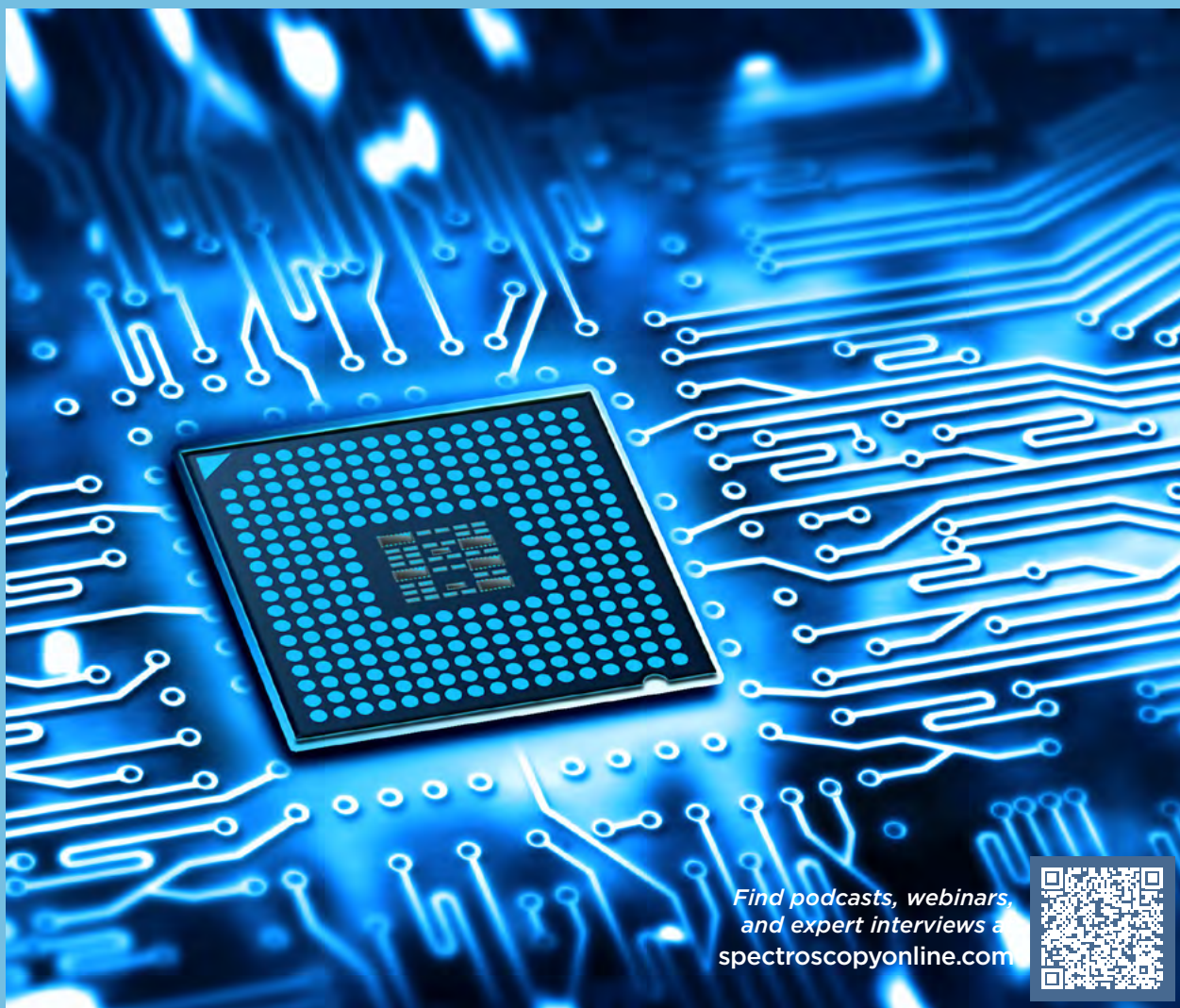


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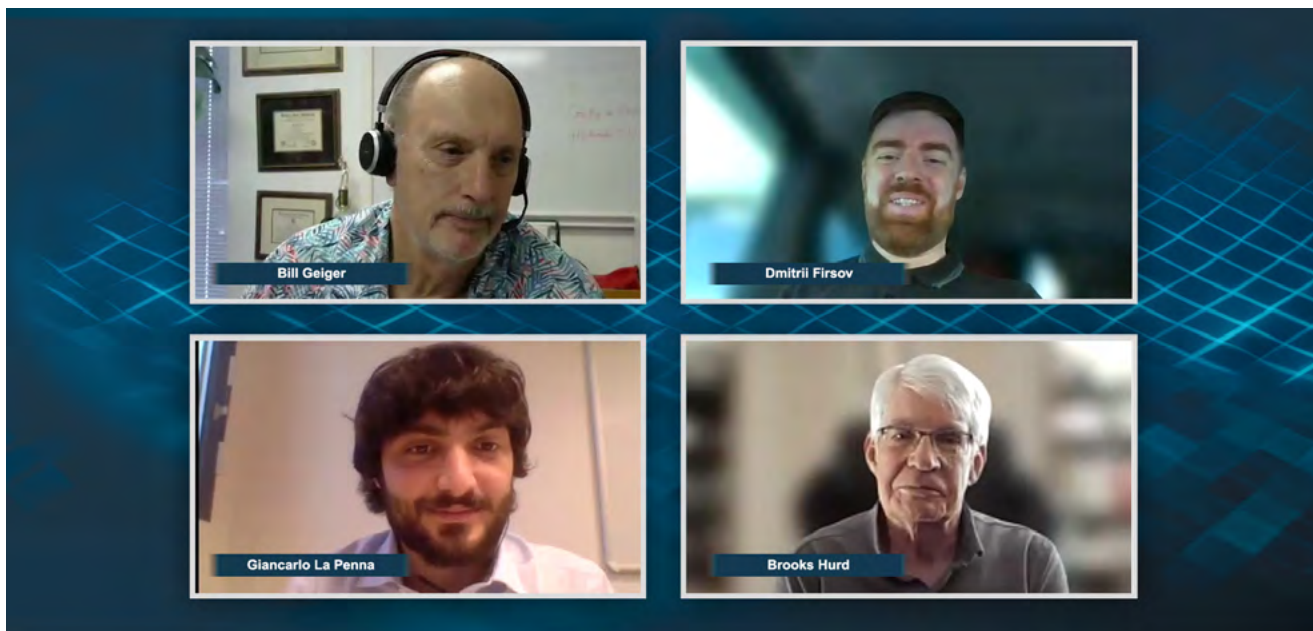
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# Best Practices for Improving Semiconductor Analysis: *A Spectroscopy Peer Exchange*

Aaron Acevedo



This executive summary highlights the key insights from a recent roundtable discussion featuring a panel of scientists. The conversation centered on the major challenges and best practices in leveraging spectroscopy for advanced semiconductor analysis.

**S**emiconductors are materials that can be engineered to either conduct or block electrical current, serving as the foundation for many modern technologies. Semiconductors—made from silicon—are the key components in devices that power advanced systems across diverse fields, such as healthcare, communications, computing, and spectroscopy (1). Silicon, the primary material in most

semiconductors, is also the main component in computer chips (2).

The importance of semiconductors is reflected in their widespread application and economic impact. According to the Semiconductor Industry Association (SIA), global semiconductor sales reached \$166.0 billion in Q3 2024, marking a 23.2% increase from Q3 2023 and a 10.7% rise compared to Q2 2024 (3).

Given the growing importance of



# “Addressing these challenges requires a coordinated effort to improve production efficiency, diversify supply sources, and develop more resilient supply chain strategies.”

-Brooks Hurd

semiconductors, scientists are intensifying efforts to achieve lower levels of detection for analyzing these critical devices. In a peer-exchange discussion moderated by Brooks Hurd, president of SiriusUHP, panelists Bill Geiger of Consolidated Sciences, Dmitrii Firsov of St. Petersburg Electrotechnical University, and Giancarlo La Penna of CEA-Leti explored the most pressing challenges in semiconductor analysis and strategies for overcoming them.

## The Biggest Hurdles in Semiconductor Analysis

In the first episode, the panel delves into key challenges in semiconductor analysis, focusing on the limitations of current techniques and the need for innovation. Firsov highlighted the complexities of analyzing two-dimensional semiconductor materials, noting that their optical signals are often limited and difficult to characterize using optical spectroscopy due to their micron-scale surfaces. La Penna emphasized the necessity for high-resolution, non-destructive techniques that can be integrated into production lines for real-time quality control (QC). Hurd addressed the complications arising from the miniaturization of semiconductor devices, stating that shrinking dimensions pose challenges for all aspects of manufacturing.

Expanding on these issues, Geiger identified sensitivity, potential interferences, calibration difficulties, and atmospheric contaminants—such as water clinging to surfaces—as persistent obstacles. These insights underscore the urgent need for advancements in spectroscopy and analytical methods to keep pace with semiconductor technology’s rapid evolution.

## Confronting Supply Chain Issues

Semiconductor manufacturing faces significant supply chain challenges, often disrupted by natural disasters striking critical chokepoints or factory shutdowns caused by fires, labor strikes, or global events (4). In episode two, La Penna highlighted how geopolitical factors and complexity of semiconductor production amplify these vulnerabilities.

“Addressing these challenges requires a coordinated effort to improve production efficiency, diversify supply sources, and develop more resilient supply chain strategies,” he said.

Hurd shared insights from his experience with rare gas supply chains, which were heavily impacted by the war between Russia and Ukraine.

“The supply is there, but if something gets disrupted, it does get disrupted. The more we can diversify the supply chain, the better it is

for everybody, if you have alternate sources,” Hurd emphasized.

## Sample Prep Pitfalls: Common Obstacles and How to Address Them

Sample preparation for semiconductor analysis presents unique challenges, particularly regarding contamination. Residues such as dust can easily compromise sample integrity, introducing unwanted variables into the analysis. In episode three, Geiger shared his experiences using gas chromatography (GC) techniques to analyze semiconductors, noting how contaminants like calcium, sodium, and iron are readily introduced.

“We have to be very careful, not only in our handling and preparing of samples for subsequent ICP-MS analysis, but we also have to ensure the instrumentation remains clean,” Geiger said. He emphasized that contamination can be so severe that it necessitates replacing instrument components between analyses.

“Once they’re contaminated, it’s difficult to fix,” he said, highlighting the care required in semiconductor sample preparation. The panelists emphasized that maintaining the cleanliness of semiconductor components and thoroughly understanding the precise specifications of the materials can help mitigate some of these challenges.

# “If artificial intelligence (AI) can help you achieve solutions faster, it’s definitely worth utilizing.”

-Dmitrii Firsov

## Spectroscopy Techniques Shaping Semiconductor Analysis

In this episode, the panelists explore the use of advanced techniques such as Fourier-transform infrared spectroscopy (FT-IR) and inductively coupled plasma mass spectrometry (ICP-MS) for semiconductor analysis, examining their benefits and limitations. FT-IR, for instance, is constrained by the fundamental physics of optical work, requiring innovative approaches like double-sided FT-IR to analyze fine structures. Despite these limitations, FT-IR remains a versatile and reliable tool for most measurement applications. Similarly, ICP-MS offers significant potential, approaching near-total accuracy in its impact. However, it often falls short of achieving the ultra-high sensitivity levels demanded by customers, underscoring the ongoing need for further refinement in these analytical methods.

## Achieving Greater Sensitivity with Spectroscopy

The penultimate episode of the roundtable focuses on the challenges of achieving greater efficiency and performance in semiconductor analysis while spotlighting advanced techniques capable of detecting trace impurities with precision. La Penna emphasized the ongoing struggle to balance the drive for higher efficiency with the com-

plexities of modern semiconductor demands. Geiger expanded on techniques designed to meet these heightened requirements, including the use of more sensitive time-of-flight mass spectrometers. Some new instrumentation can achieve detection limits in the single-digit parts-per-billion (ppb) range and, in some cases, sub-ppb levels for various compounds.

“If we can go five times more sensitive, it may not sound like much at first, but it’s quite an improvement for many of the things we analyze,” Geiger said.

## Smarter Semiconductor Analysis: The Impact of AI

In the final episode, the panelists delve into their predictions regarding the evolving role of advanced spectroscopy in shaping the future of semiconductor analysis. A central theme that emerges is the potential of artificial intelligence (AI). AI is increasingly seen as a key enabler, particularly in the realm of data analysis, where it can help researchers and manufacturers process vast amounts of complex data more efficiently.

“I think we all agree that AI will simplify things in the future by providing us with more information to help us move forward. This remains a critical issue as we continue to progress,” Hurd said.

The potential of AI in semicon-

ductor analysis is seen as a topic requiring further exploration, the panelists agreed. Both La Penna and Firsov also recognize the technology’s promise, with Firsov adding: “If AI can help you achieve solutions faster, it’s definitely worth utilizing.”

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# Analyzing Sub-100 nm Particulate and Ultrathin (~ 1 nm thick) Residue Defects

For semiconductor processes, it is crucial to eliminate sub-100 nm particulate defects and surface contaminants. While defects as small as 20 nm can be detected with survey tools, the traditional suite of analytical tools have difficulty in clearly identifying the contaminating source of defects, especially if they are organic. Infrared photo-induced force microscopy (IR PiFM) combines non-contact AFM with IR spectroscopy to acquire topographical and chemical information concurrently at nanoscale (1). Since PiF-IR spectrum matches the FTIR spectrum, IR libraries can be used to identify the defects. Given its sub-5 nm spatial resolution, even a multi-component defect can be de-composed into pure components via multivariate data analysis of PiF-IR spectra from different regions of the sub-100 nm defect.

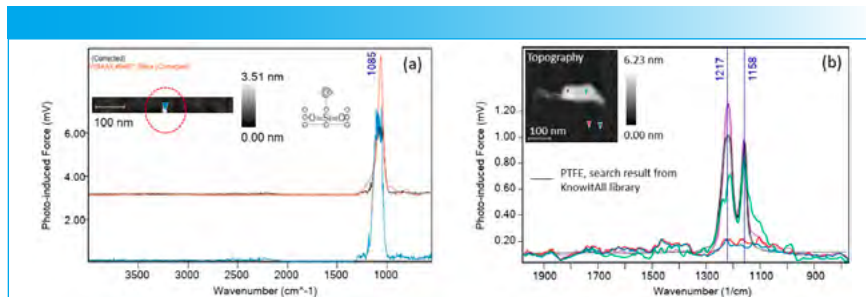
## Experimental

Surface contaminants that are common on silicon wafers along with particulate defects found on silicon wafers are characterized by IR PiFM.

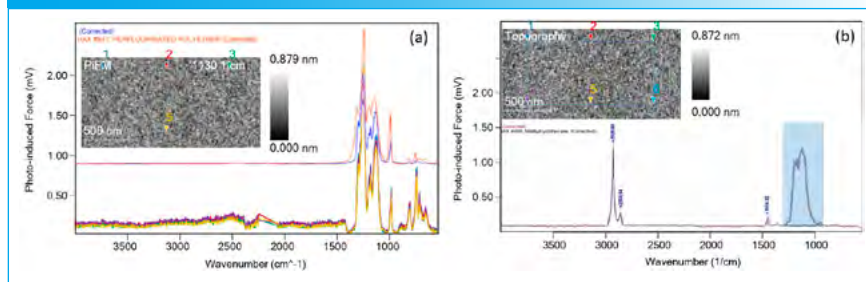
## Results and Discussion

Figure 1 shows two different defects found on silicon surfaces. In Figure 1a, we find a particle (within the red dotted circle) that is about 3 nm in height. The blue PiF-IR spectrum acquired on the particle matches the IR spectrum for silica (orange spectrum) from the Wiley IR library (2). Figure 1b shows another defect that is ~ 4 nm tall and ~ 50 nm x ~ 120 nm laterally. Two PiF-IR spectra (purple and green) on the defect match the IR spectrum (black) for PTFE.

Unwanted residue or surface contaminants need to be controlled since many semiconductor processes involve precursor molecules interacting with the surfaces. With monolayers, it is difficult to even detect its existence, let alone identify it. In Figure 2a, PiF-IR spectra acquired on a wafer from a storage container match the IR spectrum (pink) of perfluoro polyether (PFPE). When



**Figure 1.** PiF-IR spectra are used to chemically identify nano-sized defects on silicon surfaces by searching the Wiley IR library. (a) ~ 3 nm spherical silica particle (b) 3 x 50 x 120 nm<sup>3</sup> PTFE particle.



**Figure 2.** PiF-IR spectra are used to chemically identify the contaminant layer on silicon surfaces by searching the Wiley IR library. (a) PFPE (b) methylcyclohexane.

the same wafer is plasma cleaned, PFPE is removed (the strong C-F peak ~ 1250 cm<sup>-1</sup> disappears), but the surface now shows a spectrum from hydrocarbon contamination (Figure 1b); an IR library search suggests the contaminant is methylcyclohexane, which is a solvent used in some correction fluids (such as White-Out). For the search, six spectra (locations shown in the inset topography) were averaged, and the peak associated with the silicon oxide (shaded in blue) was excluded. Note that even though the surfaces are contaminated with different molecules, the micro-roughness of the silicon remains the same.

## Conclusion

IR PiFM can chemically identify sub-100 nm defects and monolayer contaminants efficiently, filling metrology needs that have been lacking. IR PiFM is available for up to 12" wafers with many automation features, including automated defect analysis based on KLARF coordinates. Contact us for a

demo on your own samples and [register for our webinar](#) for semiconductor applications of IR PiFM.

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# Analysis of Organometallic Compounds and Metallic Particles in Specialty Gases by Direct Injection Using Gas Exchange Device (GED) Coupled to Inductively Coupled Plasma–Mass Spectrometry (ICP-MS)

Chady Stephan, Aaron Hineman, and Ruth Merrifield

In this article, we introduce the concept of a gas exchange device (GED) and how it can be used to monitor organometallic compounds and metallic particles in specialty gases. The GED-inductively coupled plasma–mass spectrometry (GED-ICP-MS) workflow eliminates the need for any offline sample preparation, making it the ideal tool for online metallic impurities monitoring. This technology can be deployed to monitor specialty gas impurities in process chemicals at delivery, distribution points, and point of use.

**S**pecialty gases for the semiconductor and electronics industries range from the pyrophoric or toxic gases required for thin-film deposition and doping processes (ammonia, silane, dichlorosilane, germane, diborane, arsine, and others) to the reactive and corrosive gases needed in different etching processes (chlorine, fluorine, halocarbons, nitrogen trifluoride, and more) (1). Conventionally used methods, such as impingers or filters, suffer from various limitations, including external contamination during the collection process, solubility of the organometallic compounds, metallic particles in impinger media, loss of metallic particles information, and filter material suitability. These limitations also do not include the labor-intensive and time-consuming sample preparation, as well as impinger unsuitability to be used for moisture sensitive gases (2).

A gas exchange device coupled with inductively coupled plasma–mass spectrometry (GED-ICP-MS) overcomes all of the abovementioned challenges. A GED-ICP-MS is a fully automated workflow that can be deployed in research

and development (R&D) laboratories and in the fabrication (3). Two applications, carbon monoxide (CO) and hydrochloric gas (HCl), are discussed by comparing the results obtained by GED-ICP-MS versus the impinger (4,5).

## Introduction

The semiconductor and electronics markets are constantly changing with the emergence of new technologies like artificial intelligence (AI), machine learning (ML), edge computing, 5G connectivity, and the “internet of things” (6). These trends pushed the industry to new barriers in node size, the advent of three-dimensional (3D) stacking, and the increasing complexity of chip designs requiring more precise, efficient, and environmentally friendly etching methods. Achieving such intricate manufacturing resulted in a shift from wet to dry etching with specialty gases at its core (7).

Specialty gases are used across the manufacturing process, and they can be classified into doping gases, epitaxial gases, ion implantation gases, photolithography gases, carrier gases,



and more. Regardless of their application, specialty gases, manufacturers, transporters, and users have strict requirements for purity, composition, packaging, distribution, and storage (1).

Metallic impurities are commonly measured using a highly sensitive technique such as ICP-MS, which is capable of accurately quantifying ultra-trace levels of metallic contamination—dissolved or singular nanoparticulate (NP)—in chemicals used throughout integrated circuit (IC) manufacturing (8). However, gases are difficult to analyze directly by ICP-MS because even a small amount of these gases will extinguish the instrument argon (Ar) plasma. Complicating matters further is that the industry lacks the metallic gas standards required for accurate quantification. That said, specialty gases need to undergo sample preparation to be analyzed for metallic impurities.

Two sample preparation techniques are commonly used in the industry, the most common of which is the impinger method. This technique employs specially designed bubble tubes that flow a known volume of the sample gas into a liquid medium that will chemically or physically react with the chemical of interest. The liquid is then analyzed by ICP-MS, with the other employed technique being filtering. The sample gas flows through a series of filters that are then digested and analyzed by ICP-MS. In both approaches, sample preparation is tedious and time-consuming. Most importantly, it masks the chemical structure of the detected impurities, making it difficult to point out the source.

Gas direct injection via a GED–ICP-MS resolves those challenges while maintaining the metallic impurities structure for source identification. This technique enables direct sample gas analysis via injection into a GED—a pressured nanometer porous membrane—that exchanges the sample gas with argon while maintaining the organometallic compounds and metallic particles in its center flow, delivering them to the ICP-MS system for quantitative analysis.

In this article, we detail the main components of a GED, some of its configurations, its coupling to ICP-MS, the calibration approaches, and some selected results.

### Gas Exchange Device

In simple terms, a GED is an introduction system that enables the direct introduction of gases for metal impurities analysis to an inductively coupled plasma coupled with a mass or optical spectrometer. This hardware consists of mass flow controllers, a pressurized exchange membrane, and few gas connections. The exchange membrane and the main gas connections are temperature-controlled. Figure 1 illustrates the operating principles of a GED and the sample gas flow through a microporous membrane residing in the center of a housing that is pressured by argon. The argon penetrates the exchange membrane, sweeping the sample gas. Meanwhile, the organometallic molecules and particles remain in the center channel. These contaminants are then delivered

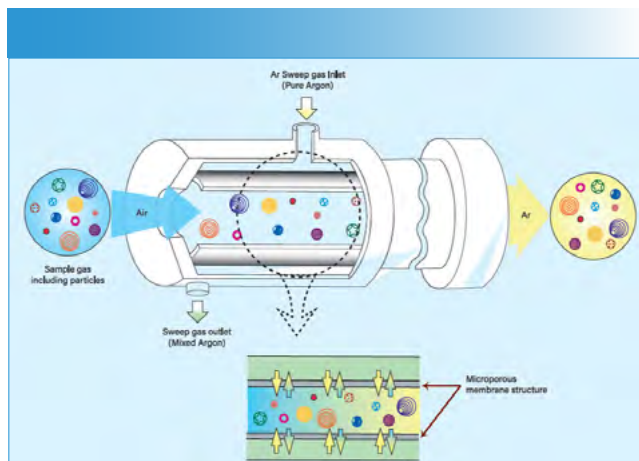


FIGURE 1: Schematic diagram of the exchange membrane in a GED.

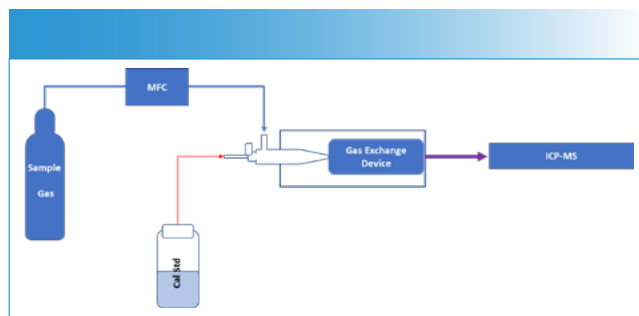


FIGURE 2: GED configuration for inert nontoxic gases.

to the ICP-MS platform in a stream of argon that maintains plasma robustness.

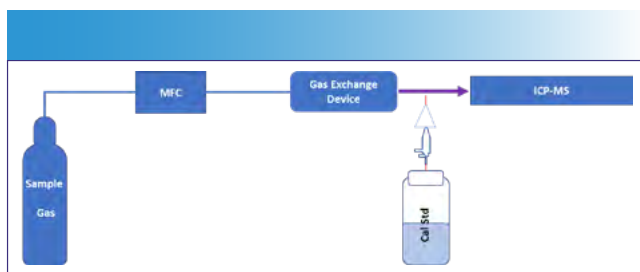
### Configurations and Calibration Approaches

As mentioned earlier, the semiconductor and electronics industries utilize many different gases for various applications. In this section, we discuss various configurations and calibration approaches depending on the sample gas chemical and physical properties.

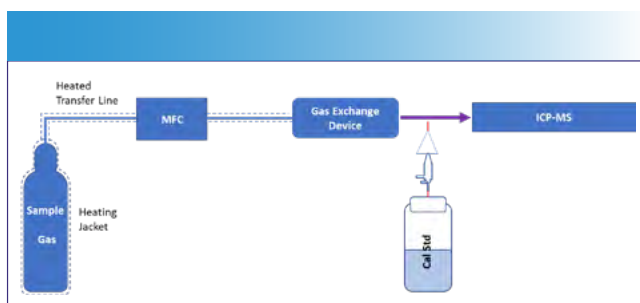
**Inert nontoxic gases:** The sample gas can be used in a similar manner, replacing argon as the nebulizer gas. The generated aerosol will enter the GED, and the sample gas gets exchanged while the impurities remain in the central channel and get introduced to the ICP-MS instrument. Calibration via standard addition is performed (Figure 2).

**Toxic and moisture reactive gases:** It is preferable to directly connect the sample gas to the GED while calibration is performed by method of standard addition (MSA) between the exit of the GED and the entrance to the ICP-MS system. These additions are performed with standard aerosol generation commonly used in the industry (Figure 3).

**Low-boiling temperature gases:** For these gases, depending on their toxicity, either of the above configurations could be used. Consideration should be taken to ensure suitable heaters are installed from the sample gas tank to the entrance of the GED. In some cases, the sample gas can



**FIGURE 3:** GED configuration for toxic gases.



**FIGURE 4:** GED configuration for low-boiling temperature gases.

be mixed with an inert gas, like argon or nitrogen, prior to its introduction to the GED (Figure 4).

### Integration with ICP-MS

The ICP-MS platform is a key component in the GED–ICP-MS system. It offers high-resolution mass spectrometry (HRMS) capabilities, enabling the precise quantification of metallic impurities even at trace levels (9). In all configurations, the output of the GED is connected to the ICP-MS injector via polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA) tubes using commonly used industry-standard fittings.

### Benefits of Combining GED with ICP-MS

- Enhanced Sensitivity and Detection Limits:** The sensitivity of ICP-MS complements the GED's ability to deliver gas samples directly. This combination results in excellent detection limits and accuracy for metallic impurity analysis.
- Removal of Gas Matrix:** The GED removes the matrix or background associated with the gas that is being tested, helping with the normalization of the plasma and ensuring better calibration and more accurate results.
- Improved Data Accuracy:** Interference removal by dynamic reaction cells (DRC) technology enhances measurement accuracy. For accurate interference removal, the reaction should be controlled by utilizing cell features such as bandpass filtering for the low-mass cut off, the ion speed, and the reaction gas flow. Furthermore, multi-quadrupole technology can refine these reactions, ensuring that even complex matrices and low-level impurities are accurately quantified.
- Streamlined Workflow:** The integration of the GED with ICP-MS creates a seamless workflow from sample intro-

duction to data analysis. The direct injection of gases into ICP-MS via the GED minimizes sample handling and preparation, reducing potential sources of error and contamination.

- Single Particle Analysis Capability:** For accurate particulate analysis, fast acquisition, short dwell times, and no settling times are required. To further improve the detection limit of nanoparticulate in the gasses, collisional focusing and Axial field technology (AFT) can be used to compress the ion plume of the particle before reaching the detector, allowing the user to monitor the gas for metallic nanoparticles.
- Advanced Calibration and Data Analysis:** ICP-MS technologies that support sophisticated calibration methods, including standard addition and internal standardization, are critical for maintaining data accuracy. Combined with the GED, this enables comprehensive and precise analysis of a wide range of metallic impurities.

### Case Example: The Analysis of Carbon Monoxide and Hydrochloric Gas

In a collaborative project with International Analytical Solutions (IAS Inc.), the NexION 5000 (PerkinElmer U.S LLC) ICP-MS system was successfully integrated with a GED for analyzing hydrochloric acid (HCl) gas. This integration also included a metal standard aerosol generation (MSAG) system to automatically and accurately generate a calibration. The MSAG-GED–ICP-MS system opens up new opportunities for analyzing metallic impurities in gases, offering a powerful analytical solution that meets the demanding needs of the semiconductor industry. Particle measurement by GED using fast acquisition and short dwell times allowed the detection of a few nanometers (nm) of particles in the HCl gas. This application demonstrated the effectiveness of the system in delivering high-resolution data with improved detection limits and robustness compared to traditional methods.

### Results

By partnering with Bio & Analytical Solution Supplier (BASS) and IAS Inc. to integrate the NexION ICP-MS platform with their respective GEDs, applications were developed for the analysis of metallic impurities in carbon monoxide (CO) and hydrochloric (HCl) gas, respectively.

This section discusses selected data from both applications, showcasing the performance of GED–ICP-MS versus impinger, focusing on the detection limits, robustness, repeatability, and ease of use.

### Detection Capability

As mentioned earlier, gas purity is the most important parameter this industry demands. GED–ICP-MS outperformed the impinger in both limit of detection (LOD) and background equivalent concentration (BEC) by factors ranging from 10 to more than 100-fold (Table I). This notice-

**TABLE I:** Detection Limit (LOD), Background Equivalent Concentration (BEC), and Coefficient of Determination ( $R^2$ ) for elements measured in CO gas using both the impinger and GDI methods, together with improvement factor of GDI over the impinger method.

Impinger Method					GDI Method					Improvement Factor	
Element	Isotope	LOD	BEC	$R^2$	Element	Isotope	LOD	BEC	$R^2$	GDI/Impinger	
		(ppb)	(ppb)				(ppb)	(ppb)		LOD	BEC
Ag	107	0.0026	0.018	0.999	Ag	107	0.00021	0.00016	0.999	12	113
Al	27	0.0263	0.2854	0.999	Al	27	0.00052	0.00123	0.999	51	232
As	75	0.0009	0.0022	0.999	As	75	0.0001	0.00066	0.999	9	3
Au	197	0.0014	0.0125	0.999	Au	197	0.00012	0.00034	0.999	12	37
Ba	138	0.0003	0.0013	0.999	Ba	138	0.00005	0.00028	0.999	6	5
Ca	40	0.0251	0.2098	0.999	Ca	40	0.00014	0.00835	0.999	179	25
Cd	111	0.0012	0.0005	0.999	Cd	111	0.00022	0.00016	0.999	5	3
Co	59	0.0005	0.0092	0.999	Co	59	0.00039	0.00032	0.999	1	29
Cr	52	0.0008	0.0148	0.999	Cr	52	0.00006	0.00034	0.999	13	44
Cu	63	0.0003	0.0026	0.999	Cu	63	0.00011	0.0012	0.999	3	2
Fe	56	0.0024	0.0396	0.999	Fe	56	0.00038	0.00152	0.999	6	26
K	39	0.0096	0.098	0.999	K	39	0.00038	0.0023	0.999	25	43
Li	7	0.0025	0.0138	0.999	Li	7	0.00044	0.00027	0.999	6	51
Mg	24	0.0041	0.0147	0.999	Mg	24	0.0002	0.00128	0.999	21	11
Mn	55	0.0003	0.0044	0.999	Mn	55	0.00009	0.00034	0.999	3	13
Mo	98	0.0003	0.0009	0.999	Mo	98	0.0002	0.0001	0.999	2	9
Na	23	0.0042	0.0467	0.999	Na	23	0.0004	0.00215	0.999	11	22
Ni	60	0.0019	0.0131	0.999	Ni	60	0.00007	0.00031	0.999	27	42
Pb	208	0	0.0006	0.999	Pb	208	0.00062	0.00035	0.999	0	2
Sn	118	0.0011	0.0076	0.999	Sn	118	0.00011	0.00015	0.999	10	51
Ti	48	0.0006	0.0031	0.999	Ti	48	0.00006	0	0.999	10	N/A
Ti	131	0.0036	0.0014	0.999	Ti	131	0.00074	0.00047	0.999	5	3
V	51	0.0004	0.0007	0.999	V	51	0.00007	0.00024	0.999	6	3
W	184	0.0006	0.0095	0.999	W	184	0.00006	0.00004	0.999	10	238
Zn	66	0.0035	0.0568	0.999	Zn	66	0.00035	0.00315	0.999	10	18

**TABLE II:** Repeatability and Robustness data – Impinger vs. GED–ICP-MS

Element (ppb)	Impinger					GED			
	Prep #1	Prep #2	Prep #3	Average	RSD	Analysis #1	Analysis #2	Average	RSD
Ba	0.029	0.004	0.001	0.011	111%	0.0003	0.0003	0.0003	0%
Ca	2.737	0.242	0.085	1.021	119%	0.0076	0.0085	0.0081	6%
Cr	0.008	0.004	0.002	0.005	53%	0.0016	0.0015	0.0016	3%
Cu	0.09	0.013	0.042	0.048	66%	0.0016	0.0017	0.0017	3%
Fe	0.358	0.06	0.018	0.145	104%	0.0041	0.0046	0.0044	6%
K	0.255	0.133	0.053	0.147	57%	0.0038	0.0035	0.0037	4%
Mg	0.214	0.1	0.103	0.139	38%	0.0792	0.0756	0.0774	2%
Mn	0.01	0.115	ND	0.063	84%	0.0008	0.0007	0.0008	7%
Na	0.318	0.132	0.019	0.156	79%	0.0022	0.0023	0.0023	2%
Zn	0.503	0.064	0.066	0.211	98%	0.0036	0.0035	0.0036	0%

able improvement in BEC and LOD derives from the direct injection ability of the GED, surpassing the need for a collection media used in the

impinger. These collection media are made from ultrapure water and other reagent chemicals that contribute to the background.

### Robustness and Repeatability

Robustness and repeatability were evaluated, comparing three different sample preparation methods using the impinger.

**TABLE III: Breakdown of Gas Sample Analysis Time - Impinger vs GED**

Procedure	Impinger	GED
Hardware cleaning	10 min	N/A
Media preparation	10 min	N/A
Sample line connection	5 min	5 min
Sample pretreatment	90 min	N/A
Analysis	5 min	5 min
Total time	120 min	10 min

The same sample gas was also analyzed by GED–ICP–MS two times, three replicates per analysis. Observing the relative standard deviation (RSD) for the selected elements (Table II), it can be seen that the high values for the common contaminants like Ca, Fe, Na, and Mn indicate that contamination usually results from the various sample preparation steps or cross-contamination from previous samples. The GED results show excellent repeatability and robustness. When comparing the obtained metal concentration between the impinger and the GED, it can be clearly seen that the latter reported lower concentrations as the impinger concentration will have contribution from ultrapure water, the reagent, and possibly random cross-contamination. The direct introduction and analysis of a sample gas by GED–ICP–MS eliminates those factors.

### Productivity

Productivity is measured by the time required to complete an analysis. This encompasses getting the instrument ready, preparing the sample, and analyzing it. Table III highlights the time required for each step needed to achieve a gas sample analysis. The impinger method is 12 times slower than the GED, with the bulk of the time being spent on sample pretreatment.

The advantages of gas direct injection analysis by GED–ICP–MS compared to the impinger is demonstrated through its ease of use and ability to analyze gas samples without prior treatments. This technology enables many use-case applications, such as performing quality control on gas cylinders, gas manifolds, and monitoring degradation of the extensive network of gases used in semiconductor fabrication plants.

### Future Advancements in GED Technology

Looking ahead, developments in GED technology could include improvements in membrane materials for better gas exchange efficiency or enhanced integration with other analytical techniques. Innovations might also focus on expanding the range of detectable impurities and reducing operational costs. As the semiconductor industry continues to evolve, these advancements will play a crucial role in meeting emerging challenges.

### Further Automation

The GED and ICP–MS combination can be further enhanced by automating the calibration and sampling of the semiconductor-grade gases, which ensures that laboratories needing to carry out these measurements will have the sophistication, flexibility, throughput, and accuracy needed to monitor all gas types.

## Conclusion

GED–ICP–MS represents a significant advancement in the analysis of metallic impurities in specialty gases. Its ability to provide real-time, accurate results without the need for extensive sample preparation sets it apart from traditional methods. This technology not only improves detection limits and repeatability, but it also enhances productivity by reducing analysis time. As industries continue to push the boundaries of technology, the GED–ICP–MS system is poised to play a pivotal role in maintaining high standards of gas purity and performance.

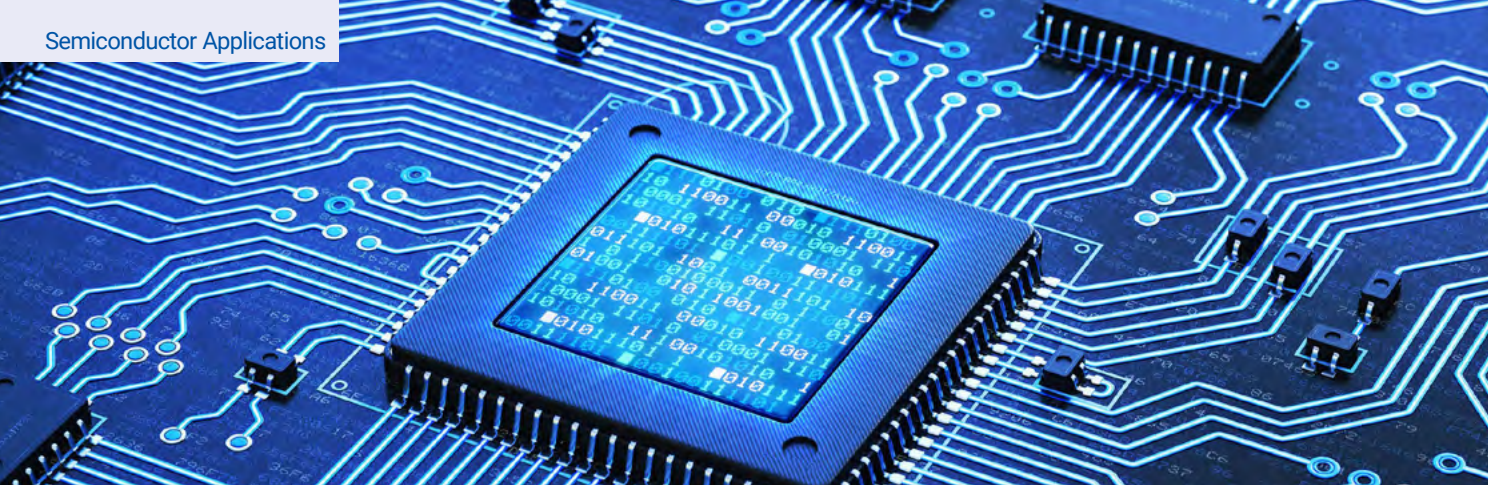
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## APPLICATION SPOTLIGHT

# Analysis of Metallic Impurities in Organic Solvents Used in IC Fabrication with the NexION 5000 ICP-MS

## The Importance of Purity of Organic Solvents

The fabrication of integrated circuits (IC) from silicon wafers takes place inside high-class cleanrooms to reduce contaminants which can affect the production yield. The most commonly used organic chemicals in the semiconductor industry are isopropyl alcohol (IPA), propylene glycol methyl ether acetate (PGMEA), propylene glycol methyl ether (PGME), and n-methyl pyrrolidone (NMP). While IPA is used frequently to clean silicon wafers, the other solvents are used as diluents or strippers of photoresist in photolithography steps. These solvents can leave behind an organic film residue with metallic and non-metallic contamination on the wafers, so for that reason, high-purity grades are required for advanced semiconductor processes.

## SEMI Specifications for Isopropyl Alcohol (IPA)

The *SEMI C41-0618 Specification and Guide for 2-Propanol* lists the impurity limits for Tier D contamination at limits of 100 ppt maximum for metallic contamination and 50 ppb for some non-metal elements. However, there are no SEMI specifications for PGMEA or PGME. In the current *SEMI C33-0213 Specifications for n-Methyl 2-Pyrrolidone*, the highest purity grade, Grade 3, sets the maximum metallic impurity levels at 5-10 ppb and non-metallic to 250-400 ppb, which are too high for the large-scale integration used in semiconductor fabrication today. Therefore, chemical producers and users are striving for a solution to deliver organic solvents with lower levels of contaminants.

## Unique Capabilities of NexION 5000 ICP-MS Universal Cell Technology

This work describes the analysis of 46 elements in IPA, PGMEA and NMP using the NexION® 5000 Multi-Quadrupole ICP-MS. The balanced and free-running RF generator, designed explicitly for ICP-MS applications, delivers improved robustness, high efficiency, and a wide power range. It ensures fast power-switching between Cold and Hot Plasma modes as well as stability while running organic solvents. Multi-mode methods can now take advantage of all new hardware features to provide superior polyatomic interference removal that further improves detection limits (DLs) and background equivalent concentrations (BECs). Reaction mode with 100% pure  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{H}_2$ , or a mixture of gases is the most effective way of removing spectral interferences by changing them into atoms or ions of a different mass or by creating a cluster ion with an analyte (Mass Shift). Some elements without spectral interferences are measured in Standard mode without any gases entering the cell. In addition, when analyzing organic solvents, it is preferred to run a higher plasma gas flow, around 18 L/min, compared with the aqueous solution analyzed at 15-16 L/min. The nebulizer flow is also lower to accommodate the  $\text{O}_2$  addition, preventing carbon from building up on the cones.

## Typical Interferences in IPA

Although argon, oxygen, and nitrogen-based interferences are well understood, there are several additional spectral interferences observed while analyzing organic solvents due to high carbon concentrations. By using 100% pure ammonia, oxygen, and hydrogen as cell gases with the MS/MS and Mass Shift modes or Cold Plasma, these interferences are removed very efficiently. Figure 1 shows scans of 500 ppt Cr in IPA run in Standard mode, and for comparison, in Reaction mode with  $\text{NH}_3$ . The reaction of  $\text{ArC}^+$  with  $\text{NH}_3$  very effectively removes huge  $\text{ArC}^+$  interference, allowing Cr to be determined accurately at very low levels. The expected isotope abundance of  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$  is a confirmation of the complete removal of  $\text{ArC}^+$  interferences.

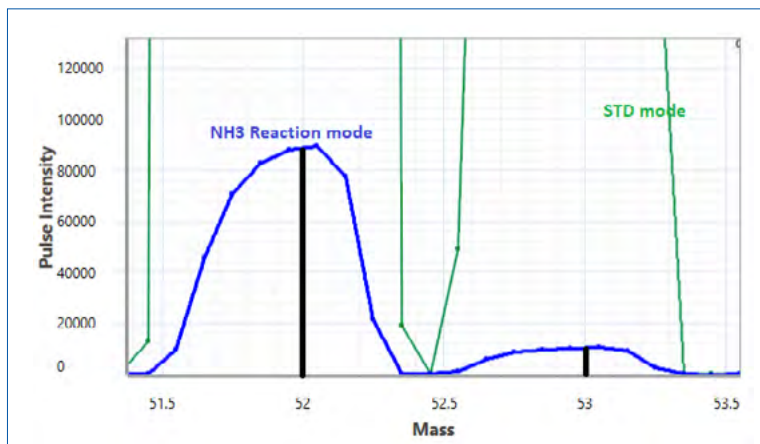


Figure 1. Scan of two Cr isotopes in Standard mode (green line) and Reaction  $\text{NH}_3$  mode (blue line).

## Quantitative Results

For DLs, BECs, and spike recovery measurements, calibration curves were established using method of standard addition (MSA). All curves correlation coefficients  $> 0.999$ , demonstrating the linearity of the analysis and the ability to measure accurately at low concentrations. As an example, the calibration curves in IPA obtained in four different modes are shown in Figure 2: Mg in Standard Cold Plasma mode, Al in Reaction ( $\text{NH}_3$ ) Cold Plasma mode, Si in Reaction ( $\text{H}_2$ ) mode, and Cr in Reaction ( $\text{NH}_3$ ) Cold Plasma mode. DLs and BECs in three organic solvents (IPA, NMP, and PGMEA) for 46 elements along with modes of operations are shown in the application note.

## Conclusion

The results presented in this work demonstrate that the NexION 5000 ICP-MS, with the combination of its unique multi-quadrupole technology and a new generation of the Universal Cell, provides the outstanding performance needed for the semiconductor industry when analyzing difficult matrices, such as organic solvents.

## Reference

Summarized from the PerkinElmer application note [“Analysis of Metallic Impurities in Organic Solvents Used in IC Fabrication with the NexION 5000 ICP-MS”](#) by Kyoko Kobayashi and Ewa Pruszkowski.

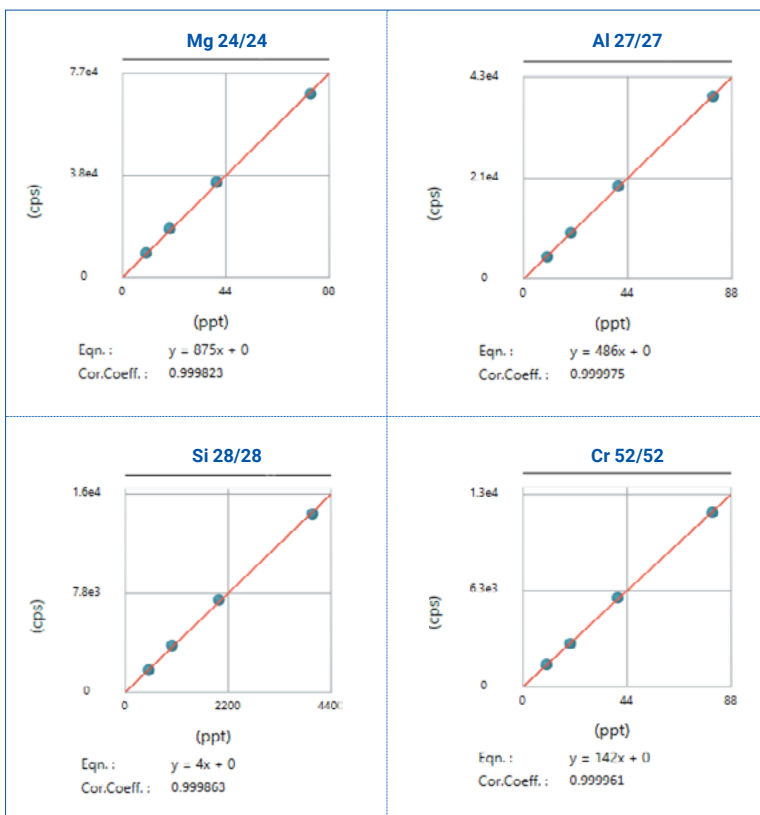


Figure 2. Calibration curves of selected elements in IPA in different modes of analysis.



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## APPLICATION SPOTLIGHT

## Ultra-Trace Elemental Analysis in High-Purity Sulfuric Acid

### The Importance of High-Purity Sulfuric Acid

The production of electronic devices is a complex process that requires the use of ultra-pure chemicals during the semiconductor fabrication process. For example, a mixture of high-purity-grade sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is used as a photoresist stripper. However, impurities in these chemicals, such as iron, copper and sodium, can diffuse rapidly in silicon during thermal processing steps, which creates defects, and as a result, degrades device performance. Therefore, as the demand for smaller chip size increases, there is a continuing need for higher-purity chemicals used in the semiconductor manufacturing process.

### SEMI Standards Specification

Even though the *SEMI C44-0618 Specification for Sulfuric Acid* lists impurity limits for Tier C at 100 ppt for several elements and 50 ppb or higher for some non-metals, these levels are already too high for many processes currently used in the industry. In this work, we evaluate the performance of the NexION® 5000 Multi-Quadrupole ICP-MS for the analysis of 52 elements in 10%  $\text{H}_2\text{SO}_4$  by measuring detection limits (DLs), background equivalent concentrations (BECs), together with 15 ppt spike recoveries and a 9-hour stability study.

### Capabilities of the NexION 5000 ICP-MS

The NexION 5000 ICP-MS leverages a host of proprietary technologies – tandem four-quad design, quadrupole-based Universal Cell and others – that come together to offer superior interference removal. For more information on these capabilities, a [product note](#) is available.

Reaction mode with either  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{H}_2$ , or a mixture of gases is the most effective way of removing spectral interferences by changing them into atoms or ions of a different mass (MS/MS mode), or by creating a cluster ion with an analyte (Mass Shift mode). In MS/MS mode, Q1 and Q3 are set to the same mass, while in Mass Shift mode, an analyte is measured as an ion product with a reaction gas at a higher mass. Some elements that do not have spectral interferences were measured in Standard mode without any gases entering the cell. By using 100% pure ammonia and oxygen as cell gases with the MS/MS and Mass Shift modes, the reaction efficiency is superior to that of diluted gas, delivering superior DLs and BECs.



## Management of Spectral Interferences in Sulfuric Acid

Titanium (Ti) is one of the most difficult elements to measure in sulfuric acid. The primary Ti isotope at mass 48 is 74.3% abundant. However, besides the  $\text{Ti}^+$  isotope,  $^{32}\text{S}^{16}\text{O}^+$ ,  $^{31}\text{P}^{16}\text{OH}^+$ ,  $^{48}\text{Ca}^+$  and other ions formed in the plasma can create direct spectral overlaps on Ti at mass 48. Ions that do not exist at mass 48 are rejected by the Q1. The Q1 allows only ions at mass 48 to reach the Universal Cell, so only  $\text{Ti}^+$ ,  $\text{SO}^+$ ,  $\text{POH}^+$  and  $\text{Ca}^+$  will enter the cell pressurized with  $\text{NH}_3$ . Here, 100%  $\text{NH}_3$  reacts rapidly with  $\text{Ti}^+$ , creating several clusters at higher masses. Thereafter, Q3 resolves  $\text{Ti}(\text{NH})_x^+$  from other masses, and the cluster ions reach the detector free from spectral interferences and can be measured at the desired mass. This is exemplified by the scan in Figure 1 which shows Ti creating several clusters with  $\text{NH}_3$  at masses 63, 80, 97, 114 and 131. As can be seen, the 131 mass was found to have the greatest sensitivity. The  $\text{NH}_3$  flow was optimized at 0.8 mL/min, which was then used for quantitation.

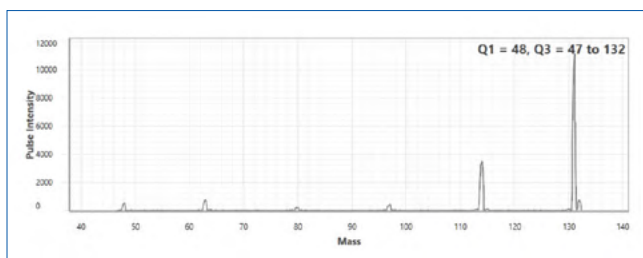


Figure 1. Scan of  $\text{Ti-NH}_3$  clusters from masses 47-132.

## Results

In this work, Mass Shift mode was used for measuring Ti, V, Zn and Ge as clusters with  $\text{NH}_3$  while P, Sc, As and Se were measured as clusters with  $\text{O}_2$ . Figure 2 shows DLs in 10%  $\text{H}_2\text{SO}_4$  for 52 elements, along with the color-coded modes of operation. DLs in 10%  $\text{H}_2\text{SO}_4$  for all elements were at 1 ppt or below with the exception of Si that was 10 ppt, exceeding the requirements of the *SEMI Guide for Sulfuric Acid (C44-0618)* by at least 10 times. Calibration curves were established with 1, 5, 10, 15 and 20 ppt standards using the method of standard addition (MSA), with the exception of P and Si which had higher standard concentrations. All curves had correlation coefficients  $> 0.999$ , demonstrating the linearity of the analysis and the ability to measure accurately at low concentrations.

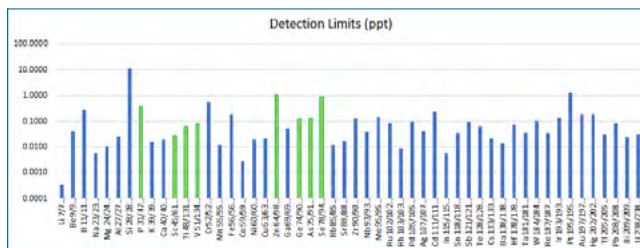


Figure 2. DLs in 10%  $\text{H}_2\text{SO}_4$  for 52 elements: blue bars – elements analyzed in MS/MS mode; green bars – elements analyzed in Mass Shift mode.

Long-term stability was also evaluated by measuring a QC standard (15 ppt for most of 50 elements with the exception of P and Si) every four samples for over 9 hours. The plot shown in Figure 3 demonstrates exceptional stability for all elements in all modes. RSDs were less than 5% for all elements and the drift was within  $\pm 15\%$  from the initial reading.

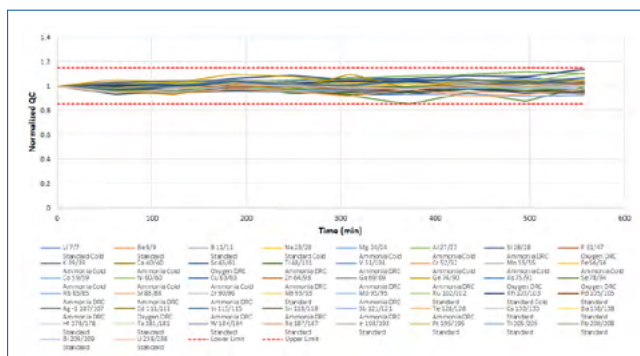


Figure 3. Spike recovery of 15 ppt of 50 analytes in 10%  $\text{H}_2\text{SO}_4$ .

## Conclusion

The results presented in this work demonstrate that the NexION 5000 ICP-MS, with its multi-quadrupole and Universal Cell technologies and up to four different pure reactive gases, provides the outstanding analytical performance needed for the semiconductor industry for such challenging matrices as 10%  $\text{H}_2\text{SO}_4$ .

## Reference

Summarized from the PerkinElmer application note "[Ultra-Trace Elemental Analysis in High-Purity Sulfuric Acid](#)" by Chady Stephan and Ewa Pruszkowski.



Download Full Application Note





# GC-ICP-MS for Process and Quality Control in Semiconductor Manufacturing

William M. Geiger, Ed McCurdy, and Mark Kelinske

Gas chromatography (GC) coupled to inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful and flexible analytical solution that is well-established for measuring organometallic compounds such as organotin, organomercury, and organolead in environmental samples, foodstuffs, and consumer products. GC-ICP-MS is also used for industrial applications, such as monitoring catalyst poisons and environmental contaminant elements in petrochemical processing and plastics manufacturing. The semiconductor industry uses a range of high-purity specialty gases and volatile liquids as precursors in wafer substrate production, and for processes such as plasma etching and deposition of thin films by chemical vapor deposition (CVD). Semiconductor manufacturers are constantly developing new integrated circuit (IC) chips with smaller sizes, higher speeds, lower power consumptions, and greater transistor densities. This trend means that contaminants must be controlled at even lower levels in process chemicals and precursors. In this article, we show how GC-ICP-MS, particularly using triple quadrupole or tandem ICP-MS (ICP-MS/MS), enables determination of the lowest levels of contaminants in the specialty gases and volatile liquids used to make the most advanced electronic devices.

**I**ntegrated circuit (IC) chips play an increasingly important role in modern life, supporting technologies from consumer electronics and self-driving vehicles to the high-speed communications and servers used in accelerated computing and artificial intelligence (AI). The manufacturing of advanced semiconductor chips requires high-purity materials, metals, and a range of process chemicals, such as ultrapure acids and solvents. Wafer manufacturers and chip fabrication plants (FABs) also use a variety of bulk and electronic specialty gases (ESGs) and volatile liquids throughout the manufacturing process (1,2). For example, silane ( $\text{SiH}_4$ ) and chlorosilanes are used as feedstocks for gas purification of silicon to the nine to eleven nines purity used to make semiconductor wafers. Nine nines (9N) Si is 99.9999999% pure, meaning there is only 1 part per billion (ppb) of total impurity elements in the solid silicon crystal. Alternative, non-silicon wafers and films are often made from "III-V compound" semiconductors, such as gallium arsenide (GaAs) and indium GaAs (InGaAs), which may use arsine gas ( $\text{AsH}_3$ ) as a precursor together with trimethyl gallium (TMG).

Fabricating an advanced IC chip involves upwards of a thousand steps where thin layers of conducting and insulating material are alternately deposited and

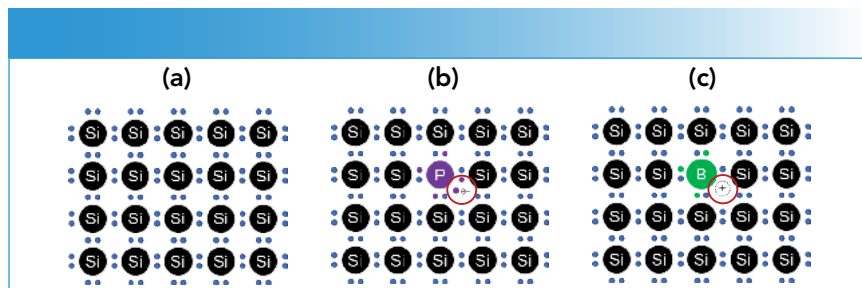
etched to create the millions of transistors and other features that make up the circuit. Dopant elements are added to modify the conductivity of the silicon substrate or surface film. High-purity gases are used extensively in these "front end" IC fabrication processes. For example, phosphine ( $\text{PH}_3$ ) is used to dope the required level of phosphorus into thin-film transistor (TFT) displays. Diborane ( $\text{B}_2\text{H}_6$ ) is used for boron doping and ion implantation, for growing metal-boron thin films, and as a component of chemical vapor deposition (CVD) of boron-phosphate-silicate-glass (BPSG) films. Fluorocarbon (FC) gases, such as 2-fluorobutane and hexafluorobutadiene, are also used in the electronics industry (for example, in dry etching and for plasma enhanced chemical vapor deposition [PECVD]). The high reactivity and low toxicity of some FC gases means they are also used to clean reaction chambers between fabrication processes. In a typical semiconductor FAB, high-purity gases can make up the second largest material cost after high-purity silicon.

Controlling the level of contaminants in specialty gases is critical to ensuring acceptable chip yield and the performance and reliability of the finished semiconductor device. To understand why contamination is so important, it is useful to consider that advances in semiconductor

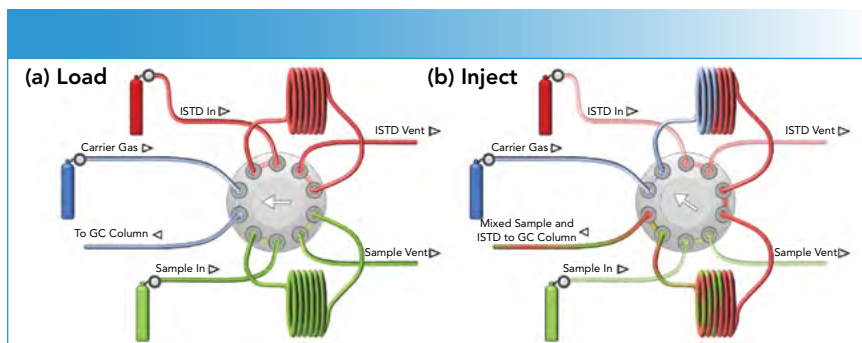
device technology are driven by reductions in scale. Packing more transistors into a smaller space improves the speed and performance of the chip. The latest chips have circuit features and line widths measured in single nanometers (nm, one millionth of a millimeter), and the presence and position of individual atoms in the silicon crystal lattice can affect the electrical properties of the device. This makes the chips highly susceptible to contamination, so controlling the levels of impurities in the high-purity gases used during fabrication is fundamental to the production process.

Controlling the levels of dopant elements and metallic contaminants in substrate materials, process chemicals, and gases, is a particular industry concern. Dopant elements are deliberately added to the silicon substrate to make it “semi-conducting” and control the electrical properties, as illustrated in Figure 1. Silicon has four valence electrons, and pure silicon forms a crystal lattice in which all these electrons are shared with the adjacent silicon atoms. As a result, pure silicon is a poor conductor of electricity. N-type (negative) dopants are Group V elements such as phosphorus, arsenic, antimony, and bismuth, which have five valence electrons, so they add one free electron to the silicon lattice. P-type (positive) dopants are Group III elements, which have three valence electrons, so they contribute a “missing” electron or a positive “hole” in the lattice. The level of doping varies depending on the intended properties, but low-level doping can add as few as one dopant atom per 100 million silicon atoms, so controlling contamination for these elements is critical.

ICP-MS instruments are already widely used in the semiconductor industry to monitor the levels of ultratrace contaminants in high-purity materials and process chemicals. Contaminants in high-purity gases often need to be controlled at lower levels than can be achieved using traditional gas chromatography (GC) detectors, which may not have sufficient selectivity for the required analysis to begin with. Also, for some matrices and compounds, standards are unstable or not available, making calibrating and quantifying contaminants difficult.



**FIGURE 1:** Schematic showing: (a) Pure silicon crystal lattice; (b) silicon doped with phosphorus, an *n*-type dopant element; (c) silicon doped with boron, a *p*-type dopant element.



**FIGURE 2:** Direct sampling of flammable and pyrophoric gases for analysis by GC-ICP-MS, using a 10-port valve to allow online addition of an internal standard to the sample gas. Showing the (a) load and (b) inject sequences.

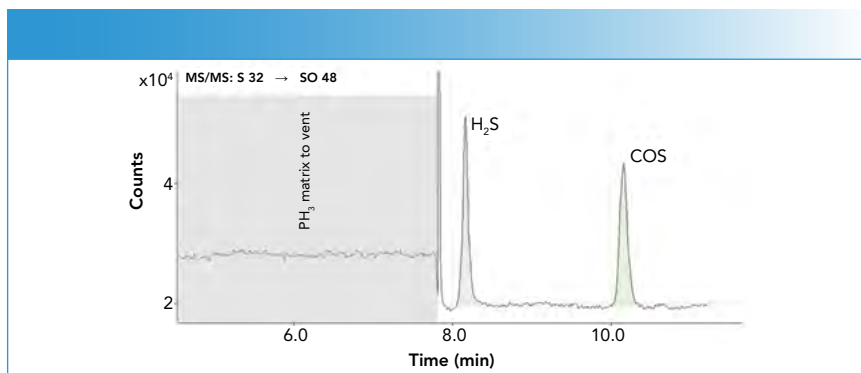
As a detector for GC, ICP-MS, particularly with a triple quadrupole or tandem mass spectrometer (MS/MS), can overcome many of the limitations of other GC detectors. GC-ICP-MS can detect and quantify almost every element at low levels in gases and volatile liquids. The technique gives element and isotope-specific analysis, and is highly selective. As a result, matrix components and other compounds have little to no impact on the signal for the target analyte. GC-ICP-MS also gives practically the same elemental signal regardless of the compound, so non-specific or “compound independent” calibration (CIC) can be used, simplifying the quantification of compounds that are unstable or for which standards are not available. GC-ICP-MS is a versatile and sensitive technique that enables semiconductor manufacturers to reliably quantify trace-level contaminants in the wide range of specialty gases and volatile liquids used in semiconductor manufacturing.

### Experimental

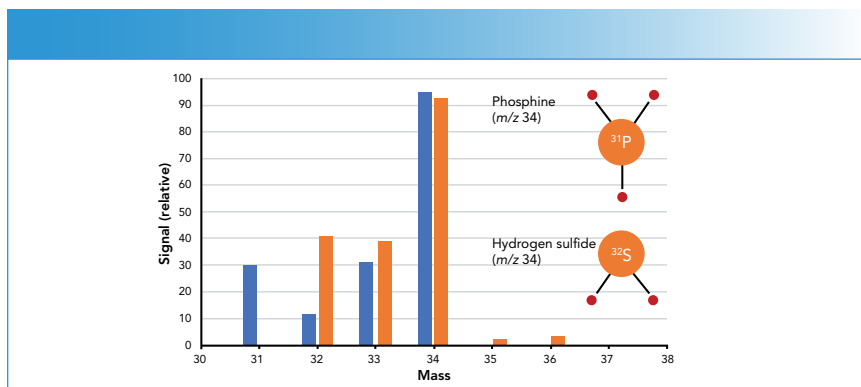
Examples of different electronic gas analysis applications are presented in this

work. The details of the specific GC columns and methods used for the different sample types and compounds measured are provided in the discussion. Specialty electronic gas analysis using GC-ICP-MS often requires a special approach to sample introduction and analysis, as many of the gases are toxic, flammable, and pyrophoric (spontaneously combust on contact with air or moisture). Silicon compounds such as silanes, siloxanes, and chlorosilanes decompose to form silica, which would deposit in a standard GC injector. Flammable and pyrophoric gases can be analyzed directly from the cylinder, using a switching valve and loop to deliver the required sample volume directly to the column in the GC injector port. A 10-port sampling valve provides the option to automatically add a second gas as an online internal standard, as illustrated in Figure 2. In a similar way, volatile liquids such as trichlorosilane (TCS) can be sampled and injected directly into the GC-ICP-MS system using a high-pressure switching valve (3).

A further consideration when GC-ICP-MS is used to analyze samples such



**FIGURE 3:** GC-ICP-MS/MS analysis of trace sulfur compounds in phosphine ( $\text{PH}_3$ ). Deans Switch diverts  $\text{PH}_3$  matrix to vent, avoiding excessive matrix loading to the ICP. Sulfur compounds at 25 ppb each. ICP-MS/MS compound DLs were approximately 1.5 ppb.



**FIGURE 4:**  $\text{H}_2\text{S}$  mass spectrum is overlapped by  $\text{PH}_3$  when measured by GC-TOF-MS. Mass-specific elemental detection of  $^{32}\text{S}$  by ICP-MS/MS avoids overlap from  $^{31}\text{P}$ , enabling interference-free, trace-level analysis of  $\text{H}_2\text{S}$  and COS (shown in Figure 3).

as silanes, chlorosilanes,  $\text{AsH}_3$ ,  $\text{PH}_3$ , and germane ( $\text{GeH}_4$ ) is that these compounds are inorganic. This means the matrix is not easily decomposed and volatilized in the ICP instrument, unlike with hydrocarbon matrices. To successfully analyze these inorganic matrices, a low-volume Deans Switch microfluidic flow control device was used to divert the matrix to vent, preventing excessive matrix load from reaching the ICP. The Deans Switch was positioned in the GC oven in the flow path between the column exit and the ICP-MS transfer line. Once the retention time of the matrix peaks were established using a low volume injection, the Deans Switch was used to divert the matrix to vent during the GC separation.

Both single and triple quadrupole (QQQ) Agilent ICP-MS systems were used for elemental detection. ICP-QQQ is a tandem MS configuration (MS/MS); as a result, it supports the use of reactive cell gases to give

more effective control of spectral overlaps. In many cases, analysis can be performed on either type of mass spectrometer, with ICP-MS/MS typically giving detection limits (DLs) that are approximately an order of magnitude lower or more, depending on the element. Because the ICP-MS plasma is "dry" (no aqueous solution), many spectral backgrounds are much lower with GC-ICP-MS than with the conventional liquid sample introduction. As a result, non-typical ICP-MS elements, such as silicon and sulfur, can be measured at their major isotopes using single quadrupole ICP-MS. However, lower DLs are possible if an ICP-MS/MS method is used with a reactive cell gas to further reduce spectral overlaps. For more typical ICP-MS elements, such as germanium and arsenic, part per trillion (ppt) level DLs are routinely achievable. As a multi-element detector, GC-ICP-MS can be used to analyze hydride gas contaminants such as  $\text{SiH}_4$ ,

$\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{GeH}_4$  at trace level (single ppb down to 10 ppt DLs) in other ultrapure hydride gases (4).

## Results and Discussion

### Trace Sulfur Compounds in Phosphine

The sulfur compounds, hydrogen sulfide ( $\text{H}_2\text{S}$ ) and carbonyl sulfide (COS), were determined as ppb-level contaminants in  $\text{PH}_3$  using a 60-m ( $2 \times 30$  m)  $\times$  0.53 mm i.d.  $\times$  20  $\mu\text{m}$  film mega-bore Plot U GC column at 50  $^\circ\text{C}$  with helium carrier gas at 17.5 psig. Sulfur was measured as the  $^{32}\text{SO}^+$  product ion using ICP-MS/MS with  $\text{O}_2$  cell gas and mass shift mode ( $\text{Q1}$  ( $m/z$  32)  $\rightarrow$   $\text{Q2}$  ( $m/z$  48)), to avoid any overlap from the  $^{31}\text{P}$  matrix peak. The chromatogram is illustrated in Figure 3, demonstrating the complete separation of the sulfur compounds from the  $\text{PH}_3$  gas. The shaded region of the time plot shows when the  $\text{PH}_3$  matrix was diverted to vent using the Deans Switch.

Measurement of  $\text{H}_2\text{S}$  in a  $\text{PH}_3$  matrix is difficult for organic MS as the two compounds both have their large molecular ion peak at  $m/z$  34 and their fragmentation patterns are similar. As illustrated in Figure 4, the only major difference in the GC-TOF-MS spectra is the  $^{31}\text{P}$  peak at  $m/z$  31, which is not useful for quantifying sulfur. Although  $\text{H}_2\text{S}$  is separated from the  $\text{PH}_3$  matrix peak chromatographically, the tail of the matrix peak causes a raised background for  $\text{H}_2\text{S}$ . By contrast, low-level determination of  $\text{H}_2\text{S}$  in a  $\text{PH}_3$  matrix is straightforward using ICP-MS, which is a mass-specific elemental detector that determines  $^{32}\text{S}$  free from any overlap from  $^{31}\text{P}$ .

### Trace Phosphine in Dichlorosilane

As discussed above,  $\text{PH}_3$  is a critical high-purity process gas, in which sulfur compounds and other hydride contaminants must be monitored at trace levels. However,  $\text{PH}_3$  also needs to be measured as a trace-level contaminant in other gases and volatile liquids used in the semiconductor industry, to avoid unwanted contamination by phosphorus, an *n*-type dopant element. Dichlorosilane (DCS) is used as a precursor for high-purity silicon crystal growth, and in combination with ammonia ( $\text{NH}_3$ ) to grow silicon nitride ( $\text{SiN}$ ) thin films by CVD. The purity of the silicon crystal or  $\text{SiN}$  film

depends on the purity of the precursor gases, so contaminants including  $\text{PH}_3$  must be monitored at ppb levels in the DCS.  $\text{PH}_3$  was determined in DCS by GC-ICP-MS/MS using a 60 m x 0.32 mm x 5.0  $\mu\text{m}$  film DB-1 column using helium carrier gas at 20 psig. The oven program had a starting temperature of 35 °C with a 15 °C/min ramp and a final temperature of 220 °C.

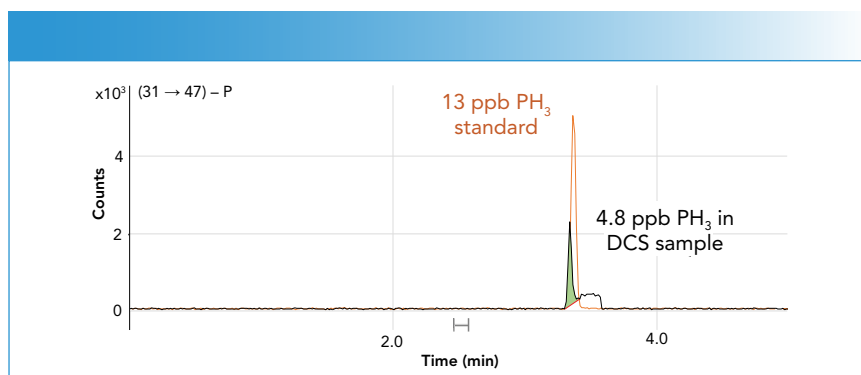
Figure 5 shows overlaid chromatograms for a  $\text{PH}_3$  standard at 13 ppb and  $\text{PH}_3$  being determined as a trace contaminant in DCS. The  $\text{PH}_3$  contaminant was quantified at 4.8 ppb. The use of ICP-MS/MS with  $\text{O}_2$  cell gas and mass shift mode ( $\text{Q1 } [m/z 31] \rightarrow \text{Q2 } [m/z 47]$ ) enabled low-level phosphorus analysis with minimal contribution from the silicon matrix.

### Higher Borane Contaminants in Diborane

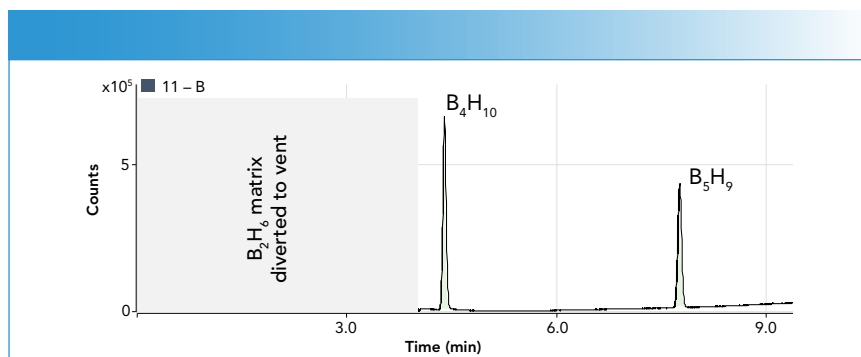
GC-ICP-MS was used to measure higher boranes as trace impurities in high-purity diborane ( $\text{B}_2\text{H}_6$ ) using a 60 m x 0.32 mm x 1.5 m Rtx-Volatiles column. The oven program used a 35 °C starting temperature with a 15 °C/min ramp and a final temperature of 240 °C. Tolerances for diborane purity are extremely tight (< 1% variation), so accurate measurement of higher boranes is essential for production control. Standards are not available or stable for higher boranes, but GC-ICP-MS provides a solution, as illustrated in Figure 6. The chromatogram shows the separation and quantification of tetraborane ( $\text{B}_4\text{H}_{10}$ ) and pentaborane ( $\text{B}_5\text{H}_9$ ) in a  $\text{B}_2\text{H}_6$  matrix. The higher boranes were quantified at single ppm levels in 2%  $\text{B}_2\text{H}_6$  using CIC against a diborane standard. Quantification by CIC is based on the consistent response for elemental boron and a simple mathematical correction for the different amounts of boron in the different compounds. ICP-MS also offers isotope specific measurement, which is beneficial in this application, as some uses of borane require  $\text{B}_2\text{H}_6$  that is isotopically enriched up to 99.99% B-11. The  $^{11}\text{B}/^{10}\text{B}$  isotopic abundances can easily be measured using GC-ICP-MS.

### Conclusions

ICP-MS and ICP-QQQ are well-established techniques that are widely used in the semi-



**FIGURE 5:** Overlaid GC-ICP-QQQ chromatograms showing trace  $\text{PH}_3$  contaminant quantified at 4.8 ppb in DCS matrix, overlaid with  $\text{PH}_3$  standard (13 ppb).



**FIGURE 6:** Tetra and pentaborane quantified at single ppm levels in 2%  $\text{B}_2\text{H}_6$  sample using compound independent calibration with  $\text{B}_2\text{H}_6$  standard.

conductor industry for measuring ultratrace levels of elemental contaminants in wafer substrate materials, metals, and process chemicals. Combining ICP-MS with GC extends the use of the technique to monitoring contaminants in bulk, specialty gases, and volatile liquids. These sample types require special GC sampling approaches, as many of the samples are toxic, flammable, or pyrophoric. Such samples can be handled safely using an appropriate switching valve or loop injection gas sampling system.

As a sensitive, multi-elemental detector for GC, ICP-MS gives low detection limits, mass-specific measurements, and excellent selectivity. GC coupled to a triple quadrupole ICP-MS system enables trace-level analysis of compounds containing elements traditionally considered difficult to determine by ICP-MS, such as silicon and phosphorus. The high temperature of the ICP ion source means that ICP-MS gives nearly equal elemental response regardless of the compound's composition. This enables the use of compound independent calibration, which is useful when

compound-specific calibration standards are unstable or unavailable.

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