

Has ICP-MS Helped to Improve the Quality of Data Obtained from Geological Samples?



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Introduction

Improvements in measurement selectivity, sensitivity, and affordability have made inductively coupled plasma mass spectrometry (ICP-MS) the predominant technique used in analytical geochemistry. These improvements make analytes accessible that were previously only quantifiable with separation and enrichment techniques. To fully benefit from the advances in this technology, however, there are important considerations to be made from sample preparation to method validation.

This summary will examine proficiency testing measurement results and sample preparation techniques for zirconium and chromium produced by ICP-MS instruments in selected reference materials and will discuss the reasons for the large difference (up to a factor of 10) in spread between ICP-MS and x-ray fluorescence (XRF) results.

Proficiency Testing

In 1951, an interlaboratory comparison was organized by the United States Geological Survey. Matrix matched calibration standards were prepared for analysis by direct current arc spectrometry. Two samples were collected: G-1 (granite) and W-1 (basalt). Samples of 40 kilograms of each were ground and bottled into 500 units. These reference materials were sent out to 30 “expert” laboratories with experience in rock analysis. The laboratories were in academia, industry, and government and samples were analyzed by two classical methods: gravimetric and titrimetric, since modern techniques such as ICP-MS and XRF were not yet in use. **Figure 1** shows the silica analysis results of one rock that had a silica content of approximately 52% (m/m), represented as the blue triangles in the upper left corner. As can be seen, this data is much more accurate and precise than the result from an International Association of Geoanalysts (IAG) proficiency testing program (GeoPT25) conducted many years later (2009) in more “routine” laboratories. This difference may be due in part to the effort put into sample analysis with classical methods. Originally, it took a week to obtain a complete major element dataset for one rock, therefore, chemists and scientists took tremendous care in the selection of samples, the production, and the interpretation of data. With modern instrumentation, it is much easier to obtain data, leading to less thought about sample selection and data production and interpretation.

A very successful proficiency testing scheme administered by the IAG has been in place since 1995, along with the production and certification of reference materials necessary to support method validation and calibration purposes. Modern proficiency testing consists mainly of two rock samples that are sent out each year to participating laboratories. In most cases,

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these samples are silicate rocks, but carbonate and cement materials have also been used. Laboratories have about three months to perform the analysis, compile the data, and issue a report. The data assessment consists of a comparison to a consensus value, which has been obtained either from the robust mean, the median, or the mode of the submitted data, depending upon the frequency distribution. Performance is then compared with the Horwitz Function, an empirical function used to assign a standard deviation. The Horwitz Function was originally created from food analysis data but still works quite well for geological material.

A specialty of this program is the differentiation between two different laboratory qualities: Group 1 are research laboratories with strict criteria of quality, and Group 2 are applied geochemistry labs, which have less strict rules for the evaluation of the data. Data are reported anonymously, according to laboratory codes, to maintain confidentiality. The data are presented in theta or z-scores, whichever is preferred; an example is illustrated in **Figure 2** for a typical distribution for the analysis of manganese oxide. In **Figure 2**, the solid lines are the criteria for the research laboratories; the dashed line the criteria for the applied laboratories. Any results outside these two lines indicate method inconsistencies requiring optimization.

The ability to collect ICP-MS data in low concentration ranges is presented in **Figure 3** for the development of ICP-MS from 1995 to 2016, where initially only 20% of laboratories contributed data for thulium, one of the least abundant rare earth elements. More recently, over 50% of all laboratories have contributed data for thulium and other rare earth elements by using ICP-MS analysis, confirming it as one of the most predominant analysis techniques for geological rock analysis.

Figure 1: Silica analysis results of a rock with silica content of approximately 52% (m/m).

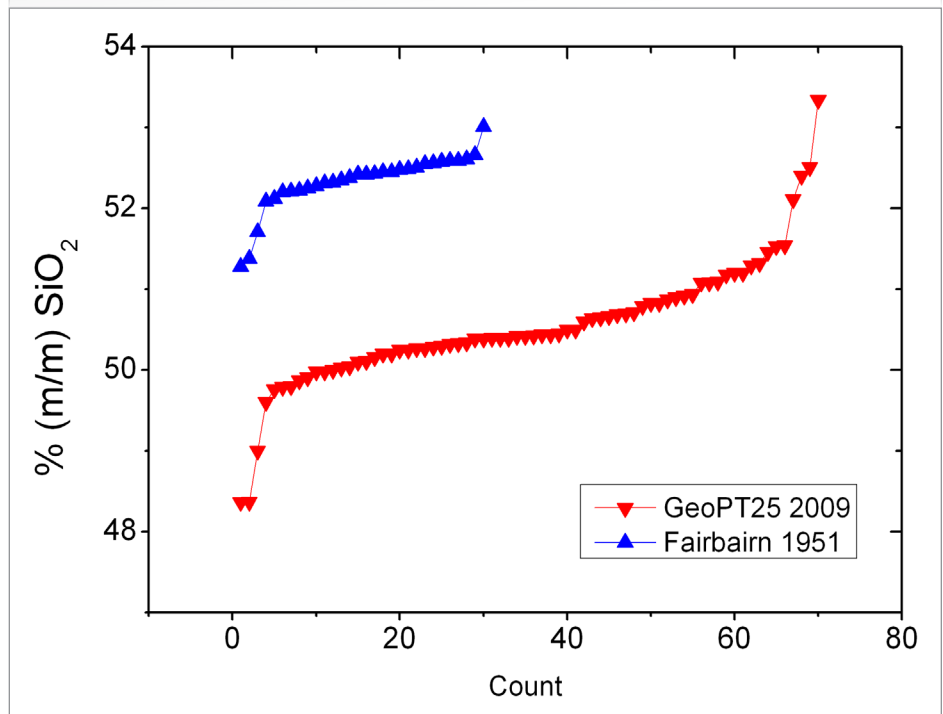
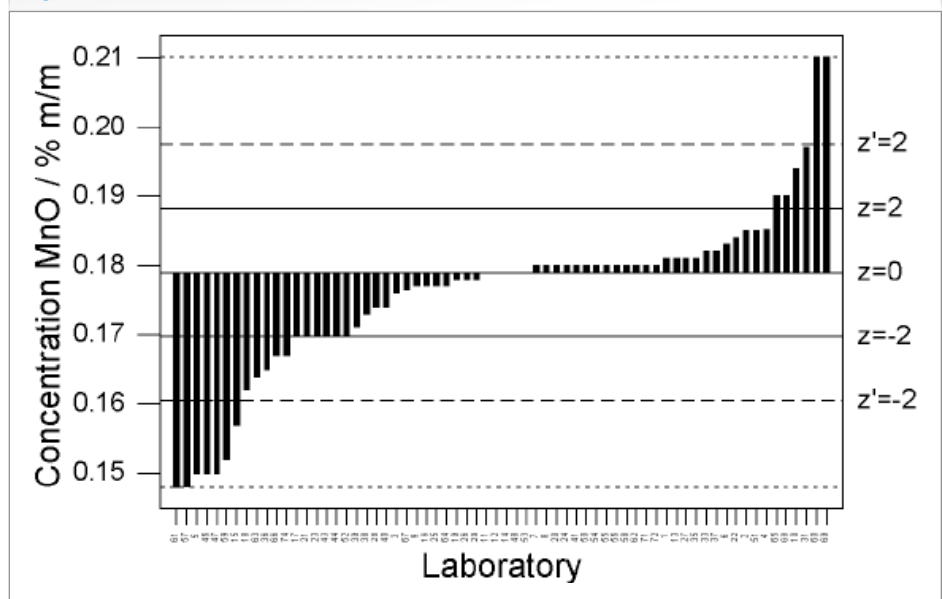


Figure 2: GeoPT20 – Barchart for MnO.



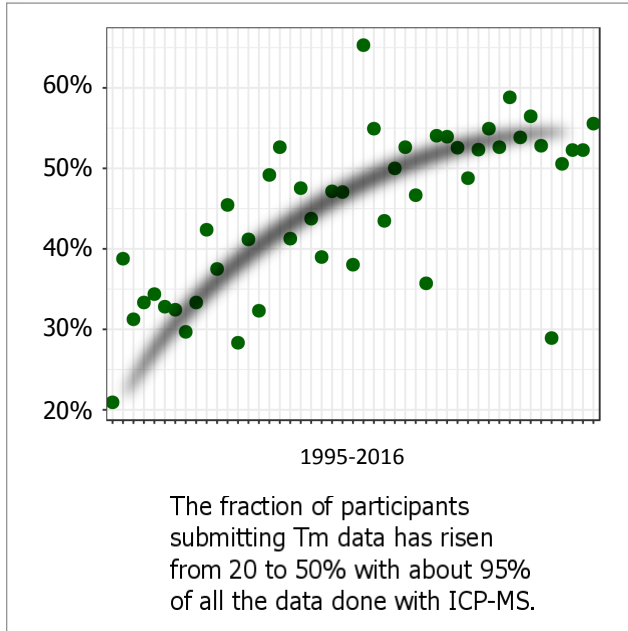
ICP-MS/MS

Although neutron activation analysis is sometimes used for geochemical analyses, there really is not a viable alternative to ICP-MS. However, not all analytes can be quantified correctly due to spectral interferences that can be caused by double-charged ions or oxidized ions. One way of solving this problem is using the newly developed technique of ICP-MS/MS analysis to improve data quality. For example, using standard

ICP-MS or even ICP-MS/MS techniques, the analysis of scandium, a mono-isotopic element, cannot be distinguished

from zirconium, which can form doubly charged ions. But by setting the first quadrupole in an ICP-MS/MS instrument to 45, and introducing oxygen between the quadrupoles, scandium will be selectively oxidized. This creates a new compound ion with a m/z of 61. By setting the second quadrupole to 61, all the other ions (e.g., the unreacted 45 scandium and the doubly charged zirconium ions) will be filtered out leaving a clean scandium oxide spectrum. Using oxygen as a reactant in this way during ICP-MS/MS analysis is referred to as mass shift mode, resulting in better correlations of the expected data of inter-laboratory reference materials versus the intensity normalized to an internal standard, which is an enormous improvement not achievable with earlier techniques.

Figure 3: Fraction of GeoPT labs that submitted thulium data.

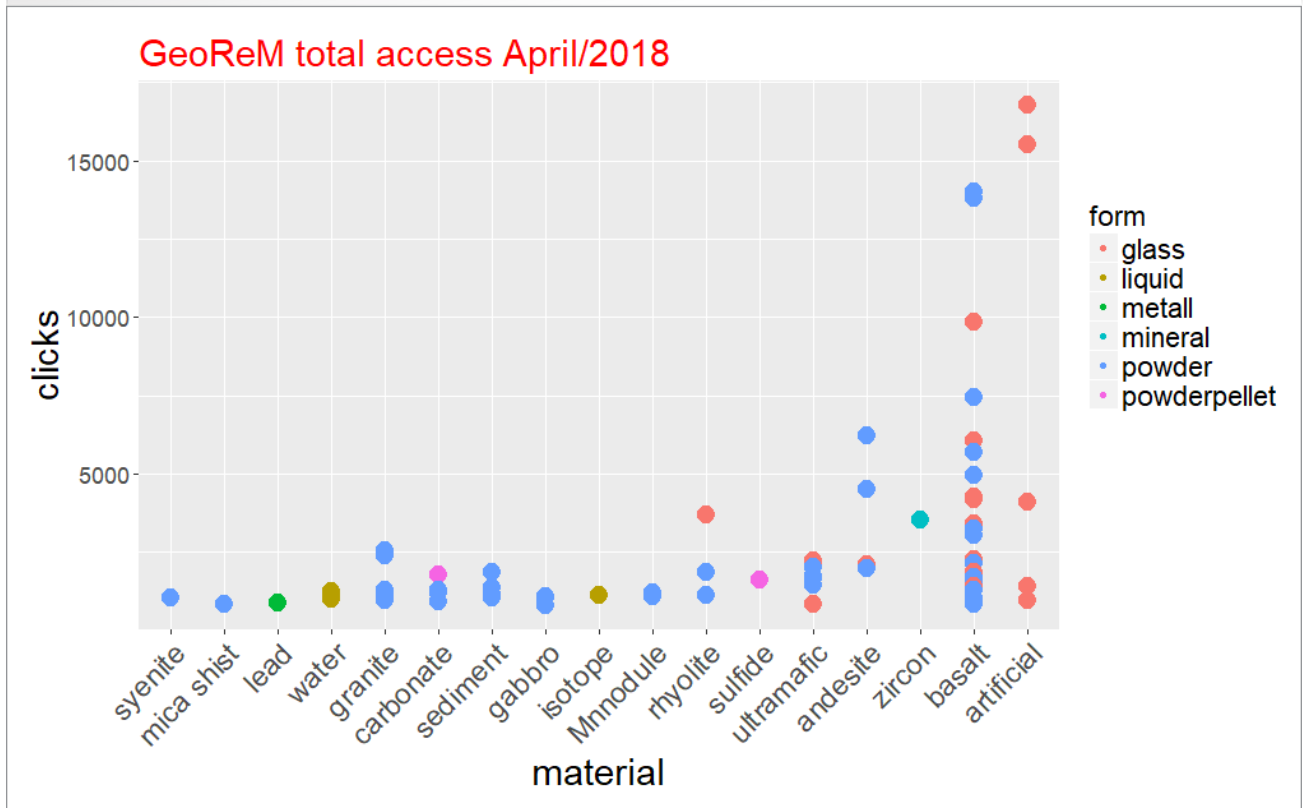


ICP-MS/MS Sample Preparation

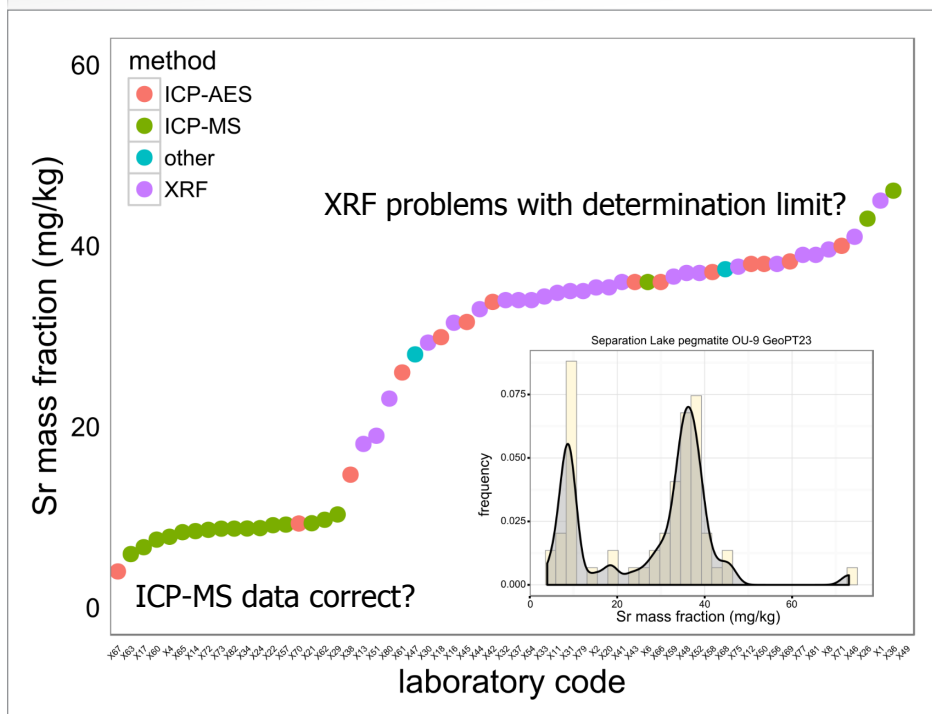
While the ICP-MS/MS technique can significantly improve the selectivity of various analyses, additional issues must be overcome such as incomplete digestions due to the lack of mineralogical and chemical knowledge or the use non-matrix matched reference materials for calibration validation and quality control purposes. Simple mineralogical matrices or materials that are easy to digest sometimes lend themselves to an observational bias where analysts only look for whatever they are searching for by looking where it is easiest.

Figure 4 summarizes some metrics from queries of a

Figure 4: Queries for various reference materials in a database maintained by the Max Planck Institute.



Source: <http://georem.mpch-mainz.gwdg.de/>

Figure 5: Separation Lake pegmatite OU-9 GeoPT23.

database maintained by the Max Planck Institute in Mainz, Germany. Data were collected from several hundred reference materials and compiled with literature data and certified data. The plot in **Figure 4** shows the number of times various reference material data were accessed up to April 2018. As can be seen in the righthand corner, the most accessed reference materials are basalts and the artificial ones that are the easiest to analyze via ICP-MS techniques.

Natural materials (basalts)—which are the most frequently accessed samples because they're simple matrices and easy to digest resulting in very good data and consensus or certified values—are often used for method validation or calibration purposes. More complicated matrices like granite are accessed much less frequently due to the so-called zircon problem. Zircon is a zirconium-bearing mineral and zircon silicate is a very refractive mineral found in the earth crust that can be up to 4.3 billion years old. It can be problematic to analyze because it is an extremely resistant mineral and very resistant to chemical digestion.

The Case for Geochemistry

Figure 5 illustrates another analysis challenge in the case of strontium, where proficiency testing revealed a significant break between data obtained via XRF and that obtained via ICP-MS analysis. Initially, it was assumed that the ICP-MS data must be correct because at low concentrations, ICP-MS is expected to be the method of choice due to its higher

sensitivity over XRF. However, rather than any true instrumental technique differences, it was determined that the different results between the two analysis techniques was due instead to the rubidium-strontium radiogenic isotope system.

Using ICP-MS, only mass 88 is monitored because it is the most abundant and interference-free mass. But mass 87 is an isotope of both strontium and rubidium and the rubidium isotope is radioactive; decaying to strontium 87 very slowly with a half-life of 48 billion years. In the case of the proficiency samples, so much radiogenic ingrowth of strontium 87 occurred that it exceeded the abundance of mass 88. ICP-MS only looks at one isotope if the other isotopes occur in abun-

dance, which in this case is not true. Since XRF analysis looks at all the isotopes at the same time, the correct results were only obtained with this technique.

Conclusion

There are many factors that can influence a measurement result; sampling, the selection of reference materials, and method selection all play a major role. In most cases, sampling must be done in solution and to get a rock sample into solution, either acid ingestion or sintering must be used. While with sintering or fusion, a complete digestion can be obtained, often it is at the cost of some contamination due to impurities in the chemicals used, resulting in a tradeoff between complete digestion and low levels of contamination. The selection of reference materials is also important as the matrix can have an enormous influence on the measurement result when performing method validation or calibration.

Method selection also has a bearing on how interferences are managed, which is best accomplished during method validation with matrix-matched calibration standards.

While collaborations between analytical chemists and earth scientists are necessary and important to obtain correct and interpretable data, it is only with the use of the right matrix-matched sample preparation techniques and improved knowledge that analysts can fully benefit from the new possibilities in geochemistry research driven by the latest innovations in analytical ICP-MS instrumentation.