THE LABORATORY QUALITY ASSURANCE COMPONENT OF ENVIRONMENTAL MONITORING: A CASE STUDY INVOLVING SUBAQUEOUS TAILINGS RESEARCH[1]

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Abstract: Assessments concerning the environmental impact of mining projects are highly dependent on reliable low-level analyses of samples collected from the receiving environment. The analytical program must be designed to maximize the reliability of the data and also provide information concerning the reproducibility, accuracy, specificity, and sensitivity of test results.

In Canada, the MEND (Mine Environment Neutral Drainage) Program has sponsored projects pertaining to comprehensive monitoring of subaqueous tailings disposal. Lake sediments, lake water, and interstitial water samples were collected and then analyzed for a host of parameters (metals, anions, physical tests, etc.). The analyses were carried out using state-of-the-art procedures and instruments. A comprehensive quality assurance-quality control (QA-QC) program was incorporated into the study with all QA-QC subsequently reported. The studies provide an ideal example of what is required, in terms of analytical approach, for projects that require extremely low detection levels and are subject to rigorous scrutiny by regulatory agencies, the scientific community, and the public.

This paper presents the QA-QC approach taken for the subaqueous tailings disposal work by discussing method selection, determination of detection limits, use of reference materials, laboratory and field QC samples, and criteria for assessing QC results. Representative QC data are presented to demonstrate validation of methodology and to show that pre-determined criteria were met. The results on all blanks were below limits of detection, the results on reference materials met suppliers 95% acceptance criteria and replicate results agreed to within ±15% of a calculated mean.

Additional Key Words: quality assurance, quality control, chemical analyses, detection limits, monitoring.

Introduction

The demand for high quality environmental laboratory services has grown rapidly, especially during the past 10 yr. Significant technical advances have been made with services and capabilities now routinely available that only a few years ago were the domain of research. There has been a dramatic trend toward multi-component determinations at very low concentrations in complex sample matrices. These requirements place an increasing burden on the laboratory and its ability to produce quality results.

The field of environmental analytical chemistry is no doubt a scientific field that has become vitally important to society by providing the required data to support environmental studies. The work produced by environmental laboratories is "under a lens", and this close scrutiny has been increasing over the years.

Government regulations have been the driving force in the rapid growth of the field of environmental analytical chemistry. In North America this sector is sophisticated and is dominated by regulatory, research, and private-sector laboratories. Laboratory managers have had to become increasingly proactive in educating industry, regulators, and the public about the field of measurement science. This has been especially important as regulators establish new

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[1] Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994.

[2] From ASL Analytical Service Laboratories Ltd., Vancouver, B.C., V5L 1K5.

Proceedings America Society of Mining and Reclamation, 1993 pp 0260-269
DOI: 10.21000/JASMR94010260

https://doi.org/10.21000/JASMR94010260

environmental standards, compliance limits, and criteria. The setting of compliance limits will undoubtedly be based on many factors; the capability to measure must be among such considerations.

As users of environmental laboratories become more educated, their expectations become enhanced. Laboratories must now routinely provide evidence that they are accredited and/or certified and that they incorporate a comprehensive quality assurance program with all work programs.

Defining Laboratory Credibility

Laboratory credibility is established through "good laboratory practice" (GLP) which involves the complete management system for laboratory operation. While laboratories will, on their own initiative, establish GLP, it is necessary to obtain official recognition in the form of certification and accreditation. Certification is the formal recognition of the proficiency of a laboratory to carry out specific tests. It is determined by a procedure of submitting proficiency samples and defining the standards that must be met by the laboratories. Accreditation is a more comprehensive system that includes, along with a proficiency component, formal site visits by properly trained laboratory auditors.

In Canada, a national accreditation program has been established by CAEAL, or the Canadian Association of Environmental Analytical Laboratories (CAEAL 1993). In the United States, the ultimate goal is a national accreditation program, but at present accreditation is offered only in some of the individual States (IAETL 1993).

Defining Laboratory Quality

The U.S. Environmental Protection Agency (EPA) defines quality assurance (QA) as the total program for assuring the reliability of monitoring data. Quality control (QC) is defined as "the routine application of procedures for controlling the measurement process" (U.S. EPA 1986). In other words, QC consists of the technical, day-to-day activities used to assess the quality of the measurement process, while QA is the overall management system that ensures a QC program is in place and is working effectively.

Quality control is primarily concerned with the tools of the measurement system. This includes internal laboratory activities or quality control steps, and the preparation and analysis of quality control samples. Analysis of quality control samples allows the determination of precision, accuracy, sensitivity, and contamination control for the sampling and analysis process. There are two types of quality control (QC) samples: internal and external. Internal or laboratory quality control samples are prepared in the laboratory and include blanks, replicates, surrogates, spikes, and reference materials. These are defined in table 1. External or field quality control samples (table 1) are prepared in the field and should be handled exactly the same way as the collected environmental samples. The data produced from these samples provide information on the sampling techniques, sampling precision and bias, analyte stability, and cleanliness of sample containers.

The results of analysis of the QC samples provide valuable information on the precision (or repeatability) and the accuracy (how close the measurement is to the true value) of the analyses. The relationship between precision and accuracy is depicted in figure 1. It is the goal of analytical chemists to utilize analysis protocols that are both accurate and precise (category B of figure 1), but some tests required for regulatory purposes do not meet such criteria (Maynard 1990).

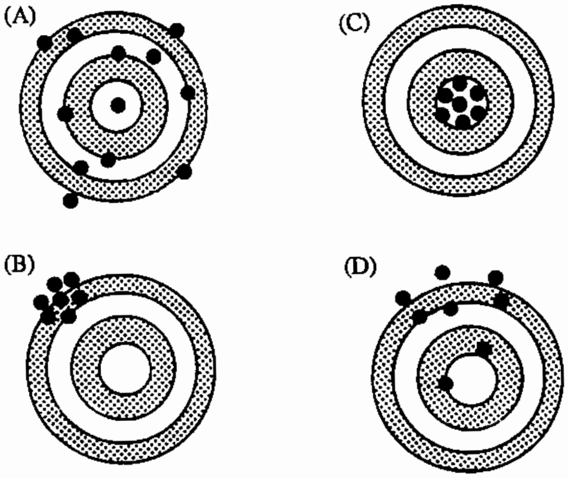

Figure 1. Relationship between precision and accuracy of analytical measurements. A, Poor precision, mean accuracy acceptable; B, good precision, good accuracy; C, good precision, poor accuracy; D, poor precision, poor accuracy.

Table 1. Definitions of laboratory and field QC samples

QC Sample	Definition	Purpose
Laboratory Method blank	Distilled water or "clean sample matrix" with added reagents, which is carried through procedure.	To monitor laboratory contamination.
Laboratory replicate	A homogenous sample that is split in the laboratory.	To monitor precision.
Surrogate compounds	Primarily used in organics analysis-consists of deuterium-labelled compounds or non-naturally-occurring fluorinated or brominated compounds which are added to the samples prior to their extraction or purging.	Quantified independently of the authentic compounds to monitor accuracy.
Sample spike	A sample to which a known amount of analyte is added.	To provide information on matrix effects and apparent accuracy.
Standard reference material (SRM)	A material that contains a known concentration of the analyte in question.	To determine accuracy.
Field Transportation blank	A sample container that contains distilled or de-ionized water and accompanies the sample containers into the field and is returned to the laboratory unopened.	To monitor contamination from the sample or shipping container.
Field blank	Distilled and de-ionized water that has been exposed to the same conditions and treatment as the environmental samples.	To monitor potential field sampling contamination.
Field analyte spike	Distilled and de-ionized water and preservation chemicals that are spiked in the field with a supplied solution containing a known concentration of the analytes of interest.	To monitor analyte degradation from the time of sampling.
Field replicate	A homogenous sample that is split in the field.	To monitor precision.

Defining Sensitivity

Sensitivity is an important component of monitoring programs required by the mining industry because ambient samples must be analyzed to detect trace (i.e., parts per billion or even parts per trillion) levels of certain analytes (especially metals). Sensitivity is defined by the detection limit, which is defined as the smallest amount of an analyte that can be measured with a stated confidence.

The American Chemical Society established a clear distinction between the detection and quantitation of an analyte (Keith et al. 1983). The limit of detection (LOD) was defined as the concentration equivalent to three times the standard deviation of the "noise" or background signal of an instrument. The limit of quantitation (LOQ) was defined as 10 times the standard deviation of the background signal.

The U.S. EPA further assessed this definition and stated that the signal-to-noise ratio provides a basis for estimating the sensitivity of the instrument alone (U.S. EPA 1985). The U.S. EPA protocols therefore required that detection limits be defined as full "method detection limits" or MDL's. The MDL is considered the most realistic approach to calculating a detection limit because it is based on a complete analytical procedure. The process involves an actual determination of detection limit by analyzing a number of low-level spikes in reagent grade water. The MDL method has been adopted by the U.S. EPA (U.S. EPA 1985) and the Canadian Association of Environmental Analytical Laboratories (Maynard 1992) and was used to define detection limits for the present program.

Summary of Monitoring Requirements for Subaqueous Tailings Disposal Project

In Canada, research has been undertaken to assess the potential impact of subaqueous disposal of mine tailings. Disposal of tailings materials under a water barrier, such as a natural lake, is thought to be one solution to stopping acid generation by preventing oxygen and bacterial action on the sulfide surfaces (Fraser and Robertson 1994).

The 1993 monitoring program involved two Canadian lakes: Anderson Lake in Manitoba and Buttle Lake in British Columbia. Both receive tailings from copper-lead-zinc mines. Details covering these studies are presented by Fraser and Robertson (1994) and by Pedersen et al. (1994).

The primary objective of the subaqueous tailings disposal monitoring program is to provide an estimation of the metal fluxes between the sediment and the water. The comprehensive sample collection process is described by Pedersen et al. (1994) and was carried out by designated field personnel. The samples collected include sediment cores, lake waters from various depths, and interstitial waters. The latter was collected by two techniques: (1) from a process involving coring, extrusion, and centrifugation and (2) utilizing in situ dialysis chambers.

All sample storage containers were cleaned and prepared by the laboratory, and the collected samples were subsequently returned within 1 to 2 days of collection. The analyses undertaken on these various samples are presented in table 2. In all cases, the methods were selected on the basis of providing optimum sensitivity, especially with respect to the various water samples, given that some parameters were expected to be at or below detection. The water quality methods are described in APHA (1992) and the sediment methods were based on EPA (1986).

Quality Program for Subaqueous Tailings Disposal Project

The subaqueous tailings disposal monitoring program requires extremely low detection limits, and the generated results are subject to rigorous scrutiny by regulatory agencies, the scientific community, and the public. For this reason the quality assurance program was expanded beyond what would be considered normal for routine environmental monitoring.

Laboratory QC

Laboratory QC samples were included with each analytical batch at a target level of about 40%, as outlined in table 3. Although batch sizes varied for different parameters and sample types, this approximate level of QC was maintained throughout the program.

Most of the interstitial water samples had insufficient volumes to replicate all of the analyses. It was, however, possible to replicate those analyses that only required low volumes (i.e., metals by graphite furnace atomic absorption spectrophotometry).

The reference materials used for this project are presented in table 4 and were selected on the basis that their matrix and concentration levels would approximate those of the actual samples. It was known, however, that these reference materials would not readily match the matrix of the interstitial water samples analyzed. For this reason, analyte spiking (for metals) was employed as additional QC.

Table 2. Analysis requirements for subaqueous tailings disposal project.

Parameter	**Lake water**	**Sediments**	**Interstitial waters**
Physical tests	✓	—	—
Anions	✓	—	—
Nutrients:			
NH3—N	✓	—	—
NO3—N	✓	—	—
Total N	—	✓	—
Total P	✓	—	—
Carbon (organic)	✓	—	—
Elements:			
As	✓	✓	✓
C	—	✓	—
Ca	✓	—	—
Cd	✓	✓	✓
Co	—	✓	—
Cr	—	✓	—
Cu	✓	✓	✓
Fe	✓	✓	✓
Hg	✓	✓	✓
K	✓	✓	—
Mg	✓	✓	—
Mn	✓	✓	✓
Na	✓	✓	—
Ni	—	✓	—
Pb	✓	✓	✓
S	—	✓	—
Zn	✓	✓	✓

✓ = analysis performed; — = analysis not performed.

Tabl. 3. Incorporation of quality control (QC) samples: target batch.

Sample type	Number per batch[1]
Actual samples	20
Method blanks	2
Sample replicates	3
Reference materials	3
% QC samples	40

[1] Total numbers varied for different parameters and sample types, but percentage QC was consistent.

For samples with analyte concentrations near or below the detection limit, a spike level of approximately four to five times the detection limit was employed. For samples with higher concentrations, the spike was carried out at two to three times the concentration in the actual sample.

The quality control data were evaluated on a batch-by-batch basis and were reported along with the sample results. Predetermined criteria were adopted for data acceptability as presented in table 5. If data did not meet the target criteria, but met the warning criteria, also listed in table 5, they were accepted, but detailed explanations were provided. If data had not met the warning criteria, the analytical batch would have been repeated.

The results of all the QC analyses were presented in the reports. A typical presentation showing blanks and reference materials is shown in table 6. These results are representative of the findings throughout the study. With few exceptions, the target criteria outlined in table 5 were met.

Table 4. Reference materials used for subaqueous tailings disposal project.

Reference material	Description
<u>Sediments</u>	
NRC[1] PACS-1	Harbour sediment certified for trace metals.
NRC[1] MESS-2	River estuary sediment certified for trace metals.
NRC[1] BSCC-1	River sediment certified for trace metals.
<u>Waters</u>	
NWRI[2] ANI-04	Lake water certified for general water quality.
NRWI[2] ION-96	Lake water certified for general water quality.
NWRI[2] TM-02	Lake water certified for trace metals.
NWRI[2] TM-21	Lake water certified for trace metals.
APG[3] (current lot)	Prepared water certified for trace metals.

[1] NRC = National Research Council of Canada (Ottawa, ON); [2] NWRI = National Water Research Institute (Burlington, ON); [3] APG = Analytical Products Group (Belpre, OH).

Table 5. Pre-determined criteria for data acceptability.

QC sample	Predetermined criteria
Target criteria	
Method blank	Below detection limit.
Laboratory replicate	Agree to within ±10% of a calculated mean[1].
Reference material	Meet manufacturers and/or suppliers' 95% acceptance criteria.
Warning criteria	
Method blank	Less than 5 times the detection limit[2].
Laboratory replicate	Agree to within ±15% of a calculated mean.
Reference material	Meet calculated 99% acceptance criteria.

[1] Only when sample concentrations are greater than 10 times the detection limit; [2] Method blank results must be less than the lowest reported result.

Table 6. Representative results for laboratory blanks and reference materials.[1]

Parameter	Results-analysis of blanks (range)[2]	Results-analysis of reference materials (range)[3]	Reference material target values
Conductivity	1.3-2.7	[4]597-617	607.3±33.7
Alkalinity	<1.0-<1.0	[4]84.6-86.8	79.6±5.52
Chloride	<.5 -<.5	[4]57-2-57.9	56.8±3.59
Sulfate	<1.0-<1.0	[4]114-116	112.3±10.2
Nitrate	<.005-<.005	[4]1.96-2.02	2.03±0.6
Cd	<.0002-<.0002	[5].0205-.0215	0.0210±0.0035
Cu	<.0005-<.0005	[5].0500-.0610	0.0541±0.0098
Fe	<.003-<.003	[5].043-.053	0.050±0.016
Pb	<.0005-<.0005	[5].0219-.0285	0.0259±0.0052
Hg	<.00001-<.00001	[6].00170-.00190	0.00173±0.00039

[1] All results are expressed as milligrams per liter (ppm); < = less than the stated detection limit; [2] n = 4; [3] n = 5;
[4] NWRI RM-ANI-04 - see table 4; [5] NWRI TM-02 - see table 4; [6] APG Lot 10369 - see table 4.

Detection Limit Validation

It was recognized that very low detection limits would be required for the subaqueous tailings disposal monitoring project. The methods employed were selected to provide optimum detection limits. All detection limits quoted for this project are MDL's. In most cases they were reverified specifically for this project. To determine the MDL's, or method detection limits, a laboratory standard, containing the analyte of interest was prepared at a concentration of five times the proposed detection limit. Eight replicates were then processed through the entire analytical procedure. Using the eight measurements obtained, the mean and standard deviation were calculated, and the MDL was computed as follows (EPA 1985):

$$\mathrm{MDL} = S \bullet t\,(n-1,\alpha=0.99),$$

where MDL = the method detection limit,
t = the Student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (for eight replicates, t=2.996),
and S = standard deviation of the replicate analyses.

Table 7 lists the reverified MDL's.

Field QC

The sampling program for the subaqueous tailings disposal monitoring required extensive field handling of the samples. All samples were prepared in an oxygen-free environment to prevent rapid oxidation of reduced species. This handling included filtration of lake waters, coring and extrusion to prepare interstitial waters, and sediment core fractionations. It was necessary to employ a rigorous field QA-QC program to demonstrate adequate contamination control and representative sample preparation.

Table 7. Validation of detection limits for trace metals.[1]

Parameters	Target detection limit[2]	Spike Level[3]	Number of Replicates	Mean	Standard deviation (S)	Calculated method detection limit
Cd	.0002	.0010	8	.00091	.00004	.0001
Cu	.0005	.0020	8	.0021	.0001	.0004
Fe	.001	.005	8	.006	.001	.003
Pb	.0005	.0020	8	.0019	.0001	.0003
Mn	.001	.005	8	.0045	.0000	.0001
Zn	.001	.005	8	.0042	.0001	.0003

[1] All results are in milligrams per liter (ppm); [2] As agreed to prior to initiating project; [3] Concentration into reagent- grade water.

Transportation blanks (normally 2 for every 20 samples) were prepared in the laboratory and sent to the field. These samples were analyzed upon their return to the laboratory. Sample replicates were collected in the field (about 2 to 3 for every 20 samples) and submitted to the laboratory as blind samples. Field filter blanks were also prepared using field filtration equipment (approximately 1 for every 20 samples).

Due to the ice on the surface and the shallow nature of the lake being studied (Anderson Lake, MB), a unique water column sampler was designed for this project. This sampler contained long lines of tubing to obtain samples from specific depths. There was concern that metals could become adsorbed onto the tubing during this process. It was also necessary to investigate the possibility of cross contamination between samples. Prior to sample collection the following laboratory-prepared solutions were pumped through one of the sampling lines:

- Distilled and de-ionized water (SAMPLER BLANK #1).
- A solution of known metal concentrations (0.2 to 5 ppb) to assess possibility of adsorption (SAMPLER SPIKE #1)..
- Then, after rinsing, a second volume of distilled and de-ionized water (SAMPLER BLANK #2).
- A solution of known concentrations that matched the more contaminated locations in Anderson Lake to assess possibility of carryover (SAMPLER SPIKE #2).
- Then, after rinsing, a third volume of distilled and de-ionized water as a second step in assessing carryover (SAMPLER BLANK #3).

All of the resulting solutions were then analyzed, and the results are presented in table 8.

Table 3. Representative results of analysis of field sampler blanks and spikes.[1]

Parameter	Blank #1	Spike #1 (low)	Blank #2	Spike #2 (high)	Blank #3
As	<.0001	.0049 (98)	<.0001	—	<.0001
Cd	<.0002	.0060 (120)	<.0002	—	<.0002
Cu	<.0005	.0047 (94)	<.0005	.052 (104)	<.0005
Fe	<.003	.005 (100)	<.003	—	<.003
Pb	<.0005	.0048 (96)	<.0005	—	<.0005
Mn	<.001	.004 (80)	<.001	—	<.001
Hg	<.00001	.00025 (71)	<.00001	—	<.00001
Zn	<.001	.002 (100)	<.001	.496(99)	<.001

[1] All results are expressed as milligrams per litre (ppm); < = less than the stated detection limit; values in parentheses are % recovery for the spike.

Summary

The subaqueous tailings disposal monitoring program described in this paper provided unique challenges with respect to sampling design, sample collection, sample analysis, and data management. Specifically, concerning the laboratory component, the procedures had to provide optimum detection limits on complex sample matrices, many of which (the interstitial water samples) were extremely low in volume. It was necessary to incorporate a comprehensive quality program to ensure that these challenges were properly met. The quality control data generated from these studies provided reliable information concerning the precision, accuracy, and sensitivity of the test procedures selected.

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Acknowledgements

This work was supported by the British Columbia (BC) Ministry of Energy, Mines and Petroleum Resources, CANMET, Environment Canada, Hudson Bay Mining and Smelting, and Placer Dome through the BC Acid Mine Drainage and Mine Environment Neutral Drainage (MEND) task forces.

We gratefully acknowledge the support of individuals involved in the actual study: W. Fraser of Hudson Bay Mining and Smelting, J. Robertson of Placer Dome, T. Pedersen and J. McNee of University of BC, and D. Flather of Rescan Environmental Services. We also acknowledge the assistance of Carol Hyde, who prepared this manuscript.