

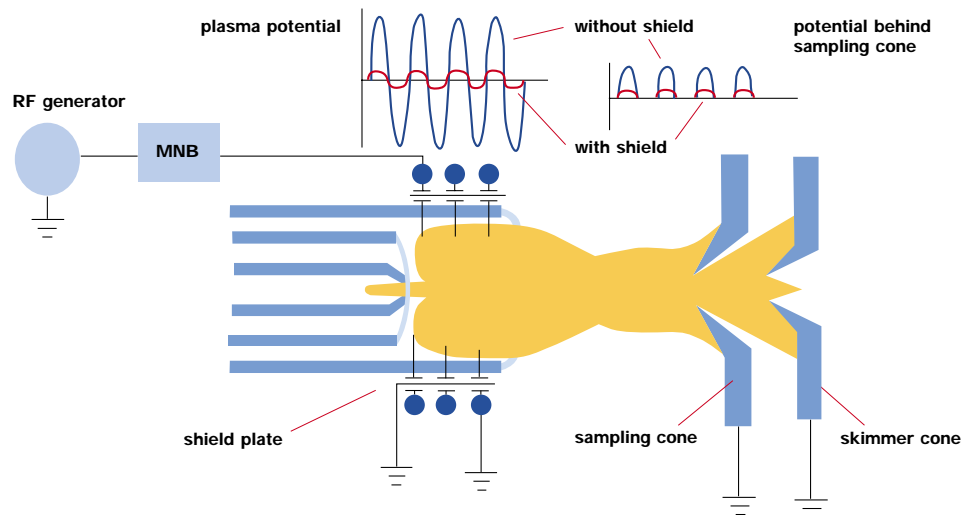
Material monitoring

The semiconductor industry has been interested in the potential applications of inductively coupled plasma mass spectrometry (ICP-MS), almost since the technique was developed in the early 1980's. Key to the acceptance of the technique has been its combination of high sensitivity, low random background and rapid multi-element measurement, but certain interferences initially proved difficult to eliminate, so limiting the widespread use of the technique. These interferences resulted from the formation of polyatomic ions, based on combinations of the components of the plasma, solvent and sample matrix. These polyatomic ions degraded detection limits for elements such as K, Ca and Fe, until the introduction of the ShieldTorch System from Agilent Technologies and Yokogawa in the early 1990's. This new technology, when used in combination with so-called "cool plasma" conditions, allowed operation of the instrument under conditions where, although the interfering polyatomic ions were formed, they were not ionised and so did not appear in the mass spectrum. As a result, K, Ca and Fe could be measured, together with the other critical contaminant elements, at the low ng/L levels required by the industry.

The Agilent Technologies 4500 ICP-MS ShieldTorch System, illustrated schematically in Figure 1, uses a grounded precious-metal plate to shield the plasma from the high voltage of the rf load coil. This removes the potential difference between the plasma and the interface, thereby preventing any possibility of re-ionisation of polyatomic clusters, such as $40\text{Ar}1\text{H}$ and $40\text{Ar}16\text{O}$. The use of long sampling depths and high carrier gas flow rates produces "cool plasma" conditions, in which virtually all background peaks are eliminated and, uniquely, the Agilent 4500 allows this background removal at high plasma powers (900 to 1000W), so allowing the analysis of high sample matrices. This new technology vastly increased the use of ICP-MS in the semiconductor industry, especially for the routine multi-element analysis of inorganic process chemicals, such as ultra-pure water, mineral acids and the chemical baths used in silicon wafer processing. However, despite this widespread adoption of the technique within the semiconductor industry, the performance of ICP-MS in the analysis of organic materials remained relatively unproven.

Direct ICP-MS analysis of organic materials has the potential to generate further polyatomic interferences, in addition to those derived from the

The selection and validation of any new analytical tool presents several practical problems to the laboratory, regardless of the industry in which it operates. Due to the nature of the semiconductor industry, however, these problems may be more severe, as the consequences of inadequately assessing a tool's routine performance and reliability may be a financial disaster.



Schematic of the Shield Torch System on the Agilent 4500

argon, as summarised in Table 1. As the elements on which these carbon-based interferences occur are considered contaminants in many semiconductor materials, their concentrations are closely monitored. Consequently, ICP-MS must be capable of removing these matrix-based interferences as well the argon-based polyatomics. Interference removal alone is not sufficient to offer a practical routine analytical technique, however, since the ICP-MS must also be capable of efficient decomposition of the heavy organic matrix associated with many organic semiconductor chemicals.

Over many years, EKC Technology has established a portfolio of products for numerous applications within the semiconductor industry, using high purity materials and specialist chemistries. Two such chemistries are Posistrip EKC830, a blend of organic solvents and primary amines, specifically designed to clean organic photoresist layers from metal interconnects, and EKC265, a blend of HDA, organic amines and corrosion inhibitors, that removes both

photoresist and plasma etch residues. Both materials have heavy organic matrices, which makes analysis difficult by many instrumental procedures. Additionally, due to the nature of the chemistries involved, common sample preparation techniques, such as acid decomposition, are highly impractical. A direct analysis method is therefore preferred, due to considerations of safety, speed and contamination control.

What follows is a description of the validation procedure carried out at EKC Technology's East Kilbride manufacturing facility, to evaluate the Agilent 4500 ICP-MS instrument, using the ShieldTorch System and cool plasma conditions for the routine analysis of a range of organic photoresist remover and post-etch cleaning chemicals. The test criteria selected and the evaluation process used may not be applicable in every validation environment, but the general procedures could serve as a model in many analytical laboratories.

Experimental

The protocol developed by EKC Technology was designed to test the analytical system's accuracy, reproducibility, and stability, during an intensive four-week evaluation. After installation in a class 1000 clean room, an Agilent Technologies 4500 ICP-MS, configured to operate under high power cool plasma conditions, was used to analyse samples of EKC Technology's Posistrip EKC830 and EKC265, for twelve elements (Al, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na and Zn).

Preliminary work, carried out by Agilent Technologies, provided an outline method of analysis, which indicated that the direct determination of these products by ICP-MS could be reproducibly and accurately completed, after a simple aqueous dilution. To eliminate operator and material variation and enable a true assessment of the system's capabilities, a single EKC Technology Analyst completed all of the tests, using a "reference" sample of each matrix. Standard addition calibrations were used for all quantification. 18.2 Mohm deionised (DI) water was used for sample dilutions and no internal standard was added, to minimise the risk of sample contamination. All sample preparation was undertaken in a Class 10 laminar flow hood.

Structure of performance testing protocol

To ensure an effective evaluation, five areas of routine analytical performance were identified for assessment, the results of which would indicate the Agilent 4500's ability to meet EKC Technology's requirements. For each area, appropriate test criteria were defined (Table 2), which were required to be exceeded if the Agilent 4500 was to be deemed acceptable for the routine analysis of organic materials.

1. Analytical Evaluation

As an initial indication of the instrument's capability, and to ensure the accuracy and precision of the data generated, an analytical assessment was completed. As no certified reference materials for this type of matrix were available, this assessment consisted of an

Table 1. Potential Spectral Overlaps in Organic Samples

Element	Isotope	Interference
B	11	12C (tail at low mass)
Mg	24	12C2
Mg	25	12C13C
Mg	26	13C2 and 12C14N
Al	27	12C14N1H
K	39	38Ar1H
Ca	40	40Ar
Cr	52	40Ar12C
Cr	53	40Ar13C
Fe	56	40Ar16O

Direct ICP-MS analysis of organic materials has the potential to generate further polyatomic interferences, in addition to those derived from the argon

analyte recovery test, together with both instrumental and method detection limit evaluations.

2. Stability Test

The stability of the system was evaluated for both short and long-term analytical drift, by the repeated analysis of a sample, over an 8 hour period. This test was developed to identify potential problems of short-term analytical imprecision (high %RSD's) and long-term signal drift (sample to sample repeatability). The former might be caused by sample droplet deposition in the spray chamber or plasma torch, which might be expected due to the viscous nature of the samples. Long-term drift might indicate problems with tuning stability, due to matrix contamination of the ion lenses.

3. Three Day Test

To evaluate the day-to-day reproducibility of the system, a three-day test was devised, where calibration response and the daily variation of the tune parameters were assessed. Calibration lines were generated twice daily (morning and afternoon) each day over the test period, to highlight possible issues with the stability of both analyte sensitivity and interference levels. Poor stability in this area might indicate a lack of robustness in the sample introduction area, whilst the need to routinely re-optimize the instrument would compromise its long-term ease of use. In order to assess the performance in a routine laboratory environment, the instrument was shutdown and restarted prior to each

calibration batch and re-tuned using a 10 ug/L cobalt standard solution, as per the manufacturer's instructions.

4. Comparative Analysis

On the successful completion of the above tests, a comparative analysis was undertaken, against equipment known to generate reproducible and accurate results. Twenty-five samples of each matrix were analysed by both ICP-MS and Electro-Thermal (also known as Graphite Furnace) Atomic Absorption Spectrometry (ETAAS), for all 12 elements of interest. To eliminate environmental variation, analyses were completed as simultaneously as the instrumentation would allow, with samples and standards being prepared from the same DI water and stock solutions.

5. Hardware Robustness Assessment

From past experience, EKC Technology staff were aware of the difficulties of analysing their sample matrices by low-power cool plasma ICP-MS, in which poorly decomposed sample residue enters the vacuum chamber and causes unacceptable signal drift and routine maintenance requirements. Therefore, as a final test, a hardware robustness evaluation was completed, where an Agilent Technologies engineer visually examined the sample introduction system and the ion lenses. Significant observable contamination or analysis problems that could be attributed to ion lens contamination would result in the Agilent 4500 failing this test criterion.

The findings

Preliminary work, completed by Agilent Technologies, demonstrated some advantages of the Agilent 4500's high-power, cool plasma set-up, when analysing EKC Technology's organic samples. Low background levels for C-based polyatomic interferences (such as ArC), as well as plasma-based polyatomics (such as ArH and ArO), indicated that the ShieldTorch System was highly efficient at removing polyatomic species from the mass spectrum. The blank organic sample spectrum is shown in Figure 2, while the good sensitivity of the 4500 system is illustrated by the addition of a 1 ppb spike (Figure 2, main spectrum). Linear calibrations were produced for the elements likely to be difficult to analyse by traditional ICP-MS. These difficulties might arise as a result of plasma interference (e.g. calcium), matrix interference (e.g. chromium), and poor ionisation (e.g. boron). In all cases, high-power cool plasma gave acceptable calibrations, which were essentially free from interference.

The on-site performance testing at EKC Technology was initiated with an

Table 2. Test Areas and Criteria

Test	Criteria	
Analytical Assessment:	Analyte Recovery	85 - 115 %, with <5 % RSD
	Detection Limits	<1 ug/L in EKC Technology material
Stability Test	Short Term	<5 % RSD per analysis
	Long Term	<10 % RSD over test period
Three Day Test		<5 % RSD per analysis
		<10 % RSD per day
		<15 % RSD over test period
Comparative Analysis	none	
Hardware Test	Down Time	<5 % down time during evaluation

Table 3. Analyte Recovery

Analyte	Na	Mg	Al	K	Ca	Cr	Mn	Fe	Ni	Cu	Zn	Pb
% Recovery from Posistrip EKC830	96	96	98	97	95	105	94	100	103	98	100	93
% Recovery from EKC265	92	101	100	96	104	95	99	96	96	98	102	9

analytical evaluation, which demonstrated that, for some sample matrices, although good analyte recoveries (Table 3) were obtained, there was a large reduction in sensitivity. This was partially expected, as a result of nebulisation efficiency and the high matrix loading, and is best illustrated by comparing the instrumental detection limits, determined by the repeat analysis of DI water, with similar limits determined by the analysis of diluted EKC265 (Table 4). Most elements were significantly affected by the presence of matrix, indicating that a large proportion of the available plasma energy was required for effective sample decomposition. Note also that these Method Detection Limits were determined in the sample matrix itself and so would be somewhat compromised by the presence of the analytes at trace levels in the sample. The matrix loading effect was not as significant in Posistrip EKC830, where the detection limits determined were very similar to those obtained from the matrix free solution. As the detection limits determined for these analytes in EKC Technology's materials were within the limits defined (<1ug/L in the original material) and good analyte recoveries were obtained, the overall analytical performance of the instrumentation was deemed to be acceptable for routine analysis.

The second section of the performance test was concerned with the system's stability, and the degree of variation apparent during both the short (each analysis) and the long (over an entire analysis run) term. The repeated analysis of a single sample indicated that, although the system gave good measurement precision for each

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individual sample, there was a noticeable drop in concentration over the first part of an analytical run. This phenomenon was initially believed to be the result of a drift in system tuning, due to matrix deposition on the ion lenses, but no trace of material was found when the ion lenses were inspected.

Increasing the uptake delay time, during which the sample is flushed through the sample introduction system prior to commencing the analytical measurement, eliminated this signal decrease, suggesting that the drift was not caused by a build up of matrix contamination. The highly invasive and solvating properties of EKC Technology's chemistries were thought to be responsible for an increased susceptibility to sample carry over, where low level contamination from previous samples was being rinsed from the system's glass surfaces during the first minutes of sample aspiration. Increasing the uptake delay time eliminated this carry-over effect, resulting in more consistent data. It is notable that the longer rinse times gave an analytical result (about 115ug/L) which was consistent with the later part of the first run, indicating that the first part of the first run was compromised due to this contamination.

The third section of the assessment, the three-day test, investigated the degree of variation in the system's response, characterised as tuning stability. Over the test period, and for each matrix of interest, it was discovered that only minimal alterations from the initial tune settings were required, and no re-tuning of the lens settings was required. The parameters that did require modification after each start-up were the torch position in the x- and y-axes, which can be controlled to 0.1mm accuracy using

the computer-controlled stepper motors. This requirement was not unexpected, as the glassware was removed and cleaned between each calibration run.

The final section of the performance test was an assessment of the hardware robustness, to ensure that no contamination of the sample introduction glassware, ion lenses and detector would occur as a result of undecomposed material being passed into the vacuum chamber of the spectrometer. No material was visible within the detector, and only minimal staining of the front-end lenses was found. This was easily removed by cleaning with DI water and propan-2-ol, and at no time has caused analysis issues or contamination problems.

Conclusion

Assessing new instrumentation and equipment, in-situ and prior to purchase, enables an evaluation to be made of the tool's routine capability. To test thoroughly any analytical equipment and to ensure its acceptability for the tasks required, EKC Technology developed the protocol detailed in this article.

The accuracy, reproducibility and stability of Agilent Technologies' 4500 ICP-MS exceeded the performance criteria set out in the testing protocol, resulting in its purchase by EKC Technology. ICP-MS has now become EKC Technology's principal method of analysis for trace contaminants in both raw materials and products, for supply to the semiconductor industry. ICP-MS has largely replaced ETAAS for routine production control purposes, due to its faster sample turn-around times and improved limits of detection for several analytes. Sample turn-around times have been reduced by 85% since introducing the Agilent 4500, the laboratory workload has been reduced by 21%, and the routine cost of analysis (instrument running costs) has been reduced by about 12%, after absorbing the initial capital expense of the instrumentation. The evaluation protocol developed by EKC Technology may not be applicable to every environment or the qualification of every analytical tool, but the principles shown and the areas detailed must, at least, be considered when assessing equipment purchases.

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For further information Enter 112

Table 4. Instrumental and Method Detection Limits

Analyte	Instrumental D.L. (µg/L)		
	DI Water	Posistrip EKC830	Method D.L. (µg/L) EKC265
Na	0.009	0.07	0.1
Mg	0.001	0.007	0.04
Al	0.002	0.009	0.2
K	0.02	0.07	0.1
Ca	0.003	0.07	0.3
Cr	0.001	0.02	0.7
Mn	0.03	0.002	0.1
Fe	0.004	0.2	0.6
Ni	0.001	0.04	0.2
Cu	0.001	0.007	0.06
Zn	0.007	0.01	0.03
Pb	0.002	0.003	0.1