Assuring the Reliability of Your Sampling Results

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Abstract

Sample analyses constitute one of the fundamental data types forming the basis of our professional work. But do the analytical results actually reflect what we think they do? Have the sampling, sample preparation, and analytical procedures been tested by a quality assurance/ quality control program that demonstrates the reliability and repeatability of the sampling results? Failure to include appropriate quality assurance/quality control procedures renders the sampling results at least suspect and potentially as totally unreliable. The inclusion of randomly selected, non-sequentially numbered duplicate samples is required at a minimum. The blind insertion of blank, standard reference, and/or control samples into the sample stream and re-analysis of sample rejects (pulps and other forms) are common steps of a quality assurance/quality control program. The analytical results of quality assurance/quality control are easily analyzed. The duplicate samples should yield the same result and standard samples should return the standard result within acceptable analytical limits. Just because a laboratory routinely runs its own quality assurance/quality control program does not demonstrate that your sample results are reliable (if it doesn't, don't use the lab). The use of independent analytical laboratories cannot in and of itself, ensure that a reliable sampling, preparation, and analytical process has occurred. You must test the process.

Introduction

The purpose of sampling is to obtain representative portions of a mineral deposit for a variety of purposes, particularly mineral content (quantity) and quality (chemistry). Additional properties such as geotechnical information, density, amenability to various types of processing, etc. can be collected from at least some types of samples. A wide variety of sample types (rock, soil, water, and air) are collected in the process of exploring for and delineating the details of a mineral deposit and determining the potential environmental impacts resulting from exploitation of the deposit.

This is not the place for a detailed discussion of the types of samples that can be collected (see for example Scott and Whateley, 1995). Rather the focus in this paper is on the procedures employed to ensure that the samples collected and the analytical results obtained from those samples provide reliable and repeatable data that can be used to model the deposit and estimate mineral resources and mineral reserves within acceptable degrees of assurance.[1] This is the function of quality assurance and quality control (QA/QC) programs. QA/QC programs should commence with the first samples taken at the beginning of exploration and continue throughout the life of the property, including the production or remediation stage, to assure that the sampling data continues to be reliable and repeatable. Failure to include appropriate QA/QC procedures renders the sampling results at least suspect and potentially as totally unreliable.

Quality assurance involves those steps taken to ensure that the sample collection, preparation, and analytical protocols are producing reliable, repeatable values. Quality control involves those steps taken to ensure that the established sample collection, preparation, and analytical protocols continue to provide reliable and repeatable results for as long as sampling continues. QA and QC are lumped together because the procedures used for one, say initial quality assurance, continue to be valid throughout the quality control portion of the sampling program.

Prior to the Bre-X fraud involving the Busang gold deposit in Indonesia that was uncovered in 1997, little formal attention was paid to QA/QC programs in the mining industry. For example, Peters, in his generally excellent *Exploration and Mining Geology*, 2nd ed. (1987, p. 479) covers the topic in two short paragraphs. Scott and Whateley (1995) provide an excellent summary discussion of various sampling and drilling methods and statistics for determining sample sizes, etc., but make no mention of QA/QC programs. Even Pitard's *Pierre Gy's Sampling Theory and Sampling Practice* (1993) does not really address QA/QC procedures of the type discussed here. Following the Bre-X fraud, more detailed attention has been paid to the subject, for example Bloom and Titaro (1997), Bloom (2000), Roden and Smith (2001), and Sinclair and Blackwell (2002, section 5.7). The facts of

1. While this paper is based on mining industry practice and thus uses terms like "deposit" and "mineral resources and mineral reserves" that are not used in the environmental field, the concepts are directly applicable to environmental work. A pollution plume can be considered a "deposit;" it has a location, X-Y-Z dimensions, and variable concentrations ("grades") within it, just like an ore body.

the *U.S. vs. Jeffus* case (2000), described below, suggest that little attention was paid to the subject in all too many environmental sampling programs.

Roden and Smith (2001) point out that,

> The key message that needs to be remembered in the area of field sampling is that errors introduced at this stage of the data generation process are, in most instances, the largest errors introduced into a program and that these errors cannot be rectified in the subsequent processing of the sample. Errors created in the field can only be rectified in the field.

Roden and Smith (2001) note that the two most common problems in field sampling are sample losses and poor sample splitting techniques. Losses depend on the sampling method involved, but can involve dust, extensive water flows during drilling, poor field handling of samples, and inadequate strength or seals on sample bags or containers. Losses of fines or "heavies" are the common result and will result in biased samples. Riffle splitters are the preferred type of splitter but they can be labor intensive. Grab sampling presents well-known problems, which can be reduced by combining several grabs that incorporate all relevant areas. Eyde and Eyde (1985) address sampling problems for industrial minerals, which include identifying the presence and impacts of even small amounts of contaminants and the need to preserve the character of the in-situ deposit when sampling clays.

Implementing a QA/QC Program

Implementing a QA/QC program is neither difficult nor does one add significantly to the sampling program's cost. The precise nature of the QA/QC program will depend on the type and purpose of the sampling program. Roden and Smith (2001) and, particularly, Bloom (2000) set out several mechanisms that can be used to monitor sample data. They include:

- routine insertion of unprepared, barren (blank) samples;
- routine submission of duplicate field samples;
- resubmission of 5 to 10% of sample preparation duplicates (sample pulps);
- insertion of control samples;
- insertion of reference (standard) samples;
- randomization of sample numbers prior to submission to the laboratory;
- comparison of multi-element trends for elements determined by different laboratory procedures;
- comparison of the results for the same element determined by different methods; and
- analysis of 5 to 10% of the sample pulps at an umpire assay or analytical lab.

Some definitions are in order.

Blank sample is material that is similar to the mineralized field samples and contains no or negligible amounts of the minerals or elements of interest. They are submitted to check on sample preparation procedures as well as the analytical procedures. If the mineral or element of interest is reported in the analysis, attention must then be directed at why the anomalous result occurred; it could come from any step in the process or from mislabeling of the samples during the process. If anomalous results in a blank sample occur when processed after a high-grade sample, cross sample contamination during sample preparation may be occurring. Regardless of the source of the error, a problem within the sampling and analytical procedures has been identified and its source can be identified and corrected through additional testing. This is particularly true when blank samples routinely have anomalous results. Bloom (2000) recommends that a blank be inserted every 20 to 50 samples.

Duplicate Field samples are collected at the same time, from the same place, and in the same manner as the other field samples. Duplicate field samples, and other types of duplicate samples (e.g., resubmitted sample pulps), provide information on the repeatability of the sampling and analytical procedures. The analytical results from duplicate samples should be within accepted analytical limits. If they are not, this may indicate a problem with the collection, preparation, and/or analytical procedures, or they may indicate that there is a significant nugget effect in the deposit. Bloom (2000) recommends that the numbers for duplicate samples should be at least 20 numbers apart so that the duplicate samples are analyzed

in different batches in the lab. As with blank samples, the number of duplicate samples required varies with the confidence in the sampling and analytical processes. Early in a project, a higher percentage is needed, say 20%. Once the reliability of sampling and analytical processes has been established, the number of duplicates can drop to 1 in every 20 to 50 samples.

Nugget effect: the nugget effect results from inhomogeneities within the sample and is common in and was first named in studies of gold deposits. A gold nugget or other large particle may represent the total gold content of a large volume, for example a cubic meter. But being a single particle, it will only be present in one sample of that volume even though duplicate samples from that volume were collected. While gold nuggets provide dramatic examples of the nugget effect (although less of an effect than gem-quality diamonds in a diamond deposit), nugget effect sampling bias can occur in a variety of deposits. Where a nugget effect is known or suspected, alternative sampling methods, and perhaps analytical methods, must be employed in order to obtain the repeatable analytical results required for mineral resource and reserve estimation.

Randomized sample numbers are a means of shipping samples to the preparation and/or analytical steps in a different sequence than the samples were collected. Randomization allows for identification of drift or bias in the sampling results. The drawback of randomization is the increased potential for introducing transcription errors and some increased handling procedures. Randomization is also best performed in large sample lots. The field data sheets for recording the information on each sample should include a column for the laboratory number corresponding to the field sample number. This is particularly needed when using randomization of sample numbers.

Reference or Standard samples are samples with known quantities of the elements or minerals of interest. Reference or standard samples have been carefully prepared in large, thoroughly homogenized batches and the analytically repeatability and analytical error limits have been determined by repeated analysis performed by a number of laboratories. They are available from a variety of sources including geological surveys and other independent groups.

Control samples are similar to reference or standard samples in that they are homogenized samples with known quantities of the minerals or elements of interest as determined by repeated analyses by several laboratories, but they have been prepared internally to the company or project. Bloom and Titaro (1997) recommended inserting a control sample in every 20-field sample group.

The particular QA/QC program adopted will depend on a number of factors including:

- whether a particular protocol is required for the type of sampling being conducted; this is particularly true for some types of environmental sampling;
- deposit delineation stage (preliminary exploration, advanced exploration, production);
- type of minerals occurring in the deposit and their abundance (precious and base metals versus coal versus an industrial mineral);
- whether a significant nugget effect exists (large variance between samples taken at the same location);
- the degree to which contamination between successive samples is likely to occur and materially affect the analytical results—this successive sample contamination can occur at the collection stage, e.g. successive composites lengths in a rotary drill hole (particularly a problem with rotary drilling in gold deposits located below the water table), or during the sample preparation process; and
- the ability to submit duplicate, blank, and reference (standard and/or control) samples in a form that conceals their identity during the sample preparation and analysis steps that follow the submission of the duplicate, blank, and reference samples; difficulties include:
  - duplicate samples may not be available in cases where whole cores are submitted as part of the routine sampling program; and
  - reference (standard and/or control) samples are already in pulp (finely ground) form to ensure the homogenization required to create useful reference standards and when the color of the reference sample may not be close to the pulps of the field samples.

An important requirement of any QA/QC program is the regular monitoring of the results. X-Y correlation plots are a common and easily prepared check, although flagging of significant variances in spreadsheets is another means of checking results. While anomalous values may indicate that a problem has cropped up, investigation of the source of the problem may isolate it to a particular sample. Was a piece of core submitted as a blank sample taken from an interval sufficiently close to the ore zone that a stray anomalous value was indeed present? Was there a transcription error in sample numbering? Anomalies should not be ignored, they should be explained. Repeated anomalous values provide the justification for detailed testing of the procedures in order to identify and correct the problem producing the anomalous results.[2]

Once the anomalous results have been resolved, Roden and Smith (2001) point out that the precision of the sampling program is easily determined from the duplicate samples; it is the Mean Percent Difference (MPD) approach, which is calculated by:

$$MPD = (\Sigma\ (\text{absolute}\ (x_1 - x_2) / ((x_1 + x_2))/2) \times 100))/n$$

where x_1 and x_2 are duplicates of the same sample and n is the number of sample pairs.[3] The individual MPD results

2. One reviewer of this paper provided the following example of an anomalous sample analysis. "Years ago I was involved in water resources and sediment quality sampling and analysis. We triplicate grabbed sediment with ponar samplers. At one site, two of the samples read BDL for Chlordane. The third sample analysis was sky high. Repeated sampling resulted in a wide range of values, and the media had a field day. I had eight of years of data in this particular stream—all good and consistent, both upstream and downstream from this particular bridge. I started talking with the neighbors and one told me about a person that had a backyard nursery and who often dumped stuff into the stream. Aha. Turned out the person had dumped an old bag of powdered Chlordane The point is that someone must maintain the sampling history, values, COC, etc."
3. The "× 100" term can be deleted from spreadsheet columns formatted for percent.

are then averaged over the range of similar samples, which provides the expected variability in analytical value for any similar sample in the database. Roden and Smith (2001, p. 76) state, "Statistical analysis of this MPD measurement has shown it to be an extremely robust measure that closely approximates the relative standard deviation. Doubling this number will therefore provide a 95 per cent confidence interval around the assay value.'

Figure 1 shows a correlation plot of 445 duplicate sample pairs. The R^2 correlation coefficient for these pairs is 0.9685 and the MPD is 16.2%. When one of the duplicate pairs reports 0.0 grade units (ppm in this case) and the other reports some detectable quantity, the mean percent difference between the two samples can be large. By eliminating those pairs reporting less than 1 ppm (well below the cut-off grade) in this example, the MPD of the remaining 379 sample pairs dropped to 6.8%.[4] These sample pairs were collected from a "nuggety" deposit and so some variance in duplicate analyses is expected.

The overall QA/QC program should include the use of different laboratories in order to test the accuracy and repeatability of the analytical results. Look carefully at detection limits (DL) and the analytical procedures that are available from a particular laboratory. What analytical procedures and detection limits do you require and what can a particular laboratory provide. For example, many labs claim to be able to test for platinum group metals (PGMs) but testing has shown that very few labs can accurately analyze for PGMs (U.S. Bureau of Land Management, 2002; Whyte, 2000). In 2000, thirteen people associated with Intertek Testing Services Environmental Laboratories, Inc. of Richardson, Texas were indicted for failure to comply with standard and accepted laboratory procedures designed to prevent cross sample contamination and to ensure accurate results. The indictment charged that the soil, water, and air samples submitted came from more than 59,000 separate projects and involved as many as 250,000 separate analyses (*U.S. v. Jeffus*, 2000).[5] These examples demonstrate that not only must one use reputable laboratories known to be able to provide reliable results for the types of analyses being run, but that these results must be independently checked and verified as a part of a thorough QA/QC program. Bloom and Titaro (1997) recommended that one in every 10 sample pulps should be sent to a second lab for reanalysis.[6]

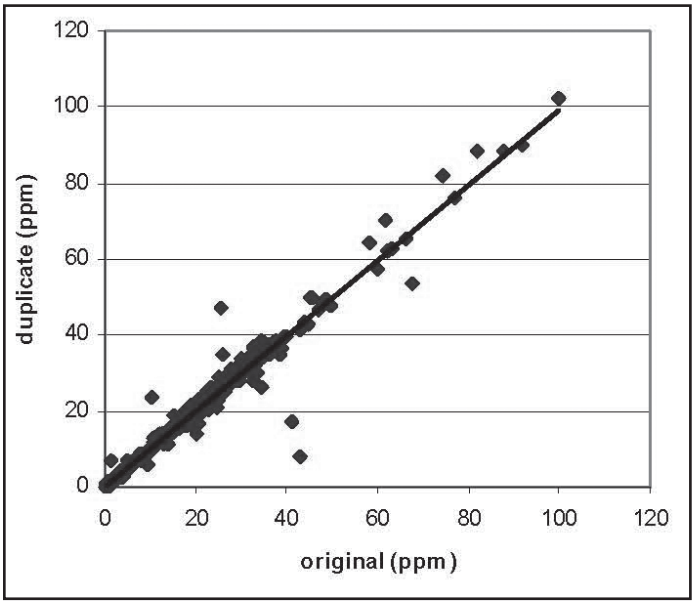

Figure 1. Correlation plot of duplicate sample pairs.

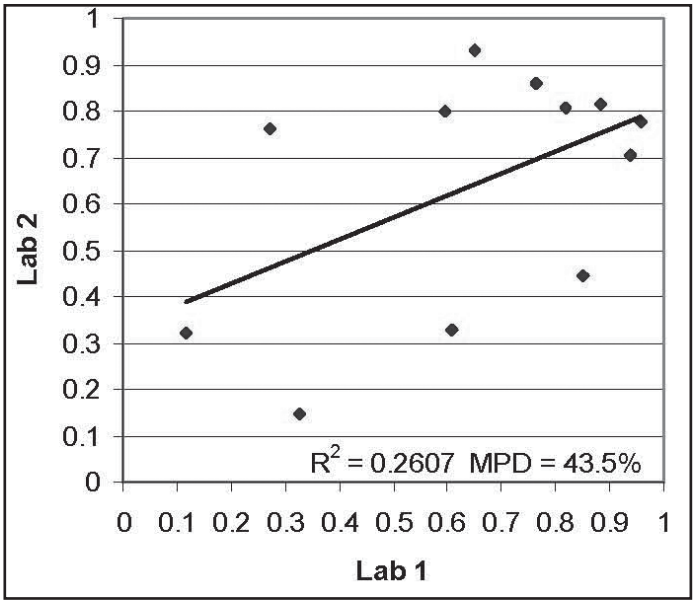

Figure 2. Correlation plot of 12 sample pairs analyzed by different laboratories.

Figure 2 is a correlation plot illustrating a problematic sample analysis example of 12 pairs of analyses from two different laboratories. The R^2 correlation coefficient for these pairs is 0.2607 and the MPD is 43.5%. Clearly, the correlation between these 12 sample pairs is very poor.

While in this case there was reason to believe that neither laboratory was capable of accurately analyzing for the elements compared in Figure 2, similar comparisons of duplicate analyses from two laboratories indicate that at least one of the laboratories is providing unreliable analytical results.

Bloom and Titaro (1997) describe some of the difficulties encountered in finding good analytical laboratories outside Australia and North America. The difficulties encountered included lack of

4. Because only the lower limit sample pairs are eliminated, the R^2 value is little affected by elimination of these sample pairs. For these lower limit sample pairs, the difference between sample pairs on a percentage basis is much higher than the difference between the sample pairs on an absolute basis.
5. Following a trial that concluded in November 2001, 8 of the 13 defendants were acquitted of the charges against them. Five others pleaded guilty prior to the trial. The not-guilty verdicts were reached in part because the sample log-in and other procedures were so lax that the government was unable to prove who was operating which piece of analytical equipment when (Abbott, 2002).
6. I don't know but suspect that the problems at Intertek were identified by those who actually followed a QA/QC program that included duplicate, blank, and standard reference samples and who also sent duplicate samples to other laboratories.

infrastructure, poor communications, bureaucracy, outdated lab equipment with high detection limits, poor lab practices, limited lab capacity, lack of ready access to high quality consumables, lack of computers that lead to transcription errors, and political risks. This does not mean that foreign laboratories are always inferior. Some may be excellent. Likewise, not all Australian or North American laboratories are reliable.[7] This is why you check results from one lab with the results of duplicate samples sent to different laboratories.

Bloom and Titaro (1997) estimated that a QA/QC program would add about 15% to direct assay costs and 1% to overall exploration program costs. The value received from this extra expenditure is assurance that the analytical results from the sampling, on which all mineral resource and reserve estimates depend, are reliable.

Other Sampling Program Issues

When reviewing a sampling program, the following questions should be asked.

- Who did the work and were the proper procedures followed?[8]
- Was there an unbroken "chain of custody"?
- How were the samples taken? Were they:
  - chip samples,
  - channel samples,
  - core samples,
  - drill cuttings, or
  - some other type?
- How was the location of the samples determined? If a GPS receiver was used, which reference map datum (geoid) was used and what are the distance errors in location? This information should be part of the data recorded on the sample data sheets.[9]
- Drilling:
  - Were drill holes surveyed (both the location of the top of the hole and downhole surveys that determine hole deviation)?
  - Was the drill hole spacing adequate? How was this determined? Has the spacing been checked?
- How and where were the assays or other analyses and tests done?
- Why were the analytical methods and tests run selected?
- Did the laboratory perform and report on its internal quality assurance/quality control program?

The appropriate answers to these and other questions will depend on the type of deposit being examined and the purpose for which the samples were taken. Reconnaissance geochemical samples may not need to be as carefully located or analyzed to the same precision as later deposit delineation samples. Rowe and Hite (1984) describe the sampling and drilling done to delineate the Crandon, Wisconsin volcanogenic massive sulfide deposit. They note that the global resource estimate did not significantly change after 40 holes were drilled. But, they note, the additional drilling done (over 180 holes) considerably improved the confidence in the knowledge of the deposit's continuity, distribution, and variability. The appropriate analyses and tests for an industrial mineral deposit vary widely depending on the industrial mineral being examined and the potential market(s) for that mineral (Eyde and Eyde, 1985). Regardless of the purpose of the sampling program, a QA/QC procedure should be part of the sampling program in order to ensure that the results obtained are indeed reliable. In those cases where the initial results are determined not to be reliable, the reasons for the lack of reliability can be examined and different sampling, sample preparation, and analytical procedures can be adopted that avoid the problems encountered with the initial program.

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7. This is particularly true for assays of platinum-group metals (PGMs), which very few labs perform accurately. Many labs in the southwestern US assay for PGMs but don't do so accurately (U.S. Bureau of Land Management, 2002).
8. A reviewer noted that in the water resources field, field samplers have to go through training / certification programs, *e.g.*, the USGS Water Resources Water Quality Sampling Training Program. Without that sampling certification, data may not be admissible in litigation cases.
9. The map datum is based on a mathematical geoid model approximating the true oblate spheroid shape of the Earth. Different map datum geoid models are used for different maps. Some one wishing to relocate your sample point needs to be using the same map datum (geoid model) you used when determining the sample's location. Common map datum geoid models include the North American Datum 1927 (NAD 27), the North American Datum 1983 (NAD 83), and the World Geodetic System 1984 (WGS 84). Even State Plane Coordinate (SPC grid) and the Universal Transverse Mercator (UTM) grid depend on a reference geoid model.

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