Importance and method of using reference materials in measuring reliability of analytical results and why customers should use them

by S. Marsland*

Synopsis

Reference materials have always been important for validating and controlling analytical methods. They have recently become even more important as quality requirements have become more stringent and customer demands for properly verified and controlled results increase. Clients, especially from the resource exploration industry, demand critical validation of all results reported. Mintek has been producing geological and semi-processed ore references since the early 1970s and recently, due to increase in demand, other manufactures have entered the South African market.

This paper describes analytical challenges from the customers' perspective, the customers being metallurgists, mine geologists, environmental scientists and geologists from resource companies. Reference materials with their appropriate use and a good understanding, can aid greatly in building confidence in the results, choosing the right laboratory for a project, deciding which set of results is correct and providing evidence to the customers' clients that the best possible results have been obtained

Introduction

Throughout the world there are hundreds of reference materials produced by over 80 organizations, and these are mainly ores, rocks, semi-processed ores and metals. Mintek is one of the top 10 producers with over 75 products. Many of these producers, including Mintek, and their respective standards organizations belong to the ISO REMCO committee and its respective work groups. This committee's main task is to draw up guidelines for using, manufacturing and certifying reference materials. In South Africa a mirror committee has recently had its inaugural meeting; its function is to give a clear mandate to the South African representative on the main ISO REMCO committee – the South African delegate has an opportunity to influence the contents of the guides.

The South African Reference Materials (SARM) programme has since 2000 increased its sales threefold; the question is why? More accountability is needed in our world. This means that the best possible analytical results are required and that the risks associated with them must be well quantified. Consider that the risk of wrong results or wrong decisions made from a result is trivial to a laboratory in comparison to the risk faced by that laboratory's customers. The consequence to a laboratory could be a loss of income or an employee losing his/her job.

The customer on the other hand, may mine thousands of tons of rock with no value in it or, worse still, fail to mine it when the grade is high. This may result in serious financial loss. Wrong results can cause incorrect conclusions about the efficiencies of metallurgical processes and may lead to the building of large, inefficient plants. Wrong decisions could be made about an environmental impact study. This is even more serious as it affects people.

The bottom line is that the results produced from inductively-coupled plasma optical emission spectroscopy (ICP—OES) can detrimentally affect people and the environment, and result in financial loss. How can the laboratory customer ensure that he or she chooses the most appropriate lab? How can the customer decide between different sets of data and know that results are unbiased?

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The customer must check the laboratories for accuracy and bias. This can be done using many techniques, including the following: (1) using duplicate samples (twin streaming); (2) sending samples to other labs; and (3) using reference materials as blind samples. The last option measures accuracy, bias and the control of methods. Every customer has had this scenario: you send a sample to a lab A and you get a certain result. You send another to lab B and get another result. Unsure of which one is right you send a sample to lab C, which provides yet another result. Now you are really frustrated: all the results are different and you can't figure out if you should combine the results or if one lab is truly bad. The solution is to use a reference material and send this with the samples to the laboratories. From the results you receive, correct conclusions for the above scenario can be made. This is achieved by using the laboratory standard deviation (LSD). Consider Table I. You can determine which result is wrong, using the LSD of 0.27. It is easy to calculate and to see that Lab 1 is the culprit. This result is further than two LSDs from the mean, which is 49.7. The result should lie within in the interval of 49.16 to 50.24. The LSD should be cited in the certificate alongside the other statistics.

Later in this paper I shall describe how LSD is derived and also what should be on a certificate of analysis. How do we choose a suitable lab for a project or ensure that our own primary lab is equal to the task?

The answer of course is LSD, reference materials and other strategies, which are: (1) proficiency testing; (2) competency documents; (3) validation reports; (4) measurement uncertainties; (5) visit them and (6) accreditation. Every aspect of the process from sample reception, preparation to reporting must be evaluated and documented. Also, at the end of an evaluation there should be a service delivery agreement between the customer and the lab. This may be a standard one or, for larger projects, a more Customer-specific agreement.

To conduct an RM performance study send the materials to the laboratories that you wish to evaluate. It is preferable to send a minimum of three to each, with plenty of sample for them towork with. When you get the results you can use the LSD to calculate the Z score, which is the distance from the mean divided by the LSD. Competent labs should be less than 1.5. The Z score can be regarded as indicating how far you are away from the centre (see Table II).

During a run of long projects, reference values can be plotted to create control charts so that the customer can be sure that the agreed-upon bias has not been exceeded and that the method is always under control.

These can be simple plots or more advanced cumulative sum (CUSUM) plots. Also, the bias from the repetitive runs of reference material can be calculated and acted upon (see Figure 1).

Table I

Laboratory standard deviation

	LAB 1	LAB 2	LAB 3
	x	y	z
SARM 74	49.01	49.75	50.20

LSD

		Cr %		
			Lab	
Certified	Value	95%	S	N
Average	49.7	49.50 - 49.83	0.27	13

Table II

Z score

LAB	AVE OF 4 RESULTS	Z SCORE
LAB 1	14.77	5.44
LAB 2	15.01	4.11
LAB 3	15.48	1.48
LAB 4	15.65	0.54
LAB 5	15.69	0.32
LAB 6	15.72	0.17
LAB 7	15.78	-0.16
LAB 8	15.87	-0.68
LAB 9	15.89	-0.79
LAB 10	15.91	-0.88
LAB 11	16.21	-2.56

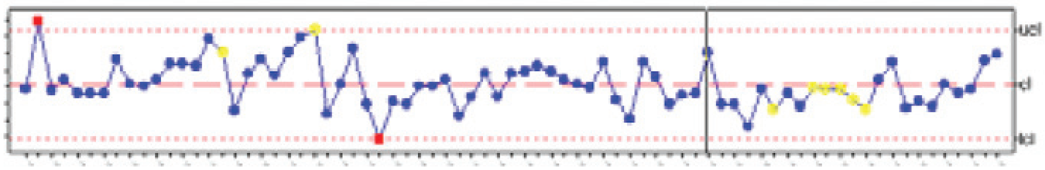

Figure 1

The question now is how many reference materials (RMs) one should use. My personal opinion this can be overdone. The information that is needed is how many reference materials the laboratory inserts. What size batches do they work with? Fire assay may work with batches of 50 samples if they have a large furnace. If you are comfortable with the laboratory's performance I would insert only one reference on every batch. If it is a new lab, insert two different references on every batch. It is a good idea to inform the laboratory manager that they are being evaluated and that insertion of RMs will be random in the batches and be marked similarly to samples. Etiquette requires that you provide feedback on the laboratory's performance. This builds an atmosphere of cooperation and transparency.

There are many situations in which suitable RMs are not available. The simple solution is to have an RM made. Mintek makes RMs for customers. This process could take between one and three months. When planning a project, ensure that this is factored in. Ideally all possible RMs should be available. This is the goal of the SARM programme and similar initiatives.

A project approach is used in making RMs at Mintek, based on the ISO guides 30 to 35. RMs must be useful for their intended purposes. For example, it is a waste of time to manufacture a product in which the overall uncertainty of the material is higher than the analytical method it will be used for controlling. For example, the ferrochrome industry will require an inter-laboratory standard deviation (LSD) of less than 0.5% while the platinum industry would need an LSD of less than 5% for measuring Pt in ore. From this the manufacturer must ensure that the homogeneity of the product falls into this requirement. The Manufacturer must ensure that the uncertainty between units and within the same unit is equivalent. To ensure this homogeneity and overall uncertainty, experiments must be planned and the results reported during the manufacturing process. Most importantly, a description of this and the result must be stated on the certificate.

The method of assigning the certified value must also be described on the certificate, and preferably with all values submitted from the round robin exercise. The reason is that after all the 'stats' and 'methodologies', the statistician at the end of day will make a judgement call regarding whether a particular result should be in or out. Also, the customer must be sure that the certified value is accurate and the assigned uncertainty is realistic. Some customers prefer to derive and compare their statistics to the reported statistics on the certificate. In my opinion this is a good attitude to have for important projects which can have a major impact on people money and the environment.

Modern practice in designing a round-robin exercise is to pick fewer labs but to ensure that they produce 'quality results.' These labs invariably have accreditation and do participate in frequent proficiency testing programmes. It also helps to contact senior role-players for recommendations. It is better to have 9 good labs producing results rather than 40 labs with results scattered all over the place. The aim is to have a data set that has normal distribution so that an arithmetic mean and standard deviation can be used rather than to use robust or non-parametric statistical methods. It is important to have a realistic estimate of uncertainty rather than an optimistically tight LSD. When choosing the labs, try to have diversification, namely some from another continent, some from a research institution and, of course, laboratories in that particular industry. Many of the industries have their own round robins and if you use only those and that whole group has drifted in particular direction, you could have an inaccurate average. The chance is small but it is there.

When all results have been submitted from the participants they should be collected and ordered and visually inspected for outliers. To aid this, a box and whisker plot should be employed. This is a graphical representation of the distribution of the data. The data should be checked for outliers using the Grubs and Chochran's test. Rejecting results should not be taken lightly and the tests should never be used more than once. This is an exercise to produce a certified value and not a 'proficiency test', and if you suspect that, for example, a participant may have made calculation errors, contact him. These kinds of errors show up clearly with the tests mentioned above. The aim is to get a normal population where the estimated arithmetic average and standard deviation are good.

In conclusion, customers must use RMs and other strategies to evaluate laboratories. The RMs must be suitable for use and customers must evaluate the certificate. The round-robin and statistical evaluation of the data is there to facilitate production of a normal population of results where obvious errors are not included. The certificate should quantify the homogeneity of the material and express realistic estimates of arithmetic means and inter-laboratory standard deviations. The laboratory standard deviation is the most important statistical parameter on the certificate as it allows one to make good judgement calls and build confidence for all players

For reference, the ISO guide 30 to 35 describes the best practice for the use and manufacture of references. For the tests mentioned previously, Shaun Burke's paper entitled 'Missing Values, Outliers, Robust Statistics and Nonparametric Methods' is excellent (LC.GC Europe online supplement). ◆

Zambian Branch gears itself for growth

After a spluttering start, the SAIMM's branch in Zambia should be officially up and running by the end of the first quarter of 2007, according to Prof. Stephen Simukanga, who was appointed last year by the president of the SAIMM to spearhead the drive to obtain official status for the branch.

The branch was informed in April last year but could not achieve official status under Zambian law until it was registered with the Registrar of Societies. Prof. Simukanga picked up the traces when the incumbent chairman left the country for Australia soon after taking up the position.

'With 29 members, our association is still disappointingly small, although the situation will change once the branch becomes fully operational,' Prof. Simukanga said. Branch activities would also increase, he said.

'We intend to work very closely with the Engineering Institution of Zambia which, as the registering authority for engineers wishing to practice in Zambia, is also a good source for SAIMM member's, he said.

Asked what activities and events the branch was planning for 2007, Prof. Simukanga said that a full executive would be appointed and installed once the registration process was completed. The branch planned to organize at least three workshops, one in Lusaka and two on the Copperbelt, during the year. Increasing membership was also a top priority, he said.

Promoting engineering as a career would be another of the branch's priorities.

'Under the Engineering Institute of Zambia, of which I am a Fellow and Registrar of the Engineer's Registration Board, we have instituted several programmes to promote engineering as a career among secondary school pupils. These include sponsoring prizes at the annual Junior Engineering, Technology and Sciences Fair (JETS), presenting career talks at schools, as well as offering two scholarships in engineering at Zambia's two universities.

'These are some of the ideas that we should adopt when the SAIMM branch becomes fully operational,' Prof. Simukanga said.

World demand for copper—notably from China and India—has resulted in a resurgence of interest in either existing mining operations or new ones on the Zambian Copperbelt and North Western Province. A number of new mines are either already in production or under construction. Some observers say that if all the projects in the pipeline come to fruition, the entire Copperbelt—the DRC included—could be producing over a million tons of copper by 2010, roughly four times what was being produced in the late 1990s when the copper price started to lift and new interest was focused on Zambia.

Prof. Simukanga believes that Zambia's share of this bounty will be in the region of 700 000 tons output a year. However, the revival of mining activity also has its problems—the shortage of manpower being a big issue in Zambia.

'There is a critical shortage of engineers in Zambia. We receive requests every day from the mines for graduate engineers, with the demand far outstripping supply. In the short-to-medium term, I believe the shortage will be overcome by the industry itself, although the mining houses are going to have to take a bigger interest by offering scholarships for students in engineering and related fields at Zambian university and colleges.

'The onset of privatization of Zambian mines has not helped matters, either. In most instances the new owners have resorted to importing specialists and graduates, understandably because they need them urgently. At the same time, they have shown little interest in helping to increase the number of graduates from our Zambian universities and technical colleges.

'Before privatization, the then ZCCM had a very good training programme both in colleges and on-the-job training. But after privatization, ZCCM stopped training and withdrew all scholarships, despite the fact that it had some shares in these new mining companies. This has not helped matters and it should have led by example by continuing to sponsor students. At the same time the new owners should have picked up from where the ZCCM left off by supporting training initiatives.

'In other words, the new owners under the government's privatization programme have been looking at this issue on a short-term basis, which is not good. Mine owners operating in Zambia need to assist in the training of our future engineers by providing scholarships or apprenticeships in the various engineering fields.

'By doing so, it will become cheaper in the long-term to use local Zambians to help run their mining operations. It will also make a big contribution towards alleviating the skills shortage in this country, while offering new employment opportunities for our Zambian youth. It is always better to have young engineers around who become very useful after five years at university and who are also cheaper to maintain than expatriates. The mining industry needs to get involved in the training of Zambians in engineering,' Prof. Simukanga said.

The attitude of some mining houses towards offering vocational training for students had been 'pathetic', he said.

'Fortunately, some mining companies, such as Lumwana Mining and First Quantum, are beginning to respond to the challenges and are sponsoring engineering students. This has been a welcome move and we urge all mining companies to follow this example as I believe that a company which has no training programmes in place is heading for trouble,' Prof. Simukanga said. ◆