Analytical Quality Control in Water Quality Monitoring

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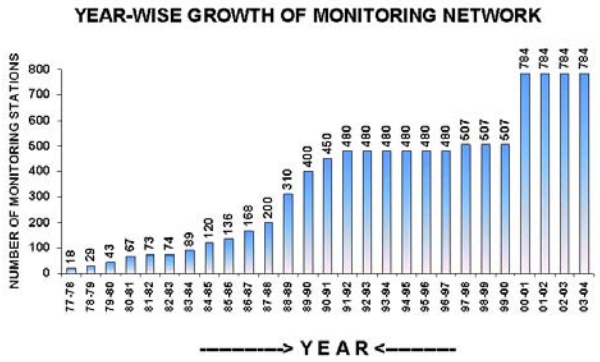
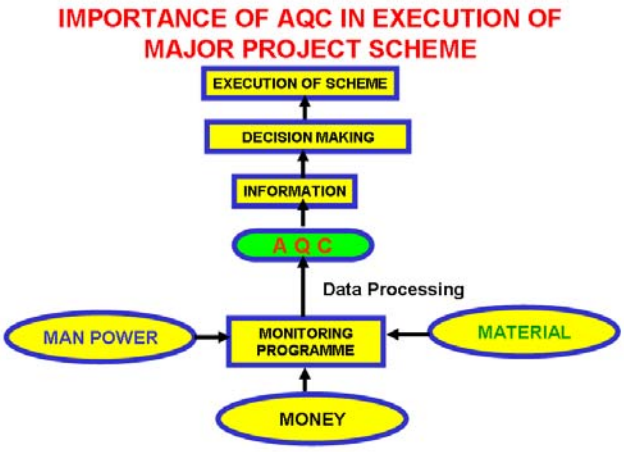
MONITORING ?
5 – Ws :

Why ?	…..	**Objective**
Where ?	…..	**Siting**
Which ?	…..	**Parameters**
When ?	…..	**Frequency**
Who ?	…..	**Agency**

HOW ?



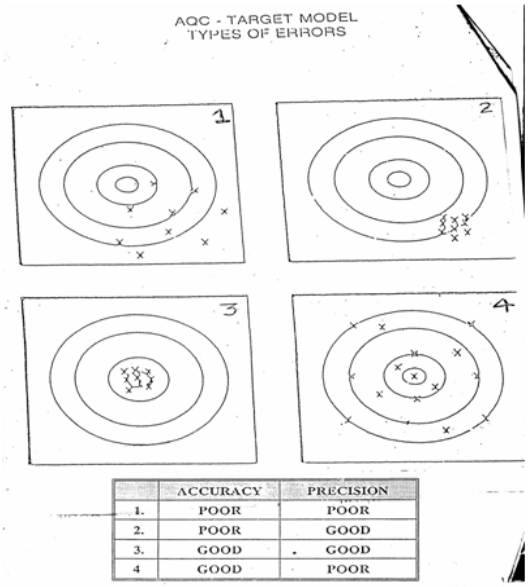


QUALITY ASSURANCE (QA)

Quality assurance is a set of operating principles that, if strictly followed during sample collection, sample pretreatment and analysis, will produce data of known and defensible quality and hence the accuracy of the analytical results can be stated with a high level of confidence.

DEFINITION OF QA TERMS

- Accuracy:
  - reflects the closeness of a measured value to the true value, combination of bias and precision of an analytical method
- Precision:
  - Value of degree of agreement among replicate analyses of a sample, also expressed as STANDARD DEVIATION
- Confidence Interval:
  - Set of possible values within the true value will lie with a specified level of probability



	ACCURACY	PRECISION
1.	POOR	POOR
2.	POOR	GOOD
3.	GOOD	GOOD
4	GOOD	POOR

QUALITY ASSURANCE PLANNING

Establish a set of operating principles that will constitute a quality-assurance program. QA plan should include:

1. **Staff organization and responsibilities.**
2. **Sample control and documentation procedures**
3. **Standard operating procedures (SOP's) for each analytical method**
4. **Analyst training requirements**
5. **Equipment/instrument preventive maintenance procedures**
6. **Calibration procedures**
7. **Internal audits and corrective actions**
8. **Internal quality control activities**
9. **Performance Audits**
10. **Data assessment procedures for bias and precision**
11. **Data validations and reporting**

What Is Proficiency Testing?

Proficiency testing is a means of assessing the ability of laboratories to competently perform specific tests and/or measurements. It therefore supplements laboratories' own internal quality control procedures by providing an additional external audit of their testing capability.

Good performance in proficiency programs provides independent evidence and hence reassurance to the laboratory and its clients that procedures, methods and other laboratory operations are under control. Proficiency testing also provides laboratories with a sound basis for continuous improvement.

Quality control and quality assessment are two important elements of quality assurance. Quality control (QC) may be either internal or external. External Quality Control is also known as "Quality Assessment". All analysts use some QC as an initiative effort to produce credible results. However, a good quality control program consists of atleast following seven elements:

1) **Certification of operators competence**
   Before an analyst is permitted to do the analytical work, his competence need to be demonstrated. To check precision and bias analyse minimum four replicates of a known sample having concentration between 5 and 50 times of method detection limit (MDL).

2) **Recovery of known additions:**
   Use the recovery of known additions as a part of a regular analytical protocol for about 10% of the samples. This ensures the absence of matrix interferences/effects. Make the known addition between 5 and 50 times the MDL or between 1 and 10 times the ambient level, whichever is greater. Use concentrated solutions so that volume change is negligible.

3) **Analysis of externally supplied standards:**
   Whenever, known additions does not result in acceptable recovery or atleast once each day, which ever is more frequent, use externally obtained standards. National Institute of Standards and Technology (NIST), USA, standard reference materials are preferred, if available. If internal reference materials are used, prepare them independently from the standards used for calibration.

4) **Analysis of Reagent Blanks:**
   Analyze reagent blanks with every batch of samples or whenever new reagents are used (about 5 % of sample load). This monitors purity of reagents and overall procedural blank.

5) **Calibration with Standards:**
   Use atleast three (preferably five) different dilutions of the standards before initiating the analysis. Subsequently, verify the standard curve daily with one standard.

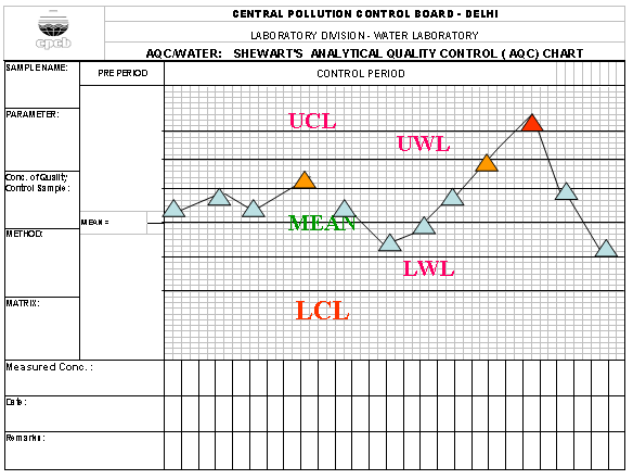
6) **Analysis of Duplicates:**
   For assessing precision, analyze about 5% of samples in duplicate.

7) **Control Charts:**
   The charts are essential instrument for quality control. Three type of control charts are commonly used:

   a. A means chart for standards

   b. A means chart for reagent blank/ background results

   c. A range chart for replicate analysis



QUALITY ASSESSMENT

Quality Assessment is the process of using external and internal quality control measures to determine the quality of data produced by the laboratory. It includes such items as performance evolution samples, laboratory inter-comparison samples, and performance audits as well as the internal QC. They are applied to test the recovery, bias, precision, detection limit, and adherence of standard operating procedure requirements.

CALIBRATION

- Basis for all measurements
- Comparison of a known with an unknown
- All methods require some form of calibration
- Calibration can be the main source of discrepancy between laboratories.
- Eliminates or reduces bias
- Provides reference system to make measurements comparable over time

CALIBRATION FREQUENCY

Depends on:

1. Type of instrument/Device
2. Factors affecting calibration
3. Accuracy requirements
4. Analyst Experience
5. Manufacturers recommendations
6. Costs

COMMON SOURCES OF ERRORS IN ANALYSIS

Types of Errors

- Systematic Error (Bias)
- Random Error (Precision)
- Blunders (Gross mistakes)

BLUNDERS

- Improper sample Labeling
- Calculation Errors
- Data reporting Errors (unit etc.)
- Sample mishandling
- Laboratory contamination
- Making changes in method without validation
- Improper calibration of Instruments.

BASIC NEEDS FOR CONDUCTING WITHIN-LABORATORIES AQC

In order to assure good and reliable water laboratory results, the following is required:

1. **Suitable Laboratory facilities**
2. **Up-to-date Laboratory Instruments, Sampling Equipment, Glassware, and Reagents;**
3. **Standardized analytical procedures covering the desired variables and ranges CG Concentration;**
4. **A well trained laboratory staff;**
5. **Well-maintained equipment and facilities**
6. **Adequate filing and reporting systems; and**
7. **A systematic Analytical Quality Control Programme.**

SUMMARY OF WITHIN-LABORATORY AQC PROGRAMME

a) Five Standards to develop a calibration curve in concentrations covering the working range, as necessary or measurement or two calibration standards to verify the existing calibration curve.

b) One method blank per run.

c) One duplicate for precision check (at least one every 20 routine samples.

d) One standard sample for recovery and calibration check (at least one every 20 routines samples). A standard should be the last sample analyzed, in each run.

e) One spiked sample for recovery check in the presence of a sample matrix (at least one every 20 routine samples).

f) Total: Seven to Ten AQC analyses may be required for runs of up to 20 routine samples, 10 to 13 AQC analyses may be required for run of 21 to 40 routine samples, etc.

g) Items (a) to (e) should be the standard practice in any laboratory.

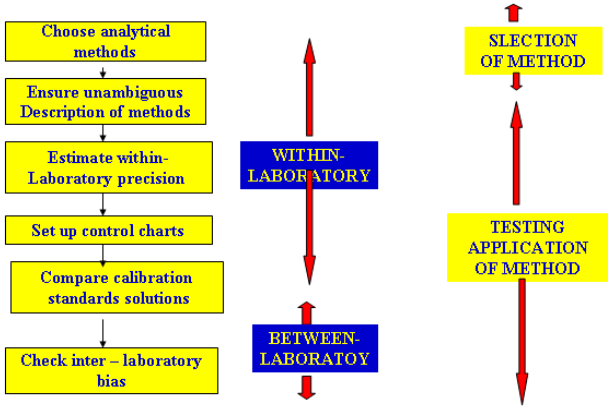
REASONS FOR NOT IMPLEMENTING AQC PROGRAMMES

Within-Laboratory, Quality Control is the most important component of any laboratory quality control programme. Experience indicates that 10-20% of the Resources (manpower, instrument utilization and consumables) of a Laboratory should be devoted to this work (20% for heavy metals, pesticides etc. and 10% for other parameters).

Various reasons for which generally AQC Programme is not implemented are:

1. Programme consumes too much time/resources I.e. 10-20%
2. Lack of information to start AQC Programme I.e. Technical description, manuals, guidelines etc, are not available to the laboratory.
3. Lack of knowledge of statistical procedures required for AQC Programme
4. Lack of understanding of the problem or lack of motivation to solve the problem.

FLOW CHART FOR APPROACH TO ACHIEVING ACCURACY OF ANA LYTICAL RESULT



Quality assurance and quality control
(Units of Operation)

- Siting of sampling location
- Sampling
- Transportation and Chain of Custody(COC)
- Sample storage
- Choice of methods
- Analysis
- Reporting
- Interpretation

22

A. QUALITY OF CHEMICALS

I. Use required quality of chemicals like A.R./G.R., L.R. etc depending upon the role of that chemical in determination

II. Keep records of chemical receiving, opening shelf life etc.

III. Label reagents properly with details like concentration, parameter for which to be used, date of preparation, shelf life etc.

B. GLASS Ware WASHING

A common source of error is contamination from improper glassware washing/ rinsing. Such errors often produce erratic results or excessive variability among analysis of method blanks.

Maintain separate sets of glassware and sample bottles for different types of analysis and type of samples fresh waters and wastewater.

24

C. INSTRUMENT/Spectrophotometer

i. Check wavelength

ii. Cuvette should not have any scratches

iii. Hold cuvette from the top only

iv. Keep cuvette always in the fixed position

v. Check zero with reagent blank in the beginning, end and intermittently (if doubts arise)

vi. Plot absorbance vs. concentration (on ordinary graph paper A = 2 -% transmission)

D. DISTILLED WATER

Purity depending upon use selection of still storage tank and any associated piping needs careful selection to ensure minimum contamination. Generally distilled water with conductivity 0.2 MSM^{-1} (2 µMHOS/CM) or less is acceptable for routine work

E ELECTRICITY SUPPLY & ELECTRICAL SERVICES

Provisions should be made for continuous supply, proper constant voltage, adequate load, etc., some instruments like spectrophotometer, flame photometer, AAS, GC, etc. require constant voltage to maintain stability and drift-free instrument operation. For such instruments voltage regulation can be achieved through stabilized and UPS system.

27

F. WEIGHING BALANCE

The most important instrument in any analytical laboratory is the analytical balance. The degree of accuracy of the balance is reflected in the accuracy of all data related to weight-prepared standards and gravimetric determinations. The balance should therefore be the most protected and cared instrument in the laboratory.

Each type of balance has its own place in the scheme of laboratory operation. But analytical single plan balance plays the most important role in the production of reliable data. The analytical balance should be mounted on a heavy shock proof table located away from the other equipments, in a dust free zone. Normally analytical balance with an accuracy and readability of 0.01 mg and weighting capacity upto 200 g is suitable for analytical laboratories.

28

AQC/ water PT programme conducted by CPCB

for the Laboratories of SPCB/PCCs and the laboratories recognized under E.P. Act, 1986

Proficiency Testing project completed/proposed by CPCB laboratory division

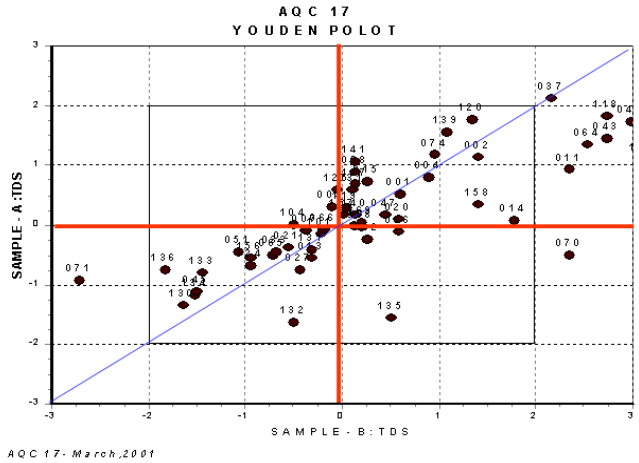
1. CPCB is conducting the AQC exercise for about 150 laboratories of SPCB, PCCs, and laboratories recognized under E.P.Act on routine basis covering 21 parameters.
2. 7 laboratories under GAP – NRCD Project during 1995-96 (Two rounds)
3. 42 laboratories under Hydrology Project during the year 1999 and 2001 (Two rounds)
4. DST – NABL sponsored a proficiency testing programme for 62 laboratories accreditated by NABL during the year 2005

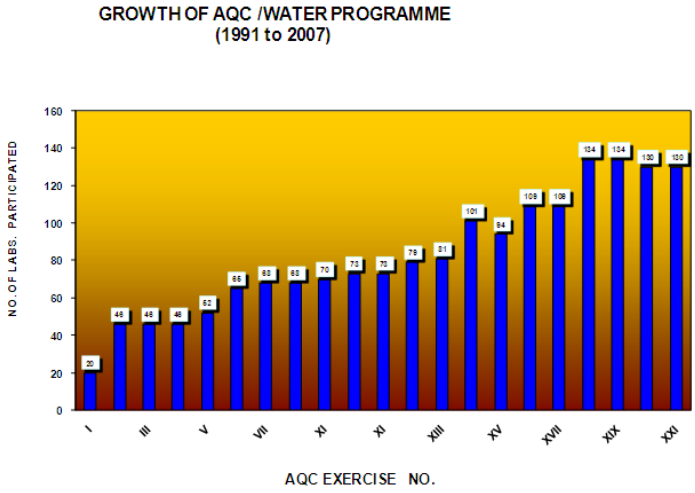
METHODOLOGY

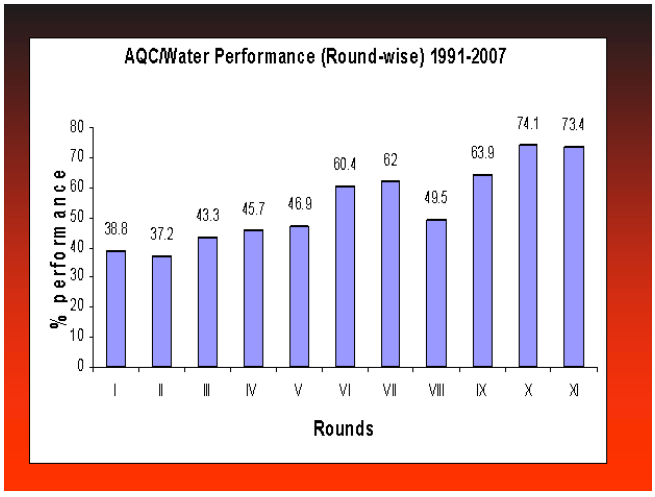
Two synthetic samples labelled as A & B of each 1 litre volume prepared in laboratory by adopting standard procedures and precautions are distributed to all participating laboratories by Courier service to avoid any transport delay. Samples were also analysed in CPCB laboratory for arriving at "Reference value" for comparison and to estimate the acceptable limits of the reported values. The acceptable limit was arrived using "Youden 2 Sample Plot" method.

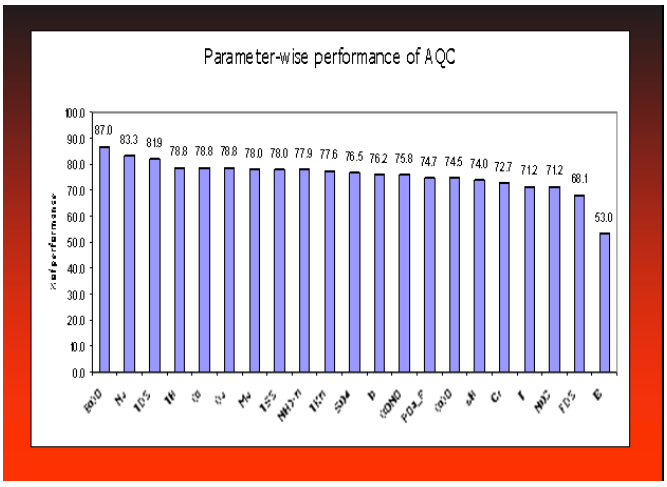
LIST OF PARAMETERS COVERED UNDER AQC / WATER PROGRAMME BY CPCB- Delhi

S. No.	Parameter	S. No.	Parameter
01.	Conductivity	16.	Chemical Oxygen Demand
02.	Total Dissolved Solids	17.	Biochemical Oxygen Demand
03.	Fixed Dissolved Solids	18.	Boron
04.	Total Hardness	19.	Chromium
05.	Calcium	20.	Total Suspended Solid
06.	Magnesium	21.	Aluminium
07.	Sodium	22.	Arsenic
08.	Potassium	23.	Cadmium
09.	Chloride	24.	Chromium
10.	Fluoride	25.	Copper
11.	Sulphate	26.	Iron
12.	Nitrate-N	27.	Lead
13.	Ammonical-N	28.	Mercury
14.	Total Kjeldahl Nitrogen	29.	Nickel
15.	Phosphate-P	30.	Zinc


AQC 17
YOUDEN POLOT
SAMPLE - A :TDS
SAMPLE - B : TDS
AQC 17 - March,2001


GROWTH OF AQC /WATER PROGRAMME
(1991 to 2007)
NO. OF LABS. PARTICIPATED
AQC EXERCISE NO.


AQC/Water Performance (Round-wise) 1991-2007
% performance
Rounds


Parameter-wise performance of AQC

PT PROGRAMME FOR SOIL & SOLID WASTE

- CPCB has started PT Programme for Soil & Solid waste samples in 2002 for the laboratories of SPCBs, PCCs.

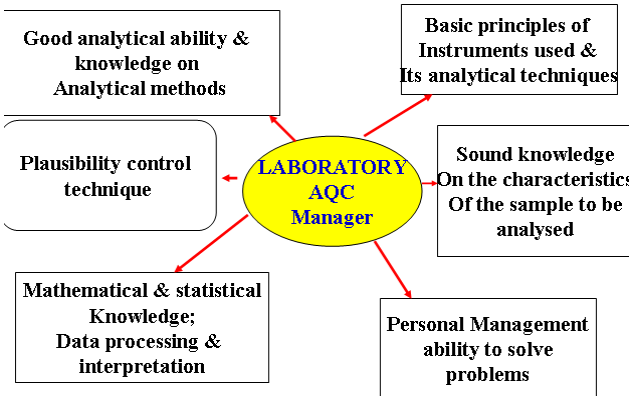
- Parameters covered under this programme are pH, Conductivity, Total Water Soluble Solids, LOI, Organic Carbon, TKN, PO_4, K, Heavy Metals, TCLP Extracts followed by physico chemical analysis etc.

Recommendations for AQC Scheme

The overall findings of the performance of AQC exercises reveal the fact that Internal AQC system in all the laboratory is to be strengthened. The analytical capability of these laboratories could be improved by adopting the following major steps.

- Strengthening of the Internal AQC System
- Periodic calibration of instruments
- Using high quality chemicals and providing adequate quantity of glassware
- Providing good quality distilled water
- Improving the laboratory work atmosphere
- Providing analytical training to laboratory analysts.
- Conducting Regional Workshop at various regions
- Adopting good quality assurance system
- Participating in Inter-laboratory AQC exercises by all laboratories of Pollution Control Boards and Committees.

QUALITY REQUIREMENT OF A LABORATORY AQC MANAGER



BEST QUALITY ASSURANCE SYSTEM