



Laboratory QA/QC Today – Its not just Control Charts

Ten years ago when a laboratory wrote an article about issues related to quality assurance (QA) and quality control (QC) they would have focused almost exclusively on control charts, frequency of QC items, and laboratory certification and accreditation. In the last decade, clients and laboratories have come to recognize that QA/QC issues include a number of other topics critical to ensuring data of suitable quality are provided for each project. In this article, a number of these current quality issues will be covered.

Changed relationship between client and laboratory

Regulatory requirements have changed the relationship between clients and laboratories with regards to QA and QC. Under the various codes of conduct including the Canadian National Instruments 43-101, and Australian Joint Ore Reserves Committee Code (JORC), minerals exploration and mining companies must now accept responsibility for the QA/QC program, including the activities of the laboratory. Clients submitting samples to any laboratory must review and oversee all of the activities of that laboratory, during analysis of their samples. Laboratories must be more open and accountable with their work. One of the impacts of this is that laboratories are asked for, and routinely provide, their internal QA/QC data. Results from participation in proficiency tests and external round robins are also requested. In addition, many companies require the laboratories use ISO17025 accredited test methods.

Even with all this evidence of laboratory quality, it is still not appropriate for any client to rely entirely on the laboratory for the QA/QC program. The laboratory QA/QC is the protocol used for running the laboratory portion of quality. Clients should have their own QA/QC program, which is focused on and covers all aspects of the project, the range of concentrations, and the sample matrices involved. This should include field duplicates, sampling protocols, and provision for oversight of the laboratory activities.

Analytical method selection – assay versus geochem precision

The first and most important QA/QC issue for any project is selection of appropriate methods and procedures. Multi-element methods now routinely report a wide range of elements and concentrations from a single digestion. The concentration range may be suitable for the project, but the completeness of the digestion, or the precision of the method, may not be. The issue can become confused by the requests for an Assay versus a Geochemical determination.

A base metals “Assay” determination used to refer to a total analysis with good precision and accuracy. The focus was

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on accurately determining the concentration of an element, and the method was typically tailored to a single element. In contrast, Exploration Geochemistry determinations focused on sufficiently low analytical detection limits to provide good contrast between “background” and “anomalous” results. “Geochem”, in its earliest applications, relied on patterns in the elements rather than absolute determinations. Total dissolution of all the elements was not critical, nor even desirable. Bias was not considered to be a problem, as long as results were consistent, and an “anomalous” result was still “anomalous” on retesting.

Precision and accuracy requirements for geochem increased as instrumentation improved. An old rule of thumb used by laboratories was that an assay had a precision of $\pm 5\%$, and geochem was $\pm 10\%$. Assays were for ore grade materials, and geochemical determinations were for ppm levels. The introduction of high quality multi-element methods, reporting concentrations from ppb to % levels, further blurred the lines between the two types of determinations.

Rather than specifying an Assay or a Geochem determination, the client is best served by selecting a procedure with the precision characteristics required for the data. A grass roots exploration program will have one precision criterion. Precision requirements in exploration drilling, where results might be used in the future for reserve calculations or estimates, will be different again. Precision specifications of a method are also useful in assessing pass or fail criteria on standards submitted to the laboratory. A method with a precision of $\pm 10\%$ will deliver failures for a control standard with limits set at $\pm 5\%$.

Laboratories should be able to provide the precision estimates for their methods. Precision specification for every method and element are available from ALS Chemex through the Standard and Duplicate Tolerance values provided in the method descriptions and on the Webtrieve™. The formulas needed for using these values

to estimate ranges at any one concentration are listed below. The equations are based on work of Thompson and Howarth (1978). These limits define a range, within which values should fall 19 times out of 20. They provide useful guidance for selecting the optimum method for a particular program.

$$\text{Range on a Standard} = \pm \text{Standard Tolerance} \times \text{Concentration} + 2 \times \text{Detection Limit} \quad (1)$$

$$\text{Difference between Duplicate Pairs} = \pm \text{Duplicate Tolerance} \times \text{Concentration} + 2 \times \text{Detection Limit} \quad (2)$$

Copper (Cu) determinations can be used to illustrate the differences that method precision has on the results. Cu methods covering the range of concentrations are listed in Table 1.

Method	Range	Duplicate Tolerance (ARD at max conc)	Number of Duplicate Pairs used in Figure 1
Cu-ICP	1 – 10,000 ppm	10% (0.1)	3950
Cu-ICPa	10 – 100,000 ppm	7% (0.07)	1617
Cu-OG	0.01 – 40%	5% (0.05)	947
Cu-VOL	0.01 – 100%	3% (0.03)	64

Table 1. Reporting Range and Duplicate Tolerance Percentage for Various Copper Methods.

With the exception of the Cu-VOL, all the procedures are multi-element ICP methods. Cu-ICPa is an intermediate method between low level exploration samples and determinations on ore grade samples.

Absolute Relative Difference (ARD) can be used to demonstrate precision of analytical data (Walsh and Shaw, 1999) by normalizing the difference between duplicate pairs, for the average value of concentration.

$$ARD = \frac{|X_1 - X_2|}{\text{Mean}(X_1, X_2)} \quad (3)$$

Duplicate pairs of results for the various methods were extracted from the ALS Chemex database. ARD was calculated on real data (as in (3) above), and the point plotted against the mean concentration. The colors show which method was used (Fig. 1). The Duplicate Tolerance specification (from (2) above) has also been added to

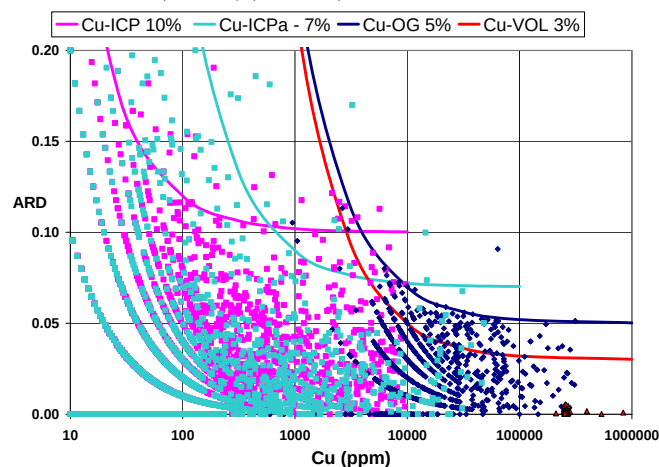


Figure 1. Absolute Relative Difference (ARD) of real data as a function of Cu concentration for various methods. (Curves represent theoretical method Duplicates Differences).

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show the theoretical method precision lines. In this case, theoretical tolerance of duplicate pairs is plotted against concentration to provide theoretical method ARD.

As is shown in Figure 1, method performance is a combination of the precision factor and the detection limit. Below 3000 ppm, the Cu-ICP method (Pink line) has the better precision (lower ARD) relative to the 100 ppm detection limit of the Cu-OG method (dark blue). Above 3000 ppm, the Ore Grade Assay method, Cu-OG (dark blue) has superior precision. The multi-element ICP assay method, Cu-ICPa (light blue), has precision performance between the two procedures, with a superiority in the range of 400 to 7000 ppm.

Method selection should be based on the precision performance required for each project. If the required precision of high level control standards for the project is $\pm 5\%$, the standard Cu-ICP method will not provide satisfactory results.

Sample tracking and control

One of the most critical QA/QC issues is sample handling and tracking. Regardless of analytical procedure and analytical quality, if the analysis is not attached to the correct sample, the result is 100% wrong. Errors in sample labeling can occur in numerous places, and it is a dual responsibility of the client and laboratory, to have

systems in place to reduce errors, and identify problems quickly.

Sample identifications

There is a trend towards using character strings as sample descriptions, to mask information about physical location. However, long character strings are easily misread, and prone to data entry errors. Providing the laboratory with a full electronic list of the sample ID's is a proactive solution to reducing data entry errors. The laboratory can then import these ID's into their database system directly. Integration of data back to the client will also be easier because sample ID formats are exactly as specified by the client.

Barcodes on samples take sample ID integrity one step further. The ALS Chemex system is set up to scan a client barcode, followed by the laboratory barcode (a unique identifier for every sample received), and to then capture the received weight. The client barcode is then transferred directly into the system as the sample ID, eliminating all clerical errors. The scan is a direct indication that the sample with that field identifier was received at the laboratory. Naturally, this system relies on the client barcodes being of sufficient quality to be reliably read by the scanner, following all the handling from the field to the sample preparation facility.

Sample received weight (SRW)

The capture and reporting of sample weight at receipt

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is an important aspect of quality and sample control. Review of Sample Received Weight (SRW) can alert the client to mislabeled, lost or spilled samples during shipment, and as a check that the collected sample mass is within specified limits. This is most valuable where the sample weights vary, as commonly occurs for drill core. SRWs are captured for all samples at ALS Chemex and reported without charge.

Audit trails

Audit trails for all aspects of laboratory systems are essential. Good protocols should allow easy and rapid review of a batch of samples to enable problems to be sorted out. ISO17025 quality systems require that a batch of samples in a laboratory can be traced back through a combination of electronic and hard copy records.

ALS Chemex is a leader in this aspect of quality management through the Open Lab initiative. Audit trails for all activities on a sample and submitted batch are generated and stored electronically. These complete

records are available online in real time, through the Webtrieve™ Audit Trail button. Tracking progress and review of activities are transparent and available to the client.

Monitoring sample preparation QC

Sample preparation protocols are designed to produce a sub-sample that is representative of the original. As stated by Pierre Gy, a sample is representative if *every particle in the lot of the material from which it is taken, has an equal probability of being included in the sample*. Two critical parameters for evaluation of preparation methods are the weight of material analyzed, and the particle size produced. Specification, measurement, and control, of grinding is required to produce quality results.

Sizing tests for sample preparation procedures, are done by the sample preparation laboratories daily, on each piece of equipment that is used at our laboratories. Results are reported as part of the QC data for each submission and available online, as shown for example in Figure 2.

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The industry commonly presents data as 75% passing 2 mm, or 85% passing 75 μm . While these specifications may be suitable for representative sampling, advanced QA/QC statistics are all developed around the 95th percentile measurements. Sample preparation procedures where the sizing criterion is also measured at the 95% level are now available. 95% passing 6 mm (for crushing) and 95% passing 105 μm (for pulverizing) are common.

Insertion of client standards, duplicates and blanks

Client QA/QC programs routinely require the insertion of their own standards, blanks and duplicates, in addition to those done by the laboratory. For these client control samples to truly reflect laboratory performance, it is important they are not treated differently than other samples. Also, they should be processed at the same time and in the same subgroups, e.g. furnace fusion groups, as critical client samples.

Ideally, control samples should be inserted in a manner completely blind to the laboratory, so the laboratory staff are not tempted to bias the estimation of performance by applying special treatment. This can be accomplished by having one laboratory prepare the samples and insert the controls, and then forwarding to another laboratory for the analytical work. An alternative is to have the laboratory prepare the samples, have the pulps returned to the client for insertion of the controls,

with return of the samples to the laboratory for analysis. The expense and time delays involved in this approach may not always be practical.

The goal is to ensure the controls are an unbiased representation of laboratory performance and that the groups of samples associated with each control sample can be clearly established. In turn, any samples requiring rework due to a failed control are readily identified. The ALS Chemex Full QC view provides the metadata required to establish this information. For each sample and analytical procedure, the sub-sample weight used, the fusion run number (or digestion run number) and the position in the fusion/digestion run are listed. Instrument runs and positions are also listed. These data can all be provided as a routine electronic format (CSVFMD), or retrieved for individual workorders, on-line through Webtrieve™ as required.

Example Gold (Au) Fire Assay data group is shown in Table 2. Sample numbers 1 to 12 and 16 to 21 were fused in the same fusion run. Results reported for sample numbers 13 to 15 come from another fusion run because the first fusions for these samples did not pass QC and the samples were re-weighed. The view also includes information on our internal QC samples for each fusion run.

Webtrieve™ also includes graphical tools for visualizing and reviewing sample order in fusion and digestion runs. Select a set of results, and click on the

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#	Sample ID	Au	WT. SAMPLE	Fusion_Seq	Fusion_Run	Instr_Seq	Instr_Run
1	144571	0.135	31.44	20	2211846	127	2216221
2	144572	0.029	31.11	21	2211846	128	2216221
3	144573	0.101	30.32	22	2211846	129	2216221
4	144574	1.550	29.93	23	2211846	309	2216221
5	144575	0.012	32.91	24	2211846	130	2216221
6	144576	0.570	30.11	25	2211846	131	2216221
7	144577	0.543	31.51	26	2211846	132	2216221
8	144578	0.465	31.02	27	2211846	133	2216221
9	144579	0.491	30.87	28	2211846	134	2216221
10	144580	0.022	31.27	29	2211846	135	2216221
11	144581	0.045	30.36	30	2211846	136	2216221
12	144582	0.044	31.28	31	2211846	137	2216221
13	144583	0.023	29.98	62	2216853	64	2218521
14	144584	0.035	30.79	63	2216853	65	2218521
15	144585	0.245	30.92	64	2216853	66	2218521
16	144586	0.342	30.34	35	2211846	141	2216221
17	144587	0.048	30.00	36	2211846	142	2216221
18	144588	0.046	31.57	37	2211846	145	2216221
19	144589	0.028	32.01	38	2211846	146	2216221
20	144590	0.010	30.66	39	2211846	147	2216221
21	144591	0.110	31.29	40	2211846	148	2216221
1	Blank03_07068920	<0.005	30.00	1	2211846	107	2216221
2	St01:OXD57_07068920	0.419	30.57	2	2211846	108	2216221
8	St07:ST-259_07068920	2.530	31.22	8	2211846	308	2216221
1	Blank02_07068920	<0.005	30.00	1	2216853	14	2218521
2	St03:OXD57_07068920	0.391	30.65	2	2216853	15	2218521
20	St09:ST-259_07068920	2.490	30.64	20	2216853	300	2218521

Table 2. Example of Full Laboratory Meta-Data Details

Sequence button in the Data Grid Display. Figure 3 shows results for the first Fusion Run, whereas Figure 4 displays the results for the reweighed samples in the second grouping. These tools can be rapid and easy ways of seeing if the laboratory is analyzing or processing control standards in an unexpected sequence or assaying smaller masses. It also allows views of sub-groups of your samples to ensure your control standards are included in fusion/digestion groups for critical samples.

Data verification and certificates of analysis

Reporting standards such as National Instruments 43:101 and the Australian Joint Ore Reserves Committee

Code (JORC) require data verification be done by the ‘qualified’ / ‘competent’ person taking professional responsibility for the results. One part of data verification involves reviewing a percentage of the data in the company’s database against the original results reported by the Assay Laboratory to ensure no errors or misrepresentations have been made.

Formerly, signed printed hard copies of the Certificates of Analysis were used for this process. Today, most laboratories provide the certificates electronically as

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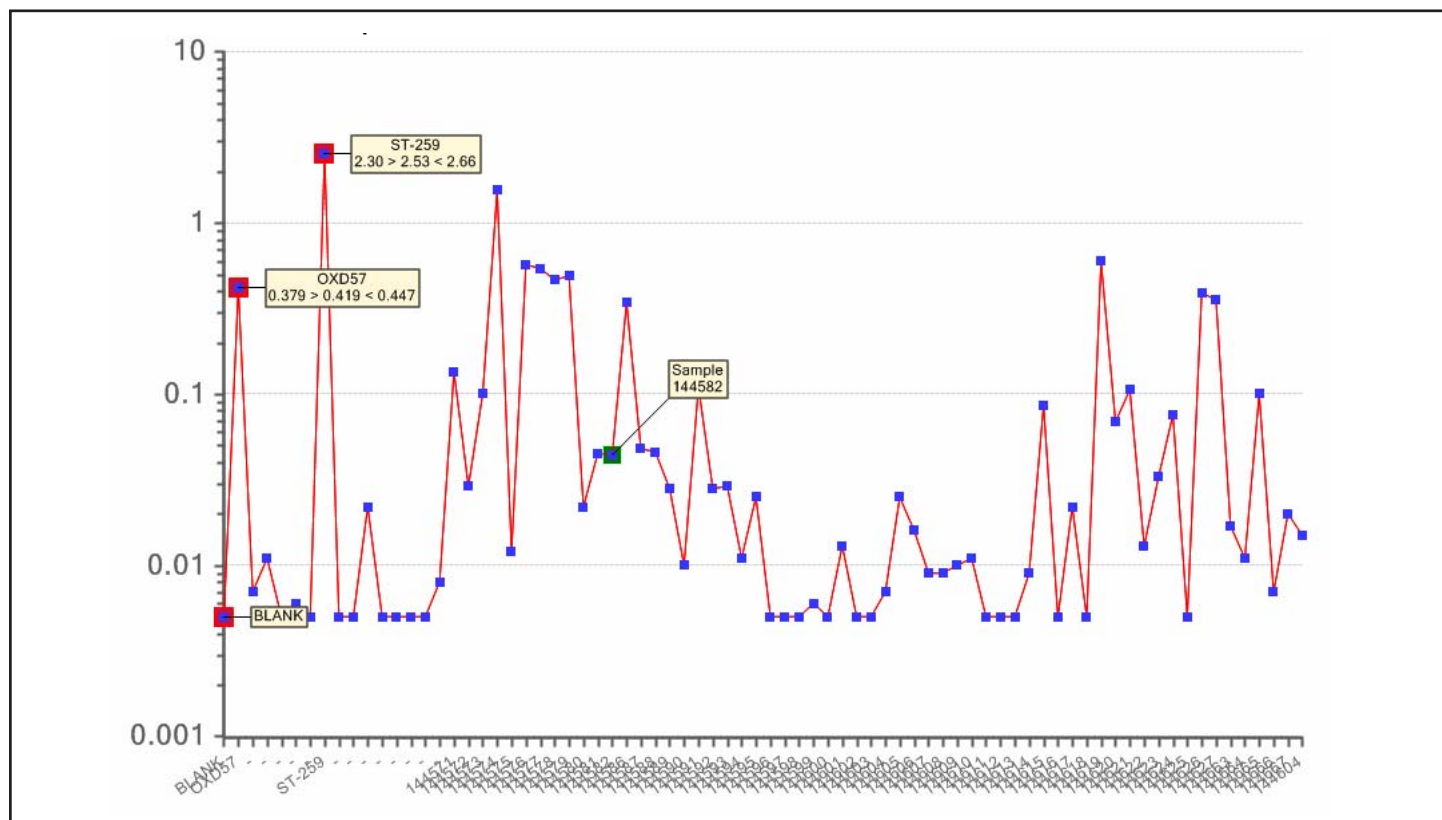
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Figure 3. Gold sequence data for fusion furnace run number 2211846.

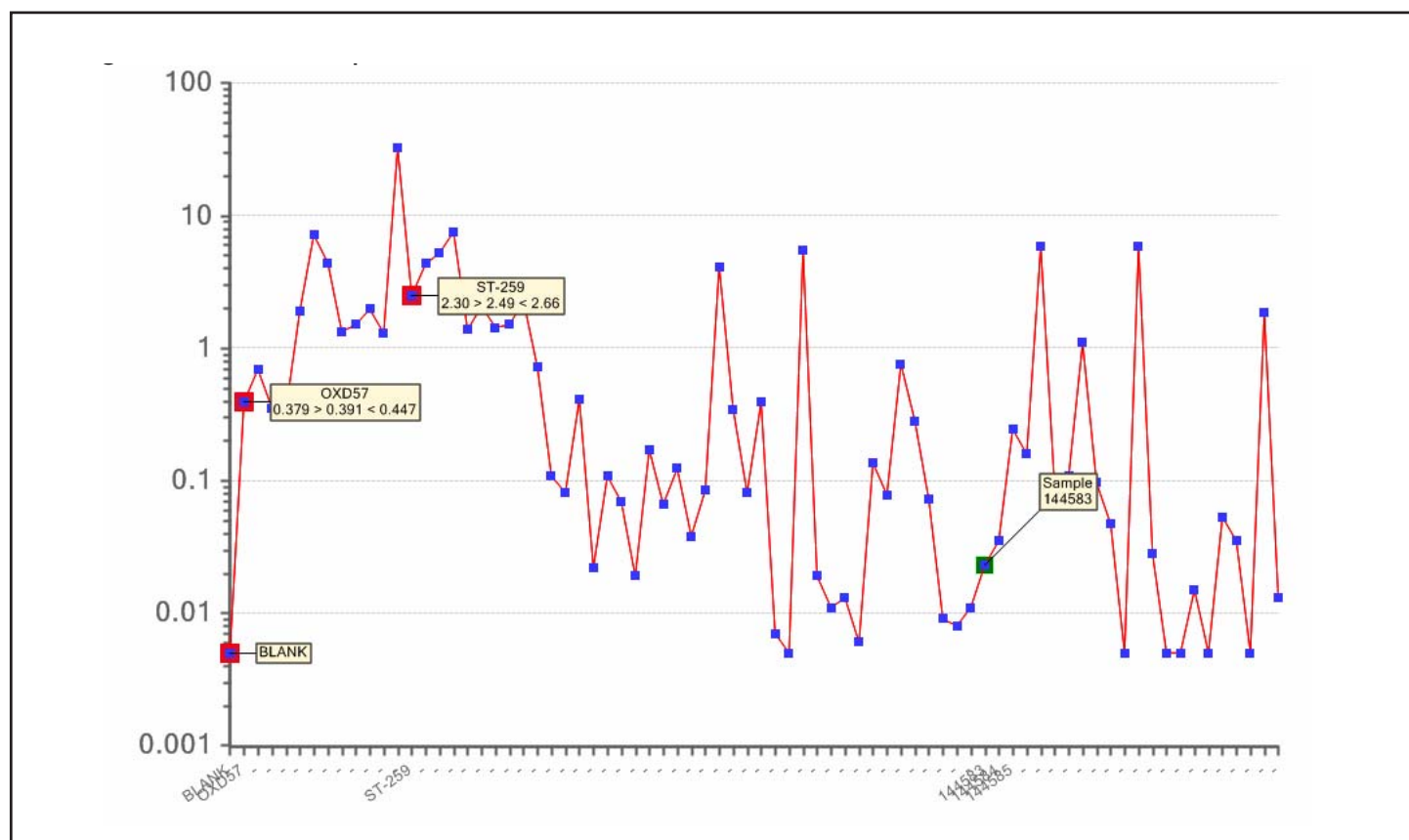


Figure 4. Gold sequence data for fusion furnace run number 2216853.

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encrypted PDFs. Some clients routinely ask that the laboratory remove the encryption so they can more easily put the PDF information into their reports. Meanwhile, regulators and other clients are asking for more sophisticated encryption on the PDF certificates, to prevent changes to the document after finalization. It is fairly apparent why a responsible laboratory cannot remove the encryption. In today's world, it is generally recognized that there is no electronic file that can not altered, and printed signed documents are no less secure.

Auditors and regulars doing data verification often ask the laboratory to provide copies of the Certificates of Analysis from the laboratory directly to them to avoid any questions about alterations. Certificates and datafiles can be redistributed electronically directly to these individuals. In addition, Webtrieve™ can allow direct access to the laboratory data and certificates once the client has given permission for the individual to view the results.

ISO 17025 – accreditation of methods

ISO17025 accreditation and ISO9001:2000 certification are external qualifications a laboratory can achieve, as evidence that its quality system meets international criteria. To become accredited for a testing method, the laboratory must pass a detailed, on-site,

technical audit of both the method, and the competence of the personnel performing it. In addition, the laboratory must correctly analysis unknown proficiency test samples, for the procedures they wish to be accredited. To maintain accreditation, the lab must continue to successfully analyze proficiency test samples twice a year, and pass biannual audits.

ISO17025 accreditation applies only for specific tests listed in the accreditation document. Sample preparation and sample handling protocols that occur prior to the analytical procedure are also critical to achieving quality outcomes. Registration to ISO9001:2000 includes independent site audits, and evidence that the location operates under a Quality Management System that meets international standards. At this time, many laboratories have ISO9001:2000 registration as evidence of the quality systems covering sample preparation activities. In the future, it is expected that specific sample preparation methods will be accredited under ISO17025.

Of course, ISO17025 accreditation or ISO9001:2000 certification is not a guarantee of quality results, but it is part of the body of evidence that the laboratory is capable of providing suitable data for your project.

Summary

It is important to recognize that quality and data suitability comes from a diverse set of activities. These activities are the dual responsibility of the person submitting the samples to the laboratory and the laboratory performing the work. Working together, the two groups can obtain the best outcome for both parties.

References

- Thompson, M. & Howarth, R.J. 1978. A new approach to the estimation of analytical precision. *Journal of Geochemical Exploration*, **9**, 23-30.
- Waltho, A.E. & Shaw W.J. 1999. Assay Program Management – Planning For Quality. *In: Good Project – Wrong Assays! Getting Sample Preparation and Assaying Right*. Seminar sponsored by MICA, AIG and AusIMM – Monday 26 July, 1999. Mineral Industry Consultants Association Technical Documents.

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