

# STUDY MODULE- VI

## Water Chemistry

(Quality Assurance and Analytical  
Quality Control Practices )

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## **Preface**

Quality assurance/quality control measures are those activities one undertake to demonstrate the accuracy (how close to the real result you are) and precision (how reproducible your results are) of monitoring. Quality Assurance (QA) generally refers to a broad plan for maintaining quality in all aspects of a program. This plan should describe how one will undertake your monitoring effort: proper documentation of all your procedures, training of volunteers, study design, data management and analysis, and specific quality control measures. Quality Control (QC) consists of the steps you will take to determine the validity of specific sampling and analytical procedures.

The scope of these manuals is to provide a baseline of consistency of analytical process in order to ensure data accountability and reliability

## **Learning Objectives**

- To understand basics of Quality Control and Quality Assurance.
- To understand the effects of non-conformances during analytical work
- To understand the quality control procedures intended to ensure Accuracy, precision and sensitivity, freedom from interference and freedom from contamination

## Table of Contents

1	Introduction to Quality Control and Quality Assurance .....	6
1.1	Quality Assurance.....	6
1.2	Quality Control .....	6
2	CALIBRATION AND CALIBRATION VERIFICATION .....	8
2.1	Calibration.....	8
2.2	Instrument Calibration .....	8
2.3	Initial calibration (IC) .....	8
2.4	Continued Calibration Verification (CCV).....	8
3	ANALYSIS OF METHOD BLANK .....	10
3.1	Method Blank: .....	10
3.2	Purpose:.....	10
3.2.1	Evaluation: .....	10
4	VERIFICATION OF REPRODUCIBILITY & REPEATABILITY .....	12
4.1	Repeatability .....	12
4.2	Reproducibility .....	12
5	ANALYSIS OF LAB CONTROL SAMPLE .....	14
5.1	Preparation of Laboratory Control Sample:.....	14
5.2	Analysis of Laboratory Control Sample: .....	14
6	CONTROL CHARTING AND CONTROL LIMITS.....	16
6.1	Preparation of Lab Control Sample for Control Chart.....	16
6.2	Analysis of Lab Control Sample.....	16
6.3	Setting Control Chart (Mean Chart) Limits .....	16
6.4	Using a Mean Chart .....	19
6.5	Interpretation of Control Chart Data.....	19
6.5.1	Control Limits:.....	19
6.5.2	Warning Limits: .....	19
6.5.3	Standard Deviation: .....	19
6.5.4	Trending:.....	19
6.6	Corrective Action:.....	20
7	COMPETENCE CHECKING OF LABORATORY ANALYST THROUGH AUDIT BLIND SAMPLES.....	22
7.1	PROCEDURE:.....	22
7.2	Handling of Lab Control Samples (LCS) .....	22

7.3	Analysis: .....	22
8	ANALYSIS OF SPIKED MATRIX SAMPLES (LABORATORY FORTIFIED MATRIX LFM).....	24
9	PROFICIENCY TESTING .....	26
9.1	Analysis of PT Samples:.....	26
9.2	Submission of Results and Final Report:.....	26
9.3	Evaluation of PT Results: .....	26
10	METHOD DETECTION LIMITS .....	29
10.1	Procedure .....	29
11	VALIDATION OF METHODS.....	31
11.1	PROCEDURE.....	31
11.2	Trueness .....	31
11.3	Precision.....	32
11.3.1	Repeatability: .....	32
11.3.2	Accuracy: .....	32
11.4	Within- Laboratory Reproducibility: .....	33
11.4.1	Working Range: .....	33
11.4.2	Analyses of Unknown Samples: .....	34
11.4.3	Equivalency Testing: .....	34
12	ANION CATION BALANCE .....	36
12.1	Correctness of Analysis: .....	36
12.1.1	Procedure: .....	36
12.2	Measure EC and ions sum: .....	36
12.3	Measured TDS to EC ratio:.....	36

## Abbreviation

Sr. No.	Abbreviation	Expanded Form
1	%	Percentage
2	µm	Micro meter
3	0C	Degree Celsius
4.	L	Liter
5.	Min	Minutes
6.	mL	Milliliter
7.	ppm	Parts per million
8.	Gm	Gram
9.	mg	Milligram
10.	mg/l	Milligram per litre
11.	NGVS	No Guideline Value Set

**Unit 01:**  
**Introduction to Quality Control**  
**and Quality Assurance**

# **1 Introduction to Quality Control and Quality Assurance**

Every organization can improve the processes it utilizes to provide products and services. Such improvement will result in more satisfied customers, lower operating costs, faster product delivery, etc.

“Quality” has many definitions; one that is widely accepted is “fitness for intended purpose”. In thinking of fitness for purpose you must consider Quality, Cost and timely Delivery. If provided correctly – All add up to customer satisfaction. Quality Control tends to be responsible for the testing and evaluation of materials including incoming raw materials, components, and final products as well as in-process testing. This testing is to ensure that the product meets the defined specifications i.e. the chemical / physical structure is as it should be and confirms that there is no contamination in the product. QC may also perform the following tasks, but this varies from organization to organization, namely, create, test and continually update specifications for testing and sampling, maintain documentation on all aspects of the team’s work, retain samples of all materials tested, investigate complaints and initiate suitable action. etc.

The role of Quality Assurance may cover aspects such as the design and monitoring of documentation systems, approval and monitoring of written procedures to produce the product, approval of written records of the processing operations, approval and monitoring of cleaning systems, regulatory control, batch or lot review, release of product etc.

## **1.1 Quality Assurance**

Quality assurance can be defined as "part of quality management focused on providing confidence that quality requirements will be fulfilled." The confidence provided by quality assurance is twofold—internally to management and externally to customers, government agencies, regulators, certifiers, and third parties. An alternate definition is "all the planned and systematic activities implemented within the quality system that can be demonstrated to provide confidence that a product or service will fulfill requirements for quality."

## **1.2 Quality Control**

Quality control can be defined as "part of quality management focused on fulfilling quality requirements." While quality assurance relates to how a process is performed or how a product is made, quality control is more the inspection aspect of quality management. An alternate definition is "the operational techniques and activities used to fulfill requirements for quality."

Before water samples are analyzed, the analytical system must be in a controlled, reproducible state from which results of known and acceptable quality can be obtained. That state is verified through the use of quality control procedures intended to ensure accuracy, precision, sensitivity, freedom from interference, freedom from contamination.

**Unit 02:**  
**Calibration and Calibration Verification**

## **2 CALIBRATION AND CALIBRATION VERIFICATION**

### **2.1 Calibration**

The word “calibration” may be used (and misused) in different contexts. Here, we are talking about metrological calibration in the world of measurement technology. Formally, calibration is the documented comparison of the measurement device to be calibrated against a traceable reference device. The reference standard may be also referred as a “calibrator.” Logically, the reference is more accurate than the device to be calibrated. The reference device should be also calibrated traceably, more on that later on. With some quantities the reference is not always a device, but can also be for example a mass, mechanical part, physical reference, reference liquid or gas.

### **2.2 Instrument Calibration**

Instrument calibration is a measure taken to verify selectivity and sensitivity of the instrument in following way:

- Calibration of instruments is accomplished through the use of reference standards or in-house standards.
- Instruments calibration according to manufacturer instructions

### **2.3 Initial calibration (IC)**

Instruments are initially calibrated with in-house standards or standard solutions made from the certified reference materials at levels appropriate for the analysis. This is called Initial Calibration (IC). Initial Calibration is performed with a minimum of three concentrations of standards for linear curves. Chose a lowest concentration at the reporting limit and a highest concentration at the upper end of the calibration range. The initial Calibration is verified at the beginning of each analytical procedure with the in-house standard solution from a different lot of reference materials.

### **2.4 Continued Calibration Verification (CCV)**

At specified intervals throughout the analytical sequence, the calibration is verified again through the analysis of independently prepared standard solutions. This is called Continued Calibration Verification (CCV). If the IC and CCV fail to meet the criteria in the analytical method, the system is recalibrated. The results of the equipment or method calibration checks are then recorded in respective logbooks.

**Unit 03:**  
**Analysis of Method Blank**

## **3 ANALYSIS OF METHOD BLANK**

### **3.1 Method Blank:**

A method blank (MB) is an analyte-free matrix such as DI Water for liquids or cleaned sand for solids and/or soils that is processed in exactly the same manner as the samples. The main function of the MB is to document contamination resulting from the analytical process. The method blank consists of reagent water and all reagents that normally are in contact with the sample during the entire analytical procedure.

### **3.2 Purpose:**

Analysis of Method blank with every analytical batch in order to determine the contribution of reagents and the preparative analytical steps to error in the measurement. Results are then recorded. An acceptable blank result must be below the Practical Quantization limit established for the analytical methods or have the value less than 10% of the concentration found in the sample. Analyze reagent blank after daily control checks.

#### **3.2.1 Evaluation:**

Evaluate reagent blank results for the presence of contamination. In case of unacceptable contamination present in the reagent blank, sources of contaminations are then identified and corrective actions are taken. Sample analyzed with an associated contaminated blank must be re-prepared and Re-analyzed as the results are suspected if analyte in the reagent blank is greater than Method Detection Limit.

The importance of the method blank is the confidence it provides in assuring the reported values found in your samples are “real” and not the result of laboratory contamination.

**Unit 04:**  
**Verification of Reproducibility & Repeatability**

## 4 VERIFICATION OF REPRODUCIBILITY & REPEATABILITY

### 4.1 Repeatability

Repeatability is the variability of the measurements obtained by one person while measuring the same item repeatedly. Repeatability is a measure of the likelihood that, having produced one result from an experiment, you can try the same experiment, with the same setup, and produce that exact same result. It's a way for researchers to verify that their own results are true and are not just chance artifacts.

To demonstrate a technique's repeatability, the conditions of the experiment must be kept the same. These include:

- Location:
- Measuring tools  
Other apparatus used in the experiment
- Observer

Time period (taking month-long breaks between repetitions isn't good practice)

Repeatability is performed by reanalyzing a pre-analyzed sample after every 10 samples and results are recorded. This procedure is followed with every analytical batch & results are recorded.

### 4.2 Reproducibility

The reproducibility of data is a measure of whether results in a paper can be attained by a different research team, using the same methods. This shows that the results obtained are not artifacts of the unique setup in one research lab. It's easy to see why reproducibility is desirable, as it reinforces findings and protects against rare cases of fraud, or less rare cases of human error, in the production of significant results.

**Unit 05:**  
**Analysis of Lab Control Sample**

## 5 ANALYSIS OF LAB CONTROL SAMPLE

A Laboratory Control Sample (LCS) contains the analyte of interest in known concentration.

It is used to evaluate the ongoing laboratory performance and to monitor accuracy of the method.

It is used to check the % recovery for the LCS used for Competence checking. This procedure is applicable to all the analytical testing

### 5.1 Preparation of Laboratory Control Sample:

A Laboratory Control Sample is prepared from solution of Certified Reference Material (Traceable to NIST)/ in de-ionized water. Stock solution and sub stock standards of desired concentrations are prepared using all glassware of Type-A, by dilution using the following formula. All the glassware used is of Type-A. Appropriate correction factors are applied to all volume preparations.

$$C1V1 = C2V2$$

Where;

C1= initial concentration

V1=Volume required

C2=concentration required

V2=final volume

### 5.2 Analysis of Laboratory Control Sample:

The Lab Control Sample is analyzed in each batch after every 10 samples. The results obtained are plotted on Control Chart. If the result of the Lab Control Sample exceeds the limits of control chart, following corrective actions are recommended.

- Check to see if the LCS was prepared and analyzed according to the method.
- Check calibration of the instrument
- Recalibrate and reanalyze LCS and samples

**Unit 06:**  
**Control Charting and Control Limits**

## 6 CONTROL CHARTING AND CONTROL LIMITS

Control Charting is a powerful and simple tool for the daily quality control of routine work. The basis is that the laboratory runs control samples together with the routine samples in an analytical run. Materials of control samples can be standard solution, real samples, blank samples, in-house control materials and certified reference materials.

The construction of a control chart is based on statistical principles, specifically on the normal distribution. The control limits are based on considerations of probability; thus decisions that a system is in control are supported. Similarly, the control limits can be used to warn of potential problems and reveal the need for corrective action. Control charts should be kept in real time so that such corrective action is taken promptly.

### 6.1 Preparation of Lab Control Sample for Control Chart

Considering the measurement range of various parameter/methods lab control samples are prepared by following steps:

- Stock solution is prepared from certified reference material/in-house standards.
- Desired standard concentration is prepared from the stock solution by using the following formula

$$C_1V_1 = C_2V_2$$

Where;

$C_1$  = Initial Concentration                       $V_1$  = Required Volume

$C_2$  = Concentration Required                       $V_2$  = Final Volume

### 6.2 Analysis of Lab Control Sample

Lab control sample of each parameter is analyzed 30 times by different analysts on different days. Results obtained are processed for following calculations:

- i) Mean
- ii) Standard Deviation (SD)

### 6.3 Setting Control Chart (Mean Chart) Limits

The mean chart is constructed from the mean and standard deviation of a specified number of measurements of the analyte of interest. The mean chart includes Upper and Lower Warning Limits (WL) and Upper and Lower Control Limits (CL). These limits are calculated as:

Upper control limit                       $UCL = \bar{x} + 3s$

Upper warning limit                       $UWL = \bar{x} + 2s$

Lower warning limit             $LWL = \bar{x} - 2s$

Lower control limit             $LCL = \bar{x} - 3s$

Where  $\bar{x}$  is the mean and  $s$  is the standard deviation. These values are derived from measures values for reference materials. The number of measurements,  $n$  or  $n-1$ , used to determine the standard deviation's, is specified relative to statistical confidence limits of 95% for WLs and 99% for CLs.

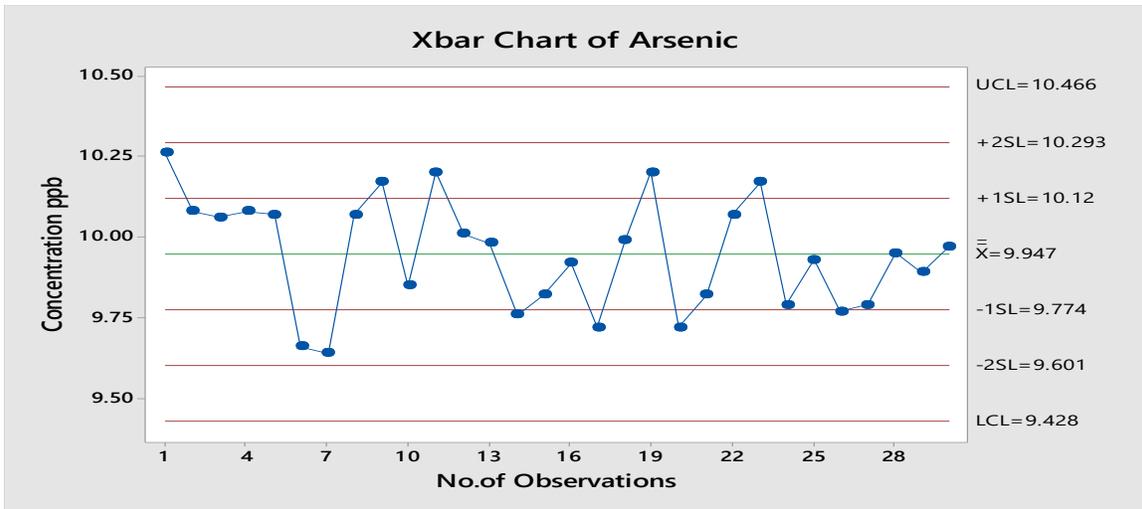
Example:

Lab Control Sample of Arsenic (As) is analyzed on Atomic Absorption Spectrophotometer (Hydride Generation) for setting the control Limits. The results and calculation are given in Table 1.

*Table 1: Data for Control Limits*

S. No	Results(ppb)
1	9.830
2	9.896
3	9.696
4	9.856
5	10.34
6	10.2
7	10.28
8	9.835
9	9.702
10	10.29
11	9.830
12	9.896
13	9.696
14	9.856

15	10.34
16	10.2
17	10.28
18	9.835
19	9.830
20	9.896
21	9.696
22	9.856
23	10.34
24	10.2
25	10.28
26	9.830
27	9.896
28	9.696
29	9.856
30	10.34
Mean	9.9858
s	0.23856
UCL =( $\bar{x}$ 3s)	10.701
UWL=( $\bar{x}$ + 2s)	10.462
LWL =( $\bar{x}$ - 2s)	9.509
LCL =( $\bar{x}$ 3s)	9.270



Date	Control Sample	Concentration ppm	Mean	Std. Dev.	Observations	Verified By	Sign
	Arsenic	10	9.9470	0.1730	30	QC Manager	

## 6.4 Using a Mean Chart

After setting the Limits, each time a result for the control samples is obtained in a batch of test samples, this result is recorded on the control chart of the attribute concerned.

## 6.5 Interpretation of Control Chart Data

**6.5.1 Control Limits:** If one measurement exceeds the CL repeat the analyses immediately. If the repeat measurement is within the CL, continue the analyses. If it exceeds the CL, discontinue the analyses, identify the root cause and correct the problem.

**6.5.2 Warning Limits:** If two out of three successive points exceeds the WL, analyze another sample. If the next point is within the WL, continue analyses, if the next point exceeds the WL, evaluate potential bias and correct the problem.

**6.5.3 Standard Deviation:** If four out of five successive points exceeds 1s, or are in decreasing or in increasing order indicate the mean shift. Analyze another lab control sample for confirmation. If the next point is less than 1s, or changes the order, continue analyses, otherwise discontinue analyses and correct the problem.

**6.5.4 Trending:** If seven successive points are on the same side of the central line, indicate that there has been a shift in the mean; work can continue, however the cause of the shift needs to be identified and the limits re-set if justified.

## **6.6 Corrective Action:**

Whenever the analytical process is out-of-control, investigation/corrective action will be initiated by authorized analyst who is able to recognize out-of-control conditions and immediately raise the non-conformance notify the Technical Manager for action plan. Following corrective actions are recommended:

- i) Review raw data quantization reports
- ii) Check instrument response using calibration standards
- iii) Recalibrate and reanalyze LCS and samples
- iv) Repeat the analysis until the observation appear within the control limits

**Unit 07:**  
**Competence Checking of Laboratory Analyst**  
**Through Audit Blind Samples**

## 7 COMPETENCE CHECKING OF LABORATORY ANALYST THROUGH AUDIT BLIND SAMPLES

This procedure provides the instructions for performance evaluation of new hired/authorized lab analysts through preparation and analysis of audit blind samples.

The Audit Blind sample is prepared and inserted by the Quality Control Section on monthly basis/when required.

### 7.1 PROCEDURE:

Audit blind samples for the purpose of performance evaluation are prepared as “Laboratory Control Samples or Matrix Spiked Samples. Method of preparation, analysis and acceptance criteria for these two types of blinds is as following:

### 7.2 Handling of Lab Control Samples (LCS)

After preparation, Laboratory Control samples (LCS) are bottled sampling bottled labeled with sample labels/sticker having sample code. After giving appropriate sample code these samples are inserted into stream of routine samples. Whereas a set of the same sample is retained by Technical Manager-Quality Control for analysis and confirmation of true values. However, it is ensured by analyst of concerned laboratory that the Laboratory control sample is received by new hired/trainee as a routine sample.

### 7.3 Analysis:

New hired/authorized laboratory analyst analyzes the LCS sample and submits the results on “Result Record Form”. The results are evaluated by calculation of percent recoveries for each parameter. The percent recovery is calculated as:

$$\text{Recovery (\%)} = \left( \frac{\text{Found Value}}{\text{True Value}} \right) \times 100$$

If the results of LCS submitted by analysts are found in the acceptance range, their evaluation is considered as “SATISFACTORY” otherwise “UNSATISFACTORY”. Objective performance criteria in the form of percent recovery calculated for chemical analyte as a part of quarterly QC practice.

**Unit 08:**  
**Analysis of Spiked Matrix Samples**  
**(Laboratory Fortified Matrix LFM)**

## **8 ANALYSIS OF SPIKED MATRIX SAMPLES (LABORATORY FORTIFIED MATRIX LFM)**

A Laboratory Fortified Matrix (LFM) is an additional portion of a sample to which known amounts of analyte of interest are added before sample preparation. In LFM sample the known amount of the analyte is added to already analyze sample. LFM is analyzed to evaluate analyte recovery and matrix interferences in a sample matrix.

QC Technical Manager evaluates the results of LFM for accuracy or percent recovery.

$$\% \text{ Recovery} = \frac{\text{LFM Sample Result} - \text{Sample Result}}{\text{Known LFM added Concentration}} \times 100$$

If LFM results are out of control, Corrective actions are required to be taken to identify the cause & ultimately rectify.

**Unit 09:**  
**Proficiency Testing**

## 9 PROFICIENCY TESTING

Proficiency testing is assessment toll and is performed to verify the test methods and external evaluation of laboratory's competency. Proficiency testing samples are prepared by an authorized independent organization outside the Laboratory. Laboratory receives and analyze PT samples in order to evaluate Laboratory performance and competence. After receiving PT samples are introduced in to the regular sample stream of the laboratory and analyzed as routine samples by authorized analysts following all the instructions provided by the PT providers for analysis.

### 9.1 Analysis of PT Samples:

Standard methods (APHA) or approved test methods are followed to analyze the PT samples.

Following guidelines are followed for analysis:

- Averaging results is prohibited.
- Only authorized employees analyze PT samples.
- Results are not discussed with outside entities prior to deadline for receipt of the results.
- No subcontracting to other laboratories for PT Sample analysis.

### 9.2 Submission of Results and Final Report:

Analyst is responsible to ensure that the laboratory results for PT samples are submitted to PT provider in designated time frame. After receiving of final report evaluation of results is carried out.

### 9.3 Evaluation of PT Results:

Evaluation of PT results is based on two types of acceptance criteria:

- Acceptance Criteria of PT Providers:

PT provider's evaluation based on Z-score is used to determine laboratory performance as per given criteria.

- Acceptance Criteria of Lab

Laboratory can set its own acceptance criteria for PT results on the basis of laboratory's own Z-score calculated by using laboratory's uncertainty. Acceptance criteria are given as following:

Sr. No	Acceptance Criteria	Items	Target	Warning	Action
1	PT Provider's	Z -score	0.00	$\pm 1$	$\pm 2$
2	NWQL	Z -score	$\pm 2$	$> 2$	$\geq 3$

Calculation of Laboratory's own Z-Score using Laboratory's Uncertainty by following formula:

$$Z = \frac{x - X}{u}$$

Where;

- x = Lab value
- X = Assigned Value
- u = Uncertainty of lab

**Unit 10:**  
**Method Detection Limits**

## 10 METHOD DETECTION LIMITS

Method detection limits are a relative measure of the performance of a particular lab, method or analyst. It is the minimum concentration that can be determined with 99% confidence that the true concentration is greater than zero.

### 10.1 Procedure

In order to calculate MDL laboratories prepare solution of concentration approximately four times the estimated limit. The prepared solution is analyzed 10 times over the course of several days. The standard deviation is calculated by the usual method. The MDL is then calculated by substituting standard deviation in the following equation:

$$\text{Method Detection Limit (MDL)} = t \times \text{Std. deviation}$$

Where ;

t = degree of freedom (n-1)

- If the MDL is much higher than the estimated detection limit, it may indicate problems with the procedure or with the analytical equipment, improperly made reagents and expiration dates for chemicals.

**Unit 11:**  
**Validation of Methods**

## 11 VALIDATION OF METHODS

### 11.1 PROCEDURE

When the testing procedure is modified from the standard or existing testing procedure and protocol, it is demonstrated that the modifications do not adversely affect the precision and accuracy of the data obtained. In order to implement the modification, the standard or existing method is first performed. Each major modification is then verified against the original method. Validation plan (NWQL/LMS/Chem-25) is initiated by the Quality Control Technical Manager, and validation report is drafted by the Laboratory Technical manager and laboratory analysts involved and verified by the Quality Manager. Validation plan addresses the parameter to be validated and relevant performance characteristics. All the Typical validation characteristics which should be considered are as following:

### 11.2 Trueness

Prepare Control Sample or Standard solution of certain concentration from Certified Reference Material. Analyzed this sample 10 times.

The trueness for the results calculated as by the following equation:

$$\text{Trueness (\%)} = \frac{\bar{X}}{\mu} \times 100$$

Where

$\bar{X}$  = mean of test results obtained for reference sample

$\mu$  = True value given for reference sample.

The best trueness we can get is 100%

Bias (Accuracy)

The bias of the results obtained can be calculated as:

$$\text{Bias (\%)} = \frac{\bar{x} - \mu}{\mu} \times 100$$

The best bias we can get is 0 %

## 11.3 Precision

### 11.3.1 Repeatability:

The measure of agreement between results obtained with the same method on identical test or reference material under the same conditions.

Make a standard solution of a certain concentration from certified reference material (following CLQA-08). Analyze this sample ten times by one person, in the same laboratory, with same equipment, at the same time or only with short time interval.

Precision is calculated as

$$\text{Precision (\%)} = \frac{s}{\bar{x}} \times 100$$

s = Standard Deviation

$\bar{x}$  = mean

The measure of the repeatability r is the standard deviation of these results sr and for not too small number of data ( $n \geq 10$ ) r is defined by (with 95% confidence)

$$r = 2.8 \times sr$$

### 11.3.2 Accuracy:

Accuracy of the test method is determined by carrying out the recovery experiment. Recovery can be defined as 'the fraction of the analyte determined after addition of a known amount of the analyte to a sample'. Spiked Matrix samples are used for percent recovery. Analysis of sample as well as the spiked sample of different concentrations is done at least 10 times and mean of the values is calculated. The equation used to calculate the percent recovery is as follows.

$$\text{Recovery (\%)} = \frac{X_s - X}{X_{\text{add}}} \times 100$$

$X_s$  = mean result of spiked sample

$X$  = mean result of un-spiked sample

$X_{\text{add}}$  = amount of added analyte

Statistically based acceptance limits are established for accuracy by evaluating spikes recoveries. These limits are used in assuring the acceptability of the subsequent accuracy of a spike and in determining if the value is true and accurate reflection of the method performance. Acceptance Limits for accuracy consist of both Warning Limits and Control Limits:

1. Warning Limits are defined as the mean from a set of data points (recovery values), +/- 2 Sigma. Sigma is the standard deviation of the n-1 population. This Calculation will give an upper and a lower warning limit for the accuracy values.

$$\text{Upper Warning Limit (UWL)} = \text{Mean} + 2 \text{ Sigma}$$

$$\text{Lower Warning Limit (LWL)} = \text{Mean} - 2 \text{ Sigma}$$

2. Control Limits are defined as the mean from a set of data points (recovery values), +/- 3 Sigma. Sigma is the standard deviation of the n-1 population. This calculation will give an upper and a lower control limit for the accuracy values.

$$\text{Upper Control Limit (UCL)} = \text{Mean} + 3 \text{ sigma}$$

$$\text{Lower Control Limit (LCL)} = \text{Mean} - 3 \text{ sigma}$$

#### **11.4 Within- Laboratory Reproducibility:**

The measure of agreement between results obtained with the same method on identical test or reference material under different conditions (execution by different persons with the same or different equipment, in the same laboratory, at different times).

- Control chart is used for the expression of the within-laboratory reproducibility. Control samples are analyzed in each batch, and the within-laboratory standard deviation is calculated when control chart is completed.
- Precision is calculated as;

$$\text{Precision (\%)} = \frac{s}{\bar{X}} \times 100$$

Where;

s = Standard Deviation

$\bar{X}$  = mean

RL = 2.8 x scc

scc = standard deviation of control chart

##### **11.4.1 Working Range:**

Calculate Method Detection limit. The determination of the upper limit is not relevant because the concentrations beyond calibration range are brought within the range by dilution.

### 11.4.2 Analyses of Unknown Samples:

Prepare standard solutions where the value is unknown to the analyst and analyze this sample in replicates by following the standard operating procedure for the method. The mean recovered should be within three standard deviations of the mean value of the standard preferably within 2 s

### 11.4.3 Equivalency Testing:

Analyze minimum of three concentrations by the alternate and by the standard method.

Test the variances of the two methods using the F-ratio statistics. the formula is

$$F = \frac{s_1^2}{s_2^2}$$

If  $F_{cal} < F_{tab}$  one can conclude with 95% confidence that there is no significant difference in precision and is accepted and if not then rejected.

Test the average values of the two methods using a Student-t statistics.

Calculate t with:

$$t_{cal} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Degree of freedom is calculated as

$$V = \frac{\frac{(s_1^2/n_1)}{n_1-1} + \frac{(s_2^2/n_2)}{n_2-1}}{\frac{(s_1^2/n_1)^2}{n_1-1} + \frac{(s_2^2/n_2)^2}{n_2-1}}$$

If the  $t_{cal} > t_{tab}$  then the null hypothesis is accepted if not then rejected.

**Unit 12:**  
**Anion Cation Balance**

## 12 ANION CATION BALANCE

### 12.1 Correctness of Analysis:

#### 12.1.1 Procedure:

The sample is analyzed for pH, Electrical conductivity and total Dissolved solids and for major Anions and Cations. Calculate the TDS by sum of the concentration of all the constituents in mg/l

Calculate the electrical conductivity as per the standard method.

Anion-cation balance is calculated by the following formula:

$$\% \text{ difference} = 100 \times (\sum \text{Cations} - \sum \text{Anions} / \sum \text{Cations} + \sum \text{Anions})$$

The anion-cation sum expressed as milliequivalent per liter must balance

The acceptance criteria is as follows

Anion Sum (meq/L)    Acceptable difference

0-3.0                    + 0.2meq/L

3.0-10.0                + 0.2%

10.0-800                + 5%

### 12.2 Measure EC and ions sum:

Measure the electrical conductivity of the sample. Sum the anions and cations. Both the anions and cations sum should be approximately 1/100 of the measured EC value. If either sum does not meet this criteria, re analyze the sample. The acceptance criteria is as follows

$$100 \times \text{anions (or cations) sum, meq/L} = (0.9 - 1.1) \text{ EC}$$

### 12.3 Measured TDS to EC ratio:

Measure the electrical conductivity of the sample. Measure the TDS of the sample. Calculate the ratio of the TDS and EC as  $\text{Measured TDS}/\text{conductivity} = 0.55 - 0.7$ . The measured TDS to EC ratio should be between 0.55 and 0.7. If it is outside these limits the either measured TDS or measure conductivity is suspect; reanalyze the sample.