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*Reference Materials and their Applications*

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## **Introduction**

Reference Materials (RMs) cover a very wide range of materials from bovine liver to gas mixtures and metal alloys. In this Workshop I am going to concentrate on solid RMs that are used for quality control in analysis for metal, particularly those manufactured by Rocklabs Ltd.

## **What makes good RM?**

In many mine laboratories, there are two types of RM. One of these is the Certified Reference Material (CRM) as manufactured by CANMET. The other type is known as an in-house standard and this is often made up by the laboratory itself from the materials around the mine. A CANMET Representative will be taking part in this Workshop, so I will not discuss their CRMs in any detail. CANMET has many years of experience on how to make a good CRM. They have a large variety of materials available, but the cost of these is high for some types of analysis, particularly for assaying for precious metals, where up to 50 grams of material are required for each assay. Hence the need for an alternative at a lower cost.

The requirement for a good RM can be summarised as:

- 1) It must be homogeneous.
- 2) It must be chemically stable.
- 3) The Recommended Value must be known to high level of accuracy.
- 4) It must be similar in composition to the sample being analysed.
- 5) It must not be too expensive.

Let us look at each of these requirements in detail.

### **1) Homogeneity**

By far the most important requirement for any RM is that it is homogeneous at the level of the aliquot taken for the analysis. For example, if an RM is analysed for gold, by fire assay of a 50 gram sample, it may be homogeneous at the 50 gram sample size but not at the 1 gram or 0.1 gram size. A copper RM will have to be homogeneous at the 1 gram size or less. Hence it is vital to know how the RM will be used and how its Recommended Value was obtained. The latter should be shown on the Certificate.

How do we at Rocklabs ensure that our RMs are homogeneous? The first step is to know the material that the RM is made from. It is impossible to make a good RM from materials with very coarse mineral or metal particles. These will not be evenly distributed, in large numbers, to ensure that each aliquot contains the same weight of metal. This is particularly so for low level RMs.

Also, the RM must be packaged before homogeneity can be determined, because the packaging process may introduce some bias or inconsistency. You cannot just mix up some ground rock in a mixer and take out a few grab samples. The bulk material must be packaged into sachets, bottles, plastic bags, etc., and then these packages be sampled in a random way. Packages need to also be checked for homogeneity within the package, unless the whole package is used for one analysis.

Once the material is demonstrated to be homogeneous, then it can be analysed to determine its Recommended Value.

For many RMs, there is a possibility that it might settle in the container. More dense particles can move towards the bottom of the container, if the container is vibrated e.g. from vehicle traffic passing the laboratory. RM containers' labels may state "Shake the bottle before using" or "Mix the contents before using" or something similar. The problem with these instructions is that the mixing process is not well defined. Should the bottle just be shaken by hand for a few seconds or mixed on a bottle roll or a mixing wheel and if so, for how long? What does mix mean?

At Rocklabs we prefer to make RMs that do not need mixing. Every RM type is checked by vibrating a jar mechanically and analysing layers down through the jar to see if the assay result is higher as the sample goes down the jar. If it does, this material is rejected.

## **2) Chemical Stability**

It is fairly obvious that once an RM is packaged it must be chemically stable. Changes to the composition will alter the Recommended Value. For example, if the RM contains sulphide materials, these will oxidise in air. In the extreme, some sulphide ores will actually burn, if exposed in the air. If a sulphide is oxidised to a sulphate, the weight of the RM will increase so the true metal level will be lower than the original Recommended Value.

What can be done to minimise these effects? It is best not to purchase RMs and use them over a long period e.g. more than a year. If usage is low per day, it is better to buy RMs in sachets rather than larger containers. If an RM jar lid is left open, there is more chance of some change taking place.

To prevent chemical change, the packaging can be flushed with inert gas, e.g. nitrogen, and then sealed e.g. a sachet. But, this adds to costs. When we have RMs that contains sulphides, we keep the particle size as coarse as possible because particles oxidise faster than large particles. Tests of our sulphide type RMs have shown an average weight gain of less than 0.4% per annum in a closed jar.

When using an RM from a sachet, the whole contents can be used for one assay, so there is very little chance of the RM absorbing moisture, as long as the sachet is not punctured. For a jar, the lid may be left open while it is being used. This could be for days, weeks or even months so Rocklabs believes that RMs should not be made of materials that absorb water e.g. dried clays. With Rocklabs RMs you use them direct from the jar; they are not dried before weighing. We aim to use mineral components that contain less than 0.5% moisture at equilibrium and have a little variation in moisture content at varying temperatures and humidities.

## **3) Recommended Value**

The exact level of metal in an RM can never be known with absolute accuracy. There is always some uncertainty in the final figure, so it is important to know not both the Recommended Value and the confidence interval (CI) at the stated level of confidence (usually 95%). Note that the CI is a statistical property that expresses confidence in the Recommended Value and is not the range that a set of results from a laboratory should fall within.

There is always an argument whether it is best to use one very good laboratory to determine the Recommended Value or more than one laboratory. One method is to prepare the RM and use it for a Round Robin of a large number of laboratories, utilising any laboratory that wants to be included. The problem with this approach is that some of the laboratories may not be doing good assays and thus the calculated Recommended Value is influenced by that group of laboratories carrying out inferior work.

At Rocklabs we use up to 30 **selected** laboratories that are invited to participate in the consensus round. Each laboratory analyses the candidate Reference Material in duplicate. The laboratories we use and the results obtained are shown on our Certificates that can be viewed on our website at [www.rocklabs.com](http://www.rocklabs.com). Sadly, some very good laboratories have closed down in recent years so we are always seeking new, high quality laboratories to analyse our perspective RMs.

#### **4) Matrix Matching**

If it was feasible, it would be a good idea to use an RM that was very close in chemical composition to the samples being analysed. This is to ensure that the assay can get the correct result on that type of material. But, this simple idea has many possible drawbacks.

The type of material may be very difficult to make a good RM from, e.g. it contains easily oxidised sulphides.

If RM manufacturers like Rocklabs had to supply many different types, the quantities of each RM would be much smaller so the cost per gram would rise, possibly substantially.

How does the laboratory know what the composition of each sample is, so that a matching RM can be used?

The laboratory would have to stock a large quantity of RMs to cover all possibilities. No Accountant would like this!

We believe that an assay procedure should be tested on a wide range of materials, including CANEMT CRMs, so the procedures can be demonstrated to be a robust technique. Once this is proven, there is no need to be re-checking the procedure by using matrix matched RMs. The RM is checking for mistakes: e.g. is the balance weighing correctly?, has there been enough flux used?, are there dispenser correctly calibrated? etc ... etc...

One method of manufacturing RMs is to use solutions of metals to provide the metal content. This can be done accurately but will not be done by Rocklabs. If the metal is in a soluble form, it will be very easily taken up by acids for example. The RM may give the correct result but the accompanying samples may not be digested or fused correctly.

Another method of manufacturing RMs is to pulverise the material very finely, even down to a micron or less. Unfortunately having a super fine matrix does not guarantee that all the gold particles are equally fine. At Rocklabs, we first of all start with material that is known to contain finely divided gold and, as an added precaution, it is screened to 200 mesh (75µm). Thus the RM is similar in particle size to what a good laboratory will achieve in its routine sample preparation. The success of an RM should depend on the selection of the best materials, not just on pulverising the matrix finely in an attempt to achieve homogeneity for gold.

#### **5) Cost of RMs**

Because fire assaying for precious metals usually requires a 30 or 50 gram sample, if an RM is used to check every batch, the annual cost for the RMs can be very high. Hence the aim of reducing costs by making your own “in-house standards”. BUT if the quality of those materials is suspect, what is the point of using them for quality control when the results of those assays may have a high uncertainty? All too often, if the assay result of the “in-house standard” is not correct, the results of all that batch are not questioned, rather, excuses are made for the “in-house standard” e.g. “It is not very homogeneous”, “It must have settled”, “Its probably absorbed a lot of moisture”, “The operator must have made a mistake”. These and other similar excuses negate the whole purpose of using an RM. If you cannot depend on the RM being of the highest quality possible, there is no point in using it for quality control purposes, no matter how little it costs.

#### **Using a RM correctly**

If the assay result for an RM is not correct, the whole procedure must be checked IMMEDIATELY. Not a week later, a month later, when the report is written up, when there is time to get around to it. The whole purpose of quality control is to give a high level of confidence to all results. If the RM assay result is not correct, i.e. within acceptable error of the Recommended Value, the results for that whole batch of assays should be questioned. Each step in the procedure must be checked, to find out what has gone wrong. (Note that it is up to the laboratory to determine what their acceptable spread of result is. Some laboratories will set action limits at two and three times the standard deviation (RSD) on a good RM between four and six percent when the gold concentration is 1ppm or more. If your laboratory is getting a RSD of less than 4% on all routine analyses, then you are doing well!!)

Every few months we get a phone call from a Rocklabs' RM user telling us that our RM is not giving the correct result. "Is there possibly something wrong with RM X?". In every case, we have been able to assist the laboratory to find out what was going wrong. What is interesting to us is that many laboratories have assumed that the RM is the problem and have contacted before checking their procedure. We believe this is because their own in-house standards have not been very high, so the procedures are the problem not the RMs. But we welcome any request for help in finding out what problems are leading to poor results.

### **Tips for use of RMs**

1. Every batch of assays is a unique event so each batch should include at least one RM. It is not adequate quality control to just use one RM per day.
2. Keep a quality control chart on paper or by computer and plot the RM results immediately after they are calculated.
3. Use two or three RMs of different levels, to cover the range of assay results reported during a normal working day.
4. Add some "unknown RMs" regularly to check that Operators are not consciously or sub-consciously getting the results that they know they should be getting. This applies particularly to manually operated AA spectrometer.

### **New ways to use RMs**

#### **1. Rocklabs' Pandora Box**

A Pandora Box is a set of 96 sachets, 12 each of eight RMs with gold values between two end members that are close together. For example, the eight RMs could vary between 1.42ppm and 2.94ppm gold (Au). The sachets have a unique number, so the purchaser knows what values each RM sachet has, but there is no value on the sachet. All sachets contents look alike.

Pandora sachets can be submitted to laboratories by customers or by the Laboratory Manager. They are a good tool for auditing the assay procedure.

Because the assay results are all similar, there is very little likelihood that an operator could guess what the correct result could be for each sachet. Sachets can be assayed over several shifts, days, even weeks or months. A quality control chart can be constructed for sachets for each value.

Pandora's boxes are not defined on our website. Only small quantities of each box are made, so the cost per sachet is higher than for standard RMs.

#### **2. Rocklabs Scientific Salting**

This new idea is a way of checking the whole process of sample preparation and assay. Normal RM use checks only from the sample weighing onwards.

With “Scientific Salting” a weighed sachet of RM material is added to a sample of crushed blank rock that has been weighed. The expected assay result can be calculated. If a “low” value is required, a normal 53 gram sachet of a high value RM can be used. If a higher value is preferred, sachets with more than 52 grams can be supplied to order.

So what does “Scientific Salting” check for, apart from the assay procedures? If the sachet is sprinkled over the bottom half of the sample bag, there is a check on whether the person loading the sample into the oven tray empties the whole sample into the tray or possibly dumps some of the bottom part of the bag.

If the oven has a very strong airflow going through it, it is possible that fine particles can be blown out of drying trays. If this happens, the assay result will be low.

If the sample preparation machines have dust extraction installed e.g. in a crusher, it is vital that the airflow takes away only the dust particles that are floating in the air and are effectively lost from the sample. There must not be mis-directed airflow which draws fine particles from a falling stream of the sample. IF this occurs, the RM material will be partly removed so the assay result will be low.

“Scientific Salting” checks for bias in the preparation process and for poor quality work which could lead to erratic results on duplicate assays i.e. a high standard deviation.

### **Conclusions:**

By reducing the cost of RMs while maintaining high quality, new ways of using RMs will be developed.