QUALITY ASSURANCE

IN THE
NATIONAL WATER QUALITY LABORATORY

HAIG AGEMIAN

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FOREWORD

The need for quality assurance has long been recognized by the Water Quality Branch. Activities undertaken by the Branch have increased the demand for measurement data and hence augmented the need for a comprehensive quality assurance program. "Quality Assurance in the National Water Quality Laboratory" describes the steps which must be taken to ensure that all measurement and data processing activities that affect the quality of the data produced in a modern laboratory satisfy preestablished standards. This document is intended as a reference manual for laboratory staff and data users. A companion volume describes field and data management quality assurance, the other activities of the data collection process.

V.E. Niemela
Director, WQB

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PREFACE

During the last decade there has been growing awareness of the impact of toxic chemicals, at trace and ultra-trace levels, on the environment. Social pressures have created a need for elucidation of the effects of chemicals on the ecosystem and humans. Increased emphasis is also being placed on how chemicals migrate in the ecosystem. Analytical data are continually being released by many laboratories and increased method sensitivity and selectivity are being sought to determine toxic chemicals at ultra-trace level.

Recently many agencies have shown a real concern about the validity of analytical data generated at ultra-trace levels. The main reason for such concern is believed to be the methodology differences, lack of documention of procedures and quality control practices used in various laboratories.

In the field of environmental analysis, Quality Control and Quality Assurance are receiving greater attention by laboratory managers and users of data. While there are a number of excellent monographs, reviews and manuals on quality control in environmental monitoring and analysis, it is nevertheless essential for each laboratory engaged in the generation of data to document the internal quality control practices and protocols, which comprise its quality assurance program. This would assist analysts in the generation of high quality of data as well as substantiate data quality to laboratory clients and data users. In addition, it is recognized that "Quality Assessment" activities, whereby the effectiveness of Quality Control practices are determined is an integral part of a successful Quality Assurance program. This is achieved by the proper documentation of Quality Control data on "Quality Assessment Forms" and their systematic evaluation.

The IWD - National Water Quality Laboratory of Environment Canada has developed a quality assurance document for analysts within the laboratory. It is also aimed at providing pertinent information to clients to indicate what precautions are taken to ensure proper calibration and standardization of instruments and analytical systems. It also describes the routine practices that are being implemented by analysts to ensure that data are generated with well defined confidence levels/intervals.

Application of these quality control practices within NWQL is a step towards a dynamic system of process deviation control. It is anticipated that by implementing these practices, systematic errors will be minimized. The topics covered in this document include; definitions of analytical terminology, protocols, quality control procedures and practices, guidelines for good laboratory practice, guidelines for instrument performance control checks and Quality Assessment Forms. By following these standard operating quality control procedures it will be possible to identify problems, improve data quality and design anticipatory actions and options to improve proficiency of analysts and the overall performance of the laboratory.

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INTRODUCTION

The National Water Quality Laboratory (NWQL) generates analytical data for Environment Canada and other government agencies to establish the trend, fate and effects of environmental contaminants in the aquatic environment. In some cases these measurements are used, or misused to establish the degree of pollution loadings and may form a basis for regulatory policy decisions.

Heightened concerns about water quality and new concerns about the possible effects of toxic chemicals at trace and ultra-trace levels have contributed greatly to an increased demand for impartial, objective and independent data which can be used to assess the impact of these contaminants in the aquatic environment.

Agencies who have been involved in environmental measurements for sometime have observed the tremendous increase in analytical sensitivity over the past 10-15 years. For some environmental contaminants, detection limits as lov as a few femtograms have been reported. At the same time greater disparities are found between the reported data at very low levels and the ability of techniques or methods to detect and measure contaminants at ultra-trace levels. In addition, it is very rare to find reported sensitivities, detection limits or data associated with degree of uncertainty (confidence levels/intervals). In many cases the numbers reported by scientists and/or laboratories are used as absolute values by other scientists and governmental agencies to predict loadings, effects and to make regulatory and control decisions. Often these numbers find their way into the media and lend to increased public concerns.

Sometimes people are un-necessarily alarmed by the apparently increasing deterioration of environmental quality without any idea that the assessments and statements are based on data which may have a large degree of uncertainty.

In view of the above, it is essential that scientists who are skilled in making these measurements, at trace and ultra-trace levels for particularly toxic chemicals, do provide valid analytical data with well defined confidence levels and intervals to facilitate the objective interpretation for regulatory policy decisions.

What are valid, reliable and quality data and how can they be assured? There is no single definition that will encompass everyone's understanding of quality. The dictionary defines quality as "excellence, the degree of excellence, relative goodness or grade". In testing laboratories such as the NWQL quality can be interpreted as the ability of the laboratory to generate accurate analytical data with well defined total error. Total error in the laboratory can be defined as the sum of random and systematic errors that can occur during the acquisition, processing, handling, analyzing and reporting of analytical data.

In order to ensure data quality, it is very important that the persons involved in generating these data are knowledgeable and fully committed to the production of high quality data. This is achieved by carefully following well established operating procedures and practices, minimization of errors during analysis, data processing and verification and data reporting.

The purpose of this document is to develop standard operating procedures for those activities of the laboratory which affect data quality. The main objectives are to:

(i) provide laboratory personnel with quality control procedures and practices that will minimize errors from the time of receipt of sample to reporting of results;

(ii) assess the quality and overall performance of the NWQL. By following these quality control practices it will be possible to ascertain that the personnel carrying out various activities within the laboratory are taking appropriate precautions during analysis to ensure that the equipment is properly standardized, calibrated and functioning in accordance with specific and well defined limits, that methods are performing within the accepted tolerance levels and that data verification is undertaken prior to reporting;

(iii) quantitatively determine single operator/multiple operator and overall precision for various determinands, and provide confidence intervals and range of variability of analytical results produced within NWQL.

(iv) institute a "Quality Assessment" program by the periodic evaluation of the effectiveness of Quality Control practices; and

(v) provide an information document to clients so they can ascertain the degree of quality in all measurements being carried out within NWQL. It is anticipated that this will result in a increased client confidence.

I

INTRALABORATORY QUALITY ASSURANCE PLAN

Quality Management involves the activities of senior laboratory managers pertaining to the development and implementation of policies and plans to ensure effective and successful Quality Assurance programs. Quality Management is implemented by the coordination and harmonization of various components of Quality Assurance to ensure optimized and fine-tuned operations and to provide high quality data within available human and financial resources.

Quality Assurance is the overall verification program which provides producers and users of data the assurance that predefined standards of quality at predetermined levels of confidence are met. The objectives of comprehensive Quality Assurance (QA) program are, to:

1. Establish policies and protocols on laboratory Quality Control.

2. Document QA methodology.

3. Standardize data quality control.

4. Provide guidelines for good laboratory practices.

5. Establish a quantitative approach to determine single/multiple operator and overall precision and confidence intervals of analytical results.

6. Make available data quality information documents for clients and data users.

7. Implement a mechanism for auditing laboratory operations.

8. Establish a framework for high calibre analytical practices.

9. Provide QC statements to support analytical practices.

These can normally be fulfilled by the implementation of comprehensive Quality Assurance program which involves the adoption of four major activities in the folowing order:

1. Operational and scientific protocols.

2. Guidelines on Good Laboratory Practices.

3. Quality Control Procedures and Practices.

4. Quality Assessment activities.

The first step includes the implementation of Quality Control protocols of operational and scientific nature. The purpose of these protocols is to establish standardization and conformity of activities throughout the analytical process from receipt of samples at the laboratory to final data reporting to clients. The implementation of these rules ensure that objective performance is maintained in all processes.

The second step in the inhouse QA program is the adoption and ongoing application of a set of guidelines called, "Good Laboratory Practices". These are aimed to provide up to standard laboratory facilities with respect to safety and working environment, staff relations and analytical proficiency, quality of chemicals, reagents and standards, performance of analytical instrumentation and apparatus, standardization, adaptation, validation and documentation of analytical methodology and data recording, reporting and documentation.

In the optimization and control of an analytical activity one must address every variable which may affect data quality. All analytical processes have a large series of factors which must be constantly fine-tuned and controlled. These are normally classified into four main groups as follows:

1. Materials - standards, chemicals, reagents, control samples, standard reference materials, consumables, etc.

2. Machines - instrument meters, recorders, detectors, laboratory equipment, etc.

3. Methods - preservation techniques, sample preparation procedures, analytical methodologies, data management and interpretation protocols.

4. Men and Women - management, supervisory, scientific and technical staff.

Each one of these elements should be optimized and controlled on an ongoing basis to ensure effective operations. The "quality" activities which are engaged to enhance the quality of the above grups of factors are the following:

1. Materials - purification, standardization, intercomparison.

2. Machines - maintenance, troubleshooting, optimization and calibration.

3. Methods - adaptation, validation, standardization, specification testing and documentation.

4. Men and Women - training, good laboratory practices, performance assessment, safety procedures, adherence to protocols and guidelines.

When both QA steps I and II are implemented and the four categories of variables are fine-tuned, then an analytical laboratory is said to have the fundamentals to monitor and evaluate the quality of their produce "data". Steps I and II ensure that all variables which affect data quality are optimized.

Step III namely, the implementation of "Quality Control Procedures and Practices" is designed to provide a quantitative measurement of the quality of the data by the analysis of a set of Quality Control samples, together with every analytical run and interpreting these data to ensure that the process in question is in control. Normally up to five types of QC sample tests may be run for a given batch of samples based on the analytical requirements. They are as follows:

1. Blanks.

2. Within run or between runs duplicates.

3. Surrogate or internal standards.

4. Spikes.

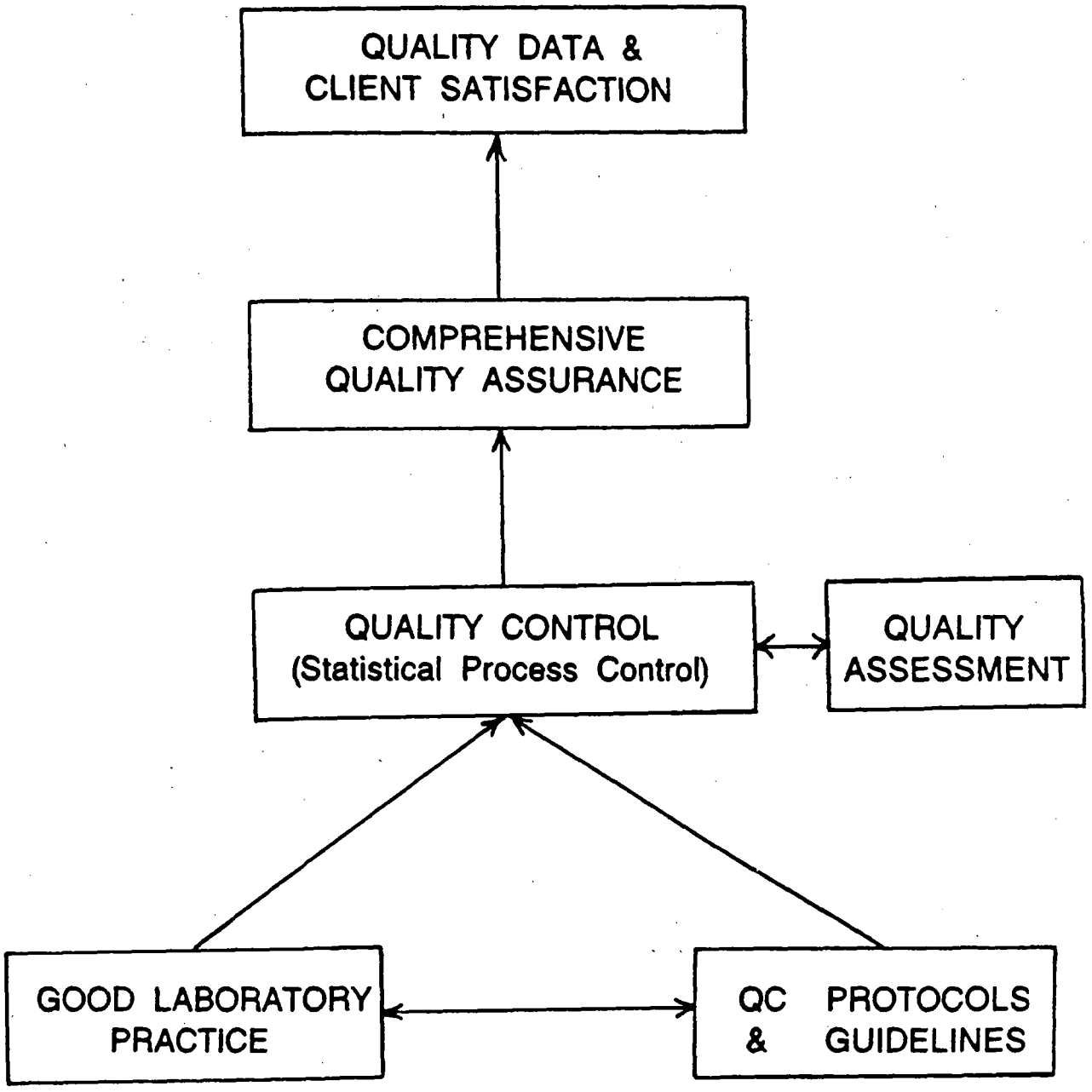
5. Reference samples (inhouse controls or standard reference materials).

These samples are called "Quality Control" samples and are analysed for each set of unknown samples. The quality control data for each batch of samples are normally evaluated to provide information on freedom from contamination (blanks), precision (between and within run duplicates), recovery (spikes), and accuracy (control samples and standard reference materials). These data can be evaluated using statistical and graphical control charting techniques (statistical process control) to provide long term, single and multi-operator performance data as well as confidence limits for analytical methods. The data may be used by laboratory analysts, supervisors and managers as well as by data users and clients to provide QC substantiation of analytical data.

Step IV of the Quality Assurance program namely "Quality Assessment" is the activities predominantly concerned with ensuring that the Quality Control step is carried out effectively. This final step involves evaluation, and auditing of quality control data and taking corrective action on an ongoing basis to fine-tune QA activities and ensure a successful program.

Figure 1 on the following page shows a schematic of the interrelationship of these four major QA steps. A comprehensive intralaboratory Quality Assurance Program is said to be in place only when every one of these areas are well coordinated with the required checks and balances to harmonize and fine-tune the QA activity. The result of a comprehensive QA program is a Quality product, namely Quality Data and a satisfied client.

INTRA-LABORATORY QUALITY ASSURANCE



II

DEFINITIONS OF ANALYTICAL TERMINOLOGY

1. DEFINITIONS

1.1 The following definitions have been adopted from currently available publications. These publications are listed at the end of this section.

2. QUALITY ASSURANCE, QUALITY CONTROL AND QUALITY ASSESSMENT

2.1 Quality assurance is the overall verification program which provides producers and users of data the assurance that predefined standards of quality at predetermined levels of confidence are met.

2.2 Quality Control is the overall system of guidelines, procedures and practices which are designed to regulate and control the quality of products or services with regards to previously established performance criteria and standards.

2.3 Quality Assessment is the overall system of activities which ensure that quality control is being performed effectively. This is carried out immediately following Q.C. and involves evaluation and auditing of Q.C. data to ensure the success of the quality control program (see Chapter VIII).

3. PRECISION

3.1 Precision or reproducibility describes the degree or closeness of agreement between the data generated from replicate or repetitive measurements by applying the same experimental procedure several times under prescribed conditions. Statistically the concept is referred to as dispersion and it measures the variability of the analytical method resulting from random errors. Precision is generally reported as the standard deviation (S.D.) or relative standard deviation (R.S.D.). The precision of an analytical method has two components which should be recorded for each method (3.2 and 3.3):

3.2 Within run precision (SD_w) measure the random error during processing of a single batch of samples analysed at the same time.

3.3 Between run precision (SD_B) measures the variability between various batches of samples analysed.

3.4 The Precision of a method is ordinarily measured by the Standard Deviation (S.D.)

$$S.D. = \sqrt{\sum_i \frac{(X_i - \bar{X})^2}{n - 1}} \qquad (1)$$

Where n = number of replicate results of the same sample.

$\bar{X}$ = mean of n determinations.

and x_i = value of i_{th} determination.

3.5 In the case where S.D. is independent of concentration (i.e. S.D. is constant for a given range of concentration), results of duplicate analyses of different samples may also be used to calculate the precision. In such a case

$$S.D. = \sqrt{\sum_{i} \frac{(x_i - y_i)^2}{2n}} \qquad (2)$$

where x_i and y_i are n paired sets of duplicate analysis results of different samples.

3.6 Often precision is expressed relative to the concentration level at which it was determined. This term is called "% Relative Standard Deviation" (% R.S.D.) or Coefficient of Variation. It is calculated as follows:

$$\% \text{ R.S.D.} = \frac{\text{S.D. x 100\%}}{\bar{x}}$$

4. ACCURACY

4.1 Accuracy refers to the correctness of the data and defines the degree of agreement of the measurements with the true value of the magnitude of the quantity concerned.

The Accuracy of a determination is expressed as % error as follows:

$$\% \text{ error} = \frac{X - X_{S.R.M.}}{X_{S.R.M.}} \times 100\%$$

Where x = mean value of replicate determinations of a standard Reference Material.

$X_{S.R.M.}$ = Certified value of Standard Reference Material (S.R.M.)

4.2 In the absence of S.R.M.'s it is possible to estimate the accuracy by determining the "spike recovery" of a given parameter. During method validation, "spike recovery" is established by spiking the analyte into an appropriate matrix at a minimum of three levels which span the range of interest. Since this procedure introduces the analyte in the soluble form, the recovery does not account for extraction efficiency from solid matrixes such as sediment and biological tissue or from suspended and colloidal matter in liquid samples. Recovery is calculated on a percentage basis as follows:

$$\% \text{ Recovery} = \frac{C_{FOUND} - \bar{C}_{BLANK}}{C_{ADDED}} \times 100$$

Where: C_{FOUND} is the measured concentration in the sample

$\bar{C}_{BLANK}$ is the average concentration of the blank

C_{ADDED} is the known concentration added to the sample.

4.3 For each method the recovery should be reported as the mean, range and standard deviation. Example:

	Mean Recovery (%)	Recovery Range (%)	Std. Dev. (%)
Pyrene - GC	63	26-129	40

4.4 Recovery is monitored by spiking at least 10% of the actual samples and calculating by the equation:

$$\% \text{ Recovery} = \frac{C_{(SAMPLE + SPIKE)} - \bar{C}_{SAMPLE}}{C_{ADDED}} \times 100$$

Where: $C_{(SAMPLE + SPIKE)}$ is the measured concentration in the spiked sample

C_{SAMPLE} is the average concentration of the unspiked sample

C_{ADDED} is the known concentration added to the sample.

4.5 Inaccuracy results from imprecision (random error) and bias (systematic error) in the measurement process.

5.0 BIAS

5.1 Bias is a systematic deviation of the average of one set of data from another.

6.0 SENSITIVITY

6.1 Sensitivity is a measure of instrumental response factor as a function of concentration. It is commonly measured as the slope of the calibration curve.

6.2 Given a linear calibration curve of the form "R = SC + I", and an intercept (I) on the ordinate "R", the sensitivity (slope) may be expressed as follows:

$$S = \frac{R}{C}$$

Where R = signal response

C = concentration

7. CONFIDENCE INTERVAL

7.1 A confidence interval is an expression of the range of values defined by upper and lower limits at a statistically defined confidence level.

7.2 The confidence interval for a "sample mean" is given by

$$\bar{X} \pm \frac{t_{(n-1)}\ S.D.}{\sqrt{n}}$$

Where: $\bar{X}$ = sample mean.
S.D. = Standard deviation.
n = Sample size.
$t_{(n-1)}$ = Two sided student's -t value with (n - 1) degrees of freedom for the specified level of confidence.

8. LIMIT OF DETECTION (LOD)

8.1 The limit of detection (LOD) is one of the most important terms used for comparison between various analytical procedures, techniques or instruments. It is defined as being the lowest concentration of analyte that can be distinguished with reasonable confidence from blank or background. In Water Quality Laboratories the confidence level of 95% is adopted as a standard for LOD for all analytes.

8.1.1 Different statistical approaches are reported in the literature to calculate limits of detection (LOD). The LOD for a determinand can easily vary an order of magnitude through the use of different statistical approaches. This problem is well documented in the literature (11.10).

Recently, detection limits for selected parameters, analysed within Water Quality Branch Laboratories, were calculated which demonstrated a significant approach employed. The study included a range of analytes covering major ions, nutrients, trace metals and trace organics. Analytical techniques employed covered titrimetry, colorimetry, atomic spectroscopy and gas chromatography. The statistical approaches for calculation of LODs included IUPAC model, graphic approach and propagation of error approach. The results of the above study confirmed that significant variation in detection limits can occur depending upon the approach employed. IUPAC model consistently gave the lowest values while the largest values were obtained using propagation of error approach.

8.1.2 A simplified version of IUPAC, described below, is selected as a standard for calculating detection limits for all analytes determined within Water Quality Branch. It is fully recognized that this approach may give the lowest values, however, the proposed approach is simple to apply and will ensure meaningful comparison and objective assessment of the sensitivity of the techniques, procedures and methods used within Water Quality Branch.

8.1.3 The LODs are represented in three different forms depending upon the requirements. These are called Instrument Detection Limit (IDL), Method Detection Limits (MOL) and Practical Detection Limit (PDL). These are discussed below.

8.2 Instrument Detection Limit (IDL)

8.2.1 The instrument detection limit is the lowest concentration of analyte that an analytical instrument can detect and which is statistically different from the response obtained from the background instrumental noise.

8.2.2 The IDL is established by adding the analyte in reagent (blank) water or appropriate organic solvent to give a final concentration within five times the estimated IDL and calculating standard deviation by introducing the solution directly into the instrumental system to obtain seven or more replicate measurements. The IDL is then calculated using the 95% confidence level, as follows:

$$IDL = t_{(n-1)} \times S.D. \text{ for } n = 7 \text{ or more}$$

Where $t_{(n-1)}$ is the value for a one sided student's t-distribution for n - 1 degrees of freedom.

The IDL should be used to indicate absolute sensitivity of the analytical technique and/or instrument.

8.3 Method Detection Limit (MDL)

8.3.1 The method detection limit is the lowest concentration of analyte in distilled water that a method can detect reliably and is statistically different from the response obtained from a blank carried through the complete method including chemical extraction or pretreatment of the sample. When the method LOD is experimentally evaluated for each matrix by the analysis of samples or spiked samples then Practical Detection Limit (PDL) is determined (see 8.4).

8.3.2 When repeated analyses of blanks show a positive response for the analyte, the LOD is defined as:

$$MDL = \bar{S}_b + t_{(n-1)} S.D.$$

Where:

$\bar{S}_b$ is the average signal (or level) for the blanks, S.D. is the standard deviation of the replicate determinations and $t_{(n-1)}$ is the one sided student's t-distribution for n-1 degrees of freedom at a confidence level of 95%.

8.3.3 If the repeated analysis of method blanks do not show a positive response for the analyste, MDL can be calculated by spiking reagent water or the samples, to give a final concentration within five times the estimated IDL and by calculating MDL using standard deviation (n = 7 or more) and 95% confidence level as shown in 8.3.2.

8.3.4 For methods requiring concentration and pretreatment MDL is determined by selecting a standard sample size (e.g. 1L in case of water), volume of final aliquot (eg. 1 mL prior to analysis by HPLC, GC, GC/MS) and volume required for analysis (eg. 2 uL for GC).

8.4 Practical Detection Limit (PDL)

8.4.1 The practical detection limit is the lowest concentration of analyte in a real sample-matrix that a method can detect reliably and is statistically different from the response obtained from a blank carried through the complete method. It is calculated in the same manner as MDL in 8.3.2.

8.4.2. For a specified method and analyte, PDL will vary with different sample matrices, since these may affect reproducibility, blanks and interference levels.

8.4.3 PDL is always equal to or greater than MDL, but will never be less then MDL.

9. LIMIT OF QUANTITATION (LOQ)

9.1 The LOQ is defined as follows:

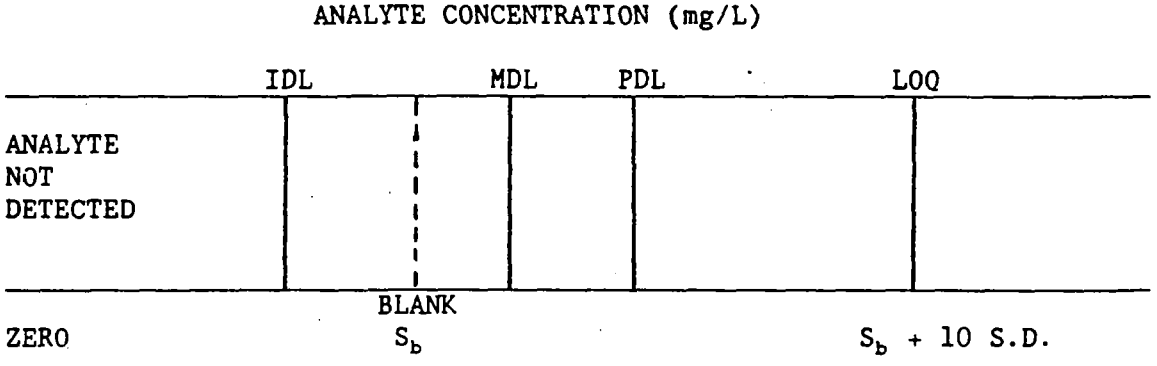
$$LOQ = \bar{S}_b + 10 \text{ S.D.}, \text{ where}$$

$\bar{S}_b$ is the average signal (or level) for the blank and S.D. is the standard deviation of the replicate determinations. This defines the level above which quantitation is reliable and also a region between MDL and LOQ, where detection is reliable but quantitation is not. The LOQ is the level above which quantitative results may be obtained with a specified degree of confidence.

10. REPORTING OF ANALYTICAL RESULTS

10.1 In no case should the term 0 (zero) be used to report an analytical result. In all cases for which no analyte was detected, the expression "ND" and "L" should be used to report the result. In this expression ND means "None Detected" and "L" means "Less than". The value following L is the MDL. If the result falls between the MDL and the PDL the value may be reported in parentheses ( ), with an explanation that the result is less than the PDL and the recovery and precision have not been evaluated at that level.

10.2 GRAPHIC SUMMARY



10.3 Reporting Data Below Method MDL

In some cases data and analyte recovery or concentration may be reported down to instrumental detection limit provided the necessary explanation is accompanied with the results indicating changes in sample size, final aliquots prior to analysis, or method of quantitation (use of internal standards or surrogates).

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III

PROTOCOLS

1. PROTOCOL FOR REJECTION OR REPORTING OF ANALYTICAL DATA BELOW THE LEVEL OF QUANTITATION

1.0 By definition, data above the limit of quantitation (LOQ) are statistically well substantiated and may be reported with a high degree of confidence. Data at levels of PDL, MDL and IDL may be reported with decreasing levels of confidence as defined in chapter II.

There are two schools of thought on the level at which data should be rejected or reported. The first, maintains that since data below the LOQ are not quantifiable, they should be totally rejected. The second, argues that concentrations below the LOQ should nevertheless be reported, since they are defined with appropriate degrees of confidence and thus have usefulness. The NWQL has taken the position expressed in the latter school of thought. It is strongly believed that a laboratory is responsible to clients in reporting all detectable analyte concentrations, provided they are well defined with appropriate levels of statistical confidence. It is felt that a laboratory that takes the initiative to censor and eliminate a certain amount of detected data, is indeed doing an injustice to data users. These data, irrespective of their level of statistical confidence may contain valuable environmental information. It is not the mandate of the NWQL to interpret data or to make decissions on their usefulness. The NWQL must endeavour to make every effort to generate high quality data which are substantiated by appropriate limits of confidence. In this way the data user would have a valuable product which can be used or not used as dictated by project needs.

2. PROTOCOL FOR VALIDATION OF ANALYTICAL METHODS

The following elements constitute "Specifications" or Performance Criteria" which characterize the capabilities and scope of an analytical method. Method validation is carried out by systematically checking these elements and documenting these results in a validation statement shown below:

2.1 Analyte (s)

2.2 Substrate (s)

2.3 Method summary

2.4 Times for Analyses (hr)
- 2.4.1 Batch samples.
- 2.4.2 Single samples.

2.5 Interferences

2.6 Range (Concentation)

2.7 Detection Criteria
- 2.7.1 Instrument detection limit (IDL)
- 2.7.2 Method detection limit (MDL)
- 2.7.3 Practical detection limit (PDL)

2.8 Sensitivity (slope of calibration curve).

2.9 Accuracy - (S.R.M.'s, spike recovery or other method compatability).

2.10 Precision (at 20%, 50% and 80% of concentration range).

3. PROTOCOL FOR APPROVAL OF NEW METHODOLOGY

The National Water Quality Laboratory has adopted specified practices to be followed in the event of modification or alterations of existing analytical methodology or the adoption of new methodology. They are as follows:

3.1 The new method or change in existing method is submitted to the chemist-in-charge for consideration. The chemist-in-charge reviews the method and ensures that the necessary validation data are available.

3.2 The method is then adopted as a "tentative method" to generate precision and accuracy data, using standard and control samples.

3.3 The method is then tested on environmental samples for the period of 3-6 months to ensure that the method covers specified scopes in terms of detection limits and the range and type of samples. The method is then documented in standard format and submitted to the laboratory manager for review.

3.4 The laboratory supervisor reviews the method and accompanying data and submits them for adoption as a routine method.

3.5 The section head, after appropriate review and peer group evaluation, recommends it for acceptance as a routine or on-line method.

3.6 The final approval is given by the Chief, National Water Quality Laboratory.

4. PROTOCOL FOR ASSIGNMENT OF NEW PARAMETER CODE TO A METHOD

When modifications to existing methods are made, it is necessary to decide whether or not the change constitutes a new method. Methodology differences in one or more of the following elements are considered to constitute a new method and thus require new parameter codes.

4.1 Substrate or Matrix

Similar methods which apply to a different substrate or matrix such as water, sediment, fish, plants etc. should be categorized separately and assigned different codes based on their classification.

4.2 Concentration Range

Each method should cover a well defined concentration range such as 1-10, 10-100, etc units. Therefore, a change in Detection Limit must constitute a significant change of at least an order of magnitude.

4.3 Instrumental Technique

Methods with similar sample preparation steps requiring different instruments for quantitative analysis should be assigned separate codes. Different models of instruments do not require different code numbers unless their operation is based on completely different scientific principles or their operation requires substantial changes to the method.

4.4 Confidence level/Interval

Methods with statistically different confidence levels/intervals should be assigned separate codes.

4.5 Clean-up

In many cases different clean-up procedures are deployed to remove certain interferences. The methods should be assigned a separate code when the clean-up procedures are different.

4.6 Derivatization

In some cases it is essential to derivatize and/or complex the analyte prior to quantitation. Methods employing different complexing agents and/or derivatization should be assigned separate codes.

5. DATA VALIDATION PROTOCOL

The following are the steps taken at the NWQL in validating data prior to release to clients and archiving.

5.1 Technician reviews analysis data to ensure blanks, spikes, replicates and SRM are within the expected ranges. If a problem is detected, unknowns and Q.C. samples are re-analyzed.

5.2 The laboratory unit head (CH-02) reviews all analytical reports and verifies data on all samples and makes a recommendation to the Laboratory Head (CH-03) for acceptance and reporting.

5.3 The Laboratory Head (CH-03) reviews data, accepts each sample, and prepares preliminary AWQUALABS sample data report.

5.4 Data on NAQUADAT samples are compared against historical ranges to ensure they are reasonable values. Outliers are re-analysed to confirm analytical results. The Laboratory Head (CH-03) then prepares a final AWQUALABS sample data report and recommends it for reporting to the Section Head (CH-04).

5.5 The Section Head (CH-04) checks approximately 5% of data against historical levels, verifies Q.C. data and reports data to client.

5.6 A record of sample data reports is kept at each level in the hierarchy from technician to Section Head and a copy of the client data report is kept in the Central Registry office at CCIW.

IV

QUALITY CONTROL PROCEDURES

1. QUALITY CONTROL PROCEDURES

Quality control procedures (QCP) are the means by which a Quality Assurance Program (QAP) is implemented. A QAP is usually divided into two classification; namely, the intra-laboratory (in-house) and inter-laboratory (between lab) quality control programs. The former program is a continuing and systematic regime carried out by each laboratory individually. Unless several appropriate standard reference materials are available for the specific parameter, substrate, sample matrix and concentration levels under study, an in-house QAP can only reflect the performance of each laboratory in isolation. In order to assess and/or ensure the reliability and compatibility of sets of data generated by different laboratories, an inter-laboratory QAP is necessary in addition to the intra-laboratory QAP.

Quality control procedures are intended to make available to analysts a standardized approach for minimizing analytical errors and in the assurance of the generation of good data with the best possible precision and accuracy. This is achieved by implementing into normal laboratory practices, steps which would ensure freedom from sources of error such as contamination, matrix effects, human and instrumental bias and random errors, fluctuating instrumental sensitivity and discrepancies in analytical standards.

Before analysts carry out any specific Analytical Quality Control procedures, they should consult the "Guidelines for Good Laboratory Practice" (Chapter VI). Good laboratory practice and Quality control procedures complement one another and together they lead to a successful Quality Assurance Program.

The following sections provide a brief description of accepted Quality Control procedures and techniques which are commonly used. It is recommended that the National Water Quality Laboratory adhere to these practices as much as possible, so that the data generated are of the best possible quality.

2. INTRA-LABORATORY QUALITY CONTROL PROCEDURES:

For every batch of analyses the following steps should be followed.

2.1 Before deciding to use an analytical standard, cross check with standards of other manufacturers in order to determine purity and/or compatability.

2.2 Run an appropriate reagent blank to check for contamination.

2.3 Spike reagent blanks at various levels of concentration to check the performance of the analytical instrument.

2.4 Spike about every tenth sample with a concentration of analyte similar to that found in the natural sample. This step checks for matrix interference effects and determines recovery.

2.5 If matrix interference is encountered, use the method of "standard additions" to calculate the concentrations of the analyte (Chapter IV, section 4).

2.6 In order to check the performance of the overall procedure, prepare synthetic samples at various concentration levels. Matching the sample matrix gives added information to the analyst.

2.7 "Close bracketing" of standards should always be exercised in order to check on changes in sensitivity. This involves running a standard about every tenth sample, as well as running the complete calibration curve before and after the samples.

2.8 Run a replicate of about every tenth sample to check the precision of the system. Use the formula (2) shown under "precision" (Chapter II, section 3.5) to calculate precision of paired determinations.

2.9 To determine the precision of "n" replicates of one sample, analyse one sample 10 or more times and use formula (1) given under "precision" (Chapter II, section 3.4).

2.10 If available, run one or more Certified Standard Reference Materials (CRM) in order to check the accuracy of the overall method.

2.11 Run secondary in-house reference materials (control samples) in order to further check on recovery. Due to the limited supply and high cost of certified SRMs, in-house reference standards (control samples) should be used. They are also useful in the preparation of Quality Control Charts.

2.12 For parameters determined routinely, "Quality Control Charts" provide a powerful tool to establish control of the analytical system. Use this technique whenever feasible (Chapter IV, section 5).

2.13 If difficulty is encountered in drawing the analytical calibration curve by the freehand technique, use the method of "Least Squares" (see chapter IV, section 6).

3. INTER-LABORATORY QUALITY CONTROL:

3.1 In addition to in-house Quality Control practices, the National Water Quality Laboratory participates in the Water Quality Inter-Regional Quality Control program in addition to any other inter-laboratory programs. These studies are designed to determine the degree of compatability of the data generated by participating laboratories. Furthermore, such studies help determine interlab precision and accuracy and to standardize analytical methodology. They also provide valuable data for the certification of Standard Reference Materials.

3.2 A well designed multi-sample inter-laboratory evaluation (Quality Assurance) program provides:

3.2.1 The necessary documented information to data users on the overall "competency" of a laboratory through time in providing data to costly environmental programs.

3.2.2 Confidence to correlate and present future data sets from a single or different laboratory since the inter-laboratory levels of confidence, through time, can be established.

3.2.3 A neutral evaluation of the effectiveness of in-house Q.C. procedures and early warning to the operational laboratories.

3.2.4 A vital mechanism to spot bias in the laboratory measurement process that is undetected in intra-laboratory Q.C.

3.2.5 Quantitative measurement of systematic bias (by a series of well-designed SRMs).

3.2.6 A valuable data base to compare different analytical systems for the same parameters.

3.2.7 Realistic criteria for "acceptability" of data.

4. STANDARD ADDITIONS METHOD:

4.1 This technique is a simple way of calculating the concentration of an unknown. Instead of the usual determination of the unknown relative to external standard solutions, several aliquots of the unknown sample are spiked at different levels of concentration of the analyte (usually one blank and 2 or more spikes). By this process, the standard is subjected to the same chemical matrix as the unknown. the technique then becomes useful whenever matrix interference prevents the complete recovery of the analyte. Therefore Standard additions removes inaccuracies caused by matrix effects. Although this technique is useful, it is not applicable to all types of interference. The effect of the interfering component on the analyte in the sample solution must be the same as that on the spiking solution. Therefore the chemical form in which the analyte is added should be as close to, if not the same, as that in the unknown. For more information on the uses and limitations of this technique, the analyst should consult ref. 7.1. Additional criteria for the proper use of this procedure are that the response should be linear in the range of the additions and that the magnitude of additions should be in the same range as that of the unknown.

4.2 Procedure:

4.2.1 Take three or more aliquots of the sample solution to be analysed.

4.2.2 Determine the concentration level at which the solutions should be spiked. Spike the solutions with concentrations of 0, 1x, 2x, 4x,... where x is the predetermined unit of concentration. The first solution is a zero spike or unspiked sample. Note: It is advantageous to make the volume of the spike negligibly small in order not to introduce a dilution factor. However, if this is not possible, the dilution factor introduced to the solutions should be constant. The "zero spike" should be diluted accordingly.

4.2.3 After analysing the solutions, plot, the scale reading or instrumental response against the concentrations of 2 or more of the additions (Fig. 1).

4.2.4 Trace a straight line through the points and extend it until it intersects the abscissa. The point of intersection on the abscissa gives the concentration of the unknown sample solution (Fig. 1).

5. QUALITY CONTROL CHARTS (REF. 7.2, 7.3):

5.1 The use of a Quality Control Chart is simply an extension of the use of a certified or in-house Standard Reference Material (SRM) for the purpose of quality assurance of analytical data. This technique allows already generated data on SRMs or data which are to be generated on them, to be used to improve the precision and accuracy of a method and to give the analyst more control of the quality of data he or she generates. Basically the technique involves the preparation of charts with specified control limits (Figures 2 and 3). The charts give the analyst a visual graphic presentation of the precision and accuracy of the system as a function of time and provides immediate detection of erroneous and unsuitable data. Furthermore, long-term variations in these data are monitored, and trends in method or operator performance can be determined. Experience has shown that the use of quality control charts, in general, improve the performance of analysts and make laboratory supervisors better informed about personnel, methods and equipment.

5.2 The essential requirement for the preparation of charts is a large enough supply of a SRM. This could either be a certified SRM purchased commercially, or an in-house bulk standard prepared by the analyst (control samples). The latter is more useful since it is much cheaper to prepare and the sample matrix can be chosen to be similar to the real samples analysed.

5.3 The SRM must be homogeneous and the concentration of the analyte in it must be in the same range as that of the real samples. Furthermore it should be large enough in quantity to last for an appreciable amount of time, during which the concentration of the analyte must be constant. The initial step of preparing the chart is to obtain about 20 pairs of data, each performed on a different day. This allows the calculation of the control limits. Once the chart is prepared, the analyste runs a pair of analyses on the SRM together with every batch of real samples analysed. Simply plotting the average and difference of the SRM results on the accuracy (Fig. 2) and precision (Fig. 3) charts respectively, determines whether the data are within the control limits or not. If they are outside the limits a problem is identified and proper steps are taken to eliminate it. If the data are within the limits, control of the system is assured and credibility is improved.

5.4 Procedure:

5.4.1 Prepare a bulk reference sample of the same background matrix as that of the majority of sample types analysed in the laboratory. Ensure sample is homogeneous, stable for the lifetime of the standard and has a concentration of analyte in the same range as the samples.

5.4.2 With the analytical method in control, collect about 20 pairs of results from different days of analysis. The daily data set need not be restricted to pairs of analyses. Statistical treatment of data can be used for any number of determinations of control samples by modifying the warning and control limits (see ref. 7.3) However for all practical purposes, pairs of analyses are all that are needed. Also since a laboratory must run control samples at different levels of the calibration curve (ideally at low, medium and high levels) minimization of the number of Q.C. samples becomes important.

5.4.3 For every pair of results (a_i, b_i) calculate the mean (x_i) and range (R_i) as follows:

$$\bar{x}_i = \frac{a_i + b_i}{2}$$

$$R_i = |a_i - b_i|$$

5.4.4 For "n" number of means and ranges calculate the grand mean $\bar{\bar{X}}$ and the average range (R) as follows:

$$\bar{\bar{x}} = \frac{(\bar{x}_1 + \bar{x}_2 + \ldots \bar{x}_n)}{n}$$

$$\bar{R} = \frac{(R_1 + R_2 + \ldots R_n)}{n}$$

where n = number of pairs of data

5.4.5 Calculate control limits CL_x and CL_R and warning limits WL_x and WL_R for x and R respectively as follows:

$CL_x = 1.880\ \bar{R}$ $\quad WL_x = 1.254\ \bar{R}$

$CL_R = 3.267\ \bar{R}$ $\quad WL_R = 2.178\ \bar{R}$

5.4.6 Prepare an accuracy control chart ($\bar{x}$ - chart) as shown in Figure 2, by drawing upper and lower control limit lines CL_x units above and below the grand mean (x) value respectively.

$$UCL_x = \bar{\bar{x}} + 1.880\ \bar{R}$$

$$LCL_x = \bar{\bar{x}} - 1.880\ \bar{R}$$

$UWL_x = \bar{x} + 1.254\ \bar{R}$

$LWL_x = \bar{x} - 1.254\ \bar{R}$

The chart is now ready for use.

5.4.7 Prepare a precision control chart (R - chart) as shown in Figure 3 by drawing upper control limit and upper warning limit lines, as follows.

$CL_R = 3.267\ \bar{R}$

$WL_R = 2.178\ \bar{R}$

The chart is now ready for use.

5.4.8 For a batch of real samples, run a pair of analyses on the designated in-house reference sample. Calculate x_i and R_i and plot them on the x and R-charts respectively. If these points lie outside the control limits a problem has been identified. At this point resolve the problem and if necessary reanalyse the samples.

5.4.9 As more $\bar{x}_i$ and R_i points become available, recalculate the control limits by taking the larger set of points available.

6. CALIBRATION CURVES BY LEAST SQUARES METHOD:

6.1 The analytical calibration curve is the means by which concentrations of unknowns could be related to standards. Since these curves provide a graphical representation of analytical standards, it is imperative that they be of good quality. Any error involved in drawing the calibration curve would affect the result. The process of drawing a curve involves plotting a set of points on a rectangular coordinate system to give a scatter diagram of the relationship of analytical signal to the actual concentration of the analyte in the standard. The next step requires the fitting of these points to the best straight line which represents the above relationship.

6.2 The common method of curve fitting is the freehand technique, where individual judgement of the analyst is used in obtaining the best line. The technique is however susceptible to human error and depending on a given case, may possibly contribute to large errors in the standardization of the analytical system.

6.3 The "least squares" method of curve fitting removes the possibility of human error by eliminating the need for individual judgement by the analyst. The technique simply makes possible the calculation of the intercept and slope of the best line, which is drawn such that the square of its distance from every point has the smallest possible magnitude. The analyst simply uses the calculated value of the slope and intercept of the straight line to obtain the mathematical expression describing the line and then uses this expression to calculate the new line.

6.4 Given a set of points (x_i, y_i) on a rectangular coordinate system, which behave in a linear fashion, the equation of the straight line which describes this relationship is as follows:

$$y = a + bx$$

where a = Y - intercept of the straight line
b = slope of the line.

Using the least squares approach "a" and "b" are calculated as follows:

and $$b = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2}$$

$$a = \bar{y} - b\bar{x}$$

where n = number of data points used.

These calculations are best performed using a simple computer program. Automated curve fitting programs are available in the AWQUALABS data management system. "TYFIT" is the general curve fitting program for first to fifth degree equations. Other curve fitting programs such as "THILO", "TYSUL", "TYCHL" etc. are also available for special cases. Curves may also be automatically plotted using the program "TYPLT". The AWQUALABS documentation should be consulted for more information. The use of automated curve fitting eliminates the inter-operator curve plotting errors and subsequent uncertainties present in a determination.

7. REFERENCES

7.1 "Standard Additions, Uses and limitations in spectrophotometric analysis", R. Klein Jr., and C. Hach, American Laboratory, 21, July 1977.

7.2 "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", United States Environmental Protection Agency, EPA-600/4-79-019, March 1984.

7.3 ASTM Manual on Presentation of Data and Control Chart Analysis, STP-15D, October 1976.

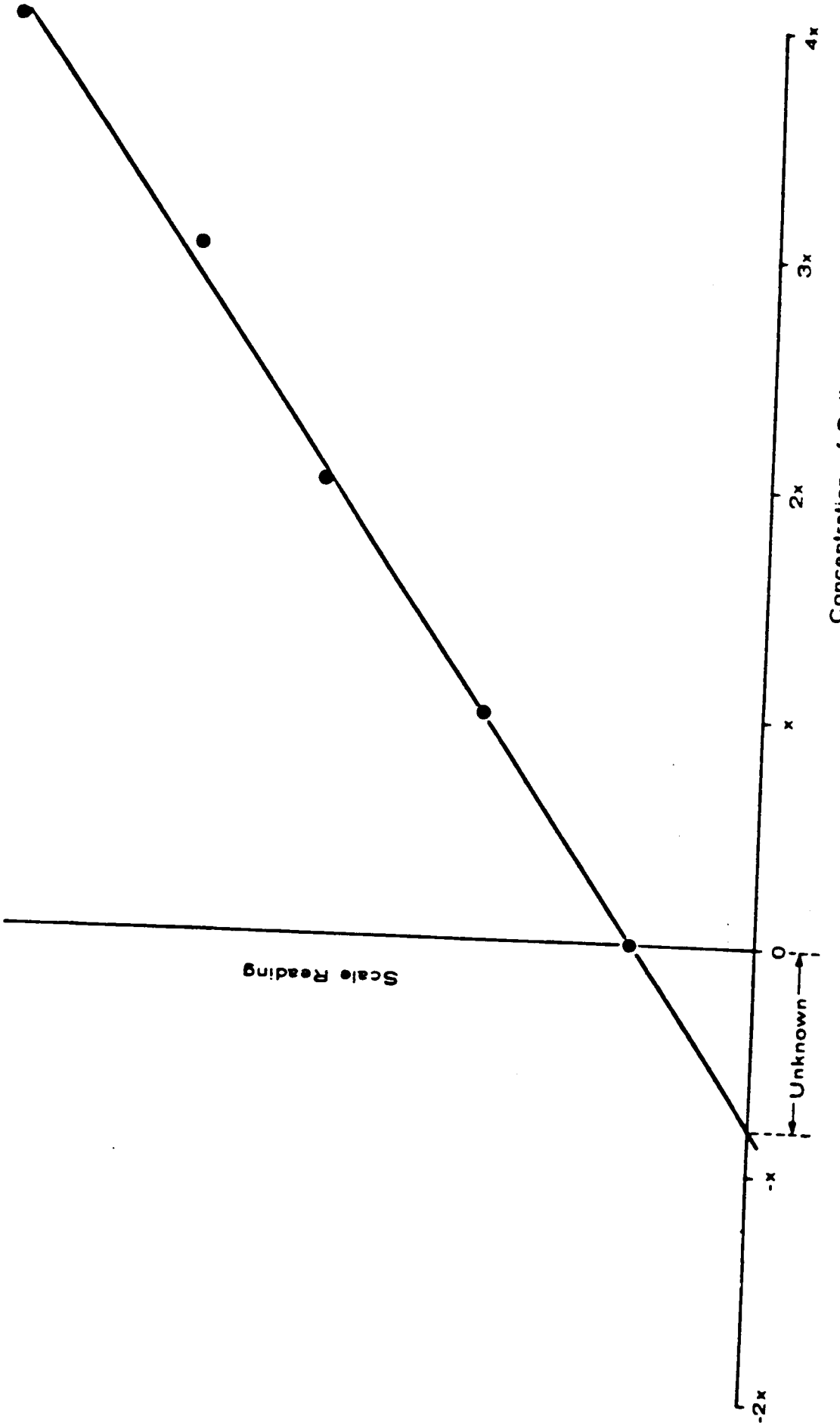

Figure 1 Standard Additions Curve

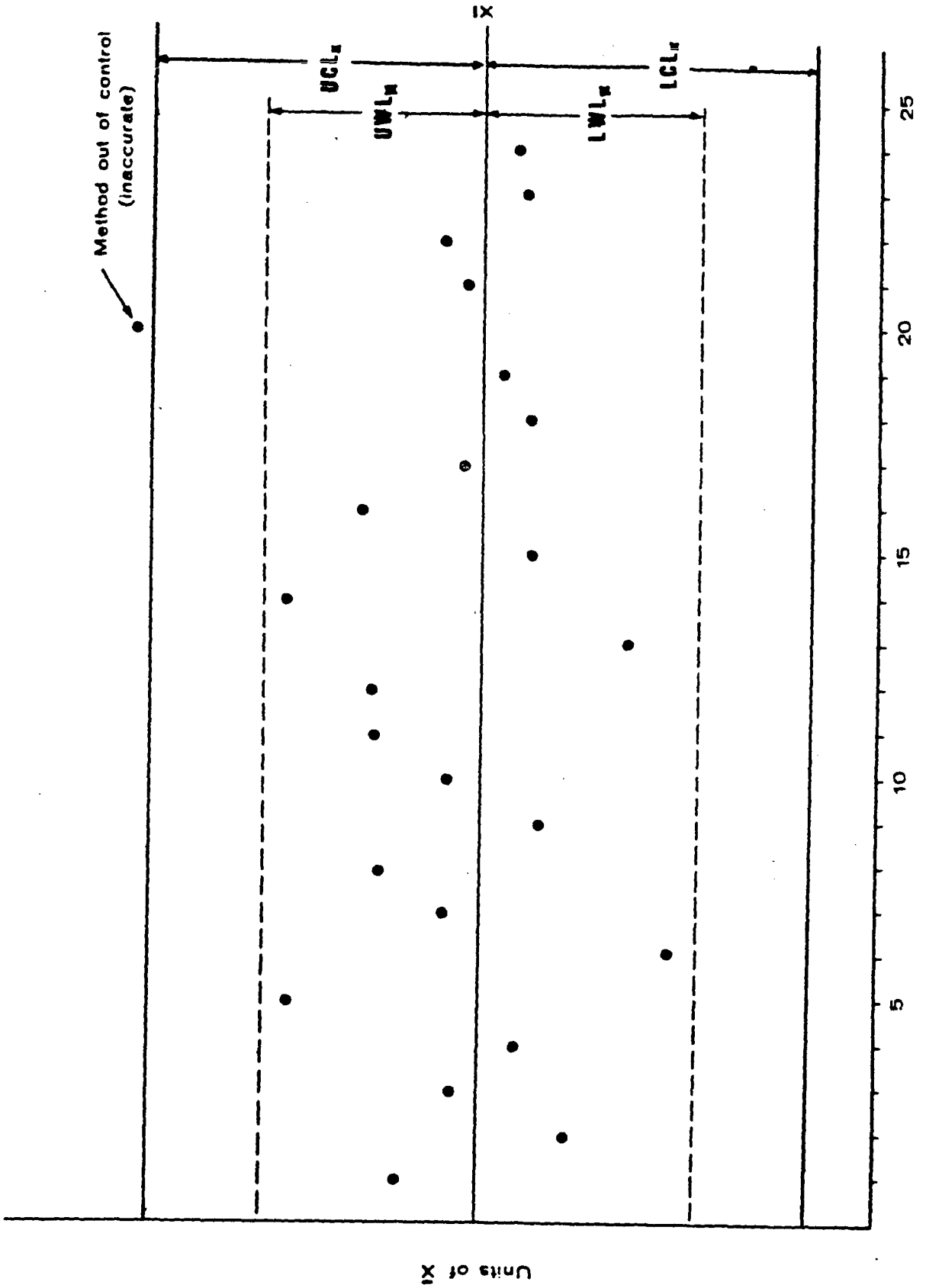

Figure 2 Accuracy Control Chart ($\bar{X}$-chart)

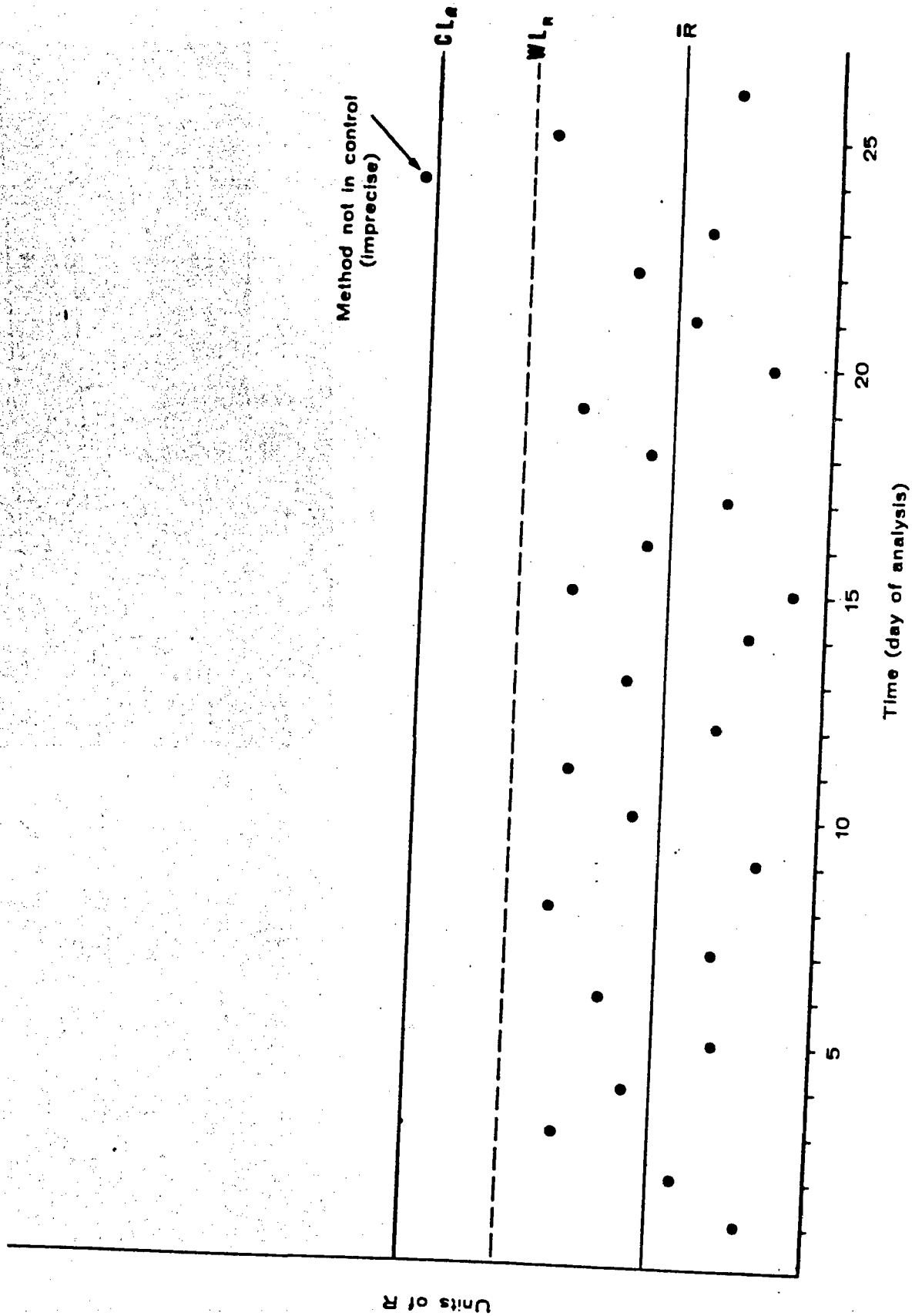

Figure 3 Precision Control Chart (R-chart)

V

QUALITY CONTROL PRACTICES

IN THE

NATIONAL WATER QUALITY LABORATORY

At the National Water Quality Laboratory a systematic intra-laboratory quality control program is recognized to be an essential element of the activites of an analytical laboratory. This practice is applied to every step of the analytical process, from sample receiving to final data reporting and recycling of field sampling containers.

The intra-laboratory Q.C. program is divided into the following areas and is customized to the various disciplines of analytical specialty.

1. Sample Receiving Facility.
2. Bottle Preparation Laboratory.
3. Major Ions, Nutrients and Physical Parameters Laboratory.
4. Atomic Spectroscopy Laboratory.
5. Organic Analysis Laboratory.
6. Gas Chromatography/Mass Spectrometry Laboratory.
7. Automated laboratory Data Management System (AWQUALABS).

Each unit within the National Water Quality Laboratory performs intra-laboratory quality control activities which consist of calibration checks, analysis of blanks, spikes, replicates and reference and/or control samples on a regular basis, as well as logistic and data validation and verification checks. The following are quality control activities which are conducted on a regular basis within the various laboratory units.

1. SAMPLE RECEIVING FACILITY:

1.1 Laboratory clients are required to accompany every batch of samples being submitted for analysis with an "Environmental Sample Submission" form (Environment Canada form 067-2152 (02/84)).

1.2 The sample submission form contains all pertinent information required to identify the samples as well as to describe the nature of requests. The information includes the following:

1. Project Number
2. Project Leader
3. Sample Submitter
4. Date of Shipment
5. Method of Shipment
6. NAQUADAT Submitter I.D.
7. NAQUADAT Station I.D.
8. Sample I.D.
9. Date and Time of Sampling
10. Sample Type
11. Analytical Request

1.3 Information on samples received at the National Water Quality Laboratory are checked immediately to verify data on submission sheets against bottle labels. Any discripancies or irregularities such as missing samples, mislabeled bottles, or damaged containers are recorded on submission sheets and information relayed to project leader.

1.4 Each sample is assigned an AWQUALABS laboratory number and appropriate analytical schemas to identify requested parameters. Samples are labelled with this information and then initialized in the AWQUALABS computer system.

1.5 A parallel set of AWQUALABS laboratory numbers is kept in a hard copy back-up log book for later verification.

1.6 Accuracy of sample identification information is verified the following day, against a list generated by the AWQUALABS system.

1.7 After verification, copies of submission forms (with AWQUALABS laboratory numbers and remarks) are returned to project leaders as aknowledgement of receipt of samples and for future reference.

1.8 Copies of submission forms are also sent to various laboratory unit heads in the National Water Quality Laboratory .

1.9 Samples are stored according to conditions specified in the "Water Quality Analytical Methods Manual", until ready for analysis.

2. BOTTLE PREPARATION LABORATORY:

2.1 The NWQL provides an on-going bottle washing and preparation service to WQB regional offices. After data are reported on analysed samples, used bottles are rewashed under strict analytical and quality control protocols and when verification is complete the clean bottles are returned to original client.

2.2 Bottles are treated according to techniques specified in the "Water Quality Analytical Methods Manual".

2.3 After cleaning, approximately 2 - 5% of every batch of clean bottles are randomly selected for quality-control analysis by the appropriate laboratory.

2.4 The Quality Control chemist inspects the data and any suspect batch of bottles is returned to the laboratory for re-washing.

2.5 A copy of the "Bottle Quality Control" report is returned with every batch of washed bottles for client information.

2.6 Bottles belonging to each WQB region are washed as a batch separate from other WQB regional sample containers and Q.C. analyses are carried out specifically for that batch.

2.7 Since bottles are color coded for each WQB region, clients are assured of obtaining bottles with a sample history pertaining only to their region.

2.8 Several times a year, as requested by the WQB regions, analytical preservatives are tested at the NWQL and forwarded to the regional central offices.

3. MAJOR IONS, NUTRIENTS AND PHYSCIAL PARAMETER LABORATORY

3.1. Operational Consideration:

3.1.1. Deionized/Distilled water blanks are monitored routinely in the laboratory. A set of two blanks are run immediately after the calibration standards and at the end of the run, following either another full set of calibration standards, or a given standard. The blanks are checked against the baseline water which usually stays unchanged from day to day operation. All containers used to store distilled deionized water for field activities such as cruises on the Great Lakes are checked for blanks. If any of the containers give positive response, they are flushed with distilled deionized water and checked again. This procedure is also done on the sample cups. The deionizing cartridges (ultrapure D0809) are changed before the meter on the deionizing column shows a conductivity reading of 0.2 megaohm.

3.1.2. Analytical Standard Preparation:

Stock standards are prepared every 6-8 months or when nearly depleted. New stock is checked against the old stock standard.

Intermediate and working standards are prepared covering different analytical ranges suitable for the various groups of parameters, as specified in the analytical method.

Working standards for nutrients and alkalinity are prepared daily and stock solutions are kept at 4°C. Major ions standards preserve well and are therefore used till they are consumed.

3.1.3. Calibration Procedures:

Instruments with Linear output (Autoanalyzers etc.) are calibrated with a minimum of two standards (mixed standard if more than one parameter is analyzed simultaneously). In case of non-Linear output, the instrument is calibrated with 4-5 standards covering low to high ranges of concentration (Ca, Mg, Na, K). Linearity test and reproducibility of calibration curves are frequently performed. Instrument response is normally monitored by keeping track of the standard calibration curve of the system. For the chloride/nitrate /sulfate ion chromatographic technique, the instrument is calibrated with three standards covering low, medium and high levels of the working range. For the chloride/sulfate/silica autoanalyser technique, the system is calibrated with 6 levels of standards.

Instrument response is monitored by keeping records of standard calibration curves on each instrument.

3.1.4. Precautions to check quality of Glassware:

The glassware used in the preparation of the reagents is washed with tap water and rinsed several times with deionized water before and after use. The graduated cylinders used for dispensing different types of acid and reagents are labelled appropriately to avoid cross contamination.

3.1.5. Use of Control Samples:

Three control samples (Hi, Med. & Lo) of known concentration are run per batch of 40-60 samples. If the analytical result falls outside the normal range of variation, then the calibration standards, reagents and blanks are checked. Analysis is resumed only when the problem is rectified.

3.1.6. Reproducibility and Performance Checks:

The within run and between run reproducibility as checked by means of reference samples and replicate samples are usually analysed at the beginning and at the end of a batch. Depending on the size of the batch, two or more replicates may be analysed. Often three blanks and two replicates are sufficient for a batch of 40-60 samples.

3.1.7 Calculation and Data Management:

Analytical data are fed into the computer either manually or by direct data capture from the analytical instrument depending on the set-up. All calculations, curve fitting, etc., are done by computer. A hard copy of the data is obtained by each technician and cross checked with the print-out from the instrument and/or recorder charts before the final transfer into the data base.

3.2. Precision, Accuracy and Bias Considerations

3.2.1. Calculation of Standard Deviation (S.D.):

S.D. is calculated on a regular basis using replicates of control samples and duplicates of real samples.

3.2.2 Re-check Analysis:

Analysis of replicates is performed on a regular basis at a rate of one per 15-20 samples.

3.2.3 Analysis of Reference Sample and Spike Recoveries:

Analysis of a spiked sample is performed and recoveries calculated once a day and plotted on a control chart on a regular basis.

3.3 Controls to Detect the Occurence of Unexpected Observations:

3.3.1. Calibration Curves:

Repeatability of calibration standards should be within the accepted limits based on the 95% confidence limits. Calibration curves are constantly monitored for linearity.

3.3.2. Reproducibility Within & Between Runs:

Difference in standards between and within run should fall within the normal range of variation characterized by the 95% confidence limits of the system.

3.3.3 Accepted Limit for Replicate:

Control Charts with the mean difference of duplicate samples are used for all methods. The upper and lower control limits are set as described in chapter III section 5 . This is done with the within run and between run duplicates. The data used for the original calculation are accumulated over a period of approximately 2-3 months. Any values that fall outside those limits are re-examined and if necessary they are re-analysed.

3.3.4 Accepted Limit for the Spike Recovery:

Control charts are also set up for spike recovery. The upper and lower limits for each parameter are based on data accumulated over a certain period of time (i.e. approx. one month). The spiked sample can either be a composite sample (i.e. a mixture of many samples) or the sample by itself. Composite samples are usually made from a large batch of samples with the same matrix (i.e., lake samples). Here again, the upper and lower limits are set as described in chapter III, Section 5.

3.3.5 Analysis of Control Samples:

Control samples are analysed on a regular basis. If the analytical result falls outside the normal control limits then the calibration, standards, reagents and blanks are checked. Analysis is resumed only when the problem is rectified.

4. ATOMIC SPECTROSCOPY LABORATORY

4.1. Operational Considerations

a) Deionized/Distilled (D/D) Water Blanks:

To ensure a good supply of D/D water, the cartridges in the deionizing column are monitored regularly, to ensure that a reading of less then 0.2 megaohm is maintained in the column.

4.1.1. Reagents Blanks

Two reagent blanks are run with every batch of fifty or less samples. In the case of the solvent extraction technique this will show the composite blank level of the D/D water, the chelating agent, buffer, acids and glassware. The blanks are studied regularly to identify possible contaminant sources.

4.1.2. Analytical Standard Preparation:

High quality certified stock standards (1000 ppm) for each metal are obtained from commercial sources. New stock solutions are checked against . old standards. Several levels of mixed intermediate standard solutions containing 12 metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn) are prepared for levels of 50 ppm, 1 ppm, and 0.1 ppm in 0.2% nitric acid. These intermediates are used for consecutive batches until exhausted (normally two months). When new intermediates are prepared they are cross checked against old standards to ensure continuity.

Working standards (mixed 12 metals) are made at levels of 1, 2, 5, 10, 20 , 50 and 100 ppb for each analytical run.

4.1.3. Calibration Procedures:

1. Atomic absorption and emmission spectrophotometers are optimized using instrumental specifications.

2. Instrument performance is tested using a standard test solution (eg. Cu^{++}) for atomic absorption spectrophotometers.

3. Batchs of an average 50 samples are run, preceeded and followed by the 7 levels of calibration standards.

4.1.4. Precautions to Check Quality of Glassware:

The glassware used is washed with deionized/distilled water, and then soaked overnight in 5% HNO_3. These glassware include volumetric flasks, graduated cylinders, pipettes etc.

All reagent containers and dispensers are properly labelled and colour coded to avoid errors and cross contaminantion.

4.1.5. Use of Reference Samples:

Two reference samples (High and Low) of known concentrations are run per batch of 50 samples or less.

4.1.6. Reproductibility and Performance Checks:

Two blanks, two replicates and one spike are analysed in a batch of 50 or less samples for each metal.

4.1.7. Calculation and Data Management:

All data are generated by automatic calibration curve fitting and necessary corrections by computer programs available in the AWQUALABS system. Data are automatically captured by the VAX 11/750 computer using AWQUALABS, and then formatted into a report on hard copy. Each technician verifies the output and cross checks with the print-out or chart tracings on the analytical instrument before data are transferred into the data base.

4.2. Precision, Accuracy and Bias Considerations:

4.2.1. Calculation of Standard Deviation (S.D.):

S.D. is calculated every three months using the pairs techniques. (Chapter II, section 3.5).

4.2.2. Within and Between Run Standard Deviation (S.D.):

Within run S.D. is calculated using duplicates of unknown samples for each metal. Between run S.D. is calculated by analyzing inhouse control samples "A" and "B" and studying reproducibility over a given period. (see 4.3.5).

4.2.3. Calibration Rerun:

Calibration curves are regularly plotted and the slope compared to the normal range of variation normally expected. (95% confidence interval). If suspected of lack of control, instrument sensitivity is checked to correct problems.

4.2.4. Replicate Analysis:

Analysis of replicates is performed on a regular basis. Every 25th sample in a batch is re-analyzed for all parameters.

4.2.5. Analysis of Reference Sample and Spike Recoveries:

Analysis of a spiked sample is performed and recoveries calculated for each run on a regular basis.

4.3 Controls to Detect the Occurence of Unexpected Observations

4.3.1. Calibration Curves:

Repeatability of calibration standards should be within the normal variation defined as the 95% confidence level.

4.3.2. Reproducibility Within and Between Runs:

Within and between run standards should be within the normal range of analytical variation.

4.3.3. Accepted Limits for Replicates:

If the variation in duplicates exceeds the 95% confidence interval, between and within runs, the analysis is repeated.

4.3.4. Accepted Limits for the Spike Recovery:

Upper and Lower Control limits (UCL & LCL) for each parameter are determined by spiking a representative sample. The spike recoveries should fall within these limits. (see chapter III, section 5).

4.3.5. Analysis of Control Samples:

Synthetic composite control samples "A" & "B" (Low and High level) are analysed on a regular basis. These control samples contain 12 metals at the following concentrations: 2 and 10 ppb, for Cd, Co, Cr, Pb, Mo, Ni and V; 5 and 20 ppb for Cu, Fe and Zn; and 10 and 50 ppb for Mn and Al. If the analytical results are not within the normal range of variation then the calibration standards, reagents and blanks are checked. Analysis is resumed only when the problem is rectified.

4.3.6. Certified Reference Materials (CRM):

CRM are analysed together with every batch of fish/sediment/water on a regular basis. Results must be within acceptable limits before data on unknowns are released.

5. ORGANIC ANALYSIS LABORATORY

5.1. Operational Considerations

5.1.1. Reagent Purity:

The purity of reagents, solvent, adsorbents, reagent grade water etc., is of great importance when determining constituents in the low parts per billion or parts per trillion range. Water blanks are monitored routinely and checked for possible interfering contaminants. Analysts must ensure that the level of purity meets the requirements of their analysis. Pesticide grade solvents and HPLC grade solvents are concentrated and analysed to ensure purity. All reagents used in the extraction and clean-up process are potential sources of contamination. It is mandatory that reagent blanks be run constantly for each analytical procedure, with final extracts being reduced to the same concentration level normally used for the sample material. A reagent blank involves the repetition of the entire procedure without including the sample itself.

5.1.2. Cleaning of Glassware:

Glassware must be entirely free of contamination. The cleaning procedure includes soaking in chromic acid cleaning solution, a distilled water rinse, rinsing with acetone and hexane followed by drying at 80°C to 100°C oven. Clean, dry glassware is stored in a dust-free cabinet.

5.1.3. Analytical Reference Standards:

A reference standard must be used in all determinations requiring comparison to a chemical substance. Storage, handling and labelling procedures must be followed to ensure the integrity of all reference standards. If a substance is not certified, the laboratory must develop and perform tests in order to assure that it is suitable for the tests intended. Reference standards are under the control of a designated staff member whose responsibility is to ensure the proper preparation and storage of analytical standard solutions.

5.1.4. Calibration Procedures:

Instruments and equipment are calibrated according to a specific schedule with four to five standards covering low medium and high ranges. Response is monitored by keeping track of the standard calibration of the instrument. Performance criteria are provided for each group of instruments to ensure that they are functioning properly. Routine maintenance is provided as specified in instrument and equipment manuals.

Written records are kept for each instrument including description, model and serial number, the date of purchase and cost, description of malfunctions and repairs including parts replaced, the date of repairs, downtime and person performing service, routine maintenance and date and a description of performance checks, specifically the identity of the standard, the method, raw data, calculations, result, operation and the date. A specific individual is responsible for instruments.

5.2. Precision Accuracy and Bias Considerations

5.2.1. Replicates:

Replicate analysis in which the entire analytical method is repeated on a portion of the same sample is carried out on every tenth sample. A blank is processed for every batch of samples analysed.

5.2.2. Recovery Studies (Spiked Samples):

To check whether losses have occured during the analysis or whether interferences exist, the analyst performs a recovery check employing the addition of a known amount of substance of interest to a sample which contains no detectable amount of the substance of interest. The concentration of spikes is normally at the same level of the expected analyte concentration in that batch of samples.

If the recovery of any parameter falls outside the normal range of variation (95% confidence interval) laboratory performance for the parameter is considered unsatisfactory and unspiked samples are suspect and are not reported. At least 10% of all samples are spiked with compounds being measured.

5.2.3. Calculation of Standard Deviation:

As part of the QC program for the laboratory, the standard deviation of the percent recovery ($S.D._p$) is calculated after the analysis of ten spiked water, fish or solvent samples. The accuracy assessment is then expressed as a percent recovery using the 95% confidence interval. The accuracy assessment is updated for each parameter on a regular basis.

5.2.4. Within Run and Between Run Precision:

Within run and between run precision is calculated on new methods introduced in the Organic Analysis Laboratory and the standard deviation is calculated on a regular basis.

5.2.5. Quality Control Check Standards:

The laboratory must on a regular basis demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. The laboratory participates in relevant performance evaluation studies whenever possible.

5.2.6. Confirmation Techniques:

When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector or mass spectrometer must be used.

5.3. Record Keeping in the Organic Laboratory

5.3.1. An integral part of good laboratory practice is to maintain adequate records of analytical activity.

5.3.2 In addition to numerical results of analysis, records should be kept with the chromatograms which provide supplemental operating data. The data and information supplied by the Organic Laboratory should include sample size, extent of concentration of the sample extract, injection volumes, elution cuts if column clean up is required, all instrumental operating parameters, and identity of the GC column. Chromatograms must be clearly identified so that they may be related to the data reported to clients. Data should include quantitation using peak heights together with calculations using peak areas. The records should clearly indicate the names of the analyst and operator of the chromatographic system.

5.3.3 Instrument operating parameters should include column type, temperature of column, length of column, detector temperature, inlet temperature, carrier flow rate, purge flow and chart speed.

5.3.4 Thorough recordkeeping is very important, especially when analysing the reasons for changed analytical performance.

5.4. Reporting

5.4.1. All information pertaining to an analysis is permanently recorded in the laboratory workbook. All valid analytical results are entered manually into the computer files and a hard copy is then checked for reporting quality, accuracy of identifying data as well as for analytical quality. If the data are acceptable to the Head, Organic Analysis Laboratory, a copy of the report is sent to the client. Furthermore, data requiring storage on the NAQUADAT system are formatted on magnetic tape and forwarded to the appropriate authority for storage.

6. GAS CHROMATOGRAPHY/MASS SPECTROMETRY LABORATORY

6.1 Introduction

Since work carried out in this laboratory is an extension of what is done by the Organic Analysis Laboratory (OAL), the quality assurance protocol practiced in that facility also forms a basis for procedures used in gas chromatography/mass spectrometry (GC/MS). Additional work must be undertaken to ensure GC/MS data are correctly acquired and interpreted and that the associated complex instrumentation is operating properly and in control.

6.2 System Applications

Analytical applications for GC/MS in the National Water Quality Laboratory (NWQL) are as follows:

6.2.1 Qualitative confirmation of positive residue detections reported by the OAL.

6.2.2 Quantitative confirmation of analytical data reported by the OAL.

6.2.3 Qualitative identification of unknown materials eluting from gas chromatographic (GC) analysis carried out in the OAL.

6.2.4 Quantitative analysis for trace levels of organic contaminants for which methods amenable to routine application in the OAL are not readily available.

6.2.5 Identification and quantitation of compounds in samples collected specifically to "screen" for unknown contaminants and characterize pollutant profiles at selected sites.

6.3 System Operational Characteristics

Equipment operated by the NWQL includes low resolution, fast scanning quadrupole mass spectrometers interfaced directly to high resolution, capillary gas chromatographs with a variety of injection modes. Mass spectrometer operating modes available are electron ionization and positive/negative (single or simultaneous) chemical ionization with filament or Townsend discharge. The instrumentation is computer controlled with acquisition modes for full scan or selected (multiple) ion monitoring.

6.4 System Performance

6.4.1 The principle components of the GC/MS systems are the gas chromatograph, the mass spectrometer and the controlling data system. QUALITY CONTROL PRACTICES FOR GC ARE SIMILAR TO THOSE DESCRIBED FOR THE OAL. The additional protocol encompasses both mass spectrometer and data system as they are always operated in conjunction.

6.4.2 The performance criteria that must be controlled are resolution, sensitivity noise and stability, both in the mass axis as well as in the intensity axis. A standard calibrant gas, FC-43 (perfluorotributylamine) is used to set up the instrument. The operating mode is selected and the appropriate parameters set according to the manufacturer's specifications.

NOTE

Reference - Finnigan Instruments
Service Handbook
Nova 3 Data System (1978)

6.4.3 The calibrant is leaked into the instrument and analog tuning of source lenses to optimize peak shape, resolution, sensitivity and uniform mass transmission is carried out. This procedure is defined by the manufacturer and is partially described in Appendix A. (6.7).

6.4.4 Upon initialization, the data system (INCOS) automatically performs internal verification of all functions and produces a diagnostic report for operator review and retention. Calibration is performed by the data system using the FC43 calibrant subsequent to tuning (6.4.2) and acquisition parameters specific to the intended analysis. Again, calibration diagnostic reports are produced. All of these reports are filed together with representative spectra and serve as an historical record of system performance and assist in isolating and diagnosing operational anomalies if and when they occur.

6.5 Applications Criteria

6.5.1 Qualitative Confirmation

Standard (recorded) mass spectrometer operating conditions applicable to the selected mode(s) of operation and GC conditions similar to those employed by the OAL are established. Either full spectra, or in the more common case of very low analyte levels selected ion scans, are acquired for both the analytical standard and the sample in question. Both are matched against standard library information using tested algorithms for "purity" and "goodness of fit" on mass assignments, ion ratios and retention index for qualitative confirmation.

NOTE

The matching of spectra is performed against the NIH/EPA mass spectral library containing some 38,760 entries.

PURITY measures the resemblance of the currently selected data to the specified library entry. If PURITY is 1000, the set of peaks LIBRary reads from the unknown are the same in mass and locally normalized intensity as those extracted from the library. A PURITY of 800 suggests that the two compounds involved are closely related. A PURITY of 600 or more suggests that the two compounds have many fragments in common.

FIT measures the resemblance of the library spectrum to the unknown, excluding peaks in the unknown not present in the library spectrum. A high FIT (800-900) with a lower PURITY (500-600) suggest that the unknown is a mixture that includes the compound selected from the library or that the two compounds have some major substructure in common.

6.5.2 Quantitative Confirmation

Quantitation is performed using a single characteristic ion and an internal standard, such as deuterium labelled anthracene or isotopically labelled analyte.

6.5.3 Qualitative Identification Of Unknown Materials

This may be carried out at various levels of confidence depending upon the nature of the original request. Identification in ascending order of reliability is as follows:

6.5.3.1 The full scan, electron ionization, mass spectral data from unknown GC eluants are subjected to computerized deconvolution and compared to similarly generated mass spectral information in a library database. "Purity" and "goodness of fit" using algorithms incorporating mass assignment and ion ratios are tested and scores assigned (as noted above). Identification must be considered tentative as many compounds have similar spectra and the identified material may very well be a homolog of the actual contaminant.

6.5.3.2 The acquired mass spectra may be examined manually by a skilled interpreter. Characteristic spectral patterns are combined and comparison with published compendia of spectra, within specified acceptance criteria, is the basis for identification.

6.5.3.3 The information derived from above may be combined with retention index/boiling point information to further increase confidence of identification. The sample is reanalysed, either

in full scan mode or in selected ion monitoring mode using five ions characteristic of the tentatively identified material.

6.5.3.4 Comparison of the unknown with the authentic material using the above criteria is highly definitive. Co-injection of the unknown with the authentic material with no observed change in retention index or mass spectrum is considered ultimate confirmation.

6.5.4 Quantitative Analysis Of Target Organic Contaminants:

NOTE

This section deals with target compound analysis using GC/MS detection techniques on parameters for which no suitable methods are presently available in the OAL.

A standard library containing the compounds of interest is prepared in the multiple ion monitoring mode using a defined set of operating conditions. Identification is based upon a unique "quantitation ion" and up to six other selected confirming ions. The standard is injected and the library conditions are calibrated. The injection includes an internal standard, deuterium labelled anthracene which is also added, in the same absolute quantity, to the sample. Sample data are compared to the calibrated library and identification based upon an algorithm incorporating mass assignments, ion ratios and retention index. Quantitation is based upon the internal standard and the calibrated response factors to the target analytes.

6.5.5 Screening And Characterization For Unknown Contaminants

Similar to (6.5.3) except that a wider range of GC and/or GC/MS operating conditions may be employed in conjunction with other chemical techniques. As this work tends to be more investigative in nature than the other categories discussed, quality assurance protocols are necessarily less clearly defined. However, specific quality assurance protocols are developed, established and applied as projects of this type evolve.

6.6. Target Compound Analysis Performance Records

Key performance data from target compound analysis are retained over time. Response factors, spike recovery data and detection criteria, computed and statistically updated through successive runs, are stored. Quality control charting is performed on the accumulated data, providing detailed information with respect to method and operator performance over time as well as early warning of impending "out of control" conditions. These charts and attendant statistical summaries are made avaliable to data users to assist with data assessment and interpretation.

6.7 APPENDIX A. - System Setup Procedure

6.7.1 INCOS Data System

6.7.1.1 FC43 calibration gas is admitted to the system such that m/z 69 is just below saturation.

6.7.1.2 System parameters are adjusted to scan from m/z 60 to m/z 510 every two seconds.

6.7.1.3 Peak intensity ratios and ion abundances are compared to historical performance records to assess mass transfer and system sensitivity; a typical spectrum with the current performance information is retained.

6.7.1.4 The system calibration program is run using the newly acquired data.

6.7.1.5 Diagnostics software compares the new calibration to manufacturer specifications for high mass transfer and quality of mass assignment with the mass table; an evaluation report is printed for use by the operator in deciding whether or not the system performance is adequate.

6.7.1.6 System software is used to establish correct "zero" and "gain" settings according to manufacturer specifications; a graphical report is provided to enable the operator to assess performance.

6.7.1.7 Upon completion of data acquisition for sample analysis, a summary diagnostic report is printed indicating to the operator if problems were encountered with respect to selection of acquisition parameters.

6.7.2 Shrader Data System

6.7.2.1 System scanning parameters are set up and acquisition is initiated without mass storage, the spectra being continuously displayed on the video terminal.

6.7.2.2 The level of admitted calibrant and acquisition parameters are adjusted based upon the display and accompanying diagnostic information within criteria recommended by the manufacturer.

6.7.2.3 Several scans are stored, averaged and the mean result displayed; mass assignments for characteristic m/z values are made by the analyst and the mass axis for the range of interest calibrated; acquisition parameters, diagnostic information form the calibration fit and the resulting calibration spectrum are stored.

6.7.2.4 The entire calibration is compared with previous similar files to detect errors such as mass mis-assignments; diagnostic data are tabulated for easy comparison over time to detect trends in system change and to highlight sporadic problems.

7. AUTOMATED LABORATORY DATA MANAGEMENT SYSTEM (AWQUALABS):

7.1 Introduction:

7.1.1 There are four general areas where the automated water quality laboratory data acquisition and management system (AWQUALABS) presently operates to support the quality assurance practices of the Water Quality National Laboratory (NWQL). These are sample initialization, sample analysis, data entry and data verification. In addition, general system and program access are restricted according to staff responsibility and date audit trails have been incorporated to minimize analytical error resulting from belated testing for labile (time) parameters.

It must be emphasized that these procedures have been designed to assist in carrying out effective quality control and do not supplant the vital role of the analyst in this regard. At selected points throughout the analytical activity, summary reports of associated quality assurance work are conveniently presented for evaluation by the appropriate technician, chemist, manager or client.

7.1.2 Present capabilities of AWQUALABS are outlined in sections 7.2 to 7.5.

7.1.3 Planned development:

Software is presently being developed to:

1. Perform a more comprehensive series of data checks,

2. Operate on quality control data that are generated during the analysis stages described above and provide a definitive and ongoing assessment of laboratory performance.

These activities are outlined in sections 7.6 to 7.9.

PRESENT ACTIVITIES

7.2. Sample Initialization

7.2.1 Certain elements of the AWQUALABS database are predefined according to project specifications. These entries are recalled at the time of individual sample initialization either as sample file entries or to verify that operator entered items are valid. Included are analytical methods (parameter dictionary), parameters and substrates for testing (analysis schemes or schemas), NAQUADAT station numbers and descriptions and analysis restrictions such as detection criteria, reporting units and significant figures.

7.2.2 Samples are initialized into a temporary file, not directly to the active database. The information in this file is reviewed independently for correctness by personnel other that those responsible for initialization.

7.3 Sample Analysis

Control of laboratory analysis is exercised through a menu driven series of programs that guide analysts systematically through the various steps necessary to carry out:

7.3.1 Identification of work to be done.

Work sheets are generated that identify samples and parameters for testing.

7.3.2 Analysis

Chemical analysis and attendant intralaboratory quality control are carried out either manually or by direct data acquisition from instruments.

7.3.3 Synchronization Of Sampling And Baseline

Samples are synchronized within a batch such that the data system knows whether an incoming value is to be associated with a sample, a standard or any one of several acceptable categories of aliquot. Baseline correction is performed automatically using blanks interspersed throughout the run. All relevant activities are identified in the final "run report".

7.3.4 Calibration

Calibration curves are prepared from measured standard solutions using linear, non-linear, multi-point or multi-level fits, depending on the requirements for analysis.

7.3.5 Measurement

Sample values are interpolated from standard calibration curve.

7.3.6 Verification

Values that do not fall within predefined criteria, such as those that lie outside upper and lower standard concentration limits are flagged.

7.3.7 Performance

Recovery (accuracy) and precision are computed based upon responses for aliquots of defined composition (spikes, splits, replicates).

7.3.8 Review

Analytical results are presented in tabular and/or graphic form for subjective review by the analyst.

7.4 Data Entry

After the analyst is satisfied with the results of testing, the data are automatically added to the sample files.

7.4.1 Predefined Sample Files

Predefinition of these files at the time of sample initialization prevents unwanted data, such as values for parameters that were not requested, from being inserted.

7.4.2 Multiple Entries

Entries for parameters that already have an associated result are flagged as rechecks and the operator informed appropriately.

7.4.3 Date Audit

The date of analysis is automatically entered with the analytical result.

7.4.4 Record Keeping

A hardcopy record of the sample file update is produced for the analyst's files. This process is rapid and free from error in transcription, the latter being a long standing source of data quality problems in laboratories.

7.5 Data Verification

There are a number of software modules both under development and in place to perform additional data verification of samples for which analyses have been completed. There are also a number of checkpoints in the database life history of a sample at which some form of approval must be provided by designated personnel in order for sample processing/reporting to continue.

Presently available are the following:

7.5.1 Ionic Balance

The difference between sums of cations and anions is calculated and compared with specified criteria for acceptability. In the case of unsatisfactory ionic balance, parameter correlations are carried out automatically and predictions as to likely sources of error (ie. those ions that are most probably incorrect) are identified for re-analysis.

7.5.2 Consistency Checks

Parameters that exhibit relative trends with respect to each other are checked and inconsistencies identified and printed. An example is verification that reported values for dissolved forms of selected parameters do not exceed those for total forms.

7.5.3 Correlation Checks

Those parameters for which there are established mathematical correlations are checked and inconsistencies identified and printed.

7.5.4 Sample Acceptance

After all tests and quality assurance checks have been completed, interim reports are printed for final review by chemists and laboratory unit heads. If everything appears satisfactory, the chemist generates a hard copy report for transmission to the client agency. The system periodically polls the sample database and when all values for a particular sample have been reported, the sample is flagged for archiving. Computer data sets may be transmitted to clients either by magnetic tape or by direct computer - computer transfer.

FUTURE DEVELOPMENT:

7.6 General Limits Screening

All data will be compared to a range of realistic and acceptable values for a specific parameter and out-of-range points will be flagged for further attention.

7.7 Site Specific Limits Screening

Where adequate historical information for particular sites is available, a table of data limits characteristic of that location will be prepared. Data for that site will be compared to historical values for early warning of changes.

NOTE

In both instances, exceedances will be verified and, if analytically correct, the information will be rapidly communicated to the appropriate project leaders to permit quick response to potential problems.

7.8 Chromatographic Decision Matrix

For chromatographic based analytical procedures, algorithms will be developed that apply selected criteria for system response from multiple column analysis and determine a confirmed residue quantitation. This will streamline the process of data interpretation for this type of work by reducing the extent of direct intervention by the analyst to results that fail to meet the established criteria. This activity will be carried out on a dedicates data acquisition system presently operating in the gas chromatgraphy laboratory.

7.9 Laboratory Performance

At the point of updating sample files in the AWQUALABS database, all the quality control information acquired to that point in time is deleted. To date, it has been the responsibility of the analyst to review these data and make subjective decisions on system performance, take corrective action as deemed necessary and carry on with the analysis. Software is being developed that will store non-sample data (standards, blanks, spikes, replicates) in a separate file. These data will be operated on to provide an ongoing assessment of laboratory performance for a specific analytical procedure. The activity will be cumulative and ultimately yield:

7.9.1. Laboratory performance over time with respect to a particular procedure, including long term definition of detection criteria.

7.9.2. Individual analyst performance over time.

7.9.3. Early diagnosis of method problems.

7.9.4. In addition, sample files will be associated with the intralaboratory quality control information derived from the same time period as the analysis, as well as with any interlaboratory studies and check samples that may have been in process in the same time frame. This latter activity will provide capability for complete data specification for all analytical work carried out by the NWQL, assess performance of indivdual staff for specific tests and of the tests themselves within the laboratory as a whole.

VI

GUIDELINES FOR GOOD LABORATORY PRACTICE

GUIDELINES FOR GOOD LABORATORY PRACTICE

One of the most important activities of analytical laboratories is the generation of data. To a large extent the success of such laboratories can be measured by the quality of their products (i.e. quality of their data). In order to ensure good quality data, every factor which contributes to the success of a laboratory must be optimized and maintained in good working order. The techniques by which success could be achieved are called "Good Laboratory Practice" (GLP). These practices involve all aspects which make the laboratory effective in accomplishing its specific goals. The following sections summarize the accepted criteria for GLP and are designed as guidelines to aid National Water Quality Laboratory staff to perform in the most effective manner and to ensure the greatest possibility of the production of good data. If properly used, these guidelines will improve laboratory performance and if performance is already satisfactory, they would help to maintain it. Furthermore GLP provides for the adoption of a mechanism by which problems may be identified and solved in the event of noncompliance to accepted practices.

1. LABORATORY FACILITIES AND SAFETY:

1.1. Facilities and safety equipment.

1.1.1. The laboratory facilities should provide an environment which is well lighted, clean, unconjested and with proper climate control (i.e. temperature and ventilation).

1.1.2. Benchs and instrument areas should be supplied with the proper electrical outlets to accommodate instruments with varying power requirements. See Treasury Board Standard 3-3 (Ref. 7.1, pages 47-65)

1.1.3. The laboratory should be equipped with properly located eye washes, showers, and breathing apparatus.

1.1.4. Laboratories should be equipped with fire extinguishers, fire alarms and sprinkler systems.

1.1.5. Separate fume hoods should be available for organics, mineral acids and perchloric acid.

1.1.6. For detailed specifications of laboratory facility design, the analyst should consult the "General Laboratory Design Criteria" of the Treasury Board Guide 5-1 (Ref. 7.1, pages 240-252).

1.1.7. If analytical activities involve different levels of the laboratory building, a freight elevator should be available for the transportation of laboratory paraphenalia, meeting the Treasury Board StandardS 3-4 (Ref. 7.1, pages 67-74).

1.1.8. All laboratory personnel should have access to an emergency first aid kit and health services within easy reach, complying with the Treasury Board Standards 3-5 and 3-8 (see Ref. 7.1, pages 75-85 and 97-101).

1.2. Safety Practices

1.2.1. Regular monthly safety tours should be conducted of laboratory premises and each laboratory unit should have representation in a safety committee.

1.2.2. A safety program should be established where laboratory personnel attend periodic seminars, courses and workshops in order to keep abreast of new developments.

1.2.3. Good records should be kept of the state of safety devices in the laboratory and of any safety related events in order to insure the efficiency of the safety program. See Treasury Board Procedures 4-1, (Ref. 7.1, pages 183-187).

1.2.4. All laboratory equipment should be regularly checked and their status recorded, in order to prevent hazardous conditions.

1.2.5. Periodic health examinations should be carried out on all personnel involved with toxic chemicals and substances with microbial contamination. See Treasury Board Standard 3-13 (Ref. 7.1, pages 139-146).

1.2.6. All personnel should ensure the use of protective gear for the eyes, face, head, skin, hands, feet, legs and the respiratory system. See Treasury Board Standard 3-14 (Ref. 7.1, pages 147-154).

1.2.7. Lab coats and other utensils used inside the laboratory, should be restricted only to their areas of use in order to prevent the transport of contamination to other areas.

1.2.8. Smoking and eating should not be permitted inside the laboratory.

1.2.9. When acid or solvent bottles are transported, they should be carried in the proper protective container, such as a rubber bucket.

1.2.10. Separate waste containers should be used for regular laboratory garbage and broken glass.

1.2.11. All contaminated materials to be discarded (broken glass, paper towels, disposable gloves, etc.) should be rinsed with water prior to being placed in waste containers in order to protect waste handlers from toxic chemicals and acids.

1.2.12. Special containers must be utilized for organic waste solvents and should be placed in a properly ventilated area such as a fume hood. Procedures for the handling and disposal of laboratory wastes should comply with Chapter 6 of the Treasury Board Guide 5-1 (Ref. 7.1, pages 284-288).

1.2.13. All personnel involved with the handling of dangerous substances and pesticides, should comply with the Treasury Board Standards 3-2 and 3-15 respectively (Ref. 7.1, pages 37-45 and pages 155-158 respectively). See also Ref. 7.2.

1.2.14. Chemicals such as solvents, acids, reducing and oxidizing agents and any substances that may not be stable in the presence of other groups of substances, should be stored separately under special conditions which allow for ventilation, proper temperature control, and isolation from areas of traffic. See Section 3.5 of the Treasury Board Guide 5-1 (Ref. 7.1, pages 265-268).

1.2.15 The use, handling and storage of compressed gas cylinders should be made in compliance with Section 3.2 of the Treasury Board Guide 5-1 (Ref. 7.1, pages 257-260).

1.2.16 Toxic volatile chemicals should be weighed and handled under ventilation and in separate quarters. The use of carcinogenic chemicals should be avoided as much as possible.

1.2.17 Laboratories should have clean-up procedures available for spills of specific chemicals used on their premises.

1.2.18 Laboratory staff should attend seminars of fire safety, and be subjected to periodic unexpected fire drills.

1.2.19 In the event that an accident does occur, the Treasury Board Guide to accident investigations should be consulted (Ref. 7.1, pages 205-228).

1.2.20 Laboratory personnel should consult the CCIW "Laboratory Safety Manual" (Ref. 7.3) whenever appropriate safety information is required.

2. STAFF RELATIONS AND WORK ENVIRONMENT:

2.1 Laboratory heads should ensure that analysts are properly trained and are qualified to perform the duties they have been assigned. Analysts should have access to the "Analytical Methods Manual" or must have detailed written instructions on the analytical technique they are to use.

2.2 Laboratory personnel should be encouraged to participate in instructive meetings, seminars and courses in order to keep abreast of latest developments in their field.

2.3 A mechanism should be present by which laboratory personnel and supervisors communicate, and where problems could be effectively solved. A system should also be present where suggestions and complaints could be looked at, and required changes be made to ensure the efficient functioning of the group.

2.4 Managers and supervisors should provide feedback on the performance of analysts, and on the results of quality control studies, in order to maintain the good calibre of work or to help make required improvements.

2.5 In the interest of keeping high morale, every effort should be made to provide continuous incentive programs.

2.6 An organization chart should be available, showing lines of authority and areas of responsibility.

2.7 Laboratory management should ensure that copies of the "Handbook of Occupational Health and Safety" are available to all personnel. Furthermore individual copies of the Treasury Board Standards, Guides and Procedures should be present at the pertinent locations and with the appropriate people so that the required information could be obtained at a glance.

3. CHEMICALS, REAGENTS AND STANDARDS:

3.1 Chemicals, solvents and standards should be dated upon receipt and discarded when their shelf-lives expire.

3.2 The level of purity of reagents, solvents and chemicals should be determined by analysing appropriate blanks with every set of analyses. Every new batch of chemicals should be checked in the above fashion.

3.3 The grade of chemicals or reagents used in an analysis, should be as specified in the analytical method.

3.4 A good source of deionized-distilled water should be available, suitable for analytical use. For organic methods, either XAD-2 cleaned water or equivalent may be necessary.

3.5 Chemical standards employed in analyses should always be "analytical grade". Standards from at least two sources of suppliers should be obtained to check one against the other. For organic parameters, it is necessary to check the purity of the standards since they are not always readily available in a pure form such as the case with inorganic standards.

3.6 Analytical grade standards should always be kept in a cool and dry place and must be dry before weighing.

3.7 For safety related aspects of the handling, storage and disposal of chemicals, consult Section 1.2.

4. APPARATUS:

4.1 Glassware and plasticware should be cleaned with the appropriate cleaner specified in the analytical method.

4.2 For parameters which are prone to contamination a separate set of glassware should be allocated.

4.3 Volumetric glassware which is deemed critical to analytical determination should be periodically calibrated.

4.4 Preventive care should be practiced for the care of all instruments.

4.5 Proper optimization and calibration of instrumental conditions should be practiced on a regular basis. Instrumentation should always be kept free of contamination and in good working condition. The instrument manual should be kept within easy reach of the system.
(See "Guidelines for Instrument Performance Control Checks", Chapter VI).

4.6 Analytical instruments should not be kept in the proximity of corrosive fumes and chemicals. If contamination occurs, the instrument should be cleaned and checked immediately.

4.7 Only instruments which meet the standards set in the analytical method should be used for analyses.

4.8 Analytical balances should be periodically calibrated with certified weights and always kept in a clean condition. Similarly, analytical meters such as pH meters, thermometers, etc. Should be calibrated and kept clean.

4.9 A systematic performance and maintenance check-list should be available for all major instruments and must be used in a regular basis. (See "Guidelines for Instrument Performance Control Checks", Chapter VI).

4.10 Records of all maintenance and performance checks should be kept and should be available for inspection.

4.11 There should be an individual person responsible for the care and maintenance of every instrument on the premises.

5. METHODOLOGY:

5.1 The techniques employed for sampling, preservation and analysis should adhere to the recommended methods in the "Analytical Methods Manual"(7.4) the "Sampling For Water Quality Manual"(7.5) or the current operational procedures with the National Water Quality Laboratory . Since all methods in the methods manual are NAQUADAT coded, alterations in the analytical precedures require a change in the code (Chapter III). Furthermore, non-adherance to the recommended procedures, may in certain cases result in noncompatability of data sets.

5.2 When methods are changed, the changes must be validated and authorized as per protocol (Chapter III), and the reasons for the changes and substantiating evidence must be documented. The new procedures should then be written up in the standard format and submitted for consideration for inclusion in to the "Analytical Methods Manual".

5.3 Sample bottles should be properly cleaned with the recommended cleaner to prevent contamination. (See Chapter V, Section 2).

5.4 For many parameters, bottle type, preservation, storage conditions and length of storage are critical and must be closely controlled. See Table I of the "Analytical Methods Manual" for the recommended conditions.

5.5 For those parameters which may be easily contaminated a separate set of containers should be set aside and reused.

5.6 Samples must be well homogenized prior to subsampling so that a representative sample may be readily obtained. The analyst should ensure that the technique employed for homogenization, does indeed affect the required result.

5.7 The sections on "Quality Control Procedures and Practices" (Chapter IV and V) should be used as a guide to the quality assurance activities of the laboratory. The laboratory should have a comprehensive quality control program to insure that the data generated meet required standards, and that satisfactory performance is maintained.

5.8 Since chromatographic techniques are not always specific, the analysis of organic parameters should be routinely confirmed by alternate techniques. Confirmation techniques include mass spectrometry, chemical derivatization and multicolumn gas, liquid, column and thin layer chromatography and others.

6. DATA RECORDING REPORTING AND DOCUMENTING:

6.1 The following should be recorded for every sample analysed, and the records must be available for inspection.

6.1.1 Date, place, time and conditions of sampling, sample identification number and name of sampler.

6.1.2 Time of preservation and preservation technique used.

6.1.3 Date of analysis and name of analyst.

6.1.4 Method employed for analysis.

6.1.5 Results of analysis including charts, calibration graphs and records of calculations.

6.2 Samples should be well identified throughout the whole period of time from sampling to analysis and calculations.

6.3 The analyst should use all analytical values obtained in a measurement. Taking the best two out of three results is frowned on since such practices may change the conclusions substantially. However, data sets may be modified if statistically based rejection techniques are used.

6.4 The accepted rules associated with significant figures should be adhered to, so that the method of calculation is uniform and standardized through the laboratory and throughout time.

6.5 The number of significant figures retained in computation and presentation of data should be as described in the ASTM manuals (7.6, 7.7).

6.6 Quality Assessment forms (Chapter VIII) should be used as the main tool for documentation of quality control data. Evaluation of this data and appropriate feedback to laboratory managers, supervisors and analysts would ensure an effective Quality Control program.

7. REFERENCE:

7.1 Treasury Board, "Handbook of Occupational Health and Safety", 2nd Edition, Cat. # BT45-3/1978, Printing and Publishing, Supply and Services Canada, Hull, Quebec, Canada, K1A 0S9.

7.2 Health and Welfare Canada, "Handbook on Chemical Safety - In the aerial application of chemical materials", Cat. # H31--1273, Information Canada, Ottawa, Ontario, 1973.

7.3 Environment Canada, Canada Centre for Inland Waters, "Laboratory Safety Manual", March, 1981.

7.4 Inland Waters Directorate, Water Quality Branch, "Analytical Methods Manual", August 1979.

7.5 Inland Waters Directorate, Water Quality Branch, "Sampling for Water Quality", 1983.

7.6 ASTM Manual on Quality Control of Materials, Prepared by ASTM Committee E-11 on Quality Control of Materials, Special Technical Publication 15-C, American Chemical Society for Testing and Materials, 1916 Race Street, Philadelphia, PA, January, 1985.

7.7 ASTM Manual on Presentation of Data and Control Chart Analysis; Special Technical Publication 15-D (1976).

VII

GUIDELINES FOR INSTRUMENT PERFORMANCE CONTROL CHECKS

The following tables provide a summary of the instrument performance control checks for systems commonly in use at the NWQL. When adhered to, these procedures should ensure that instrumental bias and variability are minimized and controlled within the accepted levels. Furthermore, they provide a framework which standardizes the maintenance, optimization and calibration activities carried out by the analyst. Since most analytical systems at the NWQL are used at sub-ppb levels, it is essential to keep instrumentation clean and properly standardized so that reproducibility and accuracy of data are kept uniform and within the accepted control limits.

1. ATOMIC SPECTROSCOPY

Instrument	Frequency of Checking	Component to Check	Procedure
Atomic Absorption Spectrophotometer (Flame)	Daily	Hollow cathode or electrodless discharge lamps.	Warm up before use to get stable current. Optimize lamp position by use of energy meter.
	Daily	Wavelength	Dial the recommended wavelength for the metal of interest and fine tune by maximizing energy meter.
	Daily	Slit	Set slit as per operator's manual.
	Daily	Cloud chamber	Wash with distilled water, and acetone and dry.
	Daily	Burner	Align burner using vertical and horizontal settings. Adjust position to peak absorbance.
		Burner o-ring	Inspect visually and replace if necessary.
		Nebulizer end cap	Inspect visually.
	Daily	NO_2 Burner	Use scraping sticks to clean carbon deposits.
	Daily	Drain level and drain tube condition.	Inspect visually and adjust or replace as necessary.

Instrument	Frequency of Checking	Component to Check	Procedure
	Daily	Gas flow meter and supply.	Inspect pressure guage to ensure appropriate setting and adjust gas flow meter as required.
	Daily	Nebulizer	Adjust by rotating knurled nut. Fine tune by maximizing sensitivity.
	Daily	External standard	Aspirate a 5 ppm Cu standard into the flame and adjust the nebulizer to maximize the absorption reading. If value is less than .250 the nebulizer should be re-assembled.
	Daily	Sensitivity	Aspirate standard solutions into flame and compare sensitivity against previous results.
	Weekly or when required	Nebulizer	Dissassemble and wash with distilled water.
	Monthly	Lamp Window	Clean with very soft lense wiping cloth.
	Quarterly	Exterior instrument cover.	Inspect visually and clean with soap and water as necessary.
	Quarterty	Burner head	Wash in dilute HCL.
	Annually or when specs. not met	Lamp output	Check with Watt meter.
Atomic Absorption Spectrophotometer (Graphite Furance)		Instrument parameters	See Flame A.A.S.
	Daily	Graphite tube	See operator's manual for model.

Instrument	Frequency of Checking	Component to Check	Procedure
	Daily	Argon gas supply	Inspect guage reading.
	Daily	Temperature compensator	Rotate adjusting pot.
	Daily	Cooling water supply	Inspect visually for correct flow, leaks, and proper operation.
	As required	Graphite cones	See operator's manual for model.
Automated Cold Vapor Analysis of Mercury	Daily	Whole system	Check lamp energy. Check for abnormal operation of parts, i.e., auto-sampler, pump, etc.
			After use aspirate the following solutions in the given order:
			a) 3% Hydroxylamine SO_4.
			b) 10% NaOH for 5 minutes.
			c) Distilled water for 2 minutes.
			d) 5% H_2SO_4 for 5 minutes.
			e) Distilled water for 5 minutes.
	Monthly	Pump tubes	Replace.
	Monthly	Gas-liquid separator	Clean with 10% NaOH.
	Monthly	U.V. cell	Clean with water and acetone or water and ethanol.
	Monthly	Column	Clean with 10% NaOH.
	Monthly	Glass coils	Clean with 10% NaOH.
	Quarterly	Transmission tubes	Replace.

Instrument	Frequency of Checking	Component to Check	Procedure
Flame Photometer (For Atomic Emission Analysis of Na and K)	Daily	Sensitivity	Aspirate standard solutions into the flame and compare sensitivity against previous results.
	Monthly	Pump tubes	Replace pump tubes monthly or sooner if excessively used.
	Semi-Annually	Transmission lines	Replace reagent, waste and lines to inspection port.
	Daily	Manifold	Rinse the system for 10 minutes with distilled deionized water and then aspirate air for two minutes to dry the flame photometer.
Inductively Coupled Argon Plasma Spectrophotometer (ARL Model ICPQ)	Daily	Spray chamber	Rinse with water.
	Daily	Sensitivity Check	With 1 ppm standard (As, Se, Sb or 16 metals.
	Daily to weekly	Profile point for simultaneous spectrometer	Run standard around position using "$ STTS".
	When torch moved or changed	Torch Position	Optimize horizontal position using "$ STTS".
	Quarterly	Computer and Instrument Check	Service contract.
Inductively Coupled Argon Plasma Spectrophotometer (ARL Model 3580)	Daily	Instrument parameters i.e., Vacuum, temperature etc.	Type "LOG (R)"
	Daily	Sensitivity Check	With 1 ppm standard (16 metals)

Instrument	Frequency of Checking	Component to Check	Procedure
	Daily	Spray chamber	Rinse with distilled water.
	Daily to Weekly	Profile point for simultaneous spectrometer	Run standard for specified channels using "IPOF" program.
		Position sequential spectrometer.	Type "pos" (DO NOT USE COMPUTER UNTIL FINISHED OR 10 MINUTES).
	Weekly	User files (All except .RES & SCN) to floppy disk	Type "BACKUP".
	Weekly	Copy .RES & SCN files to floppy disk	Initialize Disk and then copy specified files.
	Quarterly	Computer and instrument check	Service Contract.

2. MOLECULAR SPECTROSCOPY

Instrument	Frequency of Checking	Component to Check	Procedure
Technicon Auto-analyzer System for Total phosphous NO_3-NO_2, NO_2, SRP, NH_3, TKN DIC, DOC.	Each run	Accuracy and reproducibility.	The accuracy and reproducibility is checked with reference samples in duplicate at the beginning and the end of each tray.
	Each run	Calibration curve	Run a set of standard solutions (2 or more) and plot the calibration curve. The reproducibility of the calibration curve should be within the occeptance limits based on standard deviation.
	Biweekly	Pump tubes	Usually the pump tubes are replaced every two weeks but in some case they might be replaced earlier. (Refer to flow diagram of each method to replace the pump tubes).
	Monthly	Colorimeter's (optical peaking)	Follow instructions in operator's manual to optically peak the colorimeter.
	Monthly	Interference filters and optical system	The filters and lenses are removed from the colorimeter and cleaned with methanol and lens cleaning paper.
Spectrophoto-meter for Chlorophyll Analysis	Daily	Interferences	One blank and one wash sample are run every 8 - 10 samples.
	Weekly	Calibration	Instrument is calibrated with a fresh standard every 300 samples or approximately once a week when in use. Standard is run in triplicate.

3. CHROMATOGRAPHY

Instrument	Frequency of Checking	Component to Check	Procedure
Ion Chromatograph	Daily	Instrument Calibration	Calibrate as per Method's Manual.
	Daily	Accuracy	Run reference or control samples.
	Biweekly	Pump	Oil and inspect springs.
	Biweekly	Column	Check analytical retention times.
	Biweekly	Controller	Run diagnostics on software.
	Biweekly	Detector	Check sensitivity with standard solutions.
	Annually	Whole System	Complete maintenance check.

Instrument	Frequency	Component to Check	Procedure
Gas Chromatograph Electron Capture Detection	Daily	Peak Area/Height Resolution Reproducability.	Instrument is conditioned with a standard then calibrated. Standards are repeated every five samples to update calibration.
	Monthly	ECD Contamination	Detector output and background monitored for contamination. ECD are thermally cleaned over the weekend once per month.
	Monthly	Resolution	Known PCB standard injected and compared to previous month.
Gas Chromatograph Flame Ionization Detector	Annually or as needed	FID Contamination	Detector cleaned manually using HP kit.
	Daily	Peak Area/Height Resolution Reproducability	Instrument is conditioned with a standard then calibrated. Standards are repeated every five sample to update calibration.
High Pressure Liquid Chromatograph	Daily	Peak Area/Height Resolution Reproducability	Instrument is calibrated using triplicate standards. Further standards are analysed every three to five samples for recalibration.
	Daily	Contamination	An instrument blank is run prior to calibration.

Instrument	Frequency	Component to Check	Procedure
	Annually or as needed	Contamination/Interferences	Guard column is installed in system and changed when necessary or annually.
Fluorescence Detector	Monthly	Contamination	Blanks are run through the detector to check for background.
	Annually	Contamination	General cleaning and maintenance of the detector is carried out according to manual.
CHN Analyzer	Daily	Interferences	Blanks are run in duplicate everyday prior to sample analysis.
	Daily	Peak Area/Height Resolution Reproducability	Instrument is calibrated in duplicate with a known standard every morning before sample are run. A natural standard (tomato leaves) is run prior to samples.
	Monthly	Combustion	The combustion tube is changed every one to two months depending on use.
	Quarterly	Reduction	Reduction tube is changed every two to three months depending on use.
	Annually	Column	The chromatographic column is changed as needed.

Instrument	Frequency	Component to Check	Procedure
	Annually	Precision	Replicates are analysed (large number) at least yearly to determine precision of instrument and operator.

4. Mass Spectrometry

Instrument	Frequency	Component to Check	Procedure
Mass Spectrometer	Daily	Vacuum	Monitor readings on instrument panel; should show high vaccum in manifold of 10^{-6} TORR or less with .32 mm x 25m cap column at 10 psi head pressure.
	Daily	Temperature	Monitor readings on instrument panel. Manifold to be set at 100°C, source to be at 15 x 10°C for EI fragmentation.
	Daily	Calibration	Acquire 5 scans of FC43 calibration gas over a mass range of 60 to 510 amu/1.5 seconds.
			Run the CALI program then run the FIT program. If the FIT ERROR is less than 75 mu the calibration is acceptable.

Instrument	Frequency	Component to Check	Procedure
	Daily	Noise	With no input to the Preamp, and the preamp zeroed there will be fewer than 5 noise spikes seen in a 3 second measurement, each has less than 2 ADC counts.
	Weekly	Zeroing	Filament source and EM turned off. Set acquisition light until it begins to glow. Set data system with maximum sensitivity, minimum area = 0. Acquire file ZERO, monitor the acquisition using the GAIN command.
	Daily	Data System	Data capture set for 100 peaks per scan per second.
	As required	Data System - Standards	Optimum conditions set up for compounds of interest when confirmations are required.
	As required	Data System - NBS	For general screening of full scan acquisition, NBS library of 38,000 compounds used for comparison.

Instrument	Frequency	Component to Check	Procedure
Ion Source Filament	As required	Filament	Remove, clean assembly and weld new filament in place.
Gases	As required	Gas Cylinder	Replace when tank pressure drops below 500 psi.
Gas Lines	Yearly	Gas Lines	Leak check with snoop, tighten connections or replace fittings to obtain good seal.
Gas Chromatograph attachment on Mass Spectrometer	Daily	Gas	Check pressure and flow rates, adjust as required.
	As required	Injector	Change septum, clean glass liner, check column connection.
	As required	Column	Replace when parameters dictate different phase or when loss of sensitivity, resolution, or excessive column bleed pose problem.
Mass Spectrometer (VACUUM PUMPS)	Daily	Oil	Check level and temperature.
	Monthly	Recirculating Coolant	Check water level and operation.
	Semi-annually	Oil	Change oil in mechanical pumps and check for leaks. Change oil for bearings in turbo pumps.

5. MISCELLANEOUS

Instrument	Frequency of Checking	Component to Check	Procedure
Balances	Daily	Pan	Clean with brush. If needed wash with water and dry with paper cloth.
	Daily	Balance Level	Ensure balance is level by monitoring bubble in the level adjustment.
	Annually	Accuracy	Calibrate using Certified Standard Weights.
	Annually	System	Service Contract.
pH Meters	When in use.	Accuracy	Calibrate pH meter with at least two buffer solutions. The expected pH values should be as close as possible to that of the buffer.
		Probe	Keep probe submerged in distilled water at all times.

VIII

QUALITY ASSESSMENT

FORMS

In Chapter II, Section 2.3, "Quality Assessment" is defined as the overall system of activities which ensures that quality control is being performed effectively. Quality control data must be evaluated and audited in a documented form which will allow managers, supervisors and analysts to make appropriate judgements on the success of the quality control activities. The following "Quality Assessment Forms" are the instruments by which this documentation is carried out at the National Water Quality Laboratory. The information from these forms is compiled on a regular basis and used to ensure that an effective Quality Assurance Program is maintained.

NATIONAL WATER QUALITY LABORATORY

SECTION HEAD'S

QUALITY ASSESSEMENT FORM
(Semi-Annual)

Name _____

Section _____

Programs supported _____

No. of projects supported _____

F.Y. _____ P.Y.'s FTC _____ Budgets(k) O&M _____
Term _____ Capital _____
Contract _____ Other _____

1. Identify human resource utilization and distribution of time by type of activity.

Laboratory Area of Analysis	Person Years Utilized					
	Analysis	Q.C.	Meth.Adap.	Field Supp.	Other	Total
Phys./Nut./MI.						
Metals						
Organometals						
Biochemicals						
Biocides						
Industrial Chemicals						
Special						
Total						
% of PY Allocation						

2. List frequency of analytical data checked against historical values, and/or detailed analytical audit of samples.

Date	Poject #	Sample No.	Problem Parameter	Action

3. Identify frequency of client complaints about analytical or other services provided by the NWQL.

Date	Parameter/Service	Problem	Action

4. Indicate number of new analytical methods adapted, documented, implemented, or approved in your area of analysis.

Date	Method Name	Adapted	Documented	Implemented	Approved

5. List training sessions attended by your staff such as seminars, workshops, courses or conferences.

Date	Type of Activity	Benefit	Recommendation

6. Indicate unsafe laboratory facilities or work practices identified by the safety committee and action taken to resolve them.

Date	Unsafe Facility/Practice	Action

Signature of Section Head

Signature of Supervisor

NATIONAL WATER QUALITY LABORATORY

UNIT HEAD'S

QUALITY ASSESSMENT FORM
(Quarterly)

Name _____

Unit _____

Section _____

F.Y. _____ Quarter: 1 __ 2 __ 3 __ 4 __ No. of staff ____

1. Name the interlaboratory Q.C. studies in which your laboratory participated.

Study Name	Date	# of Samples	# of Tests	Performance
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2) List all new analytical methods that were characterized and documented in your laboratory during this period of assessement.

Date	Method
---	---

3. List the analytical methods that were adapted and coded during this period of assessement.

Date	Method
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4. Indicate instrument breakdowns or malfunctions and actions taken to correct problem.

Instrument	Date	Down Time	Problem	Action taken
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5. List the frequency of verification of analytical results (raw data to final results) as well as analytical data checked against historical values.

Date	Project	Parameter/Lab.No.Range	Problem (if any)	Action taken
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6. What are the multi-operator precision and accuracy of the group of tests performed in your unit during this period of assessement?

Test	Precision	Accuracy (% Recovery or SRM)

7. Identify frequency of safety checks of your laboratory facility and actions resulting from them.

Date	Observation	Action taken

Signature of Unit Head

Signature of Supervisor

NATIONAL WATER QUALITY LABORATORY

ANALYST'S

QUALITY ASSESSMENT FORM
(Monthly)

Name _____

Unit _____

Section _____

F.Y. _____ Month _____ Days Worked _____ Hours Worked _____

1. a) Indicate the variability of blanks and standards processed during this period of assessement. (Note: The units in which the following are calculated will depend on the area of analysis. For example absorbance units, concentration units or specific detector response).

		Precision (Std.Dev.)			
Test	Concentration	Blanks	Standards	Internal Spikes	Surrogates
----	----------	------	---------	-------------	----------

1. b) Indicate the precision and accuracy of the group of tests you performed on samples.

		Precision		Accuracy (% Recovery and/or SRM)				
Test	Mean	Sample Dup.	SRM	Mean	Hi	Low	Found	Theoretical
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2. a) INORGANIC LABORATORIES:

List the No. of warning limit violations for the following QC samples in your area of analysis (i.e., + or - 2 Std.Dev.).

Parameter	Spikes	Duplicates	Rechecks	Blanks	SRM/Control Smpl.

2. b) ORGANIC LABORATORIES:

Indicate No. and type of QC samples carried out with your analyses, and specify No. of outlier determinations (+ or - 2 Std.Dev.).

Parameter	Tests(#)	Blanks	Internal Spikes	Surrogates

3. INORGANIC LABORATORIES:

a) For which parameter(s) do you use control charts?

b) How many times did control charts indicate your analytical system to be out of control?

Date	Parameter	Source of Problem	Remedy Taken

4. a) How often and in what manner did you perform a sensitivity check on your analytical instrument?

4. b) Indicate the following information on Stock and/or intermediate Standard solutions you prepared.

Analyte	Date Prepared	% Deviation from Old Standard or % Purity

5. Indicate frequency of laboratory chemicals/reagents found to be impure and action taken to resolve problem.

Date	Chemical/Reagent	Action taken

6. Describe method and frequency of housecleaning procedures you used in your analytical work (i.e., glassware, instruments, fume hoods, benchs, etc.).

Signature of Analyst

Signature of Supervisor

NATIONAL WATER QUALITY LABORATORY

CONTAINER PREPARATION AND SAMPLE INITIALIZATION

QUALITY ASSESSEMENT FORM
(Monthly)

Name _____

Unit _____

Section _____

F.Y. _____ Month _____ Days Worked _____ Hours Worked _____

CONTAINER PREPARATION

1. List No. of sample containers prepared this month and sent for quality control testing.

Container Type	Containers Prepared	Q.C. Submissions

2. List No. of batches (clean containers) rejected from last month's workload, due to inadequate quality.

Container Type	No. of Batches	No. of Containers

SAMPLE INITIALIZATION

1. No. of batches submitted for analysis. _____

2. Total No. of submission forms processed. _____

3. No. of submission forms with incorrect information. _____

4. Project numbers with incorrect data on submission form or with inadequate sample.

Project	Describe Problem	Remedy to Problem

5. Verification of accuracy of sample identification information in database:

NOTE: This section is to be filled by the audit officer responsible for verifying the integrity of the sample logging information.

Details of Event	No. of Events	Action Taken

Signature of Employee

Signature of Supervisor

Date Due

~~SEP 15 2000~~			
OCT 3	2000		