

PART A
QUALITY CONTROL AND QUALITY ASSURANCE

©Her Majesty the Queen in
Right of the Province of British Columbia
2013
All Rights Reserved

Table of Contents

1. INTRODUCTION.....	4
1.1 QA Guidelines	4
1.1.1 Study Considerations	4
1.1.2 Design Considerations	5
1.1.3 Field Activities.....	5
2. GENERAL GUIDELINES.....	6
2.1 QA Manual	6
2.2 Field Sampling Record Keeping.....	6
2.3 Sample History Requirements	7
2.4 Sampling Methods Documentation	7
2.5 New Sampling Methods.....	8
2.6 Sample Preparation and Pre-Treatment.....	8
2.7 Equipment	8
2.8 Sampler Qualifications	9
2.9 Chemical Reagents and Preservatives	9
2.10 Reagent Water	10
2.11 Gravimetric Measurement	11
2.12 Volumetric Measurement	11
2.13 Sample Containers.....	11
2.14 Contamination Control	12
2.15 Calibration Practices	12
2.16 Quality Control Approaches	12
2.17 Quality Control Samples	13
2.17.1 Field and Trip Blanks.....	14
2.17.2 Field and Trip Reference Standards.....	15
2.17.3 Duplicates and Replicates	15
2.17.4 Multi-Agency Same Site Replicates	16
2.17.5 Split Samples.....	16
2.17.6 Matrix Spiking	16
2.17.7 Surrogate Spikes	18
2.18 Data Quality Objectives	18
2.19 Expression of Results	18
2.20 Performance Audits	19
2.21 Interstudy Comparison Results.....	20
3. FIELD ANALYTICAL LABORATORIES	20
4. SOURCES OF FURTHER INFORMATION.....	20
4.1 Laboratory QA/QC.....	20
4.2 Sampling QA/QC	21
5. REVISION HISTORY	22

APPENDIX 1 SAMPLER EVALUATION CHECK LIST 23

**APPENDIX 2 AUDIT TYPES, PURPOSE, AND SUGGESTED AUDIT
FREQUENCY..... 24**

**APPENDIX 3 QUALITY ASSURANCE GUIDELINES TO SUPPLEMENT THE
STANDARD EFFLUENT AND RECEIVING ENVIRONMENT QUALITY
ASSURANCE CLAUSE..... 25**

1. Introduction

A thorough program of quality assurance/quality control (QA/QC) will enable collection of meaningful and scientifically credible samples. Quality assurance (QA) includes a range of management and technical practices designed to guarantee that the delivered end product is commensurate with the intended use. For environmental- or discharge-related studies, QA ensures that the data are of adequate scientific credibility to permit statistical interpretations which lead to resource use management decisions.

One of the most important aspects of QA is quality control (QC). QC includes specific formal goals (called data quality objectives, or DQOs), collection of data to assess data quality, the statistical assessment of the data quality, and the remedial measures taken whenever the DQOs are not realized.

A successful program of QA/QC not only ensures the sampling process is in control but should also present estimates of the sampling error, especially sampling variance.

If some component of a sampling program is found not to be in control, then remedial response must be immediately initiated as soon as the problem is discovered, and both the problem and the remedial response must be thoroughly documented. Timely feedback communication between samplers and analysts is essential once a problem has been identified.

1.1 QA Guidelines

Guidelines alone cannot guarantee high quality results. However, a genuine commitment to the following guidelines should ensure that problems are identified and remedied on a timely basis.

1.1.1 Study Considerations

- Develop clearly specified study objectives for sampling programs.
- Ensure staff participate in ongoing programs of staff training.
- Ensure that every sampling program has an identifiable person designated to be responsible as the QA Officer for the program QA/QC; for large programs this should be a full time position. The QA Officer should never be the person responsible for a program's monetary budget, since budget minimization and QA optimization are often antagonistic rather than complementary responsibilities, and QA should have an independent champion.
- Ensure criteria (sometimes called data quality objectives or DQOs) are established on a formal basis and are followed. It is important that resources and monies not be wasted collecting out-of-control information.

- Involve analytical laboratory personnel in study planning and data interpretation.

1.1.2 Design Considerations

- Base sampling program design upon statistical concepts.
- Ensure each and every step of the sampling and post-sampling process follows documented protocols.
- Enhance regular documentation with photographs and video recordings.
- Ensure samples are ‘representative’ of the environment, object, or waste being sampled.
- Ensure proactive method improvement practices are performed.
- Participate on collaborative studies to ascertain accuracy and precision of the results and to ensure results are comparable to those produced elsewhere.
- If a separate study using different personnel is underway in the same or neighboring environs, initiate one or more common sites where both teams can both sample and share results. Data comparisons between different teams at one locale offer effective and timely pointers to methodology problems.
- Implement regular inspections by the QA Officer of every aspect of the sampling program on a regular basis and issue written QA/QC reports on a regular basis, usually quarterly or annually.
- Ensure that the overall sampling program is re-evaluated in detail by an outside party not less frequently than every five years.
- Minimize environmental impacts due to monitoring and sample collection. Small ecosystems may be so vulnerable as to be severely affected by the sampling process itself.
- Ensure samplers have a written “game plan” of what to do and whom to contact when something goes wrong.

1.1.3 Field Activities

- Label all samples with unambiguous identification of exact date, place and time of sampling plus name of sampler.
- Record all details relevant to the sampling in a field note book; unusual conditions and variations from usual sampling techniques especially require thorough documentation.
- Ensure instruments and equipment are regularly maintained and calibrated; maintenance logs shall be kept.
- Follow common sense approaches to avoid contaminating samples, clean sample collection equipment regularly, check equipment cleanliness and performance by running blanks and reference samples where appropriate.

- Where practical, collect samples from areas that are fairly homogeneous in time and space (i.e., avoid sampling situations where a small distance in time or space will yield very different results). Where it is not practical to avoid such situations, special attention will be required to achieve representative samples.
- Collect replicate samples towards ascertaining the precision of the sampling method, or the analytical procedure, and also the local heterogeneity. Total assay error (sum of analytical error plus sampling error) should preferably be <10% of local heterogeneity (as variance), and must not exceed 20% of local heterogeneity (as variance). Analytical error (as variance) should fall below 4% of local heterogeneity (as variance).

2. General Guidelines

2.1 QA Manual

Major sampling programs shall have a formal QA Manual which documents all resources, policies and procedures pertinent to that sampling program. The Quality Manual shall include detailed descriptions of the topics outlined in this section and shall clearly define the QA/QC responsibilities of management, supervisory staff, and field samplers.

The QA Manual shall be reviewed and updated regularly. Revisions shall be both dated and initialed.

2.2 Field Sampling Record Keeping

The Field Sampling Record System shall be designed to ensure sample and sampler traceability, including dates and samplers' initials or signatures. Dated and signed materials shall include forms, instrumental records and printouts, as well as notebooks.

If a sample numbering system is employed, it must be designed to eliminate the possibility of a sample mix-up.

The record storage system should be designed for easy retrieval. A policy on the length of the storage and disposal of records shall be established. A policy shall also be established as to the ownership of field notebooks, and as to their deposition when an individual sampler ceases employment on a project or with a company.

2.3 Sample History Requirements

Documentation and procedures on sample history shall be maintained, including:

- Method of sample collection
- Time and location of sampling
- Name of sampler(s)
- Chemical preservative added or other sample treatment
- Type of sample containers used
- Storage conditions
- Time and condition of sample on receipt at laboratory

Potential deficiencies in sample history requirements shall be monitored. Noncompliance must be identified and remedied.

2.4 Sampling Methods Documentation

An inventory of sampling methods shall be maintained that will include:

- All current methods
- All previous methods
- Date of transition from one method to another

Sampling method and procedures documentation shall include:

- A description of the procedure in sufficient detail that an experienced sampler, unfamiliar with the specific sampling method, should be able to perform the sample collection and treatment.
- Procedures for preparation of preservative reagents, if employed.
- Operating instructions for the sampling equipment, which are supplemental to the manufacturer's operating manuals.
- Method specific requirements for quality control sample preparation and analysis.
- Quality control criteria (i.e., acceptable limits).

Sampling methods and documentation shall be reviewed on a regular basis, not less than once a year. Methods shall be periodically revalidated, particularly when there has been a change in either equipment or personnel.

Where data are kept on computer files, changes in sampling methodology shall be reflected by changes in related computer codes.

2.5 New Sampling Methods

Sampling methods shall be reviewed periodically to ensure that the most up-to-date methods are being used. Sampling methods which are new to the samplers, are modifications to existing methods, or have been developed in-house must be validated. Validation shall include verification of the efficiency and adequacy of the sampling device or method over the range of conditions to be encountered. Validation shall additionally include equivalency testing to established sampling techniques.

2.6 Sample Preparation and Pre-Treatment

Documentation shall be maintained for sample preparation and pre-treatment procedures including, where relevant, the detected procedures followed for:

- Drying or removal of moisture
- Determination of moisture content
- Sub-sampling, whether in field or in-laboratory
- Preparation of geological samples including splitting, sieving, grinding, pulverizing
- Filtration and preservation of water samples
- Specialized preparation of biological samples
- Sample homogenization
- Spiking samples with radionuclides or other tracer chemicals
- Filtration
- Addition of chemical preservatives or reagents
- Freezing or freeze-drying

Complete records shall be maintained to ensure that potential problems, including cross-contamination, are traceable.

2.7 Equipment

Equipment logs shall specify:

- Manufacturer, model, serial number
- Significant modifications
- Repair and maintenance history
- Calibration history where relevant
- Performance history

Routine maintenance shall be performed according to the manufacturer's instructions and schedule.

For those instruments requiring calibration, log books or equivalent records shall be kept which document daily operating, calibration, and setup parameters.

Instrument operating instructions which supplement instructions given in the manufacturer's operating manuals should be documented.

2.8 Sampler Qualifications

Records of the qualifications and experience shall be kept for each sampler. These records shall include:

- Copy of current resume
- Records of training in new sampling or assay techniques
- Records of attendance at technical meetings or seminars
- Records of completion of relevant courses (including in-house training courses, night school classes, and courses sponsored by equipment manufacturers)

Proficiency must be demonstrated for each sampling procedure which a sampler is expected to perform.

2.9 Chemical Reagents and Preservatives

All chemical reagents and preservatives shall be reagent grade or better, and must meet specifications identified in sampling methodology protocols.

Where reagents must be prepared or mixed, the detailed procedures for both the preparation and related quality control must be included in the written documentation for the procedure. Additionally, logs must be established and maintained which document the preparation of chemical reagents and preservatives, specifying:

- Supplier, grade, and batch number
- If applicable, details as to drying, mixing, etc.
- Record of all laboratory operations performed and record of weights and volumes, plus all calculations
- Identity of person who prepared the reagent or preservative

A file of certificates for standard chemicals purchased from commercial suppliers shall be kept.

Prior to routine use, and periodically throughout its shelf life, performance of a reagent or preservative shall be verified. The performance of new and old reagents and preservatives should be compared consecutively. Written criteria should be specified setting the criteria for new versus old reagents.

All chemical reagents and preservatives must be properly labeled. Labels shall identify material, concentration, date prepared plus expiry date. Expiry dates will vary depending on the chemical composition. A general guideline for concentrated standard stock solutions is an expiry date of one year. Expired chemical reagents or preservatives are never to be used, even if the expiry date is only one day past.

Where practical, it is recommended that preservatives be pre-measured under laboratory conditions into vials or ampoules, and sealed for later use in the field without need for further measurement. Bulk preservatives intended for use with numerous samples are much more likely to become contaminated than sealed ampoules intended for single use.

2.10 Reagent Water

Reagent water shall comply with ASTM D 1193-77, Standard Specification for Reagent Water, Type I, Type II, or Type III, or Standard Methods 18th Edition (1992), Section 1080 Reagent-Grade Water, Type I or Type II. If you are not sure what the previous sentence means, then it is recommended that you have the analytical laboratory which will be analyzing your samples supply appropriate reagent water.

Reagent Water must be free from chemical substances and from microbiological organisms that might interfere with laboratory analyses of the samples. For many procedures, the presence of contaminants may be checked by submitting samples of Reagent Water as if they were genuine field collected samples. Microbiological evaluation may be performed using a Total Plate Count.

Analytical laboratories are expected to record the conductance of Reagent Water daily if it is in regular use, or weekly if it is infrequently used. Usually such thorough checking is not practical under field conditions. Therefore, firm rules must be followed to ensure an adequate quality of Reagent Water:

- Never use Reagent Water of unknown source.
- Never use Reagent Water which has passed its expiry date even if the bottle is sealed.
- When a bottle of Reagent Water is first opened note the date on the bottle and do not use Reagent Water that was first opened more than one month previous.
- Using DI water prepared by one laboratory, for samples to be submitted to another laboratory is discouraged.

2.11 Gravimetric Measurement

The accuracy of gravimetric measurements shall be ensured by referencing calibrations to class S or S-1 weights. Annual balance calibration and daily calibration checks are required, and records must be kept. (Note that “S” and “S-1” are terms defined in NIST (formerly NBS) Circular 547.)

2.12 Volumetric Measurement

The use of class A glassware will ensure accuracy of volumetric measurements.

Delivery volumes of automatic pipettes and diluters shall be checked on a routine basis and records of results maintained.

Volumetric glassware must be regularly cleaned and must not be oven dried. The effectiveness of cleaning shall be monitored by the analysis of blanks using randomly selected glassware. The results shall be recorded. Up-to-date documentation shall be kept on all glassware cleaning procedures and requirements.

2.13 Sample Containers

Sample containers should be supplied by the analyzing laboratory pre-cleaned and capped, and preferably within sealed plastic-film dust-protection. The sample containers should be checked periodically for contamination both by the analyzing laboratory and by submission of sample blanks or low level standards. Warehouse storage of uncapped bottles is not acceptable. Cleaning of old bottles for reuse may be appropriate for some situations, but is inappropriate for many situations due to increased likelihood of contamination. Good practice calls for recycling rather than reuse of bottles. (This also applies to preservative vials.)

Bottle cleaning must be carried out under laboratory conditions, and should not be done in the field. **Rinsing of bottles with sample prior to sample collection is strongly discouraged.**

Sample containers must be sufficiently robust to take fairly rough handling in the field without rupturing or leaking.

It is usual for different sample types and different groups of analytes to require specific types of sample containers and/or specific types of container lids. The analyzing laboratory should be consulted before sampling commences to ensure appropriate sample containers and lids are used. Information to this regard is in the 1994 Laboratory Manual (Permittee Edition).

As a rule, nothing but a sample and sample preservatives should ever be placed into a sample container. Never permit a thermometer, pH probe, or such like to be placed into a sample bottle, unless that bottle is a throw-away intended for no other purpose.

2.14 Contamination Control

Effective separation of incompatible activities must be ensured.

The process of sample collection or sample pre-treatment must not interfere with nor lead to contamination of other monitoring or sampling in progress. For example, a series of nearby sites sampled consecutively in a small stream should be sampled from the downstream sequentially upstream. Similarly, a series of contaminated sites should preferably be sampled from least contaminated to most contaminated.

2.15 Calibration Practices

The accuracy and stability of calibrations shall be established by setting requirements for the following, as appropriate:

- Equivalent standard/sample reagent backgrounds
- Reagent blanks to establish zero response
- Control and verification standards to verify accuracy and stability
- Associated control limits and specified corrective action

All calibration results and remedial actions must be recorded.

2.16 Quality Control Approaches

Appropriate quality control techniques shall be applied to each sample collected, series of samples collected, or series of measurements made in-situ. The QC data must be available to the client and the inclusion of QC results in reports is encouraged.

It is important that there be good communication and close cooperation between persons responsible to collect the samples and persons responsible to perform laboratory analyses upon those samples. The samplers and analysts should be involved jointly in all aspects of QC from program design to data interpretation. **It is particularly important that there be timely identification of problems, with effective feedback between samplers and analysts.** Identifying a problem five years after the fact is too late to effect corrections.

2.17 Quality Control Samples

In addition to the various environmental samples which must be collected to meet the objectives of the monitoring program, additional samples must be collected to meet the associated QA/QC objectives. These samples are known as “Quality Control Samples”. Generally, QC Samples are collected to meet two primary goals. The first goal is to give early warning if any sampling or analytical process begins to move out-of-control. The second goal is to provide data for use towards quantitating and identifying sources of systematic and random error associated with the collection and analysis of samples. The type and number of quality control samples to be analyzed should be stated in a section of the overall Quality Manual.

For samples collected and forwarded to laboratories for analysis, quality control samples shall include:

- Field and trip blanks to monitor possible contamination prior to receipt at the laboratory.
- Duplicate or replicate samples to measure both field sampling error plus local environmental variance
- In-house reference samples to monitor accuracy;

Optional Quality Control samples include:

- Analytical spikes to measure recoveries
- Surrogate spikes to measure recoveries
- Certified reference samples to monitor accuracy
- Split samples to compare 2 or more laboratories

For samples analyzed in the field, quality control samples shall include:

- Method blanks to monitor possible contamination
- Duplicate or replicate samples to measure both field sampling error plus local environmental variance
- Duplicate or replicate analyses to ascertain the method precision
- In-house plus certified reference samples to monitor accuracy
- Analytical spikes to measure recoveries
- Surrogate spikes to measure recoveries

For measurements made in-situ, quality control results shall include:

- Hysteresis plots when results are collected as vertical profiles
- Regular confirmation of the accuracy of the clock

- Regular intercomparisons either with a similar instrument or, preferably, with an instrument based on different operating principles.

Due to the wide diversity of samples collected or measurements made, it is not possible to list all QC requirements in this section. However, the Quality Manual for the study should have a comprehensive list covering every method to be employed by that study. In general, a level of QC in the range of 20 to 30% is considered appropriate, however, should serious problems be encountered, QC costs can easily rise in excess of 50% of resources. Note that large coordinated studies require far less proportion of total resources committed to QA than do small fragmented studies.

2.17.1 Field and Trip Blanks

‘Trip blanks’, sometimes called ‘transport blanks’, are aliquots of analyte-free reagent water which are sent from the laboratory to the field, and are later returned along with genuine samples. The seal remains unbroken in the field. These trip blanks are useful to determine contamination which might arise during handling, transport or storage of the samples.

‘Field blanks’, sometimes called equipment blanks or sampling blanks, are aliquots of analyte-free reagent water which are sent by the laboratory to the field, but the seal is broken in the field and the field blank sample is handled identically to a genuine sample. The purpose of field blanks is to determine contamination arising from the sample collection equipment, sample handling equipment (e.g., filtration apparatus) or from the general conditions during sampling (e.g., blowing dust). Since samplers have different preferences for where to start the field blank process (for example, some people place the field blank bottle in the sampler and lower it to water level, other start at post-collection step prior to sample handling, still other start at addition of reagents step), it is important to document in the field notebook exactly what procedure was followed. Ideally the same practice would be followed throughout a study, according to practice set out in standard protocols or in the QA Plan.

Laboratory, trip, and field blank information should be reported along with the genuine results. When interferences are identified, the cause should be investigated and the problem remedied. The extent of the contamination problem should be discussed, including the likely effect upon the data. However, good practice does not permit ‘correction’ of the data by subtraction of either trip blank nor field blank data. Note that even when submitted on a blind basis, laboratories can often identify which samples are blanks.

2.17.2 Field and Trip Reference Standards

‘Trip Reference Standards’, sometimes called ‘transport reference standards’, are aliquots of water of known analyte concentration which are sent from the laboratory to the field, and are later returned along with genuine samples. The seal remains unbroken in the field. These trip reference samples are useful to determine both contamination and analyte loss which might arise during handling, transport or storage of the samples. They also yield estimates of analytical error.

‘Field Reference Samples’, sometimes called QC Samples, are aliquots of water having known concentrations which are sent by the laboratory to the field, but the seal is broken in the field, the contents are poured out and are handled identically to a genuine sample. The purpose of field reference samples is to determine contamination or analyte loss arising from the sample collection equipment, sample handling equipment (e.g., filtration apparatus) or from the general conditions during sampling (e.g., blowing dust). Since samplers have different preferences for where to start the field reference sample process (for example, some people place the field blank bottle in the sampler and lower it to water level, others start at post-collection step prior to sample handling, still others start at addition of reagents step), it is important to document in the field notebook exactly what procedure was followed. Ideally, the same practice would be followed throughout a study, according to practice set out in standard protocols or in the QA Plan.

Laboratory, trip and field reference sample information should be reported along with the genuine results. When interferences are identified, the cause should be investigated and the problem remedied. The extent of the contamination problem should be discussed, including the likely effect upon the data. However, good practice does not permit ‘correction’ of the data by subtraction of either trip nor field reference sample data.

2.17.3 Duplicates and Replicates

Replicate samples are multiple (i.e., two or more) samples collected at the same location and time, by the same person, and using the same equipment and procedures. The smallest number of replicates is two (i.e., a duplicate). The purpose of collecting replicate samples is to obtain the precision for each analyte analyzed within these samples. The observed variance will be the sum of the local environmental variance, the analytical variance, plus the sampling variance. There are various methods to estimate the sources of variation in results. Replicate analyses of replicate samples has been reported to be a particularly useful QC approach in that it permits identification of analytical uncertainty, sampling uncertainty, and environmental heterogeneity via analysis of variance (ANOVA) calculations (Ramsey et al., 1992).

The QA Manual should include Data Quality Objectives (DQOs) for the relative proportions of categories of variance. At a minimum, the sum of the analytical variance plus sampling variance should be less than 20% of the observed local variance.

2.17.4 Multi-Agency Same Site Replicates

It often is important to show that different studies provide comparable data. For adjacent studies by different agencies, the best way to do this is by having a series of duplicate or replicate samples collected by both studies at one or more common sites. Preferably, these samples should be collected at the same time. Each sampling team or person must use the regular personnel, equipment, and procedures.

2.17.5 Split Samples

Split samples are sub-samples taken from one large sample which has been homogenized and divided into two or more sub-samples. The homogenization minimizes differences between samples due to environmental variance. Split samples usually are used to compare results between two or more methodologies or two or more laboratories. They are used for different purposes than replicate samples, and must be clearly identified so as not to be confused with true replicate samples. Similarly, repeat analyses of a sample by a laboratory, and also division of a sample into two or more sub-samples by a laboratory are both used for different purposes from replicate samples (and from each other) and must be clearly identified to avoid ambiguity.

Split samples are not appropriate where the method used to produce the split samples itself imposes significant sampling error. Most sample splitters do not perform well for samples high in non-filterable residues (= suspended solids).

2.17.6 Matrix Spiking

Matrix spiking may be employed sometimes as part of an ongoing QA/QC program either to monitor the performance of a laboratory or of a specific instrument. Changes in spike recoveries over time for similar sample matrices may indicate variation in analytical results.

Matrix spiking may also be used at the initiation of a new technique or instrument to ensure the method or instrument is appropriate to the matrix being sampled.

Very large bias, whether positive or negative, would indicate the procedure or instrument was ineffective for that matrix. Spiking may also yield information as to interference problems, recovery problems and sample stability problems.

It is recommended for both accuracy and safety reasons that spikes be prepared by trained laboratory analysts under laboratory conditions. Field spiking operations should consist solely of adding a prepared spiking solution to the sample matrix. Field personnel performing spiking must have been trained in this technique.

Additionally, the reproducibility of field spiking must be confirmed regularly through periodic replicate spikes.

Spiking solutions must be clearly labeled as to content, expiry date, added preservatives, and as to appropriate storage environment. For example, some spiking solutions may have to be kept in the dark, or may have to be kept over ice.

Spiking solutions should be of similar levels to what is expected in the environment. Spikes more than 5 times what actually occurs in the environment can mask interference effects, leading to over-optimistic estimates of analyte recovery. Spiking solutions should be small (less than 2%) of sample volumes so as not to affect the sample matrix. Spiking is not appropriate at concentrations below 5 times detection limit, nor is it appropriate for unstable chemicals for incompatible solvents. Genuine sample matrices should be used. A common fallacy is to assume that an overnight spike of sand with some contaminant has some relationship to multi-year exposure of soil with that substance.

Samples should be closely examined just prior to and after addition of spiking solution. Any colour change, or an obvious increase in sample turbidity, may be indicative of a change in sample matrix or of related problems such as semi-miscible solvent.

There are two problems to keep in mind when performing spike addition or when analyzing spike results. First, a spike program should also include a program of sample splitting or sample replication for genuine samples. Second, the spiked material may change chemically within the matrix over time. Thus, a just added spiked substance may have different chemistry than that same chemical in that same matrix for 5 or 10 years.

If performed, then spike information should be reported along with sample analysis results. However, it is not good practice to 'correct' genuine samples results based on spike recoveries.

Spike recovery is very dependent upon analyte, method of sampling and analysis used, on sample matrix, and on the concentration of analyte in both spiked and non-spiked samples. The QA Plan should specify appropriate data quality objectives specific to interpreting spike results for specific analytes. Certainly results outside three standard deviations of historic results at a particular site and matrix condition warrant further investigation.

2.17.7 Surrogate Spikes

Surrogate spikes are spikes as described previously, with the important distinction that rather than spiking with the analyte of interest, one spikes with a substance distinctly different to the analyte but having very similar chemical properties in so far as the method of analysis is concerned. This permits one, for example, to substitute a non-toxic substance for one of extreme toxicity, provided both have been proven to behave similarly for the chemical assay procedure. Surrogate substances usually are chosen such that they are unlikely to occur in genuine samples. Isotopically labeled compounds are often used for this purpose.

Surrogate spikes are a practical method to prove an assay method is in control. Surrogate spikes would not be used for a field study without close liaison with analytical laboratory personnel. Use of surrogates to adjust results, for example to compensate for evaporation loss, is strongly discouraged.

2.18 Data Quality Objectives

Data quality objectives (DQOs) are formal data quality specifications, which must be tabulated within the QA Manual. These objectives determine the maximum amount of uncertainty (or error) which can be tolerated in the data if it is to be satisfactory for the intended use. DQOs are highly specific to the intended use of the data, and also to the overall costs. The DQOs should be specified within the Quality Manual before any samples are collected, so as to avoid situations where monies are spent collecting samples which are inadequate for the intended purpose.

Once DQOs have been established and sampling has commenced, there must be regular performance checks to determine whether or not the DQOs are met.

Corrective action must be taken when DQOs fail to be met. The Quality Manual must include specific actions which must be taken to check the DQOs and also specific action must be taken when any particular DQO is not met. Out-of-control events and actions must be recorded.

Appendix 3 tabulates some example DQOs (Acceptability Criteria) and appropriate actions when these criteria fail to be met.

2.19 Expression of Results

Since it is highly likely that measurements made in the field may be subject to further calculation and data analysis, it is recommended that the numeric results be reported with additional digits beyond those of the significant figures convention.

Where practical, explicit estimates of bias and precision should form part of the record of numeric results. The procedure used to estimate bias and precision should be recorded in the Quality Manual. The practice of left-censoring of data below the detection limit is discouraged, since it results in ambiguity. Good practice suggests reporting in such situations of actual instrumentation reading plus an unambiguous estimate of laboratory uncertainty.

Variable names should be stated in consistent, unambiguous terms.

Units must be expressed in unambiguous terms, for example:

Reporting Unit Type	Example Units
weight/volume	%(w/v), mg/L, µg/L
weight/weight	%(w/w)
volume/volume	%(v/v)

2.20 Performance Audits

Sampler performance should be audited periodically to check the functioning of QC procedures. Such Performance Audits link a program to a uniform standard that may be regional, provincial, national, or international. While these audits may be performed in-house usually, it is important that the audits be performed occasionally by an independent expert. Records of audit results and of action taken should be kept.

Performance Audits should include visits to the sites where the activities to be audited are actually performed. The Auditor should check that written protocols do exist, are being followed, and do genuinely correspond to actual practice. The Auditor should check that the activities being performed correspond to the goals requiring that activity, that all staff are trained in both the activity and associated safety aspects.

The Auditor should particularly check for deficiencies where scientific methodology has advanced and old technologies are no longer appropriate. For the convenience of auditors when auditing field sampling activities, a Sampler Evaluation Check List is included as Appendix 1 of this chapter.

Recommendations as to different types of audits, purpose and relative timing are tabulated in Appendix 2 of this chapter.

External audits are intended to introduce an independent, fresh point of view. External auditors should not be employed by or be closely associated with the office being audited. Use of different persons for successive independent audits is to be encouraged.

2.21 Interstudy Comparison Results

One cannot always tell from reading printed methodologies whether the sampling and monitoring used by different study agencies yield comparable results. Therefore, agencies involved in the collection and analysis or monitoring of environmental and discharge samples are strongly urged to participate in Interstudy Comparisons Programs.

Interstudy Comparison Programs have two or more study groups simultaneously monitoring side-by-side to exchange of collected samples, for example, exchange of diatom samples for comparison of taxonomic identifications.

3. Field Analytical Laboratories

Where the equivalent to an analytical laboratory has been established in the field, the procedures specified in the British Columbia Environmental Laboratory Manual should be followed. The manual includes protocols for setting method detection limits, plus protocols for blank correction.

Since many technicians are under the impression that blank correction is mandatory, it should be emphasized during training that blank correction is only performed under specific conditions. Inappropriate blank correction will add analytical noise, rather than reduce it. Blank correction rarely is appropriate.

Note that many field laboratories may fall under Section 5 of the British Columbia Environmental Laboratory Manual. Section 5 provides for a somewhat reduced QC program for small laboratories provided they maintain a satisfactory score (PE Score >70) on the EDQA interlaboratory comparison program and also provided they run analyses in small batches (i.e., fewer than 11 samples per batch). Laboratories failing to achieve a satisfactory score on the EDQA interlaboratory comparison, or which run large batches of samples are expected to follow the full QC program.

4. Sources of Further Information

4.1 Laboratory QA/QC

Anon. Standard Methods for the Examination of Water and Wastewater, AWWA, APHA, 18th Edition (1992), Section 1000.

Creed, J. T., Martin, J. D., and Sivaganesan, M. 1995. Preservation of Trace Metals in Water Samples. *Journal AWWA*, 104-114.

Garfield, F.M. 1991. Quality Assurance Principles for Analytical Laboratories. Association of Official Analytical Chemists, USA.

Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers Inc., Chelsea, Michigan, USA.

Worthington, J.C., Coll, S.A., and TechLaw Inc. 1992. Auditing Environmental Data Systems. 46th Annual Quality Congress (May 18-20, 1992). Nashville Conference No. 18445. Pages 692-705.

4.2 Sampling QA/QC

American Society for Testing and Materials. 1990. Emergency Standard Practice for Generation of Environmental Data Related to Waste Management Activities. ASTM Designation ES 16 - 90. 14 pages. See Annual Book of ASTM Standards.

Barcelona, M.J. 1988. Overview of the Sampling Process. In Principles of Environmental Monitoring, L.H. Keith(ed.). American Chemical Society, Washington, DC, USA. 458 pages.

Beak Consultants Ltd., Brampton, Ontario. 1991. Quality Assurance Guidelines for Biology in Aquatic Environment Protection. Report prepared for the National Water Research Institute, Environment Canada, Burlington, Ontario, Canada.

Clark, M.J.R. 2000. Quality Assurance in Environmental Analysis. In: R.A. Meyers (ed.), Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester, UK, pp. 3197-3227.

Clark, M.J.R. and Whitfield, P.H. 1993. A Practical Model Integrating Quality Assurance into Environmental Monitoring. Water Resources Bulletin, **29**: 119-130.

Csuros, M. 1994. Environmental Sampling and Analysis for Technicians. Lewis Publishers, Ann Arbor, USA.

Gilbert, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York, USA, 320 pp.

Hopps, H.C. 1986. Representative Sampling of Human Tissue. Journal of the National Bureau of Standards, **91**: 47-50.

Keith, L.H. 1991. Environmental Sampling and Analysis: A Practical Guide. Lewis Publishers, Boca Raton, Florida, USA.

- Kramer, K.J.M. 1994. What About Quality Assurance Before the Laboratory Analysis? *Marine Pollution Bulletin*, **29**: 222-227.
- Kratochvil, B. and Taylor, J.K. 1981. Sampling for Chemical Analysis. *Analytical Chemistry*, **53**: 924A - 938A.
- Kratochvil, B., Wallace, D., and Taylor, J.K. 1984. Sampling for Chemical Analysis. *Analytical Chemistry*, **56**: 113R - 129R.
- Loring, D.H. and Rantala, R.T.T. 1992. Manual for the Geochemical Analyses of Marine Sediments and Suspended Particulate Matter. *Earth-Science Reviews*, **32**: 235-283.
- Prasad, S.S. 1994. Trends in Quality Assurance in the Characterization of Chemical Contaminants in the Environment. *Trends in Analytical Chemistry*, **13**: 157-164.
- Ramsey, M.H., Thompson, M. and Hale, M. 1992. Objective Evaluation of Precision Requirements for Geochemical Analysis Using Robust Analysis of Variance. *Journal of Geochemical Exploration*, **44**: 23-36
- Thompson, M. and Howarth, R. J. 1978. A New Approach to the Estimation of Analytical Precision. *Journal of Geochemical Exploration*, **9**: 23-30.
- Thompson, M. and Howarth, R. J. 1976. Duplicate Analysis in Geochemical Practice (2 parts). *Analyst*, **101**: 690-709.

5. Revision History

- February 28, 2001: Brief clarification text added to the Regent Water, the Split Sample and the Surrogate Spikes sections. Also Appendix 3 was added.
- November 1996: Initial publication.

Appendix 1 Sampler Evaluation Check List

Date:
Site:
Sampler:
Observer:

STEP or PROCEDURE	OKAY?	COMMENTS:
sampling day and shipping arrangements followed safety protocols planned to minimize transit delays		
bottles clearly labelled & dated using a permanent marking pen.		
samplers (and associated items such as ropes) are clean before use.		
bottle caps removed just before sampling, are protected from contamination i.e., placed in a clean, dry plastic bag; avoids touching inside of caps & bottles.		
exercises caution when sampling; generally safety conscious around site.		
sample taken at designated sampling site; any deviations from site location recorded.		
samples in deep, well-mixed & flowing water whenever possible.		
samples upstream when wading; avoids collecting in stirred-up water.		
avoids causing debris from falling from bridge onto the sampler.		
sample bottles are not rinsed before collection (i.e., are lab pre-cleaned).		
bottles filled to correct level & securely capped immediately after filling, i.e., room for preservatives, small air space for coliforms.		
handles preservatives carefully with appropriate safety equipment, i.e., gloves & glasses; demonstrates technique that minimizes preservative contamination; empty preservative vial re-capped, placed inside secondary container and returned to cooler.		
no contact between preservative vial or dispenser & sample water or sample bottle.		
no contact with sample water, inside of bottles or caps with anything!		
allowed thermometer to equilibrate 3 or 4 minutes in field bottle before reading; thermometer never inserted in any sample bottle.		
sampling time recorded as hh/mm (2400 hour clock); sample date as yy/mm/dd on all lab requisitions.		
packs bottles carefully with enough ice packs to cool temperature sensitive samples.		
records field measurements, observations & possible contamination sources where appropriate.		
reusable sampling & safety equipment is kept clean & stored for future use in such a manner as to minimize damage or contamination.		
shipping coolers secured (taped) for transit; destination clearly labelled on cooler(s).		

Appendix 2 Audit Types, Purpose, and Suggested Audit Frequency

Audit Type	Purpose	Audit Frequency	
		a. In-House Auditor	b. Independent Auditor
Systems Audit	Qualitative (no measurements made) walk-through of operations to ensure that all aspects of the QA Program are operational.	Not less than once per year; ideally once per quarter.	Not less than once every 5 years; preferably every other year.
Performance Audits	Detailed walk-through of operations including quantitative checks such as handing a sampler a known sample to carry through sample handling and preservation, or side-by-side collection of samples alongside the routine sampler.	Not less than once a year; preferably once per quarter. Additional Performance Audits required should there have been a major change in operations, or should either the Systems Audit or the Performance Audit reveal serious QA/QC problems.	Not less than once every 5 years; preferably every other year.
Data Audits	Several samples are selected to be followed through the overall sampling process. All documentation (e.g., field notebooks) from sample collection to final computer records are checked in detail; calculations are confirmed.	At beginning of a new sampling program and annually thereafter.	Not less than once every 5 years; preferably every other year.

Appendix 3 Quality Assurance Guidelines to Supplement the Standard Effluent and Receiving Environment Quality Assurance Clause

The following guidelines have been developed to assist in the administration of the “Standard Quality Assurance Clause” developed by the QA Clause Committee.

The objective of the standard QA Clause is to improve and maintain the quality of compliance and environmental data provided by the permittees.

The clause requires permittees regularly to demonstrate that data quality is acceptable, based on the “Quality Assurance Guidelines”, and to take timely action to correct any unacceptable sample collection and analysis so as to avoid loss of data.

This document sets quantitative guidelines for determining the acceptability of the blank, precision and accuracy data collected as an integral part of the permittee compliance and aquatic impact assessment programs. The guidelines apply to the monitoring of effluents and environmental water samples.

Production of this data will enable permittees to assess their own sampling and analytical performance on a regular basis, as well as to provide the Ministry with an objective method of evaluating permittee performance.

Quality Control Sample Types	Objective	Frequency	Acceptability Criteria	Action on When Criteria are Not Met
Laboratory Method Blanks	To determine the existence and magnitude of any contamination problem associated with laboratory methodology, environment, equipment and reagents.	Minimum of one method blank per batch run.	Laboratory method blanks preferably should not exceed the method detection limit (MDL). Where they do, they must not exceed the detection limit reported by the laboratory for the associated (same batch) samples.	All data associated with the blank must be evaluated to determine the impact upon the sample data. Sample results may require rejection or qualification based upon the degree and source of blank contamination. Note that the method blank is a control sample, and should not be used to substitute for the blank used for blank correction.
Field Blanks	To determine the existence and magnitude of any contamination problem associated with sample containers, preservation reagents, or incidental contamination associated with sample collection, sample handling and sample transportation.	Field blanks are optional for monitoring of effluent parameters known to occur in high concentrations. Field blanks should be used for environmental samples and for monitoring of effluent parameters having low permit limits (i.e., near MDL). Minimum of one field blank per sample set.	Field blank contamination preferably should not be significantly greater in concentration nor occurrence than laboratory method blank contamination.	Detectable field blanks values should be checked to determine the source of contamination, and to determine the impact of this contamination upon the sample data. This evaluation may require analyses of additional field blanks, laboratory blanks, equipment blanks and filtration blanks. Sample results may require rejection or qualification based upon the degree and source of contamination. Note that field blanks results may not be subtracted from reported results.
Laboratory Duplicates/Replicates	Measures laboratory precision.	Minimum of one lab duplicate per batch of 15 to 20 samples, or one duplicate per sample set or sample run, or randomly at an average frequency of at least 5% of all samples analysed. Where it is not possible to split a regular sample into two or more subsamples due to requirements for whole sample analysis, field duplicates should be substituted at a similar frequency.	For concentrations below 5 times the MDL, the difference between the two duplicate values shall not exceed twice the reported DL value. For concentrations at or greater than 5 times reported DL, the Relative Percent Difference (RPD, see Note 1) shall not exceed 20%. (The Ministry may establish less rigorous criteria for specific tests known to be imprecise.)	When results fall outside the allowable limits for duplicate values, preferably the entire batch of samples should be reanalysed if practicable. If this is not practicable then all data associated with the suspect data must be evaluated to determine the impact upon the sample data. Sample results may require rejection or qualification depending on the source and extent of the problem. Repeated problems over several batch runs must be thoroughly investigated and remedial measures taken. Laboratories should advise whether or not lab precision is a likely cause of the overall precision failure and QC sampling should be stepped up to pinpoint the cause.

Quality Control and Quality Assurance

Quality Control Sample Types	Objective	Frequency	Acceptability Criteria	Action on When Criteria are Not Met
Field Duplicates/Replicates	Measures overall precision of sampling and analysis plus environmental heterogeneity. Also extremely poor results may indicate lack of representative samples.	Field duplicates are optional for effluents known to be highly stable and homogeneous. Field duplicates (or replicates) are mandatory for unstable or heterogeneous effluents, and for all environmental samples. Minimum of one duplicate sample per sample set.	It should be expected that the RPD is somewhat greater than that for laboratory duplicates. If one of a set of duplicate values at or greater than five times the MDL, then RPD values >20% indicate a possible problem, and > 50% indicate a definite problem, most likely either contamination or lack of sample representativeness.	The source of the problem must be determined, and the impact upon the sample data ascertained. A special evaluation study may well be required. Note that situations where non-representative samples are common call for specialised methods of sample collection.
Laboratory Reference Samples	Laboratory reference samples are SRMs, CRMs or lab-prepared samples handled identically to a genuine sample. Laboratory reference samples can be used to determine accuracy (bias) and multiple reference samples can be used to determine precision.	Minimum of one laboratory reference sample per batch run. Preferably SRMs or CRMs should be used, but where these are not available or practical, then in-house manufactured references may be employed. Where those are not practical, spikes or surrogates may be employed.	Preferably all values should meet the CRM or SRM manufacturer's specified confidence interval for the true value, or within 85% to 115% of the long-term mean, the design value, or the certified target value. However, tests for many organic substances are not this accurate nor precise. It is useful to plot results from laboratory reference samples on control charts. All values should fall within +/- 3 standard deviations of the mean or design value, whichever employed. (Control charts usually have additional decision rules regarding sequential values or runs.)	Where samples are stable, they should be re-analyzed. If this cannot be done, then the impact of the problem must be evaluated. Sample results may require rejection or qualification based on the scale of the problem.
Field Reference Samples	Field reference samples are SRMs, CRMs or lab-prepared samples shipped from lab to field, seal broken, sample poured out and handled identically to a genuine sample. Field reference samples can be used to determine accuracy (bias) and multiple reference samples can be used to determine precision.	It is suggested that field reference samples (and similarly field spikes and surrogates) not be mandatory. They may be employed in special studies to characterise particular problems.	(Study specific)	(Study specific)

Note 1: Whereas replicate data are usually reported in terms of relative standard deviation (RSD) or confidence intervals (CI), duplicate results are usually reported as Relative Percent Difference (RPD). For two duplicate values A and B, where A is larger than B, the $RPD = 2 \cdot (A-B)/(A+B) \cdot 100\%$

Note 2: With regard to both laboratory duplicates and field duplicates, duplicate analysis of blank samples may not be substituted for duplicate analyses of genuine samples.

Note 3: Calibration solutions must not be employed as reference materials. Also blanks may not be substituted for reference materials.

Note 4: For reference samples both the design (manufacturer's) value and the recovery should be reported.

Note 5: Handling of QC samples on a blind basis is recommended where practical, but is not mandatory.

Note 6: Field Duplicates/Replicates preferably should be collocated samples, either samples collected simultaneously side by side or as one large sample split into several sub-samples by a sample splitter. Sequential samples are not encouraged because of environmental heterogeneity.

Note 7: Accuracy is usually measured and reported as % Recovery -- whether for results from SRMs, CRMs, in-house standards, spikes and surrogates.