

Rising to the Challenge – Applications of Cell-Based ICP-MS to the Analysis of Geological Samples

Introduction

Geologists have always relied on quantitative analysis in order to further their understanding of rock petrogenesis, just as other scientists require assays to measure their experimental progress or explorationists require ore grades. Throughout history, from alchemists attempting to transmute metals into gold to modern day analysts using complex instrumentation, assaying the amount of different elements in a sample has been a tried and trusted method of furthering science, although this approach does require a homogenous solution of the sample. Paracelsus, for example, was a sixteenth century doctor and prototypical chemist whose quest throughout his life was to find the alkahest, a mythical liquid that was said to dissolve anything ‘as warm water dissolves ice’ (Ball 2006). Alas, he was ultimately unsuccessful in his search, but inspired many others to follow in his footsteps.

Many reputable analysts would contend that the modern equivalent of Paracelsus’ quest, and just as foolish, is the attempt by geoanalysts to find a single instrument that can measure all the elements in a rock simultaneously! This is effectively the Holy Grail of modern geological analysis, as it would provide fast, accurate analysis at a reasonable cost for the large numbers of samples generated in an exploration program, especially as modern digestion processes have solved many of the dissolution problems. However, most analytical procedures for geological samples have to resort to multiple instruments for a complete elemental analysis. This problem is exacerbated by the range and complexity of today’s exploration targets.

Until recently, exploration programs have typically been aimed at discovering precious and base metal commodities. However, technological innovations such as hybrid car batteries, more powerful magnets and the ubiquitous iPhone®, have increased demand for more exotic elements in the far reaches of the periodic table. This demand has resulted in assays being required for 50-60 elements that can vary widely in concentration. In addition, requests for lower detection limits and isotopic ratios have resulted in the need for new approaches to analysis that must continue to remain practical, both in terms of cost and numbers of different determinations. ICP-MS is ideally situated to meet these demanding expectations, as it combines multi-element capability with detection limits significantly below other widely used analytical instruments. The aim of this article is to show how cell-based ICP-MS instruments are now being utilized to meet the challenging analytical demands of today’s exploration

programs and attempting to provide a single point analysis for the geologist.

Cell-Based ICP-MS Technology

The typical configuration of a commercial quadrupole ICP-MS is shown in Figure 1a. Although each manufacturer has their own approach, the basic tenets of the argon plasma to produce ions, a lens system to focus the ion beam, a quadrupole mass spectrometer to separate individual ions on a mass to charge ratio, and an electron multiplier detector to amplify very small signals, remain the same. This set-up is used successfully in many geological applications, but does have limitations because of interferences. Other drawbacks include the inability of the instrument to measure high concentrations of ions and inherent fluctuations in the plasma prohibiting the precise measurement of individual isotopes needed for isotopic ratio measurements.

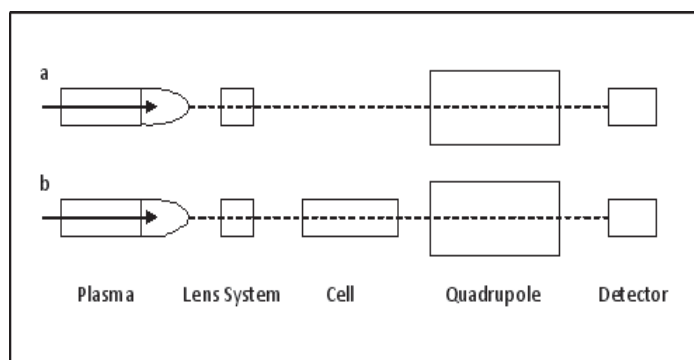


Figure 1. Schematic diagram for a Quadrupole ICP-MS: (a) The sample is aspirated into the plasma (arrowed line) where ions are formed (dotted line). They are focussed using the lens system and then separated into individual masses using the quadrupole mass analyser. Individual ion masses are measured using an electron multiplier detector: (b) The cell is pressurized with a gas to effect interference reduction, either by collisions or chemical reactions before the mass analyser.

When ICP-MS was first developed, it was thought that it would be mostly interference-free as only single masses were being measured and it did not have the complex spectra of emission spectroscopy. How hard could that be? Well, for many high mass elements it is not hard at all, but at masses below 80 there are many polyatomic ions formed in the intense heat of the plasma that can cause interferences. These include staples such as oxygen that interferes with sulphur, to more esoteric argon-based interferences on elements like

continued on page2

Rising to the Challenge — ... continued from page 1

chromium (e.g. $[^{40}\text{Ar}^{12}\text{C}]^+ = ^{52}\text{Cr}^+$), resulting in higher detection limits.

To overcome these interferences, a cell can be placed between the lens system and the quadrupole (Fig. 1b). This cell can be filled with either an inert or reactive gas. The gas collides or reacts with the ions in the system and breaks up polyatomic interferences. An ion guide is used to push the analyte ions through the cell in order to minimize losses through collisions with the gas molecules (Tanner et al. 2002). Cell-based systems have been used successfully in many areas of chemical analysis over the past decade or so, and are now being applied to the complexities of geological analyses.

SGS Minerals Services uses PerkinElmer instruments that employ a quadrupole as the ion guide in the cell. This cell is known as a Dynamic Reaction Cell (DRC) and works by performing reactions to break down polyatomic interferences, rather than the collision approach of other systems (Baranov & Tanner 1999). Figure 2 shows an illustration of how the DRC works. A mixture of the analyte and the interference enter the cell, pressurized with a reactive gas such as ammonia. The gas reacts with the interference, breaking it apart through charge transfer reactions. The parameters of the quadrupole inside the DRC are adjusted to prevent interferences from re-forming, allowing

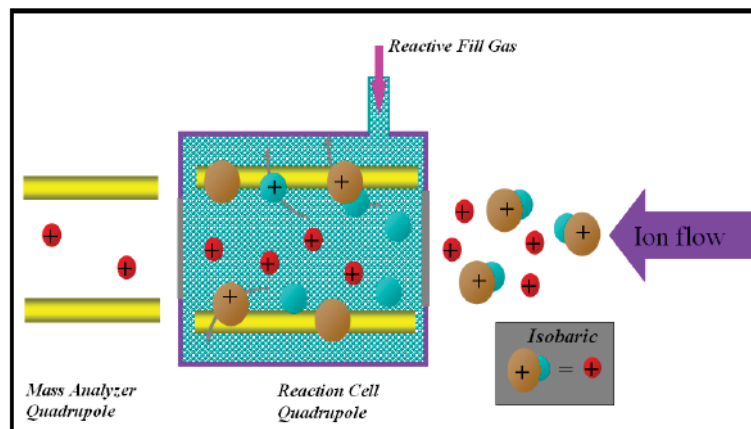


Figure 2. Interference removal using the Dynamic Reaction Cell (DRC). Polyatomic Interferences (brown and blue) of the same mass (isobaric) as the analyte (red) enter the cell, pressurized with a reactive gas. The gas molecules react with the interference, breaking them apart. The parameters of the quadrupole inside the reaction cell are adjusted to only allow the analyte ion through. (© PerkinElmer Inc., used with permission).

only the analyte ion to exit the cell (Tanner & Baranov 1999). This filtering, or bandpass tuning, allows for a number of different applications, including:

- Electronic signal control to measure both high and low concentrations of elements in a single pass (extended dynamic range, or EDR);
- Detection limit improvement by either interference removal or reaction with the analyte to measure at a non-interfered higher mass;
- Use of a non-reactive gas to improve measurement precision in isotopic ratios.

These applications can lead to exciting new methodologies that stretch the boundaries of typical geological applications, as described in the examples below.

Determination of High Concentrations of Rare Earth Elements (REE) using EDR

Interest in the determination of high concentrations of REE has spiked recently because of their extensive use in batteries, magnets and electronic technologies. The REE are listed in Table 1, along with typical ranges detected in geological materials. They are determined using a variety of instrumental techniques, including: neutron activation analysis (NAA); X-ray fluorescence (XRF); and both ICP-AES and ICP-MS. Most methodologies were developed to measure low-levels (parts per million) of REE found in most rocks, and for these types of material ICP-MS is ideal, because it has the ability to measure all of the rare earth series to low (sub ppm) concentrations. In comparison to XRF or ICP-AES, there are fewer interferences for the REE elements using ICP-MS, while NAA is not able to measure all of the REE in a single run.

Higher concentrations of REE (>5000 ppm total REE) found in ore bodies are harder to measure by a single process because of the large differences in concentration, from percentage levels of light REE to single parts per million for the

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Rising to the Challenge — ... continued from page 2

heavy REE. To achieve this analysis, a new method has been developed by SGS Minerals Services that involves the use of a specific digestion procedure, followed by ICP-MS analysis using extended dynamic range (EDR). This is an attenuation process based on the characteristics of the quadrupole inside the reaction cell. No cell gas is used here, but the conditions in the cell are changed to allow fewer ions through, culminating in a drop in signal and consequently the ability to measure very high concentrations of specific REE, whilst retaining detection limit capabilities for others.

The extraction consists of sintering the sample with a sodium peroxide flux, followed by digestion in dilute nitric acid. The resultant solution is measured by ICP-MS to determine all of the REE in a single pass. EDR is used to measure the high concentrations of light REE, in conjunction with the heavy REE to produce detection limits and measurement ranges listed in Table 1. Cerium, for example,

can be measured at concentrations in excess of 15%, whilst still maintaining <1 ppm detection limit for elements such as holmium and thulium. Furthermore, additional elements can be added to the analysis to increase the range of applications as required by exploration geologists.

Detection Limit Improvements for Mobile Metal Ion (MMI™) Weak Leach Extractions using Cell-Based ICP-MS

Mobile Metal Ion (MMI™) Technology is one of several commercially available weak leaches that are used for a variety of resource identification and lithological mapping projects (e.g., Mann et al. 1998). The principle of MMI™ is that mobile ions associated with an ore body migrate to the surface over a period of time. These mobile ions adhere to soil particles at the surface and can be selectively extracted by mixing the sample with MMI™ solution. The resultant extract is measured for a variety of elements using ICP-MS

Element		DL	Typical Range*	Element		DL	Typical Range*
Lanthanum	La	50	1000ppm - 10%	Terblum	Tb	1	20 - 500ppm
Cerium	Ce	50	1000ppm - 20%	Dysprosium	Dy	1	100 - 5000ppm
Praesodymium	Pr	10	1000ppm - 5%	Holmium	Ho	0.1	20 - 500ppm
Neodymium	Nd	50	1000ppm - 10%	Erbium	Er	0.5	50 - 1000ppm
Samarium	Sm	10	100 - 5000ppm	Thulium	Tm	0.1	10 - 50ppm
Europium	Eu	1	100ppm - 1%	Ytterbium	Yb	1	50 - 500ppm
Gadolinium	Gd	5	100 - 5000ppm	Lutetium	Lu	0.2	5 - 50ppm

Table 1: List of Rare Earth Elements in ascending atomic number, including detection limits using the cell-based method and typical ranges seen in the laboratory. La to Eu are referred to as the light REE and Gd to Lu as the heavy REE. * Ranges are given to show approximate levels seen in typical high concentration REE samples only.

continued on page 5

Rising to the Challenge — ... continued from page 4

in order to detect a buried ore body through identification of anomalies over background levels. This has proven valuable for many target elements, but some critical elements cannot be measured at low levels because of matrix and sample interferences (Table 2).

Analyte	Mass	Major Interference	Reaction Gas	Det. Lt. (ppm)
Vanadium	51	ClO^+	Ammonia	0.001
Chromium	52	ArC^+	Ammonia	0.001
Selenium	78	Ar_2^+	Ammonia	0.002
Sulphur	34*	O_2^+	Oxygen	0.1

*Table 2: Enhanced MMI™ elements measured using cell-based ICP-MS. Ammonia reacts with the interferences, allowing lower detection limits for V, Cr and Se. Detection limit for Cr is 0.1 ppm for standard ICP-MS analysis, while the other elements are not determined. For Sulphur, the excess oxygen is used to move the sulphur ion to a higher mass, enabling a lower detection limit to be achieved. * Sulphur is actually measured as the oxide, SO^+ , at mass 50.*

Chromium is an important element in the discovery and identification of kimberlites for diamond exploration and for other ultramafic lithologies for nickel exploration. Vanadium has potential uses in uranium exploration and selenium is a useful pathfinder element for several types of mineral deposits including various polymetallic ores and ores containing gold and uranium. All three elements suffer from interferences in quadrupole ICP-MS (Table 2). To overcome these limitations, a cell-based method has been developed using ammonia gas. Ammonia reacts with the interfering polyatomic ions and removes them from the ion beam, resulting in low detection limits required for exploration work. All other elements are measurable in the same analysis to provide a comprehensive sample analysis required for target resource identification.

Sulphur is key element for nickel or oil and gas exploration, but is notoriously difficult to measure by ICP-MS because of oxygen interferences. However, a new cell-based method has been developed that utilizes the ability of the reaction cell to move an analyte away from interferences. In this case, oxygen gas is used in excess to react with the sulphur ions to produce SO^+ ions that are measured at a higher mass away from interferences. Again, the parameters of the quadrupole in the cell are optimized to remove other potential interferences and all other elements can be measured in the same analysis.

Precise Isotopic Ratios of Copper using DRC-ICP-MS

Copper consists of two isotopes, mass 63 (with nominally 69.17% abundance) and mass 65 (30.83% abundance). Studies of copper isotopic ratios have shown that there are small differences in copper from various sources. The difference in isotopic ratios is given as the delta value ($\delta^{65}\text{Cu}\text{‰}$), defined as the difference in the $^{65}\text{Cu}/^{63}\text{Cu}$ ratio relative to the NBS976 isotopic standard, expressed in parts per thousand (‰) (Maréchal et al. 1999). It is this delta value that

can potentially be used in exploration geology to distinguish copper from various reservoirs. For example, it has been shown using a specialized technique that Cu oxides rimming a vein of chalcocite from El Salvador, Chile, had significantly lighter isotopic signatures (by approximately $+1 \delta^{65}\text{Cu}\text{‰}$). These were then used to evaluate the extent of veining of copper mineralization (Mathur et al. 2009). Additionally, the leach cap minerals have lower delta values than the primary mineralization and potentially this tool can be used to vector into blind mineralization.

ICP-MS has been utilized for the measurement of isotopic ratios in a variety of matrices, but the precision is typically limited to ca. 0.5% R.S.D., mainly because of fluctuations of the ion density in the extracted beam. By the time you move from measuring one isotope to the next, there is a small difference in the counts. Considering that a $\delta^{65}\text{Cu}\text{‰}$ difference of 1 is equivalent to a 0.1% difference in the isotopic ratio, the difficulty of measuring these values using conventional ICP-MS is apparent. Currently, precise isotopic ratios are typically determined using multi-collector or thermal ionization mass spectrometric techniques that are expensive, time-consuming and, thus, not easily applicable to geological exploration surveys.

In order to determine precise isotopic ratios using ICP-MS, the cell-based system is pressurized with a non-reactive gas. This pressurization effectively homogenizes the ion beam by increasing the residence time of the ions in the cell due to collisions with the gas, thus eliminating most of the fluctuations from the plasma source (Bandura et al. 2000). Copper determinations carried out using neon gas produced isotopic ratio results with precisions of $\pm 0.5 \delta^{65}\text{Cu}\text{‰}$. This precision is illustrated in Figure 3, where the small differences in delta values required for exploration purposes were measured by spiking the NBS976 standard with differing levels of enriched copper to simulate changes in the delta value.

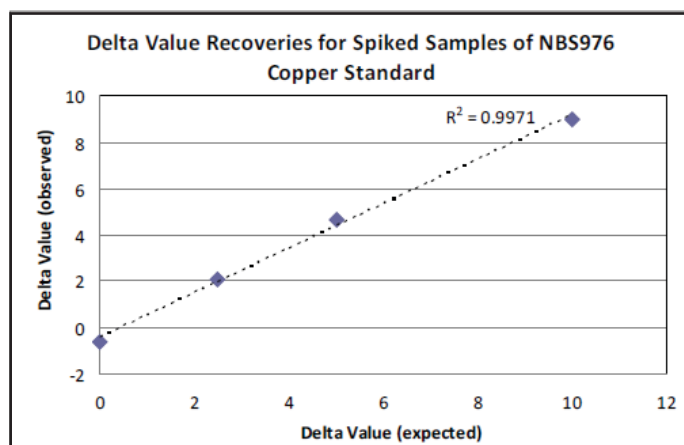


Figure 3: Plot of delta ($\delta^{65}\text{Cu}\text{‰}$) values for copper isotopic ratios measured using cell-based ICP-MS. NBS976 (nominal $\delta^{65}\text{Cu}\text{‰} = 0$) was spiked at +2, +5 and +10 $\delta^{65}\text{Cu}\text{‰}$ equivalents using an enriched ^{65}Cu standard solution to show that the method was capable of distinguishing between delta values of 1 unit.

Rising to the Challenge — ... continued from page 5

A similar approach is available for the determination of lead isotopic ratios that are important in uranium exploration. A multi-elemental scan (from an aqua regia digest or MMI™ extraction, for example) is used to screen samples for potential lead isotopic anomalies. Samples of interest are then measured precisely using a cell-based isotopic ratio method. This is particularly effective with uranium exploration, because there is a significant shift in isotopic signature that can be detected using the quadrupole ICP-MS and refined using the cell-based approach to provide high quality isotopic data for target resource identification.

Conclusions

Cell-based ICP-MS has allowed the expansion of analysis into various areas of recent interest, in order to respond to the ever-increasing demands of geological analysis. The examples given above are now routinely measured and are effectively 'tip of the iceberg' applications of this exciting technology, as we strive for a simplified approach to geological analysis. Whilst there is still considerable work to be done, the use of digestion processes such as fusions and selective weak leaches, combined with cell-based ICP-MS technology have succeeded in pushing us closer towards the end of the quest for a single dissolution and measurement process for specific target commodities.

But what of the alkahest, the ultimate solvent that Paracelsus strived in vain for? Alchemists kept looking for it well into the eighteenth century, even after the German chemist

Kunkel correctly noted in 1702 that if anyone actually discovered the alkahest, there would not be anything to contain it!

Acknowledgement

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Nicholas Turner

*Global ICP/ICP-MS Technical Manager
SGS Minerals Services, Geochemistry
E-mail: Nicholas.Turner@sgs.com*

