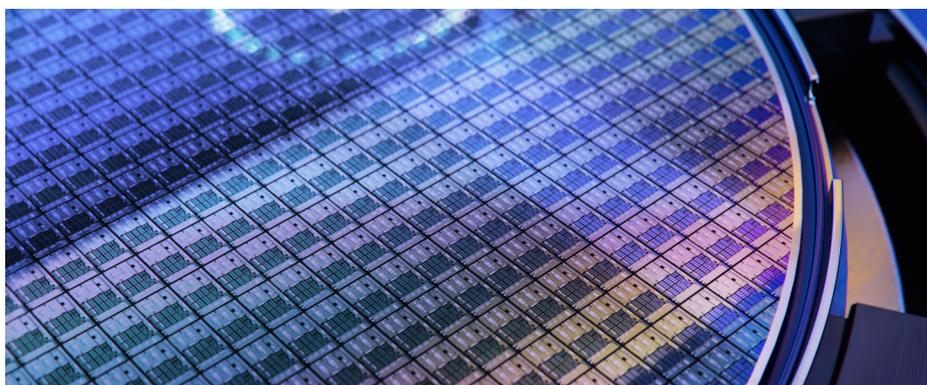


Determination of Ultratrace Impurities in Semiconductor Photoresist Using ICP-MS/MS

Monitoring 20 elemental contaminants in IC photoresist by Agilent 8900 ICP-QQQ after simple dilution in PGMEA solvent



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Introduction

With the rapid development of the consumer electronics industry and the expanding use of computer chips in homes, vehicles, telecommunications, manufacturing automation, AI, and a range of other high-tech products and industries, demand for semiconductors is increasing rapidly. The most advanced integrated circuit (IC) fabrication factories (FABs or “foundries”) currently produce chips at the 7, 5, or 3 nanometers (nm) process node (approximately 130–250 million transistors per square millimeter). Ongoing industry developments are targeting production of chips at the 2 nm process node by 2025. Higher device densities provide benefits in size, speed, and power consumption, all of which are valuable attributes for portable electronics. To achieve the required performance and quality at these small device dimensions, the level of contaminants in the silicon (Si) substrate and process chemicals used during manufacturing must be strictly controlled.

Photoresist (PR) is one of the key materials used in the lithography step of IC fabrication, where intricate patterns are etched into the surface of the wafer to build up the IC circuit. Photolithography uses a UV image, projected onto the wafer surface, to reproduce the specific patterns required for each layer of the circuit, and PR is the crucial material for the lithography process. Different classifications of PR are used depending on whether the FAB is manufacturing printed circuit boards (PCBs), liquid crystals (LCs) and liquid crystal displays (LCDs), or ICs. In this work, IC PR, which is mostly used in the IC fabrication process and therefore requires the highest level of purity, was analyzed.

PR is coated directly onto the wafer surface for each lithography step, and tens of lithography steps may be required to build up the alternating conducting and insulating layers in a completed circuit. Therefore, the purity of the PR must be strictly controlled to avoid contaminating the wafer surface. Metal impurities in the PR are particularly problematic, as they can affect the electrical properties and reliability of the final semiconductor device, so the specification of metal impurities in PR are constantly being reduced. The maximum acceptable levels of metallic impurities in IC PR are currently in the range of 1–10 ppb per element and will be reduced to less than 1 ppb in the future. Monitoring these elements at ultratrace levels in PR is therefore extremely important and is routinely carried out by PR suppliers and IC manufacturers (1).

As IC dimensions continue to shrink, the smaller line width circuit features are even more at risk from dissolved and particulate metallic contaminants, so impurities must be monitored at even lower levels. As a result, it is important that the performance of the analytical instruments used to measure elemental impurities in raw materials continually improve to be able to meet the needs of the semiconductor industry. Process chemicals and ultrapure water (UPW) used in advanced semiconductor processes require elemental impurities to be controlled at ppt or even sub-ppt levels; triple quadrupole ICP-MS (ICP-QQQ) is increasingly used in the semiconductor industry to meet these requirements. The Agilent 8900 ICP-QQQ is a tandem ICP-MS (ICP-MS/MS) that offers high sensitivity, extremely low background (typically <0.1 cps), and highly effective control of spectral interferences. This unique combination delivers detection limits (DLs) at the sub-ppt level for the critical semiconductor elements, enabling chemical suppliers and IC manufacturers to meet the industry requirements for accurate analysis of elemental impurities in the highest purity semiconductor materials.

In this study, an 8900 ICP-MS/MS was used to analyze 20 critical trace elements in several different IC-grade photoresist samples obtained from suppliers to the semiconductor industry. The PR samples were simply diluted in Propylene Glycol Methyl Ether Acetate (PGMEA) solvent and analyzed against an external calibration prepared in PGMEA. Excellent precision and recovery were achieved for repeated measurement of a 0.1 ppb spike in photoresist over 1 hour of sample running. The results demonstrate the stability, robustness, and sensitivity of the 8900 ICP-MS/MS method.

Experimental

Reagents

All the samples were diluted in semiconductor G5 grade (specification of <10 ppt for each contaminant element) PGMEA. The ultrapure water (UPW) was prepared in the laboratory using a UPW system from Organo Corp (Tokyo, Japan).

Sample preparation

PR contains a blend of photoacid generators (PAG) selected for their ability to generate microstructures with the specific dimensions required for the circuit. The PR also contains resins, solvent, and other additives depending on the intended application. The resins strongly influence the physical properties of the PR and also affect aspects of the analysis procedure, such as the dilution factor required to enable the sample solution to be nebulized in the ICP-MS. IC PR typically contains relatively low concentrations of resin, so the IC PR samples in this study only required 10 times dilution, which enabled measurement of ultratrace impurities in the original samples. The PR samples were diluted in PGMEA, which is the solvent typically used for PR sample preparation.

Calibration standards

A multi-element calibration containing all the required elements was prepared in N-Methyl-2-Pyrrolidone (NMP) with the addition of 2% HNO₃ to stabilize the analytes. NMP can be dissolved in both UPW and PGMEA, making it a useful intermediate solvent for organic sample analysis. In this work, the final calibration standards were prepared in PGMEA to match the sample diluent. The following Agilent stock solutions were used to cover the full list of required analytes:

- Agilent multi-element calibration standard 2A (p/n 8500-6940)
- Agilent multi-element calibration standard-4 (p/n 8500-6942)
- Agilent tin standard: 1,000 µg/mL Sn (p/n 5190-8583)

Instrumentation

The Agilent 8900 (#200) Semiconductor configuration ICP-MS/MS is the recommended model for high purity sample analysis, such as the PR samples analyzed in this work. The 8900 #200 ICP-MS/MS includes a fifth (option gas) Agilent Mass Flow Controller (AMFC) gas controller for addition of oxygen (O₂) to the plasma for the analysis of organic samples. The 8900 #200 sample introduction system comprises a 200 µL/min MicroFlow PFA nebulizer, quartz spray chamber, and quartz connecting tube with gas port for option gas addition. The 8900 #200 instrument also includes Pt-tipped interface cones and the s-lens, which provides high ion transmission and is compatible with cool plasma operation. The 8900 was fitted with the organic solvent sample introduction kit (G3280-60580), which includes solvent resistant tubing and a quartz torch with 1.5 mm internal diameter (ID) injector, suitable for analysis of most organic solvents. An optional 1.0 mm ID injector torch (G3280-80081) is available for analysis of the most volatile solvents.

When high carbon samples such as organic solvents are analyzed by ICP-MS, carbon can deposit on the sampling cone, clogging the orifice and reducing sensitivity. When solvents are analyzed using an Agilent ICP-MS, the fifth AMFC gas controller is used to add oxygen to the carrier gas to decompose the carbon matrix and prevent carbon deposits. For safe handling of gases in the laboratory, it is advisable to use a mixture of 20% oxygen in argon (O₂/Ar), rather than 100% O₂. And it is recommended to add the O₂/Ar mix through the T-connector between the spray chamber and torch. The 8900 (Advanced Applications and Semiconductor configurations) includes the fifth gas controller and T-connector for O₂/Ar option gas addition.

Together with the carbon, hydrogen, and oxygen derived from the organic matrix, and the argon and nitrogen from the plasma gas and surrounding atmosphere, the PR samples analyzed in this study also contained sulfonic acid, which would contribute sulfur ions to the spectrum. The combination of background ions could potentially cause polyatomic ion interferences on some key elements such as Mg, Al, Ti, Cr, Fe, and Zn, shown in Table 1.

Table 1. Spectral interferences caused by the sample matrix.

Analyte Ion	Main Polyatomic Ion Interferences
²⁴ Mg ⁺	¹² C ₂ ⁺
²⁷ Al ⁺	¹² C ¹⁴ NH ⁺ , ¹³ C ¹⁴ N ⁺
³⁹ K ⁺	³⁸ ArH ⁺ , ¹² C ₂ ¹⁴ NH ⁺
⁴⁸ Ti ⁺	³⁶ Ar ¹² C ⁺ , ³² S ¹⁶ O ⁺
⁵¹ V ⁺	³⁴ S ¹⁶ OH ⁺
⁵² Cr ⁺	⁴⁰ Ar ¹² C ⁺
⁵⁶ Fe ⁺	⁴⁰ Ar ¹⁶ O ⁺ , ¹² C ₂ ¹⁶ O ₂ ⁺
⁶⁴ Zn ⁺	³² S ₂ ⁺ , ³² S ¹⁶ O ₂ ⁺ , ³⁶ Ar ¹² C ¹⁶ O ⁺ , ³⁸ Ar ¹² C ¹⁴ N ⁺

To achieve the lowest background equivalent concentration (BEC) for each analyte in the photoresist samples, the ICP-MS/MS operating conditions were optimized for measurement of the different elements. The 8900 ICP-MS/MS provides high-sensitivity and extremely low random background – typically <0.1 cps – so signal-to-noise is exceptionally high. This underlying performance is combined with flexible reaction cell operation using MS/MS mode to resolve spectral interferences. The 8900 supports rapid and automated switching between plasma conditions to enable the optimum settings to be applied to each analyte within a single analysis.

In this study, several reaction cell gases were used as appropriate to give the lowest BECs and detection limits (DLs) for the analytes monitored in the semiconductor supply chain. Ammonia (NH₃) reaction gas mode was combined with optimized “warm” plasma conditions (1000 W forward power, longer sampling depth, and increased carrier gas flow). These plasma conditions are effective for controlling the intense carbon-based spectral backgrounds that occur in organic samples, while maintaining the good plasma robustness necessary for PR sample analysis. All Agilent ICP-MS systems include a makeup gas line as well as the nebulizer gas line. This additional makeup gas controller allows the total carrier gas flow through the plasma to be varied without affecting the nebulization process, ensuring optimum settings for a variety of plasma conditions. The operating parameters of the 8900 ICP-MS/MS are given in Table 2.

Table 2. Agilent 8900 ICP-MS/MS operating conditions.

Tune Mode	NH ₃	H ₂	O ₂
MS/MS Acquisition Parameters			
Replicates/Sample	3		
Sweeps/Replicate	100		
Integration Time/Mass (s)	0.6		
Plasma			
RF Power (W)	1000*	1550	
Sampling Depth (mm)	18.0	7.0	
Nebulizer Gas (L/min)	0.65		
Makeup Gas (L/min)	0.60	0	
O ₂ /Ar Option Gas (L/min)	0.25	0.20	
Spray Chamber Temp (°C)	-5		
Ion Lenses			
Extract 1 (V)	-150	4.3	
Extract 2 (V)	-15	-250	
Omega bias	-80	-140	
Omega lens	5	10	
Collision/Reaction Cell			
He Flow Rate (mL/min)	1.0		
H ₂ Flow Rate (mL/min)		4.0	
NH ₃ Flow Rate (mL/min)**	2.0 (20%)		
O ₂ Flow Rate (mL/min)			0.45 (30%)
Octopole Bias (V)	-15	-16	-4
Axial Acceleration (V)	0.5		1.5
KED (V)	-8	0	-8

* 1000 W plasma power gives high energy, matrix tolerant, "warm" plasma conditions appropriate for optimum removal of carbon-based spectral overlaps in organic matrices.
 ** NH₃ cell gas was a mix of 10% NH₃ in He.

Results and discussion

Calibration curves

The multi-element mixed stock standard was spiked into the PGMEA blank to give calibration standards with final concentrations of 200, 500, and 1000 ng/L (ppt). Examples of the calibration curves for some of the difficult, interfered elements are shown in Figure 1.

The good linearity of the plots and excellent precision of the calibration standards demonstrate the ability of the 8900 ICP-MS/MS to reliably measure the most difficult, interfered analytes at ppt levels in the PGMEA solvent.

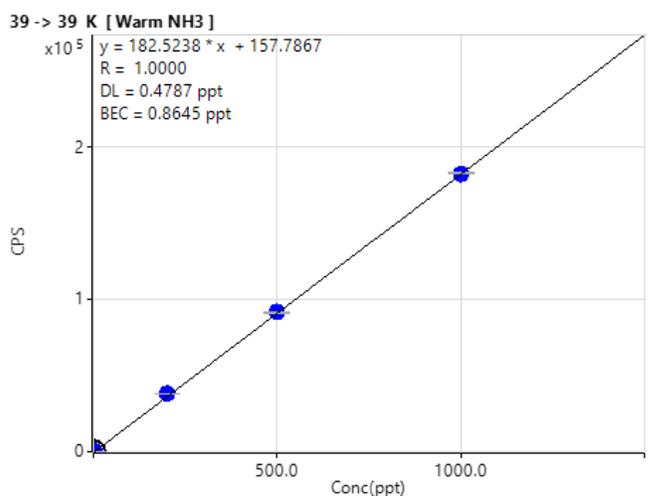
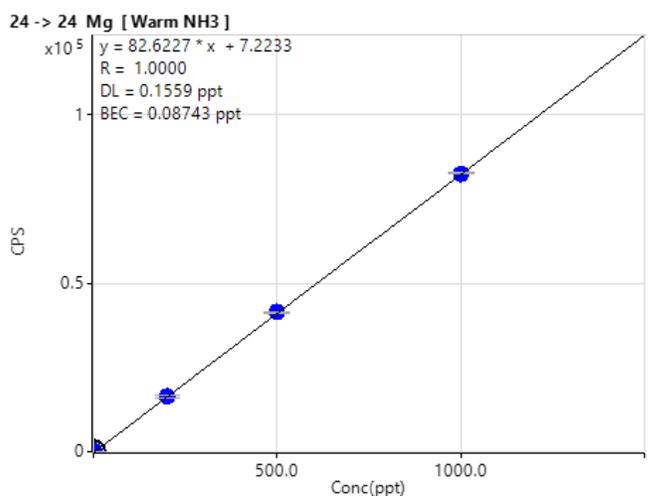
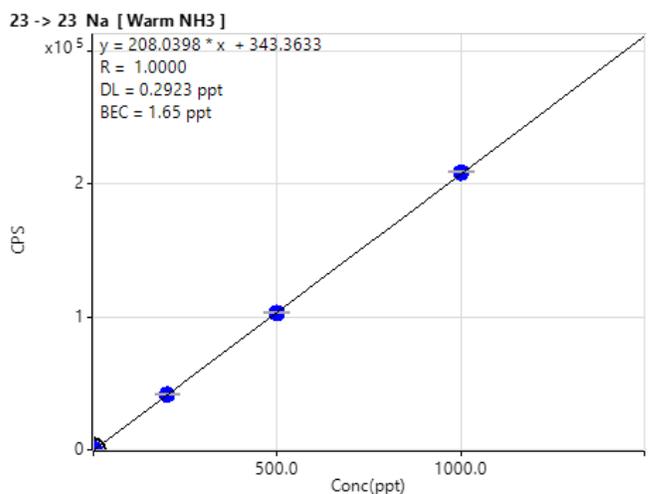


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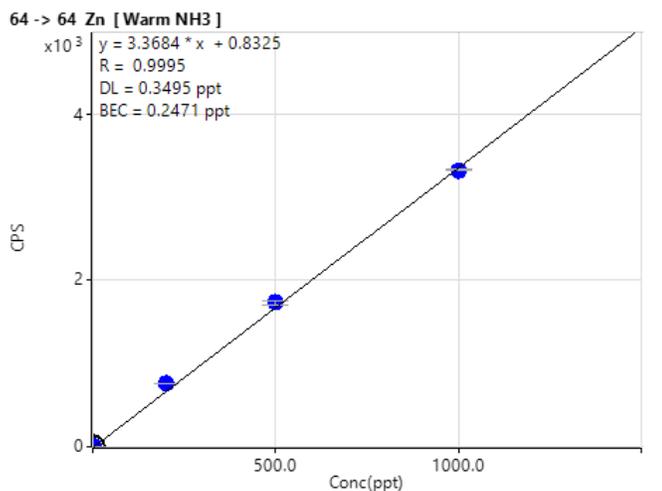
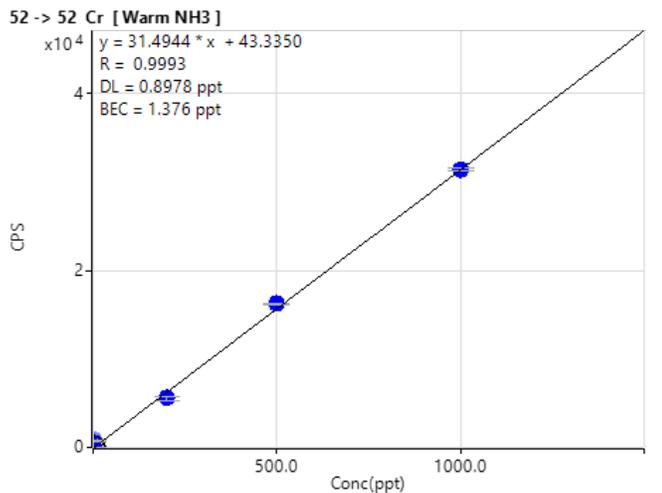
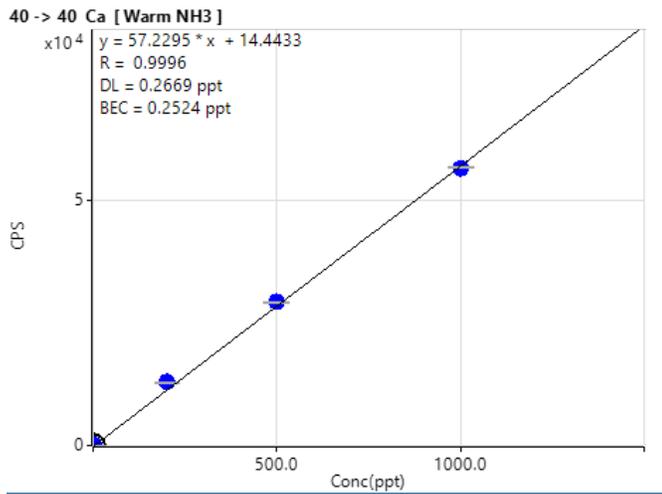


Figure 1. Calibration curves prepared in PGMEA.

The calibrations were used to calculate BECs and DLs for all the measured analytes, as shown in Table 3. DLs below 1 ppt were obtained for all elements except Pb, which was present as a low-level (<2 ppt) contaminant in the PGMEA. The BECs were mostly far below 0.5 ng/L with only Na, Cr, Fe, and Pb above 1 ng/L, due to trace contamination of these elements in the PGMEA. Even these contaminant elements were present at less than 3 ng/L in the PGMEA solvent, well below the specification (of <10 ppt) for this grade of PGMEA. The low BECs and DLs obtained demonstrate not only the suitability of high purity PGMEA as a solvent for IC grade PR, but also the capability of the 8900 ICP-MS/MS to effectively resolve matrix-based interferences on all the analytes, including the intense carbon-based interferences on elements such as Mg, Ti, Cr, and Zn.

Table 3. Analyte masses, tune modes, BECs, and DLs in PGMEA solvent used for analysis of contaminant elements in IC PR.

Element	Q1/Q2	Tune Mode	DL (ng/L)	BEC (ng/L)
Li	7/7	NH ₃	0*	0*
Na	23/23	NH ₃	0.29	1.70
Mg	24/24	NH ₃	0.16	0.09
Al	27/27	NH ₃	0.28	0.39
K	39/39	NH ₃	0.48	0.86
Ca	40/40	NH ₃	0.27	0.25
Ti	48/64	O ₂	0.31	0.33
V	51/67	O ₂	0.06	0.47
Cr	52/52	NH ₃	0.90	1.40
Mn	55/55	NH ₃	0.08	0.02
Fe	56/56	NH ₃	0.38	2.50
Co	59/59	NH ₃	0.06	0.01
Ni	60/60	NH ₃	0.39	0.15
Cu	63/63	NH ₃	0.36	0.29
Zn	64/64	NH ₃	0.35	0.25
Ag	107/107	NH ₃	0.10	0.02
Cd	114/114	O ₂	0**	0.32
Sn	118/118	H ₂	0.64	0.50
Ba	138/138	O ₂	0.44	0.34
Pb	208/208	O ₂	1.20	1.80

* Zero counts were measured for Li in all replicates of the blank, so no DL and BEC could be calculated.

** The same number of counts were measured in all replicates of the blank, so the standard deviation (SD) was zero and therefore no DL could be calculated.

Sample measurement

Three different IC PR samples were measured in this study after diluting the samples 10 times in PGMEA. The concentrations of the analytes present in the PR samples were determined against the external calibrations in PGMEA, and the dilution-corrected results (in $\mu\text{g/L}$ in the original PR samples) are shown in Table 4. Generally low levels of contamination were found in all three PR samples. A few elements were present at raised levels, for example Fe, Zn, and Sn in PR Sample 1 and Ca in Sample 2. However, none of the analytes were above the current maximum 1–10 ppb range for contaminant elements in IC PR. Sample 3 did not contain any of the monitored elements at levels above 0.2 ppb, meeting future requirements for <1 ppb contaminant levels in PR.

Table 4. Quantitative results for key semiconductor contaminant elements in three IC PR samples. Results in $\mu\text{g/L}$ (ppb) in the original PR samples, after correction for the 10x dilution.

Element	PR Sample 1 ($\mu\text{g/L}$)	PR Sample 2 ($\mu\text{g/L}$)	PR Sample 3 ($\mu\text{g/L}$)
Li	0.00*	0.00*	0.00*
Na	0.31	0.57	0.12
Mg	0.03	0.05	0.01
Al	0.52	0.05	0.03
K	<BEC	0.57	0.01
Ca	0.25	1.50	0.02
Ti	1.00	0.33	0.05
V	0.09	0.02	0.05
Cr	0.63	0.33	0.05
Mn	<BEC	0.01	0.001
Fe	2.40	0.22	0.05
Co	<BEC	0.001	0.001
Ni	0.03	0.04	0.01
Cu	0.20	0.02	0.01
Zn	1.20	0.08	0.06
Ag	0.19	0.01	0.001
Cd	0.11	0.02	<BEC
Sn	1.40	0.04	0.01
Ba	<BEC	<BEC	<BEC
Pb	<BEC	<BEC	<BEC

* Zero counts were measured for Li in all replicates of the samples, so no concentration could be determined.

Recovery check by comparing PR sample results at different dilutions

The different (higher) viscosity of PR compared to the PGMEA solvent used to prepare the calibration standards could lead to differences in sample flow rate and nebulization. In non-semiconductor applications, differences in sample flow rate due to non-matrix matched calibration standards are typically corrected using internal standards (ISTDs) added to all solutions. The measured results for the analytes in the samples are corrected relative to the signal difference for the ISTDs in the samples compared to the standards. However, analysts in semiconductor laboratories aim to reduce sample handling and minimize the risk of contamination, so these users typically prefer not to add ISTDs.

In this work, the PR results calculated using the non-matrix matched (PGMEA) calibration were validated by measuring two different dilutions of a PR sample. The same PR sample was diluted 10x (1 part sample to 9 parts PGMEA) and 20x (1 part sample to 19 parts PGMEA) and the two solutions were measured against the PGMEA calibration. The results, corrected for the appropriate dilution factor, are shown in Table 5, together with an analysis of the relative difference in the concentrations reported in the two dilutions. Of the 15 elements where valid results above the BEC were reported, 11 were within $\pm 20\%$ difference and a further two were within $\pm 50\%$. This good agreement demonstrates the robustness and matrix tolerance of the 8900 method, especially considering that many of the analytes were present at single digit ppt in the undiluted PR.

Table 5. Recovery check by analysis of the same PR sample run at two different dilutions (×10 and ×20). Analyte results are shown in µg/L (ppb) in the original PR sample, after correction for the dilution factor.

Element	×10 Diluted PR (µg/L)	×20 Diluted PR (µg/L)	Relative Difference (10x/20x)
Li	0.000	0.000	NA
Na	0.308	0.272	0.12
Mg	0.053	0.052	0.02
Al	0.547	0.523	0.04
K	0.011	0.049	-3.45
Ca	0.326	0.391	-0.20
Ti	0.040	0.043	-0.07
V	0.091	0.135	-0.48
Cr	0.679	0.701	-0.03
Mn	<BEC	<BEC	NA
Fe	0.080	0.078	0.03
Co	<BEC	<BEC	NA
Ni	0.029	0.040	-0.38
Cu	0.198	0.207	-0.05
Zn	0.119	0.112	0.06
Ag	0.005	0.013	-1.60
Cd	0.019	0.017	0.11
Sn	0.065	0.052	0.20
Ba	<BEC	<BEC	NA
Pb	<BEC	<BEC	NA

NA = not applicable.

Spike recovery test

The accuracy of the external, non-matrix matched calibration in PGMEA was further validated by measuring the spike recovery for a PR sample spiked with the multi-element standard at a concentration of 0.1 ppb. The concentration results and spike recoveries are shown in Table 6. The average recoveries for three replicate measurements of the sample spiked at 0.1 ppb level were within the range of ±10% for all the elements.

Table 6. Spike recoveries in PR sample diluted 10x in PGMEA (n=3).

Element	Unspiked PR Sample (µg/L)	0.1 ppb Spiked PR Sample (µg/L)	Spike Recovery Average (%)
Li	0.001	0.107	106
Na	0.038	0.146	108
Mg	0.012	0.103	91
Al	0.048	0.152	104
K	0.049	0.159	110
Ca	0.048	0.152	104
Ti	0.061	0.162	101
V	0.001	0.095	94
Cr	0.034	0.141	107
Mn	0.004	0.106	102
Fe	0.109	0.206	97
Co	0.001	0.107	106
Ni	0.030	0.122	92
Cu	0.024	0.132	108
Zn	0.105	0.212	107
Ag	0.027	0.118	91
Cd	0.001	0.110	109
Sn	0.011	0.104	93
Ba	0.001	0.097	96
Pb	0.038	0.139	101

Long-term stability

The long-term stability and robustness of the 8900 ICP-MS/MS method were evaluated by analyzing a 10x diluted PR sample repeatedly over a one-hour period with a total of 10 replicates. The stability test results, corrected for the 10x dilution, are shown in the plot in Figure 2. These results demonstrate the exceptional stability of the 8900 for ultratrace level measurements. For the analytes that were present in the PR sample at concentrations above 0.2 µg/L (>20 ng/L in the 1:10 diluted sample), the RSDs were around 5% or below over the one hour of analysis. Good stability of around 10% RSD or below was obtained for ultratrace level contaminants, such as Al (11% RSD at 0.05 µg/L), Ca (8% RSD at 0.07 µg/L), and Mn (12% RSD at 0.005 µg/L).

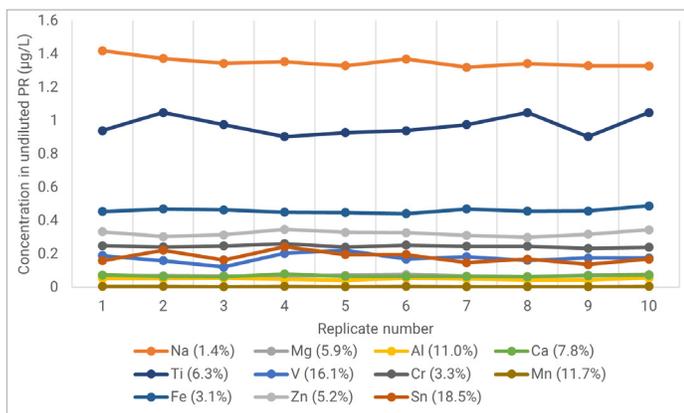


Figure 2. Stability of analytes measured in a PR sample run repeatedly over a period of one hour (n=10). Some ultra-low level elements omitted for clarity. Excellent stability was obtained, with RSD of 5% or below for analyte concentrations at levels above 0.2 ppb in the undiluted PR (>20 ppt level measured in the 10x diluted sample).

Conclusion

This work demonstrates the performance of the Agilent 8900 ICP-MS/MS for the measurement of 20 critical contaminant elements in IC grade photoresist samples. The optimized plasma conditions used for organic solvent analysis ensured high sensitivity for the analytes without compromising the ICP-MS matrix tolerance. The reproducibility (stability) results of all elements in the PR samples confirmed that the robust plasma conditions could tolerate the PR sample matrix for extended routine analysis runs.

The 8900 ICP-QQQ was operated in MS/MS mode using a multitune method with different cell gases to achieve extremely low, single- or sub-ppt BECs for all the elements in a single acquisition. The low BECs showed that the 8900 ICP-MS/MS method could effectively remove all the spectral interferences, including intense polyatomic ion interferences caused by the high carbon matrix and the other components—such as sulfur—in the PR samples.

www.agilent.com/chem/8900ICP-QQQ

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The interference removal capability of the 8900 ICP-QQQ for the measurement of trace metals in PR samples was further demonstrated through accurate spike recoveries. And the accuracy of the external PGMEA calibration was confirmed by the good agreement between the results measured in different dilutions of the sample PR sample. The robustness of the 8900 was assessed by running a PR sample repeatedly for one hour, achieving excellent stability even for ultratrace level analytes.

The 8900 ICP-MS/MS offers the performance to meet the current and future requirements for PR used in the most advanced manufacturing processes for the high-performance ICs on the semiconductor industry roadmap.

Reference

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