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## 1 Quality Assurance

### 1.1 Need for quality Assurance

Many studies have shown that analytical results are often subject to serious errors, particularly at the low concentrations encountered in water analysis. In fact, the errors may be so large that the validity of actions taken regarding management of water quality may become questionable.

Nutrients, N and P, in very small concentrations can cause eutrophication of waterbodies. An analytical quality control exercise (AQC) exercise conducted by United States Environmental Protection Agency (US-EPA) showed a wide variation in results when identical samples were analysed in 22 laboratories:

Nutrient	Concentration, mg/L	Range of results, mg/L
Ammonia	0.26	0.09 - 0.39
	1.71	1.44 - 2.46
Nitrate	0.19	0.08 - 0.41
Total phosphorus	0.882	0.642 - 1.407

It is seen that the range of values reported are significantly large,  $\pm 50\%$  for ammonia and  $\pm 100\%$  for nitrates, compared to the actual concentrations. Therefore, the need for nutrient control programme and its results become difficult to assess.

Many laboratories under Hydrology Project (HP) report total dissolved salts (TDS) calculated from the electrical conductivity (EC) value:

$$\text{TDS, mg/L} = A \times \text{EC, } \mu\text{S/cm}$$

where A is a constant ranging between 0.55 and 0.9 depending on the ionic composition of salts dissolved in the water.

An inter-laboratory AQC exercise conducted by Central Pollution Control Board (CPCB) showed that for measurement of EC of a standard solution, out of 44 participating laboratories only 34% reported values in the acceptable range. See Figure 1.

Thus, the reliability of iso-concentrations of TDS in groundwaters, drawn based on data of several laboratories may become questionable on two counts; use of an arbitrary value for the constant A and variation in inter-laboratory measurements.

These examples amply demonstrate the need for quality assurance (QA) programmes.

## 1.2 Quality assurance programme

The QA programme for a laboratory or a group of laboratories should contain a set of operating principles, written down and agreed upon by the organisation, delineating specific functions and responsibilities of each person involved and the chain of command. The following sections describe various aspects of the plan.

**Sample control and documentation:** Procedures regarding sample collection, labelling, preservation, transport, preparation of its derivatives, where required, and the chain-of-custody.

**Standard analytical procedures:** Procedures giving detailed analytical method for the analysis of each parameter giving results of acceptable accuracy.

**Analyst qualifications:** Qualifications and training requirements of the analysts must be specified. The number of repetitive analyses required to obtain result of acceptable accuracy also depends on the experience of the analyst.

**Equipment maintenance:** For each instrument, a strict preventive maintenance programme should be followed. It will reduce instrument malfunctions, maintain calibration and reduce downtime. Corrective actions to be taken in case of malfunctions should be specified.

**Calibration procedures:** In analyses where an instrument has to be calibrated, the procedure for preparing a standard curve must be specified, e.g., the minimum number of different dilutions of a standard to be used, method detection limit (MDL), range of calibration, verification of the standard curve during routine analyses, etc.

**Analytical quality control:** This includes both *within-laboratory* AQC and *inter-laboratory* AQC.

Under the within-laboratory programme studies may include: recovery of known additions to evaluate matrix effect and suitability of analytical method; analysis of reagent blanks to monitor purity of chemicals and reagent water; analysis of sample blanks to evaluate sample preservation, storage and transportation; analysis of duplicates to assess method precision; and analysis of individual samples or sets of samples (to obtain mean values) from same control standard to check random error.

Inter-laboratory programmes are designed to evaluate laboratory bias.

It may be added that for various determinands all of the AQC actions listed may not be necessary. Further, these are not one time exercises but rather internal mechanisms for checking performance and protecting laboratory work from errors that may creep in. Laboratories who accept these control checks will find that it results in only about 5 percent extra work.

**AQC is:**

- an internal mechanism for checking your own performance
- protecting yourself from a dozen of errors that may creep into analytical work
- to avoid human errors in routine work
- practised by responsible chemists
- not useless work
- common practice in certified laboratories

**AQC is NOT:**

- much work
- to be carried out for each and every routine sample
- consultants checking and reporting the quality of your work
- a one time exercise to be forgotten soon

**Data reduction, validation and reporting:** Data obtained from analytical procedures, where required, must be corrected for sample size, extraction efficiency, instrument efficiency, and background value. The correction factors as well as validation procedures should be specified. Results should be reported in standard units. A prescribed method should be used for reporting results below MDL.

An important aspect of reporting the results is use of correct number of significant figures. In order to decide the number of significant digits the uncertainty associated with the reading(s) in the procedure should be known. Knowledge of standard deviation will help in rounding off the figures that are not significant. Procedures regarding rounding off must be followed.

### **1.3 Definitions and basic statistics**

**Bias:** Bias is a measure of systematic error. It has two components, one due to method and the other due to laboratory use of method.

**Precision:** Precision is a measure of closeness with which multiple analyses of a given sample agree with each other.

**Random error:** Multiple analyses of a given sample give results that are scattered around some value. This scatter is attributed to random error.

**Accuracy:** Combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to the true value.

**Frequency distribution:** Relation between the values of results of repetitive analyses of a sample and the number of times (frequency) that a particular value occurs.

**Mean:** Mean is the central value of results of a set of repetitive analyses of a sample. It is calculated by summing the individual observations and dividing it by the total number of observations.

**Normal distribution:** Normal distribution is a frequency distribution, which is symmetrical around the mean. In a normal distribution 95.5% and 99.7% of the

observations lie in  $\pm$  two times standard deviation and  $\pm$ three times standard deviation range around the mean, respectively. See also Figure 2.

**Standard deviation:** Standard deviation is a measure of spread of results of repetitive analyses of a sample around its mean value. It is a measure of precision of the analytical method. It is calculated by taking square root of sum of squares of deviation of the observations from the mean divided by the number of observations minus one.

**Coefficient of variation:** Comparison of standard deviation values for results of repetitive analysis, of two samples having different concentration of the determinand, may sometimes give wrong conclusion regarding precision of the measurement. Coefficient of variation (CV), which is calculated as  $CV = \text{standard deviation}/\text{mean} \times 100$ , is a better parameter for such comparison. For example, for results of two sets of analyses, performed on two different samples, if the mean values are 160 and 10 mg/L and standard deviations are 8 and 1.5 mg/L, respectively, comparison of standard deviation would indicate lower precision for the first set of observations (standard deviation 8 mg/L), while the CV values work out to be 5 ( $8/160 \times 100$ ) and 15 ( $1.5/10 \times 100$ ) percents respectively. Indicating a better precision for the second set of observations.

#### **1.4 Interpretations of Shewhart control charts**

If a set of analytical results is obtained for a control sample under conditions of routine analysis, some variation of the observed values will be evident. The information is said to be statistically uniform and the analytical procedure is said to be under statistical control if this variation arises solely from random variability. The function of a control chart is to identify any deviation from the state of statistical control.

Shewhart control chart is most widely used form of control charts. In its simplest form, results of individual measurements made on a control sample are plotted on a chart in a time series. The control sample is analysed in the same way as the routine samples at fixed time intervals, once or twice every week, or after 20 to 50 routine samples.

Assuming the results for the control sample follow the Normal frequency distribution, it would be expected that only 0.3% of results would fall outside lines drawn at 3 standard deviations above and below the mean value called upper and lower control limits, UCL and LCL, respectively. Individual results would be expected to fall outside these limit so seldom (3 out of 1000 results), that such an event would justify the assumption that the analytical procedure was no longer in statistical control, i.e., a real change in accuracy has occurred.

Two lines are inserted on the chart at 2 standard deviations above and below the mean value called upper and lower warning limits, UWL and LWL, respectively. If the method is under control, approximately 4.5% of results may be expected to fall outside these lines. This type of chart provides a check on both random and systematic error gauged from the spread of results and their displacement, respectively

Standard Methods lists the following actions that may be taken based on analysis results in comparison to the standard deviation.

**Control limit:** If one measurement exceeds the limits, repeat the analysis immediately. If the repeat is within the UCL and LCL, continue analyses; if it exceeds the action limits again, discontinue analyses and correct the problem.

**Warning limit:** If two out of three successive points exceeds the limits, analyse another sample. If the next point is within the UWL and LWL, continue analyses; if the next point exceeds the warning limits, discontinue analyses and correct the problem.

**Standard deviation:** If four out of five successive points exceed one standard deviation, or are in increasing or decreasing order, analyse another sample. If the next point is less than one standard deviation away from the mean, or changes the order, continue analyses; otherwise discontinue analyses and correct the problem.

**Central line:** If six successive points are on one side of the mean line, analyse another sample. If the next point changes the side continue the analyses; otherwise discontinue analyses and correct the problem.

Figure 3 to Figure 7 illustrate the cases of loss of statistical control for analysis of individual samples based on the above criteria.

## 2 Report on within-laboratory AQC exercise

### 2.1 Response/reasons

Out of 30 laboratories nominated for the exercise 21 responded, an overall degree of participation of exactly 70%. The degree of participation for state organisations is somewhat higher:

type of lab	degree of participation
CWC	5 out of 8 nominated (60%)
CGWB	4 out of 7 nominated (57%)
state laboratories	12 out of 15 nominated (80%)

None of the laboratories in Orissa of either state or central agencies responded. In terms of requested parameters (30 laboratories times 4 parameters =120) the actual response of 61 reported parameters is only slightly higher than 50%. This is mainly due to lack of functioning spectrophotometer for NO<sub>2</sub> analysis. The central organisations' response was better with respect to NO<sub>2</sub><sup>-</sup>. Some laboratories spontaneously analysed NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> or Cl<sup>-</sup> instead.

Our biggest concern is the response time. Only one laboratory was able to respond within the timeframe envisaged by the consultants (2 months after receiving the AQC booklet). Most laboratories needed a lot of pushing and persuasion before the work started.

We can think of the following reasons for this below 100% performance:

1. the topic was new and not yet appreciated
2. the topic was misunderstood and too much work was envisaged
3. the topic was found difficult by some, -e.g. in terms of statistics involved
4. the necessary equipment for the tests was not functioning properly or missing, such as balance
5. the necessary chemicals for the tests were not readily or at all available
6. the workload of some laboratories was too high
7. there were two evident errors in the booklet provided (in the NO<sub>2</sub><sup>-</sup> analytical method)

### 2.2 Discussion of results

The most important parameter to evaluate in the results is the precision. The statistical term to evaluate precision is standard deviation. The numerical value of the standard deviation depends on the average concentration (standard deviation also has the unit of concentration). Numerical values of standard deviations of low concentration solutions are usually smaller than those of solutions with higher concentrations. The precision of measurement for low concentration solutions is generally lower and therefore the numerical value of standard deviation is not a universal measure for precision. Therefore the coefficient of variation or normalised standard deviation (CV = standard deviation/mean x 100) will be used to evaluate precision. This is particularly useful when comparing results of analysis for samples having different concentrations.

Before evaluating the results one should answer the question 'what is the desired precision for an analyses?'. In fact this question should be answered by the so called 'data users'. The use of the data determines the required precision, e.g. detection of trends may require more precise results (in order to actually detect small changes in the cause of time) than checking water for use (a rough comparison with a standard). Laboratory staff should always ask for the purpose for which they are performing the requested test.

As a minimum goal for precision, however, the precision that can be obtained by correctly and adequately following the method prescribed by the APHA Standard Methods for the examination of water and wastewater may be adopted (see Table 1).

**Table 1** Coefficient of variation for Total Solids, Total Hardness and Electrical Conductivity from three sources: Standard Methods (1995), Central Pollution Control Board New Delhi (1992-1997) and US-Environmental Protection Agency (around 1980). The underlined numbers are the proposed precision goals.

Reference	TS		EC		TH	
	average mg/L	cv %	average umho/cm	cv %	average mg/L	cv %
<b>Standard Methods</b>	15	33	-	1 to <u>2</u>	610	<u>2.9</u>
	242	10				
	1707	0.76				
	293	<u>7.2</u>				
<b>EPA</b>	58.1	23.1	119	14.6	299	0.9
	298	7.4		10.4	300	2.2
<b>CPCB</b>	68.3	6.9	171	2.3	47.17	8.4
	145.4	5.3	214	2.5	61.43	4.3
	152	8.5	231	1.9	65.25	6.2
	171.8	5.7	256	2.6	75.25	4.5
	238.1	3.0	294	1.8	84.08	6.3
	244.9	5.4	305	2.0	84.71	3.9
	249.7	3.6	401	2.6	111.92	2.9
	472.3	2.8	478	1.5	135.00	3.7

Results of the first round of the within-laboratory AQC exercise are shown in shown in Table 2 and Figure 8 to Figure 10. The 'goal' CV values from Table 1 are represented in the figures by arrows indicating the range.

**Table 2** Results from the laboratories that participated in the first round within laboratory AQC.

Lab Id	TS			EC			TH			NO2		
	avg	sd	cv	avg	sd	cv	avg	sd	cv	avg	sd	cv
1	146.1	7.7	5.3 ✓	256.4	8.7	3.4 ×	99.2	4.1	4.1 ×	0.417	0.018	4.3 ✓
2	149.37	4.8	3.2 ✓	283	5.39	1.9 ✓	99.4	5.2	5.2 ×			
3	157.4	3.19	2.0 ✓	325	5.2	1.6 ✓	10.03	0.035	0.3 ✓			
4	202.3	11.08	5.5 ✓	350.9	2.23	0.7 ✓	776.5	0.12	0.05 ✓			
5	147.7	1.4	1.0 ✓	115.6	1.6	1.4 ✓	100.24	0.9	0.9 ✓			
6	141.1	2.8	2.0 ✓	141.8	7.91	0.6 ✓	101.6	2.48	2.4 ✓			
7	142.7	2.66	1.9 ✓	280	4.4	1.6 ✓	98.15	5.1	5.2 ✓			
8	148.8	3.5	2.4 ✓	285	5.27	1.8 ✓	99.9	0.7	0.7 ✓			
9	148.8	3.5	2.4 ✓	285	5.27	1.8 ✓	99.9	0.7	0.7 ✓			
10	156.8	6.47	4.1 ✓	285	5.27	1.8 ✓	101.4	0.9	0.9 ✓			
11	146.1	7.7	5.3 ✓	256.4	8.7	3.4 ×	99.2	4.1	4.1 ×	0.002	1.6	✓
12	146.1	7.7	5.3 ✓	256.4	8.7	3.4 ×	99.2	4.1	4.1 ×	100	3.7	3.7 ✓
13	146.1	7.7	5.3 ✓	256.4	8.7	3.4 ×	99.2	4.1	4.1 ×	99.4	2.91	2.9 ✓
14	146.8	0.72	0.5 ✓	283.67	1.19	0.4 ✓	99.8	2.7	2.7 ✓	0.008	0.8	✓
15	136.0	10.5	7.7 ×	274.10	2	0.7 ✓	93.4	0.9	1.0 ✓	0.985	0.012	1.2 ✓
16	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
17	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
18	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
19	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
20	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
21	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
22	140.0	3.3	2.4 ✓	276.10	3	1.1 ✓	95	0.9	0.9 ✓			
<b>Results for EC</b>												
1	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
2	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
3	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
4	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
5	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
6	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
7	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
8	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
9	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
10	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
11	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
12	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
13	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
14	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
15	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
16	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
17	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
18	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
19	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
20	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
21	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
22	710	1.2	0.2 ✓	104.7	1.1	1.1 ✓						
<p>Except one lab all laboratories work within the precision goal set by Standard Methods (2.0%) Figure 9. This is a remarkable result because consultants feel that this is a stringent precision goal that is only achievable under ideal conditions. This feeling is supported by the 2 higher CV values reported by CCB and USEPA (2.4%) although the latter might be partly caused by old equipment.</p> <p>Especially for pictures that depend on instrument reading the precision will depend strongly upon the time between the successive readings (were all 20 readings taken in one hour or did it take several days?).</p> <p>Control solutions: TH=100mg/L, EC=200-250µmho/cm at 25C, TS=149mg/L and NO2=1.0mg/L.</p> <p>In inter-laboratory tests, EC is on of the parameters that shows a high bias.</p> <p>Bold numbers indicate a different solution was used (e.g. stock).</p>												

**Results for TH**

Only three laboratories reported cv values outside Standard Methods limits, Figure 10. The largest class (7 laboratories) reported 0-1% of precision. This precision seems to be very high compared to EPA, Standard Methods and CPCB. This high precision is not achievable when the method as prescribed is carried out by standard laboratory glassware. Three laboratories have used the standard CaCO<sub>3</sub> solution instead of the ten times diluted control sample resulting in 0.6% precision. For the other 4 laboratories no explanation can be given.

The expected precision of the TH determination according to the prescribed procedure is estimated in appendix A. The effect of the accuracy of the burette and the pipette gives an estimated cv of 1%. The largest contribution comes from the 2.5mL EDTA titration by

the burette. This calculation does not include the effect of all other sources of error mentioned and therefore the actual precision must be less and CV value higher than 1%.

### **2.3 Potential sources of error**

#### **Potential sources of error affecting precision of TS analysis**

- i. balance precision and calibration
- ii. handling of glassware/paper to avoid addition of weight from other sources
- iii. weighing while dish is still hot (air turbulence)
- iv. small amounts of solid dried results in accumulating errors due to differential method
- v. large amount of solids (water-trapping crust formation)
- vi. hygroscopic solids require prolonged drying
- vii. poor storage during cooling in desiccator
- viii. human errors

#### **Potential sources of error affecting precision of TH analysis**

- i. balance precision
- ii. standardisation of titrant on day of analysis using primary standard
- iii. reading of burette during titration: a sample volume between 5 and 20mL is optimal for a 50mL (0.1mL readability)
- iv. reagent blank correction (titration of distilled water)
- v. indicator in blank and standard should be of same quality
- vi. preparation of dilutions (volumetric flask)
- vii. determination of endpoint: colour change (light conditions, white background)
- viii. determination of endpoint: speed of adding the last drops
- ix. correct pH (buffer solution) during titration

#### **Potential sources of error affecting precision of EC measurement**

- i. calibration of the instrument
- ii. accuracy in preparation of the calibration solution (0.01M KCl)
- iii. quality of the de-mineralised water used for the calibration solution
- iv. measurement of the sample temperature and temperature correction
- v. condition of the conductivity cell
- vi. procedure (rinsing, temperature equilibrating, temperature correction etc.)

### **2.4 Interpretation of reported Shewhart control charts**

#### **Laboratories 2, 3, 6, 8, 10, 13, 14, 17, 18, 21 and 23**

The exercise was not carried out according to the instructions provided in the booklet. These laboratories performed the first 20 analysis on their control sample (analysis spread over a two week period) and used these data to calculate warning and action limits for the construction of the Shewhart control chart.

Unfortunately, they did not analyse another 10 or so analyses in the next say 10 days. Instead, the same 20 data that were used to calculate the warning and control limits were plotted in the chart. Per definition, exceeding the control limits is very rare in this

approach. Careful reading of instructions and appreciating the merits of the exercise is essential for the future.

*Therefore, the actual exercise for these laboratories is yet to start!*

### **Laboratory 20**

This laboratory has carried out 20 repetitive analysis on a sample from one of their regular monitoring sites (river water). We like to stress that this is not needed for any AQC exercise. Only control samples (artificial solutions prepared by the laboratory itself) should be analysed in a within laboratory AQC exercise.

Repeated analysis on a natural sample from the field is less suitable for evaluation of method precision because of potential disturbance of the sample with time.

### **Laboratory 7**

Commented that 10 times diluting the stock for EC (2826 umho/cm) will not exactly lead to a value of 283 as suggested in the AQC booklet.

If a solution is diluted, say ten times, the EC value of the diluted solution will be *higher* than the EC based on the dilution factor. In other words, the same ions contribute more to the EC in a diluted solution. At higher salt levels, the ionic strength causes screening. The effect is of practical importance. If a 0.02M yields 2765 umho/cm (standard methods) a 0.002M solution will be around 296 umho/cm at 25°C, about 10% higher than expectations based on dilution only.

It is however important to realise that for a *within laboratory* exercise this *bias* is not relevant since only precision is under investigation.

**Statistical control of analytical procedure**

Interpretation of the charts of all laboratories is summarised in Table 3.

**Table 3** Results of Shewhart control charts for all laboratories that participated in the within laboratory AQC

Lab	TS	EC	TH
1	√	T	√
2	T	√	√
3	A	A	A
4	√	√	√
5	√	A	A
6	A	T, A	√
7	T	T	√
8	√	√	T
9	T	-	T
10	T	√	√
11	√	C, A, W	√
12	√	T, W	√
13	√	T	√
14	√	√	√
15	√	C	A
16	√	√	√
17	√	√	√
18	√	T	√
19	-	√	√
20	-	A	√
21	-	-	-
22	-	√	√
23	-	-	-
Number of times out of control (all laboratories)	$\frac{6}{18} = 33\%$	$\frac{11}{20} = 55\%$	$\frac{5}{24} = 26\%$
Number of times failed more than one criterion	$\frac{0}{6} = 17\%$	$\frac{3}{11} = 27\%$	$\frac{0}{5} = 0\%$
√ = under statistical control C = 2 successive points out of Control (Action) Limit W = 3 out of 4 successive points out of Warning Limit S = 5 out of 6 successive points out of standard deviation limit T = 5 out of 6 successive points having the same trend A = 7 successive points on one side of the average - = parameter not reported or insufficient repetitions for statistical evaluation			

**Laboratory 10 – TS (Figure 11)**

The concentration of TS is decreasing in time and more than 5 points do show the same trend so the analysis is not under statistical control and the problem(s) should be corrected. High values of TS may indicate poor drying of the sample, e.g. caused by too low oven temperature (oven out during weekend and nights?) or too long stay of dried samples in poorly functioning desiccator etc.

**Laboratory 13 – TS**

This laboratory uses 50ml sample for drying. By weighing 50ml of the control solution (146mg/L), the amount of solid remaining after drying is only  $50/1000 \times 146 = 7.3\text{mg}$ . Standard Methods prescribes a minimum yield of 10mg!

With a good analytical balance, with an error of  $\pm 0.1\text{mg}$ , a relative error of 0.14% can be achieved in this case. In this laboratory the error of the analytical balance is much higher however (estimated at  $\pm 0.4$  to  $0.5\text{mg}$  based on the raw data provided by the laboratory, See also Appendix B). If the laboratory is aware of the performance of their balance and the propagation of errors during differential weighing methods, the relative error can be reduced by 50% by drying double the amount of sample volume.

Some laboratories are aware of the -poor- quality of their this because they vary the sample volume from 100ml up to 200ml (two successive portions of 100ml). Even then the result is not as precise as it should be:  $CV = 3.5\%$ . Probably the balance has an error of more than  $\pm 0.5\text{mg}$  in these cases.

**Laboratory 5 –TH (Figure 12)**

The distribution (all 10 below the average of 100.5 mg/L) suggests that the analysis is no longer under statistical control. The precision of the 10 data plotted in the chart is much higher than the precision of the first 20 analysis on which the warning and control limits of the Shewhart control chart are based (around 5%).

Since the precision for this analysis in this lab is the lowest among all participating laboratories it is likely that a systematic error is involved somewhere (change of analyst, solutions, indicator). The laboratory itself should investigate this prior to taking part in an inter-laboratory programme.

**Laboratory 15 – TH (Figure 13)**

The concentration of the control solution prepared by the laboratory (100 mg/L) is not found back in the average of the first 20 titrations (93.4 mg/L). The next 10 titrations tend to be all below this average (negative trend line). If a laboratory does not find back the concentration of a solution prepared in its own laboratory, the analysis is not carried out correctly! Most probably, the EDTA solution is not standardised against the Standard  $\text{CaCO}_3$  solution!

More than seven successive points are below the central line, the problem should be corrected.

**Laboratory 14 – TH (Figure 14)**

The chart shows a very symmetric pattern with only discrete variations of  $\pm 4\text{mg/L}$ . Four mg/L corresponds to a burette reading of  $\pm 0.1\text{mL}$ , whereas a reading precision  $\pm 0.05\text{mL}$  is achievable. Moreover, the 16 data plotted are also used for constructing the chart so the actual AQC exercise has yet to start in fact.

**Laboratories 4, 11 and 15 – EC (Figure 15)**

These laboratories have done 20 repetitive analyses for EC in a short time (on one day?) and find a very low CV of 0.8%, 0.7% and 0.7% respectively. When the control sample was checked within a period of a month afterwards, this very high precision could not be maintained. A more realistic precision (e.g. based upon the last 10 measurements) should replace the control and warning limits on the control chart.

**2.5 Calculating revised limits when continuing the exercise**

Warning and control limits should be recalculated periodically. Especially when new techniques are introduced, the precision improves when experience is gained with the technique. A good time for recalculating the control and warning limits is at the time when the control chart is full and a new graph has to be created anyway. At this point, use the 20 most recent data on the old chart for construction of LCL, LWL, average, UWL and UCL.

**2.6 Errors that cannot be detected by within-lab AQC**

- i. balance bias (malfunctioning)
- ii. improper storage between drying and weighing (desiccator)
- iii. human errors (e.g. blowing through a pipette, short person reading a high positioned burette)
- iv. old EC-cells that are not in good condition (e.g. not platinised regularly)

A laboratory on its own cannot detect many sources of bias. A good example to illustrate this is the total hardness method. If the analytical balance in a lab always reads 10% too much all solution prepared will have a 10% higher concentration: the Standard  $\text{CaCO}_3$  solution, the EDTA titrant and also the control sample containing  $\text{CaCO}_3$ . This error can only be detected by analysing a sample prepared by a laboratory with a correctly functioning balance. The current lab will underestimate the concentration of such a inter-laboratory sample by 10% because their EDTA titrant is '10% too strong'.

### **3 Inter-laboratory AQC exercise**

#### **3.1 Objectives**

The within-laboratory exercise of individual measurements does not tell much about bias. It focuses mainly on precision and whether the system is under statistical control. Only in some circumstances it may point towards freshly introduced bias, for example the total solids values of individual measurements being consistently on one side of the previously calculated mean.

The main objectives of an inter-laboratory AQC exercise are:

1. To test for possible bias in measurements in a laboratory.
2. To provide direct evidence of comparability of results among laboratories in a common water quality-monitoring programme such as Hydrology Project. Some related objectives and benefits are listed below:
  - to assess the status of analytical facilities and capabilities of concerned laboratories.
  - to identify the serious constraints (random & systematic) in the working environment of laboratories.
  - to provide necessary assistance to the concerned laboratories to overcome the short comings in the analytical capabilities.
  - to validate the water quality monitoring data.
  - to promote scientific and analytical competence of the concerned laboratories to the level of excellence for better output.
  - to enhance the internal and external quality control of the laboratories in an organised manner.

#### **3.2 Results of AQC conducted by Central Pollution Control Board**

The Central Pollution Control Board (CPCB) is monitoring water quality at 180 stations under GEMS, MINARS, GAP, NRCD programs through various State Pollution Control Boards (SPCBs). The water samples are being analysed in central or regional laboratories of SPCBs for 22 parameters. In order to obtain reliable and accurate analytical data, CPCB has started regular AQC exercises with the concerned laboratories from 1991 onwards.

### List of Parameters covered

1. Conductivity	2. Total dissolved solids (TDS)
3. Fixed dissolved solids (FDS)	4. Total Hardness
5. Calcium	6. Magnesium
7. Sodium	8. Potassium
9. Chloride	10. Fluoride
11 Sulphate	12. Nitrate - N
13. Ammonical - N	14. Total Kjeldahl nitrogen(TKN)
15. Phosphate P	16. Boron
17. Chromium hexavalent	18. Chemical oxygen demand (COD)
19. Biochemical oxygen demand (BOD)	

The above listed 19 parameters are covered in 2 groups of exercises in one year period, to make it as one full round. As on 31st March, 1997, four rounds of exercises were completed covering all 19 parameters.

### Methodology

Two synthetic samples labelled as A & B each of 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 acceptability of results was determined using "Youden 2 sample plot" method. See Figure 16.

### Findings

The findings of nine exercises conducted during 1991 to 1997 by CPCB by involving various laboratories of SPCBs, Pollution Control Committees and laboratories recognised under E.P. Act are summarised below.

- The number of laboratories participating in AQC programme has increased from 20 in 1991 to 70 in 1997.
- At present, 52 laboratories of Pollution Control Boards and 18 other environmental laboratories recognised under E. P. Act are participating in the program.
- The response of laboratories was always more than 80% and the maximum was in the 9<sup>th</sup> AQC exercise as 94.2 %.
- The overall performance of all the 4 rounds of exercises carried out in 8 slots during 1992 to 1997 covering 19 parameters in terms of laboratories found within the acceptable limits for all the 19 parameters is shown in Figure 1
- A perusal of this Figure 1 indicates that in general performance of these laboratories for titrimetric methods of analysis is better than colorimetric and complex type analyses.

### **Suggestions**

- Since overall performance of the AQC Exercises reveals that colorimetric and complex type of analysis are not up to the expectation, it is necessary to give more attention towards those methods of analysis to reduce possible analytical errors.
- As the performance of the most of analytical parameters were found lacking in accuracy, it is necessary to take corrective measures.
- Improvement in within laboratory AQC is to be made with reference to selection of method, grade of chemicals, glassware, analytical balance and preparation of control charts.
- Known reference samples are to be provided to participating laboratories for improving within laboratory AQC.
- Inter-laboratory AQC programme for participating laboratories is to be conducted regularly and all the laboratories should participate regularly to assess the analytical competence among various laboratories with a view to take necessary corrective measures for reducing analytical errors.
- Training programme on AQC with special emphasis on hands-on training on internal AQC programme is to be organised.
- Laboratory visits should be performed to advise necessary corrective measures.
- Central and Regional level workshops should be organised to sort out analytical problems.

It is suggested that laboratories that are not participating in MINARS & GEMS programmes may also participate in the AQC programme conducted by CPCB in order to improve the analytical capability and performance.

## **4 Planning of first round inter-laboratory AQC**

### **4.1 Co-ordinating Laboratory**

The co-ordinating laboratory distributes identical portions of the same standard solution or sample to each participating laboratory, which analyses the portion it receives. Results from the different laboratories are analysed by the co-ordinating laboratory to estimate the bias of results of each laboratory.

Thus, it is essential that a laboratory able to act in this co-ordinating role is available and has sufficient time and resource for the very careful work involved. Such a co-ordinating laboratory should be a member of the working group of analysts. On satisfactory completion of the tests, any of the participating laboratories may then act as co-ordinating laboratory

### **4.2 Test samples**

The objective of distributing a solution or sample is that each participating laboratory should receive and analyse a portion containing the same concentration of the determinand. For standard solutions, the co-ordinating laboratory should know this concentration to accuracy appreciably better than that required of normal analytical results otherwise the results of the exercise will be worthless. The need for great care in the preparation and distribution of solutions cannot, therefore, be over-emphasised. Generally, it will often be desirable for the co-ordinating laboratory alone to make preliminary tests to ensure that its procedures do achieve the above requirement.

### **4.3 Purity of material used to prepare standard solutions**

The chemicals used to prepare solutions should be of standard quality whose purity is guaranteed by a written specification; 99.5% or better purity is usually adequate. High purity water (de-ionised or distilled) is generally satisfactory, but absence of the determinand in such water should not be assumed.

### **4.4 Errors in preparing the test solution or samples**

In preparing a standard solution, it is useful for two analysts independently to calculate the weight of standard material required in making up the desired volume of solution. A second analyst should check the balance readings. When the standard material is weighed, and also independently calculated, the weight of material is taken.

All apparatus used must be scrupulously clean and, in particular, free from traces of the determinand of interest. Great care must be taken to avoid contamination of materials and apparatus before and during the preparation. Manipulations such as quantitative transfers and diluting solutions to a graduation mark must be conducted with the utmost care.

When the standard solution has been prepared a question arises whether the concentration of the solution should be checked by analysis. The approach recommended is to prepare the solution as a primary standard using all the classical precautions associated with such a preparation. The freshly prepared solution should be analysed for the determinand of interest, a sufficient number of replicates being made for

the purposes of stability testing. The estimate of initial concentration also serves as a check for gross errors in the preparation. The true concentration for the collaborative test should, however, be taken as the nominal concentration of the solution as a primary standard and not the analytical result obtained in the concentration check.

#### **4.5 *Determinand stability and contamination***

When the distribution is carried out, several portion of solution should be retained at the co-ordinating laboratory for stability checks, and for replacements if required. The solution should be stored in containers of the type used in the distribution and under the storage conditions specified to participating laboratories. The concentration of the determinand of interest should be checked at the end of the collaborative exercise and should not have changed significantly from the initial value. For most determinands, this usually means 1% of the nominal concentration, and sufficient replicate analyses should be made to achieve that precision.

It is vitally important that the concentration of the determinand of interest in the samples should be stable throughout the period of the tests, and a preservative may some times be added to ensure this stability. However, some preservatives may cause interference in certain analytical methods, and so the possible effect of any proposed preservative on all methods of analyses must always be investigated carefully before the preservative is used.

The material of which sample bottles are made should neither absorb nor release the determinand, and bottles must be scrupulously cleaned to be free of the determinand of interest. Particular care is necessary for many trace impurities to ensure that bottle stoppers and caps are not a source of contamination.

#### **4.6 *Participating laboratories***

The participating laboratories should be thoroughly familiar with the recommended analytical procedure. They should have satisfactorily completed a within-laboratory exercise for the determinand producing results of acceptable precision.

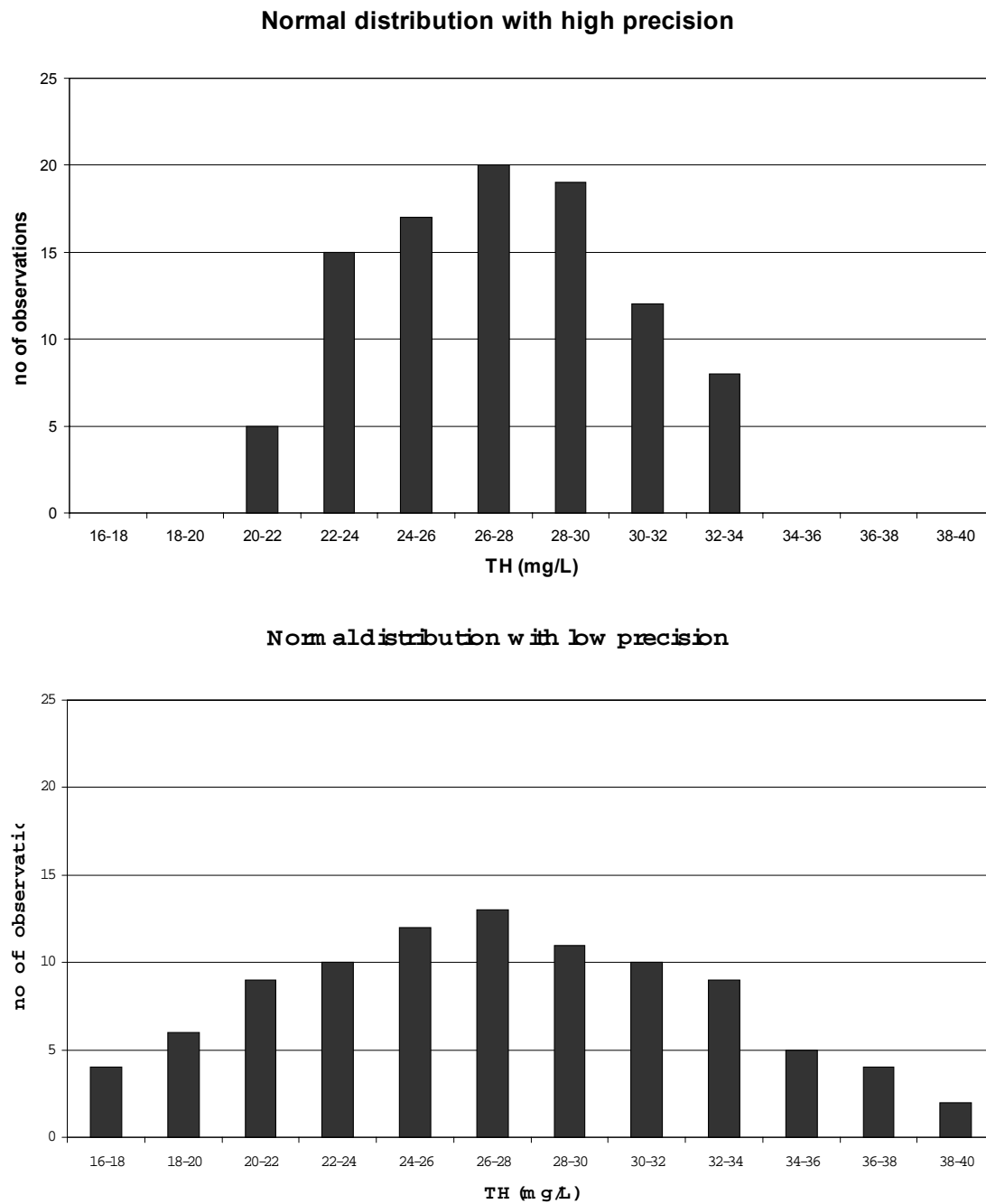
The participating laboratories can easily assess sources of bias resulting from the use of impure chemicals, poor quality distilled water and sub-standard. If such errors are detected, they should be removed before starting the inter-laboratory exercise.

#### **4.7 *Proposal***

The exercise will be started by sending two samples by courier to the participating laboratories. The laboratories are requested to analyse both samples for various parameters. Each sample should be analysed in duplicate. The results must be reported within three weeks after receipt of the bottles. Within two weeks after receipt of the results the laboratory will be informed about the result (within limits / outside limits). The results of the performance of all laboratories will be reported after wards. Consultants offer assistance in solving analytical problems if so appears necessary.

Central Pollution Control Board (CPCB) laboratory at New Delhi was identified as the reference co-ordinating laboratory. The laboratory is conducting such programmes for the last several years for many laboratories in the country.

**Figure 1** The overall performance of all the 4 rounds of exercises carried out by CPCB in 8 slots during 1992 to 1997 covering 19 parameters. Laboratories found within the acceptable limits for all the 19 parameters.



**Figure 2** Example of two normal distributions with the same mean value, the upper one being more precise (having a lower standard deviation and CV)

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**Figure 3** Example of loss of statistical control by the *Control Limit* criterion

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**Figure 4** Example of loss of statistical control by the *Warning Limits* criterion

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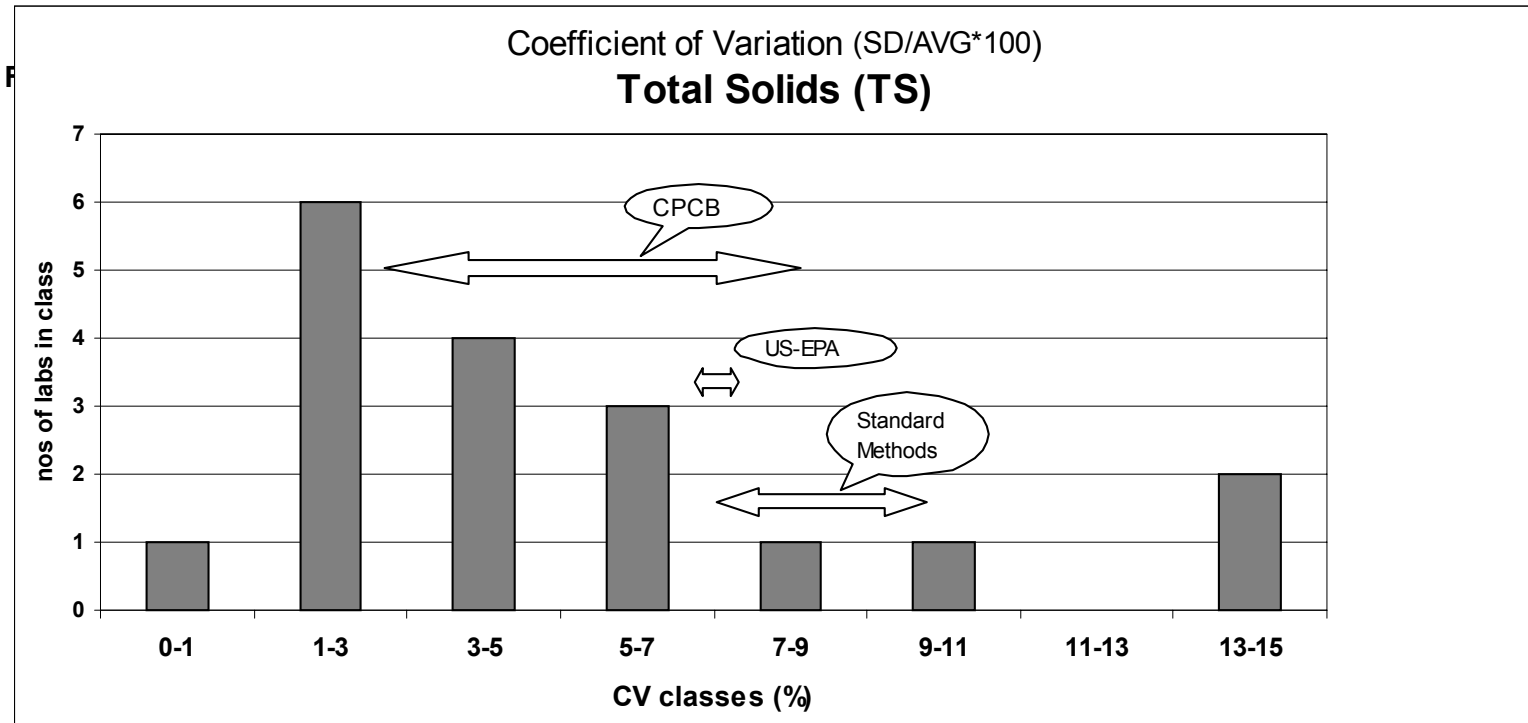
**Figure 5** Example of loss of statistical control by the *Standard Deviation* criterion

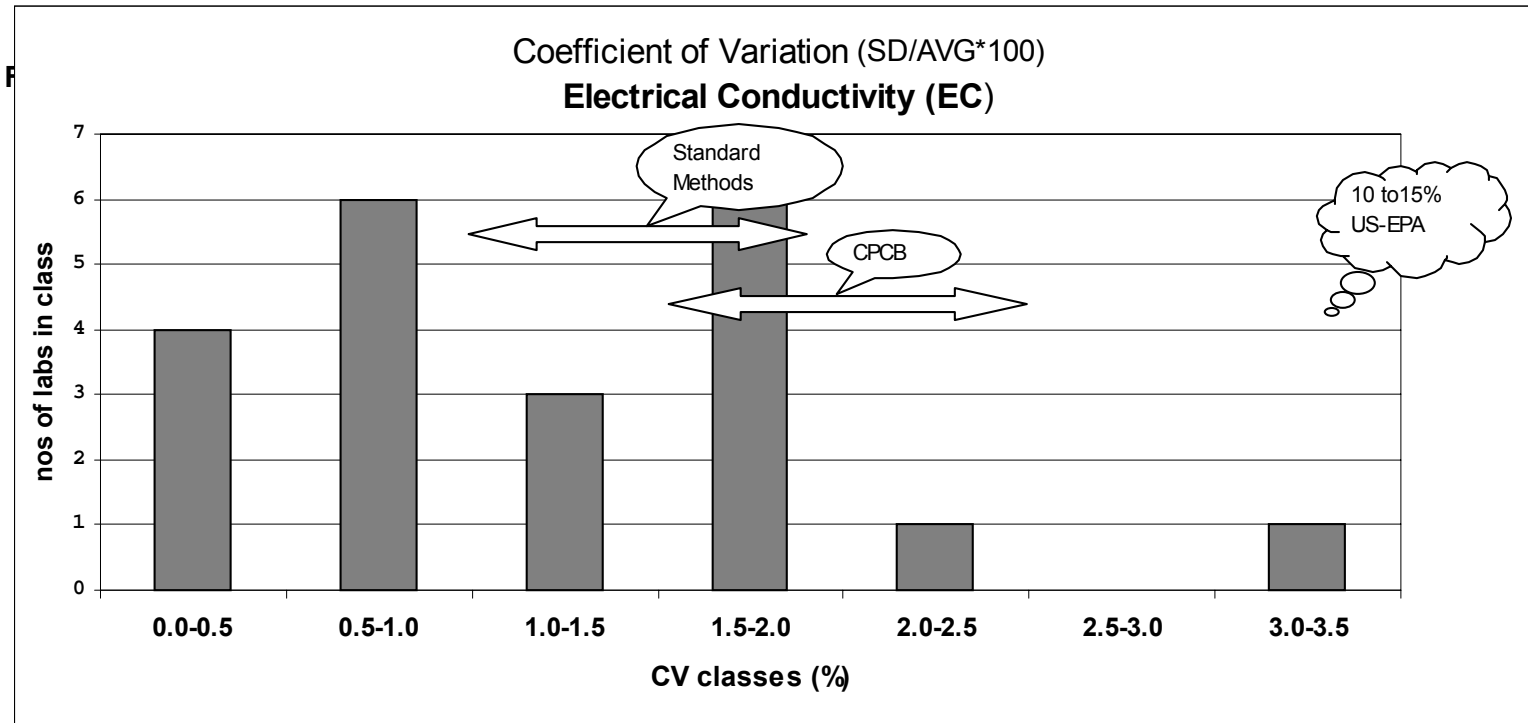
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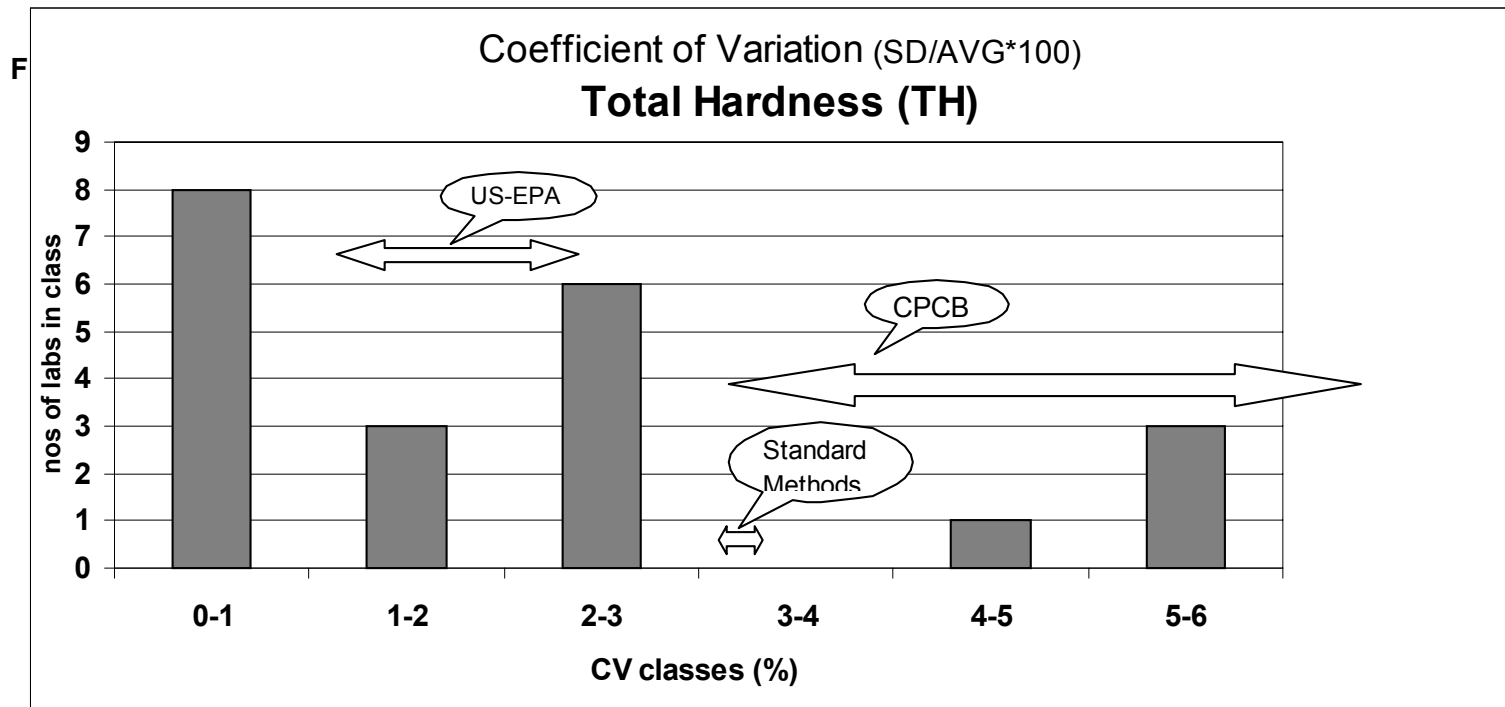
**Figure 6** Example of loss of statistical control by the *Trend* criterion

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**Figure 7** Example of loss of statistical control by the Average (*Central Line*) criterion







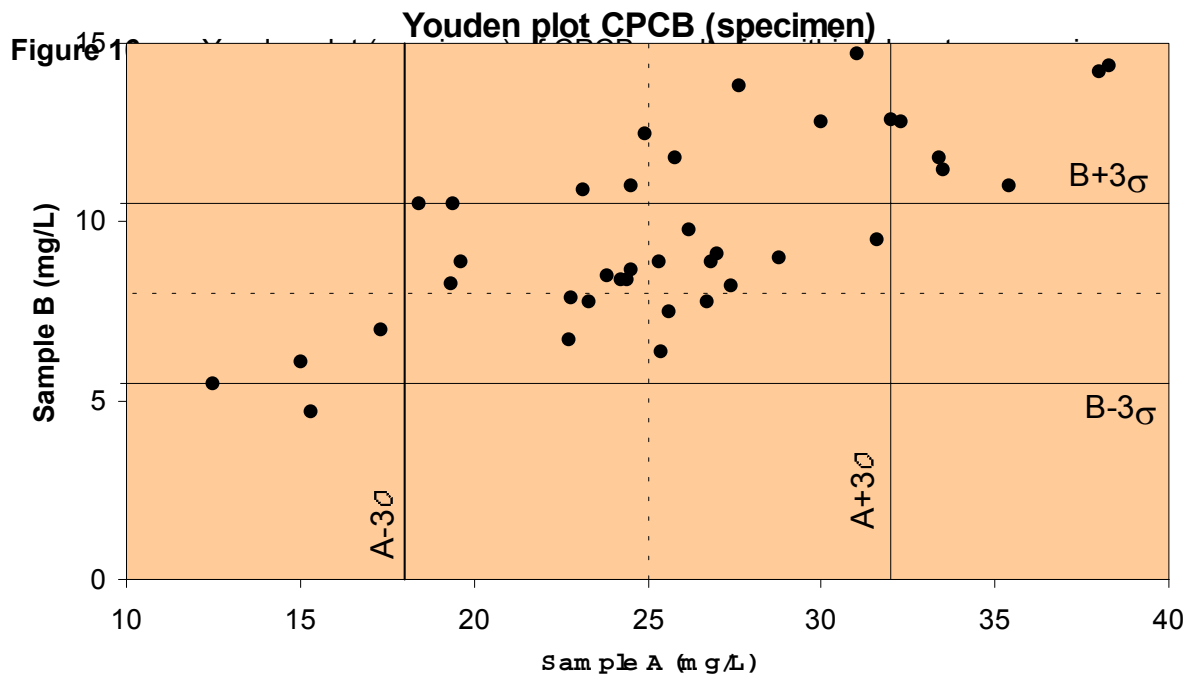
**Figure 11** Shewhart control chart for TS by laboratory 10

**Figure 12** Shewhart control chart for TH by laboratory 5

**Figure 13** Shewhart control chart for TH by laboratory 15

**Figure 14** Shewhart control chart for TH by laboratory 14

**Figure 15** Shewhart control chart for EC by laboratory 15



## Appendix A

Estimation of error in TH

burette accuracy (50mL type) is  $\pm 0.05\text{mL}$

pipette accuracy (15mL type) is  $0.03\text{mL}$

EDTA titrant =  $0.01\text{M}$  (standardised)

standard Ca solution:  $0.01\text{M} = 1000\text{ mg/L}$

control sample is 10x diluted standard Ca solution =  $100\text{mg/L}$

Procedure: take  $25\text{mL}$  of control sample and titrate this with approximately  $2.5\text{mL}$  EDTA until colour changes.

Formula:  $TH = \frac{A}{\text{mL}} \times B \times 1000$  gives TH in mg/L

where A = mL EDTA titrated for sample

mL = milliliters of sample titrated

B = mgCaCO<sub>3</sub> equivalent to 1.0 mL of EDTA

Estimation of the error in TH of the control sample:

Total error TH =  $\%Error_A + \%Error_{\text{mL}} + \%Error_B$

$\%Error_A = 15\text{mL} \pm 0.03 \rightarrow 0.2\%$  (pipette)

$\%Error_{\text{mL}} = 2.5\text{mL} \pm 0.05 \rightarrow 2\%$  (burette)

Determination of B is again a titration and therefore:

$\%Error_{B-A} = 15\text{mL} \pm 0.03 \rightarrow 0.2\%$  (pipette)

$\%Error_{B-\text{ml}} = 15\text{mL} \pm 0.05 \rightarrow 0.3\%$  (pipette)

Sum of all four errors =  $0.2 + 2 + 0.2 + 0.3 = \pm 2.8\%$ ! The estimated cv is then  $\pm 1.0\%$ , assuming  $\%error = 3\sigma$ . The largest contribution comes from the  $2.5\text{mL}$  EDTA titration by the burette. A larger sample volume requiring larger EDTA titrant quantity reduces the relative error.

Note that this is a theoretical calculation based upon accuracy's of burette and pipette only. The actual precision is probably less because of other potential sources of error mentioned (e.g. caused by judging the colour change).

## Appendix B

Effect of sample volume on precision for Total Solids analysis

		<b>Based on 100mL</b>	<b>Based on 50mL sample</b>
Dish	mg	14000 ± 0.5	14000 ± 0.5
dish range	mg	13999.5 to 14000.5	13999.5 to 14000.5
dish + solids	mg	14015 ± 0.5	14007.5 ± 0.5
dish + solids range	mg	14014.5 to 14015.5	14007.0 to 14008.0
differences	mg	14, 16, 14, 15	7.5 8.5 6.5 7.5
average weight	mg	<b>15 ± 1.0</b>	<b>7.5 ± 1.0</b>
	% error	-	± 6.7%
sample volume	ml	<b>100 ± 2.0</b>	<b>50 ± 2.0</b>
	% error	-	± 4%
average concentration	mg/l	150	150
differences	mg/l	142.9 137.3 163.3 156.9	135.4 125.0 177.1 165.5
	error (%)	-	<b>8.7%</b>
	cv (%)	-	<b>2.9%</b>
			<b>17.4%</b>
			<b>5.8%</b>

