



Multi-Element Determination of Geological Samples using ICP-OES and ICP-MS – Which Technique . . . and When?

Introduction

The determination of major, minor and trace elements in geological samples has always been of paramount importance in the geochemical exploration of elements of economic interest and the evaluation of potential resources. However, these types of samples pose an unusual set of challenges for the analyst, including: the range of analyte concentrations present; the number of elements required per sample; and the amount of samples produced by a typical exploration survey. These factors are further compounded by the presence of a complex range of matrices and the potential for widely different compositions within an analytical batch of samples (Riddle 1993).

Over the past two decades, inductively coupled plasma optical emission spectrometry (ICP-OES) has proven to be a fast and reliable technique for the quantitative measurement of major, minor and trace level elements in geological samples. By simultaneously measuring all of the elements in a sample digest, the speed and cost-effectiveness of analysis are considerably improved. The advent of inductively coupled plasma mass spectrometry (ICP-MS) has further pushed the boundaries of both detection limits and the range of determinable elements available to the exploration geologist. Using either one, or a combination of these powerful techniques, it is now possible to quantitatively measure most elements in the Periodic Table.

An increasingly sophisticated understanding of elemental behaviour and the development of software for handling multi-element arrays, has gone hand in hand with the development of the multi-element capability of the two techniques, leading to the use of a large suite of elements as pathfinders for mineralization. It is important for the geologist to use the appropriate analytical procedure when evaluating exploration survey samples in order to obtain the pertinent information required to identify ore mineralization. Like most commercial analytical laboratories, SGS Minerals Services has developed a comprehensive range of multi-element techniques depending upon the analytical and budgetary requirements of the client. Table 1 provides a brief summary of the typical analytical packages available, although these are often tailored to specific requests. The choice of digestion type has been discussed elsewhere (Chao et al. 1992) and suffice it to say here that initial reconnaissance samples (or soil samples) generally require a partial or weak extraction – the hydrochloric/nitric

continued on page 2

Multi-Element Determination of Geological Samples... *continued from page 1*

Method	ICP-OES	ICP-MS	ICP-OES+ICP-MS
2 Acid Extraction (HNO ₃ and HCl)	32 elements Major and trace levels	36 elements Major, trace and ultratrace levels	52 elements Major, trace and ultratrace levels
4 Acid 'near-total' Digestion (HNO ₃ + HCl + HF + HClO ₄)	32 elements Major and trace levels	—	50 elements Major, trace and ultratrace levels
Sodium Peroxide Fusion	28 elements Major and trace levels	—	54 elements Major, trace and ultratrace levels
Lithium Borate Fusion	16 elements Major and trace levels	31 elements Trace and ultratrace levels	47 elements Major, trace and ultratrace levels
MMI-M Selective Weak Extraction	—	45 elements Major, trace and ultratrace levels	—
Sodium Peroxide Fusion Assay	Co, Cu, Ni, Pb & Zn Major components	—	—

Table 1: Summary of typical multi-element exploration packages offered by SGS Minerals Services, showing the range of digestions and instrumental finishes available. 'Ultratrace' is used to differentiate the lower ICP-MS detection limits for particular elements.

acid extraction or partial weak extraction (MMIM) – followed by an elemental scan to provide information concerning anomalies above background levels. Follow-up drilling, delineation, and rock samples are generally analysed using the four-acid digestion (a combination of nitric, hydrochloric, perchloric and hydrofluoric acids) to provide more complete information about composition. Fusion digestions are used to dissolve refractory phases unaffected by acid dissolution, providing a complete multi-element determination of geological samples and high precision assays for ore level concentrations of base and other metals of interest.

Multi-element scans can thus provide a wealth of elemental data in rapid timeframes for the large volumes of samples required by exploration geology. The aim of this paper is to attempt to answer the question of what

technique is appropriate for different types of sample and concentrations of elements of interest. Following a brief introduction to the concepts behind the techniques will be a discussion on how advances in instrumental design have enabled SGS Minerals Services to improve their application to geological analysis in two specific areas. These are the lack of sensitivity of ICP-OES in measuring low concentrations of many trace elements, and the inability to measure high concentrations of elements by ICP-MS. In overcoming these limitations, both ICP-OES and ICP-MS can provide unparalleled analytical data for the geologist at all stages of the exploration process.

Inductively Coupled Plasma (ICP)

The argon plasma is used in atomic spectroscopy as an efficient energy source for the excitation and ionization of atoms. The plasma is initiated through partial ionization of argon by seeding it with electrons. A Radio Frequency generator provides high frequency current to an induction coil and the resultant magnetic field is used to accelerate the electrons. Adding energy to the electrons in this manner is called *inductive coupling*. A chain reaction is set up whereby the accelerated electrons collide with argon atoms, causing ionization and more electrons that collide with other atoms. This reaction results in a stable plasma held within the induction coil by the magnetic field. The plasma has core temperatures of between 8000 and 10000°C, into which samples can be aspirated, producing the required excitation and ionization of elements in solution.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES utilizes the ICP as an energy source to excite atoms and ions, which, as they return to ground

continued on page 3

Note: This EXPLORE article has been extracted from the original EXPLORE Newsletter. Therefore, page numbers may not be continuous and any advertisement has been masked.

Multi-Element Determination of Geological Samples... *continued from page 2*

state, emit light at characteristic wavelengths that can be measured using an appropriate detector. Modern instruments differentiate the light into its component wavelengths using an Echelle diffraction grating with efficient light throughput. The diffracted light from the grating is measured using a Charge-Coupled-Device (CCD) detector. By comparing the intensities of the sample with a standard containing known quantities of each element of interest, the concentrations of those elements in the sample can be determined.

The main advantages of the ICP-OES system for the analysis of geological samples include the ability to measure many elements from a single sample digest, in order to provide maximum information about the sample, and a variety of strong acid and fusion matrices can be determined directly, since only light enters the instrument. The large number of spectral emission lines available enables analytically useful wavelengths to be found for most elements. In addition, both major (percentage levels) and trace (parts per million levels) elements can be determined from the same solution, without the need for serial dilutions, which take more time and can impact analytical precision. Finally, the robustness of the technique makes it a powerful tool in the analysis of large numbers of samples.

The limitations of analyzing geological samples by ICP-OES methodologies include: potential compromises

in analytical data due to the digestion procedure involved; the enormous number of emission lines and the nature of the plasma source can lead to significant interferences for some elements; and the sensitivity of the instrument tends to be limited for some elements, (e.g. Sn, W and Sb) due to emission lines in the low UV wavelengths that can be absorbed in the air before entering the spectrometer. Whilst the first two limitations can be overcome by carefully choosing the appropriate digestion (see Table 1) and analytical wavelengths, plus interference correction where necessary, the third problem can be improved by using a dual-view approach.

Lower Detection Limits for ICP-OES – The Dual View Approach

Traditionally, plasmas have been viewed from the side (or *radially*), analogous to atomic absorption spectroscopy where viewing occurs along the line of the burner.

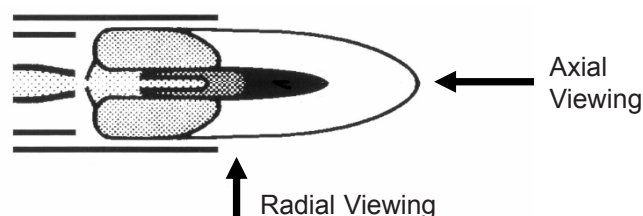


Figure 1. Dual view configuration of the ICP-OES. Axial and dual view instruments have horizontally orientated plasmas and view both across and down the plasma. Radial instruments have a vertically orientated plasma and view through the analytical zone only.

continued on page 4

Multi-Element Determination of Geological Samples... continued from page 3

However, the plasma also can be viewed end-on, or *axially* (Fig. 1). The advantage of axial viewing is that more of the light enters the instrument, resulting in greater intensities. Even though backgrounds are also increased and there are potential problems with spectral re-absorption in the plasma tail for easily ionizable elements, axial measurements tend to give sensitivities that are an order of magnitude higher for many trace elements of geological significance. An ICP-OES with a combination of axial and radial viewing is known as a dual view instrument (Nölte 2003).

SGS Minerals Services utilizes the dual view approach (Optima 5300DV ICP-OES, PerkinElmer Life and Analytical Sciences, USA) for the multi-element analyses detailed in Table 1. The radial view is used for high concentrations of elements, and the axial view for trace elements. Thus, measurement of a wide concentration of elements is achieved in a single determination and has the

Element	Radial Detection Limit	Axial Detection Limit
As	7.2	2.7
Bi	5.8	0.5
Co	0.7	0.1
Cr	1.2	0.3
Cu	0.5	0.2
Hg	2.6	0.5
Mo	1	0.2
Ni	1.8	0.2
Pb	8.5	0.6
Sb	4	0.8
Sn	12.1	0.3
W	2	0.6
Zn	4.4	0.1

Table 2: Comparison of two-acid extraction detection limits for ICP-OES using radial and axial modes. Results show the increased sensitivity of the axial mode for many trace elements. Detection limits are determined from three times the standard deviation (3 σ) of seven method blank solutions. Detection limits are based upon a 0.25 g sample digestion, diluted to a final volume of 20 mL. All results are in ppm.

advantage of providing lower detection limits for many elements. Table 2 shows a comparison of detection limits determined using both radial and axial instruments for a two-acid extraction digest. These limits are based upon a 0.25 g sample digestion diluted to a final volume of 20 mL. As can be seen, the axial view produces significant

	Axial		
	ICP-OES	ICP-MS	Difference
Sample-1	15	13.3	2
Sample-2	14	14.8	1
Sample-3	13	11.3	1
Sample-4	15	13.5	1
Sample-5	13	12.2	1
Sample-6	15	14.8	1
Sample-7	15	14.0	1
Sample-8	26	25.2	1
Sample-9	9	9.1	<1
Sample-10	4	2.8	1
Sample-11	9	7.6	1
Sample-12	9	6.7	2
Sample-13	13	11.0	2
Sample-14	10	9.2	1
Sample-15	8	7.8	1
Sample-16	17	16.4	1
Sample-17	15	15.2	<1
Sample-18	16	15.7	<1
Sample-19	14	14.2	<1
Sample-20	22	21.5	<1

Table 3: Comparison of axial ICP-OES recoveries for low-level Pb containing samples with ICP-MS using a four acid digestion. All results are within ± 2 ppm, showing the ability of the axial mode to achieve acceptable precision at low concentration levels. ICP-OES detection limit is 2 ppm for this analysis. Results are based upon a 0.2 g sample digestion, diluted to a final volume of 12 mL. All results in ppm.

improvements for Hg, Pb, Sn, Sb, and other important trace elements compared with the radial approach. Table 3 shows recoveries for a series of samples containing low concentrations of Pb, determined by axial ICP-OES and ICP-MS, following a multi-acid digestion of 0.2 g

continued on page 5

Multi-Element Determination of Geological Samples... *continued from page 4*

sample diluted to a final volume of 12 mL. The data confirm that acceptable precision (± 2 ppm) can be obtained, even at less than 10 ppm Pb concentration. Table 4 illustrates the recoveries for twelve reference standards analysed using a two-acid extraction (0.25 g sample digested to a final volume of 20 mL) and shows

Standard	Axial ICPOES	Expected Value	% Recovery
LKSD-1	82	84	97
LKSD-2	38	40	95
LKSD-3	25	26	96
LKSD-4	91	93	98
STSD-1	35	34	102
STSD-2	65	66	99
STSD-3	40	39	103
STSD-4	13	13	103
TILL-1	14	12	118
TILL-2	22	21	107
TILL-3	17	16	106
TILL-4	37	36	102

Table 4: Comparison of Pb recoveries for a two acid extraction of reference standards by axial ICP-OES. Acceptable recoveries are obtained for all standards (Lynch 1990 and Lynch 1996). Results are from a 0.25 g sample digestion, diluted to a final volume of 20 mL. All results are averages of five digestions. All results are in ppm.

that accurate values can be measured for Pb at less than 20 ppm in the sample using this technique.

Thus, ICP-OES can be utilized to measure not only high concentrations of elements, but also trace levels by using the dual view instrument. The flexibility of the dual view instrument is shown in other applications as well. For instance, in the determination of low level precious metals by fire-assay, the axial mode provides a detection limit of 1 ppb for Au, compared with the 5 ppb detection limit achievable by radial ICP-OES and atomic absorption spectrometry. Also, for assay quality analysis (<5% for both precision of duplicates and accuracy) on higher concentration samples, the radial mode is used in conjunction with element-specific certified reference materials (CRMs). However, as powerful as the dual view ICP-OES technique has become, there are many cases where even lower detection limits are required for a range of elements and it is then that ICP-MS becomes the technique of choice.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS utilizes the plasma as an efficient heat source for the formation of positive ions. A small portion of the ion beam enters the instrument, is focused using a lens system, and then passed into a quadrupole mass spectrometer, where ions are separated based on their mass to charge ratio. An electron multiplier is used to detect the ions as they pass out of the mass spectrometer.

As with ICP-OES, comparing intensities from known standard solutions to the unknown sample allows the concentration of the analyte to be determined. The instrument measures elements sequentially by scanning up and down the mass range. Hence, the more analytes that are required to be measured, the longer the analysis will take.

The advantages of ICP-MS include: the sensitivity of the technique allows for the determination of many elements in the sub parts per million range (e.g. rare earth elements); the multi-element capabilities of the instrument allow for the analysis of a wide range of elements at different concentration levels in one pass; and the reliability of contemporary instrumentation makes it a powerful tool in the analysis of the large volumes of samples generated in geochemical analysis.

The main limitations of ICP-MS are: the technique cannot directly determine elements in solutions containing high levels of dissolved solids, such as rock digests; the high temperature of the plasma can cause polyatomic interferences (such as argides and oxides of other elements in the sample digest); and the increased sensitivity of the instrument (typically >1000 times that of ICP-OES) makes it inappropriate for measuring high analyte concentrations. Whilst the first two disadvantages can be overcome by diluting the sample prior to analysis, choosing the appropriate isotope and where necessary performing interference corrections, the measurement of increased ion beam intensities from high element concentrations requires a different approach.

ICP-MS was initially developed to measure trace amounts of elements in solutions. However, the proliferation of the technique and its widespread use in many analytical areas, including geological samples, created a requirement for increased dynamic range to allow for the determination of different concentration levels without the need for further dilution. The introduction of the two stage detector enabled the expansion of the use of ICP-MS to measure high concentrations whilst retaining its low detection limit capabilities.

Increased Dynamic Range for ICP-MS – The Dual Stage Detector

Commercially available ICP-MS instruments (SGS Minerals Services uses the Elan 9000, PerkinElmer SCIEX, Canada) contain a two-stage, or dual detector, for the measurement of low (sub parts per billion) and high (parts per million) solution concentrations in a single pass. High intensity ion signals emanating from the quadrupole mass spectrometer are measured by the *analogue* stage, whereas low concentrations pass into the electron multiplier for amplification and measurement – the *pulse* stage (Fig. 2). It is this amplification that enables the ICP-MS to detect very low concentrations of elements in solution.

By measuring solutions containing significant concentrations of an analyte using both stages of the detector, a cross calibration coefficient can be determined (Fig. 2). This determination can be repeated for all

continued on page 6

Multi-Element Determination of Geological Samples... *continued from page 5*

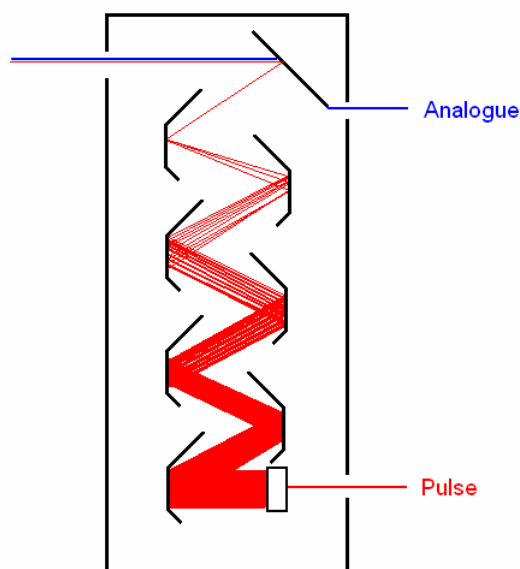


Figure 2. The Dual Stage Detector. A high concentration of the element (in blue) is detected by the analogue stage, whereas the low concentration signal enters the electron multiplier (red). By measuring appropriate concentrations using both stages of the detector, a graph can be drawn and the coefficient between the two stages calculated. This can be used to convert the analogue result to the pulse calibration, creating an extended linear range.

elements of interest to create a dual detector calibration. Due to the linear nature of the detector, sample digests containing a wide range of concentrations can now be determined in a single pass, without the need for further dilution. Table 5 illustrates the measurement of high levels of Pb in a four-acid digestion of geological samples. The results are from a 0.2 g sample digestion, diluted to 12

Sample	ICPMS	ICP	%Recovery	Expected
Unknown-1	S	38200	n/a	
Unknown-2	12270	12500	98	
Unknown-3	325	320	101	
Unknown-4	12600	12700	99	
Unknown-5	2440	2270	107	
Unknown-6	4090	3960	103	
Unknown-7	1660	1640	101	
Unknown-8	36	35	101	
Unknown-9	3660	3390	108	
Unknown-10	4770	4470	107	
SRM2710	5480	5385	99*	5532
SRM2711	1180	1170	102*	1162

Table 5: Comparison of Pb results using ICP-MS and ICP-OES for a range of unknown samples and two reference twenty times was made before analysis. S = signal saturated and could not be measured. Reference Standard results are averages from five replicate digestions. * Based on ICPMS comparison to reference values (Govindaraju 1994). All results in ppm.

mL for ICP-OES, and then diluted a further twenty times for analysis by ICPMS. As can be seen, there are acceptable correlations between the ICP-MS, ICP-OES and expected values for the standards. The ICP-MS results are within 10% of the expected value for both the reference standards and the results obtained by ICP-OES for unknown samples. The calibration for this determination has a maximum point of 60ppm in the sample, enabling the quantitative determination of Pb up to over 200 times higher, with saturation only occurring at much greater than 10 000ppm (or 1%). This confirms that ICP-MS can be used to measure not only trace levels of elements, but also significantly higher concentrations as well. A two-acid partial extraction can be measured by ICP-MS for a range of major components (such as Fe, Ca, Al, Mg), percentage levels of base and other metals, as well as trace levels of other elements. However, ICP-OES is still preferred for major component analysis of geological samples in multi-acid and fusion digests, due to its ability to measure the considerably higher amounts of

continued on page 7

Multi-Element Determination of Geological Samples... *continued from page 6*

major elements extracted into solution using these digestion techniques.

Partial weak extractions, such as Mobile Metal Ion Geochemistry (MMI), have become a significant tool in geochemical exploration over the past decade (Mann et al. 1998). Earlier versions of these leaches measured four or five indicator elements at low concentrations using ICP-MS in order to determine locations of buried gold and base metal mineralization. The recent introduction of MMI-M, a pH-neutral extraction that aids in the identification of polymetallic targets and multi-element associations for specific styles of mineralization, has placed the emphasis on ICP-MS to deliver quantitative results for a much larger range of elements. As well as measuring base and precious metals, the package has been used in the determination of rare earth elements (significant in the geochemistry of nickel sulphide deposits) and major elements such as Fe, Ca and Mg. In total, ICP-MS can be used to measure over 45 elements present in concentrations ranging from sub parts per billion (e.g. Au), through to hundreds of parts per million (e.g. Mg and Ca), further illustrating the major advantage of the dual detector approach to analysis by ICP-MS.

Conclusion

There is an increasing need for high precision analyses of geological samples for a greater range of elements and concentrations. Modern exploration methods involve statistical analysis of data from a set of elements in order to assess possible ore deposits. The challenge for analytical techniques is to evolve to meet these ever-changing demands. These can include: the addition of more elements, lower detection limits, and increased ranges of concentrations. ICP-OES and ICP-MS have been shown to provide reliable results for geological samples and the constant improvement in both techniques, such as use of the dual view for ICP-OES to lower detection limits, and the dual detector in ICP-MS to increase dynamic ranges only strengthens their applicability in a wide variety of situations for both now and the future.

The answer to the question of which technique to use is always contentious, as a number of factors have to be taken into consideration that may be unique to a particular situation. However, the following are some general guidelines:

- For initial reconnaissance work using a weak extraction, use either ICP-OES or ICP-MS to obtain information about a set of elements. For two-acid extraction, use a combination of the two techniques to determine additional elements (such as S, Hg, REE, Th and U).
- For drill cores and rock samples, use either a multi-acid or fusion digestion, followed by ICP-OES for major components and trace elements. Combine this with ICPMS to determine additional elements (such as REE, Rb, Nb, Th, U).

- For individual elements required in high-grade samples (percentage levels), a specialized assay technique is used, combining a larger weight sodium peroxide fusion with ICP-OES determination, and utilizing appropriate element-specific certified reference standards.

Note: classical chemistry is used for the settlement quality analyses of payable elements in very high-grade materials

The use of both ICP-OES and ICP-MS provides the most comprehensive sample analysis for the greatest range of elements in exploration situations. The two techniques have become synonymous with geological sample analysis and their unrivalled ability to produce high quality data in a timely and cost-effective manner makes them a powerful tool for the exploration industry.

References

- Chao, T.T. & Sanzolone, R.F. 1992. Decomposition Techniques. *Journal Geochemical Exploration*, **44**, 65-106.
- Govindaraju, K. 1996. 1994 Compilation of Working Values and Sample Description for 383 Geostandards. *Geostandards Newsletter*, Vol. 18, Special Issue, 1-158.
- Lynch, J.J. 1990. Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4. *Geostandards Newsletter*, **14**, 153-167.
- Lynch, J.J. 1996. Provisional elemental values for four new geochemical soil and till reference materials TILL-1, TILL-2, TILL-3 and TILL-4. *Geostandards and Geoanalytical Research* **20**(2), 277-287.
- Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B. & Perdix, J.L. 1998. Application of mobile metal ion technique to routine geochemical exploration. *Journal Geochemical Exploration*. **61**, 87-102
- Nölte, J. 2003. *ICP Emission Spectrometry*. Wiley-VCH.
- Riddle, C. (ed.), 1993. *Analysis of Geological Materials*. Marcel Dekker.

Nicholas Turner

*Global Technical Manager, ICP-OES/ICP-MS
SGS Minerals Services,
1885 Leslie Street, Toronto, ON
CANADA M3B 2M3
Tel: (416) 445 5755
Email: Nicholas.Turner@sgs.com*

