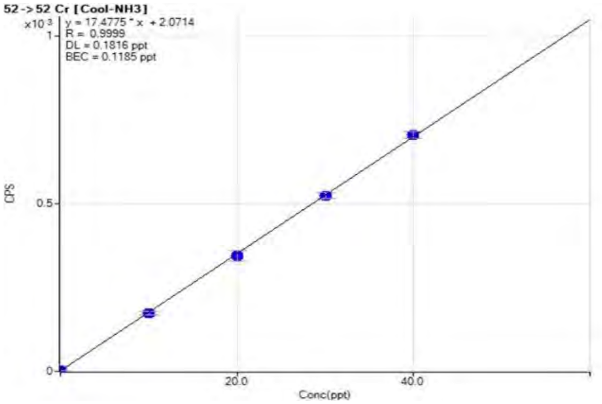


Figure 1. ^{52}Cr calibration curve obtained using cool plasma and NH_3 cell gas, showing low BEC and good linearity.

The same approach is effective for the determination of other interfered elements such as K. Figure 2 shows that the interference from $H_2{}^{37}Cl^+$ on $^{39}K^+$ was suppressed using cool plasma and NH_3 cell gas, giving a BEC and DL for K of 0.17 ppt and 0.09 ppt, respectively.

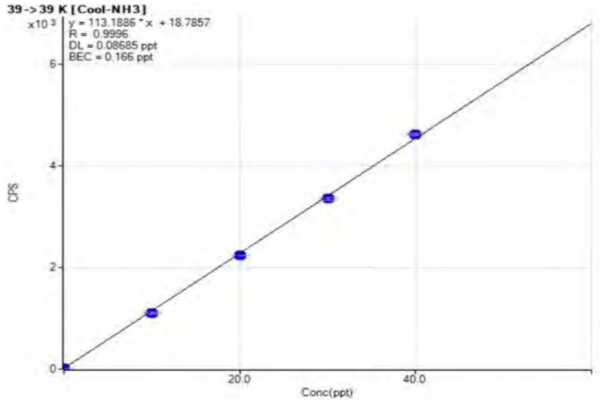


Figure 2. ^{39}K calibration curve obtained using cool plasma and NH_3 cell gas.

V and Ge determination

ICP-QMS fitted with a CRC operating in helium collision mode can successfully eliminate many polyatomic ions using He collision cell gas and kinetic energy discrimination (KED) [3]. However, ICP-QMS has some serious limitations when highly reactive cell gases, such as NH_3, are used in the CRC. ICP-QMS has no mass selection step before the cell, so all ions enter the CRC. It is likely, therefore, that new reaction product ions will form in the CRC that may overlap the target analyte mass of interest. Bandpass ICP-QMS instruments, where all ions within a certain mass range (usually about 10 u) of the target analyte can enter the cell and react, have similar limitations to traditional ICP-QMS in terms of controlling reaction chemistry with highly reactive cell gases.

ICP-QQQ with MS/MS removes this limitation, as the first quadrupole mass filter (Q1), which is located before the CRC, allows precise selection of the specific mass of ions that are allowed to enter the cell. This extra mass selection step ensures that reaction processes in the cell are controlled, which removes the potential for non-target product ion overlaps and dramatically improves the detectability of the analyte ions.

MS/MS acquisition mode using NH_3 as the reaction cell gas was used for the trace determination of V and Ge. The ClO^+ interference on ^{51}V was removed using NH_3 on-mass mode. Potentially, $^{14}NH_2{}^{35}Cl^+$ could form in the cell and interfere with V at *m/z* 51. However, the unit mass resolution of Q1 on the 8900 ICP-QQQ ensures that only ions at *m/z* 51 can enter the cell. All other matrix and analyte ions, e.g. $^{35}Cl^+$, are prevented from entering the cell and cannot, therefore, contribute to the signal at the analyte mass. This simple approach avoids the formation of any new product ion interferences on ^{51}V.

The $ClCl^+$ interference on ^{74}Ge was avoided by measuring a Ge-ammonia cluster ion, $^{74}Ge[^{14}NH_2(^{14}NH_3)]^+$, in mass-shift mode at mass 107. Q1 (set to *m/z* 74 to allow the $^{74}Ge^+$ precursor ions to enter the cell) rejects all non-target masses, including $^{107}Ag^+$, which would otherwise overlap the Ge-NH_3 product ion mass. Q1 (in contrast to a bandpass filter) also rejects all other nearby analyte ions, $^{70}Zn^+$, $^{71}Ga^+$, $^{73}Ga^+$, $^{75}As^+$, $^{78}Se^+$, etc., preventing them from forming potentially overlapping ammonia clusters at the target product ion mass.

Representative calibration curves for V and Ge are shown in Figure 3, again illustrating the low BEC (0.19 ppt for V and 0.77 ppt for Ge) and DL (0.11 ppt for V and 0.32 ppt for Ge) achieved with the 8900 with NH_3 cell gas in MS/MS mode.

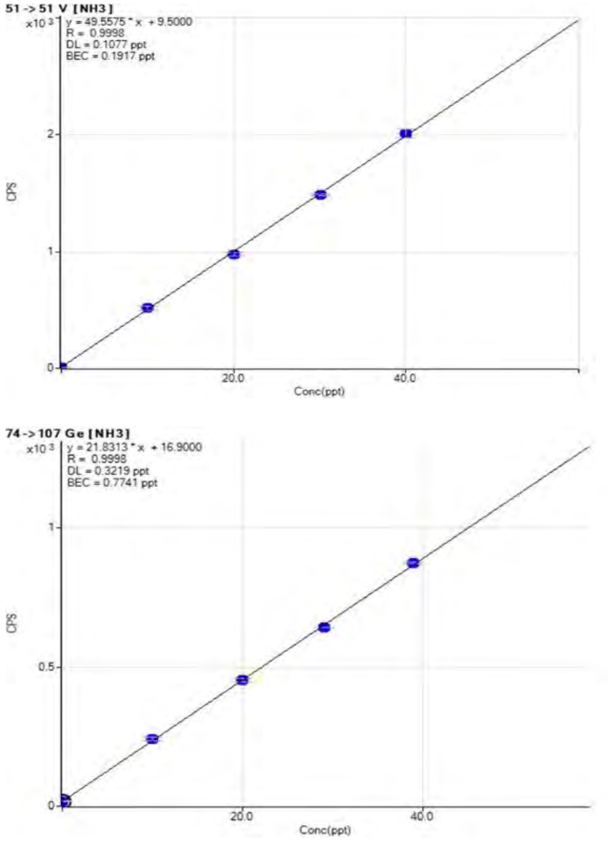


Figure 3. ^{51}V and ^{74}Ge calibration curve obtained using NH_3 cell gas.

Determination of As

Arsenic has a single isotope at *m/z* 75 that suffers an interference from the polyatomic ion $^{40}Ar^{35}Cl^+$. Since $ArCl^+$ readily forms in a chloride matrix, the polyatomic interference compromises the determination of As at ultratrace levels in concentrated HCl using ICP-QMS. Oxygen can be used as the cell gas to avoid this overlap, with As being measured as the AsO^+ product ion at *m/z* 91. However, with ICP-QMS, the AsO^+ product ion at mass 91 suffers an interference from $^{91}Zr^+$. Helium collision mode in the Agilent ORS cell can reduce $ArCl^+$ effectively, allowing a BEC of less than 20 ppt to be achieved by ICP-QMS [3]. But, as semiconductor industry demands become more stringent, this sensitivity may not be sufficient for the lowest level of ultratrace analysis.

Using the 8900 ICP-QQQ with MS/MS, the $^{91}Zr^+$ ion is removed by Q1, which is set to the As^+ precursor ion mass of 75. MS/MS mode allows O_2 cell gas to be used successfully, with As being measured as the AsO^+ product ion at *m/z* 91 without overlap from $^{91}Zr^+$. A further benefit of O_2 cell gas is that measuring AsO^+ provides more sensitivity that direct measurement of As^+ in He mode.

A calibration curve for As in 20% HCl (Sample 3) is shown in Figure 4, demonstrating a BEC of 6.17 ppt and a DL of 0.73 ppt. While lower than the industry requirements for high-purity HCl, this BEC doesn't represent the best performance that can be achieved with the 8900 ICP-QQQ, so further investigation was done to identify the cause of the relatively high background.

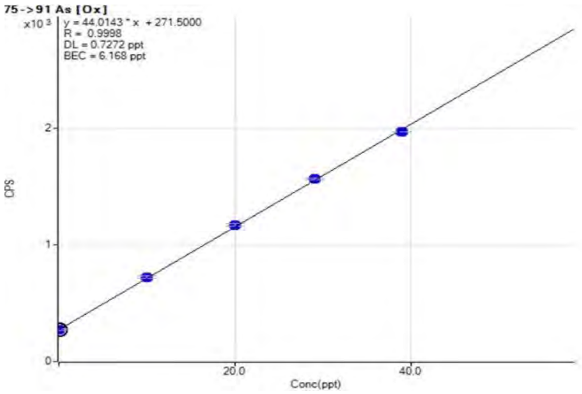


Figure 4. ^{75}As MSA calibration curve obtained in Sample 1 using O_2 cell gas.

Investigation of arsenic contamination

As the measured result for As was relatively high in high purity HCl Sample 1 (Table 4), the signal count at *m/z* 91 (mass of the product ion AsO^+) was investigated further. In a high Cl matrix, the polyatomic ion $^{40}Ar^{35}Cl^+$ forms in the plasma and during ion extraction. This polyatomic ion has the same nominal mass as the target $^{75}As^+$ precursor ion, so it passes through Q1 and enters the cell. While not thermodynamically favored, the $ArCl^+$ might react with the O_2 cell gas to form $ArClO^+$, which would therefore remain as an interference on AsO^+ at *m/z* 91. This possibility can be checked by comparing the isotopic signature of the Cl-based product ions observed in the mass spectrum. Since chlorine has two isotopes, 35 and 37, the ratio of the natural abundances of these isotopes (75.78%: 24.22%) can be used to confirm whether a product ion is Cl-based.

The signals of the mass-pairs 75/91 and 77/93, representing the potential Cl interferences $^{40}Ar^{35}Cl^{16}O^+$ and $^{40}Ar^{37}Cl^{16}O^+$ respectively, were measured by ICP-QQQ with MS/MS. A neutral gain scan spectrum (where Q1 and Q2 are scanned synchronously, with a fixed mass difference between them) was measured and the scan is presented in Figure 5. For this neutral gain scan, Q1 was scanned across the mass range from 74 to 78 u to pass any precursor ions to the CRC, and Q2 was scanned synchronously at Q1 + 16, monitoring any product ions formed by O-atom addition. The peak at mass-pair *m/z* 75/91 that caused the relatively high BEC for As in Sample 1 is clearly visible. However, if the signal at 75/91 was due to interference from $^{40}Ar^{35}Cl^{16}O^+$, there would also be a corresponding signal from $^{40}Ar^{37}Cl^{16}O^+$ at mass-pair 77/93. Since there was no signal observed at 77/93, we can conclude that the signal at *m/z* 75/91 is not due to any contribution from $ArClO^+$, and the high reported concentration of As in Sample 1 is due to contamination.

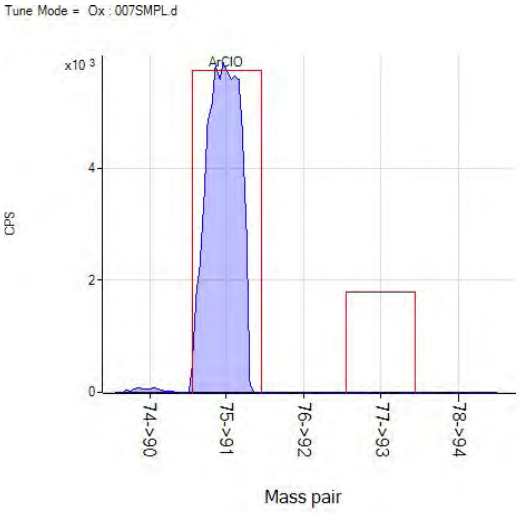


Figure 5. Neutral gain scan spectrum for 20% high purity HCl showing the theoretical isotope template for $^{40}Ar^{35}Cl^{16}O^+$ and $^{40}Ar^{37}Cl^{16}O^+$. Q1 was scanned from *m/z* 74 to 78, while Q2 was set to Q1 + 16.

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Conclusions

The high performance of Agilent ICP-QQQ systems for the analysis of trace metallic impurities in concentrated HCl has been described previously [4]. Now, the Agilent 8900 Semiconductor configuration ICP-QQQ with flexible cell gas support, unique MS/MS capability, and unparalleled cool plasma performance, further improves the detection limits for the analysis of a wide range of trace metal contaminants in high purity acids. The advanced reaction cell methodology supported by the 8900 ICP-QQQ allows the SEMI elements, including those elements with potential matrix-based interferences such as K, V, Cr, Ge, and As, to be determined at lower concentrations in a chloride matrix than was previously possible.

References

1. SEMI C27-0708, Specifications and guidelines for hydrochloric acid (2008)

2. Junichi Takahashi and Katsuo Mizobuchi, Use of Collision Reaction Cell under Cool Plasma Conditions in ICP-MS, 2008 Asia Pacific Winter Conference on Plasma Spectroscopy

3. Junichi Takahashi, Direct analysis of trace metallic impurities in high purity hydrochloric acid by Agilent 7700s/7900 ICP-MS, Agilent publication, 2017, 5990-7354EN

4. Handbook of ICP-QQQ Applications using the Agilent 8800 and 8900, Agilent publication, 2017, pp 13-14, 5991-2802EN

More Information

When analyzing 20–36% HCl on a routine basis, it is recommended to use the following options:

• G3280-67056	Pt sampling cone (18 mm insert)
• G4915A	Upgrade to dry pump
• G3666-67030	Interface valve kit - ball type valve

Since hydrochloric acid is corrosive, avoid placing open sample bottles near the instrument.

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Analysis of silicon, phosphorus and sulfur in 20% methanol using the Agilent 8800 Triple Quadrupole ICP-MS

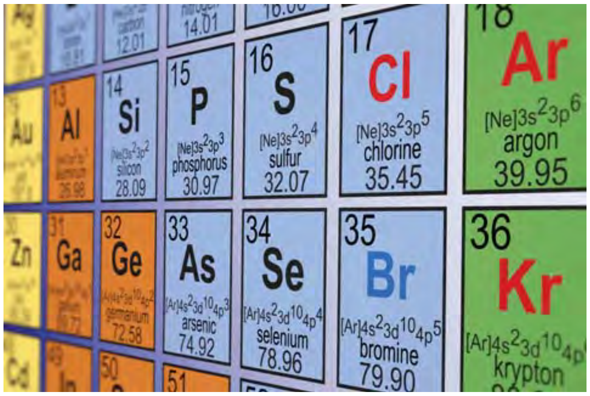
Application note

Semiconductor analysis; metallomics; energy & fuels

Author

Emmett Soffey, Bert Woods and
Steve Wilbur

Agilent Technologies
Bellevue, WA, USA



Introduction

Analysis of trace elements in organic solvents presents a number of challenges to ICP-MS, many of which have been overcome to varying degrees on Agilent's 7700 Series quadrupole ICP-MS systems, using technological advances including a Peltier-cooled spray chamber, fast variable-frequency impedance matching solid state RF generator and octopole-based collision/reaction cell (ORS^3). However, even with these advances, several elements remain challenging in organic solvents, particularly silicon, phosphorus and sulfur. All three elements are subject to intense interferences from polyatomic ions based on carbon, nitrogen and oxygen, which are difficult to completely remove using conventional ICP-MS. Examples include CO, COH, N_2 and NO on silicon 28, 29 and 30, COH, NOH, N_2H, NO and CO on phosphorus 31, and O_2, NO, NOH and NOH_2 on sulfur 32 and 34. Additionally, phosphorus and sulfur have high first ionization potentials (IP) of 10.5 eV and 10.4 eV respectively, resulting in relatively poor sensitivity compared to more typical elements whose IPs are in the range of ~6-8 eV.

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Silicon, phosphorus and sulfur are all important analytes in organic solvents used in the semiconductor manufacturing industry, which is largely silicon based. Phosphorus is a common dopant in wafer manufacturing, and sulfur hexafluoride gas is used as an etchant. Contamination of the wafer by trace elements including P and S, even at ultratrace levels, can render a chip unusable, so the control of these elements in the water, acids and organic solvents that come into contact with the wafer surface is a critical requirement in semiconductor manufacturing.

Sulfur and phosphorus are important trace analytes in the organic solvents used in many other applications outside the semiconductor industry, including hydrocarbon processing, and particularly in life sciences research. Because ICP-MS is an elemental detector and therefore gives the same response for a given sulfur concentration regardless of the compound in which it occurs, ICP-MS analysis of sulfur permits the quantification of sulfur-containing proteins and peptides without the requirement for compound-specific calibration standards. This technique is called compound independent calibration (CIC) and is a major benefit of ICP-MS for life science research. Other developing applications for ICP-MS include the quantification of nucleotides (DNA and RNA) based on their phosphorus content. Additionally, regulation of enzyme activity through phosphorylation is an important area of biological research that requires highly sensitive and specific phosphorus determination. Speciation analysis of biomolecules typically involves separation by HPLC, followed by analysis using ICP-MS. Since LC mobile phases commonly contain methanol, the ability to determine trace Si, P and S in methanol was tested using the new Agilent 8800 Triple Quadrupole ICP-MS.

Experimental

Ultra pure methanol was diluted 1:5 with ultrapure water and spiked with silicon, phosphorus and sulfur at 1, 5, 10 and 50 ppb. These standards were measured using the Agilent 8800 ICP-Triple Quad in several operational modes in order to evaluate the optimum conditions for the simultaneous analysis of all three analytes.

The 8800 combines two quadrupole mass filters, Q1 before and Q2 after the Octopole Reaction System (ORS^3) cell (Figure 1), in a tandem mass spectrometer (MS/MS) configuration. The normal mode of operation of the 8800 is MS/MS mode, where the first quadrupole works as a unit mass filter, restricting the ions entering the ORS^3 cell to a single mass to charge ratio (m/z) at any given time. In this way, ions entering the collision reaction cell are precisely controlled, resulting in the ability to exactly control the reaction chemistry occurring in the cell, even if the sample composition changes. This is in contrast to conventional quadrupole reaction cell instruments, where there is no control over the ions that enter the cell and undergo reactions with the cell gas. MS/MS supports both direct, 'on-mass' measurement, and indirect or 'mass shift' mode. On-mass measurement is used when the analyte is unreactive and is measured at its natural mass, while

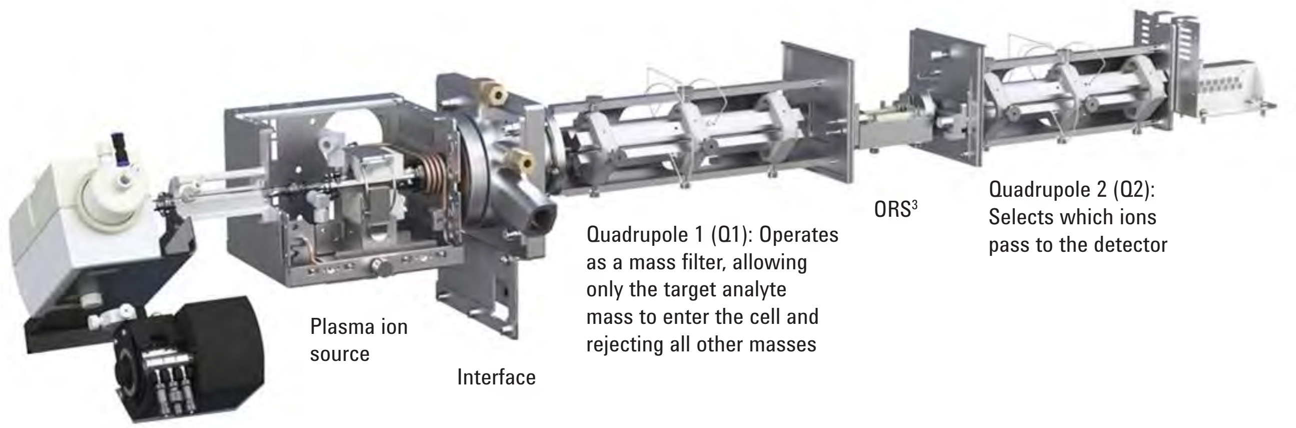

Figure 1. Schematic of the Agilent 8800 Triple Quadrupole ICP-MS

the interferences are reactive and are removed. Mass-shift mode is used when the analyte is reactive and the analyte ions are moved away from the interfering ion overlaps at the original *m/z* through the formation of an analyte reaction product ion at a new mass. The 8800 can also be operated in single quad mode, where the first quadrupole acts as a low mass cutoff filter, essentially transmitting all ions above a specified mass to the ORS, and the second quadrupole is used for mass analysis. In single quad mode, the 8800 operates in a similar way to a conventional quadrupole ICP-MS. In this work, hydrogen and oxygen reaction gases were evaluated, with H_2 cell gas used in both single quad and MS/MS modes. In addition, helium collision gas was investigated in both single quad and MS/MS mode to determine the effects of using MS/MS mode with a non-reactive cell gas.

The instrument conditions used are outlined in Table 1, which includes the five analysis modes evaluated. Two single quad modes were tested, using He or H_2 in the cell, to simulate the capability of a conventional quadrupole ICP-MS. In addition, three MS/MS modes were tested using H_2, He or O_2 as the cell gas. It is notable that plasma and ion optic (extraction lens settings) conditions were identical for all five modes, making it fast and simple to switch between the various modes.

Results and discussion

The background equivalent concentration (BEC) and detection limit (DL) results are summarized in Tables 2–4, for silicon, phosphorus and sulfur respectively, for all five analysis modes tested. Single quad and optimum MS/MS results are in bold type for comparison. The two masses listed under *m/z* monitored in MS/MS mode are the settings for Q1 and Q2 respectively. For example, Table 2 shows silicon monitored in O_2 MS/MS mode using masses 28 and 44. With Q1 set to *m/z* 28, only silicon 28 and any on-mass interferences are allowed to enter the ORS^3 cell. The silicon 28 in the cell reacts with the oxygen cell gas to form the product ion $^{16}Si^{16}O^+$, and Q2 is set to measure this reaction product ion at Q1 + 16 ($m/z = 44$), ensuring that only the + ^{16}O reaction transition is measured. This specific mass-shift monitoring capability is unique to MS/MS mode and means that the isotopic pattern of the analyte is maintained, since possible isotopic overlaps such as $^{28}Si^{18}O^+$ on $^{30}Si^{16}O^+$ cannot occur. The polyatomic ions that interfered with direct measurement of Si at m/z = 28 do not react with oxygen to form product ions at *m/z* = 44, and so are eliminated by Q2.

Table 1. Agilent 8800 ICP-MS acquisition conditions tested, including five operational modes: two single quad modes, and three MS/MS modes. 'Q2 offset mass' is the mass difference between Q1 and Q2 to measure analyte reaction product ions.

Tune	**He mode**	**H_2 mode**	**H_2 MS/MS**	**He MS/MS**	**O_2 MS/MS**
Scan mode	Single quad	Single quad	MS/MS	MS/MS	MS/MS
RF power (W)	1550				
Sample depth (mm)	8				
Carrier gas flow rate (mL/min)	1.05				
Ext 1 (V)	0				
Ext 2 (V)	-190				
Cell gas/flow rate (mL/min)	He / 5	H_2 / 7	H_2 / 7	He / 5	O_2 / 0.4
KED (V)	5	0	0	5	-7
Q2 offset mass (amu)	N/A	N/A	0, 2, 3	0	0, 16, 32

Table 2. Detection limits (DLs, 3σ) and background equivalent concentrations (BECs) for silicon. Silicon was not measurable at the spiked concentrations in helium mode.

Mode	*m/z* monitored	BEC (ppb)	DL (ppb)
H_2 single quad	**28**	**25.46**	**0.12**
H_2 MS/MS	**28/28**	**2.17**	**0.03**
O_2 MS/MS	28/44	85.54	28.21
O_2 MS/MS	30/46	99.09	21.26

Table 3. Detection limits (DLs, 3σ) and background equivalent concentrations (BECs) for phosphorus. Phosphorus was not measurable at the spiked concentrations in hydrogen single quad mode.

Mode	*m/z* monitored	BEC (ppb)	DL (ppb)
He single quad	**31**	**3.81**	**0.63**
He MS/MS	31/31	2.99	0.72
H_2 MS/MS	31/33	0.56	0.07
H_2 MS/MS	31/34	0.58	0.67
O_2 MS/MS	31/47	0.40	0.05
O_2 MS/MS	**31/63**	**0.41**	**0.02**

Table 4. Detection limits (DLs, 3σ) and background equivalent concentrations (BECs) for sulfur. Sulfur was not measurable at the spiked concentrations in helium or hydrogen mode.

Mode	*m/z* monitored	BEC (ppb)	DL (ppb)
O_2 MS/MS	34/34	51.17	4.37
O_2 MS/MS	**32/48**	**3.13**	**0.10**
O_2 MS/MS	34/50	3.11	0.20

The sample calibration plots in Figure 2 are displayed in pairs showing the results using single quad mode with a typical cell gas, compared with MS/MS mode using the optimum conditions.

It can be seen that in all cases, the use of MS/MS mode significantly improves both the BEC and instrument detection limit when compared with single quad mode. The most notable improvement was for sulfur (Figure 2, bottom), which cannot be measured at the spiked concentrations (1, 5, 10, 50 ppb) in single quad He mode due to the intense polyatomic background resulting from the methanol:water matrix. For this reason, trace level analysis of sulfur using the 7500 or 7700 Series quadrupole ICP-MS has typically been performed using Xe reaction mode, which gives the best reduction of the O_2 interference. However, Xe is very expensive and Xe reaction mode is not ideal for other elements, due to severe loss of sensitivity for low mass ions due to scattering from the large Xe molecules in the cell. This has made the simultaneous analysis of sulfur with other analytes difficult in chromatographic applications.

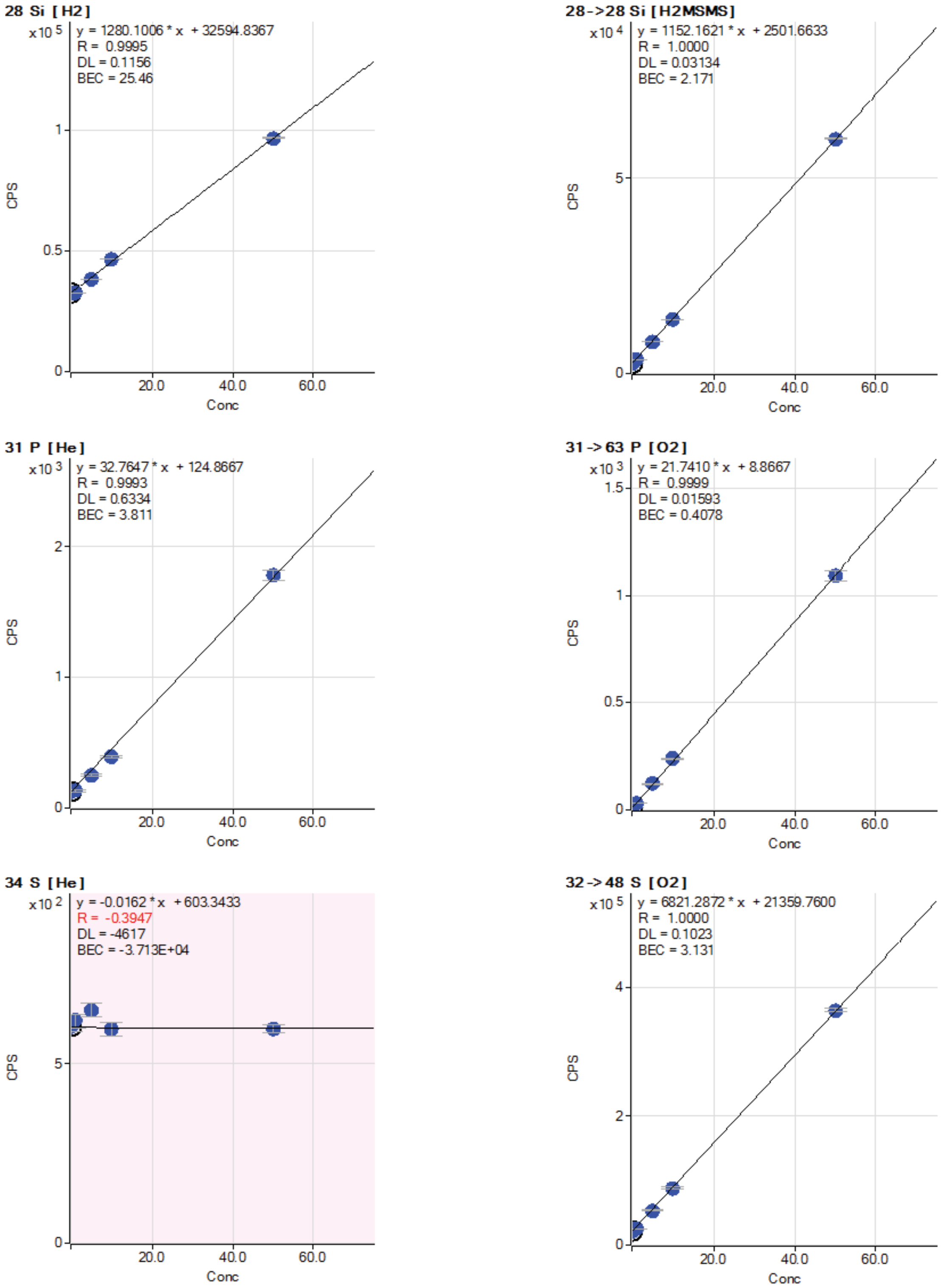

Figure 2. Example calibration curves for silicon, phosphorus, and sulfur showing single quad results (left) compared with MS/MS results (right). Sulfur is not measurable at the spiked concentrations in methanol in single quad mode due to the intense polyatomic interference (left). All concentration units are ug/lL (ppb).

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Conclusions

The Agilent 8800 ICP-Triple Quad provides significantly enhanced sensitivity and interference reduction for the challenging elements; silicon, phosphorus and sulfur in organic matrices when compared with conventional quadrupole ICP-MS systems. The 8800 achieves this superior performance by utilizing MS/MS mode, where the first quadrupole eliminates all but the analyte mass and any interfering ions at the same *m/z*. By rejecting all non-target masses, the reaction chemistry in the cell is controlled and consistent, resulting in highly efficient and predictable interference removal. Q1 also rejects any off-mass ions that might overlap the analyte product ions created in the cell, thereby greatly improving the accuracy and reliability of reaction gas modes that use mass-shift. In addition, the higher sensitivity and lower background of the 8800 provide improved detection limits compared with quadrupole ICP-MS, even when operated in single quad mode.

Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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Determination of trace elements in ultrapure semiconductor grade sulfuric acid using the Agilent 8900 ICP-QQQ in MS/MS mode

Application note

Semiconductor

Authors

Michiko Yamanaka,
Kazuo Yamanaka and
Naoki Sugiyama,
Agilent Technologies, Japan

Introduction

In the semiconductor industry, it is extremely important to reduce contamination within the manufacturing process, as particle-, metallic-, or organic-based contaminants degrade the quality and reliability of the final device. Organic materials, such as photoresist polymer patterns, must be thoroughly removed from the surface of the silicon wafer following ion implantation; this cleaning step is performed using a piranha solution; a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). Ensuring a low level of metal impurities in these chemicals is vital to ensure that contamination of the wafer surface is avoided at this stage in the manufacturing process.

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Since its inception, ICP-MS has been widely utilized for the analysis of elemental impurities in chemicals and materials used by semiconductor-related industries. More recently, collision/reaction cell (CRC) technology, which was first developed for quadrupole ICP-MS (ICP-QMS), has been implemented to remove polyatomic ions that cause problematic spectral interferences on many analytes. In certain sample matrices, however, not all polyatomic species can be completely removed using CRC-ICP-QMS, hindering accurate measurement of a few important elements at low-levels. For example, high concentration sulfur matrices generate polyatomic ions with a low ionization potential, such as SO^+, which interferes with Ti. Since SO^+ has a high dissociation energy of 5.4 eV, it is not easily dissociated using a CRC operating in collision mode with an inert cell gas.

The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) has a unique tandem MS configuration, comprising two quadrupole mass filters (Q1 and Q2), separated by an octopole reaction system (ORS^4) cell. The MS/MS configuration allows reaction chemistry to be applied to the most complex and challenging interference problems that hinder ICP-QMS. As more reactive gases (e.g. NH_3 or O_2) can be used in ICP-QQQ in a controlled way, the reaction pathways and product ions formed in the cell are not affected by changes in the sample matrix or by other co-existing analyte ions. Using MS/MS, Ti can be analyzed in a sulfur matrix, using NH_3 reaction gas mode, by measuring a suitable ammonia cluster product ion that is free from polyatomic ion interference. In addition, the new axial acceleration technology of the 8900 ICP-QQQ, which accelerates product ions generated in the ORS^4 cell, leads to an increase in sensitivity of product ions, including Ti/NH_3 cluster ions.

In this study, the Agilent 8900 ICP-QQQ was used for the analysis of 42 analytes in sulfuric acid, including Ti and other elements which are difficult to determine at trace levels in a high sulfur matrix.

Experimental

Sample preparation

All sulfuric acid samples were prepared using pre-cleaned PFA containers. High purity 98% H_2SO_4 (TAMA Chemicals Co. Ltd. Japan) was diluted ten-fold with ultrapure water (UPW). All calibration and quantification was done using the method of standard additions (MSA). Standard solutions were prepared from a mixture of XSTC-331, XSTC-7, XSTC-8 (SPEX CertiPrep, USA) and a Si single element standard (Kanto Chemical Co., Inc., Japan).

Instrumentation

An Agilent 8900 ICP-QQQ (#200, Semiconductor configuration) was used throughout. The sample introduction system comprised a quartz torch with a 2.5 mm i.d. injector, quartz spray chamber, a PFA concentric nebulizer and platinum-tipped interface cones. The sample was self-aspirated using an Agilent I-AS autosampler. MS/MS mode, in which Q1 and Q2 both act as unit mass filters, was used for all measurements. To run ten-fold diluted sulfuric acid routinely, it is recommended that the large (18 mm) insert Pt cone is fitted. Long-term corrosion of internal ICP-MS components can be minimized by fitting the dry pump option and ball-type interface valve kit.

Evaluation of different reaction gases

For multi-element trace analysis, O_2, NH_3, H_2 and He were evaluated as cell gases. O_2 is often used in mass-shift methods to move the target analyte from its elemental ion mass to its oxide product ion mass (MO^+) by setting Q2 to 16 amu higher than Q1 [1]. NH_3 is highly reactive and used as a cell gas in both on-mass mode and mass-shift mode depending on the interference to be removed. H_2 and He were used with O_2 or NH_3, to assist the cell gas reaction process. He cell gas was used in collision mode to eliminate many common background polyatomic interferences.

Results and discussion

As is typical with analyses at the ultra-trace level, the optimum plasma mode (normal or cool plasma) and cell gas type was selected for each element. Most higher-mass analytes are free from significant interference in high-purity reagents, but element-specific optimization is particularly important for the ultra-trace analysis of Ti, V, Cr, Zn, Ge and As, which suffer from S-based polyatomic interferences in a sulfur-matrix. Instrument operating parameters used are shown in Table 1.

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Table 1. ICP-QQQ operating parameters.

<table>
<tr><th></th><th>Cool-NH_3</th><th>NH_3-1
(for Ti and V)</th><th>NH_3-2
(for Zn)</th><th>O_2</th><th>O_2+ H_2
(for P)</th><th>He mode[1]</th></tr>
<tr><td>RF power, W</td><td>600</td><td colspan="5">1600</td></tr>
<tr><td>Sampling depth, mm</td><td>18.0</td><td colspan="5">8.0</td></tr>
<tr><td>Carrier gas, L/min</td><td colspan="6">0.7</td></tr>
<tr><td>Makeup gas, L/min</td><td>0.75</td><td colspan="5">0.49</td></tr>
<tr><td>Extraction lens 1, V</td><td>-150</td><td>5.3</td><td>5.1</td><td colspan="2">5.0</td><td>4.5</td></tr>
<tr><td>Extraction lens 2, V</td><td>-15</td><td colspan="2">-200</td><td>-250</td><td>-190</td><td>-155</td></tr>
<tr><td>Octopole bias, V</td><td>-10.0</td><td>-17.0</td><td>-13.5</td><td>-11.0</td><td>-4.0</td><td>-100.0</td></tr>
<tr><td>Axial acceleration, V</td><td colspan="2">1.0</td><td>0.2</td><td colspan="2">1.0</td><td>0.0</td></tr>
<tr><td>Energy discrimination, V</td><td>-5.0</td><td>-18.2</td><td>-20.0</td><td>-13.0</td><td>-8.0</td><td>5.0</td></tr>
<tr><td>NH_3 flow[1], mL/min</td><td>2</td><td>1</td><td>4.5</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>O_2 flow, mL/min</td><td>-</td><td>-</td><td>-</td><td>0.7</td><td>0.2</td><td>-</td></tr>
<tr><td>He flow, mL/min</td><td>1</td><td>9</td><td>1</td><td>-</td><td>-</td><td>9</td></tr>
<tr><td>H_2 flow, mL/min</td><td>-</td><td>-</td><td>-</td><td>-</td><td>1</td><td>-</td></tr>
</table>

[1] High engergy He mode conditions

[2] 10% NH_3 balanced with 90% He

O_2 mass-shift mode for As, Se and Si

Oxygen mass-shift mode detects analyte ions (M^+) as reaction product ions at the oxide ion mass (MO^+). For example, $^{75}As^+$ is detected as AsO^+ at *m/z* 91. This method is used when the analyte ion reacts efficiently with O_2 gas to form an oxide ion, while the interfering ion reacts slowly or not at all with the O_2 gas, so does not contribute significantly to the signal at the new mass of the analyte product ion. The lowest detection limits (DLs) and background equivalent concentrations (BECs) for Si, As and Se were obtained with a relatively high O_2 cell gas flow rate (0.7 mL/min), which encourages the formation of O-atom addition product ions for these analytes, especially Se.

O_2 + H_2 mass-shift mode for P

In a sulfur matrix, on-mass measurement of ^{31}P is affected by the peak tail of the large adjacent ^{32}S peak. This can be addressed using ICP-QQQ, which benefits from the high abundance sensitivity (AS) of MS/MS mode. The AS in MS/MS mode is the product of the AS of the two quadrupoles, so Q1 AS x Q2 AS. On the Agilent 8900, each of the two quadrupoles has an AS specification of 10^{-7}, so the overall AS is theoretically 10^{-14}, meaning that peak tailing, even from very intense background peaks, is practically eliminated. However, on-mass measurement (e.g. using He mode) does not give sufficiently low backgrounds for the measurement of P at ultra-trace levels. As an alternative, O_2 mass-shift mode can be used to effectively eliminate the NO^+ or NOH^+ interference on P^+, since the oxidation of P^+ is exothermic, while the oxidation of NO^+ or NOH^+ is endothermic. Hence, these background polyatomic ions are avoided by shifting the P^+ away from the interfering ions, and measuring it as the PO^+ product ion at *m/z* 47. Interestingly, P sensitivity was improved 1.5 times by adding H_2 gas to the cell together with O_2. In this study, O_2 + H_2 mass-shift mode was used for P analysis to obtain maximum sensitivity. However, O_2 alone would deliver sufficient performance for the analysis of semiconductor grade H_2SO_4. Optimum gas conditions were 0.2 mL/min of O_2 and 1 mL/min of H_2.

NH_3 mass-shift mode for Ti

The two most abundant isotopes of titanium, ^{48}Ti and ^{46}Ti, suffer interferences from $^{32}S^{16}O$ and $^{32}S^{14}N$ respectively, so the minor isotope, ^{47}Ti, is usually selected for analysis using ICP-QMS. However, MS/MS mode with ICP-QQQ allows control of the complex reaction chemistry that occurs with ammonia cell gas, allowing the major Ti isotopes to be measured as a suitable Ti-NH_3 cluster ion and thereby avoiding the S-based interferences. Single ng/L level BECs can be achieved using this approach [2]. ^{48}Ti could also potentially suffer an isobaric overlap from the minor ^{48}Ca isotope (0.187% abundance), but this is not a problem in semiconductor reagents as the concentration of Ca is low.

When a heavy cell gas such as O_2 or NH_3 is used at a high flow rate, analyte ions entering the cell significantly slow down due to suffering multiple collisions with the cell gas molecules, resulting in an increased transit time through the cell. Some ions may even lose so much energy that their progress through the cell stops, which causes a loss of sensitivity. Furthermore, product ions formed in the cell are generally very slow as a result of the reaction with cell gas molecules. If the transmission of these product ions through the cell reduces, so does the sensitivity. The ORS^4 CRC of the 8900 Semiconductor configuration ICP-QQQ benefits from axial acceleration; an electrical field is established by a potential gradient in the axial direction of the cell so that positively charged analyte ions are accelerated towards the cell exit. Axial acceleration can improve the transmission of slow-moving product ions, and thus increase the sensitivity for certain analytes. In practice, changing the axial acceleration voltage from 0 V to +1 V resulted in a 5-fold increase in the sensitivity of the ammonium cluster ion selected for titanium analysis, $^{48}TiNH(NH_3)_3^+$ ($m/z = 114$). An axial acceleration voltage of 1 V was used for Ti analysis using MS/MS mass-shift mode with NH_3 cell gas.

Multi-element analysis

Representative calibration curves obtained using MSA are shown in Figure 1. Good linearity was observed for all analytes (R > 0.9995), and sub-ppt detection limits were achieved for all elements apart from Si (44 ppt), P (3 ppt), and Zn (1.5 ppt). The quantitative results of the analysis of 9.8% H_2SO_4 are shown in Table 2. The DLs were determined from 10 x replicate measurements of the blank 9.8% H_2SO_4 solution. Recoveries and RSDs were determined from 10 replicate measurements of a 20 ng/L spiked solution of 9.8 % H_2SO_4. Excellent performance was achieved for all elements, including Ti, V and Zn, indicating the effective suppression of S-based matrix interferences.

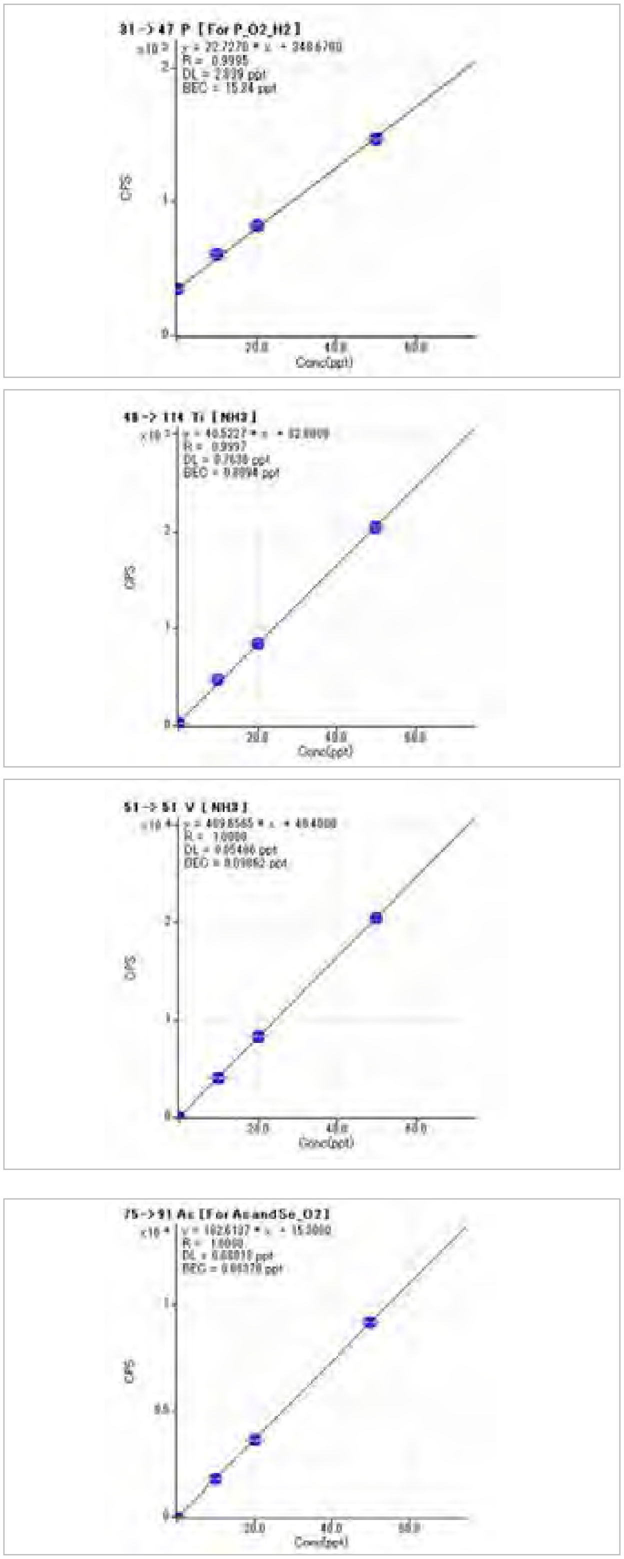

Figure 1. Calibration curves of P, Ti, V and As in 9.8% H_2SO_4

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Table 2. Quantitative results for 42 elements in 9.8% H_2SO_4.

Analyte	Mode	Q1 Mass	Q2 Mass	DL (ng/L)	BEC (ng/L)	20 ng/L Spike Recovery (%)	20 ng/L RSD (%)
Li	Cool-NH_3	7	7	0.13	0.13	104	2.1
Na	Cool-NH_3	23	23	0.37	0.73	102	1.8
Mg	Cool-NH_3	24	24	0.15	0.05	106	2.4
Al	Cool-NH_3	27	27	0.18	0.09	107	1.8
Si	O_2	28	44	44	480	*98	*1.7
P	$O_2 + H_2$	31	47	2.8	15	96	3.5
K	Cool-NH_3	39	39	0.36	0.66	104	2.1
Ca	Cool-NH_3	40	40	0.57	0.18	106	1.8
Ti	NH_3-1	48	114	0.76	0.81	99	2.9
V	NH_3-1	51	51	0.05	0.10	101	0.5
Cr	Cool-NH_3	52	52	0.51	0.37	106	2.8
Mn	Cool-NH_3	55	55	0.16	0.11	103	3.0
Fe	Cool-NH_3	56	56	0.40	0.28	101	2.7
Ni	Cool-NH_3	58	58	0.12	0.02	100	3.6
Co	Cool-NH_3	59	59	0.23	0.03	102	2.3
Cu	Cool-NH_3	63	63	0.57	0.58	101	2.8
Zn	NH_3-2	68	85	1.5	1.8	99	4.1
Ga	Cool-NH_3	69	69	0.08	0.01	102	2.0
Ge	He	74	74	0.40	0.24	101	3.3
As	O_2	75	91	0.08	0.08	101	1.1
Se	O_2	78	94	0.14	0.22	103	2.0
Rb	Cool-NH_3	85	85	0.12	0.03	102	2.6
Sr	He	88	88	0.02	0.004	100	1.9
Zr	He	90	90	0.03	0.005	101	1.1
Nb	He	93	93	0.03	0.05	100	1.3
Mo	He	98	98	0.19	0.12	104	1.9
Ru	He	101	101	0.19	0.10	101	3.6
Pd	He	105	105	0.04	0.004	102	3.1
Ag	He	107	107	0.16	0.15	99	1.2
Cd	He	114	114	0.16	0.04	102	3.5
In	He	115	115	0.02	0.008	101	1.1
Sn	He	118	118	0.35	0.33	102	2.3
Sb	He	121	121	0.09	0.03	101	3.1
Cs	He	133	133	0.10	0.17	103	1.7
Ba	He	138	138	0.03	0.007	102	1.3
Ta	He	181	181	0.26	0.42	100	1.6
W	He	182	182	0.28	0.07	99	4.4
Au	He	197	197	0.41	0.30	99	3.3
Tl	He	205	205	0.09	0.07	100	2.6
Pb	He	208	208	0.56	0.93	95	4.1
Bi	He	209	209	0.03	0.004	100	2.2
U	He	238	238	0.02	0.003	101	2.7

*2 µg/L spike

Conclusions

Forty-two elements were determined successfully at ultra-trace levels in semiconductor grade H_2SO_4 using the Agilent 8900 Semiconductor configuration ICP-QQQ. Excellent spike recoveries for all elements were achieved at the 20 ppt level (2 ppb for Si) in the 1/10 diluted H_2SO_4, demonstrating the suitability of the 8900 ICP-QQQ method for the routine analysis of high purity process chemicals.

Problematic spectral interferences that hinder the measurement of some key elements by ICP-QMS were eliminated using ICP-QQQ in MS/MS mode with suitable reaction cell gas conditions. The axial acceleration function of the 8900 ICP-QQQ provided significant improvements in the product ion sensitivity used for the determination of Ti, Zn and P etc. Sub-ppt level DLs and BECs were obtained for almost all analytes in 9.8 % H_2SO_4.

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1. 'Agilent 8800 Triple Quadrupole ICP-MS: Understanding oxygen reaction mode in ICP-MS/MS', Agilent publication, 2012, 5991-1708EN.

2. J. Takahashi, 'Determination of challenging elements in ultrapure semiconductor grade sulfuric acid by Triple Quadrupole ICP-MS', Agilent publication, 2015, 5991-2819EN

More information

When analyzing 9.8% sulfuric acid on a routine basis, it is recommended to use the following options:

- G3280-67056 Pt sampling cone (18 mm insert)
- G4915A Upgrade to dry pump
- G3666-67030 Interface valve kit - ball type valve

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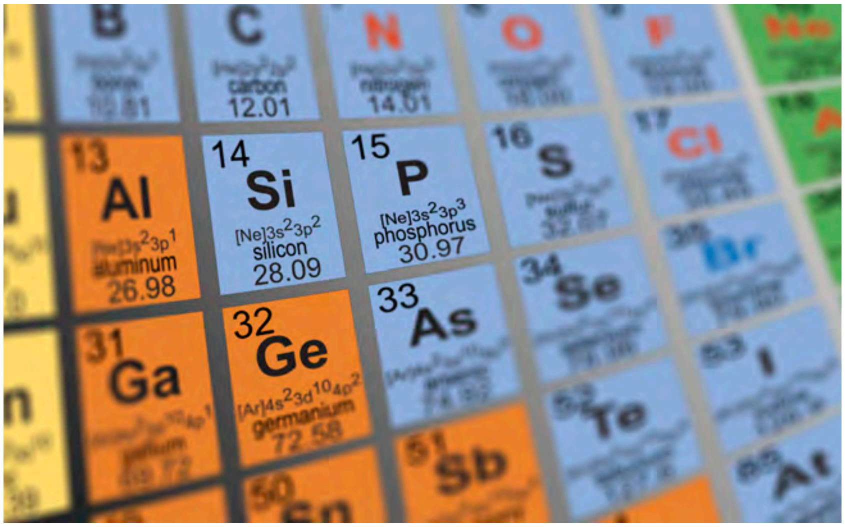
Ultra-low level determination of phosphorus, sulfur, silicon and chlorine using the Agilent 8900 ICP-QQQ

Application note

Semiconductor

Author

Kazumi Nakano,
Agilent Technologies, Japan



Introduction

Quadrupole ICP-MS (ICP-QMS) is one of the most sensitive and versatile analytical tools used in inorganic analysis. With sensitivity approaching 1,000 million counts per second/part per million (1 G cps/ppm) and background signals typically less than 1 cps, the latest instrumentation achieves detection limits (DL) in the ppq (pg/L) range for most of the elements in the periodic table. Detection limits tend to be lowest for elements at masses higher than 80 amu, while some lower mass elements are more difficult to measure at trace levels due to the presence of spectral overlaps from polyatomic interferences. ICP-QMS can utilize cool plasma and/or collision/reaction cell methods to address the problem of background interferences, with successful results in many applications.

More recently, the introduction of triple quadrupole ICP-MS (ICP-QQQ) has dramatically improved the reliability and performance of reaction cell methods by allowing a double mass filter (MS/MS) to be applied to control reaction chemistry in the cell. This now allows analysts to resolve interferences on a wide range of elements in a controlled and effective manner [1].

With the introduction of Agilent's second generation ICP-QQQ instrument, the Agilent 8900 Triple Quadrupole ICP-MS, reaction cell operation with MS/MS mode has been further refined. This note describes the performance of the 8900 ICP-QQQ for the analysis of some of the most challenging elements for ICP-MS: phosphorus (P), sulfur (S), silicon (Si), and chlorine (Cl). The first ionization potentials of these elements are relatively high, which reduces the degree of ionization and therefore the analyte signal. Furthermore, the background signals are elevated due to plasma-, solvent- and matrix-based polyatomic ions, making low-level analysis even more difficult. As ICP-MS technology has developed, there has been a growing demand and expectation to measure these difficult elements together with more conventional elements in high purity chemicals and materials. Details of the methods used to control the interferences on the four elements are presented, together with background equivalent concentrations (BECs) and detection limits (DLs) for P, S, Si and Cl in ultra-pure water (UPW), and P, S and Si in the highest grade hydrogen peroxide (H_2O_2).

Experimental

Instrumentation

An Agilent 8900 ICP-QQQ (#200, Semiconductor Configuration) was used for all measurements. The sample introduction system comprised a PFA concentric nebulizer, a quartz spray chamber and torch, and platinum interface cones. The 8900 #200 ICP-QQQ is fitted with a new argon gas flow control system specially designed to minimize sulfur/silicon contamination from the gas line components.

Normal, hot plasma conditions were used throughout. Extraction lens voltages were optimized for maximum sensitivity using an Agilent 1 ppb tuning solution containing Li, Y, Ce and Tl. Operating and tuning parameters are summarized in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating parameters

Parameter	Unit	Value
RF power	W	1500
Sampling depth	mm	8.0
Carrier gas flow rate	L/min	0.70
Makeup gas flow rate	L/min	0.52
Extraction lens 1	V	4.0
Extraction lens 2	V	-210
Omega lens bias	V	-80
Omega lens	V	8.0

Method and cell tuning

Based on previous studies, oxygen (O_2) mass-shift mode was used for the analysis of P and S [2], hydrogen (H_2) on-mass mode was used for Si, and Cl was determined using H_2 mass-shift mode [3]. The reaction processes used for removal of the primary interference on each analyte were as follows:

Sulfur by oxygen mass-shift mode

The intense polyatomic interference from ${}^{16}O_2^+$ on the primary isotope of S, ${}^{32}S^+$ at *m/z* 32, is avoided by shifting S^+ away from the interfering O_2^+ ion, using an O-atom addition reaction. S^+ reacts readily with O_2 cell gas to form the product ion SO^+, which can be measured free of interference at M + 16 amu (*m/z* 48 for the primary ${}^{32}S^{16}O^+$ isotope product ion), as shown in the following equations:

$$^{32}S^+ + O_2 \text{ <cell gas>} \rightarrow {}^{32}S^{16}O^+ + O$$

$$^{16}O_2^+ + O_2 \text{ <cell gas>} \rightarrow \text{no reaction}$$

Phosphorus by oxygen mass-shift mode

A similar mass-shift approach is used for the measurement of P as PO^+. The native mass of P (*m/z* 31) suffers an intense background interference from ${}^{14}N^{16}O^1H^+$, ${}^{15}N^{16}O^+$, and ${}^{14}N^{17}O^+$. These background polyatomic ions are avoided by reacting P^+ with O_2 cell gas, shifting the P^+ away from the interfering ions, and measuring it as the PO^+ product ion at *m/z* 47:

$$^{31}P^+ + O_2 \text{ <cell gas>} \rightarrow {}^{31}P^{16}O^+ + O$$

$$NOH^+/NO^+ + O_2 \text{ <cell gas>} \rightarrow \text{no reaction}$$

Table 2. Cell mode related tuning parameters

Parameter	Unit	O_2 mass-shift	H_2 on-mass	H_2 mass-shift
Element		^{31}P, ^{32}S	^{28}Si	^{35}Cl
Mass pair	(Q1 ⟶ Q2)	(31 ⟶ 47), (32 ⟶ 48)	(28 ⟶ 28)	(35 ⟶ 37)
Cell gas		O_2	H_2	
Flow rate	mL/min	0.41	5.0	
OctpBias	V	-3	-18	
KED	V	-8	0	
Axial acceleration	V	1	0	
Cell exit	V	-90	-70	
Deflect	V	8	-6	
Plate bias	V	-60		

Silicon by hydrogen on-mass mode

The analysis of Si uses on-mass measurement with H_2 cell gas, as the primary interferences on the major Si isotope at *m/z* 28, $^{14}N_2^+$ and $^{12}C^{16}O^+$, react readily with H_2, while Si^+ does not react. Thus the N_2^+ and CO^+ interferences can be removed, and $^{28}Si^+$ can be measured free from the interferences at its original mass:

$$^{28}Si^+ + H_2 \text{ <cell gas>} \longrightarrow \text{no reaction}$$

$$^{14}N_2^+ + H_2 \text{ <cell gas>} \longrightarrow N_2H^+ + H$$

$$^{12}C^{16}O^+ + H_2 \text{ <cell gas>} \longrightarrow COH^+ + H$$

Chlorine by hydrogen mass-shift mode

Cl is a difficult element to analyze at low concentrations using ICP-MS, because it is a common contaminant and is often present in reagents used in the laboratory environment. In addition, its first ionization potential of 12.967 eV is higher than that of any other commonly measured element, meaning that Cl is very poorly ionized, so the sensitivity for Cl^+ is extremely low. A further issue for low-level Cl analysis is the presence of a polyatomic interference from $^{16}O^{18}O^1H^+$ on the primary Cl isotope at *m/z* 35. The O_2H^+ overlap can be avoided by measuring Cl as a ClH_2^+ product ion, produced from sequential reaction with H_2 reaction gas:

$$^{35}Cl^+ + H_2 \text{ <cell gas>} \longrightarrow {}^{35}Cl^1H^+ + H$$

$$\text{Followed by } {}^{35}Cl^1H^+ + H_2 \text{ <cell gas>} \longrightarrow {}^{35}Cl^1H_2^+ + H$$

$$^{16}O^{18}O^1H^+ + H_2 \text{ <cell gas>} \longrightarrow \text{no reaction}$$

In all of these methods, the Agilent 8900 ICP-QQQ was operated in MS/MS mode (where both Q1 and Q2 function as mass filters) ensuring that only the target ion or product ion was measured. MS/MS means that potentially overlapping ions are excluded from the collision/reaction cell, so the reaction chemistry is controlled and consistent, even if other matrix elements or analytes are present in the sample. For example, in the case of $^{32}S^{16}O^+$ product ion measured at *m/z* 48, the product ion mass could be overlapped by other ions, such as $^{48}Ca^+$, $^{48}Ti^+$, and $^{36}Ar^{12}C^+$, if these ions were not rejected by Q1. This is the main reason for the improved reaction mode performance of ICP-QQQ compared to ICP-QMS, as ICP-QMS has no mass filter step before the collision/reaction cell.

The ORS^4 collision/reaction cell of the 8900 #200 instrument has the facility to utilize an axial acceleration voltage, which was found to be effective to increase sensitivity in the O_2 mass-shift method used for the determination of P and S. Cell parameters were optimized separately for each mode while aspirating a 1 ppb standard solution of each of the elements. Cell tuning parameters are summarized in Table 2.

Reagents

Standard solutions for P, S and Si were prepared from single element standards purchased from SPEX CertiPrep (NJ, USA), by serial dilution with UPW. The UPW was supplied from ORGANO Corp (Tokyo, Japan). The Cl standard was prepared from high purity HCl purchased from Wako Pure Chemicals Industries Ltd (Osaka, Japan). The highest purity grade H_2O_2, TAMAPURE-AA-10, was purchased from TAMA Chemicals Co Ltd (Kanagawa, Japan). The calibration standard addition spikes were added directly to the undiluted H_2O_2. A 1% TMAH alkaline rinse was used during the analysis of Cl to maximize the effectiveness of the washout between samples, and prevent any carryover. All pipette tips, vials and bottles were thoroughly cleaned using diluted high purity acids, and rinsed in UPW prior to use.

Results and discussion

To prepare the ICP-QQQ for the analysis, a 1% HNO_3 solution was aspirated overnight to thoroughly clean the sample introduction system. Running the plasma for several hours would also help to remove any contaminants in the Ar gas flow line. P, S and Si were measured together, and Cl was analyzed in a separate batch since it benefited from an alkaline rinse between solutions. Figures 1 and 2 show the calibration curves of the four elements in UPW and P, S and Si in H_2O_2, respectively, measured using the method of standard addition (MSA). The background level of Cl present in the H_2O_2 sample was too high to permit accurate analysis at the spike levels used.

Good linearity at low and sub-ppb levels was observed for all elements measured in both of the sample matrices. The DL for each element was calculated as 3 times the standard deviation of 10 replicates of the blank using an integration time of 1 sec for each element. The results are summarized in Table 3.

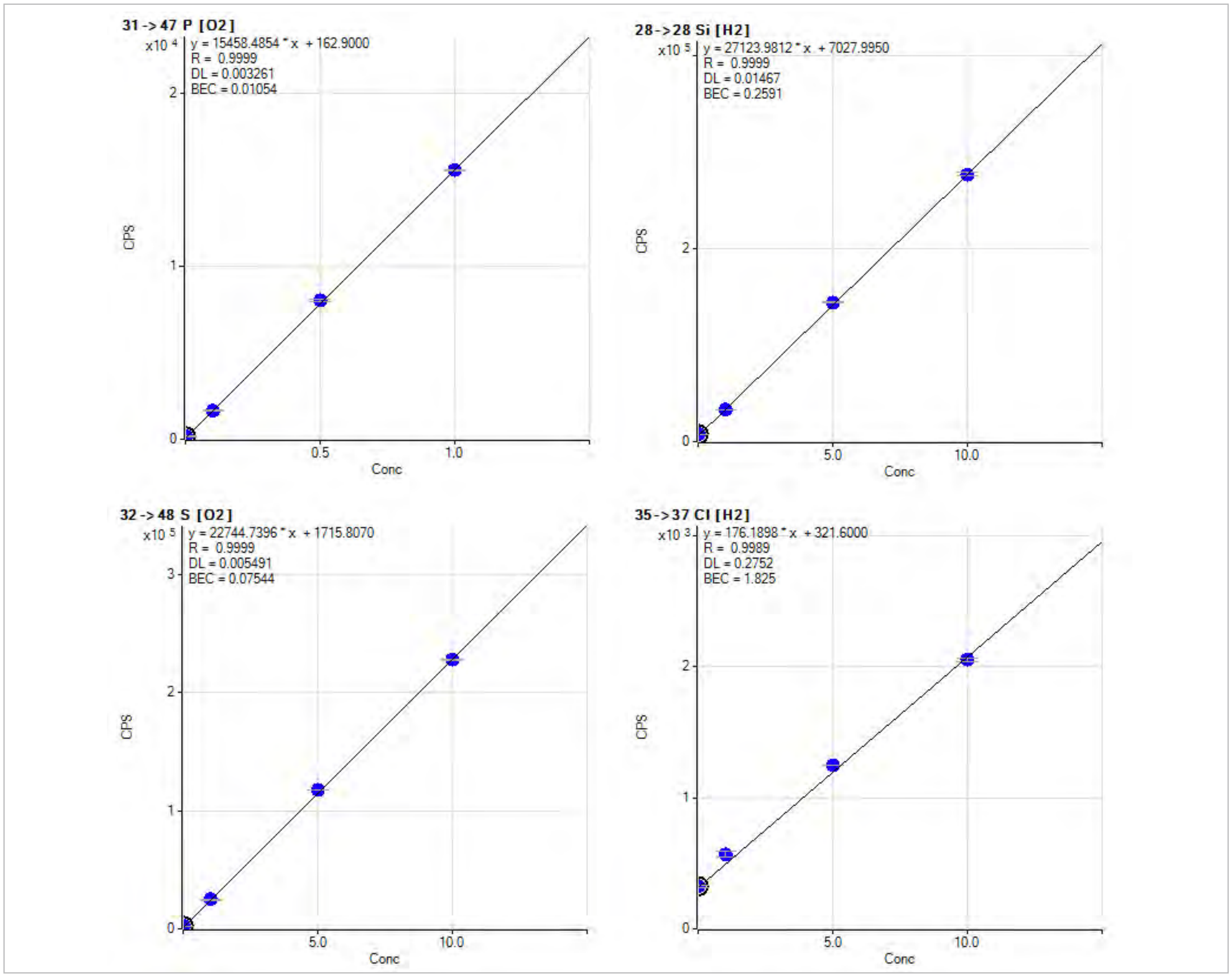


Figure 1. Calibration plots of P, S, Si and Cl in UPW . All values in ug/L (ppb).

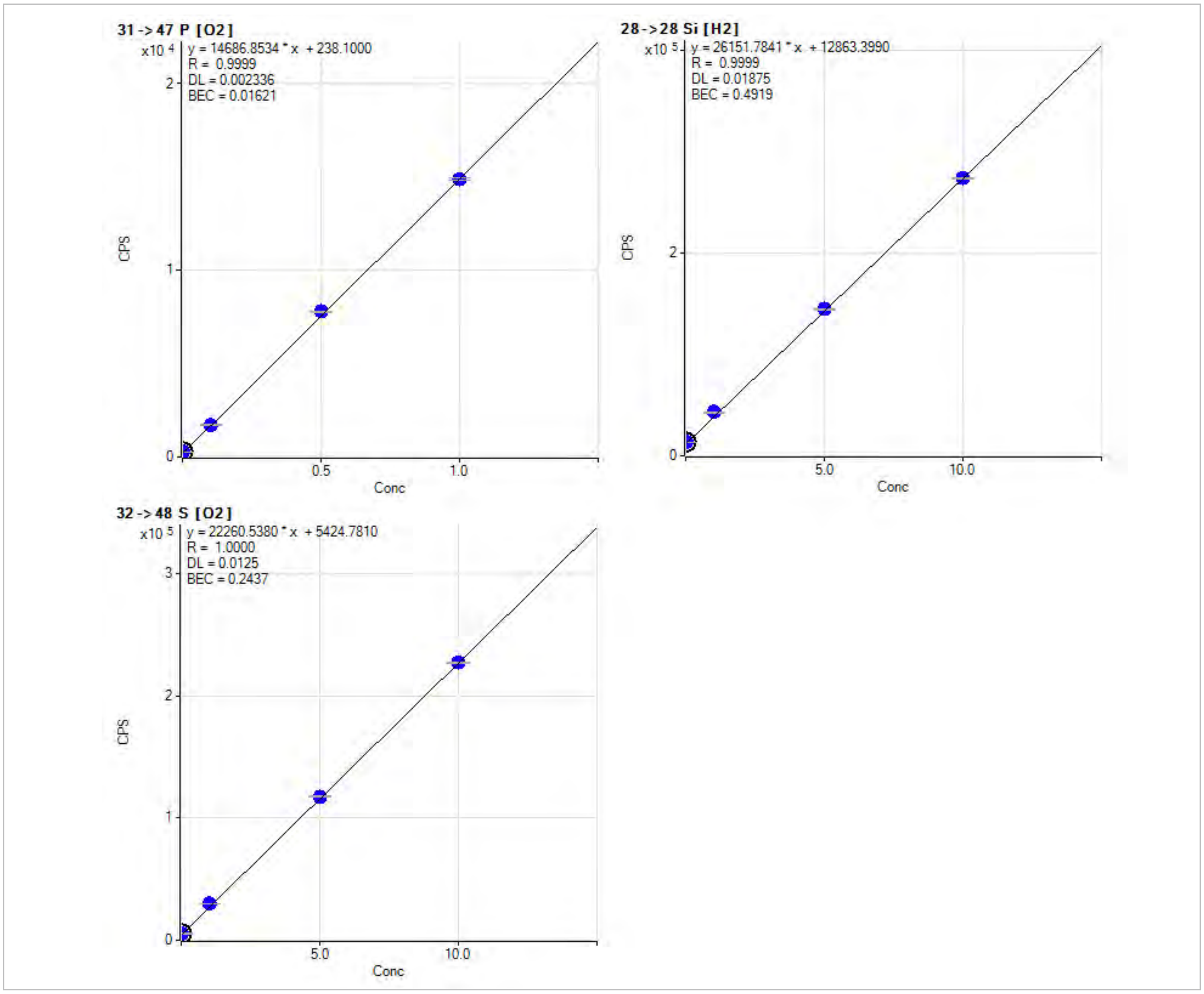


Figure 2. Calibration plots of P, S and Si in H_2O_2

Table 3. BEC and DL of P, S, Si and Cl in UPW and P, S and Si in the highest grade H_2O_2

	P (ppt)		S (ppt)		Si (ppt)		Cl (ppb)	
Element	BEC	DL	BEC	DL	BEC	DL	BEC	DL
UPW	10.5	3.3	75.4	5.5	259	14.7	1.83	0.28
H_2O_2	16.2	2.3	244	12.5	492	18.8		

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode with O_2 and H_2 cell gases successfully eliminated problematic spectral interferences on non-metallic impurities P, S, Si and Cl in UPW and P, S and Si in H_2O_2. The results highlight the advanced performance of the second generation ICP-QQQ for the analysis of challenging elements, by achieving the lowest ever reported BECs for the four elements in UPW.

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Ultra trace measurement of potassium and other elements in ultrapure water using the Agilent 8800 ICP-QQQ in cool plasma reaction cell mode

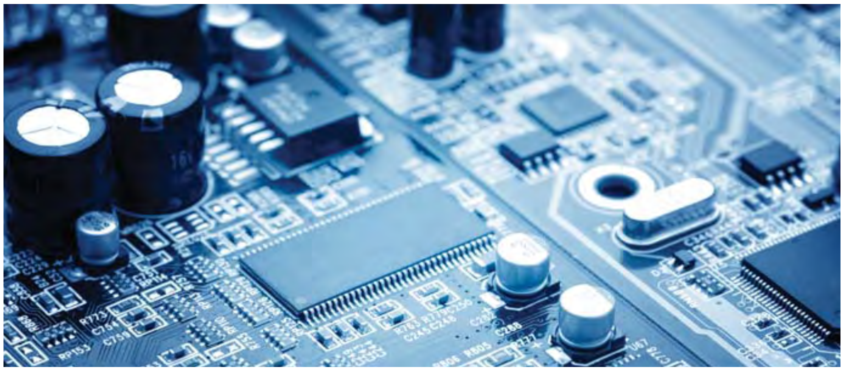
Application note

Semiconductor

Author

Katsuo Mizobuchi
Masakazu Yukinari

Agilent Technologies Japan Ltd



Introduction

The drive to downsize semiconductor components is relentless, as the industry responds to the market demands for more compact devices, faster operational speeds, lower power consumption and lower cost. The trend for ever smaller and higher density device architecture requires that higher purity chemicals and materials are used in the semiconductor manufacturing process, since any impurities present in the process chemicals may contaminate surfaces and directly affect the performance and yield of the final product. Consequently, semiconductor applications have always required the highest performance, cutting edge technology, and specific, clean sampling techniques to keep pace with evolving analytical demands.

Since its inception, ICP-MS has been of interest for the elemental impurity analysis of chemicals and materials used by semiconductor industries; however, some analytical challenges remain unsolved. The development of collision/reaction cells (CRC) for quadrupole ICP-MS (ICP-QMS) addressed some of the analytical difficulties by allowing specific interferences to be

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removed by chemical reaction in the CRC. However, these ICP-QMS reaction mode methods are unable to achieve the extremely low limits of detection now required by the industry.

Cool plasma is an ICP-MS mode of analysis that was developed more than 20 years ago for the determination of difficult, interfered elements such as Na, Mg, Al, K, Ca and Fe at trace levels [1]. The concentrations of K, Ca and Fe are strictly controlled in semiconductor device manufacturing processes and chemicals, but they are difficult elements to determine by ICP-MS due to argide interferences e.g. ArH^+ on $^{39}K^+$, Ar^+ on $^{40}Ca^+$ and ArO^+ on $^{56}Fe^+$. Cool plasma employs a lower temperature plasma that has sufficient energy to ionize the analytes but not the argide interferences, thereby allowing the analyst to measure the interfered elements at trace (ppt) levels, free from the interfering ions. The low temperature plasma also prevents the re-ionization of Easily Ionized Elements (EIEs) such as Li and Na that may be deposited on the interface of the ICP-MS. Even after the introduction of a high concentration of EIEs, cool plasma ensures a low background level of these elements is maintained.

Agilent ICP-MS systems (the 7900 ICP-MS and 8800 Triple Quadrupole ICP-MS (ICP-QQQ)) are available in two configurations; the standard configuration is for general applications while the “s” configuration (option #200) is optimized for semiconductor applications. The “s” configuration includes a specially designed “s-lens” to support cool plasma performance, which remains the semiconductor industry standard technique for a number of high-purity chemical applications. Both the 7900 ICP-MS and the 8800 ICP-QQQ instruments also support CRC operation, giving total flexibility for method optimization for the extremely high performance capability required in the semiconductor industry.

This note describes how the Agilent 8800 ICP-QQQ provides improved cool plasma performance combined with unique MS/MS mode reaction cell methodology to achieve a Background Equivalent Concentration (BEC) of 30 ppq for K in ultrapure water (UPW) and BECs at the ppq level for all the other elements studied: Li, Na, Mg, Al, Ca, Cr, Mn, Fe, Ni and Cu.

Experimental

A semiconductor configuration Agilent 8800 Triple Quadrupole ICP-MS was used. The sample introduction system features a quartz torch with a 2.5 mm i.d. injector, quartz spray chamber, and a PFA concentric nebulizer. The semiconductor configuration also includes platinum interface cones, which were fitted for the analysis. The sample was self-aspirated at about 180 µL/min using a carrier gas flow rate of 0.7 L/min. An Agilent I-AS autosampler was used, with a flowing rinse port kit (Organo Corp., Tokyo, Japan) fitted in one of the I-AS rinse port positions. The rinse port kit continuously supplies fresh UPW for the probe rinse during analysis; this eliminates the possibility of the buildup of trace contamination that may occur in a static (non-flowing) rinse container.

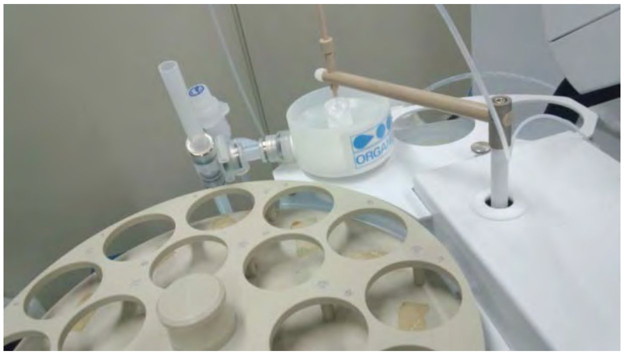

Figure 1. Photograph of the Organo flowing rinse port kit fitted to the Agilent I-AS autosampler

High purity HNO_3 (TAMAPURE-AA-10, TAMA Chemicals Co. Ltd. Kanagawa, Japan) was used to acidify the blanks and samples. Standard solutions were prepared by serial dilution from a SPEX 331 mixed standard (SPEX CertiPrep, NJ, USA).

Cool plasma conditions were used throughout, and the plasma parameters are shown in Table 1. A low-temperature plasma dramatically reduces the formation of argide-interferences e.g., Ar^+, ArH^+ and ArO^+. To establish cool plasma conditions, the total injector gas flow rate (carrier gas flow rate + make up gas flow rate) is increased, the RF forward power is decreased, and a longer sample depth (SD) is used. With the low temperature plasma conditions of cool plasma, hard extraction (significantly negative voltage applied to extraction lens 1) is recommended.

The 8800 ICP-QQQ has a tandem MS configuration which enables operation in MS/MS mode (where both quadrupoles are operated as unit mass filters). MS/MS mode ensures that the reaction chemistry in the CRC is controlled and predictable, as only the target analyte ion and direct, on-mass interferences are passed to the cell. This ensures that the reactions are consistent even when using a highly reactive cell gas such as ammonia. In this study, a cell gas of 10% NH_3 in He (99.99%) was used, introduced using the 8800 ICP-QQQ's third cell gas line. The performance was compared for cool plasma mode (with no cell gas), and cool plasma with NH_3 MS/MS reaction mode.

Table 1. Agilent 8800 ICP-QQQ operating parameters

Tuning parameters	Unit	Cool plasma	Cool plasma + NH_3 reaction
RF power (RF)	W	600	
Sample depth (SD)	mm	18	
Carrier gas flow rate (CRGS)	L/min	0.7	
Make up gas flow rate (MUGS)	L/min	0.8	
Scan mode	-	MS/MS	
Extraction lens 1 (Ex1)	V	-100	
Extraction lens 2 (Ex2)	V	-12	
Omega bias	V	-70	
Omega lens	V	6.7	
OctpBias	V	-20	-10
KED	V	15	-10
Cell gas	-	NA	10% NH_3 in He
Cell gas flow rate	mL/min	NA	1

Results and discussion

Investigation of the background signal at *m/z* 39 under cool plasma conditions

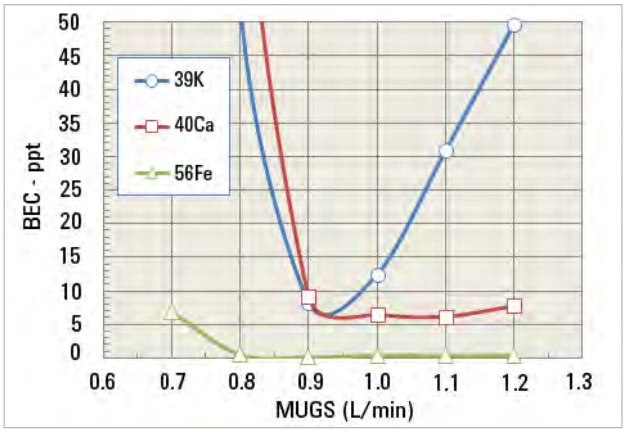

Figure 2: BEC of K, Ca and Fe as a function of makeup gas (MUGS) flow rate

Figure 2 shows the BEC of ^{39}K, ^{40}Ca and ^{56}Fe in UPW as a function of makeup gas (MUGS) flow rate. As shown, an increase in MUGS (cooler plasma conditions) results in a decrease of the BEC for each element. This indicates a reduction in the production (ionization) of the argide ions that overlap each of the analyte ion masses. However, above a MUGS flow rate of 0.9 L/min, the BEC of ^{39}K starts to increase again. This indicates that, apart from the ionization of ArH^+, there is another factor that also affects the background signal at *m/z* 39. The first factor is the decreasing formation of $^{38}ArH^+$ with higher MUGS flow rate (lower plasma temperature). Second, we suspect the presence of a water cluster ion, $H_3O(H_2O)^+$, which is likely to form under low temperature plasma conditions. To test this hypothesis, we monitored two signal ratios; R1 (signal at *m/z* 37 to signal at *m/z* 39) and R2 (signal at *m/z* 41 to signal at *m/z* 39). If the background signal at *m/z* 39 is mainly due to ArH^+, R2 should match the ratio of the Ar 40/38 isotope abundance ($^{40}ArH^+/^{38}ArH^+$) = 1581. If the signal at *m/z* 39 is mainly due to the water cluster ion, R1 should match the ratio of the abundance of the water cluster ions consisting of the different oxygen isotopes, ^{16}O and ^{18}O (99.5/0.409 = 243), as shown in Table 2.

Table 2. Abundance of water cluster ions

Water cluster ion	Mass number	Abundance %
$(H_3{}^{16}O+)(H_2{}^{16}O)$	37	99.5
$(H_3{}^{16}O^+)(H_2{}^{18}O)$ or $(H_3{}^{18}O^+)(H_2{}^{16}O)$	39	0.409

Figure 3 is a plot of the signal ratios R1 and R2 as a function of MUGS. It shows that R2 is close to 1581 when the MUGS flow is low, indicating that the signal at *m/z* 39 is dominated by ArH^+ at low MUGS flow. However, when the MUGS flow is high (> 1 L/min), R1 approaches 243, indicating that the signal at *m/z* 39 is dominated by the water cluster ion at high MUGS flow. This result confirms the background at *m/z* 39 is due to the combination of two interfering ions, ArH^+ and the water cluster ion. The findings suggest that it may not be possible to completely remove the background signal at *m/z* 39 simply through applying cool plasma conditions, as there is no plasma temperature where both interferences on $^{39}K^+$ are at a minimum level.

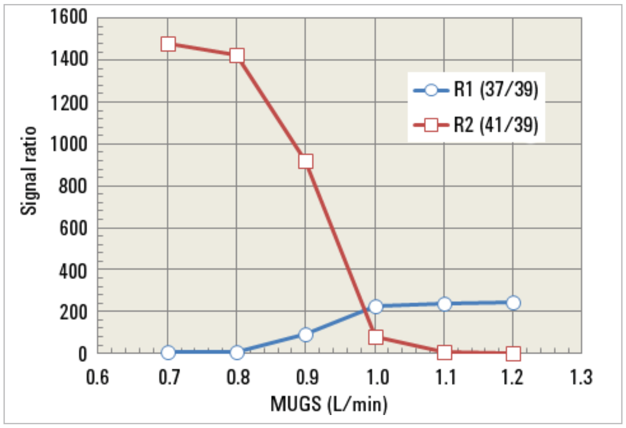

Figure 3. Signal ratio of R1 and R2 as a function of MUGS

Cool plasma/NH_3 reaction cell mode for K analysis

The water cluster ion is known to react with deuterated ammonia (ND_3) via the fast proton transfer reaction shown below [2].

$$H_3O(H_2O)^+ + ND_3 \rightarrow NHD_3{}^+ + 2H_2O$$

It is reasonable to assume that the water cluster ion reaction with NH_3 would proceed at a similar rate to the reaction with ND_3, offering a NH_3 reaction cell method to remove the water cluster ion.

Ammonia reaction gas mode under cool plasma conditions was used to determine K in UPW. The BEC was measured at 30 ppq. A comparative study carried out using a 7500cs ICP-QMS in cool plasma/NH_3 reaction mode achieved a BEC of 500 ppt for K [3]. We attribute the improvement of BEC achieved with the 8800 to the MS/MS reaction capability of the ICP-QQQ technique. In ICP-QMS, all ions formed in the plasma enter the reaction cell and react with NH_3 and product ions that are formed in the cell. These reactions lead to the formation of new product ions at *m/z* 39. In contrast, MS/MS prevents any unwanted precursor ions from entering the cell thus minimizing the formation of undesired product ions.

Multi-element analysis using cool plasma/NH_3 MS/MS reaction mode

The new cool plasma method with MS/MS and NH_3 reaction mode was applied to the multi-element analysis of UPW. As can be seen from the results in Table 3, BECs < 0.05 ppt (ng/L) or 50 ppq were achieved for all elements except Ca, Fe and Ni, all of which had BECs < 150 ppq.

Table 3. DL and BEC of elements in UPW determined using ICP-QQQ in cool plasma/NH_3 reaction mode

Mass/Element	Sensitivity, cps/ppt	DL, ppt	BEC, ppt
7 Li	6.2	0.000	0.000
23 Na	94.0	0.014	0.035
24 Mg	44.0	0.010	0.005
27 Al	42.7	0.010	0.002
39 K	96.8	0.000	0.030
40 Ca	42.5	0.035	0.091
52 Cr	36.5	0.029	0.037
55 Mn	64.5	0.020	0.011
56 Fe	42.2	0.488	0.134
60 Ni	13.4	0.270	0.101
65 Cu	15.5	0.014	0.029

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Conclusion

The Agilent 8800 ICP-QQQ was used to confirm the presence of a water cluster ion, $H_3O(H_2O)^+$, which contributes to the background signal for K at *m/z* 39 under cool plasma conditions. This water cluster ion was removed successfully using NH_3 cell gas in MS/MS mode. The 8800 ICP-QQQ BEC for ^{39}K was more than a factor of 10 lower than that achieved using a conventional quadrupole ICP-MS. This demonstrates the benefit of MS/MS reaction mode, which stops any non-target, plasma-derived ions from entering the cell, and thereby prevents the creation of potentially interfering cell-formed product ions. This enabled the Agilent 8800 ICP-QQQ to achieve a BEC of 30 ppq for K in UPW and a BEC < 150 ppq for all other elements, including Ca, Fe and Ni.

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Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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Ultratrace measurement of calcium in ultrapure water using the Agilent 8800 Triple Quadrupole ICP-MS

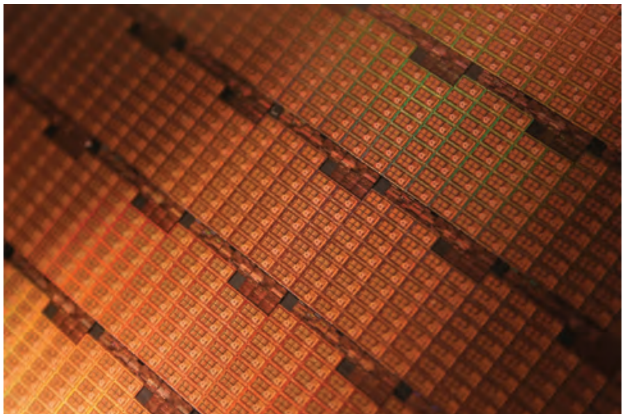
Application note

Semiconductor

Authors

Albert Lee, Vincent Yang, Jones Hsu, Eva Wu and Ronan Shih
BASF Taiwan Ltd., Taipei, Taiwan

Katsuo Mizobuchi
Agilent Technologies, Tokyo, Japan



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Introduction

In the semiconductor industry, the control of metal impurities in the process chemicals used in the manufacture of semiconductor devices is critical to achieve the required product performance and yield. As device performance is continually increasing, the required impurity control becomes ever more stringent. For example, metal content of the ultra pure water (UPW) used in the manufacturing process must be at the sub-ppt level. ICP-MS is the standard technique used for the trace metals analysis of semiconductor chemicals and devices. The most common instrument and measurement technique used in the semiconductor industry is single quadrupole ICP-MS (ICP-QMS) with cool plasma. The cool plasma technique [1], developed in the mid 1990's, enables the quantification of key contaminant elements at the single ppt level. Collision and reaction cell ICP-QMS, developed from 2000 onwards, enabled the direct analysis of more complex semiconductor matrices, but did not improve on the detection limits or background

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equivalent concentration (BEC) of cool plasma. To achieve measurement at the sub-ppt level, reduction of the BEC is required.

The Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) provides new reaction cell technology that enables a BEC of 100 ppq for Ca. This application note describes the theory and operation of the Agilent 8800 ICP-QQQ to achieve the sub-ppt measurement of Ca in UPW.

Experimental

Instrumentation

A standard Agilent 8800 Triple Quadrupole ICP-MS mainframe (option #200 semiconductor version) was used. The sample introduction system features a quartz torch and spray chamber, and a concentric PFA nebulizer (which was operated in self-aspiration mode). Platinum interface cones were also used. Cool plasma conditions were used throughout and plasma parameters are shown in Table 1.

Table 1. Agilent 8800 ICP-QQQ operating parameters

Parameter	Value
RF (W)	600
Carrier gas (L/min)	0.7
Make up gas (L/min)	1
Sampling depth (mm)	18

As can be seen in Figure 1, compared to conventional ICP-QMS, the 8800 features an additional quadrupole mass filter (Q1), situated in front of the Octopole Reaction System (ORS^3) cell and quadrupole mass filter (now called Q2). The Agilent 8800 ICP-QQQ can be operated in two scan modes: single quad mode and MS/MS mode. Single quad mode emulates ICP-QMS: Q1 is fixed and operates simply as an ion guide.

MS/MS mode is unique to ICP-QQQ: Q1 operates as a 1 amu window mass filter, selecting the ions that enter the cell. Because plasma ions are eliminated from the cell by Q1, ion transmission through the cell is greatly increased. When a reaction gas is added, reaction efficiency is also greatly enhanced, enabling the use of lower reaction gas flow rates which also increases ion transmission and, therefore, sensitivity.

Calibration standards

A Ca standard was prepared in UPW acidified with 0.1% high purity HNO_3. This was used to make 50 ppt and 100 ppt additions to a UPW blank acidified with 0.1% high purity HNO_3.

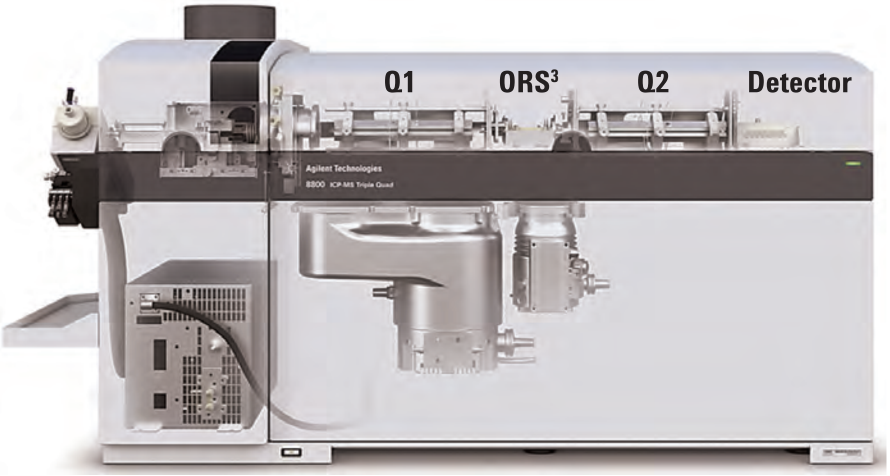

Figure 1. Cutaway diagram of the Agilent 8800 ICP-QQQ

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Results

The sample was acidified to be 0.1% HNO_3. Figure 2 shows the BECs obtained for Ca using method of standard additions (MSA), using three different operating conditions: single quad mode with no cell gas, MS/MS mode with no cell gas, and finally MS/MS mode with an H_2 cell gas flow of 1 mL/min. The first operating condition emulates the Agilent 7700 ICP-QMS operated in cool plasma mode. The obtained BEC of 6.8 ppt is similar to that routinely achieved with the Agilent 7700.

Using MS/MS mode (without cell gas) improved the BEC to 1.4 ppt. MS/MS mode with H_2 at 1 mL/min in the cell further improved the BEC down to 0.041 ppt (41 ppq). The obtained MSA plot is shown in Figure 3. The Agilent 8800 achieved a BEC for Ca in UPW two orders of magnitude lower than the BEC obtained using conventional ICP-QMS.

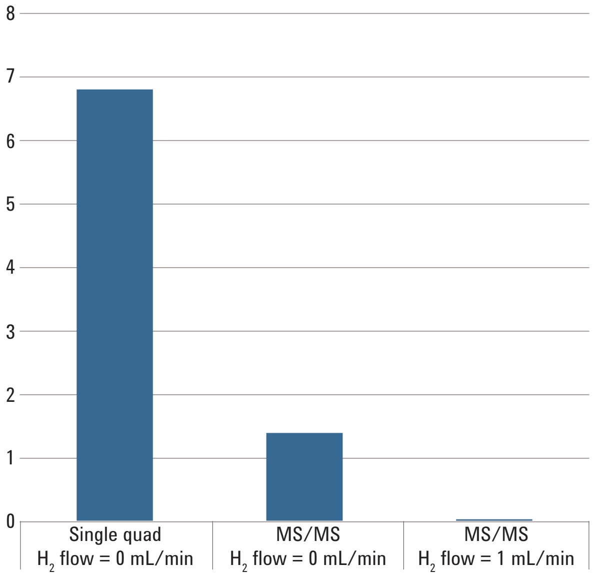

Figure 2. BECs for Ca obtained using single quad mode with no cell gas [6.8 ppt], MS/MS mode with no cell gas [1.4 ppt], and MS/MS mode with an H_2 cell gas flow of 1 mL/min [0.041 ppt].

Discussion

Figure 4 shows the spectrum obtained from UPW using cool plasma mode and single quad mode (no cell gas).

As can be seen, Ar^+ is suppressed under the low temperature plasma conditions and two intense peaks are observed at $m/z = 19$ and 30. These are $(H_2O)H^+$ and NO^+, respectively. With single quad mode, all ions formed in the plasma including these two intense ions pass through to the cell. Even with no cell gas, an unexpected reaction occurs in the cell which causes a new interference at $m/z = 40$. The likely reaction occurring in the cell is:

$NO^+ + Ar \rightarrow Ar^+ + NO$ (charge transfer reaction)

which increases the BEC for Ca by several ppt. Although the ionization potential (IP) of NO (IP = 9.26 eV) is lower than that of Ar (IP = 15.7 eV), a metastable ion, NO^+ exists close to the ionization potential of Ar [2]. So it is reasonable to assume that the charge transfer reaction shown occurs in the cell. With the MS/MS mode, Q1 rejects all non-target ions such as NO^+ and $(H_2O)H^+$, preventing unwanted reactions from occurring in the cell, which lowers the BEC. The addition of H_2 in the cell also removes any residual $^{40}Ar^+$ that is formed even under cool plasma conditions.

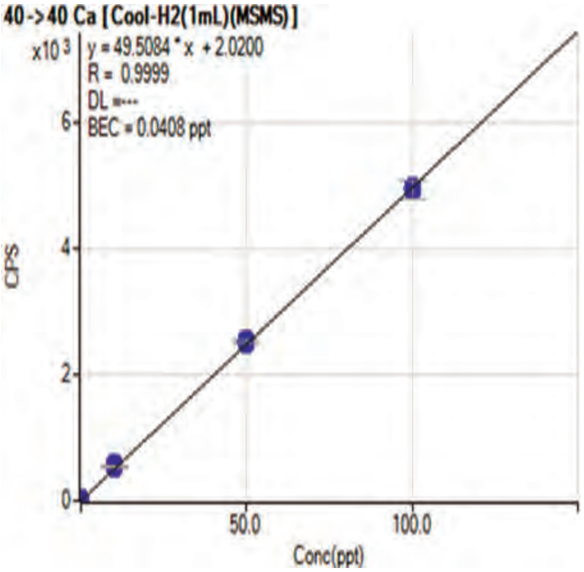

Figure 3. MSA calibration plot for Ca using MS/MS mode with H_2 cell gas at 1 mL/min.

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Conclusions

The plasma derived polyatomic ion NO^+, which is formed in cool plasma mode, can generate small amounts of Ar^+ in the cell by charge transfer reaction, which interferes with Ca at $m/z = 40$. The Agilent 8800 ICP-QQQ operated in MS/MS mode, which is unique to ICP-QQQ, stops plasma derived ions from entering the cell, preventing unwanted reactions from occurring. This enabled the Agilent 8800 Triple Quadrupole ICP-MS to achieve a BEC of 41 ppq for Ca in UPW.

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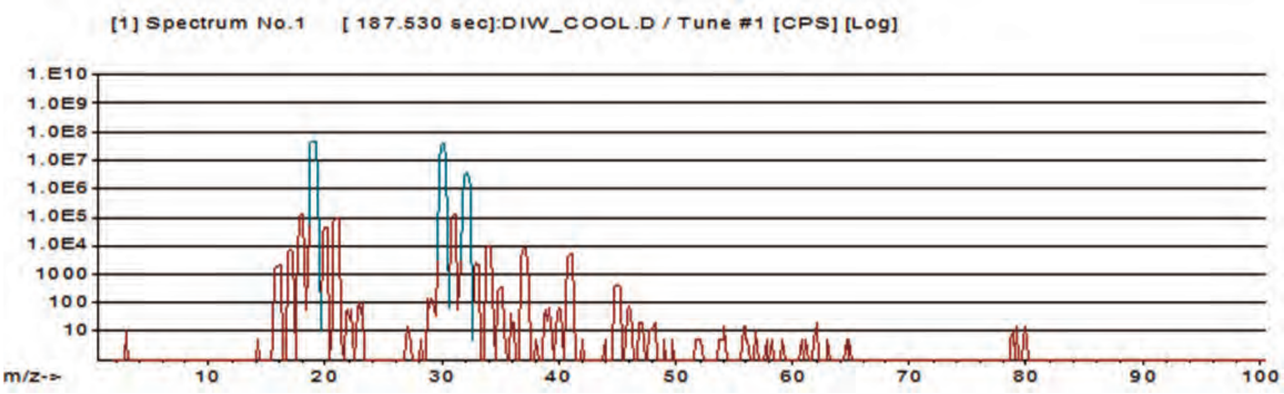

Figure 4. Spectrum of UPW acquired using cool plasma mode and single quad mode (no cell gas)

Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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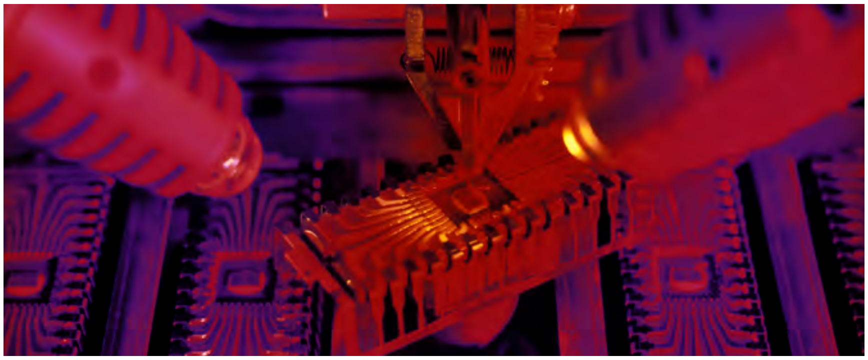
Application Note

Semiconductor

Automated Analysis of Semiconductor Grade Hydrogen Peroxide and DI Water using ICP-QQQ

Online MSA calibration using prepFAST S automated sample introduction and Agilent 8900 ICP-QQQ



Authors

Kazuhiro Sakai
Agilent Technologies, Japan

Austin Schultz
Elemental Scientific, USA

Introduction

Maximizing product yield and performance of semiconductor devices requires manufacturers to address the potential for contamination at every stage of the production process. Contamination from particles, metals, and organic residues can affect the electrical properties of the semiconductor, reducing the quality and reliability of the final product. For example, following each photolithography step during wafer processing, the organic photoresist mask must be completely removed from the silicon wafer surface. A mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) known as a sulfuric/peroxide mix (SPM) is used for this cleaning procedure. SPM is also used for degreasing the wafer surface. H_2O_2 is also used in the RCA Standard Clean steps (SC-1 and SC-2) used to clean silicon wafers, and for etching metallic copper on printed circuit boards.

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Ultrapure water (UPW) is used throughout the wafer fabrication process. As well as working as a rinse solution between processing steps, UPW is also the diluent for many process chemistries such as SC-1 and SC-2 solutions. As these chemicals are in frequent and prolonged contact with the wafer surface, minimizing metal impurities is essential to prevent wafer surface contamination.

Semiconductor Equipment and Materials International (SEMI) publishes standards for semiconductor process chemicals. The standard for H_2O_2 is SEMI C30-1110 – Specifications for Hydrogen Peroxide (*1*). SEMI Grade 5 is the highest purity level, with maximum contamination levels of 10 ppt for most trace elements.

Quadrupole ICP-MS (ICP-QMS) is the standard technique used to monitor trace element contaminants in the semiconductor industry. However, the drive for ever smaller device architectures and higher yields requires an increasing number of contaminant elements to be monitored at lower concentrations.

In addition to trace elements, SEMI Standard C30-1110 specifies the maximum concentration of sulfate and phosphate allowed in high purity H_2O_2, with a limit of 30,000 ppt. This limit equates to an elemental concentration of sulfur (S) and phosphorus (P) of 10,000 ppt. Due to the relatively high detection limits achievable with conventional single quadruple ICP-MS, these two elements are not currently measured using ICP-MS.

Triple quadrupole ICP-MS (ICP-QQQ) provides much lower limits of detection for S and P (among many other elements). Uniquely, the technique offers the potential for the sulfate and phosphate analysis to be combined with the other trace metals. The adoption of ICP-QQQ therefore enables all SEMI specified elements to be monitored using a single technique (*2, 3*).

Contamination control

Ultratrace analysis at the pg/g (ppt) or fg/g (ppq) level is susceptible to contamination from the lab environment, reagents, or errors arising from manual tasks, such as pipetting. To deliver consistently accurate results at these ultratrace concentrations, a skilled and experienced analyst is typically required.

One approach to simplifying the analysis for less expert analysts is to use an automated sample introduction system. These systems automate typical sample handling steps such as dilution, acidification, and spiking. They can also automatically generate a calibration curve using either external standards or Method of Standard Additions (MSA).

In this study, an automated procedure was developed to quantify ultratrace elemental impurities in de-ionized (DI) water and H_2O_2 using an Agilent 8900 ICP-QQQ fitted with an ESI prep*FAST* S automated sample introduction system. The prep*FAST* S automates sample preparation and calibration, saving time and minimizing the risk of sample-contamination from manual sample handling operations.

Experimental

Reagents and samples

TAMAPURE-AA-10 hydrogen peroxide (35%, Tama Chemicals, Japan) and ultrapure DI water (Milli-Q water, Molsheim, France) were used as the samples.

Standard stock solution for MSA: a 1000 ppt mixed multi-element standard solution was prepared by diluting a 10 ppm mixed multi-element standard solution (SPEX CertiPrep, NJ, US) with 1% HNO_3.

Nitric acid for sample acidification: a 10% nitric acid solution was prepared by diluting 68% ultrapure HNO_3 (TAMAPURE-AA-10) with DI water. HNO_3 was automatically added the H_2O_2 samples, giving a final concentration of 0.5% HNO_3 to stabilize the spiked elements. UPW samples are often also acidified to ensure trace element stability (see reference 2). However, in this work, the DI water was analyzed unacidified, without the addition of a HNO_3 spike, providing results that can be compared with the earlier work.

The standard stock and HNO_3 spike solutions were loaded on the prep*FAST* S. All solutions run in the analysis were automatically prepared from these stock solutions by the prep*FAST* S system. The prep*FAST* S method used DI (Milli-Q) water as the carrier solution, at a flow rate of 100 µL/min.

All preparation and analysis steps were performed in a Class 10,000 clean room.

Instrumentation

A standard Agilent 8900 semiconductor configuration ICP-QQQ instrument was equipped with a PFA concentric nebulizer that is included with the prep*FAST* S automated sample introduction system. The semiconductor configuration ICP-QQQ is fitted with a Peltier cooled quartz spray chamber, quartz torch (2.5 mm id), platinum-tipped sampling and skimmer cones, and s-lens.

The 8900 ICP-QQQ was connected to the ESI prep*FAST* S automated sample introduction system. The prep*FAST* S is a specialized, semiconductor version of the standard ESI prep*FAST*. The S version has a high purity, low-contamination, inert sample path and features an automated MSA spike addition mode. ICP-QQQ instrument operating conditions are given in Table 1.

Table 1. ICP-QQQ operating conditions.

Tune	Cool-no gas	Cool-NH_3(1)	Cool-NH_3(2)	No gas	H_2	He	O_2(1)	O_2(2)
Acquisition mode	Single Quad	MS/MS						
RF power (W)	600			1500				
Carrier gas (L/min)	0.70							
Makeup gas (L/min)	0.90			0.48				
Sampling depth (mm)	18.0			8.0				
Ext 1 (V)	-150.0		-100.0	4.2	4.7	4.2	4.5	3.5
Ext 2 (V)	-18.0	-17.0	-12.0	-250.0				-120.0
Omega bias (V)	-70.0			-140.0				-70
Omega lens (V)	2.0			10.0	8.0	10.0	10.5	4.0
Q1 entrance (V)	-15.0		-50.0					
NH_3 flow (mL/min)*	-	3.0 (30%)**		-	-	-	-	-
He flow (mL/min)	-	1.0		-	-	5.0	-	-
H_2 flow (mL/min)	-	-	-	-	7.0	-	-	-
O_2 flow (mL/min)	-	-	-	-	-	-	4.5 (45%)**	
Axial acceleration (V)	0.0	1.5		0.0			1.0	
Energy discrimination (V)	15.0	-5.0		5.0	0.0	3.0	-7.0	

*10% NH_3 balanced with 90% He
* Values in parentheses are % of the maximum flow of the gas controller, as displayed in the tuning pane of ICP-MS MassHunter software

The most advanced semiconductor manufacturing facilities require the lowest possible levels of contamination, so they require analytical techniques that can deliver the lowest possible detection limits (DLs). This requirement is critical in the analysis of trace contaminants in process chemicals such as UPW and H_2O_2, which are used at multiple stages of the wafer fabrication process. UPW and H_2O_2 also come into direct contact with the wafer surface.

The 8900 ICP-QQQ satisfies this requirement by offering the flexibility to optimize the measurement parameters (plasma conditions, quadrupole scan mode, cell gas type, and flow rate) to give the highest sensitivity and lowest background for each analyte.

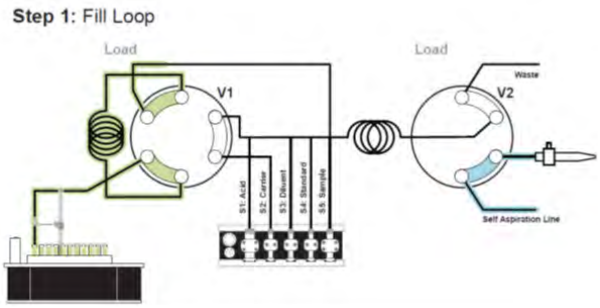
In this work, several reaction cell gases (He, H_2, O_2, and NH_3) were used in the collision/reaction cell (CRC) of the 8900, as appropriate for the large number of analytes being measured. Since DI water and H_2O_2 are low-matrix samples, cool plasma conditions were also applied for the elements where this mode provides the lowest background equivalent concentrations (BECs).

The tuning steps were 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 maximum sensitivity for the analytes. Q1 and Q2 settings are shown in Table 2 along with DLs, BECs, and quantification results.

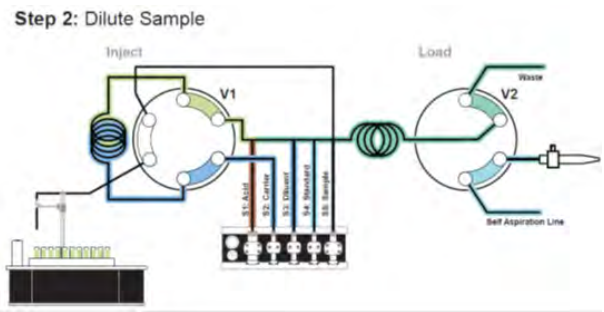
ESI prep*FAST* S operation

The prep*FAST* S automated sample introduction system combines an autosampler with a system of ultrapure valves (S1 -5), and a set of high precision syringe pumps. Undiluted chemicals can be placed on the autosampler and the system will perform the actions—such as dilution, acidification, and spiking—required to prepare the sample for introduction to the ICP-MS or ICP-QQQ. The operation of the prep*FAST* S is outlined in the four schematics shown in Figure 1.

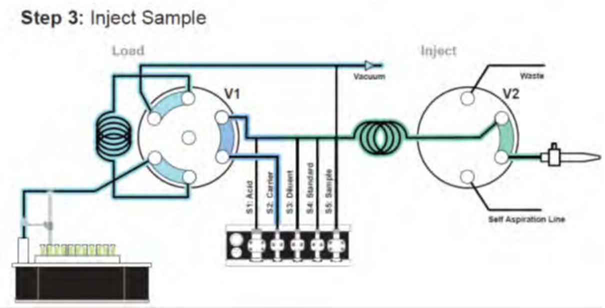
1. Loading of sample: Syringe S5 loads a precise amount of sample to the loop of valve 1 (V1).



2. Sample dilution and sample spiking: Syringes S1, S2, S3, and S4 mix the acid, sample, diluent, and spike solution into a loop connecting V1 and V2.



3. Sample injection: The prepared sample is introduced into the ICP-QQQ via the carrier solution pumped by S2. S2 provides a precise flow rate regardless of sample type. The V1 loop is washed simultaneously.



4. Valve wash: UPW or acidified UPW is used to clean the lines between V1 and V2.

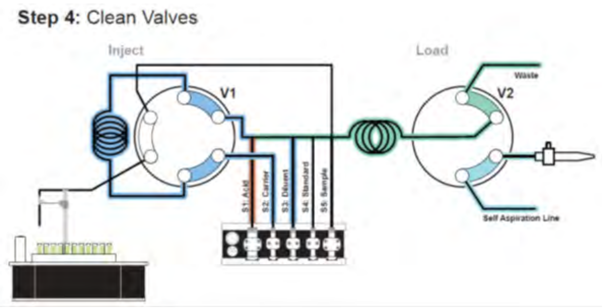


Figure 1. ESI prep*FAST* S system schematic, illustrating four distinct steps: sample loading during spray chamber rinse, sample preparation, injection, and cleaning.

The prep*FAST* S removes the need for analyst intervention in the analysis of semiconductor grade chemicals, reducing the risk of sample contamination. The integrated system offers the following advantages for the ultratrace elemental analysis of semiconductor samples:

1. Automated dilution of samples
2. Automated creation of external or MSA calibrations
3. Automated acidification of samples
4. Injection of samples at a precise flow rate
5. High speed rinsing of the ICP-MS sample introduction system

Results and Discussion

Figures 2 and 3 show calibration curves for Na, K, Si, P, and S in DI water and Ca, Zn, and As in H_2O_2, respectively. All elements were measured using the MSA calibration prepared automatically using the prep*FAST* S. These elements are difficult to analyze at low levels due to raised backgrounds. The analytes Si, P, and S are not commonly measured with conventional single quadrupole ICP-MS, due to the presence of intense polyatomic interferences. However, the controlled reaction chemistry of the 8900 ICP-QQQ operating in MS/MS mode gives far superior control of background interferences. MS/MS mode allows these elements to be calibrated and quantified at ppt concentrations.

Good linearity at the ppt level was observed for all elements measured in both sample matrices, although Si, P, and S had relatively high BECs of 85, 10, and 118 ppt, respectively. These elements are typically present at higher levels than the trace metals, as they are more difficult to control in the lab environment and in reagents. They are also less critical contaminants, as reflected in the higher levels for P and S (of 30 ppb for phosphate and sulfate) permitted in high purity H_2O_2. However, despite the higher BECs, the calibration curves for Si, P, and S were still linear over the calibration range from 10 to 50 ppt. The same calibration levels were used for all analytes, as the mixed stock standard contained all elements at the same concentration.

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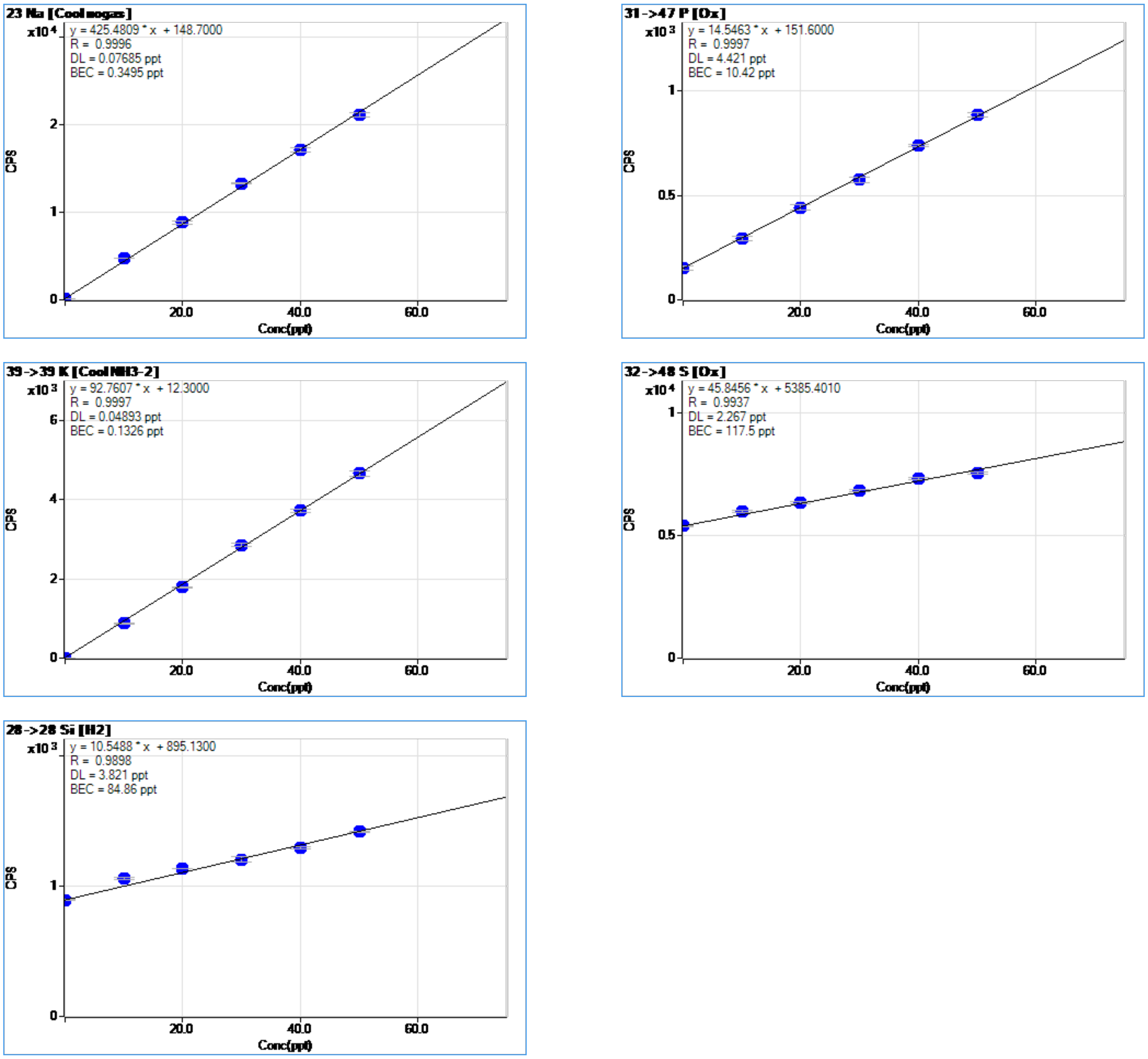

Figure 2. Calibration plots for Na, K, Si, P, and S in DI water. All values in ng/L (ppt).

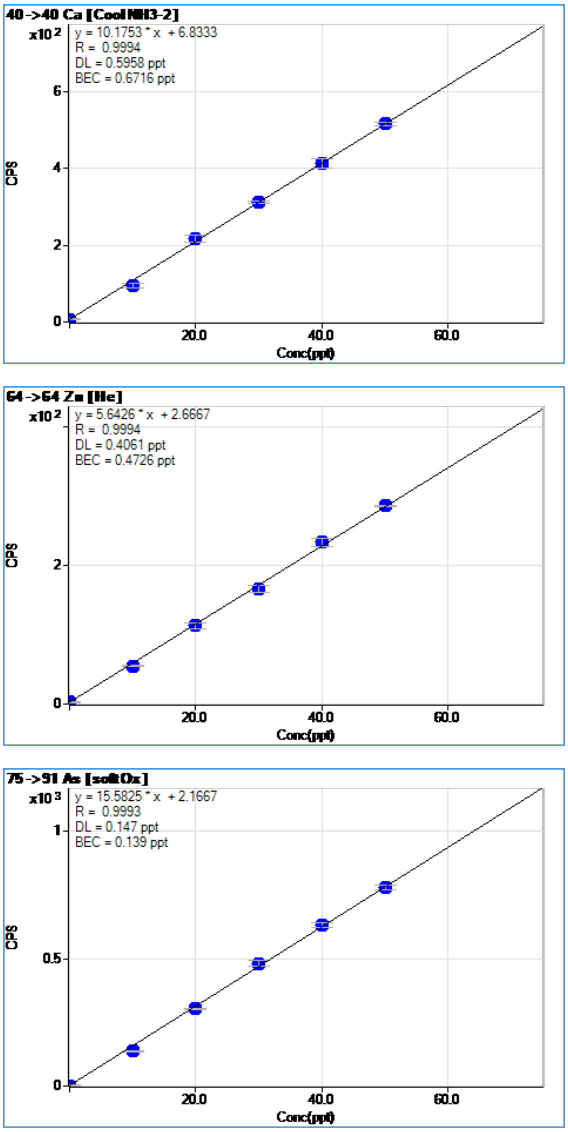

Figure 3. Calibration plots for Ca, Zn, and As in H_2O_2. All values in ng/L (ppt).

DLs and quantitative results

Forty-nine elements in total, including all the elements listed in SEMI C30-1110, were measured by MSA in DI water and H_2O_2, using the 8900 multi-tune mode method. Data was acquired in an automated sequence of cool plasma, no gas, and gas modes, during a single visit to the sample vial. Data for each of the modes was combined automatically into a single report for each sample.

Quantitative results, DLs, and BECs for all analytes—including all the SEMI specified elements—are shown in Table 2. Detection limits were calculated as 3-sigma of 10 replicate measurements of the blank DI water or H_2O_2 sample.

DLs <1 ng/L (ppt) were obtained for 46 elements in DI water. The DLs for the remaining 3 elements, Si, P, and S, were at the single-ppt level. Measured concentrations of all elements apart from B, Si, P, and S were <1 ng/L or <DL, confirming the purity of the sample. This analytical performance easily meets the requirements for monitoing UPW in semiconductor manufacturing.

In H_2O_2, DLs <1 ng/L were obtained for 45 elements. The DLs for B, P, and S, were at the single-ppt level, while the DL for Si was 26 ppt. All elements were measured at <1 ng/L or <DL apart from B (22 ppt), Na (1.1 ppt), Si (500 ppt), P (9.4 ppt), and S (220 ppt) in 35% H_2O_2. Only B and Si exceed the 10 ppt maximum limit in the SEMI specifications, and of these, only B is a SEMI specified element. P and S were quantified well below the 10,000 ppt SEMI specified limit in H_2O_2.

Table 2. Quantification of trace elements in DI water and 35% H_2O_2. SEMI specification elements are in bold.

	Q1	Q2	Scan type	Tune mode	DI Water			H_2O_2		
					DL ng/L	BEC ng/L	Conc ng/L	DL ng/L	BEC ng/L	Conc ng/L
Li		**7**	**SQ**	**Cool no gas**	**0.003**	**0.001**	**<DL**	**0.025**	**0.022**	**<DL**
Be	9	9	MS/MS	No gas	0.096	0.040	<DL	0.089	0.017	<DL
B	**11**	**11**	**MS/MS**	**No gas**	**0.52**	**1.7**	**1.7**	**1.9**	**22**	**22**
Na		**23**	**SQ**	**Cool no gas**	**0.077**	**0.35**	**0.35**	**0.11**	**1.1**	**1.1**
Mg		**24**	**SQ**	**Cool no gas**	**0.015**	**0.009**	**<DL**	**0.040**	**0.053**	**0.053**
Al		**27**	**SQ**	**Cool no gas**	**0.040**	**0.028**	**<DL**	**0.22**	**0.63**	**0.63**
Si	28	28	MS/MS	H_2	3.8	85	85	26	500	500
P	**31**	**47**	**MS/MS**	**O_2**	**4.4**	**10**	**10**	**2.6**	**9.4**	**9.4**
S	**32**	**48**	**MS/MS**	**O_2**	**2.3**	**120**	**120**	**7.5**	**220**	**220**
K	**39**	**39**	**MS/MS**	**Cool NH_3 (2)**	**0.049**	**0.13**	**0.13**	**0.19**	**0.45**	**0.45**
Ca	**40**	**40**	**MS/MS**	**Cool NH_3 (2)**	**0.082**	**0.044**	**<DL**	**0.60**	**0.67**	**0.67**
Ti	**48**	**64**	**MS/MS**	**O_2 (2)**	**0.042**	**0.021**	**<DL**	**0.24**	**0.21**	**<DL**
V	**51**	**67**	**MS/MS**	**O_2 (2)**	**0.021**	**0.026**	**0.026**	**0.058**	**0.068**	**0.068**
Cr	**52**	**52**	**MS/MS**	**Cool NH_3 (1)**	**0.085**	**0.047**	**<DL**	**0.24**	**0.69**	**0.69**
Mn	**55**	**55**	**MS/MS**	**Cool NH_3 (1)**	**0.010**	**0.010**	**0.010**	**0.039**	**0.020**	**<DL**
Fe	**56**	**56**	**MS/MS**	**Cool NH_3 (1)**	**0.070**	**0.076**	**0.076**	**0.29**	**0.17**	**<DL**
Co	59	59	MS/MS	Cool NH_3 (1)	0.017	0.002	<DL	0.025	0.005	<DL
Ni	**60**	**60**	**MS/MS**	**Cool NH_3 (1)**	**0.080**	**0.016**	**<DL**	**0.24**	**0.18**	**<DL**
Cu	**63**	**63**	**MS/MS**	**Cool NH_3 (1)**	**0.12**	**0.11**	**<DL**	**0.17**	**0.12**	**<DL**
Zn	**64**	**64**	**MS/MS**	**He**	**0.063**	**0.28**	**0.28**	**0.41**	**0.47**	**0.47**
Ga		71	SQ	Cool no gas	0.011	0.001	<DL	0.032	0.031	<DL
Ge	74	74	MS/MS	He	0.36	0.32	<DL	0.27	0.20	<DL
As	**75**	**91**	**MS/MS**	**O_2 (2)**	**0.072**	**0.035**	**<DL**	**0.15**	**0.14**	**<DL**
Se	78	78	MS/MS	H_2	0.20	0.14	<DL	0.40	0.13	<DL
Rb		85	SQ	Cool no gas	0.031	0.015	<DL	0.052	0.035	<DL
Sr	88	88	MS/MS	He	0.024	0.002	<DL	0.000*	0.000*	0.000*
Nb	93	93	MS/MS	He	0.018	0.010	<DL	0.030	0.029	<DL
Mo	98	98	MS/MS	He	0.093	0.045	<DL	0.065	0.063	<DL
Ru	101	101	MS/MS	He	0.077	0.058	<DL	0.075	0.014	<DL
Rh	103	103	MS/MS	O_2 (2)	0.057	0.10	0.10	0.018	0.097	0.097
Pd	105	105	MS/MS	No gas	0.078	0.12	0.12	0.055	0.090	0.090
Ag	107	107	MS/MS	No gas	0.099	0.14	0.14	0.031	0.016	<DL
Cd	**114**	**114**	**MS/MS**	**No gas**	**0.045**	**0.021**	**<DL**	**0.047**	**0.009**	**<DL**
In	115	115	MS/MS	No gas	0.009	0.003	<DL	0.022	0.019	<DL
Sn	**118**	**118**	**MS/MS**	**No gas**	**0.038**	**0.059**	**0.059**	**0.20**	**0.17**	**<DL**
Sb	**121**	**121**	**MS/MS**	**H_2**	**0.029**	**0.032**	**0.032**	**0.028**	**0.005**	**<DL**
Te	125	125	MS/MS	No gas	0.18	0.043	<DL	0.000*	0.000*	0.000*
Cs		133	SQ	Cool no gas	0.074	0.020	<DL	0.088	0.059	<DL
Ba	**138**	**138**	**MS/MS**	**H_2**	**0.023**	**0.014**	**<DL**	**0.039**	**0.018**	**<DL**
Ta	181	181	MS/MS	No gas	0.024	0.041	0.041	0.12	0.28	0.28

Table continues....

...Table continued.

	Q1	Q2	Scan type	Tune mode	DI Water			H_2O_2		
					DL ng/L	BEC ng/L	Conc ng/L	DL ng/L	BEC ng/L	Conc ng/L
W	182	182	MS/MS	No gas	0.037	0.009	<DL	0.044	0.044	0.044
Re	185	185	MS/MS	No gas	0.040	0.037	<DL	0.062	0.056	<DL
Ir	193	193	MS/MS	No gas	0.023	0.016	<DL	0.040	0.027	<DL
Pt	195	195	MS/MS	H_2	0.28	0.33	0.33	0.088	0.39	0.39
Au	197	197	MS/MS	No gas	0.051	0.048	<DL	0.22	0.15	<DL
Tl	205	205	MS/MS	No gas	0.036	0.082	0.082	0.015	0.010	<DL
Pb	**208**	**208**	**MS/MS**	**No gas**	**0.042**	**0.066**	**0.066**	**0.056**	**0.035**	**<DL**
Bi	209	209	MS/MS	No gas	0.034	0.048	0.048	0.027	0.054	0.054
U	238	238	MS/MS	No gas	0.004	0.001	<DL	0.012	0.008	<DL

SQ: single quadrupole. *Measured value was zero counts in all replicates.

Conclusions

By combining superior detection limits with a high degree of automation, the Agilent 8900 ICP-QQQ fitted with ESI's prep*FAST* S automated sample introduction system provides unmatched performance. The method also simplifies the elemental analysis of semiconductor process chemicals.

User handling of the samples is limited to loading the multielement stock standards, acid used for spiking, and samples into the prep*FAST* S automated sample introduction system. All subsequent steps, including introduction of the sample to the ICP-QQQ, are performed automatically by the prep*FAST* S. Benefits of the method include:

- Autodilution of samples
- Auto-acidification of samples
- Auto-creation of MSA calibrations
- Injection of samples at a precise flow rate
- High-speed rinsing of the ICP-MS sample introduction system.

A complete analysis of the two samples, meausred using separate, automated MSA calibrations, was achieved in less than 30 minutes.

Automating the sample handling steps speeds up the analytical procedure, while also making the overall analysis easier for the analyst to perform. Eliminating manual tasks such as sample dilution and spiking lowers the risk of contamination during ultratrace analysis. 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.

All the elements specified in SEMI C30-1110, including P and S, were measured at sub-ppt to ppt levels in DI water and high purity 35% H_2O_2. The results easily meet the current SEMI Grade 5 specifications for H_2O_2.

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Gas chromatographic separation of metal carbonyls in carbon monoxide with detection using the Agilent 8800 ICP-QQQ

Application note

Petrochemical, semiconductor

Authors

William M. Geiger, Blake McElmurry
and Jesus Anguiano
CONSCI, Ltd., Pasadena, Texas, USA

Introduction

Carbon monoxide (CO) gas is used in a number of industries and applications. For example, the semiconductor industry uses it to moderate the etch rate of silicon wafers and improve selectivity for greater control of the process. In pharmacology, CO has been used therapeutically to mitigate organ rejection in transplant patients. It can also be a major constituent in cogeneration gas or syngas. However, CO can form a metal carbonyl on contact with various metals including chromium, molybdenum, iron, nickel, cobalt, and several more. Iron carbonyl [$Fe(CO)_5$] and nickel carbonyl [$Ni(CO)_4$] are the most common examples [1].

Metal carbonyls are highly toxic and the therapeutic use of carbon monoxide can lead to exposure to carbonyls that may be more harmful than the CO itself. In the etching process, if a metallic carbonyl residue forms on the surface of the wafer, it can cause electronic device failure. Similarly, if CO is present at high levels in syngas, the deposition of carbonyls on gas turbine fan blades may lead to the catastrophic failure of the turbine. Because of the potential harm caused by metal carbonyls, it is important that the

concentration of metal carbonyls in CO used in mixed gases is known or controlled before the gas is used.

Gas chromatography with electron capture detection (ECD) can be used for the analysis of nickel and iron carbonyl, with excellent sensitivity [2]. However, the method requires a laborious and complicated calibration strategy that can lead to poor accuracy due to errors introduced during sample handling and analysis. A novel approach using a GC coupled to a triple quadrupole ICP-MS (ICP-QQQ) operating in MS/MS mode offers an efficient and elegant alternative approach for the analysis of Ni, Fe and other metal carbonyls.

There are several challenges that need to be addressed for GC-ICP-QQQ analysis to be successful. Since metal carbonyl gas standards are not readily available, a calibration strategy must be developed. As both nickel and iron carbonyls can easily form or deposit on steel surfaces in a carbon monoxide matrix, a chromatographic system without metal in the flow path must be used to avoid erroneous measurements. Finally, for optimum performance, two tune conditions are required for the ICP-QQQ as the best performance for nickel is achieved using helium gas in the ORS collision/reaction cell, while performance for iron is superior with hydrogen cell gas.

Experimental

Instrumentation

An Agilent 7890B Gas Chromatograph was coupled to an Agilent 8800 Triple Quadrupole ICP-MS, using a combined gas/liquid introduction interface, as illustrated in Figure 1.

All sample wetted parts were composed of PEEK, including tubing, sampling lines, and a Valco 10 port gas sampling valve (GSV). The GSV was used to introduce two gas volumes to the GC column (Figure 2). A sample loop of 280 µL was used for the introduction of the calibration standard or carbon monoxide sample, and a standard addition loop of 70 µL was used as an internal calibration/check standard.

The combination GC-ICP-QQQ interface (with both GC effluent connection and conventional nebulizer/spray chamber) enabled the liquid standard solution or blank (introduced via the nebulizer) to be mixed with the gaseous effluent from the GC, before being passed to the plasma torch [3]. GC operating conditions are given in Table 1.

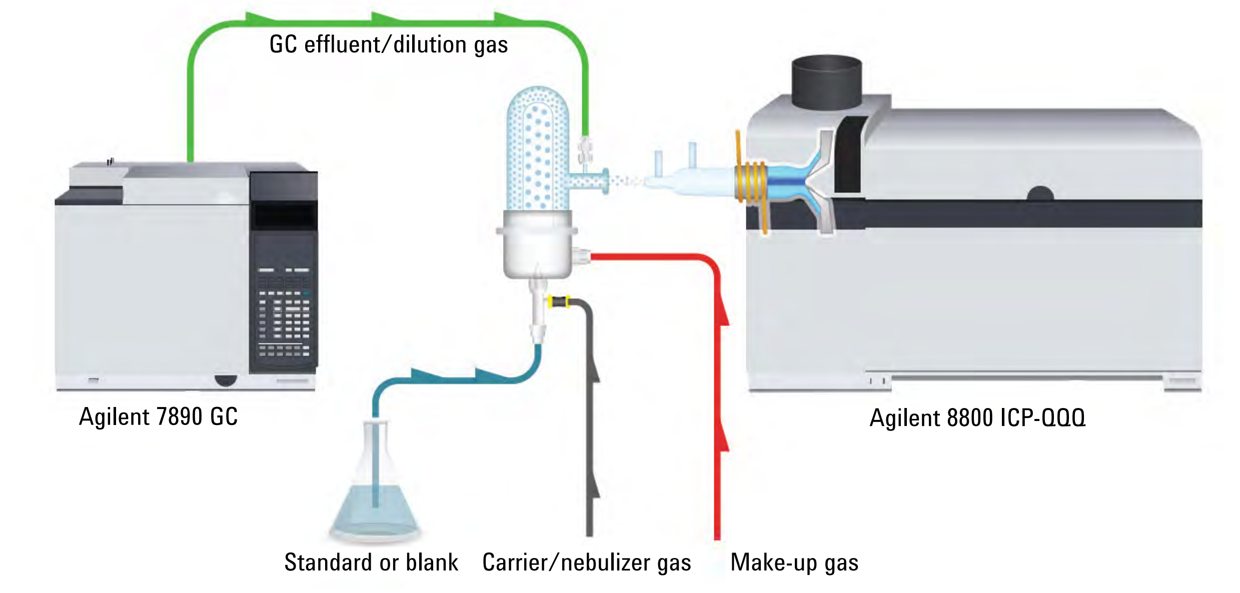


Figure 1. GC-ICP-QQQ interface for the simultaneous aspiration of liquid standard or blank and GC effluent

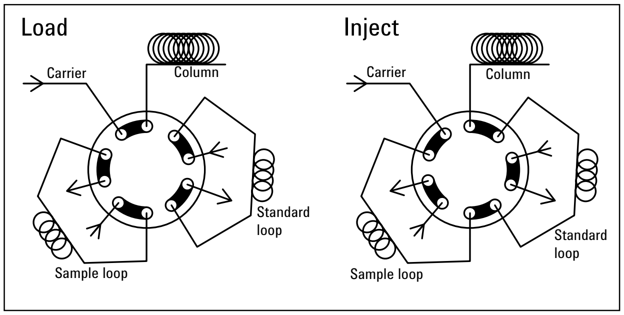


Figure 2. Valco 10 port PEEK gas sampling valve (GSV) flow path providing standard addition capability

Table 1. Agilent 7890 GC conditions

Carrier	Helium @ 13 psig
Column	30 m x 0.53 mm x 1.5 µm DB-5
Oven	40 °C Isothermal
Sample size	280 µL

Acquisition conditions

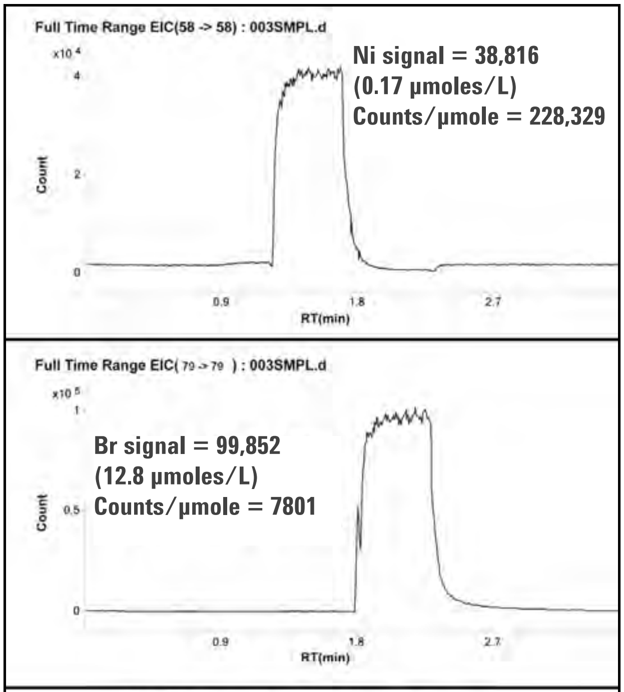
In this study, the 8800 ICP-QQQ was operated in MS/MS mode using helium as the collision gas for the on-mass measurement of Ni at *m/z* 58 (integration time 0.1 seconds/mass). Hydrogen cell gas mode was used for the on-mass measurement of Fe at *m/z* 56 (integration time 0.5 seconds/mass). Tuning conditions were almost identical for the two modes, the only differences were in the KED voltage and the cell gas flow. Bromine was determined in He mode at *m/z* 79 (integration time 0.1 seconds/mass).

Table 2. Agilent 8800 ICP-QQQ operating conditions

	He mode	H_2 mode
RF power (W)	1550	
Sample depth (mm)	8.0	
Dilution gas flow (L/min)	0.2	
Extract 1 (V)	0.0	
Extract 2 (V)	-165.0	-160.0
Kinetic Energy Discrimination (V)	3.0	0.0
Cell gas flow (mL/min)	3.30	7.00
Integration time/mass (seconds)	Ni, Br: 0.1	Fe: 0.5

Calibration

Calibration was performed by the aspiration of aqueous standards (Inorganic Ventures, Christiansburg, Virginia, USA, standard IV-ICPMS-71A) of nickel (0.17 µmoles/L), iron (0.18 µmoles/L), and a bromine standard (12.8 µmoles/L). This allowed the relative response of Ni and Fe to Br to be determined, as illustrated for Ni in Figure 3. In order to determine nickel or iron carbonyl concentrations, a gas standard of methyl bromide (101 ppb) was introduced to the GC via the GSV. Relative response factors were used to quantitate for the unknowns as illustrated in Figure 4 [4]. The methyl bromide gas phase standard was prepared at 101 ppb by dynamically diluting a higher level standard (certified as 9.90 ppm NIST traceable, sourced from United Specialty Gases, Houston, Texas, USA).



Ni signal = 38,816 (0.17 µmoles/L) Counts/µmole = 228,329

Br signal = 99,852 (12.8 µmoles/L) Counts/µmole = 7801

X RRF_{Ni} = 7801/228,329 = 0.0342

Figure 3. Calculation of relative response factor (RRF) for Ni, from aspiration of aqueous nickel and bromine standards

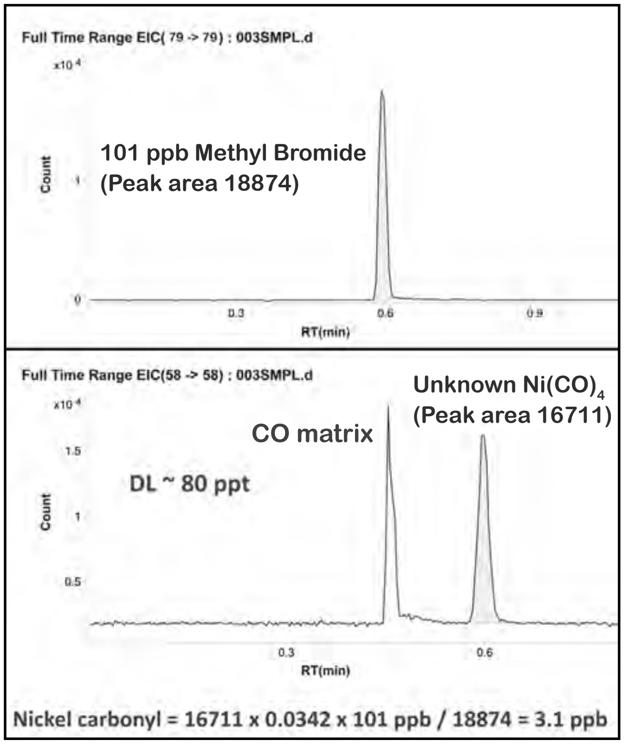


Figure 4. Analysis of known gas phase bromine standard as a surrogate standard for the determination of unknown nickel carbonyl

The ICP-MS MassHunter software allows multiple tune conditions to be applied in series during a single time resolved analysis (TRA) acquisition. Mode switching allows the acquisition mass and cell mode to be changed mid-run, so nickel and iron can be measured under optimum conditions (using helium and hydrogen cell gas, respectively), in the same analytical run. As there is a reasonable interval between the elution of nickel carbonyl and iron carbonyl, there is sufficient time for switching tune conditions so that both elements can be measured from a single injection. Since two tune modes were used in the analysis (He mode for Ni and Br, and H_2 mode for Fe) there was a virtual gain in sensitivity when switching mode since only one mass was monitored at a time allowing for better signal averaging. This is illustrated in Figure 5.

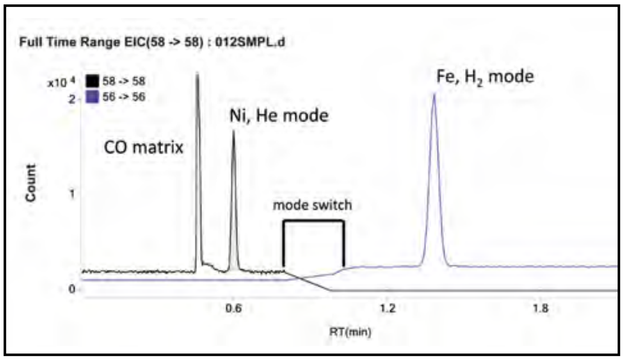


Figure 5. Tune mode switching for optimum measurement conditions during TRA acquisition

Limits of Detection

The detection limit (DL) for nickel carbonyl was estimated to be 80 ppt based on 2x signal-to-noise (S/N). Since the iron carbonyl peak is broader, the integration time was increased from 0.1 to 0.5 seconds/mass in the second tune so that the S/N ratio was improved. For comparison purposes, two different methods were used to establish the DL for iron carbonyl. A simple 2 x S/N calculation gave a DL of ~70 ppt. Applying a t-test to eight replicate analyses resulted in a more statistically valid value of 140 ppt. The nickel DL was improved at least twofold using He gas mode compared to no gas. Similarly, the DL for iron was improved about three fold using hydrogen versus helium as the cell gas.

An important matter in achieving very low detection limits, particularly for iron carbonyl, is the cleanliness of the blank solution. Figure 6 shows the signal plot for a suspect blank compared to a five level calibration. Note that the suspect blank is over 2 ppb on a weight basis, which would raise the noise level and therefore the detection limit for the gas phase analysis.

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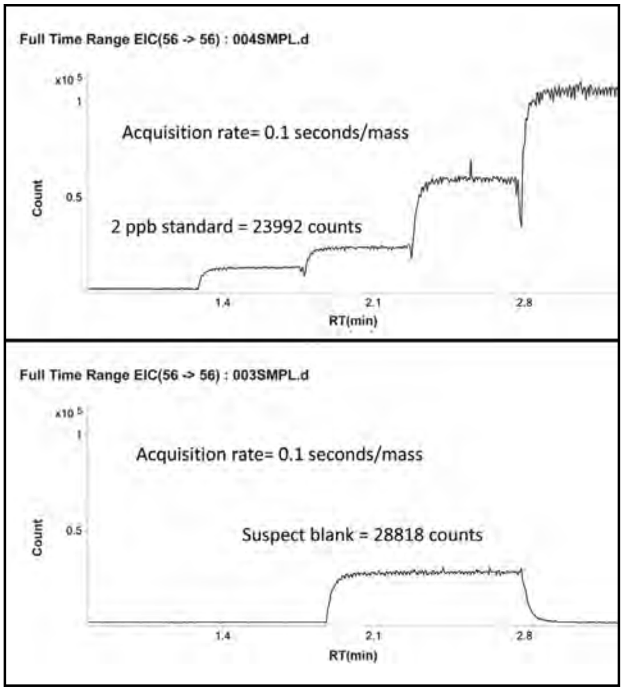

Figure 6. Aqueous standards (top) versus contaminated blank (bottom)

Conclusions

The Agilent 8800 ICP-QQQ's ability to use multiple tune conditions in a single chromatographic analysis makes it possible to use optimum acquisition settings for each analyte. This enables the GC-ICP-QQQ to achieve excellent detection limits for nickel carbonyl and iron carbonyl, two of the most analytically challenging contaminants in carbon monoxide. The detection levels of 70-80 ppt are comparable to GC-ECD detection and are well below what is currently required by the various industries. However, the multi-element capability of ICP-QQQ ensures that other metal carbonyls can also be successfully measured with this method, including $Co_2(CO)_8$, $Cr(CO)_6$, $Mo(CO)_6$, and $Fe_2(CO)_9$.

The GC was interfaced to the ICP-QQQ via a second inlet connection to the standard ICP spray chamber, to allow simultaneous aspiration of an aqueous standard. This approach is essential to performing quantitative measurements of carbonyl species, for which gas phase standards are not typically available. The simultaneous aspiration of an aqueous standard also provides sufficient oxygen to prevent carbon buildup on the torch or cones from the carbon monoxide, avoiding the need to add additional oxygen.

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Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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Direct Analysis of Trace Metallic Impurities in High Purity Hydrochloric Acid by 7700s/7900 ICP-MS

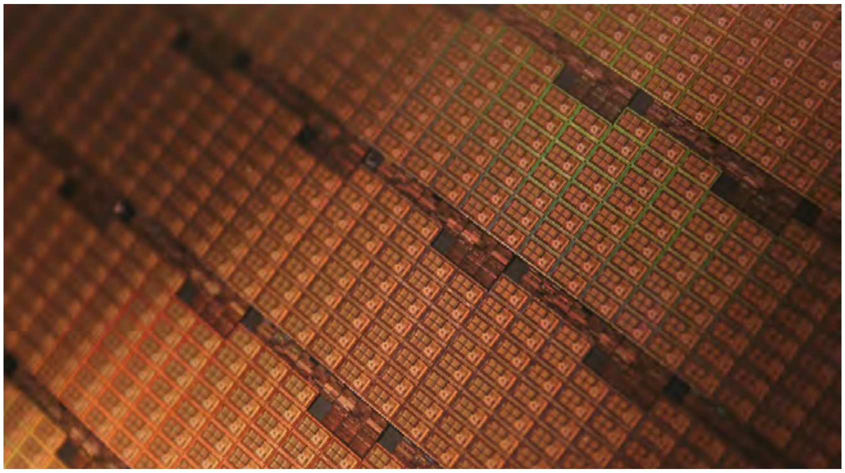
Application note

Semiconductor analysis

Author

Junichi Takahashi

Agilent Technologies
Tokyo, Japan



Abstract

This application note illustrates the advanced analytical performance and robustness of the Agilent 7700s/7900 ICP-MS for the direct determination of metallic impurities in high purity concentrated hydrochloric acid (HCl). The 7700s/7900 incorporates an Octopole Reaction System (ORS), which effectively removes polyatomic interferences, allowing ultimate detection limits to be achieved for elements that suffer from severe chloride-based interferences. For example, the polyatomic ion $^{40}Ar^{35}Cl^+$ can be eliminated by the ORS allowing the direct measurement of As at mass 75, and permitting accurate analysis of As at trace levels in undiluted concentrated HCl. Enabling direct analysis of concentrated acids eliminates the dilution step from the sample preparation procedure, and so significantly reduces the potential for sample contamination.

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Introduction

Hydrochloric acid is frequently used to remove metallic impurities on the surface of silicon wafers. Together with hydrogen peroxide, this cleaning method is well known as RCA Standard Clean 2 (SC-2). The manufacturing process of semiconductor devices requires routine monitoring of contaminants in HCl, and ICP-MS is the accepted tool for this purpose. Although HCl is diluted prior to use for SC-2, the concentration of industrial grade HCl is usually 20% or 35%, depending on the method of production. Because HCl is highly corrosive; direct introduction of concentrated HCl into an ICP-MS is normally avoided. Moreover, introduction of HCl at high concentration leads to the formation of a large number of polyatomic ions in the ICP, which cause significant spectral interferences with some key elements of interest, for example, $H_2{}^{37}Cl^+$ on $^{39}K^+$, $^{35}Cl^{16}O^+$ on $^{51}V^+$, $^{35}Cl^{16}OH^+$ on $^{52}Cr^+$, $^{35}Cl^{37}Cl^+$ on $^{72}Ge^+$, $^{37}Cl_2{}^+$ on $^{74}Ge^+$, and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Consequently, some methodology for the analysis of high purity HCl by ICP-MS has recommended sample pre-treatment steps to remove the chloride matrix, which can lead to analyte loss and sample contamination. However, the Agilent 7700s/7900 ICP-MS is manufactured using robust and anti-corrosive materials, which means that undiluted HCl can be analyzed directly, while the ORS drastically improves the efficiency of removing polyatomic ions, allowing many elements to be determined at lower detection limits than were previously possible.

Experimental

Instrumentation

An Agilent 7700s ICP-MS fitted with an optional third cell gas mass flow controller (in addition to the standard collision (helium) and reaction (hydrogen) gas lines) was used throughout. The optional cell gas line is required for specialized applications, including analyses where optimum interference removal requires a highly reactive cell gas such as ammonia. The standard 7700s ICP-MS sample introduction system was used, consisting of a platinum sampling cone, platinum skimmer cone, PFA nebulizer, and quartz torch.

Materials and reagents

High purity hydrochloric acid, TAMAPURE-AA100 (20%), was purchased from TAMA Chemicals, Japan. Undiluted HCl was introduced directly into the ICP-MS, to eliminate any sample preparation steps and thereby significantly reduce the potential for sample contamination.

Calibration standard solutions were prepared by spiking a mixed multielement standard (SPEX Certiprep) into an acid blank at 10, 20, 50 and 100 ppt.

Results and Discussion

Detection limits and background equivalent concentrations

Forty two elements were measured using the Agilent 7700s ICP-MS operating in multiple tune modes. Data was acquired in an automated sequence of cool plasma, no gas and gas modes, during a single visit to the sample vial. The sample-to-sample run time was approximately 6 minutes. Data for each of the modes was combined automatically into a single report for each sample. Detection Limits (DLs) and Background Equivalent Concentrations (BECs) are show in Table 1. DLs were calculated from 3σ of 10 measurements of the acid blank.

Table 1. Agilent 7700s ICP-MS DLs and BECs in 20% high purity HCl.

Element	*m/z*	Mode	DL (ppt)	BEC (ppt)
Li	7	Cool	0.016	0.004
Be	9	No gas	0.13	0.11
B	11	No gas	4.5	9.7
Na	23	Cool	0.44	1.3
Mg	24	Cool	0.11	0.22
Al	27	Cool	0.79	1.1
K	39	Cool/NH_3	0.40	0.50
Ca	40	Cool/NH_3	1.1	2
Ti	48	He	0.71	0.68
V	51	NH_3	2.1	2.0
Cr	52	Cool/He	4.5	12
Mn	55	He	1.57	2.84
Fe	56	Cool	2.4	4.2
Co	59	He	0.20	0.13
Ni	60	He	3.03	4.43
Cu	63	Cool	0.49	0.59
Zn	64	He	2.1	2.9
Ga	71	He	0.47	0.31
Ge	74	He	2.1	13
As	75	He	4.0	16
Se	78	He	5	5.5
Sr	88	He	0.21	0.061
Zr	90	He	0.11	0.03
Nb	93	He	0.34	0.43
Mo	98	He	0.52	0.67
Ru	101	He	0.05	0.01
Pd	105	He	0.57	0.51
Ag	107	He	0.056	0.033
Cd	114	He	0.41	0.52
Sb	121	He	2	2.8
Te	125	He	5.4	1.1
Ba	138	He	0.076	0.067
Hf	178	He	0.06	0.015
W	182	He	0.094	0.13
Re	185	He	0.49	0.54
Ir	193	He	0.1	0.07
Au	197	He	0.15	0.4
Tl	205	He	0.054	0.024
Pb	208	He	0.37	0.56
Bi	209	He	0.44	0.33
Th	232	He	0.01	0.003
U	238	He	0.032	0.013

Cr and K determination

Cool plasma is a proven technique used to remove plasma-based interferences. Although it has been largely superseded by Collision Reaction Cell (CRC) methodology, cool plasma remains the most effective analytical mode for some elements in certain matrices. Furthermore, the Agilent 7700s/7900 ICP-MS provides an enhanced cool plasma mode of operation, delivering improved robustness and stability due to the use of the new frequency matching RF generator. Used together with the ORS, cool plasma has recently been demonstrated to provide a new, powerful mode to remove interferences [1].

Because the major isotope of chromium ($^{52}Cr^+$) suffers an interference from $^{35}Cl^{16}O^1H^+$, chromium was determined using cool plasma and He mode. With cool plasma (low plasma RF power), production of $ClOH^+$ ions is suppressed because of its high ionization potential (I.P.) of 11 eV [2]. For further analytical improvement, He mode was used in combination with the cool plasma conditions to completely eliminate any remaining $^{35}Cl^{16}OH^+$ ions. The resultant calibration curve for ^{52}Cr is shown in Figure 1.

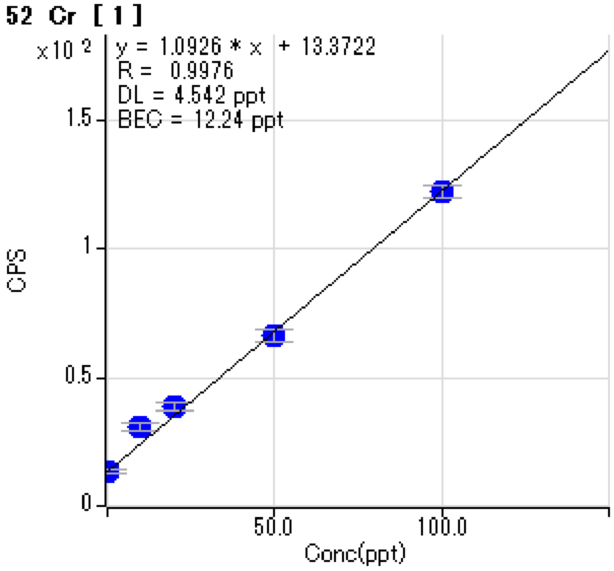


Figure 1. ^{52}Cr calibration curve obtained using He mode and cool plasma.

The approach of using the ORS with cool plasma is also effective for other elements such as potassium. In order to suppress the interference of $H_2{}^{37}Cl^+$ on $^{39}K^+$, ammonia was selected as the cell gas with cool plasma. While there are very few cases where such highly reactive cell gases are required, there are some specific cases where such gases offer the lowest DLs. The intense $H_2{}^{37}Cl^+$ interference that affects K at mass 39 is not very reactive with H_2, so H_2 cell mode does not give sufficiently good interference removal for the lowest DL to be achieved in the highest purity HCl. The calibration curve for K (shown in Figure 2) illustrates the effective removal of the $H_2{}^{37}Cl^+$ interference using this novel mode of acquisition, providing a K BEC of 0.5 ppt and DL of 0.4 ppt in undiluted (20%) HCl.

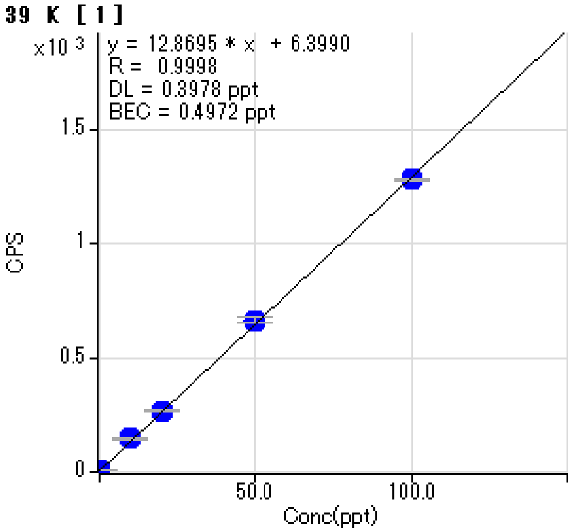


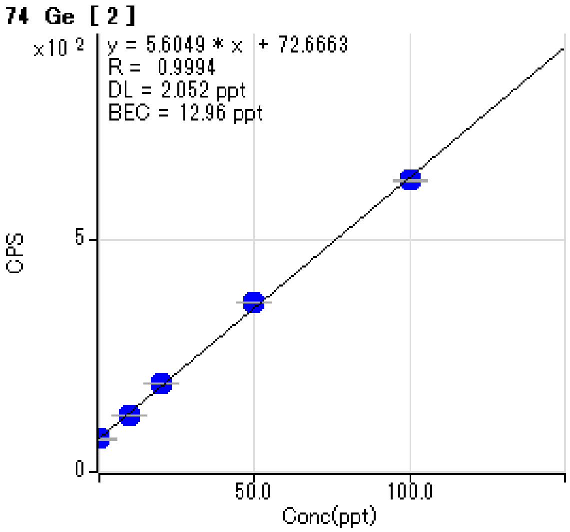
Figure 2. ^{39}K calibration curve obtained using NH_3 mode and cool plasma.

Ge and As determination

The ORS of the Agilent 7700s/7900 ICP-MS improves the removal of polyatomic interferences using He mode with Kinetic Energy Discrimination (KED), and also promotes Collision Induced Dissociation (CID) for relatively weakly bound polyatomic ions.

Germanium has 3 major isotopes at 70, 72 and 74 u that suffer from Cl-based polyatomic interferences, namely $^{35}Cl^{35}Cl^+$, $^{35}Cl^{37}Cl^+$ and $^{37}Cl^{37}Cl^+$. As the dissociation energy of $Cl_2{}^+$ is approximately 4 eV (3.95 eV for $^{35}Cl^{35}Cl^+$)[3], CID of $Cl_2{}^+$ would be unlikely to happen with the previous generation ORS, which provided a collision energy of only 0.9 eV in He mode. In contrast, in the later generation ORS the collision energy is increased to 5 eV, facilitating CID of several polyatomic ions including $Cl_2{}^+$. The performance of the 7700s with the ORS operating in high energy He mode is illustrated in Figure 3, which shows the calibration curve, DL and BEC for ^{74}Ge in a matrix of 20% HCl.

Figure 3. ^{74}Ge calibration curve obtained using high energy He mode.



Arsenic has a single isotope at *m/z* 75, that can suffer an interference from the polyatomic ion $^{40}Ar^{35}Cl^+$ that readily forms in a chloride matrix, making it extremely difficult to determine ^{75}As at low levels directly at mass 75. The ArCl interference on As can be avoided by indirectly measuring As at 91 u as the AsO^+ ion, which is formed either by applying cool plasma conditions or via the use of O_2 cell gas in the CRC. The latter approach utilizes hot plasma conditions but the measurement of As at mass 91 can still be affected by a $CaClO^+$ interference that forms from $CaCl^+$ when O_2 cell gas is used. Furthermore, AsO^+ at mass 91 suffers an isobaric interference from $^{91}Zr^+$, an overlap that does not occur under cool plasma conditions, since Zr is not ionized in a cool plasma. However, as with $Cl_2{}^+$, the higher collision energy of He mode in the ORS of the 7700s/7900 means that the $ArCl^+$ ion can also be dissociated by CID. This allows As to be determined at low levels directly at 75 u in 20% HCl, thus avoiding the use of both cool plasma and O_2 cell gas. A typical calibration curve for As in 20% HCl is shown in Figure 4.

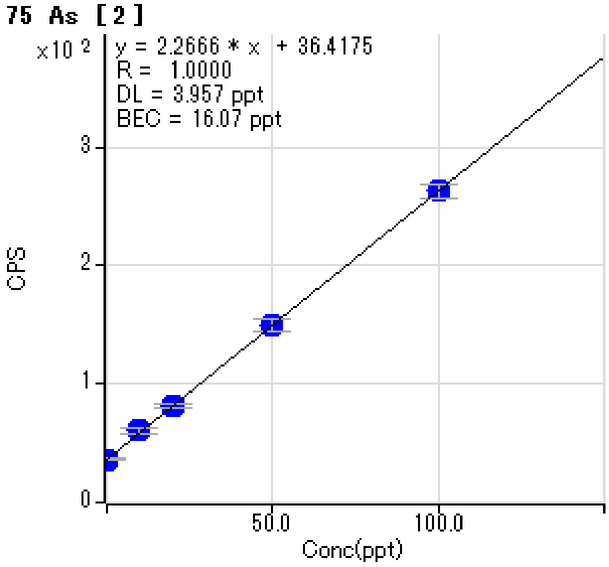


Figure 4. ^{75}As calibration curve obtained using high energy He mode.

V determination

The $^{35}Cl^{16}O^+$ interference on $^{51}V^+$ can also be eliminated using NH_3 as the cell gas, but under normal hot plasma conditions (1600 W). The increased collision energy of the ORS improves the reaction efficiency and gives a significant improvement in the DL and BEC, as shown in Figure 5.

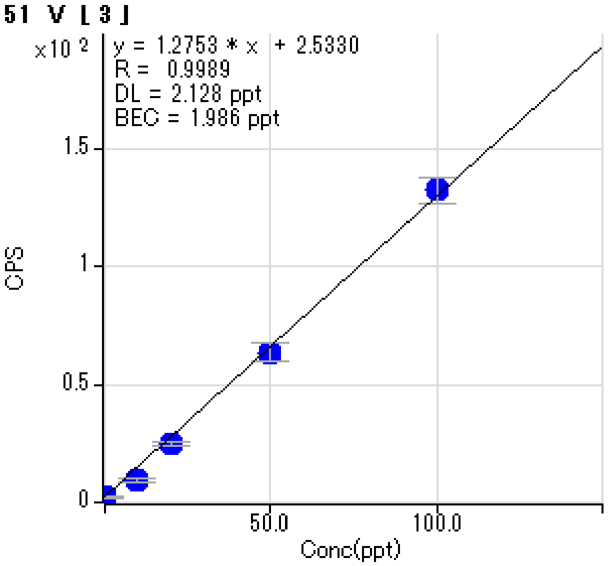


Figure 5. ^{51}V calibration curve obtained using NH_3 and normal plasma mode.

Conclusions

Agilent ICP-MS systems have been used for the analysis of trace metallic impurities in concentrated HCl for many years. Now, the Agilent 7700s/7900 ICP-MS with unparalleled cool plasma performance and ORS collision/reaction cell further improves the detection limits for the analysis of high purity acids. The ORS can be fitted with up to 3 cell gas lines (2 are included as standard), allowing total flexibility in both collision and reaction modes. The ORS cell improves performance for several critical elements by increasing the efficiency of both collision and reaction mode, and providing enhanced dissociation of certain polyatomic ions by CID. These developments now allow several elements like Cr, K, Ge, As and V to be determined at lower concentrations than previously possible in a chloride matrix.

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Semiconductor configuration

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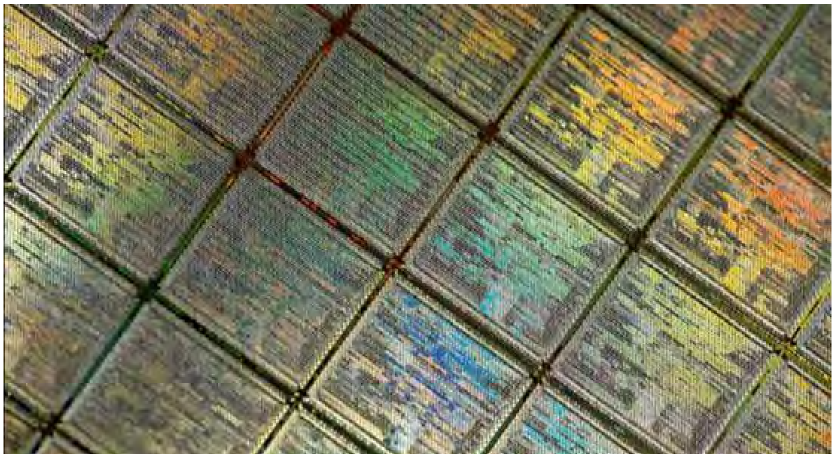
Direct Measurement of Metallic Impurities in 20% Ammonium Hydroxide by 7700s/7900 ICP-MS

Application Note

Semiconductor



Authors

Junichi Takahashi

Agilent Technologies
Tokyo, Japan

Abstract

Ammonium hydroxide (NH_4OH) is a chemical used in the manufacture of semiconductor devices, and must therefore be analyzed for trace metal impurities. The direct analysis of undiluted (20%) NH_4OH using ICP-MS is challenging because its high vapor pressure causes plasma instability. However, dilution of the samples would degrade detection limits, so the ability to directly analyze 20% NH_4OH is important. The Agilent 7700s/7900 ICP-MS employs a unique, high-speed frequency-matching ICP RF generator that can maintain a stable plasma even when 20% NH_4OH is aspirated. The 7700s/7900 also features effective technologies for removing spectral interferences in high-purity chemicals, making it ideally suited to semiconductor chemical analysis. An Agilent 7700s, using an inert sample introduction system, was used to measure trace elements in high purity 20% NH_4OH. Detection limits in the single digit ppt or sub-ppt range were obtained for 48 elements, and long term (~7 hours) stability of approximately 5% RSD was achieved for a spike level of 100 ppt in 20% NH_4OH, demonstrating the ability of the 7700s to routinely measure trace contaminants in high purity 20% NH_4OH.

Agilent Technologies

Introduction

Many chemicals are used throughout the manufacturing process of semiconductor devices. Metallic impurities present in the chemicals and chemical mixes used can cause contamination and give rise to defects in the final product, so their levels must be strictly controlled. ICP-MS is the standard technique used for the measurement of metallic impurities in semiconductor chemicals. Among all the process chemicals, those that are used as part of the silicon wafer cleaning process are particularly important, as they are in direct contact with the wafer and can therefore impart impurities to the wafer surface. There are over 100 cleaning steps throughout the manufacture of a typical semiconductor device, and one of the typical solutions used for wafer cleaning is a chemical mix developed by RCA, commonly referred to as Standard Clean 1 (SC-1). SC-1 is a mixture of NH_4OH, hydrogen peroxide (H_2O_2) and ultra-pure water (UPW) in the ratio 1:1:5, and is used to remove surface particles by lightly etching the wafer. There is a clear requirement for a highly sensitive and reliable analytical methodology to measure metallic impurities in the high purity chemicals from which SC-1 is produced.

While UPW and H_2O_2 are easy matrices to analyze, the analysis of high purity NH_4OH by ICP-MS is very difficult for two reasons. Firstly, NH_4OH is a strong alkali, which causes some metals to readily precipitate as insoluble hydroxides. This presents difficulties for determination using the method of standard additions (MSA), because MSA is performed by sequentially spiking an acid-based multi-element standard into the sample. At higher concentrations, some metals will precipitate when spiked into the undiluted NH_4OH, making accurate determination by MSA impossible. However, the NH_4OH used in SC-1 is high purity grade with a maximum metallic impurity level of 100 ppt, so higher level spikes can be avoided if the ICP-MS detection limits are sufficiently low. If MSA spikes are at the low ppt level (<100 ppt), minimal precipitation should occur, and MSA can in fact be used to analyze undiluted NH_4OH. To be able to produce good MSA calibrations below 100 ppt of course requires the interference removal technology employed in the ICP-MS to be extremely effective for all interferences.

The Agilent 7700s/7900 ICP-MS, with the Octopole Reaction System (ORS), has a wide range of interference removal technologies. In addition to conventional no gas mode, the ORS operates in both collision (He) mode and reaction (e.g. H_2) mode, and cool plasma mode is also available. The interference removal approach selected depends on the analytical requirement: for this application, calibration down to the 10 ppt level is required for all analytes and therefore the most efficient interference removal mode is required for every analyte. Switching between modes is fully automated and all analytes are measured with a single visit to the sample vial. The small size of the ORS cell allows very fast switching between cell gas modes so the additional time required for multi-mode operation is minimized.

The second challenge when analyzing undiluted NH_4OH is that the plasma becomes unstable due to the high vapor pressure of undiluted NH_4OH, so routine, direct analysis of undiluted NH_4OH has not previously been possible. The accepted method of analyzing NH_4OH is to remove the matrix by heating to near dryness and then re-dissolving the residue in 1% HNO_3 prior to measurement by ICP-MS [1]. Although this method is widely used, laboratories favor elimination of the sample preparation step, to shorten analysis time and reduce the risk of sample contamination and loss of volatile analytes. The 7700/7900 ICP-MS features a unique RF plasma generator design with high-speed frequency-matching that can instantaneously adjust to changes in plasma load—for example when switching from aqueous to a high vapor pressure solvent. This produces a very stable plasma capable of tolerating the direct aspiration of undiluted NH_4OH.

The combination of high sensitivity, effective removal of interferences, and high-speed frequency-matching ICP RF generator enables the 7700s/7900 ICP-MS to measure low ppt level metallic impurities directly in undiluted high purity NH_4OH.

Experimental

An Agilent 7700s was fitted with an inert sample introduction system (Agilent part # G4912-68002) comprising a PFA double pass spray chamber and demountable torch fitted with a 1.5 mm ID sapphire injector. Standard Pt interface cones and PFA concentric nebulizer were used. A solution of Li, Zn, Sn, and Pb prepared in 2% NH_4OH was used to tune the instrument. These elements were chosen since they form amphoteric oxides or hydroxides (which can display both acidic and basic properties), and are therefore stable in NH_4OH. The normal tuning solution containing Li, Y, Ce and Tl in 2% nitric acid may also be used, but a thorough rinsing with UPW prior to analysis is necessary to prevent residual acid mixing with the NH_4OH standard and samples. Once the tuning conditions have been established, the system should be rinsed with UPW and then 20% NH_4OH for an hour to ensure that the sample introduction system is free from acid. Operating parameters are shown in Table 1. The acquisition used a multi-tune mode method, performed with a single visit to the sample vial, and data for each of the modes (cool plasma, no gas, He mode and H_2 mode) was combined automatically into a single report for each sample. Total run time per sample, including uptake and rinse, was 8 m 20s.

High purity grade NH_4OH (20% as NH_3) was used (TAMAPURE-AA100, TAMA Chemicals, Kawasaki, Japan), and the MSA calibration standard solutions were prepared by spiking a mixed multi-element standard (SPEX CertiPrep, Metuchen, NJ, USA). Calibration levels, added sequentially into a blank of undiluted NH_4OH, were at 10, 20, 50 and 100 ppt.

Results and Discussion

DLs and BECs

3 σ detection limits (DLs) and background equivalent concentrations (BECs) obtained for 48 elements in high purity NH_4OH are shown in Table 2. For Se and Te, the lowest detection limits were obtained using H_2 mode, while for Na, Mg, Al, K , Ca, Cr, Mn, Fe, Co, Ni, and Cu, cool plasma mode was used. For the remainder, He mode was used except for Be and B which were run using no gas mode. The DLs were calculated from 10 measurements of the blank. All DLs were single figure ppt or lower, as were the BECs, aside from Ca at 11 ppt. This demonstrates the ability of the 7700s to remove spectral interferences, and also the high quality of this NH_4OH product. Since no individual analysis mode gives the best DLs for every element, the 7700s offers excellent performance for semiconductor chemical analysis by allowing the user to automate analysis methods with no gas, He, and H_2 modes, plus cool plasma. This flexibility, coupled with pre-defined methods and simple, automated optimization routines makes the 7700s/7900 the most powerful single quadrupole ICP-MS for semiconductor analysis.

Table 1. ICP-MS operating parameters.

	Cool	No gas	He	H_2
RF power (W)	600	1600		
Carrier gas (L/min)	0.8			
Make up gas (L/min)	0.5	0.1		
Sampling depth (mm)	18	7		
He gas flow (mL/min)	-	-	5	-
H_2 gas flow (mL/min)	-	-	-	6
Energy discrimination (V)	-	3		
Uptake time (s)	60			
Acquisition time (s)	350			
Rinse time (s)	90			

Table 2. 7700s ICP-MS DLs and BECs in 20% NH_4OH.

Element	m/z	Mode	DL (ppt)	BEC (ppt)
Li	7	cool	0.014	0.003
Be	9	no gas	0.33	0.1
B	11	no gas	2.6	16
Na	23	cool	0.43	0.38
Mg	24	cool	0.17	0.32
Al	27	cool	0.26	0.67
K	39	cool	0.25	0.38
Ca	40	cool	1.9	11
Ti	48	He	2.4	1.4
V	51	He	0.67	0.31
Cr	52	cool	0.3	0.4
Mn	55	cool	0.078	0.026
Fe	56	cool	1.5	2.1
Co	59	cool	0.23	0.052
Ni	60	cool	0.88	0.42
Cu	63	cool	3	1.8
Zn	66	He	1.7	0.8
Ga	71	He	1.7	0.68
Ge	72	He	4.3	1.6
As	75	He	6.5	3.8
Se	78	H_2	8.4	4.6
Rb	85	He	0.022	0.028
Sr	88	He	0.86	0.29
Zr	90	He	0.35	0.2
Nb	93	He	0.057	0.076
Mo	98	He	0.24	0.16
Ru	101	He	0.26	0.1
Rh	103	He	0.41	1.4
Pd	105	He	0.18	0.092
Ag	107	He	0.11	0.12
Cd	111	He	0.66	0.35
Sn	118	He	2.3	1.5
Sb	121	He	2.3	0.92
Te	125	H_2	1.3	1.3
Cs	133	He	0.41	0.21
Ba	138	He	0.27	0.13
Hf	178	He	0.24	0.086
Ta	181	He	0.047	0.036
W	182	He	0.16	0.071
Re	185	He	0.14	0.061
Ir	193	He	0.15	0.16
Pt	195	He	0.39	0.48

Table 2 continued...

Element	m/z	Mode	DL (ppt)	BEC (ppt)
Au	197	He	0.4	0.17
Tl	203	He	0.21	0.27
Pb	208	He	0.75	1.1
Bi	209	He	0.16	0.15
Th	232	He	0.085	0.025
U	238	He	0.064	0.013

Calibration linearity

Figures 1a and 1b show examples of the calibration plots achieved for elements in two different modes: V (He mode) and Fe (cool plasma mode). Excellent linearity at the ppt level was achieved in each case, demonstrating the interference removal power of the 7700s in both modes.

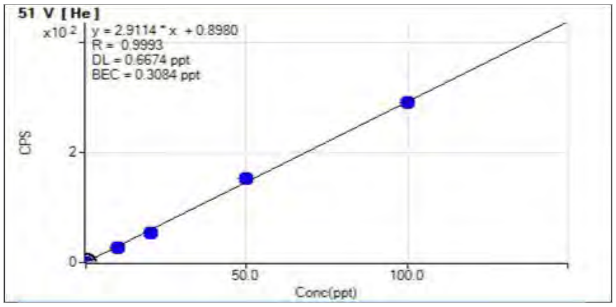


Figure 1a. Calibration plot showing spikes at 0, 10, 20, 50, and 100 ppt for V in 20% NH_4OH.

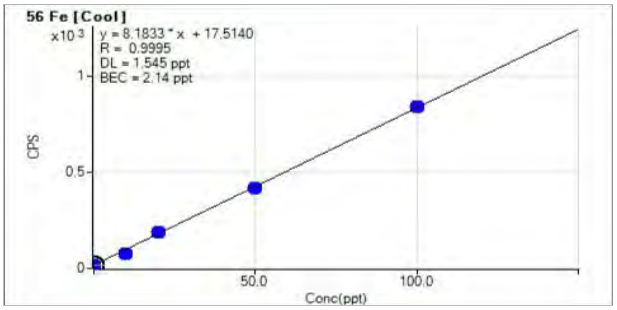


Figure 1b. Calibration plot showing spikes at 0, 10, 20, 50, and 100 ppt for Fe in 20% NH_4OH.

Long term stability

If present at a high enough concentration in an alkaline solution, many metals form insoluble hydroxides which easily form precipitates or can be adsorbed on to the surface of the vessel wall, and the likelihood of precipitation or adsorption increases with time. Keeping metal concentrations low (at a maximum of 100 ppt) reduces the risk of precipitation, and monitoring signal stability over an extended period is an effective way to confirm the chemical stability of the analytes. A long term (just under 7 hours) stability test was performed for 22 elements spiked at 100 ppt in 20% NH_4OH. Signal intensity was measured every 45 min while blank samples of 20% NH_4OH were introduced between each spike measurement. Figure 2 shows the excellent stability (approx. 5% RSD) of the spikes over the test period, confirming the applicability of direct analysis using MSA at spike concentrations up to the 100 ppt level in 20% NH_4OH.

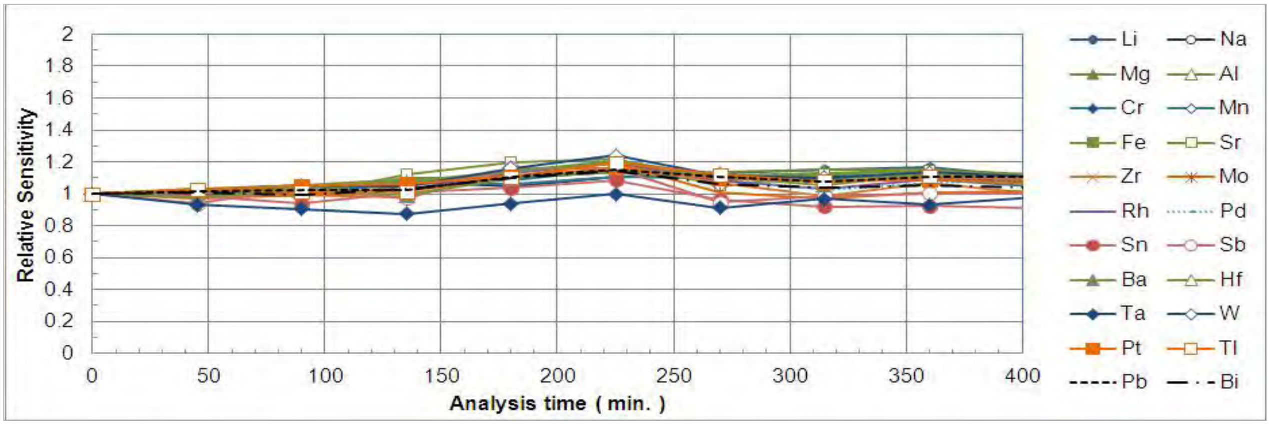


Figure 2. Signal stability of a representative selection of 22 elements spiked at 100 ppt in 20% NH_4OH.

Conclusions

The direct analysis of 20% NH_4OH was performed successfully using an Agilent 7700s ICP-MS. The high speed frequency-matching RF generator of the ICP-MS produces a stable plasma when 20% NH_4OH is aspirated, while the availability of multiple interference removal technologies assures low DLs and BECs for all 48 elements measured. The routine applicability of direct measurement using MSA has been demonstrated by limiting spike concentrations to 100 ppt, which avoids precipitation in the alkaline matrix. As a result, labs are no longer forced to carry out matrix removal in order to analyze high purity 20% NH_4OH by ICP-MS, and direct analysis is routinely possible.

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Determination of Trace Metal Impurities in Semiconductor Grade Phosphoric Acid by High Sensitivity Reaction Cell ICP-MS

Application

Semiconductor

Author

Junichi Takahashi
Kouichi Youno
Agilent Technologies
9-1 Takakura-Cho, Hachioji-Shi
Tokyo, 192-0033
Japan

Abstract

Metallic impurities in semiconductor grade phosphoric acid were determined by a newly developed high sensitivity reaction cell inductively coupled plasma mass spectrometer (ICP-MS). The Agilent 7500cs ICP-MS, which features an Octopole Reaction System (ORS) for interference removal, was used to analyze 85% (w/w) phosphoric acid (H_3PO_4) following a 100-fold dilution, for elements specified in SEMI C36-0301, Specifications and Guidelines for Phosphoric Acid. By pressurizing the ORS with simple gases, hydrogen and helium, all plasma and matrix based polyatomics that interfere with the measurement of elements such as Ca, Fe, Ti, Co, Ni, Cu, and Zn are easily attenuated while maintaining excellent sensitivity for all other elements in non-gas mode. The ShieldTorch System (STS) and new ion lens assembly used in the Agilent 7500cs provides excellent signal/background resulting in exceptional detection limits for all elements (0.06–28 ppt range). Excellent spike recovery data at the 50 ppt level in 0.85% H_3PO_4 further highlights the suitability and accuracy of the Agilent 7500cs for the determination of SEMI required elements at trace levels in H_3PO_4.

Introduction

Contamination control in semiconductor processing is increasingly important as device critical dimensions (CD) continue to shrink. Particulate contamination, which can lead to device defects, needs to be minimized at each of the manufacturing stages. Impurity levels present in the various process chemicals are controlled and monitored closely. Phosphoric acid (H_3PO_4) is used for wet chemical etching of silicon nitride films (Si_3N_4). It is critical that the wafer surface is not contaminated by any metallic impurities present in the acid, as micro-contamination accounts for over 50% of the yield losses in IC manufacturing [1]. In order to minimize this risk, many incoming chemicals, including H_3PO_4, are analyzed for their chemical purity and the etching baths are sampled regularly.

Interference Removal

Plasma and matrix-based polyatomic overlaps on critical elements present specific analytical problems for conventional quadrupole ICP-MS for many semiconductor applications. The introduction of the ShieldTorch interface with the original HP 4500 in 1994 revolutionized the use of ICP-MS in the semiconductor industry, resulting in the acceptance of cool plasma as the standard technique for ultratrace analysis. This was due to the unique capability of cool plasma to remove plasma-based polyatomic interferences on the key elements K

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(ArH), Ca (Ar), and Fe (ArO) [2]. However, with the introduction of the high-sensitivity 7500cs reaction cell ICP-MS, which has been specifically designed for semiconductor applications, analysts now have the flexibility to attenuate matrix interferences using reaction cell technology. The 7500cs also features a new extraction lens design which reduces Easily Ionized Elements (EIE) background equivalent concentrations (BECs) close to cool plasma levels, under normal plasma conditions. All applications can be performed at 1500W forward power with the added advantage of Agilent cool plasma performance still being available for those users who have exisiting and proven methodology based on cool plasma.

The analyst has complete flexibility over choice of analysis mode: normal, He, H_2, or cool plasma. The 7500cs ChemStation software allows data to be acquired automatically in multiple modes, with the results combined into a single report.

Analysis of H_3PO_4

Phosphoric acid is a high viscosity acid (65cP viscosity at 20 °C); therefore, a 100 times dilution in ultrapure water is required prior to analysis. Also, since H_3PO_4 cannot be purified by distillation, metal impurity levels are normally above 1 ppb. Maximum allowable levels (ppb), as stated in the SEMI C36-0301 Specifications and Guidelines for Phosphoric Acid document, appear in Table 3.

The analysis of H_3PO_4 by ICP-MS is challenging for conventional systems because of the presence of various molecular species that interfere with many key semiconductor elements. In addition to the plasma-based interferences on ^{39}K ($^{38}Ar^{1}H$), ^{40}Ca (^{40}Ar), and ^{56}Fe ($^{40}Ar^{16}O$), the analysis of Ti, Co, Ni, Cu, and Zn in H_3PO_4 is made more challenging by the presence of the matrix-based polyatomics (shown in Table 1), which interfere with some important elements.

Table 1. Phosphorus Polyatomic Interferences on Ti, Co, Ni, Cu, and Zn

Polyatomic ions	Mass	Analyte
PNH	46	Ti
PO	47	Ti
POH	48	Ti
POH_2	49	Ti
PCO, PN_2	59	Co
PN_2H	60	Ni
PO_2, P_2H	63	Cu
PO_2H	64	Zn
PO_2	65	Cu
PO_2H	66	Zn

Even though these plasma and matrix-based interferences can be minimized by the Agilent 7500s ICP-MS operating in cool plasma mode, the BECs for the semiconductor critical elements Ti, Zn, and Cu are greatly improved by using the 7500cs ORS ICP-MS, as seen in the data presented in Table 2.

Table 2. Comparison of ORS-Based Performance (7500cs) with Non-reaction Cell Performance (7500s)

	7500cs - ORS ICP-MS		7500s non-cell ICP-MS	
Analyte	mode	BEC ppt	mode	BEC ppt
Ti (46)	Helium	36	Normal	170
Co (59)	Helium	0.47	Cool	0.4
Ni (60)	Helium	21	Cool	23.7
Cu (65)	Helium	3.9	Cool*	2700*
Zn (66)	Helium	9.6	Normal	36

*Copper measurements determined on mass 63

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Instrumentation

The instrument used in this application was an Agilent 7500cs ICP-MS equipped with an ORS, ShieldTorch System (STS), and PFA Inert Kit. The PFA Inert Kit (Agilent part number G3139A #301) consists of a PFA-100 high efficiency, self-aspirating micro flow nebulizer, 35-mm PFA Pure-Cap end cap, 35-mm PFA spray chamber, 2.0-mm O-ring free platinum injector, and precision quartz torch. A low flow nebulizer and platinum interface cones were used to prevent deterioration of the interface by the acid.

Argon and matrix-based polyatomic ions on key elements like Ca, Fe, Ti, Co, Ni, Cu, and Zn were eliminated by pressurizing the Octopole Reaction cell with H_2 or He. Several methods of interference removal are provided with the ORS [3]. Using He as a cell gas promotes collisional dissociation and energy discrimination (this allows the ORS to discriminate between analyte ions and larger polyatomic ions). Efficiency in collision mode is greatly improved by Agilent's STS, which produces ions with very low and uniform ion energies. Hydrogen induces ion-molecular reactions used for the efficient removal of the intense peaks due to plasma-based species, CO^+, N_2^+, Ar^+, ArO^+, and Ar_2^+.

The 7500cs ChemStation software controls all instrument operations including tuning and data acquisition – automatically combining different acquisition modes, data analysis, and reporting.

Methodology

Sample Preparation

Because of the high viscosity of H_3PO_4 (2.4 times higher than sulfuric acid), samples were diluted 100 times in ultrapure water prior to analysis. Analyses were performed using the method of standard additions (MSA). Calibration curves were prepared at concentrations ranging from 20 to 500 ng/L (ppt). A single MSA curve was established and converted into an external calibration curve, thereby eliminating the need to spike each subsequent sample to be analyzed. Once an external calibration curve is established from the MSA curve, all other sample concentrations can be determined against it. No internal standards were used in this study to minimize the risk of sample contamination. Following quantitation, H_3PO_4 samples were spiked at a level of 50 ppt (ng/L) to assess the accuracy of the measurement.

ICP-MS Analysis

The sample was self-aspirated at an uptake rate of 100 µL/min. To demonstrate the range of operation modes available, data were acquired using both ORS mode and cool plasma conditions to eliminate matrix interferences. Comparative data for the two modes are shown in Table 4, page 4. Data for all SEMI specified analytes is given except for Si and Sb: Sb is present at high levels in H_3PO_4, which significantly increases BEC and detection limits (DL) values, and accurate spike recovery at the 50 ppt level is not possible. Further method development is required for the accurate measurement of Si in H_3PO_4 at ultratrace levels by ICP-MS.

Results and Discussion

The results shown in Table 3 show 3-sigma DL (ppt), BECs (ppt) and spike recovery data (%) for a standard suite of semiconductor elements in 0.85% H_3PO_4. Note the excellent performance for elements such as K, Ca, Ti, Co, Ni, Cu, and Zn, which suffer plasma and matrix-generated interferences. The results for Ti, Co, Ni, Zn, and Cu particularly highlight the effectiveness of the 7500cs for removing the phosphorus based interferences (see Table 1, page 2), allowing the direct analysis of these elements in H_3PO_4. The Cr and Fe values suggest that there were some impurities present in the sample, and the level of Sb was not reported as it was above the top calibration standard. Results for all other elements were well below the maximum allowable levels (ppb) stated in the SEMI Specifications and Guidelines for Phosphoric Acid document (C36-0301), and all recoveries were within the SEMI acceptable range of 75%–125%.

Table 4 shows the comparison between the data for EIE acquired at 1500W and the cool plasma (600W) results. The new ion lens system on the 7500cs eliminates the extraction of these EIE from the interface region when high RF power is used. This

Table 3. DL (3 sigma) and BECs and Spike Recoveries of SEMI Specified Elements in 0.85% H_3PO_4

Element (mass)	Plasma power	H_2 Gas flow (mL/min)	He Gas flow (mL/min)	DL 3 sigma, n = 10 (ppt)	BEC (ppt)	*SEMI Grade 3 spec - max level (ppb)	Spike recovery (%) 50 ppt spike (*200 ppt)
Li (7)	Normal	4.5	–	0.58	0.44	10	99*
B (11)	Normal	–	–	28	110	50	79*
Na (23)	Normal	4.5	–	3.4	34	250	97*
Mg (24)	Normal	4.5	–	2.3	15	50	99*
Al (27)	Normal	4.5	–	3.4	7.0	50	100*
K (39)	Normal	4.5	–	3.0	19	150	101*
Ca (40)	Normal	5.0	–	5.7	24	150	92
Ti (46)	Normal	–	4.5	10	36	50	104
V (51)	Normal	–	4.5	0.50	0.31	–	97
Cr (52)**	Normal	–	4.5	10**	55**	50	113
Mn (55)	Normal	5.0	–	0.80	3.4	50	98
Fe (56)**	Normal	5.0	–	22**	180**	100	95
Co (59)	Normal	–	4.5	0.40	0.47	50	98
Ni (60)	Normal	–	4.5	4.5	21	50	90
Cu (65)	Normal	–	4.5	1.7	3.9	50	96
Zn (66)	Normal	–	4.5	5.3	9.6	50	90
As (75)	Normal	–	4.5	5.3	9.5	50	93
Sr (88)	Normal	–	–	0.07	0.13	10	100
Cd (111)	Normal	–	–	2.2	5.0	50	107
Sb (121)	Normal	–	–	–	>500	1000	–
Ba (138)	Normal	–	–	0.20	0.45	50	102
Au (197)	Normal	–	–	0.70	1.8	50	99
Pb (208)	Normal	–	–	1.4	7.0	50	101

Normal plasma power = 1500W, *Maximum acceptable levels in undiluted phosphoric acid, **Suggests impurities in H_3PO_4.

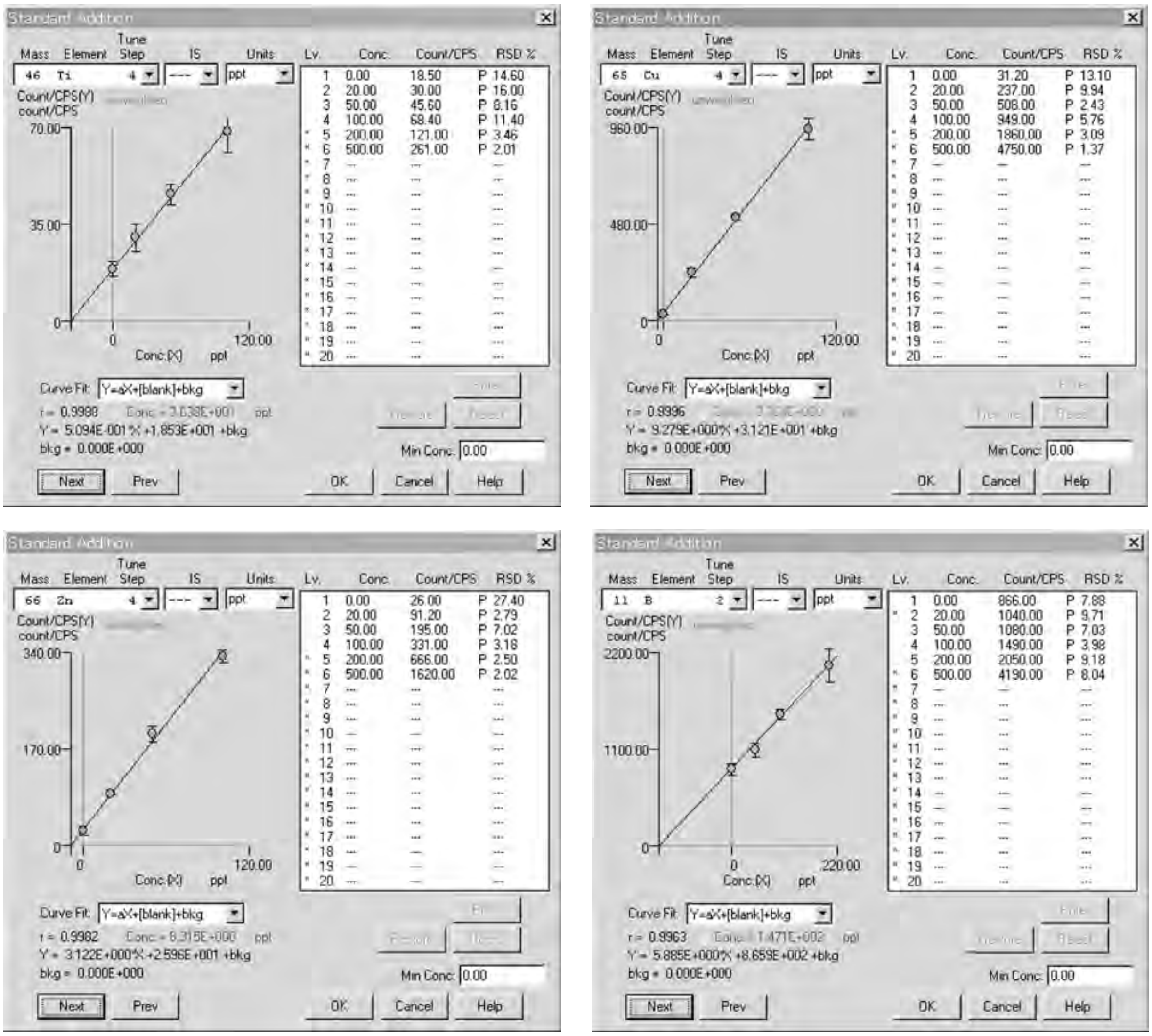
reduces backgrounds, allowing the ultratrace measurement of Li, Na, Mg, Al, and K even at high-plasma power (1500W). Though BEC and DL values obtained at high power for some EIE are slightly higher than with cool plasma, they compare favorably with previously reported values obtained in 1%w/w H_3PO_4 using reaction cell ICP-MS [4].

Representative calibration curves are given in Figure 1. Excellent correlation coefficients were obtained for all elements.

Table 4. Comparison of DL (3 sigma) and BECs for EIEs in 0.85% H_3PO_4 Acquired Using Cool and Normal Plasma Power. H_2 was Added at a Flow Rate of 4.5 mL/min

	DL (ppt)		BEC (ppt)	
Element (mass)	Cool	Normal + H_2	Cool	Normal + H_2
Li (7)	0.10	0.58	0.070	0.44
Na (23)	6.7	3.4	28	34
Mg (24)	2.8	2.3	13	15
Al (27)	1.1	3.4	4.1	7.0
K (39)	1.3	3.0	2.4	19

Detection limits were calculated using three times the standard deviation (n = 3) of the raw counts of the H_3PO_4 blank divided by the slope of the calibration curve. The reported DLs are good and are dependent upon the trace metal content in the blank. This provides an opportunity for even further improvement upon the reported values should higher purity H_3PO_4 become available. All DLs are in the range 0.1–28 ppt (ng/L) in the 0.85% H_3PO_4.



Mass: 46 Element: Ti Tune Step: 4 IS: --- Units: ppt

Lv.	Conc.	Count/CPS	RSD %
1	0.00	18.50	P 14.60
2	20.00	30.00	P 16.00
3	50.00	45.60	P 8.16
4	100.00	68.40	P 11.40
5	200.00	121.00	P 3.46
6	500.00	261.00	P 2.01
7	---	---	---
8	---	---	---
9	---	---	---
10	---	---	---
11	---	---	---
12	---	---	---
13	---	---	---
14	---	---	---
15	---	---	---
16	---	---	---
17	---	---	---
18	---	---	---
19	---	---	---
20	---	---	---

Curve Fit: Y=aX+[blank]+bkg
r = 0.9988 Conc = 3.638E+001 ppt
Y = 5.094E-001*X +1.853E+001 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Mass: 65 Element: Cu Tune Step: 4 IS: --- Units: ppt

Lv.	Conc.	Count/CPS	RSD %
1	0.00	31.20	P 13.10
2	20.00	237.00	P 9.94
3	50.00	508.00	P 2.43
4	100.00	949.00	P 5.76
5	200.00	1860.00	P 3.09
6	500.00	4750.00	P 1.37
7	---	---	---
8	---	---	---
9	---	---	---
10	---	---	---
11	---	---	---
12	---	---	---
13	---	---	---
14	---	---	---
15	---	---	---
16	---	---	---
17	---	---	---
18	---	---	---
19	---	---	---
20	---	---	---

Curve Fit: Y=aX+[blank]+bkg
r = 0.9996
Y = 9.279E+000*X +3.121E+001 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Mass: 66 Element: Zn Tune Step: 4 IS: --- Units: ppt

Lv.	Conc.	Count/CPS	RSD %
1	0.00	26.00	P 27.40
2	20.00	91.20	P 2.79
3	50.00	195.00	P 7.02
4	100.00	331.00	P 3.18
5	200.00	666.00	P 2.50
6	500.00	1620.00	P 2.02
7	---	---	---
8	---	---	---
9	---	---	---
10	---	---	---
11	---	---	---
12	---	---	---
13	---	---	---
14	---	---	---
15	---	---	---
16	---	---	---
17	---	---	---
18	---	---	---
19	---	---	---
20	---	---	---

Curve Fit: Y=aX+[blank]+bkg
r = 0.9982 Conc = 8.315E+000 ppt
Y = 3.122E+000*X +2.596E+001 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Mass: 11 Element: B Tune Step: 2 IS: --- Units: ppt

Lv.	Conc.	Count/CPS	RSD %
1	0.00	866.00	P 7.88
2	20.00	1040.00	P 9.71
3	50.00	1080.00	P 7.03
4	100.00	1490.00	P 3.98
5	200.00	2050.00	P 9.18
6	500.00	4190.00	P 8.04
7	---	---	---
8	---	---	---
9	---	---	---
10	---	---	---
11	---	---	---
12	---	---	---
13	---	---	---
14	---	---	---
15	---	---	---
16	---	---	---
17	---	---	---
18	---	---	---
19	---	---	---
20	---	---	---

Curve Fit: Y=aX+[blank]+bkg
r = 0.9963 Conc = 1.471E+002 ppt
Y = 5.885E+000*X +8.659E+002 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Figure 1. Representative calibration curves for Ti, Cu, Zn, and B obtained using method of standard addition (Blank, 20, 50, 100, 200, and 500 ppt).

A short-term stability study was performed by adding a 100 ppt standard into the 0.85% H_3PO_4 and analyzing the spiked sample over a 3-hour period. Instrument stability over this period was excellent, with %RSD values typically less than 15%. A stability plot of representative elements is shown in Figure 2.

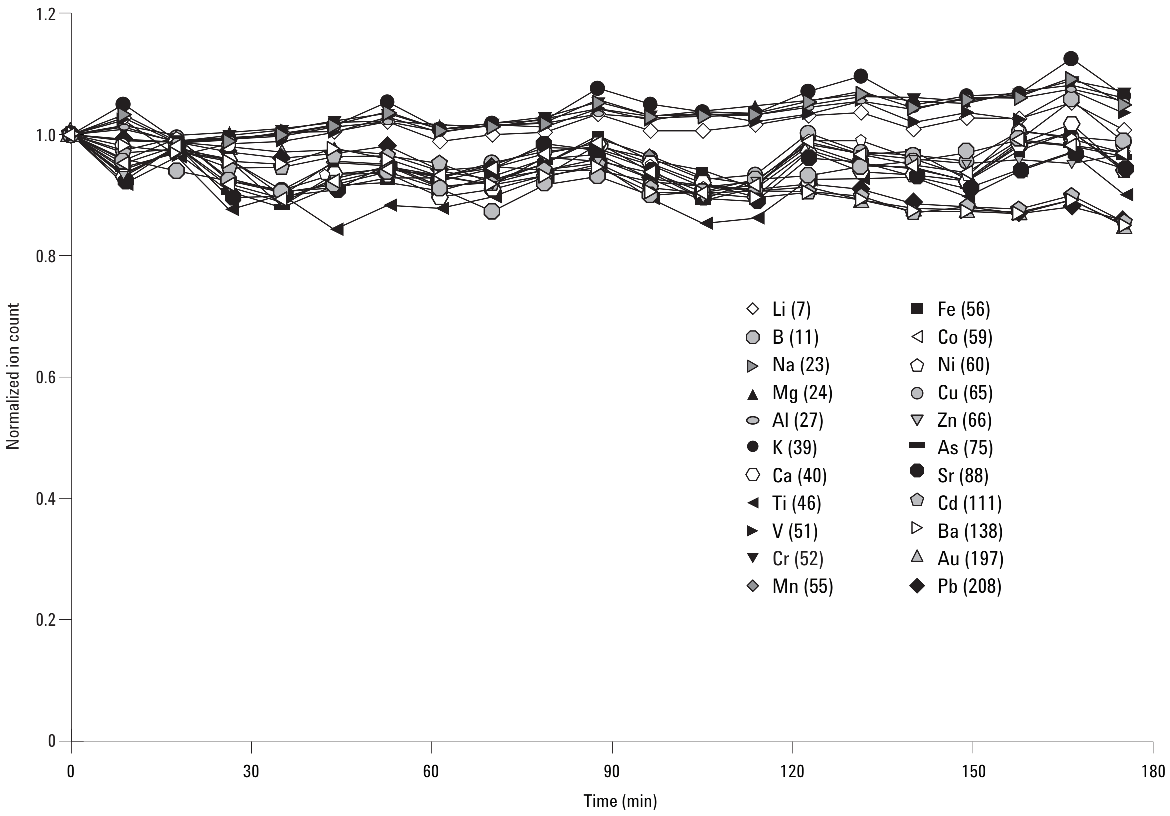


Figure 2. Analysis of 100 ppt multi-element standard spiked into 0.85% H_3PO_4 measured repeatedly over a 3-hour period. Analysis time per sample including 60 s of sample uptake was 185 s (0.33 s integration time, except Ti - 1 s, three replicate measurements).

Conclusions

A newly developed high sensitivity reaction cell ICP-MS was used to analyze 85% (w/w) H_3PO_4 following a 100-fold dilution for elements specified in SEMI Specifications and Guidelines for Phosphoric Acid. The Agilent 7500cs features a new-design ion-lens system for high ion transmission and an ORS cell for interference removal. By pressurizing the cell with simple gases like hydrogen and helium, argon and phosphate-based polyatomics are removed, allowing the direct, ppt-level measurement of Ti, Cu, and Zn in H_3PO_4.

The new extraction lens design also reduces the BECs for the EIEs to close to cool plasma levels even at 1500W or 1600W forward power (normal plasma). All applications can be performed at normal power with the added advantage of Agilent cool plasma performance still being available, if required. Even though BEC and DL values obtained at high power for EIEs are slightly higher than with cool plasma, they are appropriate for the measurement of trace contaminants in H_3PO_4 and they compare favorably with previously reported values obtained in 1%w/w H_3PO_4 using reaction cell ICP-MS [4].

The DL, BEC, spike recovery and stability data presented in the application note highlight the suitability and accuracy of the Agilent 7500cs ICP-MS to determine ppt level impurities in H_3PO_4 for all of the important SEMI specified elements. All analytes were measured directly on mass, in a single analytical run with automatic switching of cell and plasma parameters. A typical total analysis time for this application is 4 minutes. All data is automatically combined into a single report.

Samples were analyzed using the MSA. Only the first sample is spiked with the calibration standards and a MSA regression is generated, which is then converted to an external calibration curve. This method eliminates the need to spike all subsequent samples aiding sample throughput.

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Polymer Comparisons for the Storage and Trace Metal Analysis of Ultrapure Water with the Agilent 7500cs ICP-MS

Application

Semiconductor

Authors

Brad McKelvey, Shelley McIvor, and Bill Wiltse
Seastar Chemicals Inc.
10005 McDonald Park Rd. PO Box 2219
Sidney, BC, Canada V8L 3S8
www.seastarchemicals.com

Abstract

The aim of this study was to find a cost-effective means of storing ultrapure water (UPW). The target was to find a low cost material that was free from contaminating metals that might leach into the UPW during storage. Results for selected metals from the analysis of UPW stored over short and long periods are presented. Low-density polyethylene (LDPE) and high-density polyethylene (HDPE) were compared with PTFE perfluoroalkoxy polymer resin (PFA) and PTFE fluorinated ethylene-propylene (FEP).

Introduction

Cation contamination of samples or high-purity reagents from storage vessels is a critical consideration and a major challenge for analytical laboratories performing ultra trace metal analysis by inductively coupled plasma mass spectrometry (ICP-MS). Many times, poor instrument blanks and subsequently poor limit of detection (LOD) and background equivalent concentration (BEC) values can be traced to reagent/solution impurities.

For almost 30 years, Seastar Chemicals Inc. (Canada), manufacturers of high-purity acids and ammonia for the laboratory market, has specialized in part-per-trillion (ppt) and sub-ppt multielement analytical determinations for the quality control of high-purity reagents. Ultrapure water (UPW) production and storage is a critical platform on which we build our reagent distillation, lab solutions/dilutions, and trace metal clean room work. Therefore, a major R&D focus at Seastar includes materials leaching and analysis for the improvement of product storage. Maintaining the trace metal quality of our products requires chemically inert engineered materials that are trace metal clean or leachable to an acceptable level. With the recent acquisition of our Agilent 7500cs, we are continuing to explore the lower limits of ICP-MS analytical capabilities to globally provide the highest purity acids available for trace metal analysis.

Seastar's high-purity acid products are corrosive, therefore more expensive PTFE perfluoroalkoxy polymer resin (PFA) or PTFE fluorinated ethyene-propylene (FEP) are used for storage and shipping where polyethylene would be inappropriate. Because UPW is relatively inert, this study highlights short- and long-term storage results for select metals in UPW with less-expensive low-density polyethylene (LDPE) and high-density polyethylene (HDPE) compared with PTFE PFA and PTFE FEP.

Instrumentation and Sample Preparation

All samples were analyzed using the Agilent 7500cs ORS ICP-MS. The instrument is located in a class 1000 cleanroom with the autosampler located directly under ultra low penetrating air (ULPA) filtered air. All sample handling prior to analysis is done under class 100 or better conditions. All reagents used are Seastar Chemicals Baseline

Agilent Technologies

Quality. Many of our customers use our products in semiconductor applications; therefore, Seastar's quality control clean room handling and product certifications subscribe to SEMI guidelines for analysis and recoveries.

The ICP-MS operating parameters are shown in Table 1.

Table 1. 7500cs ORS ICP-MS Operating Parameters

Parameters	Cool Plasma Mode	No Gas and Gas Mode
RF Power (W)	640	1500
Sampling Depth (mm)	18	10
Carrier Gas (L/min)	0.7	0.8
Makeup Gas (L/min)	0.75	0.32
Reaction Gas (mL/min)	0	0 (6 for H_2, 5.2 for He)
Extract 1 (V)	−120	6
Extract 2 (V)	−6	−50
QP Bias (V)	−5	−3 (−12 for H_2, −14 for He)
Oct P Bias (V)	−20	−6 (−17 for H_2, −16 for He)

Nalge Nunc International (Rochester, NY) manufactured the bottles used in this study. The bottles are made from virgin resins with no pigments, additives, or stabilizers. The PTFE FEP and PTFE PFA bottles are manufactured using resins and conditions specific to Seastar Chemicals Inc.

All bottles analyzed were 1 liter capacity for comparable surface area leaching. For this study, all bottles were washed with soap and water to remove manufacturing surface dust, then thoroughly rinsed with deionized water. Preleached bottles were filled with dilute high-purity acid and stored at 50 °C for two weeks, followed by thorough rinsing with deionized water. All sample preparation and data acquisition was performed in Class 100 or better clean room conditions.

Six bottles of each polymer, three preleached and three nonleached, were filled with UPW and stored upright at room temperature for 21 days. Ten milliliter aliquots were decanted from each bottle, acidified with nitric acid to 2% (v/v) and analyzed by external calibration. Each bottle was then acidified with nitric acid to 2% (v/v), and allowed to leach for 24 hours at room temperature. Small aliquots were again analyzed by external calibration.

Results and Discussion

In preliminary investigations, unacidified UPW that was stored in both preleached and nonleached bottles had equivalent BECs to 2% v/v high-purity nitric acid. This suggests that no metals were being extracted from the polymer at the pH of ultrapure water (pH 5.2). To test the effect of pH, the same bottles were acidified with nitric acid to 2% (v/v) and stored again for 24 hours. The data in Table 2 summarizes the average result for each of the polymer types. The most common elements extracted were Ca, Fe, Mg, Al and Cu. All of the PTFE preleached bottles have no measurable extractables. Preleached LDPE had only four detectable elements that were all less than 10 ppt. Preleached HDPE had six detectable elements, which included

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significant amounts of Ca and Al. For most applications, preleached LDPE containers are the best economical choice for UPW and dilute acid solutions.

Table 2. Nonleached and Preleached Polymer Comparisons for Ultrapure Water Acidified to 2% (v/v) HNO_3

	LDPE		HDPE		PTFE PFA		PTFE FEP	
H_2 Mode	Nonleached	Preleached	Nonleached	Preleached	Nonleached	Preleached	Nonleached	Preleached
Isotope	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt
Ca 40	160 70	<20	600 600	30 20	440 150	<20	70 60	<20
Cr 52	<3	<3	<3	<3	<3	<3	<3	<3
Fe 56	110 60	4 3	110 140	<3	45 13	<3	22 8	<3
Se 78	<6	<6	<6	<6	<6	<6	<6	<6
Tl 205	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Bi 209	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

	LDPE		HDPE		PTFE PFA		PTFE FEP	
He Mode	Nonleached	Preleached	Nonleached	Preleached	Nonleached	Preleached	Nonleached	Preleached
Isotope	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt	avg/SD/ppt
Ti 48	<0.8	<0.8	4 3	2 2	1.3 0.3	<0.8	<0.8	<0.8
V 51	0.2 0.2	<0.05	3 0.5	5 5	<0.05	<0.05	<0.05	<0.05
Ni 58	<4	<4	<4	<4	7 9	<4	6 2	<4
Co 59	0.2 0.1	<0.07	0.1 0.1	0.08 0	1 0.2	<0.07	6 2	<0.07
Zn 64	8 3	<3	9 6	<3	<3	<3	<3	<3
Ga 71	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Ge 72	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
As 75	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Sr 88	0.5 0.2	<0.09	2 2	<0.09	4 2	<0.09	0.3 0.1	<0.09
Zr 90	<0.2	<0.2	<0.2	<0.2	5 1	<0.2	<0.2	<0.2
Nb 93	<0.005	<0.005	<0.005	<0.005	0.02 0	<0.005	0.04 0	<0.005
Mo 98	<0.2	<0.2	<0.2	<0.2	1.4 0.8	<0.2	1.2 0.6	<0.2
Cd 114	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Sn 120	<0.5	<0.5	2 2	<0.5	<0.5	<0.5	<0.5	<0.5
Sb 121	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ba 138	2 2	0.3 0.3	8 5	<0.1	2 1	<0.1	0.7 0.5	<0.1
W 182	<0.3	<0.3	<0.3	<0.3	4 4	<0.3	0.6 0.2	<0.3

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Table 2. Nonleached and Preleached Polymer Comparisons for Ultrapure Water Acidified to 2% (v/v) HNO_3 (continued)

Normal Mode	LDPE		HDPE		PTFE PFA		PTFE FEP	
Isotope	Nonleached avg/SD/ppt	Preleached avg/SD/ppt	Nonleached avg/SD/ppt	Preleached avg/SD/ppt	Nonleached avg/SD/ppt	Preleached avg/SD/ppt	Nonleached avg/SD/ppt	Preleached avg/SD/ppt
Be 9	0.6 0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B 11	<30	<30	<30	<30	<30	<30	<30	<30
Au 197	<5	<5	<5	<5	<5	<5	<5	<5
Pb 208	3 1	<0.2	3 1	<0.2	1.8 0.5	<0.2	0.9 0.6	<0.2
Th 232	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
U 238	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08

Cool Mode	LDPE		HDPE		PTFE PFA		PTFE FEP	
Isotope	Nonleached avg/SD/ppt	Preleached avg/SD/ppt	Nonleached avg/SD/ppt	Preleached avg/SD/ppt	Nonleached avg/SD/ppt	Preleached avg/SD/ppt	Nonleached avg/SD/ppt	Preleached avg/SD/ppt
Li 7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na 23	<5	<5	86 24	<5	8 6	<5	<5	<5
Mg 24	15 5	4 4	27 25	2 1	26 8	<1	12 15	<1
Al 27	70 30	9 8	120 130	40 40	9 2	<3	5 2	<3
K 39	<7	<7	9 10	<7	<7	<7	<7	<7
Mn 55	4 1	<0.2	3 2	<0.2	0.8 0.3	<0.2	0.5 0.4	<0.2
Cu 63	36 30	1.0 0.8	21 2	<0.9	10 2	<0.9	5 3	<0.9
Ag 107	<1	<1	<1	<1	<1	<1	<1	<1

To quantify the capability of preleached LDPE to maintain trace metal quality UPW over time, three separate bottles were analyzed after one year, two years, and three years. The data is summarized in Table 3. All elements were undetectable.

Table 3. Individual ultrapure water samples stored in preleached low-density polyethylene for one, two, and three years.

H_2 Mode	Preleached LDPE		
Isotope	1 yr ppt	2 yr ppt	3 yr ppt
Ca 40	<20	<20	<20
Cr 52	<3	<3	<3
Fe 56	<3	<3	<3
Se 78	<6	<6	<6
Tl 205	<0.3	<0.3	<0.3
Bi 209	<0.1	<0.1	<0.1

He Mode	Preleached LDPE		
Isotope	1 yr ppt	2 yr ppt	3 yr ppt
Ti 48	<0.8	<0.8	<0.8
V 51	<0.05	<0.05	<0.05
Ni 58	<4	<4	<4
Co 59	<0.07	<0.07	<0.07
Zn 64	<3	<3	<3
Ga 71	<0.3	<0.3	<0.3
Ge 72	<0.4	<0.4	<0.4
As 75	<0.8	<0.8	<0.8
Sr 88	<0.09	<0.09	<0.09
Zr 90	<0.2	<0.2	<0.2
Nb 93	<0.005	<0.005	<0.005
Mo 98	<0.2	<0.2	<0.2
Cd 114	<0.09	<0.09	<0.09
Sn 120	<0.5	<0.5	<0.5
Sb 121	<0.1	<0.1	<0.1
Ba 138	<0.1	<0.1	<0.1
W 182	<0.3	<0.3	<0.3

Table 3. Individual ultrapure water samples stored in preleached low-density polyethylene for one, two, and three years. (continued)

Normal Mode	Preleached LDPE		
Isotope	1 yr ppt	2 yr ppt	3 yr ppt
Be 9	<0.1	<0.1	<0.1
B 11	<30	<30	<30
Au 197	<5	<5	<5
Pb 208	<0.2	<0.2	<0.2
Th 232	<0.09	<0.09	<0.09
U 238	<0.08	<0.08	<0.08

Cool Mode	Preleached LDPE		
Isotope	1 yr ppt	2 yr ppt	3 yr ppt
Li 7	<0.01	<0.01	<0.01
Na 23	<5	<5	<5
Mg 24	<1	<1	<1
Al 27	<3	<3	<3
K 39	<7	<7	<7
Mn 55	<0.2	<0.2	<0.2
Cu 63	<0.9	<0.9	<0.9
Ag 107	<1	<1	<1

Conclusions

All labware for ultra trace metal analysis must be preleached prior to use with acidic solutions. The high standard deviations for elements detected in the nonleached bottles indicate significant bottle-to-bottle variability. If possible, all bottles and labware should be uniquely identified and blank tested. The elemental signature of the extractables can later be used to determine the source of contamination problems. It is the experience of this laboratory that each manufacturer of polymeric bottles and labware exhibits unique elemental signatures and the value of extractables may differ from those reported in this study.

The preleached LDPE bottles maintained elemental concentrations under 10 ppt for dilute nitric acid solutions and UPW with long-term storage. From a trace metal perspective, preleached LDPE is an excellent, cost-effective alternative to PTFE PFA and FEP for UPW and dilute acid solutions.

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Process Chemicals

ICP-MS is used to monitor the contamination of chemicals used during the wafer/IC fabrication process.

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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.

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.

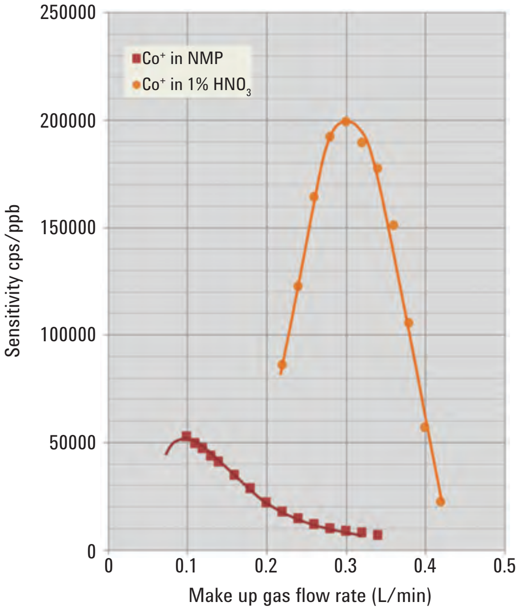

Figure 1. 1 ppb Co signal in 1% HNO_3 and acidified NMP as a function of MUGS flow rate

The optimum MUGS flow rate for NMP analysis is 0.20 L/min lower than that for 1% HNO_3, and Co sensitivity in NMP is about four times lower than in 1% HNO_3. 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 (H_2) and oxygen (O_2) were used as reaction gases in the Octopole Reaction System (ORS^3). 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	
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 O_2 worked well for P and S measurement in NMP. The reactions of P and S with O_2 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.

$$P^+ + O_2 \rightarrow PO^+ + O \qquad \Delta Hr = -3.17 \text{ eV},$$
$$kr = 4.9 \times 10^{-10} \text{ cm}^3/\text{s/molecule}$$
$$S^+ + O_2 \rightarrow SO^+ + O \qquad \Delta Hr = -0.34 \text{ eV},$$
$$kr = 1.5 \times 10^{-11} \text{ cm}^3/\text{s/molecule}$$

Figures 2 and 3 show calibration plots obtained using the O_2 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 O_2 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 O_2, allowing the analytes to be separated from the interferences.

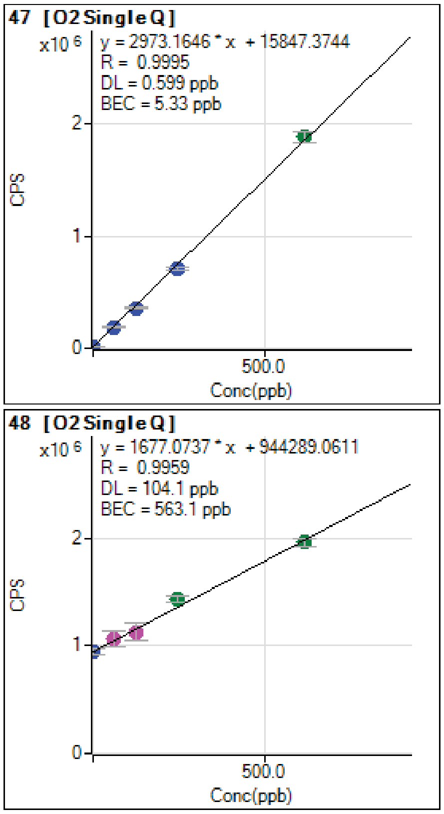

Figure 2. Calibration curve of O_2 mass-shift method for P (top) and S (bottom) in NMP with single quad scan, emulating conventional ICP-QMS

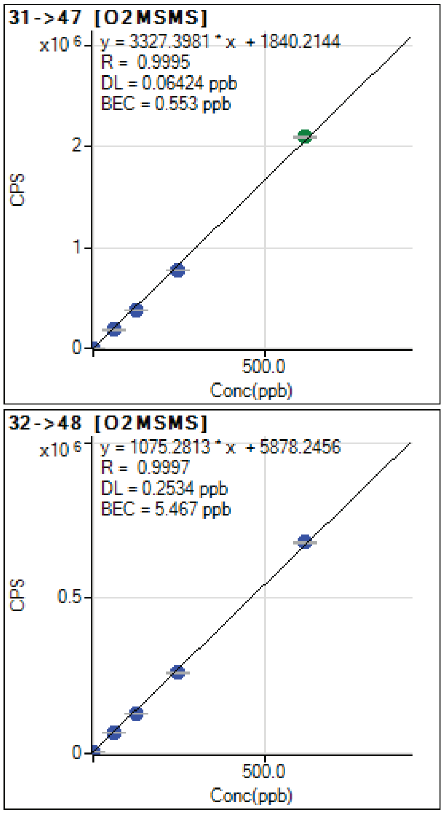

Figure 3. Calibration curve of O_2 mass-shift for P (top) and S (bottom) in NMP with MS/MS scan

Si in NMP

H_2 and O_2 cell gases were both applied to the measurement of Si in NMP. The reaction kinetics for Si and its major interferences with H_2 cell gas are shown below. The reaction rate data suggests that Si does not react with H_2 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 H_2 is endothermic, the reactions of the major interfering ions on Si at mass 28 (N_2^+ and CO^+) are exothermic, and these interferences are therefore neutralized or reacted away.

$Si^+ + H_2 \rightarrow SiH^+ + H \quad \Delta Hr = 1.30eV,$

$kr = 5 \times 10^{-13}\ cm^3/s/molecule$

$N_2^+ + H_2 \rightarrow HN_2^+ + H \quad \Delta Hr = -0.60\ eV,$

$kr= 2.1 \times 10^{-9}\ cm^3/s/molecule$

$CO^+ + H_2 \rightarrow COH^+ + H \quad \Delta Hr = -1.63eV,$

$kr = 1.8 \times 10^{-9}\ cm^3/s/molecule$

Oxygen cell gas was also tested. As shown below, the reaction of Si^+ with O_2 to form SiO^+ is endothermic. However, collisional processes in the cell provide additional energy which promotes the reaction, enabling the O_2 mass-shift method to be applied.

$Si^+ + O_2 \rightarrow SiO^+ + O \quad \Delta Hr = 0.11eV$

$kr = < 1 \times 10^{-11}\ cm^3/s/molecule$

Unfortunately a major interference on Si at *m/z* 28 (CO^+) also reacts with O_2, so the BEC achieved using the O_2 mass-shift method to measure Si as SiO^+ (Q1=28, Q2=44) was not satisfactory. Fortunately, another Si reaction product ion (SiO_2^+) also forms and this can be measured at *m/z* 60 (Q1 = 28, Q2 = 60) giving better results, as shown in Figure 4.

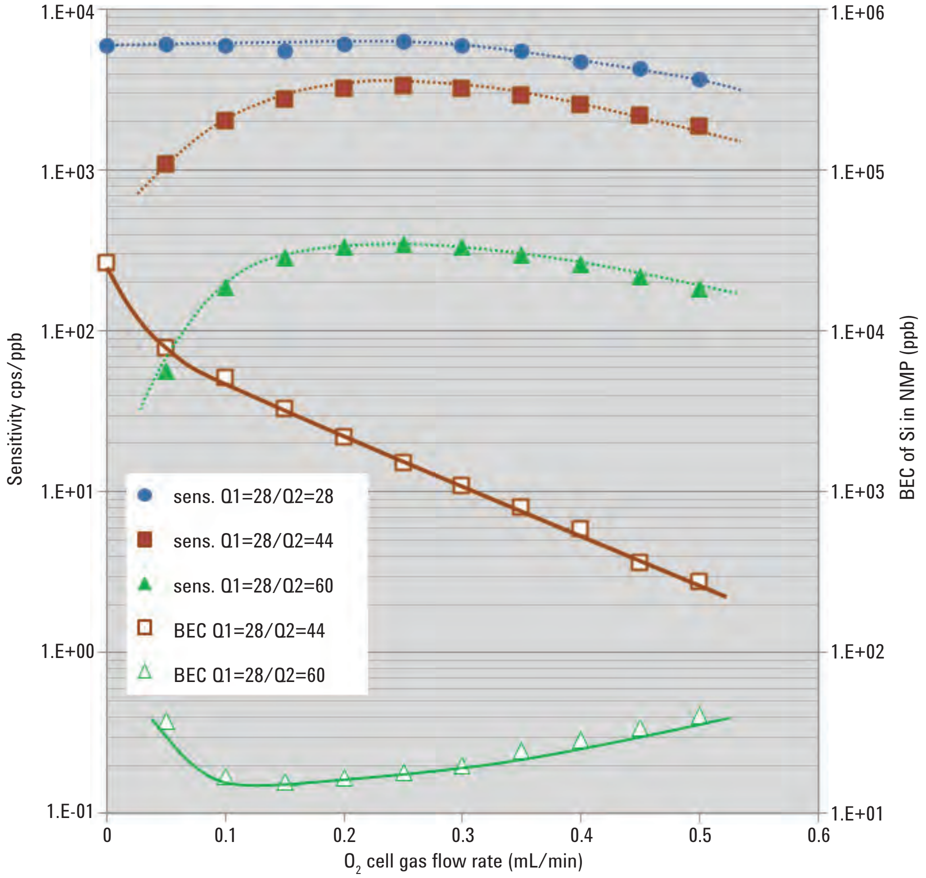

Figure 4. BECs of Si in NMP obtained using product ions SiO^+ and SiO_2^+, as a function of O_2 cell gas flow rate

The results obtained are shown in Figure 5 (top). The H_2 on-mass method achieved a BEC of 15.8 ppb for Si in NMP. Using the O_2 mass-shift method to measure SiO_2^+ gave a BEC of 11.9 ppb (Figure 5, bottom) for Si in NMP.

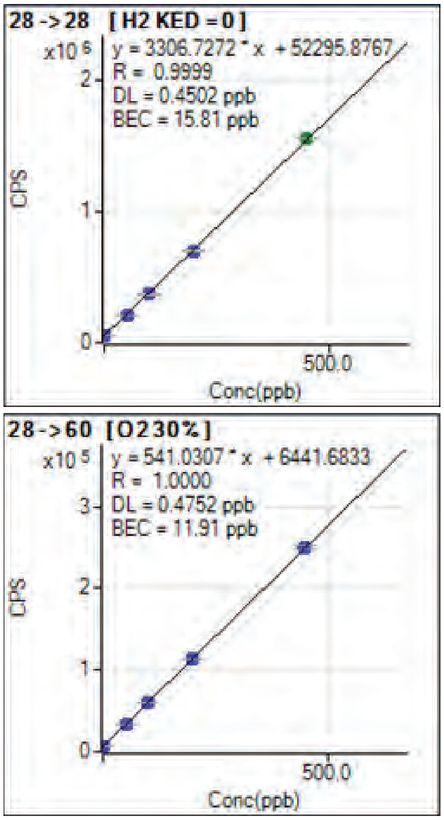

Figure 5. Calibration plots for Si in NMP. Top: H_2 on-mass method (Q1=Q2=28). Bottom: O_2 mass-shift method (Q1=28, Q2=60)

Cl in NMP

Cl^+ reacts with H_2 exothermically to form HCl^+ as shown below. HCl^+ continues to react via a chain reaction to form H_2Cl^+. Preliminary tests showed the reaction is more efficient than the reaction with O_2 to form ClO^+, so the H_2 mass-shift method (Q1=35, Q2=37) was applied to the measurement of Cl in NMP.

$$Cl^+ + H_2 \rightarrow HCl^+ + H \qquad \Delta Hr = -0.17 eV,$$
$$kr = 9.2 \times 10^{-10}\ cm^3/s/molecule$$

$$HCl^+ + H_2 \rightarrow H_2Cl^+ + H \qquad \Delta Hr = -0.39 eV,$$
$$kr = 1.3 \times 10^{-9}\ cm^3/s/molecule$$

Figure 6 (top) shows calibration plots obtained for Cl in NMP using the H_2 mass-shift method. The plot obtained using the O_2 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 H_2 mass-shift method.

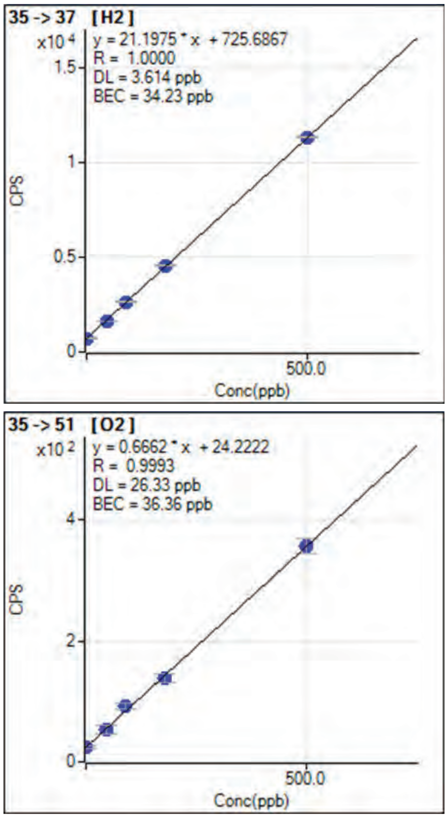

Figure 6. Calibration plots for Cl in NMP. Top: H_2 mass-shift method (Q1=35, Q2=37). Bottom: O_2 mass-shift method (Q1=35, Q2=51)

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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 O_2 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.

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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.

Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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Sub-ppb detection limits for hydride gas contaminants using GC-ICP-QQQ

Application note

Semiconductor and petrochemical

Authors

William Geiger

CONSCI, Ltd., Pasadena, Texas, USA

Emmett Soffey, Steve Wilbur and Chris Scanlon

Agilent Technologies Inc., USA

Introduction

Hydride gases, such as phosphine and arsine, are important contaminants in process chemicals used in both the petrochemical and semiconductor industries. For example, the presence of phosphine, arsine, hydrogen sulfide and carbonyl sulfide in polymer grade ethylene or propylene can have a deleterious effect on catalysts used in the production of polypropylene plastics. Accurate data on the concentrations of these contaminants at trace levels enables prediction of catalyst lifetime and minimizes production downtime.

In the semiconductor industry, phosphine is used as a precursor for the deposition of group III-V compound semiconductors, and as a dopant in the manufacturing of semiconductor devices, such as diodes and transistors. In the case of group III-V compound materials, such as indium phosphide (InP), absence of other hydride dopant impurities e.g., silane, germane or hydrogen sulfide (and moisture) is critical, as they can have a profound effect on the performance of the final device. In particular, incorporated sulfur from hydrogen sulfide and carbonyl sulfide may affect the electrical properties of

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the device, such as carrier concentration and electron mobility. In the case of arsine, which is used in the manufacture of high electron mobility transistors (HEMTs) and field effect transistors (FETs), product performance can be adversely affected by the presence of germane.

To date, measurement of these contaminants at ppb levels has been sufficient, but increasing competition within the industry and evolving performance criteria are pushing specifications ever lower. In addition, high purity gas manufacturers often require analytical detection limits 5–10 times lower than reported specifications. Earlier generation quadrupole ICP-MS (ICP-QMS) detectors were capable of measuring sulfur and silicon species at the 10 ppb level. More recently, the Agilent 7900 ICP-MS has demonstrated the ability to measure these elements at the 1–2 ppb level. In anticipation of increasing industry demand for even lower levels, a new high sensitivity GC-ICP-MS method using the Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) was developed for this application.

Experimental

Instrumentation

An Agilent 7890 GC was coupled to an Agilent 8800 ICP-QQQ using the Agilent GC-ICP-MS interface. The GC operating parameters given in Table 1 were also used for a parallel GC-ICP-MS study using an Agilent 7900 ICP-MS.

Table 1. GC operating parameters

Parameter	Setting
Column	100 meter x 0.53 mm x 5.0 µm DB-1
Flow	Pressure control isobaric @ 20 psig
Column exit pressure	4 psig
Temperature	Isothermal ambient
Gas sampling valve and sample size	6 port valve with 400 µL loop

The 8800 ICP-QQQ features two quadrupole mass filters (Q1 and Q2), situated either side of the Octopole Reaction System (ORS^3) collision/reaction cell (CRC). In MS/MS mode, Q1 operates as a mass filter, allowing only the target analyte mass to enter the cell, and rejecting all other masses. Because plasma, matrix and all non-target analyte ions are excluded by Q1, the reaction processes in the ORS^3 are precisely controlled and consistent, so accurate measurements can be performed even in complex, high matrix samples, while sensitivity is significantly increased. The ORS^3 cell can be pressurized with either a collision gas to remove polyatomic ions by kinetic energy discrimination (KED), or by collision-induced dissociation (CID), a reactive gas to selectively react with either the interfering or the target ion to attain interference-free measurement, or a combination of both.

In this study, the 8800 ICP-QQQ was operated in MS/MS mass-shift mode using oxygen as the reaction gas for the measurement of Ge, As, P, and S. Hydrogen cell gas mode was used for the on-mass measurement of the primary isotope of Si at *m/z* 28. Tuning conditions were almost identical for the two modes, the only differences being in the KED voltage and the cell gas flow.

Table 2. Agilent 8800 ICP-QQQ operating conditions

	O_2 mode	H_2 mode
RF power (W)	1350	
Sample depth (mm)	8.4	
Argon carrier (makeup) gas flow (L/min)	0.85	
Extract 1 (V)	-150	
Extract 2 (V)	-190	
Omega bias (V)	-120	
Omega lens (V)	2.2	
Cell entrance (V)	-50	
Cell exit (V)	-60	
Kinetic Energy Discrimination (V)	-4	0
Cell gas flow (mL/min)	0.35	5.0

Reagents

Gas standards of silane, phosphine, germane, arsine (all balanced with H_2), and hydrogen sulfide and carbonyl sulfide (balanced with Ar) were supplied by Custom Gas Solutions at a nominal value of 10 ppmv. These standards were dynamically diluted in helium using a pressure/fixed restrictor based diluter supplied by Merlin MicroScience.

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Results and discussion

Low level phosphine analysis

The purpose of this experiment was to establish a detection limit for phosphine (PH_3) using GC-ICP-QQQ under ideal conditions. Q1 was set to *m/z* 31 (the precursor ion $^{31}P^+$) and Q2 was set to *m/z* 47 to measure the reaction product ion $^{31}P^{16}O^+$. Since the eluting peaks are relatively narrow, with duration of no more than ~12 seconds, a maximum of 1 second was set for the total scan time. For the single element analysis of phosphine (measured as PO^+), an integration time of 1.0 second was used. A multi-point calibration curve was generated for PH_3 at concentrations of 8.2, 18.8 and 50.8 ppb (Figure 1). This covers the representative concentration range required for the measurement of this contaminant.

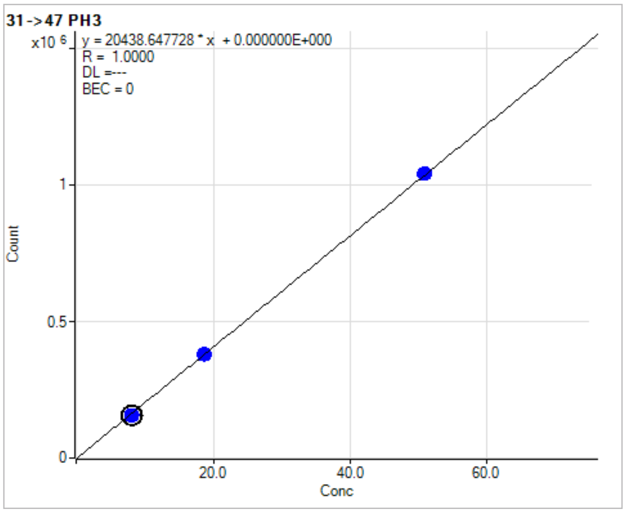

Figure 1. Phosphine calibration curve with an R value of 1.000 over the concentration range

A low level phosphine standard (~0.42 ppb) was also prepared, to allow the detection limit (DL) to be calculated. Two different methods for DL calculation were used:
i. Two times the signal to noise (S/N) of the phosphine peak in the low level standard based on “Peak to Peak” noise method, and
ii. The standard deviation of the concentrations measured in seven replicate analyses of the low level standard.

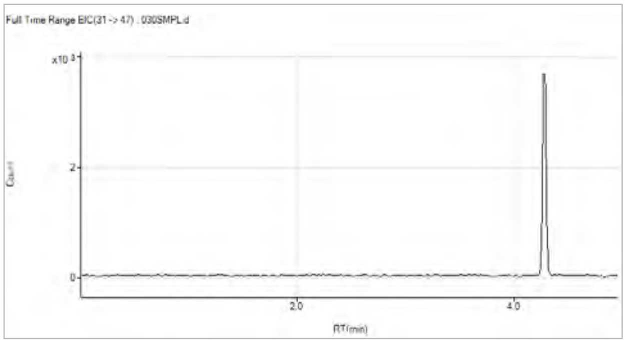

Figure 2. Chromatogram of 0.42 ppb PH_3 standard. S/N: 96.9

In the chromatogram shown in Figure 2, a S/N ratio of 96.9 was determined for the phosphine peak. Using the equation DL = 2 x ((concentration of standard) / (S/N)), a detection limit approximation of 8.67 ppt was calculated based on 2 x ((0.42 ppb) /(96.9)). Using the standard deviation method, where multiple replicates of the low level standard were analyzed, the detection limit was 19 ppt.

Multielement analysis of germane, arsine and phosphine

In order to check the performance of the method when measuring multiple masses within a single analysis, Ge, As and P were analyzed together and integration times were adjusted so as to not exceed the 1 second scan time limit. Ge and As were measured as their O_2 reaction product ions: GeO^+ and AsO^+, as was the case with P (PO^+). The total integration time for all three mass pairs was 0.908 seconds, as shown in Table 3.

Table 3. Acquisition parameters for P, Ge and As

Element	Q1 -> Q2	Integration time/Mass (sec)
P	31 -> 47	0.5000
Ge	74 -> 90	0.2000
As	75 -> 91	0.2000

Linear multipoint calibration curves were generated from phosphine, germane and arsine standards at 4.1, 8.8 and 18.3 ppb. The detection limits for all three analytes, calculated from the S/N measured using the low level calibration standard, are shown in Table 4.

Table 4. GC-ICP-QQQ detection limits for P, Ge and As

	Calibration R value	S/N of 4.1 ppb standard	DL using S/N (ppb)
PH_3	1.0000	671	0.012222
GeH_4	1.0000	2111	0.00388
AsH_3	1.0000	6373	0.00129

Analysis of hydrogen sulfide and carbonyl sulfide

Hydrogen sulfide (H_2S) and carbonyl sulfide (COS) were analyzed using O_2 mass-shift mode based on the ICP-QQQ measurement of sulfur as the $^{32}S^{16}O^+$ reaction product ion at *m/z* 48. An integration time of 0.75 seconds was chosen and a calibration curve was generated from standards at 4.28, 7.49 and 17.04 ppb. A chromatogram of the 4.28 ppb standard is shown in Figure 3. A low level standard (~2.3 ppb) was also prepared, to allow the DL to be calculated. DLs for H_2S and COS, calculated from the S/N analysis of the 2.3 ppb standard and the analysis of 7 replicate measurements of the low standard, are shown in Table 5.

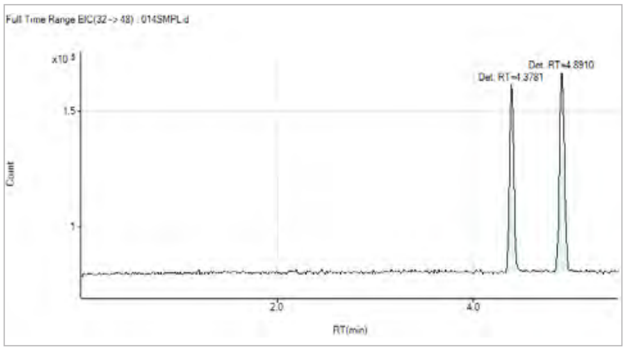

Figure 3. Chromatogram of 4.28 ppb standard of H_2S and COS

Table 5. MDL calculations for H_2S and COS

	Calibration R value	S/N of 2.3 ppb standard	DL using average S/N (ppb)	DL based on 7 replicates (ppb)
H_2S	1.0000	46	0.10602	0.20506
COS	1.0000	44.8	0.1085	0.11893

Analysis of silane

The primary polyatomic interferences on $^{28}Si^+$ are $^{12}C^{16}O^+$ and $^{14}N_2^+$ due to the presence of CO_2, N_2, and O_2 in the argon supply and from air entrainment into the plasma. H_2 was selected as the reaction gas for Si analysis, as both the CO^+ and N_2^+ interferences react readily with H_2 cell gas. Si^+ remains unreactive and so can be measured, free from interferences, at its original mass.

Data acquisition was performed using on-mass MS/MS mode with both Q1 and Q2 set to mass 28, and using an integration time of 0.75 seconds. A calibration curve for silane was prepared at 4.2, 7.8 and 18.1 ppb and an R value of 1.00 was achieved over this concentration range. MDLs for SiH_4 calculated from the S/N analysis of the 4.2 ppb standard and analysis of seven replicate measurements of the low standard are shown in Table 6.

Table 6. MDLs for silane based on 4.2 ppb standard

	Calibration R value	DL using average S/N (ppb)	DL based on 7 replicates (ppb)
SiH_4	1.0000	0.196764	0.141877

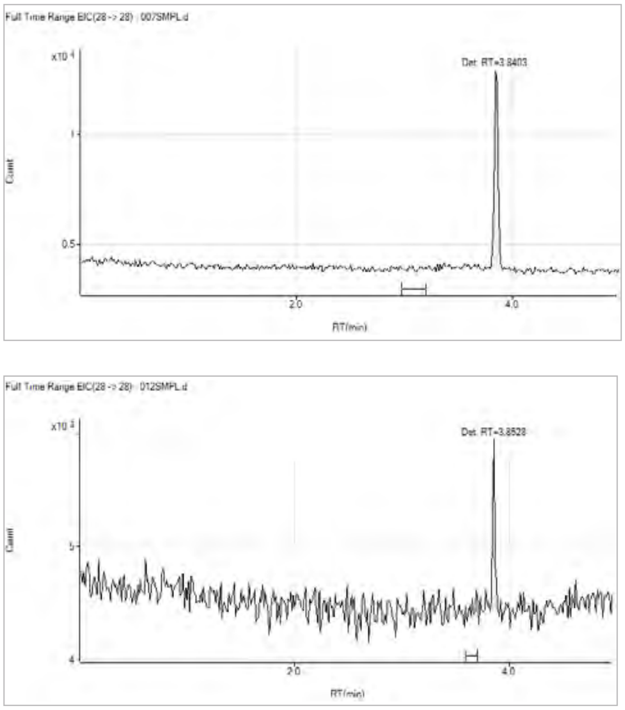

Figure 4. Chromatogram of 4.2 ppb silane standard (upper) and ~0.4 ppb silane (lower)

It should be noted that the elevated background at mass 28 in the silane chromatograms shown in Figure 4 is most likely due to column bleed from the thick film DB-1 column (methyl silicone stationary phase) used in these experiments. This Si background signal might be reduced by using a porous polymer type column.

Comparison of GC-ICP-QQQ and GC-ICP-MS DLs

For comparison purposes, H_2S, COS, PH_3, GeH_4, AsH_3, and SiH_4 were analyzed by both GC-ICP-QQQ with the 8800 ICP-QQQ, and GC-ICP-MS using the same GC method with an Agilent 7900 conventional quadrupole ICP-MS. A summary of the detection limits (DLs) for both techniques is given in Table 7. For analytes where the background noise is very low (Ge-74, As-75), single digit ppt level detection limits are easily achieved using either GC-ICP-MS or GC-ICP-QQQ. However, for analytes that are prone to higher backgrounds (P-31 and S-32), significantly lower detection limits can be achieved using MS/MS with O_2 cell gas and measuring the oxygen addition reaction product ions PO^+ and SO^+ in mass-shift mode. In addition, MS/MS mode with H_2 cell gas provides effective removal of background interferences at mass 28, allowing on-mass measurement of Si at its primary isotope.

Table 7. Detection limit comparison between GC-ICP-QQQ and GC-ICP-MS

Hydride gas	8800 ICP-QQQ		7900 ICP-MS	
		DL, ppb		**DL, ppb**
H_2S	**32->48 (O_2)**		**32 (No gas)**	
	MDL 7 reps	0.21	MDL 7 reps	0.62
	MDL 2 x S/N	0.11	MDL 2 x S/N	0.22
COS	**32->48 (O_2)**		**32 (No gas)**	
	MDL 7 reps	0.12	MDL 7 reps	0.51
	MDL 2 x S/N	0.11	MDL 2 x S/N	0.21
PH_3	**31->47 (O_2)**		**31 (No gas)**	
	MDL 7 reps	0.019	MDL 7 reps	0.139
	MDL 2 x S/N	0.009	MDL 2 x S/N	0.077
GeH_4	**74->90 (O_2)**		**74 (No gas)**	
	MDL 7 reps	NA	MDL 7 reps	0.013
	MDL 2 x S/N	0.0038	MDL 2 x S/N	0.0013
AsH_3	**75->91 (O_2)**		**75 (No gas)**	
	MDL 7 reps	NA	MDL 7 reps	0.016
	MDL 2 x S/N	0.0013	MDL 2 x S/N	0.006
SiH_4	**28->28 (H_2)**		**28 (H_2)**	
	MDL 7 reps	0.14	MDL 7 reps	1.09
	MDL 2 x S/N	0.196	MDL 2 x S/N	1.18

NA = not available

Conclusions

The significantly lower background and higher sensitivity of the Agilent 8800 ICP-QQQ resulted in a GC-ICP-QQQ method that shows a clear advantage for the determination of a range of contaminants in high purity gases at the low detection levels demanded by the industry. Compared to GC-ICP-MS with conventional quadrupole ICP-MS, GC-ICP-QQQ DLs for silane, phosphine, hydrogen sulfide, and carbonyl sulfide were lower by a factor of 5 to 10, with silane detection limits in the ~200 ppt range and phosphine detection limits in the ~15 ppt range.

More Information

Find out more about CONSCI at www.consci.com or contact William Geiger at bill@conscicorp.com

Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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Direct Analysis of Photoresist and Related Solvents Using the Agilent 7500cs ICP-MS

Application

Semiconductor

Authors

Junichi Takahashi
Kouichi Youno
Agilent Technologies, Inc.
9-1 Takakura-Cho, Hachioji-Shi
Tokyo, 192-0033
Japan

Abstract

A simple method for analyzing photoresists using reaction cell inductively coupled plasma mass spectrometry is discussed. The Agilent 7500cs ICP-MS, which features a high sensitivity version of the Octopole Reaction System (ORS), was used to analyze photoresist for a full suite of elements. The ORS eliminates all plasma and matrix based polyatomics that interfere with the measurement of elements such as B, Mg, Al, K, Ca, Ti, Cr, Fe, and Zn, which would otherwise limit standard quadrupole ICP-MS operation for this application. Sample preparation is a simple 10× dilution of the photoresist sample (30% resin) in a suitable solvent, followed by direct analysis by the 7500cs.

Introduction

Manufacturing integrated circuits (ICs) is a complex process involving numerous steps over a period of weeks. Without constant testing, metal contaminants can be unwittingly introduced at any step of the manufacturing process and particularly during the critical lithography stage. Once a layer of material, such as an oxide layer, is grown or deposited onto the silicon wafer surface, a light-sensitive liquid-photoresist layer is applied. After it has cured, the photoresist prevents etching or plating of the area it covers. There are several different classifications of resists. In this application note, the analysis of positive resist (p-type), which becomes soluble when exposed to ultraviolet (UV) light, is considered. When processing a wafer with a positive resist, a mask having the required template is aligned between an UV light source and the wafer. UV light shines through the clear portions of the mask thereby exposing the template onto the photo-sensitive resist. The exposed resist becomes soluble to a developer for example, tetra-methyl ammonium hydroxide (TMAH, 2.38%), and is removed from the wafer surface. The "mask pattern" is then etched onto the wafer using either a wet or dry etching process, the remaining undeveloped/hardened photoresist is removed and the process is repeated.

Metal impurities present in the photoresist can cause a distortion of the electrical properties and reliability of the final semiconductor devices, so acceptable limits of impurities are constantly being reduced. Current acceptable levels of metallic impurities in the photoresist (such as Na, Mg, K, Ca, Cr, Mn, Fe, Ni, Cu, and Zn) are in the range 10–30 ppb per element and will become less than 10 ppb soon. Consequently, monitoring these elements in photoresist at ultratrace levels is critical and is routinely carried out by photoresist suppliers and some integrated circuit manufacturers.

A photoresist sample is usually prepared by acid digestion or dry ashing, followed by graphite furnace atomic absorption spectroscopy (GFAAS) analysis. This method is used extensively although it is time-consuming and potentially hazardous. Also, acid digestion or dry-ashing sample preparation can lead to the loss of volatile elements such as boron and arsenic. Other limitations of this approach include the potential introduction of contaminants from the apparatus, acid mixture and other reagents, and the poor sample throughput capabilities of GFAAS. More recently a different approach was developed. Photoresist can be analyzed directly for multiple elements by a combination of simple dilution in an appropriate solvent and analysis using inductively coupled plasma mass spectrometry (ICP-MS). There are a variety of solvents suitable as photoresist diluents, including N-methyl-2-pyrrolidone (NMP), propylene glycol monomethyl ether (PGME) and ethyl lactate. The detection capability of impurities in photoresist is strongly affected by the level of impurities in the solvent. Despite this fact, commercially available ultrahigh purity solvents are difficult to find. This report describes the analysis of photoresist by ICP-MS following a simple dilution in PGME. The solvent was purified in the laboratory prior to the analysis.

Instrumentation

The Agilent 7500cs ICP-MS instrument is equipped with the Octopole Reaction System (ORS) for the removal of polyatomic species that can interfere with the measurement of some elements as shown in Table 1. A 7500cs fitted with an organic solvent introduction kit (part number G1833-65038) was used in this study. The kit consists of a quartz narrow-bore injector torch (1.5-mm id) with a tapered tip, and spray chamber drain fitting for organic solvents. The Agilent quartz concentric nebulizer (part number G1820-65138) was self aspirated at a sample uptake rate of 68 µL/min. The specially engineered tapered injector torch, exclusive to Agilent, (part number G1833-65424) is suitable particularly for the analysis of photoresist because the torch requires a narrow injector and is difficult to block. The temperature of the quartz spray chamber was maintained at –5 °C.

Removal of Carbon

The high carbon content of photoresist, which typically consists of a carrier solvent, photoactive compound, and polymers, can lead to deposition of carbon on the sampling cone, eventually leading to clogging of the orifice and a reduction in sensitivity. To prevent this, a small amount of oxygen is added into the argon gas line to burn carbon. Oxygen gas is added through a T-connector before the torch. For safety reasons, oxygen should not mix with argon in the spray chamber and it is advisable to use oxygen (20%) diluted with argon. Platinum-tipped interface cones are used instead of nickel cones, which quickly deteriorate, in the much more reactive plasma environment produced by adding oxygen.

Removal of Spectral Interferences

The photoresist used in this study contains not only carbon, hydrogen, and oxygen but also sulfur as sulfonic acid, giving rise to potential matrix-based polyatomic interferences shown in Table 1. With the introduction of the high-sensitivity 7500cs reaction cell ICP-MS, these spectral background ions can be attenuated using a controlled environment within the ORS cell or by Agilent's cool plasma technology. In this report, data obtained using the 7500cs ORS in helium and hydrogen mode is presented.

Table 1. Potential Interferences on Preferred Analyte Isotopes

Analyte	Mass	Polyatomic ions
B	10, 11	^{12}C
Mg	24	$^{12}C_2$
Al	27	$^{13}C^{14}N$, $^{12}C^{14}NH$
K	39	^{40}ArH, $^{12}C^{14}N^{12}CH$
Ca	40	^{40}Ar
Ti	46,	$^{12}C^{16}O_2$
Ti	46, 47, 48	$^{14}N^{16}O_2$
Ti	48, 49	$^{32}S^{16}O$, $^{32}S^{16}OH$
Cr	52	$^{40}Ar^{12}C$
Fe	56	$^{40}Ar^{16}O$
Zn	64	$^{32}S^{16}O_2$

Experimental

A simple analytical method was used to analyze the photoresist samples, see Table 2 for the operating parameters used. The optional gas flow rate was set at 0.2 L/min of oxygen (20%) mixed with argon and the torch sampling depth was 8 mm.

Ion lens parameters and ORS gas flow rates were optimized using a blank PGME and a 1-ppb tuning solution containing ^{7}Li, ^{59}Co, ^{89}Y, and ^{205}Tl in PGME. In non-gas mode, operating conditions were tuned by maximizing the counts for Li, Y, and Tl. In hydrogen gas mode, the signal response in counts per second (cps) for ^{59}Co was maximized and the signal response for Ar at mass 40 and ArC at mass 52 were minimized. In helium gas mode, ^{59}Co was maximized and the background counts at mass 63 and 64 were minimized. The ICP-MS ChemStation software features Multi-tune, which automatically combines different tuning conditions in one analytical run. Results for all elements are presented in a single report.

As photoresist precipitates on contact with water, it is important to ensure there is no water present in the sample introduction system of the ICP-MS. Following ignition of the plasma, when an aqueous solution is used, water is eliminated by introducing a solution of PGME for at least 10 min. Oxygen is added to the plasma gas during this cycle.

Table 2. 7500cs Operating Conditions

RF power	1600 W
Sampling depth	8 mm
Carrier gas flow rate	0.6 L/min
Makeup gas flow rate	0 L/min
Optional Gas Flow	20% oxygen in argon
Spray chamber temperature	–5 °C

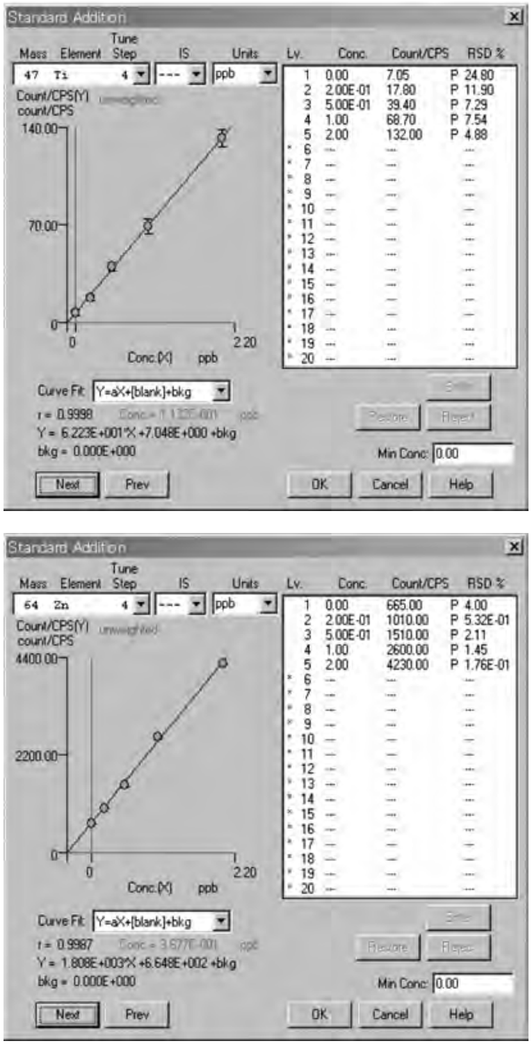
Sample Preparation

Sample preparation consisted of simply diluting the photoresist samples 1:10 with PGME.

Method of Quantification

Due to the difference of viscosity between photoresist and PGME, each sample was analyzed separately and the results for PGME were subtracted from the photoresist data to give a net analytical value. Calibrations for each sample were performed using matrix matched PGME and photoresist standards. First, an aliquot of PGME was spiked with a multi-element standard (SPEX) to final concentrations of 0.5, 1.0, and 2.0 ppb. The concentration of the analytes present in the solvent was determined against this external calibration. No internal standards (ISTDs) were added to avoid the risk of contamination. The external calibration avoided the need for time-consuming standard additions, which requires the need to spike every sample. The process was repeated for photoresist. An aliquot of photoresist (diluted to 3% resin in PGME) was spiked to final concentrations of 0, 0.2, 0.5, 1.0, and 2.0 ppb. All other photoresist sample concentrations were determined against this external calibration. Again, no ISTD was used. Concentrations obtained were corrected to account for the dilution factor. Detection limits for each element were obtained from the calibration curves.

The effectiveness of the external, matrix-matched calibration was gauged by spiking the photoresist sample with a multi-element standard at a concentration of 0.5 ppb and calculating recoveries. Figure 1 illustrates representative calibration curves in the matrix matched solution for Ti and Zn. Note the excellent linearity and superb precision that was obtained.



Mass Element: 47 Ti
Tune Step: 4
IS: ---
Units: ppb

Lv.	Conc.	Count/CPS	RSD %
1	0.00	7.05	P 24.80
2	2.00E-01	17.80	P 11.90
3	5.00E-01	39.40	P 7.29
4	1.00	68.70	P 7.54
5	2.00	132.00	P 4.88
* 6	---	---	---
* 7	---	---	---
* 8	---	---	---
* 9	---	---	---
* 10	---	---	---
* 11	---	---	---
* 12	---	---	---
* 13	---	---	---
* 14	---	---	---
* 15	---	---	---
* 16	---	---	---
* 17	---	---	---
* 18	---	---	---
* 19	---	---	---
* 20	---	---	---

Curve Fit: Y=aX+[blank]+bkg
r = 0.9998
Y = 6.223E+001*X +7.048E+000 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Mass Element: 64 Zn
Tune Step: 4
IS: ---
Units: ppb

Lv.	Conc.	Count/CPS	RSD %
1	0.00	665.00	P 4.00
2	2.00E-01	1010.00	P 5.32E-01
3	5.00E-01	1510.00	P 2.11
4	1.00	2600.00	P 1.45
5	2.00	4230.00	P 1.76E-01
* 6	---	---	---
* 7	---	---	---
* 8	---	---	---
* 9	---	---	---
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* 11	---	---	---
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* 15	---	---	---
* 16	---	---	---
* 17	---	---	---
* 18	---	---	---
* 19	---	---	---
* 20	---	---	---

Curve Fit: Y=aX+[blank]+bkg
r = 0.9987
Conc = 3.677E-001 ppb
Y = 1.808E+003*X +6.648E+002 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Figure 1. Photoresist matrix matched calibration curves for ^{47}Ti and ^{64}Zn. Helium gas mode was used for both measurements.

Data Acquisition

The photoresist sample was allowed to self-aspirate into the ICP-MS using standard 0.3-mm capillary tubing from the Integrated Autosampler (I-AS) – a clean autosampler designed specifically to avoid contamination at the sample introduction stage (product number G3160A). The integration time for each element was 1 s, except for Ti which was 3 s, with three replicate measurements. For the analysis of a suite of 35 elements per sample, the time required was 3.5 min per sample. However, a rinse step using PGME between samples is strongly recommended to prevent signal drift resulting from photoresist precipitation.

Results

Table 3 shows the detection limits (DL) obtained during this study, for the 1:10 diluted photoresist sample. DLs were calculated using three times the standard deviation (n = 7) of the raw counts of the photoresist divided by the slope of the calibration curve. Using the slope of the calibration curve, rather than counts obtained from a standard, takes into account any matrix suppression. The reported DL are fundamentally limited by the metal impurities in the solvent blank (B) that is, in PGME.

Table 3. **Three Sigma DL in Photoresist and Spike Recovery Data at 0.5-ppb Level for a Full Suite of Elements**

Element (mass)	Plasma power (W)	H_2 Gas flow (mL/min)	He Gas flow (mL/min)	Photoresist DL (ppb)*	Photoresist (A) (ppb)*	PGME (B) (ppb)	A - B (ppb)	Spike recovery (%) 0.5 ppb
Li (7)	1600	–	–	0.01	0.029	0.007	0.022	97
Be (9)	1600	–	–	0.004	0.003	0.003	<0.004	95
B (10)	1600	5	–	0.2	0.279	0.123	<0.2	87
Na (23)	1600	5	–	0.07	2.677	0.027	2.650	82
Mg (24)	1600	5	–	0.03	0.366	0.003	0.364	94
Al (27)	1600	5	–	0.03	0.217	0.019	0.198	93
K (39)	1600	5	–	0.04	1.220	0.059	1.201	93
Ca (40)	1600	5	–	0.02	0.328	0.023	0.269	96
Ti (47)	1600	–	4.5	0.1	0.113	0.008	<0.1	104
V (51)	1600	–	4.5	0.009	0.017	0.004	<0.009	99
Cr (52)	1600	5	–	0.04	0.732	0.001	0.728	97
Mn (55)	1600	5	–	0.004	0.025	0.019	0.024	94
Fe (56)	1600	5	–	0.07	2.317	0.051	2.298	98
Co (59)	1600	–	4.5	0.003	0.020	0.002	0.019	97
Ni (60)	1600	–	4.5	0.06	0.330	0.002	0.281	93
Cu (63)	1600	–	4.5	0.03	0.262	0.001	0.211	97
Zn (68)	1600	–	4.5	0.02	0.369	0.001	0.366	89
As (75)	1600	–	–	0.008	0.010	0.004	0.008	93
Sr (88)	1600	–	–	0.001	0.004	0.040	0.003	91
Zr (90)	1600	–	–	0.007	0.090	0.001	0.089	91
Nb (93)	1600	–	–	0.002	0.010	0.003	0.006	93
Mo (95)	1600	–	–	0.04	0.679	0.005	0.639	96
Ag (107)	1600	–	–	0.001	0.003	0.002	0.002	92
Cd (111)	1600	–	–	0.005	0.008	0.001	0.006	90
Sn (118)	1600	–	–	0.008	0.064	0.001	0.059	89
Sb (121)	1600	–	–	0.003	0.027	0.001	0.025	87
Ba (138)	1600	–	–	0.001	0.007	0.003	0.007	88
Ta (181)	1600	–	–	0.05	0.015	0.002	<0.05	89
W (182)	1600	–	–	0.006	0.032	0.002	0.029	87
Au (197)	1600	–	–	0.003	0.004	0.003	<0.003	86
Tl (205)	1600	–	–	0.001	0.005	0.002	0.003	88
Pb (208)	1600	–	–	0.005	0.019	0.002	0.016	87
Bi (209)	1600	–	–	0.001	0.001	0.003	<0.001	87
Th (232)	1600	–	–	0.0009	0.002	0.001	<0.0009	85
U (238)	1600	–	–	0.0006	0.000	0.001	<0.0006	86

*Photoresist sample was diluted 1:10 with PGME to give a 3% solution

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Table 3 also illustrates 0.5-ppb spike recoveries in 1:10 diluted photoresist for 35 elements. All data was acquired under normal plasma operating conditions that is, 1600W RF forward power. The spike recoveries are good, particularly for difficult elements such as B, Mg, Al, K, Ca, Ti, Cr, Fe, and Zn which suffer matrix and argon based interferences. The results highlight the effectiveness of the ORS for preventing polyatomic ions from reaching the detector.

A 2-hour stability study was performed by adding a 0.5-ppb standard into 1:10 diluted photoresist (3% resin) sample and repeatedly analyzing the spiked sample over a 2-hour period. Instrument stability over this period was excellent with %RSD values typically less than 3% for the majority of elements, despite the complex matrix. A stability plot for all elements is summarized in Figure 2.

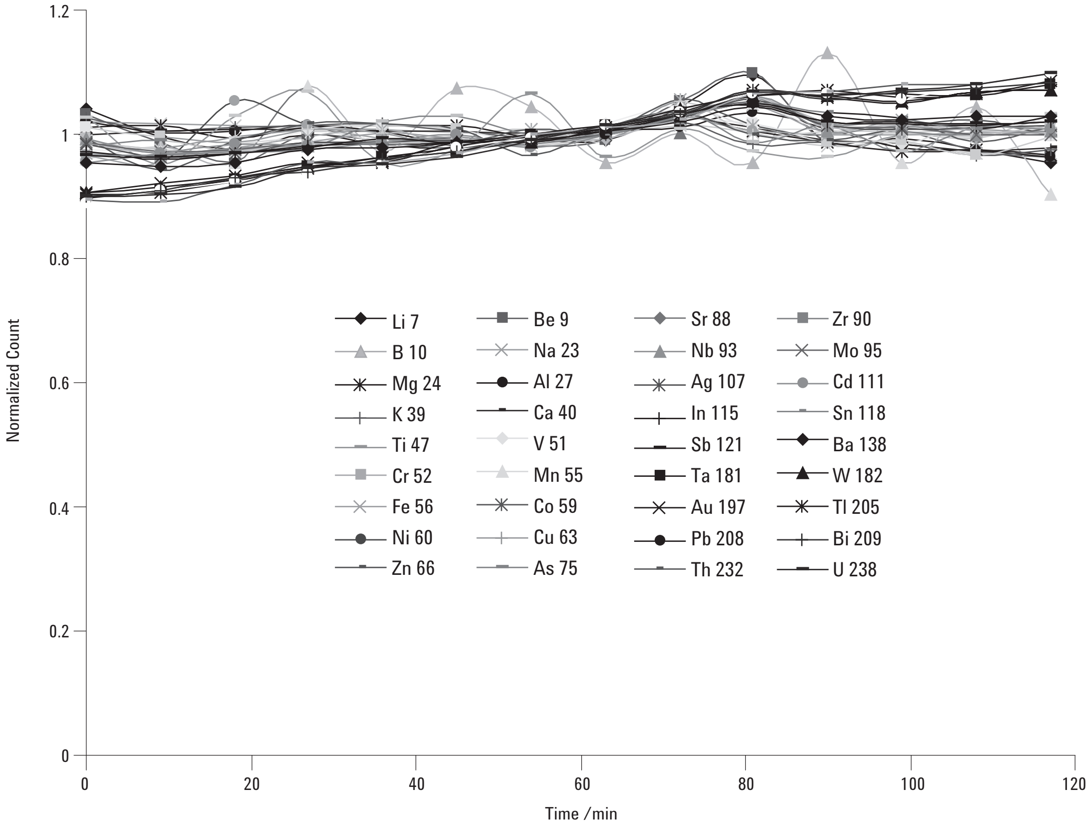

Figure 2. Two-hour stability plot for 35 elements in 3% photoresist sample.

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Conclusions

Reliable photoresist analysis can be carried out following simple dilution in a suitable solvent so long as the ICP-MS meets several key design considerations:

- The sample introduction system is optimized to handle high sample matrices over extended periods of time. This includes the use of low-flow nebulizers, cooling of the spray chamber and use of a torch injector designed to minimize sample deposition.
- A flexible gas-control mechanism is available to accommodate the need for oxygen addition when analyzing organic solvents.
- There is an effective reaction cell for elimination of polyatomic interferences while maintaining sufficient sensitivity for trace level analysis.

The Agilent 7500cs ICP-MS with ORS meets all of the design criteria outlined above. The results outlined in this application note demonstrate that:

- The optimized sample-introduction system in the 7500cs effectively breaks down the heavy-resist matrix (sample analyzed as 3% resins).
- The ORS eliminates matrix-based interferences on B, Mg, Al, Ti, Cr, and Zn, as well as Ar-based interferences on K, Ca, and Fe.

The combination of these two powerful features provides reproducible measurements of the key analytes at the levels required by the industry.

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Silicon and Other Materials

ICP-MS is used to assess metal contamination in silicon wafer substrates as well as that associated with layers and coatings applied to the silicon.

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Improvement of ICP-MS detectability of phosphorus and titanium in high purity silicon samples using the Agilent 8800 Triple Quadrupole ICP-MS

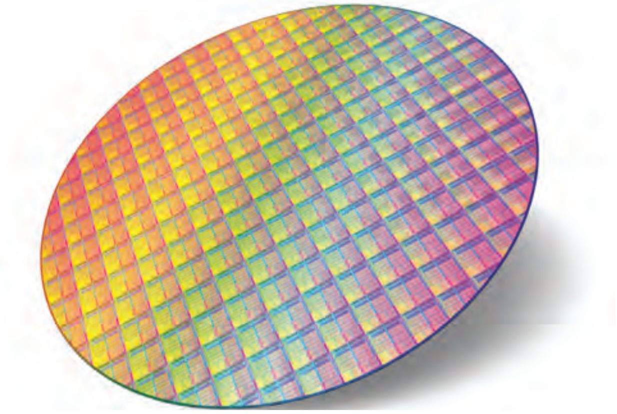
Application note

Semiconductor

Authors

Junichi Takahashi

Agilent Technologies, Tokyo, Japan



Introduction

In the past three decades monitoring and controlling metallic impurities in semiconductor device manufacturing has become increasingly important. During the period between 1983 and 1985, the first generation of commercial ICP-MS appeared on the market. These first generation ICP-MS systems had high enough sensitivity to determine many trace elements, such as Rare Earth Elements, uranium and thorium, which were free from interference, but could not determine important elements such as potassium, calcium, chromium and iron at low levels because of high background signals from interfering polyatomic ions.

In 1994 HP (Agilent) introduced the 4500 ICP-MS, which included the first reliable commercial implementation of cool plasma operation, and the analysis of trace alkaline and transition metals became possible. In fact, argon and argon-based polyatomic ions could be completely eliminated by

cool plasma technology, enabling ICP-MS to measure the complete suite of metals typically monitored in high-purity semiconductor chemicals. Due to the success of ICP-MS using cool plasma, it became a vital instrument in the field of semiconductor manufacturing. The main downside of cool plasma was its poor tolerance of high matrix samples, as the lower-power plasma suffered a greater degree of ionization suppression compared to normal "hot" plasma conditions. Cool plasma is not ideal for the routine analysis of high-matrix samples, as the less efficient decomposition of the matrix also leads to more deposition of material on the interface cones and ion lens. The development of collision/reaction cell (CRC) technology in quadrupole ICP-MS (ICP-QMS) offered an alternative means to remove the intense polyatomic backgrounds. Hydrogen or ammonia reaction gas is introduced into the cell to neutralize the argon and argon-based polyatomic ions, as a result of which, trace Ca and Fe can be determined even under a hot plasma conditions. Moreover, helium collision mode can be utilized to reduce or remove other (matrix-based) polyatomic ions, eliminating sulfur- and chlorine-based interferences on other key semiconductor analytes.

However, even the performance of collision/reaction cell is not sufficient for some of the most intense and problematic interferences on the analytes considered "difficult" by ICP-QMS. Analysis of phosphorus and titanium in silicon-rich samples is an example where improved performance is required. Phosphorus is monoisotopic at *m/z* 31 and a high silicon matrix will lead to a polyatomic ion $^{30}SiH^+$ which interferes with $^{31}P^+$. Surface layer contamination of silicon wafers is measured using an etch with HF vapor known as VPD (vapor phase decomposition), and samples prepared in this way usually contain both Si and HF. In this matrix, Si will form the polyatomic ions SiF^+ as well as SiO^+, making trace analysis of Ti in VPD samples nearly impossible because of the interferences from:

- $^{30}Si^{16}O^+$ on $^{46}Ti^+$
- $^{28}Si^{19}F^+$ on $^{47}Ti^+$
- $^{29}Si^{19}F^+$ and $^{30}Si^{18}O^+$ on $^{48}Ti^+$
- $^{30}Si^{19}F^+$ on $^{49}Ti^+$

ICP-QMS with reaction gas mode does not offer a reliable solution to these interferences, because all ions from the sample enter the reaction cell, and so multiple polyatomic ions are created from all the matrix components and other (variable) analytes present in the sample. If any component of the sample changes, the product ions created in the cell will also change, so new and unpredictable overlaps are created.

The development of triple quadrupole ICP-MS technology finally solves these problems, as MS/MS mode controls the reaction processes in the cell, allowing reaction cell gases to be used reliably and routinely. Phosphorus reacts with hydrogen to produce $^{31}PH_4^+$ which is detected at *m/z* 35 by the second quadrupole mass analyzer (Q2). Any previously existing ions present as *m/z* 35 will already have been excluded by the first quadrupole (Q1), which is set to allow transmission of only ions at *m/z* 31. An alternative method for measuring P in high Si matrix utilizes oxygen reaction gas. Q1 is set to *m/z* 31 to allow $^{31}P^+$ into the cell. $^{31}P^{16}O^+$ product ion is produced in the cell by reaction with the O_2 cell gas, and is detected by Q2 which is set to *m/z* 47. $^{30}SiH^+$ which also occurs at *m/z* 31 will also pass through Q1 and enter the cell, but SiH^+ does not react with oxygen in the cell and thus will not produce a $SiOH^+$ product ion that interferes with $^{31}P^{16}O^+$. Oxygen cell gas can also be used for titanium determination using the same reaction principle. Q1 will transmit $^{48}Ti^+$ and any isobaric interfering ions at *m/z* 48 such as SiF^+. Only the titanium ions react with oxygen to produce TiO^+, which can be detected free from overlap by Q2 which is set *m/z* 64. In this report, such methodology and figures of analytical merit of the Agilent 8800 Triple Quadrupole ICP-MS with MS/MS capability are described with regard to metallic impurity analysis of Si rich samples.

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Experimental

Sample preparation

In a VPD scanner, a solution droplet is scanned across the wafer surface to collect the surface contaminants dissolved from the Si matrix by the HF vapor. The scan droplet is usually composed of HF and H_2O_2, and contains a matrix of dissolved Si, the concentration of which is dependent upon the nature of the oxide layer on the Si wafer. The thickness of the silicon oxide layer on a naturally oxidized wafer is less than 1 nm and the resultant scan solution contains 20 to 30 ppm Si at the most. In contrast, a thermally oxidized silicon wafer has a much thicker silicon oxide layer, and the Si concentration in the VPD scan droplet may reach levels up to 2000 ppm in the final solution. We prepared solutions by dissolving bulk silicon to simulate those two types of VPD samples. Approximately 3 g of silicon pieces were cut from a silicon wafer and thoroughly cleaned with 1:1 HCl/HNO_3. After rinsing with ultra-pure water (UPW), pieces were cleaned with HF and re-rinsed with UPW. This process was repeated twice. The silicon pieces were then dissolved with 40 mL each of 38% HF and 68% HNO_3 in a lightly capped PFA bottle. UPW was added to make 3% Si stock solution from which 30 ppm Si and 2000 ppm Si final matrix solutions were prepared by further diluting with UPW. Therefore, beside silicon and its impurities, the sample solutions contain a high concentration of nitric and hydrofluoric acids.

Instrumentation

Instrument, peripherals and major operating parameters are described below. Because the sample volume of a VPD scan droplet is usually limited to as low as 0.5 mL, an ultralow uptake nebulizer was used. The number of tune modes was also minimized to reduce the total analytical time.

- ICP-MS: Agilent 8800 Triple Quadrupole ICP-MS
- Nebulizer: C-flow 50 PFA nebulizer (uptake volume: 45 µL/min)
- Inert sample introduction system: PFA spray chamber, end cap and connector tube; demountable torch with 2.5 mm internal diameter (i.d.) sapphire injector
- Interface: Pt sampling cone and Pt/Ni skimmer cone
- Reaction cell gases: Oxygen and hydrogen
- Standard solution: Pre-mixed standard solution from SPEX Corporation
- Phosphorus and sulfur standards were prepared from semiconductor grade phosphoric acid and sulfuric acid, respectively

Table 1. Agilent 8800 ICP-QQQ tuning conditions

			Low Si Conc Tuning			**High Si Conc Tuning**		
	Tune step		Cool	No gas	O_2	No gas	H_2	O_2
	Stabilization time	sec	5	30	15	5	15	15
	Scan mode		MS/MS			MS/MS		
Plasma								
	RF power	W	600	1600		1600		
	Sample depth	mm	18	8		8		
	Carrier gas	L/min	0.7	0.7		0.7		
	Makeup gas	L/min	0.95	0.56		0.58		
Lenses								
	Extract 1	V	-180	5		0		
	Extract 2	V	-14	-250		-250	-235	-205
Cell								
	He flow	mL/min	-	-	3	-	-	3
	H_2 flow	mL/min	0.5	-	-	-	10	-
	O_2 flow	mL/min	-	-	0.5	-	-	0.5
	OctP bias	V	-18	-8	-20	-8	-25	-20
	KED	V	13	-20	-20	-20	-5	-20

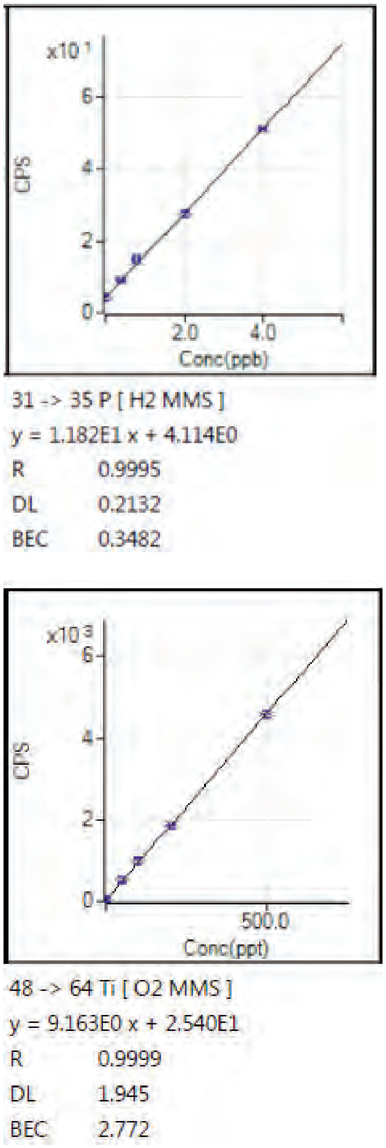
Cool plasma conditions can be used successfully for low concentration silicon sample analysis, delivering superior BEC and DL for several elements with low ionization potential. However cool plasma conditions accelerate silicon dioxide crystal deposition on the skimmer cone if used during the analysis of high concentration Si matrix samples. It is not recommended to use cool plasma when the Si concentration is higher than 50 ppm in the sample solution. In order to improve the detection of some elements, particularly Ca, in cool plasma mode, a small flow of hydrogen was added to the cell [1].

Analysis of high matrix samples, such as 2000 ppm Si solution, requires a robust tuning for best long-term stability. In addition to high plasma power, the lens setting can also be optimized for matrix tolerance by applying 0 volts to the first extraction lens. With a slight sacrifice of sensitivity, less signal suppression and better long term stability are obtained. Ion lens voltages except those in Table 1 were all optimized by the auto-tune function of the instrument.

Results

Calibration plots for the challenging elements P and Ti, measured in the optimum MS/MS mode in 2000 ppm Si sample, are given in Figure 1. P was measured in H_2 reaction mode (product ion PH_4^+ at *m/z* 35), while Ti was measured in O_2 reaction mode (product ion TiO^+ at *m/z* 64). P can also be measured in O_2 reaction mode (product ion PO^+ at *m/z* 47). Preliminary tests showed that O_2 mode provided BEC of 5.86 ppb, while H_2 mode yielded a significantly lower BEC of 0.35 ppb.

In addition to the two difficult elements P and Ti discussed above, a full suite of elements of interest in the semiconductor industry was also measured in the Si matrix samples. Results for DL and BEC for all analytes are shown in Tables 2 and 3. These results were calculated from standard addition curves generated by spiking the multi-element standard into the 30 ppm and 2000 ppm Si matrix solutions. The acid concentration in all cases was 3.8% HF and 6.8% HNO_3. It is worth noting that a common scanning solution of VPD contains 2% HF and 2% H_2O_2, but no HNO_3. However, this experiment required the use of HNO_3 with HF to dissolve the bulk Si wafer. Even after dilution in UPW, the final concentration of acid was several percent. It is well known that HNO_3 increases the background counts at mass 31 and accelerates SiO_2 deposition on the skimmer cone. Therefore, it should be noted that the experimental conditions applied here are more severe than actual VPD sample analysis.



31 -> 35 P [H2 MMS]

y = 1.182E1 x + 4.114E0

R	0.9995
DL	0.2132
BEC	0.3482

48 -> 64 Ti [O2 MMS]

y = 9.163E0 x + 2.540E1

R	0.9999
DL	1.945
BEC	2.772

Figure 1. Calibration curve of P (MS/MS; H_2 mode) and Ti (MS/MS; O_2 mode) in 2000 ppm Si sample

Table 2. DL and BEC of elements in 30 ppm Si solution (ppt except S, ppb)

Element	Mass	Tune	DL	BEC
Li	7	Cool	0.01	0.01
Be	9	No gas	0.93	0.18
B	11	No gas	11	29
Na	23	Cool	0.09	0.94
Mg	24	Cool	0.47	0.17
Al	27	Cool	1.7	0.63
P	31/35	H_2	110	210
S	34/50	O_2	2.1	34
K	39	Cool	1.0	1.7
Ca	40	Cool	3.0	1.1
Ti	48/64	O_2	0.90	0.70
V	51/67	O_2	0.34	1.7
Cr	52	Cool	1.7	0.72
Mn	55	Cool	0.01	0.01
Fe	56	Cool	1.9	1.2
Co	59	Cool	0.01	0.01
Ni	60	O_2	1.0	1.0
Cu	63	O_2	2.8	8.8
Zn	64	O_2	5.2	19
Ga	71	Cool	0.01	0.01
Ge	74/90	O_2	5.3	4.1
As	75/91	O_2	4.5	12
Se	78/94	O_2	6.2	6.3
Rb	85	Cool	0.36	0.90
Sr	88	Cool	0.01	0.01
Zr	90/106	O_2	0.01	0.01
Nb	93/125	O_2	0.40	0.08
Mo	98/130	O_2	1.5	1.3
Ru	101	No gas	0.63	1.1
Rh	103	O_2	0.64	8.1
Pd	105	O_2	1.6	0.43
Ag	107	Cool	0.01	0.01
Cd	114	O_2	0.01	0.01
Sn	118	O_2	1.1	1.1
Sb	121	O_2	0.79	0.33
Te	125	O_2	2.4	0.80
Cs	133	Cool	0.01	0.01
Ba	138	O_2	0.01	0.01
Hf	178/194	O_2	0.01	0.01
Ta	181/213	O_2	0.26	0.09
W	182/214	O_2	1.8	0.50
Re	185	No gas	0.21	0.06
Ir	193	No gas	0.20	0.31
Pt	195	O_2	1.6	1.2
Au	197	O_2	0.45	0.09
Tl	205	No gas	0.36	0.21
Pb	208	Cool	0.01	0.01
Bi	209	No gas	0.04	0.01
Th	232/248	O_2	0.01	0.01
U	238/254	O_2	0.02	0.01

Long term stability over three hours of continuous analysis was confirmed for 2000 ppm Si solution. In Figure 2, typical examples of phosphorus (4 ppb), sulfur (40 ppb) and titanium (500 ppt) signal plot are shown.

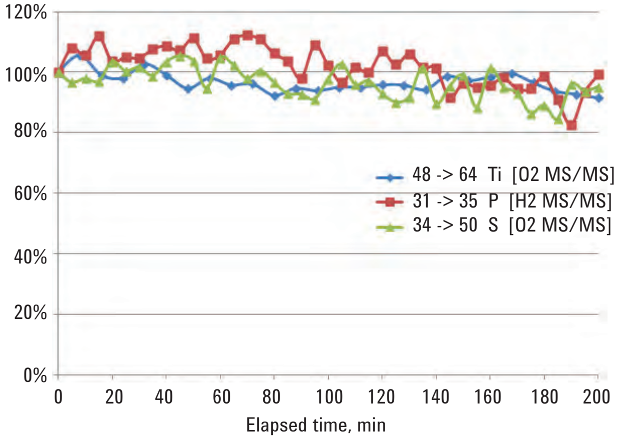


Figure 2. Three hour long-term stability test for 2000 ppm Si sample

Conclusions

MS/MS mode on the Agilent 8800 ICP-QQQ was shown to be very useful and effective for the determination of P, Ti, and other trace elements in high purity silicon matrices of different concentrations (30 ppm and 2000 ppm). Very low BECs and DLs could be realized for all elements, and MS/MS mode ensured reliable separation of the target product ions from potential overlapping product ions from other analytes. This capability is unique to MS/MS mode on the 8800 ICP-QQQ. Even by using an ultra low flow nebulizer, excellent sensitivity and low DLs were obtained, and good signal stability was demonstrated over a three hour testing period for the 2000 ppm Si sample.

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Verified for Agilent
8900 ICP-QQQ

Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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Trace Elemental Analysis of Trichlorosilane by Agilent 7700s/7900 ICP-MS

Application note

Semiconductor analysis

Author

Junichi Takahashi

Agilent Technologies
Tokyo, Japan

Abstract

Metallic impurities in trichlorosilane (TCS), an intermediate product used in the production of photovoltaic (PV) silicon, must be strictly controlled in order to produce the high purity PV silicon necessary for the manufacture of solar cells. A successful analytical method was developed, featuring measurement of impurities in TCS by an Agilent 7700s/7900 ICP-MS, following a sample preparation approach developed by Agilent. A spike recovery test demonstrated the validity of the method for 33 elements including boron and phosphorus, and two TCS samples were also analyzed. The ability to analyze TCS allows PV silicon manufacturers to check the TCS intermediate chemical for metallic impurities prior to the manufacture of PV silicon.

Introduction

The search for alternative energy resources is continuing due to the exhaustion of natural fossil fuel resources and their contribution to global warming, together with associated geological, environmental, and political concerns. Among the many alternative methods of generating electricity, solar power or photovoltaic (PV) is a booming industry with enormous increases in capacity each year. Photovoltaic panels, which are generally silicon wafer-based, convert energy from the sun into electricity, but the efficiency of this process is relatively low. Improving conversion efficiency and reducing production costs are key goals within the industry. The metallic impurity level in the polycrystalline silicon (polysilicon) used in the manufacture of the wafers that go into the PV panels must be strictly controlled, as impurities degrade the conversion efficiency. An effective method for the analysis of PV grade silicon by ICP-MS has already been developed by Agilent [1]. In an effort to further increase device efficiency, PV silicon manufacturers want to measure impurities in the chemicals used in the manufacture of polysilicon. This application note describes the use of the Agilent 7700s/7900 ICP-MS with Octopole Reaction System (ORS) for the analysis of TCS. TCS is commonly used in the manufacture of ultrapure polysilicon.

Experimental

Instrumentation

A standard Agilent 7700s ICP-MS was fitted with an Agilent Inert Sample Introduction kit. The kit consisted of a PFA concentric nebulizer, PFA double pass spray chamber and a demountable torch with 2.5 mm inner diameter platinum injector.

The 7700s/7900 ICP-MS have a wide range of available interference removal technologies. In addition to conventional no gas mode, the 7700s/7900 can be operated in cool plasma mode and in ORS mode, which provides effective interference removal in both collision mode using an inert cell gas (He), and in reaction mode using a reactive cell gas (such as H_2). The 7700/7900 ICP-MS includes an ORS cell that features a longer, smaller internal diameter octopole, operating at higher frequency than in previous ORS versions. The ORS can also be operated at higher cell gas flow rates and with higher bias voltages, which promotes greater collision energy. In combination, these features give improved interference removal efficiency in both collision and reaction modes.

The interference removal approach is selected depending on the analytical requirement. For this application, ultimate sensitivity is required for all analytes and therefore the most effective interference removal mode is required for every analyte/interference. A data acquisition protocol featuring four steps was used, and all instrument operating parameters are given in Table 1. During method development, some analytes were run in multiple modes, and the mode that gave the best detection limits in the sample matrix was determined for each analyte.

Table 1. ICP-MS operating conditions.

	Method step			
	Step 1	**Step 2**	**Step 3**	**Step 4**
Plasma	Cool	Normal		
RF power (W)	600	1600		
Sample uptake rate (µL/min)	~160 (free aspiration)			
Sampling depth (mm)	16	8		
Carrier gas flow rate (L/min)	0.7			
Makeup gas (L/min)	0.8	0.5		
He cell gas flow rate (mL/min)	0		5	2
KED (V)	13	3		135

Analytes:		
	Step 1	^{7}Li, ^{23}Na ^{24}Mg, ^{27}Al, ^{39}K, ^{40}Ca, ^{55}Mn, ^{56}Fe, ^{63}Cu, ^{71}Ga
	Step 2	^{10}B, ^{138}Ba, ^{178}Hf, ^{181}Ta, ^{182}W
	Step 3	^{48}Ti, ^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{64}Zn, ^{75}As, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{114}Cd, ^{118}Sn, ^{121}Sb, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U
	Step 4	^{31}P

The analytes measured in each step in the final method are also shown in Table 1. Step 1 employed cool plasma mode, and all remaining steps used normal or hot plasma. Step 2 used conventional no gas mode, Step 3 used He collision mode, and Step 4 was a modified He collision mode optimized for phosphorus determination. In the past, P has been measured indirectly as $^{31}P^{16}O$ at *m/z* 47, using cool plasma or O_2 cell gas. The improved

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performance of the ORS enables a greater reduction of the interferences $^{15}N^{16}O$ and $^{14}N^{16}O^{1}H$ that overlap P at mass 31, lowering the detection limit of P in He collision mode by a factor of 50, and making direct measurement of P possible at the required levels. Switching between modes is fully automated and all analytes were measured with a single visit to the sample vial, which helps to minimize sample contamination. The small size of the ORS cell allows for very fast switching between modes, so the additional time required for multimode operation is minimized. The total analysis time was eight minutes per sample.

Sample preparation

Trichlorosilane (TCS) is an intermediate compound used in the manufacture of high purity polysilicon. Since TCS is a volatile liquid that can easily be purified by distillation, it can be made from low-grade metallurgical grade silicon, purified, and then converted to high purity polysilicon. TCS is liquid at room temperature with high volatility (BP 31.8 °C). It easily decomposes to SiO_2 in air by hydrolysis, as shown below:

$$SiHCl_3 + 2H_2O \rightarrow SiO_2 + 3HCl + H_2$$

The direct sampling and on-line ICP-MS analysis of TCS in the manufacturing line is not feasible, because SiO_2 would deposit in the transfer tube and on the ICP-MS sample introduction and interface components. In addition, TCS must be chilled and handled in an inert environment to avoid evolution of HCl gas, and so an ICP-MS inside a clean mini-environment would need to be installed at each sampling point. The only practical approach is therefore to transfer liquid TCS to the lab for analysis. In this work, liquid TCS was transferred to a clean laboratory following appropriate safety precautions, and analyzed after careful sample preparation using the following procedure: Liquid TCS was converted to SiO_2 via gentle hydrolysis in an inert gas atmosphere, dissolved in HF solution and Si removed (as SiF_4 gas) by heating to dryness. The dry residue was then re-dissolved in 0.4% HCl solution before analysis by ICP-MS.

WARNING **Chemical Hazard**

As with all sample preparation methods that utilize HF, use great care when handling the acid. Use all appropriate personal protective equipment and follow all appropriate safety procedures.

For more information of safe handling of TCS, please contact your local Agilent Applications team.

Calibration standards

External calibration in a matrix of 0.4% HCl was used for quantification of the trace elements. Since the Si matrix is removed during the sample preparation, the sample residue re-dissolved in 0.4% HCl, is essentially free of any matrix. Four multielement calibration standard solutions were prepared at 0, 1, 2, and 5 ppb in 0.4% HCl. No internal standardization was used, to avoid the possibility of adding contamination.

Results and Discussion

Detection limits

Detection limits (DLs) were calculated from 3 sigma of the calibration blank and are shown in Table 2. Low ppt DLs for V and As demonstrate the efficient removal of the ClO (on ^{51}V) and ArCl (on ^{75}As) polyatomic interferences in the HCl matrix. Also the phosphorus DL of 0.1 ppb shows the effectiveness of the optimized He collision mode parameters used in Step 4 for the removal of NO/NOH on P. DLs in the original sample were also calculated, by multiplying by a dilution factor of 7.5*, and all DLs were under 1 ppb in the original TCS sample.

Quantitative analysis

Table 2 also shows the results from the quantitative analysis of two TCS samples, after reagent blank subtraction. Sample A was a high purity TCS sample obtained from a semiconductor company and stored in a glass vial. Sample B was also obtained from a semiconductor company, but shipped in a stainless steel pressure vessel.

As is clearly shown in Table 2, Sample B contained significantly higher levels of Fe, Ni and Cr than Sample A, indicating metallic contamination from the steel container. Sample A was found to be of high purity with only four elements above 1 ppb in the original sample.

Table 2. Detection limits and quantitative analysis.

m/z	Element	DL (final solution) (ppb)	DL (original sample) (ppb)	Analysis — Sample A (ppb)	Analysis — Sample B (ppb)
7	Li	0.0003	0.002	0.007	0.007
10	B	0.08	0.60	1.4	5.5
23	Na	0.002	0.01	0.53	15
24	Mg	0.001	0.010	2.5	1.4
27	Al	0.006	0.04	0.75	8.5
31	P	0.1	0.7	2.7	4.2
39	K	0.02	0.15	0.23	3.6
40	Ca	0.006	0.05	0.83	26
48	Ti	0.001	0.008	0.08	2.3
51	V	0.008	0.06	0.08	0.6
52	Cr	0.02	0.12	0.12	22
55	Mn	0.001	0.008	0.01	1.6
56	Fe	0.01	0.08	1.9	180
59	Co	0.0001	0.001	0.02	0.3
60	Ni	0.001	0.008	0.08	14
63	Cu	0.002	0.01	0.08	0.8
64	Zn	0.001	0.01	0.38	3.5
71	Ga	0.001	0.006	0.01	0.03
75	As	0.02	0.14	0.14	0.02
88	Sr	0.0001	0.0004	0.01	0.1
90	Zr	0.0002	0.001	0.08	1.0
93	Nb	0.0002	0.001	0.007	0.02
98	Mo	0.0003	0.002	0.08	1.3
107	Ag	0.004	0.03	0.03	0.02
111	Cd	0.0001	0.001	0.007	0.04
118	Sn	0.003	0.02	0.38	1.7
121	Sb	0.001	0.01	0.08	0.5
138	Ba	0.0002	0.002	0.007	1.4
181	Ta	0.0001	0.0004	0.007	0.2
182	W	0.0003	0.002	0.007	0.3
208	Pb	0.0002	0.002	0.007	0.8
232	Th	0.0001	0.001	0.007	0.007
238	U	0.0001	0.0002	0.007	0.007

Recovery test

In order to test the recovery efficiency of the method, and in particular to check for loss of volatile elements during the sample preparation procedure, a high purity sample of TCS was purchased (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan). The TCS sample was divided into four aliquots, each containing 1.5 g of TCS, and sample preparation was performed as previously described. After hydrolysis and HF addition, but prior to the heating step to remove Si, one of the aliquots was spiked at the 5 ppb level with a multielement standard (Spex, Metuchen, NJ, USA). The samples were then evaporated to dryness and the dry residue was taken up in 0.4% HCl and analyzed. Figure 1 shows the recoveries achieved for the 5 ppb spiked sample. All elements gave good recoveries, including B, which can be problematic due to its volatility, demonstrating the validity of both the sample preparation and analytical methods.

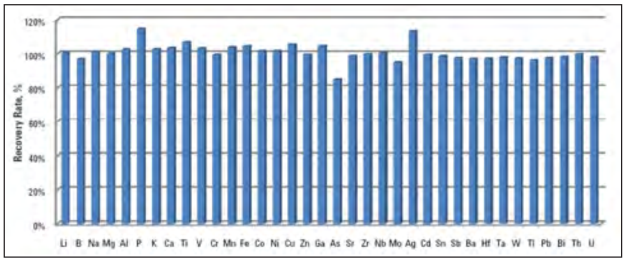

Figure 1. 5 ppb spike recovery test in TCS, confirming no loss of volatile elements during sample evaporation, and accurate recovery (between 80 and 120%) for all analytes.

Conclusions

Trichlorosilane has been successfully analyzed using the Agilent 7700s ICP-MS, following a sample preparation approach developed by Agilent. The ORS cell improves He collision cell performance significantly, achieving a DL of 0.1 ppb for phosphorus from a direct measurement at *m/z* 31. A spike recovery test demonstrated the validity of the sample preparation and analytical methods for all elements including boron. The ability to analyze TCS allows PV silicon manufacturers to check the TCS intermediate product for metallic impurities prior to the manufacture of PV silicon.

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7900 ICP-MS
Semiconductor configuration

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Characterization of Surface Metal Contamination on Silicon Wafers Using Surface Metal Extraction Inductively Coupled Plasma Mass Spectrometry (SME-ICP-MS)

Semiconductor

Authors

Tom Gluodenis
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

Surface Metal Extraction (SME) can be combined with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to characterize trace metal contaminants on a silicon wafer surface. Wafer sample preparation and analysis can be performed in less than 20 minutes thus allowing real time wafer production monitoring. Detection levels determined using this technique exceed the requirements for surface metallic contamination specifications for the year 2009.

Introduction

The current industry trend is toward the manufacture of semiconductor devices which exhibit faster operational speeds, smaller feature sizes, larger scales of integration, and lower manufacturing costs from yield enhancements and defect reduction. As device features continue to shrink to satisfy these goals, the need to characterize trace metal contamination on silicon wafer surfaces becomes more important. Contamination currently accounts for over 50% of the yield losses in semiconductor IC device manufacturing.

Surface contamination concentration techniques such as SME-ICP-MS have been used to determine the purity of both the native and thermal oxide layer on silicon wafers. This analysis can provide valuable information on the type, the source, and the levels of metallic contamination at almost every processing step in semiconductor manufacturing. Advantages of SME-ICP-MS include accurate analysis of up to 40 elements in a single droplet, excellent detection limits (part per trillion and sub part per trillion) and a 20-minute turn-around time for wafer preparation and analysis. These features of the SME-ICP-MS technique make it uniquely suited to perform real time wafer production monitoring.

The SME-ICP-MS application is particularly challenging due to the small sample volume, silicon rich matrix, and ultra-trace levels at which metal contaminants need to be measured. The instrument used in this application was an Agilent 7500s ICP-MS equipped with a MicroFlow nebulizer operating at 20uL/min. The exceptional sensitivity characteristic of the Agilent 7500s ICP-MS was

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further enhanced by operating the instrument in the soft extraction mode[1,2]. This mode of operation leverages the unique twin extraction lens design of the 7500s to apply a slight positive voltage to the first extraction lens. This counter-intuitive optimization procedure dramatically reduces the background across the entire mass range without any sacrifice in sensitivity. The result is a 10 to 100 fold increase in the signal-to-background ratio for most elements.

Potentially troublesome argon polyatomic ions were virtually eliminated using Agilent's exclusive ShieldTorch System (STS). Unlike traditional cool plasma conditions which require plasma powers of 500 – 550W, the Agilent 7500s is able to effectively eliminate argon based polyatomic interferences while operating at higher, more robust plasma conditions. This is primarily due to the 27.12 MHz generated, higher temperature plasma which promotes more efficient sample matrix dissociation and hence, higher sensitivity relative to cooler 40.68MHz generator designs. Also, the STS is highly efficient at reducing the plasma potential to approximately 1 eV – significantly lower than with non-shield plasma locking devices. This leads to better ion focusing and more efficient interference removal thereby alleviating the need for sample pretreatment or complex scanning reaction/collision cell technologies.

The use of a MicroFlow nebulizer, Peltier cooled spray chamber, wide bore torch injector, and highly efficient 27MHz plasma generator ensured complete ionization of the sample matrix thereby eliminating concerns regarding analytical stability. In addition, the flat mass response curve of the robust Omega II ion lens system resulted in efficient transmission of the analyte ions to the quadrupole mass filter with the same high sensitivity across the entire mass range. Combined, these design features minimized ion suppression resulting from the silicon rich sample matrix thereby eliminating the need for MSA (method of standard additions), matrix matching, or internal standards which could potentially contaminate the samples undergoing ultra-trace analysis.

METHODOLOGY

Sample Preparation

The silicon wafer was placed in a cleaned PTFE chamber and exposed to HF to dissolve the SiO_2 surface layer. The wafer surface was then scanned with a 250 uL extraction droplet. This can be done manually or with an automated wafer scanner. The extraction droplet collects the contents of the dissolved silicon layer as it is moved across the wafer surface. The extraction droplet was then pipetted from the wafer surface, deposited into an autosampler, and analyzed by ICP-MS. The calibration blank and standards used in this study were prepared at 0, 100, 250 and 500 ppt in 5% HF and 6% H_2O_2.

High purity silicon was cleaned in HF and peroxide then dissolved in 10g HF (49%), 18g H_2O_2 (30%), and 72g of UPW. Note that some small degree of metals contamination may be present from the silicon, which has gone through all the manufacturing steps from crystal growth through wafer thermal processing. This final solution, containing 0.59ppm Si (verified independently) was used as a synthetic SME matrix to determine spike recoveries. A synthetic matrix was used rather than an actual SME droplet due to the difficulties associated with spiking into a small sample volume without diluting the sample matrix. This method of sample preparation offers a much more rigorous test of instrument performance than simply spiking a standard solution of Si.

ICP-MS Analysis

An Agilent 7500s ICP-MS equipped with the ShieldTorch System and a Micro Flow nebulizer was used for this analysis. The sample was self-aspirated at an uptake rate of 20 uL/min. Instrument operating conditions are given in Table 1.

Table 1. ICP-MS operating conditions

Parameter	STS Conditions	Soft Extraction Conditions
RF Power	800W	1540 W
Sampling Depth	14.2 mm	9.2 mm
Carrier Gas Flow	0.8 L	1 L
Makeup Gas Flow	0.75 L	0 L
Extraction Lens 1	- 152 V	+ 4 V
Extraction Lens 2	- 22 V	- 46 V

Switching between STS conditions and soft extraction mode is completely automated using Agilent's Multi-tune software. Multi-tune allows complete data collection in a single acquisition, with a single visit to the sample vial, thereby saving time and reducing the potential for sample contamination. In addition, all resulting data is compiled in a single report. Stabilization time in switching between operating modes is minimal with only 20 seconds required when switching from soft extraction to STS conditions. The stability of switching between operating modes over prolonged periods has been previously demonstrated to be

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stable to approximately 3% RSD over an 8 hour period of time[3].

Three sigma detection limits were determined using the constructed calibration curve. A synthetic SME sample matrix containing 5% HF, 6% H_2O_2, and 0.59 ppm silicon (typical of native oxide layers – the most common application of SME) was analyzed to evaluate the magnitude of any physical or spectral interferences arising from the matrix. The synthetic SME matrix was then spiked with a multielement standard at a concentration of 10ppt. The spiked and unspiked matrix droplets were analyzed and spike recoveries calculated.

Results and Discussion

The results shown in Table 2 show detection limits for a standard suite of semiconductor elements both in the calibration matrix and in the simulated SME matrix. Note the exceptional performance even for more difficult elements such as Ca, K, and Fe. A small trace of Co was observed in the calibration matrix and this has biased the result for this particular element high; however, at 1.38ppt, this remains well within industry guidelines. All other elements, including Co in the high silicon matrix, return sub-ppt detection limits. Also note that these results were obtained with a 20 uL/min sample uptake rate and that the detection would be improved even further if the more common 100 uL/min MicroFlow Nebulizer were used. Representative calibration curves are given in Figure 1.

Table 2. Detection limits (parts per trillion) in the SME matrix

Element	Mass	No Silicon 7500 DL (ppt)	0.59 ppm Silicon 7500 DL (ppt)	450 mm Wafer DL (atoms/cm2)	NTRS 2009 Requirements
Li	7	0.03	0.02	4.1 E5	<1.0 E11
Na	23	0.20	0.27	8.2 E5	<2.5 E9
Mg	24	0.17	1.00	6.6 E5	<1.0 E11
Al	27	0.05	0.16	1.8 E5	<1.0 E11
K	39	0.57	3.3	1.4 E6	<2.5 E9
Ca	40	0.26	0.97	6.1 E5	<2.5 E9
Cr	52	0.04	0.81	7.3 E4	<2.5 E9
Mn	55	0.02	0.18	3.4 E4	<2.5 E9
Fe	56	0.3	0.95	5.1 E4	<2.5 E9
Co	59	1.4	0.58	2.2 E6	<2.5 E9
Ni	60	0.74	1.0	1.2 E6	<2.5 E9
Cu	63	0.25	0.14	3.7 E5	<2.5 E9
Zn	68	0.86	3.0	1.2 E6	<2.5 E9
Zr	90	0.22	0.27	2.3 E5	NA
Sn	118	0.29	0.48	2.3 E5	NA
Ta	181	0.03	0.04	1.6 E4	NA
Au	197	0.09	0.12	4.3 E4	NA
Pb	208	0.02	0.09	9.1 E3	NA

A comparison of the detection limits measured in the calibration matrix with that obtained in the SME synthetic matrix exhibits no significant differences. These results highlight the effectiveness of the ShieldTorch interface in effectively removing matrix-based polyatomic interferences while efficiently ionizing elements with high ionization potentials, such as Zn, in the high silicon matrix. Further evidence of the effectiveness of the ShieldTorch System in eliminating matrix based interferences without loss of sensitivity has been documented previously by Howard et. al in which the authors demonstrated quantitative recovery of a 495ppt multielement spike solution in SME matrices containing 100, 250, 500, and 1000 ppm silicon[4].

If there were a loss of plasma ionization energy due to the SME sample matrix, poor spike recoveries would be expected. Elements with a high ionization energy, such as Zn, would show the greatest signal loss and the lowest spike recovery. The results given in Table 3 demonstrate excellent spike recoveries for all elements, therefore indicating negligible plasma ionization suppression from the SME sample matrix. The quantitative recovery also indicates the absence of any nebulization or transport interferences. Note: all recoveries were determined without the use of an internal standard therefore simplifying sample preparation and eliminating a potential source of contamination.

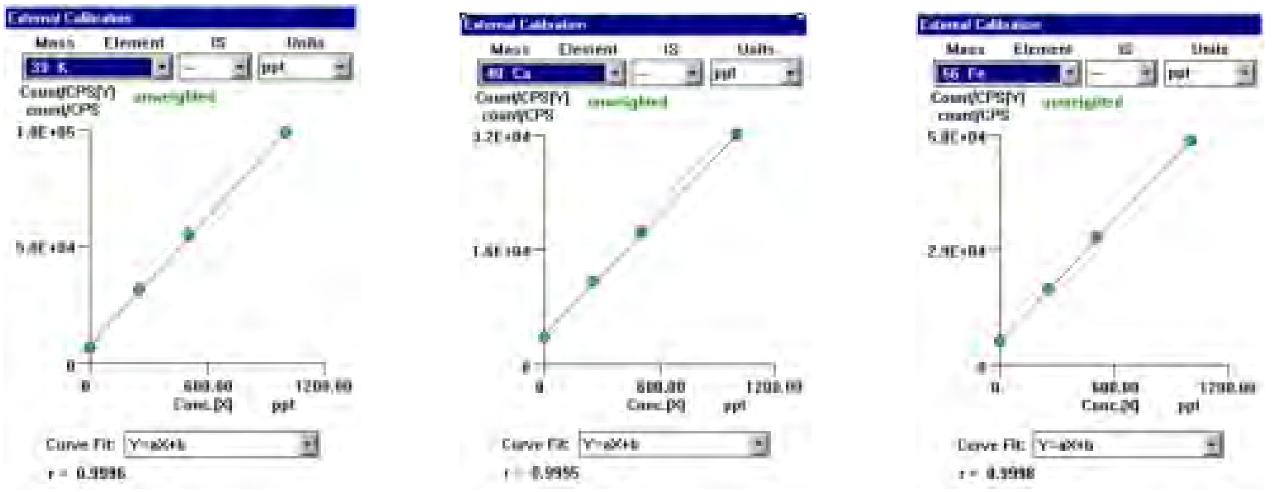

Figure 1. Representative calibration curves for K, Ca and Fe at 0, 250, 500 and 1000 ppt

Table 3. Spike recoveries in the synthetic extraction droplet

Element	Mass	Conc (ppt)	% Recovery	Element	Mass	Conc (ppt)	% Recovery
Li	7	9.8	98	Cu	63	9.9	99
Be	9	11.0	110	Zn	68	11.5	115
B	11	9.5	95	Ga	69	9.9	99
Na	23	9.5	95	Ge	70	10.6	106
Mg	24	9.8	98	As	75	9.1	91
Al	27	10.3	103	Sr	88	10.2	102
K	39	9.9	99	Zr	90	10.3	103
Ca	40	9.6	96	Cd	111	9.5	95
Ti	47	10.8	108	Sn	118	10.0	100
V	51	9.9	99	Sb	121	9.6	96
Cr	53	9.4	94	Tl	205	10.0	100
Mn	55	10.0	100	Pb	208	10.0	100
Co	59	10.0	100	Bi	209	9.9	99
Ni	60	10.1	101				

The detection limits given in Table 2 were used to calculate the corresponding wafer detection limits (atoms/cm^2) for surface metals on a 450-mm wafer. The current performance of the SME-ICP-MS technique described exceeds the projected requirements for 450-mm wafer surface contamination for the year 2009.

Conclusions

The SME-ICP-MS technique offers a sensitive and accurate method for the characterization of trace metals on silicon wafer surfaces. Silicon wafers can be prepared and analyzed in less than 20 minutes providing real time data for manufacturing quality assessments. Potential physical interferences associated with the analysis of the SME droplet matrix by ICP-MS can be virtually eliminated using STS conditions. This combined with the soft extraction mode of operation results in detection capability that is orders of magnitude below what the National Technology Roadmap will require for 450mm wafers to the year 2009.

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Ultratrace Analysis of Solar (Photovoltaic) Grade Bulk Silicon by ICP-MS

Application Note

Semiconductor

Author

Junichi Takahashi
Agilent Technologies
Tokyo Analytical Division
9-1 Takakura-cho
Hachioji, Tokyo 192-0033
Japan

Abstract

A new quantitative method for the determination of ultratrace elemental impurities present in photovoltaic grade silicon is described using the Agilent 7500cs ICP-MS. Boron (volatile element) and phosphorus (subject to Si-based interferences) are of particular importance to the industry; therefore, special attention was given to the sample pretreatment stage in order to analyze these elements by ICP-MS. Good recovery results for all elements validated the sample preparation strategy. Example data for a range of elements present in 13 different Si samples is presented, along with a list of detection limits. B and P can be determined at the low ppb level in the solid and other elements studied can be measured at the ppt level.

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Introduction

Research into alternative energy sources is accelerating with one of the most dynamic areas of interest being the development of devices to harness solar energy. According to the "solar grand plan," 69% of total electricity in the USA could be sourced from solar power by 2050 (*Scientific American*, January 2008). The growing demand for solar power devices requires highly efficient energy converters, principally silicon. Impurity control of solar (or photovoltaic) grade silicon, particularly for boron and phosphorus, is critical to the efficiency of the finished device. Historically the analysis of phosphorus has been performed by inductively coupled plasma optical emission spectroscopy (ICP-OES), but with a demand for lower detection limits (DLs), a more sensitive method is needed. This work describes the sample preparation and analysis of 31 analytes in bulk silicon (used for the manufacture of solar silicon devices) using an Agilent 7500cs inductively coupled plasma mass spectrometer (ICP-MS).

Analytical Challenges

The latest industry requirement for impurity levels in silicon is lower than 10 ppb in the solid. Boron and phosphorus are of particular importance but are difficult elements to analyze by ICP-MS. In a Si matrix, the polyatomic ion $^{30}Si^{1}H$ interferes with ^{31}P. An alternate strategy is to determine P indirectly by measuring $^{31}P^{16}O$ at mass 47, but here $^{28}Si^{19}F$ also interferes (see Recovery Test section for more detail). Boron is a volatile element that is easily lost during the sample preparation stage. It is critical, therefore, that a new method removes Si for the determination of P, while avoiding the loss of B.

Silicon Sample

Pieces of silicon taken from a block of silicon were analyzed for the following analytes: Li, B, Na, Mg, Al, K, Ca, P, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Sr, Zr, Nb, Mo, Cd, Sn, Sb, Ba, Ta, W, Pb, Th, and U. The method can also be applied to polysilicon granules or chips.

Sample Preparation

Two sample preparation procedures were followed: one for the analysis of all elements except boron, and a slightly modified procedure for boron. First, the sample surface was cleaned with HF. The sample pieces were then dissolved in HF/HNO_3. A small aliquot of H_2SO_4 was added, except to samples being prepared for boron analysis (the higher temperature generated during the evaporation of the H_2SO_4 solution would result in the loss of volatile boron). Sample solutions were heated to near dryness, and then dissolved in 0.5% v/v HNO_3.

Calibration Standard Solution

The calibration blank solution contained 0.34% (w/w) HNO_3 and 0.33% (w/w) H_2SO_4 . Calibration standards were prepared by spiking the blank solution with a multielement standard solution (Spex, Metuchen, NJ, USA) at the following concentrations: 0, 0.1, 0.2, 0.5, and 1 ppb.

Instrumentation

An Agilent 7500cs ICP-MS with Octopole Reaction System (ORS) was used throughout the study. The sample introduction configuration included an Agilent Micro Flow 100 nebulizer, inert PFA spray chamber with sapphire torch injector, and platinum sampling cone and skimmer cone with a brass skimmer base. An Agilent Integrated Autosampler (I-AS) with tray type F sample vials was used. Instrument operating conditions are given in Table 1.

Table 1. Agilent 7500cs ICP-MS Operating Parameters

		Method step (stabilization time)		
		Step 1 (5 sec)	**Step 2 (45 sec)**	**Step 3 (30 sec)**
Parameter	**Unit**	**Cool**	**No gas**	**He**
RF power	W	600	1600	1600
Sampling depth	mm	20	8	8
Carrier gas	L/min	0.8	0.8	0.8
Makeup gas	L/min	0.8	0.46	0.46
ORS He gas	mL/min	0	0	5
Analytes		^{7}Li, ^{23}Na ^{24}Mg, ^{27}Al ^{39}K, ^{40}Ca ^{45}SiO, ^{47}PO ^{55}Mn, ^{56}Fe ^{63}Cu, ^{71}Ga	^{11}B, ^{138}Ba ^{181}Ta ^{182}W	^{47}Ti, ^{52}Cr ^{59}Co, ^{60}Ni, ^{68}Zn, ^{75}As ^{88}Sr, ^{90}Zr ^{93}Nb, ^{95}Mo ^{111}Cd, ^{118}Sn ^{121}Sb, ^{208}Pb ^{232}Th, ^{238}U

Notes: The purity of the He cell gas used was >99.995%. Sample uptake time was 60 sec and rinse time between samples was 60 sec. Integration time was 0.66 sec × 3 points for all elements with the exception of: ^{45}SiO (1 sec × 3 points), ^{75}As (2 sec × 3 points), ^{47}Ti (3 sec × 3 points), and ^{47}PO (5 sec × 3 points). Total analysis time per sample (3 replicates) was 9 min.

Recovery Test

When silicon is dissolved in HF/HNO_3, a significant amount of silicon remains in solution, even after heating. Phosphorus determination at mass 31 is normally performed in helium collision mode. However, any Si present in solution creates ^{30}SiH in the plasma, which interferes with ^{31}P; $^{14}N^{16}OH$ also overlaps at mass 31. Another approach for the determination of P is to measure the PO polyatomic ion at mass 47, which can be produced using cool plasma conditions (reduced plasma power). In this case the background equivalent concentration (BEC) for P is very low at 20 ppt. Although Ti has an isotope at mass 47, it is not ionized under cool plasma conditions, so there is no Ti interference on PO. Conversely, Ti can be measured using He collision mode under normal plasma conditions as PO does not form in a hot plasma. Using a combination of measurement modes, both PO and Ti can be determined effectively. It is worth noting that because any Si remaining in solution with HF would give rise to $^{28}Si^{19}F$, which interferes with $^{31}P^{16}O$, complete elimination of Si from the sample solution is absolutely necessary in order to determine phosphorus, regardless of the measurement mode used. This is achieved by the addition of H_2SO_4. However, when heating the sample solution with H_2SO_4, the high temperature results in the loss of boron as BF_3. Therefore a slightly modified, lower temperature sample prep, without the addition of H_2SO_4 (as complete removal of the silicon matrix is not required), is used for boron. A recovery test was performed to validate this sample preparation strategy.

As significant inhomogeneity in the Si block was observed for Fe, Mn, and Ni, the recovery test was performed by dissolving a larger amount of sample to make a bulk solution: 2.0 g of sample was dissolved in 25 mL HF and 25 mL HNO_3 in a 250-mL PFA beaker. A further 15 mL of HF and 15 mL of HNO_3 were added, the beaker was capped, and the solution was left overnight. Six 10-mL aliquots of the bulk solution were transferred to PFA beakers A, B, C, D, E, and F. Beakers G and H were left empty (for reagent blanks). 0.5 mL of 1:10 H_2SO_4 was added to beakers A, B, C, and G. Beakers C and F were spiked with 75 µL of 1 ppm standard solution. All the solutions were heated for approx 2 hours. After cooling, 0.5 mL of 1:10 H_2SO_4 was added to beakers D, E, F, and H in order to match the acid matrix. Then the residue was dissolved in 1:200 HNO_3 and analyzed. To confirm the efficiency of matrix removal, silicon (^{28}Si) was determined by H_2 reaction mode. Concentrations in solution (ppb) are shown in Table 2 and Figure 1.

Table 2.. Concentrations in Solution (ppb) and Recovery Data for 5-ppb Spikes Added to Si Samples Prepared With and Without the Addition of H_2SO_4 (Note: Reagent blank is the mean value from beakers G and H.)

			H_2SO_4 added				**No H_2SO_4 added**		
	Reagent blank	**A**	**B**	**C**	**Recovery (%)**	**D**	**E**	**F**	**Recovery (%)**
7 Li	0	0	0	5	100	0	0.0012	5.3	110
11 B	0.0051	0.021	0.03	0.086	1	0.083	0.06	5	99
23 Na	0.023	0.31	0.61	5.8	110	1.3	1.6	7.4	120
24 Mg	0.0011	0.52	0.95	5.6	98	0.7	0.72	5.3	92
27 Al	0.0062	0.19	0.44	5.1	95	0.62	0.37	4.8	87
28 Si	0.11	0.28	0.55	0	—	450	14000	25000	—
39 K	0.012	0.09	0.17	5.2	100	0.31	0.37	8.9	170*
40 Ca	0.0091	0.38	0.81	5	88	0.77	0.96	5.9	100
$^{31}P^{16}O$	0	0.026	0.096	4.2	84	3	90	190	3000
47 Ti	0	0.056	0.14	5.4	110	0.13	0.19	5.4	100
52 Cr	0	0.003	0.0068	5.4	110	0.0048	0.016	4.8	97
55 Mn	0	0	0.0014	4.9	97	0.0023	0.0015	4.5	89
56 Fe	0.0024	0.048	0.12	4.9	96	0.31	0.12	4.7	89
59 Co	0	0	0.0011	5.4	110	0.0011	0.0011	5.2	100
60 Ni	0	0.022	0.038	5.5	110	0.035	0.036	5.2	100
63 Cu	0	0.0064	0.015	4.8	95	0.018	0.041	5.1	100
68 Zn	0.0044	0.022	0.043	5.3	110	0.048	0.047	5.5	110
71 Ga	0	0	0	5	100	0	0	5.2	100
75 As	0	0.0016	0.0029	5.1	100	0.0028	0.0024	5.1	100
88 Sr	0	0.0065	0.012	5.4	110	0.056	0.064	5.2	100
90 Zr	0	0	0	5.3	110	0.0021	0	5.2	100

*Poor recovery probably due to contamination

(Continued)

Table 2. Concentrations in Solution (ppb) and Recovery Data for 5-ppb Spikes Added to Si Samples Prepared With and Without the Addition of H_2SO_4 (Note: Reagent blank is the mean value from beakers G and H.) (continued)

		H_2SO_4 added				No H_2SO_4 added			
	Reagent blank	**A**	**B**	**C**	**Recovery (%)**	**D**	**E**	**F**	**Recovery (%)**
93 Nb	0	0	0.0017	5.3	110	0.0045	0.0048	5.2	100
98 Mo	0	0.0018	0.0013	5.3	110	0.0006	0.046	5.2	100
111 Cd	0	0	0	5.4	110	0	0	5.5	110
118 Sn	0.0015	0.0023	0.005	5.4	110	0.0045	0.0056	5.4	110
121 Sb	0	0	0	5.3	110	0.0024	0.002	5.4	110
138 Ba	0	0.001	0.0022	5.6	110	0.0044	0.0041	5.6	110
181 Ta	0	0.043	0.075	5.5	110	0.11	0.2	4.9	95
182 W	0	0.032	0.071	5.7	110	0.053	0.063	5.6	110
208 Pb	0	0.0012	0.0021	5.6	110	0.0036	0.0032	5.8	120
232 Th	0	0	0	5.8	120	0	0	6	120
238 U	0	0	0	5.9	120	0	0	6.1	120

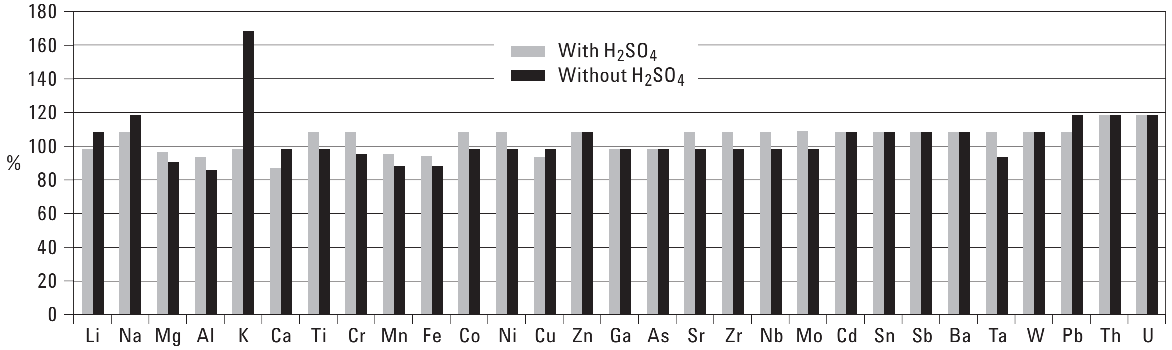

Figure 1. Recovery of 5-ppb spikes added to sample solution.

From the recovery test results (Table 2 and Figure 1), it can be concluded that the addition of sulfuric acid removes the silicon matrix completely (as well as boron), due to the higher temperature evaporation process, which makes it possible to determine phosphorus at the low ppb level in the solid. The results also show that a simple evaporation without sulfuric acid is effective for the determination of boron. Although it has been reported that the addition of mannitol stabilizes boron in solution, acceptable recoveries can be obtained without the addition of mannitol, provided high solution temperatures are avoided. With no H_2SO_4 added, it is important to closely monitor the evaporation of the sample. If the sample is allowed to evaporate to dryness, Nb, Ta, W, and Au will be lost. The concentration of silicon remaining in the non-H_2SO_4 prep solution was 10 to 20 ppm.

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Detection Limits

Three sigma detection limits (DLs) were calculated from the calibration curves as shown in Table 3. DLs in the solid were obtained by multiplying the solution DL by 50 (0.3 g made up to 15 mL).

Table 3. Detection Limits (3 s) in Solution and in the Solid. All Units: ppt

	ng/L in solution	ng/kg in solid
7 Li	0.011	0.55
11 B	20	1000
23 Na	0.78	39
24 Mg	0.16	8
27 Al	0.56	28
39 K	0.13	6.5
40 Ca	4.3	215
47 PO	17	850
47 Ti	2.2	110
52 Cr	1.3	65
55 Mn	0.067	3.35
56 Fe	0.8	40
59 Co	0.015	0.75
60 Ni	0.21	10.5
63 Cu	0.31	15.5
68 Zn	4.6	230
71 Ga	0.080	4
75 As	0.13	6.5
88 Sr	0.037	1.85
90 Zr	0.11	5.5
93 Nb	0.046	2.3
98 Mo	0.27	14
111 Cd	0.24	12
118 Sn	0.4	20
121 Sb	0.26	13
138 Ba	0.093	4.65
181 Ta	0.058	2.9
182 W	0.34	17
208 Pb	0.42	21
232 Th	0.16	8.2
238 U	0.014	0.7

Quantitative Analysis

Samples taken from 13 different polysilicon blocks were analyzed by ICP-MS. The concentration data for elements present in the different samples are shown in Table 4. Concentrations are expressed as ppb in the original solid. Note the inhomogeneity for elements such as Fe, Mn, and Ni.

Conclusions

Ultratrace elemental impurities in solar grade silicon can be quantitatively analyzed following an appropriate sample pre-treatment stage and measurement by the Agilent 7500cs ICP-MS. The sample preparation detailed in this report is quite simple and reproducible. B and P can be determined at the low ppb level in the solid and other elements studied can be measured at the ppt level.

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Table 4. Quantitative Data (ppb in the Original Solid) for Samples Taken from 13 Different Polysilicon Blocks

	#A	**#B**	**#C**	**#D**	**#E**	**#F**	**#G**	**#H**	**#I**	**#J**	**#K**	**#L**	**#M**
7 Li	0.067	0.097	0.077	0.057	0.26	0.051	0.049	0	0.012	0.098	0.11	0.1	0.076
11 B	62	62	100	13	21	39	29	14	6.8	12	6.1	10	9.3
23 Na	2.8	15	2.5	6.2	450	0	2.5	28	17	0	25	61	140
24 Mg	1.9	3.8	3.1	0	0	0	0	0	0	0	1.6	0	0
27 Al	100	100	270	130	130	150	170	43	39	86	120	110	150
39 K	1.4	3.5	1.1	4.2	210	0.41	3.7	14	7.5	0.83	5.3	11	3
40 Ca	6.8	5.5	9	0	56	0	0	20	0	0	0.57	2.5	0.63
$^{31}P^{16}O$	64	59	70	61	99	97	110	25	41	110	91	87	110
47 Ti	0	2.5	310	0	0	0	0	0	0	2.9	8.7	2.9	1.3
52 Cr	0.34	0.64	16	1.1	2.1	0	0	2.4	1.2	1	0.61	0.18	1.1
55 Mn	0.022	0.027	3.4	0.31	0.32	0	0	0.16	0.87	0.017	0.061	0.21	0.078
56 Fe	5.7	5.1	1700	42	29	3.5	4.9	36	140	3	3.7	32	10
59 Co	0.28	0.19	7.6	0.35	1.6	0.21	0.33	3.3	0.35	0.036	0.087	0.054	0.1
60 Ni	13	2.5	270	6.1	16	17	18	21	12	1.4	3.3	2.3	12
63 Cu	1.6	2.8	40	5.2	24	2.6	6.1	39	4.5	2.2	3.9	1.9	2.1
68 Zn	0.3	0.073	0.015	1.8	41	0	0	7.4	3.3	0	0.47	4.1	0
71 Ga	0.077	0.11	0.28	0.1	0.14	0.073	0.07	0	0.016	0.096	0.11	0.11	0.099
75 As	0.18	0.22	0.17	0.17	0.2	0.01	0	0.28	0.22	0.086	0.086	0.07	0.034
88 Sr	0.017	0.013	0.071	0.022	0.23	0	0	0.19	0.077	0.014	0.027	0.057	0.074
90 Zr	0.028	0.04	13	0.15	0.32	0	0	0.28	0.11	0	0	0.037	0.027
93 Nb	0	0.012	2	0	0	0	0	0.064	0	0.013	0.027	0.011	0.27
95 Mo	0.092	0.55	5.4	0.032	0	0	0	3.7	0.6	0	0.39	0.048	10
111 Cd	0	0.016	0	0	0	0	0	0	0	0	0.023	0.023	0
118 Sn	2.3	11	0.18	9.6	11	2.7	2.6	0.55	0.074	7.9	9	7.7	2.4
121 Sb	0.42	1.1	0.038	1	1.2	0.39	0.34	0.6	0.32	0.81	0.97	0.8	0.36
138 Ba	0.029	0.039	0.25	0	0.15	0	0	5.6	0.57	0.12	0.17	0.11	0.029
181 Ta	0	0	0.52	0	0.91	0	0	0	0	0	0	0.013	0.033
182 W	38	34	28	15	12	25	6.8	200	8.4	12	11	14	8.8
208 Pb	0	0.016	0.022	0	1.8	0	0	1	0.4	0.12	0.31	0.45	0.053
232 Th	0	0	0.049	0	0	0	0	0	0	0	0	0	0
238 U	0	0	0.5	0	0	0	0	0	0	0	0	0	0

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Analysis of Electroceramics by Laser Ablation ICP-MS

Application

Semicondutor

Author

Masahiro Oishi and Keiichi Fukuda
Materials Analysis Center
Technology Group
TDK Corporation,
Japan

Abstract

TDK is one of the leading electronic component manufacturers supporting the advance of cell phones, personal computers, and car electronics. As the electroceramic chip parts used in these devices become smaller, thinner, and lighter, new analytical methodology is needed to meet the demand for faster, more sensitive methods of quantitative analysis of solid materials. In addition, environmental regulations are expected to become increasingly stringent, which will impact on the need for reliable methods for the trace analysis of solids. To meet these challenges, researchers at TDK have developed a method based on laser ablation inductively coupled plasma mass spectrometry which offers simultaneous quantitative analysis of major and minor elements with high sensitivity, spatial resolution of 10 µm, robustness, and rapid analysis. The results are based on a new normalization method which can compensate for the sample introduction rate differences between samples or between different sites. The technique is applicable to the simultaneous analysis of major, minor, and trace elements in electroceramics as well as other sample types in other industry sectors.

Introduction

All ceramics, including electroceramics, can be defined as polycrystalline nonmetallic materials. By using precisely controlled compositions and additives, their unique electrical (dielectric, piezoelectric), optical, and magnetic properties can be optimized for use in many key technologies such as communications, electronics, and automation. For example, dielectric materials are used in chip capacitors, whereas magnetic materials are used in transformer coils using ferrite, chip beads, and other components.

Currently, there is a drive to make electroceramics lighter and more compact, and to achieve thinner packages, higher compositeness, and lower levels of power consumption [1]. For instance, ceramic capacitors are one form of electroceramics that are in high demand. They were initially comprised of a single layer, but with developments in multilayering and chip technology, larger capacity and more compact capacitors are now widely used. The ability to make multilayer ceramic chip capacitors smaller, lighter, and thinner has contributed greatly to the propagation of mobile devices such as cellular telephones. As these materials continue to become smaller and thinner, there is an increased need to conduct composition analysis at lower limits of detection (LOD).

Furthermore, the need for fast, high-sensitivity analysis is not restricted to the production and processing industry. Electroceramics are used

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primarily in electrical and electronic devices, and in recent years, environment-related regulations pertaining to electrical and electronic devices have grown increasingly stringent worldwide. Two new environmental regulations that will take effect in the European Union (EU) in 2006 are the directive on Waste Electrical and Electronic Equipment (WEEE) and Restriction on the Use of Certain Hazardous Substances (RoHS). The WEEE directive is associated with the disposal of waste electrical and electronic equipment; while RoHS, restricts the use of certain hazardous substances present in electrical and electronic equipment. The proposal for the RoHS directive will prohibit the use of mercury, cadmium, lead, hexavalent chromium, and other toxic substances from electrical and electronic equipment. Also, in Japan there are pressures on the electronics industry to eliminate lead and to restrict the use of other toxic substances.

In this application note, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to analyze electroceramics. A method was developed that enables rapid, convenient, and highly sensitive compositional analysis. Further details were described in a previous report [2].

Inorganic Analysis of Electroceramics

The techniques generally used for the inorganic analysis of electroceramics are X-ray fluorescence (XRF), inductively coupled plasma atomic emission spectroscopy (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS). Inorganic analysis of micro portions is generally performed using an electron probe micro-analyzer (EPMA) or an energy dispersive X-ray analyzer attached to a scanning electron microscope.

The XRF enables convenient analysis of major elements and minor components. XRF measurement targets include bulk, particle, and thin film samples. The technique is extremely effective in characterizing unknown samples; however, conducting high-sensitivity analysis requires a larger measurement diameter and is relatively slow. When measurements are required at lower LODs than is possible via XRF analysis, the sample is usually dissolved using acid, or fused with alkali and then dissolved and analyzed using ICP-AES or ICP-MS. Drawbacks associated with these methods include: the additional time required for sample dissolution, the risk of sample contamination during sample preparation, and the fact that “local” analysis of solids is not possible. In many cases, microfield analysis, EPMA, which has an element mapping function, is used. However, EPMA requires some sample preparation, and because the sample chamber is contained within a vacuum, time is required before measurements can be performed. In addition, analysis cannot be performed at a sufficiently high level of sensitivity, with typical detection limits (DL) at ppm levels.

Thus, conventional methods of analysis have fallen short of the mark with regard to speed, convenience, sensitivity, dynamic range, and microfield analysis. In contrast, LA-ICP-MS enables local analysis of solid samples while maintaining the high sensitivity of ICP-MS. ICP-MS also offers a wide linear dynamic range. For example, the working analytical range of the Agilent 7500 ICP-MS extends to nine orders with very high sensitivity. In addition, the detection circuit used in the 7500 Series ICP-MS means acquisition speed is not compromised when analyzing higher concentration elements and ensures that transient signals from a laser ablation pulse can be measured over such a wide dynamic range. This is a key advantage in the determination of trace and major elements in inclusions, where the analyte signal is very short-lived, and analyte concentrations vary widely.

This report summarizes investigations into the possibility of applying a new LA-ICP-MS method to compositional and impurities analysis of electroceramics.

Analysis Using Laser Ablation ICP-MS

Evaluation of LA-ICP-MS

LA-ICP-MS is widely used to determine inorganic elements in solid samples. A laser is used to irradiate the solid sample and to generate microparticles. The particles are carried on a steady gas stream to the ICP-MS, where the sample is ionized and measured. Thus, solid samples can be analyzed directly without preprocessing, and element analysis can be performed at a high level of sensitivity. LA-ICP-MS is often used as a means of qualitative analysis, although it is also used in quantitative analysis. Typical applications include the determination of trace elements in iron [3] and the characterization of geological samples [4, 5, 6]. At the same time, however, the elements involved in these analyses are trace components, and few studies have been conducted on assays that included everything from principal to trace components.

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Advantages of the technique include:

- Measurement speed: There is no need to draw the sample chamber into a vacuum, so sample measurements can be carried out rapidly.
- High sensitivity and wide dynamic range: Gases and micro-particles generated by laser ablation are introduced directly into the ICP-MS for measurement, enabling high-sensitivity analysis. Moreover, the ICP-MS has a wide dynamic range, enabling a broad spectrum of analysis ranging from principal component elements to impurity elements.
- Local analysis is possible: The laser beam is narrow and a charged coupled device (CCD) camera can be attached, enabling local analysis of specific subsections of the sample.
- Changing the analysis field: The area being analyzed can be modified by changing the diameter of the laser beam.
- Analyzing a wide range of samples: Almost any sample can be fused and ablated using the fourth higher harmonic (266 nm) or fifth higher harmonic (213 nm) of an Nd:YAG laser, or using an excimer laser (193 nm).
- Measuring samples of various shapes: Bulk, particle, thin film and other types of samples can be measured. However, a smoother sample field, that has no bumps or projections, achieves more stable results.

Some disadvantages include:

- Problems with stability: The efficiency with which samples can be introduced varies for each sample, so analysis values are sometimes not stable.
- Quantitative analysis is difficult: Quantitative analysis of solutions by ICP-MS is carried out using a method of calibration that uses external standards or standard addition. However, in the case of LA-ICP-MS, internal standards are difficult to add to solid materials. The internal standardization can be used if there are principal component elements for which the concentrations are already known, but then the method cannot be applied in all types of analysis.

Semiquantitative Analysis

Because quantitative analysis using external standards is difficult via LA-ICP-MS, generally the concentration conversion coefficient is calculated separately for each element being measured, and semiquantitative analysis is performed. In this case, either National Institute of Science and Technology (NIST) 611, 612, 613, or 614 glass, which contains multi-elements, or a manufactured standard that is similar to the material being tested, is used for calculating the concentration conversion coefficient (k). If NIST glass is used, the concentration conversion coefficients of the various elements contained in the NIST glass are calculated ahead of time. Then the actual test sample is analyzed and the semiquantitative values for the actual test sample are determined from the data obtained using the concentration conversion coefficients. However, when NIST glass is used, the sample introduction efficiency is different for the material being measured, in many cases. This increases the error in the semiquantitative values. When a standard sample that is similar to the material being tested is used as the standard sample, there are also problems such as the sample introduction efficiency being different depending on the location being analyzed.

Given these challenges with the semiquantitative analysis of electroceramics, we developed a method in which the semiquantitative values are standardized in order to suppress fluctuation of the sample introduction efficiency. Moreover, in order to reduce the error of the semiquantitative values, a solid reference sample was used that was similar to the material being measured. To carry out standardization, however, it was necessary to measure all of the elements and determine the semiquantitative values. In other words, it was necessary to calculate the concentration conversion coefficients (k) for all of the elements. Because the solid reference sample contained only some of the components of the electroceramic, it was not possible to calculate the concentration conversion coefficients (k) for all of the elements. In this case, a concentration conversion coefficient (k-aqua) was calculated by measuring the SPEX multi-element standard solution (XSTC-1, 7, 8, 13). This value was then corrected to take account of the element being present in the solid rather than in solution, to give a k-aqua* value. The k-aqua* values were used as the concentration conversion coefficient (k) for the calculations.

The procedure for semiquantitative analysis of the electroceramic test sample is described below:

1. Using pneumatic nebulization, aqueous standards containing SPEX XSTC-1,7,8,13 were measured over the entire mass range (m/z 2 to 260 amu).
2. Semiquantitative factors (SF) were calculated for the elements in the aqueous standard.
3. Using LA-ICP-MS a solid standard was measured across the entire mass range (m/z = 2–260).

4. For those elements where the concentration is known, semiquantitative factors (SF) were calculated in the solid standard.
5. For those elements that occur in both the aqueous and solid standard and for which SF values were calculated, the coefficient (k) was generated.
6. The k coefficient can be used to convert SF values obtained using the aqueous standard into those useful for solid standards (SF obtained by pneumatic nebulization ICP-MS) × (coefficient (k)). This way, SF values of elements that are not in the solid standard could be generated.
7. The concentration conversion values for all elements were converted to the equivalent oxide.
8. Using the sum of the oxide conversion values of the detected elements, standardization was performed, and the standardized semiquantitative values were determined. For an example of semiquant factor calculations see Table 2.

Oxide conversion was carried out at this time because electroceramics are primarily oxides.

Table 2. Semiquant (SQ) Factor Calculation

Case 1

	SQ Factor of LA	SQ Factor of nebulizer
Fe	100	200
Co	?	1000
Ni	2000	4000

Coefficient (k) of Fe is 100/200	= 0.5
Coefficient (k) of Ni is 2000/4000	= 0.5
Coefficient (k) of Fe and Ni is same	
Co SQ factor is 1000 × 0.5	= 500

Case 2

	SQ Factor of LA	SQ Factor of nebulizer
Fe	100	200
Co	?	1000
Ni	3000	4000
Cu	?	2000
Zn	4000	4000

Coefficient (k) of Fe is 100/200	= 0.5
Coefficient (k) of Ni is 3000/4000	= 0.75
Coefficient (k) of Zn is 4000/4000	= 1.0
Co SQ factor is 1000 × ((0.5 + 0.75)/2)	= 625
Cu SQ factor is 2000 × ((0.75 + 1.0)/2)	= 1750

Using the above method results in the following advantages:

- Elements not contained in the solid reference sample can be measured.
- Standardization processing makes it possible to correct the sample introduction efficiency between samples, or for each of the measurements, thus minimizing disparities and offset from the true values.

Using this method of analysis, we investigated the possibilities of semiquantitative analysis of an area measuring several mm^2 on a ferrite bulk sample. In addition, we attempted analysis of a spot on a barium titanium oxide ($BaTiO_3$) disk, to determine whether we could apply this method of analysis to local analysis of an area measuring several tens of µm^2.

Semiquantitative Analysis of Ferrite Bulk Samples

Ferrite is a typical magnetic material for electroceramics, and is used for a wide range of components, from bulk-shaped parts such as transformer coils and deflecting yoke coils to chip-shaped parts such as chip beads. Two types of ferrite samples with different compositions were used. The samples were manufactured in-house and measured 2.0 cm in length, 1.0 cm in width, and 0.5 cm in height. For a solid reference sample, we used a nickel-copper-zinc (NiCuZn) ferrite sample, and calculated the concentration conversion coefficient. Table 1 shows the measurement conditions used in the test. A 100-µm beam diameter at 2 mJ output energy and repetition rate of 10 Hz was used. The measurement was carried out over the entire mass range ($m/z = 2 \sim 260$), and the integration time for the various masses was set at 0.05 s, with measurements being performed three times. To compare the analysis values, the same sample was analyzed using XRF. The results measured using the LA-ICP-MS for the two types of ferrite samples are shown in Figures 1 and 2 respectively.

There was excellent agreement between the principal composition and the reference values

Table 1. Laser Ablation and ICP-MS Conditions

Laser ablation		**ICP-MS**	
New Wave Research LUV266X		Agilent 7500s	
Wavelength:	266 nm	RF power:	1200 W
Pulse frequency:	10 Hz	Carrier gas:	1.15 L/min
Laser energy:	2 mJ for Ferrite	Plasma gas:	16.0 L/min
Ablation pattern:	Raster, 100-µm spot diameter for Ferrite,	Number of masses:	m/z = 2 to 260
Scan speed:	50 µm/s for Ferrite	Integration time:	0.05 s
Laser warm-up:	10 s		

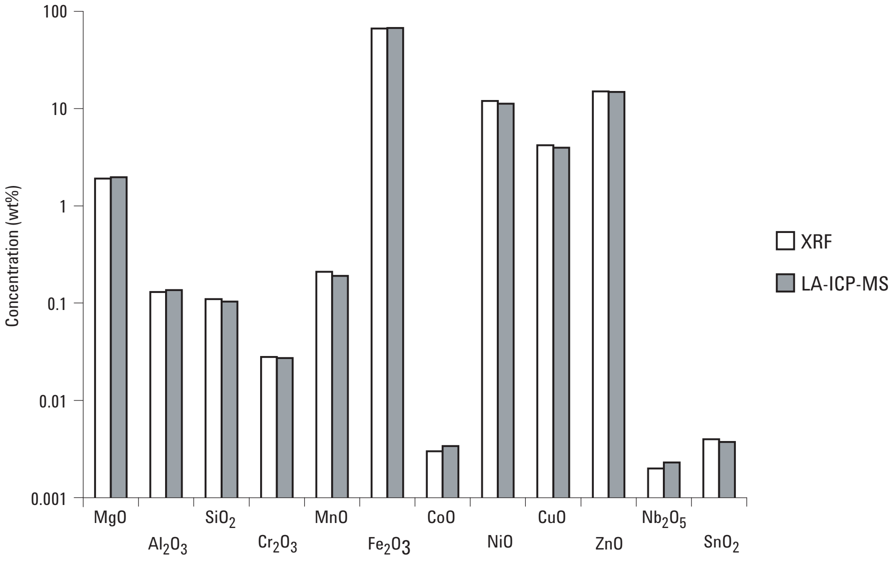

Figure 1. **Comparison of results of semiquantitative analysis using LA-ICP-MS and XRF analysis conducted on ferrite sample A.**

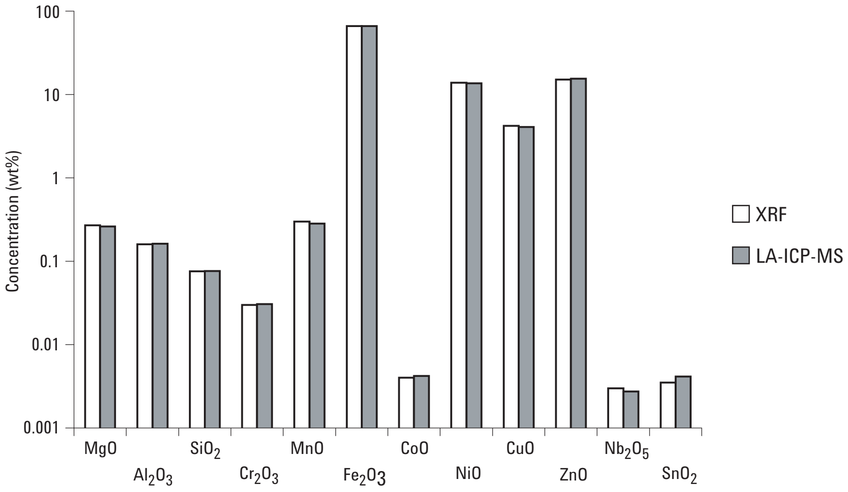

Figure 2. **Comparison of results of semiquantitative analysis using LA-ICP-MS and XRF analysis conducted on ferrite sample B.**

obtained via XRF, with variations of only several percent. Even for the trace components, the difference from the reference value was within 10%. The disparity among the three measurements was approximately 5% to 10% for the bulk elements, and approximately 20% for the trace elements. Using this analysis method, it was possible to suppress the fluctuation in the sample introduction efficiency that is peculiar to LA-ICP-MS. Table 3 shows the analysis values for all of the elements detected with the LA-ICP-MS measurement of ferrite sample A.

Table 3. A Comparison of the Principal Components and Trace Element Concentrations (wt %) of Ferrite Sample A with the Concentrations Obtained from XRF (The % RSD for the LA-ICP-MS Indicates the RSD for the Three Measurements)

Elements	XRF	LA-ICP-MS	
	Reference value	Mean	%RSD
MgO	0.27	0.26	11.0
Al_2O_3	0.16	0.16	9.7
SiO_2	0.076	0.076	10.1
Cr_2O_3	0.030	0.031	4.1
MnO	0.30	0.28	0.8
Fe_2O_3	66.0	66.0	0.5
CoO	*	0.004	3.1
NiO	13.8	13.6	2.8
CuO	4.2	4.1	0.8
ZnO	15.1	15.5	2.3
Y_2O_3	*	0.00004	18.9
ZrO_2	*	0.001	20.8
Nb_2O_5	*	0.003	6.5
MoO_3	*	0.004	8.6
In_2O_3	*	0.00004	8.1
SnO_2	*	0.004	14.7
Sb_2O_3	*	0.0002	17.0
BaO	*	0.001	15.6
WO_3	*	0.0004	4.1
Bi_2O_3	*	0.0001	11.7

* Not detectable

Trace components, such as V_2O_5, Y_2O_3, ZrO_2, MoO_3, Sb_2O_3, BaO, WO_3, and Bi_2O_3, which could not be detected with XRF, could be measured using the LA-ICP-MS. Heavy elements could also be measured and have sub-ppm DLs. Although not included in our samples, the technique offers good DLs for cadmium, lead, mercury and other elements which will be targeted by the RoHS directive, so the proposed method will be effective in the analysis of toxic metals.

The time required for analysis was 40 seconds per measurement, and the total time for the three repititions, including the time spent changing the samples, was approximately 5 minutes. Moreover, no sample preparation was carried out when the measurements were taken. In our opinion, this semiquantitative LA-ICP-MS method satisfies the requirements for electroceramics analysis in terms of speed, convenience, and high sensitivity.

Semiquantitative Analysis of Spots on a $BaTiO_3$ disk

Next, we investigated whether the technique could be applied to feature (local) analysis of a dielectric material. A 1-cm diameter $BaTiO_3$ disk, manufactured in-house, was used. $BaTiO_3$ is a major component of chip capacitors. Depending on the elements added to $BaTiO_3$, the baking conditions, and other parameters, black spots sometimes appear on the surface during manufacture. The LA-ICP-MS quantitative technique described above was used to characterize both these spots and normal areas on the $BaTiO_3$ disk. The following laser conditions were used in this measurement: beam diameter of 10 µm at 10 Hz and 0.02 mJ. In addition, for comparison purposes, we analyzed the entire disk using XRF. The results are shown in Figure 3.

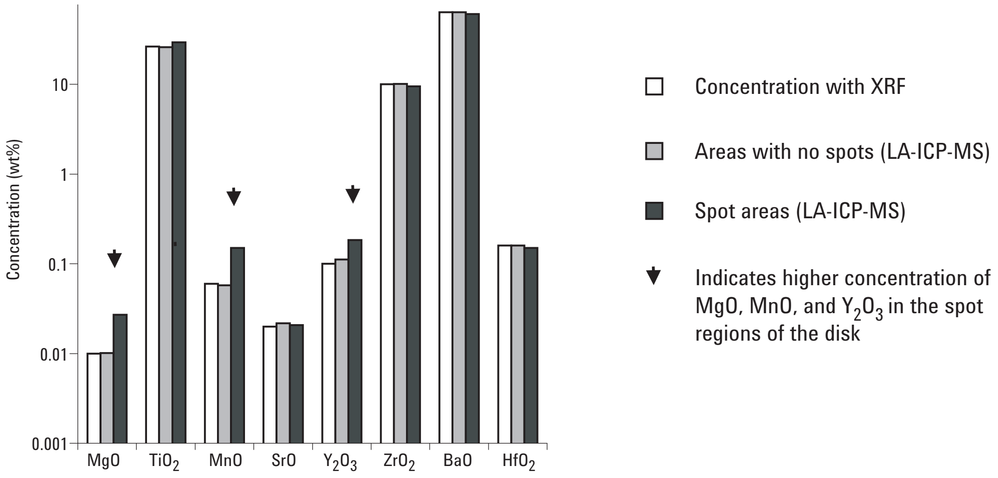

Figure 3. **A comparison of results obtained using the LA-ICP-MS for semiquantitative analysis of areas of the $BaTiO_3$ disk with no spots and areas with spots, compared with the results obtained using XRF analysis.**

The calculated semiquantitative values for the normal areas of the $BaTiO_3$ disk using LA-ICP-MS were approximately equal to the results for the disk as a whole, as obtained using XRF. Analysis of the black spots (an area of several micrometers) on the $BaTiO_3$ disk indicated significant disparities in the amounts of MgO, MnO and Y_2O_3. Figure 3 illustrates the analysis of the spots compared to the normal areas of the $BaTiO_3$ disk. It is thought that the spots on the $BaTiO_3$ disk were caused by aggregation of MgO, MnO, and Y_2O_3. Figures 4 and 5 show a CCD image of the $BaTiO_3$ disk before and after LA-ICP-MS analysis, and, as the photographs illustrate, there was very little damage to the sample with the laser diameter set at 10 µm.

As described above, our analyses indicate that the LA-ICP-MS method of semiquantitative analysis is effective as a means of local analysis of areas measuring several tens of micrometers in diameter.

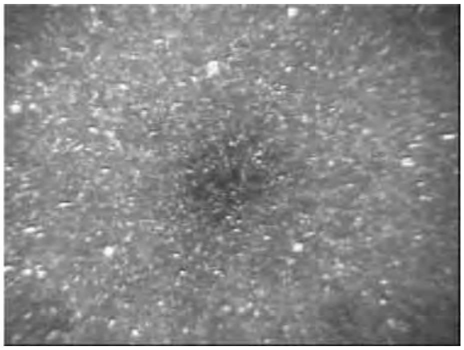

Figure 4. **CCD image of the $BaTiO_3$ disk prior to laser irradiation.**

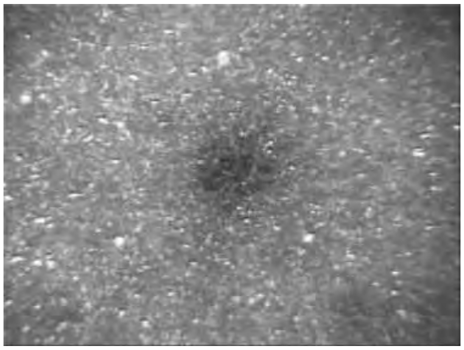

Figure 5. **CCD image of the $BaTiO_3$ disk after laser irradiation showing minimal damage (laser diameter was 10 µm).**

Conclusions

Not only are electroceramics becoming smaller and more heavily layered, but the boards themselves are becoming more hybridized as capacitors and magnetic elements begin to share space on the same board. To keep apace with these developments, methodology for the trace analysis of impurities will continue to evolve. In addition, environmental regulations are expected to become increasingly stringent, which will impact on the need for reliable methods for the trace analysis of solids. Therefore, the demand for newer, faster, and more convenient methods of semiquantitative analysis, such as the LA-ICP-MS technique discussed in this application note, will continue to grow.

Using concentration conversion coefficients obtained from an aqueous standard and solid reference samples and by measuring all of the elements, we found that LA-ICP-MS provides an effective technique for rapid semiquantitative analysis. The technique can be applied to measurements across a wide dynamic range from bulk to trace components of materials. Furthermore, this method is not limited to electroceramics and can be applied to various other materials and substances.

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