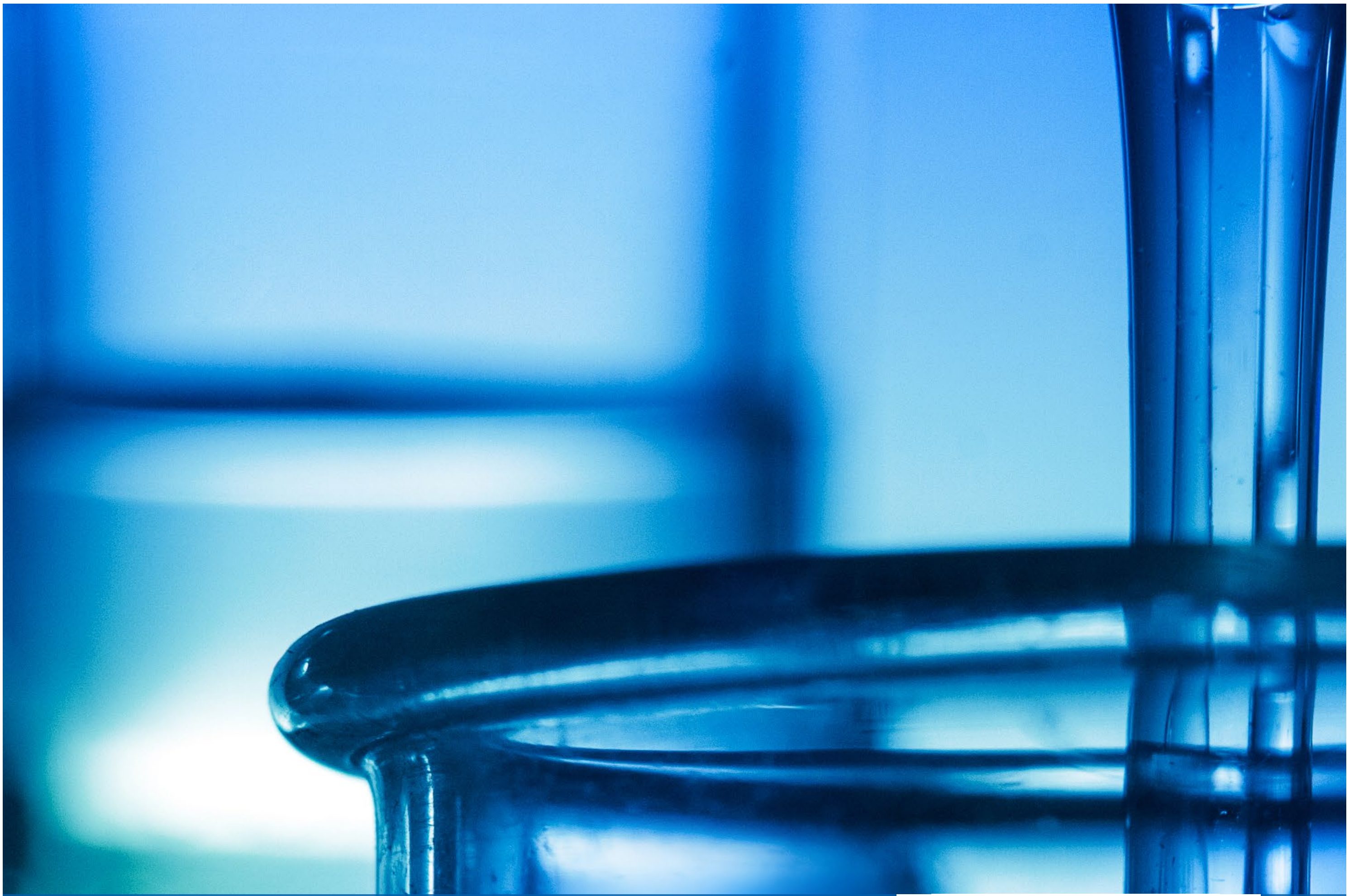

DIGEST OF
APPLICATION SPOTLIGHTS
NEXION 5000 MULTI-QUADRUPOLE ICP-MS

NEXION 5000 ICP-MS
The Industry's First and Only Four-Quadrupole ICP-MS System

PerkinElmer®
For the Better

Welcome to the application digest for PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS.

The multi-award-winning* NexION 5000 is the industry's first and only four-quadrupole ICP-MS system, engineered to remove the most complex interferences and address the most challenging applications requiring ultra-trace-level detection. The combination of its tandem four-quad design and a range of proprietary features brings its performance beyond traditional triple-quad and high-resolution ICP-MS to deliver exceptionally low background equivalent concentrations and outstanding detection limits, key to ensuring accurate, repeatable results.

*THE NEXION 5000 ICP-MS IS THE PROUD WINNER OF TWO COVETED FIRST-PLACE AWARDS FROM RESPECTED ORGANIZATIONS:

- **Wiley Analytical Science Award 2021**
- **The Analytical Scientist Innovation Award 2020**

This digest offers a selection of application spotlights across different market segments (see below Table of Contents) with the opportunity to download the full application notes.

But before diving into the applications, let's first start with a quick overview of what makes the NexION 5000 ICP-MS the ideal analytical solution for labs conducting multi-elemental analyses that require ultra-trace-level detection.

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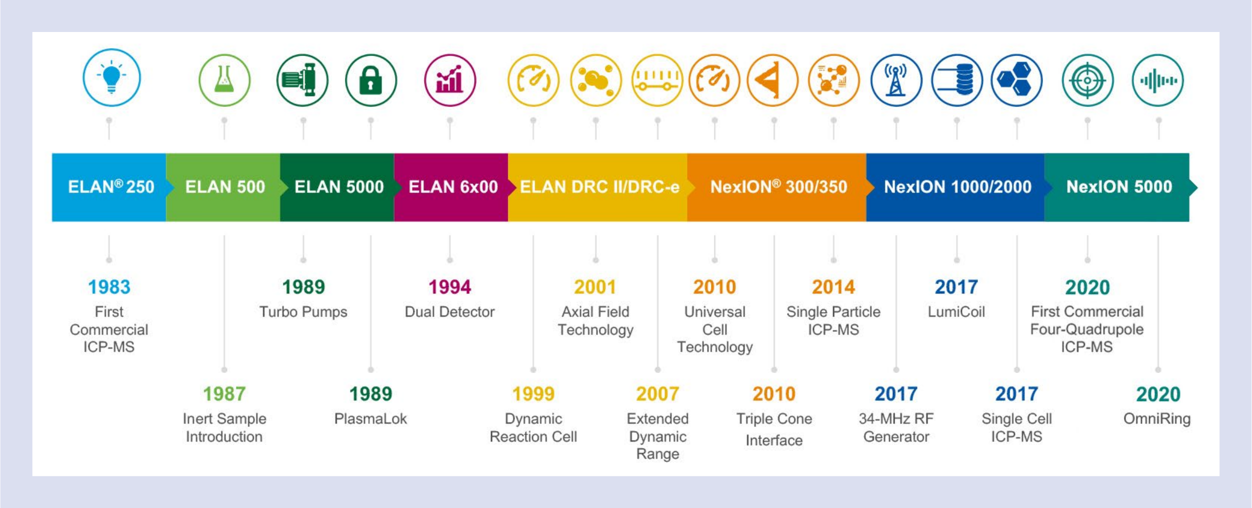


The NexION 5000 builds on a long and rich tradition of innovation in ICP-MS technology at PerkinElmer. Our ICP-MS systems have always delivered exceptional detection capabilities. But we've raised the stakes on sensitivity and performance with the NexION 5000 ICP-MS, and here are some of the features that set this system apart.

Superior Interference Removal

Unlike triple-quad systems, the NexION 5000 Multi-Quadrupole ICP-MS delivers four stages of mass resolution. The combination of its tandem four-quad design and other proprietary technologies, such as its quadrupole Universal Cell with dynamic bandpass tuning, creates an environment for the best interference removal. Plus, it boasts the added flexibility of using up to four cell reaction gases with on-the-fly gas mixing. These unique features come together to provide the most efficient spectral interference elimination, delivering parts-per-quadrillion detection limits and up to 12 orders of magnitude linear dynamic range when combined with Extended Dynamic Range.

Excellent Stability

Everything about the NexION 5000 ICP-MS says stability – for the instrument and the results. Let's start with its free-running 34-MHz RF generator. This system is the only RF generator on the market specifically designed to meet the needs of ICP-MS applications and delivers the fastest impedance matching on the market. Plus, the instrument's Triple Cone Interface with wide-aperture cones offers unparalleled resistance to clogging even in tough matrices. And finally, the ability to use pure reaction gases, such as ammonia, in its quadrupole Universal Cell creates controlled reactions for unparalleled spectral interference removal, delivering outstanding reproducibility in the results.

Unmatched Matrix Tolerance

The NexION 5000 ICP-MS is the perfect solution for testing labs requiring extremely low detection limits and background equivalent concentrations in a variety of different matrices, from aqueous to organic, from ultrapure water to high total dissolved solids. Its powerful All Matrix Solution (AMS) sample introduction system is able to deliver up to 200x dilution and support samples even with 35% TDS without needing to manually dilute. Moreover, its innovative free-running RF generator with patented LumiCoil™ technology provides accurate impedance matching to easily handle even the most difficult matrices. And last but certainly not least, the second-generation Triple Cone Interface with OmniRing™ technology provides unique solutions to space-charge effects.

Lowest Maintenance

Uptime is key to keeping labs running at peak performance, and the NexION 5000 ICP-MS eliminates almost all maintenance requirements for unsurpassed instrument uptime. First, its patented LumiCoil™ RF coil is guaranteed for life and requires no active water or gas cooling. Then, its second-generation Triple Cone Interface features a unique hyper-skimmer cone with OmniRing™ technology that produces a tightly focused ion beam. Furthermore, the interface's wide-aperture cones maximize signal stability and minimize cone clogging during extended high-TDS sample runs. And finally, the patented combination of the Triple Cone Interface and Quadrupole Ion Deflector controls and focuses the beam in the downstream ion optics, ensuring no cleaning or replacing is needed for any of the spectrometer components.

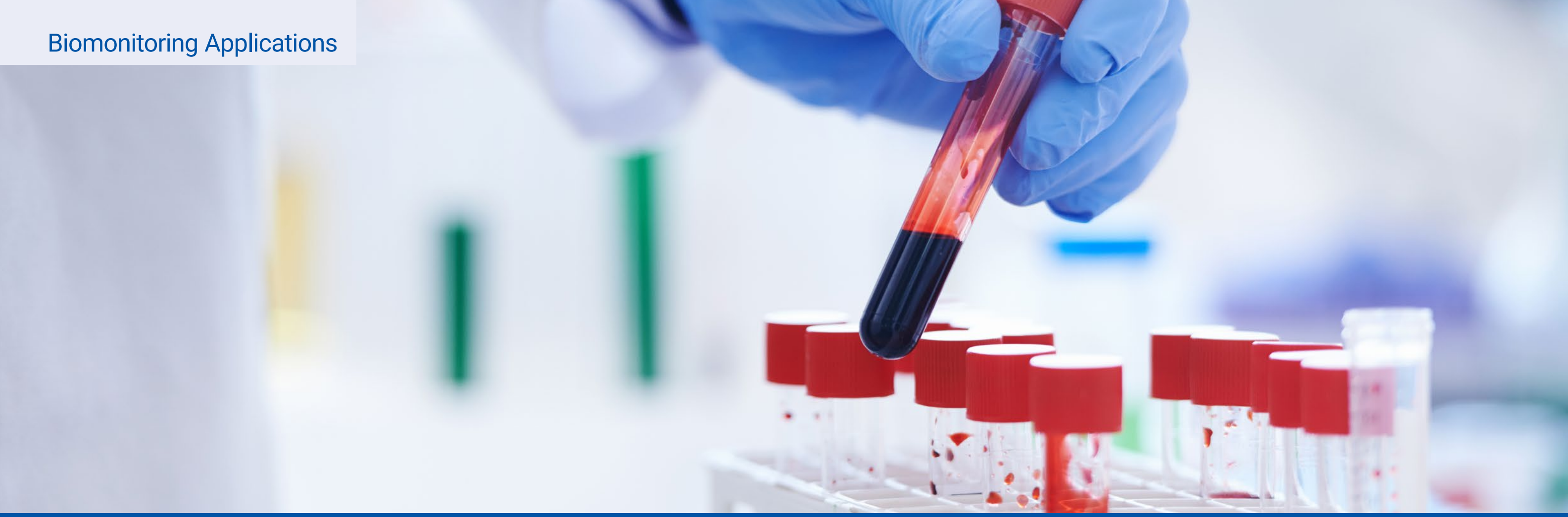
For more information on these innovative technologies, download our technical notes:

Interferences in ICP-MS: Do we still have to worry about them?

All Matrix Solution System for NexION ICP-MS Platforms

Advantages of a Novel Plasma Generator for the NexION 1000/2000/5000 ICP-MS Systems

Advantages of a Novel Interface Design for NexION 5000 ICP-MS



APPLICATION SPOTLIGHT

Analysis of Blood Using the NexION 5000 ICP-MS

The Importance of Measuring Low and High Levels of Elements in Bodily Fluids

For many years, ICP-MS has been the tool of choice for the analysis of toxic and nutritional elements in human bodily fluids and tissue samples. Historically, researchers have found correlations between these panels of elements and human diseases, metabolic disorders, environmental exposures, and nutritional deficiencies. However, owing to the increased popularity of orthopedic implants, elements like titanium (Ti) and cobalt (Co) have also been added to the list of commonly tested analytes. Although these elements are not classified as either essential or toxic, they can give medical practitioners valuable information on the implant's degradation.

Challenges of Biological Samples

Blood and serum are two common biological fluids which present challenges for trace metal analysis. Blood is a complex mixture of water, proteins, glucose, mineral salts, hormones, as well as red and white blood cells, while serum has a similar composition, but without the blood cells. This work provides a summary of an optimized analytical method using the NexION® 5000 Multi-Quadrupole ICP-MS for the rapid measurement of low and high levels of analytes in one analytical run, based upon a simple dilution of the blood sample.

Standards and Sample Preparation

To determine the accuracy of the method, three levels of a ClinChek® Blood Control reference material (normal, elevated and high) were analyzed. Sample preparation involved diluting the sample matrices 50-fold with a mixture of 0.5% HNO_3 + 0.05% Triton™ X + 0.25 mg/L gold (Au). The low concentration of nitric acid was required to keep elements stable in solution, but also to prevent precipitation of proteins and cell debris. Triton™ X was used to help rinse the spray chamber and to aid the solubilization of proteins and cell membranes, while the addition of gold aided mercury stability and washout. Internal standards (2 ppb of Rh and Ir) were also prepared in the same diluent and mixed on-line with a switching valve.

Instrumental Conditions for this Analysis

The main benefit of the multi-quadrupole capability of the NexION 5000 is the ability to reject ions that are not the analytes of interest by the Q1 quadrupole and the possibility of using not only MS/MS but also Mass Shift mode. The use of Universal Cell Technology (UCT) along with four cell gases allows the optimal conditions to be chosen for each analyte, whether it is Reaction, Collision, or Standard mode. In Reaction mode, ammonia is the most effective cell gas for eliminating the argon-, carbon- and chloride-based interferences on several elements, such as Mg, Cr, Mn, Co and others, delivering single-ppt detection limits in biological matrices. On the other hand, oxygen is the most efficient reaction gas for eliminating the metal-oxide interferences on cadmium (MoO^+) and mercury (WO^+) by changing interferences into different oxide ions. Also, O_2 reacts and creates clusters with some elements like P, As and Se, allowing the application of Mass Shift to measure those elements as oxide ions at higher masses where there are no spectral interferences. Moreover, for high mass analytes with no polyatomic interferences, Standard mode is preferred. This approach results in enhanced ease-of-use and efficient interference removal, so all analytes could be measured within a single analytical run.

Interference Management

The capabilities of the NexION 5000 technology are demonstrated below. Figure 1a shows a Q3 scan (Single Quad mode) of a 100 ppt multi-element standard from mass 75 to 92 while O_2 was introduced into the Universal Cell. In this mode, the Q1 quadrupole acts as ion guide transmitting all masses. The analyzed standard is a mixture of 50 elements including Ge, Zr. Multiple peaks from components of this standard are displayed and a peak formed by AsO^+ is present at mass 91, while in Figure 1b, the same mixed-element standard solution was scanned in Product Ion Scan mode with O_2, with Q1 set to mass 75 operating at a resolution of 0.7 amu. It shows a clean background with only two peaks – a small one at mass 75 (CoO^+ and $ArCl^+$) and a much larger one at mass 91, arsenic as AsO^+. Arsenic is measured in Mass Shift mode after a reaction with O_2 without any worry about potential interferences from Ge, Zr and Cl.

Results

Figure 2a shows normalized results to the mean values of ClinChek I, II and III CRM, which are all within the control range and also very close to the mean values. With the accuracy established, the stability of the methodology was explored next by analyzing pooled-blood samples (spiked with 2 ppb of a mixed standard) over 6.5 hours and monitoring a QC standard every 10 samples. The resultant plot shown in Figure 2b clearly demonstrates the exceptional stability of the multi-mode method and the lack of long-term drift, a direct result of the robust design of the NexION 5000 system.

Conclusion

This work has demonstrated the ability of the NexION 5000 Multi-Quadrupole ICP-MS to perform reproducible analyses of blood samples with excellent stability over long sample run times. Accurate results were attained using a method with MS/MS mode using NH_3, O_2 or no-gas and Mass Sift Mode with O_2.

Reference

Summarized from the PerkinElmer application note "Analysis of Blood Using the NexION 5000 ICP-MS" by Ewa Pruszkowski.

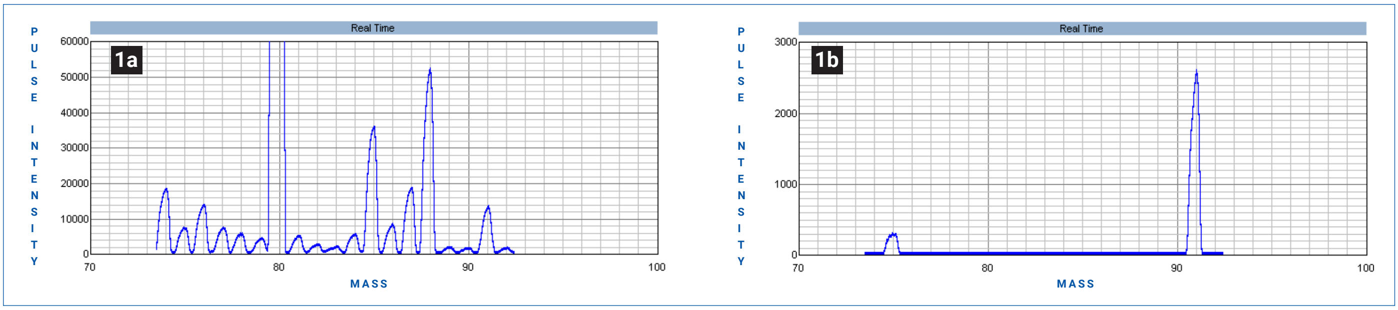


Figure 1a: Scan in Single Quad mode; and Figure 1b. Scan in Mass Shift mode using O_2.

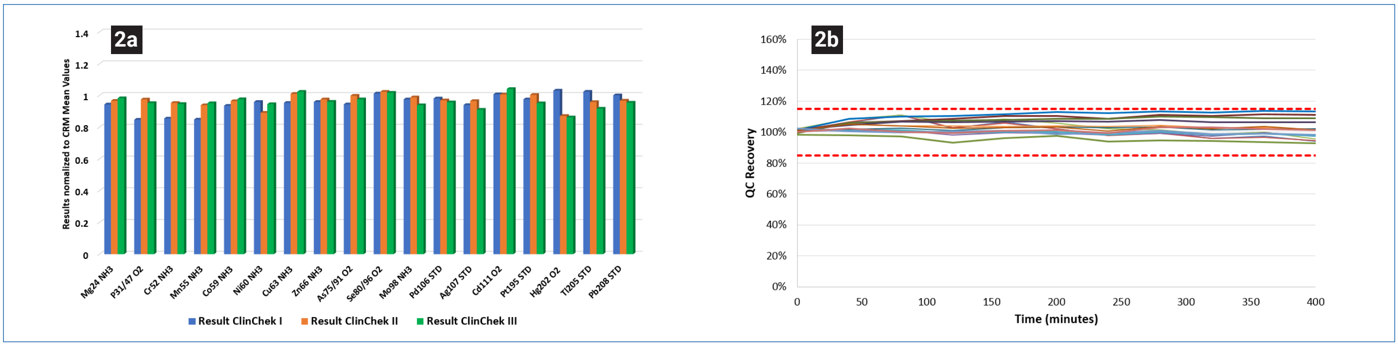


Figure 2a. ClinCheck I, II, III CRM normalized mean values for a panel of analytes using different modes; and Figure 2b. 6.5-hour stability run of the same analytes.

APPLICATION SPOTLIGHT

Analysis of Samples Rich in Rare Earth Elements Prepared by Lithium Borate Fusion on the NexION 5000 ICP-MS

The Demand for the Analysis of Rare Earth Minerals

Rare earth elements (REEs) have many uses in the advanced technology and electronics that are utilized in automobiles, airplanes, camera lenses, medical devices, televisions, smartphones, and computers. Since geological materials that contain REEs are usually only found in low concentrations, an essential component of geological exploration is the ability to accurately quantify trace levels of REEs. The measurement of REEs by ICP-MS following sample preparation using a fusion flux or acid digestion method is a widely used analytical technique. Lithium borate flux is commonly used for matrices that are very refractory and otherwise hard to digest. However, they can present some unique challenges in sample introduction and matrix effects for ICP-MS due to the increased amount of total dissolved solids (TDS). Moreover, REEs are usually present in very low concentrations, and many have isotopic and oxide overlaps that can provide additional complications.

This work describes the analysis of three certified REE reference materials (CRMs) prepared by lithium borate fusion using the NexION® 5000 Multi-Quadrupole ICP-MS. The combination of the instrument's All Matrix Solution (AMS), an online argon dilution system, second-generation Triple Cone Interface with OmniRing™ technology, four gas channels with on-line gas mixing, Universal Cell Technology (UCT), and multi-quadrupole design provides many of the outstanding tools needed to overcome these challenges.

Sample Preparation

Three CanMET CRMs (REE-1, REE-2, and REE-3) that had already undergone lithium borate fusion and subsequent dissolution in 5% HNO_3 were supplied by an external lab. An additional dilution of 100x was performed on each CRM before analysis using a diluent of 0.5 % HNO_3. The standard concentrations prepared for all samples were 0.2, 2 and 20 ppb, with the exception of Al, Ca, Fe, K, Mg, Na, and Si, which were 0.2, 2, 20, 200, and 400 ppb. In addition, 10 ppb rhodium was used as the internal standard and added via the High Throughput System (HTS) flow-injection module.

Instrumental Conditions

Multiple cell modes were used to best leverage the interference removal capabilities. Optimization of collision and reaction gas flows, dynamic bandpass filtering within the quadrupole Universal Cell and analyte mass selection for the resolving quadrupoles were all automated through Syngistix™ for ICP-MS software. The ion guide mode for all analytes was selected based on the mode which delivered the lowest background equivalent concentrations (BECs) for the analytes of interest. Depending on the interferences present on a specific analyte, the combination of pure reaction gases and multi-quad technology in the NexION 5000 ICP-MS offers superior analytical capabilities. For example, a significant advantage of multi-quadrupole instruments is the ability to mass-shift a target element by reacting with a reactive gas to a higher mass and away from interferences, resulting in potentially erroneous results. Oxygen can be used to form oxides on the target elements, shifting 16 amu higher. In contrast, gases such as pure ammonia can create cluster ions with certain elements, shifting even further up the mass range and away from potential interferences. All these reactions need to be actively controlled to prevent unwanted side reactions from taking place. The customizable dynamic bandpass tuning of the unique quadrupole UCT provides users the flexibility to actively prevent reaction by-products from forming by further reacting with the reaction gas or impurities in the gas.

Results

The recoveries of a suite of REEs and other transition and heavy metals are shown in Figure 1. It can be seen that all the generated data are within 10% of the certified values. In particular, it's worth emphasizing the conditions used for Si and P as an example of the flexibility of the Universal Cell's reaction capability. For Si, ammonia (NH_3) and hydrogen (H_2) gases are mixed online in the cell for the best interference removal of N_2 and CO on mass 28. Phosphorus, on the other hand, is monoisotopic with 100% isotopic abundance at 31 amu. However, there are interferences from N and Si on this mass (NOH^+, SiH^+ NO^+), which can typically make the analysis challenging for single quadrupole instruments. However, with multi-quadrupole ICP-MS technology and O_2 as a reaction gas, P is mass shifted to PO^+ at mass 47 and quantified free of these interferences, providing excellent CRM recoveries.

Long-term stability was also assessed with a 7-hour analysis of the lithium borate fusion samples. The stability run consisted of multiple analyses of each CRM, repeated in sequence, as well as matrix blanks and simulated samples in the same fusion matrix, to demonstrate the effect of analyzing samples with high total dissolved solids (TDS) on the sample introduction and components of the NexION 5000's interface region.

The 10 ppb rhodium internal standard recoveries relative to the calibration blank were monitored and are shown in Figure 2. All recoveries were within 20% of the true value, further validating the robustness of the method and analytical instrumentation.

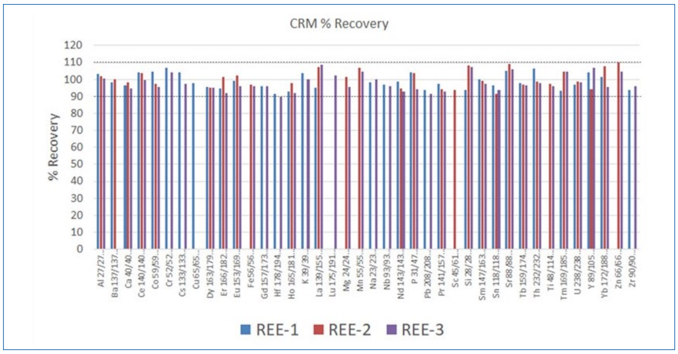


Figure 1. Analyte recoveries in CanMET certified reference materials REE-1, REE-2, and REE-3.

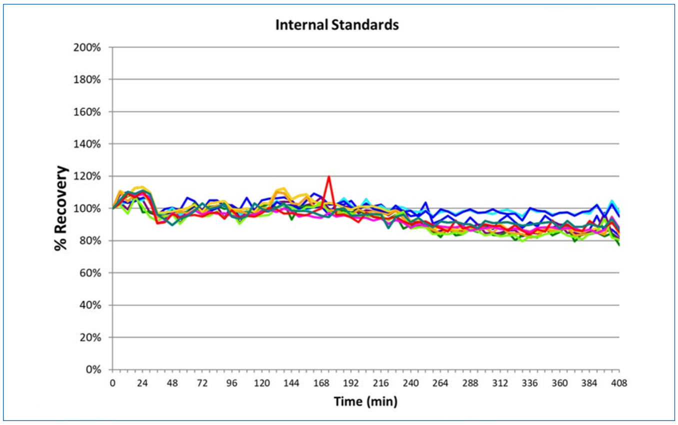


Figure 2. Long-term stability based on internal standard (Rh) measured over 7-hour run with multiple gas modes.

Conclusion

This work demonstrates the outstanding accuracy and long-term stability of REEs and other elements of interest in complex geological samples using the NexION 5000 Multi-Quadrupole ICP-MS system. In addition, superior interference removal was achieved on all analytes of interest by controlling the ions and the reactions within the cell. Furthermore, having four gas channels enabled maximum specificity in the reaction chemistry such that the most effective single or mixed reaction gases could be used without compromise for each of the analytes.

Reference

Summarized from the PerkinElmer application note "Analysis of Samples Rich in Rare Earth Elements Prepared by Lithium Borate Fusion on the NexION 5000 ICP-MS" by Andrew Rams.

APPLICATION SPOTLIGHT

Determination of Impurities in Lithium Materials with the NexION 5000 ICP-MS

The Importance of Measuring Impurities in Lithium Salts

One of the most common uses of lithium (Li) is in the manufacture of batteries found in electric vehicles, computers, cell phones, and many other portable electronic devices. With the demand for higher-capacity batteries with longer lifetimes, current battery production technology requires better control of the raw materials used and their physical properties. For example, lithium salts are commonly refined from a highly concentrated solution of NaCl, which must be removed since excess sodium can lead to battery overheating. Therefore, the capability to identify the presence of impurities in lithium battery materials is critical to ensure that the final battery performance is not compromised.

Although there is no industry standard yet for the purity of Li salts required in battery production, the purity requirements from many manufacturers have risen from 99% to 99.9% and can become even more stringent in the future. This work describes the analysis of four Li salts for 50 elemental impurities using the NexION® 5000 Multi-Quadrupole ICP-MS configured with a High Throughput System (HTS), a valve-and-loop system that minimizes both sample uptake and washout times, coupled with an autosampler for automated sample introduction.

Sample Preparation

250 mg of each tested Li salt was weighed accurately and combined with 50 mL 1% nitric acid (v/v). The samples were allowed to degas for an hour and then diluted 100x with 1% nitric acid for analysis. Each sample was prepared in triplicate to assess both robustness and reproducibility. All measurements were made against external calibration curves, with standards prepared in 1% nitric acid.

Results and Discussion

During the analysis of high-purity materials, both the matrix elements and impurities may need to be measured. However, there are analytical challenges associated with the measurements of both major and minor elements in one method since their concentrations are very different. Moreover, analysis of matrix elements without additional dilution could lead to saturation of the detector. However, in the NexION series of ICP-MS instruments, the signal of user-selected masses can be selectively attenuated in the Universal Cell using the quadrupole DC voltage rejection parameter (RPa). It can be applied to a single mass without affecting the other masses in the method or requiring an additional internal standard. In this work, RPa was optimized for both ^{6}Li and ^{7}Li, to ensure that all analytes in the standards and samples were measured at the same stage of the detector. Table 1 shows the lithium results from three separate sample preparations of lithium carbonate, showing that the mean results of the three samples are within 0.1% for ^{6}Li and ^{7}Li, confirming the high accuracy of the method.

With the accuracy of Li analysis established, the impurity measurements in the four different Li samples were carried out. Impurity levels in 99% Li salts were traditionally measured by ICP-OES, and as a result, elemental analysis was limited to a small handful of elements including Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn. However, purity requirements changed with battery manufacturers demanding a minimum of 99.9% purity and a more comprehensive panel of elements. For that reason, the four Li salts were analyzed for 50 elemental impurities using a combination of MS/MS, Mass Shift and Standard modes with pure ammonia (NH_3) and oxygen (O_2) as reaction gases. Table 2 shows the total impurity concentrations of all 50 elements, together with the % purity of the four different Li salts.

Table 1: Results from analysis of three separate preparations of Li carbonate (99.998%).

Sample Number	^{6}Li Lithium Carbonate (%)	^{7}Li Lithium Carbonate (%)
1	19.00	18.64
2	18.31	18.88
3	18.53	18.61
Mean	18.61	18.71
STD	0.35	0.15
RSD	1.89	0.80

Table 2: Total impurity concentrations of 50 elements, together with the % purity of the four different Li salts.

	Impurity (µg/g)			
Analyte	LiOH 98%	LiOH 99.995%	Li_2CO_3 99%	Li_2CO_3 99.998%
Impurity (µg/g)	1653.904	77.054	595.694	51.337
% Impurity	0.1654%	0.0077%	0.0596%	0.0051%
% Purity	99.8346%	99.9923%	99.9404%	99.9949%

When measuring impurities in Li compounds, sodium (Na) and sulfur (S) are critically important elements, because high impurity levels lead to reduced battery life and possible explosive events. The challenge when analyzing trace Na in a Li matrix using ICP-MS is the lithium oxide (LiO) interference which occurs at the same mass of Na at mass 23. Since Na is monoisotopic, there are no alternative masses which can be used. However, on the NexION 5000 ICP-MS, the LiO^+ interference is removed by reacting it with 100% ammonia in the Universal Cell, resulting in neutral LiO particles, which are no longer detected at mass 23. Sodium ions do not react with ammonia; therefore, they can be analyzed in MS/MS mode at mass 23.

Sulfur is another difficult element to measure with ICP-MS as all isotopes occur at the same masses as O_2^+ interference. However, S^+ reacts with O_2 to form SO^+ at mass 48. Therefore, by adding O_2 to the Universal Cell, S^+ is readily converted to SO^+. Unfortunately, titanium (Ti) and calcium (Ca) isotopes also exist at mass 48. Because Ti^+ reacts rapidly with O_2 to create TiO^+, it does not interfere with SO^+. However, Ca^+ does not react with O_2 and will interfere with SO^+. In single quadrupole instruments, a correction equation must be applied to compensate for the Ca interferences at 48. However, this can be overcome with the NexION 5000 by setting the first resolving quad (Q1) to mass 32, allowing only O_2^+ and S^+ to pass into the Universal Cell, removing Ca. The sulfur then reacts with oxygen to form SO^+, and the second resolving quad (Q3) is set to mass 48, so that only SO^+ reaches the detector. For that reason, there is no need for correction equations as neither ^{48}Ti nor ^{48}Ca make it past Q1.

Conclusion

Lithium batteries are an important commodity in today's world, and the demand for longer life and higher efficiency will only increase as the world turns away from fossil fuels. Li salts used in the production of batteries are typically extracted from brines and, subsequently, have high impurity levels. The purity of these salts can impact battery lifetime, stability and efficiency, pushing the need for higher purity levels in these raw materials. In this study, we have shown that as the purity of Li salts increases, it becomes necessary to analyze more than just a few traditional impurity elements. For this analysis, the NexION 5000 ICP-MS offers outstanding detection limits and interference removal capabilities thanks to the combination of its multi-quadrupole technology and other proprietary features.

Reference

Summarized from the PerkinElmer application note "Determination of Impurities in Lithium Materials with the NexION 5000 ICP-MS" by Ruth Merrifield.

Download Full Application Note

APPLICATION SPOTLIGHT

Determination of Trace Rare Earth Impurities in High-Purity Europium Oxide Using the NexION 5000 ICP-MS

The Demand for Rare Earth Materials

Rare earth elements (REEs) play an extremely important role in today's high-tech photoelectromagnetic industry, including luminescent phosphors and powders, crystalline materials, optical fibers, optical glass, as well as for use in high-tech fields of electronic and magnetostrictive applications. As an example, high-purity europium oxide (Eu_2O_3) is used to make energy-saving lamp and self-luminous powders for today's high-definition displays (HDP), which require higher purity materials with smaller particle size.

Analytical Challenges

Generally, REE matrices have to be preprocessed before ICP-OES and ICP-MS measurements to separate analytes from the matrix causing spectral interferences. For example, in the measurement of ultra-trace REE in Eu_2O_3, direct determination of thulium (Tm), a mono-isotopic element at mass 169, is challenging by ICP-MS due to the interference of $^{153}Eu^{16}O^+$. However, in this work, the NexION® 5000 Multi-Quadrupole ICP-MS is used for the direct determination without any preprocessing of 14 trace rare earth impurities in high-purity Eu_2O_3 by eliminating matrix-based interferences.

Unique Capabilities of the NexION 5000 ICP-MS for this Application

The NexION 5000's quadrupole-based Universal Cell controls reaction chemistry within the cell when pressurizing with a reaction gas. This is achieved by applying dynamic bandpass tuning within the cell, preventing by-products of the original reaction from forming new interferences. The reaction cell's bandpass allows predictable and reproducible interference removal using either 100% pure or a mixture of highly reactive gases in the cell. In addition, the instrument provides four gas channels, which allows on-the-fly gas mixing of reaction and/or collision gases within the same analytical method, delivering ultimate flexibility in removing interferences. In this work, reaction gases (NH_3, O_2) were used to remove spectral interferences by changing them into atoms or ions of a different mass or creating a cluster ion with an analyte (Mass Shift). 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.

Results and Discussion

For the analysis of trace rare earth impurities in high-purity Eu_2O_3 the most challenging REE to measure is Tm. It has only one isotope at mass 169, which has a direct interference from $^{153}Eu^{16}O^+$. Mass Shift mode with O_2 does not effectively remove the EuO^+ interference on Tm^+. However, MS/MS mode with NH_3 can be used to remove $^{153}Eu^{16}O^+$ interferences on Tm due to high EuO^+ reactivity with NH_3. Gadolinium (Gd) in Eu_2O_3 was also investigated in this study. Unlike EuO^+, Gd^+ reacts with NH_3 very inefficiently, and was therefore measured on mass in MS/MS mode with NH_3. For comparison, all the REEs were measured also in Standard mode and Mass Shift mode with O_2 except Tm, which was measured in Standard mode only. In Mass Shift mode with O_2, the Q3 mass is set 16 amu higher than the Q1 mass. All the REEs can react with the oxygen but with variable efficiencies forming MO^+. The results are shown in Figure 1.The values of Tm and Gd measured in MS/MS mode with NH_3 gas were lower than in Mass Shift mode with O_2. Other REE values were equivalent to Standard mode and Mass Shift mode with O_2; therefore, as a result, they were measured in Standard mode. It also confirmed that the other REEs had no interferences in the 500 ppm Eu_2O_3.

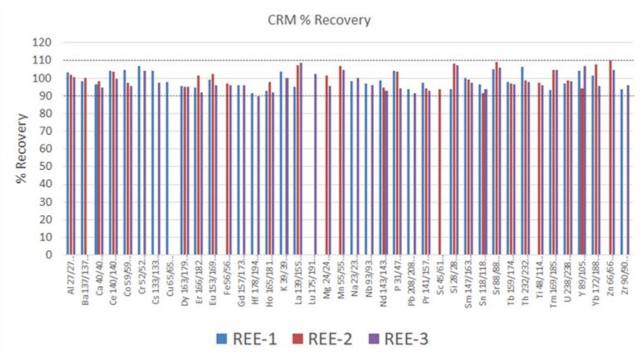


Figure 1. Measured concentrations of REE impurities in 500 ppm Eu_2O_3, showing that the values of Tm and Gd by MS/MS mode with NH_3 gas were lower than by Mass Shift mode with O_2.

The results of 14 REE impurities in high-purity Eu_2O_3 are listed in Table 1. Note: yttrium (Y) has no spectral interference in high-purity Eu_2O_3, so the relatively high value may be the result of contamination of Y from the manufacturer's other products. When the yttrium contamination is controlled, the NexION 5000 ICP-MS can seamlessly measure a suite of rare earths in 99.9999% ultra-high purity Eu_2O_3.

Table 1: Results of REE impurities in Eu_2O_3.

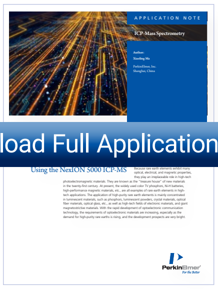
Element	Q1	Q3	Mode	Concentration (ng/L)	Content (µg/g)
La	139	139	Standard	52.8	0.11
Ce	140	140	Standard	9.58	0.02
Pr	141	141	Standard	14.2	0.03
Nd	142	142	Standard	35.9	0.07
Sm	147	147	Standard	12.1	0.02
Gd	157	157	Ammonia	116	0.23
Tb	159	159	Standard	73.1	0.15
Dy	163	163	Standard	13.9	0.03
Ho	165	165	Standard	5.24	0.01
Er	166	166	Standard	20.4	0.04
Tm	169	169	Ammonia	16.2	0.03
Yb	174	174	Standard	19.4	0.04
Lu	175	175	Standard	26.0	0.03
Y*	89	89	Standard	875.4	1.7

Conclusion

The results presented in this work demonstrate the analysis of 14 REEs in high-purity europium oxide. The interference of EuO^+ on the mono-isotopic element Tm was dramatically reduced by using 100% NH_3. Moreover, the outstanding analytical performance of the NexION 5000 Multi-Quadrupole ICP-MS was made possible thanks to the unique 34-MHz RF plasma generator with LumiCoil RF load coil and the Universal Cell with its ability to use a 100% pure reactive gas.

Reference

Summarized from the PerkinElmer application note "Direct Determination of Trace Rare Earth Impurities in High-Purity Europium Oxide Using the NexION 5000 ICP-MS" by Xiaoling Ma.



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APPLICATION SPOTLIGHT

Direct Determination of Trace Rare Earth Impurities in High-Purity Praseodymium Oxide Using the NexION 5000 ICP-MS

The Importance of Measuring Impurities in High Purity Rare Earths

Rare earth elements (REEs) are widely used in a variety of traditional industrial fields, such as metallurgy, ceramics, textiles, as well as in novel materials, such as permanent magnets, hydrogen storage alloys and catalysts. Moreover, the purity of the REE material is of critical importance, as this can have a direct impact upon the end product's quality, performance and yields. A particularly important application is the use of high-purity praseodymium oxide (Pr_6O_{11}) in optoelectronic communication technology used in the production of crystal materials and optical glasses.

However, one of the biggest challenges in the analysis of impurities in purified REE compounds, such as Pr_6O_{11}, is that the impurities are often present at extremely low concentrations. For this reason, multi-quadrupole ICP-MS has become the technique of choice for the measurement of very low impurity levels in REE compounds.

Even though the capability of interference reduction such as MO^+, MOH^+, MH^+, MOH_2^+ is possible with triple-quad systems, pure reaction gases and a quadruple-based reaction cell (UCT) in the NexION® 5000 ICP-MS facilitate fast and complete removal of such interferences.

In this work, the NexION 5000 Multi-Quadrupole ICP-MS was used for the direct determination of trace REE impurities in a high-purity Pr_6O_{11} matrix. Fourteen REE impurities were analyzed using multi-quad technology combined with gas reactions in the UCT for detection at ultra-trace levels.

Experimental

Approximately 0.100 g of Pr_6O_{11} was weighed into a 100 mL PFA bottle followed by 10 mL 2% HNO_3 to dissolve it at room temperature and then diluted to 50 mL. with 2% HNO_3.

The method of standard addition (MSA) was used for the analysis of 14 REEs in the high-purity Pr_6O_{11} sample solution. MSA calibration standards were prepared from a 10 ppm Multi-Element Rare Earth Element Standard. Calibration standard solutions were prepared at concentrations of 20, 100, and 500 ng/L in solutions of 500 ppm Pr_6O_{11}. Rhenium was used as internal standard and added on-line to all standards and samples.

Instrumentation

The PerkinElmer NexION 5000 Multi-Quadrupole ICP-MS (cleanroom model) was used for all analyses. Reaction gases (NH_3 and O_2) were used in the Universal Cell to assist in the removal of interferences, along with dynamic bandpass tuning to actively prevent new interferences from forming in the cell. Since most of the REEs readily react with the oxygen to form MO^+, oxygen was used as the reaction gas in many cases, whereas some analytes were measured with pure ammonia. Both MS/MS and Mass Shift modes were used. In MS/MS mode, Q1 and Q3 are set to the same mass, and the interference reacts with the reaction gas. In Mass Shift mode, Q1 and Q3 are set to different masses where the 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 in the cell.

Results and Discussion

The concentrations measured in Standard mode and Mass Shift mode with the reaction gas (O_2 or NH_3) were very similar for La, Ce, Nd, Sm, Eu, Dy, Ho, Er, Tm, Lu, and Y. Since both modes produced comparable results, it was concluded that there were no significant interferences from 500 ppm of Pr_6O_{11} matrix on these elements, so Standard mode was used for their analysis. The recoveries for all the REEs are shown in Figure 1.

However, the most challenging REE to measure in this matrix is terbium (Tb) because it is monoisotopic, having only one isotope at mass 159 which has a direct interference from $^{141}Pr^{16}OH_2^+$, resulting in an apparent concentration of almost 5000 ppt Tb in 500 ppm Pr_6O_{11} when measured in Standard mode, as shown in Figure 1. Figure 2a shows an overlay of a product ion scan in Mass Shift mode with O_2 for a 500 ppm Pr_6O_{11} sample solution both unspiked and spiked with 500 ppt Tb. The spectrum of the spike solution has a clear peak at mass 175, while the unspiked solution does not have the peak signifying that Tb^+ is transformed to TbO^+, and $^{141}Pr^{16}OH_2^+$ does not react effectively with oxygen. Figure 2b shows an overlay of a product ion scan in Mass Shift mode with NH_3 for 500 ppm Pr_6O_{11}, both unspiked and spiked with 500 ppt Tb. It can be seen from the spectrum that the spike solution has a clear peak at mass 242, while the sample solution is flat, which means that Tb^+ is transformed to $TbNH(NH_3)_4^+$, and $^{141}Pr^{16}OH_2^+$ does not react effectively with NH_3. Therefore, the effect of the interference can be reduced dramatically with Mass Shift mode using O_2 or NH_3, with the lowest values being achieved when using NH_3 as a reaction gas, which delivers significantly lower BECs.

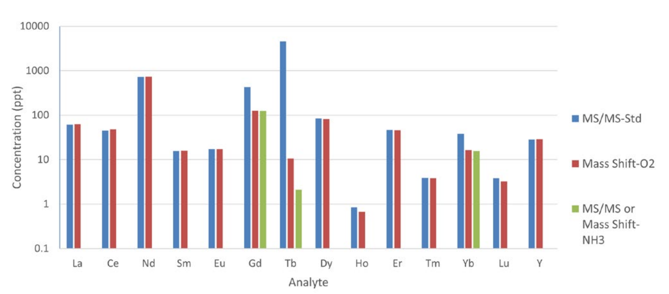

Figure 1. Concentration of REE impurities (ppt) in 500 ppm Pr_6O_{11} utilizing different modes of operation and with different reaction gases.

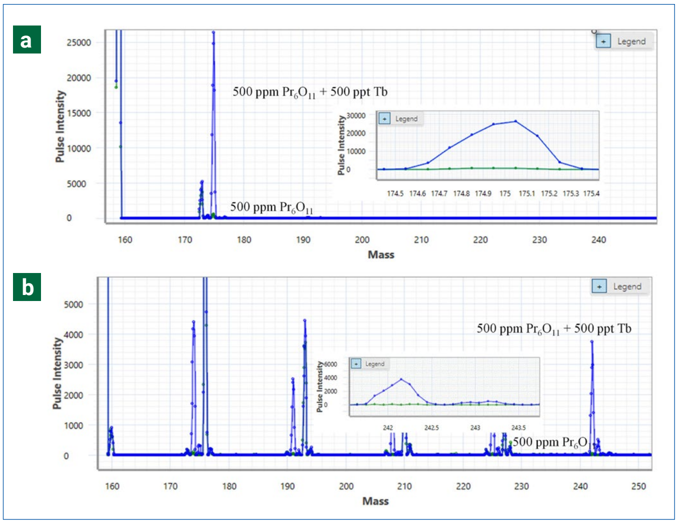

Figure 2. (a) Mass spectrum for 500 ppm Pr_6O_{11} with and without 500 ppt Tb in Mass Shift mode with O_2; (b) Mass spectrum for 500 ppm Pr_6O_{11} with and without 500 ppt Tb in Mass Shift mode with NH_3.

Conclusion

The results presented in this work demonstrate the ability of the NexION 5000 Multi-Quadrupole ICP-MS to accurately and directly measure 14 ultra-trace REE impurities in a high-purity Pr_6O_{11} matrix. Using a combination of the true quadrupole Universal Cell, multi-quadrupole technology and pure NH_3 reaction gas, the Pr polyatomic interferences on Gd, Yb, and Tb were eliminated, ensuring accurate results.

During the analysis, elements which were not thought to have an interference on them were analyzed in Standard mode. These assumptions were validated by analyzing the element in Mass Shift mode with O_2. Since no significant differences in the concentrations between Standard and Mass Shift modes were observed, these elements were analyzed in Standard mode.

Reference

Summarized from the PerkinElmer application note "Direct Determination of Trace Rare Earth Impurities in High-Purity Praseodymium Oxide with the NexION 5000 ICP-MS" by Xiaoling Ma.

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APPLICATION SPOTLIGHT

Determination of Bromine in Ultra-High-Purity Copper Using the NexION 5000 ICP-MS

The Importance of Measuring Bromine in High-Purity Copper

Ultra-pure copper (Cu)wire is widely used in integrated circuit boards as well as for audio device cables because of its high electrical and thermal conductivity, strong corrosion resistance, and excellent workability. However, the presence of impurities, such as bromine (Br), will reduce its performance to varying degrees and is a limiting factor on the material's quality. Bromine has two naturally occurring isotopes at masses 79 and 81, both of which suffer from copper oxide spectral interferences. In addition, the low ionization efficiency of Br (5%) makes the determination of bromine in copper extremely challenging. This work describes the capabilities of the NexION® 5000 Multi-Quadrupole ICP-MS to effectively remove oxide interferences using hydrogen as a reaction gas, prevent additional interferences from forming, and accurately quantify trace impurities of Br in 99.999% ultra-high-purity copper.

Interference Management

Although Br has two isotopes at ^{81}Br and ^{79}Br which can be used for quantitation, ^{81}Br has interferences from $^{65}Cu^{16}O^+$, $^{63}Cu^{16}OH_2^+$ and $^{40}Ar_2H^+$. However, the latter two interferences do not react with H_2 reaction gas, and as a result would not be removed, making low-level Br determinations at this mass more challenging. Therefore, ^{79}Br is the preferred mass for analysis, but in order to remove the oxide interference, high-purity hydrogen (99.9999%) was used as a reaction gas to mass shift the $^{63}Cu^{16}O^+$ interference to $^{63}Cu^{16}OH_2^+$ away from the $^{79}Br^+$ and an RPq rejection parameter was applied in the Universal Cell to prevent any further side reactions from taking place.

Method Development

As part of the initial method development, an automated optimization routine in the software was run, which allows the conditions for the lowest background equivalent concentration (BEC) for the analyte of interest to be obtained. Using H_2 as a reaction gas, an automated cell gas optimization was used to identify the optimal cell gas flow which delivered the best BECs for ^{79}Br.

The second part of the method development was to carry out an assessment of the copper oxide interferences on bromine at mass 79. Figures 1a and 1b show a product ion scan for a pure Cu sample solution and a Cu solution which has been spiked with 37.5 ppb Br, where Q1 was set to mass 79 which eliminates all other masses except ^{79}Br and the ^{63}Cu^{16}O interference. Q3 was then set to scan the product ion formation from mass 79-83. As can be seen in the product ion mass spectrum, the CuO interference, which would otherwise have shown a significant signal on mass 79, is mass shifted during the reaction with H_2 away to mass 81. This reaction proceeds rapidly, as evidenced by the disappearance of CuO^+ at mass 79 and formation of $CuOH_2^+$ at mass 81. Figure 1a, demonstrates that the $^{63}Cu^{16}O^+$ is completely eliminated with the use of H_2 in the cell. The same experiment was repeated, except the copper solution was spiked with Br and a product ion scan was carried out at masses 79-83, as shown in Figure 1b. Compared to Figure 1a, a peak is seen at mass 79, which is due to $^{79}Br^+$.

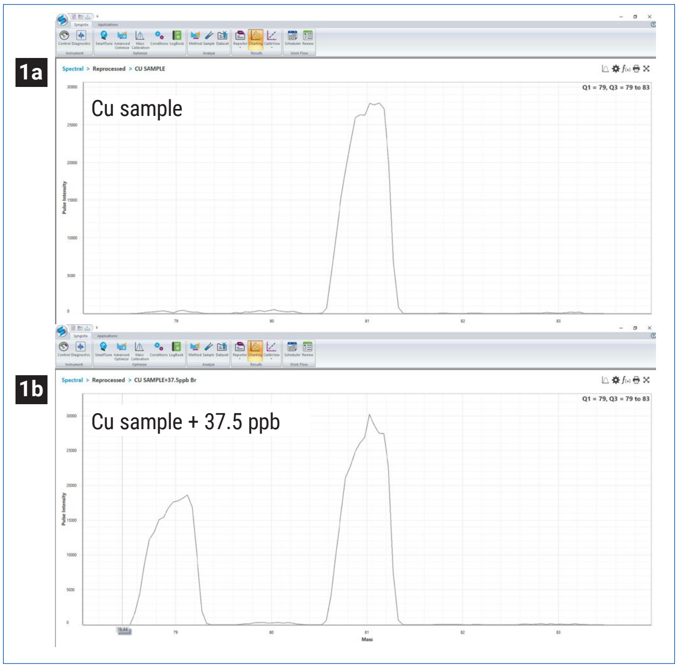

Figure 1a. Mass spectrum for Cu in H_2 Reaction mode; and Figure 1b. Spectrum for Cu spiked with 37.5 ppb Br in H_2 Reaction mode.

Results

Using these instrumental conditions and the method of standard addition, Br was measured in a 1000 ppm high-purity copper solution and was found to be present at concentrations of 0.122 µg/g. To validate these findings, a spike recovery of 10 µg/L Br was evaluated and determined to be 102%. Figure 2 shows the calibration curve for ^{79}Br in the concentrated copper solution which demonstrates excellent linearity across the defined range (r^2=0.9998).

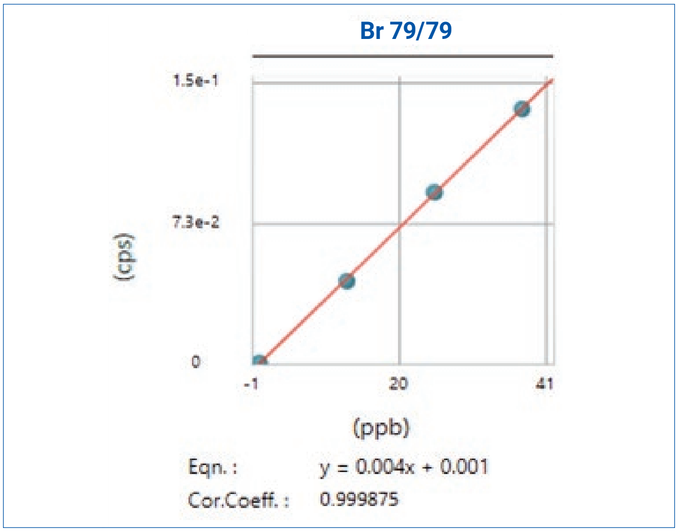

Figure 2. Method of standard addition calibration curve for ^{79}Br.

Conclusion

This work demonstrates the ability of the NexION 5000 Multi-Quadrupole ICP-MS to determine low-concentration Br impurities in an ultra-pure copper material by removing oxide interferences on ^{79}Br with pure H_2 as a reaction gas. The generated analytical results were both accurate and repeatable.

Reference

Summarized from the PerkinElmer application note "Determination of Bromine in Ultra High-Purity Copper Using the NexION 5000 ICP-MS" by Xiaoling Ma.

APPLICATION SPOTLIGHT

Measurement of Impurities in High-Purity Copper Concentrate Using the NexION 5000 ICP-MS

The Importance of Measuring Impurities in Copper Ores

The processing of copper (Cu) ores and concentrates can be influenced by the presence of minor valuable metals, such as nickel, cobalt, silver, gold, palladium, and platinum, as well as other deleterious elements, such as arsenic, lead and uranium. Most of the copper concentrates produced around the world contain some impurities, which can affect the price as copper concentrates containing high levels of impurities are not accepted by some smelters. This can render them unsaleable in some countries, as in the case for the high-arsenic-containing concentrates from the Pacific Rim. To permit treatment and to maximize the value of a copper concentrate, the levels of impurities in the concentrate need to be reduced below the limits set by the smelters and, in some cases, the authorities in the producing and receiving countries.

Challenges of Analyzing Copper Concentrates by ICP-MS

To measure the lowest possible levels of impurities in copper concentrates by ICP-MS, the technique must be capable of accurate measurements in the parts per trillion (ppt) range. However, to achieve these levels, both polyatomic and doubly-charged interferences must be minimized. These interferences originate from the plasma and the sample matrix. In this study, we describe the challenges encountered in analyzing impurities in copper concentrate, and in particular comparing accuracy and precision for external calibration versus the method of standard addition (MSA). Moreover, the study also emphasizes the importance of using ammonia and oxygen as reaction gases for this application.

Instrumental Conditions for Copper Matrices

For this analysis, the NexION® 5000 Multi-Quadrupole ICP-MS was used in a variety of different modes. The OmniRing™ technology in combination with the hyper-skimmer cone, a component of the second-generation Triple Cone Interface, was set to Extraction or Focusing modes, depending upon the element of interest. Three different scan types were used to obtain the best results for the different analytes: Single Quad (Q3), MS/MS and Mass Shift; the latter two modes were used with different reaction gases in the Universal Cell (UCT) because the high Cu matrix has the potential for creating new interferences. Some of these would be formed in the plasma, while others may be formed in the cell with the reaction gas that is being used. Table 1 shows all the potential interferences and which analytes may be affected.

The UCT Advantage for Copper Matrices

In a conventional triple-quad system where the interference is formed in the plasma and has the same mass as the analyte of interest, both the interferent and analyte will pass through Q1 and into the cell. Collision or Reaction mode will then be used to remove the interference or mass shift the analyte to a different mass. However, there is the potential for unwanted side reactions to take place and new interferences to form from the reaction gases and impurities in the reaction gas. This is not a problem for the interference removal capabilities of the NexION 5000's UCT because a bandpass of the true scanning quadrupole can be applied to prevent new interferences from forming in the cell by not only controlling the ions which enter the cell but also controlling the side reactions within the cell.

Table 1: Potential polyatomic interferences on a suite of elements in a copper-rich matrix.

Element	Possible Interference	Scan Type	Cell Gas	Q1 (amu)	Q3 (amu)
Ag		Q3			109
Al	N_2 spread	MS/MS	Ammonia	27	27
As	$^{40}Ar^{35}Cl$, $^{59}Co^{16}O^+$, $^{12}C^{31}P^{16}O_2^+$	Mass Shift	Oxygen	75	91
Au		Q3			197
Bi		MS/MS		209	209
Cd		Q3			111
Co	$^{24}Mg^{35}Cl^+$	MS/MS	Ammonia	59	59
Cr	$^{40}Ar^{12}C^+$ $^{35}Cl^{16}OH^+$	MS/MS	Ammonia	52	52
Fe	$^{40}Ar^{16}O^+$, $^{40}Ca^{16}O^+$, $^{28}Si_2^+$	MS/MS	Ammonia	56	56
Ir		Q3	Ammonia		193
Mg	$^{12}C_2^+$	MS/MS	Ammonia	24	24
Mn	$^{40}Ar^{14}NH$	MS/MS	Ammonia	55	55
Na		MS/MS	Ammonia	23	23
Ni	$^{44}Ca^{16}O^+$, $^{43}Ca^{16}OH^+$, $^{44}Ca^{16}O^+$, $^{23}Na^{37}Cl^+$, $^{25}Mg^{35}Cl^+$	MS/MS	Oxygen	60	60
P	$^{63}Cu^{++}$, $^{14}N^{16}OH^+$	Mass Shift		31	47
Pb	$^{190}Pt^{16}O^+$	Q3			208
Pd	$^{40}Ar^{65}Cu^+$, $^{36}Ar_2{}^{16}O^{17}O^+$	Q3			106
Pt		Q3	Ammonia		195
Rh	$^{40}Ar^{63}Cu^+$	MS/MS	Ammonia	103	103
Ru	$^{36}Ar^{63}Cu^+$	MS/MS	Ammonia	104	104
Sb	$^{61}Ni^{37}Cl^+$	MS/MS	Oxygen	121	121
Se	$^{40}Ar^{38}Ar^+$, $^{63}Cu^{17}O^+$, $^{65}Cu^{170+}$, $^{62}Ni^{16}O^+$ $^{46}Ca^{16}O_2^+$	Mass Shift	Ammonia	78	94
Si	$^{14}N_2^+$, $^{12}C^{16}O^+$	MS/MS		28	28
Te		MS/MS	Ammonia	130	130
Zn	$^{40}Ar^{14}N_2^+$, $^{40}Ar^{12}C^{16}O^+$, $^{63}CuH^{3+}$, $^{52}Cr^{16}O^+$	MS/MS		68	68

A mechanism for the removal of the $^{63}Cu^{40}Ar^+$ interference on $^{103}Rh^+$ using NH_3 is exemplified in Figures 1a-1d. Pure ammonia (at 100%) is an ideal reaction gas to remove the $CuAr^+$ interference on Rh due to its fast reaction with $CuAr^+$ and slow reaction with Rh^+.

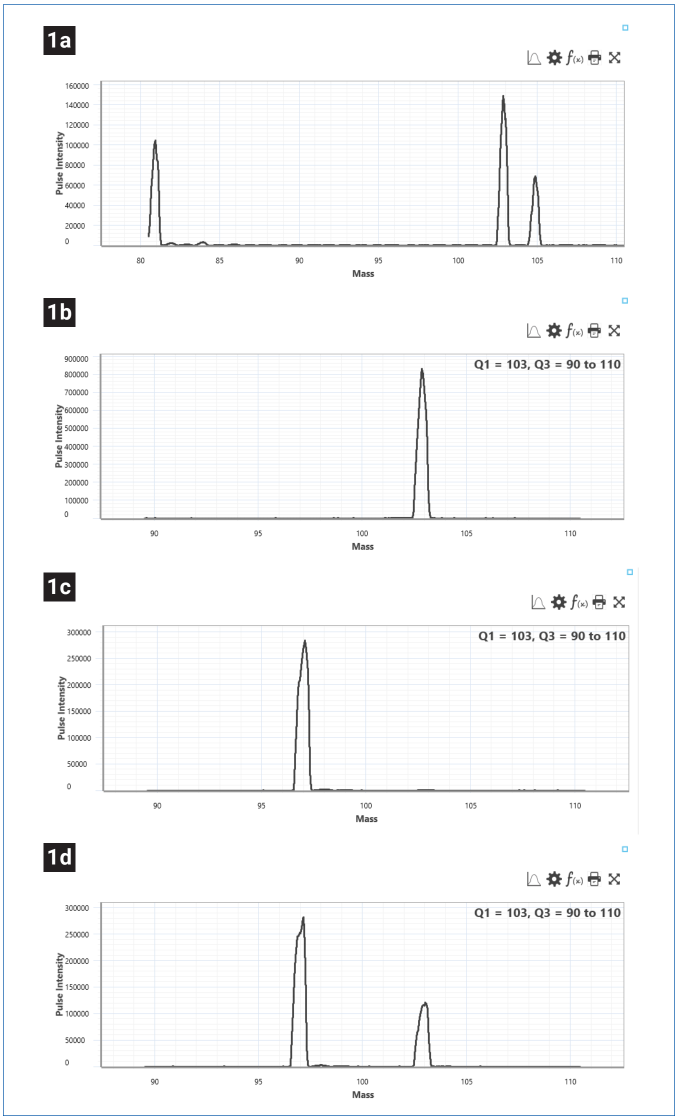

Figure 1. Mechanism of removing spectral interferences on Rh: (a) Product Ion scan of 1 ppm Cu solution in Q3 only mode; (b) Product Ion scan of 1 ppm Cu solution in MS/MS mode; (c) Product Ion scan of 1 ppm Cu solution in MS/MS mode with NH_3 as a reaction gas; (d) Product Ion scan of 1 ppm Cu and 1 ppb Rh solution in MS/MS with NH_3 as a reaction gas.

Results

Detection limits and spike recoveries were carried out on a copper sulphate solution using this method. Method DLs are shown in Figure 2.

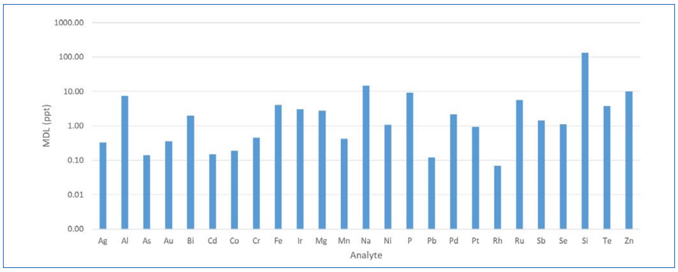

Figure 2. MDLs determined in 1% nitric acid using the scan types indicated in Table 1.

Conclusion

The unique capabilities of the NexION 5000 Multi-Quadrupole ICP-MS and Universal Cell Technology were proven to be effective at removing spectral interferences, as demonstrated for the removal of the $CuAr^+$ polyatomic interference on Rh^+. The MDLs obtained permit the determination of extremely low-level impurities in Cu concentrates, whereas excellent spike recoveries demonstrate the accuracy and reliability of the method.

Reference

Summarized from the PerkinElmer application note "Measurement of Impurities in High-Purity Copper Concentrate Using the NexION 5000 ICP-MS" by Ruth Merrifield and Chady Stephan.

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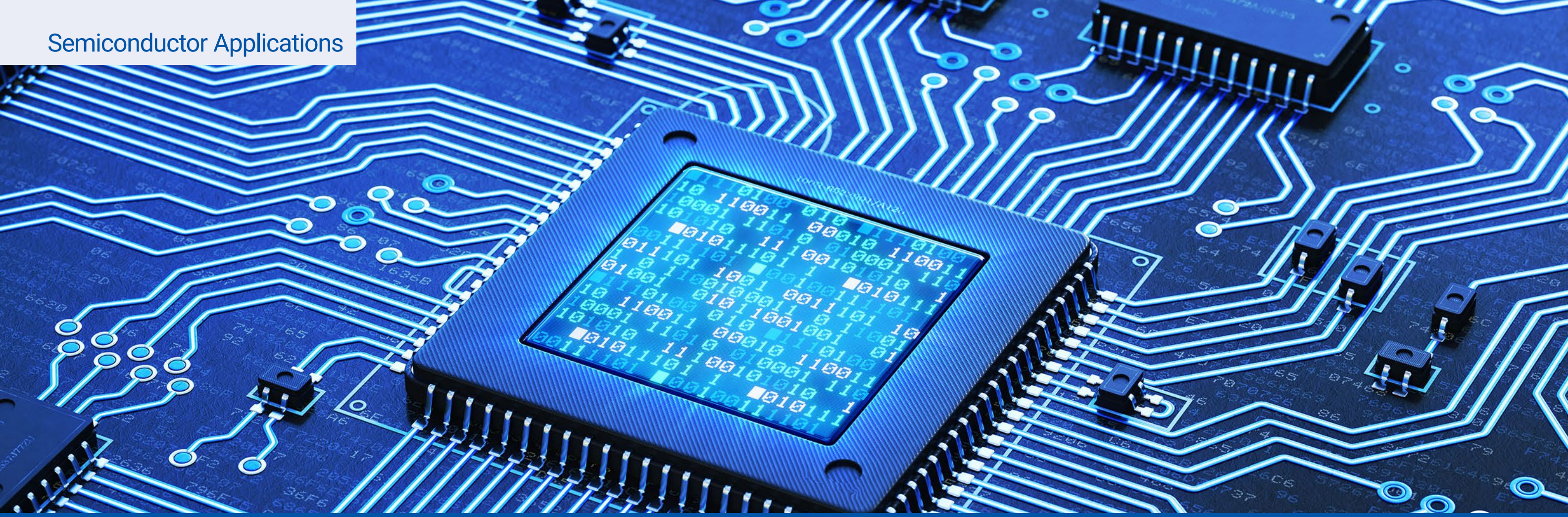


APPLICATION SPOTLIGHT

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 NH_3, O_2, 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 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 NH_3. The reaction of ArC^+ with NH_3 very effectively removes huge ArC^+ interference, allowing Cr to be determined accurately at very low levels. The expected isotope abundance of ^{52}Cr and ^{53}Cr is a confirmation of the complete removal of ArC^+ interferences.

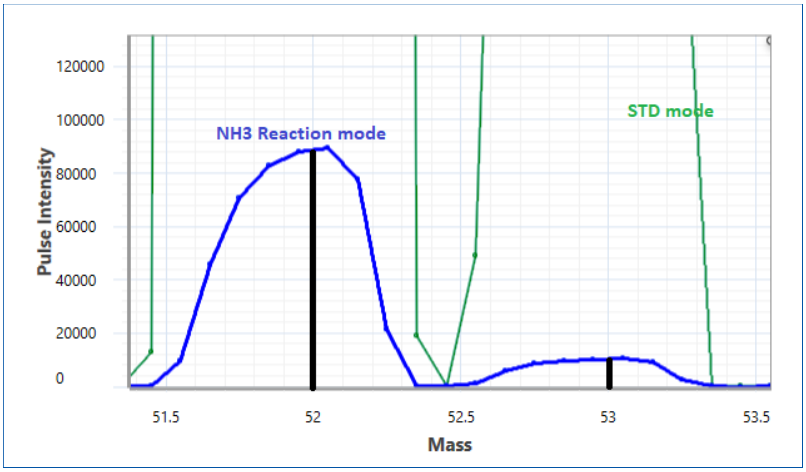


Figure 1. Scan of two Cr isotopes in Standard mode (green line) and Reaction NH_3 mode (blue line).

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 (NH_3) Cold Plasma mode, Si in Reaction (H_2) mode, and Cr in Reaction (NH_3) Cold Plasma mode. DLs and BECs in three organic solvents (IPA, NMP, and PGEMEA) for 46 elements along with modes of operations are shown in the application note.

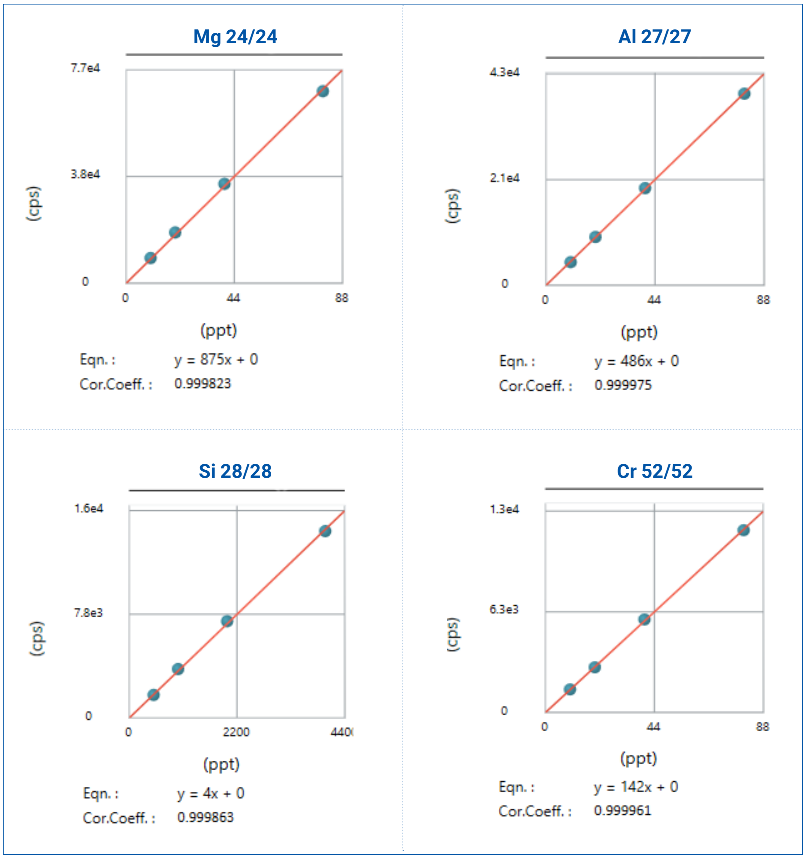


Figure 2. Calibration curves of selected elements in IPA in different modes of analysis.

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.

APPLICATION SPOTLIGHT

Analysis of Metallic Impurities in Silicon Wafers Using Fully Automated VPD-ICP-MS

The Importance of Measuring Impurities in Silicon Wafers

As more industries utilize silicon-based semiconductor devices, there is an increasing demand for minimal impurities due to ever-growing scale of component integration on a chip. Since Si wafer production involves many microfabrication steps, an essential component of the quality control (QC) process is to have a reliable technique that can identify metallic impurities introduced during production.

The standard approach is to check each manufacturing step with a control wafer and analyze the Si wafer's surface for impurities using total reflection x-ray fluorescence (TRXF). While the method is ideal for analyzing the film's surface, impurities inside the film cannot be analyzed since detection limits are inadequate for current requirements and some light mass elements are almost impossible to analyze. To improve the detection capability of the analysis, vapor phase decomposition (VPD) was developed.

Given the disadvantages of TRXF analysis, ICP-MS can be used instead to directly analyze the scanned solution, easily achieving a detection limit of E5-E7 atoms/cm^2, which meets the current industry requirements.

System Setup

This work describes the instrument setup, instrument parameters, and analytical steps taken to identify metallic impurities on and within Si wafers. The instrumentation utilized in this work consisted of coupling the Expert_PS™ fully automated VPD device (IAS Inc., Hino, Tokyo, Japan) with two 12-foot front opening unified pod (FOUP) load ports to PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS. The full VPD and instrument setup will not be discussed here but detailed information is given in the full application note.

VPD Chemistry

Most films can be etched by HF vapor, but some films, such as Si epitaxial, polysilicon, WSi, and Ti, cannot be etched by HF only. The Expert_PS system has the bulk-etching option that uses a mixture of HF vapor and ozone (O_3) gas, which can etch these films and Si substrate. The bulk-etching option can be used for a depth profile of metallic impurities in an ion-implanted Si wafer or metal diffusion behavior in Si substrate with high temperature. The dual scan nozzle and the N_2 wall option significantly improve the scan solution's holding capability, allowing the scanning of hydrophilic glass or sapphire wafer. The Expert_PS system has the patented module that enables the scan of the specified area of the bevel and edge.

Typical critical contamination elements are Fe, Cr, Mn, Ni, Cu, Zn, and Ti, which exist commonly in the environment and can be recovered using a normal scan solution, i.e., a mixture of HF and H_2O_2. However, for various new elements that have have been recently used in the manufacturing process, a different chemistry is required to recover these elements from Si substrate. Aqua regia scan solutions effectively recover noble metals, such as Ru, Au, Pt, and Ag.

Results and Discussion

The scan solution was self-aspirated from the autosampler rinse port. The on-line positioned ASAS device can automatically prepare and deliver calibration standards, QC solutions and internal standards.

Table 1 shows the results from the Si bare wafer as well as a 1 µm bulk-etched Si wafer. The concentration of impurities on the Si bare wafer surface were calculated as atoms/cm^2 based on the actual scan area. The bulk-etched Si wafer depth was calculated by the weight loss of the Si wafer before and after the bulk etching. The concentration of the impurities in the bulk-etched Si wafer were calculated in atoms/cm^3.

The recovery of noble metals on the Si wafer was also assessed. A spiked wafer was prepared by dropping a 1000 µL of 1 ppb multi-element standard solution on a Si bare wafer. The scan was repeated three times using the concentrated aqua regia scan solution after the VPD. The scanned aqua regia solution was automatically diluted with DIW 10 times before ICP-MS analysis. As can be seen in Table 2, some elements showed lower recoveries with the normal HF + H_2O_2 scan solution, whereas the aqua regia scan solution improved analyte recoveries.

Finally, the depth profile of ^{11}B implanted Si wafer was evaluated by bulk etching a 0.1 µm wafer 20 times. The target ^{11}B implanted depth was at 1 µm, and the depth profile showed good agreement. However, some impurities, such as Al and Fe, were detected at a shallower level as shown in Figure 1.

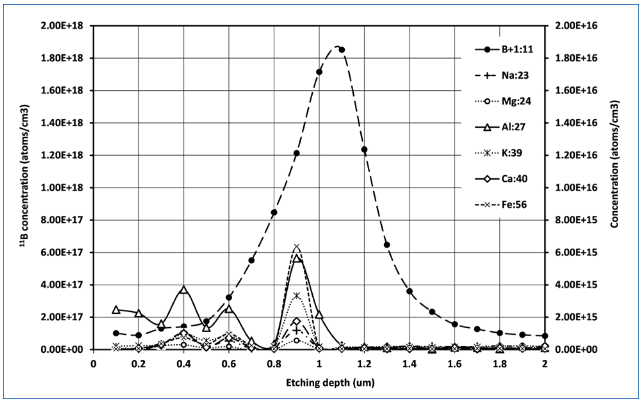


Figure 1. Depth profiling study of ^{11}B implanted Si wafer.

Table 1: Results of Si Wafer Analysis.

Analyte	Mode	Q1/Q3	Cell Gas Flow (mL/min)	RPq	Bare Wafer		1 µm Bulk Etching	
					Found (ppt)	Found (atoms/ cm^2)	Found (ppt)	Found (atoms/ cm^3)
^{7}Li	STD	7/7	0	0.25	< 0.12	< 1.6E + 07	< 0.12	< 1.6E + 10
^{23}Na	STD	23/23	0	0.25	1.2	4.8E + 07	2.7	1.1E + 11
^{24}Mg	STD	24/24	0	0.25	0.14	5.3E + 06	6.0	2.3E + 11
^{27}Al	DRC (NH_3)	27/27	0.6	0.45	1.1	3.7E + 07	3.1	1.1E + 11
^{39}K	DRC (NH_3)	39/39	0.6	0.45	1.9	4.4E + 07	1.1	2.6E + 10
^{40}Ca	DRC (NH_3)	40/40	1.0	0.45	1.2	2.7E + 07	18	4.1E + 11
^{48}Ti	DRC (NH_3)	48/131	0.6	0.25	< 0.2	< 3.8E + 06	2.1	4.0E + 10
^{51}V	DRC (NH_3)	51/51	0.3	0.45	<0.046	8.2E + 05	0.4	7.2E + 09
^{52}Cr	DRC (NH_3)	52/52	0.6	0.45	1.6	2.8E + 07	2.0	3.5E + 10
^{55}Mn	DRC (NH_3)	55/55	0.6	0.45	0.13	2.2E + 06	0.5	8.3E + 09
^{56}Fe	DRC (NH_3)	56/56	0.6	0.45	1.9	3.1E + 07	2.2	3.6E + 10
^{59}Co	DRC (NH_3)	59/59	0.3	0.45	0.10	1.6E + 06	< 0.088	< 1.4E + 09
^{60}Ni	DRC (NH_3)	60/60	0.3	0.45	0.7	1.1E + 07	2.4	3.7E + 10
^{63}Cu	DRC (NH_3)	63/63	0.3	0.45	1.1	1.6E + 07	1.3	1.8E + 10
^{66}Zn	DRC (NH_3)	66/66	0.3	0.45	0.69	9.6 + 06	< 0.52	< 7.3E + 10
^{69}Ga	DRC (NH_3)	69/69	0.6	0.45	< 0.031	< 4.1E+05	< 0.031	< 4.1E + 08
^{74}Ge	DRC (NH_3)	74/90	0.3	0.45	0.27	3.4E + 06	3.2	4.0E + 10
^{75}As	DRC (O_2)	75/91	1.1	0.45	< 0.64	< 7.8E + 06	8.1	9.9E + 10
^{88}Sr	DRC (NH_3)	88/88	0.6	0.45	< 0.025	< 2.6E + 05	0.15	1.6E + 09
^{90}Zr	STD	90/90	0	0.25	< 0.1	< 1.0E + 06	< 0.1	< 1.0E + 09
^{98}Mo	DRC (NH_3)	98/98	0.6	0.45	0.33	3.1E + 06	< 0.31	3.0E + 09
^{107}Ag	STD	107/107	0	0.25	< 0.19	< 1.6E + 06	3.9	3.3E + 10
^{111}Cd	STD	111/111	0	0.25	< 0.18	< 1.5E + 06	< 0.18	< 1.5E + 09
^{118}Sn	STD	118/118	0	0.25	< 0.28	< 1.5E + 06	12	9.2E + 10
^{138}Ba	STD	138/138	0	0.25	< 0.048	< 3.2E + 05	< 0.048	< 3.2E + 08
^{184}W	STD	184/184	0	0.25	< 0.15	< 7.4E + 05	< 0.15	< 7.4E + 08
^{208}Pb	DRC (NH_3)	208/208	0.6	0.45	< 0.13	< 5.7E + 05	< 0.13	< 5.7E + 08

Table 2: Recovery (%) of Elements from Si Wafer with Different Scan Solutions.

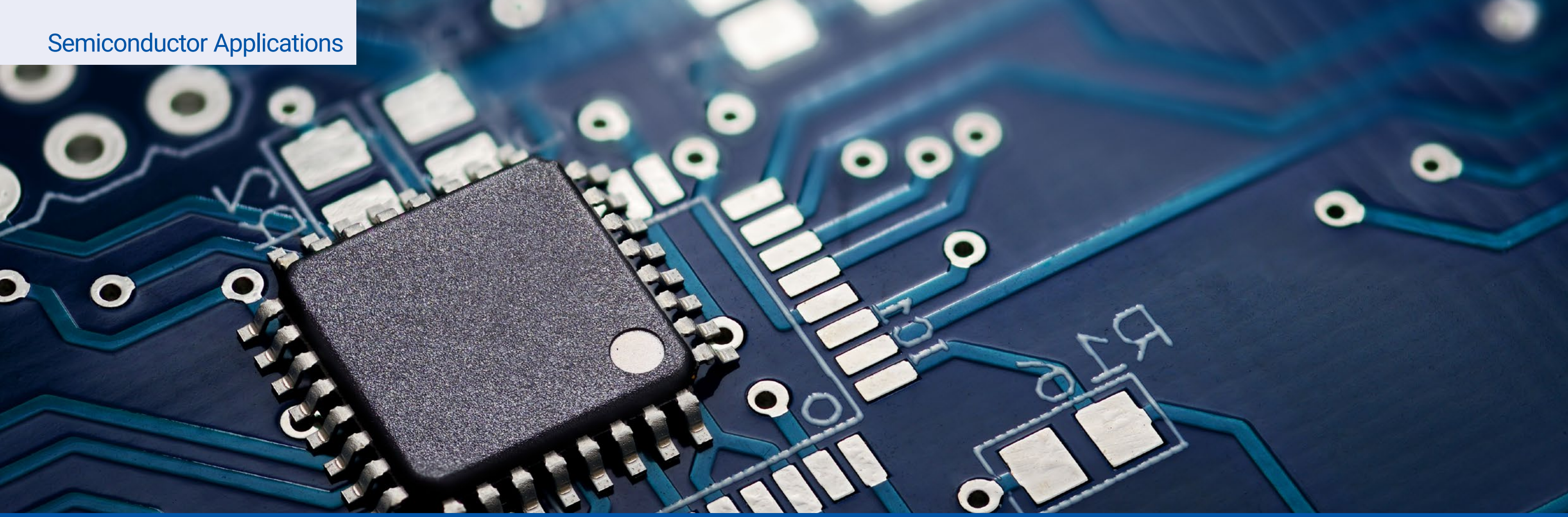
Scan Solution	Element						
	Au	Ir	Pt	Rh	Ru	Pd	Ag
3% HF + 4% H_2O_2	7	28	20	25	26	14	9
Aqua Regia	99	99	89	91	92	98	99

Conclusion

The results presented in this work, performed in collaboration between PerkinElmer Inc. and IAS Inc., demonstrate that the Expert_PS VPD system can be coupled with the NexION 5000 Multi-Quadrupole ICP-MS to provide a fully automated solution for the analysis of metallic impurities in Si wafers. This is due to the sensitivity of the ICP-MS and its ability to remove spectral inferences when performing trace analysis in combination with the VPD system that eliminates manual operation and chemical exposure to operators to prevent Si wafer contamination.

Reference

Summarized from the PerkinElmer application note "Analysis of Metallic Impurities in Silicon Wafers Using Fully Automated VPD-ICP-MS" by Mina Ichikawa, Yoko Kishi, Tatsu Ichinose, and Katsu Kawabata at IAS Inc.



APPLICATION SPOTLIGHT

Analysis of Semiconductor-Grade Hydrogen Peroxide Using the NexION 5000 ICP-MS

The Importance of Purity of H_2O_2 in Semiconductors

Contaminants in high-purity chemicals used in the manufacturing of integrated circuits (ICs) have a direct impact on product yield and reliability of semiconductor devices. In particular, the removal and cleaning of organic photoresist solvents from the wafer surface using hydrogen peroxide mixtures is critical to ensure that diffusion, implantation and/or deposition is carried out correctly. For example, mixtures of ammonia (NH_4OH) and hydrochloric acid (HCl) with hydrogen peroxide (H_2O_2) are effective in the removal of particulates and metal contaminants, while a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide is used in the removal of organic residues. Moreover, hydrogen peroxide mixed with hydrofluoric acid (HF) is also employed in vapor phase decomposition (VPD) for metal contamination studies on the wafer surfaces.

SEMI Specifications for Hydrogen Peroxide

Semiconductor Equipment and Materials International standard for H_2O_2, *SEMI C30-1110 Specifications for Hydrogen Peroxide SEMI Grade 5*, specifies maximum contamination levels of 10 ppt for most trace elements. While a conventional quadrupole ICP-MS (ICP-QMS) technique could be used to monitor trace-element contaminants at ppt levels, the detection capability for silicon (Si), phosphorus (P) and sulfur (S) is limited to ppb levels. With modern semiconductor devices getting down to 5 nm geometry, it is becoming imperative to be able to analyze Si, P and S at much lower levels. In this work, we describe the analysis of 46 elements in 35% H_2O_2 using the NexION® 5000 Multi-Quadrupole ICP-MS.

Unique Capabilities of NexION 5000 ICP-MS Universal Cell Technology

The NexION 5000's Universal Cell (UCT) is a true quadrupole reaction cell that allows the control of reaction chemistry within the cell. This is achieved through the application of a bandpass within the cell, preventing by-products of the original reaction from forming new interferences with the cell gas. Moreover, the bandpass of the reaction cell allows predictable and reproducible interference removal using either 100% pure or a mixture of highly reactive gases in the cell, utilizing up to four gas channels within the same analytical method.

Typical Interferences in Hydrogen Peroxide

The most abundant spectral interferences in H_2O_2 analysis are argon, nitrogen and oxygen-related polyatomic species. A combination of MS/MS, Q3 and Mass Shift in Standard and Reaction (with NH_3, O_2 and H_2) modes using both hot and cold plasma conditions were applied to the analysis. It's also worth pointing out that the Mass Shift mode is a very powerful technique for removing spectral interferences on those elements that can efficiently create cluster ions with reactive gases. Mass Shift allows to move an element of interest as a cluster to a higher mass where no other ions exist and measure it virtually interference-free. In this work, Mass Shift mode was used for measuring phosphorus (P), sulfur (S), titanium (Ti), arsenic (As), and selenium (Se) as clusters with O_2. For example, Ti at mass 48 (the most abundant isotope) is one of the challenging analytes due to the presence of many spectral interferences at its mass. Figure 1 shows a scan of 100 ppt Ti in H_2O_2 solution without the addition of oxygen to the cell (Standard mode). Here, Ti stays at mass 48, while Figure 2 shows that Ti^+ at mass 48 is shifted and measured at mass 64 as TiO^+ after the reaction with O_2 in the UCT.

Quantitative Results

The measurement of 46 elements was carried out by the method of standard addition (MSA) in undiluted 35% H_2O_2 acidified by 0.2% HNO_3. The NexION 5000 ICP-MS provides the flexibility to measure these elements using multiple modes within a single method. Background equivalent concentrations (BECs), detection limits (DLs) and spike recoveries can be found in the full application note. Detection limits were calculated as 3-sigma of seven replicate measurements of the H_2O_2 blank sample. With the exception of B, Si, P and S, DLs less than 1 ng/L (ppt) were obtained for all other elements, with many of them even below 0.1 ppt. The DLs for B and P were at the single-digit ppt level, while the DLs for Si and S were at 16 and 26 ppt respectively. More importantly, BECs were below 1 ppt for most elements, with many well below the detection limits. The exceptions were non-metals B and P with BECs at single-digit ppt and Si and S with BECs < 1 ppb. Spike recoveries were performed at 5 ppt level (1 ppb for Si and S) with all elements achieving recoveries within ±25% as required by the *SEMI C1-0310* standard.

It is imperative that besides producing the best BECs and DLs, the ICP-MS must also be able to provide good long-term stability. A 5-hour analysis of H_2O_2 was performed with a QC (H_2O_2 spiked with 10 ppt) measured at 20-minute intervals for 5 hours. Relative standard deviations (RSDs) were less than 5% for all elements and the drift was within ±15% against an average value.

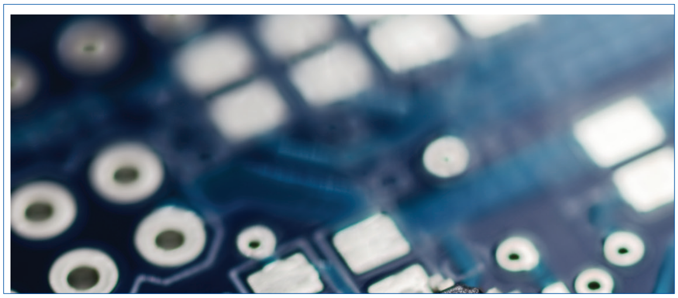


Figure 1. A scan of 100 ppt Ti in H_2O_2 at mass 48 solution without the addition of oxygen to the cell.

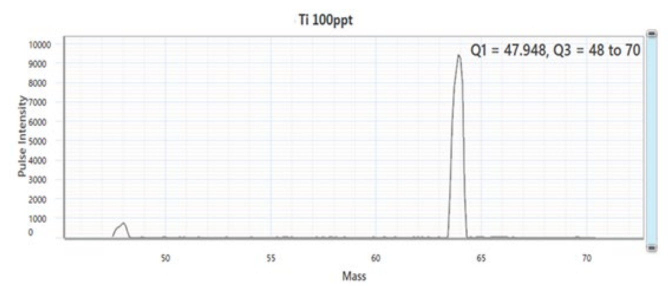


Figure 2. Ti^+ at mass 48 is shifted and measured at mass 64 as TiO^+ after the reaction with O_2.

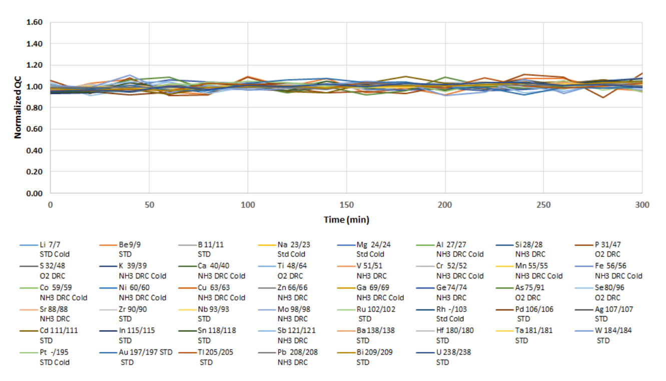


Figure 3. Long-term stability (5 hours) of 10 ppt spiked in 35% H_2O_2.

Conclusion

The NexION 5000 Multi-Quadrupole ICP-MS has shown to be robust and suitable for the routine quantification of ultra-trace impurities at the ng/L level in 35% H_2O_2. Syngistix for ICP-MS software simplifies the optimization procedure of different operating modes and allows various modes of operation such as MS/MS, Mass Shift as well as Hot and Cold Plasma to be used in a single method. All the elements specified in *SEMI C30-1110*, including Si, P and S, were measured.

Reference

Summarized from the PerkinElmer application note "Analysis of Semiconductor-Grade Hydrogen Peroxide Using the NexION 5000 ICP-MS" by Kenneth Ong, Kyoko Kobayashi and Ewa Pruszkowski.

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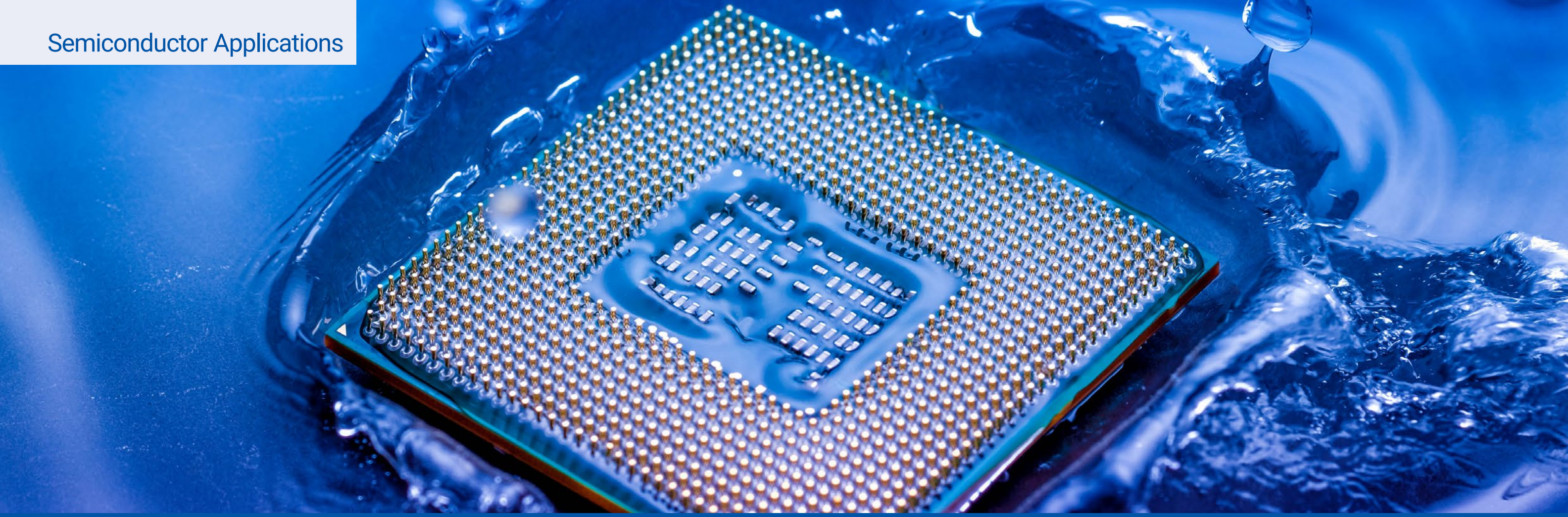

APPLICATION SPOTLIGHT

Characterization of Ultrapure Water Using the NexION 5000 ICP-MS

The Importance of Characterizing High-Purity Water

For decades, the semiconductor industry has been continuously developing new devices that are smaller, faster and consume less power than their predecessors. To maintain this trend, these devices must have fewer defects, which requires the use of higher-purity materials with extremely low levels of contaminants. Ultrapure water (UPW) is one of the most important chemicals in the production of semiconductor devices as it is used for wafer rinsing and the dilution of chemical baths. For that reason, the measurement of metallic contaminants in UPW is of critical importance, as otherwise the impurities could cause defects, resulting in a component failure.

Semiconductor Industry Standards

In the most recent *SEMI F63-0918 Guide for Ultrapure Water Used in Semiconductor Processing*, the target values for the majority of the 26 metallic contaminants are less than 1 ppt. The only technology that can realistically determine this suite of elements at such low levels in a high-throughput sampling environment is inductively coupled plasma mass spectrometry (ICP-MS). In this work, we describe the analytical methodology and results for the analysis of UPW using the NexION® 5000 Multi-Quadrupole ICP-MS.

Instrumental Conditions

The main component of the Cell (UCT) in the NexION 5000 ICP-MS is a scanning quadrupole, which has the ability to control the reaction chemistry through the implementation of the RF rejection parameter (q). This parameter is able to prevent by-products of the original reactions from forming new interferences. In addition, controlling the chemistry allows the use of highly reactive, undiluted gases in the cell, which greatly enhances the elimination of interferences and ensures predictable reactions. The UCT function, in combination with multi-quad technology, is a winning solution for removal of spectral interferences.

Background equivalent concentrations (BECs) and detection limits (DLs) were run in hot plasma or cold plasma conditions, depending on the element. A Reaction mode using either NH_3 or O_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 in MS/MS mode, or by creating a cluster ion with an analyte at a higher mass in Mass Shift mode. In MS/MS mode, the bandpass of Q1 and Q3 are set to the same mass, and quantitation is carried out at the analyte mass, while in Mass Shift mode, the analyte is moved away from the interference with a reaction gas and measured as a product ion at a higher mass. For detailed instrumental conditions, download the full application note.

Calibration

For the BEC and DL measurements, calibration curves were established with 10, 20, 40 and 60 ppt standards. All curves had correlation coefficients > 0.999, demonstrating the linearity of the analysis, the ability to accurately measure at low concentrations, and the effectiveness of the interference removal. Figure 1 shows four typical calibration curves for B (11/11) in Standard MS/MS mode, Ca (40/40) in Reaction MS/MS mode (using NH_3) and Ti (48/64) and As (75/91) respectively in Reaction Mass Shift mode (using O_2).

Results

Detection limits (DLs) in Hot Plasma mode in conjunction with MS/MS for all 26 essential elements were found to have concentrations lower than 0.3 ppt, easily meeting the <1 ppt requirement by *SEMI* standards, with background equivalent concentrations (BECs) for most of the elements less than 0.5 ppt. In Cold Plasma mode, even better DLs and BECs can be achieved for elements that have Ar-based interferences or whose sensitivity is enhanced by the reduction of Ar ions in the plasma gas.

DLs for all 26 elements using both hot and cold plasma conditions are shown in Figure 2, demonstrating the effectiveness of the gas reactions and the several analytical modes in removing spectral interferences.

Conclusion

The data has shown that the NexION 5000 Multi-Quadrupole ICP-MS system provides outstanding analytical performance in terms of DLs and BECs to meet the current and future demands of the semiconductor industry.

Reference

Summarized from the PerkinElmer application note "Characterization of Ultrapure Water Using NexION 5000 ICP-MS" by Ewa Pruszkowski.

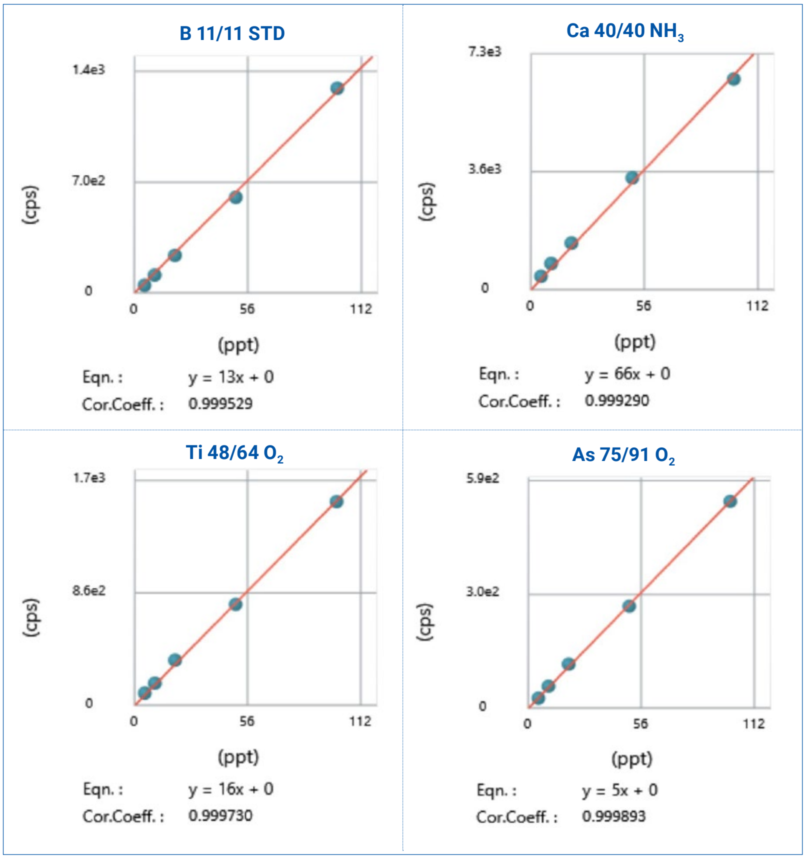

Figure 1. Calibration curves for B (Standard MS/MS), Ca (Reaction-NH_3 MS/MS) and Ti and As (Reaction-O_2 Mass Shift).

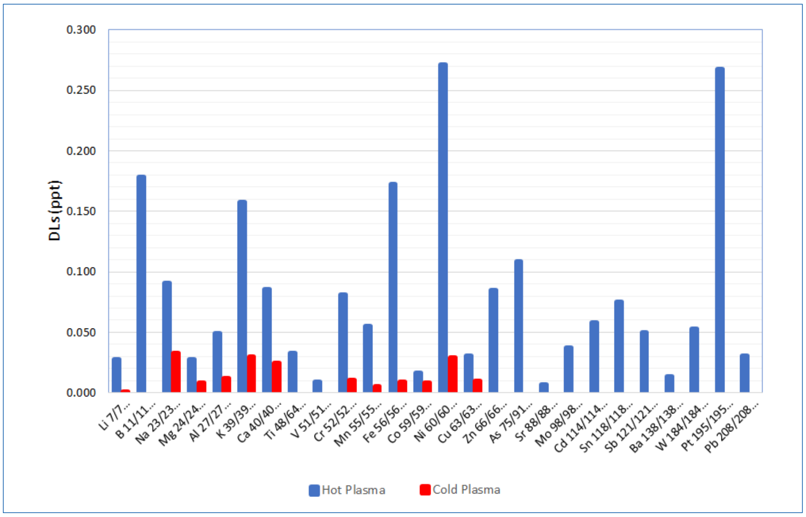

Figure 2. DLs for all 26 elements in ultrapure water (UPW).

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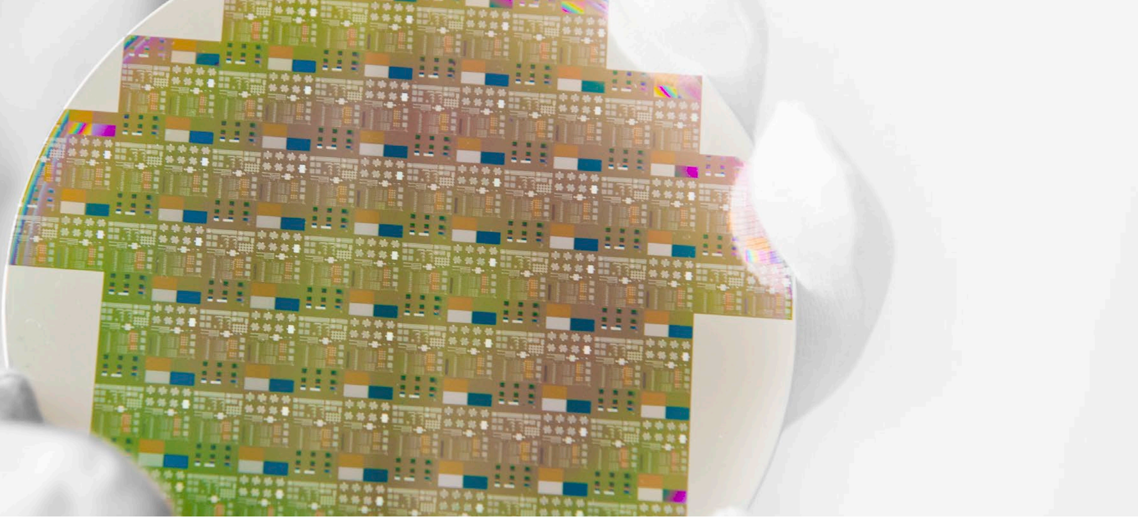

APPLICATION SPOTLIGHT

Determination of Impurities in Electronic-Grade Hydrochloric Acid with the NexION 5000 ICP-MS

The Importance of High Purity Cleaning Chemicals

During the production of semiconductor devices, silicon wafers go through a wet cleaning process to ensure they are free of contaminants and impurities before the high-temperature processing steps of oxidation, diffusion, and vacuum deposition. In this cleaning procedure, organic films and metal particles are first removed, followed by hydrous oxide stripping. The final step uses a cleaning solution of a mixture of H_2O:HCl:H_2O_2 (6:1:1 by volume) to remove the remaining traces of metallic ion contamination and create a thin inert layer that protects the surface from further contamination. The use of high-purity chemicals during the cleaning process is therefore critical to the overall quality and performance of the semiconductor device. For this reason, the measurement of elemental contaminants in high-purity hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) is critically important to the device's performance and specification. With more and more elements added into the list of critical analytes by the semiconductor manufacturers, the determination of ultra-trace impurity levels is now commonly carried out using inductively coupled plasma mass spectrometry (ICP-MS).

SEMI Standards Specification

In the most recent *SEMI C27-0918 Specification and Guide for Hydrochloric Acid* specifies that the maximum concentration of 26 elemental contaminants in 37% HCl according to Tier C guidelines should be less than 100 ppt (ng/L). In addition, it also specifies that spike recoveries of 75-125% should be achieved at 50% of the specified level. This work demonstrates analytical methodology, detection limits (DLs), background equivalent concentrations (BECs) and recoveries for 10 ppt spikes in 20% HCl, along with a 50 ppt 5-hour stability study, using the NexION® 5000 Multi-Quadrupole ICP-MS.

Instrumental Conditions

Universal Cell Technology (UCT) in the NexION 5000 ICP-MS is based on a scanning quadrupole, which has the ability to control the reaction chemistry through the implementation of the RF rejection parameter (q). This parameter, as a component of dynamic bandpass tuning, is able to prevent by-products of the original reaction from forming new interferences. In addition, by controlling the chemistry, it allows the use of highly reactive, undiluted gases in the cell, which greatly enhances the elimination of interferences and ensures predictable reactions. The UCT function, in combination with multi-quadrupole technology, is a winning solution for removal of spectral interferences.

Background equivalent concentrations and detection limits for all elements were run in Hot Plasma mode using 1500 W RF power, while for elements that work well at a lower temperature plasma, cold plasma conditions (700 W) were used. Reaction mode using either NH_3 or O_2 or H_2 is the most effective way of removing spectral interferences by changing them into atoms or ions of a different mass in MS/MS mode, or by creating a cluster ion with an analyte known as Mass Shift mode. In MS/MS mode, Q1 and Q3 are set to the same mass, and quantitation is carried out at the analyte mass, while in Mass Shift mode, the analyte is moved away from the interference with a reaction gas and measured as a product ion at a higher mass.

Calibration Routine

For the BEC and DL measurements, 20% HCl was analyzed using the method of standard addition (MSA). The calibration curves for all elements had correlation coefficients > 0.999. Even though they were obtained using different modes (MS/MS and Mass Shift), reaction gases (NH_3 and O_2) and plasma conditions (hot and cold), they demonstrate good linearity.

Management of Spectral Interferences

An example of the interference removal capabilities of the NexION 5000 system is demonstrated by the $^{35}Cl^{16}O^+$ and $^{35}Cl^{16}OH^+$ interference elimination on ^{51}V and ^{52}Cr. V^+ and Cr^+ ions have a low reactivity rate with NH_3, while $^{35}Cl^{16}O^+$ and $^{35}Cl^{16}OH^+$ react spontaneously. This reaction will also create by-product ions such as $^{35}ClNH_2^+$ and $(NH_3)_2NH_4^+$, which would interfere with V^+ and Cr^+ if it wasn't for the bandpass control of the UCT. The importance of bandpass tuning is demonstrated by a spectral scan of an HCl sample with a minimal presence of V, when Q1 is set to mass 51 (^{51}V and $^{35}Cl^{16}O^+$), and Q3 is scanning masses from 34 to 53. With RPq set to a low value of 0.25, significant counts are observed at mass 35, and some at masses 51 and 52, which can be attributed to $NH_3NH_4^+$ at mass 35 and to $^{35}ClNH_2^+$ and $(NH_3)_2NH_4^+$ at masses 51 and 52 respectively. When RPq is increased to a higher value, the side reactions that produce the by-product interferences at masses 35, 51 and 52 are eliminated, allowing very low BEC detection of V and Cr in HCl (Figure 1).

Results

DLs of 43 elements in 20% HCl are shown in Figure 2, while a 5-hour stability plot of 26 elements in HCl is shown in Figure 3.

Conclusion

The data has clearly shown that the NexION 5000 Multi-Quadrupole ICP-MS is suitable for the routine quantification of ultra-trace impurities at the ng/L level in concentrated HCl, demonstrating excellent interference removal, low DLs, BECs and outstanding long-term stability.

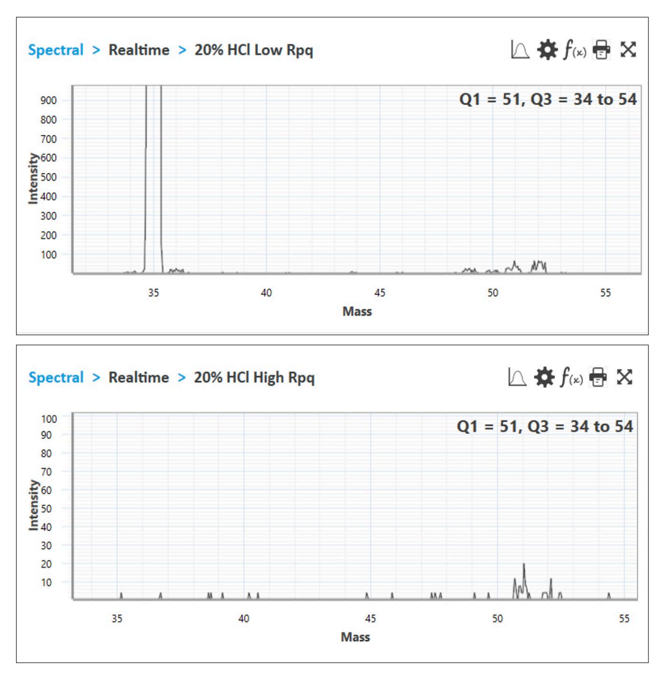

Figure 1. Product Ion scan of a 20% HCl with Q2 bandpass (low RPq) acting as a simple ion guide (top) compared to Q2 with bandpass filter (high RPq) for mass-dependent cut off (bottom).

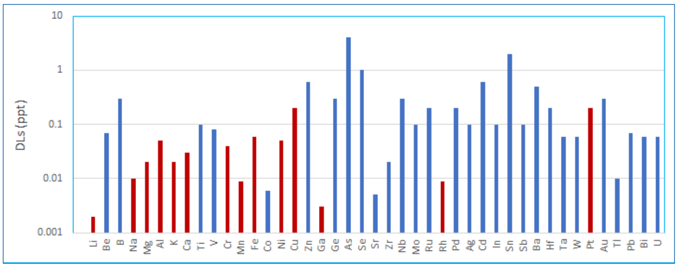

Figure 2. DLs of 43 elements in 20% HCl (blue bars: hot plasma; red bars: cold plasma).

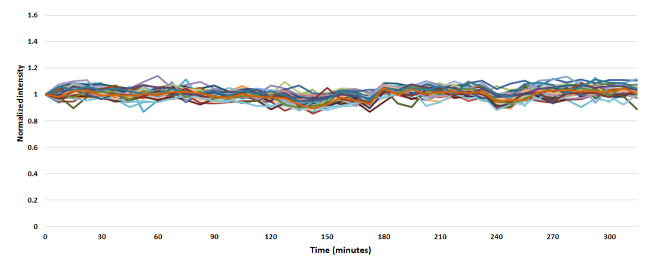

Figure 3. 5-hour stability plot of 26 elements in HCl.

Reference

Summarized from the PerkinElmer application note "Determination of Impurities in Electronic-Grade Hydrochloric Acid with the NexION 5000 ICP-MS" by Kenneth Ong, Kyoko Kobayashi, and Ewa Pruszkowski.


APPLICATION NOTE

ICP - Mass Spectrometry

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Kyoko Kobayashi
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clean process before high-temperature operations. The most commonly used technique is called RCA Clean, developed by Werner Kern from Radio Corporation of America in 1965.[1] In the four-step procedure of cleaning, organic films, some metals and particles are first removed, followed by hydrous oxide stripping. The final step uses the so-called RCA-2 solution to remove the remaining traces of metallic ion contamination and create a thin inert layer that protects the surface from further contamination. The RCA-2, commonly referred to as SC-2 (Standard Clean 2) or HPM (Hydrogen Peroxide Mixture), is a mixture of $H_2O:HCl:H_2O_2$ (6:1:1 by volume).

The use of high-purity chemicals during the cleaning process is critical to the semiconductor product's overall quality and performance. Therefore, it is essential to analyze electronic-grade hydrochloric acid (HCl) and hydrogen peroxide[2] for the presence of trace metal contaminants. The SEMI Standard C27-0918[3] specifies the maximum concentration of metal contaminants by element and tier for hydrochloric acid. With more and more elements added into the list of critical analytes by the semiconductor manufacturers, the determination of ultra-trace impurity levels is now commonly carried out using inductively coupled plasma mass spectrometry (ICP-MS).

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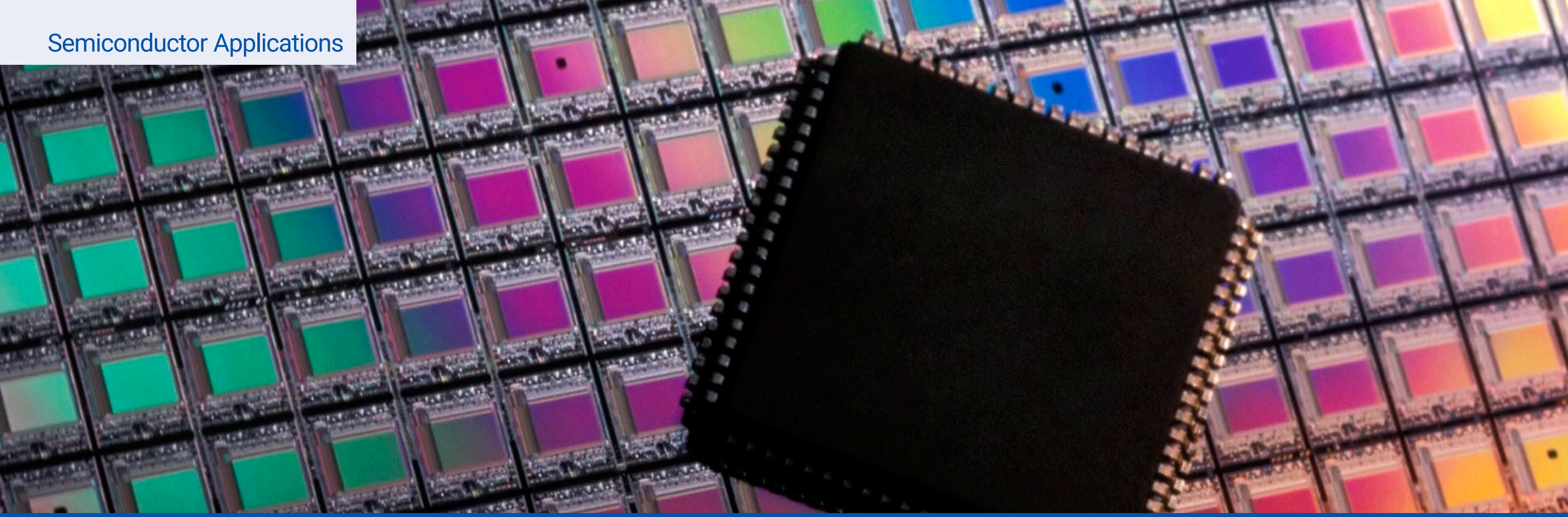

APPLICATION SPOTLIGHT

Rapid Ultra-Trace Analysis of Impurities in Ultrapure Water Using the NexION 5000 ICP-MS

Reasons for Rapid Ultra-Trace Analysis of Ultrapure Water

Impurities in ultrapure water (UPW) have a direct impact on the quality and overall yield of semiconductor products.[1] With the use of UPW in extremely high volumes in semiconductor device fabrication, the ability to deliver sub-ppt detection limits by ICP-MS within a relatively short period of time is critically important. For that reason, it is necessary to address interferences as efficiently as possible, as these can impact analysis run times. It is well recognized that reaction gases are far more effective at removing argon-based interferences than collision gases because interferences very often exceed four orders of magnitude compared to the analyte signal. So even though pure, highly reactive gases offer the most complete interference removal, there are some countries where the use of such gases as NH_3 is restricted due to regional safety regulations, and as a result, other gases, such as O_2 or H_2, are typically used. However, H_2 is very flammable, and for that reason, many laboratories prefer to use hydrogen generators to deliver high-purity gas on demand. This work describes a method for the determination of the detection limits (DLs) and background equivalent concentrations (BECs) of 12 impurities in ultrapure water using the NexION® 5000 Multi-Quadrupole ICP-MS with Universal Cell Technology (UCT), utilizing hydrogen from a hydrogen generator as a reaction gas under cold plasma conditions.

Instrumental Conditions for this Application

The NexION 5000 ICP-MS offers the ability to control the mass range entering the high-vacuum region of the ion optics via the Quadrupole Ion Deflector (QID - Q0). The ions are then mass-separated in the first Transmission Analyzer Quadrupole (Q1) where only the masses of interest are allowed to proceed to the Universal Cell (Q2). Here, the analyte ion and interferences undergo controlled reactions in the cell where the reaction by-products are ejected before they have a chance to react and form new interferences. Thereafter, the analyte mass is selected in the second Transmission Analyzer Quadrupole (Q3) for detection. Reaction mode was used for certain analytes typically required by the semiconductor industry in order to eliminate interferences from Si, C, O and Ar. Reaction mode with a low gas flow rate was also used for analytes which are relatively free from interferences – namely lithium (Li), beryllium (Be) and sodium (Na) – in order to shorten the analytical run time since rapid analysis and high sample throughput was the particular focus of this work. Higher gas flows were used for $^{39}K^+$, $^{40}Ca^+$ and $^{56}Fe^+$ to eliminate the argon-based polyatomic interferences of ArH^+, Ar^+, and ArO^+ respectively. All analyses were carried out in MS/MS mode under cold plasma conditions.

Calibration

Calibration curves for all twelve analytes were plotted and were found to have correlation coefficients ≥ 0.999 (four standards + blank), showing that the calibrations were adequately linear for all analytes. Four of those elements are exemplified in Figure 1 — for the complete set, please refer to the full application note.

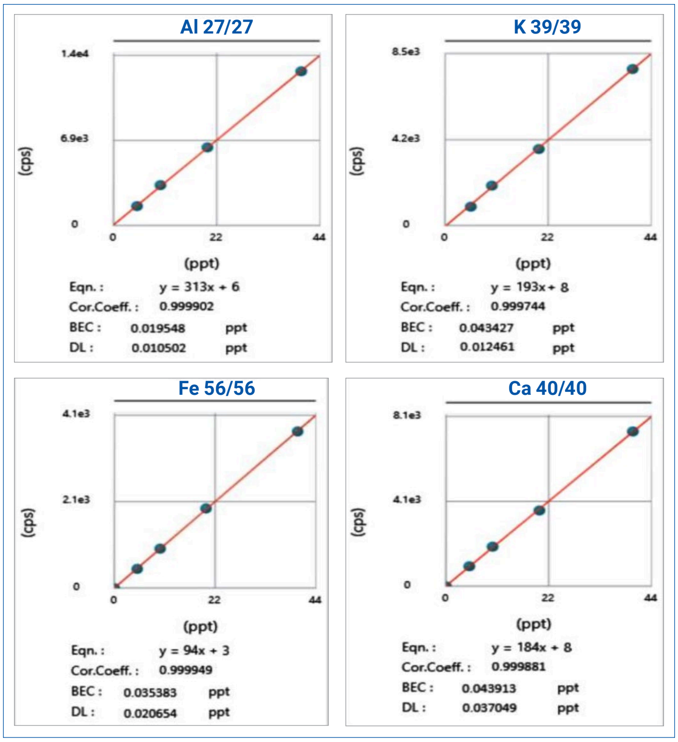

Figure 1. Calibration plots of four of the analytes determined in this study.

Results

DLs and BECs were then determined in UPW and were calculated using the traditional 3σ method. As can be seen in Figure 2, sub-ppt DLs and BECs were obtained for all analytes evaluated using a single reaction gas and set of plasma conditions, where the analysis time for each sample was less than 2 minutes. Despite the presence of large polyatomic interferences – ArH+, Ar$^+$, and ArO$^+$ on ^{39}K$^+$, ^{40}Ca$^+$, and ^{56}Fe$^+$ respectively – and the lower effectiveness of hydrogen as a reaction gas when compared to NH_3, these elements can be easily quantified at parts per quadrillion (ppq) concentrations using cold plasma conditions. Moreover, elements, such as Li, Be, Na, that have few interferences remain relatively unaffected by the lower gas flows of the hydrogen reaction gas, yet still deliver outstanding BECs while maintaining high sensitivity.

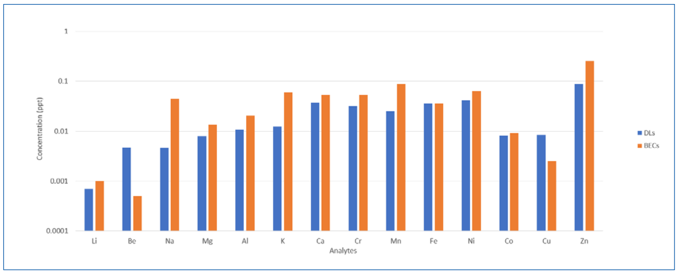

Figure 2. DLs and BECs for all 12 elements in ultrapure water.

Conclusion

This work demonstrates the ability of the NexION 5000 Multi-Quadrupole ICP-MS to deliver outstanding DLs and BECs for Li, Be, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Co, Cu and Zn, allowing for the accurate quantification of these elements at the ppq level with hydrogen as a reaction gas. The hydrogen reaction gas generated with a hydrogen generator was found to deliver the level of purity required by this semiconductor application. In addition, a single Cold Plasma mode allowed for analysis times of less than 2 minutes per sample, supporting the rapid sample throughput needs for UPW analysis in semiconductor laboratories.

Reference

Summarized from the PerkinElmer application note "Rapid Ultra-Trace Analysis of Impurities in Ultrapure Water using the NexION 5000 ICP-MS" by Chung Ryu and Sooyoung Yoon.

1. Characterization of Ultrapure Water Using the NexION 5000 ICP-MS.

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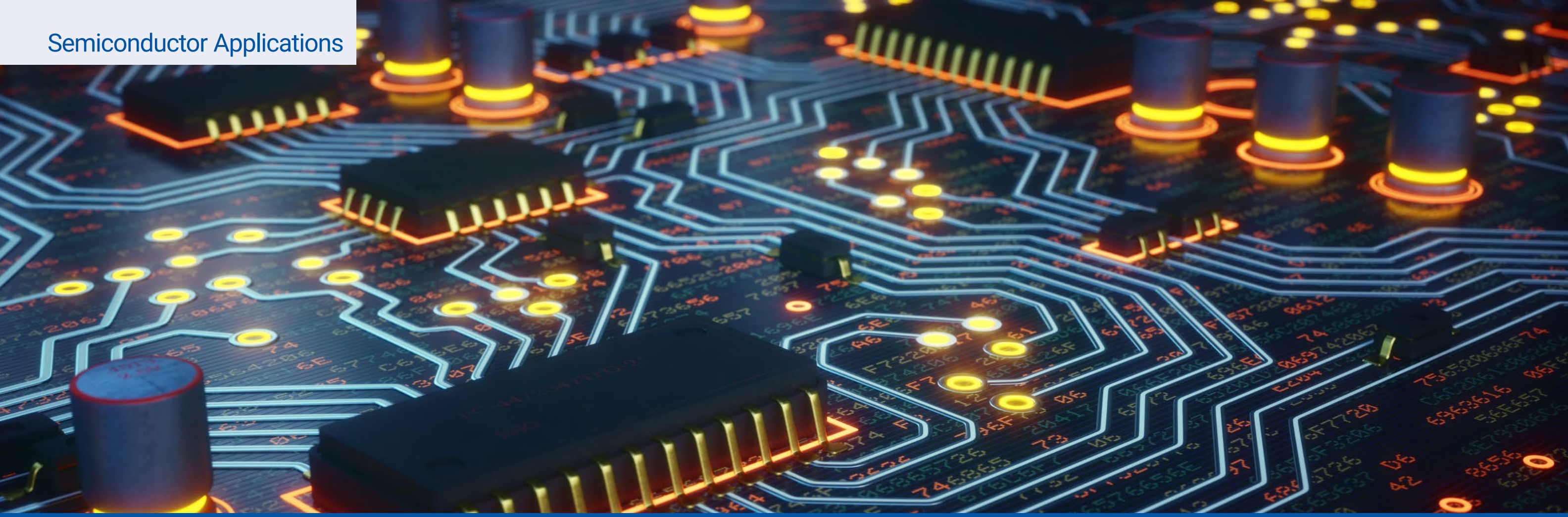

APPLICATION SPOTLIGHT

Ultra-Trace Determination of Non-Metallic Elements in Dilute Nitric Acid Using NexION 5000 ICP-MS

The Need for the Measurement of Trace Impurities of Non-Metals in Nitric Acid

High-purity nitric acid is widely used throughout the semiconductor industry for wet etching of silicon and other metals, in addition to being blended with other chemicals for polishing metal components on circuit board interconnections. As a result, there is a need for ever-lower detection limits of a broad range of impurities, including non-metallic elements, to meet manufacturing requirements. Due to the presence of complex spectral interferences resulting from plasma gases and the sample matrix, the low-ppt quantification of non-metallic elements – such as arsenic (As), bromine (Br), chlorine (Cl), iodine (I), phosphorus (P), sulfur (S), selenium (Se) and silicon (Si) in high-purity nitric acid can be challenging using conventional ICP-MS.

Unique Capabilities of the NexION 5000 ICP-MS for this Application

In this work, the NexION® 5000 Multi-Quadrupole ICP-MS was used because of its ability to not only filter the ions before they enter the collision-reaction cell but to also control the reactions in the cell. This ensures that there are no side reactions with reaction by-products, allowing predictable and repeatable interference removal to be achieved, regardless of the sample matrix. This results in outstanding detection limits (DLs) and background equivalent concentrations (BECs) of non-metallic impurities in a single analytical run using both hot (all analytes except Si) and cold plasma (Si) conditions.

Method Development

To eliminate spectral interferences on P, S, Se, and As, these elements are often reacted with O_2 to form PO^+, SO^+, SeO^+ and AsO^+ respectively via exothermic mass-shift reactions. Since quadrupole-based Universal Cell Technology (UCT) works on frequency modulation, it is able to control the reaction and ensures that undesired endothermic reactions do not proceed, as this can produce potentially unwanted products that could later interfere with the analyte. Moreover, the dynamic bandpass tuning capability of UCT eliminates precursor species of other unwanted exothermic reactions by making them unstable in the cell, ensuring that these reactions do not proceed. While Si exothermically combines with O_2 to form a stable SiO^+ ion, polyatomic interferences from N_2^+ and CO^+ also easily react with O_2 and shift masses along with the analyte of interest. As such, O_2 is not regarded as being an efficient reaction gas for the analysis of Si, so H_2 is often used as a reaction gas for this analyte.

In this example, exothermic reactions hydrogenate N_2^+ and CO^+, while the hydrogenation of Si proceeds through a slow endothermic reaction. The difference in reactivity between the analyte ion and the polyatomic species with hydrogen is significant, resulting in the easy separation of Si from N_2^+ and CO^+ by shifting the polyatomic interferences instead of the analyte. While Cl can also produce ClH^+ ions via an exothermic reaction with H_2, the ClH^+ ions undergo a chain reaction and eventually form H_2Cl^+. By applying a low RPq of 0.25 to the cell, this reaction is allowed to proceed unhindered. The analytical conditions are summarized in Table 1.

Table 1: Isotope selection and cell conditions used in this study.

Element	Isotope Selection (Q1/Q3)	Cell Mode	Cell Gas
Si	28 / 28	MS/MS	H_2
P	31 / 47	Mass Shift	O_2
S	32 / 48	Mass Shift	O_2
Cl	35 / 37	Mass Shift	H_2
Se	80 / 96	Mass Shift	O_2
As	75 / 91	Mass Shift	O_2
Br	79	Single Quad (Q3)	None
I	127 / 127	MS/MS	None

Results

Correlation coefficients of > 0.9995 were achieved for all six non-metal analytes, confirming the excellent linearity of the calibration. From these results, the BECs and DLs were determined and are exemplified in Figure 1. The results show that the detection limits of Si and S in 0.7% HNO_3 were around 1 ppt (ng/L); P, Se, As, and I were 1 ppt; Cl was 0.1 ppb; while Br was < 3 ppt, which is currently the lowest reported detection limit value in the open literature for this type of low-matrix samples, including ultrapure water, hydrogen peroxide, dilute HNO_3 and HCl.

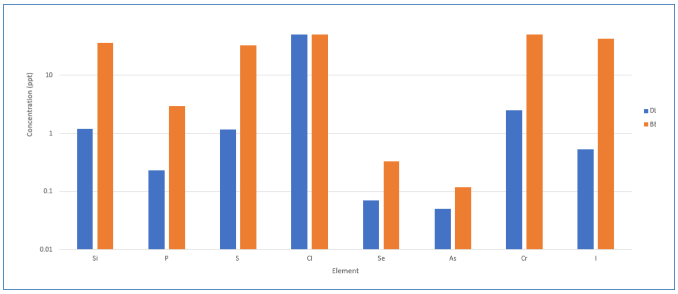

Figure 1. BECs and DLs of elements of six non-metal analytes in 0.7% HNO_3.

Conclusion

Because of the unique multi-quadrupole capabilities of the NexION 5000 ICP-MS, outstanding BECs and DLs for non-metals in a 0.7% nitric acid solution were achieved. The mixed-mode method utilizing both hot and cold plasma conditions was carried out, where the plasma conditions were rapidly switched without the need to create additional methods or repeat the analysis under different plasma conditions. Although nitric acid introduces additional spectral interferences through the enhancement of the nitrogen concentration, the UCT rapidly removed these interferences to achieve the lowest known reported BECs and DLs for these elements under hot plasma (P, S, Cl, As, Se, Br, and I) and cold plasma (Si) conditions.

Reference

Summarized from the PerkinElmer application note "Ultra-Trace Determination of Non-Metallic Elements in Dilute Nitric Acid Using NexION 5000 ICP-MS" by Chung Ryu and Soo Young Yoon.

APPLICATION BRIEF

ICP - Mass Spectrometry

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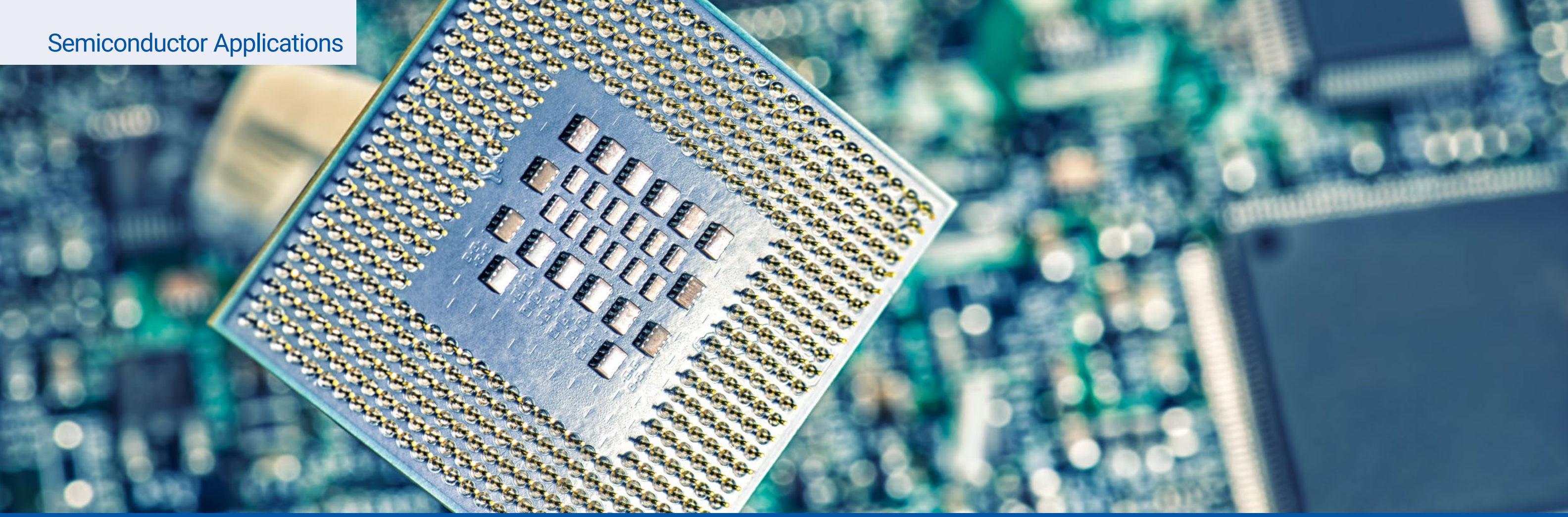
NexION 5000 ICP-MS



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 (H_2SO_4) and hydrogen peroxide (H_2O_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% H_2SO_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 NH_3, O_2, 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 Ti^+ isotope, $^{32}S^{16}O^+$, $^{31}P^{16}OH^+$, $^{48}Ca^+$ 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 Ti^+, SO^+, POH^+ and Ca^+ will enter the cell pressurized with NH_3. Here, 100% NH_3 reacts rapidly with Ti^+, creating several clusters at higher masses. Thereafter, Q3 resolves $Ti(NH)_x^+$ 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 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 NH_3 flow was optimized at 0.8 mL/min, which was then used for quantitation.

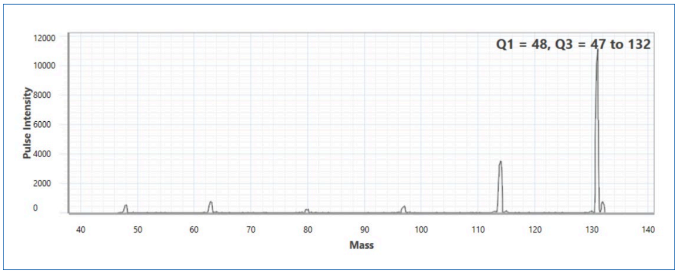


Figure 1. Scan of Ti-NH_3 clusters from masses 47-132.

Results

In this work, Mass Shift mode was used for measuring Ti, V, Zn and Ge as clusters with NH_3 while P, Sc, As and Se were measured as clusters with O_2. Figure 2 shows DLs in 10% H_2SO_4 for 52 elements, along with the color-indicated modes of operation. DLs in 10% H_2SO_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.

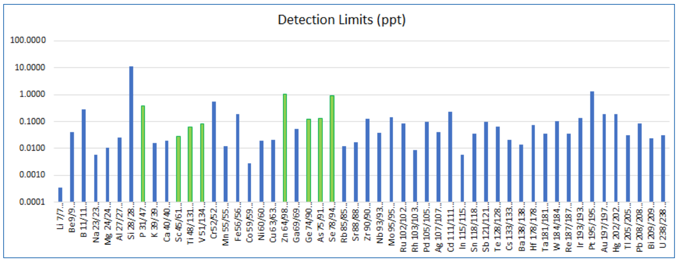


Figure 2. DLs in 10% H_2SO_4 for 52 elements: blue bars – elements analyzed in MS/MS mode; green bars – elements analyzed in Mass Shift mode.

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 ±15% from the initial reading.

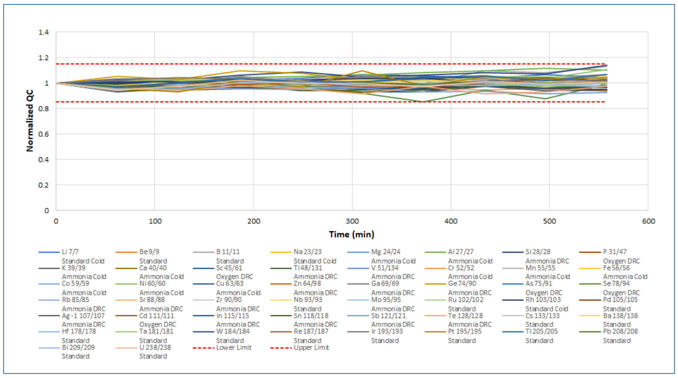


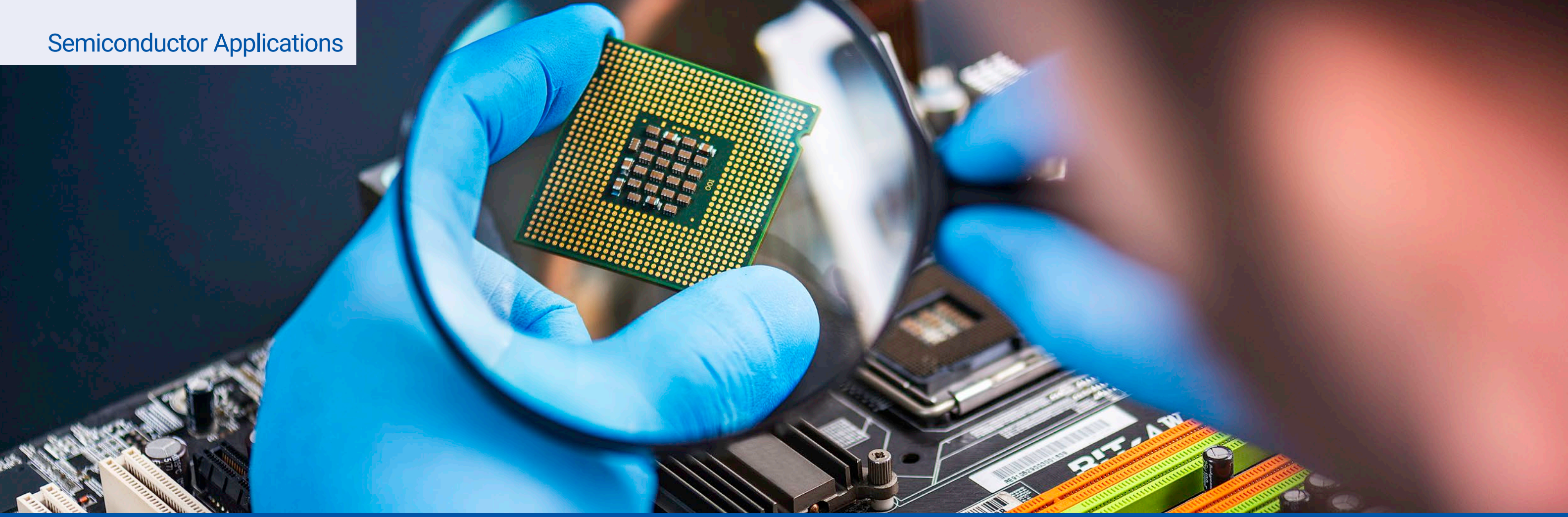
Figure 3. Spike recovery of 15 ppt of 50 analytes in 10% H_2SO_4.

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% H_2SO_4.

Reference

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



APPLICATION SPOTLIGHT

Ultra-Trace Quantification of Non-Metals in Sulfuric Acid Solutions Using the NexION 5000 ICP-MS Under Different Cell Gas Conditions

The Importance of Quantifying Non-Metals in Sulfuric Acid

In the semiconductor industry, there is a growing demand for ICP-MS instrumentation to analyze non-metals – such as boron (B), phosphorus (P), silicon (Si), germanium (Ge), arsenic (As), selenium (Se), bromine (Br) and iodine (I) – at ultra-trace concentrations in sulfuric acid matrices where the presence of sulfur, argon, nitrogen, oxygen, hydrogen and carbon can interfere with the analytes by forming polyatomic interferences. The use of an ICP-MS that has a resolving quadrupole before the collision/reaction cell as well as the ability to control the reaction within the cell can dramatically improve detection limits, which allows quantification of non-metallic elements at ultra-trace levels. This work describes how a NexION® 5000 Multi-Quadrupole ICP-MS utilizing different cell gases, optimized instrumental parameters and multi-quad technology delivered the best detection limits (DLs) and background equivalent concentrations (BECs).

Interference Reduction Using the NexION 5000 ICP-MS

Instrumental conditions can be found in the full application note. Mass Shift mode was applied to P, Ge, Se and As, which allowed the removal of polyatomic interferences via exothermic reactions using oxygen as the reaction gas to form PO^+, GeO^+, SeO^+ and AsO^+ respectively. Although silicon forms the stable molecular ion SiO^+ in the presence of oxygen gas via an exothermic reaction, N_2^+ and CO^+ have the same mass as silicon and also easily react with oxygen. Consequently, in order to analyze silicon, it is necessary to employ a different means of interference reduction. When reacted with hydrogen, N_2^+ and CO^+ undergo hydrogenation through a spontaneous exothermic reaction, while silicon only undergoes an endothermic reaction. Due to this difference in reaction speeds, silicon can easily be isolated from N_2^+ and CO^+ by employing a high rejection parameter q (RPq) in the quadrupole Universal Cell. As such, in this experiment, reaction with H_2 and MS/MS modes were used to remove interferences from N_2^+ and CO^+ on silicon.

Calibration

The calibration curves of the analytes using different cell gas conditions in 9.8% sulfuric acid all had a correlation coefficient of at least 0.9999 with the exception of silicon which had a correlation co-efficient of 0.9998 as determined using the method of standard addition (MSA) for all these analytes.

Results

Figure 1 shows the detection limits (DLs) in 9.8% H_2SO_4 where two sets of reaction gases were used for Si and P, as well as two different isotopes using Mass Shift mode for Se. In the case of silicon, the analysis was carried out at two different cell gas conditions, where the first set of conditions used hydrogen alone as the reactive gas and the second set used hydrogen mixed with ammonia via an on-line gas mixing manifold. Both methods resulted in a DL of 10 ppt (ng/L). For phosphorous, the analysis was done using first oxygen alone and also using oxygen with hydrogen which were mixed online. For this analyte, the DL was found to be 0.6 ppt with pure oxygen and 0.3 ppt with a mixture of oxygen and hydrogen. The DLs were <0.1 ppt for germanium and arsenic, *ca.* 0.5 ppt for selenium and iodine, and 2 ppt for bromine. The DL for boron, which was run in Standard mode, was excellent at 0.03 ppt, the lowest published DL for this element in the open literature to date.

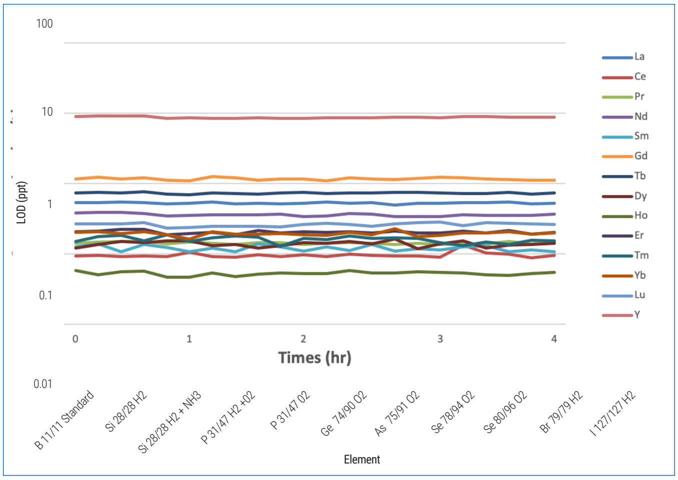


Figure 1. Detection limits for B, P, As, Se, Si, Ge, Br and I in 9.8% sulfuric acid.

This method was then used to quantify concentrations of eight non-metal contaminants in purified and non-purified 9.8% (v/v) H_2SO_4. These data also showed that most of the impurities were effectively removed from the sulfuric acid solution via distillation with the exception of phosphorus, which could not be effectively removed. This is thought to be due to the chemical properties of phosphorus and sulfur and their tendency to form non-volatile compounds. Concentration results from the purified acid can serve as BECs for all analyzed elements.

Conclusion

Being able to achieve ultra-low DLs and BECs for non-metals that are typical contaminants in process chemicals is of critical importance to the semiconductor industry. Excellent detection limits of 0.1 ppt for B, Ge, and As; 0.5 ppt for P, Se, and I; and 10 ppt for Si and 2 ppt for Br were achieved and are the direct result of the proprietary capabilities of the NexION 5000 ICP-MS, including Universal Cell Technology (UCT), the ability to mix cell gases on the fly, and the patent-pending Triple Cone Interface with OmniRing™ technology.

Reference

Summarized from the PerkinElmer application note "Ultra-Trace Quantification of Non-Metals in Sulfuric Acid Solutions Using the NexION 5000 ICP-MS Under Different Cell Gas Conditions" by Chung Ryu and Sooyoung Yoon.

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