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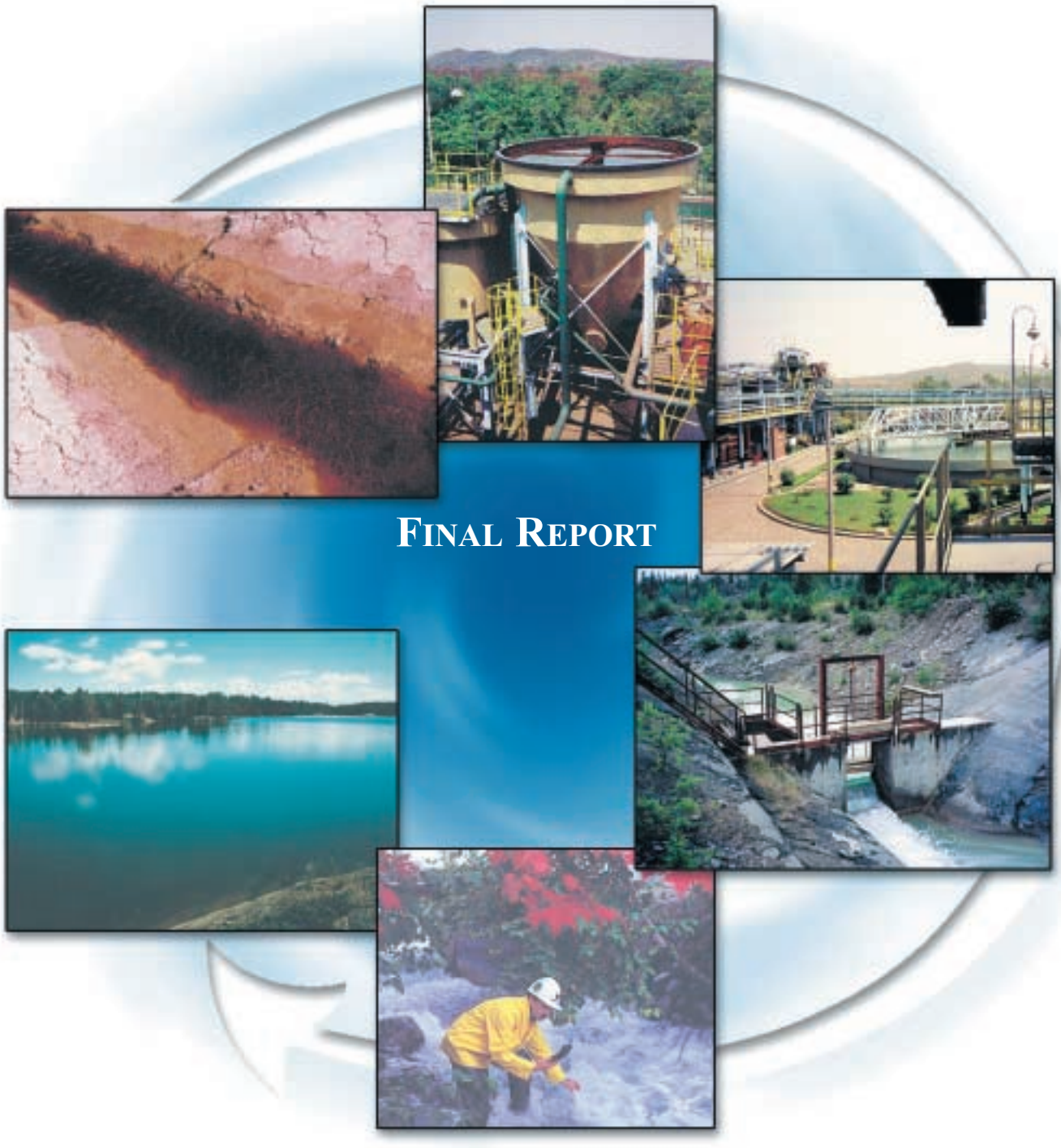
Guidance Document for the Sampling and Analysis of Metal Mining Effluents



Final Report

EPS 2/MM/5 – April 2001
Minerals and Metals Division
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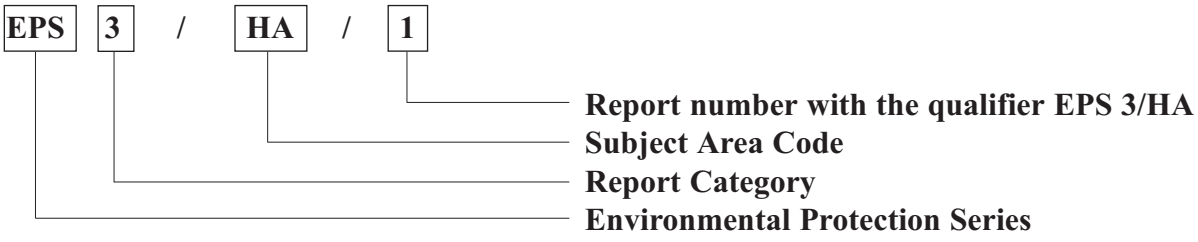

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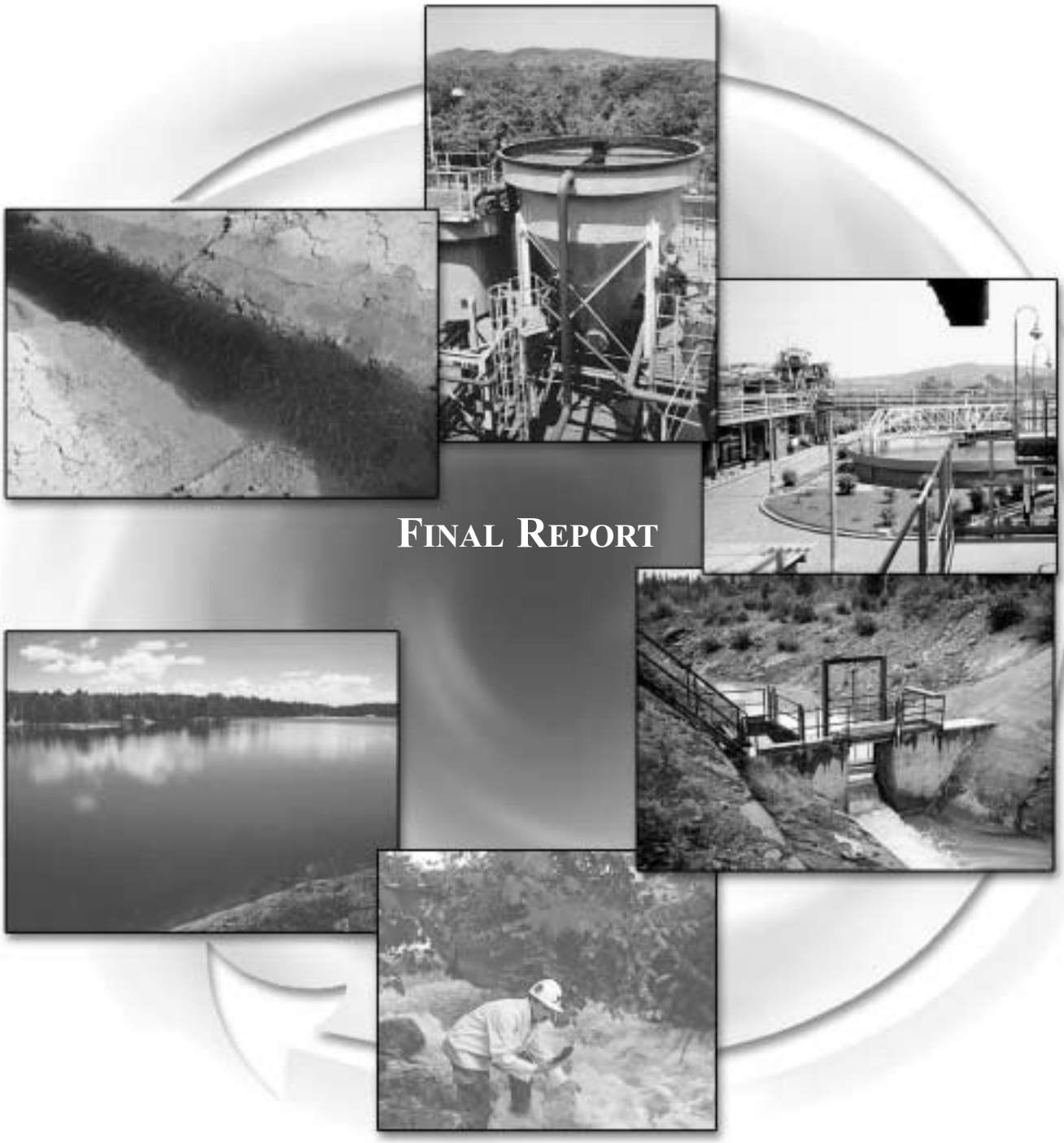

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ABSTRACT

This document discusses sampling and chemical analysis considerations and procedures for use with metal mining effluents. The document stresses performance-based methods and how such methods should be applied to the mining industry. Data quality measures and objectives and overall quality control procedures are outlined for effluent sampling and analysis. References to suitable analytical methods are also provided.

The information presented is to support implementation of the proposed *Metal Mining Effluent Regulations* (MMER) under the *Fisheries Act* by Environment Canada.

More information on the *Metal Mining Effluent Regulations* and associated guidance documents is available on Environment Canada's Green Lane at www.ec.gc.ca/nopp/metals/english/index.cfm .

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SUMMARY

This document outlines performance-based method criteria to support implementation of activities related to the sampling and analysis of metal mining effluents under the proposed *Metal Mining Effluent Regulations* (MMER). The performance-based approach permits flexibility in the selection of procedures, as long as the target data quality objectives (DQOs) are achieved, and this can be demonstrated by reporting of appropriate quality assurance/quality control (QA/QC) data. The document identifies target DQOs and provides guidance on QA/QC activities by which data quality can be tracked and reported. It suggests sampling and analytical techniques and provides references to suitable analytical methods, which can be used to achieve the desired data quality.

Target DQOs are presented in terms of analytical precision and accuracy, as well as method detection limits (MDLs) and calibration criteria for a variety of chemical parameters relevant to metal mining effluents. These targets provide a benchmark against which the quality of the data can be evaluated. Data quality evaluations may trigger investigative or corrective actions and provide a basis for flagging any data of lesser quality for special consideration by data users.

Sampling techniques are discussed with respect to appropriate sampling locations and frequencies, sample volumes, containers, preservatives, holding times and field QC samples. The use of Standard Operating Procedures (SOPs) for sampling is recommended, and an outline is provided of information typically included in sampling SOPs. The importance of documenting the sampling effort is emphasized, and guidance is provided on use of field log books, sample labeling, shipping and custody records, and reporting of the sampling information.

Analytical techniques are discussed with respect to appropriate sample preparation, method principles and laboratory QC samples. The use of SOPs for analysis is recommended, and an outline is provided for information typically included in analytical SOPs. Method validation is discussed and use of validated methods is recommended. Guidance is provided on components of both internal and external QC programs to ensure that DQOs are achieved and that data quality can be demonstrated. The elements of complete data reporting are described. Laboratory accreditation is discussed in the context of external QC, and use of accredited laboratories is recommended.

1.0 INTRODUCTION

The purpose of this document is to outline performance-based method criteria to support implementation of activities related to the sampling and analysis of metal mine effluents under the proposed *Metal Mining Effluent Regulations* (MMER) that are to be promulgated by Environment Canada under the *Fisheries Act*. Data quality objectives (DQOs), quality assurance and quality control (QA/QC) criteria and examples of acceptable analytical methodology are included. The intent of the document is to provide performance-based guidance permitting flexibility in the procedures selected, examples of objectives to be achieved and suggestions as to how to make the process work. This document is intended for the use of mine environmental and operational staff and managers, Environment Canada Inspection and Enforcement personnel, and members of provincial environmental agencies and territorial water boards.

This document does not address water quality monitoring studies in the receiving environment. Recommended procedures and methods for receiving water quality monitoring are presented in Environment Canada's *Metal Mining Guidance for Aquatic Environmental Effects Monitoring*.

Sampling and analysis methods suggested in this document should not be considered as restrictive, but should be viewed rather as suggestions of methods to be used when there is no compelling reason to use alternatives. If the range of possibilities can be narrowed to a few reliable methods, the resulting data might be more comparable than they would be if many methods were used.

The performance-based approach allows organizations to adapt a method appropriate to their situation. The options chosen should, however, be documented as Analytical Methods or Standard Operating Procedures and used consistently. They should be available for review on request by an Inspector under the *Fisheries Act* or other federal or provincial/territorial legislation.

Analysis methods must be implemented by the regulated industry and their laboratories to provide data to comply with the proposed MMER. Some chemical parameters are regulated, with concentration limits specified in the proposed MMER, while others are characterization parameters. The latter do not have regulatory limits. Target DQOs for analysis are listed in Table 1.

Table 1 Target Analytical Data Quality Objectives for Metal Mining Effluents

Chemical Parameter	Precision	Accuracy	MDL[4]
Arsenic[1]	10% RSD[2]	100 ± 10%[3]	0.01 mg/L
Copper[1]	10% RSD	100 ± 10%	0.01 mg/L
Lead[1]	10% RSD	100 ± 10%	0.03 mg/L
Nickel[1]	10% RSD	100 ± 10%	0.02 mg/L
Zinc[1]	10% RSD	100 ± 10%	0.01 mg/L
Total Suspended Solids[1]	15% RSD	100 ± 15%	2 mg/L
Radium 226 (total)[1]	10% RSD	100 ± 10%	0.01 Bq/L
Total Cyanide[1]	10% RSD	100 ± 10%	0.01 mg/L
pH[1]	0.1 pH unit	0.1 pH unit	N/A
Aluminum	10% RSD	100 ± 10%	0.03 mg/L
Cadmium	10% RSD	100 ± 10%	0.002 mg/L
Iron	10% RSD	100 ± 10%	0.02 mg/L
Manganese	10% RSD	100 ± 10%	0.05 mg/L
Molybdenum	10% RSD	100 ± 10%	0.02 mg/L
Mercury	10% RSD	100 ± 10%	0.0001 mg/L
Selenium	10% RSD	100 ± 10%	0.005 mg/L
Uranium	10% RSD	100 ± 10%	0.02 mg/L
Fluoride	10% RSD	100 ± 10%	0.1 mg/L
Total Ammonia Nitrogen	10% RSD	100 ± 10%	0.25 mg/L
Nitrate+Nitrite	10% RSD	100 ± 10%	0.25 mg/L
Total Phosphorus	10% RSD	100 ± 10%	0.1 mg/L
Chloride	10% RSD	100 ± 10%	2.0 mg/L
Sulphate	10% RSD	100 ± 10%	5.0 mg/L
Calcium	10% RSD	100 ± 10%	0.2 mg/L
Magnesium	10% RSD	100 ± 10%	0.05 mg/L
Potassium	10% RSD	100 ± 10%	1.0 mg/L
Sodium	10% RSD	100 ± 10%	0.1 mg/L
Conductivity	10% RSD	100 ± 10%	5 µS/cm
Hardness	10% RSD	100 ± 10%	1.0 mg/L
Alkalinity	10% RSD	100 ± 10%	1.0 mg/L
Acidity	10% RSD	100 ± 10%	1.0 mg/L

NOTES:
(1) Prescribed deleterious substance under the proposed MMER; other parameters for characterization only.
(2) Relative standard deviation (RSD) at concentrations 10 times above the Method Detection Limit (MDL).
(3) Analyte recovery at concentrations 10 times above MDL.
(4) Mines participating in the MISA program should achieve MISA target MDLs if these are lower than those in Table 1.
N/A: Not applicable.

2.0 PERFORMANCE-BASED METHODS

A performance-based method specifies the data quality objectives (DQOs) that are to be achieved but leaves the laboratory and its customer to determine the chemical and instrumental procedures by which the DQOs are to be met. DQOs and performance standards are established based on the needs of the end users of the data. For the purposes of this Guidance Document, the end users are the regulated companies, Environment Canada inspectors and provincial compliance officers. Some DQOs can be specified as quantitative values, while others are qualitative descriptions. In either case a description of the procedure to be followed if the DQO is met or not met should be specified in Standard Operating Procedures. When DQOs are clearly defined, it is easy for the company or compliance officers to evaluate whether the criteria were met and to accept the data or ask for reruns.

The goal of a performance-based method is to provide reasonable flexibility in the choice of analytical method and instrument used. This allows for technical advances in measurement science to be implemented in the future and permits the analyst to modify methods to deal with the realities of the sample such as matrix effects, interferences, limitations in sample size, etc. It also allows for continuous improvement in the quality of laboratory operations.

DQOs and performance standards are needed for such method characteristics as precision, accuracy, method detection limit (MDL) and method validation for applicable sample types. Each of these method characteristics needs to have a logical, consistent and generally accepted definition that is used by both the laboratory and data user. The data quality results determined for each of these attributes should be within the required performance specifications needed by the end user of the data. If DQOs cannot be met due to problems with specific samples, the results for those samples should be flagged and explained in the data report.

Laboratories must demonstrate clearly their ability to work within a performance-based system. This is most easily done by participating in an accreditation program operated under ISO/IEC Guide 25, General Requirements for the Competence of Calibration and Testing Laboratories; taking part in relevant interlaboratory performance evaluation (PE) programs; and using a documented method validation process. ISO Standard 17025 will replace ISO/IEC Guide 25. The Canadian standard, numbered CAN-P-4D, is identical and will be available from the Standards Council of Canada web site (www.scc.ca).

3.0 DEFINITIONS

Many terms used in chemistry and in the reporting of chemical data are loosely defined or have a number of different possible definitions. Terms such as detection limit and quality control are commonly used, but often have quite different meanings to different people. It is important that the laboratory, the regulated company and compliance officers agree upon a common set of definitions. A glossary of technical terms relevant to the proposed MMER can be found in Appendix 1.

4.0 PARAMETERS MEASURED

Parameters relevant to the monitoring and characterization of metal mining effluents are listed in Table 2. Chemical Abstracts Service (CAS) numbers and required reporting units for the proposed MMER are also shown.

The regulated parameters are those recommended by the Assessment of the Aquatic Effects of Mining in Canada (AQUAMIN) final report (April 30, 1996). The rationale for these parameters is outlined in the AQUAMIN report. Many of the characterization parameters were also identified in the AQUAMIN report. These parameters are of interest either as effluent tracers or as modifiers of effluent toxicity. It should be noted that AQUAMIN referred to Total Suspended Matter (TSM), whereas this document and the proposed MMER refer to Total Suspended Solids (TSS). These two parameter names refer to the same parameter.

It should be noted that analyses of all of these parameters are carried out on the total unfiltered sample. Therefore, except for TSS, the analytical result will include all soluble and particulate matter. Arsenic includes species of all valences. Cyanide is the total cyanide including all the metal complexes of cyanide.

Table 2 Parameters Measured

Chemical Parameter	Symbol	CAS #	Reporting Units
Arsenic(1)	As	7440-38-2	mg/L
Copper(1)	Cu	7440-50-8	mg/L
Lead(1)	Pb	7439-92-1	mg/L
Nickel(1)	Ni	7440-02-0	mg/L
Zinc(1)	Zn	7440-66-6	mg/L
Total Suspended Solids(1)(2)	TSS	None	mg/L
Radium 226 (total)(1)	^{226}Ra	None	Bq/L
Total Cyanide(1)	CN^-	57-12-5	mg/L
pH(1)	pH	None	pH units
Aluminum	Al	7429-90-5	mg/L
Cadmium	Cd	7440-43-9	mg/L
Iron	Fe	7439-89-6	mg/L
Manganese	Mn	7439-96-5	mg/L
Molybdenum	Mo	7439-98-7	mg/L
Mercury	Hg	7439-97-6	mg/L
Selenium	Se	7782-49-2	mg/L
Uranium	U	7440-61-1	mg/L
Fluoride	Fl	None	mg/L
Total Ammonia Nitrogen	Am-N	None	mg/L
Nitrate+Nitrite	N-N	None	mg/L
Total Phosphorus	TP	7723-14-0	mg/L
Chloride	Cl	None	mg/L
Sulphate	SO_4	None	mg/L
Calcium	Ca	7440-70-2	mg/L
Magnesium	Mg	7439-95-4	mg/L
Potassium	K	7440-09-7	mg/L
Sodium	Na	None	mg/L
Conductivity	Cond	None	µS/cm
Hardness	Hardness	None	mg/L
Alkalinity	Alk	None	mg/L
Acidity	Acidity	None	mg/L

NOTES:

(1) Prescribed deleterious substance under the proposed MMER; other parameters for characterization only.

(2) TSS is defined as any solid matter that is retained on a 1.5 micron pore filter paper after sample filtration and oven drying. The filter may not retain small colloidal particles.

5.0 Sample Types

Performance-based criteria found in this document apply to the final effluent discharge points of all Canadian metal mines subject to the proposed MMER, including base metal, iron ore, uranium and gold mines.

Sample types may include mine water effluent, mill process effluent, tailings impoundment area effluent, treatment pond or treatment facility effluent, seepage and surface drainage. Specifically excluded are in-plant samples such as effluents from unit operations, non-contact cooling water and recycle water. Samples of receiving water and the aquatic environment near the mine are also excluded. Requirements for water quality monitoring in the receiving environment are addressed through the metal mining Environmental Effects Monitoring (EEM) program.

6.0 SAMPLING

Personnel experienced in sampling activities and working under standard documented operating conditions should do the sampling. The objective of sampling is to collect a representative set of samples that is suitable for chemical analysis to assess compliance with the limits set by the regulations. Since compliance decisions are made from analysis of the sample, it is essential that the sample be properly taken in a quality-controlled manner for submission to a laboratory and that the sample be representative of the effluent stream being sampled.

The final discharge point in the metal mining industry is very often from a tailings pond. Tailings ponds typically have residence times measured in weeks or months. With such long retention times, the effluent chemistries are often fairly stable; changes are typically observed over the course of several days or weeks rather than hourly or daily. For this reason, weekly grab sampling is considered appropriate for the purpose of monitoring compliance with the proposed MMER, provided that the sampling location has been demonstrated to be the discharge of a pond with adequate retention time to provide consistency in the quality of the effluent. Grab samples can also highlight transient effects, which can occur with mining effluents.

Composite samples are also considered suitable in the proposed MMER. These can be collected using automatic sampling equipment (e.g., ISCO) with compositing over a 7- to 24-hour period, again with a weekly frequency. Samplers should be programmed to collect equal aliquots at regular intervals (e.g., hourly) over the compositing period. Composite samples can give a better representation of average effluent quality, particularly when transient effects are present.

Sampling in practice often requires work to be done under less than ideal conditions. The quality of data generated is closely related to the care given to the sampling equipment, as well as the expertise and training of the sampling staff. There are many considerations in collection of suitable samples. Site conditions often require changes to the sampling plans. Success is dependent upon keeping the goals of the sampling operation in mind, then recording and communicating any deviations from sampling plans, and their reasons, to the parties involved. A good knowledge of the principles of environmental sampling and a documented QC program will provide solutions to most sampling problems.

Although it is expected that the discharge samples from Canadian mines will not be hazardous to sampling personnel, some of the process chemicals and effluent constituents such as arsenic and cyanide can pose a personal hazard if they are in high concentration. The acids and bases used for sample preservation are hazardous, so samplers should consult material safety data sheets (MSDSs) for safe handling of these chemicals. The sampling locations may pose hazards to personnel if they are in remote or cold areas. A sampling plan should address these and other relevant safety issues.

The most common quality problems introduced in sampling are the mislabeling or switching of bottles, failure to add proper preservatives, improper storage conditions, sample contamination from sampling equipment or other sources, and holding time exceedance. It is recognized that the distance between the sampling point and the laboratory may make the time between sampling and analysis longer than recommended. This should be noted in the report. Each of these items should be addressed in the sampling plan.

Detailed information on sampling is available from several sources including the Ontario Ministry of Environment's *Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater* (1994; a draft 1998 version is available) and Water Technology International's *Multi-Media Sampling Training Course Reference Manual* (1996). Samplers can also refer to *The Inspector's Guide: A Sampling Manual and Reference Guide for Environment Canada Inspectors* (1995) and *The Inspector's Safety Guide: A Field Guide for Environment Canada Inspectors* (1995).

6.1 Sampling – Standard Operating Procedures

Sampling should be planned and executed under Standard Operating Procedures (SOPs). SOPs should be written to describe exactly how, where and when a sample is to be taken and what happens to that sample. The goal of sampling SOPs is to ensure consistency of sampling over time, particularly when different people take the samples.

A sampling SOP should provide very specific instructions to the sampler on where the sample is to be taken, how to take the sample, and how to preserve and handle the sample. Appropriate sample collection, preservation and handling methods will vary by parameter (Table 3). The SOP also covers sampling materials, field QC samples, equipment calibration and use, transportation of the sample, submission to the laboratory, chain of custody and documentation required. In the event that a company has more than one effluent discharge point at a mine, a separate SOP or section of the SOP should address the specifics of sampling each discharge such as access, safety and transportation of the samples. Sampling SOPs should also discuss personnel qualifications and training, and specify safety procedures.

Although a sampling SOP is necessary, it is acceptable for the SOP to cite other documents for many of the details listed above. Failure to use a sampling SOP often results in inconsistent sampling over time, particularly when there are changes in sampling staff. Improvements in sampling and solutions to sampling problems are difficult to achieve or demonstrate without an SOP or equivalent documentation.

A suggested format for a sampling SOP is presented in Appendix 2.

6.2 Field QC Samples and Measurements

Field QC samples are used to determine if any errors are being introduced during the sampling process so that corrective action can be taken if necessary. It should be noted that field QC samples are distinct from laboratory QC samples, as they measure sampling effects in addition to laboratory effects.

The purpose of field QC samples is to establish background contamination and precision of sampling. This can be accomplished using field blanks and field duplicates. Field blanks are prepared by obtaining blank water from the laboratory to be used, sending it to the sampling location, handling the blank water with the sampling equipment where appropriate, and preserving it as appropriate in the field. This field blank should be treated just like the actual samples to the extent possible.

Field duplicates are two separate samples taken at the same time and location. Field duplicates are used to evaluate homogeneity of the sample stream and the ability of the sampling system to take the sample the same way every time. A field duplicate must be a completely separate sample taken from the sampling location, not a split of a single sample into two bottles. Split samples can be used to assess bias attributed to sub-sampling in the field.

Other types of QC samples such as field spikes can be used to observe sample stability during shipment and storage if deemed necessary, but the parameters regulated under the proposed MMER are unlikely to exhibit stability problems if samples are taken and preserved according to generally accepted procedures.

The number of field QC samples can be derived from statistical considerations. However, such calculations are often difficult, so general quality control rules based on experience can apply. Generally, field QC samples should make up 5% to 10% of the total number of samples. Thus, in an annual set of 52 final effluent samples, there should be three to five sets of QC samples, or approximately one set per quarter. The proportion of QC samples can be increased if necessary to monitor errors due to sampling and matrix heterogeneity, or if the total number of samples taken is low.

If field QC samples are not used, any inaccuracy or imprecision introduced in the sampling process will go undetected, which may lead to inappropriate characterization of the effluent.

Suggested field QC samples for each parameter are listed in Table 3.

Field measurements of pH and conductivity can be useful for quality assurance purposes. These measurements are recorded and should be in reasonable agreement with laboratory results. If they are not, a change in the sample prior to analysis or a sample mix-up or data transcription error may be indicated.

6.3 Location

The sampling location(s) under the proposed MMER must be the final discharge point(s) that is (are) identified by the owner or operator of the mine in accordance with the regulations. **Provisions must be made to collect a representative sample in the same manner and from the same location every time.** The sampling location must be selected where there

Table 3 Appropriate Sampling Method Specifications

Chemical Parameter	Bottle Type	Preservative	Typical Sample Volume	Maximum Storage Time	Sample Type	Field QC Samples
As[1]	Glass or plastic	HNO_3 to pH <2	100 mL	30 days	Grab or Composite	Blank, Duplicate
Cu[1]	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Pb[1]	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Ni[1]	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Zn[1]	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
TSS[1]	Glass or plastic	None	500 mL	7 days at 4°C	Grab or Composite	Blank, Duplicate
^{226}Ra[1]	Glass or plastic	HNO_3 to pH <2	1000 mL	30 days	Grab or Composite	Blank, Duplicate
CN^-[1]	Glass or plastic	NaOH to pH >12	500 mL	7 days	Grab or Composite	Blank, Duplicate
pH	Glass or plastic	None	100 mL	4 days at 4°C	Grab or Composite	Duplicate, Field Measure
Al	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Cd	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Fe	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Mn	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Mo	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Hg	Glass with plastic-lined cap	HNO_3 to pH <2 and 0.5 mL $K_2Cr_2O_7$ or BrCl	200 mL	7 days	Grab or Composite	Blank, Duplicate
Se	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
U	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
Fl	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate
Am-N	Glass or plastic	H_2SO_4 to pH 1.5 to 2	100 mL	10 days	Grab or Composite	Blank, Duplicate
N-N	Glass or plastic	None	50 mL	5 days	Grab or Composite	Blank, Duplicate
TP	Glass or plastic	H_2SO_4 to pH 1.5 to 2	75 mL	30 days	Grab or Composite	Blank, Duplicate
Cl	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate
SO_4	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate

Table 3 Appropriate Sampling Method Specifications (cont'd)

Chemical Parameter	Bottle Type	Preservative	Typical Sample Volume	Maximum Storage Time	Sample Type	Field QC Samples
Ca	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate
Mg	Glass or plastic	HNO_3 to pH <2	500 mL	30 days	Grab or Composite	Blank, Duplicate
K	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate
Na	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate
Conductivity	Glass or plastic	None	75 mL	4 days	Grab or Composite	Blank, Duplicate Field Measure
Hardness	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate
Alkalinity	Glass or plastic	None	250 mL	1 day	Grab or Composite	Blank, Duplicate
Acidity	Glass or plastic	None	50 mL	28 days	Grab or Composite	Blank, Duplicate

NOTES:
Analytes with the same bottle and preservation requirements can be determined from the same bottle as long as sufficient volume is collected and storage times are respected. See also Table 5, note 3.
(1) Prescribed deleterious substance under the proposed MMER; other parameters for characterization only.

is reasonable mixing or turbulence so that it is possible to collect a representative sample of any solids, floating materials or separate phases that might exist in the sample stream. The sampling location must also represent the stream in which the flow is measured. These factors should be documented in the sampling SOP.

6.4 Frequency

The frequency of sampling and analysis is specified in the proposed MMER to be weekly, at least initially, for regulated parameters. However, there is provision to reduce the frequency of analysis for some parameters based on the results obtained.

6.5 Sample Handling and Preservation

Samples must be collected and preserved such that degradation or alteration of the sample is avoided. This involves using the containers and sample preservation chemicals listed in Table 3, and storing and transporting samples to a laboratory as soon as possible to complete chemical analysis within generally accepted holding times.

For metal mining effluents, it is generally acceptable to use high-density polyethylene (HDPE) containers as they are less expensive than glass and are less likely to break, especially if samples are inadvertently frozen. Glass bottles are also acceptable. Sample bottles should preferably be new and unused and should be purchased as certified clean. If bottles are to be reused, they should be cleaned and proofed by a documented cleaning procedure with a bottle lot number control system. If bottles are reused, cleanliness must be demonstrated by rinse analysis of cleaned bottles and by the use of blanks. Frequency of field blanks should be at least 5% of all samples, as noted in Section 6.2.

Chemical preservatives must be added where appropriate in quantities that do not materially dilute the samples, generally at less than 1% of the total sample volume. American Chemical Society (ACS) reagent or better grade chemicals should be used as preservatives to avoid introducing contamination. The same preservatives should be used for the samples and the field blanks. Bottles should generally not be precharged with preservatives, as concentrated preservatives can cause leaching of metals and other chemicals from the plastic. Zinc and lead have been used as lubricants in the production and stabilization of plastic bottles and, if present, may leach into the sample. Preservatives should be tested for contamination by the laboratory before use. In addition, preservatives should be added to reagent water and stored in the laboratory as reagent blanks to be analyzed concurrently with regular samples.

Samples should generally be cooled to between 2°C and 10°C for shipping and storage as soon as possible after collection. This is critical for pH, cyanide and TSS. Determination of pH should be as soon as possible after arrival in the laboratory and definitely within the maximum holding time.

Decisions need to be made on what to do with extraneous material in the sample such as sticks, floating material and grease. If these are deemed to be part of the sample, they should be included and the sampling system designed to include them. If they are to be excluded, this must be specified in the sampling SOP.

Samples must be clearly labeled with the date and time of sampling, location or source of the sample, whether the sample is a grab or composite, what preservatives were used, analysis required and the identity of the individual who collected the sample. The sample must be labeled in a manner that clearly identifies it and distinguishes it from all other samples. Labels must be filled out in indelible ink and fixed to the sample container such that they will not fall off when wet or during transport.

When a sample could be considered as evidence in an investigation, rigorous chain of custody procedures are required. Chain of custody requires demonstration that samples have not been tampered with at any point in handling and shipping and that the individuals in charge of the samples can be identified at every stage in the sampling and analysis operation. Sample labels, chain of custody forms and log books should be correctly and legibly filled out in ink, and the sample should have an intact chain of custody seal applied to the bottle cap. Individuals who receive the sample should sign the chain of custody form and understand the chain of custody procedures. If samples are to be shipped by courier under chain of custody, the samples should be sealed in a container with a chain of custody seal, which can be verified as intact (or not) by the receiver of the samples. Further details can be found in Environment Canada or provincial inspectors' manuals.

6.6 Field Log Book

The field log book is an integral part of the sampling program and forms the basis of the sampling record. Items documented in the log book are highly relevant to interpreting the subsequent laboratory data. These items should include recording of any measurements made in the field such as pH or conductivity, the label information noted above, any deviations from the sampling plan, and any other relevant observations about the sample or the sampling location. Sample handling requirements should be part of the sampling SOP and listed in the sampler's field log book.

Some of the most common deficiencies in field log books are failure to make planning notes, failure to make notes at the time events occur, failure to sign and date entries, and having too many people use the log book. The log book should stay in the custody of the sampler and should not be shipped with the samples. However, photocopies of relevant pages can be sent along with the samples to the laboratory if not all details are transferred to a laboratory submission sheet.

6.7 Minimum Volume

Sample volumes are important, since the sample taken must be large enough to be representative of such discharge characteristics as solids and floating material. The samples must also be of sufficient volume to complete all the chemical analyses required and accommodate laboratory quality control samples. Typical sample volumes are shown in Table 3, but volumes required should first be confirmed with the laboratory. It is often a good idea to send twice the volume of sample required to accommodate retests and quality control samples.

6.8 Sample Packaging and Shipping

Samples collected in the field must be sent quickly and safely to a laboratory for analysis. No matter how they are sent, samples should be packaged carefully so as to arrive unbroken. Broken samples not only represent a waste of time and money, they also constitute a safety hazard to the individual who unpacks them. Moreover, the labels of all the samples can be obliterated by one leaking bottle. Samples that are to be analyzed for pH and TSS should be sent in a cooler with ice or ice packs to keep them cool during shipping.

Samples should be sent along with corresponding request for analysis forms or chain of custody forms supplied by the laboratory that is to receive the samples. These forms should be filled out completely and should specify which analyses are requested, identify that the samples are for regulatory purposes, and list any other specific requirements.

In Canada, the *Transport of Dangerous Goods Act* (TDG) requires that each shipment of dangerous material be packaged properly and accompanied by prescribed documentation. The acids and bases used as preservatives for metal mining effluent parameters may require compliance with TDG. Normally, samples for analysis can be exempt from TDG if the package is less than 10 kg in weight and is labeled "Test Samples". Shipping documents must contain the name and address of the shipper. Nitric acid is exempt if its concentration is less than 20%, which is the case with preserved samples but may not be the case with the preservative container itself. Transport Canada or a shipping company can provide detailed advice, but it is best to confirm any information received by referring to the regulations.

6.9 Field Quality Control Program

Companies that conduct sampling pertaining to the proposed MMER should operate a documented internal quality control program. This should include maintenance of sampling records so that all sampling information can be associated with laboratory results for each sample, cross-checking of field measurements with laboratory results (e.g., for pH or conductivity), corrective actions when large sampling errors or field-lab discrepancies are indicated, equipment maintenance, and staff training and evaluation programs.

7.0 Laboratory Analysis

Laboratory analysis should be carried out in a qualified laboratory by trained personnel operating under quality-controlled conditions and using documented SOPs. Information typically included in an analytical method SOP is presented in Appendix 3. It is recommended that laboratories that are accredited under ISO/IEC Guide 25 be used to generate data for any federal or provincial regulation.

7.1 Selection of Analytical Methods

The performance-based approach allows for selection of analytical methods that will meet the data quality objectives of the proposed MMER. The methods selected should meet the criteria in this document plus any other objectives defined by the mine operator, Environment Canada and other relevant regulatory agencies. The project manager and the laboratory need to confirm that the parameters of interest will be measured unambiguously and that holding times can be met. The laboratory and analysis method should be selected before the sample is collected to ensure that the laboratory sample requirements are met.

Methods selected should be generally accepted and in common use in laboratories in Canada. The overall method principle should be peer reviewed, widely documented and readily available so that it can be located easily for details. Unpublished and in-house analytical methods often lack documented SOPs, validation and quality information and are difficult to review.

The methods chosen should be capable of reliably measuring any concentration that approaches the maximum authorized concentrations under the proposed MMER (i.e., any concentration above about one-tenth of the maximum authorized grab sample concentration). The precision and accuracy objectives of Table 1 are achievable at this one-tenth concentration, which is approximately 10 times the MDL for the regulated metal parameters. Typical data quality performance for a competent laboratory is illustrated in Table 4.

For metals, absorption or emission lines can be subject to interference or overlap. Spectral overlap and inter-element correction factors should be recognized and used. Both the instrument manual and the technical literature should be consulted to find possible interference.

For ^{226}Ra, other radionuclides or other isotopes of radium can provide interfering emissions. If the radon emanation method is used, sufficient time must elapse for decay of short-lived isotopes.

For TSS, a glass fibre filter with 1.5 µm particle retention is required. The filter should be dried at 104°C to constant weight before and after the sample is filtered using the filter paper.

The pH of samples must be measured using a pH meter with appropriate electrodes. Indicator paper is not appropriate for measurement of samples, but is acceptable to confirm that sufficient acid or base has been added for preservation of the samples for other analyses. pH can be measured at the sampling site, provided that proper calibration and quality control procedures are used. In the event that on-line pH monitors are used, the output from the on-line monitor must be verified and recorded monthly by the operator.

For cyanide, colourimetric, ion selective electrode and ion chromatographic methods are often used. Each of these methods has its own specific interferences, which have to be recognized. Interference due to sulfur species, cyanate and thiocyanate are well known, and methods exist to accommodate these interferences. Cyanide can exist as a number of metal complexes, which are difficult to break down during analysis. Strong acid digestion and distillation is generally used for such samples. Since the chemistry of each mine's effluent is different, validation should include interference studies and should demonstrate the ability of the method to recover complex cyanides expected at that mine.

Suggested method principles that can be used when providing data to the proposed MMER are presented in Table 5. This table is not intended to be comprehensive. References for examples of acceptable methods are provided in Appendix 4. The instrumental methods are generally preferred over colourimetric methods, since they are less labour intensive. Any of these methods or alternatives that are selected by the regulated companies or their laboratories must be validated for use in those laboratories, and the validation should be documented.

Table 4 Typical Laboratory Data Quality Performance

Chemical Parameter	MDL and Units	Single Lab Precision (difference between duplicates)		Single Lab Accuracy (recovery of spiked blank)		Single Lab Accuracy (recovery of spike from a sample)	
		Average (%)	Standard Deviation (%)	Average (%)	Standard Deviation (%)	Average (%)	Standard Deviation (%)
As	0.01 mg/L	1.3	1.6	101	1.7	100	2.5
Cu	0.005 mg/L	1.4	2.0	101	1.5	100	1.7
Pb	0.005 mg/L	1.5	2.0	99.8	1.9	100	1.7
Ni	0.01 mg/L	2.2	2.3	99.9	2.0	99.7	2.4
Zn	0.01 mg/L	1.8	2.3	100	1.4	99.8	1.6
TSS	2.0 mg/L	11	11	99.1	8.9	NA	NA
^{226}Ra	0.01 Bq/L	7.1	2.8	104	6.2	NA	NA
CN^-	0.01 mg/L	6.7	5.9	93.9	7.2	99.6	4.7
pH	NA	0.2	0.1	100	0.3	NA	NA
Al	0.002 mg/L	1.0	1.4	101.6	2.1	101.7	2.1
Cd	0.003 mg/L	0.5	1.2	100.3	2.1	100.6	2.9
Fe	0.006 mg/L	1.1	1.8	100.8	1.7	100.2	1.4
Mn	0.001 mg/L	1.5	2.1	101	1.6	100.7	2.0
Mo	0.006 mg/L	1.2	2.4	99.8	1.7	100.3	1.6
Hg	0.00006 mg/L	1.1	1.4	101.4	2.8	100.4	2.8
Se	0.00003 mg/L	1.4	2.1	10.9	1.3	101.5	1.7
U	0.15 mg/L	NA	NA	98.6*	3.0*	99	4.0
Fl	0.488 mg/L	4.0	3.9	99	2.8	97.3	9.5
NH_3-N	0.1 mg/L N	2.5	3.7	97.6	4.7	92.7	18.3
NO_2	0.345 mg/L	1.6	2.8	103	6.7	97.5	5.2
NO_3	0.345 mg/L	3.8	4.5	98.1	3.5	97.3	4.9
TP	0.182 mg/L P	4.2	4.2	101	5.7	97.1	8.3
Cl	0.0460 mg/L	1.7	2.2	97.3	2.3	100.4	2.6
SO_4	0.907 mg/L	2.4	2.5	100.1	2.7	100	3.6
Ca	0.002 mg/L	1.1	0.9	100.8	1.6	100.4	2.1
Mg	0.0004 mg/L	1.3	1.1	101.1	1.7	101.3	2.4
K	0.236 mg/L	0.9	0.7	100.9	2.4	98.4	2.8
Na	0.050 mg/L	2.9	2.8	99.9	1.7	99.1	1.5
Conductivity	0.428 µmhos/cm	0.3	0.7	99.5	1.8	NA	NA
Hardness	3.50 mg/L $CaCO_3$	4.8	12.1	100	1.4	88.3*	19.4*
Alkalinity	5.5 mg/L $CaCO_3$	1.5	1.3	100.1	1.4	100.1*	0.2*
Acidity	3.0 mg/L $CaCO_3$	2.1*	3.3*	97.5*	3.9*	NA	NA

NOTES:
NA: Not applicable.
Most data in Table 4 are from 30 sequential QC samples run in WTI Environmental Chemistry Laboratory (concentrations approximately 10 times MDL).
QC data for ^{226}Ra were supplied by SRC Analytical using the gross alpha counting method.
* Value calculated on fewer than 30 data points.

Table 5 Summary of Commonly Accepted Method Principles

Parameter	Sample Preparation	Normally Accepted Methods	Lab QC Samples
As	Acid Digestion	HGAA, GFAA, ICPMS, ICP	Blk, Dup, Ref, Spk
Cu	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Pb	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Ni	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Zn	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
TSS		Filter and dry at 104°C(1)	Blk, Dup, Ref(4)
^{226}Ra	Co-precipitation with $BaSO_4$	α spectrometry, radon emanation, α counting(2)	Blk, Dup, Ref, Spk
CN^-	Acid Distillation	Colourimetry ion selective electrode ion chromatography	Blk, Dup, Ref, Spk
pH	Stir at room temperature	pH meter and electrode(3)	Dup
Al	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Cd	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Fe	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Mn	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Mo	Acid Digestion	AA, GFAA, ICP, ICPMS	Blk, Dup, Ref, Spk
Hg	Acid Digestion	CVAA, CVAFS, HGAA, ICP, ICPMS	Blk, Dup, Ref, Spk
Se	Acid Digestion	HGAA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
U	Acid Digestion	AA, GFAA, ICP, ICPMS, Colourimetry	Blk, Dup, Ref, Spk
Fl	As appropriate for measurement system	Colourimetry, ion selective electrode, or ion chromatography	Blk, Dup, Ref, Spk
Am-N	Distillation	Colourimetry, ion selective electrode, titration or ion chromatography	Blk, Dup, Ref, Spk
NO_3+NO_2	As appropriate for measurement system	Colourimetry or ion chromatography	Blk, Dup, Ref, Spk
TP	Digestion with 5:1 ratio of HNO_3 to H_2SO_4	Colourimetry or ICP	Blk, Dup, Ref, Spk
Cl	As appropriate for measurement system	Ion chromatography, colourimetry or titration	Blk, Dup, Ref, Spk
SO_4	As appropriate for measurement system	Ion chromatography	Blk, Dup, Ref, Spk
Ca	Acid Digestion	AA, ICP, ICPMS	Blk, Dup, Ref, Spk
Mg	Acid Digestion	AA, ICP, ICPMS	Blk, Dup, Ref, Spk
K	Acid Digestion	AA, ICP, ICPMS	Blk, Dup, Ref, Spk
Na	Acid Digestion	AA, ICP, ICPMS	Blk, Dup, Ref, Spk
Conductivity	As appropriate for measurement system	On-line analyzer, meter	Blk, Dup
Hardness	As appropriate for measurement system	Titration, or calculation by concentration of Ca and Mg	Blk, Dup
Alkalinity	As appropriate for measurement system	Titration	Blk, Dup
Acidity	As appropriate for measurement system	Titration	Blk, Dup

NOTES:

(1) Use glass fibre filter with 1.5 µm pore size.

(2) Suitable if the total α activity is less than the limit for ^{226}Ra.

(3) pH can be measured by an on-line analyzer, provided that a split grab sample taken monthly agrees with the result of the on-line analyzer.

(4) Infusorial earth can be used as a reference for TSS.

LEGEND:

AA	Atomic absorption spectrophotometry (flame)
CVAA	Cold vapor generation atomic absorption spectrophotometry
CVAFS	Cold vapour atomic fluorescence spectrometry
HGAA	Hydride generation atomic absorption spectrophotometry
GFAA	Graphite furnace atomic absorption spectrophotometry
ICP	Inductively coupled plasma emission spectrometry
ICPMS	Inductively coupled plasma mass spectrometry
Colourimetry	Colourimetric wet chemistry
Blk	Blank
Dup	Duplicate
Ref	Reference standard
Spk	Spiked sample

7.2 Analytical Methods – Standard Operating Procedures

Chemical analysis methods, once selected, should be documented as Standard Operating Procedures (SOPs) within the laboratory. An example of items useful in a chemical analysis SOP is presented in Appendix 3.

7.3 External Quality Control Program

It is strongly recommended that laboratories selected to provide analysis data pertaining to any regulation be accredited under ISO/IEC Guide 25 for the relevant chemical parameters. In Canada, the Canadian Association for Environmental Analytical Laboratories (CAEAL) and the Province of Quebec operate laboratory accreditation programs.

The CAEAL assessment program is currently based on the application of Canadian National Standard CAN/CSA-Z753-95 – Requirements for the Competence of Analytical Environmental Laboratories. The Canadian Standards Association, in co-operation with CAEAL, prepared CAN/CSA-Z753-95. It takes the generic requirements of ISO/IEC Guide 25, the internationally recognized accreditation standard, and makes these requirements specific to environmental laboratories. It will be reviewed or replaced during 2000.

The requirements include a well-documented quality assurance/quality control (QA/QC) program, as well as demonstrated proficiency in analysis of performance evaluation (PE) samples. Based on a site audit by CAEAL assessors and successful analysis of PE samples, the laboratory is accredited for particular chemical parameters. The assessment and accreditation is updated every two years.

Users of laboratories should verify that their laboratory is currently accredited for the chemical parameters of interest. Accreditation information is available on the Standards Council of Canada web site (www.scc.ca/certific/labs.html).

Laboratories that provide analysis data pertaining to the proposed MMER should demonstrate proficiency in analysis of PE samples for the relevant parameters whenever such PE samples are available. CAEAL provides suitable PE samples for all of the proposed MMER parameters except ^{226}Ra. Results of any PE sample analysis should be made available to compliance officers and program managers upon request. Corrective action must be documented for any deficiencies identified by the PE program.

Additional information on the CAEAL accreditation program can be found by contacting:

> Canadian Association for Environmental Analytical Laboratories
> 265 Carling Avenue, Suite 300,
> Ottawa, ON, K1S 2E1 — Tel.: (613) 233-5300
> www.caeal.ca

In Quebec, the Centre for Expertise in Environmental Analysis of Quebec (Centre d'expertise en analyse environnementale du Québec) deals with the accreditation of private, municipal and institutional laboratories in order to comply with provincial regulations. The accreditation program is based in power granted to the Minister in article 118.6 of the Law on the Quality of the Environment of Quebec (Loi sur la qualité de l'environnement du Québec [L.R.Q., chap. Q-2]).

The Accreditation Program for Environmental Analysis Laboratories (Programme d'accréditation des laboratoires d'analyse environnementale [PALAE]) is made up of a set of standards and requirements governing the quality assurance procedures for laboratories. It was drawn up in 1984 to ensure the quality of the analyses performed by laboratories accredited for the supervision of drinking water, groundwater, industrial and municipal waste waters, sludge from water purification plants, contaminated soil, dangerous wastes, grease and oil wastes and atmospheric emissions. The program's objective is to ensure and maintain a sufficiently high level of analytical quality that the clients making use of these laboratories may call upon their services with confidence in the analytical information generated.

The PALAE process ensures the reliability of the analytical results produced by accredited laboratories. It rests mainly on "performance evaluations," permitting the verification of analytical capability of accredited laboratories using quality control samples or reference materials. Furthermore, laboratory audits are carried out, allowing the application of quality management and quality assurance procedures to be verified.

More information about this accreditation program can be found by contacting:

Centre d'expertise en analyse
environnementale du Québec
Service de l'accréditation
360, rue Franquet, bureau 40
Sainte-Foy, QC, G1P 4N3
Tel.: (418) 646-6898
www.menv.gouv.qc.ca/ceaeq/index.htm

7.4 Internal Quality Control Program

Laboratories that provide analysis data pertaining to the proposed MMER should operate a documented internal quality control program. This should include items such as calibration schedules, use of quality control samples, established control specifications with corrective actions if specifications are not met, data validation, equipment maintenance, and staff training and evaluation programs. Guidance on internal quality control is outlined in ISO/IEC Guide 25 and CAN/CSA-Z753-95. Another good reference is *Quality Assurance of Chemical Measurements* by John K. Taylor (1987).

7.5 Performance-Based Data Quality Objectives

Performance-based DQOs can be expressed in terms of method detection limit, precision, accuracy, calibration criteria, and type and frequency of quality control samples. Suggestions for numerical DQOs are given in Table 1. Laboratories contributing data pertaining to the proposed MMER should be able to produce a report similar to that in Table 4.

Method detection limit (MDL) is defined as the lowest concentration that can be distinguished from zero at the 99% confidence interval. It is calculated by analyzing seven or more replicate low-level standards and calculating their 99% confidence level. Good examples of MDL calculations are given by the Ontario MISA program and the AWWA Standard Methods for Examination of Water and Wastewater. Laboratory MDLs should be about a factor of 10 less than the required lowest concentration for discharges specified in the regulations.

Precision is the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation. Precision reflects random errors and is a measurable and controllable parameter. Precision can be separated into two further concepts, repeatability and reproducibility. Repeatability is the closeness of agreement between successive measurements of the same parameter carried out under the same conditions. Repeatability means the standard deviation obtained from the same analytical run and is called within-run precision. Reproducibility is the closeness of agreement between the results of measurement of the same parameter carried out under changed conditions of measurement. Reproducibility means the standard deviation obtained measuring the same sample in different analytical runs and is called between-run precision. Between-run precision includes variability due to calibration on different days, instrument drift and many other factors.

For purposes of the proposed MMER, reproducibility, or the day-to-day variability, should be used to assess precision. Precision must be estimated by processing separate sample aliquots through the entire analytical method. A laboratory must monitor its precision and be able to report precision using several days of recent data. For the metals, radium and cyanide, precision should be within 10%, and for TSS it should be within 15%, at concentrations greater than 10 times the MDL. For pH, precision should be within ± 0.1 pH unit.

Accuracy is concerned with the correctness or closeness of a measurement to the true value of a parameter in a sample. Accuracy is measured as per cent recovery of known concentrations such as certified reference materials, spiked samples or reference samples prepared by the laboratory and analyzed as samples.

Bias is a systematic error caused by something in the measuring system resulting in the data being high or low. This is usually reflected in the accuracy measure, although some systematic errors may be picked up in the precision measure. Bias can be caused by a number of factors including contamination, mechanical losses, spectral interference, calibration errors or the influence of different operators. Bias can also be introduced by blank correction procedures. If blank correction is performed, the procedure and the blank value used should be noted in data reports.

Whether data are considered accurate or inaccurate is relative to the final use of the data. Errors of 10% to 20% are often considered acceptable in environmental data. A laboratory must monitor its accuracy and be able to report it using several days of recent data. For the metals, radium and cyanide, accuracy should be within 10%, and for TSS it should be within 15%, at

concentrations greater than 10 times the MDL. For pH, accuracy should be within ± 0.1 pH unit.

Calibration criteria (procedures) as outlined in this section should be met unless other methods that are currently accredited under ISO/IEC Guide 25 are used.

For arsenic, metals and cyanide, on each day that analyses are performed, the laboratory must prepare a calibration curve using calibration standards at a minimum of three concentrations plus a blank. The standards should contain the analytes of interest and be within the applicable concentration range of the samples as they are presented to the instrument. The lowest concentration standard should be within a factor of 10 of the MDL. The chemical matrix of the standards presented to the instruments should be chemically similar to that of the prepared samples. For each calibration standard, there should be a check standard from a separate source to check for consistency with the calibration standard. Samples must be prepared such that they are within the calibration range of the instrument.

For radium, the count rates and counting efficiency of the counter or spectrometer should be confirmed using a standard ^{226}Ra source at the beginning and end of each counting run. The physical matrix of the standard counting source presented to the instruments should be similar to that of the prepared samples.

For TSS, calibration of the analytical balances must be checked each day with traceable check weights and the results written in the balance log book. Balances must be inspected by qualified individuals and serviced as necessary, at least annually.

For pH, calibration must be done with certified (e.g., NIST traceable) pH buffers, which should bracket the pH of the samples. A check pH buffer with a pH value different from that of the calibrating buffers should be analyzed to ensure the continued suitability of the primary buffer used to calibrate the pH meter.

For all analyses, the calibration standard should be verified on a daily basis with a check standard that is prepared independently of the calibration standard. The lowest calibration standard should be within a factor of 10 of the MDL.

Laboratory quality control (QC) samples are samples of known or defined composition, which are treated like analytical samples and processed through the entire analytical method. Quality control samples should include:

- blanks – analysis of deionized water to ensure that there is no contamination due to laboratory procedure;
- duplicates – a replicate analysis of a homogeneous sample to show method precision;
- spikes – a replicate sample spiked with a known amount of stock standard solution to show both method precision and accuracy and to check for any interferences; and
- reference materials – a National Institute of Standards and Technology (NIST) or other suitable certified reference material to show method accuracy.

All of the above laboratory QC samples should be run regularly. Results should be compared to DQOs and be used to flag sample results where DQOs are not met. Control samples should be run at a minimum frequency of 10% of the samples for analysis. Quality records should be kept and should be available for inspection. Control charts are a very useful form of quality record.

7.6 Method Validation

Before analyzing any samples, the laboratory should demonstrate that the selected analytical methods can provide valid data under practical conditions in the laboratory. The laboratory should have in place a method validation process and data to demonstrate that validation has occurred and that the methods chosen can meet the DQOs.

The uncertainty of the results, detection limits, selectivity of the analysis, and robustness of the analysis in the hands of different staff should be tested and documented. Techniques used for validation include results obtained on certified or other reference materials, comparison of results with data obtained using other methods, interlaboratory comparison data, systematic assessment of factors that could influence the results, and assessment of uncertainty based on accuracy and precision. The influence of instrumental, human and environmental factors should be considered.

Method validation should be documented in a report with a statement that the method is fit for use on mining effluent samples.

8.0 Reporting of Data

The chemical analysis results should be reported to the regulated company within a time frame agreed to by all parties. The data should be reported accurately, clearly, unambiguously and objectively, in accordance with any specific instructions received. These instructions should clearly reflect any requirements of the appropriate regulation. Results are reported as a test or analysis report and should include all relevant data needed to assess the validity of the data. Items that should appear in a data report include:

- report title (e.g., Test Report, Report of Analysis, Quality Report);
- name, address and location of the laboratory and the site tested;
- unique identification of the report so it can be traced easily (serial number, group number, etc.);
- name and address of the client;
- identification or description of the sample tested;
- condition of the test item (unpreserved, leaking bottle, etc.);
- date of sample receipt; date of report;
- identification of the analysis method and description of any non-standard tests;
- reference to sample date and sampling method (grab sample, time-proportioned composite sample, etc.);
- deviations from the usual test method (filtering, pH adjustment, standard addition, etc.);
- the analytical result with units clearly identified;
- statement indicating whether the results were corrected for blanks;
- laboratory and field quality control data, identified as such;
- qualification flags to indicate if samples did not meet DQOs or other QC tests (sample size too small, etc.);
- signature of accountable person and date authorized;
- clear identification of any subcontractors;
- updates or corrections to reports, clearly identified as such; and
- client notification if new information invalidates reports already issued.

Data below the analytical detection limit should be clearly reported as such along with the applicable MDL for that sample.

Sampling information should accompany laboratory results in reporting of data from the regulated company to regulatory authorities. At a minimum, this information should indicate when, where and how the samples were collected, with reference to SOPs as needed. It should include any data qualifications based on a review of field QC data and sampling records, and should identify a company contact who can supply additional sampling information as needed.

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List of Abbreviations

AA	Atomic Absorption (Spectrophotometry)
ACS	American Chemical Society
AQUAMIN	Assessment of the Aquatic Effects of Mining in Canada
AWWA	American Water Works Association
CAEAL	Canadian Association for Environmental Analytical Laboratories
CSA	Canadian Standards Association
CVAA	Cold vapor generation atomic absorption spectrophotometry
CVAFS	Cold vapour atomic fluorescence spectrometry
DQO	Data Quality Objective
GFAA	Graphite Furnace Atomic Absorption (Spectrophotometry)
HDPE	High-Density Polyethylene
HGAA	Hydride Generation Atomic Absorption (Spectrophotometry)
ICP	Inductively Coupled Plasma (Emission Spectrometry)
ICPMS	Inductively Coupled Plasma Mass Spectrometry
ISCO	ISCO Inc., Environmental Division, Lincoln, NE
ISO	International Organization for Standardization
MDL	Method Detection Limit
MISA	Municipal Industrial Strategy for Abatement
MMER	*Metal Mining Effluent Regulations*
MSDS	Material Safety Data Sheet
NIST	National Institute of Standards and Technology
NRC	National Research Council
NWRI	National Water Research Institute
PE	Performance Evaluation
QA/QC	Quality Assurance/Quality Control
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SCC	Standards Council of Canada
SOP	Standard Operating Procedure
SRC	Saskatchewan Research Council
TDG	Transport of Dangerous Goods
TSM	Total Suspended Matter (= TSS)
TSS	Total Suspended Solids (= TSM)
WEF	Water Environment Federation
WTI	Wastewater Technology Institute

APPENDIX 1 GLOSSARY OF TERMS

Acceptable	evaluation rating indicating that laboratory being audited is following the audit guidelines and fulfilling all test requirements.
Accuracy	the combination of bias and precision of an analytical method that reflects the closeness of a measured value to the true value of a sample.
Analyst	a qualified person responsible for work of analyzing and reporting tests according to accepted and current procedure.
Analyst Intervention	an action on the part of the analyst that is a deviation from normal method procedure.
Analyte	a physical or chemical parameter that is measured in a chemical analysis.
Analyte Spike Recovery	recovery of analyte spike added to sample prior to sample preparation. Determination of spike recovery is based on results provided by spiked and unspiked sample. Used to account for matrix effects and sample preparation losses.
Blank	the measured value obtained when a target analyte or parameter is not supposed to be present during measurement. Used to monitor contamination and purity of test supplies and materials.
Calibration	a set of operations that establish, under specified conditions, the relationship between values indicated by a measurement instrument or measuring system and the corresponding known values of the material being measured.
Calibration Curve	relationship used to define the relation between analyte concentration and analytical response. Normally, at least three to five appropriately placed calibration standards are needed to adequately define the curve. The curve should incorporate a low standard not exceeding 10 times the detection limit. Analytical response, where appropriate, is zeroed using a reagent blank. Standards and samples must have equivalent reagent backgrounds.
Certified Reference Samples	reference samples with concentration values certified by a recognized standards supplier (e.g., NIST, NRC and NWRI).
Chain of Custody	written train of signatures or appropriate identification of the person(s) responsible for the content and security of information, sample(s) or other material.
Check Standard	a standard that is prepared independently of the calibration standard and used to validate the calibration standard.
Chemical Preservation	appropriate chemical manipulation of a sample that facilitates optimum preservation or target parameter of analyte.
Confidence Intervals	limits of confidence for a set of values using the formula: $$\text{confidence limits} = \overline{X} \pm \frac{txs}{\sqrt{n}}$$
Control Chart	graphical plot of test results with respect to time or sequence of measurement upon which control and warning limits are set to guide in detecting whether the system is in a state of control.

Control Limits	limits or combination of limits that, when exceeded, trigger analyst intervention. These limits may be defined statistically or based on protocol requirements. Control limits may be assigned to method blanks, check standards, spike recoveries, duplicates and reference samples.
Data Quality Objectives (DQOs)	predefined criteria for the quality of data generated or used in a particular study, so as to ensure that the data are of suitable quality to meet the needs of the program.
Detection Limit	the smallest concentration or amount of parameter or analyte that can be measured with a stated level of confidence or quality assurance.
Documentation	evidence of relevant written or printed material that contains authorization and/or instructions.
Duplicate	a quality control sample, often chosen randomly from a batch of samples, that undergoes separate but identical sample preparation and analysis, and whose purpose is to monitor method precision and sample homogeneity, that contains a deteriorous substance.
Effluent	for purposes of this document, effluent as defined by the proposed MMER includes mine water effluent, mill process effluent, tailings impoundment area effluent, treatment pond or treatment facility effluent, seepage and surface drainage.
Field Blank	a quality control sample in which the target analytes or parameters are not present, which is taken to a field or sampling site. Used to monitor contamination of samples during sampling, preservation, handling and transportation. It also monitors the purity of preservation materials.
Field Duplicate	a quality control sample taken randomly during sampling by collecting a separate but duplicate sample from the sampling site, whose purpose is to monitor repeatability of the sampling process. A field duplicate must be a completely separate sample taken from the source, not simply a split of a single sample.
Flag	a record, signal or symbol used to alert an observer of a notable deviation from an expected result or method.
Gravimetric Measurement	measurement by weight.
Holding Time	time elapsed between sample collection and sample preparation and/or analysis as required.
Laboratory	a body or part of an organization that is involved in calibration and/or testing.
Linearity	a simple straight-line relationship between two variables, functions or characteristics. Linearity is often demonstrated using linear regression with a coefficient of variation (r^2) of greater than 0.995.
Material Safety Data Sheets (MSDSs)	written information that defines and describes pertinent physical and chemical characteristics that affect safety, transportation, incompatibility with other materials, flammability, storage and handling of contained material.
Matrix	the material or substance, form or state in which the analyte is embedded.

Matrix Spike	a sample aliquot to which a known amount of target analyte has been added.
Method Blank	a quality control sample that is free of the target parameter or analyte and that undergoes the same analysis procedure as the unknown sample. Used to monitor possible contamination sources.
Method Detection Limit (MDL)	the smallest concentration at which the true physical and chemical characteristics of a target analyte or parameter can be measured and statistically distinguished from zero at a specified confidence level (usually 99%).
Non-Conformances	items, actions, data and/or substitutions that have taken place regarding the analytical test that are deviations from expected results and/or procedures.
Parameter	a limit, state, constant or defined physical and/or chemical characteristic that describes a variable or group of variables and is the subject of a test.
Precision	the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation. Precision is affected by random errors and is a measurable and controllable parameter. Precision can be separated into two further concepts, repeatability and reproducibility. Repeatability is the closeness of agreement between successive measurements of the same parameter carried out under the same conditions (within runs). Reproducibility is the closeness of agreement between the results of measurement of the same chemical carried out under changed conditions of measurement (between runs). Between-run precision includes variability due to calibration on different days, instrument drift and many other factors.
Quality Assurance (QA)	an integrated system of internal and external activities involving quality planning, quality control, quality assessment, quality reporting and quality improvement to ensure that data meet the needs of users.
Quality Manager	a person who has responsibility and authority to implement and maintain a quality system.
Quality System	a functional unit or network accountable for connecting and recording all procedures and actions relating to and affecting the degree of excellence.
Reagent	a substance or component used in preparation, preservation and analysis of a sample or standard.
Reagent Blank	a quality control sample that contains only the reagents used in an analytical test procedure. Used to monitor contamination problems and purity.
Reference Material	a material, consisting of one or more substances, whose properties are sufficiently well established to be used for the calibration of instruments and equipment.
Reference Samples	samples, including matrix spikes, with known analyte concentrations. Used to assess analytical accuracy.

Relative Response Factor (RRF)	ratio of slopes provided by calibration curves for analyte and corresponding internal standard (or surrogate and corresponding internal standard). Calibration curves may be determined by two precisely determined calibration points. Analytical responses must be demonstrated to be linear.
Sample	a portion of a lot or population consisting of one or more single units.
Sample Analysis	all procedures carried out on a sample and standards subsequent to sample preparation. Includes any chemical alteration to sample as well as subsequent measurement.
Sample Collection	all procedures carried out on a sample at the time of sample collection, including filtration to (i) remove unwanted material from the sample or (ii) isolate the sample.
Sample Container	a receptacle used to collect and seal a sample; it is matrix-specific and ensures contaminant-free preservation of target analyte or parameter.
Sample Preparation	all procedures used on samples and corresponding standards, before analysis.
Sample Preservation	physical or chemical action(s) needed to secure and protect target analyte or parameter integrity within a sample.
Sample Pretreatment	all pretreatment procedures carried out on a collected sample prior to sample preparation or analysis, including removal of unwanted material, removal of moisture, sub-sampling and homogenization.
Significant Figures	numerical digits considered to be statistically important in representation of a quantity.
Spiked Blank	a blank matrix (e.g., reagent water) to which a known amount of target analyte has been added; it is analyzed using the same materials and methods as the samples. The control sample is used to assess recovery in the absence of sample interferences.
Spiked Sample	a control item to which a known quantity of target analyte has been added that is analyzed using the same material and methods as the client sample. Used to monitor matrix effects and sample preparation losses. $\%\ \text{Recovery} = \frac{\text{Measured Conc.} - \text{Unspiked Conc.}}{\text{Expected Spike Conc.}} \times 100$
Standard Operating Procedure (SOP)	a written document that details methods of analysis, operation or action. Techniques and procedures that are thoroughly prescribed and that are accepted as the method for performing certain routine or repetitive tasks.
Storage Conditions	conditions relevant to sample integrity during sample transport and sample storage at the laboratory.
Traceability	the property of an item such as a record, method, measurement or qualification that completely demonstrates the origin or validity of the item.
Units	the descriptor used to indicate the type or scale of measurement that is reported as a numerical (e.g., mg/L = milligrams per litre).

Validation	signature and title of laboratory employee who is responsible for the confirmation and reliability of test results and for minimizing transcription errors.
Validator	a laboratory employee, often a supervisor, who is responsible for the confirmation of analytical results generated by a qualified analyst.
Warning Limit(s)	a boundary or combination of limits that, when exceeded, triggers analyst intervention.

Appendix 2 Information Typically Included in a Sampling Standard Operating Procedure (SOP)

The purpose of a sampling SOP is to provide a description of the type, location and number of samples to be taken, and to detail all quality control (QC) measures, equipment and procedures. The SOP also identifies personnel, training requirements and responsibility levels. Safety issues should also be addressed in the SOP, if not addressed in other documentation such as a field safety plan or manual. It is often an advantage for an organization to have a standard format for SOPs.

Information useful in a sampling SOP includes:

Objectives

Provide a statement of objectives and goals explaining why the sample is to be taken and what will be done with the sample and the resulting data.

Summary of the sampling procedure

Briefly describe the sampling location(s), the matrix to be sampled, chemicals to be analyzed, sampling equipment to be used, and field QC procedures. This section should be written such that it can be transferred directly to final reports where a brief description of sampling is needed.

Safety considerations

List known chemical and physical hazards as well as methods to safely address these factors. Note the location of material safety data sheets (MSDSs) and detail personal protective equipment that might be needed.

Responsibility

Specify who is to collect the sample and what qualifications are needed in sampling staff. Specify who has prepared and validated the sampling plan.

Equipment and supplies

Describe exactly what is to be used, what specifications and grades of equipment and materials are to be used. State where material can be purchased and provide a list of typical suppliers. List cleaning procedures and reagent preparation instructions.

Sampling and sample size

Document the exact proposed sampling procedure, including:

- Location and timing of sampling
- Container sizes, types and numbers
- Labels and labeling requirements
- Field log books
- Sampling devices
- Equipment calibration
- Minimum sample volumes
- Compositing requirements
- Preservation instructions
- Chain of custody procedure
- Transportation instructions
- Field measurements and observations needed (temperature, weather, etc.)

Quality control

Discuss the number and types of field QC samples and where to take them. Also discuss how QC sample results will be used (e.g., to flag other sample results). If possible, provide a checklist of activities needed to ensure sample quality.

Corrective action

List any anticipated deviations from the sampling procedure or deviations experienced in the past. Actions expected from the samplers when they encounter problems may be listed. Discuss what actions a sampler can take for future improvement or resampling if field data quality objectives are not met.

Documentation required

Note that field notes or log books should contain details on:

- Site name
- Exact location
- Weather conditions
- Date and time of arrival and departure

- Names of people present
- Name of sample collector
- Sample numbers, time, method of collection
- QC samples, time, method of collection
- Sampling equipment, method, description
- Calibration data
- Appearance of the outfall and the sample (photographs may be useful)
- Measurements taken on-site (pH, temperature, flow)
- Deviations from the plan (if needed)
- What laboratory is to be used; when and how sample is to be sent
- Any issues and concerns arising before, during or after the sampling activity
- Signature of accountable person and the date

Sampling report

List all items to be included in the report.

Pollution prevention procedures

Outline procedures for safe disposal of samples, reagents, wash water, etc.

Decontamination and clean-up procedures

List washing procedures for sampling equipment, and storage procedures and locations.

Definitions

Define any terms that are new or that could be misinterpreted, and explain technical jargon used.

Appendix 3 Information Typically Included in an Analytical Method Standard Operating Procedure (SOP)

The purpose of an analytical SOP is to provide a description of the analyses to be performed, and to detail all quality control (QC) measures, equipment and procedures. The SOP also identifies personnel, training requirements and responsibility levels. Safety issues should also be addressed in the SOP. The SOP should discuss any standard worksheets or forms to be used and how they are used to prevent errors or omissions. It is often an advantage for an organization to have a standard format for SOPs.

Information useful in an analytical SOP includes:

Scope and application

Explain what parameters are to be analyzed, the concentration range, and to what sample matrices the method is applicable. A table of parameters analyzed might be appropriate here. Discuss the situations where this method may be used.

Summary of method principle

Provide a brief summary description of the method principle, including but not limited to sample handling, sample preparation and method of analysis. This section should be written such that it can be copied directly into data reports if asked for a method description.

Safety considerations

Note the location of material safety data sheets (MSDSs). Explain particular hazards involved with the samples, analytes and reagents (e.g., acid digestion with presence of cyanide compounds can pose health risks).

Interferences, contamination control, limitations

Describe what interferes with the method and what steps must be taken to control errors caused by interfering chemical, physical or other factors. Discuss possible sources of contamination or loss that are particular to this method. Discuss any limitations of the method such as unavoidable interferences or shortcomings.

Equipment, reagents, supplies specifications

Describe exactly where the materials can be purchased, what has previously been purchased, what the specifications are and why those specifications are important. This section explains exactly what materials to get and where to get them.

Reagents, water and standards

List all reagents that are used and what grade of chemicals are needed. This will include all solvents, reagents and calibration standards, as well as specific wash or dilution water types if necessary. Complete preparation instructions for reagents used in the analysis should be given. Labeling requirements and shelf life for reagents must be specified. Also specify dilutions for stock and working standards commonly used.

Apparatus/equipment

List all instruments, glassware and consumables. Provide a complete description of the equipment or apparatus used, including model number or part number if applicable.

Glassware preparation

Provide a detailed description of glassware preparation procedures or refer to a glassware cleaning SOP.

Sampling and sample size

Specify the method of field preservation and storage. Holding times, container type and any sample pretreatment such as shaking, removal of unwanted material, homogenization, etc. are described. The sample size refers to the usual amount of sample taken and might be a maximum or minimum amount of material that can be used without dilution or concentration. Sample storage and preparation of quality control samples can be explained. A detailed description of sample bottle requirements, cleaning and preparation procedures, or references to a glassware cleaning SOP should be included in this section.

Sample preparation and extraction

Describe how the sample is digested, extracted or otherwise manipulated to transform the sample into something that can be analyzed for the parameters of interest. This section can be quite detailed. It should discuss method options and criteria for selecting those options. Since the digestion step can involve hazards to the analyst, the hazards should be reiterated in this section.

Sample analysis procedure

Describe all steps in the analysis of a sample, including sample preparation. Included in this section are subsections on Method Calibration and Method Quality Control. Instructions on the operation of instruments or ancillary procedures (e.g., glassware cleaning, instrument start-up) may reference manufacturer instructions.

Quality control samples

Describe how QC samples are prepared and used:

- Method blanks
- Duplicates
- Spikes
- Reference materials

Are any other quality control samples needed or are there any special considerations for this analysis?

Method calibration

Note what materials and concentrations are used for calibration, and that the lowest concentration needs to be less than 10 times the method detection limit (MDL). Note how many calibration points are used. How is the calibration handled–by the instrument, a PC program, graph paper, etc.? After how many samples should the calibration be repeated? Is it to be repeated at the end of the sample run? What deviation from the initial calibration is tolerated in subsequent calibrations? What is the mathematical formula to use? Are response factors used, standard additions, internal or external standards? Are different analytes added together to give a total response?

Instrument operation/measurement procedure

Discuss how any instruments used are started or set up. List the usual operating parameters or settings. The run format for a particular analysis can be specified. Each run usually begins with the analysis of standards, followed by quality control samples and analytical samples that could be run in a specific order. The order may be fixed by the analysis system or may be somewhat flexible. Control and warning limits based on historical data should be listed here. This section can refer to an instrument operating manual if the manual provides detailed operating information.

Calculations

Describe how the calibration curve is used to calculate sample values. How are data, quality control samples and method detection limits reported? What are the reporting units? All calculations and formulae that are required to generate data should be shown in this section. Any blank correction used should be noted in the data report. Any qualifiers that are reported with the data should be defined (e.g., ND, Tr, LT, <, etc.) so they are not misunderstood. An example of the correct use of significant digits for this analysis should also be given.

Detection limit and method validation

Use historical data, if possible, to provide a statement of MDL, precision of duplicates, recovery of standards, spikes and reference samples. Provide a statement on the average and standard deviation of recoveries. Performance in round robins and laboratory certifications for this method should be listed. The calculations and method for determining MDLs should be stated.

Corrective actions/intervention

Describe any deviations from accepted practices or standard conditions with respect to sample handling and analysis. Areas for consideration include but are not limited to condition of sample container, preservation of sample, condition of sample, duplicate precision, absolute value of method blank, spike recoveries, check standard data and external reference material results.

Pollution prevention procedures and disposal of samples/reagents

State any procedures for safe disposal or destruction of samples or reagents. Are there specific considerations as to how waste can be minimized and

environmental harm avoided during the analysis and disposal of reagents, consumables and samples?

References

Provide literature references for the method.

Definitions

Explain any terms that apply to this method so that analysts clearly understand the terminology.

Appendices

Add any relevant background information.

APPENDIX 4 EXAMPLES OF ACCEPTABLE METHODS

Acceptable analytical methods include but are not limited to the following. Although these methods are current at the time of writing, laboratories must ensure that they keep up-to-date with future revisions of methods and documents.

Arsenic

Ontario MOE method E3302A – Determination of Arsenic, Selenium and Antimony in Liquid Industrial Wastes and Landfill Leachates by Hydride Generation – Flameless Atomic Absorption Spectrophotometry, June 12, 1997.

Alberta Research Council ICP-MS Method – Arsenic, October 1, 1996; Speciation of Arsenic (III) and (V), 1999.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 3114 – Arsenic and Selenium by Hydride Generation/Atomic Absorption Spectrometric Method, 1998.

MEF-MA. 200 – *Mét. 1.0 : Détermination des métaux; méthode par spectrométrie de masse à source ionisante au plasma d'argon.*

Metals

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 3120 – Metals by Plasma Emission Spectroscopy, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 3111 – Metals by Flame Atomic Absorption Spectrometry, 1998.

Ontario MOE method E3094B – Determination of Metals in Final Effluent, Industrial Waste and Landfill Leachates by Inductively Coupled Plasma – Atomic Emission Spectrometry, June 5, 1997.

Alberta Research Council (by A. Wittmeier and S. Wu) – Metals by Inductively Coupled Argon Plasma Mass Spectrometry, 1996.

MEF-MA. 200 – *Mét. 1.0 : Détermination des métaux; méthode par spectrométrie de masse à source ionisante au plasma d'argon.*

Total suspended solids

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2540 D – Total Suspended Solids Dried at 103–105°C, 1998.

Alberta Research Council – Solids, Total Suspended (Gravimetric Method), October 1, 1996.

Ontario MOE method E3188B – The Determination of Solids in Liquid Matrices by Gravimetry, June 5, 1997.

MEF-MA. 115 – *S.S. 1.0 : Effluents – Détermination des solides en suspension totaux et volatils; méthode gravimétrique.*

Radium 226

Standard Methods for the Examination of Water and Wastewater, 19th Edition, Method 7500 – Radium, 1995.

Ontario MOE method E3001A – The Determination of Gross Alpha and Beta Activity in Water, May 10, 1997.

CANMET – National Uranium Tailings Program – Radioanalytical Methods Manual, NUTP-3E, ISBN 0-660-12138-7.

Cyanide

Alberta Research Council – Cyanide, Total (Automated Pyridine – Barbituric Acid Method), October 1, 1996.

Ontario MOE method E3015A – Determination of Total Cyanide Aqueous Samples by Colourimetry, May 11, 1999.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Cyanide, 1998.

OI Analytical Method, Method OIA-1677: Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, USEPA, July 7, 1998, Federal Register (63 FR 36810).

MEF-MA. 300 – *CN 1.0 : Eaux – Détermination des cyanures totaux; méthode colorimétrique automatisée avec la pyridine et l'acide barbiturique.*

pH

Ontario MOE method E3218 – The Determination of Conductivity, pH and Alkalinity in Water and Effluents by Potentiometry, June 12, 1997.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – pH Value, 1998.

MEF-MA. 100 – *pH 1.0 : Détermination du pH; méthode électrométrique.*

Selenium

Ontario MOE method E3302A – Determination of Arsenic, Selenium and Antimony in Liquid Industrial Wastes and Landfill Leachates by Hydride Generation – Flameless Atomic Absorption Spectrophotometry, February 2, 1996.

Alberta Research Council ICP-MS Method – Selenium, October 1, 1996.

MEF-MA. 204 – *Se 1.0 : Détermination du sélénium; méthode automatisée par spectrophotométrie d'absorption atomique après digestion et formation d'hydrures.*

Mercury

Ontario MOE method E3301 – The Determination of Mercury in Liquid Industrial Waste, Landfill Leachate and Sewage Samples by Cold Vapour – Flameless Atomic Absorption Spectrophotometry (HYD-FAAS), June 12, 1997.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 3112 – Metals by Cold-Vapor Atomic Absorption Spectrometry, 1998.

MEF-MA. 200 – *Hg 1.0 : Détermination du mercure; méthode par spectrophotométrie d'absorption atomique, génération de vapeur.*

Alberta Research Council – Ultra Trace Level Total Mercury in Waters, 1999.

Fluoride

Ontario MOE method E3369 – The Determination of Fluoride in Water, Leachates and Effluents by Colourimetry, February 19, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Fluoride, 1998.

MEF-MA. 300 – *F 1.0 : Détermination des fluorures; méthode colorimétrique.*

Ammonia nitrogen

Ontario MOE method E3366 – The Determination of Ammonia Nitrogen, Nitrite Nitrogen, Nitrite Plus Nitrate Nitrogen and Reactive Ortho-Phosphate in Water, Sewage, Leachate and Industrial Effluents by Colourimetry, June 5, 1997.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Ammonia, 1998.

MEF-MA. 300 – *N 1.0 : Détermination de l'azote ammoniacal; méthode colorimétrique automatisée avec le salicylate de sodium.*

Nitrate and nitrite

Ontario MOE method E3366 – The Determination of Ammonia Nitrogen, Nitrite Nitrogen, Nitrite Plus Nitrate Nitrogen and Reactive Ortho-Phosphate in Water, Sewage, Leachate and Industrial Effluents by Colourimetry, June 5, 1997.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Nitrate, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Nitrite, 1998.

MEF-MA. 315 – *NO3 1.0 : Effluents – Détermination des nitrates et nitrites; méthode colorimétrique automatisée avec le sulfate d'hydrazine et le N.E.D.*

Total phosphorus

Ontario MOE method E3036 – The Determination of Total Phosphorus in Water by Colourimetry (Dorset), June 5, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Phosphorus, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 3120 – Metals by Plasma Emission Spectroscopy, 1998.

MEF-MA. 315 – *P 1.0 : Effluent – Détermination du phosphore total, digestion à l'autoclave avec le persulfate; méthode colorimétrique automatisée.*

Alberta Research Council – Total Phosphorus, October 1, 1996.

Chloride

Ontario MOE method E3016 – The Determination of Chloride in Drinking Water, Surface Water, Sewage and Industrial Waste by Colourimetry, September 21, 1999.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Chloride, 1998.

MEF-MA. 300 – *Ions 1.0 : Eaux – Détermination des anions; méthode par chromatographie ionique.*

Sulfate

Ontario MOE method E3172 – The Determination of Sulphate in Water by Automated Ion Chromatography (IC), December 6, 1999.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Sulfate, 1998.

MEF-MA. 300 – *Ions 1.0 : Eaux – Détermination des anions; méthode par chromatographie ionique.*

Major cations (Ca, Mg, K, Na)

Ontario MOE method E3217 – The Determination of Cations in Water, Sewage, Health Samples, Industrial Waste and Landfill Leachates by Atomic Absorption Spectrophotometry (AAS), June 12, 1997.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Calcium, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Magnesium, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Potassium, 1998.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 – Sodium, 1998.

Conductivity

Ontario MOE method E3218 – The Determination of Conductivity, pH and Alkalinity in Water and Effluents by Potentiometry, January 12, 2000.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2510 – Conductivity, 1998.

MEF-MA. 115 – *Cond 1.0 : Effluents – Détermination de la conductivité; méthode électrométrique.*

Hardness

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2340 – Hardness, 1998.

Alkalinity

Ontario MOE method E3218 – The Determination of Conductivity, pH and Alkalinity in Water and Effluents by Potentiometry, January 12, 2000.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2320 – Alkalinity, 1998.

Acidity

Ontario MOE method E3248 – The Determination of pH and Acidity in Water by Potentiometry and Titrimetry, October 26, 1999.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2310 – Acidity, 1998.