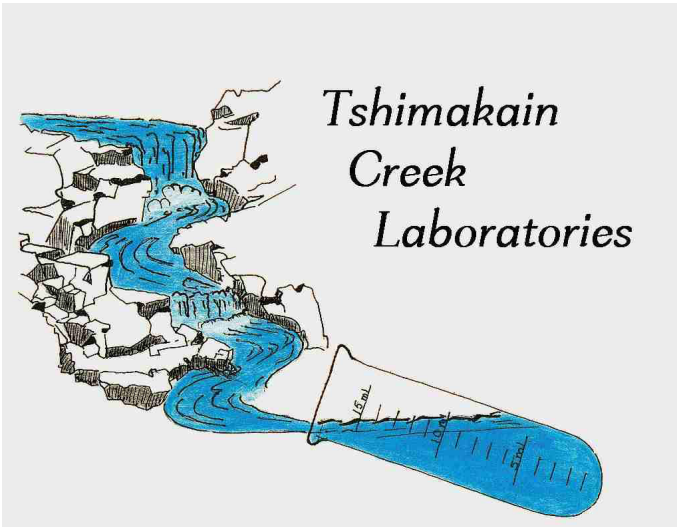


Tshimakain Creek Laboratories Quality Assurance Plan



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APPROVED FOR RELEASE:

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1. INTRODUCTION

This manual is issued to describe the quality assurance program (QAP) utilized at Tshimakain Creek Laboratories. (TCL). TCL is committed to providing accurate and defensible data; this manual fully explains the means in which TCL maintains quality and integrity of data obtained in the laboratory.

TCL is an analytical laboratory specializing in the performance of tests and parameters used in the characterization of environmental samples. Since 1993, TCL has analyzed water, soil, sediment, sludge, vegetation, and other sample types.

TCL facilities are specifically designed and organized to ensure an efficient mode of operation. The laboratory building has been modified to the specific needs of an analytical laboratory. State-of-the art analytical equipment is employed to obtain highly accurate and quality data.

1.1 Organizational Chart/Key Personnel

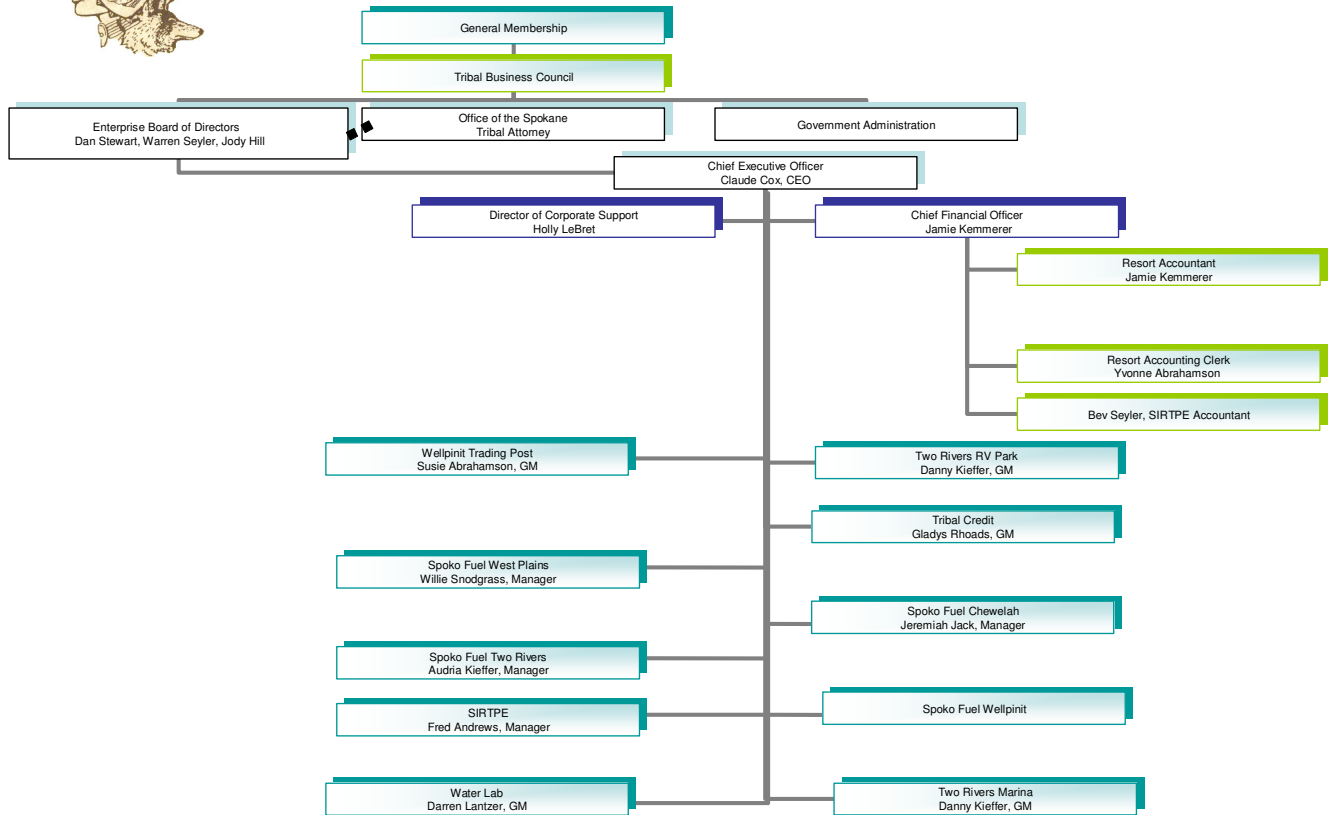
The organizational structure of TCL follows a traditional scheme of management with a few modifications. The lab is an enterprise that is owned by the Spokane Tribe of Indians. The first in command is the Spokane Tribe of Indians Enterprises Chief Executive Officer. The Laboratory Manager is next in command, followed by laboratory technicians. A complete organizational chart is shown below.

Brief resumes follow in this document

Position	Employee	Degree	Lab Experience
Owner	Spokane Tribe of Indians		
Enterprise Chief Executive Officer			
Laboratory Manager	Darren Lantzer	MS 1995	16
Laboratory Technician	Joshua Flett	Currently Attending College	5
Laboratory Technician	Brittany Rough	Currently Attending College	1



Spokane Tribe Enterprise Office Organization Chart



1.2 Resumes

Darren Lantzer

Title: Laboratory Manager

Education: Master of Science, Biology 1995
Eastern Washington University, Cheney, WA
Bachelor of Science, Biology 1993
Eastern Washington University, Cheney, WA

Completed course instruction on Viva-Jr® Operator Training for UA analysis.

Responsibilities: Oversee all aspects of laboratory operations, train and supervise lab technicians, operate and maintain all laboratory equipment, client interaction, quality control/quality assurance, billing, internal audits, external audits and report writing. Collection and analysis of UA samples. Interpret and report UA results to clients.

Joshua Flett

Title: Laboratory Technician

Education: Working on a degree at Eastern Washington University.

Responsibilities: Analyze surface water samples for total suspended solids, turbidity, and fecal coliform. Data entry, client interaction, log in samples, glassware preparation, logbook monitoring. Use of IC and flow injection units on surface water samples to analyze anions and nutrients.

Brittany Rough

Title: Laboratory Technician

Education: Working on a degree at Spokane Community College.

Completed course instruction on Viva-Jr® Operator Training for UA analysis.

Responsibilities: Analyze surface water samples for total suspended solids, turbidity, and fecal coliform. Data entry, client interaction, log in samples, glassware preparation, logbook monitoring. Use of IC and flow injection units on surface water samples to analyze anions and nutrients. Assist in collection and analyze UA samples. Interpret and report UA results to clients.

2. Equipment

Model #	Manufacture/Quantity & Type
	Dionex
DX-500	1 - Ion Chromatograph
	Hach
2100N	1 – Turbidimeter
45900	1 -- Block Incubator
15E	1 – Incubator
	Mettler
AG204	1 – Analytical Balance
PB602-S	1 - Analytical Balance
	Refrigerators
CTX18	1-Hot point (Samples)
TAX4SNTB	1-GE (Reagents)
	Fisher Scientific
09-328	1 – Conductance Meter
Iso-Temp 500	1 - Drying Oven
	Barnstead/ Thermolyne
5P131325	1-Hot plate/stirrer
	VWR
AS12	1 – Sterilizer
1213	1- Water Bath
	UVP
UVL-56	1 - UV Lamp
	Alpkem O.I. Analytical
FS-3000	1 – Flow Solution 3000
	AI Scientific
AIM500	1 - Digester

3. Analytical Procedures

Samples are analyzed according to TCL Standard Operating Procedures (SOPs) that are created using established procedures. The SOPs are available upon request. References for creating SOPs are listed below. TCL is also able to design procedures to meet the needs of clients when approved or recommended procedures are not available.

3.1 References

- ◆ “Methods for Chemical Analysis of Water and Wastes”, EPA/600/4-79/020.
- ◆ “Test Methods for Evaluating Solid Wastes”, SW 846, Sept 1986
- ◆ “Standard Methods for the Examination of Water and Wastewater”, 21st Edition, 2005

4. Documentation

Complete documentation of laboratory operations requires several types of manuals, logbooks and forms. The following types of documents are used at TCL.

- ◆ Quality Assurance Manual – The QA Manual establishes the guidelines for QA/QC procedures, documentation, and protocol.
- ◆ Standard Operating Procedures (SOPs) – SOPs provide detailed instructions for analytical methods and procedures.
- ◆ Bench Sheets – This includes all bench sheets for analysis that have been analyzed in the lab. Besides having a record what has been analyzed it also includes the work order folder number where the raw data can be found.
- ◆ Material Safety Data Sheets – MSDS are kept for all chemicals used in the lab. They can be used for emergency purposes or review of chemical information.
- ◆ Log Books – Many log books are kept to record daily, weekly, and monthly records which includes (but not all) refrigerator temperatures, turbidimeter calibration, and IC reagents.

4.1 Document Retention

Historical revisions of the QA Manual, SOPs, Bench Sheets, Raw Data, and Clients Reports will be kept for a minimum of seven years. Client records can be held longer with written request from the client.

5. Ethics and Data Integrity Agreement

The pledge of TCL is to provide its clients with accurate and defensible data and meeting all client requirements for data quality and integrity. Data is useless unless this commitment is adhered to. All employees agree to follow TCL's policy regarding ethics and data integrity, which is characterized in the items listed below.

- ◆ All work performed shall be in accordance with appropriate work order agreements, specified methods, SOP's, contracts, etc.
- ◆ All data values reported (e.g. sample results), including analysis dates and times, represent actual values obtained and are not modified, or manipulated in any manner which is not described in the referenced method.
- ◆ Analysts performing technical methods in the name of Tshimakain Creek Labs, shall not represent work which was performed by other individuals as their own.
- ◆ TCL shall keep client results strictly confidential and released to a third party only with written permission.

6. Quality Assurance/Quality Control Procedures

TCL realizes that an all-encompassing quality control program is essential to providing analytical data, which is legally defensible, technically accurate, and scientifically meaningful.

At TCL, quality control begins once samples are received and continues until data is reported to the client. Control procedures are defined for every step of the program and detailed in current Standard Operating Procedures (SOPs).

Without these controls adhered to in every aspect of laboratory operations, data becomes suspect and therefore, of little or no use to our clients. Hence, TCL is dedicated to providing data of the highest quality, usability, and defensibility for every project we undertake.

6.1 Quality Assurance Policy and Objectives

The goal of the QAP is to define quality control procedures for all activities that take place in the laboratory. These include the following: receipt, handling, and storage of samples; preparation and maintenance of standards, reagents, gases, and water; calibration and maintenance of analytical equipment; performance, and evaluation of analytical methodologies. The objective is to provide a uniform basis for instrument maintenance, document control, analytical methodologies, data generation, quality assurance, and quality control. The procedures outlined in this manual are the basis of the TCL Quality Assurance Plan (QAP).

6.2 Quality Assurance Management

At TCL the Laboratory Manager is also the Quality Assurance Coordinator. The Quality Assurance Coordinator is responsible for the management and implementation of the quality assurance program. The QA Coordinator is responsible for recommending corrective actions as necessary.

In addition, the Quality Assurance Coordinator develops quality control programs; monitors quality assurance activities to determine conformance with policies and procedures; evaluates and maintains records of data quality and other pertinent performance information; and coordinates quality-problem investigations.

6.3 Sample Collection and Handling

This section describes the quality control procedures to be followed in the collection and handling of samples for TCL. These procedures are recommended to all clients submitting samples for chemical analysis. All samples submitted for microbiological analysis must follow sampling protocols described in method SM9060A and/or instructions on back of bacteriological sample collection chain-of-custody form. Glassware preparation is included in this section because it is an integral part of any sampling program. It is assumed that the objectives of a study for which samples are to be collected have been stated and the number of samples, types of samples, frequency of collection, and duration of the sampling program has been established. Finally, it is assumed that all personnel involved in sample acquisition are aware of the above factors. If utilized, the procedures characterized here result in more confidence in the data produced and the samples are processed more efficiently. The most important aspects of quality control for sample collection and handling are sample integrity and representivity.

6.3.1 Sample Integrity

Sample preservation is critical for sample integrity given the potential for transportation delays and hold ups. Chemical reactions may occur and some chemical species begin to change upon sample collection. Unfortunately, for most samples immediate analysis is neither economically feasible nor logistically possible. TCL strongly recommends the preservation methods, container type, sample size and estimated maximum holding times for collection of water and wastewater samples summarized in Table 5-1. If samples cannot be delivered to the lab during the same day as collection samples can be kept on ice or stored in a designated refrigerator free of any food. This is only acceptable if analysis can begin within holding time requirements.

Solid samples are best preserved by refrigeration at $4\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. Analysis begins as soon as possible after lab receives samples. TCL does its utmost to ensure that all holding times are met for water samples as listed in Table 5-1. A complete record is maintained on each sample to provide a history of handling from the time of collection through analysis and sample disposal.

6.3.2 Sampling Precision and Bias

Sampling precision is a means of determining sample representivity as measured by collecting duplicate samples until seven (7) pairs of data are available. These samples can be obtained either at seven (7) different sampling sites or at the same sampling site on seven (7) different trips, depending on the parameters being tested. These data are used to determine acceptable sampling precision limits. Generally, sampling precision is determined in the initial phase of a long-term sampling program. It is checked thereafter with a single duplicate sample, preferably accompanying every sample delivery group.

Field blanks allow identification of systematic sample contamination, which may result from the sampling equipment, storage containers, sampling agents, or chemicals added to preserve samples. Filling a randomly selected sample container with distilled water and the appropriate chemical preservative can check this contamination. Field blanks are analyzed as samples and therefore, are treated exactly as samples: all aliquots, preservation, filtration, storage and handling procedures are performed as if the field blanks are samples. To achieve accurate and meaningful data, field blank "sample" containers are filled at the sampling site, not after returning to the field laboratory. The following notes may be helpful in reducing the impact upon data of contamination, which is encountered through collection, and handling in the field.

Two general classifications of contamination exist, random and systematic. Random contamination causes imprecision in analytical results as noted by significant differences between results of duplicate analyses. Systematic contamination generally results in consistent shifts in baseline concentrations; this is demonstrated through the use of field blanks. The point is that systematic contamination is much easier to eliminate and to deal with in interpreting the data. The best way to restrict contamination of the systematic type is to treat every sample, blank, replicate, sub-sample, split sample, etc., exactly alike within the limits of preservation, holding and procedural prerequisites. It may, therefore, be necessary to do a few dry runs through filtering or preservation procedures to achieve a routine. The vast majority of contamination of this type occurs with analyses detected in levels of trace concentrations only.

Many sources of possible sample contamination exist including the following:

- ◆ Contaminated sample containers.
- ◆ Unclean glassware and filters.
- ◆ Impure solvents and reagents.
- ◆ Use of cleaning products inappropriate for the proposed analysis.
- ◆ Inadequate rinsing of glassware during the cleaning process.
- ◆ Inadequate presample rinsing--the sample bottle should be rinsed two (2) to three (3) times with small volumes of the sample before the bottle is filled to overflowing.

Presample rinsing is not possible for certain parameters (e.g., oil and grease) or when pre-preserved or sterile bottles are used.

- ◆ Particulate matter (hair, tobacco smoke, dust)-- all sample handling should be done in as clean an area as possible. Filtration apparatus should be protected from contamination. As an example, Kimwipes™ must be used with caution during handling of samples scheduled for trace metals analyses since they may contain appreciable amounts of zinc.
- ◆ It is advisable to rinse filters several times with distilled water between samples and also to pre-rinse filter with 50 mls of sample, which is run through the walls of the filter funnel (under vacuum). This filtrate is then discarded.
- ◆ Use of improper sample container for the parameter specified; e.g., trace metals samples are not to come in contact with any metallic surface.

Table 6-1. Preservation, container type, sample size/type and storage times for analytes.*

Analyte	Container	Minimum Sample Size <i>ml</i>	Sample Type	Preservation	Maximum Storage Recommended/ Regulatory
Alkalinity	P,G	200	g	Cool to 4 °C	24h/14d
Chloride	P,G	100	g, c	none required	28d
Chlorophyll	P,G	500	g, c	analyze immediately	30d/N.S.
Coliform bacteria	Sterilized P,G	100	g	analyze immediately Cool to 4 °C	6h/30h
Conductivity	P,G	500	g, c	Cool to 4 °C	28d/28d
Fluoride	P	300	g, c	none required	28d/28d
Hardness	P,G	100	g, c	Add HNO ₃ to pH<2	6 months/6 months
Metals, general	P(A),G(A)	500	g	Add HNO ₃ to pH<2 For dissolved metals filter immediately,	6 months/6 months
Mercury	P(A),G(A)	500	g	Add HNO ₃ to pH<2, Cool to 4 °C	28d/28d
Nitrogen: Ammonia	P,G	100	g, c	Analyze ASAP or add H ₂ SO ₄ to pH<2 Cool to 4 °C	7d/28d
Nitrate	P,G	100	g, c	Analyze ASAP or Cool to 4 °C	48h/48h(28d for chlorinated samples)
Nitrite	P,G	100	g, c	Analyze ASAP or Cool to 4 °C	asap/48h
Kjeldahl	P,G	500	g, c	Cool to 4 °C, add H ₂ SO ₄ to pH<2	7d/28d
pH	P,G	200	g	analyze immediately	2h/stat
Total Phosphorus	P,G(A)	100	g	Cool to 4 °C	48h/N.S.
Ortho-Phosphorus	P,G(A)	100	g	filter immediately; Cool to 4 °C	48h/N.S.
Solids	P,G	500	g, c	Cool to 4 °C	7d/2-7d
Sulfate	P,G	100	g, c	Cool to 4 °C	28d/28d
Turbidity	P,G	300	g, c	Analyze same day; store in dark up to 24h,Cool to 4 °C	24h/48h

P = Plastic (polyethylene or equivalent)

G = Glass

(A) = Rinsed with 1:1 HNO₃

g = grab

c = composite

• * Standard Methods (APHA 1995)

6.3.3 Cleaning Procedures for Sample Containers and Filtering Equipment

6.3.3.1 Glassware for General Use

Immediately after use, glassware is immersed in a solution of synthetic detergent. It is scrubbed with a brush, rinsed several times with hot tap water, and subsequently rinsed with deionized water. Glassware thus treated may be used for procedures contingent upon the performance of additional steps specific for that particular parameter.

6.3.3.3 Microbiology Sample Containers (Total Coliforms)

Sterile Whirl-Pak® bags and sterile bottles are commercially obtained for sampling and analysis for the Presence-Absence Coliform Test. Sterility is determined on each lot by inoculation of a container with 100ml Tryptic Soy Broth and incubation for 24 hours.

A sterilized (autoclaved) 500 ml HDPE bottle is supplied when membrane-filter analysis of fecal coliform or E. Coli is to be determined.

6.3.4 Sample Receipt and Handling

Sample receipt and handling procedures at TCL, are based upon the EPA guidelines to ensure efficient generation of high quality analytical results. Each sample is checked for visible damage, leakage, temperature, proper preservation, improper sampling vessel, and over holding time (30 hours). If one or more of these criteria are not met the samples are rejected and the client is notified immediately. Rejection can also happen if background growth results in inhibition of coliform organisms during incubation (i.e. high turbidity). See Table 5-1 for proper handling, sampling, and preservation criteria.

6.3.4.1 Requesting Analysis

The field personnel shall complete a request for analysis. It is imperative that the Order for Analytical Services (TCL's is in the form of a chain-of-custody) or an equivalent be provided which defines analytical requirements and enables the lab to meet sample holding times.

6.3.4.2 Chain-of-Custody

Improper sample and data handling and inadequate chain-of-custody procedures affect the credibility and acceptability of analytical results, regardless of their accuracy and precision. Therefore, it is essential that all samples be properly collected, handled, and analyzed. It is imperative that a chain-of-custody be maintained to document the proper processing of samples, from the time of collection to the time of analysis. Use of a Chain-of-Custody or an equivalent form filled out using indelible ink is required to document this process.

6.3.4.3 Sample Handling

Each batch of samples received at TCL, is given a unique job number consisting of the day, month, and year received and a sequential identifier. For example, a sample that was received April 6 2005 would be given the job number 5040601 with the sample identifier of 5040601-01 with the next sample from the same job 5040601-02; the next job received the same day would have 5040602 with the first sample labeled 5040602-01. This unique number remains with the sample throughout the analytical process. The sequential nature of the laboratory identification numbers allows for quick identification of job and sample status during the analytical process. Samples are labeled with their unique numbers soon after they are received.

6.3.4.4 Bench Sheets and Batch Numbers

Batches are created for each group of samples with the same analyses. Bench sheets are then created from the batch information and printed for the laboratory personnel analyzing the samples. Batches and bench sheets are given a unique number consisting of the day, month, year, and a sequential number if more than one produced on the same day. For example, the first batch and bench number created April 6 2005 would have the number B5D0601. The sequential batch and bench number for the same day would be given the number B5D0602.

6.3.4.5 Sample Storage and Security

Samples, which require refrigeration, are stored in a cooler at 4°C(1°C-5°C), except at times of sample prep or analysis. Samples that do not require refrigeration are maintained in a sample storage area. Samples are retained at TCL for a minimum of 30 days (or longer if required by the client) after a data report is issued to the client so as to facilitate the resolution of potential analytical problems. At the end of the specified period, samples are returned to the client or discarded.

6.4 Reagents, Standards, Gases, and Water

In an effort to keep contamination to a minimum, TCL recognizes the importance of using quality materials in the analytical process. Detailed below are descriptions of the procedures practiced at TCL, to maintain contaminant free reagents, standards, gases, and water.

6.4.1 Reagent chemicals

The most significant source of sample contamination for trace metal and organic analyses results from the acids and solvents used in digestion and extraction, respectively. To minimize this potential for contamination, TCL, uses BAKER INSTRA-ANALYZED or better grade reagents for all environmental analyses.

An approximate amount of reagent required is dispensed into a secondary (clean) vessel; reagents are never dispensed directly from the reagent container. Excess reagent is not returned to the bottle but discarded to appropriate waste container.

6.4.2 Microbiology Media

All media used in microbiological analysis is commercially obtained. Media is checked for quality and contamination. Each Lot of media is checked for proper pH and performance with positive and negative culture controls when received and every 90 days.

6.4.3 Standards

The sources and quality of all standards, reagents, and chemicals used by TCL are documented. A record is maintained which indicates the name of the person preparing a standard, the source of the standard being used, weight or volume measurements, units, and dilutions.

6.4.4 Gases

All carrier, oxidant, and fuel gases used by TCL meet or exceed instrument manufacturers' specifications.

6.4.5 Water

The primary general use water in the laboratory is filtered through a charcoal filter and then a reverse osmosis system. Water then flows through a micro-pore filter with a minimum of one (1) ion-exchange resin cartridge and one (1) High-purity Cartridge. This satisfies the specifications of ASTM Type I water. The water registers a resistance of at least 18.00 M Ω -cm; this meets the specifications of ASTM Type I water.

6.5 Calibration and Maintenance of Analytical Equipment

The following are descriptions of key instruments of concern which detail the routine calibration and maintenance procedures employed at TCL.

6.5.1 Analytical Balances

The precision (0.0001) balance is checked weekly over a seven-point range of Class S weights. The higher capacity top loading (.01) balance is not checked on a routine basis due to it seldom being used. Therefore, it is checked just before each use using a six-point range of Class S weights. An independent contractor calibrates both balances annually. Upon completion of this annual calibration, a calibration status label is affixed to each balance.

6.5.2 Ion Chromatograph

The Dionex ion chromatograph is operated in accordance with manufacturer's instructions. All maintenance specified in the instruction manual is performed at the time intervals specified. Auto-calibration for the instrument is established through the use of standards, performed immediately following maintenance of the instrument and after that on an "as needed" basis. The calibration curve is verified before each use with many different second source standards (ICV1, ICV2, ICV3, MDL1, MDL2) and the acceptance criteria is a result of $\pm 10\%$ of true value. In addition, a CCV1, CCV2 and CCB are performed at a frequency of 10%.

6.5.3 Culture Incubators

The Hach incubators are set at the appropriate temperatures for specific culture growth. The block incubator is set at $44.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ and Air incubator is set at $35.0^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. Temperature is recorded twice during each 24-hour incubation period with a minimum four hours separating each reading. Thermometers in each incubator are checked against a NIST traceable thermometer a minimum of once per year.

6.5.4 Temperature Monitoring Device

Glass/mercury thermometers graduated in 0.1°C increments are used in all incubator units. Calibration of in-use thermometers are checked yearly against a reference NIST thermometer and recorded.

6.5.5 pH Meter

The pH meter is calibrated in accordance with manufacturer's instructions. When the meter is used for determining pH three standards are used to calibrate. Buffer standards of pH 7, pH 10, and pH 4 are used to calibrate and slope is recorded. An old WS or WP sample is checked and result compared to true value. Re-calibration is done if slope is not within acceptance limits of 95% to 105%.

6.5.6 Turbidimeter

The turbidimeter is calibrated and operated in accordance with manufacturer's instructions. Calibration standards are made from commercially manufactured 4000 ntu Formazin solution. Secondary standards (gel) are checked and recorded in the logbook each time meter is used. If results are not within 10% of the expected value then the meter is calibrated.

6.5.7 Conductance Meter

The conductance meter is calibrated and operated in accordance with manufacturer's instructions. Quarterly the meter is calibrated with a 0.01M KCl solution.

6.5.8 Automated Flow Analyzer w/autosampler

The Flow Solution 3000 is operated in accordance with manufactures instructions. All

maintenance specified in the instruction manual is performed at the time intervals specified. Calibration curves are established from analysis of four or five standards, of which the stock solutions are made fresh daily. The initial calibration verification (ICV) is made with a second source standard that is close to the midpoint of the calibration curve and is analyzed at the beginning of the run. Continuing calibration blanks (CCB) and a continuing calibration verifications (CCV) are analyzed at a frequency of 10%.

6.6 Quality Control Protocols

6.6.1 Blanks

Preparation blanks are analyzed at a minimum of one per every batch of twenty (20) or fewer samples or each matrix type whichever is more frequent. A preparation blank consists of laboratory pure water that is processed through all procedures, materials, and labware used for sample preparation and analysis.

6.6.2 Laboratory Control Samples

A laboratory control sample (LCS) is a sample of known value used to validate the analytical procedure. One LCS is analyzed with every batch of twenty (20) or fewer samples or each matrix type whichever is more frequent. Sample batches containing LCS's that are out of control limits are re-prepared. Control limits for solid LCS's are set by the supplier (typically $\pm 3\sigma$). Water or other aqueous LCS's have control limits of $\pm 10\%$ or limits set by the supplier.

LCS samples, for both organic and inorganic analyses, are prepared from different reference materials than those used in the preparation of the instrument calibration standards. Control limits specified by the method are used to monitor system performance.

6.6.3 Control Cultures

Culture control samples are cultures to test microbiological media for positive and negative performance. Each lot of media used is tested. If performance fails the whole lot of media is discarded. Culture control samples are obtained commercially. (Hach provides cultures)

6.6.4 Duplicate Sample

These are aliquots made in the laboratory of the same sample, each aliquot is treated exactly the same throughout the analytical method. The relative percent difference (RPD) between the values of the duplicates, as calculated below, is taken as a measure of the precision of the analytical method.

$$RPD = \frac{|S - D|}{(S + D) \div 2} \times 100$$

WHERE RPD = Relative Percent Difference

S = First Sample Value (original)
D = Second Sample Value (duplicate)

One duplicate sample is used for every batch of twenty (20) or fewer samples or each matrix type whichever is more frequent. The tolerance limit for percent difference typically does not exceed ± 20 RPD. However, the duplicate is also a measure of the homogeneity of the sample matrix. An abnormally high RPD may be an indication of a non-homogeneous sample.

6.6.5 Check Standards and Control Standards

A check standard is prepared in the same manner as a calibration standard. The concentration is usually mid-range for the specific calibration curve. Control Standards are used to validate an existing calibration curve, and are values that are located mid-range on the calibration curve. The control standard is from a different (second) source than that of the standards and check standards. A "control standard" is defined as the Initial calibration verification standard (ICV) and the "check standard" as the "continuing calibration verification standard" (CCV). Check standards are run at a frequency of 10%. The check standard can provide information on the accuracy of the total analytical method and of instrumental performance and response consistency independent of various sample matrices and of the sample preparation procedure. Specific requirements and procedures for calibration and check standards are outlined in the specific analytical procedures (SOPs).

6.6.6 Matrix Spikes and Blank Spikes

A sample matrix spike is prepared by adding a known amount of a pure compound to the environmental sample prior to digestion or extraction. This compound is identical to the analyte for which the sample is being assayed. The calculated percent recovery of the matrix spike is considered to be a measure of the relative accuracy of the total analytical method, i.e., sample preparation and analysis. A blank spike is prepared the way a matrix spike is prepared but the matrix is the blank solution used in the analytical method and provides information concerning sample preparation without concern of matrix interference.

An analytical spike is prepared by adding a known amount of analyte(s) to a digestate or extract of a sample for which the analyte(s) concentration has been determined. These spikes simulate the background and interferences found in the actual sample. The calculated percent recovery of the analytical spike is considered to reflect the relative accuracy of the sample analysis procedure only. Both the matrix spike and the analytical spike are also an indication of the effect of the sample matrix on the ability of the methodology to detect the specific analyte. When no change in volume due to the spike occurs, it is calculated as follows:

$$\% \text{ Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

WHERE SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

Tolerance limits for acceptable percent recoveries are established by client's data quality objectives, but normally are $\pm 25\%$. A blank spike acceptable limit is $\pm 15\%$.

6.6.7 QA Reports / Control Charts

A complete review of the data contained in each client's report is performed including a review of the Chain-of-custody, holding times, and the invoice. All QC sample calculations are reviewed and all raw data results are verified against the reported results. If there are any QC data discrepancies qualifiers are appointed to results after a thorough review of raw data.

Control Charts are maintained for all analytical procedures using QC results. The charts include upper and lower warning levels and upper and lower control levels. Corrective action is taken if QC data that exhibit a trend or are outside acceptance limits in the analytical process. The goals of control charts are to eliminate out-of-control events and to reduce the causes.

6.7 Audits

The success of any QA program is the implementation of internal and external audits. Due to the size of TCL, external audits play an important role in the evaluation of the QA program established at the laboratory.

6.7.1 Performance Evaluations

At TCL performance evaluation samples are obtained commercially to evaluate the accuracy of employed analytical methods. Analysts are required to analyze performance evaluations before they are allowed to generate data.

6.7.2 External Performance Evaluations

TCL participates in the USEPA WS and State of Washington DOE WP Performance Evaluation study series (comprised of 3 studies annually) for a variety of parameters. Copies of the most recent results are available upon request.

6.8 Corrective Action

Any analysis not conforming to the control limits must be halted if all steps to remedy the situation have failed to produce values within the limits. The analyst must correct the problem before analysis may commence.

6.9 Standard Operating Procedures

Standard Operating Procedure (SOP) as defined by the EPA, is a written document which provides directions for the step-by-step execution of an operation, analysis, or action that is commonly accepted as the method for performing certain routine or repetitive tasks.

All operational procedures at TCL conform to a uniform numbering scheme and standard format. It is the policy of TCL to create and maintain SOPs that are useful, accurate, current, and accessible to all employees at TCL.

6.10 Method Detection Limits (MDL)

Before data may be obtained from an instrument utilizing an approved method a Method Detection and Instrument Detection study must be performed, after which studies are performed on a yearly basis, when methods are modified, or when new operators/analysts begin to execute procedures.

A method detection limit is the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. For seven replicates of the sample, the mean must be $3.14s$ above the blank where s is the standard deviation of the seven replicates. The MDL is obtained by replicate measurements one to five times the actual MDL.

At TCL the measured MDL will equal to the limits of reporting. MDL studies are on file and are available upon request.

6.11 Initial Demonstration of Performance

Before an analyst may be allowed to execute an analytical procedure he/she must first, perform a method detection limit study and second, analyze a performance evaluation sample.

Results of the method detection limit study must be consistent with historical values and the measured value of the performance evaluation sample must be $\pm 10\%$ of the true value, before analyst may be allowed to perform the analysis of interest.

7. Certifications

7.1 Drinking Water Certification

Since, TCL is owned by The Spokane Tribe of Indians, a Federal Indian Tribe, the EPA shall certify the laboratory and not the State Department of Health. TCL has been granted Drinking Water Certification as of December 1998. Bob Rieck (chemistry) and Dr. Stephanie Harris (microbiology) conducted a laboratory evaluation on September 23/24, 1998 which resulted in the certification of the laboratory to analyze drinking waters for inorganic and microbiology parameters.

United States Environmental Protection Agency

7.2 State Certification

State of Washington Department of Ecology

8. Glossary

Below you will find a list of terms in this manual and their intended definition.

Accuracy

The degree of agreement of a measured value with the true or expected value of the quantity of concern.

Aliquot

An exact fraction of a solution or suspension.

Bias

A systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system. Temperature effects and extraction efficiencies are examples of the first kind. Blanks, contamination, mechanical losses, and calibration errors are examples of the latter kinds. Bias may be both positive and negative, and several kinds can exist concurrently so that net bias is all that can be evaluated, except under special conditions.

Blank

An artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used.

Reagent Blank Aliquot of analyte-free water or solvent analyzed with the analytical

batch. Prep Blanks are reagent blanks that are created at the time of sample preparation using all the reagents used in the preparation of the samples (i.e., digestion, distillation or extraction).

Method Blank Reagent blank which are put through all the steps of a specific method along with the samples.

Field Blank Randomly selected sample container that is filled with distilled water and the appropriate chemical preservative in the field.

Trip Blank A specific type of field blank. A trip blank is not opened in the field. It is a check on sample contamination origination from sample transport, shipping, and site conditions.

Blind Sample

A sample submitted for analysis whose composition is known to the submitter but unknown to the analyst. A blind sample is one way to test proficiency of a measurement process.

Calibration

Comparison of a measurement standard or instrument with another standard or instrument to report or eliminate by adjustment any variation (deviation) in the accuracy of the item being compared.

Check Standard

A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method.

Contamination

There are two general classifications of contamination; random and systematic. Random contamination causes imprecision in analytical results as noted by significant differences between results of duplicate analyses. Systematic contamination generally results in consistent shifts in baseline concentrations as demonstrated by field, trip or equipment blanks.

Control Limits

The limits shown on a control chart beyond which it is highly improbable (within a 99.7% probability) that a point could lie while the system remains in a state of statistical control.

Control Chart

A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control.

Detection Limit

The smallest concentration/amount of some component of interest that can be measured by a single measurement with a stated level of confidence.

Double Blind

A sample known by the submitter but submitted to an analyst in such a way that neither its composition nor its identification as a check sample are known to the latter.

Duplicate Samples

An aliquot taken in the laboratory of the same sample, treated exactly the same throughout the analytical method. The relative percent difference (RPD) between the values of the duplicates, as calculated below, is taken as a measure of the precision of the analytical method. The relative percent difference for original sample and duplicate is calculated as follows:

$$\text{RPD} = \frac{|S - D|}{(S + D) \div 2} \times 100$$

RPD= Relative Percent Difference

S= First Sample Value (original)

D= Second Sample Value (duplicate)

Homogeneity

The degree to which a property or substance is randomly distributed throughout a material. Homogeneity depends on the size of the sample under consideration. Thus a mixture of two minerals may be non-homogeneous at the molecular or atomic level but homogeneous at the particulate level.

Instrument Detection Limit (IDL)

The smallest concentration detectable on a specific instrument.

Laboratory Control Sample (LCS)

A material of known composition that is analyzed concurrently with test samples to evaluate a measurement process.

Matrix Spike

A sample to which a known amount of analyte(s) has been added. Designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added prior to sample extraction/digestion and analysis. Individual component sample recoveries are calculated as follows:

$$\% \text{ Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

SSR= Spiked Sample Result

SR= Sample Result

SA= Spike Added

Mean

The sum of all observations divided by the number of observations.

Method

An assemblage of measurement techniques and the order in which they are used.

Method Detection Limit (MDL)

The smallest concentration detectable by a specific method (the standards used for this determination are carried through all the steps required by the method).

Performance Audit

A process to evaluate the proficiency of an analyst or laboratory by evaluation of the results obtained on known test materials.

Precision

The degree of mutual agreement characteristic of independent measurements as the results of repeated application of the process under specified conditions.

Procedure

A set of systematic instructions for using a method of measurement or sampling or the steps or operations associated with them.

Quality Assurance

A system of activities, which the purpose is to provide to the producer or user of a service the assurance that it meets, defined standards of quality.

Quality Control

The overall system of activities whose purpose is to control the quality of a service so that it meets the needs of users.

Relative Standard Deviation

The standard deviation divided by the mean and multiplied by 100.

$$RSD = \left[\frac{s}{\bar{x}} \right] \times 100$$

Sample

A representative sample of any material (aqueous or non-aqueous) collected from any source for which determination of composition or contamination is requested or required.

Standard Operating Procedure (SOP)

A procedure adopted for repetitive use when performing a specific measurement or

sampling operation. It may be a standard method or one developed by the user.

Subsample

A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, a test portion may be a subsample of a laboratory sample.

Standard Deviation

The positive square root of the variance (i.e., σ for populations and s for a sample set of the population). A measure of the average spread around the mean.

Variance

The value approached by the average of the sum of the squares of deviations of individual measurements from the mean. Mathematically, it may be expressed as:

$$\frac{\sum (X_i - m)^2}{n} \rightarrow \sigma^2 \text{ as } n \rightarrow \infty$$

Ordinarily, it cannot be known but only its estimate s^2 , which is calculated by the expression:

$$s^2 = \frac{\sum (X_i - m)^2}{n}$$

Warning Limits

The limits on a control chart within which most of the test results are expected to lie (within a 95% probability) while the system remains in a state of statistical control.