



Optimised Detection Limits for Multi-Element Geochemical Analysis

A few years ago some rock samples were submitted to our laboratory by a client requiring gold analysis. We found the levels to be <1 ppb in all samples and reported them as such. The client then came back to us asking how much gold that was. Even after explaining the samples were below the detection limit, the client still replied: “Yes, I understand. But how much is there?”

The concept of a detection limit has always been difficult to explain, since it can be expressed in so many ways. It is also a somewhat controversial subject in geochemistry, as there is a commercial advantage to having lower reporting limits and seemingly offering the geologist better information about their samples. There is also the oft believed concept that a lower detection limit means that one method is ‘better’ than another one. This is not necessarily true as there are many factors that influence the efficacy of a method – sampling procedure, homogenization and digestion procedure to name but three. Nevertheless, there is a decades long trend in the geochemical laboratory industry towards reporting lower concentration levels of elements, but what is the value of these data, in terms of practical use and reliability, particularly given field sampling representation and sample homogeneity issues? Furthermore, what constitutes a method detection limit as opposed to an instrumental detection limit and what is the best way of determining it?

It is the responsibility of the analytical chemist to ensure that data are meaningful, and this becomes more important as lower element concentrations are reported. “Instruments do not write scientific papers, since they have no opinions. Scientists must give them voice.” stated Nobel laureate John Polanyi recently, adding that “truth . . . is the astonishing belief that unites us as scientists” (Polanyi 2015). It was with this goal in mind that we decided to investigate the concept of detection limit for geological analysis using inductively coupled plasma mass spectrometry (ICP-MS) and mobile metal ion (MMI®) extractions as examples of technique and methodology. The rise of ICP-MS in the past two decades, combined with advances in geochemistry that have championed the use in exploration for a large array of pathfinder elements, has resulted in laboratories offering a wide range of elements and digestion procedures. SGS Minerals Services, for example, offers standard packages for a variety of methodologies, from weak leaches through acid digests to fusion procedures that offer in excess of 55 elements reported to very low concentrations. For this study, MMI® was chosen as the methodology as it is a single pass analysis that provides data

on a wide range of elements. In addition, samples from all over the world are analysed and this variety provides a good cross-section of different terrains and soil types.

Mobile Metal Ion (MMI®) Analysis

MMI® is one of a number of weak partial extraction methods used in soil geochemistry (Mann et al. 1998). It works on the principle that mobile ions from buried ore deposits migrate to the water table and then are transported towards the surface. Over time they accumulate just below the organic layer of the soil in the active plant root zone. These mobile ions are preferentially extracted from the substrate by using a ligand based solution (MMI-M) that releases them from the soil particles. The resultant solution is then measured using ICP-MS for a wide range of elements. MMI-M has been used in a wide variety of geochemical exploration programs since 2004 due to its high selectivity, low matrix interferences and low background noise (Mann 2010). However, recent improvements in instrumentation and methodology necessitated a review of whether these reporting limits were appropriate for each element.

ICP-MS

ICP-MS offers very low detection limits for many elements, even after the typical digestion procedures required for geological samples. It can do this because of its architecture – the argon plasma is an extremely efficient heat source that can ionize elements in a solution which can then be extracted and separated by a quadrupole mass spectrometer. An electron multiplier detector allows the measurement of very low concentrations of many elements. Due to the fast scanning of the quadrupole, analysis of the majority of elements in the periodic table can be measured in a matter of a few minutes. To put the instrument sensitivity in perspective, a 0.1ppb detection limit for gold for example, is approximately the same as picking out one person from the population of the entire world. The main factors governing detection limits by ICP-MS include:

- **Ionization Potential:** the degree to which a particular ion behaves in the plasma and forms positive ions will govern the amount of signal achieved for it. For example, cobalt is 93% ionized in the plasma, whereas platinum is only 63% ionized and will give less signal for the same concentration (Houk 1986).
- **Isotopic Abundance:** Mono-isotopic elements such as cobalt at mass 59 will have a greater sensitivity than platinum with six isotopes, the largest of which is 33% abundance.

continued on page 3

Optimised Detection Limits for Multi-Element Geochemical Analysis... *continued from page 1*

- Measurement time of the element in the solution.
- Contamination: Due to its abundant sensitivity, small traces of any element will be detected from sampling instruments, sample containers, reagents, glassware etc.
- Matrix Effects: The matrix itself can cause issues with signal suppression if it is too concentrated in the plasma.
- Interferences: Due to the high temperature of the plasma, polyatomic species from elements in the sample can be formed that interfere with the analyte, such as $^{43}\text{Ca}^{16}\text{O}$ on ^{59}Co or $^{179}\text{Hf}^{16}\text{O}$ on ^{195}Pt (May & Wiedmeyer 1998).

Thus it is important to understand what the issues are when determining a detection limit for an element in a particular matrix. Whilst the first four are somewhat constant, the last two can vary considerably from sample to sample, especially in geological samples. Matrix effects are minimized by the use of sample dilution, internal standards and matrix matched calibration standards but these approaches do have adverse effects on the detection limit for a method. Interferences are particularly difficult to deal with in geological samples compared with most other chemical analyses, because of the mineralogical variety and the subsequent changes in elements concentrations in any given sample. Whilst blood, seawater and other heavy matrices can be difficult to deal with, they are at least homogenous – you are not going to suddenly get a blood sample with 1% zirconium for instance, whereas the major elements in geological samples vary with each batch, and often dramati-

cally within a batch as well. Interferences can be corrected for mathematically or reduced using a variety of cell-based techniques. In the latter approach, a cell is placed before the quadrupole and filled with either an inert or reactive gas. The gas collides or reacts with the ions in the system, breaking up polyatomic interferences but allowing the ion of interest to exit the cell into the quadrupole (Tanner et al. 2002). Both concentration range and interferences have to be taken into consideration when determining detection limits as they affect the overall measurement uncertainty of the analytical process.

Standard Approach for Determining Detection Limits

Typically, a detection limit is based on instrument sensitivity combined with a sense of the crustal abundance of an element. This leads to several ranges of detection limits – higher levels (ppm and %) for the major elements such as Fe, Ca, Mg etc., medium levels for elements like base metals, Ba, Sr etc. (5 to 10ppb) and then low levels for elements such as precious metals (0.1 to 1ppb). This is particularly relevant in ICP-MS, where there is no point in having a very low detection limit for iron, for example, since all samples tend to contain appreciable concentrations. A common approach is to take ten method blank solutions and then measure them against the calibration. The limit of

continued on page 4

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.

Optimised Detection Limits for Multi-Element Geochemical Analysis... continued from page 3

.....

detection (L.O.D.) is defined as 3 X SD (standard deviation) of these solutions. This infers that the analyte can be detected above the background, but not necessarily quantified. A better measure is the limit of quantitation (L.O.Q.) defined as ten times the standard deviation (10 X SD) of ten method blanks measured against the calibration. Table 1 illustrates these results for several MMI-M elements. These values are then evaluated with the typical range of the elements in samples and known interference issues to arrive at values for the detection limits as shown in the table. The Pd detection limit, for instance, is significantly higher than the calculated value due to the presence of interferences from samples.

	Mn	Co	Cu	Pd	Pt	Au
Blank 1	0.05	0.23	2.64	-0.005	0.006	-0.004
Blank 2	0.03	0.14	1.58	0.009	0.029	-0.013
Blank 3	0.02	0.04	2.69	0.015	0.023	0.014
Blank 4	0.06	0.20	2.39	-0.016	0.003	-0.009
Blank 5	0.05	0.19	2.06	0.005	0.040	-0.013
Blank 6	0.02	-0.00	1.67	-0.006	0.011	-0.008
Blank 7	-0.06	0.06	2.33	0.010	0.040	-0.008
Blank 8	0.02	0.07	2.32	-0.012	0.023	-0.003
Blank 9	-0.04	0.12	2.46	-0.002	0.039	-0.016
Blank 10	-0.03	0.07	1.81	-0.007	0.028	-0.008
Average	0.013	0.113	2.193	-0.001	0.024	-0.007
SD	0.04	0.08	0.40	0.010	0.014	0.008
LOD	0.1	0.2	1.2	0.03	0.04	0.03
LOQ	0.4	0.8	4.0	0.10	0.14	0.08
Det Lt.	10	5	10	1	0.1	0.1

Table 1: An example of a common approach to the determination of the limits of detection and quantitation using 3X and 10X standard deviations (SD) of 10 method blanks for selected MMI-M elements. All results in ppb.

This approach does give justifiable detection limits but it suffers from some drawbacks:

- it is based on a single idealized test usually measured on a cleaned instrument
 - there is no allowance for differences in instrument performance with time
 - it does not necessarily reflect typical sample levels.
- In order to address these shortcomings, a more holistic approach to the detection limit was taken by using a database of method blanks and duplicate analyses. The concept of optimising the detection limit to the levels that can both be seen and are seen in a technique, using real samples over time, was the basis of this approach, with the idea being to achieve an appropriate detection limit for each element in a methodology that would allow the geologist to use the data to its fullest extent.

Determination of Optimized Detection Limits

The long term analysis of method blanks was used to monitor the analysis over time. The use of more than 1200 randomly placed method blanks meant that all scenarios of instrument performance and sample concentrations were covered and allowed for. Here, the detection limit of an element must fall below the 95th percentile of the method blanks (Quarles et al. 2014). Furthermore, the duplicates over the same period of time were investigated to see the typical levels of elements in samples. This is invaluable as it informs whether the detection limit is appropriate for the element. As an example, the results for Cu are given in Figure 1. (See page 6.) It can be seen that the 95th percentile for the method blanks is 10 ppb which is where the detection limit is set. An analysis of the duplicates indicates that Cu tends to be relatively abundant in samples, with 90% of samples containing greater than 100 ppb. Because the lowest quartile of results is considered background in terms of anomaly determination, it can be seen that an optimised detection limit of 10 ppb will be appropriate to highlight any potential anomaly, but will not be affected by variation in the background value over time.

This approach was taken for all elements in the MMI-M scheme and example elements are given in Table 2.

	Mn	Co	Cu	Pd	Pt
No. of Method Blanks	1335	1340	2170	1257	1272
Blank: 95th Percentile	13	0.8	9.9	0.04	0.01
Current Detection Limit	10	5	10	1	1
New Detection Limit	100	1	10	1	0.1

Table 2: New reporting limits based on a combination of the LOQ, long term 95th percentile blank data and levels found in samples. All results in ppb.

It can be seen that some detection limits have been lowered, some remain the same, and Mn has increased. Cobalt for example, has been lowered from 5 ppb to 1ppb, since the 95th percentile of the blanks is 0.8 ppb. Furthermore the distribution of duplicates indicates that 50% are in the 1 to 50 ppb range. Thus 1ppb is an appropriate detection limit

Optimised Detection Limits for Multi-Element Geochemical Analysis... *continued from page 4*

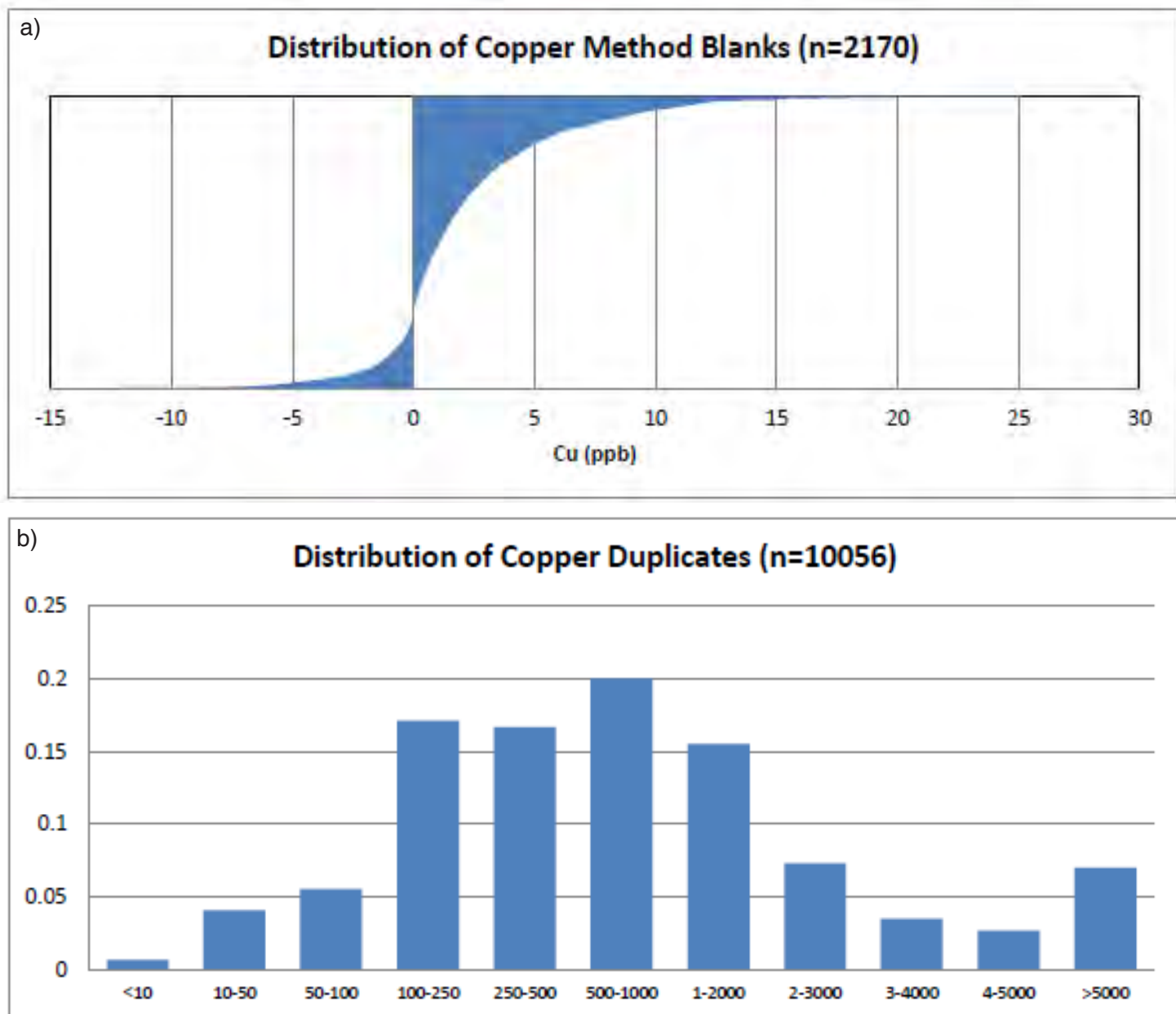


Figure 1: Analysis of long term method blank and duplicate data for Cu in order to determine the optimised detection limit. a) Method blank distribution for Cu. Bar chart illustrates the spread of 2170 method blank results around the origin. The 95th percentile value for the method blanks is 10 ppb. b) Distribution of duplicates for Cu showing that the majority of values are greater than 100 ppb in solution, indicating that the optimized detection limit is appropriate at 10ppb. Results are in ppb.

for the delineation of anomalies (Figure 2). The results for Mn illustrate that the 95th percentile method blank is at 13ppb. However, analysis of the duplicates indicates that 95% of samples are much greater than 100 ppb. Thus for Mn the detection limit has been set at 100 ppb to reflect the high levels found in all samples. This approach was applied to all elements and it was found that many elements required a lower reporting limit, based on duplicates and method blank data. Calibration ranges were also adjusted where necessary to reflect the levels found for some elements. Full results are given in Table 3 (*see page 8*). These

robust detection limits mean that low concentration results can be better used by the geologist for data evaluation.

A couple of important elements do not achieve reporting limits that make them particularly useful for anomaly targeting due to low concentrations found in samples, or interferences causing restrictions on reporting limit. Platinum does not show anomalies particularly well because it occurs at very low levels, has low ionization in the plasma, and has six isotopes resulting in diminished signal for each. Similarly, palladium is hard to measure at low concentrations due both to its relative insensitivity, low concentra-

continued on page 7

Optimised Detection Limits for Multi-Element Geochemical Analysis... *continued from page 6*

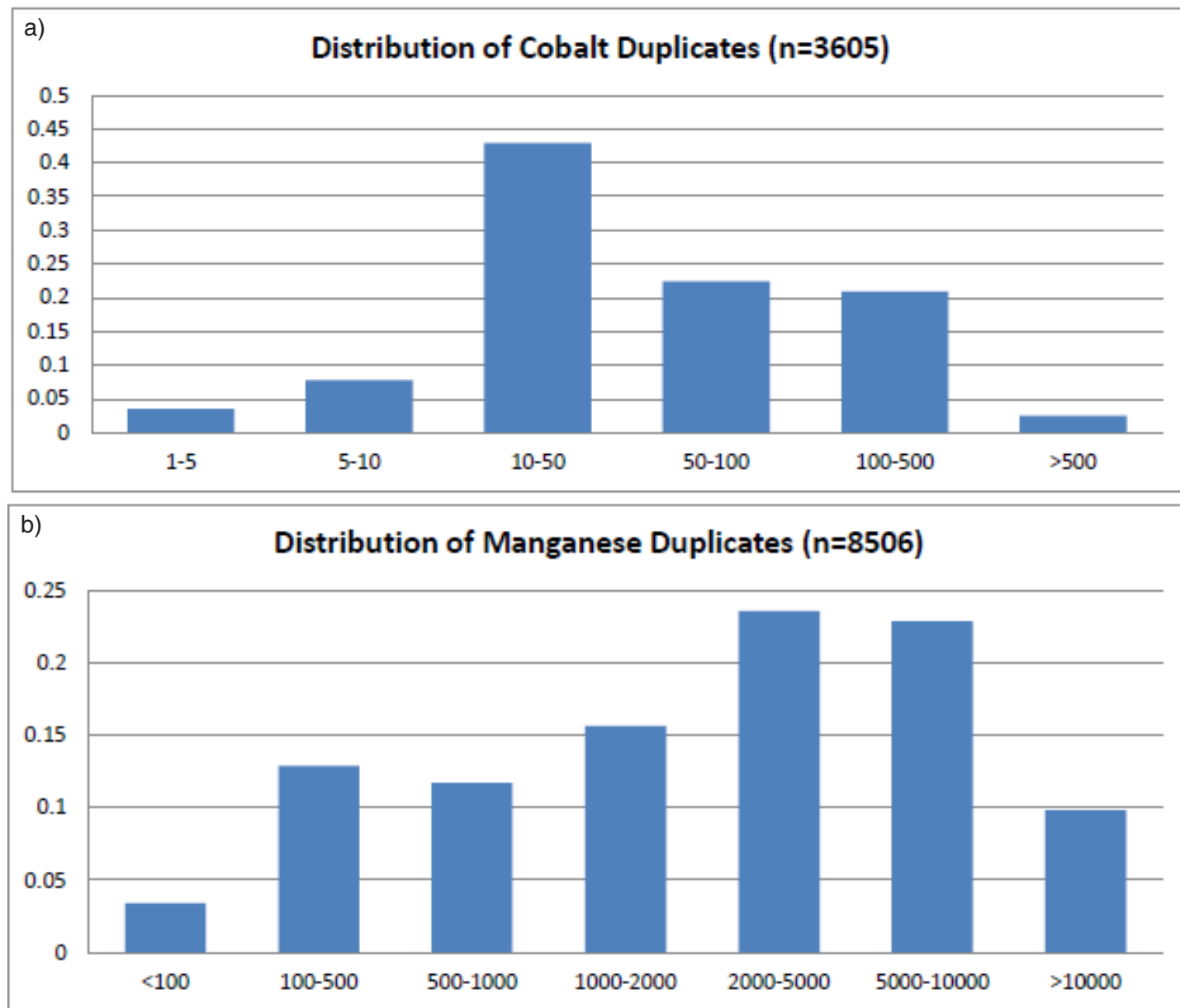


Figure 2: Analysis of long term duplicate data for Co and Mn for the determination of detection limits. a) Most Co duplicates are >10 ppb, so a detection limit lower than 1 ppb is not appropriate for detecting anomalies. b) Distribution of duplicate data for Mn, illustrating that all samples are >10 ppb initial detection limit and >95% of samples are more than 100 ppb. This indicates that the optimized detection limit should be raised to 100 ppb. Results are in ppb.

tion in samples and potential interferences from common elements such as Sr, Zr and Y. Even though the LOQ and the 95th percentile of method blanks indicate that Pd can be measured at lower detection limits, the plethora of interferences associated with the element in this method indicated that the 1 ppb detection limit was appropriate.

To address this, a separate method (MMI-MP) was developed that allowed the detection limits for these elements to be lowered to 0.1 ppb for Pd and 0.02 ppb for Pt. This was achieved through a combination of increased measurement time for the two elements and a rigorous interference correction procedure to combat effects at very low concentrations. Since ICP-MS is a sequential technique,

it is possible to measure individual masses more precisely using longer dwell times and more readings. However, this does increase the overall time of analysis and can affect the stability of the instrument due to the amount of sample passing through the spectrometer. In this case, an acceptable compromise was reached by reducing the number of elements being measured, resulting in an 11 element package focused on evaluation of precious and base metal commodity elements. This method is now being offered in Canada as an alternative to MMI-M for particular situations where palladium and platinum are required.

continued on page 8

Optimised Detection Limits for Multi-Element Geochemical Analysis... continued from page 7

	OLD DL	NEW DL		OLD DL	NEW DL		OLD DL	NEW DL
Ag	1	0.5	Gd	1	0.5	Sb	1	0.5
Al	1	1	Hg	1	1	Sc	5	5
As	10	10	In	0.5	0.1	Sm	1	0.5
Au	0.1	0.1	K	0.1	0.5	Sn	1	1
Ba	10	10	La	1	1	Sr	10	10
Bi	1	0.5	Li	5	1	Ta	1	1
Ca	10	2	Mg	1	0.5	Tb	1	0.1
Cd	1	1	Mn	10	100	Te	10	5
Ce	5	2	Mo	5	2	Th	0.5	0.5
Co	5	1	Nb	0.5	0.5	Ti	3	10
Cr	100	100	Nd	1	1	Tl	0.5	0.1
Cs	0.5	0.2	Ni	5	5	U	1	0.5
Cu	10	10	P	0.1	0.1	W	1	0.5
Dy	1	0.5	Pb	10	5	Y	1	1
Er	0.5	0.2	Pd	1	1	Yb	1	0.2
Eu	0.5	0.2	Pr	1	0.5	Zn	20	10
Fe	1	1	Pt	1	0.1	Zr	5	2
Ga	1	0.5	Rb	5	1			

Reporting Limit Unchanged

Reporting Limit Lowered

Reporting Limit Increased

Table 3: Reporting limits for the MMI-M scheme before and after the investigation. All limits in ppb except Al, Ca, Fe, K, Mg, P, which are in ppm.

Conclusions

Most approaches to the determination of detection limits for a method use a standard test of method blanks measured in a single pass. This work used long term data to calculate detection limits and resulted in:

- Detection limits that reflect technical improvements to the MMI methodology
- The use of randomized method blanks in conjunction with the common approach to detection limit calculation in order to provide true or more representative reporting limit capabilities for each element.
- Optimized detection limits related to the typical levels found in samples that are potentially more appropriate for targeting anomalies.
- The development of a new method, MMI-MP, to address the case of Pd and Pt where it was found that the MMI-M method was not sensitive enough for some situations.

Although improvements in methods, instrumentation, and sampling protocols have benefitted geochemical exploration, better handling of detection limits is important in providing high quality data for the geologist. It can be seen that the lowest detection limit is not always the best, but the use of optimized detection limits provides reliable data at low concentrations.

Acknowledgment

This article benefited from a review by Ryan Noble (CSIRO).

References

- HOUK, R. S. 1986. Mass spectrometry of inductively coupled plasmas. *Analytical Chemistry*, **56**, 91A - 105A.
- MANN, A. W., BIRRELL, R.D., MANN, A.T., HUMPHREYS, D. B. & PERDIX, J. L. 1998. Application of the mobile metal ion technique to routine geochemical exploration. *Journal of Geochemical Exploration*, **61**, 87-102.
- MANN, A. W. 2010. String versus weak digestions: ligand-based soil extraction geochemistry. *Geochemistry: Exploration, Environment, Analysis*, **10**, 17-26
- MAY, T. W. and WIEDMEYER, R. H. 1998, *Atomic Spectroscopy*, **19**, 150-155.
- POLANYI, J. 2015. *Toronto Star*, January 5.
- QUARLES, C. D. Jr., JONES, D. R., JARRETT, J. M., SHAKIROVA, G., PAN, Y., CALDWELL, K. & JONES, R.L. 2014. *Journal of Analytical Atomic Spectrometry*, **29**, 297-302.
- TANNER, S. D., BARANOV, V.I. & BANDURA, D. R. 2002. Reaction cells and collision cells for ICP-MS: a tutorial review. *Spectrochimica Acta*, **57**, 1361-1452.
- Nicholas Turner**
 Global ICP/ICPMS Technical Manager,
 SGS Minerals Services Geochemistry
 Email: Nicholas.Turner@sgs.com

