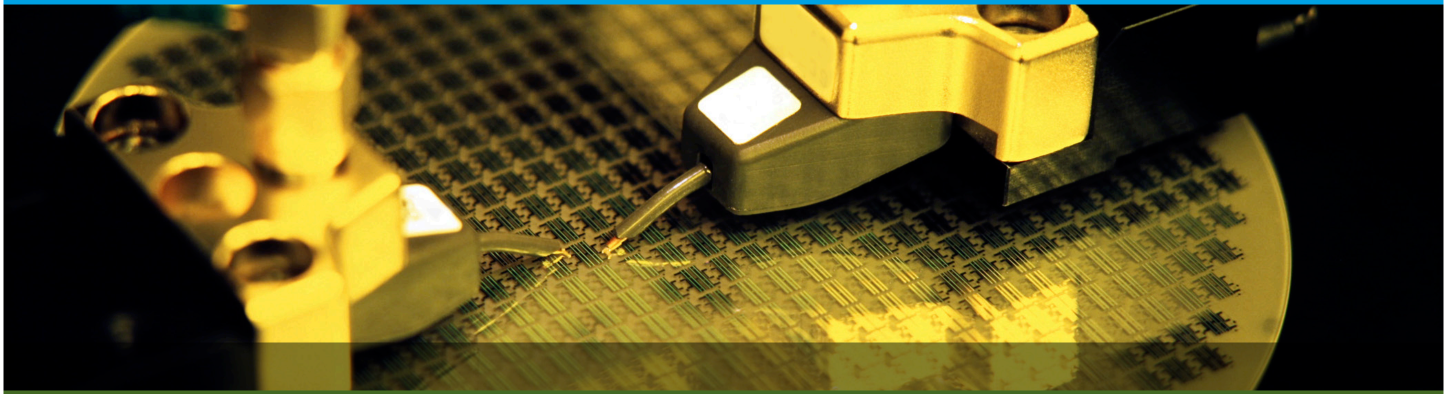
Applications of ICP-MS

Measuring Inorganic Impurities in Semiconductor Manufacturing

Application Compendium



Agilent ICP-QQQ

10 Years of enabling semicon industry advances

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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 smaller than 10 nanometers (equivalent to about 40 Si atoms). Doped regions are added, depositing or implanting specific atoms to alter the conductivity of the silicon.

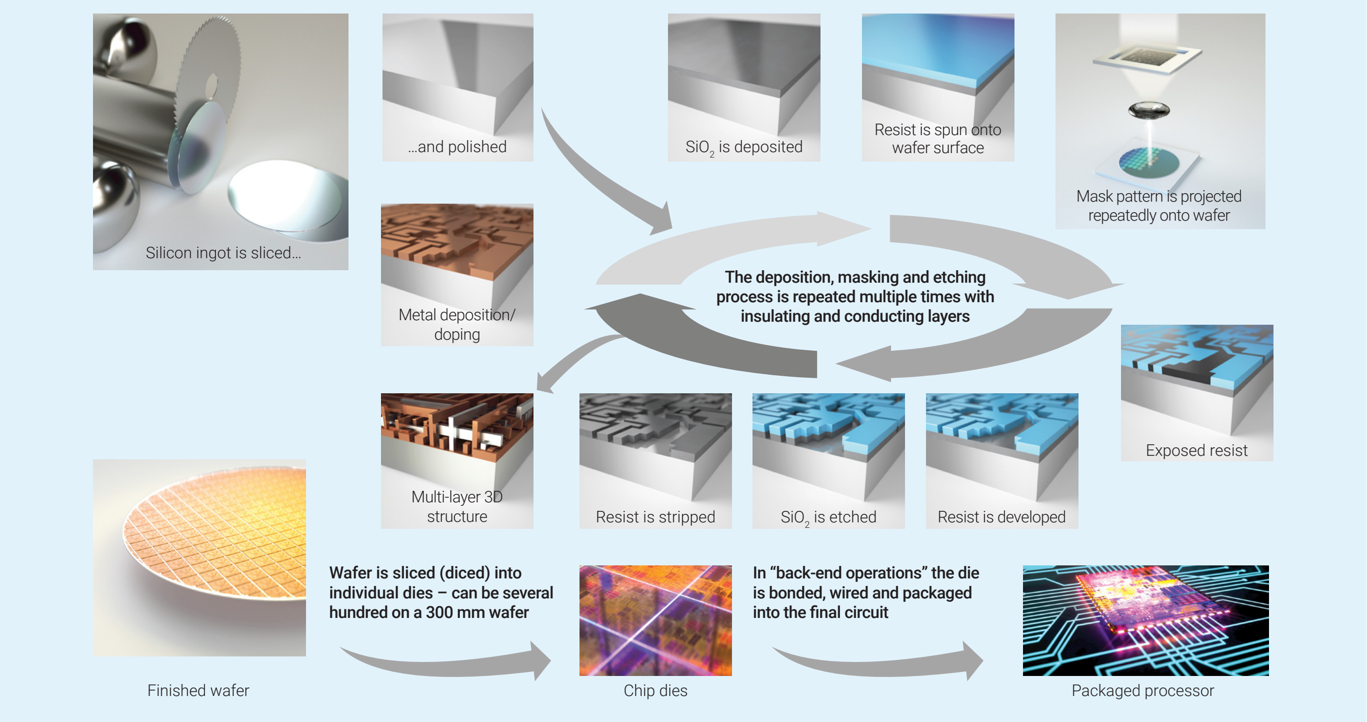

Figure 1. Simplified schematic showing typical steps in silicon wafer fabrication.

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An IC with "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.

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. Arsine gas (AsH_3) is used as a precursor for non-Si semiconductors such as GaAs, AlGaAs, and InGaAsN. High-k dielectric materials include chlorides and alkoxides 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 (monoethanol amine)
Polishing	CMP (chemical mechanical planarization) slurries, oxalic acid, NH_4OH

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Agilent Has Three Decades of ICP-MS Experience Driving 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

The Agilent 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 a powerful 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 Semiconductor configuration is specifically designed for semiconductor applications, providing high sensitivity, coupled with the unique, high power 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 or O_2 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.

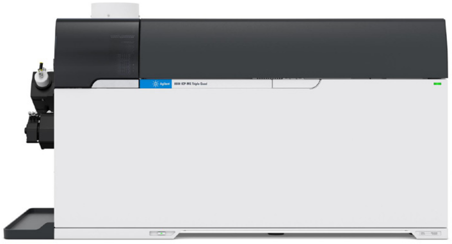

Figure 4. The Agilent 8900 triple quadrupole ICP-MS Semiconductor configuration is designed specifically to meet the current and future needs of the semiconductor industry.

To meet facility requirements for ammonia cell gas handling, the instrument is available in two versions, as follows:

- 8900 #200: 10% NH_3/He for cell gas
- 8900 #210: Pure NH_3 for cell gas

The following pure gas kits are also available:

- Pure Ammonia Cell Gas Kit (G5726A) for 8900 #200
- Pure Oxygen Option Gas Kit (G5725A) for 8900 #200 and #210

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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
- Elemental Scientific Inc, USA

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

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 (which 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 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 an Agilent ICP-QQQ.

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

Figure 8. Radian automated VPD-ICP-MS system from Elemental Scientific Inc., USA with integrated Agilent 7900 or 8900 ICP-MS.

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 with Peltier cooling
- 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 fifth 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. Less robust ICP-MS systems may require extreme low temperatures (e.g. –20 °C) to tolerate such solvents.

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 is added using a fifth (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. Oxygen can be added as an O_2/Ar (20% O_2) mix or 100% O_2 via the Pure Oxygen Option Gas Kit. The kit is compatible with the 8900 Semiconductor (#200 and #210) and Advanced Applications (#100) ICP-QQQ models.

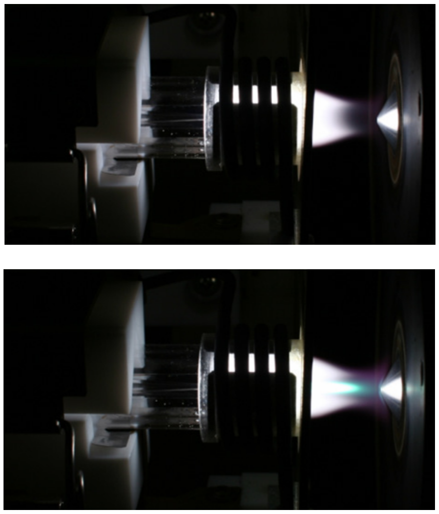

Figure 9. How the ICP-MS plasma looks when aspirating aqueous solutions (top) and organic solvents (bottom).

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 9.

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.

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.*

*** O_2 is often 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. However, when using 100% O2 as an option gas, please use the Pure Oxygen Option Gas Kit and the appropriate version of ICP-MS MassHunter software. Note that the O2 gas flow rates will not match the values in this table, so please consult your local specialist for more information.*

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 Agilent 7900 ICP-MS and Agilent 8900 ICP-QQQ Semiconductor ICP-QQQ 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 and #210)
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 line	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)	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 or pure O_2 option for organics (8900 ICP-QQQ only), or He for laser.*

*** Add pure NH_3 via third cell line (standard on #210, Pure NH_3 Kit needed for #200).*

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

Figure 10. 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 10) 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. The standard Agilent 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*

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Expanding Capabilities with Accessories and Software

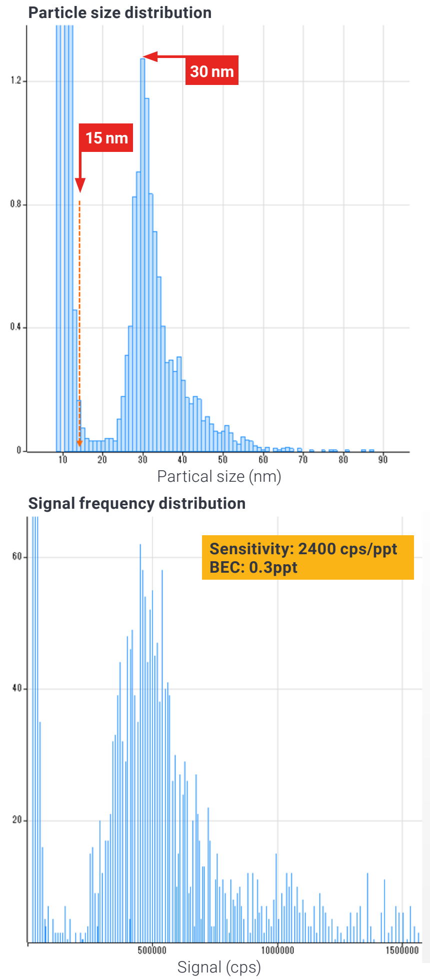
Nanoparticle analysis

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 less than 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 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. The portfolio of Agilent NP solutions also includes support of Field Flow Fractionation (FFF)-ICP-MS for bulk characterization of samples containing multiple sizes and types of nanoparticles.


Particle size distribution

Signal frequency distribution

Figure 11. Analysis of Fe nanoparticles (30 nm, 6 ppt) in butyl acetate.

Integrated, contamination-free autosampler

The Agilent I-AS integrated autosampler (shown in Figure 12) 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.

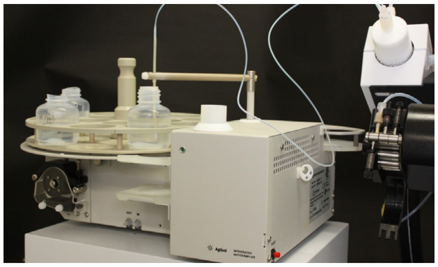


Figure 12. The Agilent I-AS integrated autosampler.

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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.

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 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 13). 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.

The ESI scoutDX* and scoutNANO on-line chemical monitoring systems (shown in Figure 14) control up to 20 remote sampling modules. Each module collects a small amount of a chemical or stream and transfers it to the central scoutDX or scoutNANO 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.

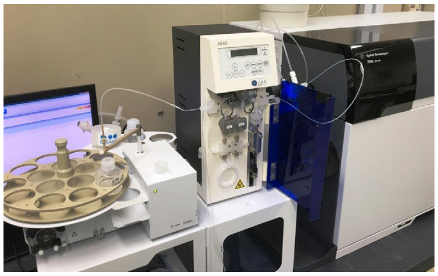

Figure 13. The ASAS automated standard addition device, part of the CSI online monitoring system from IAS Inc., Japan.

Figure 14. The ESI scoutNANO automated online process monitoring system, Elemental Scientific Inc., USA

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*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

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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 the Agilent website for later publications.

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Ultrapure Process Chemicals Analysis by ICP-QQQ with Hot Plasma Conditions

Authors

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Meeting single- and sub-ppt guideline levels for ASTM/SEMI elements in ultrapure water using an Agilent 8900 ICP-QQQ

Introduction

Contamination control is critical in semiconductor device fabrication (FAB) facilities (*1*). Contaminants may be introduced via the wafer substrate, or the chemicals and reagents used during the manufacturing process. Impurities—particularly metal ions and particles – adversely affect device performance and production yield, so FABs use the highest purity reagents and follow strict protocols to control contaminants during the manufacturing process. Ultrapure water (UPW) is used throughout the wafer fabrication process including in the RCA standard cleaning (SC-1/SC-2) procedure to remove chemical contaminants and particulate impurities from the wafer surface. UPW is one of the most critical process chemicals for contamination-control as the water is in direct contact with the wafer surface at many stages of manufacturing. Any impurities present in the UPW could directly affect the electrical properties of the finished device, for example, by reducing dielectric breakdown voltage.

ASTM International and Semiconductor Equipment and Materials International (SEMI) publish standards regarding the specifications for semiconductor process chemicals and reagents, including UPW. ASTM D5127-13, 2018 and SEMI F63-0521, 2021 provide guidance for the quality of UPW needed to produce devices with linewidths < 0.045 microns (*2, 3*). Both standards require detection limits (DLs) of less than 0.5 ppt (boron has a higher limit of 15 ppt) and background equivalent concentrations (BECs) less than 1 ppt (50 ppt for B). The semiconductor industry standard method for monitoring trace element contaminants is ICP-MS, with laboratories increasingly switching to triple quadrupole ICP-MS (ICP-QQQ or ICP-MS/MS) for its superior detection limits. The Agilent 8900 ICP-QQQ is a tandem MS instrument, which uses MS/MS operation to further improve the performance of the technique compared to single quadrupole ICP-MS instruments.

The 8900 ICP-QQQ meets the electronic and semiconductor industry's need for trace and ultratrace element analysis due to its high sensitivity, low background, and interference removal capabilities. The 8900 has the flexibility to operate in several modes to give optimum performance across different applications. For example, semiconductor labs often use cool plasma conditions to achieve the lowest BECs and DLs for interfered elements and easily ionized elements (EIEs). Cool plasma reduces EIE backgrounds and suppresses the formation of intense argon-based interferences such as Ar^+, ArH^+, and ArO^+, allowing low-level analysis of ^{40}Ca, ^{39}K, and ^{56}Fe, respectively.

Cool plasma gives excellent results in low matrix samples, such as UPW, H_2O_2, HNO_3, and HCl (*4*). However, high matrix samples, such as silicon and metal digests, are difficult to run using cool plasma due to the higher level of matrix suppression. More robust, hot plasma (low CeO/Ce ratio) conditions are preferred for such sample types. For labs wishing to use only hot plasma, the 8900 ICP-QQQ can be fitted with an optional skimmer cone and m-lens that provide optimum performance in hot plasma conditions. In a recent study, an 8900 fitted with the optional m-lens was used to determine 38 elements in two digested silicon samples prepared at 10 and 100 ppm Si (*5*). The m-lens and the skimmer cone that it is paired with have an optimized geometry that minimizes EIE backgrounds when using normal, hot plasma conditions. Using m-lens, the 8900 was able to measure all required elements at ppt levels in the Si matrix without using cool plasma.

The 8900 with m-lens can also be used to analyze ultratrace elements in low matrix semiconductor samples – such as UPW – using only normal, hot plasma conditions. In this study, hot plasma was combined with no gas mode and two cell gas modes to resolve spectral interferences, achieving single- or sub-ppt BECs and DLs for all analytes.

Experimental

Reagents and sample preparation

UPW (Organo Corp, Tokyo, Japan) was acidified to 0.1% with high purity 68% HNO_3 (TAMAPURE AA-100, Japan). Acidification ensures that elements are retained as soluble ions in solution, although adding acid can potentially contribute to the level of contamination.

Calibration standards

The 8900 ICP-QQQ was calibrated using the method of standard addition (MSA), as is typical for the analysis of high-purity semiconductor samples. A mixed multi-element standard (SPEX CertiPrep, NJ, US) was prepared and spiked into the UPW to give standard additions at 5, 10, 20, and 40 ppt.

Instrumentation

The 8900 Semiconductor Configuration ICP-QQQ was fitted with standard components including a PFA-100 MicroFlow nebulizer, quartz spray chamber, quartz torch with 2.5 mm injector, and Pt sampling cone. The standard s-lens was replaced with an optional m-lens (part number G3666- 67500) and optional Pt-tipped, Ni-based skimmer cone for m-lens (part number G3666-67501). The 8900 includes the ORS^4 collision/reaction cell (CRC) and two quadrupoles (Q1 and Q2), one either side of the CRC, enabling double mass selection (MS/MS). Q1 rejects all nontarget ions before they enter the cell, allowing only analyte ions and on-mass interference ions to pass to the cell. The analyte and interfering ions can then be separated using predictable, consistent, and reproducible reaction chemistry (*6, 7*). Q2 then ensures that only the analyte ions (on-mass mode) or analyte-product ions (mass-shift mode) pass to the detector, free of interferences.

Agilent ICP-MS MassHunter instrument control software for the 8900 provides simple method setup to measure analytes in different cell gas modes using a single multitune acquisition. In this analysis no gas mode, ammonia reaction mode (using a mixture of ammonia and hydrogen cell gases), and oxygen reaction mode were used to remove interferences using a combination of on-mass and mass-shift measurement. During data acquisition, the cell gases and measurement modes were switched automatically, giving a fast and automated analysis using the best mode for each analyte. Instrument acquisition and operating parameters are given in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating conditions.

	No Gas	NH_3+H_2	O_2
Acquisition Parameters			
Scan Mode		MS/MS	
Replicates (standards)		3	
Replicates (blank)		10	
Integration Time per Mass (s)		1.0	
Plasma			
RF Power (W)		1600	
Sampling Depth (mm)		8.0	
Nebulizer Gas (L/min)		0.70	
CeO^+/Ce^+ (%)		2	
Cell			
He Flow Rate (mL/min)	-	1	-
H_2 Flow Rate (mL/min)	-	2	-
*NH_3 Flow Rate (mL/min)	-	2.0 (20%)	-
O_2 Flow Rate	-	-	0.45 (30%)
KED (V)	3	−10	−7

**Mix of 10% NH_3 in 90% He*

Results and discussion

Calibration curves

Four representative MSA calibration curves for K, Ca, Fe, and Ni in UPW are shown in Figure 1. No background subtraction or blank correction was performed. The four analytes are representative of the EIEs (K), elements with severe background interferences (Ca), elements of particular importance for the semiconductor industry (Fe), and elements that could indicate contamination from the ICP-MS interface (Ni). All the SEMI element calibrations showed excellent linearity (r > 0.999) and low BECs. This performance confirms the high sensitivity of the 8900 and the effectiveness of the reaction cell method with m-lens to control elemental backgrounds and resolve interferences.

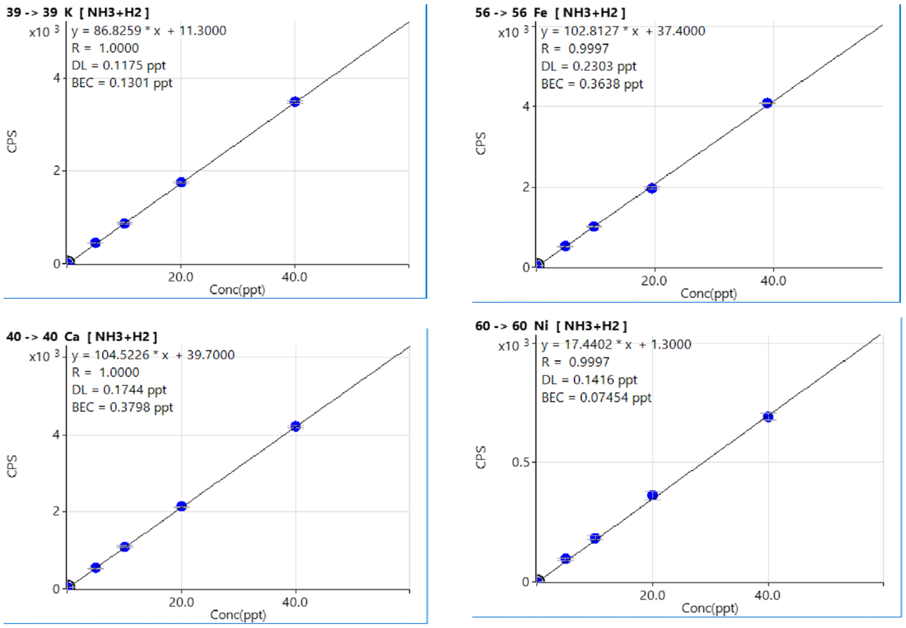

Figure 1. Representative MSA calibration plots for K, Ca, Fe, and Ni in UPW.

BECs and DLs

BECs and DLs for 26 elements were calculated automatically by the ICP-MS MassHunter software (Table 2). BECs below 0.5 ppt and DLs below 0.3 ppt were obtained for 25 SEMI elements, easily meeting the limits for UPW specified by ASTM and SEMI. The higher specified limits for boron (50 ppt BEC and DL of 15 ppt) were also easily achieved (measured BEC of 1.11 ppt and DL of 1.18 ppt). Backgrounds are highly dependent on water quality, but the BEC achieved in this work was a factor of 50 lower than the SEMI guideline, easily meeting current industry requirements. Critical metallic (conductive) contaminants such as Al, Cr, Fe, Co, Ni, Cu, Zn, and Mo were measured with BECs and DLs substantially below 0.5 ppt, again easily meeting industry requirements.

The results, which are also shown in Figure 2, demonstrate the suitability of the 8900 ICP-QQQ using hot plasma for the analysis of ultratrace contaminants in high purity semiconductor process chemicals.

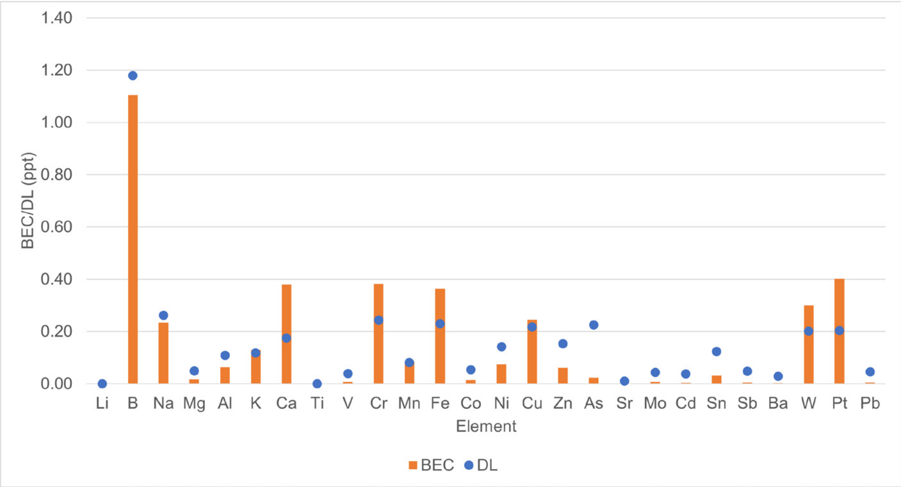

Figure 2. BECs and DLs for SEMI specified elements in UPW measured using the 8900 ICP-QQQ with hot plasma conditions.

Conclusion

The study has demonstrated the suitability of the Agilent 8900 ICP-QQQ with optional m-lens for the measurement of ultratrace-level contaminants in low-matrix semiconductor reagents such as UPW. The m-lens ensured that background signals for the EIEs – K, Na, Ba, and Li – were minimized, allowing all 26 SEMI-critical elements to be measured at ppt levels using hot plasma conditions (CeO/Ce ratio < 2%). All potential spectral interferences were resolved by operating the 8900 in MS/MS mode using a single multitune method with no gas and two reaction gas modes.

Standard addition calibration curves from 0 ppt to 40 ppt concentration range showed excellent linearity and sensitivity for all elements. The low BECs showed that the method successfully removed all spectral interferences, including argon-based interferences that typically form under hot plasma conditions. The 8900 method resolved the intense interferences such as Ar^+, ArH^+, and ArO^+, allowing sub-ppt analysis of ^{40}Ca, ^{39}K, and ^{56}Fe, respectively.

The BECs and DLs for all elements were well below the recommendations set by ASTM and SEMI for the quality of UPW related to semiconductor-industry manufacturing at < 0.045 m linewidths.

Table 2. Agilent 8900 ICP-QQQ DLs and BECs and ASTM/SEMI requirements for 26 elements in UPW.

				Measured in UPW by 8900		ASTM D5127-13 (2018) Requirements	SEMI F63-0521 (2021) Requirements	
Analyte	Tune Mode	Q1	Q2	DL (ppt)	BEC (ppt)	BEC (ppt)	BEC (ppt)	MDL (ppt)
Li	No gas	7		0	0	<1	<1	0.5
B	No gas	11		1.18	1.11	<50	<50	15
Na	No gas	23		0.26	0.23	<1	<1	0.5
Mg	NH_3+H_2	24		0.05	0.02	<1	<1	0.5
Al	NH_3+H_2	27		0.11	0.06	<1	<1	0.5
K	NH_3+H_2	39		0.12	0.13	<1	<1	0.5
Ca	NH_3+H_2	40		0.17	0.38	<1	<1	0.5
Ti	O_2	48	64	0	0	<10	<1	0.5
V	NH_3+H_2	51		0.04	0.01	<10	<1	0.5
Cr	NH_3+H_2	52		0.24	0.38	<1	<1	0.5
Mn	NH_3+H_2	55		0.08	0.09	<10	<1	0.5
Fe	NH_3+H_2	56		0.23	0.36	<1	<1	0.5
Co	NH_3+H_2	59		0.05	0.01	<1	<1	0.5
Ni	NH_3+H_2	60		0.14	0.07	<1	<3	1.6
Cu	NH_3+H_2	63		0.22	0.24	<1	<1	0.5
Zn	NH_3+H_2	64		0.15	0.06	<1	<1	0.5
As	O_2	75	91	0.23	0.02	<1	<1	0.5
Sr	NH_3+H_2	88		0.01	0.002	<1	<1	0.5
Mo	NH_3+H_2	98		0.04	0.01	<1	<1	0.5
Cd	NH_3+H_2	114		0.04	0.004	<10	<1	0.5
Sn	NH_3+H_2	118		0.12	0.03	<10	<1	0.5
Sb	NH_3+H_2	121		0.05	0.01	<1	<1	0.5
Ba	NH_3+H_2	138		0.03	0.003	<1	<1	0.5
W	O_2	184	216	0.20	0.30	<1	<1	0.5
Pt	O_2	195		0.20	0.40	<1	<1	0.5
Pb	NH_3+H_2	208		0.05	0.005	<1	<1	0.5

BEC and DL values of "0" are reported for Li and Ti because zero counts per second were measured for these elements in all 10 replicates of the blank UPW.

References

1. Applications of ICP-MS: Measuring Inorganic Impurities in Semiconductor Manufacturing, Agilent publication 5991-9495EN
2. ASTM D5127-13, Standard Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries, https://www.astm.org/Standards/D5127.htm
3. SEMI F63 - Guide for Ultrapure Water Used in Semiconductor Processing, https://store-us.semi.org/products/f06300-semi-f63-guide-for-ultrapure-water-used-in-semiconductor-processing
4. Kazuo Yamanaka, Determination of Ultratrace Elements in High Purity Hydrogen Peroxide with Agilent 8900 ICP-QQQ, Agilent publication 5991-7701EN
5. Yu Ying, Analysis of Ultratrace Impurities in High Silicon Matrix Samples by ICP-QQQ, Agilent publication 5994-2890EN
6. Technical Overview of Agilent 8900 Triple Quadrupole ICP-MS, Agilent publication 5991-6942EN
7. Naoki Sugiyama and Kazumi Nakano, Reaction data for 70 elements using O_2, NH_3 and H_2 with the Agilent 8800 Triple Quadrupole ICP-MS, Agilent publication 5991-4585EN

Determination of Ultratrace Elements in SEMI Grade 5 High Purity Hydrogen Peroxide

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Keywords

SEMI, H_2O_2, hydrogen peroxide, semiconductor, high purity chemicals

Introduction

Hydrogen peroxide (H_2O_2) is one of the most important process chemicals used in semiconductor device manufacturing. As a strong oxidizer, it is used for cleaning silicon wafers, removing photoresists, and etching metallic copper on printed circuit boards.

Semiconductor Equipment and Materials International (SEMI) publishes standards regarding the specifications for semiconductor process chemicals including H_2O_2 (SEMI C30-1110). SEMI Grade 5 is the highest purity level, with maximum contamination levels of 10 ppt for most trace elements. The industry therefore requires analytical methods capable of measuring the trace elements at single- or sub-ppt level background equivalent concentrations (BECs). SEMI C30-1110 also includes specifications for the maximum concentrations of sulfate and phosphate allowed in high purity H_2O_2, with a limit of 30 ppb. This limit equates to elemental concentrations of sulfur and phosphorus of 10 ppb. These two contaminants are not currently measured by ICP-QMS. However, the recent development of triple quadrupole ICP-MS (ICP-QQQ) permits much lower limits of detection for S and P. It is now possible to monitor all SEMI elements using a single technique.

Experimental

Instrumentation: Agilent 8900 Semiconductor configuration ICP-QQQ.

Tuning: To achieve the lowest DLs, a multi-tune method was used. The tuning parameters are summarized in Table 1. For data acquisition, a 2 s integration time was used for all isotopes with three replicates (10 replicates for the blank to calculate the DLs).

Table 1. ICP-QQQ tuning conditions.

	Cool	Cool-NH_3 (1)	Cool-NH_3 (2)	No gas	H_2	He	O_2 (1)	O_2 (2)
Scan mode	Single Q	MS/MS						
RF power (W)	600			1500				
Nebulizer gas flow (L/min)	0.70							
Make-up gas flow (L/min.)	0.90			0.48				
Sampling depth (mm)	18.0			8.0				
Ex1 (V)	-150.0		-100.0	4.2	4.7	4.2	4.5	3.5
Ex2 (V)	-18.0	-17.0	-12.0	-250.0				-120.0
Omega (V)	-70.0			-140.0				-70.0
Omega Bias (V)	2.0			10.0	8.0	-10.0	10.5	4.0
Q1 Entrance (V)	-15.0		-50.0					
Cell gas	–	NH_3		–	H_2	He	O_2	
Cell gas flow (ml/min)		2.0	2.0		7.0	5.0	0.3	0.3
Axial Acceleration (V)	0.0	1.5		0.0			1.0	
KED (V)	15.0	-5.0		5.0	0.0	3.0	-7.0	

Sample Preparation

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 one part of 70% HNO_3 to 1000.

Results and discussion

Table 2 shows quantitative results and detection limits for the SEMI specification elements in high purity 35% H_2O_2. Comparative quantitative results and DLs are also shown for the same elements in ultrapure water. 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 generated at the beginning of the sequence. The spiked samples were then run as unknown samples for a total analysis period of 3 h 40 min. The RSDs of the 13 results are shown in Table 2 (Stability RSD %).

Table 2. ICP-QQQ tuning conditions.

					Hydrogen peroxide			Ultrapure water	
Element	Q1	Q2	Scan mode	Tune	Conc. (ppt)	DL (ppt)	Stability 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	0.5	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	0.2	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	0.02	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

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Conclusion

All the elements specified in SEMI C30-1110 were measured at sub-ppt to ppt levels in high purity 35% hydrogen peroxide using the Agilent 8900 ICP-QQQ. 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 in a high purity 35% hydrogen peroxide sample analysis sequence that lasted 3 hours 40 minutes. This performance demonstrates the suitability of the Agilent 8900 Semiconductor configuration ICP-QQQ instrument for the routine analysis of the highest-purity semiconductor reagents and process chemicals.

More information

Determination of ultratrace elements in high purity hydrogen peroxide with Agilent 8900 ICP-QQQ, Agilent publication, 5991-7701EN

Automated analysis of semiconductor grade hydrogen peroxide and DI water using ICP-QQQ

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Online MSA calibration using prep*FAST* S automated sample introduction and Agilent 8900 ICP-QQQ

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.

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)*.

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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.Tuning: To achieve the lowest DLs, a multi-tune method was used. The tuning parameters are summarized in Table 1. For data acquisition, a 2 s integration time was used for all isotopes with three replicates (10 replicates for the blank to calculate the DLs).

Table 1. ICP-QQQ operating conditions.

	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 Q	MS/MS						
RF power (W)	600			1500				
Carrier gas (L/min)	0.70							
Make-up gas (L/min.)	0.90			0.48				
Sampling depth (mm)	18.0			8.0				
Ex1 (V)	-150.0		-100.0	4.2	4.7	4.2	4.5	3.5
Ex2 (V)	-18.0	-17.0	-12.0	-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					
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.

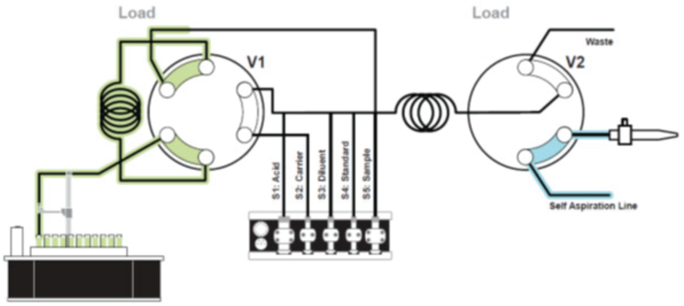
In this work, several reaction cell gases (He, H_2, O_2, and NH_3) were used in the collision/reaction cell (CRC) of the 8900, as appropriate for the large number of analytes being measured. Since DI water and H_2O_2 are low-matrix samples, cool plasma conditions were also applied for the elements where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

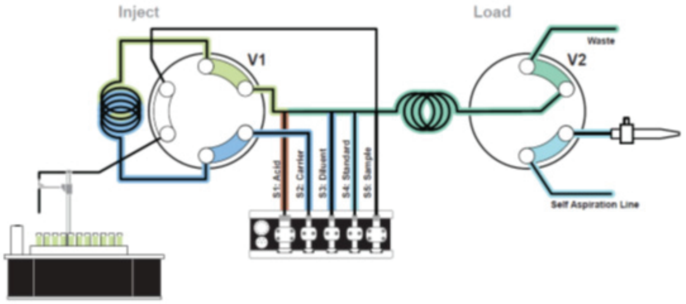
The prepFAST S automated sample introduction system combines an autosampler with a system of ultrapure valves (S1 -5), and a set of high precision syringe pumps. Undiluted chemicals can be placed on the autosampler and the system will perform the actions—such as dilution, acidification, and spiking—required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



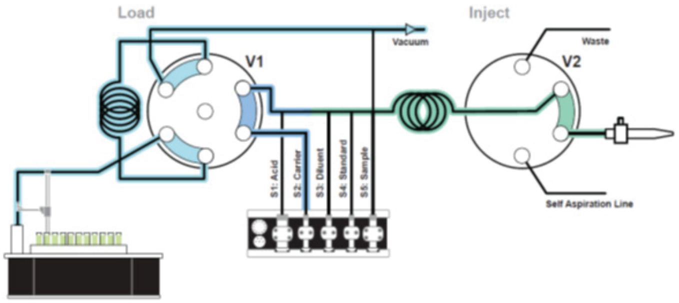
Step 1: Fill Loop

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.



Step 2: Dilute Sample

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.



Step 3: Inject Sample

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

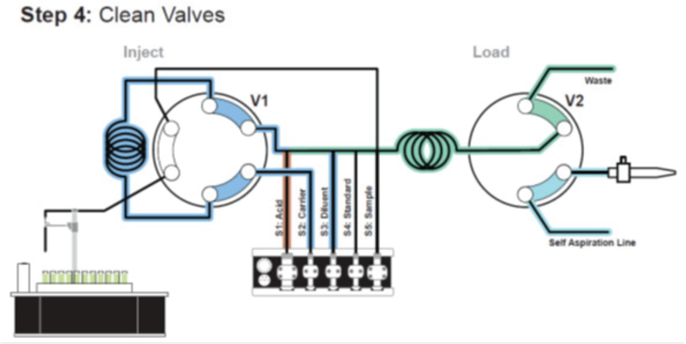


Figure 1. ESI prep*FAST* S system schematic, illustrating four distinct steps: sample loading during spray chamber rinse, sample preparation, injection, and cleaning.

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.

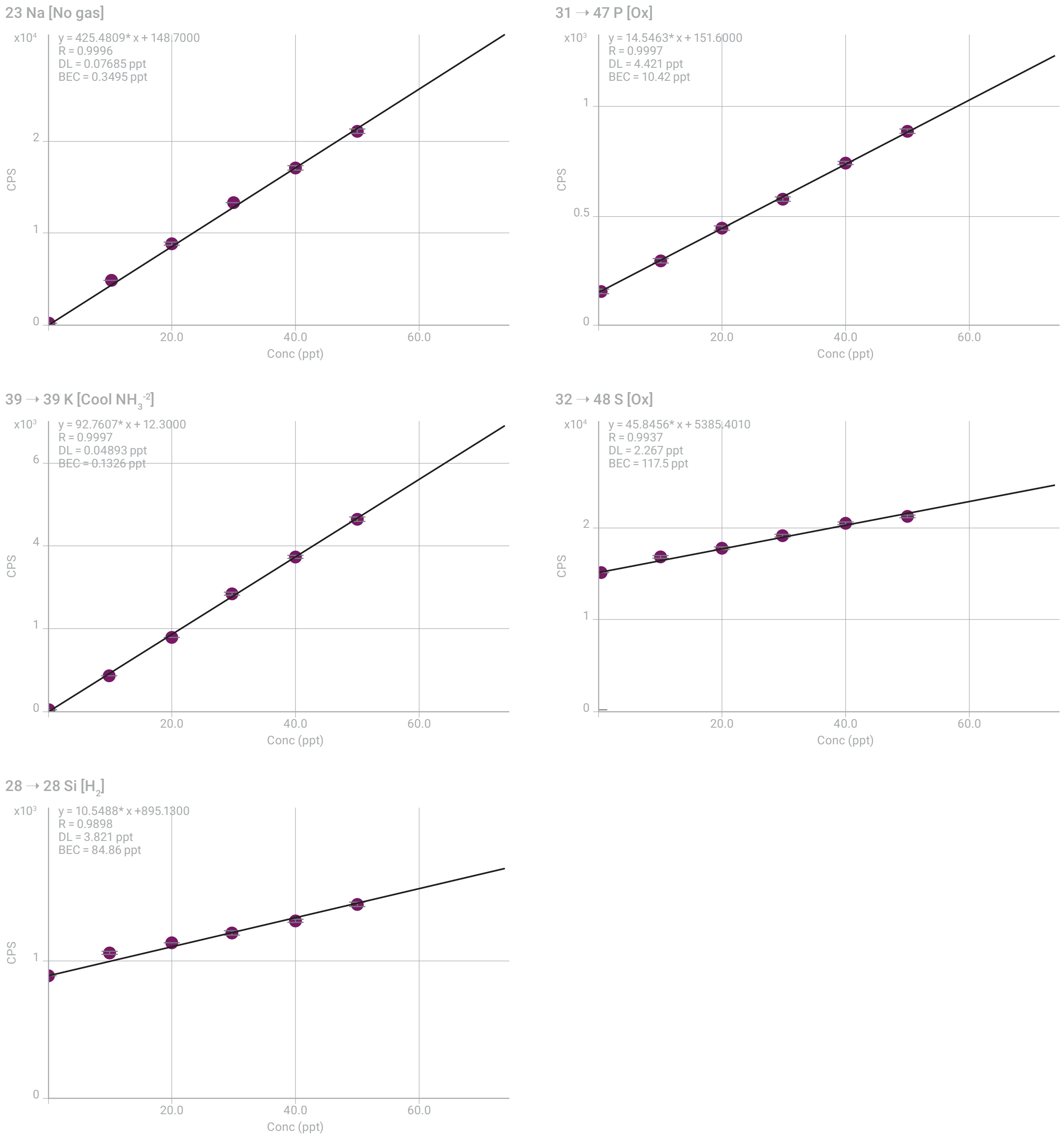


Figure 2. Calibration plots for Na, K, Si, P, and S in DI water. All values in ng/L (ppt).

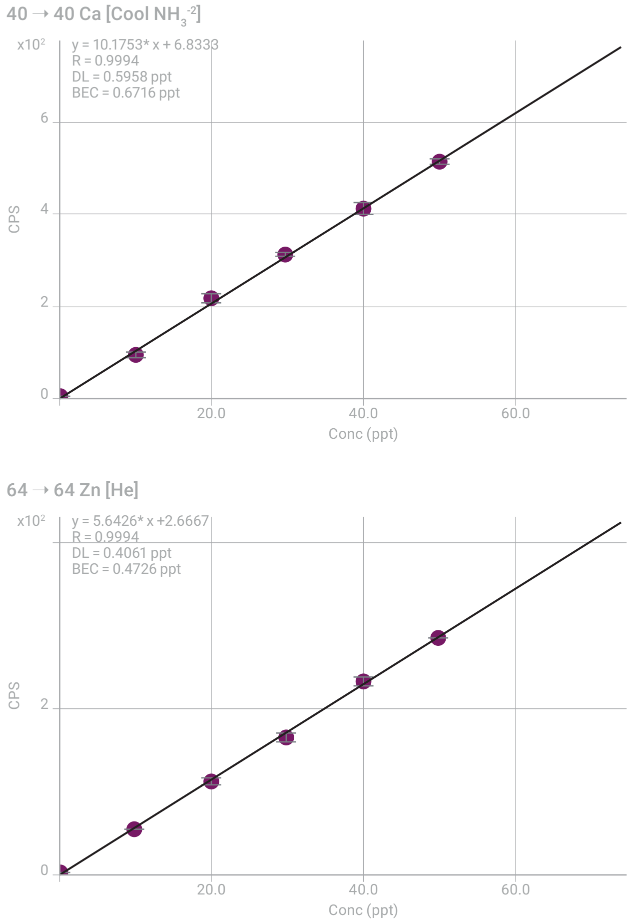


Figure 3. Calibration plots for Ca, Zn, and As in H_2O_2. All values in ng/L (ppt).

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 monitoring 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.

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Table 2. Quantification of trace elements in DI water and 35% H2O2. 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	MS/MS	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
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	H_2	0.023	0.016	<DL	0.040	0.027	<DL
Pt	195	195	MS/MS	No gas	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**	**SQ**	**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.

Conclusion

By combining ultra low 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 performance ideally suited to the high demands of the semiconductor industry. 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, measured 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.

References

1. SEMI C30-1110, Specifications for hydrogen peroxide, 2010.
2. Kazuo Yamanaka, Determination of ultratrace elements in high purity hydrogen peroxide with Agilent 8900 ICP-QQQ, Agilent publication, 2016, 5991-7701EN
3. Kazumi Nakano, Ultra-low level determination of phosphorus, sulfur, silicon, and chlorine using the Agilent 8900 ICP-QQQ, Agilent publication, 2016, 5991-6852EN

Ultratrace Measurement of Calcium in Ultrapure Water

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Keywords

semiconductor, process chemicals, ultra pure water, UPW, calcium, method of standard additions, hydrogen on-mass

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 1990s, 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 DLs or BECs of cool plasma for low-matrix samples. To achieve measurement at the sub-ppt level, reduction of the BEC is required. As outlined in this paper, the Agilent 8800 ICP-QQQ provides new reaction cell technology that enables a significant reduction in the BEC that can be achieved for Ca, to 100 ppq.

Table 1. Cool plasma operating conditions.

Parameter	Unit	Tuning value
RF	W	600
Sampling depth	mm	18
Carrier gas flow	L/min	0.7
Make-up gas flow	L/min	1.0
Spray chamber temp.	°C	2

Experimental

Instrumentation: Agilent 8800 #200.

Plasma conditions: For the ultratrace measurement of Ca, cool plasma operating conditions were used (Table 1). The sample was self-aspirated at a carrier gas flow rate of 0.7 L/min.

Reagents and sample preparation: 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.

Results and discussion

Ultra-low BEC for Ca using MS/MS mode

Figure 1 shows the BECs obtained for Ca, measured at its major isotope of ^{40}Ca, using the method of standard additions (MSA) under three different operating conditions on the 8800 ICP-QQQ: Single Quad mode with no cell gas, MS/MS mode with no cell gas, and finally MS/MS mode with a H_2 cell gas flow of 1 mL/min. The Single Quad mode uses operating conditions with Q1 acting as an ion guide, to emulate the Agilent 7700 ICP-QMS. The obtained BEC of 6.8 ppt is similar to that routinely achieved with the Agilent 7700 operated in cool plasma mode.

Using MS/MS mode (without cell gas) improved the Ca 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 2. The Agilent 8800 ICP-QQQ in MS/MS mode with H_2 cell gas achieved a BEC for Ca in UPW two orders of magnitude lower than the BEC obtained using conventional ICP-QMS.

Figure 3 shows the spectrum obtained for UPW using cool plasma conditions in Single Quad mode with no cell gas. As can be seen, Ar^+ (*m/z* 40) is suppressed under the lower temperature plasma conditions, but two intense background peaks are observed at *m/z* = 19 and 30. These are $(H_2O)H^+$ and NO^+ respectively. In Single Quad mode, all ions formed in the plasma, including these two intense ions, pass through to the cell. Even with no gas added to the cell, a reaction occurs in the cell which causes a new interfering ion 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 MS/MS mode on the 8800 ICP-QQQ, Q1 rejects all non-target ions such as NO^+ and $(H_2O)H^+$, preventing unwanted reactions from occurring in the cell, which lowers the Ca BEC. The addition of H_2 in the cell also removes any residual $^{40}Ar^+$ that is formed even under cool plasma conditions.

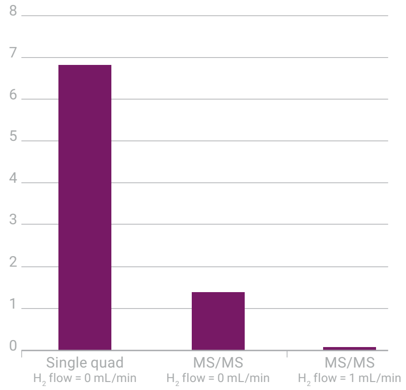

Figure 1. BECs for Ca obtained using Single Quad mode with no cell gas [6.8 ppt], MS/MS mode with no cell gas [1.4 ppt], and MS/MS mode with an H_2 cell gas flow of 1 mL/min [0.041 ppt].

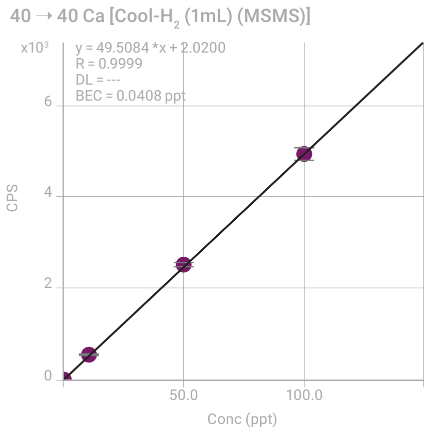

Figure 2. MSA calibration plot for Ca using MS/MS mode with H_2 flow of 1 mL/min.

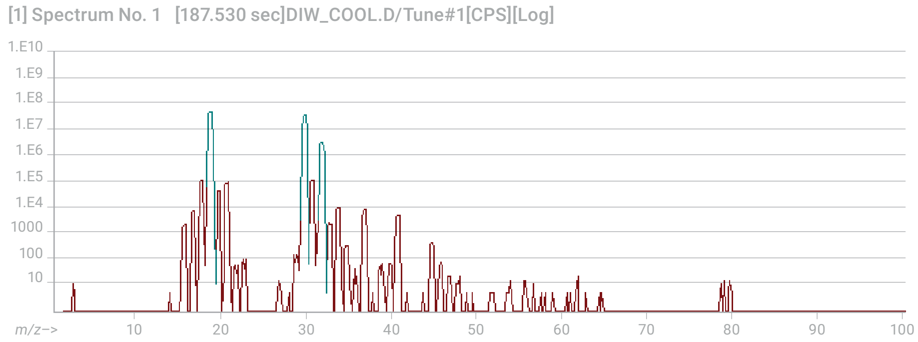

Figure 3. Spectrum of UPW acquired using cool plasma conditions in Single Quad mode with no gas mode.

References

1. K. Sakata and K. Kawabata, Reduction of fundamental polyatomic ions in inductively coupled plasma mass spectrometry, *Spectrochimica Acta*, Part B, **1994**, 49, 1027.
2. R. Marx, Y.M. Yang, G. Mauclaire, M. Heninger, and S. Fenistein, Radioactive lifetimes and reactivity of metastable NO$^+$($a^3\Sigma^+$,v) and O^+_2($a^4 \Pi_u$,v) , *J.Chem. Phys.*, Vol. 95, No. 4, 2259-2264, **1991**.

Ultratrace Measurement of Potassium and Other Elements in UPW Using ICP-QQQ in Cool Plasma/Reaction Mode

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Keywords

semiconductor, process chemicals, ultra pure water, UPW, potassium, cool plasma, ammonia on-mass

Introduction

The level of metal contaminants is strictly controlled in semicon device manufacturing processes, but the elements K, Ca and Fe are difficult 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 relatively low temperature plasma to remove the argide interferences allowing the analyst to measure these elements at trace levels. The low temperature plasma also reduces the background signal from any Easily Ionized Elements (EIEs) such as Li and Na that may deposit of on the interface of the ICP-MS. Even after the introduction of high concentration of EIEs, cool plasma ensures a low background level of these elements is maintained.

The Agilent 8800 ICP-QQQ provides improved cool plasma performance in combination with reaction cell technology, to enable a BEC of 30 ppq for K to be achieved 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.

Table 1. Cool plasma operating conditions.

Parameter	Unit	Tuning value
RF	W	600
Carrier gas	L/min	0.7
Make-up gas	L/min	0.8
Sampling depth	(mm)	18
NH_3 (10% in He) cell gas flow rate	mL/min	1

Experimental

Instrumentation: Agilent 8800 #200 (semiconductor configuration).

Plasma conditions: Cool plasma operating conditions (Table 1).

Reagents and sample preparation: The blanks and samples were acidified using high purity HNO_3 (TAMAPURE-AA-10, TAMA Chemicals Co. Ltd. Kanagawa, Japan). Standard solutions were prepared by serial dilution from a SPEX 331 mixed standard (SPEX CertiPrep, NJ, USA).

Cool plasma/NH_3 reaction cell mode

Investigation of the signal at *m/z* 39 under cool plasma conditions indicated the presence of $^{38}ArH^+$ which decreases with lowering plasma temperature, indicating a reduction in the ionization of the polyatomic ion. However, there was also a contribution from a water cluster ion, $(H_3O^+)(H_2O)$, which is likely to form under low temperature plasma conditions. The combination of these two interferences means that there is no plasma temperature at which both interferences can be minimized (Figure 1). As the water cluster ion is known to react with deuterated ammonia (ND_3) via a fast proton transfer reaction [1], it was assumed that reaction with NH_3 would proceed at a similar rate, so this cell gas mode was investigated in order to remove the water cluster ion in cool plasma conditions.

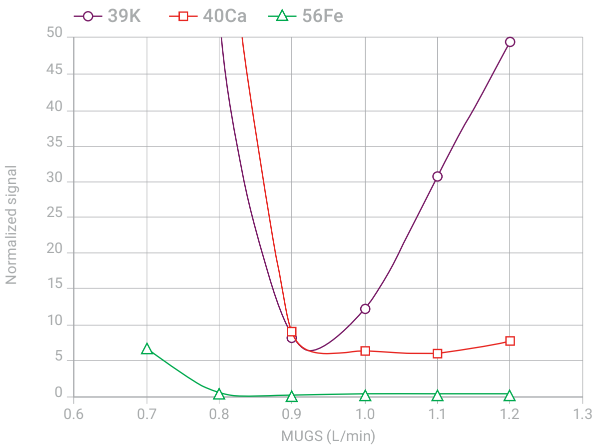

Figure 1. Investigation of the background signal under cool plasma conditions. BEC of K, Ca and Fe as a function of make-up gas (MUGS) flow rate.

Results and discussion

Ultra-low BEC for K using MS/MS mode

Ammonia reaction gas mode under cool plasma conditions was used to determine K in UPW. The BEC of K was measured at 30 ppq. A comparative study carried out using a 7500cs quadrupole ICP-MS in cool plasma/NH_3 reaction mode achieved a BEC of 500 ppt for K [2]. It would be reasonable to attribute the improvement of BEC achieved with the 8800 to the MS/MS reaction capability of the ICP-QQQ. In conventional quadrupole ICP-MS, ions formed under cool plasma conditions enter the reaction cell and react with NH_3 or with impurity residues present in the cell to form product ions at *m/z* 39. MS/MS prevents any unwanted precursor ions from entering the cell, thus minimizing the production of undesired product ions.

Multielement analysis

The cool plasma/NH_3 reaction mode method was applied to the multielement analysis of UPW. As can be seen from the results in Table 2, a BEC < 150 ppq was achieved for all elements, including K, Ca and Fe.

Table 2. DL and BEC of elements in UPW.

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

Conclusion

The Agilent 8800 ICP-QQQ was used to show the background signal at *m/z* 39 under cool plasma conditions was due to a water cluster ion, $H_3O(H_2O)^+$, which was removed using NH_3 cell gas. The 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 mode for reaction gas methods: MS/MS mode prevents all non-target ions from entering the cell, and thereby eliminates the possibility of unwanted reactions from occurring.

References

1. V. G. Anicich (2003.11), An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics (p369), NASA
2. Junichi Takahashi et al., Use of collision reaction cell under cool plasma condition in ICP-MS, Asia Pacific Winter Plasma Conference 2008 (O-10)

More information

Ultratrace measurement of potassium and other elements in ultrapure water using the Agilent 8800 ICP-QQQ in cool plasma reaction cell mode, Agilent publication 5991-5372EN

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

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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 u, 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.

With the introduction of the second generation Agilent 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
Make-up 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, hydrogen (H_2) on-mass mode was used for Si, and Cl was determined using H_2 mass-shift mode [1]. 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 u (*m/z* 48 for the primary $^{32}S^{16}O^+$ isotope product ion), as shown in the following equations:

$^{32}S^+ + O_2$ <cell gas> → $^{32}S^{16}O^+ + O$

$^{16}O_2^+ + O_2$ <cell gas> → 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:

$^{31}P^+ + O_2$ <cell gas> → $^{31}P^{16}O^+ + O$

$NOH^+/NO^+ + O_2$ <cell gas> → no reaction

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:

$^{28}Si^+ + H_2$ <cell gas> → no reaction

$^{14}N_2^+ + H_2$ <cell gas> → $N_2H^+ + H$

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

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 $^{16}O^{18}O^{1}H^+$ 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:

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

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

$^{16}O^{18}O^{1}H^+ + H_2$ <cell gas> $\rightarrow$ 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.

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		

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.

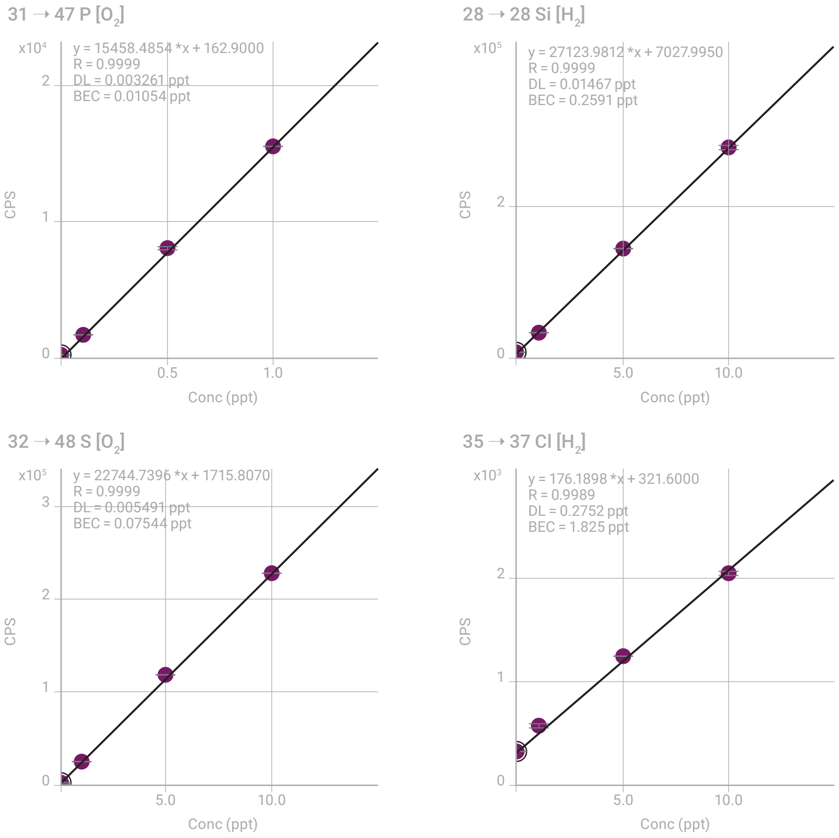

Figure 1. Calibration plots of P, S, Si and Cl in UPW. All values in ug/L (ppb).

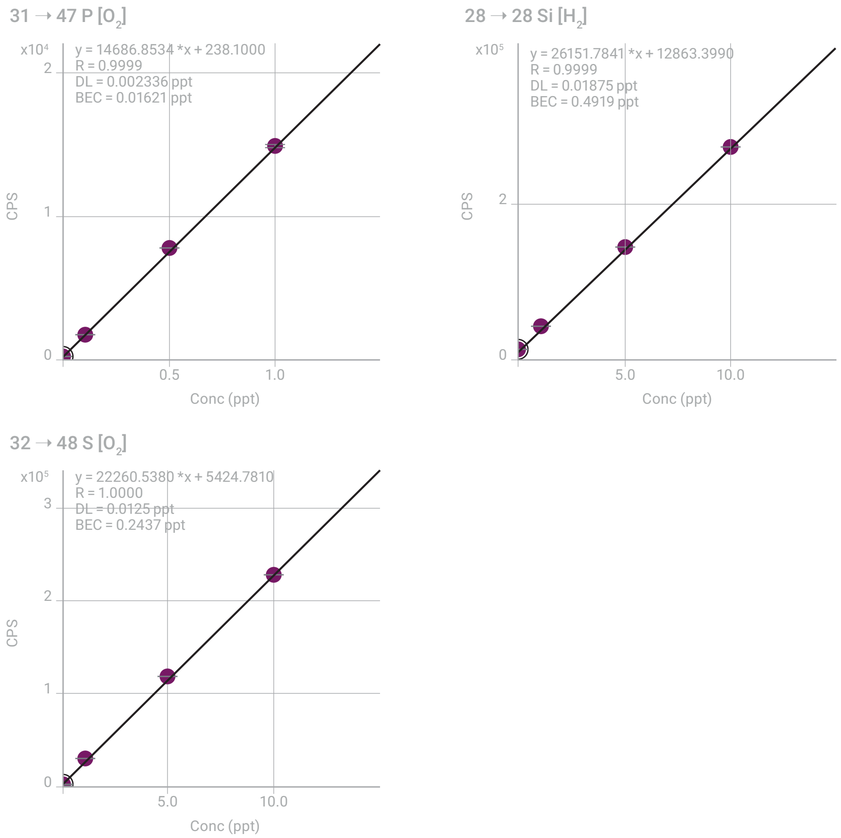

Figure 2. Calibration plots of P, S and Si in H_2O_2.

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 (ppt)	
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**		

Conclusion

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.

References

1. N. Sugiyama, Trace level analysis of sulfur, phosphorus, silicon and chlorine in NMP using the Agilent 8800 Triple Quadrupole ICP-MS, Agilent application note, 2013, 5991-2303EN

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Direct analysis of trace metal impurities in high purity nitric acid using ICP-QQQ

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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.

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.

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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					
Make-up gas (L/min)	0.78	0.36				
Ex1 (V)	-150	4.2	4.7	4.2	4.5	3.5
Ex2 (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)	-	-	-	-	4.5 (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 samples) 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 %
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	H_2	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

Element	Tune	Q1	Q2	DL (ng/L)	BEC (ng/L)	30 ppt Recovery %	Stability test RSD %
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

DLs were calculated as 3-sigma of 10 replicate measurements of a blank HNO3 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].

Table 3. 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.

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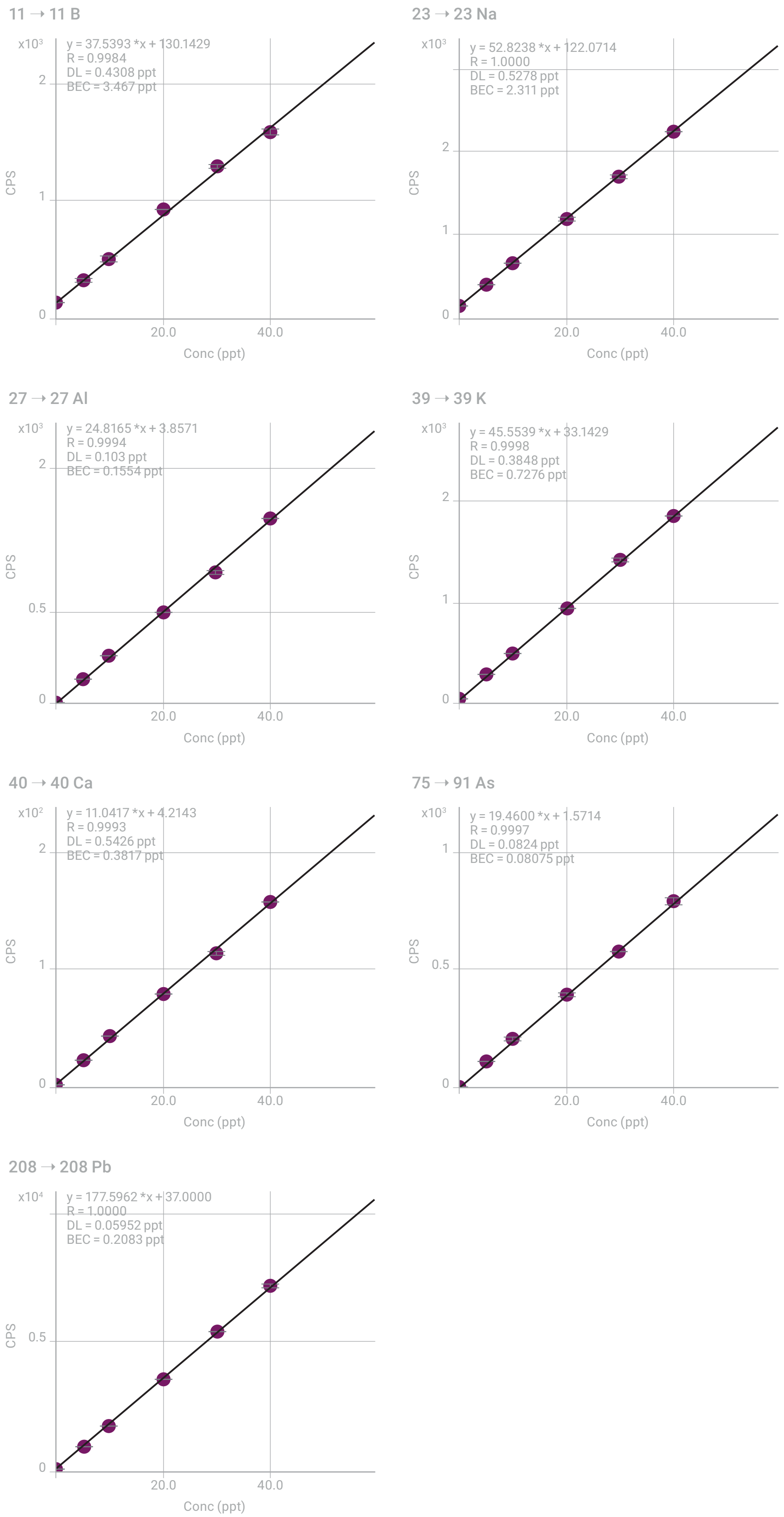

Figure 1. Calibration curves for several SEMI specification elements in high purity 68% HNO_3.

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.

Conclusion

The Agilent 8900 ICP-QQQ operating in MS/MS mode provides the sensitivity, low backgrounds, and effective 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

Direct Determination of V, Cr, Ge, and As in High-Purity 20% Hydrochloric Acid

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Keywords

semiconductor, RCA Standard Clean, silicon wafer, hydrochloric acid, vanadium, chromium, germanium, arsenic, ammonia on-mass, ammonia mass-shift, oxygen mass-shift

Introduction

Since the 1970s, the RCA Standard Clean (SC) method has been used extensively in many countries for cleaning silicon wafer surfaces. SC-2 refers to a mixture of HCl and H_2O_2 that is used to remove ionic and metallic contaminants from the surface of silicon wafers. Because cleaning solutions are in direct contact with semiconductor devices, ultra high purity is required for these solutions. The SEMI standard Tier-D protocol for HCl defines the contaminant level to be <10 ppt for each element. Some elements have been very difficult to determine at ppt level by quadrupole ICP-MS (ICP-QMS) due to significant spectral interferences arising from the Cl matrix, even when analyzed by ICP-MS equipped with a collision/reaction cell (CRC). Consequently, some methods for the analysis of high purity HCl by ICP-MS have recommended sample pre-treatment steps to remove the chloride matrix, which can lead to analyte loss and sample contamination. In this study, ICP-QQQ was used to analyze undiluted HCl directly. Using MS/MS mode with mass-shift to remove polyatomic ions, the most problematic elements, such as V, Cr, Ge and As could be determined in HCl at single-figure ppt detection limits.

Experimental

Instrumentation: Agilent 8800 #200. Operating parameters are given in Table 1.

Reagents: 20% TAMAPURE-AA-100 HCl (metallic impurities are guaranteed to be below 100 ppt) was purchased from Tama Chemicals Co., Ltd. (Kanagawa, Japan). The undiluted HCl was introduced directly into the ICP-QQQ.

Table 1. ICP-QQQ operating conditions.

		O_2 MS/MS[1)	NH_3 MS/MS[2)
RF power	W	1600	
Sampling depth	mm	8	
Carrier gas flow rate	L/min	0.8	
Make-up gas flow rate	L/min	0.41	
Octopole bias V	V	-20	
KED	V	-20	
He	mL/min	3	1
O_2	mL/min	0.4	0
NH_3	mL/min	0	3

1) 100% O_2 (purity 99.995%)
2) 10% NH_3 balanced with 90% He (purity 99.995%)

Results and discussion

Determination of BECs of V, Cr, Ge, and As in high purity HCl

ICP-QMS with a CRC using He collision mode can successfully eliminate some polyatomic ions such as ArCl [1], and the use of NH_3 as a reaction gas also works to remove the ClO^+ ion for the determination of V. However, ICP-QMS has some serious limitations when highly reactive cell gases (such as NH_3) are used in the CRC. Principal among these limitations is the fact that all ions enter the CRC, so predicted reaction pathways can be disrupted and new reaction product ion overlaps can be formed if the analyte levels in the sample change. ICP-QQQ with MS/MS removes this limitation, as the first quadrupole mass filter (Q1) allows precise selection of the ions that are allowed to enter the cell. This ensures that reaction processes and product ions are strictly controlled, dramatically improving detectability of the analyte ions shown in Table 2.

Table 2. Spectral interferences arising from the Cl matrix on some key elements.

Polyatomic interference	*m/z*	Analyte ion
ClO^+	**51, 53**	**$^{51}V^+$**
$ClOH^+$	**52, 54**	**$^{52}Cr^+$, ($^{54}Fe^+$)***
$ClCl^+$	**70, 72, 74**	**$^{70}Ge^+$, $^{72}Ge^+$, $^{74}Ge^+$**
$ArCl^+$	**75, 77**	**$^{75}As^+$, ($^{77}Se^+$)***

***Alternative isotopes can be chosen to avoid spectral interferences on Fe and Se.**

The MS/MS acquisition mode using O_2 or NH_3 as the reaction gas enables the determination of trace ^{51}V (measured directly as V^+ using NH_3 cell gas), Cr as $^{52}Cr^{16}O^+$ (using O_2), Ge as $^{74}Ge^{14}NH_2^+$ (using NH_3) and As as $^{75}As^{16}O^+$ (using O_2). In the case of As, the $^{91}Zr^+$ ion is removed by Q1 (which is set to the As^+ precursor ion mass of *m/z* 75), so the potential overlap from Zr on the AsO^+ product ion at *m/z* 91 is also removed. The complete cut-off of cluster ions by Q1 also eliminates the possibility that $^{14}NH_2{}^{35}Cl$ is created in the cell, so the potential new product ion interference on ^{51}V is avoided. Representative calibration curves for V and Ge are shown in Figure 1. BECs and DLs determined by the ICP-QQQ for V, Cr, Ge, and As are given in Table 3.

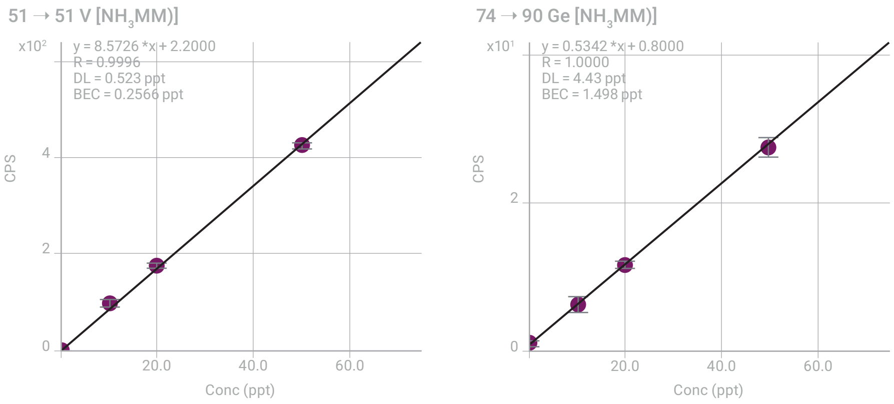

Figure 1. Calibration curves of V (NH_3 on-mass mode) and Ge (NH_3 mass-shift mode) in 20% HCl.

Table 3. BECs and DLs for V, Cr, Ge and As in 20% HCl.

Element	Ti	Cr	Ge	As
Mode (cell gas)	MS/MS (NH_3)	MS/MS (O_2)	MS/MS (NH_3)	MS/MS (O_2)
Measured ion	$^{51}V^+$	$^{52}Cr^{16}O^+$	$^{74}Ge^{14}NH_2^+$	$^{52}Cr^{16}O^+$
Mass pair	Q1 = Q2 = 51	Q1 = 52, Q2 = 68	Q1 = 74, Q2 = 90	Q1 = 75, Q2 = 91
BEC - ppt	0.3	8.0	1.5	19.7
DL - ppt	0.5	1.1	4.4	3.4

Investigation of arsenic contamination

As the BEC for arsenic in high purity HCl was relatively high (Table 3), the signal count at *m/z* 91 was investigated further. The signals of the mass-pairs 75/75, 77/77, 75/91 and 77/91 were measured by ICP-QQQ with MS/MS, the mass pair number represents the set mass of Q1 followed by the set mass of Q2, so an MS/MS mode acquisition of mass pair 75/91 represents a mass-shift mode with Q1 = 75 and Q2 = 91, for example. The four mass pairs were measured in HCl blanks from three different lots, and the results are shown in Table 4.
The following observations were made:

1. The ratio of the signal of 75/75 to 77/77 is around four, which is close to the ratio of the abundance of ^{35}Cl to ^{37}Cl, i.e. 3.13.
2. The ratio of the signal of 75/91 to 77/93 is 200–1000, which is far in excess of the ratio of ^{35}Cl to ^{37}Cl.
3. While the signals of 75/75 and 77/77 are similar for the three HCl blanks, those of 75/91 and 77/93 vary.

Table 4. Comparison of background counts (cps) in 3 different lots of 20% HCl*.

Mass pair	75->75	77->77	75->91	77->93
Sample A	509.3	133.5	584.4	2.5
Sample B	508.4	126.0	1172.6	1.9
Sample C	612.7	130.0	3175.6	2.6

***All the samples were obtained from the new bottles of high purity HCl.**

Finding #1 suggests that the remaining signal on 75/75 and 77/77 was mostly from $ArCl^+$. This is a reasonable assumption since $ArCl^+$ doesn't react with O_2 very efficiently so most $ArCl^+$ remains at the original masses of 75 and 77. Finding #2 suggests that the signal of 75/91 is not due to $ArCl^+$. Assuming that all counts of 77/93 arise from $^{40}Ar^{37}Cl$, the contribution of $^{40}Ar^{35}Cl$ to the signal of 75/91 in the HCl blank is estimated to be just 7-8 cps, which is two orders of magnitude lower than the signal that is actually observed. Observation #3, together with #1 and #2, suggests the high count obtained for 75/91 in HCl is due to As impurity in the acid.

Reference

1. Direct analysis of trace metallic impurities in high purity hydrochloric acid by Agilent 7700s ICP-MS, Agilent application note, 5990-7354EN.

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Analysis of trace metal impurities in high purity hydrochloric acid using ICP-QQQ

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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	18.0 8.0					
Nebulizer gas (L/min)	0.70						
Make-up gas (L/min)	0.90	0.48					
Extract 1 (V)	-150		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 samples) 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

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

Element	Cell gas mode	Q1 mass	Q2 mass	DL ng/L	BEC ng/L
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

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.

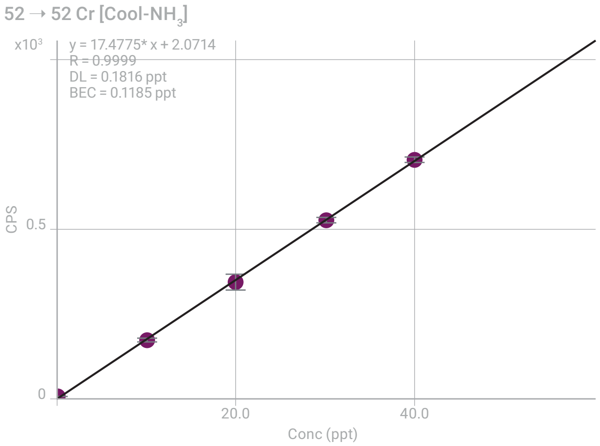

Figure 1. ^{52}Cr calibration curve obtained using cool plasma and NH$_3$ cell gas, showing low BEC and good linearity.

The same approach is effective for the determination of other interfered elements such as K. Figure 2 shows that the interference from H^{237}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.

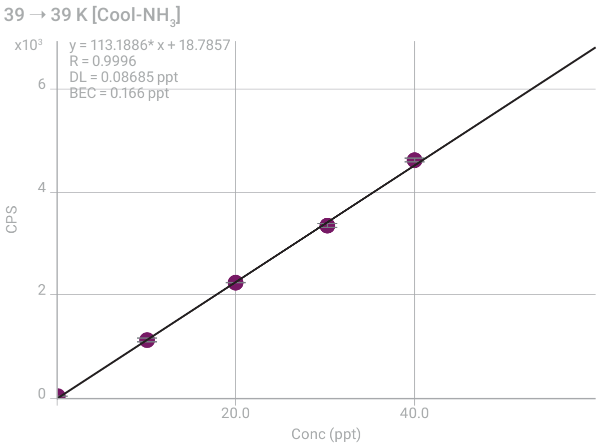

Figure 2. ^{39}K calibration curve obtained using cool plasma and NH$_3$ cell gas.

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.

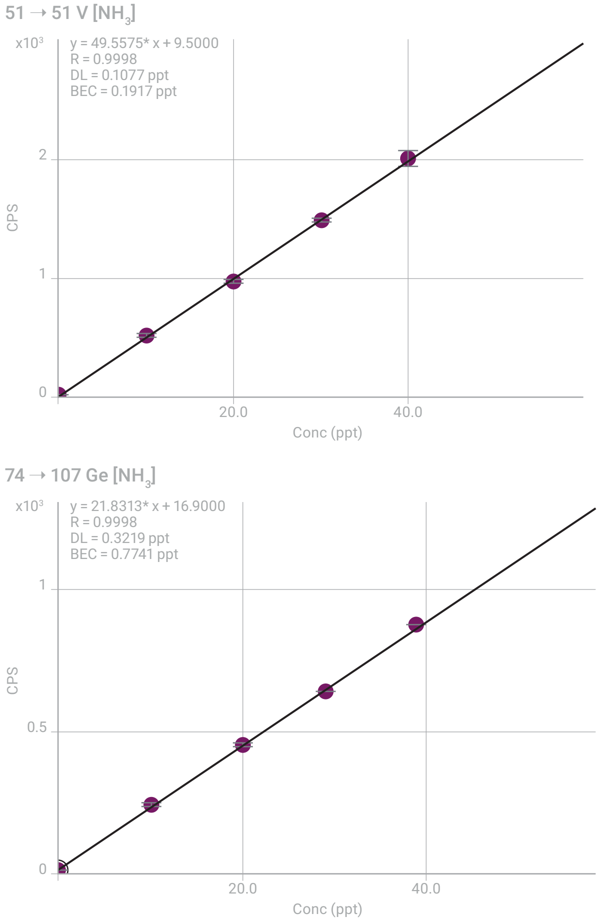

Figure 3. ^{51}V and ^{74}Ge calibration curve obtained using NH_3 cell gas.

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.

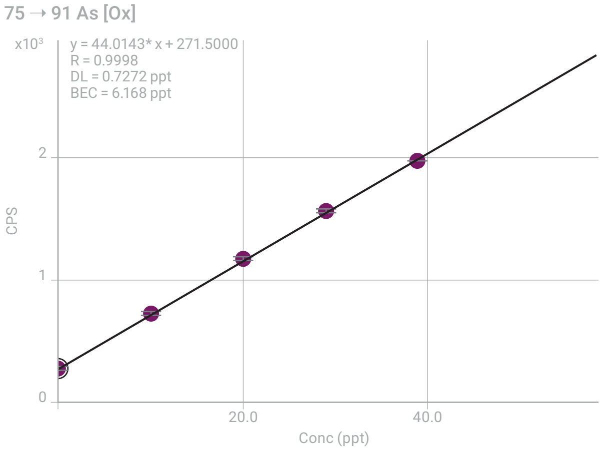

Figure 4. ^{75}As MSA calibration curve obtained in Sample 1 using O_2 cell gas.

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.

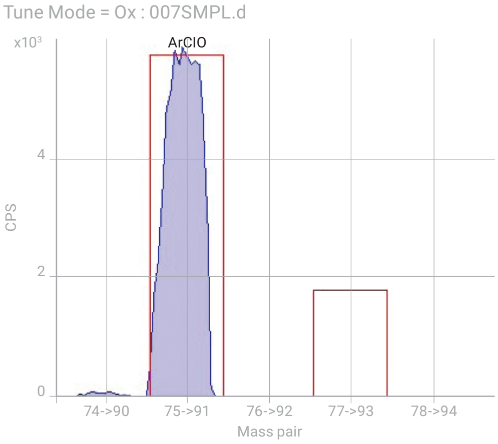

Figure 5. Neutral gain scan spectrum for 20% high purity HCl showing the theoretical isotope template for $^{40}Ar^{35}Cl^{16}O^+$ and $^{40}Ar^{37}Cl^{16}O^+$. Q1 was scanned from *m/z* 74 to 78, while Q2 was set to Q1 + 16.

Conclusion

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, powerful MS/MS capability, and proven 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

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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Determination of Ti, V, and Cr in 9.8% Sulfuric Acid

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Keywords

semiconductor, process chemicals, ultra pure water, UPW, calcium, method of standard additions, hydrogen on-mass

Introduction

High purity H_2SO_4 is frequently used in the manufacturing of semiconductor devices, in processes such as the removal of organic substances from the surface of silicon wafers. The required metallic impurity level is lower than 100 ppt in the concentrated (usually 98%) acid. ICP-MS is the technique of choice for the measurement of trace metal impurities in semiconductor process chemicals. There are, however, some limitations for the measurement of elements such as Ti, V and Cr in H_2SO_4. Because of its high viscosity of 27 cP, it is not possible to introduce H_2SO_4 directly into the ICP without dilution. A 10 times dilution in UPW is normally applied, thus the BEC of the calibration curve must be lower than 10 ppt in the 9.8% H_2SO_4 solution measured. In addition, spectral interferences from SO^+, S_2^+ and ArS^+ originating from H_2SO_4 make it difficult to determine elements such as Ti and Cr at low concentration even by quadrupole ICP-MS (ICP-QMS) equipped with collision/reaction cell (CRC). As outlined in this report, the Agilent 8800 ICP-QQQ with MS/MS mode allows the successful determination of the most problematic elements including Ti, V and Cr in H_2SO_4.

Experimental

Instrumentation: Agilent 8800 #200. Operating parameters are given in Table 1.

Reagents and sample preparation: Highly purified H_2SO_4, TAMAPURE-AA-100 (98% H_2SO_4) was purchased from Tama Chemicals Co., Ltd. (Kanagawa, Japan). 5 g of H_2SO_4 was diluted by a factor of 10 in a chilled PFA bottle.

Table 1. ICP-QQQ operating conditions.

		O_2 MS/MS 1)	NH_3 MS/MS 2)
RF power	W	1600	
Sampling depth	mm	8	
Carrier gas flow rate	L/min	0.8	
Make-up gas flow rate	L/min	0.41	
Octopole bias V	V	-20	
KED	V	-20	
He	mL/min	3	1
O_2	mL/min	0.4	0
NH_3	mL/min	0	3

1) 100% O_2 (purity 99.995%)
2) 10% NH_3 balanced with 90% He (purity 99.995%)

Results and discussion

Of the potential polyatomic interferences formed from the H_2SO_4 matrix, the SO^+ ion is very stable and difficult to eliminate because its dissociation energy is as high as 5.44 eV. In addition, its ionization potential is 10.3 eV, which is almost the same as that of S, 10.36 eV. The spectral interferences caused by SO^+ and SOH^+ overlap with ^{48}Ti ($^{32}S^{16}O$), ^{51}V ($^{33}S^{18}O$, $^{34}S^{16}OH$ and $^{32}S^{18}OH$) and ^{52}Cr ($^{34}S^{18}O$). Quadrupole ICP-MS operating in He collision mode provides BECs of 60 ppt for ^{47}Ti (the BEC for the preferred isotope ^{48}Ti is much higher), 3 ppt for V and 8 ppt for Cr in 9.8% H_2SO_4. The BEC of Ti, in particular, is not acceptable for producers and users of semiconductor grade H_2SO_4.

Appropriate reaction gases to remove SO^+ successfully in ICP-QMS are difficult to find. NH_3 can reduce SO^+ by two orders of magnitude but the background signal remains too high for this application. Additionally, cluster ions of NH_3 such as N_mH_n produced by the reaction between Ar^+ and the NH_3 cell gas lead to new reaction product ion interferences that increase the background at *m/z* 51, for example.

The 8800 ICP-QQQ operating in MS/MS mass-shift mode with NH_3 or O_2 reaction gas provides reliable and consistent measurement of Ti as $^{48}Ti^{14}NH(^{14}NH_3)_3$ (Figure 1) and Cr as $^{52}Cr^{16}O$ in H_2SO_4. Furthermore, in MS/MS mode, the Ar^+ ion is removed by Q1, preventing it from reacting with NH_3 to form new product ion interferences in the cell. This reduces the background at *m/z* 51 improving the BEC for V, as shown in Figure 2. The final BECs obtained by ICP-QQQ in 9.8% high purity H_2SO_4 are summarized in Table 2.

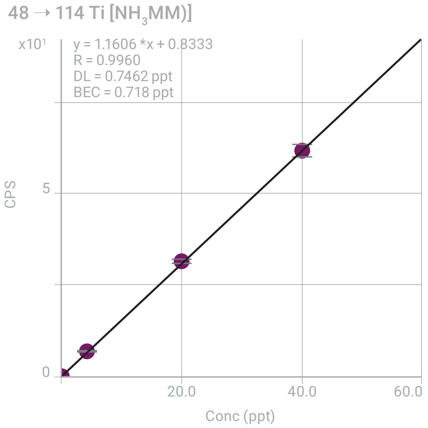

Figure 1. Calibration curve of Ti in 9.8% H_2SO_4.

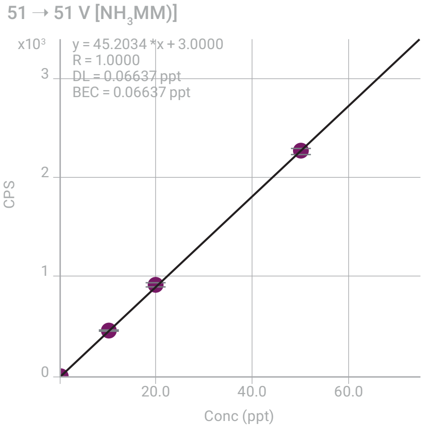

Figure 2. Calibration curve of V in 9.8% H_2SO_4.

Table 2. BECs of Ti, V and Cr in 10x diluted 98% H_2SO_4, measured by ICP-QQQ.

Element	Ti	V	C
Mode (cell gas)	MS/MS (NH_3)	MS/MS (NH_3)	MS/MS (O_2)
Measured ion	$^{48}Ti^{14}NH(^{14}NH_3)_3+$	$^{51}V^+$	$^{52}Cr^{16}O^+$
Mass pair	Q1 = 48, Q2 = 114	Q1 = Q2 = 51	Q1 = 52, Q2 = 68
BEC - ppt	0.72	0.07	3.70

Conclusion

ICP-QQQ operating in MS/MS mode provides a reliable means for manufacturers of high purity H_2SO_4 to guarantee all metallic impurity concentrations at less than 100 ppt in the concentrated acid.

More information

Determination of challenging elements in ultrapure semiconductor grade sulfuric acid by Triple Quadrupole ICP-MS, Agilent publication, 5991-2819EN

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

Authors

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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.

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.

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.

Table 1. ICP-QQQ operating parameters.

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

[1] *High engergy He mode conditions*

[2] *10% NH_3 balanced with 90% He*

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.

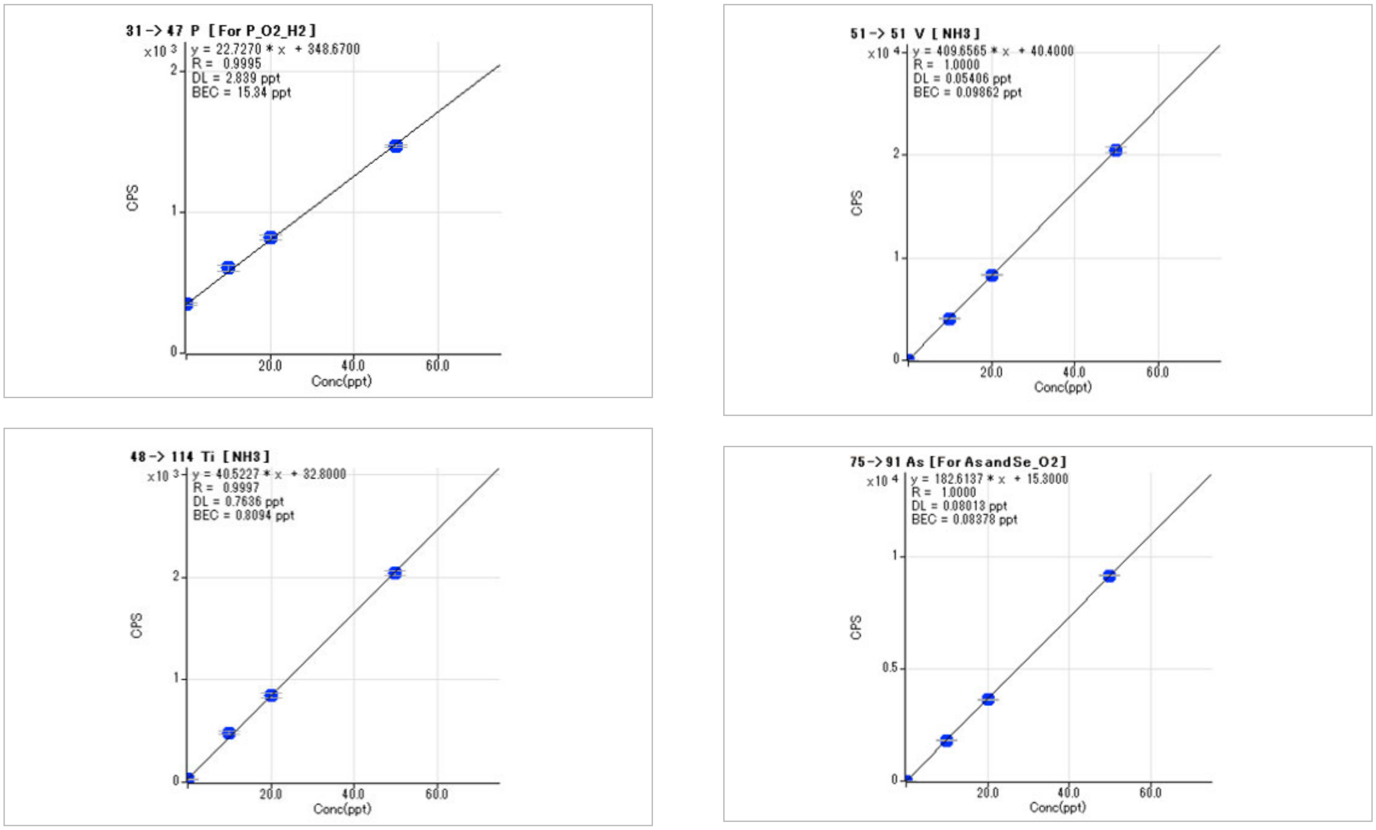

Figure 1. Calibration curves of P, Ti, V and As in 9.8% H_2SO_4

Table 2. Quantitative results for 42 elements in 9.8% H2SO4.

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.

References

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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Multielement Nanoparticle Analysis of Semiconductor Process Chemicals Using spICP-QQQ

Authors

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Characterization of Ag, Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs in TMAH in a single analytical run

Introduction

Technologies such as smartphones, cloud computing, the Internet of Things (IoT), and development of autonomous vehicles continue to drive demand for semiconductor products. To meet the requirements for higher integrated circuit (IC) performance and improved device yield, contamination must be controlled in the wafer substrate and on the surface of the device during fabrication. Given the nanometer scale of device features, there is a critical need to monitor metallic nanoparticles (NPs), as well as dissolved metals. Analysis of NPs present in bulk chemicals, silicon wafers, and cleaning bath solutions is important. If a particle is present between two metal lines, it may cause electrical shorting to occur, and surface defects can affect the growth of new layers on the silicon wafer. To fully investigate the cause/source of any particle contamination, multi-element analysis of NPs is necessary. ICP-MS is used increasingly to measure nanoparticles directly in sample solutions, using single particle inductively coupled plasma mass spectrometry (spICP-MS). With growing interest in characterizing NPs in various semiconductor samples, the technique is currently being evaluated within the industry.

The Single Nanoparticle Analysis software module available for ICP-MS MassHunter provides the method setup, analysis, and data interpretation tools for single particle ICP-MS analysis. spICP-MS has been used for a range of studies, from the analysis of gold NPs in simple matrices to TiO2 NPs in complex samples (1–4). To facilitate multiple element NP analysis, Agilent has developed Rapid Multi-Element Nanoparticle Analysis software. The software can collect data sequentially for up to 16 elements in a single sample analysis, using optimum conditions for the measurement of each individual element (6). This function saves time and reduces the risk of sample contamination compared to conventional spICP-MS analysis, as data for multiple elements can be obtained with only one visit to the sample vial.

In this study, multiple element NPs including Ag, Fe3O4, Al2O3, Au, and SiO2 were measured in semiconductor grade tetra methyl ammonium hydroxide (TMAH). TMAH is widely used as a basic solvent in the development of photoresist in the photolithography processing of ICs. Since TMAH comes into direct contact with the wafer surface, avoiding contamination of the chemical is critical. The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used for the analysis because of its high sensitivity, low background, and effective interference removal capability.

Experimental

Sample reagents and NP standards

A 60 nm silver NP (Sigma Aldrich, P/N 730815) reference material (RM) was used to measure the nebulization efficiency, which is required for the calculation of particle size and particle concentration. The value was calculated using RM size and the sensitivity of an ionic Ag solution (Kanto Chemical, Japan).

Solutions containing 30 nm iron oxide (Fe_3O_4) NPs (Sigma Aldrich, P/N 747408), 30~60 nm aluminum oxide (Al_2O_3) NPs (Sigma Aldrich, P/N 642991), 200 nm silica (SiO_2) NPs (nanoComposix, P/N SISI200), and 60 nm gold NPs (NIST 8013) were used as NP standards. The sample comprised 25 wt% TMAH diluted to 1 wt % (25 times dilution) with de-ionized water (Organo, Japan).

Sample preparation

To verify the method for the measurement of multiple element NPs, the Ag RM and four NP standards were dispersed in 1 wt % TMAH using the preparation procedure shown in Figure 1. To prepare the intermediate solutions, 1% TMAH was used as the diluent for Al_2O_3 NPs, while DIW was used for the other NPs. Better dispersion was obtained for Al_2O_3 NPs using TMAH as the diluent.

Instrumentation

An Agilent 8900 ICP-QQQ (Semiconductor configuration) was used for all measurements. The sample introduction system comprised a quartz torch with a 1.5 mm i.d. injector, quartz spray chamber, a PFA concentric nebulizer, and platinum-tipped interface cones. The samples were self-aspirated using an Agilent I-AS integrated autosampler.

The 8900 ICP-QQQ was operated in MS/MS mode for all measurements, with Q1 and Q2 acting as unit mass filters. Q1 selects which elements enter the ORS[4] collision/reaction cell (CRC), allowing controlled reaction chemistry to take place in the cell when a reactive cell gas such as hydrogen (H_2) or ammonia (NH_3) is used. The 8900 can also operate in helium (He) collision mode, which is effective for the elimination of many common polyatomic ions using kinetic energy discrimination (KED).

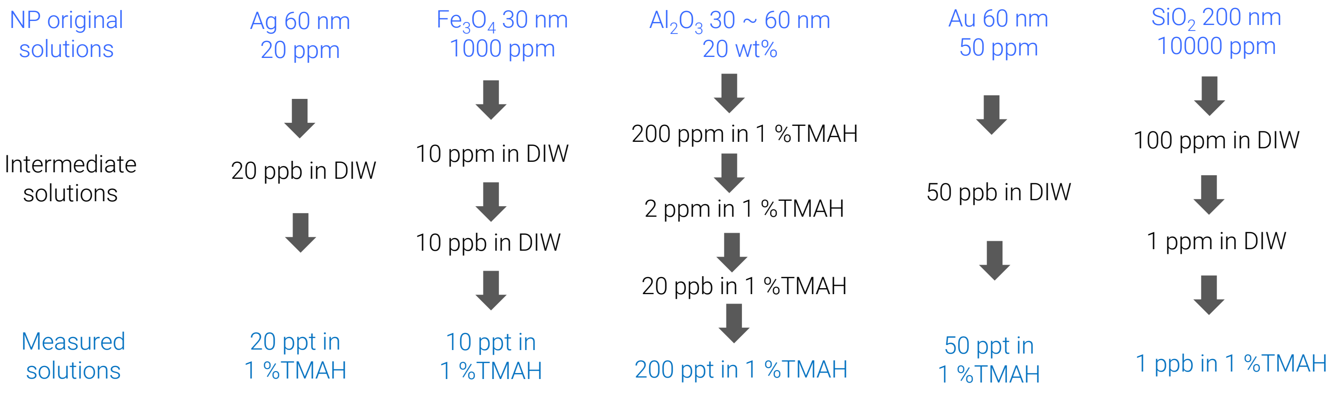

Figure 1. Sample preparation procedure.

NPs containing ^{28}Si, ^{197}Au, ^{27}Al, ^{56}Fe, or ^{107}Ag were measured in fast Time Resolved Analysis (fast TRA) mode. Fast TRA allows single element acquisition at a sampling rate of 100 µs (10,000 measurements per second) with no settling time between measurements (*7*). All elements were measured on-mass in MS/MS mode, with Q1 and Q2 set to the same mass. H_2 cell gas was used to eliminate any on-mass polyatomic interferences on ^{28}Si, such as $^{12}C^{16}O$ and $^{14}N_2$. NH_3 mode was used to control the ArO and C_2O_2 interference on Fe at *m/z* 56 and the C_2H_3 and CNH interferences on Al at *m/z* 27. NH_3 was also used to eliminate any of potential interferences from the carbon matrix on Ag at *m/z* 107. Au is less susceptible to polyatomic interference so can be measured using He or no gas mode. During the analysis, ICP-MS MassHunter changes between each tune step sequentially, ensuring that optimum conditions are used for the measurement of each element.

Multiple element NP data acquisition and analysis were performed using the Rapid Multi-Element Nanoparticle Analysis mode of the Single Nanoparticle Application Module of ICP-MS MassHunter. In Rapid Multi-Element Nanoparticle Analysis mode, multi-element data is collected sequentially from a single sample acquisition, with the multi-element data being combined into a single data file. This approach saves time, as only one sample uptake and rinse time is required for all analytes. Data quality is likely to be improved, as the risk of sample contamination using a single analysis-approach is significantly reduced compared to performing multiple, separate analyses.

The operating conditions of the Agilent 8900 ICP-QQQ are detailed in Table 1.

Table 1. ICP-MS operating conditions.

Parameter	Value		
	H_2 mode	He mode	NH_3 mode
RF power (W)	1200		
Sampling depth (mm)	12		
Nebulizer gas (L/min)	0.70		
Makeup gas (L/min)	0.20		
Sample uptake rate (mL/min)	0.216 (self aspiration)		
Spray chamber temp. (°C)	2		
Extraction lens 1 (V)	−100		
Extraction lens 2 (V)	−10		
Octopole bias (V)	−18	−8	−8
Axial acceleration (V)	1	1	1.5
Energy discrimination (V)	3	3	−10
H_2 cell gas flow rate (mL/min)	6	0	0
He cell gas flow rate (mL/min)	0	2	1
NH_{3*} cell gas flow rate (mL/min)	0	0	3.0 (30 % of full scale)
Dwell time (µs)	100		
Masses monitored *(m/z)*	Si (Q1:28, Q2:28)	Au (Q1:197, Q2:197)	Al (Q1:27, Q2:27) Fe (Q1:56, Q2:56) Ag (Q1:107, Q2:107)
Data acquisition time (s/element)	30		

Results and discussion

Nebulization efficiency measurement

To convert the signals measured using spICP-MS to the particle content of the original sample, it is necessary to calculate the nebulization efficiency.
The nebulization efficiency is the ratio of the amount of analyte entering the plasma to the amount of analyte delivered to the nebulizer. Here, the nebulization efficiency was calculated by measuring a reference material (Ag NP) of known particle size. A 60 nm Ag NP RM dispersed in 1% TMAH and an ionic Ag solution (in 1% TMAH base) were measured. The Single Nanoparticle software automatically calculated the nebulization efficiency as 0.081 (8.1%). The signal distribution and the size distribution graphs of Ag NPs in 1% TMAH are shown in Figure 2.

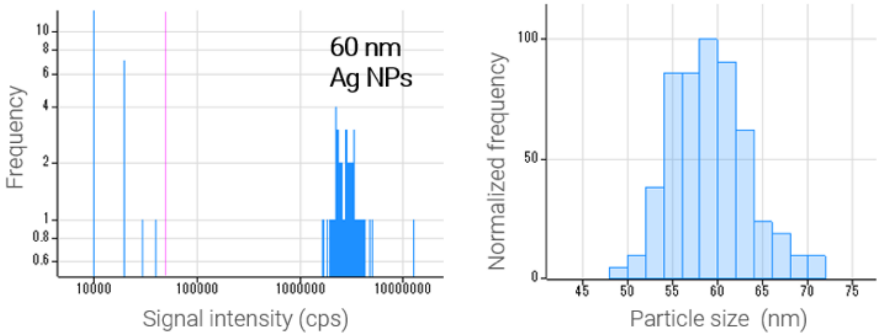

Figure 2. Signal distribution (left) and size distribution (right) of Ag NPs in 1% TMAH solution.

Analysis of various kinds of NPs in TMAH

Blank TMAH and TMAH solution spiked with Fe_3O_4, Al_2O_3, Au, or SiO_2 NPs were measured using the multi-element spICP-MS method. The time resolved signal, signal distribution, and size distribution for Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs are shown in Figure 3.

The Rapid Multi-Element Nanoparticle Analysis software enabled multiple element NP data to be quickly collected. Less than six minutes were required for the measurement of all elements, which equates to a saving of 7 minutes compared to separate, single sample analyses. The time-saving per sample can be calculated using the following equation, which means that more time can be saved if more elements are measured.

Time saving per sample = (number of measured elements -1)
× (sample uptake time + rinse time)

The improved Single Nanoparticle Application Module software automatically sets the signal baseline in the TRA data, which is shown in light blue in the time charts in Figure 3. The improved software also sets the particle threshold, which separates particle-generated signals from the background or ionic signals. The particle threshold is shown by the vertical red/pink line in the signal distribution graphs in Figure 3.

The measured size and size distribution data for all four spiked NP samples agreed with the expected results (Figure 3). The results for Fe_3O_4 and SiO_2 NPs show that both NPs were present in the blank TMAH solution analyzed in this study, although not all TMAH solutions are likely to contain NPs.

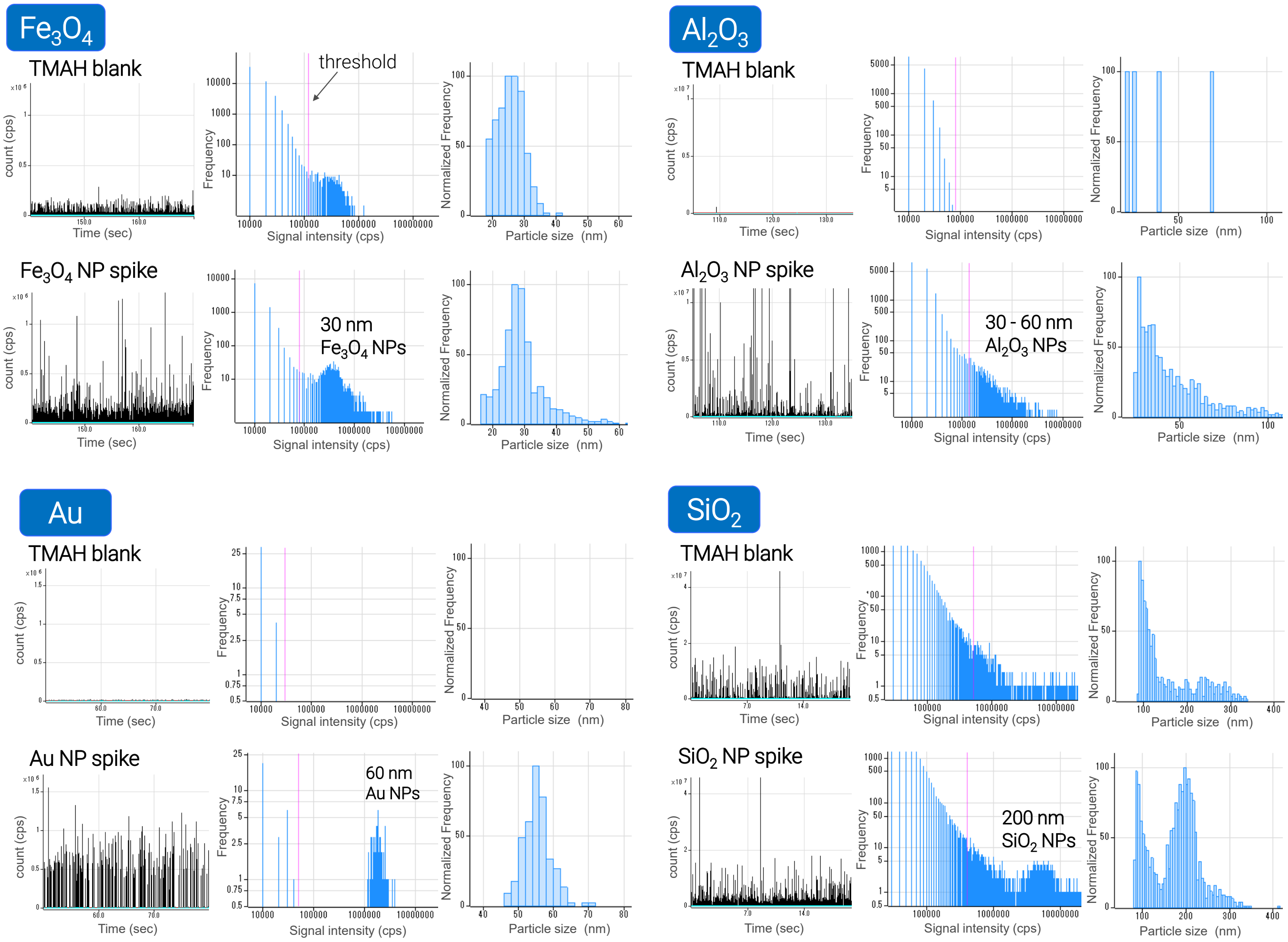

Figure 3. Time resolved signal, signal distribution, and size distribution graphs for Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs. The upper graphs for each NP show the results from 1% TMAH without NP spike; the lower graphs show the results with NP spike.

Figure 4 summarizes the size data for multiple element NPs in 1% TMAH. The blue histograms show NPs present in the unspiked (original) TMAH solution. The green histograms show NPs present in the spiked TMAH solution. The results show that all five NPs were detected separately, even in the mixed NP TMAH solution. Using the multiple element spICP-MS method, small particles (e.g. 30 nm Fe_3O_4) can be clearly measured with good accuracy even in the presence of larger particles (e.g. 200 nm SiO_2).

Long-term stability test

Figure 5 shows the stability of particle concentration and particle size for five NPs in 1% TMAH over 10 hours. For Ag NPs, both the particle concentration and the size decreased over time, suggesting that Ag NPs are easily dissolved in 1% TMAH solution. For Fe_3O_4 NPs, the size was constant, but the particle concentration decreased over time. Rather than being dissolved in TMAH, Fe_3O_4 NPs are likely to settle or be adsorbed onto the surface of the sample container. Al_2O_3 and SiO_2 NPs were stable in terms of particle concentration and size over 10 hours. The size profile of the Au NPs remained constant over 10 hours, while the particle concentration remained broadly stable over 10 hours after a slight change during the first three hours.

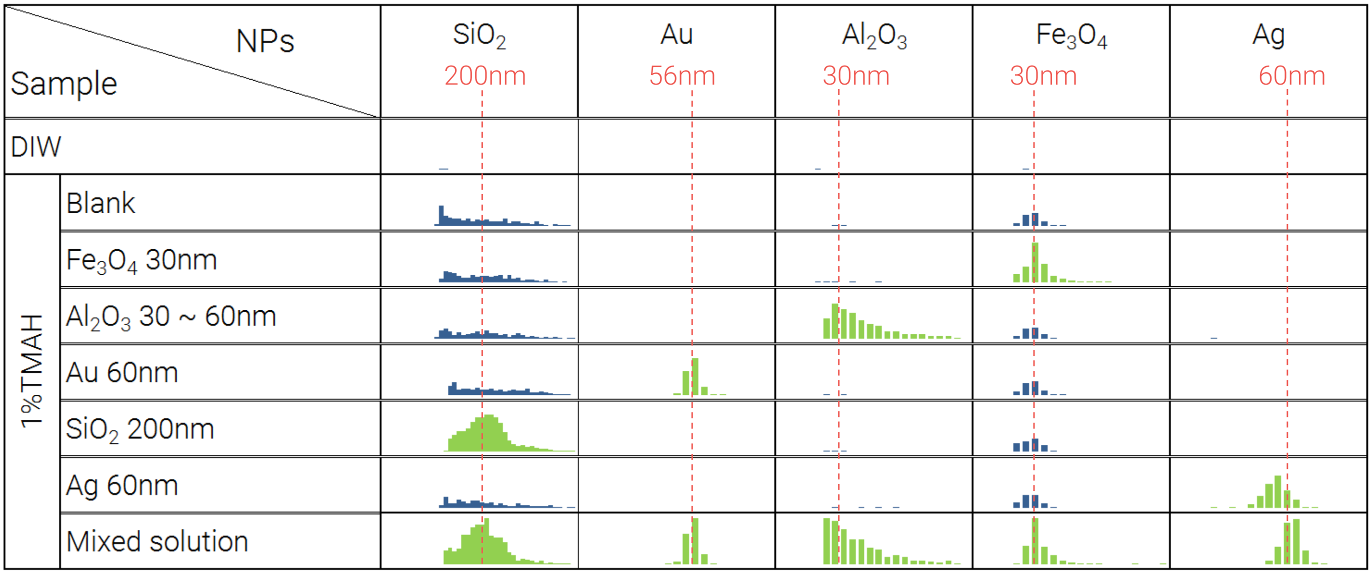

Figure 4. Size distribution overview for multiple element NPs in 1% TMAH. The results for the unspiked TMAH solution are shown in blue and the spiked TMAH solution results are shown in green.

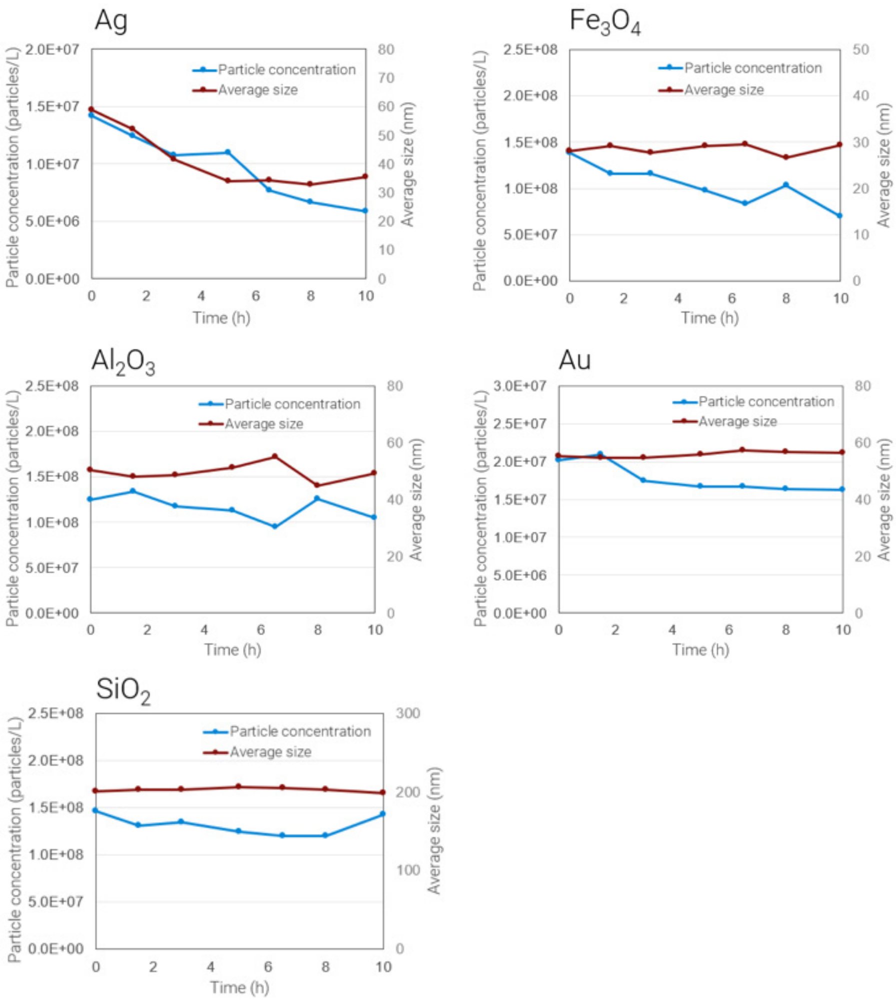

Figure 5. Long-term stability of NP solutions of Ag, Fe_3O_4, Al_2O_3, Au, and SiO_2. The blue line shows the particle concentration and the red line shows the average particle size.

Conclusion

Multiple element nanoparticles were determined and characterized in 1% TMAH using the Agilent 8900 ICP-QQQ operating in multi-element spICP-MS mode. The MS/MS method delivered the low background, high sensitivity, and interference control necessary for the analysis of multiple element NPs in semiconductor grade chemicals.

Using specially developed Rapid Multi-Element Nanoparticle Analysis software, multi-element data for Ag, Al_2O_3, Fe_3O_4, Au, and SiO_2 NPs were collected from a single sample acquisition and combined into a single table of results. The table provides comprehensive information about the nanoparticles containing each of the measured elements. The results showed that small particles such as 30 nm Fe_3O_4 NPs could be measured in solutions containing larger particles, such as 200 nm SiO_2 NPs. The particle size and particle concentration of Al_2O_3 and SiO_2 NPs were stable in 1% TMAH solution over 10 hours, while the particle concentration of Fe_3O_4 and Ag NPs decreased over time. The results suggest that Fe_3O_4 and Ag NPs in TMAH solutions should be measured as soon as they are prepared. While the particle size of Fe_3O_4 NPs remained stable in 1% TMAH, the variation in the concentration of NPs over time requires further investigation.

The study showed that samples containing nanoparticles composed of different and/or multiple elements can be determined quickly and accurately using spICP-MS. Compared to acquiring data separately for each NP, the Rapid Multi-Element Nanoparticle Analysis software simplifies the analytical method and shortens the sample run times by seven minutes. If more elements are measured, more time can be saved.

References

1. Susana Nunez, Heidi Goenaga Infante, Michiko Yamanaka, Takayuki Itagaki, Steve Wilbur, Analysis of 10 nm gold nanoparticles using the high sensitivity of the Agilent 8900 ICP-QQQ, Agilent publication, 5991-6944EN
2. Jenny Nelson, Michiko Yamanaka, Francisco Lopez-Linares, Laura Poirier, Estrella Roge, Single Nanoparticle Analysis of Asphaltene Solutions using the Agilent 8900 ICP-QQQ: ICP-MS MassHunter software module simplifies spICP-MS analysis, Agilent publication, 5991-9498EN
3. Michiko Yamanaka, Steve Wilbur, Accurate Determination of TiO_2 Nanoparticles in Complex Matrices using the Agilent 8900 ICP-QQQ, Agilent publication, 5991-8358EN
4. Michiko Yamanaka, Takayuki Itagaki, Steve Wilbur, High sensitivity analysis of SiO_2 nanoparticles using the Agilent 8900 ICP-QQQ in MS/MS mode, Agilent publication, 5991-6596EN
5. Michiko Yamanaka and Steve Wilbur, Measuring Multiple Elements in Nanoparticle using spICP-MS: Acquire NP data for up to 16 elements in Rapid Multi-Element Nanoparticle Analysis Mode, Agilent publication, 5994-0310EN
6. Craig Jones, Emmett Soffey, Mark Kelinske, Rapid Multielement Nanoparticle Analysis Using Single-Particle ICP-MS/MS, *Spectroscopy*, **2019**, 34, 5, 10–20. Link.
7. Steve Wilbur, Michiko Yamanaka, and Sebastien Sannac, Characterization of nanoparticles in aqueous samples by ICP-MS, Agilent publication, 5991-5516EN

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Silicon Wafer Analysis by ICP-QQQ: Determination of Phosphorus and Titanium in a High Silicon Matrix

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Keywords

semiconductor, silicon wafer, phosphorus, titanium, Vapor Phase Decomposition, VPD, oxygen mass-shift

Introduction

The semiconductor industry first used ICP-MS for trace element analysis in the early 1980s. Nowadays the technique is widely used for control of trace impurities in materials and chemicals, particularly by silicon device manufacturers. The major challenge for quadrupole ICP-MS (ICP-QMS) is the presence of spectroscopic interferences on key contaminant elements, although performance has been gradually improved through developments such as cool plasma and collision/reaction cells (CRC), and improved performance has also been provided by high resolution ICP-MS. Consequently, metallic impurity control of silicon wafers can be successfully monitored by ICP-MS in the case of low silicon samples such as Vapor Phase Decomposition (VPD) of native silicon wafers. However, difficulties of Si-based spectral interferences, particularly on P and Ti, still affect the analysis of samples that contain high concentrations of Si, such as VPD samples of thermally oxidized wafers and samples relating to bulk silicon wafers. These interferences cannot be reduced adequately by ICP-QMS and have required HR-ICP-MS. In this paper, we evaluate triple quadrupole ICP-MS with MS/MS technology for the determination of ultratrace P and Ti in a high Si matrix.

Experimental

Instrumentation: Agilent 8800 #200 with an inert sample introduction kit including a low flow nebulizer (PFA-20) and a Pt/Ni skimmer cone. The actual sample uptake rate was 36 µL/min. The sample was self-aspirated from an Agilent I-AS autosampler.

Plasma conditions: Robust tuning conditions were applied as summarized in Table 1.

Ion lens tune: Extract 1 = 0 V was used and other lens voltages were optimized using Auto tune.

Sample preparation: Silicon wafer samples were dissolved in TAMAPURE HF/HNO_3 and the final Si concentration was adjusted to 2000 ppm.

Table 1. Robust tuning conditions.

		O_2 MS/MS	H_2 MS/MS
RF power	W	1600	
Sampling depth	mm	8	
Carrier gas flow rate	L/min	0.6	
Make-up gas flow rate	L/min	0.6	
He	mL/min	3	0
O_2	mL/min	0.4	0
H_2	mL/min	0	10

Results and discussion

Phosphorus is monoisotopic at *m/z* 31, and suffers an interference from ^{30}SiH. While P^+ can be detected as PO^+ under cool plasma conditions, it is difficult to maintain cool plasma when the matrix concentration is high. Si sample solutions always contain HF, so Si will form SiF (IP: 7.54 eV) that also interferes with Ti. Table 2 shows the Si-based spectral interferences on P and Ti. Using the 8800 ICP-QQQ operating in MS/MS mode with O_2 mass-shift, P and Ti can be determined as their oxide ions, avoiding the Si-based interferences.

Table 2. Spectral interferences of Si on P and Ti.

Polyatomic interference	*m/z*	Analyte ion
$^{30}SiH^+$	31	$^{31}P^+$
$^{30}Si^{16}O^+$	46	$^{46}Ti^+$
$^{28}Si^{19}F^+$, $^{30}Si^{16}OH^+$	47	$^{47}Ti^+$, $^{31}P^{16}O^+$
$^{29}Si^{19}F^+$, $^{30}Si^{18}O^+$	48	$^{48}Ti^+$
$^{30}Si^{19}F^+$	49	$^{49}Ti^+$

For Ti analysis, Q1 is set to *m/z* 48, and so will transmit $^{48}Ti^+$ and any other interfering ions at mass 48, such as $^{29}Si^{19}F^+$ and $^{30}Si^{18}O^+$. But only ^{48}Ti reacts with oxygen in the CRC, producing the product ion $^{48}Ti^{16}O^+$, which is transmitted by setting Q2 to *m/z* 64. NH_3 can be used as an alternative reaction gas, as it produces $^{48}Ti^{14}NH^+$ that can be detected at *m/z* 63.

$^{31}P^+$ reacts readily with O_2 to form $^{31}P^{16}O^+$. The selection of ions at *m/z* 31 by Q1 eliminates the spectral interference of $^{28}Si^{19}F$. However, ^{30}SiH passes through Q1 and reacts with O_2 to create $^{30}Si^{16}OH$. In order to determine P in a high Si matrix, H_2 mass-shift is a preferred option, despite the relatively low efficiency of production of PH_3^+ or PH_4^+ ions. The MSA calibration curves for P and Ti in a matrix of 2000 ppm Si are shown in Figure 1. The calculated BECs are summarized in Table 3. A long term stability test was carried out by analyzing a spiked sample repeatedly over five hours (Figure 2).

Table 3. BECs of P and Ti in 2000 ppm Si.

Element	P	Ti
Mode (cell gas)	MS/MS (H_2)	MS/MS (O_2)
Measured ion	$^{31}PH_4^+$	$^{48}Ti^{16}O^+$
Mass pair	Q1 = 31, Q2 = 35	Q1 = 48, Q2 = 64
BEC - ppt	227	13

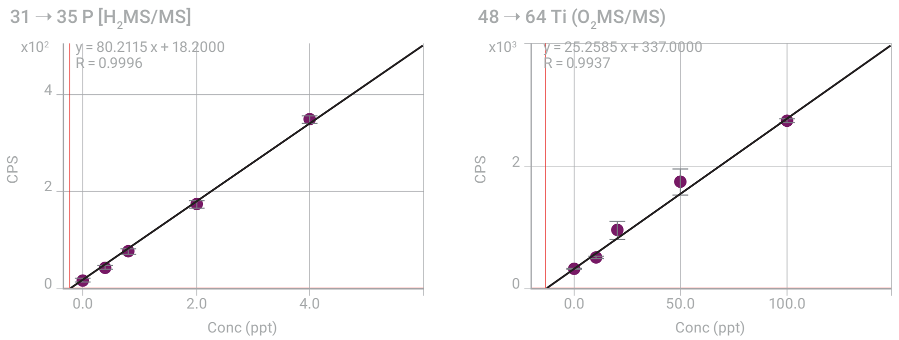

Figure 1. MSA curves of P and Ti in 2000 ppm Si.

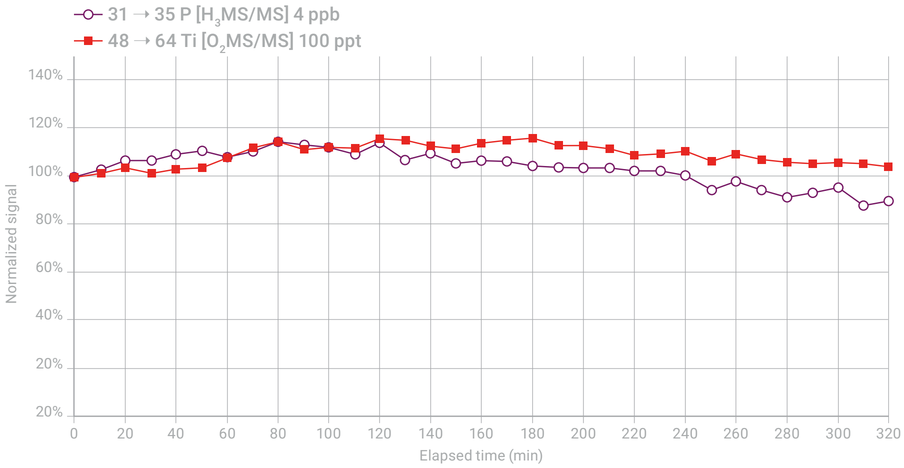

Figure 2. Five-hours test of P and Ti spiked in 2000 ppm Si.

Conclusion

The MS/MS mass-shift mode of the ICP-QQQ is effective for the determination of P, Ti and other trace elements in high purity silicon matrices, providing effective removal of the potential Si-based polyatomic interferences.

More information

Improvement of ICP-MS detectability of phosphorus and titanium in high purity silicon samples using the Agilent 8800 Triple Quadrupole ICP-MS, Agilent publication 5991-2466EN

Analysis of Ultratrace Impurities in High Silicon Matrix Samples by ICP-QQQ

Authors

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Determination of 38 elements in high matrix samples using an Agilent 8900 ICP-QQQ with optional m-lens

Introduction

Rapid developments in the emerging fields of artificial intelligence (AI) and the Internet of Things (IoT) are driving innovation in the integrated circuit (IC) sector of the semiconductor industry. IC fabrication plants (known as FABs or IC foundries) are increasing production of ICs to meet the requirements of this expanding market, as well as serving ongoing demand from other high-tech industries. Silicon (Si) is essential to the IC industry, as most modern electronics are based on Si semiconductors. These devices are made from millions of individual transistors (or switches) packed onto a Si wafer chip. Smaller transistors give higher core density, faster processing speed, lower power consumption, and less heat generation, critical factors for mobile devices. Currently, FABs are producing chips with transistor "gates" 10, 7, or even 5 nanometers (nm) long, with ongoing research projects to reduce the gate length even further. Manufacturing ICs at this small scale and high density requires excellent control of the quality of the Si substrate and process chemicals. It is important that the performance of the analytical instruments used to detect metallic impurities in raw materials evolves to meet the needs of the semiconductor industry.

Single quadrupole ICP-MS is the most widely used atomic spectrometry technique for the measurement of trace elements in many semiconductor applications due to its sensitivity and multi-element capability (*1*). However, more advanced semiconductor processes require elemental impurities on the Si wafer to be less than 1.0 x 10^7 atom/cm^2 level. While it is difficult to meet these specifications using single quadrupole ICP-MS, triple quadrupole ICP-MS (ICP-QQQ) with MS/MS operation has further improved the sensitivity, background, and interference removal capabilities of the technique. With detection limits (DLs) for many elements at the sub-ppt level, ICP-QQQ is increasingly used in the semiconductor industry for the accurate analysis of the highest purity semiconductor materials (*1*).

Another challenge of measuring trace metal impurities in a high Si matrix by ICP-MS relate to physical effects arising from the matrix. The high levels of Si in the sample can lead to deposition of Si on the sampling cone and suppression of analytes, leading to instability and signal drift. Operating single quadrupole ICP-MS with a “cool” or reduced-energy plasma has been widely used in the semiconductor industry for many years for the analysis of high-purity chemicals and materials. Cool plasma suppresses the formation of intense argon-based interferences such as Ar^+ and ArO^+, allowing low-level analysis of ^{40}Ca and ^{56}Fe, respectively. A lower-temperature plasma also causes less re-ionization of traces of easily ionized elements (EIEs) from the cones and ion lens, giving lower

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background signals for these elements than normal plasma conditions. However, the lower power used with cool plasma conditions provides insufficient energy to decompose some sample matrices, including high Si matrix samples.

The Agilent 8900 ICP-QQQ fitted with an optional "m-lens" ion lens uses normal plasma conditions to analyze silicon-rich samples. The m-lens has an optimized geometry that minimizes background signals from EIEs deposited on the ICP-MS interface components. The 8900 with m-lens provides ppt-level background equivalent concentrations (BECs) for the elements of interest in the semiconductor industry, including the easily-ionized alkaline elements. The low BECs enable the monitoring of ultra-trace ppt-level impurities in high Si matrices using high-power, robust, matrix tolerant plasma conditions.

In this study, the 8900 ICP-QQQ was used to analyze two Si samples prepared at matrix levels that are typically analyzed in the semiconductor industry. Excellent precision was achieved for the measurement of 50 ppt spikes in the Si matrix samples over a 1 hour analytical run, demonstrating the effectiveness, robustness, and sensitivity of the method.

Experimental

Reagents

All samples and standards were prepared in semiconductor grade TAMAPURE AA-100 nitric acid (HNO_3) and hydrofluoric acid (HF) bought from Tama Chemicals Co. Ltd, Kanagawa, Japan. The ultrapure water (UPW) was supplied from Organo Corp (Tokyo, Japan).

Sample preparation

Pieces of electronic grade (9N purity) poly-silicon were weighed to the nearest 0.05 g and the sample surfaces were cleaned with HNO_3 and rinsed with UPW. To prepare a 1000 ppm Si matrix solution, the Si pieces were digested in a 1:1 (w/w) acid mix of 38% HF and 55% HNO_3. The Si matrix solution was then diluted to provide two typical Si matrix samples. A 10 ppm Si solution was used to represent the Si matrix level in a sample prepared by scanning the wafer using a vapor phase decomposition (VPD) device. A 100 ppm Si matrix solution was used to represent the matrix level that would be present in a digested poly-silicon sample.

Calibration standards

Simple, aqueous (no Si matrix) calibration standards were prepared in the same acid concentration as the 10 and 100 ppm Si samples using Agilent stock solutions. Multi-element calibration standards included "2A" (p/n 8500-6940) and "4" (p/n 8500-6942). Single element standards at 1000 µg/mL were used for antimony (p/n 5190-8562) and tin (p/n 5190-8583).

A multi-element spike solution containing all elements was also prepared from the stock solutions. The spike solution was added to the 10 and 100 ppm Si matrix samples at 50 ng/L (ppt).

Instrumentation

An Agilent 8900 ICP-QQQ was used for the analysis. The 8900 was fitted with an inert (HF-resistant) sample introduction system comprising a 200 µL/min MicroFlow PFA nebulizer, a PFA spray chamber, endcap, and connector tube, and a demountable torch with a 2.5 mm internal diameter (i.d.) sapphire injector. A Pt-tipped sampling cone was used, together with the optional m-lens (G3666-67500), and Pt-tipped, Ni-based skimmer cone for m-lens (G3666-67501). The PFA nebulizer and Pt tipped sampling cone are standard on the 8900 #200 (Semiconductor Applications model). The other sample introduction parts (PFA spray chamber, endcap, connecting tube, and demountable torch) are included in the Inert Kit (G4912A #001). The sample introduction and interface parts listed are also compatible with the 8900 #100 (Advanced Applications model).

A high Si matrix leads to the formation of several polyatomic ions, which cause significant spectral interferences on some important elements such as Ti, Fe, Ni, Cu, and Ge (Table 1). To achieve the lowest BEC for each analyte in the silicon-rich samples, optimized ICP-QQQ acquisition conditions were used for different elements. Using ICP-MS MassHunter instrument control software, it is simple to measure different analytes in different cell gas modes using a single multitune method. During data acquisition, the ORS^4 cell gases and measurement modes are switched automatically, giving a fast and automated analysis using the best mode for each analyte.

In this study, several reaction cell gases (He, H_2, O_2, and NH_3) were used as appropriate for the large number of analytes being measured. Details of the configuration and principles of ICP-QQQ and MS/MS are explained elsewhere (*2, 3*). The operating parameters of the 8900 ICP-QQQ are given in Table 2.

Results and discussion

Background equivalent concentrations

The blank, 10 ppm, and 100 ppm Si samples were measured by external calibration method and the BECs of each sample were calculated using ICP-MS MassHunter. The BECs of all 38 analytes were lower than 50 ng/L in both the 10 and 100 ppm Si matrix blank samples, with most below 5 ng/L (Table 3). The low BECs show the effectiveness of the ICP-QQQ method at removing interferences on all analytes, including Si-based interferences on Ti, Fe, Ni, Cu, and Ge (Table 1). The relatively high BECs for some analytes may be due to the contamination during sample preparation.

Spike-recovery and stability test

The stability, robustness, and matrix tolerance of the instrument and method were tested over an hour of continual measurements. The unspiked (blank) Si samples were measured three times and each spiked sample was measured 11 times over the 60 minute run. The average recoveries of the 50 ng/L spikes ranged from 90 to 110% for all elements apart from Fe at 112% in the 10 ppm Si sample (Table 3). The slightly higher recovery of Fe was likely due to sample contamination from the laboratory environment. The 8900 ICP-QQQ also provided excellent sensitivity and accuracy for all elements, including EIEs, as shown by the spike recoveries in both Si matrices.

The relative standard deviation (RSD) of the measurements (n=11) was <6% for all 38 elements in both Si matrices, indicating minimal signal drift during the run using the 8900 with m-lens. Figure 1 shows the stability test results of some typical elements of importance to IC foundries such as Fe in the 100 ppm Si matrix sample.

Table 1. Potential spectral interferences in a Si matrix digest with HF.

Analyte Ion	Interference
$^{46}Ti^+$	$^{30}Si^{16}O^+$
$^{47}Ti^+$	$^{28}Si^{19}F^+$ $^{30}Si^{16}OH^+$
$^{48}Ti^+$	$^{29}Si^{19}F^+$ $^{30}Si^{18}O^+$
$^{49}Ti^+$	$^{30}Si^{19}F^+$
$^{58}Ni^+$	$^{28}Si^{30}Si^+$ $^{29}Si^{29}Si^+$
$^{60}Ni^+$	$^{28}Si^{16}O_2^+$ $^{30}Si^{30}Si^+$
$^{56}Fe^+$	$^{28}Si^{28}Si^+$
$^{63}Cu^+$	$^{28}Si^{16}O^{19}F^+$
$^{65}Cu^+$	$^{30}Si^{16}O^{19}F^+$ $^{28}Si^{18}O^{19}F^+$
$^{72}Ge^+$	$^{28}Si^{28}Si^{16}O$
$^{74}Ge^+$	$^{28}Si^{28}Si^{18}O$ $^{30}Si^{28}Si^{16}O$

Table 2. ICP-QQQ operating conditions.

	No Gas	H_2	NH_3	He
Acquisition Parameters				
Scan Mode	MS/MS			
Stabilization Time (s)	15	25	25	20
Replicates	3			
Sweeps/Replicate	100			
Integration Time (s)	0.6			
Plasma				
RF Power (W)	1550			
Sampling Depth (mm)	8.0			
Carrier Gas (L/min)	0.8			
Makeup Gas (L/min)	0.4			
Lenses				
Extract 1 (V)	1.5			
Extract 2 (V)	−70			
Omega Bias	−20			
Omega Lens	6			
Cell				
He Flow Rate (mL/min)				4.0
H_2 Flow Rate (mL/min)		10.0		
*NH_3 Flow Rate (mL/min)			2.0	
Octopole Bias (V)	−8	−18	−6	−20
Axial Acceleration (V)	0	1	1.5	0
KED (V)	3	−8	−10	5

Table 3. Analysis results of 10 and 100 ppm Si matrix samples and matrix-spiked samples, n = 11.

			10 ppm Si Matrix Sample			100 ppm Si Matrix Sample		
Element	Q1/Q2	Cell Gas	BEC (ng/L)	%RSD of 50 ppt-Spiked Samples	50 ppt Spike Recovery Average (%)	BEC (ng/L)	%RSD of 50 ppt-Spiked Samples	50 ppt Spike Recovery Average (%)
Li	7/7	No gas	0.38	3.7	101.4	0.60	3.4	107.3
Be	9/9	No gas	0.00	3.6	99.4	0.87	4.7	105.7
B	11/11	No gas	16.1	4.0	105.9	30.2	3.2	109.7
Na	23/23	H_2	5.13	5.6	101.8	13.3	2.9	96.7
Mg	24/24	H_2	1.45	3.0	93.9	5.82	4.4	108.2
Al	27/27	H_2	8.52	3.8	103.1	46.6	2.6	97.7
K	39/39	H_2	10.8	2.3	93.6	10.3	2.6	105.1
Ca	40/40	H_2	7.99	2.1	95.8	7.79	3.3	108.9
Ti	48/114	NH_3	5.35	5.4	101.3	4.55	5.4	101.7
V	51/67	NH_3	0.00	2.5	90.8	0.30	4.6	102.3
Cr	52/52	NH_3	4.30	2.5	95.9	9.71	2.8	101.4
Mn	55/55	NH_3	35.7	3.8	103.8	43.3	1.5	96.2
Fe	56/56	H_2	21.6	6.0	112.0	23.6	3.9	106.9
Ni	58/58	NH_3	6.75	2.4	90.0	4.69	3.2	99.1
Co	59/59	NH_3	2.37	4.0	92.2	5.56	2.3	96.7
Zn	64/64	NH_3	1.92	5.6	99.4	34.8	5.9	94.5
Cu	65/65	NH_3	4.19	5.1	101.1	33.6	5.7	95.7
Ga	69/69	H_2	0.34	2.4	94.8	6.13	2.8	109.8
Ge	74/74	H_2	4.26	2.0	90.7	4.30	1.7	98.1
As	75/75	H_2	0.86	4.7	90.3	0.29	5.9	100.4
Se	78/78	H_2	1.24	5.0	90.4	1.60	4.5	97.2
Rb	85/85	H_2	0.62	2.0	96.5	18.4	4.5	100.6
Sr	88/88	H_2	0.02	2.0	95.3	0.03	2.5	101.2
Zr	90/90	H_2	0.08	1.9	94.9	0.03	2.3	102.2
Nb	93/93	He	0.43	2.6	91.5	0.12	2.7	98.2
Mo	95/95	He	0.12	2.9	93.8	0.53	4.3	98.0
Ag	107/107	No gas	0.12	1.9	98.2	0.18	1.6	100.8
Cd	114/114	NH_3	0.02	1.7	95.9	0.00	2.5	98.1
Sn	118/118	NH_3	0.51	2.5	96.7	1.12	2.1	97.6
Sb	121/121	NH_3	0.14	2.3	93.9	0.24	2.6	95.3
Cs	133/133	He	0.03	2.7	94.6	0.03	1.8	97.0
Ba	138/138	H_2	0.42	2.3	97.6	0.43	1.9	98.4
Ta	181/181	He	0.17	2.2	98.8	0.09	1.6	96.4
W	182/182	He	3.48	4.2	99.2	0.12	2.2	96.1
Re	185/185	He	0.00	2.9	95.8	0.01	1.9	95.9
Tl	205/205	No gas	0.15	3.0	104.2	0.12	1.3	103.2
Pb	208/208	NH_3	0.31	2.2	98.0	0.19	1.9	96.1
U	238/238	No gas	0.00	3.3	103.2	0.00	1.0	101.2

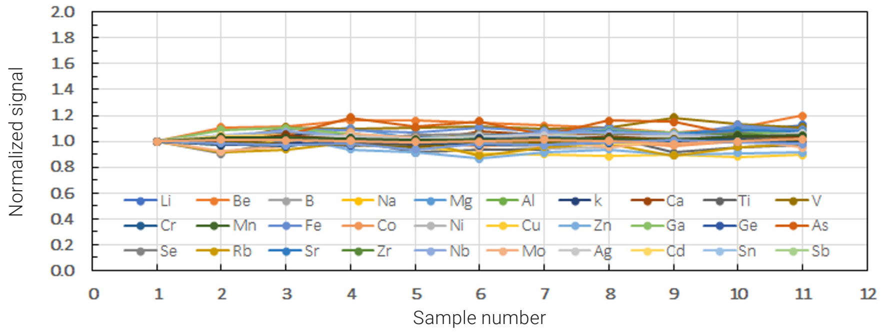

Figure 1. Stability results for multiple elements spiked at 50 ppt in a 100 ppm Si matrix sample.

Conclusion

The robustness of the Agilent 8900 ICP-QQQ with m-lens was demonstrated for the determination of 38 elements in two digested silicon samples containing 10 and 100 ppm Si. The optional m-lens ensured that the background signals for the EIEs were minimized, allowing all elements to be measured at ppt levels using matrix tolerant, high-power plasma conditions.

The best BECs for all elements were achieved by operating the 8900 ICP-QQQ in MS/MS mode using a single multitune method with different cell gases. The low BECs showed that the method successfully removed all spectral interferences, including Si-based interferences on Ti, Fe, Ni, Cu, and Ge.

The reproducibility (stability) results for the 50 ppt spikes in the two high silicon samples were between 1 and 6% RSD for all elements in a sequence lasting 1 hour. These results showed that there was minimal signal suppression or drift caused by Si deposition on the interface under the robust plasma conditions.

The study demonstrates the suitability of the 8900 ICP-QQQ for the characterization of trace metals in silicon-matrix samples. The method has the potential to meet the evolving needs and future specifications of the most advanced manufacturing processes that are required to meet the demand for higher IC performance.

References

1. Applications of ICP-MS: Measuring Inorganic Impurities in Semiconductor Manufacturing, Agilent publication, 5991-9495EN
2. Eduardo Bolea-Fernandez, Lieve Balcaen, Martin Resano, Frank Vanhaecke. Overcoming spectral overlap via inductively coupled plasma-tandem mass spectrometry (ICP-MS/MS). A tutorial review, *J. Anal. At. Spectrom.*, **2017**, 32, 1660–1679
3. Ed McCurdy, Glenn Woods, Naoki Sugiyama. Method Development with ICP-MS/MS: Tools and Techniques to Ensure Accurate Results in Reaction Mode, *Spectroscopy*, **2019** (9):20–27, http://www.spectroscopyonline.com/method-development-icp-msms-tools-and-techniques-ensure-accurate-results-reaction-mode

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Analysis of Sulfur, Phosphorus, Silicon, and Chlorine in N-methyl-2-pyrrolidone

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Keywords

N-methyl-2-pyrrolidone, NMP, semiconductor, process chemicals, sulfur, phosphorus, silicon, chlorine, method of standard additions, oxygen mass-shift

Introduction

N-Methyl-2-Pyrrolidone (NMP), 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 photo resist 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 (Table 1).

Table 1. ICP-QMS BECs obtained in no gas mode 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

Instrumentation: Agilent 8800 #200 with narrow injector (id =1.5 mm) torch (G3280-80080) typically used for the analysis of organic solvents. A C-flow 200 PFA nebulizer (G3285-80000) was used in self-aspiration mode. An option gas flow of 20% O_2 in Ar was added to the carrier gas to prevent carbon build up on the interface cones.

Plasma conditions: NMP analysis requires hotter plasma conditions than normal. This was achieved by reducing Make-up Gas (MUGS) by 0.2 L/min. Plasma tuning conditions are summarized in Table 2.

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

CRC conditions: Table 3 summarizes the cell tuning parameters (gas flow rate and voltages) used.

Table 3. CRC operating conditions.

Parameter	Unit	O_2 reaction cell		H_2 reaction cell	
Method	-	On-mass	Mass-shift	On-mass	Mass-shift
Cell gas	-	O_2		H_2	
Gas flow rate	mL/min	0.30		4.0	
Octopole bias	V	-14		-10	
KED	V	-5	-5	0	-5

Reagents and sample preparation: Electronic industry grade NMP was distilled at 120 °C and acidified by adding high purity HNO_3 to a concentration of 1% w/w.

Results and discussion

NMP was analyzed directly using the method of standard additions (MSA). Three replicate measurements (ten replicates for the blank) were acquired for S, P, Si and Cl using an integration time of 1 s per isotope.

P and S measurement 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; therefore P^+ and S^+ are efficiently 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.

$P^+ + O_2 \rightarrow PO^+ + O \quad \Delta Hr = -3.17\ eV$

$S^+ + O_2 \rightarrow SO^+ + O \quad \Delta Hr = -0.34\ eV$

In MS/MS mode, Q1 rejects $^{36}ArC^+$ before it can enter the cell, preventing it from overlapping SO^+. This allows ICP-QQQ to control the reaction chemistry pathways and reaction product ions, ensuring that the analyte product ion is measured free from overlap, regardless of the levels of other co-existing analyte (or matrix) elements. MS/MS mode with the O_2 mass-shift method achieved BECs of 0.55 ppb and 5.5 ppb for P and S respectively in NMP. The low BECs and linear calibration plots achieved in MS/MS mode also prove that the matrix-based interferences do not react with O_2, allowing the analytes to be separated from the interferences.

Si measurement in NMP

H_2 cell gas was 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.

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

$N_2^+ + H_2 \rightarrow N_2H^+ + H$ $\Delta Hr = -0.60\ eV$

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

The results obtained are shown in Figure 2 (top). The H_2 on-mass method achieved a BEC of 15.8 ppb for Si in NMP.

Oxygen cell gas was also tested of the measurement of Si in NMP. 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.

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

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 a BEC of 11.9 ppb for Si in NMP (Figure 2, bottom).

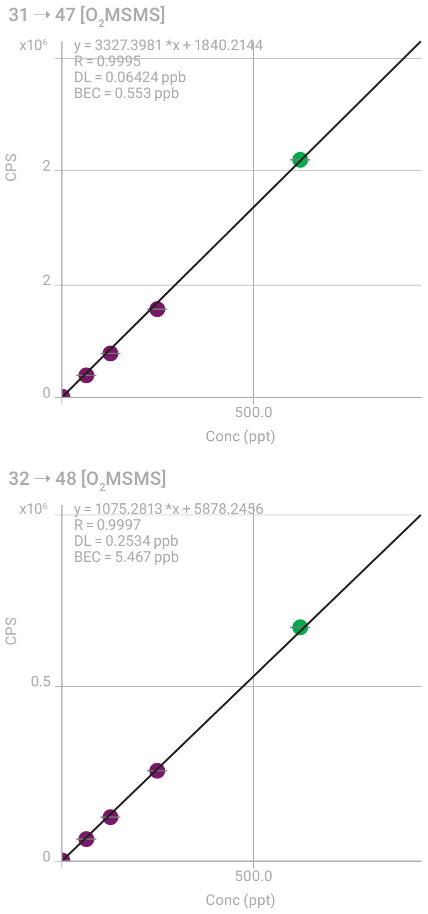

Figure 1. Calibration curve using MS/MS with O_2 mass-shift for P (top) and S (bottom) in NMP.

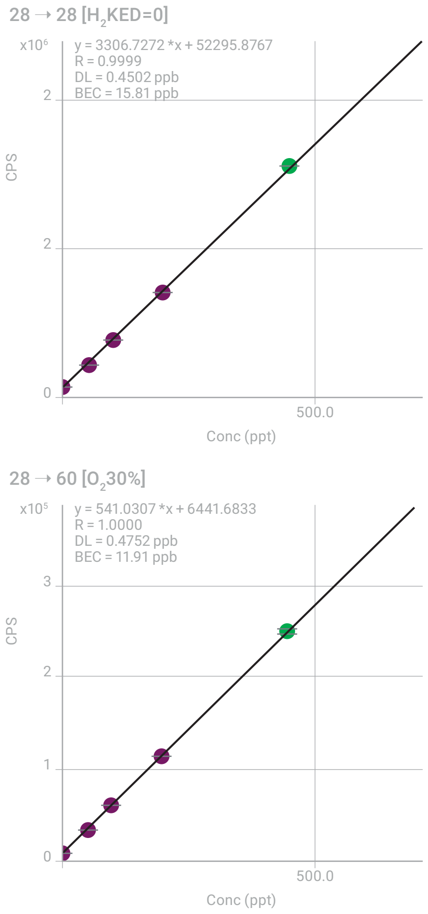

Figure 2. Calibration plots for Si in NMP. Top: H_2 on-mass method (Q1=Q2=28). Bottom: O_2 mass-shift method (Q1=28, Q2=60).

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Cl in NMP

Cl^+ reacts exothermically with H_2 to form ClH^+ as shown below. ClH^+ continues to react via a chain reaction to form ClH_2^+.

$Cl^+ + H_2 \rightarrow ClH^+ + H$ $\Delta Hr = -0.17$ eV

$ClH^+ + H_2 \rightarrow ClH_2^+ + H$ $\Delta Hr = -0.39$ eV

Figure 3 (left) 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 3, below) is also shown for comparison. A slightly better BEC of 34.2 ppb was achieved with much higher sensitivity for Cl in NMP using the H_2 mass-shift method.

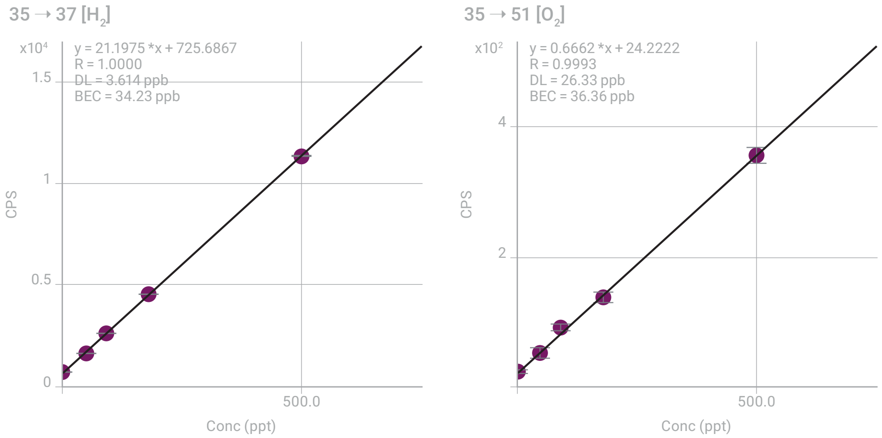

Figure 3. Calibration plots for Cl in NMP. Left: H_2 mass-shift method (Q1 = 35, Q2 = 37). Right: O_2 mass-shift method (Q1=35, Q2=51).

More information

Trace level analysis of sulfur, phosphorus, silicon and chlorine in NMP using the Agilent 8800 Triple Quadrupole ICP-MS, 2013, Agilent publication, 5991-2303EN

Analysis of Silicon, Phosphorus, and Sulfur in 20% Methanol

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Keywords

organic solvents, methanol, silicon, phosphorus, sulfur, hydrogen on-mass, oxygen mass-shift

Introduction

Analysis of organic solvents for trace metals presents a number of challenges to ICP-MS, many of which have been overcome to varying degrees on the Agilent 7700 Series quadrupole ICP-MS systems. 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 quadrupole ICP-MS (ICP-QMS). 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.

Experimental

Instrumentation: Agilent 8800 #200.

Plasma conditions and ion lens tune: RF power =1550 W, Sampling depth = 8.0 mm and Carrier gas flow rate = 1.05 L/min were used with soft extraction tune, Extract 1 = 0 V and Extract 2 = -190 V.

Ultra pure methanol was spiked with silicon (Si), phosphorus (P) and sulfur (S) at 1, 5, 10 and 50 ppb and measured using the ICP-QQQ in several operational modes in order to evaluate the optimum conditions for the simultaneous analysis of all three analytes. Hydrogen and oxygen reaction gases were evaluated, with H_2 cell gas used in both Single Quad (SQ) and MS/MS modes. In addition, helium collision gas was investigated in both SQ and MS/MS mode to determine the effects of using MS/MS with a non-reactive cell gas.

The CRC conditions are outlined in Table 1, which includes the five analysis modes evaluated. Two Single Quad modes were tested, using both He and H_2 in the cell, to simulate the capability of a single quadrupole ICP-MS. In addition, three conditions using MS/MS mode were tested using H_2, He and O_2 as cell gases.

Table 1. 8800 ICP-QQQ acquisition conditions tested, including five operational modes.

Parameter	Unit	He SQ	H_2 SQ	H_2 MS/MS	He MS/MS	O_2 MS/MS
Acquisition mode		SQ	SQ	MS/MS	MS/MS	MS/MS
Cell gas		He	H_2	H_2	He	O_2
Cell gas flow rate	mL/min	5.0	7.0	7.0	7.0	0.40
KED	V	5	0	0	5	-7

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Results and discussion

The BECs and DLs results are summarized in Tables 2–4, for silicon, phosphorus and sulfur respectively, for all 5 analysis modes tested. SQ and optimum MS/MS results are in bold type for comparison. A few mass-pairs were measured in each mode as shown. For example, Table 2 shows silicon monitored in MS/MS mode with O_2 cell gas, using a mass-pair of Q1 = 28 and Q2 = 44. With Q1 set to *m/z* 28, only silicon 28 and any on-mass interferences are allowed to enter the ORS cell. The silicon 28 in the cell reacts with the oxygen cell gas to form SiO^+, and Q2 is set to measure at Q1 + 16 (*m/z* = 44), ensuring that only the M + ^{16}O reaction transition is measured.

Table 2. DLs and BECs for silicon. Silicon was not measurable at the spiked concentrations in helium mode.

Mode	Mass or mass pair	BEC (ppb)	DL (ppb)
H_2 SQ	Q2=28	25.46	0.12
H_2 MS/MS	Q1=28, Q2=28	2.17	0.03
O_2 MS/MS	Q1=28, Q2=44	85.54	28.21
O_2 MS/MS	Q1=29, Q2=45	N/A	N/A
O_2 MS/MS	Q1=30, Q2=46	99.09	21.26

Table 3. DLs and BECs for phosphorus. Phosphorus was not measurable at the spiked concentrations in H_2 Single Quad mode.

Mode	Mass or mass pair	BEC (ppb)	DL (ppb)
He SQ	Q2=31	3.81	0.63
He MS/MS	Q1=31, Q2=31	2.99	0.72
H_2 MS/MS	Q1=31, Q2=33	0.56	0.07
H_2 MS/MS	Q1=31, Q2=34	0.58	0.67
O_2 MS/MS	Q1=31, Q2=47	0.40	0.05
O_2 MS/MS	Q1=31, Q2=63	0.41	0.02

Table 4. DLs and BECs for sulfur using MS/MS mode with O_2 cell gas. Sulfur was not measurable at the spiked concentrations in helium or hydrogen mode.

Mode (cell gas)	Mass or mass pair	BEC (ppb)	DL (ppb)
MS/MS (O_2)	Q1 = 34, Q2 = 34	51.17	4.37
MS/MS (O_2)	Q1 = 32, Q2 = 48	3.13	0.10
MS/MS (O_2)	Q1 = 34, Q2 = 50	3.11	0.20

Sample calibration plots are displayed in Figure 1. They are displayed in pairs showing the results obtained using SQ mode with a typical cell gas (upper calibration), compared to MS/MS mode using the optimum conditions (lower calibration).

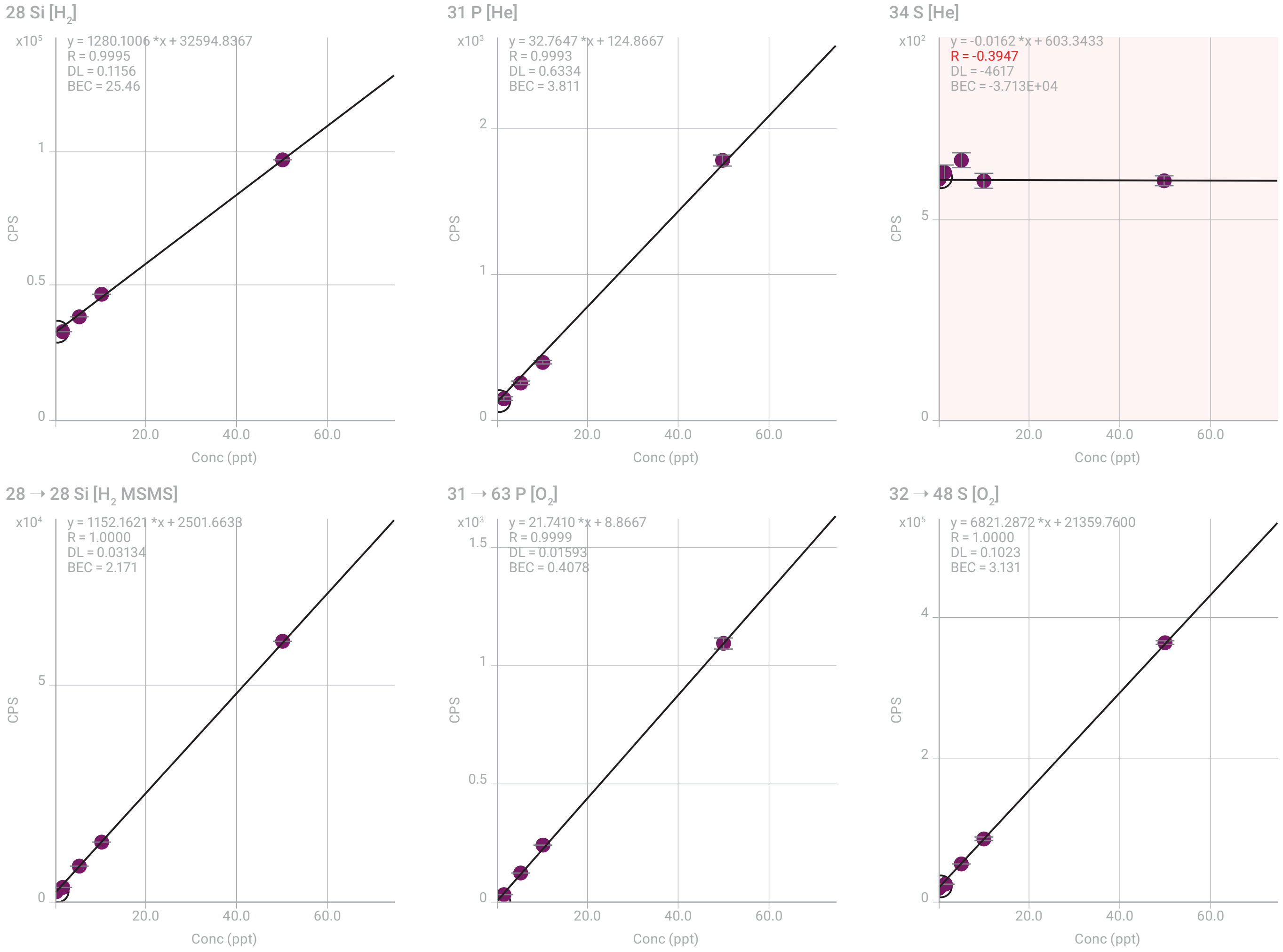

Figure 1. Calibration curves for Si, P and S showing SQ results (upper) compared with MS/MS results (lower). ^{32}S was not measurable at the spiked concentrations in methanol in SQ mode due to the intense $^{16}O_2^+$ polyatomic interference.

Conclusion

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 to Single Quad mode. The most notable improvement was for sulfur which cannot be measured at the spiked concentrations (1, 5, 10, 50 ppb) in SQ He mode due to the intense polyatomic background resulting from the methanol matrix. By contrast, on the 8800 ICP-QQQ using MS/MS mode with O_2 mass-shift, S can be measured with a DL of 0.1 ppb.

More information

Analysis of silicon, phosphorus and sulfur in 20% methanol using the Agilent 8800 Triple Quadrupole ICP-MS, Agilent publication, 5991-0320EN

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Automated ultratrace element analysis of isopropyl alcohol with the Agilent 8900 ICP-QQQ

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

Introduction

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

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

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

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

Experimental

Reagents and samples

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

A 1 µg/L (ppb) mixed multi-element standard solution was used to create the MSA calibration spikes. The working standard solution was prepared by diluting a 10 ppm mixed multi-element standard (SPEX CertiPrep, Metuchen, NJ, US) with distilled IPA. To stabilize the spiked elements, nitric acid (68% ultrapure HNO_3) was added to the IPA samples at a final acid concentration of 1%.

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

Instrumentation

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

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

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

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

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

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits for each analyte. Laboratories measuring ultratrace levels of contaminant metals often use a multitune method, where several tuning steps are applied sequentially during the measurement of each solution. This approach allows the tuning conditions to be optimized for the removal of different types of interferences, while maintaining sensitivity for each analyte. In this work, several reaction cell gases (He, H_2, O_2, and NH_3) were used for the analytes being measured.

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

Table 1. Agilent 8900 ICP-QQQ operating conditions.

	H_2 (cool plasma*)	NH_3 (cool plasma*)	O_2 He	H_2	He	No gas
Scan type	MS/MS					
RF power (W)	1500					
Sampling depth (mm)	18.0					
Nebulizer gas flow rate (L/min)	0.70					
20% O_2 Ar balance gas flow rate (L/min)	0.30 (30%)**					
Spray chamber temp (°C)	–5.0					
Make-up gas flow rate (L/min)	0.80	0.70	0.50			
Extract 1 (V)	-100					
Extract 2 (V)	-10.0					
Omega bias (V)	-70.0					
Omega lens (V)	4.0					
Q1 entrance (V)	-50.0					
He cell gas flow rate (mL/min)	-	1.0	12.0	-	5.0	-
H_2 cell gas flow rate (mL/min)	5.0	-	-	10.0	-	-
NH_3 cell gas flow rate (mL/min)***	-	2 (20%)**	-	-	-	-
O_2 cell gas flow rate (mL/min)	-	-	0.075 (5%)**	-	-	-
OctP bias (V)	-18	-5	-3	-30	-20	-10
Axial acceleration (V)	1.0			0		
Energy discrimination (V)	0	-10			3	

Table 2. Acquisition parameters.

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

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

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

*** 10% NH_3 balanced with 90% He.

Automated Standard Addition System (ASAS)

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

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

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

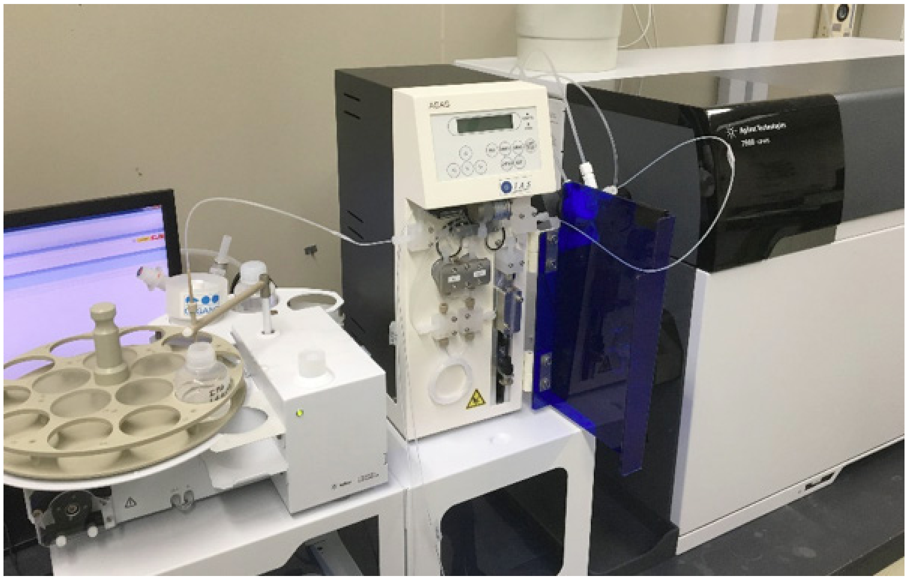
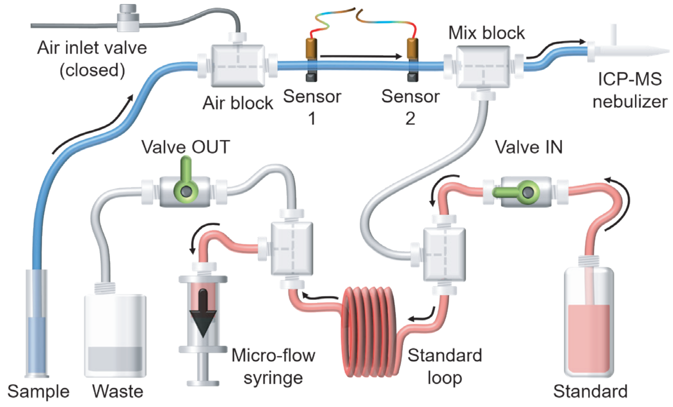


Figure 1. An Agilent ICP-MS fitted with an IAS ASAS automated standard addition system and the Agilent I-AS integrated autosampler.

ASAS operation consists of the following four steps:

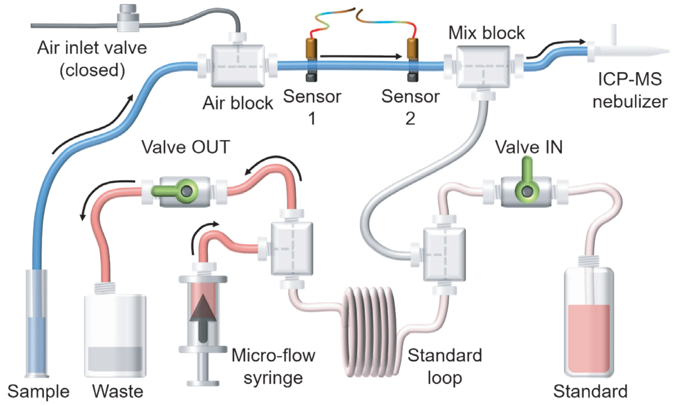
Step 1: Loop is filled with the standard solution.

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



Step 2: Excess standard solution is pumped to waste.

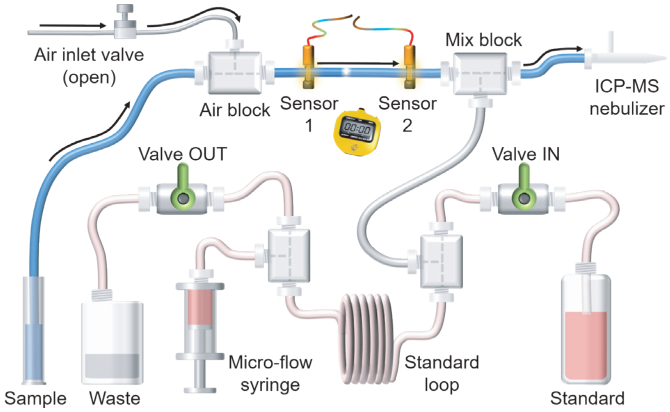
"Valve OUT" in the standard line opens, "Valve IN" closes, and the syringe pump discharges, pumping the remaining standard solution to the waste bottle—bypassing the loop.



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

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

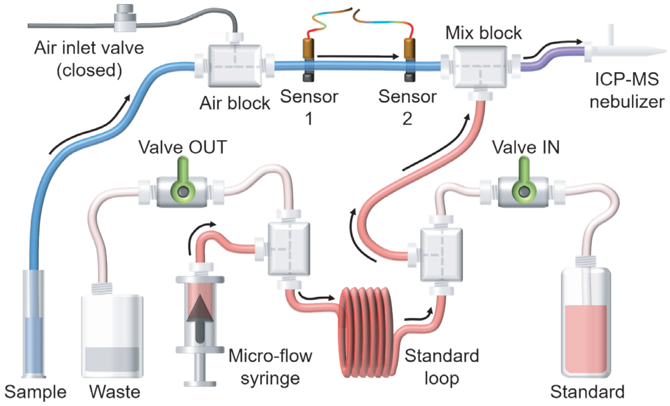
- When the autosampler probe moves to the sample vial, it triggers measurement of the sample uptake rate.
- An air bubble is introduced via the "Air inlet valve".
- Optical fiber sensors measure the elapsed time between the air bubble passing Sensor 1 and Sensor 2. The elapsed time is inversely proportional to the sample flow rate, allowing the actual solution flow rate to be calculated.



Step 4: MSA spikes are added automatically.

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

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



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

- A 1 ppb spike standard is prepared and placed in a sample bottle connected to the Standard line of the ASAS.
- The microflow syringe loads the spike standard into the ASAS loop via the dedicated uptake line.
- The autosampler moves to the next sample vial.
- The ASAS measures the sample uptake line flow rate (as previously outlined in Step 3). In this example, we will use a nominal flow rate of 200 µL/min.
- Based on the measured sample flow rate, the ASAS software calculates the flow rate of the 1 ppb stock standard required to give a 50 ppt spike concentration. In this case, to achieve a spike level of 50 ppt in the sample flow of 200 µL/min, the standard would need to be introduced at a flow rate of 10.0 µL/min (20x dilution of the 1 ppb standard).
- The standard in the loop is added to the sample via the “Mix Block” at the calculated flow rate. The mixed, spiked sample then passes to the ICP-MS for analysis.

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

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

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

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

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

Results and discussion

DLs and BECs

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

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

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

Analyte	Q1	Q2	Tune mode	DL (ng/L)	BEC (ng/L)	20 ng/L Recovery (%)	20 ng/L n=10 RSD (%)	SEMI standard C41-0705 Grade 4 (ng/L)
Li	7	7	$*H_2$	0.010	0.040	99	2.4	< 100
Be	9	9	No gas	0.023	0.005	99	2.4	
B	11	11	No gas	1.2	12	96	8.0	< 100
Na	23	23	$*NH_3$	0.060	0.97	109	5.7	< 100
Mg	24	24	$*NH_3$	0.020	0.082	102	2.7	< 100
Al	27	27	$*NH_3$	0.042	0.16	100	2.8	< 100
P	31	47	O_2 He	2.6	43	99	7.9	<16,000*
K	39	39	$*NH_3$	0.64	1.1	107	4.9	< 100
Ca	40	40	$*NH_3$	0.19	0.62	108	4.7	< 100
Ti	48	64	O_2 He	0.23	1.3	99	2.4	< 100
V	51	67	O_2 He	0.020	0.030	99	2.3	< 100
Cr	52	52	$*NH_3$	0.16	0.48	92	1.7	< 100
Mn	55	55	$*NH_3$	0.030	0.030	102	2.4	< 100
Fe	56	56	$*NH_3$	0.16	0.72	101	2.5	< 100
Co	59	59	He	0.020	0.020	99	2.1	
Ni	60	60	He	0.43	0.80	101	2.0	<100
Cu	63	63	O_2 He	0.38	6.4	97	2.3	<100
Zn	64	64	He	0.71	0.72	98	6.9	<100
Ga	71	71	O_2 He	0.013	0.005	100	2.8	
Ge	74	74	He	0.30	0.070	96	8.1	
As	75	91	O_2 He	0.41	0.26	108	2.7	<100
Rb	85	85	H_2	0.17	0.59	101	2.4	
Sr	88	88	O_2 He	0.005	0.002	98	2.4	
Zr	90	90	O_2 He	0.030	0.020	99	2.7	
Nb	93	93	H_2	0.14	0.41	102	4.0	
Mo	98	130	O_2 He	0.17	0.11	103	4.1	
Ru	101	101	He	0.080	0.03	99	2.9	
Rh	103	103	O_2 He	0.070	0.18	99	2.1	
Pd	105	105	O_2 He	0.070	0.040	100	2.5	
Ag	107	107	O_2 He	0.014	0.006	97	2.6	
Cd	111	111	O_2 He	0.035	0.004	98	4.0	<100
In	115	115	O_2 He	0.012	0.008	99	1.8	
Sn	118	118	O_2 He	0.058	0.034	100	4.9	<100
Sb	121	121	O_2 He	0.056	0.009	103	2.3	<100
Te	125	125	O_2 He	0.78	0.29	97	8.9	
Cs	133	133	$*H_2$	0.060	0.022	96	4.2	
Ba	138	138	O_2 He	0.009	0.004	99	2.4	<100

Analyte	Q1	Q2	Tune mode	DL (ng/L)	BEC (ng/L)	20 ng/L Recovery (%)	20 ng/L n=10 RSD (%)	SEMI standard C41-0705 Grade 4 (ng/L)
Hf	178	178	He	0.000	0.000	105	5.1	
W	182	214	O_2 He	0.21	0.049	97	5.7	
Re	185	185	O_2 He	0.000	0.000	96	3.0	
Ir	193	193	No gas	0.060	0.006	101	6.7	
Pt	195	195	O_2 He	0.51	0.45	100	3.0	
Tl	205	205	O_2 He	0.018	0.008	99	2.1	
Pb	208	208	O_2 He	0.047	0.042	100	2.7	<100
Bi	209	209	O_2 He	0.021	0.004	98	1.6	
Th	232	248	O_2 He	0.11	0.022	97	4.6	
U	238	254	O_2 He	0.18	0.048	91	6.6	

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

** < 16,000 ppt is the concentration limit for elemental P that is equivalent to the SEMI specified limit of 50 ppb (50,000 ppt) for PO_4.

Resolving polyatomic interferences on Mg, Al, and Cr

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

Table 4. Main interferences arising from organic solvent matrix.

Analyte	Interferences	DL (ng/L)	BEC (ng/L)
^{24}Mg	$^{12}C_2^+$	0.020	0.082
^{27}Al	$^{12}C^{15}N^+, ^{13}C^{14}N^+, ^{12}C^{14}N^1H^+$	0.042	0.16
^{31}P	$^{15}N^{16}O^+, ^{14}N^{17}O^+, ^{13}C^{18}O^+$	2.6	43
^{52}Cr	$^{40}Ar^{12}C^+$	0.16	0.48

The major isotope of magnesium, $^{24}Mg^+$, suffers an intense polyatomic interference from $^{12}C_2^+$ in organic samples. Cool plasma conditions can suppress the ionization of C_2, and CRC mode can also be employed successfully to resolve the interference. In this work, the lowest DLs for Mg were achieved using a combination of high-power cool plasma conditions and on-mass measurement in MS/MS mode with NH_3 cell gas. The calibration curve for ^{24}Mg shows that the $^{12}C_2^+$ interference was removed successfully, achieving a BEC less than 0.1 ng/L (ppt), and a detection limit of 0.020 ppt (Figure 2).

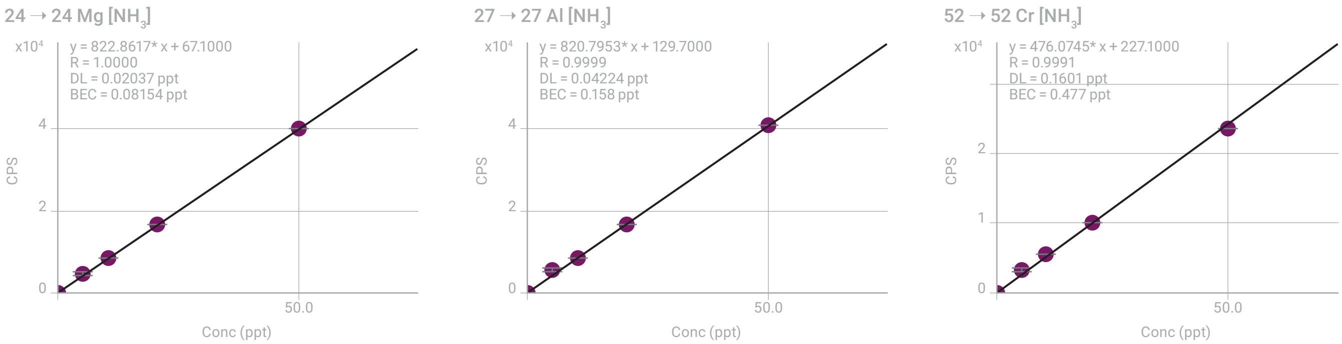


Figure 2. MSA calibration curves for ^{24}Mg, ^{27}Al, and ^{52}Cr.

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

P determination

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

The analysis of P in IPA needs an ORS cell mode that can resolve P from the normal plasma background polyatomic ions formed from N and O – $^{14}N^{16}O^1H^+$, $^{15}N^{16}O^+$, and $^{14}N^{17}O^+$. In addition, potential carbon-based interferences that overlap P^+ at *m/z* 31 must also be resolved. MS/MS mass shift operation with oxygen reaction cell gas has been shown to be suitable for the analysis of P. Using this method, the P^+ ions react with O_2 cell gas to form a reaction product ion PO^+ at *m/z* 47, mass-shifted away from the original on-mass interferences.

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

The measurement conditions for P described in reference 3 were also used in this study. The calibration curve in Figure 3 shows good linearity from 5 to 50 ppt for P. The BEC was 43 ng/L (ppt) and the DL was 2.6 ppt (Table 3). Given the much higher typical contaminant levels for P compared to the other trace metals, it would be reasonable to calibrate P at a higher concentration level than the other elements. This modification could easily be applied to the ASAS methodology

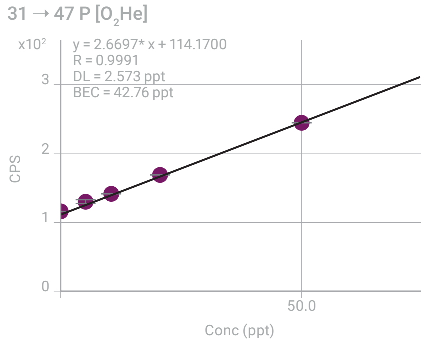


Figure 3. MSA calibration curve for ^{31}P.

described here, if a higher P concentration was added to the working stock standard solution. The ASAS would then prepare and inject the online MSA spikes from the mixed standard, including the higher P spike levels. The upper limit for P defined in SEMI Grade 4 purity chemicals is also much higher than for the other trace elements. The relatively high BEC of 43 ppt is still several orders of magnitude lower than the 16,000 ppt concentration limit specified for P.

Conclusion

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

Eliminating manual sample handling steps during ultratrace analysis lowers the risk of contamination. Limiting the handling of reagents and samples also reduces the likelihood of errors arising during the experimental procedure. Automating calibration and spike addition leads to increased consistency and higher confidence in the quality of the results.

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

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

References

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

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Analysis of Nanoparticles in Organic Reagents by Agilent 8900 ICP-QQQ in spICP-MS Mode

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Determination of 25 and 30 nm Fe_3O_4 NPs in low particle concentration solutions

Introduction

Semiconductor device manufacturing involves several processes including lithography, etching, ion implantation, and peeling. Even small amounts of impurities present in processing reagents such as developer, rinse solution, and etching liquid can cause defects, resulting in a reduction of product yield and degradation of product reliability. Metallic nanoparticles (NPs), especially iron (Fe) NPs, can lead to the occurrence of 'cone defects' on the surface of wafers, which cause shorting of electrical signals (*1*). To prevent these problems from arising, an accurate analytical method is required to determine metallic NPs in semiconductor process chemicals.

Single particle ICP-MS (spICP-MS) is a powerful tool that is used increasingly to characterize the NP content of various types of samples (*2–4*). spICP-MS allows the simultaneous determination of the number, concentration, and size of particles, plus the dissolved element concentration. It can be applied to the measurement of semiconductor grade organic solvents such as isopropyl alcohol (IPA), propylene glycol methyl ether acetate (PGMEA), and butyl acetate (BuAc), as well as aqueous solutions (*3*). To detect very small-sized NPs using spICP-MS, an instrument with a low background and high sensitivity such as the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) is needed. Also, since some metallic NPs suffer from spectral interferences, the advanced interference removal capability of the 8900 ICP-QQQ is advantageous for the application.

In this study, Fe NPs were measured in semiconductor grade IPA, PGMEA, and BuAc using the Agilent 8900 ICP-QQQ operating in spICP-MS mode.

Experimental

Sample preparation

Two kinds of Fe_3O_4 NP (Fe NP) solutions, 25 nm (Sigma Aldrich, p/n 900027) and 30 nm (Sigma Aldrich, p/n 747408), were used as NP standards. The Fe NPs were spiked into IPA, PGMEA, and BuAc. These organic solvents were introduced directly to the ICP-QQQ. To measure the ionic sensitivity of Fe, an aqueous Fe standard (1000 ppm, Kanto Chemicals, Japan) was diluted with each organic solvent.

Instrumentation

An Agilent 8900 ICP-QQQ (#200, Semiconductor configuration) and Agilent SPS 4 autosampler were used for all measurements. The sample introduction system comprised a quartz torch with a 1.5 mm i.d. injector, quartz spray chamber, and platinum-tipped interface cones. The SPS 4 autosampler was fitted with a sample rack (produced in Taiwan) designed to accommodate larger sample bottles (100 to 500 mL). Being able to load the same bottles used for sample preparation into the SPS 4 rack reduces the risk of contamination as the samples don't need to be transferred to smaller bottles. Also, larger bottles are convenient for the long-term stability test. The samples were self-aspirated using an Agilent PFA nebulizer, which is part of the SPS 4 probe kit (p/n G3139-68000). Clean argon gas was purged into the cover of the autosampler and there was a constant flow of ultrapure water via a continuous flow rinse port fitted to the SPS 4.

The 8900 ICP-QQQ was operated in MS/MS mode for all Fe measurements. Both Q1 and Q2 (unit mass filters) were set to *m/z* 56. Q1 selects which elements enter the ORS[4] collision/reaction cell (CRC), allowing controlled reaction chemistry to take place in the cell when a reactive cell gas is introduced. Ammonia cell gas was used to control the ArO and C_2O_2 interferences that overlap Fe at *m/z* 56.

The signal generated by a single NP lasts for about 1 ms, so Fast Time Resolved Analysis (TRA) mode of the 8900 ICP-QQQ was used to acquire the data. Fast TRA allows single element acquisition at a sampling rate of 100 µs (10,000 measurements per second) and no settling time is needed between measurements. Data analysis was performed using the Single Nanoparticle Application Module of the Agilent ICP-MS MassHunter software.

The operating conditions of the Agilent 8900 ICP-QQQ are detailed in Table 1. As shown, slightly different parameters were used to achieve optimum sensitivity for the determination of Fe NPs in each solvent. To enable the direct injection of organic solvents to the ICP-QQQ without the deposition of carbon on the cones, oxygen gas (20%, Ar balanced) was added to the sample gas flow.

Table 1. ICP-QQQ operating conditions.

Parameter	Value		
	IPA	PGMEA	BuAc
RF power (W)	1400	1500	1500
Sampling depth (mm)	18.0		
Nebulizer gas (L/min)	0.70		
Makeup gas (L/min)	0.50	0.60	0.45
*Option gas (L/min)	0.40 (40%)	0.20 (20%)	0.40 (40%)
Spray chamber temp. (°C)	2		
Extraction lens 1 (V)	-150	-125	-125
Extraction lens 2 (V)	-10	-15	-15
Octopole bias (V)	-10	-3	-3
Axial acceleration (V)	1.5		
Energy discrimination (V)	-10	-7	-7
He flow rate (mL/min)	1		
**NH_3 flow rate (mL/min)	2 (20%)	3 (30%)	3 (30%)
Dwell time (µs)	100		
Masses monitored	Fe (Q1: 56, Q2: 56)		
Data acquisition time (s)	60		

**20% O_2 balanced with Ar added using the option gas mass flow controller, which is fitted as standard on the Agilent 8900 Semiconductor ICP-QQQ.*
***10% NH_3 balanced with He.*

Results and discussion

Analysis of Fe NPs in IPA, PGMEA, and BuAc

Solutions of IPA, PGMEA, and BuAc containing 30 nm Fe NPs spiked at 5 ppt were measured using the 8900 ICP-QQQ. The signal distribution and size distribution plots for Fe NPs in each of the samples are shown in Figure 1. The signals generated from the Fe NPs were clearly separated from the background signals. Also, the mean measured particle size was around 30 nm in all spiked solvents, which is consistent with the nominal Fe NP diameter (30 nm). The Single Nanoparticle Application Module software automatically sets the particle threshold, which is shown by the pink line in the signal distribution plots.

The spICP-MS software automatically calculates the nebulization efficiency, which is the ratio of the amount of analyte entering the plasma to the amount of analyte delivered to the nebulizer. By measuring 30 nm Fe NP, the nebulization efficiency (calculated by size) was found to be around 0.30 (30%) for all three organic solvents. The sensitivity of ionic Fe ranged from 1500 cps/ppt to 2400 cps/ppt depending on the solvent. The background equivalent concentration (BED) of the blank reagents was around 6 nm.

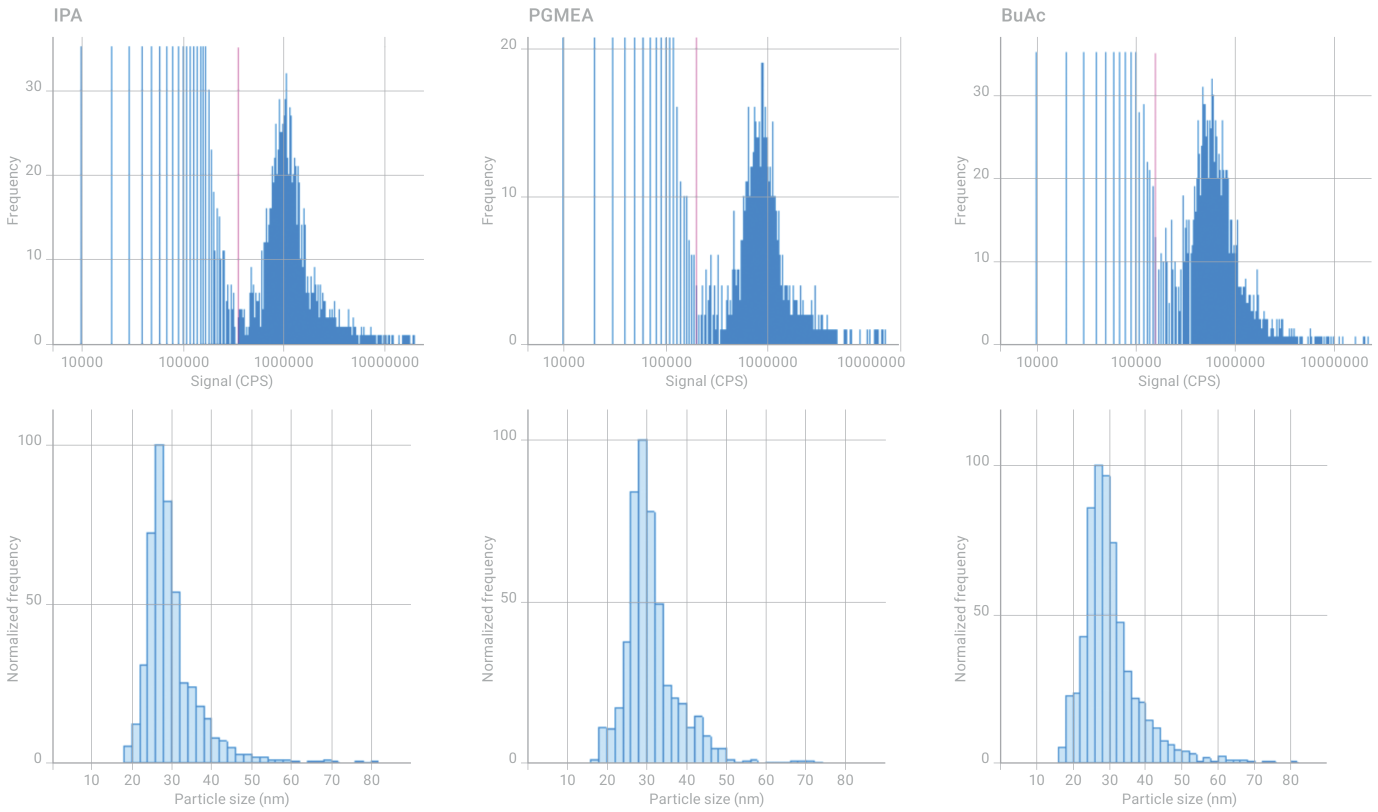

Figure 1. Signal distribution (upper) and size distribution (lower) of 30 nm Fe NPs in solutions of IPA, PGMEA, and BuAc.

Linearity of detected particle number concentration in terms of spiked concentration

Figure 2 shows the size distribution of 25 nm Fe NPs dispersed in IPA solution at several concentrations (0, 0.1, 0.5, 1, and 2 ppt). The graph clearly indicates a Gaussian distribution for 0.5, 1, and 2 ppt of Fe NPs. It wasn't possible to detect NPs smaller than 18 nm due to the background signal from the small amount of ionic Fe present in the sample (BEC = 0.6 ppt).

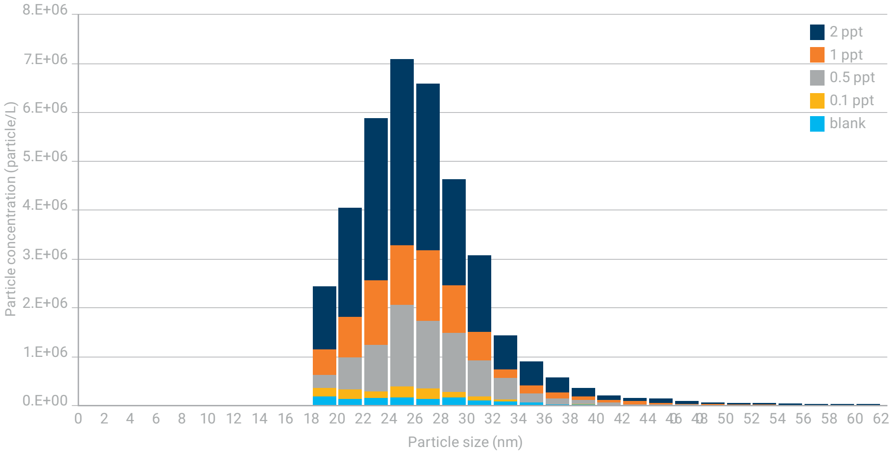

Figure 2. Size distribution data for 25 nm Fe NPs spiked at 0, 0.1, 0.5, 1, and 2 ppt in IPA. The vertical axis shows the particle number concentration for each range of particle sizes (each bar represents a size range of 2 nm).

Figure 3 shows the relationship of measured particle number concentration (particle/L) against the spiked concentration of Fe NPs in IPA. Almost perfect linearity ($R^2 = 0.998$) was obtained across the concentration range of 0.1 to 2 ppt. These results show that 25 nm Fe NPs can be determined in IPA solutions containing very low concentrations of Fe NPs using the 8900 ICP-QQQ operating in spICP-MS mode.

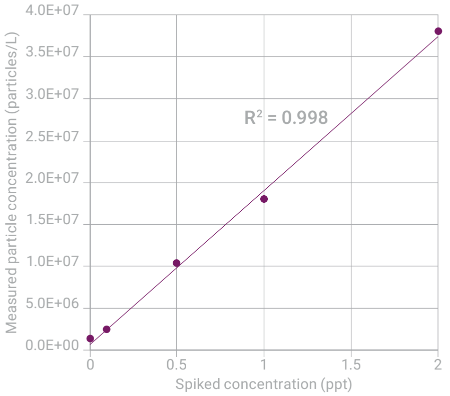

Figure 3. Relationship between the spiked concentration of 25 nm Fe NPs and measured particle number concentration in IPA.

Long-term stability test

Figure 4 shows the stability of detected particle number (representing particle number concentration) and particle size for 30 nm Fe NPs in the three solvents over 12 hours. Both the detected particle number and the size were constant over 12 hours, as indicated by the %RSDs. The stability of Fe NPs in each solvent means they can be measured accurately, even a long time after sample preparation.

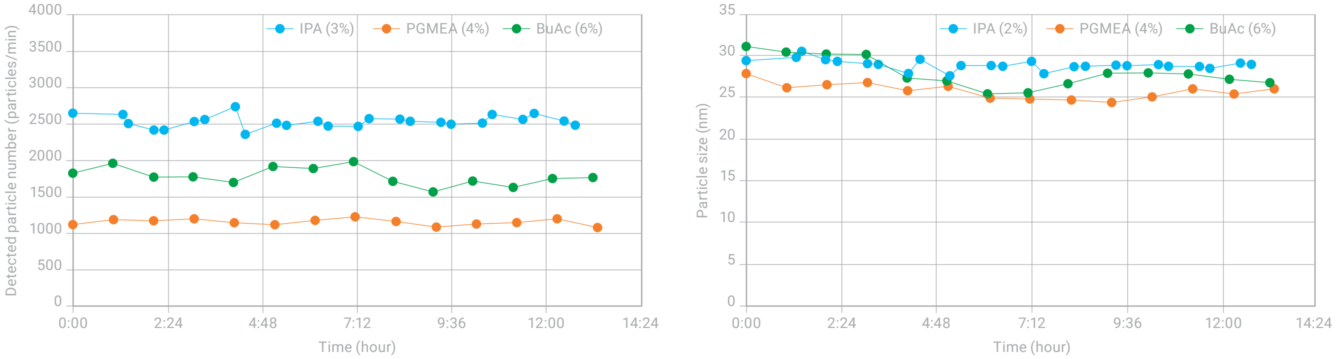

Figure 4. Long-term stability of 30 nm Fe NPs in IPA, PGMEA, and BuAc over 12 hours. The left graph shows the detected particle number and the right graph shows the average particle size. The numbers in parentheses are RSD%.

Conclusion

Using an spICP-MS method, the Agilent 8900 ICP-QQQ operating in MS/MS mode was used for the determination and characterization of iron-based nanoparticles in IPA, PGMEA, and BuAc.

Standards containing 25 or 30 nm Fe_3O_4 nanoparticles were spiked into the organic solvents and the particle size and the particle number concentration were determined using the spICP-MS method. The small-sized particles were successfully measured in solutions with a particle concentration ranging from 0.1 to 2 ppt. Also, the particle size and particle concentration of Fe NPs were stable in each of the three organic solvents over 12 hours.

Overall, the method delivered the low background, sensitivity, and spectral interference removal necessary for the analysis of small-sized NPs in semiconductor grade organic solvents.

References

1. Takuya Hagiwara, Kentaro Saito, Hiraku Chakihara, Shuji Matsuo, Masao Inoue, Seiji Muranaka, Yuki Ota, Masazumi Matsuura, Study on Cone-defects during the Pattern Fabrication Process with Silicon Nitride, *J. Photopolym. Sci. Technol.*, 28, No.1, **2015**, 17–24
2. Michiko Yamanaka and Steve Wilbur, Measuring Multiple Elements in Nanoparticle using spICP-MS: Acquire NP data for up to 16 elements in Rapid Multi-Element Nanoparticle Analysis Mode, Agilent publication, 5994-0310EN
3. Yoshinori Shimamura, Donna Hsu, and Michiko Yamanaka, Multielement Nanoparticle Analysis of Semiconductor Process Chemicals Using spICP-QQQ: Characterization of Ag, Fe_3O_4, Al_2O_3, Au, and SiO_2 NPs in TMAH in a single analytical run, Agilent publication, 5994-0987EN
4. Michiko Yamanaka and Steve Wilbur, Accurate Determination of TiO_2 Nanoparticles in Complex Matrices using the Agilent 8900 ICP-QQQ, Agilent publication, 5991-8358EN

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Analysis of 15 nm Iron Nanoparticles in Organic Solvents by spICP-MS

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Using the exceptional sensitivity and low background of the Agilent 8900 ICP-QQQ

Monitor metallic nanoparticles in process chemicals

In semiconductor device manufacturing, even small amounts of impurities present in processing reagents can affect product yield and reliability. There is growing awareness that metallic nanoparticles (NPs), especially Fe NPs, can lead to the occurrence of defects on the surface of wafers. Single particle ICP-MS (spICP-MS) is a powerful tool that is used increasingly to characterize the NP content of various types of samples, including semiconductor process chemicals.

Measurement of 15 nm Fe NPs using spICP-MS

The Agilent 8900 ICP-QQQ (semiconductor configuration) was fitted with a quartz torch with a 1.5 mm i.d. injector. Interferences on ^{56}Fe from ArO and C_2O_2 were resolved using oxygen as the cell gas. The Agilent SPS 4 autosampler was used, so large bottles (100 to 500 mL) could be used for long-term stability tests. The samples were self-aspirated using an Agilent PFA nebulizer with SPS 4 probe kit (G3139-68000). Data analysis was performed using the optional Single Nanoparticle Application module of Agilent ICP-MS MassHunter software.

Table 1. 8900 ICP-QQQ operating parameters used for spICP-MS method.

Parameter	Setting	Parameter	Setting
RF Power (W)	1200	Energy Discrimination (V)	−8.0
Sampling Depth (mm)	16	Cell gas (O_2) Flow (mL/min)	0.38 (25%)
Neb Gas Flow (L/min)	0.75	Dwell Time (us)	100
Makeup Gas Flow (L/min)	0.5	Scan Mode	Single quad mode
*Option Gas (O_2) Flow (L/min)	0.12 (12%)	Mass Monitored	56 (Fe)
Spray Chamber Temp (deg)	−2	Data Acquisition Time (s)	60
Axial Acceleration (V)	2		

**Direct injection of organic solvents was possible by adding oxygen (50% balanced with Ar) to prevent the deposition of carbon on the cones.*

The spICP-MS method was used to measure isopropyl alcohol (IPA), propylene glycol methyl ether acetate (PGMEA), and propylene glycol monomethyl ether (PGME) spiked with 15 nm Fe_2O_3 NPs (Sigma Aldrich). Figure 1 shows the signal distribution (upper) and size distribution plots (lower) for Fe NPs in each of the samples. The NP signals were clearly separated from the background signals. Also, the mean measured particle size was around 15 nm in all spiked samples, which is consistent with the nominal Fe NP diameter of 15 nm.

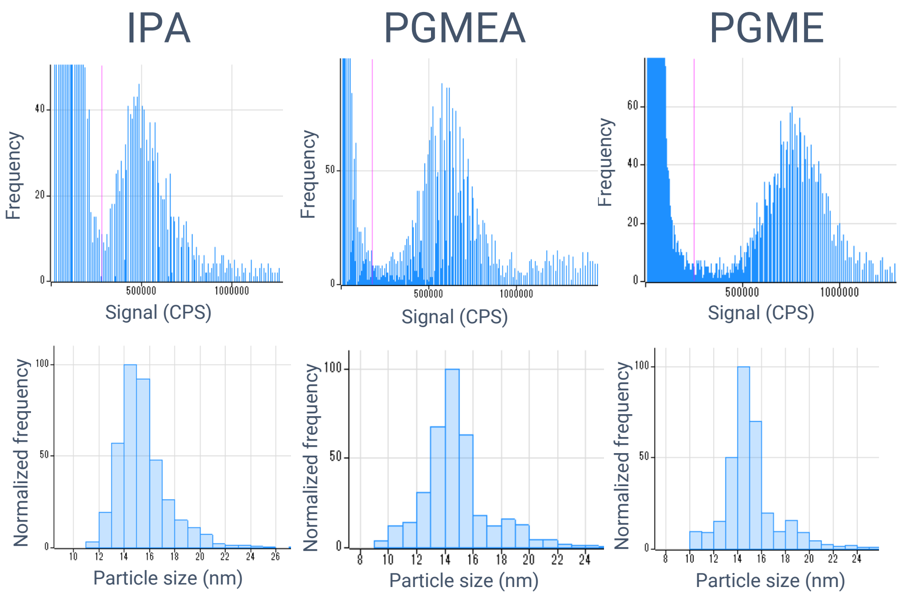

Figure 1. Signal distribution (upper) and size distribution (lower) of 15 nm Fe NPs in solution of IPA, PGMEA, and PGME.

Size ratio of 15 and 30 nm particles

Table 2 shows the average signal intensities from one particle with a 30 nm diameter and one particle with a 15 nm diameter, and the ratio of these intensities (30 nm/15 nm). As the signal intensity is proportional to the cube of the diameter of the particle, the ratio of signal intensities from the 15 and 30 nm NPs should be 8. The measured ratio was 8.44, which is acceptable, considering the accuracy of the nominal diameters.

Table 2. Average particle signal intensities and ratio of the intensities.

Average signal intensity from one particle (cps)		Ratio (30 nm/15 nm)
30 nm	15 nm	
5,216,482	617,736	8.44

Long-term stability tests

Figure 2 shows the stability of detected number (representing particle number concentration) and particle size for 15 nm Fe NPs in two of the solvents over 10 hours. Both the detected particle number and the size were constant over 10 hours, as indicated by the %RSDs.

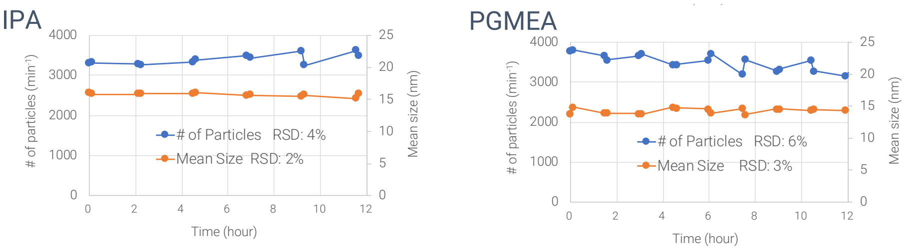

Figure 2. Long-term stability of 15 nm Fe NPs in IPA and PGMEA over 10 hours.

Figure 3 shows the size distribution profiles of 30 nm Fe NPs in IPA on the day of sample preparation and six months later. After six months, the signals from 30 nm Fe NPs were clearly observed and the shape of the size distribution is almost the same as the one in the fresh solution. The results show that Fe NPs are stable in IPA for a long period, suggesting that they don't dissolve into or precipitate out of the solvent.

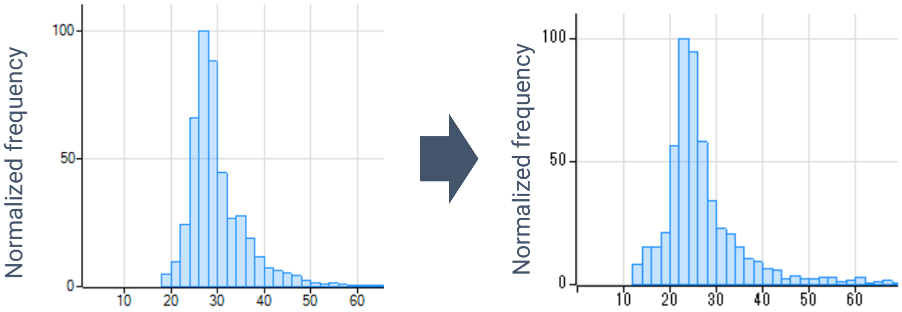

Figure 3. Size distribution of 30 nm Fe NPs in IPA on the day of preparation (left) and six months later (right).

Single particles in high purity solvents

The 8900 spICP-MS method satisfies the emerging needs of the semiconductor industry to monitor low concentrations of small sized particles in high purity solvents.

GC-ICP-QQQ Achieves Sub-ppb Detection Limits for Hydride Gas Contaminants

Authors

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Keywords

semiconductor, petrochemical, phosphine, arsine, hydrogen sulfide, carbonyl sulfide, germane, silane, oxygen mass-shift, hydrogen on-mass

Introduction

Hydride gases, such as phosphine and arsine, are important contaminants in process chemicals used in both the petrochemical and semiconductor industries. 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. 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. The presence of unwanted hydride gas impurities can have a profound effect on the performance of the final device.

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. In anticipation of increasing industry demand for lower level detection, a new high sensitivity GC-ICP-QQQ method was developed for this application.

Experimental

Instrumentation: An Agilent 7890 GC was coupled to an Agilent 8800 #200 using the Agilent GC-ICP-MS interface.

Acquisition conditions: MS/MS mass-shift mode using oxygen as the cell gas for the measurement of Ge, As, P and S. MS/MS mode with hydrogen cell gas was used for the on-mass measurement of the primary isotope of Si at *m/z* 28.

Table 1. Agilent 8800 ICP-QQQ operating conditions.

	O_2 mode	H_2 mode
RF power (W)	1350	
Sample depth (mm)	8.4	
Argon carrier (make-up) gas flow (L/min)	0.85	
Extract 1 (V)	-150	
Extract 2 (V)	-190	
Kinetic Energy Discrimination (V)	-4	0
Cell gas/flow (mL/min)	0.35	5.0

Reagents and sample preparation: 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.

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 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. This covers the representative concentration range required for the measurement of this contaminant.

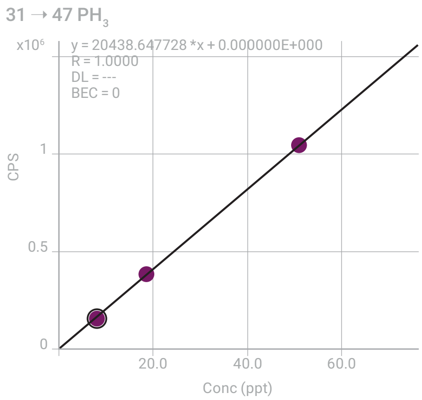

Figure 1. Phosphine calibration curve with an R value of 1.000 over the concentration range.

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

ii. The standard deviation of the concentrations measured in seven replicate analyses of the low level standard.

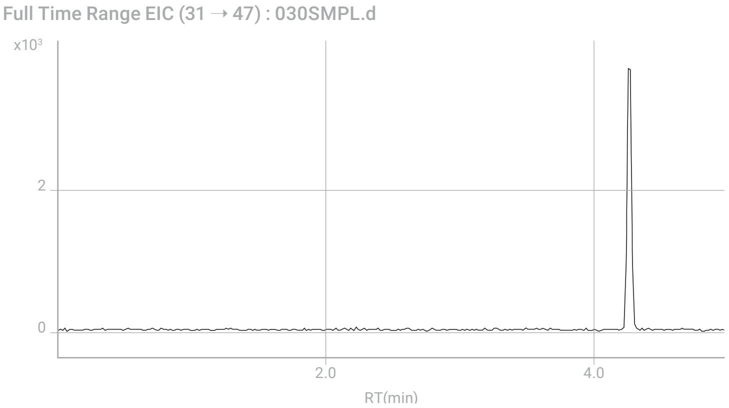

Figure 2. Chromatogram of 0.42 ppb PH_3 standard. S/N: 96.9.

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.

Analysis of additional hydride gases

The GC-ICP-QQQ method was applied to the multielement analysis of germane, arsine and phosphine within a single analysis. Ge and As were measured as their O_2 reaction product ions, GeO^+ and AsO^+, as was the case with P (PO^+). Hydrogen sulfide (H_2S) and carbonyl sulfide (COS) were also 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. For the analysis of silane, Si was measured directly (on-mass) at its major isotope ^{28}Si, using H_2 cell gas. 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 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.

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 1. 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 by 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 1. 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

GC-ICP-QQQ sets benchmark detection limits

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

Sub-ppb detection limits for hydride gas contaminants using GC-ICP-QQQ. Agilent Publication 5991-5849EN

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Determination of Trace Impurities in Electronic Grade Arsine by GC-ICP-QQQ

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Sub-ppb detection limits for hydride gas contaminants using a single column, single injection volume, and multi-tune method

Introduction

Most electronic devices use silicon-based semiconductors. However certain applications can benefit from alternative semiconductor materials, such as III-V compound semiconductors. These compounds are made of elements from groups III and V of the periodic table, usually Al, Ga, or In combined with N, P, As, or Sb. The appeal of these compounds is that they have much higher “carrier mobility” than silicon, which means they offer high performance and greater chip density with lower power consumption and less heat generation. These are critical factors in microelectronics, leading to increased use of III-V compound semiconductors in high electron mobility transistors (HEMT) and field effect transistors (FET).

Unlike Si semiconductors, III-V compound semiconductors are also able to emit light, which makes them essential for the large and growing field of optoelectronics. Light emitting diodes (LED) are widely used in lighting, displays, illuminated switches, and infrared remote controls. Other III-V compound semiconductor devices include vertical-cavity surface-emitting lasers (VCSEL), which are used in optical fiber communications.

Among the most widely used III-V compounds are gallium arsenide (GaAs), aluminum gallium arsenide (AlGaAs), and indium gallium arsenide nitride (InGaAsN), all of which require arsine gas as a precursor for manufacture.

Dopants are added deliberately to modify the electrical properties of semiconductor materials, but incorporation of unwanted dopant elements into III-V compound semiconductor structures can be problematic, even at trace levels (*1*). The unwanted dopants will introduce energy levels in the energy gap of the semiconductor, altering the electrical and optical properties of the semiconductor substrate through an increase in electron mobility, leakage current, or photoluminescence.

For example, n-type dopants such as Ge, Si, P, and S increase leakage current and reduce the gain of transistors. Therefore, it is critical to determine the concentration of germane (GeH_4), silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) impurities in arsine to prevent them affecting the performance of the final device. There may be some slight variation in the gas purity levels required for the manufacture of each type of device, but, in general, process gases need to be free of dopant impurities. Because Ge is of particular concern in the manufacture of many devices, there is a need to measure GeH_4 impurities at or below single digit ppb levels in arsine. However, the ability to detect such low level impurities requires a highly sensitive analytical method.

Gas chromatography (GC) coupled with ICP-MS is currently the only technique capable of measuring germane in arsine at sub-ppb levels (*2–4*). The non-atmospheric molecular impurities typically determined by GC-ICP-MS are H_2S, SiH_4, PH_3, and GeH_4. Occasionally, stibine (SbH_3), hydrogen selenide (H_2Se), and stannane (SnH_4) are also of interest.

The goal of this work was to measure as many of the critical hydride gas impurities as practically possible in arsine, using a single GC-ICP-MS injection and a multi-tune "time program" acquisition method. This approach avoids the need to use different detectors, columns, methods, and even instruments to cover the full range of impurities.

Experimental

Sample and standard preparation

Standards of SiH_4, PH_3, GeH_4, and H_2S were made using a 10 ppm standard mixture (Custom Gas Solutions, Durham, NC, USA) and dynamically diluting it to a value of 24 ppb using a UHP-MMSD dilution system (CONSCI, Pasadena, TX). Standards for H_2Se, SbH_3, and SnH_4 are difficult to obtain due to the labile nature of these compounds. Only qualitative retention time standards were made using hydride generation with sodium borohydride. Although H_2Se, SbH_3, and SnH_4 can be determined by GC-ICP-MS, they were not studied quantitatively in this investigation.

Instrumentation

An Agilent 7890B GC was used for the separation of impurities in arsine and an Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used as the detector. The standard Agilent GC-ICP-MS interface was modified using a high flow Deans switch, as shown in Figure 1. This configuration allowed the arsine matrix to be vented at its elution time, preventing the matrix from entering the ICP-MS torch. The column was selected based on a previous study that used an Agilent 8800 ICP-QQQ (*3*). The GC operating parameters are given in Table 1.

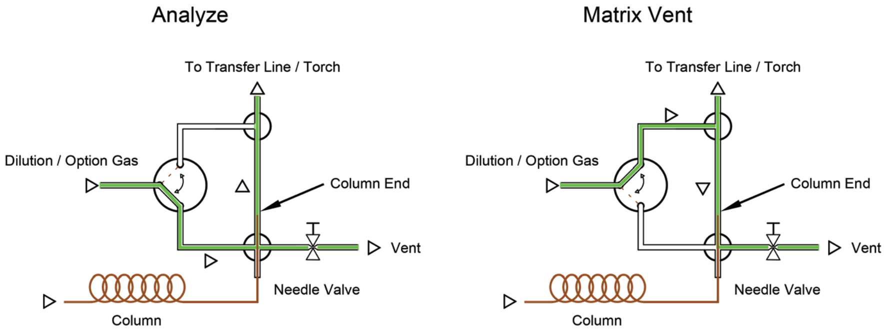

Figure 1. Schematic of the Deans switch used to vent arsine eluted by the GC column, preventing the matrix from being passed to the 8900 ICP-QQQ.

Table 1. GC operating parameters.

Parameter	Setting
Column	Two 100 m x 0.53 mm x 5.0 µm DB-1
Carrier Gas (psig Ar)	20
Oven Temperature (°C)	30 (isothermal)
Sample Size (µL)	60
Transfer Line Temperature (°C)	120

Standard instrument operating parameters for the ICP-MS recommended by Agilent were used. To optimize the ICP-QQQ, a standard containing 5 ppm sulfur hexafluoride, xenon, and krypton in argon (CSI Gas, Texas City, TX) was used. The standard was introduced into the argon dilution gas flow path at 2 mL/min and the signal at *m/z* 32 was maximized. The S, Kr, and Xe peaks were used to optimize torch position and confirm mass calibration.

As described in a previous study (*3*), Agilent ICP-QQQ instruments feature two identical, full-sized quadrupole mass filters (Q1 and Q2), situated either side of the Octopole Reaction System (ORS) collision/reaction cell (CRC). This configuration enables double mass selection (MS/MS), which is vital for successful interference removal using reactive cell gases. Like Q2, Q1 operates in a high vacuum region, so it provides excellent resolution and abundance sensitivity while also maintaining high transmission. This allows precise selection of the ions that enter the cell, ensuring the reactions used to remove interferences on analyte ions are consistent and predictable. A reactive cell gas such as hydrogen, oxygen, or ammonia is used to react with either the interfering ion or the analyte ion (M^+) to attain interference-free measurement. Analytes are measured in 'on-mass' or 'mass-shift' mode. When the cell gas reacts with the interferent, but not the analyte ion, the analyte is measured at its natural mass (on-mass) and the interference ions are removed by Q2. When the analyte ion reacts more readily with the cell gas than the interference ions do, the analyte forms a reaction product ion e.g. MH^+ or MO^+. These product ions are then measured at a new mass, away from the interfering ion overlaps.

The ICP-QQQ can also be operated in no gas mode or the ORS cell can be pressurized with a collision gas, such as helium (He). He mode removes many common polyatomic ion interferences by kinetic energy discrimination (KED) or by collision-induced dissociation (CID).

Compared to the 8800 ICP-QQQ used in the previous study (*3*), the 8900 uses newer technology, such as an ORS^4 cell, which provides higher sensitivity and lower backgrounds. In addition, the 8900 #100 (Advanced Applications) model used in this work includes inert, low sulfur and silicon argon gas lines, which reduce instrumental backgrounds for these elements. To identify the best method conditions for the application, three different MS/MS tune modes were investigated: no gas, hydrogen, and oxygen with and without a mass-shift. Instrument operating conditions are listed in Table 2.

Table 2. ICP-QQQ operating parameters.

Parameter	No Gas	H_2	O_2
RF Power (W)	1450		
Sampling Depth (mm)	3		
Dilution Gas Flow (L/min)	0.7		
Extract 1 (V)	–20		
Extract 2 (V)	–250		
Kinetic Energy Discrimination (V)	5	2	–7
Cell Entrance (V)	–50		
Cell Exit (V)	–80	–70	
Cell Gas Flow Rate	NA	2 mL/min	0.6 mL/min (40% of full scale)

Method development

The method conditions that provided the best detection limits (DLs) for each compound are summarized using bold text in Table 3. The DLs were calculated from signal-to-noise value multiplied by three (as described later). For analytes where the background noise is low due to the absence of interferences (e.g. ^{74}Ge), single digit ppt level DLs were easily achieved using GC-ICP-QQQ operating in no gas, H_2, or O_2 mode. For analytes that are prone to higher backgrounds, such as ^{31}P, ^{32}S, and ^{28}Si, lower DLs were achieved using a reactive cell gas method. The presence of CO_2, N_2, and O_2 in the argon supply and from air entrainment into the plasma leads to the formation of spectral interferences. These interferences include $^{12}C^{18}OH^+$, $^{14}N^{16}OH^+$, $^{15}N_2H^+$, $^{15}N^{16}O^+$ and $^{13}C^{18}O^+$ on $^{31}P^+$, $^{16}O_2{}^+$ and $^{14}N^{18}O^+$ on $^{32}S^+$, and $^{12}C^{16}O^+$ and $^{14}N_2{}^+$ on $^{28}Si^+$. P and S react quickly with O_2, so both analytes were measured as reaction product ions, $^{31}P^{16}O^+$ and $^{32}S^{16}O^+$, at *m/z* 47 and 48, respectively, in mass-shift mode. H_2 cell gas provided effective removal of the background interferences at mass 28, allowing on-mass measurement of $^{28}Si^+$ at *m/z* 28.

The measurement of different analytes in different reaction modes is simple to set up and run using a single multi-tune method on the 8900. In the acquisition method, the cell gases and measurement modes are switched automatically during the analysis, giving a fast and automated analysis using the optimum mode for each analyte. Switching conditions during the run allows the analyst to use the best cell conditions, as well as increase the analyte acquisition times to improve sensitivity.

Increasing the injection volume would provide even lower DLs for all compounds except for H_2S. A 60 µL (or smaller) sample size is needed for the separation of H_2S from the arsine matrix.

Table 3. Comparison of GC-ICP-QQQ method conditions for each gas mode.

	No Gas				
	Mass	Integration Time (s)	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
Silane	28 > 28	0.2	165967	14	5
Germane	74 > 74	0.2	447435	8260	0.01
Phosphine	31 > 31	0.2	32118	870	0.08
Hydrogen sulfide	32 > 32	0.2	234053	175	0.41
	Hydrogen				
	Mass	Integration Time (s)	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
Silane	28 > 28	0.2	79068	42	1.7
Germane	74 > 74	0.2	272006	8300	0.01
Phosphine	31 > 31	0.2	17919	650	0.11
Hydrogen sulfide	32 > 32	0.2	145124	180	0.40
	Oxygen				
	Mass	Integration Time (s)	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
Silane	28 > 28	0.2	51499	34	2
Silane	28 > 44	0.2	34201	37	2
Germane	74 > 74	0.2	422359	8000	0.01
Germane	74 > 90	0.2	15577	1240	0.06
Phosphine	31 > 31	0.2	0	0	NA
Phosphine	31 > 47	0.2	29011	1500	0.05
Hydrogen sulfide	32 > 32	0.2	22579	13	6
Hydrogen sulfide	32 > 48	0.2	218640	290	0.24

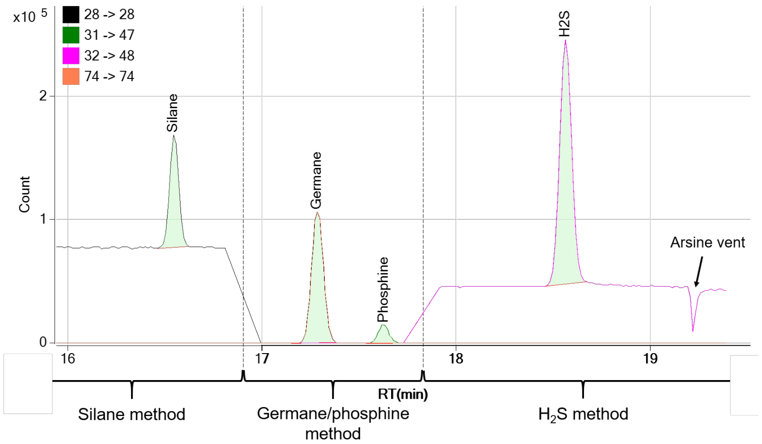

Figure 2. Overlaid chromatograms of SiH_4, PH_3, H_2S, and GeH_4 in arsine by GC-ICP-QQQ obtained using a multi-tune method.

Multi-element analysis of SiH_4, PH_3, H_2S, and GeH_4

Since the best sensitivity (peak area) was obtained using different cell gas conditions for each analyte compound, a time program method was used where the acquisition conditions were changed during the run. The optimized single-method parameters are given in Table 4 and the chromatograms are shown in Figure 2. If analysts preferred to simplify the analysis and use a single cell gas, O_2 would provide acceptable data, with some loss of sensitivity compared to the multi-tune method.

Table 4. Multi-tune method parameters.

	Acquisition Time (s)	Retention Time (s)	Gas Mode	Q1 -> Q2	Integration Time/Mass (s)
Silane	1008	992	H_2	28 -> 28	0.8
Germane	77	1037	O_2	74 -> 74	0.2
Phosphine		1057	O_2	31 -> 47	0.4
Hydrogen sulfide	89	1112	O_2	32 -> 48	0.8

Table 5. DLs for SiH_4, GeH_4, PH_3, and H_2S.

	Mass	Integration Time (s)	Gas Mode	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
Silane	28 > 28	0.8	H_2	308146	140	0.51
Germane	74 > 74	0.2	O_2	438374	8000	0.01
Phosphine	31 > 47	0.4	O_2	60451	4700	0.02
Hydrogen sulfide	32 > 48	0.8	O_2	883099	490	0.15

Results and discussion

The DLs reported for SiH_4, GeH_4, PH_3, and H_2S (Table 5) were determined using the chromatograms (Figure 2) that were obtained using the parameters outlined in Table 4. The ICP-MS MassHunter software signal-to-noise (S/N) tool was used. The software divides the concentration of the analyte by the S/N value followed by multiplication by three to determine the DL. The EPA protocol MDL and a Student T-test could have been applied if a standard 10 times or less than the expected DL had been available (*5*). That level standard was not available for this work.

Other compounds of potential interest in the quality control testing of arsine including H_2Se and SbH_3 eluted well beyond the arsine retention time (not shown in Figure 2). The relative retention time of SnH_4 and arsine prevented SnH_4 from being separated on a boiling point column, so an Agilent Select Low Sulfur column (p/n CP8575) was used instead. DLs for SnH_4, H_2Se, and SbH_3 were estimated at 1 ppb or lower, based on their relative response in aqueous samples and their first ionization potentials.

Conclusion

GC-ICP-QQQ was used to separate and measure all hydride gas contaminants in arsine at or below single digit ppbv levels. Germane, which is probably the most critical contaminant in semiconductor-grade arsine, was determined at low ppt levels. Measurements of SiH_4, PH_3, H_2S, GeH_4, H_2Se, and SbH_3 were performed using a single GC column and a single injection.

The best detection limits for all compounds were achieved by operating the 8900 ICP-QQQ in MS/MS mode with H_2 and O_2 cell gases. Using a single multi-tune method allowed us to maximize signal averaging, and therefore achieve low DLs with a single injection.

The determination of dopants/contaminants in arsine provides extra process control to aid in the quality of the manufacturing process, thus improving the yield and performance of micro-electronic and opto-electronic devices.

References

1. J. Feng, R. Clement, M. Raynor, Characterization of high-purity arsine and gallium arsenide epilayers grown by MOCVD. *J. of Chrystal Growth*, **2008**, 310, 23, 4780–4785
2. C. J. Meyer and W. M. Geiger, The Chromatographic Analysis of Trace Atmospheric Gases. In J. D. Hogan (Ed.), Specialty Gas Analysis: A Practical Guidebook. 1997, 76–77. New York: Wiley-VCH.
3. W. M. Geiger and E. Soffey, GC-ICP-QQQ Achieves Sub-ppb Detection Limits for Hydride Gas Contaminants. In *Agilent 8800 ICP-QQQ Application Handbook*, Fourth edition, **2020**, 37–40, Agilent publication 5991-2802EN
4. D. Decker and L. M. Sidisky, Gas Chromatographic Column Considerations. In W. M. Geiger, & M. W. Raynor (Eds.), Geiger, W. M., and Raynor, M. W. (2013). *Trace analysis of specialty and electronic gases*. (pp. 251–274). Hoboken, N.J: John Wiley & Sons, Inc.
5. G. Wells, H. Prest, C. W. Russ IV, Signal, Noise, and Detection Limits in Mass Spectrometry, Agilent publication, 5990-7651EN

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Gas Chromatographic Separation of Metal Carbonyls in Carbon Monoxide with Detection using the Agilent 8800 ICP-QQQ

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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.

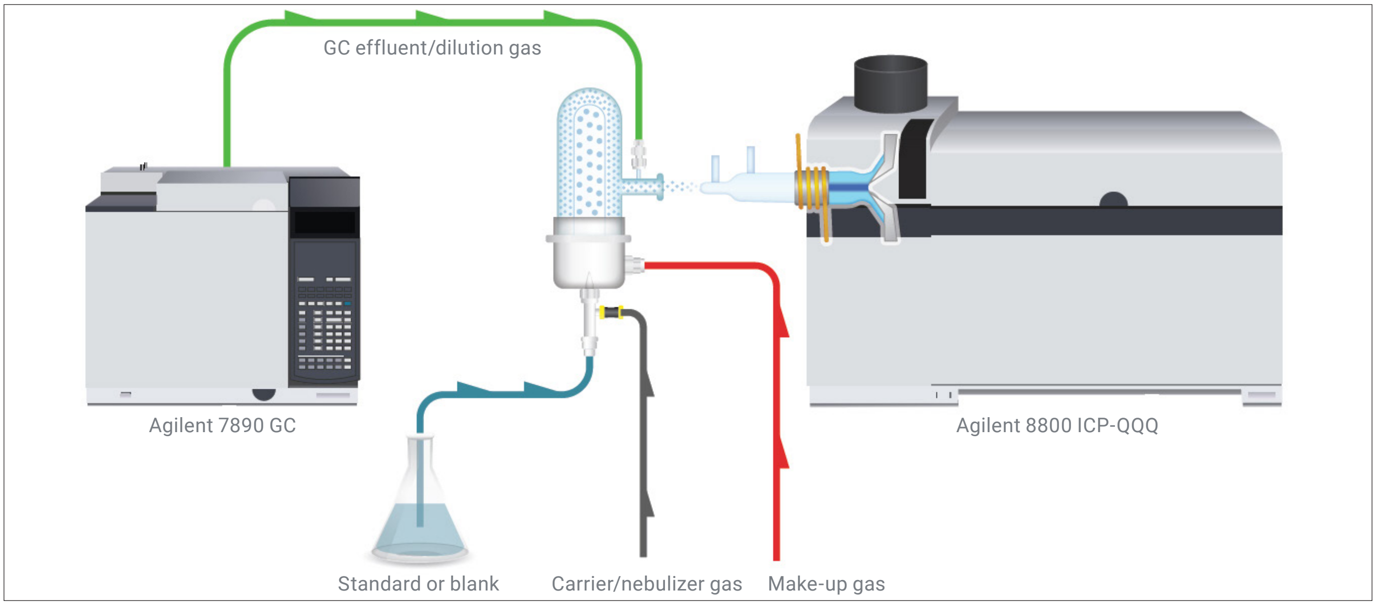

Figure 1. GC-ICP-QQQ interface for the simultaneous aspiration of liquid standard or blank and GC effluent.

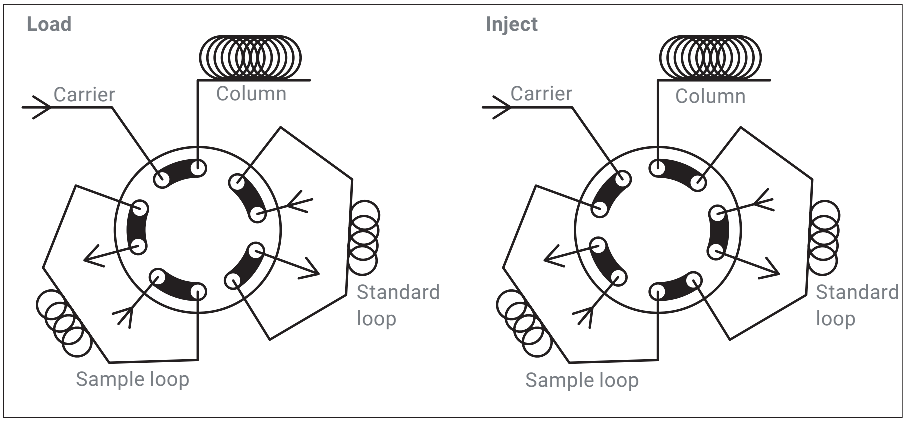

Figure 2. Valco 10 port PEEK gas sampling valve (GSV) flow path providing standard addition capability.

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).

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.

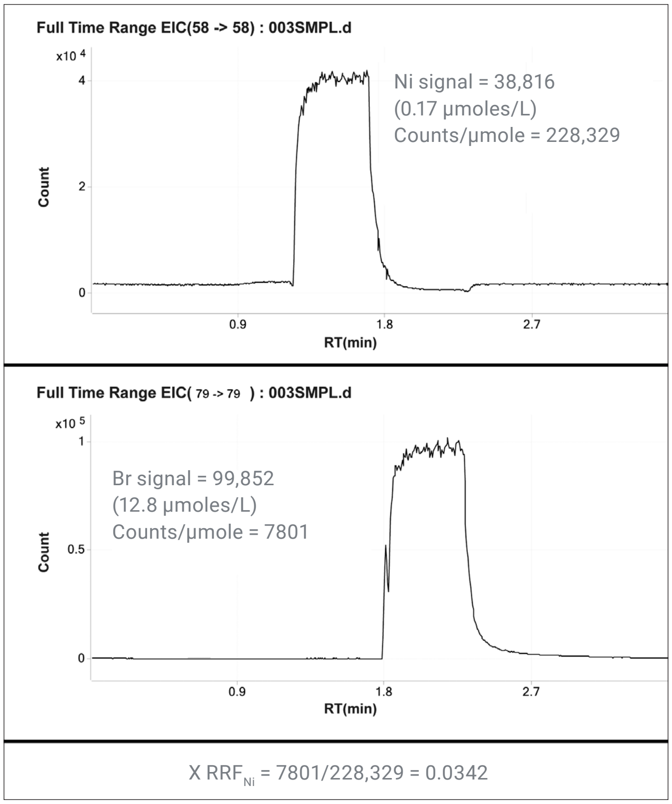

Figure 3. Calculation of relative response factor (RRF) for Ni, from aspiration of aqueous nickel and bromine standards

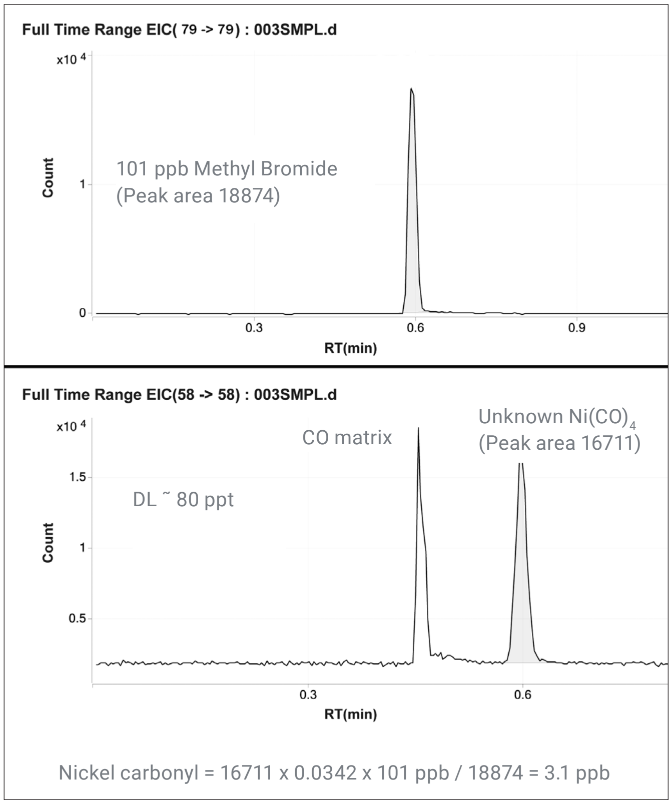

Figure 4. Analysis of known gas phase bromine standard as a surrogate standard for the determination of unknown nickel carbonyl

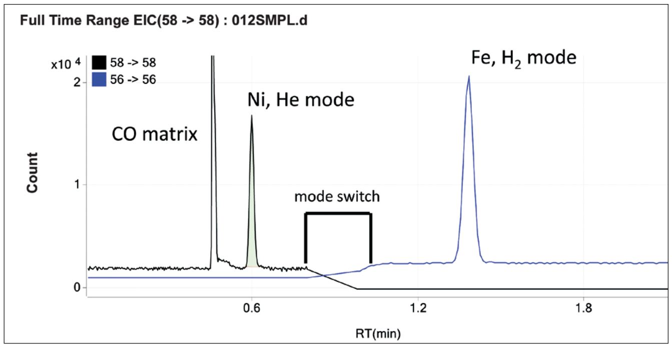

Figure 5. Tune mode switching for optimum measurement conditions during TRA acquisition

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.

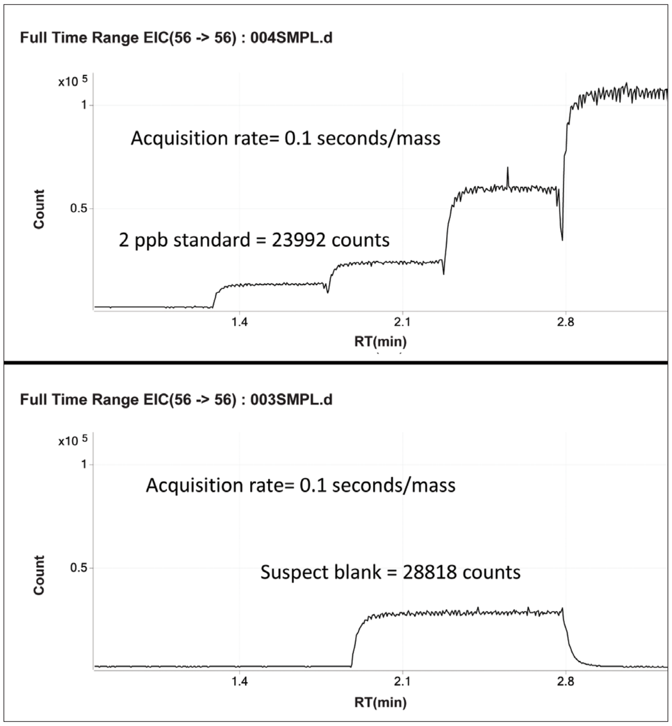

Figure 6. Aqueous standards (top) versus contaminated blank (bottom)

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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 $Fe2(CO)_9$.

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.

References

1. D.H. Stedman, D.A. Hikade, R. Pearson, Jr., E.D. Yalvac, *Science*, 1980, 208, 1029
2. A. Harper, *Analyst*, 1991, 149-151
3. E.M. Krupp, et. al., *Spectrochimica Acta* Part 56, 2001, 1233-1240
4. W.M. Geiger, M.W. Raynor, D. Cowles, *Trace Analysis of Specialty and Electronic Gases*, 2013, Wiley, Chapter 6, 182-185.

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