# Fully Simultaneous ICP-MS

## The new approach to isotope geochemistry

*Elemental analysis and the measurement of the ratio of their isotopes are well established techniques in geochemistry, extensively used for geological dating and for "fingerprinting" rocks, minerals and ceramics. The so-called Rare Earth Elements (REE's) are widely used as diagnostic indicators, requiring accurate measurements at extremely low concentrations. A related technique, isotope dilution, is an evaluation method that can provide extremely precise measurements of trace element concentrations in geological samples. Isotope dilution is also often used in the preparation of standard reference materials (SRM's).*

*Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a widely used analytical method for such measurements, in which a solution of the sample is introduced into the high temperature environment of inductively coupled plasma. The plasma atomizes the sample and then ionizes the atoms (isotopes). The resulting ions are then transferred into a mass spectrometer that separates them according to their mass/charge ratios. Most instruments scan across a range of mass numbers, measuring each isotope sequentially. Because only one mass/charge ratio is measured at a time, any fluctuations due to the sample introduction process, the plasma, or the detection system can introduce errors in the observed isotope ratios. Furthermore it may be desirable to measure a range of elements to establish an elemental "fingerprint" of the sample and to allow evaluation of various calculation strategies using different isotope combinations. Today's instruments often suffer from the limitation of measuring at best only a narrow mass range. Others work with a pulsed ion beam, limiting the sensitivity and the dynamic working range. Instruments that scan relatively slowly or over a limited mass range are also clearly at a disadvantage when handling transient signals, as in hyphenated measurements with techniques like HPLC or sample introduction by laser ablation. Instrument technology has evolved to reduce these problems, but until now the majority of ICP-MS instruments have relied on scanning to a greater or lesser extent, and its attendant problems.*

The new SPECTRO MS from SPECTRO Analytical Instruments is the first commercially available ICP-MS capable of truly simultaneous mass spectrometry. A revolutionary new detector placed at the focal plane of the mass spectrometer simultaneously and quantitatively measures the entire mass spectrum, from lithium to uranium. This has the immediate benefit that all isotopes are measured at the same instant in time, allowing ratio measurements that are free of noise from the sample introduction system such as flicker noise from the plasma itself or pulsation from the peristaltic pump used to introduce the sample. It also greatly improves the instrument's ability to handle transient signals. The accuracy and precision of the measurements and hence the reliability of the conclusions drawn from them are vastly improved. Additionally, collecting the entire mass spectrum allows future analysis utilizing any element in the sample, even when the sample is no longer available. Productivity is also improved: the complete mass spectra of up to 100 samples per hour can be recorded with no limitations on the number of elements or isotopes measured.

## INTRODUCTION TO ISOTOPE GEOCHEMISTRY

Isotope Geochemistry gives insight into the origin, formation and ages of rocks and minerals by studying the relative isotope abundances of elements. The geological processes by which elements become distributed in different minerals are complex and beyond the scope of this paper, but a few examples may serve to illustrate the role and importance of isotope analysis.

Earth's evolution can best be understood through detailed analysis of minerals from various geological periods. In the billions of years that have elapsed since the solar system was formed, the distribution of isotopes of different elements has been subject to changes, as the result of chemical reaction, radioactive decay, melting, differentiation, compression, and/or crystallization processes, etc.

It is well known that some of the isotopes of elements found in minerals are present because of the process of radioactive decay. For example, the uranium 238 isotope ($^{238}$U) decays to lead 206 ($^{206}$Pb) with a half-life of approximately 4.5 billion years. In a closed system (i.e. one in which isotopes cannot exchange with the outside (e.g., a crystal) the ratio of these isotopes will depend on the time elapsed since the rock formed by crystallization. Therefore, measurement of the relative ratios of the appropriate isotopes offers insight into the sample's age. One mineral frequently used for this purpose is zircon ($ZrSiO_4$). During crystallization, atoms of uranium and thorium (another precursor of lead) are preferentially incorporated into the zircon crystal lattice. Since any lead found in the crystal is likely to be there as the result of radioactive decay, measuring the relative abundances of lead and its precursors in the zircon yields the time since the zircon crystallized and hence the age of the rock. Other elements used in similar dating schemes are Rb/Sr, Sm/Nd, Lu/Hf and Re/Os.

Another important method for gaining insight into the history and origin of minerals utilizes the fact that some elements, based on their ionic properties (size and charge) tend to have higher concentrations during the formation of a particular solid phase (rock), while others will tend to stay in the liquid magma phase. The former are known as compatible elements, the latter as incompatible elements. The relative abundance of compatible and incompatible elements in a given rock can provide key information regarding the history and origin of tectonic units. Rare Earth Elements, usually present as traces, have broadly similar chemical properties. They are particularly useful as indicators of these processes.

For certain rocks originating from a defined tectonic environment and of a certain age, the following element ratios can be used as a quality indicator for the chemical analysis. Deviation from these values may indicate interferences in the analytical process (like an incomplete sample digestion procedure) or a different geochemical environment.

*Table 1:*
*Element ratios as quality indicator*

| Elements | Ratio |
|---|---|
| Zr / Hf | 36 - 37 |
| Nb / Ta | 17 - 18 |
| Y / Ho | 28 |

Some of the oldest known rocks are meteorites or "Chondrites", and these are believed to have derived from small asteroids and similar bodies that, when they formed from the cosmic dust, were too small to undergo the heating, melting, partition and crystallization processes that have occurred in larger bodies such as the Earth. Chondrites are therefore regarded as a baseline to which all "younger" minerals can be compared. This has led to the concept of chondrite normalization, where all element concentrations are normalized to the values found in chondrites. Changes due to geological processes then show up as deviations from these normalized values.

Analytical techniques of extremely high sensitivity, accuracy and precision are necessary to detect and quantify trace elements and isotopes at levels encountered in minerals. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) is one of the available techniques capable of this level of performance. It is often the preferred analytical techniques for determining isotope ratios, element ratios and absolute element concentrations in geochemical samples.

## ICP-MS: THE BASICS

An ICP-MS spectrometer works by separating ionized atoms according to their mass/charge ratio. In conventional ICP-MS, a sample solution is converted into a fine aerosol via a pumped nebulizer system, and introduced into a high temperature argon plasma where the analyte is atomized and subsequently ionized. These charged ions are then transferred into the mass spectrometer, where species of different mass/charge ratios are separated by magnetic and/or electrostatic fields and subsequently detected.

A basic ICP-MS comprises the main components shown in figure 1.

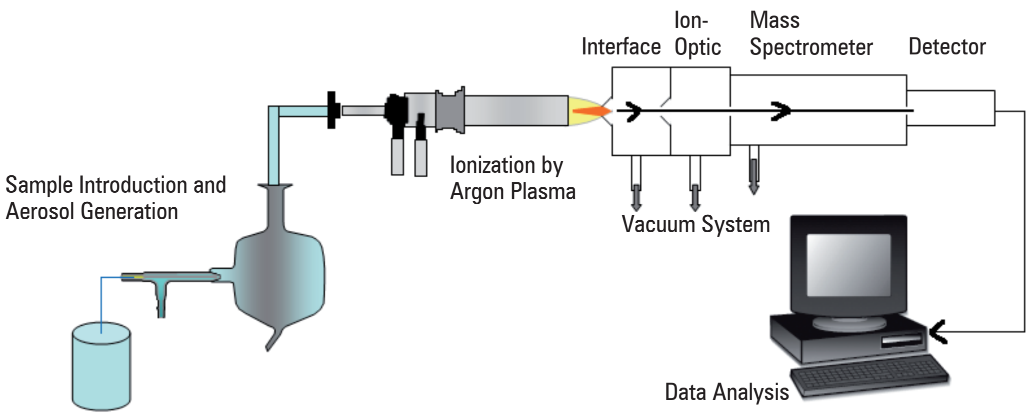


*Figure 1: ICP-MS Schematic*

The system illustrated is designed for continuous measurements, i.e. the sample is introduced over a period of several seconds to minutes and the detector signal integrated over time. Noise and fluctuations in any of the system components will be superimposed on the detector signals and adversely impact the achievable limits of detection. In isotope ratio or dilution studies, the abundances of two or more isotopes of interest have to be compared mathematically, so unless their concentrations are measured under exactly the same conditions, errors can be introduced. Most conventional MS detectors involve "scanning" the mass/charge ratio of the ions arriving at the detector over time, and while many efforts have been made to minimize the time interval between detection of individual masses, short-term fluctuations in the sample introduction system or the plasma can still lead to errors. For similar reasons, transient signals may not be accurately tracked, a problem known as signal "skew". The only real solution is simultaneous and continuous detection of the masses of interest. In attempting to achieve this simultaneous detection using conventional technology, large expensive instruments were fabricated which provided two or more movable detectors which could be laboriously set to monitor a limited number of individual isotope masses. None of these instruments provided the ideal capability of simultaneously observing the whole mass spectrum. The new SPECTRO MS, utilizing an entirely new concept in detectors, is the first isotope ratio instrument to offer all the advantages inherent in the simultaneous observation of the entire mass spectrum. Before describing the revolutionary new detector that makes this possible, it is useful to consider some of the conventional types of mass spectrometer, and their limitations for isotope analysis.

## MASS SPECTROMETER DESIGNS

### The Quadrupole

The most commonly used ICP mass spectrometers are quadrupole instruments.

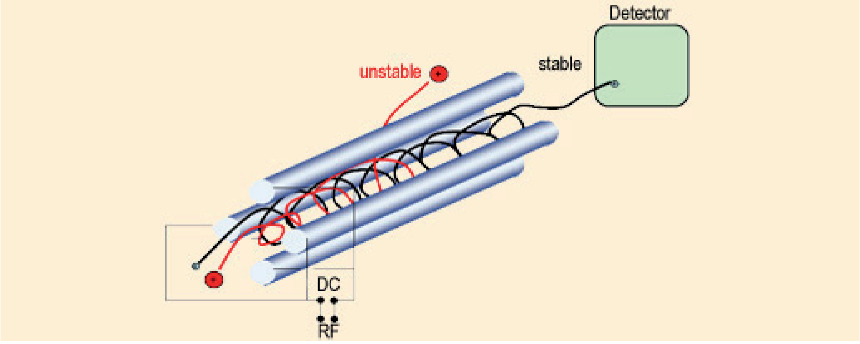


*Figure 2: Quadrupole ICP-MS instrument*

A quadrupole is constructed from four straight rods with opposing rods connected. A combination of high frequency and DC voltages is applied to the rod pairs. With the appropriate combination of high frequency and DC voltages, only ions with one mass/charge ratio are able to traverse the resulting electrical field and emerge from the end of the quadrupole. This type of analyzer actually acts as a mass filter. A mass spectrum can be obtained by ramping the RF and DC voltages and sequentially measuring the intensity of the ions passing through the quadrupole. A quadrupole based ICP-MS instrument can measure about ten spectra per second in the mass range of interest in ICP-MS studies.

This means that different isotopes are measured sequentially only for about $400\,\mu s$ each, so that time-dependent effects like plasma flicker or pump pulsations can lead to higher noise and poorer detection limits. In normal use to optimize the duty cycle, i.e., the proportion of time used for actual measurement, these instruments are programmed to "jump" from isotope to isotope of interest. The rest of the mass spectrum is not measured and the information about unexpected elements and/or interferences is lost.

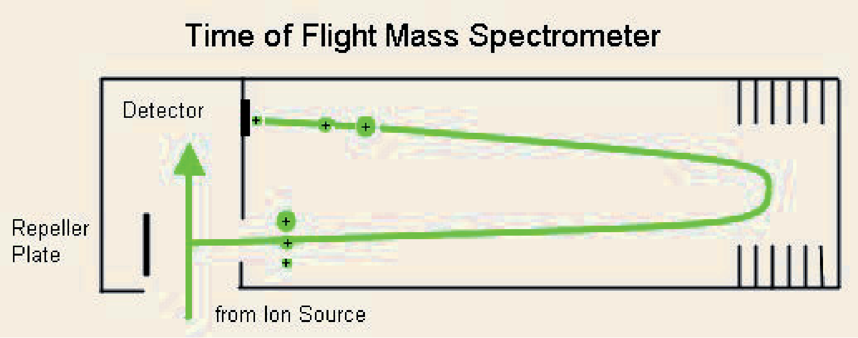


*Figure 3: Time-Of-Flight ICP-MS instrument*

## Time-Of-Flight

There are several designs of Time-of-Flight (TOF) mass spectrometer. In the depicted orthogonal geometry, a packet of ions, generated at the same point in time in the plasma, is ejected from the ion stream by an electrostatic pulse from a "repeller" plate, in a direction perpendicular to the ion stream. The ions then enter a field free region called the flight tube. Since all ions are accelerated to the same kinetic energy by the repeller plate, light mass ions have a higher velocity compared to the heavier mass ions and thus will arrive at the detector first. In this way, the complete mass spectrum can be detected measuring one mass to charge ratio of ions after the other from the light mass ions to the heavier mass ions. The reflectron arrangement (pictured), with an ion mirror at the end of the flight tube, is very common. This design doubles the flight path through the tube and compensates for slight variations in the energy of ions of the same mass/charge ratio thus improving resolution. Depending on the mass range, these instruments can measure 20,000 to 40,000 spectra per second, but multiple spectra have to be integrated to achieve acceptable signal to background ratios. Furthermore, while one packet of ions is being analysed, all others passing through the instrument are lost. The TOF spectrometer also has a dynamic range limited by the counting rate of the detector to around five to six orders of magnitude.

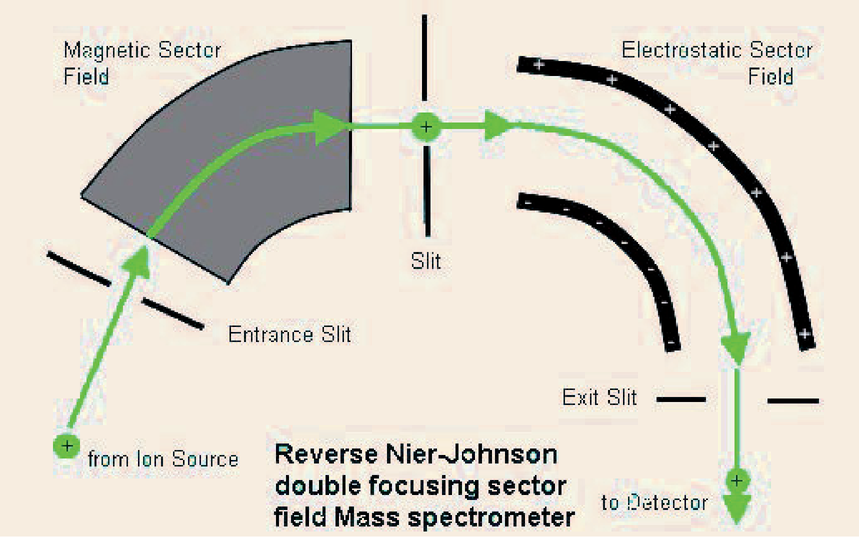


*Figure 4: Magnetic Sector ICP-MS instrument*

## Magnetic Sector

Nier-Johnson double focusing magnetic sector instruments use a combination of a magnetic sector field and an Electrostatic Analyzer (ESA). The magnetic sector deflects and focuses ions based on their mass/charge ratio and the ESA deflects and focuses ions based on their kinetic energy. Slits are used to admit the ion stream and to select the ions passed to the detector. Changing the strength of the magnetic field and/or the voltages of the electrostatic analyzer results in the scanning required to transport one mass/charge ratio after the other to the single detector, so again time-dependent variables can be superimposed on the results, impairing precision.

Attempts have been made, in so-called "multi-collector" instruments (MC-ICP-MS), to improve the situation by using multiple detectors to collect information from the separated isotopes simultaneously. Clearly, because of the physical size of the detectors there are mechanical limitations to this approach, and the mass ranges that can be covered simultaneously are very limited. Detectors can be optimized to detect specific combinations of elements or isotopes, but for any others scanning will still be necessary, and a complete, simultaneously measured mass spectrum is still not achievable.

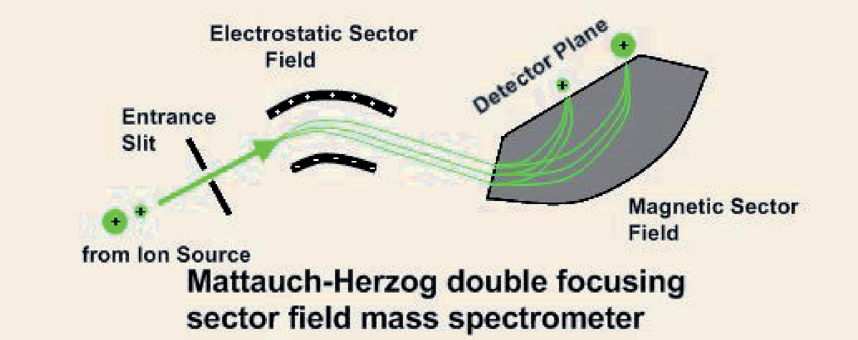


Figure 5: Mattauch Herzog double-focusing sector field mass spectrometer

It is thus obvious that all these designs are not optimal for isotope ratio investigations. One configuration, however, has the potential to overcome all the problems associated with "scanning" spectrometers by allowing all the isotopes to be measured simultaneously. This is the double focusing sector field mass spectrometer in the Mattauch-Herzog geometry, which also uses an ESA and a magnet, but in a specific geometric configuration that focuses ions of different masses on to the same flat focal plane, but spatially separated. This is achieved without the need for varying either the voltages applied to the ESA or the strength of the magnetic field. Unfortunately, however, until now there has been no commercially available detector capable of detecting and measuring this spatially resolved mass spectrum. Photographic plates have been used, but these have obvious limitations.

The SPECTRO MS solves all these problems by combining the Mattauch-Herzog geometry with a revolutionary new detector that measures the entire mass spectrum simultaneously.

## The "Ion 120" Direct Charge Detector

Specially developed for SPECTRO, the Ion 120 is a 12cm long CMOS (Complementary Metal Oxide Semiconductor) array that covers the entire mass range from Li to U in 4800 separate channels. Each of these channels incorporates separate high- and low-gain detector elements, allowing each channel to independently handle a wide range of signal levels. This in part accounts for the extremely wide dynamic range of the system, up to 8 orders of magnitude in the basic integration cycle. The dynamic range is extended even further by the readout system used when the measurement is longer than the basic integration cycle. In the basic integration cycle, each channel is monitored by the electronics at very short time intervals (every 20ms). If the signal integrated in this time interval nears the threshold of the channel, the integrated signal of that channel is automatically logged and the channel is reset and begins to collect information again. This is repeated until the end of the set measurement time, when all the collected data is integrated to produce the final signal. This means that the detector is always working within its linear response range and that longer integration times can be used without fear of detector saturation.

The basic principle of the detector is similar to that of a Faraday Cup: when a charged ion arrives at the detector, it is discharged by receiving an electron, generating a detector signal. This detector is referred to as a Direct Charge Detector (DCD) because every ion arriving at the detector contributes to the signal. The DCD can therefore be regarded as 100% efficient. Furthermore, with 4800 detector elements covering the mass range (from~5 to 240 amu) every mass unit is on average covered by 20 separate elements, resulting in a true mass spectrum rather than a single point for each amu.

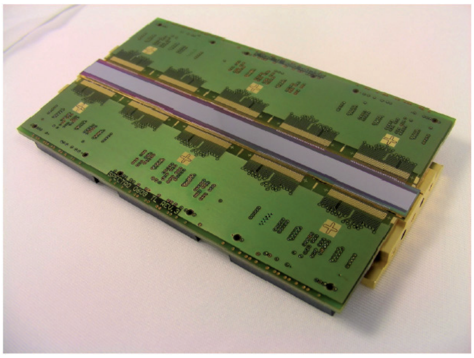


*Figure 6: The Ion 120 direct charge detector*

Some conventional MS detectors, like the SEM (Secondary Electron Multiplier), and even the less sensitive Faraday Cup can show aging effects. SEM's are particularly prone to these aging effects and have to be replaced from time to time, making them an expensive consumable.

Advantages gained by using this new detector may be summarized as:

- Elimination of noise from the sample introduction system
    - Flicker noise from the plasma
    - Pulsation from the peristaltic pump
- Improved quantitative precision

- Element ratios (internal standards, isotope ratios) are calculated on readings obtained simultaneously and therefore under identical conditions
- Improved precision, theoretically by 1-2 orders of magnitude
- Complete mass spectrum from every single measurement
- Method development can be conducted after the sample is measured to:
  - See unexpected interferences
  - Detect unexpected elements
  - Make interference corrections after the measurement is completed
  - Review spectra of samples that no longer exist
  - Determine additional elements
- Improved handling of transient signals
  - No signal skew when measuring many different isotopes
  - Full duty cycle on all elements independent from the number of elements monitored – all are measured, all the time.
  - Better precision with transient sample introduction techniques (HPLC, Laser Ablation)

## THE SPECTRO MS

The benefits of simultaneous detection can only be fully realized if the rest of the instrument is functioning optimally, and the SPECTRO MS incorporates many other refinements:

### Sample Introduction

The SPECTRO MS can be fitted with virtually any sample introduction system normally used in ICP-MS. The large sampling area can accommodate most types of nebulizer/spray chamber combinations, with a 12-roller, 4-channel, computer-controlled peristaltic pump fitted as standard. In addition to sample and drain, additional channels can be used for a variety of purposes such as online addition of internal standards.

### The Plasma

The generator used to power the plasma in the SPECTRO MS has an output of 1700W, more than enough for even the most difficult organic solutions.
The generator is of the free-running type, running at a nominal frequency of 27.12MHz. This frequency is chosen in preference to 40.68MHz, the other "permitted" frequency commonly used for ICP, because while the analytical performance of an ICP system differs little between the two, the frequency range (the "allowed bandwidth") over which a free-running generator may adjust to compensate for sample loading is considerably wider at 27 MHz.

### The Spectrometer Interface

The spectrometer interface provides the route between the plasma (at up to 10,000K and atmospheric pressure) and the mass spectrometer (at ambient temperature and high vacuum). The SPECTRO MS interface is an optimized two-stage design with "sampler" and "skimmer" cones. At the sampler cone, the pressure drop across the cone accelerates the ions to supersonic speed towards the skimmer cone in an expanding beam. At the skimmer cone the ions are further accelerated into the vacuum chamber of the spectrometer. Both cones "peel off" the outside of the plasma, removing most of the argon while maintaining the composition of the ions in the central channel. The cones are made of either nickel or platinum for aggressive acid and organic samples. Since these items require regular inspection and cleaning, the SPECTRO MS is configured such that a single mouse click brings the interface assembly into a convenient service position for maintenance without losing vacuum in the spectrometer.

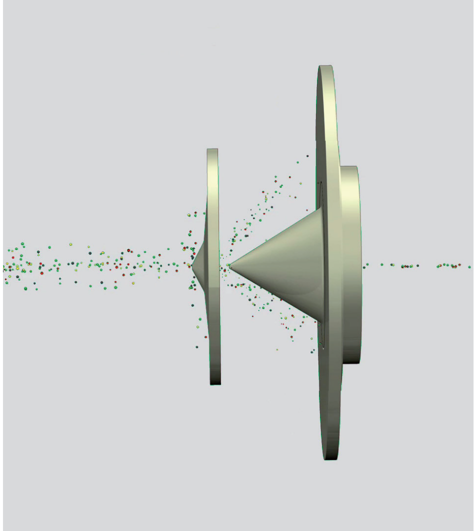


Figure 7: SPECTRO MS Interface

## Ion Optics

After passing through the interface, the stream of ions still contains unwanted particles such as neutral atoms, electrons, photons and dirt. The ion stream also needs to be shaped to conform to the entrance slit of the spectrometer. In the SPECTRO MS this task is carried out by the components of the instrument's sophisticated ion optics:

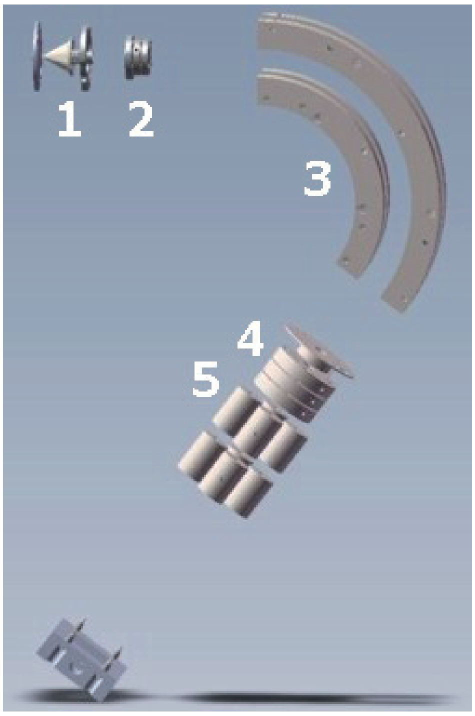


*Figure 8: Ion Optics*

1. The interface
2. Einzel lens, focuses the ion stream into
3. Pre filter, deflects the ions into a curved flight path, while neutral species, dirt and other particles fly straight on
4. Einzel lens, extracts the ions from the filter and focuses them onto the spectrometer entrance slit via
5. Quadrupole doublet, shapes the ion beam to optimally fill the spectrometer entrance slit.

## The Spectrometer

As noted above, the spectrometer in the SPECTRO MS is a double focusing sector field mass spectrometer in Mattauch-Herzog geometry, with an Electrostatic Analyzer (ESA) followed by a magnetic sector. The ESA separates ions based on their kinetic energy and the magnetic sector on the basis of their mass/charge ratio. All the ions are focused by the magnet onto the same focal plane, the location of the Ion 120 detector. The complete mass spectrum is available for detection, without scanning: the ESA is at a fixed potential and the magnetic sector is a permanent magnet. This eliminates yet more potential variables from the system.

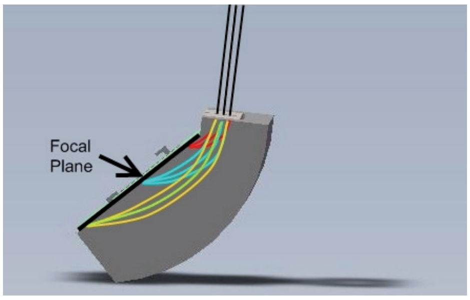


*Figure 9: The Magnet and Detector*

## Signal and Result Processing for Isotope Analysis

The software suite in the SPECTRO MS is called MASS ANALYSER VISION and is based on SPECTRO's highly successful SMART ANALYSER VISION software used with their Optical Emission Spectrometers (OES), with special functionality for processing mass spectra.

Compared to ICP-OES, the ICP-MS spectrum is simple, with the complete mass spectrum of the periodic table containing only approximately 220 masses of interest, compared to tens of thousands of emission lines for the optical emission spectrum. Every element is represented in the mass spectrum by one or more isotopes.

In spite of the relative simplicity of the mass spectra, spectral interferences between elements can still occur because isotopes of different elements can have identical mass/charge (m/z) ratios. Examples are Ba, Ce and La all of which have isotopes with mass/charge 138. This is called an isobaric interference and normally cannot be resolved by spectroscopic means such as higher resolution. However all these elements have other isotopes that do not interfere with each other and can be measured independently to derive correction factors using isotope ratio calculations. These interferences are known and documented, so their correction by software is relatively straightforward – provided that measurements of the alternate isotopes, obtained under identical conditions, are available. One of the unique advantages of the SPECTRO MS is that the complete mass spectrum is always available, and can be recalled even when the sample no longer exists.

Doubly charged interferences can occur with divalent ions such as 138Ba++. This has a mass of 138, but being doubly charged has an effective m/z of 69 and would therefore interfere with 69Ga+, also with an m/z of 69. This can be treated similarly to an isobaric interference, as 71Ga does not suffer from a 138Ba interference. A doubly charged ion of 137Ba has m/z 68.5, so in a low resolution instrument could interfere with 69Ga and 68Zn, but the SPECTRO

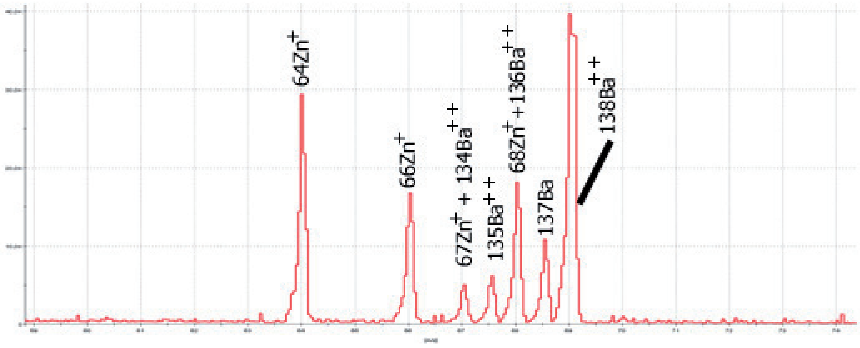


*Figure 10: Interferences*

MS can separate these fractional masses and the correction can then be handled by the software in the same way as isobaric interferences. These interferences occur mainly with elements having a low ionisation potential, such as the alkaline earth and rare earth elements (REE's). These elements are particularly significant in isotope geochemistry, so an ability to deal with these interferences effectively is important in this application.

A third type of spectral interference can occur when polyatomic charged species such as BaO+ are formed in the plasma. This ion could interfere with the determination of Nd, Sm, Eu and Gd. Again, these interferences are known and documented, and corrections can be applied in the same way.

The SPECTRO MASS ANALYSER VISION software includes all the necessary data about these interferences, and can make the appropriate corrections. As mentioned above, having the entire mass spectrum available makes this process much more reliable, to the extent that the SPECTRO MS has a "Semi-Quant" analysis mode that can use all this information combined with a "response table" containing sensitivities for all the elements, to give a good approximation of what an unknown sample contains even if no standards are available and the instrument has never been calibrated for some of the elements. Such a measurement takes only 10 seconds with the SPECTRO MS and can yield precision and accuracy in the range of 10-15% or better

The software also contains the resources to handle Isotope Ratio and Isotope Dilution calculations. In all isotope ratio studies, the fully simultaneous measurement of the complete mass spectrum improves accuracy and precision of the results by eliminating any noise from the sample introduction system and the plasma. For absolute concentration measurements, precision of 0.01% can be achieved using isotope dilution with the SPECTRO MS.

The software operates in the familiar Windows™ environment and is fully EPA, FDA, CLP and 21 CFR Part 11 compliant. The software also continuously monitors and documents the status of the instrument and uses SPECTRO's ICAL logic to ensure that the instrument is always in an optimum state of operation.

## Performance and Results

For meaningful trace element geochemistry, low limits of detection are required. This is partly because the concentrations of many of the elements of interest are low in the original rock samples – parts per million or parts per billion, and partly because further dilution takes place in the dissolution process. Limits of Detection (LOD's) at the parts per trillion level (in the sample solutions presented to the instrument) are needed. The SPECTRO MS achieves these levels over the whole mass range.

*Table 2: Detection Limits*

| Element | Mass | LOD [ppt] |
|---|---|---|
| Li | 7.00 | 20.00 |
| Co | 59.00 | 3.00 |
| In | 115.00 | 0.30 |
| Ba | 138.00 | 0.80 |
| Tb | 159.00 | 0.70 |
| Bi | 209.00 | 0.30 |
| U | 238.00 | 0.30 |

One of the great advantages of simultaneous ICP-MS is that element concentrations, element ratios and isotope ratios on all the elements of geochemical interest can be determined with a single measurement. In this experiment, a measurement was performed using a 100 µg/l multi-element solution (B at 1000 µg/l) with a sample uptake rate of 0.8 ml/min and 3 replicates, each of 30 seconds measurement time. The total sample consumption was therefore less than 2 ml. A sample introduction system with a concentric nebulizer and a cyclonic spray chamber was used.

*Table 3: SPECTRO MS Isotope Ratio Measurements*

| **Ratio** | **Li6/7** | **B10/11** | **Sr86/88** | **Sr87/88** | **Ag107/109** | **Pb204/208** | **Pb206/208** | **Pb207/208** |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.08031 | 0.24503 | 0.11687 | 0.08578 | 1.08513 | 0.02491 | 0.45227 | 0.43387 |
| 2 | 0.08039 | 0.24516 | 0.11694 | 0.08591 | 1.08541 | 0.02499 | 0.45267 | 0.43350 |
| 3 | 0.08038 | 0.24515 | 0.11699 | 0.08592 | 1.08465 | 0.02494 | 0.45216 | 0.43396 |
| **Average** | **0.08036** | **0.24511** | **0.11693** | **0.08587** | **1.08506** | **0.02495** | **0.45237** | **0.43378** |
| SD | 0.000044 | 0.000072 | 0.000060 | 0.000078 | 0.000384 | 0.000040 | 0.000268 | 0.000244 |
| RSD % | 0.054 | 0.030 | 0.052 | 0.091 | 0.035 | 0.162 | 0.059 | 0.056 |

SD = Standard Deviation, RSD = Relative Standard Deviation

The same level of precision can be achieved on lower concentrations by using a longer integration time. The isotope ratio for Boron (Boron 10/11) was measured using a integration time of 60 sec and 10 replicates with a 100 $\mu$g/l solution. The standard solution was alternately measured with a solution spiked with the $^{10}$B isotope. A wash solution was aspirated between the measurements for 180 seconds.

*Table 4: SPECTRO MS Isotope Ratio Measurements*

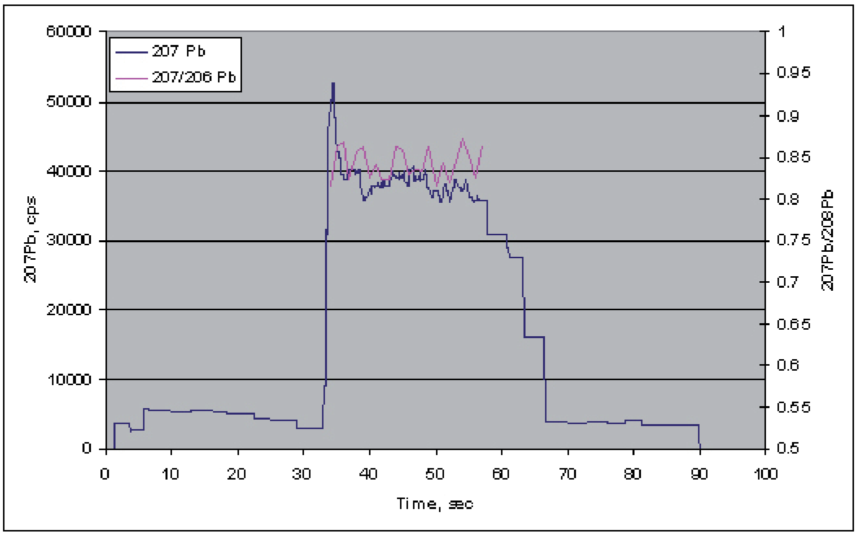
| | **Standard** | **Spike** | **Standard** | **Spike** | **Standard** | **Spike** | **Standard** | **Spike** | **Standard** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.247990 | 0.331940 | 0.247460 | 0.332830 | 0.247990 | 0.332140 | 0.247460 | 0.332830 | 0.247680 |
| 2 | 0.247530 | 0.332230 | 0.247630 | 0.332510 | 0.247530 | 0.332230 | 0.247630 | 0.332510 | 0.247390 |
| 3 | 0.247150 | 0.331890 | 0.247440 | 0.332550 | 0.247150 | 0.332890 | 0.247440 | 0.332550 | 0.247790 |
| 4 | 0.247630 | 0.332630 | 0.247550 | 0.331860 | 0.247630 | 0.332630 | 0.247550 | 0.332860 | 0.247880 |
| 5 | 0.247300 | 0.332270 | 0.247820 | 0.332010 | 0.247300 | 0.332270 | 0.247820 | 0.332010 | 0.247250 |
| 6 | 0.247590 | 0.331940 | 0.247800 | 0.332530 | 0.247590 | 0.332940 | 0.247800 | 0.332030 | 0.247870 |
| 7 | 0.247240 | 0.331810 | 0.247530 | 0.332360 | 0.247240 | 0.332810 | 0.247530 | 0.332360 | 0.247500 |
| 8 | 0.247500 | 0.332350 | 0.247830 | 0.332780 | 0.247500 | 0.332350 | 0.247830 | 0.332980 | 0.247950 |
| 9 | 0.247410 | 0.332740 | 0.247040 | 0.332630 | 0.247410 | 0.332740 | 0.247040 | 0.332630 | 0.247320 |
| 10 | 0.247450 | 0.332540 | 0.247120 | 0.332470 | 0.247450 | 0.332540 | 0.247120 | 0.332470 | 0.247890 |
| **Average** | **0.247479** | **0.332234** | **0.247522** | **0.332453** | **0.247479** | **0.332554** | **0.247522** | **0.332523** | **0.247652** |
| SD | 0.000236 | 0.000332 | 0.000274 | 0.000308 | 0.000236 | 0.000292 | 0.000274 | 0.000327 | 0.000264 |
| RSD % | 0.09545917 | 0.09994085 | 0.11088351 | 0.09275497 | 0.09545917 | 0.08776317 | 0.11088351 | 0.0984539 | 0.10669429 |

SD = Standard Deviation, RSD = Relative Standard Deviation

## LA-ICP-MS

Using Laser Ablation as a sample introduction system for ICP-MS has several advantages. Measurements are made directly on the sample, so there is no need for a sample digestion procedure with its potential errors and possibilities of contamination. Furthermore, spatially resolved information about element and isotope ratio distributions can be obtained. The following graph shows the $^{207}$Pb signal and the Pb 207/206 ratio using ratios using a 193 nm ArF Laser with 60 $\mu$m spot size and 12 J/cm2 at an ablation frequency of 25Hz using the NIST 612 glass CRM.

Note that whereas the $^{207}$Pb signal has the commonly observed initial peak at the beginning of the ablation, the 206/207 ratio is constant throughout. Increasing the ablation frequency but using the same number of shots improves the obtainable precision on the isotope ratio measurement as shown in table 5.



Data: B. Hattendorf, D. Günther, ETH Zürich

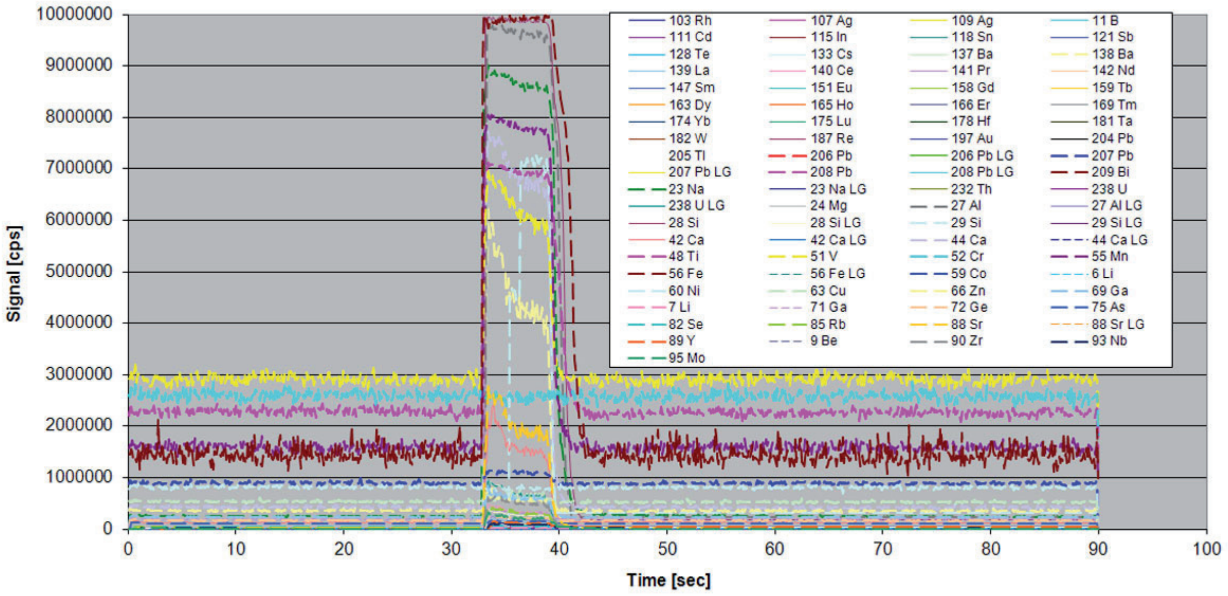
*Figure 11: LA-ICP-MS for Pb 206/207*

*Table 5: Effect of Ablation Frequency*

| | 10 Hz | 25 Hz | 50 Hz | 100 Hz |
|---|---|---|---|---|
| Mean | 0.830257 | 0.842393 | 0.821995 | 0.861152 |
| RSD | 3.92 | 2.26 | 2.45 | 1.98 |

*Data: B. Hattendorf, D. Günther, ETH Zürich*

The combination of Laser Ablation with simultaneous ICP-MS is immensely powerful, as it means that all the elements of geochemical interest can be available for ratio measurements on a given sample. The following composite graph shows the data of 81 separate isotopes monitored using Laser Ablation at 100 Hz ablation frequency on the BCR 2G CRM. The instrument readout frequency was 10 Hz with a basic integration time of 20ms.



*Data: B. Hattendorf, D. Günther, ETH Zürich*

*Figure 12: Completely simultaneous LA-ICP MS for 81 isotopes*

## CONCLUSION

Fully simultaneous ICP-MS can improve the precision of isotope ratio, isotope dilution and element ratio measurements in geological applications compared to sequential measurements commonly used in ICP-MS. The unique capability of the SPECTRO MS to measure the complete relevant inorganic mass range fully simultaneously from a permanent, non-pulsed ion beam extends these possibilities to geological applications. Until now, the simultaneous determination of all rare earth elements and their ratios was impossible for most available instruments. In addition, post-measurement reprocessing of the complete mass data can give access to information on elements that were not of interest at the time of measurement, even when the samples no longer exist. When the SPECTRO MS is used for hyphenated techniques like Laser Ablation, the measurement duty cycle for each element is independent of the number of elements to be determined. Measuring one isotope per element for the complete periodic table (i.e. ca. 80 isotopes determined simultaneously), measurements can be performed at a 10 Hz frequency over extended periods of time without sacrificing limits of detection, counting statistics or precision compared to a single element measurement. The combination of a unique new innovation in array detection used in conjunction with an ultra-modern Inductively Coupled Plasma Mass Spectrometer and advanced software technologies offers a revolutionary new tool for geochemical investigations.

**www.spectro.com**

GERMANY
SPECTRO Analytical Instruments GmbH
Boschstrasse 10
D-47533 Kleve
Tel: +49.2821.892 2102
Fax: +49.2821.892 2202
spectro.info@ametek.com

U.S.A.
SPECTRO Analytical Instruments Inc.
91 McKee Drive
Mahwah, NJ 07430
Tel: +1.800.548 5809
+1.201.642 3000
Fax: +1.201.642 3091
spectro-usa.info@ametek.com

HONG KONG (Asia-Pacific)
SPECTRO SPECTRO Analytical Instruments
(Asia-Pacific) Ltd.
2303-4 Sino Favour Centre
1 On Yip Street
Chaiwan
Tel: +852.2976.9162
Fax: +852.2976.9132
spectro-ap.info@ametek.com

Subsidiaries:
CHINA: Tel +86.10.8526.2111, Fax + 86.10.8526.2141, spectro-china.info@ametek.com.cn, FRANCE: Tel +33.1.30 68 89 70, Fax +33.1.30 68 89 79, spectro-france.info@ametek.com, GREAT BRITAIN: Tel +44.(0)1162.462950, Fax +44.(0)1162.740160, spectro-uk.info@ametek.com, INDIA: Tel +91.22.28 36 47 50, Fax +91.22.28 36 36 13, sales.spectroindia@ametek.com , ITALY: Tel: +39.02.94693.1, Fax +39.02.94693650, spectro-italy.info@ametek.com, JAPAN: Tel: +81-(0)3 3740 5172, Fax: +81-(0)3 3740 5307, spectro-japan.info@ametek.com, SWEDEN: Tel: +46.8.519-060 31, Fax: +46.8.519.060 34, spectro-nordic.info@ametek.com, SOUTH AFRICA: Tel +27.11.9794241, Fax +27.11.9793564, spectro-za.info@ametek.com.
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