Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 49

Quality Assurance and within Laboratory AQC

New Delhi, September 2000

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DHV Consultants BV & DELFT HYDRAULICS

with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1. Module context

This module discusses the need for Quality Assurance programme and describes the procedure for setting up a within-laboratory AQC programme.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

Modules in which prior training is required to complete this module successfully are listed in the table below.

No.	Module	Code	Objectives
1.	Basic Statistics	**WQ – 47**	• Understand difference between accuracy and precision • Calculate, descriptors of frequency distribution
2.	Applied Statistics	**WQ – 48**	• Apply common statistical tests for evaluation of the precision of data

2. Module profile

Title	:	Quality Assurance and within Laboratory AQC
Target group	:	HIS function(s): Q2, Q3, Q5, Q6
Duration	:	one session of 60 min
Objectives	:	After the training the participants will be able to*:* • Understand the need for QA programmes • Set up with-in laboratory AQC programme
Key concepts	:	• Quality Assurance • With-in laboratory AQC
Training methods	:	Lecture, exercises, OHS
Training tools required	:	Board, flipchart
Handouts	:	As provided in this module
Further reading and references	:	• Standard Methods: for the Examination of Water and Wastewater, APHA, AWWA, WEF/1995. APHA Publication • Statistical Procedures for analysis of Environmenrtal monitoring Data and Risk Assessment', Edward A. Mc Bean and Frank A. Rovers, Prentice Hall, 1998.

3. Session plan

No	Activities	Time	Tools
1	***Preparations***		
2	***Introduction***: • Ask participants how can they be sure of the correctness of their results. • Discuss the need for quality assurance programmes	10 min	OHS
3	***Review*** • Precision, bias and accuracy • Definitions from statistics	15 min	OHS
4	***With-in laboratory AQC*** • Discuss precision and statistical control • Shewhart charts • Interpretation of results	30 min	OHS
5	***Conclusion***	5 min	OHS

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Quality Assurance

- Need for QA
  - *Analytical results are subject to errors*
  - *EPA studies showed ± 50% and ±100% errors in results of ammonia and nitrate analyses*
  - *Only 34% of SPCB laboratories reported acceptable EC results for standard sample.*
- *Actions taken on such results become questionable.*

Quality Assurance

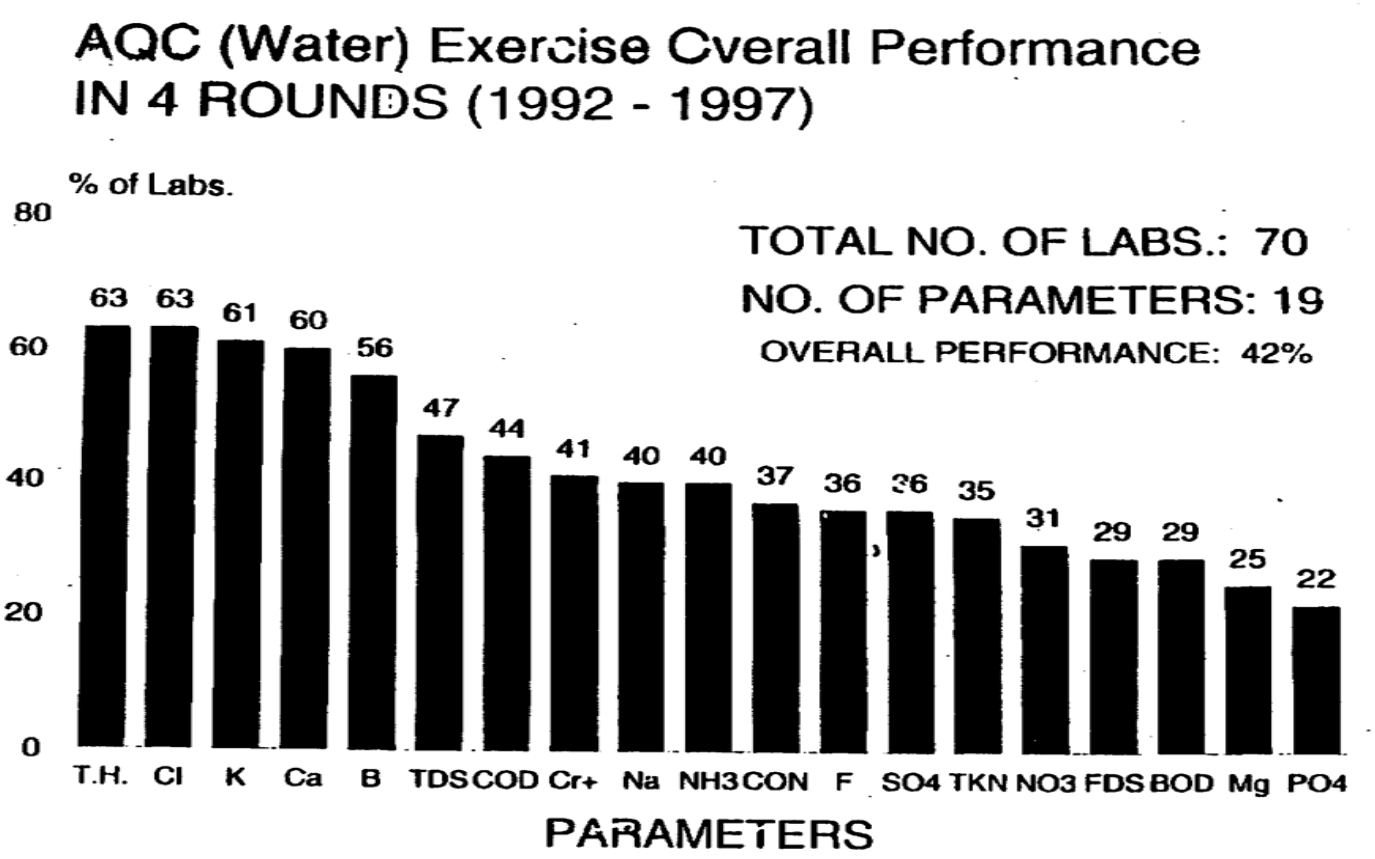

Figure 1: **The overall performance of all the 4 rounds of exercises carried out by CPCB in 8 slots during 1992 to 1997 covering 19 parameters. Laboratories found within the acceptable limits for all the 19 parameters.**

QA Programme

- Sample control and documentation
- Standard analytical procedures
- Equipment maintenance
- Calibration procedures
- AQC, within-laboratory and inter-laboratory

Within-Laboratory AQC

- Suitability of analytical methods
- Purity of chemicals
- Sampling techniques
- Sample preservation
- Data reporting
- Method precision, Shewhart charts

Shewhart Control Chart (1)

- Focuses on precision – state of ‘Statistical Control’
- Construction of charts
  - *Make 20 replicate analyses on a standard solution*
  - *Calculate mean and standard deviation*
  - *Establish warning limits at* $\bar{x} \pm 2S$ *and control at* $\bar{x} \pm 3S$
- Repeat analysis of control after 20 to 50 routine samples and plot results

Shewhart Control Chart (2)

- Evaluate performance
  - *Loss of statistical control*
  - *Newly introduced bias*
  - *Revised control limits*

Shewhart Control Chart (3)

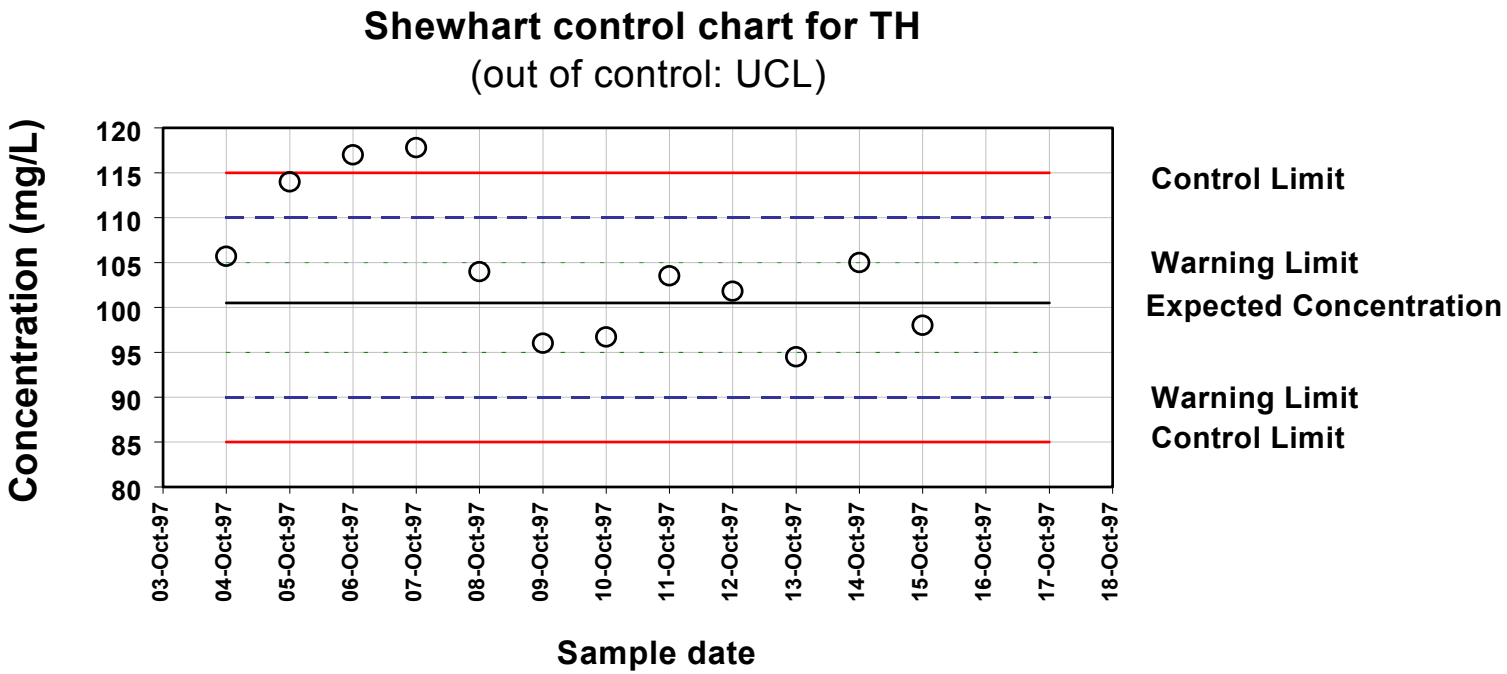

Figure 3: Example of loss of statistical control by the Control Limit criterion

Shewhart Control Chart (4)

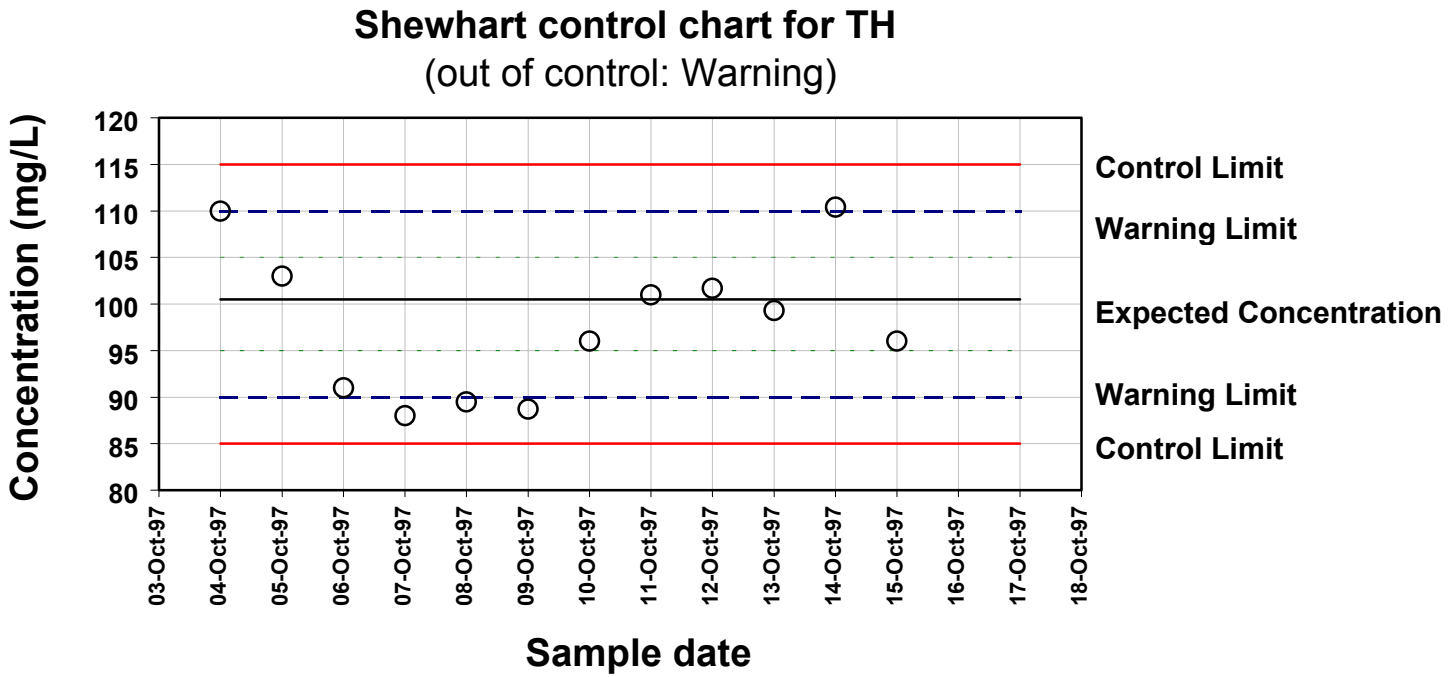

Figure 4: Example of loss of statistical control by the Control Limit criterion

Shewhart Control Chart (5)

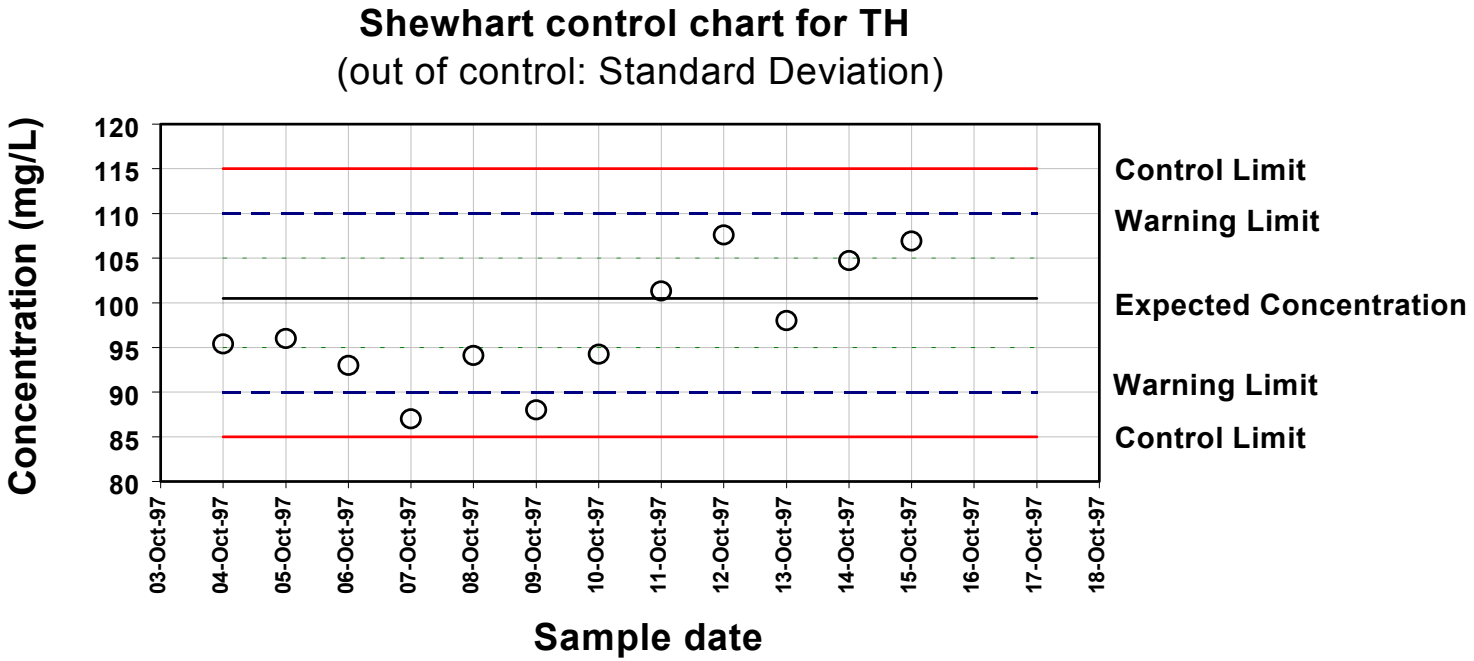

Figure 5: Example of loss of statistical control by the Standard Deviation criterion

Shewhart Control Chart (6)

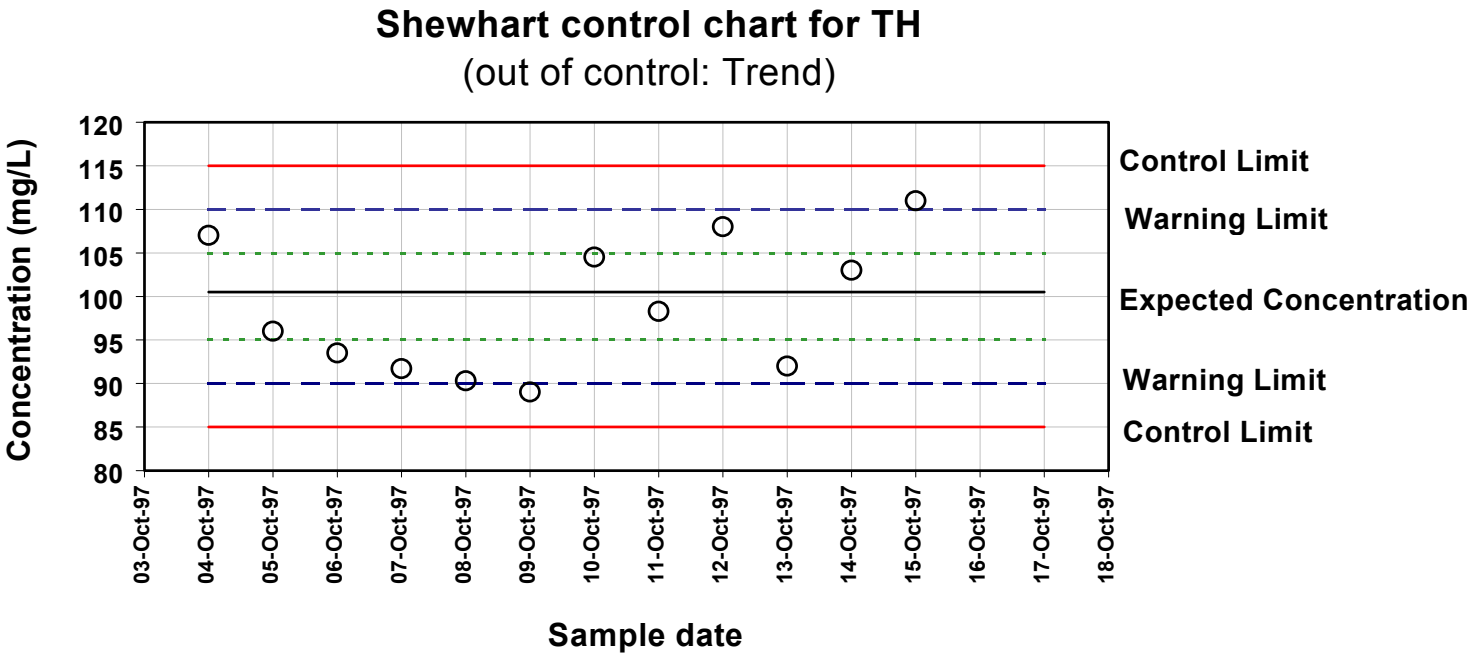

Figure 6: Example of loss of statistical control by the Trend criterion

Shewhart Control Chart (7)

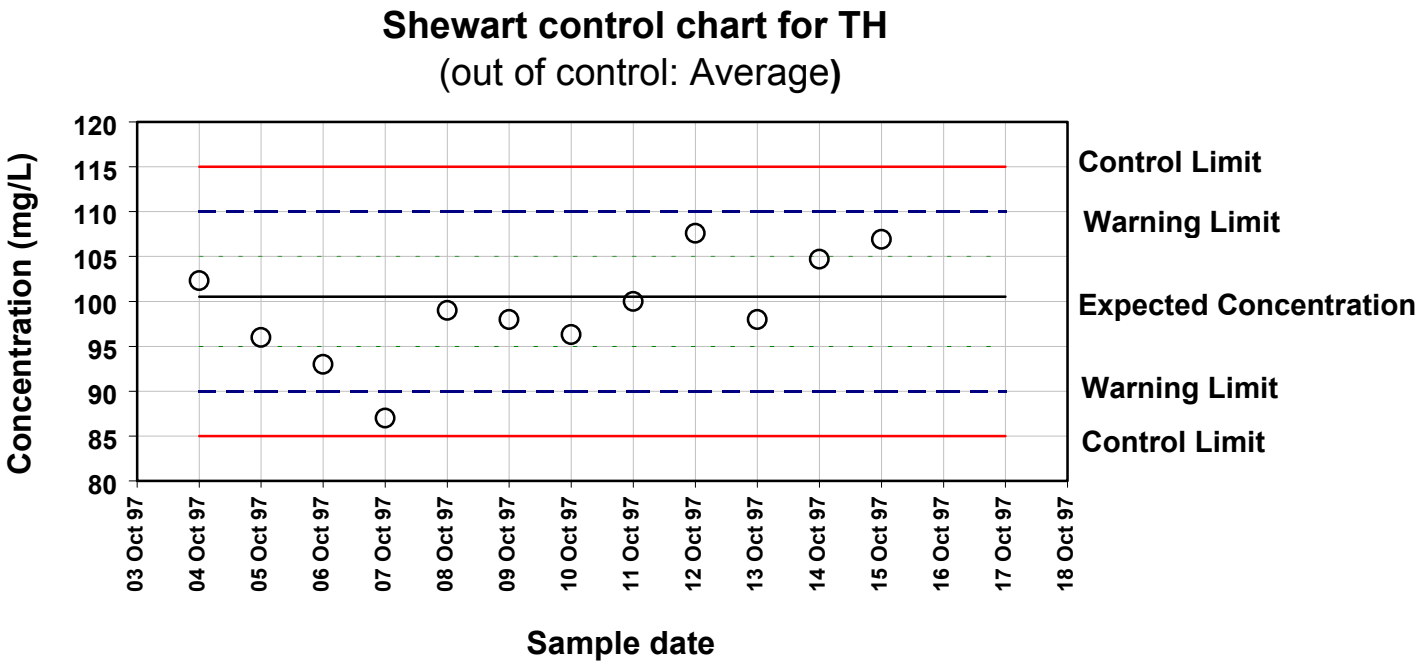

Figure 7: Example of loss of statistical control by the Average (Central Line) criterion

Conclusion

- Within-laboratory AQC measures precision
- An internal mechanism to check performance
- Practised by responsible chemists
- It is not much additional work
- It should not be a one time exercise

5. Evaluation sheets

6. Handout

Quality Assurance

- Need for QA
  - *Analytical results are subject to errors*
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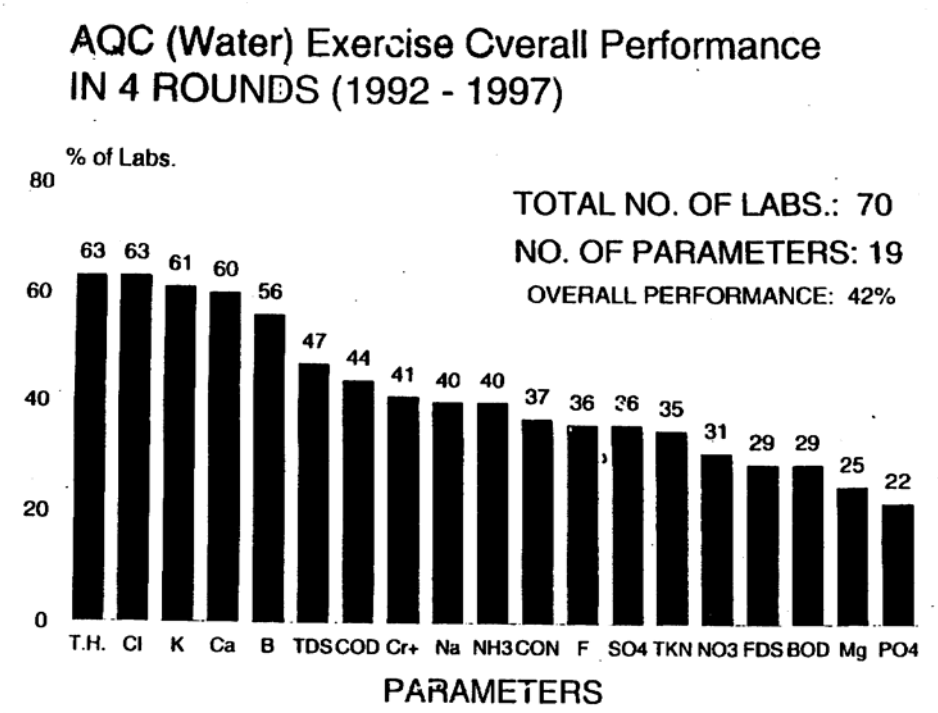

QA Programme

- Sample control and documentation
- Standard analytical procedures
- Equipment maintenance
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- AQC, within-laboratory and inter-laboratory

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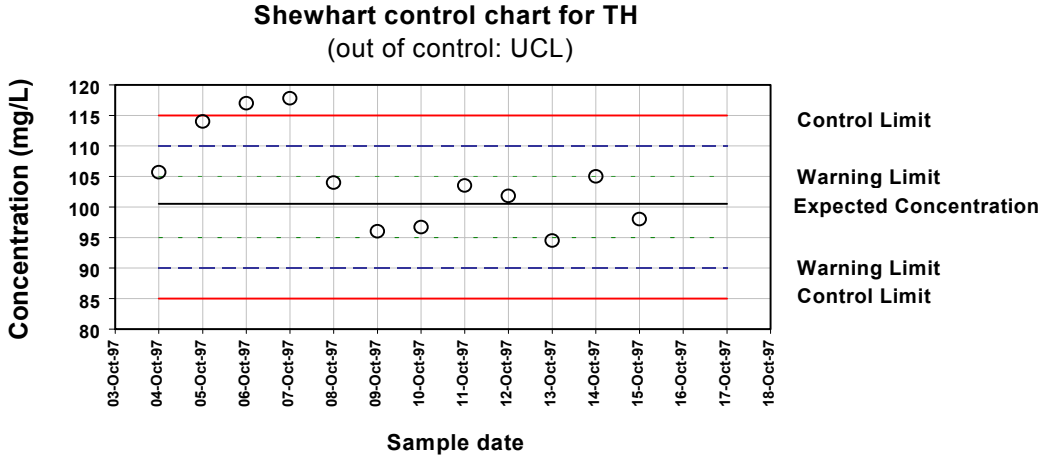

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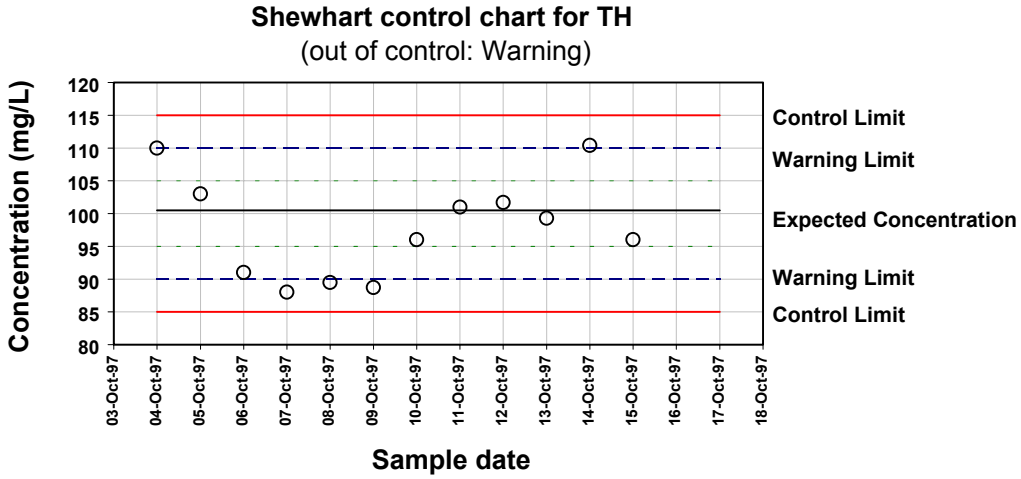

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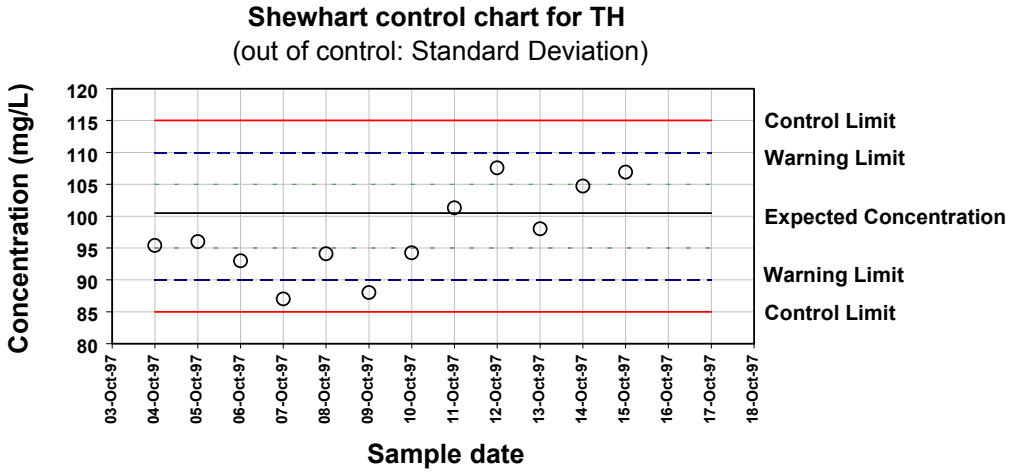

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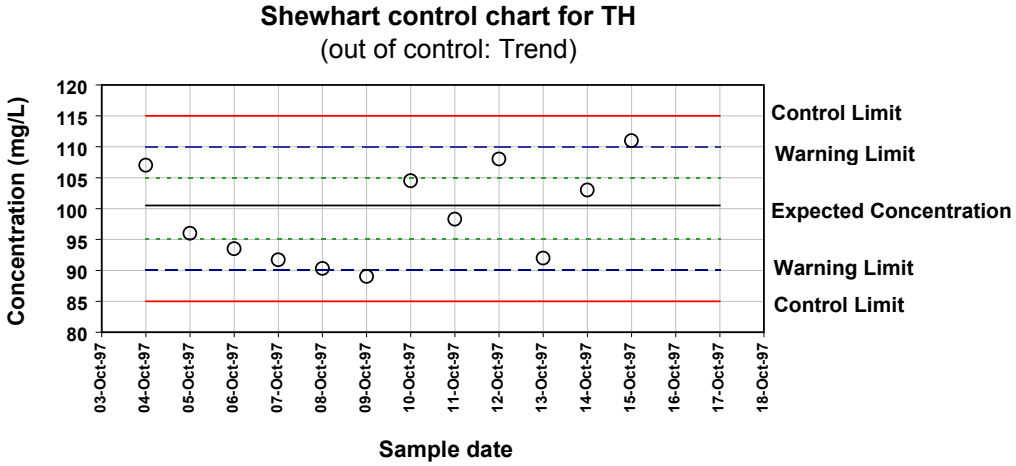

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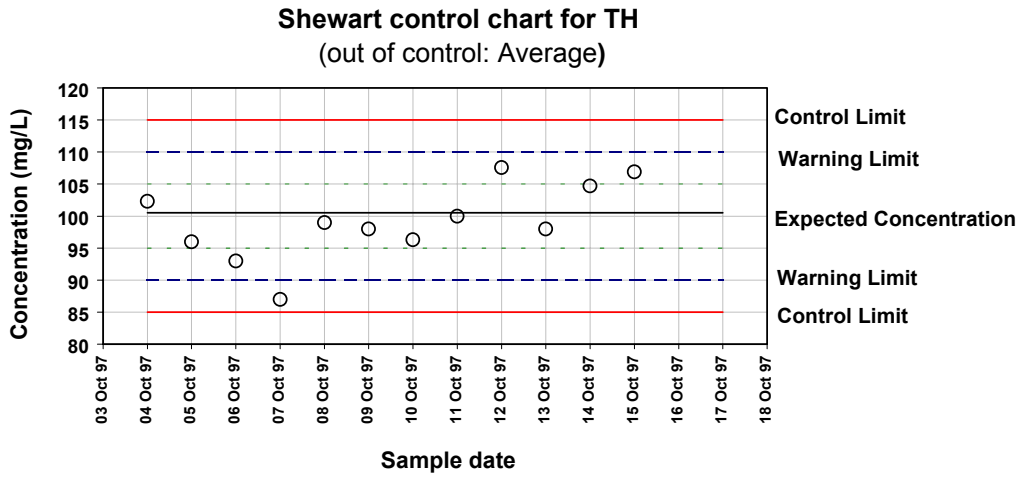

Conclusion

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- An internal mechanism to check performance
- Practised by responsible chemists
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Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8. Main text

Contents

Quality Assurance and within Laboratory AQC

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, ±50% for ammonia and ±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. 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.

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 programmes

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 asses 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.

In Summary:

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
- practiced 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
- 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.

3. Review of 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.

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. Figure 2.

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 = standard deviation/mean X 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 X 100) and 15 (1.5/10 X 100) percents respectively. Indicating a lower precision for the second set of observations.

4. 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.

5. Discussion of results

5.1 Precision

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. Therefore the coefficient of variation, defined earlier, should 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, say for irrigation. 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

5.2 Calculating revised limits when continuing the exercise

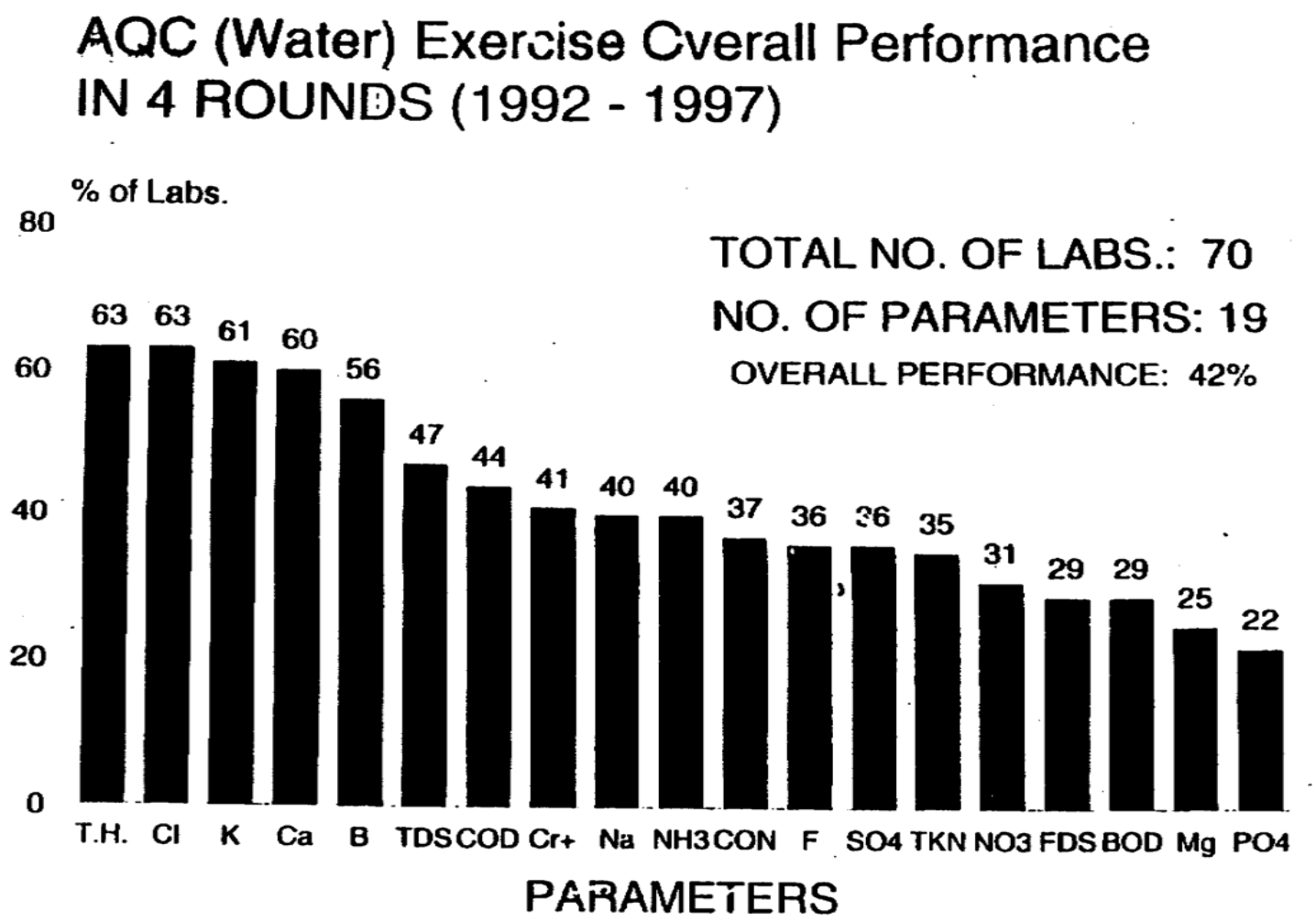
Warning and control limits should be recalculated periodically. Especially when new techniques are introduced, the precision improves when experience is gained with the technique. A good time for recalculating the control and warning limits is at the time when the control chart is full and a new graph 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.

5.3 Errors that cannot be detected by within-laborartory AQC

The within-laboratory AQC exercise focusses mainly on precision. 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 $CaCO_3$ solution, the EDTA titrant and also the control sample containing $CaCO_3$. This error can only be detected by analysing a sample prepared by a laboratory with a correctly functioning balance. The current laboratory will underestimate the concentration of such a inter-laboratory sample by 10% because their EDTA titrant is '10% too strong'.

In some cases freshly introduced bias may be detected. For example, if the measurements consistently fall on one side of the previously calculated mean, it indicates a freshly introduced bias.

An inter-laboratory AQC exercise should be conducted for detecting bias or accuracy for analysis.



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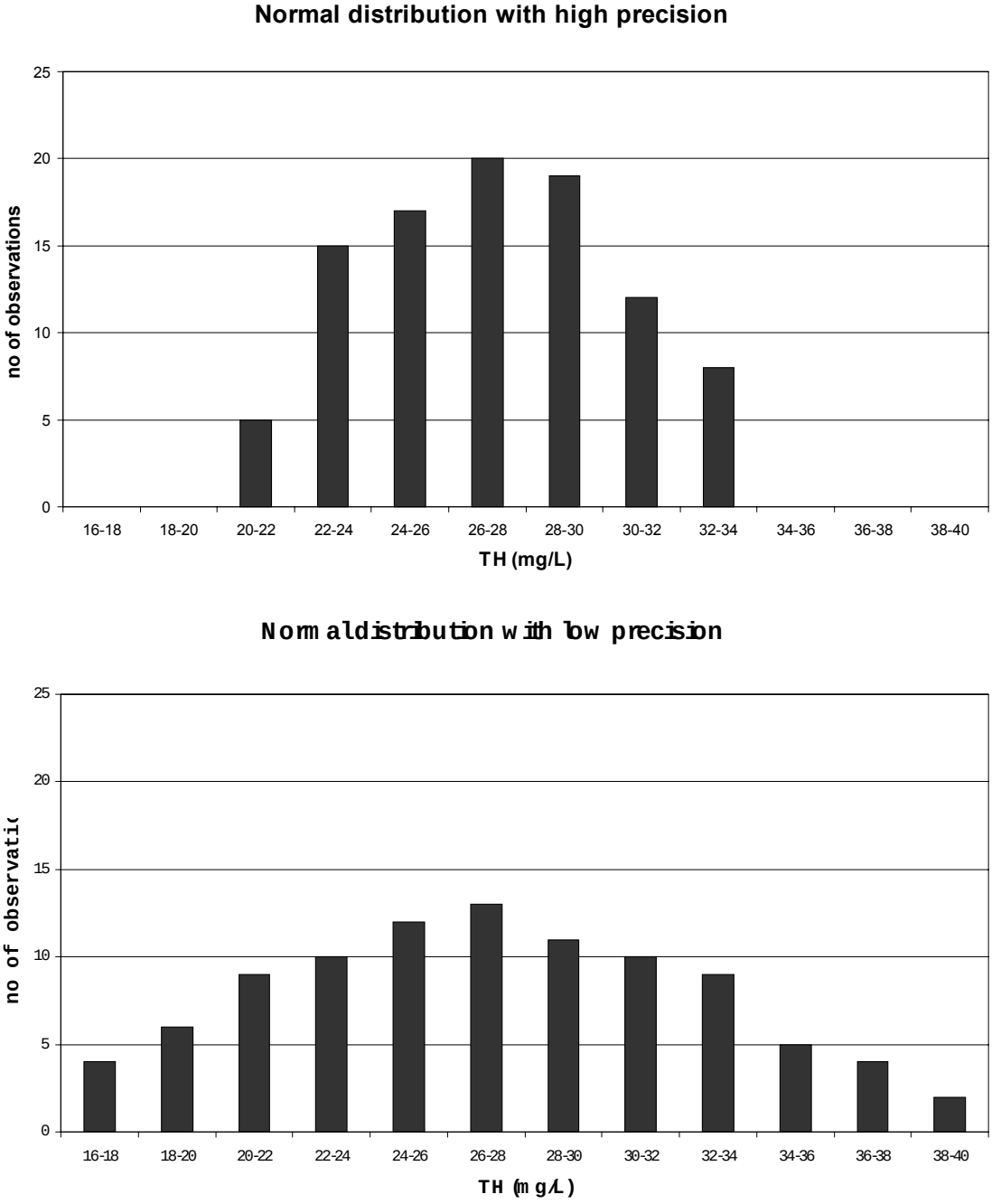
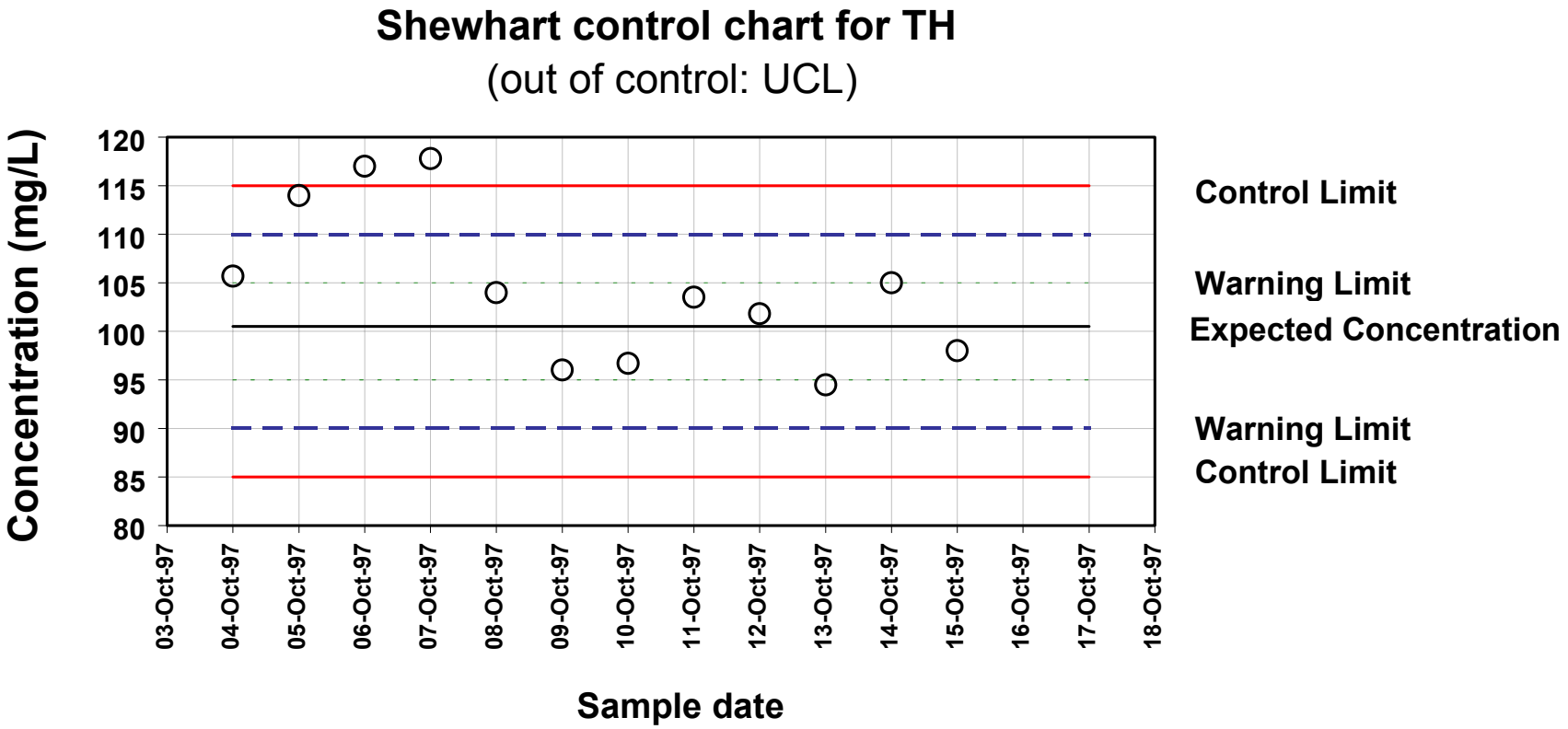


Figure 2: Example of two normal distributions with the same mean value, the upper one being more precise (having a lower standard deviation and CV)



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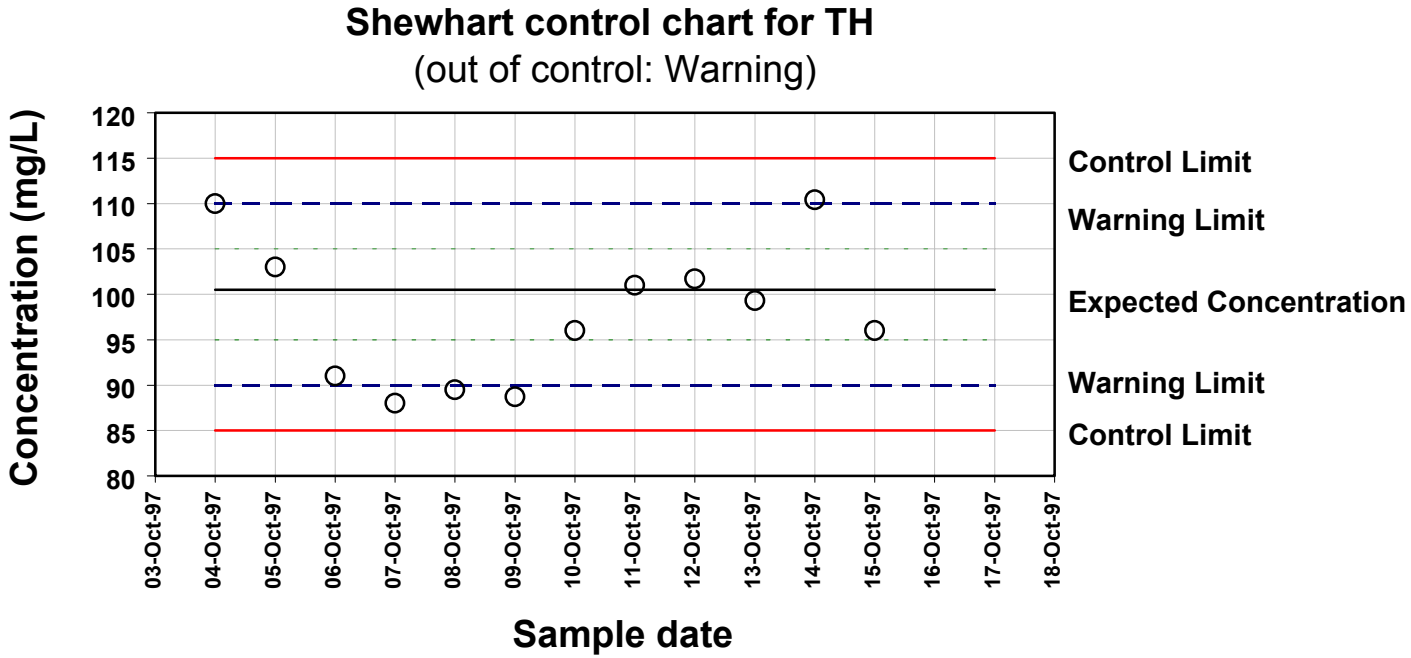

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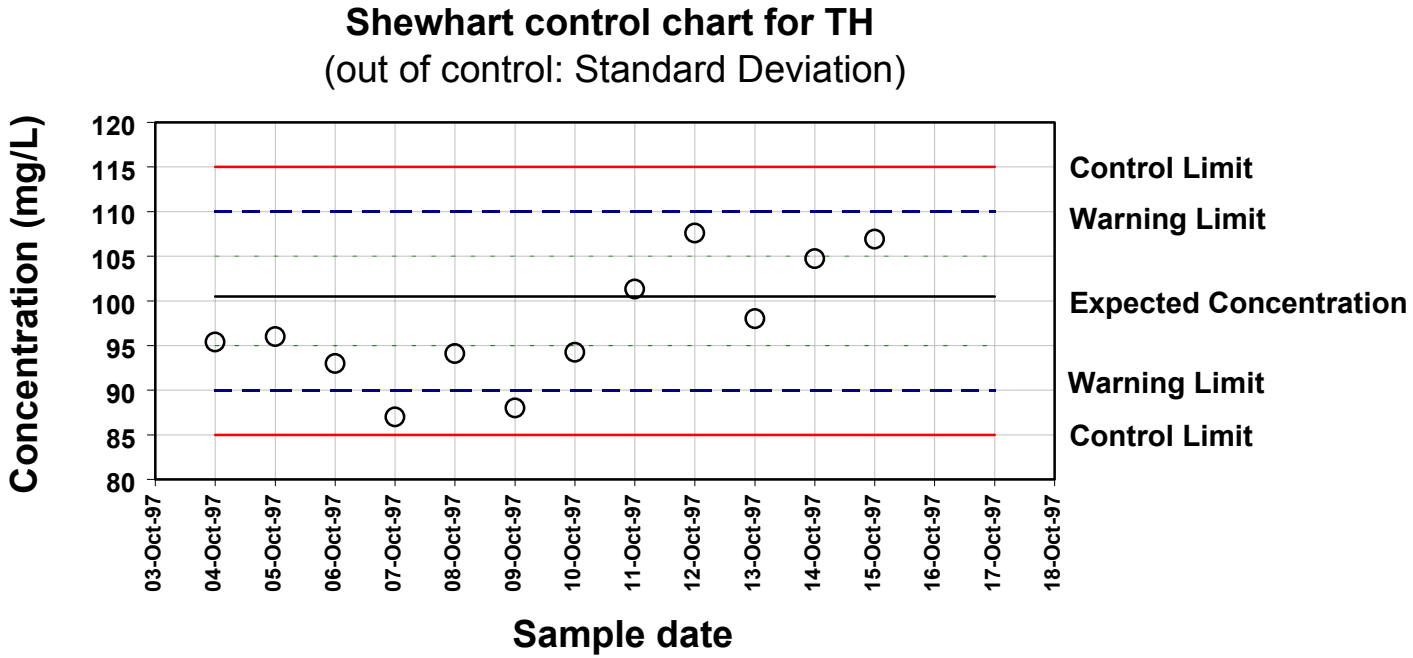

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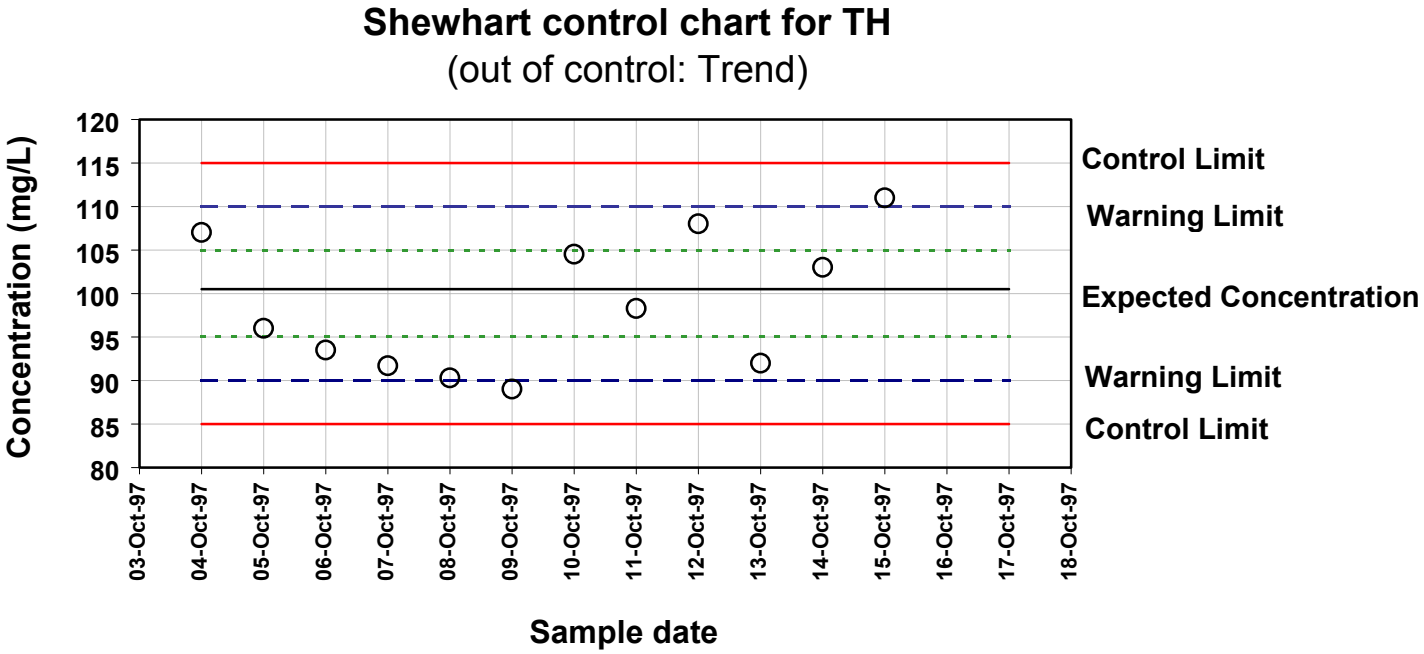
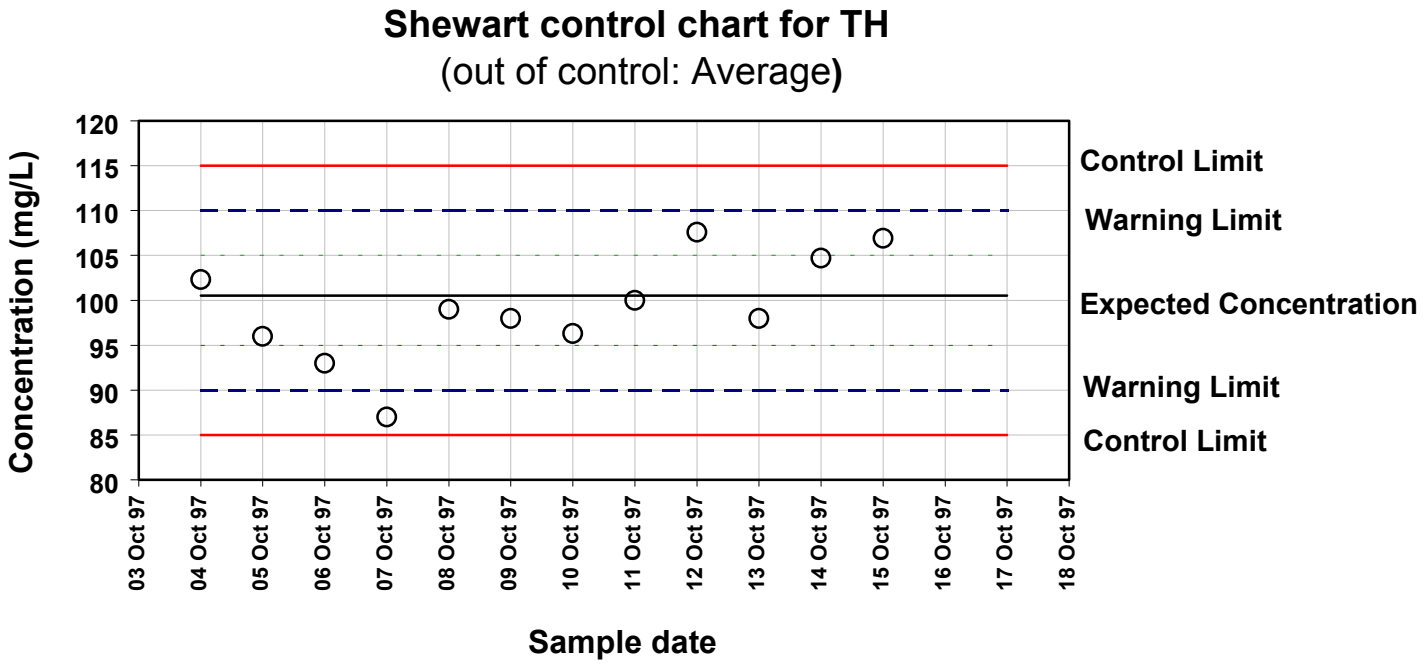


Figure 6: Example of loss of statistical control by the Trend criterion



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