

A New Direction in ICP-MS

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Inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful technique for elemental and isotopic analysis that combines the efficiency and ease of use of the ICP component with the sensitivity and selectivity of MS. Sensitivity is a key factor in detection limits, and with environmental and other regulations calling for increasingly lower detection limits, ICP-MS has gained international acceptance as the preferred elemental analysis technique.

Recently, Varian introduced an ICP instrument designed to further improve the sensitivity of this technology. This quadrupole ICP-MS can produce tunable gigahertz sensitivity (1000 million cps/mg/L) in combination with low interference and

reduced levels of background noise. The improvements can be traced to a new direction in the ion beam such that, instead of ions traveling linearly through the ICP-MS interface and quadrupole, the analytical ion beam is reflected through 90°. This is achieved by a new reflecting ion optics system that efficiently reflects and focuses analyte ions into the quadrupole mass analyzer. As much as 80% or more of the analyte ions passing through the skimmer cone are reflected by the ion mirror and directed to the quadrupole, explaining the heightened sensitivity of the new system (1).

New ICP-MS Technology

The unique 90° reflection of the ion beam is the result of its in-

teraction with Varian's patented ion mirror (2), as depicted in Figure 1. The ion mirror is a hollow ring of four electrodes, each individually computer controlled. The electrical potentials applied to the electrodes create a parabolic electrostatic field that reflects the ion beam to a focal point at the quadrupole entrance. In optical terms it is similar to the focusing characteristics of a parabolic mirror. One of the key benefits of this approach is that the parabolic field ensures that ions of higher kinetic energy are brought back to the focal point where ions of lower kinetic energy are naturally positioned. This is especially important in ICP-MS to ensure maximum ion transmission efficiency regardless of the mass of the ion (3).

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Figure 1. The 90° reflecting ion optics system of the Varian ICP-MS system. Ions enter through the interface region via the skimmer cone (1) before being reflected (arrow) and focused by the ion mirror (2). The analyte ions are reflected while photons and neutrals pass directly through the ring to a V-301 turbomolecular pump that is connected to the second-stage vacuum chamber. The turbomolecular pump (3) is shown swung away from its operating position (4). Analyte ions are focused into the quadrupole mass analyzer. A set of curved fringe rods (5) create a double off-axis system that further contributes to the low background of the new ICP-MS.

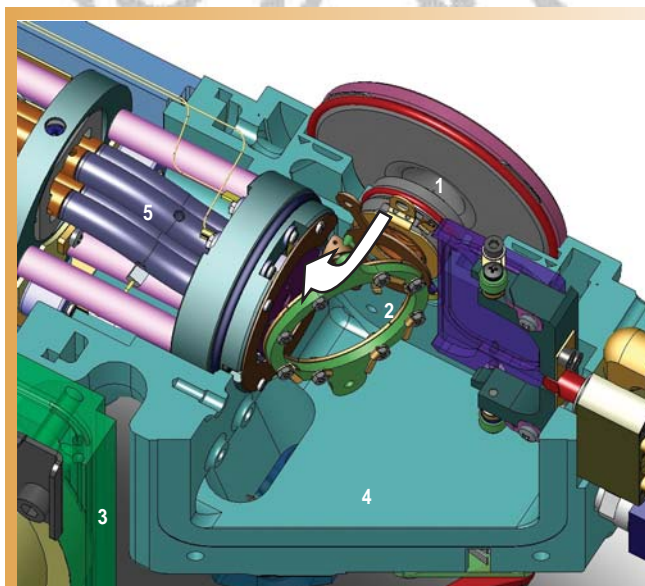
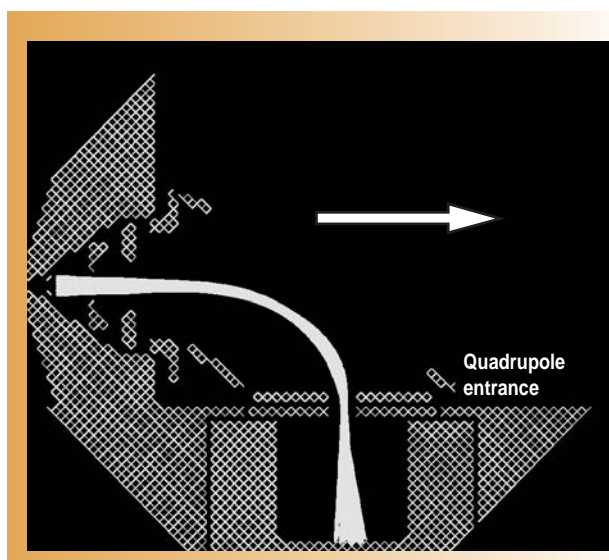


Figure 2. Computer modeling of ion trajectories at low, mid, and high mass for the ion mirror reflecting optics, showing the high efficiency transfer of analyte ions to the entrance of the quadrupole optics. The arrow shows the flight path of photons and neutrals that pass through to the vacuum pump.



The new 90° reflecting ion mirror achieves a transmission efficiency gain of as much as 200 times compared with the theoretical calculations for conventional linear ICP-MS systems (4). This translates into sensitivity that can be adjusted on the fly from low megahertz (millions of cps/mg/L) to gigahertz (1000 Mcps/mg/L). Sensitivity can be adjusted instan-

taneously during any individual sample analysis from low to high, via computer-controlled tuning of the ion mirror and extraction optics. This changes the focal point of the ion beam so that a lower sensitivity setting can be used for highly concentrated elements and a higher sensitivity setting can be used for lower concentration elements.

Real-time, multimode tuning can also be used to adjust performance for different sample types employing lower sensitivity settings for analytes in matrices such as diluted soils, sediments, sludges, and wastes, and the highest sensitivity for the analysis of chemicals in the semiconductor industry and trace environmental applications. The adjustable gigahertz sensitivity of the Varian ICP-MS is also ideal for laser ablation applications, allowing microscopic features to be analyzed while maintaining measurable signal levels.

A significant development is that these impressive sensitivity figures are achieved without compromising performance for background and interferences. Example performance figures are shown in Table I. Further improvements in interferences can also be achieved using specialist sample introduction systems. The CeO^+/Ce^+ ratio is an important indicator because it demonstrates that the high sensitivity of the system is not being achieved simply by introducing more sample into the ICP-MS, a quick fix that may involve loading the plasma with water and oxygen. Enhancing sensitivity by using more sample may compromise the performance of the introduction system, reduce dynamic range and result in greater drift due to cone blockage when more highly concentrated samples are used.

High sensitivity can contribute to lower detection limits, but to be valuable, a detection system with a wider dynamic range is required so that gains in detection limits are not lost in a more restricted upper dynamic range. The ideal characteristics of a detector would be to combine wide linearity, with low noise and ease of use. Traditional ICP-MS detectors combine an insensitive analog section with a pulse counting section for lower concentration ranges. There are two well-documented problems with this dual-mode approach however.

Firstly, it requires time-consuming multipoint cross calibration between the pulse and the analog sections that tend to drift with aging of the analog section. Second, the linear dynamic range of the pulse-only section can have an upper concentration limit of just 10–50 µg/L. This means the responses



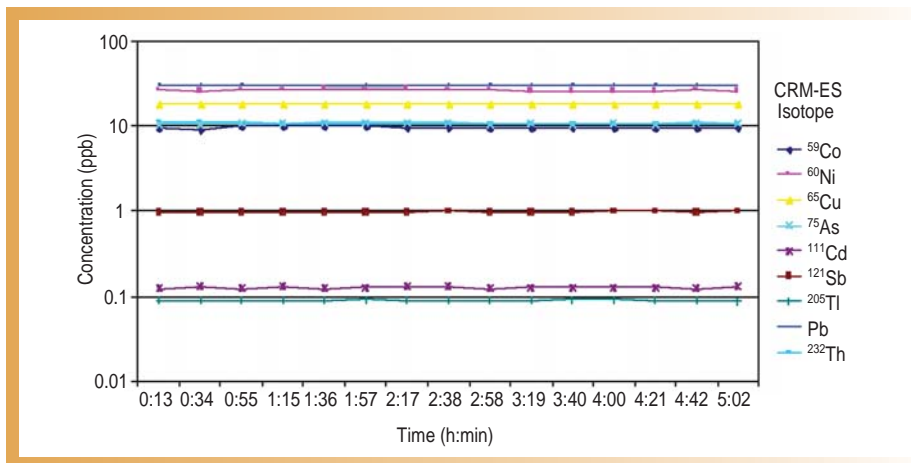


Figure 3. Stability study over 5 h showing results for estuarine sediment CRM. The stability for all analytes is less than 3.0% RSD over the 5-h period. During this period the estuarine sediment CRM was presented alternately with the other CRMs, to simulate significant changes in sample matrix over time.

Table I. Typical performance specifications for the Varian ICP-MS

High Sensitivity Mode, Mcps/mg/L

⁹ Be	>50
¹¹⁵ In	>1000
²³² Th	>500
Precision (10 replicates, 20 min)	<3%
Oxides	CeO ⁺ /Ce ⁺ < 3%
Doubly charged	Ce ⁺⁺ /Ce ⁺ < 2%
Background	<5 at 5 amu

Low Sensitivity Mode, Mcps/mg/L

⁹ Be	>5
¹¹⁵ In	>50
²³² Th	>20
Precision (10 replicates, 20 min)	<3%
Long term stability (10 µg/L multielement standard aspirated for 4 h)	<4%
Oxides	CeO ⁺ /Ce ⁺ < 1%
Doubly charged	Ce ⁺⁺ /Ce ⁺ < 2%
Background	<2 at 5 amu

Table II. Recoveries for river sediment CRM.

Isotope	Measured (µg/L)	Certified (µg/L)	Recovery (%)
⁵¹ V	25.4	25	101.6
⁵⁹ Co	10.1	10	101.0
⁶⁰ Ni	49.1	50	98.2
⁶⁵ Cu	93.9	100	93.9
⁶⁶ Zn	1338	1500	89.2
⁷⁵ As	60.2	60	100.3
⁸² Se	2.4	2	120.0
¹¹¹ Cd	10.4	10	104.0
¹²¹ Sb	48.3	50	96.6
¹³⁷ Ba	47.5	50	95.0
²⁰⁵ Tl	1.0	1	100
²³² Th	2.2	2	110
²³⁸ U	1.1	1	110

for most elements must be cross-calibrated. The Varian ICP-MS uses an ETP AF250 electron multiplier detector, an all-digital pulse counting detector with an effective count rate upper limit that is 10,000 times that of standard pulse counting multipliers (5). The AF250 consists of three sections:

- ion conversion where incoming ions are converted into measurable electrons
- control section where the signal is dynamically attenuated from 90% efficiency for trace signals to 1 in 10,000 efficiency for intense signals
- amplification section where the resultant signals are finally processed for measurement.

The AF250 is an all pulse counting design that eliminates the need for analog to digital calibrations, a complex and time-consuming process that is required by other dual-mode designs. The AF250, produced by ETP Electron Multipliers Pty. (Sydney, New South Wales, Australia), has the ideal dynamic range to match the tunable gigahertz sensitivity of the Varian ICP-MS.

Applications and Results for Adjustable Tuning Mode

The Varian ICP-MS was tested for wide range operability by examining suitable normal sensitivity conditions for difficult sample types and the ultimate high sensitivity conditions for low-level laser

Table III. Recoveries for soil CRM.

Isotope	Measured ($\mu\text{g/L}$)	Certified ($\mu\text{g/L}$)	Recovery (%)
⁵¹ V	10.6	10	106.0
⁵⁵ Mn	12.6	10	126.0
⁶⁰ Ni	30.5	30	101.7
⁶⁵ Cu	30.9	30	103.0
⁶⁶ Zn	104.1	100	104.1
⁷⁵ As	20.6	20	103.0
⁸² Se	1.0	1	100.0
¹¹¹ Cd	0.3	0.3	100.0
¹²¹ Sb	3.1	3	103.3
¹³⁷ Ba	459.6	500	91.9
Pb	39.5	40	98.8
²³² Th	10.6	10	106
²³⁸ U	1.1	1	110

Table IV. Recoveries for estuarine sediment CRM.

Isotope	Measured ($\mu\text{g/L}$)	Certified ($\mu\text{g/L}$)	Recovery (%)
⁹ Be	2.1	2	105.0
⁵¹ V	96.0	100	96.0
⁵³ Cr	83.0	80	103.8
⁵⁹ Co	9.8	10	98.0
⁶⁰ Ni	30.9	30	103.0
⁶⁵ Cu	20.7	20	103.5
⁶⁶ Zn	156.8	150	104.5
⁷⁵ As	10.9	10	109.0
⁸² Se	4.6	5	92.0
Pb	30.0	30	100.0
²³² Th	10.6	10	106.0

Table V. Duplicate analysis results of NIST glasses by LA-ICP-MS.*

Isotope	NIST 616	NIST 616	NIST 614	NIST 614
	(mg/kg in the solid) Found	(mg/kg in the solid) Certified	(mg/kg in the solid) Found	(mg/kg in the solid) Certified
¹¹ B	0.21	(0.2)	1.30	(1.3)
⁴⁷ Ti	2.54	(2.5)	3.11	(3.1)
⁵⁷ Fe	11.19	(11)	12.6	(13.3)
⁵⁹ Co	0.07	N/A	0.76	(0.73)
⁶⁰ Ni	0.81	N/A	1.09	(0.95)
⁷¹ Ga	0.26	(0.23)	1.50	(1.3)
⁸⁵ Rb	0.1	(0.1)	0.88	0.855
¹⁰⁷ Ag	0.08	N/A	0.48	0.42
¹¹¹ Cd	0.19	N/A	0.56	(0.55)
²⁰⁶⁻⁸ Pb	2.41	N/A	2.68	2.32
²³⁸ U	0.077	0.0721	0.84	0.823

* Values in parentheses are not certified and are for information only. At these low levels many element values are not certified.

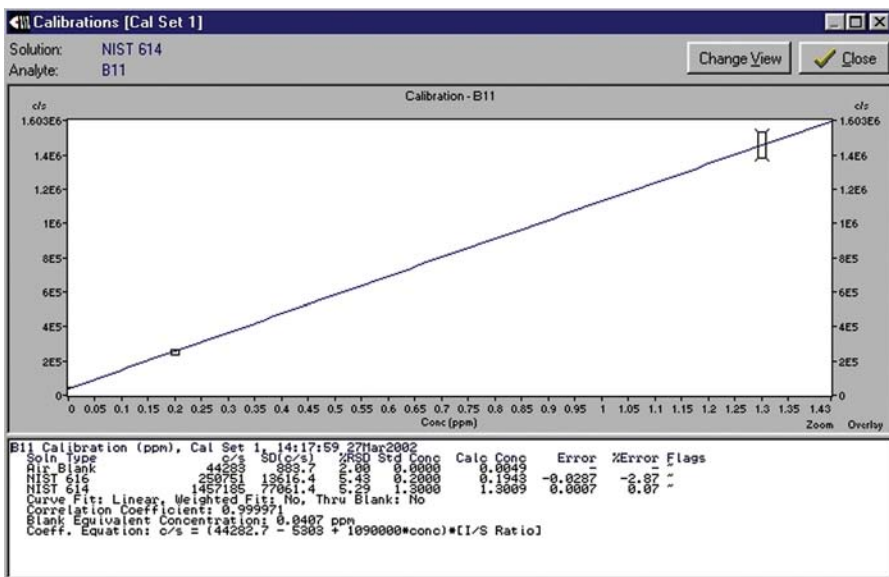


Figure 4 (left). LA-ICP-MS calibration for B using NIST 616 and NIST 614 glass reference materials. The correlation coefficient is 0.99997.

ablation applications.

Normal Sensitivity Analysis of Digested Environmental Samples

A series of reference solutions was prepared equivalent to 1 g of sample digested into a final volume of 100 mL

and then diluted a further 10 times for analysis. Aqueous calibration standards were prepared in 1% nitric acid. Internal standards of ⁶Li, ⁸⁹Y, ¹¹⁵In, ¹⁵⁹Tb, and ²⁰⁹Bi were used. The certified reference materials (CRM) were river sediment solution A: CRM-RS-A, soil solu-

tion A: CRM-Soil-A, and estuarine sediment solution CRM-ES and were measured in duplicate. Our results on the estuarine sediment were erroneous for Cd and Sb due to contamination in our laboratory and are not reported.

The Varian ICP-MS was tuned to normal sensitivity conditions, a mid-mass sensitivity of approximately 44 Mcps/mg/L was selected with a CeO⁺/Ce⁺ ratio of just 0.7%.

Recovery results for these certified reference materials are shown in Tables II–IV. It can be seen that recoveries for these varying sample types are achieved across the mass range. To assess long-term stability, the CRMs were then analyzed in continuous sequence with no rinsing for a period of 5 h. The CRMs were alternated to create significant variations in the ion flux entering the ICP-MS. As can be seen from Figure 3, stability for all analytes is less than 3.0% RSD stability over the 5-h period.

High Sensitivity Analysis – Lower Detection Limits for Laser Ablation ICP-MS

In laser ablation ICP-MS (LA-ICP-MS), a laser is directed to the surface of a solid sample and the resultant ablated material is swept up into the plasma of the ICP-MS. Spot sizes refer to the size of the crater left on the surface of the sample and these vary with the nature of the laser, the efficiency of the coupling of the laser to the sample, and the controlling parameters used (6, 7). A typical laser crater might measure 10–50 μm in diameter with a desirable goal being to reduce spot sizes so as to allow the examination of smaller and smaller features and, critically, to minimize damage to the sample. Higher sensitivity will be required if smaller spot sizes are to be used routinely.

LA-ICP-MS can be used for important applications where these discrete features can yield important information such as the analysis of growth bands in coral to obtain information about historical seawater temperatures

and the analysis of fish otoliths to monitor pollution history. In geochemistry, both bulk laser and small spot laser ablation techniques are used. An example of the latter is the analysis of fluid inclusions in geochemical structures. Microscopic fluid inclusions in minerals reveal important information about the chemical composition of crustal fluids and are used in the study of hydrothermal transport of metals and ore forming processes (8).

In bulk geochemical LA-ICP-MS, it is common practice to prepare samples by fusion techniques to create a glassy pellet. The LA-ICP-MS can then be calibrated using a series of NIST standard reference glasses so as to quantify analytes found in geochemical samples that have been fused before analysis. The NIST glass series is available in four standards of varying concentrations covering a dynamic range of 10,000 times in concentration from a fraction to hundreds of milligrams per kilogram. The most widely used of these glasses is NIST 612 that includes elements at concentrations readily measurable by conventional LA-ICP-MS. However, the least concentrated of the standards, NIST 616 and NIST 614, are very rarely used in LA-ICP-MS because many of the elements are undetectable at these concentrations.

The high sensitivity, on-the-fly adjustment feature of the Varian ICP-MS permits the analysis of these very trace level

analytes in the lowest NIST glasses. This is a significant development and confirms the use of high sensitivity LA-ICP-MS for analyses that were previously deemed too insensitive. In this work, a CETAC Technologies (Omaha, NE) LSX-200 laser ablation system (266 nm) was used to obtain the successful calibration of these NIST glasses.

A sample calibration is shown in Figure 4 for boron. Note that the concentration of B in the lowest standard is 200 $\mu\text{g}/\text{kg}$ (parts per billion) in the solid material.

After calibrating, the glasses were read back as samples in duplicate with recoveries for all elements in the 10–100 $\mu\text{g}/\text{kg}$ range, as shown in Table V.

Conclusions

The new Varian ICP-MS represents a significant change in direction for this widely acclaimed technique for elemental analysis. The patented 90° reflecting and focusing ion mirror has enabled the development of the world's first gigahertz quadrupole ICP-MS. The new ICP-MS enables on-the-fly, multimode tuning within any sample, and optimized tuning for specific applications. The product demonstrated both capacity recoveries and stability for dense matrix environmental samples using normal sensitivity tuning, and extremely low detection limits using high sensitivity tuning — suitable for the analysis of solids using laser ablation techniques.

The increased sensitivity of the Varian ICP-MS also offers advantages to industries such as semiconductor chemicals and wafer manufacturing, which will be the focus of future articles.

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