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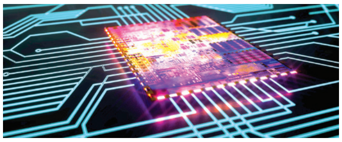

How Semiconductor Industry Requirements Drive Innovation in Agilent‘s ICP-MS

Ed McCurdy, ICP-MS Product Marketing, Agilent UK

In this issue of the ICP-MS Journal, we take an in-depth look at the role of ICP-MS and ICP-QQQ in the semiconductor industry. Working closely with leading semiconductor manufacturers and chemical suppliers since the 1990s, 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.

Figure 1. Agilent 8900 Semiconductor configuration Triple Quadrupole ICP-MS and I-AS covered autosampler

ICP-MS and ICP-QQQ in the Semiconductor Industry

Katsuo Mizobuchi, Abe Gutierrez, Bert Woods, and Ed McCurdy, Agilent Technologies

Introduction to Semiconductors

Semiconductor device fabrication requires strict control of sources of contamination; industry estimates suggest that contamination accounts for around 50% of yield losses.

Contamination control 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.

In addition to the high purity wafer substrate, the purity of chemicals used throughout the wafer fabrication process must be carefully controlled to avoid adding contaminants. Metallic contaminants are of concern because they can affect the electrical properties of the finished device, for example by reducing dielectric breakdown voltage.

A simplified schematic of the wafer fabrication process is shown in Figure 1. Each conducting or insulating layer is deposited, masked, and etched, leaving an intricate pattern of features with line widths as small as 10 nanometers (nm). 10 nm is equivalent to about 40 Si atoms. Doped regions are added, where specific atoms are deposited or implanted to alter the conductivity of the silicon.

A Si-based integrated circuit (IC) contain millions of individual transistors. These are built from patterned layers of oxide, polysilicon, silicon nitride dielectric, and conducting metal interconnects. Layers are connected by "vias" to form a 3D structure.

The current "10 nm" geometry contains features approximately 1000 times smaller than could be manufactured in circuits 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 ICP-MS performance.

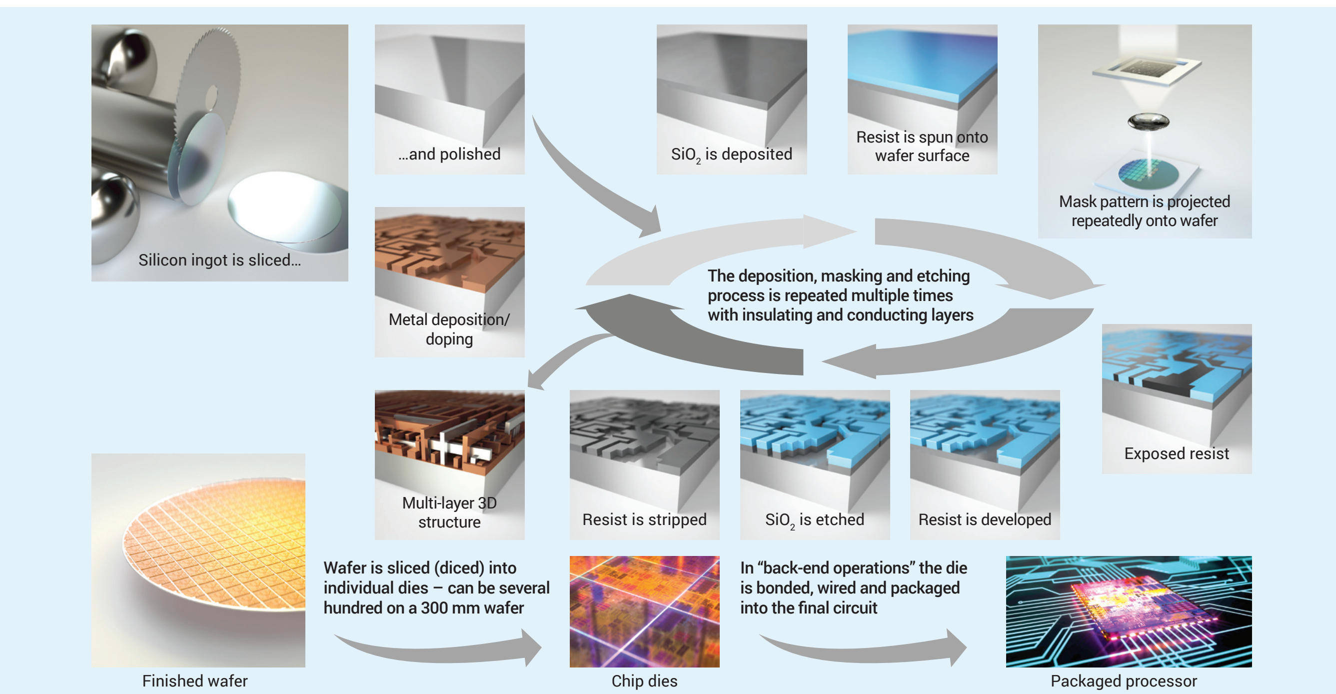

Figure 1. Simplified schematic showing typical steps in silicon wafer fabrication.

ICP-MS in Semiconductor Manufacturing

ICP-MS technology development: 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 increased rapidly in the 1990s, with the development of “cool plasma” on the HP 4500. 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.

ICP-MS manufacturers have continued to improve the technique, most recently with the release of triple quadrupole ICP-MS (ICP-QQQ). Launched in 2012, Agilent’s 8800 ICP-QQQ provided higher sensitivity, lower backgrounds, and better control of interferences than single quadrupole ICP-MS. This allowed a greater number of contaminant elements to be monitored at lower concentrations, including difficult elements such as Si, P, S, and Cl. With the release of the 8900 ICP-QQQ, Agilent continues to support the semiconductor industry in its drive for ever-smaller device architectures, higher yield, and improved device performance.

Materials: Metal contamination in the silicon wafer substrate and associated layers and coatings can be monitored using surface metal extraction (SME) or vapor phase decomposition (VPD). In the VPD technique, the surface layer (bare Si, or naturally or thermally oxidized SiO_2) is dissolved using HF vapor and the dissolved metals are collected for ICP-MS analysis in a droplet of H_2SiF_6. Other materials used in chip manufacturing are suitable for analysis using ICP-MS, including metal organic compounds such as trimethyl gallium (TMG), trimethyl aluminum (TMA), dimethyl zinc (DMZ), tetraethoxysilane (TEOS) and trichlorosilane (TCS). Such compounds are precursors used to grow thin metal films or epitaxial crystal layers in metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition. Pure metals such as Al, Cu, Ti, Co, Ni, Ta, W, and Hf are used as sputtering targets for physical vapor deposition (PVD) to create thin metal films on the wafer surface. High-k dielectric materials include chlorides and 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.

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.

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

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.

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, which requires the higher performance of ICP-QQQ.

More Information

Please refer to the application notes listed on pages 5 and 8.

Analysis of High-Purity Acids Used in Semiconductor Fabrication

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Introduction

High purity acids play an important role in the fabrication of semiconductor devices, so they need to be of ultrahigh purity. HNO_3 is widely used in wafer processing, including for wet etching of single crystal silicon, polycrystalline silicon, and aluminum. HCl combined with H_2O_2 and deionized water is used as part of the standard wafer cleaning process.

In this article, we discuss the analysis of sub-ppt level trace elements in HNO_3 and HCl.

Nitric acid: The Agilent 8900 ICP-QQQ was used for the direct analysis of undiluted commercial grade (61-68%) HNO_3. Direct analysis simplifies sample preparation and avoids the potential introduction of contaminants during dilution.

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. Good linearity and sub-ppt detection limits (DLs) were obtained for all SEMI target elements. Representative standard addition calibration curves are shown for Na, K, Ca, and Fe (Figure 1). All 49 elements

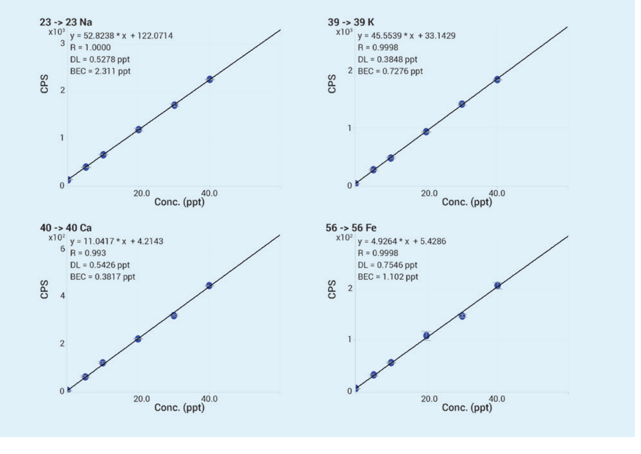

Figure 1. Calibration curves for several SEMI specification elements in high purity 68% HNO_3

were determined at significantly lower levels than the <1 µg/L (ppb) maximum limit specified for 69-70% HNO_3 in SEMI standard C35-0708 Tier-B [1].

Hydrochloric acid: Semiconductor grade HCl is 37-38%, compared to 20% or 36% for commercial grades (as used in this study). In all grades, the very high chloride 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 $^{75}As^+$. In total, 50 elements including all SEMI standard C27-0708 Tier-C 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.

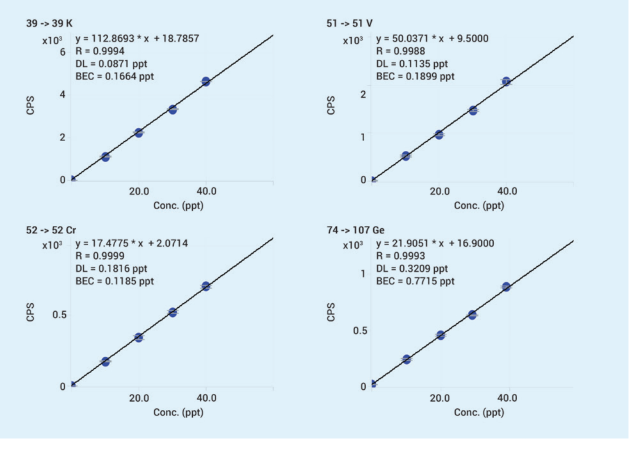

Figure 2. Method of Standard Addition (MSA) calibration curves for ^{39}K, ^{51}V, ^{52}Cr, and ^{74}Ge in high-purity 20% HCl, showing low BECs and good linearity.

DLs and MDLs: Single figure ppt or sub-ppt DLs and BECs were achieved for all 50 elements in 20% HCl.

Quantitative results: Table 1 shows quantitative data for all SEMI specification elements determined by MSA in high purity 20% HCl and lower purity 36% HCl.

Table 1. Quantitative results for SEMI specification elements in high purity HCl.

Element	Sample 1 20% HCl	Sample 2 36% HCl	DL	Element	Sample 1 20% HCl	Sample 2 36% HCl	DL
	ng/L				ng/L		
Li	<DL	<DL	0.032	Fe	0.27	7.6	0.24
B	4.1	15	0.55	Ni	<DL	<DL	0.66
Na	0.15	6.4	0.064	Cu	0.12	0.57	0.10
Mg	<DL	6.5	0.077	Zn	<DL	1.1	0.14
Al	<DL	23	0.20	As*	48	39	0.73
K	0.17	1.5	0.087	Cd	0.10	0.34	0.090
Ca	0.68	13	0.44	Sn	3.3	2.3	0.57
Ti	0.074	1.4	0.051	Sb	1.5	0.95	0.66
V	0.19	4.6	0.11	Ba	0.005	<DL	0.005
Cr	<DL	0.55	0.18	Pb	0.023	0.13	0.028
Mn	<DL	0.071	0.016				

*The As DL was measured in a different high-purity grade HCl (34% high purity grade diluted to 20% with DIW), due to suspected contamination for this element in Sample 1. The As contamination was confirmed from the product ion spectrum measured at *m/z* 91 and 93. Please refer to Agilent publication 5991-8675EN for details.

The results show that the 8900 ICP-QQQ can measure contaminants in HCl at much lower levels than the 100 ppt maximum limit in the SEMI Tier-C specifications [2]. The SEMI specification is for semiconductor grade (37–38%) HCl, while the data presented here is for 20% and 36% HCl. But even allowing for this difference, it is clear that the 8900 ICP-QQQ is able to measure contaminants at levels far lower than current industry requirements for high-purity semiconductor grade HCl.

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode provides the high sensitivity, low backgrounds, and unmatched control of interferences required for the analysis of ultratrace elements in high purity HNO_3 and HCl.

References

1. SEMI C35-0708, Specifications and guidelines for nitric acid (2008)
2. SEMI C27-0708, Specifications and guidelines for hydrochloric acid (2008)

Semiconductor-related Application Notes

- Analysis of Trace Metal Impurities in High Purity Hydrochloric Acid Using ICP-QQQ, 5991-8675EN
- Direct Analysis of Trace Metal Impurities in High Purity Nitric Acid Using ICP-QQQ, 5991-8798EN
- Determination of Ultratrace Elements in High Purity H_2O_2 with Agilent 8900 ICP-QQQ, 5991-7701EN
- Determination of Trace Elements in Ultrapure Semiconductor Grade Sulfuric Acid using the Agilent 8900 ICP-QQQ in MS/MS mode, 5991-7008EN
- Ultra-Low-Level Phosphorus, Sulfur, Silicon and Chlorine Analysis, 5991-6852EN
- Ultratrace Measurement of Calcium in UPW using Agilent 8800 ICP-QQQ, 5991-1693EN
- Direct Analysis of Trace Metallic Impurities in High Purity HCl by ICP-MS, 5990-7354EN
- Direct Measurement of Metallic Impurities in 20% Ammonium Hydroxide by ICP-MS, 5990-7914EN
- Trace Elemental Analysis of Trichlorosilane by ICP-MS, 5990-8175EN

Determination of Trace Metals in E-Cigarettes

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Introduction

The use of electronic (e-)cigarettes is increasing, despite uncertainties about their toxicity and health effects. Electronic nicotine delivery systems (ENDS) typically use a battery-powered metal heating coil to heat a liquid, which usually contains vegetable glycerin, propylene glycol, flavorings, and nicotine. The heated liquid forms an aerosol or vapor and, by inhaling the vapor (vaping), the user gets a nicotine "hit" from a tobacco-free source. E-cigarette vapor doesn't contain the harmful combustion products found in tobacco smoke, so vaping may offer a less hazardous – though not entirely safe – alternative to smoking. In this study, triple quadrupole ICP-MS (ICP-QQQ) was used to investigate the transfer of metals from the e-cigarette heating coil to the liquid in the tank, and to the aerosol vapor produced.

Experimental

Instrumentation: An Agilent 8800 ICP-QQQ was used for all measurements. The instrument was operated in single-quadrupole mode using no-gas and helium (He) mode (cell gas flow rate of 4.0 mL/min He).

Samples: Samples were taken from the refilling dispenser, the aerosol, and the e-liquid from the tank of 56 e-cigarette users' devices.

Results and Discussion

Quantitative results: The concentrations (µg/kg) of the metals measured were highly variable between devices (Figure 1). Compared to the concentrations in the refill liquid, the median values found for all elements apart from Fe were significantly higher in the aerosol samples and the liquid taken from the tank. The results indicate that the metals come from the heating coils. The median Pb concentration in the aerosols was more than 25 times greater than the median level in the refill dispensers. Almost 50% of aerosol samples had Pb concentrations higher than health-based limits defined by the US EPA. Median aerosol concentrations of Ni, Cr, and Mn also approached or exceeded safe limits.

Conclusions

The study shows that e-cigarettes are a potential source of exposure to several toxic metals. The higher concentrations in the aerosol and tank samples compared to the refill liquid indicates that the contamination arises from the heating coil.

More Information

Metal Concentrations in e-Cigarette Liquid and Aerosol Samples: The Contribution of Metallic Coils, https://ehp.niehs.nih.gov/ehp2175/

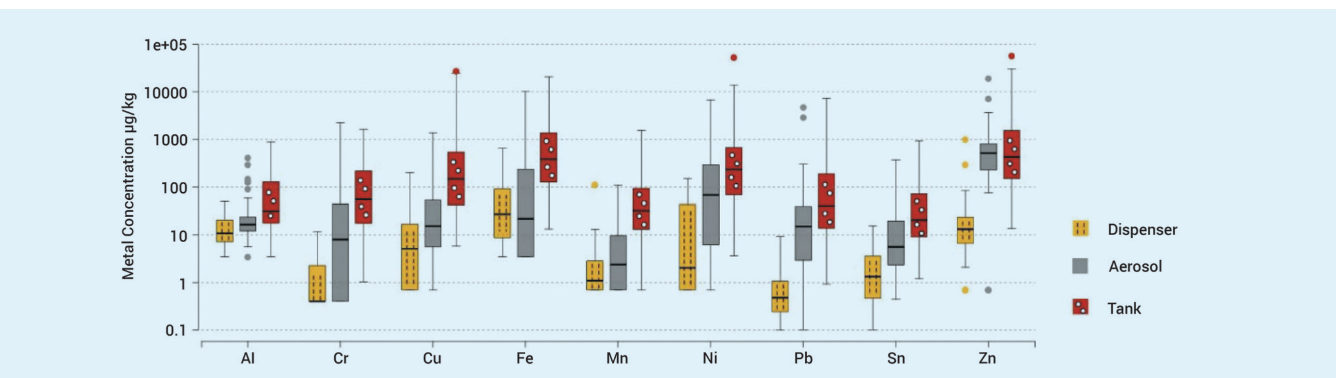


Figure 1. Boxplots of metal concentrations in e-cigarette liquid refill dispenser, aerosol, and tank samples.

Thoughts from the US Winter Plasma Conference

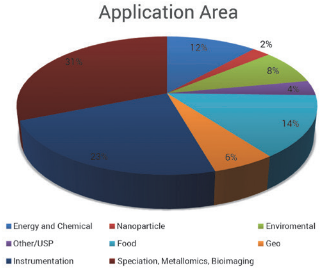
Chuck Schneider, North American Spectroscopy Marketing Manager, Agilent Technologies

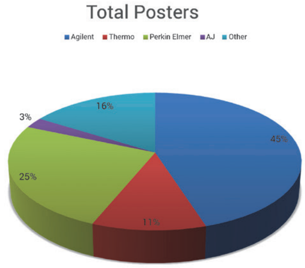
Twentieth Conference in Biennial Series

The 2018 Winter Conference on Plasma Spectrochemistry (WPC) took place at the Omni Amelia Island Plantation Resort, Amelia Island in Florida. Around 600 delegates traveled from all parts of the world to discuss the major topics of interest in plasma spectrochemistry. Similar to the topics discussed at the recent Asia Pacific WPC, single nanoparticle and single cell analysis, laser ablation, isotope ratio and isotope dilution, and speciation were among the many subjects covered during the six-day conference. Triple quadrupole ICP-MS remains the hot topic in plasma instrumentation.

A Closer Look at the Poster Presentations

A review of poster presentations showed a wide variety of application areas including energy and chemicals, food, environmental, single nanoparticle, and pharmaceuticals. The greatest focus was on speciation analysis and instrumentation. The review also showed that Agilent ICP-MS and ICP-QQQ systems were used in almost half of the posters.





Agilent's Contribution - A Global Team Effort

Reflecting the international scope of the conference, Agilent was well represented with a global team of technical experts. Representatives from Agilent's ICP-MS, ICP-OES, and MP-AES marketing and R&D teams joined colleagues from the North American applications team. Between them, the team presented close to 40 posters or oral presentations, and Agilent hosted five different customer events.

The first-ever Agilent Software Boot Camp allowed customers to benefit from hands-on experience with ICP Expert and ICP-MS MassHunter software. The workshop, which was designed to improve skills around method development, method optimization, and reporting, was very well received by all attendees.

Mark Kelinske, Agilent ICP-MS Applications Engineer, hosted a lunch seminar on the hot topic of MS/MS (unit mass resolution) for controlling interferences. At another lunch seminar, Agilent's Paul Krampitz showed how new software features in ICP Expert can improve the quality of ICP-OES data.

Agilent also hosted an 8800/8900 users group meeting. The keynote address was given by Dr Hakan Gurleyuk, Technical Director, Brooks Applied Labs (BAL). Dr Gurleyuk spoke about the role that the ICP-QQQ systems are playing in the success of his lab.

Attendees at the Agilent Customer Appreciation Event traveled by trolley cars to the Amelia Island Museum of History. Guests explored Amelia Island's history of piracy, with some getting into role with the aid of the Pirate Punch served along the tour. After the museum visit, dinner was hosted at a nearby restaurant where the DJ got the crowd moving and a photo booth captured the event.

Agilent's Lindsey Whitecotton, Patrick Simmons, and Jenny Nelson.

Looking ahead: The European Winter Conference on Plasma Spectrochemistry will take place in Pau, France, February 3-8, 2019.

Serving the Semiconductor Industry: Agilent innovations

When ICP-MS was first introduced in the 1980s, it was quickly adopted by semiconductor manufacturers and suppliers because of its high sensitivity. Since then, Agilent has led the way in ICP-MS developments to meet the evolving needs of the industry. Innovations that address the demanding requirements of the semiconductor industry are often of benefit to other users of ICP-MS, including:

- The very high sensitivity offered by the off-axis ion lens systems of all Agilent systems.
- Cool plasma, perfected on the HP 4500, 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 controls contamination and provides the ability to handle very small sample volumes (such as <500 µL VPD droplets).
- The stainless-steel chassis and clean room preparation 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.
- Agilent's applications expertise in the analysis of high-purity and high-performance materials.

Additional Semi-Related Application Notes

- Gas Chromatographic Separation of Metal Carbonyls in Carbon Monoxide with Detection using the Agilent 8800 ICP-QQQ, 5991-6432EN
- Sub-ppb Detection Limits for Hydride Gas Contaminants using GC-ICP-QQQ, 5991-5849EN
- Quantitative Analysis of High Purity Metals using Laser Ablation Coupled to an Agilent 7900 ICP-MS, 5991-6156EN

Agilent ICP-MS Publications

To view and download the latest ICP-MS literature, go to www.agilent.com/chem/icpms

- **Application note:** Determination of Diclofenac and Its Related Compounds using Gradient Elution Reversed Phase HPLC-ICP-QQQ, 5991-9077EN
- **Application overview:** Analysis of 10 nm Gold Nanoparticles using the Agilent 7800 ICP-MS, 5991-8827EN
- **Application note:** Speciated Arsenic Analysis in Wine Using HPLC-ICP-QQQ: Validation of an extended FDA Elemental Analysis Manual method, 5991-8833EN

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