UNREALISTIC EXPECTATIONS OF ASSAY RESULTS

The integrity of a resource database is pivotal to a company's success in securing debt or equity finance for a new mining project. The quality of data and thus the validity of the database can only be guaranteed when appropriate sampling and assaying protocols have been implemented. No amount of mathematical sophistry can replace them.

This paper examines the key sampling, analytical and quality assurance factors impacting on project success and how a project manager should set about establishing an analytical protocol in liaison with a commercial laboratory. What can really be expected from assay data? Laboratories are not perfect, mistakes can happen we are all human, even geologists make mistakes. It is the duty of both the chemist and geologist to minimise mistakes, and ensure that assay data is fit for purpose. An analytical performance specification should be clearly defined in contract documents ensuring laboratories deliver technically sound and legally defensible assay results. It is irresponsible to assay samples using a "cheap and nasty" geochemical technique if the project involves resource estimation.

It is assumed that the project manager has done his homework and minimised the potentially greatest source of error, field sampling. Field sampling errors can only be minimised by developing and thoroughly testing a sampling protocol that defines minimum subsample size for the sampling regime (particle size and sample recovery), and clearly describes an efficient subsampling protocol. Naturally, this is in addition to diligence by explorers at the sampling site.

Establishing an Analytical Protocol
When a project manager approaches a contract laboratory with a schedule of work he will be armed with information about the elements of interest. In consultation with the client an analytical scheme needs to be developed. Without a protocol that considers all the following items explorers may find that analytical data produced by the laboratory does not measure up to expectations when results are critically evaluated.

Specification of samples
- Sample type,
- Sample treatment e.g. drying temperatures or sieving,
- Size of sample to be processed,
- Crushing - jawcrush, Boyd crush, hammermill or coarse disc grinding,
- Splitting - Jones riffle or rotary splitter or cone and quarter, and
- Pulverisation - Keegor mill or ring grinder - quality control check for sizing.

Analytical Scheme
- Dissolution procedure – partial leach, selective leach techniques, Mobile Metal Ion, "total acid digest", ore grade digestion, fusion,
- Analyte detection – gravimetric, atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), hydride generation for As, Sb, Se, Te etc, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA), classical chemical analysis,
- Detection limit and precision requirements, and
- Controls – replicates, splits, certified reference materials (CRM's), frequency of use, control data used to demonstrate statistical control i.e. control chart.

Tender Process and Contractual Requirements
- Specification of samples and analytical scheme - analytical quality and price compromise,
- Sample turnaround,
- Analytical performance specification defined, and
- Penalty clauses for non-compliance.

Review
- Laboratory audit by client,
- Statistical review – Quality Control Report to client – turnaround performance, standard performance, blank performance, replicate and split performance, and
- Statistical review by client.

Although geologists work closely with commercial laboratories, there still exists a lack of understanding and appreciation between the two disciplines. The establishment and maintenance of good lines of communication between the project manager and the laboratory manager is essential for success of both exploration and resource evaluation projects. Good communication and a sound working relationship with the contract laboratory can result in project savings. The stages of establishing an analytical protocol are examined.

Sample Preparation

Exploration usually involves various stages, e.g. grassroots exploration, reconnaissance, detailed follow up, anomaly delineation and target definition, resource estimation and reserve calculation. Good sample preparation practice at all of these stages is essential to obtaining meaningful and reliable analytical data. An accurate assay is of limited value if the sample preparation has not been carried out to the same standard.

Taking gold as an example, over the past decade, sample preparation techniques have improved significantly. Principles of sampling theory developed by Pierre Gy (1979) have been used by the mining industry to calculate the minimum mass required to obtain a representative sample, this is defined by:

$$\mathbf{M} = \frac{\mathbf{kd^{\alpha}}}{\mathbf{S^2_{FE}}}$$

Where:
M is the sample mass (g)
S^2_{FE} is the Fundamental Sampling Error expressed as a relative variance
d is the diameter of the largest particle in the sample (cm)
α is an exponent characterising the deposit of interest
k is a sampling constant and is defined by

$$\mathbf{k = c \, f \, g \, d_L^{\,3-\alpha}}$$

Where:
c is the composition factor
f is the shape factor of particles or fragments
g is the particle size distribution factor
d_L is a function of the particle size and the liberation size

The normal preparation practice for gold assays today involves total pulping of up to 3.5kg to a nominal particle (90% passing 75μm), with a grab sample of approximately 200g taken for analysis and the remainder of the pulp transferred to a bulk reject bag. If historical sample preparation techniques are examined to determine likely total sampling errors using sampling nomograms, today's practices are considerably closer to Gy's guidelines. Explorationists' demands for accurate and precise assays at lower and lower detection limits have increased with interest in lower grade deposits. The level of gold in the sample dictates the type of preparation and the assay sample size required.

Using Gy's formula and assuming a 90% confidence level and a 15% relative error, the minimum mass of a sub-sample can be calculated, Table 1.

Table 1. Minimum mass required using Gy's formula, assuming 90% confidence level and a 15% relative error, Analabs (1992).

Particle Size (mm)	REQUIRED SAMPLE SIZE Au g/tonne				
	0.01	0.10	1.00	10.0	30.0
50.0	1.43Mt	143kt	14.3kt	1.43kt	477t
10.0	11.4kt	1.14kt	114t	11.4t	3.81t
5.00	1.43kt	143t	14.3t	1.43t	477kg
1.00	11.43t	1.14t	114kg	11.4kg	3.81kg
0.50	1.43t	143kg	14.3kg	1.43kg	477g
0.10	11.4kg	1.14kg	114g	11.4g	3.81g
0.05	1.43kg	143g	14.3g	1.43g	0.48g
0.01	11.4g	1.14g	0.11g	0.01g	3.81mg

If samples are not prepared as outlined above with total pulping of the sample presented to the laboratory, that is samples are subsampled at different size fractions, then homogeneity checks need to be undertaken at each subsampling step. Although multiple subsampling steps in sample preparation is no longer considered best practice, exploration in some developing countries still relies on this protocol. Regardless of the sample preparation protocol used, particle size testing should be carried out at each stage of comminution. Wet sieving to check pulverisation, should be a part of a laboratory's quality assurance program. It should also be an integral part of an explorer's quality assurance program. The results of the laboratory's wet sieving quality assurance program should be part of the reporting process.

A major problem for any geochemical laboratory is sample contamination from preceding samples, caused by carryover during the crushing and pulverising stages. Laboratories use barren flushes during the pulverising stage, e.g. barren feldspar, usually between batches and jobs, to reduce carryover. Blank or barren samples i.e. expected low grade, should be submitted by the explorer to quantify contamination between samples during sample preparation or assaying. Other potential sources of contamination include airborne dust, tramp metal, jewellery worn by sample preparation staff and metal contamination from crushers and pulverisers. Laboratories normally use vacuum systems as the primary tool for cleaning sample preparation equipment this minimises the use of compressed air thus reducing airborne dust. The composition of the pulveriser head (bowl and rings or puck) needs to be taken into account when trace element analysis is undertaken, to minimise contamination of analytes. Specialist materials are available; these include carbon steel, tungsten carbide, alumina and zirconia. To avoid contamination explorers should not prepare exploration samples at mine site laboratories. When samples are analysed at commercial laboratories, project managers should ensure that separate preparation facilities are available for exploration and grade control samples, this is particularly relevant for regional laboratories.

It should now be clear that the sample preparation step is pivotal in obtaining good assay results. No matter how much care is taken and sophisticated instrumentation used in the next analytical stages, if the sample preparation protocol is flawed then assay results will not live up to the explorer's expectations.

Analytical Scheme
Exploration and mining involves a number of distinct stages; the reconnaissance exploration, detailed follow-up, anomaly delineation and target definition, resource estimation and reserve calculation, and the final stages of process/grade control at mine development and operation. Analytical requirements at each of these stages should be considered independently because requirements differ.

Analytical results are judged on their accuracy, precision and bias, so these terms should be clearly defined, Taylor (1987):
Accuracy: The degree of agreement of a measured value with the true or expected value of the quantity of concern.
Accuracy will depend on both random and non-random (systematic) errors.

Precision: The degree of mutual agreement characteristic of independent measurements as a result of repeated application of the process under specified considerations. Precision is a measure of random errors alone.

Bias: A systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system. Temperature effects and extraction inefficiencies are examples of the first kind. Blanks, contamination, mechanical, mechanical losses, and calibration errors are examples of the latter kinds. Bias may be both positive and negative, and several kinds can exist concurrently so that net bias is all that can be evaluated, except under special conditions.

The terms accurate, inaccurate, precise and imprecise are relative to the end use of the analytical data.

Gold Analysis:
The three main methods used in laboratories for gold analysis are:
- Fire assay with a gravimetric, AAS finish or ICP-MS
- Aqua regia digestion with a DIBK extraction and an AAS finish
- Cyanide extraction (BLEG)

Each of these methods is examined in turn.

Fire assay
The fire assay technique is a small-scale pyrometallurgical process, and is one of the oldest analytical techniques still in use. Unfortunately the traditional skilled fire assayer has disappeared and has been replaced by furnace hands trained "on the job". Despite the high volumes, margins are small, and commercial laboratories can simply not afford such skilled staff. A fire assay determination is about 40% cheaper than it was 10 years ago. No longer does the fire assayer decide on an appropriate flux composition for samples but rather uses a proprietary flux mix, which will successfully fuse most samples. Generally commercial laboratories are using a five pot pour system and rely on furnace hands to take note of the consistency of each "pour", and alert supervisors to problems of "shotting", viscous pours or incomplete fusion. Most samples can be successfully fused although some may require changes in the flux proportions or in sample size. The second stage of the fire assay process is the cupellation stage where the noble metals are separated from the lead. Again problems can be experienced in the cupellation process; high levels of copper, nickel, antimony, arsenic, bismuth, tellurium and selenium can lead to cupellation failure. If the laboratory is aware of the sample composition through consultation with the client, steps can be taken to reduce or eliminate the problems. Laboratories rely heavily on quality control samples to demonstrate the integrity of sample batches.

The fire assay method is the most reliable routinely available analytical technique for gold and is therefore favoured by most mining companies for resource evaluation. But problems arise for the fire assay technique when samples exhibit a "nugget" effect. This nugget effect occurs because some gold mineralisation can occur as coarse grains and furthermore gold is often found as the free metal. During the sample pulverising step any coarse-grained gold is normally flattened and not comminuted because of the ductile nature of the metal. In commercial laboratories the sample charge for a fire assay is normally limited to about 50g, in this case reproducibility will be severely affected and results of limited value. The screen fire assay provides a method for overcoming the problems associated with irregularities in the gold mineralisation. A weighed 1kg of sample is screened through a nominated mesh size and information is reported on the size fraction distribution, the coarse and fine fraction gold content and the total gold content. Since the technique is expensive as it requires three gold assays, one on the course fraction and duplicate analysis on the fine fraction, it is usually only used in the later stages of exploration but it is extremely important to recognise coarse grain mineralisation at the regional exploration stage.

Typical detection limits for fire assay techniques:

Lead collection, gravimetric finish	3ppm
Lead collection, flame AAS detection	0.01ppm
Lead collection, DIBK extraction, flame AAS detection	0.001ppm
Lead collection, graphite furnace AAS detection/ICP-MS detection	0.001ppm

Precision of the method:
10% with a 95% confidence at concentrations greater then 50 times the detection limit

Aqua regia leach assay

The aqua regia digestion is a partial leach and is most applicable to the analysis of reconnaissance exploration samples, that is prepared or pre-sieved soil, drill or stream sediment material. This digestion suffers problems if samples contain significant quantities of sulfide, carbonate or organic carbon. The extent of leaching depends on the sample weight and the particle size, the content of reductants, the solvent volume, the exact nature of the dissolution procedure and the mode of occurrence of the gold. The success of this dissolution procedure relies on the diligence of the laboratory staff to recognise samples rich in sulfides, carbonaceous substances, carbon or iron oxide rich samples, as each requires a different pre-treatment. Naturally communication with the laboratory can ensure that the correct pre-treatment is undertaken. Incomplete removal of reductants decreases the recovery of gold, as does very fine gold trapped in quartz or other mineral resistant to aqua regia digest. Aqua regia results have been compared to fire assay results over the years and the amount of gold leached usually exceeds 90% of the total content, Sulcek and Povondra (1989).

Typical detection limits for aqua regia techniques:

25g, DIBK extraction, flame AAS detection	0.02ppm
50g, DIBK extraction, flame AAS detection	0.01ppm
25g, DIBK extraction, graphite furnace AAS detection	0.001ppm
50g, DIBK extraction, flame AAS detection	0.001ppm
25-100g, DIBK extraction, Zeeman graphite furnace AAS detection	0.0001ppm

Precision of the method:
15% with a 95% confidence at concentrations greater than 50 times the detection limit

Cyanide leach assaying

Bulk leach extractable gold (BLEG) is a partial leach method utilising a cold cyanide extraction and is applicable to large samples i.e. 0.5-10kg. The technique was developed as a grassroots exploration tool and is ideally suited to regional-scale stream and soil surveys. Commercial laboratories using many variations, these include:

- Sample weight – from 0.5 to 10kg
- Concentration of the cyanide liquor – normally 0.1 - 0.2% w/v
- Period of extraction – 12 to 48 hours
- Type of agitation – bottle roll, tumble or static (no agitation)
- Use of accelerated cyanide extraction e.g. LeachWELL™ 60X catalyst
- Preconcentration techniques
  - Activated carbon satchels
  - DIBK extraction
- Analytical detection
  - Flame AAS
  - ICP-AES
  - Graphite furnace AAS
  - ICP-MS
  - INAA
- Detection limits vary from 0.0002 to 1ppb depending on the sample weight, preconcentration and analytical detection

The degree of gold extraction will depend on:

- Period of extraction
- Type of agitation
- Sample matrix – presence of carbonaceous or cyanide consuming minerals – pyrrhotite, pyrite, malachite, azurite and arsenic and antimony minerals
- Form of the gold – colloidal, free gold, adsorbed on clays,
- Accessibility of the gold to the cyanide leachate

LeachWELL™ 60X catalyst is used to accelerate the rate of dissolution of gold, silver and copper in 5% cyanide leaches. This accelerated leach is usually faster than fire assay and reports gold levels that would be extracted

in commercial gold CIL or CIP treatment plants. This accelerated cyanide extraction is only partial and mirrors plant performance so is not suitable when a total gold content is required.

Because of the sensitivity of the BLEG technique, sample contamination due to gold jewellery is an issue both in the laboratory and in the field during sample collection. Personnel handling samples both in the field and the laboratory should not wear any gold jewellery.

Multi-element Analysis:
A trend over the last decade is for lower detection limits on important indicator elements including the target element. Similarly, for partial extraction systems used on exploration samples, analytical techniques are required to discriminate between subtle analyte concentration related to ore deposits and the background. Increasingly ICP-MS and GFAAS techniques are used by commercial laboratories to analyse these ore and pathfinder elements, with detection limits usually several orders of magnitude lower than either flame AAS or ICP-AES.

Dissolution procedures
Dissolution in acids is the most common method of sample decomposition and can provide a solution suited for introduction into AAS, ICP-AES or ICP-MS. Hot acids used singly or in combination provide partial digestion of geochemical samples with the extent of dissolution dependent on the sample mineralogy and acid combinations. Acid dissolution techniques used by commercial laboratories can be divided into two categories; geochemical trace and ore grade analysis.

Geochemical trace element dissolutions are normally carried out in glass or Teflon® test tubes on relatively small sample weights and are made to volume in the test tubes with a dispenser, assuming a standard acid loss. Precision is typically 15% when analyte concentrations are 100 times detection limit, while accuracy will depend on the analyte and the sample matrix.

Ore grade analysis dissolutions are normally carried out in either glass or Teflon® beakers and digests are made to volume in volumetric flasks. Precision is typically 10% when analyte concentrations are 50-100 times detection limit, while accuracy will depend on the analyte and the sample matrix.

Perchloric Acid: A powerful oxidising and dehydrating agent which solubilises metals as perchlorates leaving silicates largely undissolved. Perchlorates are readily water soluble except for potassium, rubidium or caesium. Iron and manganese may be incompletely extracted while lead, zinc and silver may be low if high concentrations of barium or manganese are present in the sample matrix. Chromium values may be low due to incomplete dissolution of chromite or loss of chromium as volatile chromyl chloride.

Hydrofluoric acid / nitric acid / perchloric acid / hydrochloric acid: This dissolution is sometimes referred to as a "total" dissolution but is in fact still only a partial dissolution although it provides a near complete dissolution of silicate minerals. As with all digests the host mineralogy dictates the extent of dissolution, and this may be incomplete for minerals that are difficult to dissolve even in this acid combination; zircon, topaz, rutile, all polymorphous modifications of Al_2SiO_5, tourmaline, staurolite, cassiterite, chromite and baryte etc. Losses of some analytes during the decomposition have also been reported, these include; arsenic, antimony, selenium, boron and silicon. Precipitation or occlusion of analytes can also lead to low assay results.

Fusion: Whole rock analysis by alkaline fusion, usually lithium metaborate or lithium tetraborate, provides a solution that can be used to determine major, minor and trace elements by ICP-AES and ICP-MS. Fusions are normally used for the dissolution of refractory and acid insoluble minerals. The high flux to sample ratio of a fusion means that detection limits are usually higher than acid dissolution. Accuracy and precision are good but can depend on sample matrix.

Atomic Absorption Spectrometry (AAS)
Flame AAS is one of the most commonly used instrumental techniques in the mining and mineral exploration industry, especially in regional laboratories. Like routine ICP-AES and ICP-MS, the success of this technique relies on the sample digestion stage. AAS is a sequential technique and even with the introduction of "fast" sequential analysis is still best suited to the analysis of small suites of elements, up to eight. ICP techniques are better suited to the multi-element suites. This technique is relatively free from spectral interference but some elements suffer from chemical and ionisation interference. Accuracy is generally good and depends on the

sample digest and freedom from interferences while precision is reasonable and highly suited to exploration analysis.

Graphite furnace atomic absorption spectrometry (GFAAS) detection limits are generally 2-3 orders of magnitude better than flame AAS and 1-2 orders better than ICP-AES, although the dynamic linear working range is limited. Despite low detection limits, the application of GFAAS to geological applications has remained relatively specialised because of the requirement to separate the analyte from the sample matrix in order to avoid the complex matrix interferences. The success of the technique ultimately depends on the ability to accurately correct for non-specific molecular absorption. Three types of background correction are available: the traditional deuterium background correction; corrections based on the Zeeman effect; and the Smith-Hieftje hollow cathode reversal system. Deuterium background correction is adequate for background correction of flame and some graphite furnace AAS applications. The determination of low level gold after a fire assay separation is well suited to deuterium background correction while the determination of indicator elements from an aqua regia digest requires a more sophisticated background correction. The technique is relatively expensive due to large consumable costs and requires skilled laboratory staff to develop methods due to the complex nature of sample matrices.

Cold vapour AAS is well suited to the trace determination of mercury. There are two major problems that occur with this technique: interferences from matrix elements and contamination from reagents. Matrix elements can interfere with the release of mercury vapour by competing reactions involving the formation of amalgams, selenides, tellurides or other stable mercury compounds. Hydride generation AAS for the determination of arsenic, antimony, selenium and tellurium in geological materials also suffers from matrix interferences. It is essential that all analyte be converted to the correct oxidation state before the hydride gas is generated. The principle interference arises from matrix elements, typically Ni, Co and Cu, interfering with the reduction to the hydride. Since these techniques are prone to matrix interferences in the generation stage it is essential to check recoveries by spiking. Spike recovery evaluation should be a part of the laboratory's quality assurance system for cold vapour and hydride techniques therefore mining companies should request this data be reported.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
ICP-AES is a well established analytical technique with a large linear dynamic range, low detection limits and can offer accurate and precise simultaneous multielement analysis of major, minor and trace elements. The technique has made significant advances over the last decade although detection limits have not changed significantly with radial view plasma. The simultaneous determination of analytes requires that the chemist choose a compromise of optimum conditions to accommodate all elements. Parameters include:
- Power,
- Plasma gas flow,
- Auxiliary gas flow,
- Nebuliser gas pressure or flow rate,
- Sample uptake rate, and
- Viewing height.

The analysis of geological materials can pose tough analytical challenges to chemists in contract laboratories. The biggest challenge to overcome is spectral interferences from concomitant elements and this can be done in two ways:
- Choosing an alternative spectral line, this is not an option for traditional fixed line polychromators, and
- Applying corrections through interelement correction factors or by creating a mathematical model for correction.

Contract laboratories need to be vigilant in monitoring instrument performance through assessment of quality control data, instrument drift and sample introduction carry over. Instrumental drift in not normally corrected by internal standards as for ICP-MS but rather by monitoring standards within each sample batch.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
ICP-MS has moved from the research laboratory and has now firmly established itself as a routine analytical technique in contract laboratories. In this demanding, high-production environment trace element determinations in complex geological matrices are a challenge for laboratory chemists. Detection limits are extremely low,

typically 0.05-1ppm in the rock, with good accuracy and precision for most elements. The challenges facing chemists include:

- Small levels of contamination caused by poor analytical technique will be observable due to the high sensitivity of ICP-MS,
- Reduction of oxide and doubly charged ions
- Space-charge effects, observable when low-mass analytes are determined in a high-mass sample matrix
- Mathematical correction for isobaric and molecular interferences
- Use of suitable internal standards, to correct for changes that occur due to differences between standards and samples, primarily physical effects.
- Sample matrix and high solids loading, total dissolved salts to approximately 1000ppm
- Memory effects, which is dependant upon the relative concentration differences between samples analysed sequentially

Flow injection has now been successfully coupled to ICP-MS and has dramatically increased laboratory productivity. This technique offers several advantages for ICP-MS:

- High sample throughput, typically 1100 samples/day
- Small sample volumes, typically 50-500μl. Due to the transient nature of the FIA injection profile the sample introduction system and ICP-MS interface are exposed to much lower levels of sample matrix.
- Automated on-line sample preparation, i.e. hydride generation, addition of internal standard

Contract laboratories need to be vigilant in monitoring instrument performance through assessment of quality control data and sample introduction carry over.

X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence spectrometry has now reached maturity in its development as an analytical technique for the analysis of geological materials, although some interesting advances have recently been commercialised with the introduction of polarising XRF. Samples are prepared as either pressed powder pellets, normally used for heavy major and trace elements or as fused glass discs for the light element as well as major and minor elements. Detection limits for wavelength dispersive XRF for many trace elements lie in the range 1-10ppm. This technique is well suited to the determination of trace refractory elements because assays are carried out directly on the solid sample and do not rely on acid digestion.

When evaluating XRF results it is essential to distinguish between accuracy and precision. The precision of the XRF technique is normally very high and is simply demonstrated by evaluation of replicate results. Accuracy on the other hand depends heavily on two factors: the attenuation-enhancement correction procedure used to correct matrix effects caused by concomitant elements, and calibration procedures. Laboratories analysing samples with variable matrices require a person that is highly skilled and proficient in the XRF technique in order to produce accurate data. Methods worked up for one matrix need to be examined before it is indiscriminately applied to another. Control standards need to be in the same matrix as the samples and at appropriate concentrations.

Neutron Activation Analysis

INAA is a relatively simple, sensitive, precise and non-destructive analytical technique and is remarkably free from analytical interferences with matrix effect being small, Potts (1996). Since the original solid sample is analysed, the problems associated with incomplete dissolution, volatilisation and precipitation are not an issue. Contamination control is still important, although not from added chemicals, but rather from gold jewellery during sample handling.

Instrumental neutron activation analysis (INAA) can be used for the determination of gold in a variety of sample types, Garnett (1988).

- Particulate samples (pulverised rocks, soils, stream sediments)
- Biogeochemical samples
- Activated charcoal from bulk cyanide leaching
- Hydrogeochemical samples
- Prills from conventional fire assay with lead collection for gold, platinum and palladium
- Platinum group elements (PGE) and gold rich residues isolated after NiS fusion of samples

INAA can analyse large samples, typically 10–30g, but can accommodate even larger samples. The technique has the unique advantage in that it can report at least 31 other elements besides gold on the same analytical sample making it a cost effective multi-element technique. Detection limits are in the ppb to low ppm range for most elements, see Table 2, and depend on:

- Sample weight analysed
- Neutron flux in the reactor or the concentration of neutrons available for irradiation
- Duration of irradiation
- Probability that the parent nucleus will absorb a neutron
- Efficiency and resolution of the gamma ray detector
- Elapsed time after irradiation

Table 2. Typical detection limits achievable on rocks, soils and stream sediments, Becquerel Laboratories, Lucas Heights.

Element	DL (ppm)	Element	DL (ppm)	Element	DL (ppm)
Au	0.005	Fe	200	Se	5
Ag	5	Hf	0.5	Sm	0.2
As	1	Ir	0.02	Ta	1
Ba	100	K	2000	Te	5
Br	1	La	0.5	Th	0.5
Ca	1%	Lu	0.2	U	2
Ce	2	Mo	5	W	2
Co	1	Na	100	Yb	0.5
Cr	5	Rb	20	Zn	100
Cs	1	Sb	0.2	Zr	500
Eu	0.5	Sc	0.1		

There are two main advantages with the fact that the spectrum of a sample changes with time, firstly a sample can be recounted after a suitable decay period when photopeak interferences activity has substantially disappeared and secondly the time when samples are counted can be used to optimise detection limits. The most serious instrumental sources of error are in photopeak overlaps in gamma spectra, maintaining reproducible sample geometry and self-shielding which can occur in coarse grains which contain large amounts of easily activated elements.

INAA is best suited to the early phases of mineral exploration when regional geochemical patterns are being defined and lithogeochemical indicators may be as important as the ore elements themselves. The technique can also be used as an independent check on assay results and to test the homogeneity of quality control samples.

There are a number of disadvantages with INAA:

- Requirement for a nuclear reactor
- Unable to provide useful analytical data on a number of base metals e.g. Cu, Pb, and Ni.
- Turnaround time, typically 10-12 days

Precision of the method:
5% with a 95% confidence at concentrations greater than 10 times the detection limit

General Comments on Analytical Scheme

When an analytical scheme is chosen in consultation with a contract laboratory the decision should be made with the clear understanding of the end use of assay results. The analytical requirements for different stages of the exploration process, i.e. reconnaissance exploration or resource estimation, are quite different. It is useless choosing an analytical technique on the basis of price alone - the data must be fit for purpose. It is also important that geochemical databases identify different sample types, different analytical methods or laboratories so that each can be evaluated on its merits. If analytical schemes are chosen with due consideration of the required accuracy and precision then explorers should expect to obtain assay results that are technically sound.

Review

Mining Companies Obligations to Ensure Quality of its Data

Field Sampling Check Samples: Potentially field sampling is the greatest source of error and accordingly duplicate samples should be taken during this stage of the project. Statistical analysis of duplicate sample will quantify the total error, i.e. sampling in the field, sample preparation, and the assay procedure.

Control Standards: Submission of control standards to monitor performance of a laboratory, is a vitally integral part of any exploration or mining project. Control standards monitor accuracy and these standards require inter-laboratory test work so that a "true or accepted" value can be established. Companies should examine the spread of published assay results used to determine recommended standard values on typical industry standards. For a 50g fire assay for gold, after outlier results have been removed, the spread of analytical results averages about 20-30%, while base metal result spread can be anything up to an order of magnitude, see Figure 1. If this is a typical spread for "round robin" sample results, when it can be assumed that laboratories take a little bit of extra care, what accuracy can realistically be expected from industry samples?
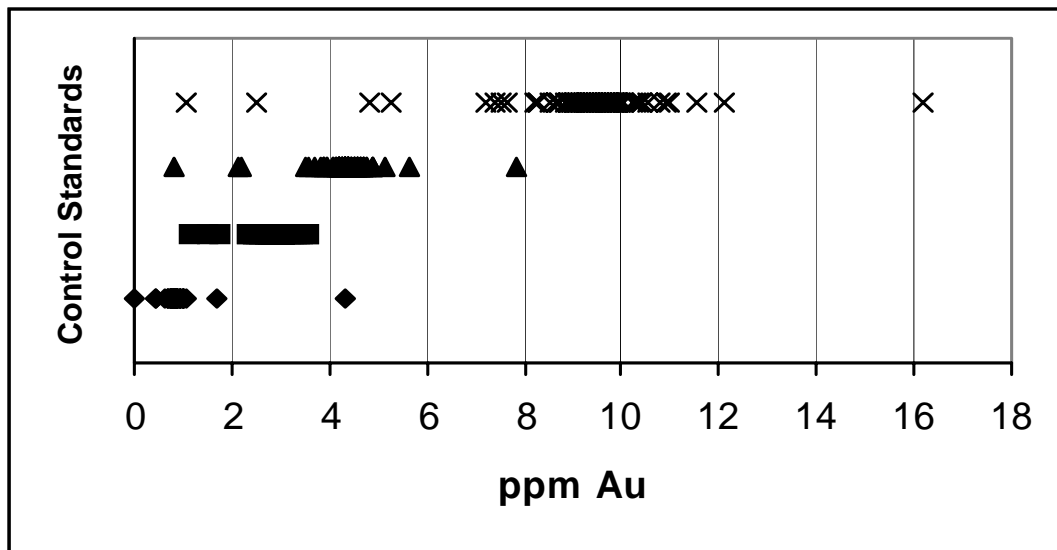

Figure 1. Typical spread of gold assay results obtained in round robin surveys to establish recommended values on four control standards. Data was obtained using 50g fire assay deteminations and includes all statistical outliers.

The mining industry should understand that "not all standards are created equal" and should critically examine the quality and usefulness of available standards. Following this critical assessment, when appropriate control standards have been purchased or developed and validated "in-house", then the identity and concentration of analytes should not be known to the laboratory. To this end, control standard labeling, packaging and physical and chemical composition should mimic those of the routine samples to mask the identity of the samples to the laboratory. Unless these measures are taken laboratories may differentiate between samples and standards, establish values for the standard materials, and in a worst case senario could use these standards to "normalise" sample results. It is important that the development of control standards is carefully planned. For large scale projects, use reject material and prepare standards with two standards that have similar analyte concentrations for each grade, so that laboratories can't differentiate without accurately analysing them. When explorers have properly developed control standards they have an equally important obligation to check the laboratories performance before data is entered into a resource database. Like the laboratory, control charting is the simplest method to monitor control standard performance.
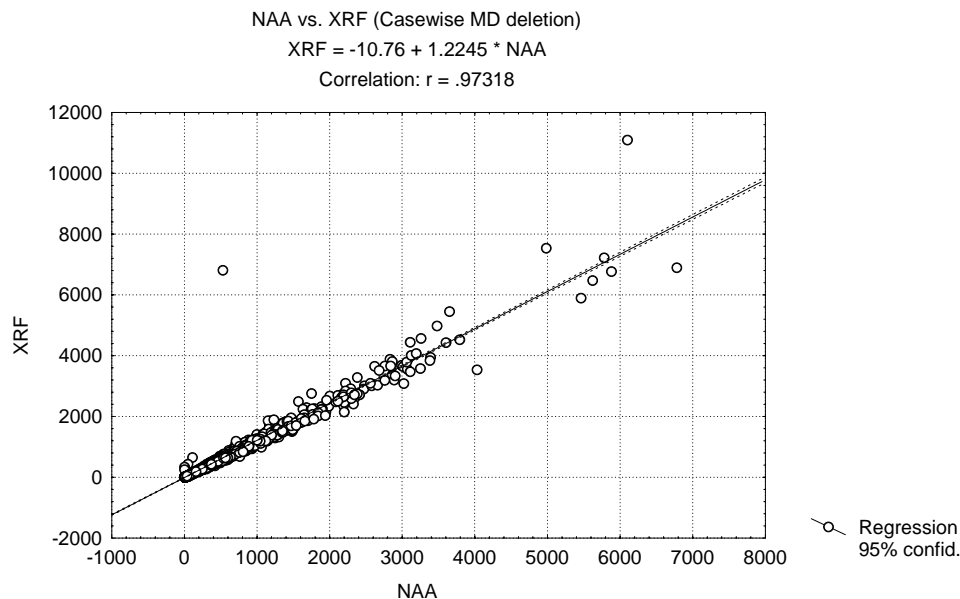
Traceability of analytical data is an important part of a laboratory's quality assurance systems and also AS ISO/IEC 17025. If in doubt about assays or problems are perceived then most laboratories have the ability to

provide an audit trail on all analytical results, this is available through most laboratory information management systems (LIMS).

Check Assays: The mining company should have a procedure in place where a predetermined percentage of samples are randomly resubmitted with new sample numbers to the laboratory for check analysis when the pulps are returned. Check assays should be carefully chosen, the results statistically compared to original data and plotted on scatterplots with corrective action taken when necessary. This check procedure should not be left until the end of the project when corrective actions are too late to implement. Feedback to the laboratory on performance is encouraged even when statistical analysis of data indicates good correlation. Poor check assays usually indicate poor sample preparation or poor analytical determinations. Check assays can be sent to an independent laboratory or the same laboratory using a different technique to monitor accuracy of analytical determinations, Figure 2. Explorationists should submit barren samples as part of the check assay program to monitor contamination during the sample preparation and assay process, i.e. monitor blank samples following high-grade samples. To effectively monitor laboratory performance a standards program has to be well planned and executed.

NAA vs. XRF (Casewise MD deletion)
XRF = -10.76 + 1.2245 * NAA
Correlation: r = .97318

Figure 2. Scatterplot showing bias between analytical techniques

Laboratory Quality Control: Laboratories as a part of in-house quality control procedures monitor performance by analysing:

- Certified reference materials or properly validated "in-house" standards
- Second splits
- Replicates
- Blanks

Mining houses should request as part of the contractual requirements, that laboratories report their in-house quality control data. This is normally a requirement for environmental testing conducted by contract laboratories.

Laboratory Audit: All contract laboratories should have a quality assurance system in place and mining companies have an obligation to audit the laboratory and ensure it has met its contractual obligations to report high quality fit for purpose analytical data. By conducting audits that examine all aspects of the laboratory quality assurance system, mining companies are one step closer to ensuring that the quality of their assay result matches their expectations.

Laboratories Quality Assurance Obligations

Quality assurance involves all the activities undertaken by a laboratory to ensure customer satisfaction and consists of two separate but related activities: quality control and quality assessment. Both must be operational and coordinated, Eames (1998). Quality management activities have the following definitions:

- Quality assurance: A system of activities whose purpose is to provide to the client the assurance that analytical data meets defined standards of quality with a stated level of confidence, see Figure 3.
- Quality control: The overall system of activities whose purpose is to control the quality of analysis so that it meets the needs of clients. The aim is to provide analytical data that is satisfactory, adequate, dependable, and economic.
- Quality assessment: The overall system of activities whose purpose it is to provide assurance that the overall quality control job is being done effectively. It involves a continuing evaluation of the analytical data and the performance of the analytical scheme.
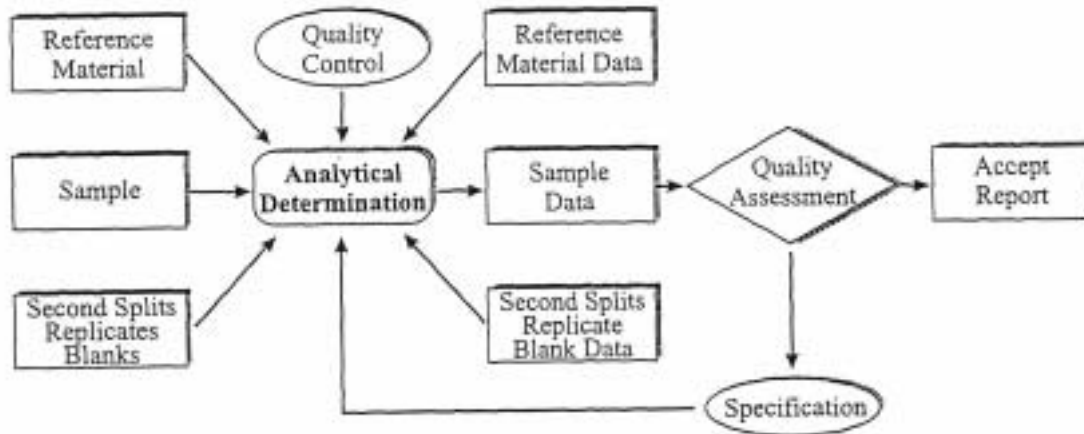

Figure 3. Quality assurance aspects of a typical measurement process

Quality control procedures are used to tune and maintain the system in a state of statistical control while quality assessment procedures are used to evaluate the quality of the data that is produced. Laboratory data that is produced must be both technically sound and legally defensible. Good quality assurance practices are central to achieving both goals.

Quality Control
To ensure quality control, all practices and procedures used in leading to statistical control and achieving the desired accuracy and precision of the analytical measurement must be considered. The basic elements of quality control are considered in detail below.

Human Resources
Adequate competence and expertise of laboratory staff commensurate with the skill requirements of the analytical task. Laboratory management that has the technical knowledge, experience and skill to train new employees and for periodic review of long-term employees. On-the-job training should be a continuing activity which motivates and commits staff and also helps indoctrinate them in the laboratory's quality assurance program

Laboratory Facilities and Equipment
- Appropriate laboratory facilities and equipment required for analyses
- Calibration schedule

- Routine maintenance of equipment and facilities

Documentation and Validation
- Use and operation of all relevant equipment
- Appropriate work instructions (methods and procedures) for all calibrations and analytical tasks and related activities (sample preparation) within its responsibility
- Full validation of all non-standard analytical tasks
- Implementation of Good Laboratory Practices (GLP) (AS ISO/IEC 17025)

Quality System
- Laboratory Quality Manual as required by:
  - ISO 9001:2000 Certification
  - NATA accreditation

There seems to be a misconception in the mining industry about laboratory certification and accreditation. Laboratory certification to ISO 9000 ensures that a management system is in place that is aimed primarily at achieving customer satisfaction by preventing non-conformity at all stages of production, while laboratory accreditation to ISO/IEC 17025 assesses a laboratory's technical competence by peer review. The requirements for NATA accreditation are basically the necessities of good laboratory practice. In a recent Canadian study (1999), the following recommendation has been made:

We encourage the adoption of laboratory accreditation programs by all jurisdictions with the mining industry and the accreditation of laboratories in those jurisdictions, so that the use of accredited mineral analysis laboratories becomes common practice worldwide in the mining industry.
We recommend that Canadian securities regulatory authorities require that analytical results from mineralised rock samples reported by companies on exploration programs must be analysed by an accredited laboratory. Laboratories in Canada should be accredited under ISO/IEC Guide 25 as supplemented by CAN-P-1579, or in other jurisdictions under ISO/IEC Guide 25 or the local equivalent of ISO/IEC Guide 25. Where an accredited laboratory is not available, an appropriate number of samples as determined by the Qualified Person should be re-analysed at an accredited laboratory.

Quality Assessment
Quality assessment techniques are the ways in which measurement process is monitored in order to infer the quality of the analytical data reported to the client. These techniques provide assurance that statistical control is achieved and maintained and as well provide estimates of the accuracy of the analysis data. The basic elements of quality assessment are considered in detail below.

Reference Materials
- CRM (certified reference material - issued and certified by an organisation considered technically competent)
- Reference materials are widely used in analytical chemistry to:
  - Evaluate accuracy and precision of analysis schemes
  - Develop "in-house" secondary standards
  - Direct calibration of instrumentation (XRF)
  - Internal quality assurance
- Validity of use will depend on how well the reference material mimics the sample suite with respect to both matrix and analyte concentration
- When samples are profiled into a LIMS system, the laboratory would normally specify the frequency of quality control samples per sample batch

Independent Methodology
- Analytical data should be free from measurement bias, including analyst, instrumentation and methodology biases. Commercial laboratories possess a wide range of analytical instrumentation ensuring that internal bias can be investigated by using independent techniques e.g. AAS, GFAAS, ICP-AES, ICP-MS as well as definitive techniques like INAA.

Proficiency Testing Programs
- Contract laboratories participate in proficiency testing exercises. This gives laboratories the opportunity to compare analytical performance with other laboratories
- Larger contract laboratories have laboratories both nationally and internationally, allowing the development of "in-house" standards and exchange of samples on a regular basis to evaluate analytical performance.

Spikes
- To ensure recovery of some analytes, spikes can be added and the recovery monitored

Replicate Analysis
- When samples are profiled into the LIMS system, it can adopt a standard format for the frequency of quality control samples per sample batch:
    - Second splits   - two packets of the same sample material are created following the final stage of sample preparation
    - Replicates – repeats performed on the identical sample from the same packet
    - Blanks – analytical blank that follows the sample batch through the entire process to monitor analyte background levels as well as contamination

Laboratory Audits
- Laboratories serious about quality assessment see that quality audits are an essential part of the quality assessment progress, and as such, two types of audits should be undertaken:
    - Qualitative evaluation of the operational details of the Quality System
    - Performance audits to quantitatively evaluate analytical data
- Both internal and external audits should be conducted
- Laboratory audits should cover all aspects of a laboratory:
    - Administrative information
    - Equipment
    - Human resources
    - Quality assurance systems
    - Control charts
    - Reference materials
    - Records
    - Reports
    - Sample management
    - Audits
    - Training

Performance Charting and Statistical Analysis
Laboratories should monitor performance regularly and control charting is possibly the simplest method. The centre line of the chart defines the certified or agreed value of the control standard, and plots incorporate established warning (2σ) and control (3σ) limits. Trend analysis using these charts can be an invaluable diagnostic tool. On multi-element techniques, key analytes should be monitored regularly with other analytes monitored on a less frequent basis.

Quality assurance must be more than a plan of activities; it must be a philosophy, a way of life within the contract laboratory. As a plan that is mechanically followed it is doomed to failure but when quality assurance is approached as both a philosophy and a program then the laboratory has an excellent opportunity of reporting high quality analytical data.

What can go Wrong and the Effect on Resource Analysis

Adoption of poor practices can ultimately lead to defence of these practices in a court of law. Recently a case settled in the Supreme Court involved the underestimation of a grade of mineralisation in a resource model. Listed below are some of the contributing factors that led to the resource being underestimated:

- Failure to apply principles of well established sampling theory
- Failure to design and implement effective quality control protocols
- Poor choice and implementation of analysis methodology
- Use of defective statistical tools and absence of skilful interpretation
- Failure to act on expert advice provided both internally and by consultants

Explorationists need to examine laboratory assay data throughout the project, ask questions early and don't leave it to the end of the project to discover problems with the quality of the analytical data. The integrity of sulfide rich samples may be compromised and repeat analysis impossible. This was recently the case for an explorer analysing precious metals in a sulfide matrix, repeat assays were not an option, essentially too late to show concern at the integrity of the database.

In another incident a mining company suspected the quality of its assays and acting responsibly questioned the laboratory and embarked on a check assay program with independent laboratories. Despite repeated communication with the laboratory it embarked on a second major drilling and assay program using the same suspect analytical method. The issue of assay quality had not been adequately resolved. Mining companies often maintain integrity of their data by using the same assay method, but the assay method needs to be appropriate. Assay data must be fit for purpose. It is irresponsible to use geochemical trace determinations if conducting a resource evaluation program.

Laboratories need to know the stage of exploration i.e. reconnaissance or resource evaluation, so that an appropriate analytical schedule can be quoted. Accuracy and precision requirements need to be clearly spelt in contract documents. Analytical data is required to be both technically sound and legally defensible, that is to say it must be defensible against any reasonably adversarial inquiry or action, legal or otherwise. There is a difference in these requirements and both need to be met. Technically sound includes all things that a competent analytical chemist should do, while the second includes proof that sound work was done. A sound and properly implemented laboratory quality assurance program is an essential factor in achieving both requirements.

Conclusions

Ensuring an accurate and precise assay result and the integrity of a resource database is a process that commences at the beginning of an exploration project. Field sampling protocols need to be tested and implemented to minimise sampling errors and an appropriate analytical scheme must be developed with the contract laboratory. It is no good examining the data at the end of a project and deciding that assay quality is poor because an inappropriate analytical scheme was chosen or because scheme selection was based on price alone. Every analytical technique has an associated error and it is up to the mining company in collaboration with the contract laboratory to ensure that assay schemes are fit for purpose. Good communication with the laboratory throughout the life of the project is integral to its success. The mining company also needs to ensure that it has a comprehensive system of checks in place to monitor laboratory performance.

The contract laboratory has an obligation to ensure that its analytical data is both technically sound and legally defensible. To this end the laboratory must have in place a quality assurance program which contains all the key elements outlined in this text and must stand up to the rigors of external and internal audits.

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