

What is the preferred upper end of concentration for base metals and pathfinder elements in ICP-MS? When should the geochemist switch to routine ICP-AES?

Commercial ICP-MS multi-element packages are now widely used as an exploration tool, providing pathfinder elements at trace concentration levels. The detection limits achievable by ICP-MS for low level concentrations of elements and elements with low crustal abundances have proved their worth in determining new targets and increased information about geological sites.

The combination of multi-element analytical packages and computing power to manage data from for multiple elements over a project has made the collection of these data common place. The range of concentrations in geochemical analysis that needs to be addressed is wide. Major elements are present at % levels. Trace elements such as Se and Te have crustal abundances in the sub-ppm level and require the sensitivity of ICP-MS. Important trace element indicator elements such as arsenic can range from a few ppm to hundreds of ppm. Levels of other elements may cover wide ranges: Cu at sub-ppm in a selective leach, 10's of ppm in grass roots exploration and % levels for on-site and target drilling. These are challenging demands but are being met by current analytical options.

Analog detector on the mass spectrometer. ICP emission range is from ppm to % levels. The extended range is due to the ability to access emission lines of different sensitivities that allow extension of linear range for any element. It is common within one project to have requirements for different elements that cross all these ranges.

The need for a combination of instruments to cover the range in geological samples is illustrated in Figure 1. Typical crustal abundances for a number of elements are plotted in increasing order against the instrumental ranges for ICP-MS and ICP-AES. ICP-MS optimum analytical range is shown in yellow and ICP-AES optimum range in blue. Gray represents where the two techniques overlap. The instrumental ranges are estimated based on a 1 g to 25 ml digestion.

Best Methods to Provide Results across the Ranges

The standard ICP-MS packages at ALS Chemex have always included both an ICP-AES *and* an ICP-MS ion determination on each sample to provide optimum precision and accuracy for each element over a wide concentration range. Trace elements and low level concentrations are reported from the ICP-MS determination. Major element concentrations are reported from the ICP-AES determination. Elements with concentrations in the mid-range between the techniques are measured by both procedures. Results are cross-checked for correctness to ensure there are not interferences in one technique and to ensure linearity of the reporting between the two techniques. Within a submission, an element such as arsenic or copper might be reported from the ICP-MS, from the ICP-AES, or from a comparison of both instruments at the mid-range. This ensures that from the two determinations, the data reported are the best available between the two instruments. This was established at the early stages of implementation at ALS Chemex owing to concern for quality data for each element reported, and recognition that some elements at certain ranges are better reported from ICP-AES rather than ICP-MS, whereas other elements can only be measured by ICP-MS.

The procedures and calculations for the instruments and reporting protocols are the same across the company globally. The global protocol includes primary isotope and emission line selection for each elements, secondary

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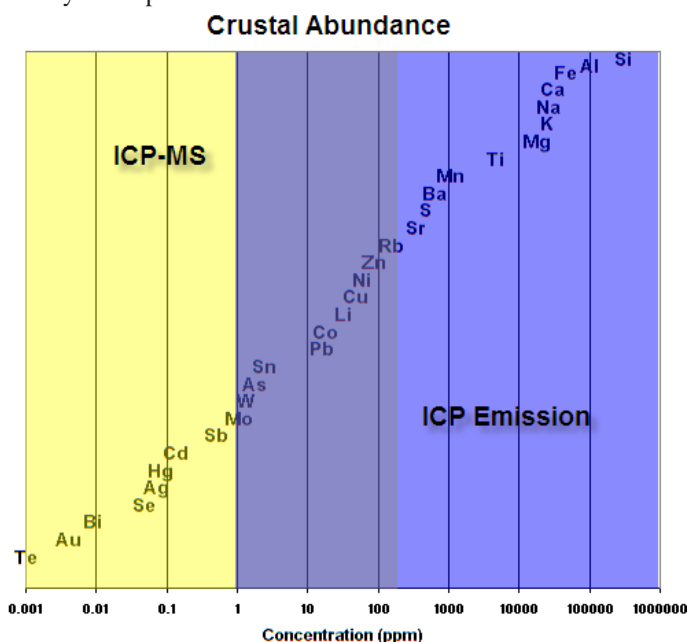


Figure 1: Crustal abundances of various elements versus analytical ranges for ICP-MS and ICP-AES.

Range of ICP-MS and ICP Emission Instruments

Most samples are now analyzed by either ICP emission spectrometry or ICP-MS, or a combination of these two instruments. The range of ICP-MS for most elements is 10 ppb to 250 ppm (in the sample itself). Extension of this upper limit can be done by using the

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choices, rules for when secondary choices are used, switching points between techniques, plus calibration protocols and levels. The software for calculation of results from instrument data, and review and approval of data are centrally controlled. In addition to this, all choices made by the analysts during the data review process are captured in an audit trail and are available. Within the procedure, a number of the inserted Quality Control reference standards are used by all laboratories globally. Review of control charts and long-term trends are monitored to ensure consistency amongst all the labs. The outcome is that comparable results are obtained by these methods from all our sites.

Over Limits – when to switch to another method

When the concentration of an element exceeds the range of the procedure, another method is used to determine the element abundance. For instance, fire assay with an AA finish may indicate high-grade samples which are repeated by a fire assay Au with gravimetric finish. We might determine the Cu by a 'geochem'

method up to 1% (with a precision of $\pm 10\%$) and then, at the 1% level, use an assay procedure with an appropriate digestion and finish to determine the concentrations with better precision (i.e. $\pm 5\%$).

The concept of range is important. Range for a procedure is the concentration upper and lower limits which meet the precision, accuracy and performance requirements for the method. Range includes not just the analytical finish but also the appropriateness of the digestion, the volume controls and accuracy, calibration checks and precision of method control.

When a sample exceeds that standard calibration for a method, there are choices to be made in order to determine the content. Oftentimes, a lab will be asked to simply 'dilute' the sample and report a value. In most cases, this is not appropriate. The digestion for the original determination, typically 0.5 g to 25 mL in a test-tube, is not likely appropriate for a highly mineralized sample. The volume control in the test-tube volume ($\pm 3\%$), added to the dilution error (too often done as 1 ml with an Eppendorf pipette plus 9 ml with an autodispenser) now has a volume error of greater than 5%. When this is coupled with other errors in the procedure, the error limits of the 'diluted' value can make the results misleading and not of value.

When an element exceeds the limits of an ICP-MS range, the sample can be determined directly on the ICP emission instrument without dilution. If the sample exceeds the calibration range of the primary emission line,

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in many cases, there are secondary emission lines that can be used to extend the calibration without resorting to dilution. This is a case of using the 'right' instrument to analyze the sample. However, at a certain level, all are better served by using the 'right' method – i.e. a specific digestion with volumetric flasks – to provide an appropriate result that is fit for purpose.

In our opinion, it is not responsible to use dilution and a single digestion and instrumental procedure cover the range for sub-ppm up to tens of percent for one element.

Under Limits

In many cases, the detection limits from the ICP-MS packages are not required and, for most of the samples in the project or for most elements, ICP emission detection limits are adequate. This cost-effective choice can be made. Generally though there are a few elements or a few samples where the concentrations are below emission detection limits and an ICP-MS determination would be of value. These can be managed by "Under Limits". Just as you might specify, 'if Cu > 5000 ppm, do an assay', the specification of 'if Bi < 20 ppm, use ICP-MS' can be requested and automatically managed in the system.

A project can have ICP-MS done for a few key elements on every sample, or it can be done by having ICP-MS done only when the concentration for the element is below a trigger level.

ICP-MS to Determine Trace Elements in Ore-Grade Samples and Concentrates

Trace element characterization of a highly mineralized sample or concentrate can add value to a project. ALS Chemex has developed ICP-MS packages for concentrates and high-grade samples. It is not appropriate to have these samples analyzed by the routine exploration package. These packages use slightly higher sample/volume ratios but include a number of other features. In the case of a copper concentrate, high-concentration copper samples are run to correct for any interferences on other elements that may not be corrected for during routine determinations. Separate equipment is used to prevent any carry-over contamination to other work. The commodity element will not be reported by this procedure but trace characterization can be very useful.

Summary

Knowledge of the nature of your project and expected concentration ranges will allow you, in discussion with the analysts at the laboratory, to select the best analytical protocols for your project. This may will include a number of methods, for instance both ICP-MS and ICP emission spectrometry, and selected 'over limits' and 'under limits' to give data quality that is suitable for the needs of the project. The procedures established at ALS Chemex are designed to provide quality determinations

for elements at a variety of ranges, with the system set up to automatically provide the optimal procedures if the initial determination is not optimal. The geochemist is not required to request these because they are part of the ALS system. However, collaboration between the geochemist and analyst at the start of the project is always preferable to establish the optimum analytical methods to match the sample concentrations, matrix, and mineralogy.

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