# Quality Control for Sampling and Chemical Analysis

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# What is QA/QC?

- Quality Assurance (QA)
  - Are we doing the right things?
  - Management
- Quality Control (QC)
  - Are we doing things right?
  - Technical

# Quality Control

Are we doing things right?

A technical concept:

- Did we do the test?
- Did the results pass or fail the criteria?
- If the results failed did we perform a corrective action?

# Purpose of QA/QC

- Determine precision and accuracy,
- Demonstrate absence of interferences,
- Demonstrate absence of contamination (from sampling equipment, glassware, and reagents)

# Quality Assurance

Are we doing the right things?

A management concept:

- Planning
- Assessment
- Continued improvement

# What Qualities do We Want to Control?

- Accuracy - closeness to the “true” value
- Precision - repeatability

# Accuracy

- Composed of precision and bias
- Measure of the overall agreement of a measurement to a known value
  - when random errors are tightly controlled, bias dominates the overall accuracy
  - when random errors predominate, variance (imprecision) dominates the overall accuracy
- Use bias and precision as separate measures rather than accuracy

# Precision

- Precision is the measure of agreement among repeated measurements under identical conditions
- A precision QC is a quantitative indicator of the random errors or fluctuations in the measurement process
  - e.g., standard deviation or variance

# Sensitivity

- Usually regarded as detection limit
- Capability of a method or instrument to discriminate between measurement responses
  - but this term is often used without defining what is intended (minimum detection or quantitation)
- A sensitivity QC describes the capability of measuring a constituent at low levels
  - a Practical Quantitation Level describes the ability to quantify a constituent with known certainty
    - e.g., a PQL of 0.05 mg/L for mercury represents the level where a precision of +/- 15% can be obtained

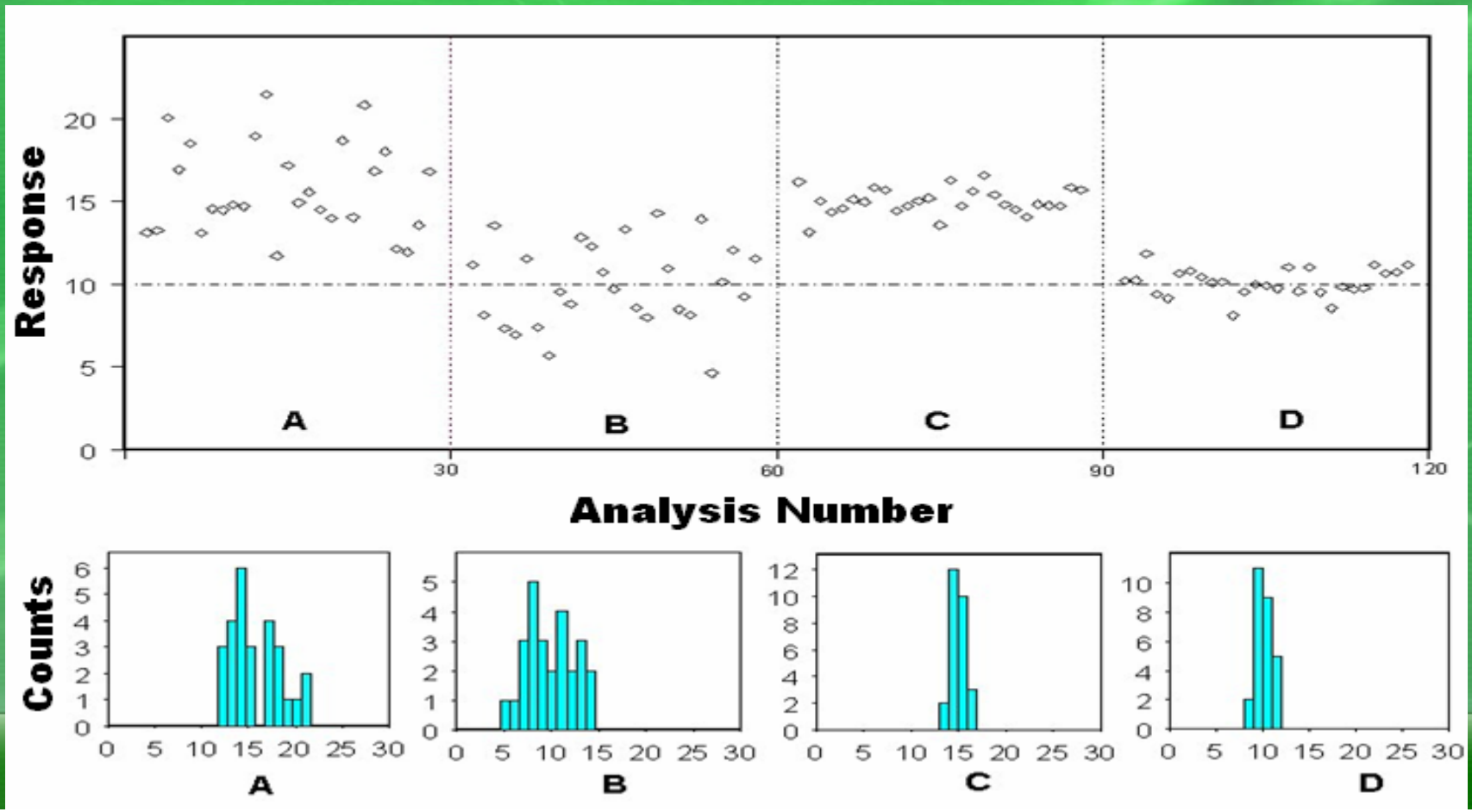
# Bias

- Bias is systematic or persistent distortion of a measurement process that causes error in one direction

- A bias can result from:
  - biased sampling design
  - calibration errors
  - response factor shifts
  - unaccounted-for interferences
  - chronic sample contamination

# Influence of Bias and Imprecision on Overall Accuracy

*Imprecise and biased* | ***Imprecise and unbiased*** | *Precise and biased* | *Precise and unbiased*



# Data Verification

- The procedures needed to ensure that a set of data is a faithful reflection of all the processes and procedures used to generate the data
  - verification entails the examination of objective evidence that the specified method, procedures, and contractual requirements were fulfilled

# Data Validation

- Analyte and sample matrix-specific process to determine the analytical quality of a data set
  - inspection of data handling practices for deviations from consistency,
  - review of quality control (QC) information for deviations,
  - assessment of deviations,
  - assignment of data qualification codes
- Validation can entail the examination of the data with respect to the QA Project Plan

# Accuracy

Closeness to the “true” value

Types of QC to assess accuracy:

- Matrix Spike
- Laboratory Control Sample
- Laboratory Fortified Blank
- Standard Reference Material

# Bias

Error in a specific direction

Blanks are used as an indication of bias

- Field Blank
  - analyte contamination - positive bias
- Method Blank
  - analyte contamination - positive bias
- Calibration Blank
  - analyte contamination - negative bias
  - Matrix mismatch – positive or negative bias
- Calibration Check Blank or Instrument Blank
  - Instrumental drift over time - positive or negative bias

# Data Integrity

- Lack of integrity affects all aspects of data interpretation, especially data used for decision making

- Lack of integrity includes:
  - manipulation of QC measurements
  - dry-labbing (complete falsification of data)
  - manipulation of results during analysis
  - failure to conduct required analytical steps
  - post-analysis alteration of results

# Precision

Precision = repeatability

Types of QCs to assess precision:

- Duplicate Field Sample
- Duplicate Lab Sample
- Duplicate Matrix Spike
- Duplicate Laboratory Control Sample
- Duplicate Laboratory Fortified Blank

# QC – Tools for the Analyst

1. Use Quality Control samples to identify accuracy and precision problems,

1. AND to isolate the problems,

1. AND to address the problems

# Field Blank

Field blanks should be of the same quality as laboratory blanks. Also called Trip Blank or Preservation Blank.

Confirms that the source of contamination was not from laboratory contamination.

Equipment Blanks - some field blanks are actual washings of field equipment, and should be so designated. These blanks may well show some elements above detection.

# Calibration Blank

- Used to set the zero end of the calibration curve.
- If contaminated, can skew the whole curve - biasing the sample results low, especially at low concentrations.

# Method Blank

- Analyte-free matrix taken through the same laboratory preparation and analysis process as the samples.
- Lab needs to set criteria of acceptance range
- Typically, if contamination is found in the method blank but at less than 1/10 of the sample concentration, the method blank contamination is disregarded for that sample.

# Calibration Check Blank

An instrument blank (the same blank that used for calibration) must be run:

- Immediately after calibration
- Minimum frequency – after every 10 samples
- At the end of the analysis run

Calibration is the set of operations which establish, under specified conditions, the relationships between values indicated by a measuring instrument or measuring system , or values represented by a material measure or reference material, and the corresponding values of a quantity realized by a reference standard.

**Calibration can be carried out for three possible purposes viz.**

I) Determining whether or not a particular instrument or standard is within some established tolerance in respect of its deviation from a reference standard.

**ii)** Reporting of deviation in measurements from nominal values.

iii) Repairing /adjusting the instrument or standard to bring it back within the established tolerance.

# Calibration System

In a calibration system, the following items shall be defined.

1. Classification of calibration

2. Standard and levels of standard.

3. Interval of calibration and limit of correction

4. Procedures of calibration

5. Action after calibration

6. Conditions to use measuring instrument

7. Procedures of measurement

# Why Measurements?

Measurements are basic tools in S & T. Said a German philosopher:
If I can define it, I can measure it.
If I can measure it, I can analyze it.
If I can analyze it, I can control it.
If I can control it, I can improve it.

Measurements are needed to
**Choose ,develop,** and **validate models** used to **predict, control** or **Improve** various phenomena. Measurements provide the very basis Of all control actions.

# What are Measurements?

**Measurement :**

A Process that follows a defined sequence of steps/activities involves physical, material and technological resources;and results in a numerical value/a set of numerical values that is assigned to an item in respect of a defined property/ parameter/ characteristic.

Measurement : The output of a (measurement) process.

- a numerical value

## Errors in  Measurements:

Errors in the observed results of a measurements (process) give rise to uncertainty about the true value of the measured as is obtained (estimated) from those results. Both systematic and random errors affecting the observed results (measurements) contribute to this uncertainty.

Random errors presumably arise from unpredictable and spatial Variations of influence quantities ,for example.

- the way connections are made or the measurement method employed
- uncontrolled environmental conditions or their influences

- inherent instability of the measuring equipment

- personal judgment of the observer or operator, etc.

These cannot be eliminated totally but can be reduced by exercising appropriate controls.

Various other kinds of errors, recognized as systematic, are also observed.

Some common type of these errors are

- those reported in the calibration certificate of the reference standards/instruments used.

- those due to different influence conditions at the time of measurement compared with those prevalent at the time of calibration of the standard(quite common in length and d. c. measurements) etc.

It should be pointed out that errors which can be recognized as systematic and can be isolated in one case may simply pass off as random in another case.

# Quality in Measurements

Quality of measurements is comprehended in terms of accuracy and Precision, based on systematic/random errors respectively that get reflected in repeat measurements. A more recent development takes care of both random and systematic errors and results in a measure of Uncertainty about the true value.

Accuracy is the critical parameter, and is not the same as precision. Accuracy is closeness to the true value (of the measured), while precision implies consistency among repeat measurements(not always available).

# NABL Requirements :Technical Criteria

- Standard required : ISO/IEC 17025 : 2005
- What are Technical requirements ? Need to be satisfied in order to establish technical competence of a Laboratory to carry out the Testing and Calibration activities of the Organization

- **Note** : Whatever we speak these three days, the single most important purpose is to find the true value of the parameter we want to measure(measured) as close as possible.

- In ISO/IEC 17025, the Technical requirements are elaborated in Section 5.0.

## ❖ The requirements are:

5.1 General
5.2 Personnel
5.3 Accommodation and Environmental conditions
5.4 Test and Calibration Methods and Method Validation
5.5 Equipment
5.6 Measurement Traceability
5.7 Sampling
5.8 Handling of Test and Calibration items
5.9 Assuring the Quality of Test and Calibration Results
5.10 Reporting of Results

You can very well imagine that all these factors can affect the correctness and reliability of the test results performed by a laboratory.

## Personnel

- This is the human factor and is an important one , since error(random) will be introduced due to personnel who are involved in carrying out the tests, evaluate and sign test reports.
- Basic concepts of this requirement is to ensure competence of the person/persons in a particular testing or calibration activity. This involves both operation of the equipment correctly and carrying out test according to the laid down validated test methods.

## How can we do that?

- We can ensure educational part by specifying qualification and experience during recruitment of Scientist/Technical Officer/ Technical Assistant at a certain level.
- CSIR has a definite Recruitment policy to take care of this criteria.

# Accommodation and Environment

- All aspects discussed here are basically for leading to create a conducive atmosphere for conducting the tests accurately and reliably.

**Policy should be framed so that:**

- All technical requirements of space, temperature, power, atmosphere should be met in the testing area.
- The laboratory should provide facilities for the effective monitoring, control and recording of environmental conditions as appropriate
- Adequate measures are to be taken to ensure good house keeping in the laboratory.
- Testing areas should be separated from neighboring areas and access should be limited.

**Procedures:** how to implement these policies

- Procedures can be laid down according to the convenience and practice followed by the laboratory.
- Some improvements in practices should be done taking advantage of the NABL requirements

## ❖ What is validation?

Validation is the confirmation by examination and the provision of objective evidence that the particular requirements for
a specific intended use are fulfilled.

## ❖ What to validate?

- Standard methods, national or international, do not need validation.
- Not-standard methods, laboratory developed methods, standard methods used outside their intended scope , amplifications and modifications of standard methods need validation
- Should be extensive to check that it meets the need of the given application/field of application
- Should record the results obtained, procedure used for validation and a statement indicating suitability
- Validation may include sampling, handling and transportation

## ❖ How to validate?

**By following one or a combination of the following methods**:

- Calibration using reference standards or reference materials
- Comparison of results achieved with other methods
- By participating in Interlaboratory comparisons
- Systematic assessment of the factors influencing the result
- Assessment of the uncertainty of the results based on scientific understanding of the theoretical principles of the method and practical experience

## ❖ Uncertainty of measurement

A Testing laboratory or a Calibration laboratory has to apply a procedure to estimate the uncertainty of measurement for each test.

# Reference Standards and Reference Materials(RM)

- **RM** is a generic term
- **Definition**: Material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process
- properties can be quantitative, e.g. identity of substances or species.
- Uses may include the calibration of measurement system, assessment of a measurement procedure, assigning values to other materials , and quality control.
- A single RM cannot be used for both calibration and validation of results in the same measurement procedure.

**Certified Reference Material(CRM**) –Reference material characterized by a metro logically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

N.B.Intermediate checks, transport and storage of the RM should also be taken care of

## ❖ Reporting of results

- ISO 17025 gives a specific format for Test Report(clause 5.10.2 of IS/ISO/IEC 17025)
- In addition, the followings should be mentioned
  - deviations from, additions to or exclusions from the test method and information on specific test condition such as environmental conditions.
  - a statement of compliance/non-compliance with requirement or specification
  - a statement on the estimated uncertainty of measurement, if applicable
  - opinions and interpretations, if needed
  - details on sampling

## ❖ Opinions and Interpretations

- This standard offers the scope of giving opinions and interpretations based on test results

## ❖ Amendments of test report/calibration certificate

- Further document should be issued which should include the following:
  "Supplement to test report/Calibration Certificate, serial no. or any other identification no"

# LATEST TERMINOLOGIES AND TRENDS IN CALIBRATION

- **Nominal Value:-** A target value intended as the general value to be measured
- **True Value:-** A value measured without any errors.
- **OFFSET:-** The difference between the Nominal value and the true value which can be corrected for "It is what we want to measure".
- **ERROR:-** The difference between the true value and measured value.

# LATEST TERMINOLOGIES AND TRENDS IN CALIBRATION

**. . . . contd**

- **UNCERTAINITY:-**

  An estimate of the range of values which contains the true values of a measured quantity. It is usually reported of probability that the true value lies within a stated range of values.

  Errors also can never be known exactly only estimated.

  Error is not the same as uncertainty

- It is an additional factor applied to the measured value to allow for the Presence of measurement error.

  Measurement = Measured value +/- M. Uncertainty

## Basic requirements of a Calibration Lab

- Instruments(Standards)
- Personnel
- Documentation

# ADVANTAGES OF CALIBRATION

1. Insures that all tools & test standards properly agree

2. Verifies compatibility of parts, systems & assemblies

3. Obtain peak performance of all systems in use

4. Insures that everyone in the company stays working to the same standard

**contd . . .**

5. Ensures performance after recalibration

6. Avoids damage during performance checking because of improperly calibrated or functioning instruments

# STANDARDS

Standards means physical realization of various units of measurements

Standards in terms of hierarchy

- **International Standards**
- **Primary National Standards**
- **secondary Standards**
- **Working Standards or Industrial Standards**

**International Standards** are constructed as per specification of an International agreement. They represent the units of measurements of various physical quantities of the highest possible accuracy.

**Primary National Standards** represent the fundamental and derived quantities and are calibrated by absolute measurements. These are maintained normally by the National Laboratories, e.g., Standard for Temperature using “Freezing Point of Pure Metal”

***secondary Standards*** includes devices which carries down the SI units from the primary local standards. It is normally used to either calibrate or enhance the performance of calibrator.

**Some more types of standards which are also used are**

***Consensus Standards*** which can be an artifact or a process that is mutually acceptable to supplier/customer, having no national standard. Example: Particle contamination

***Indirectly Derived standards*** which are inferred by measuring other quantities. example: Direct Current even as one of the SI units, not directly traceable to national standards. Current is standardized through measurement of voltage developed according to Ohms Laws.

# ERRORS IN MEASUREMENT

***Types of error***

Gross error

Random error

Systematic  error

# ERRORS IN MEASUREMENT

**Contd. . .**

**Gross errors**

Are strictly under the control of individual (independent of instrumentation)

Examples-

- Misreading of instrument
- Making incorrect adjustments
- Improper application of instruments
- Recording interpolated data

Can be avoided by-

- Care and attention
- Close supervision
- More systematic training

# ERRORS IN MEASUREMENT

**contd…**

**Random errors**

- A scatter about an average when a multiple no. of measurements are taken
- As a result of:
  - Variations in measuring system
  - Changes in quality being measured
- Detectable when:
  - Repeated measurements are taken with a seemingly constant set-up and consistent technique

# Internal Standard

Some tests (e.g., ICP-MS) make routine use of internal standards.

For each specific analysis, the limits on the recovery of the internal standards are determined by the lab.

# Matrix Spike and Duplicate Spike

Spike – add a known amount of analyte to a separate aliquot of sample from the same sample container and take it through the entire prep and analysis procedure.

Analyze a matrix spike/duplicate pair for every 10 samples, with a minimum of one for each batch from a survey.

Two matrix spikes are evaluated separately as matrix spikes, and the pair is evaluated as above for a sample/duplicate pair.

The matrix spike/duplicate pair should be evaluated together for evidence of sample homogeneity problems.

Matrix spike duplicates may be used in place of sample duplicates.

# Analytical Spike

Some tests (e.g., GFAA) make routine use of analytical spikes.

The limits on the recovery of the analytical spikes is determined by the lab.

Indicates bias of results.

# Laboratory Control Sample (LCS)

- An LCS is a sample of known concentration for the analyte of interest.
- Made from a standard from a source independent of the calibration standard source (referred to as “second source”)
- Prepared and analyzed with the samples.
- Limits on recovery are determined by the lab.
- The LCS may be the only independent check of the standards used to prepare the calibration curve.

# Instrument Performance Check

Some methods (ICP, ICP-MS) have instrument performance checks periodically performed to confirm the instrument is operating properly before analysis.

- Spectral Position Optimization
- Interference Check Samples:
- ICP-MS Tuning:
- Short-Term Stability Check

# Which QC to use?

## Your QC Tools:

1. Field Blank
2. Field Dup
3. Lab Blank
4. Lab Dup
5. LCS
6. Matrix Spike
7. Matrix Spike Dup
8. Spike Blank
9. Calibration Check Blank (initial and continuing)
10. Calibration Check Standard (initial and continuing)
11. Special QC

# QC for Titration

- Field Blank
- Field Dup
- Lab Blank
- Lab Dup
- LCS
- Matrix Spike
- Matrix Spike Dup
- Spike Blank

# QC for a simple analysis e.g. Colour

1. Field Blank
2. Field Dup
3. Lab Blank
4. Lab Dup

# QC for Instrumental Analysis

- Field Blank
- Field Dup
- Lab Blank
- Lab Dup
- LCS
- Matrix Spike
- Matrix Spike Dup
- Spike Blank
- Calibration Check Blank (initial and continuing)
- Calibration Check Standard (initial and continuing)

# QC for ICP

- Field Blank
- Field Dup
- Lab Blank
- Lab Dup
- LCS
- Matrix Spike
- Matrix Spike Dup
- Spike Blank
- Calibration Check Blank (initial and continuing)
- Calibration Check Standard (initial and continuing)
- Inter-Element Correction Factor Check
- Reporting Limit Check
- Spectral Optimization Check

# USEPA Websites for QA/QC

- Agency-wide Quality System Documents (EPA Order; QMPs: QA/R-2; QAPPs: QA/R-5, QA/G-5, QA/G-5G, QA/G-5S, QA/G-5M)
- http://www.epa.gov/quality/qa_docs.html

- Training courses on QA/QC activities
- http://www.epa.gov/quality/trcourse.html

- Quality Management Tools – QAPP (FAQs, checklist, and all QA/R & G documents)
- http://www.epa.gov/quality/qapps.html

- Doing Business with EPA:  Quality Specifications for non-EPA Organizations
- http://www.epa.gov/quality/exmural.html

# Thanking you