# Importance and Method of using Reference Materials in measuring reliability of Analytical results and Why Customers should use them.

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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 1970's and recently due to increase in demand other manufactures have entered the South African Market.

This paper describes Analytical challenges from the customer's perspective. The customer being the metallurgist, mine geologist, environmental scientist and geologists from resource companies. Reference Materials and their appropriate use and good understanding of them can aid greatly in building confidence in the results, choosing the right Laboratory for a project, deciding which set of results are correct and providing evidence to the customer's clients that the results obtained are the very best possible.

Throughout the world there are hundreds of reference materials produced by over 80 organisations and these are mainly ores, rocks, semi processed ores, metals, and many more. Mintek is one of the top 10 producers with over 75 products. Many of these producers including Mintek and their respective standards organisations belong to the ISO REMCO committee and their respective work groups. This committee's main task is to draw up guide lines for the use, manufacturing and certifying reference materials. In South Africa a mirror committee has recently had its inaugural meeting the function is to give 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 SARM program has since the year 2000 increased its sale three fold, the question is why? There is more accountability needed in our world. That means Analytical results have to be the very best possible and risks associated to them must be well quantified. Consider that the risk of wrong results or wrong decisions made from a result is trivial to laboratory, in comparison to the laboratories customers. The consequence to a laboratory could be a loss of income or some one may lose their job. To the customer he may dig up 1000 of ton's of rock with nothing in it or worse still don't mine it when the grade is high enough. This is serious money. Wrong results can cause incorrect conclusions about the efficiencies of metallurgical processes and may lead to building of large in-efficient plant, this is money again. Wrong decisions

could be made about an environmental impact study. This is even more serious, this affects people. The bottom line is the results produced from an ICP – OES can detrimentally affect people, environment and money. How can the laboratory customer ensure that he chooses the most appropriate lab, decide between different sets of data and know that results are unbiased?

The customer must check the laboratories for precision accuracy and bias. This can do using many techniques namely: - (1) duplicate samples (twin streaming) (2) send samples to other labs (3) use reference materials as blind samples. The last option measures accuracy, bias and control of methods.
Every customer has had this scenario you send sample to lab a you get a result. You send another to lab B gets another result then you don't know which the right one is so you send a sample to lab C. 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 answer is to use a reference material, 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 the table below and 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 LSD 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 along side the other statistics.

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

LSD

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

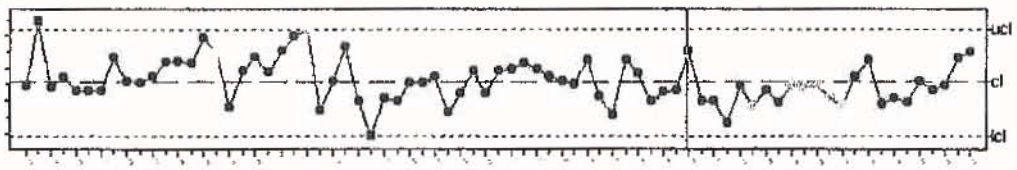
Later in this paper I will describe how LSD derived and also what should be on a certificate of analysis.
How do we choose a suitable lab for a project or ensure that our own primary lab is up to the game.
The answer of course is LSD, reference materials and of course other strategies' which are :- (1) proficiency testing (2) competency documents (3) validation reports (4) measurement uncertainties (5) visit them (6) others (7) accreditation. Every aspect of process from sample reception, preparation to reporting must be evaluated and documented.

Also at the end of an evaluation there should be service delivery agreement between the customer and the lab. This may be standard default one and for larger projects a more customer specific.

To do a RM performance study send them to the laboratories that you whish to evaluate preferable minimum of three each with plenty of sample for them to work with. When you get the results back you can use the LSD to calculate the Z - score, this 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 how far you are away from the centre.

| 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 |

During a run of long projected reference 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 to more advanced CUSUM plots. Also the bias from the repetitive runs of reference material can be calculated and acted upon.




The question now is how many RM one should use? My personal opinion this can be over done. 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 laboratories performance I would insert only one reference on every second batch if it is a new lab every batch. Also I would try to use two different references and alternate there insertion. Personally I would inform the laboratory manager that you are being checked and insertion of RM will be random in the batches and be marked similar to samples. Also it would be good etiquette to give feed back on there performance. This builds an atmosphere of cooperation and transparency.

There are lots of situation where suitable references materials are not available the simple answer here is get one made! Mintek makes RM for customers. This process could take between one and three months! When planning a project ensure that this is factored in. Ideally all possible RM should be available that is goal of the SARM program and other similar programs in the world.

Project based approach is used in making RM at Mintek this based on the ISO guides 30 to 35. Reference materials must be useful for their intended purposes, for example it is a waste of time manufacturing product where 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) less than 0.5% while the Platinum industry would need a LSD less than 5 % for measuring Pt in ore. From this the manufacturer must ensure that the homogeneity of the product fall into this requirement he must ensure that the uncertainty between units and inside the same unit are less than the LSD. To ensure this Homogeneity and overall uncertainty, certain experiments must be planned and the results reported and verified during the manufacturing process. Most importantly a description of this and the result must be on the certificate.

Method of assigning the certified value must also be described on the certificate and preferable with an 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 if a particular result should be in or out. Also customer must be sure that certified value is accurate the assigned uncertainty is realistic. These customers prefer to derive and compare there statistics to the reported statistics on the certificate. In my opinion this is good attitude to have for important projects which can have large impact on people money and the environment.

Modern practice in designing a round robin exercise is to pick a fewer labs but ensure that they produce "Quality Results" These labs invariably have accreditation and do participate in frequent proficiency testing programs, also contacting senior role players for recommendations helps. The short side of this is that 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 get involved in robust or non - parametric statistical methods. It is important to have realistic estimate of uncertainty rather than optimistically tight LSD. When choosing the labs try to have diversification namely some from another continent another from research institution and of course laboratories in that particular industry. Many of the industries have there own round robins and if you use only them 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 box and whisker plot should be employed. The data should be checked for outliers using Grubs and Chochran's test. Rejecting results should not be taken lightly and the tests should never be use more than once. Since this is an exercise to produce a certified value and not a "Proficiency Test" and if you suspect for example a participant may have made calculation error's then contact him. These kinds of errors show up clearly with 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 Reference materials and other strategies to evaluate laboratories. The RM 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 you to make good judgment 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 and for the tests mentioned previously the paper by Shaun Burke "Missing Values, Outliers, Robust Statistics & Non-parametric Methods" is excellent. (LC.GC Europe online supplement )