Guide to the Use of Control Charts in Water Analysis

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A GUIDE TO THE USE OF CONTROL CHARTS IN WATER ANALYSIS

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SUMMARY

I OBJECTIVES

To give guidance on the use of quality control charts in water laboratories. The construction of various types of Shewhart control charts and their interpretation is described.

CONTENTS

SECTION 1 - INTRODUCTION

Any study of water quality, whatever its purpose, will involve the collection and comparison of analytical results. On the basis of these results decisions will be made and appropriate action taken. It is essential, therefore, if the correct conclusion is to be arrived at, to be able to examine analytical data of adequate accuracy.

If the errors associated with analytical results were always very small, the correctness of any decisions would rarely be in doubt. However, it has been established by many investigations that the errors arising in the analysis of samples may often be so large as to affect seriously the validity of decisions based upon them.

It is essential that the intended uses of analytical data are clearly defined so that the requirements for analytical accuracy may be established. Steps can then be taken to control the size of analytical errors such that the results are of an accuracy adequate for their purpose. This is the function of the techniques and activities which go under the collective name of Analytical Quality Control (AQC).

Once the requirements for the accuracy of analytical results have been established, the analyst is in a position to select analytical methods which are capable of meeting these requirements.

It is not sufficient for a laboratory to adopt a suitable, well-tested analytical method and assume that, thereafter, the results will be of adequate accuracy. Whilst such methods are of great value, there can be little control over many factors which may affect analytical accuracy. Differences in the interpretation of the method, in the reagents and equipment used, in the laboratory environment, and in the skill and conscientiousness of analysts may all produce analytical errors of different magnitude, both in a given laboratory on different occasions and between different laboratories. Thus, the achievement of analytical results of adequate accuracy requires:

1. selection of an analytical method capable of the required performance, and
2. the correct application of the method in routine analysis.

The chosen method should be tested when it is first established in the laboratory, to ensure that it produces results of adequate accuracy. Subsequent routine tests are necessary to check that this performance is maintained, and it is in this aspect of AQC that control charts are employed. (It should be noted, however, that within-laboratory AQC cannot assess all potential sources of error, and cannot, therefore, ensure that results from different laboratories are comparable. This requires an AQC programme involving between-laboratory testing (1).

Control charts, then, are a component in the process of Analytical Quality Control and should, ideally, be used as a part of a more comprehensive system of AQC designed to ensure that analytical results meet the needs for which they were obtained (2).

Some familiarity with basic statistical concepts and terminology is assumed so as to avoid a document of undue length.

SECTION 2 - SCOPE

2.1 SYMBOLS

i 1, 2 .....m number of batches of analysis

j 2, 2 .....n number of control determinations within a batch of analysis

σ population standard deviation

s estimate of σ

s_t estimate of total standard deviation - the standard deviation of results taken at random from any batch of analysis

A recovery of an added spike of determinand

s_a estimate of standard deviation of recovery

Sp quantity of determinand added as a spike (expressed in concentration terms)

D difference between replicate analysis

s_D estimate of standard deviation of differences between replicate analysis

R range of observed results

s_j estimate of standard deviation of j determination performed within a batch of analysis

2.2 GENERAL

This report introduces the principles of control charts as applied to the analysis of water. Emphasis is placed on the use of the conventional type of chart, sometimes referred to as the Shewhart chart (3,4), with a brief description of the cumulative sum chart.

SECTION 3 - PRINCIPLES OF CONTROL CHARTS

When preliminary tests have shown that errors are satisfactorily small, and the analytical method has been put into routine use, a continuing check on the accuracy of results is needed because many factors can cause a deterioration of accuracy with time.

A control chart is a statistical tool for the analysis of data obtained during a continuing process. It consists of a chart on which the values of the measured quality characteristic, such as concentration or pH, are plotted in the order in which they were obtained. The presentation of the information in this way is an aid to the understanding of the operation of the process and can form the basis, when supplemented by technical knowledge. for process control.

Process control has two main features:

1. the detection of a change in the performance of the process, and
2. identification of the causes of the change and appropriate corrective action.

If a set of data, consisting of measurements of some quality characteristic such as the concentration of a determinand of interest, is obtained under conditions of routine analysis, some variation of the observed value is bound to be evident. The information is said to be statistically uniform and the process is said to be under statistical control if this variation arises solely from a given set of what can be considered as sources of random analytical variability. These causes of variation can be assumed to be equally likely to result in analytical errors in a positive or negative direction and will affect, to an extent dependent on their magnitude, all measurements. Loss of statistical control is characterised by the introduction of sources of systematic error or by a change in the size of the random error operating in the analytical method.

The application of statistical techniques to results subject to random variation will allow an estimation of error and an objective evaluation of the worth of the information available. Thus, whilst results are in statistical control, an estimate of the expected error associated with any result in a series of measurements can be made. If a change in the magnitude of random error occurs, this estimate will no longer be valid.

In the application of control charts to water analysis the objective, therefore, is to maintain the production of analytical results in a state of statistical control.

SECTION 4 - SHEWHART CONTROL CHARTS

The most widely used form of control chart is the Shewhart chart (4). This takes the form of a chart on which the quality characteristic of interest is plotted against time (see Figure 1). The observed values of the variable are compared with either the expected or the true value. Much information can be gained by the experienced operator merely by a visual examination of the chart. In addition, however, guide lines are provided to aid in an objective assessment of the accuracy of analytical results.

For example, suppose a standard solution were analysed with each batch of analysis as a check on accuracy. These results could be plotted on a chart (see Figure 1), in the order in which they were obtained. Assuming the results for the standard solution follow the Normal distribution and that only chance causes of variation were operating, it would be expected that only 0.3% of results would fall outside lines drawn at 3 standard deviations above and below the population mean value. Individual results would be expected to fall outside these limits so seldom that such an event would justify the assumption that the analytical procedure was no longer in statistical control - ie a real change in accuracy had occurred, and hence that remedial action was required.

Therefore, insertion of lines corresponding to: (a) the mean value, μ, expected for results, and (b) the limits $\mu \pm 3\sigma$ (where σ is the standard deviation of results, see Figure 1) provides objective criteria for the interpretation of the chart. The limits $\mu \pm 3\sigma$ are called the "action limits" of the control chart (see Section 7).

It is also useful to insert two other lines on the chart at $\mu \pm 2\sigma$. If the method is under statistical control, approximately 5% of results may be expected to fall outside these lines, the so-called "warning limits" of the chart. The fact that one result falls outside these limits need warrant no action provided the next result is inside. Such an occurrence serves as a warning of loss of statistical control and indicates that a possible source of increased error (either random or systematic) may be present. The observation of two consecutive results outside the warning limits is often regarded as cause for remedial action (see Section 7). Such an occurrence in which both results were on the same side of the mean value could be taken as an indication of increased systematic error. Alternatively, if the two results were on opposite sides of the mean, there would be stronger evidence for increased random error.

SECTION 5 - MEASUREMENTS REQUIRED FOR CONTROL CHARTS

Control charts can be used for all analytical techniques, but the tests required may vary in detail from one technique to another. However, the principles for choosing the control charts and tests to use are as follows:

a. A standard solution of known concentration is analysed at regular intervals (for example, in every batch of analysis) and the results are plotted on a control chart with the nominal concentration of the standard as the expected value. The scatter of the individual results gives a check on precision and their average value indicates any systematic changes in calibration. Provided that there is evidence that precision is similar for samples and standards (something which should not be assumed) this type of chart also provides indirect evidence on precision for routine samples. This control test is the most generally useful, and is therefore recommended as the minimum for normal use.

   Ideally, all control standards would be presented to the analyst as routine samples so that any possibility of falsely optimistic estimates of precision is avoided. However, this is often difficult to achieve, and an alternative approach may be useful. For this, a second analyst provides the first with control standards whose concentrations are varied, from batch to batch, within a narrow range around a fixed value. Variation between 80% and 120% of the chosen concentration is unlikely to result in any problems of interpretation caused by a dependence of standard deviation upon determinand concentration. The actual concentration of each solution analysed is not revealed until after analysis, the differences between the observed and true concentration being plotted on the control chart. Such a chart, having an expected value of zero, provides the desired information on accuracy.

   It is highly desirable that the stock standard solution used for the preparation of the control standard is different from that used to prepare the calibration standards. If the two standards were

prepared from the same source, then a deterioration in the stock standard solution and the consequent error in calibration could go undetected.

b. Direct evidence on the precision of sample analysis can be obtained by analysing two portions of a water sample, and plotting the difference between the two results on a control chart with zero as the expected value. If it is known that the precision of the analytical method concerned is significantly different from one sample type to another, care should be exercised in the choice of sample to be used for this chart. If this is the case it will be necessary to plot a separate chart for each sample type. Again, any tendancy to falsely precise results may be reduced by presenting the second portion of the sample to the analyst as an additional rather than as a replicate sample. This type of chart also provides a check on systematic error between duplicate determinations within a batch and may allow detection of such effects as drifting calibration during a batch of analysis.

c. Control tests (a) and (b) provide no direct evidence on the systematic error caused by the presence of other substances in samples. If the analytical method was selected on the basis of its freedom from interferences, the likelihood of systematic error arising from this source should be small. A routine check can be made by carrying out "spiking" recovery tests on samples and plotting the observed recoveries on a control chart with the theoretical recovery as the expected value. This type of test is not capable of detecting systematic errors which are independent of determinand concentration, but provides a valuable indication of the presence of some sources of systematic error - especially certain interference effects.

d. It is also useful to plot a control chart of blank determinations to aid in the detection of abnormal values, such as may be introduced by the use of a batch of contaminated reagents. This chart cannot be interpreted in the same way as those described in (a) to (c) above, because the fact that results of blank determinations are

higher or more variable (from one batch of analysis to another) than usual does not necessarily mean that the accuracy of results is affected. However, erratic variations in blank results are generally undesirable since they call into question the validity of the blank value as a suitable correction to be made to sample responses and may indicate the introduction of some source of sample contamination. This chart is to be used merely as a guide and there is therefore no need to insert warning or action lines.

The use of controls of different types is summarised in Table 1. Ideally, all these control charts would be maintained but in practice, owing to limitations on available time and effort, some compromise is often necessary. It is recommended, therefore, that, as a minimum, control tests of type (a) are included in each batch of analysis. Other tests can be made if more time and effort are available or if a particular type of error is considered to be likely (see Table 1).

Table 1. The use of control tests for checking different types of analytical error

Type of control test	Type of error checked
a. Standard solution; single determination in each batch of analysis.	Random error (total standard deviation). Systematic error due to calibration or blank determination.
b. Real sample; replicate determinations in each batch of analysis.	Random error (within-batch standard deviation). Systematic differences between replicate determinations in a batch (eg due to "carryover" or calibration drift).
c. Spiking recovery	Systematic error dependent on the determinand concentration.
d. Blank determination.	Some types of blank error (eg contamination problems).

SECTION 6 - CHOICE OF CONTROL SOLUTIONS

a. When samples always contain very similar concentrations of the determinand, that concentration is recommended for control standard solutions described in 5 (a) above. When samples contain a wide range of concentrations and standard deviation varies with concentration, at least two control standards of different concentration should ideally be analysed. However, the required effort may not be available, and if only one control standard is to be used, a decision on the best concentration is needed. Changes in the slope of the calibration curve are best detected by the use of control standards whose concentration is that at which the relative standard deviation is a minimum. This concentration usually corresponds to, or is close to, the upper limit of the concentration range of the method. A concentration near the upper limit of the analytical method is therefore suggested, if no other guide is available to the choice of control standard (for example, it may be desired to monitor analytical accuracy at some specified concentration of interest defined, perhaps, by a standard for water quality).

b. In control tests of the type described in 5 (b) above, it is suggested that samples for duplicate analysis are chosen with two criteria in mind. Control samples should be representative of the samples routinely analysed in terms both of their determinand concentration and of their sample type. It is necessary, for the successful interpretation of the control chart, that each observed difference between replicate determinations is a reflection of the same underlying variability. In other words, the samples should be chosen such that there is no change in the true standard deviation of measurements from batch to batch. Standard deviation may change with determinand concentration or with sample matrix. Some knowledge of the performance characteristics of the method is therefore necessary before suitable control samples can be chosen. Again, it may be desirable to maintain more than one chart, each chart covering a sample type and a range of concentration for which analytical variability can be considered to be constant.

c. In control tests of the type described in 5 (c), if the amount of determinand used for spiking is small, it is difficult (because the analytical precision is often relatively poor at lov concentration) to detect systematic error in the recovery, while if the amount added is large, the results for recovery may not reflect the errors for routine samples. Some compromise should be made on the spiking concentrations used; it is suggested that the concentration of the spiked sample is made as small as possible consistent with relatively precise determination of recovery. (See reference 2 for further discussion of this subject.)

SECTION 7 - CONSTRUCTION OF CONTROL CHARTS

The general principle of the construction of control charts is fairly simple and has been outlined above; however, it may be useful to provide guidance on the different approaches which may be adopted and the methods of estimating the appropriate standard deviation.

7.1 CONTROL CHARTS OF SINGLE RESULTS

During an initial period of, say, 20 batches one analysis of the control sample is carried out in each batch. The control sample should be analysed in the same way as routine samples (eg with respect to replication of analysis).

An estimate of the mean:

$$\bar{x} = \frac{\sum_{i=1}^{m} x_i}{m}$$

is calculated. This is used as the control line of the chart. For a control solution of fixed concentration - of the type described in 4 (a) - the total standard deviation of analytical results (ie the standard

deviation of any one result taken from any batch of analysis), σ_t, is required for the construction of the chart. An estimate, s_t, of total standard deviation will be obtained, if one is not already available from tests of the performance characteristics of the analytical method, by performing one determination on the chosen control sample in each batch of analysis for m batches:

$$s_t = \sqrt{\frac{\sum_{i=1}^{m} (x_i - \bar{x})^2}{m-1}}$$

where x_1 to x_m are the results obtained in batches 1 to m and $\bar{x}$ is the mean result from the m batches. This estimate of standard deviation will have m-1 degrees of freedom. As the chart progresses and more data points become available, the estimate, s_t, should be recalculated with a correspondingly greater number of degrees of freedom. The estimate, s_t, should not be considered a reliable indicator of the population standard deviation, σ_t, unless its associated number of degrees of freedom is greater that approximately 25. Thus, in the initial stages of the use of the chart until an estimate of s_t with at the very least 25 degrees of freedom is available, any control limits which may be drawn should be regarded as tentative. Nevertheless, it may be helpful, in the early stages of plotting a given chart, to draw in tentative control lines after an estimate of s_t with 10 degrees of freedom has been gained. These lines will aid in the early interpretation of the chart. It is also possible to vary the concentration of the control standard - within a range over which the precision of determinations can be considered to be constant. This allows the true value of the control solution used in any particular batch to be kept confidential from the analyst concerned. In this situation s_t remains the relevant standard deviation, but the difference d = O - E, (with due regard for their sign) are plotted on the chart as described in 4 (a), where O and E are the observed and expected concentrations, respectively. The expected value for the chart is zero.

7.2 CONTROL CHARTS OF MEAN RESULTS

Here the approach is the same as for single results except that n determinations are performed on the control sample in each batch analysis. The advantage of this chart over one consisting of individual measurements is that the influence of routine random error is reduced by a factor of $\sqrt{n}$ and therefore the probability of detecting a small bias is increased.

Again, the chart is plotted against the overall mean. The appropriate standard deviation (s_{tn}) is that which relates to the precision of the mean of n determinations from batch to batch. It can be estimated from

$$s_{tn} = \sqrt{\frac{\sum_{i=1}^{m} (\bar{X}_i - \bar{\bar{X}})^2}{m-1}}$$

where m is the number of batches for which data are available and $\bar{x}_i$ is the mean of the ith batch of n determinations and $\bar{\bar{x}}$ is the overall mean.

7.3 CONTROL CHART OF SPIKING RECOVERY

In this case the parameter of interest is the recovery of a known quantity(s) of determinand added to a natural sample. Two determinations are required one on the unspiked (X_o) and one on the spiked samples (X_s). ("Spiking" refers to the division of a sample into 2 portions to one of which is added a known quantity of determinand - the "spike".) The percentage recovery (A) is calculated:

$$A\% = \frac{(\bar{X}_s - \bar{X}_o) \times 100\%}{Sp}$$

(Note: (a) The added quantity, Sp, should be chosen so that the concentration of the spiked sample is near the upper limit of the range of the sample (7). (b) Any volume change caused by the spiking process must be corrected for when the recovery is calculated.) For control charts of spiking recovery, the relevant standard deviation, s_A, is given by:

$$s_A = \sqrt{\frac{\sum_{i=1}^{m} (A_i - \bar{A})^2}{m-1}}$$

where A_i is the recovery, in concentration terms, (it the observed difference between the concentration of the spiked and unspiked portions of the sample, uncorrected for the blank) in the ith batch and $\bar{A}$ is the mean recovery for m batches.

7.4 CONTROL CHART OF DIFFERENCES

For a chart of the differences between the results for duplicate determinations on real samples - as described in 4 (b) - the differences, D (R_1 - R_2), are plotted on the chart, where R_1 and R_2 are the results (uncorrected for the blank) for the first and second portions analysed in the ith batch. It is essential always to subtract the second result from the first and plot the differences with due regard to their sign. The expected value for the chart is zero. The relevant standard deviation, s_D, is calculated from:

$$s_D = \sqrt{\frac{\sum_{i=1}^{m} (D_i - \bar{D})^2}{m-1}}$$

where $\bar{D}$ is the mean difference between duplicates over m batches of analysis. The remarks made earlier (see 6 (a)) regarding the

recalculation of s_t to provide an estimate with a greater number of degrees of freedom apply equally here.

The requirement that the population standard deviation should be constant (ie that the same sources of variability should be operating during each control analysis) can create particular difficulty in this type of control test as compared with those involving standard solutions. When the standard deviation of results (and hence of differences between replicate determinations) changes markedly with determinand concentration, and there is not the possibility to choose, for the control analysis, samples of relatively constant determinand concentration, no one standard deviation will apply and the interpretation of the chart becomes very difficult. This type of chart is, therefore, principally of value when the determinand concentrations in samples lie within a sufficiently narrow range that essentially the same value of standard deviation is applicable to all samples. Of course, several control charts may be established for a number of relatively narrow concentration ranges and the results from duplicate analyses of samples entered on the appropriate charts.

If the relative standard deviation, r%, of analytical results if constant within the range of sample concentrations, the problem of non-homogeneity of variance may be overcome by plotting $200D/(R_1 + R_2)$ on the control chart instead of D. The expected value for the chart is the 0% and the warning and action limits are given by $2\sqrt{2}$ r% and $3\sqrt{2}$ r% respectively.

7.5 CONTROL CHARTS OF RANGE

A more general case of the control chart of differences is the control chart of range. In each batch of analysis a control sample is analysed n times ($n > 2$). The range is the difference between the greatest and smallest result.

The mean range $\bar{R}$ is calculated from the ranges R_i obtained in each of the m batches of analysis:

$$\bar{R} = \sum_{i=1}^{m} \frac{R_i}{m}$$

The action and warning limits are calculated as multiples of the mean range. (The standard deviation of range can be estimated from the mean range - for a given value of n.)

$$\text{Upper action limit} = D_2 \bar{R}$$
$$\text{Lower action limit} = D_1 \bar{R}$$

$$\text{Upper warning limit} = \bar{R} \left[\frac{1 + 2 (D_2 - 1)}{3} \right]$$

where D_1 and D_2 are obtained from Table 2 below:

Table 2. Factors for the computation of the upper and lower action limit of the range control chart (6)

n	D_1	D_2
2		3.267
3		2.575
4		2.282
5		2.115
6		2.004
7	0.076	1.924
8	0.136	1.864
9	0.184	1.816
10	0.223	1.777

7.6 CONTROL CHART FOR STANDARD DEVIATIONS

If more that 10 replicate analyses are carried out for a control sample within a batch, the control chart of standard deviations is superior to the range control chart.

For each subgroup (sample) the standard deviation s_j is calculated. The action and warning limits are derived from:

$$s = \sqrt{\sum_{j=1}^{m} \frac{s_j^2}{m}}$$

Upper action limit = $B_2 \cdot s$
Upper warning limit = $B_1^2 \cdot s$

Table 3. Factors for the computations of warning and action limit of a standard deviation control chart (6)

n	B_1	B_2
1		3.267
2		2.568
3		2.266
5		2.089
6	0.030	1.970
7	0.118	1.882
8	0.185	1.815
9	0.239	1.761
10	0.284	1.716
11	0.321	1.679
12	0.354	1.646
13	0.382	1.618
14	0.406	1.594
15	0.428	1.572
16	0.448	1.552
17	0.466	1.534
18	0.482	1.518
19	0.497	1.503
20	0.510	1.490

SECTION 8 - THE INTERPRETATION OF CONTROL CHARTS

Control charts, or at least the control limits, such as those described above are strictly valid only when the analytical results follow the Normal distribution. A closer approximation to the Normal distribution can be obtained by making n replicate determinations of a given control solution in a given batch, and plotting the mean results (the relevant standard deviation is then equal to the standard deviation of individual determinations divided by $\sqrt{n}$). However, it is recognised that the necessary effort will seldom be available. For many applications in the field of analysis the Normal distribution is likely to be sufficiently well obeyed for the recommendations above to be used generally.

The interpretation of control charts is not a subject about which it is possible to formulate rules specifying the course of action to be followed in any given situation. Although the action and warning limits provide a statistical basis for deciding whether or not the underlying performance has changed, the decision as to what should be done when lack of control is indicated will depend on many external factors. The knowledge of the factors which affect the performance of the analytical method, and the likely consequences of errors of increased size will all play a part in determining the interpretation of the charts.

The fact that a result is observed as out of control should not be disregarded if, for example, the method involved is easily capable of meeting the requirements for analytical accuracy. The power of one control analysis per batch (often performed on a standard solution which may not be subject to errors as large as real samples) to indicate a deterioration in analytical performance may not be very great (see below). Thus, it is advisable to take action when loss of control is signalled, since the control analysis may be a warning of increased error which may have been introduced some time previously and which may be more severe for real samples. It is therefore emphasised that control charts provide objective guidance in the control of analytical errors which should be viewed together with other information.

Another feature which should be considered in the interpretation of control charts is their ability to detect a given change in performance. A measure of the effectiveness of a control chart in this respect is the average run length (ARL). This is the average number of points which will be plotted on the chart before a result falls outside the control limits. Ideally, therefore, the ARL should be large in the absence of systematic error or increased random error and small when such factors are present.

Suppose a step change in the mean value of the measure variable occurs. The average number of points which would be plotted before such a change was signalled by a point outside the control limits would depend on the size of the change. Table 4 gives the ARL for the detection of changes of different sizes in the mean result from the true or expected value. For example, if a change in the observed value for the determination of a standard solution changed by an amount s, where s is the standard deviation of determinations at this concentration (perhaps due to the incorrect preparation of a stock calibration standard solution), then, on average, 44 batches of analysis would be performed before the control chart indicated a change in analytical accuracy by a point outside the 3s control limits. This response of the control chart may be considered, in some applications, rather less sensitive than required.

The ARL can be made shorter by adopting the rule that either a result outside the 3s control limits or two consecutive results outside the 2s control limits requires investigation. The effect of this for changes in the mean value of results and for changes in the standard deviation of results is shown in Tables 4 and 5, respectively. The ARL is made substantially shorter by adoption of this rule of interpretation, but the price paid for this increased sensitivity to changes in performance is an increase in "false alarms" (ie results out of control when there has been no change in mean or standard deviation). It is considered, however, that the benefit of more rapid detection of problems will outweigh this small disadvantage, in most applications. It is recommended, therefore, that action be taken when either action limit is crossed once or when two consecutive results fall outside the same warning limit, or opposite warning limits.

Table 4. Average Run Length for Shewhart charts for a change in mean value

Deviation of mean from true or expected value	Average Run Length	
	Rule 1	Rule 2
0.0 σ	370	276
0.1 σ	352	260
0.3 σ	253	174
0.5 σ	155	98
1.0 σ	44	25
1.5 σ	15	8
2.0 σ	6	4
3.0 σ	2	2

σ is the standard deviation of control determinations.
Rules of interpretation
Rule 1 - action is taken if one value is outside the 1 3σ action limits.
Rule 2 - as for Rule 1 but action is also taken if two consecutive values are outside the 2σ warning limit - on the same side of the chart.

Table 5. Average Run Length for Shewhart charts for an increase in standard deviation

Increase in standard deviation	Average Run Length	
	Rule 1	Rule 1
+ 0.0 σ	370	220
+ 0.1 σ	157	97
+ 0.3 σ	48	32
+ 0.5 σ	22	15
+ 1.0 σ	7	6
+ 2.0 σ	3	3

σ is the standard deviation of control determinations.
Rules of interpretation.
Rule 1 - action is taken if one value is outside the 1 3σ action limits.
Rule 2 - as for Rule 1 but action is also taken if two consecutive values are outside the 2σ warning limits (either upper or lower limit).

(Note that, in Table 4, the second action rule refers only to two consecutive results outside the warning limit on the same side of thechart. This has been done to illustrate the improvement in the detection of systematic error which such a rule can achieve. In practice, however, the rule described above is recommended to improve the ability to detect both systematic and increased random error.)

Other decision rules may be used to supplement the two described above. Two examples are given below.

- 8 successive results on the same side of the x-axis.
- 8 successive results showing an increasing or decreasing trend.

The consequence of adopting these additional decision rules will vary according to the type of error which is of interest. For example, the decision to treat 8 consecutive results on the same side of the x-axis as "out of control" will be of no benefit in detecting increased random error. It will, however, aid in the identification of small biases. As noted above, any increased power to detect departure from the state control will be accompanied by an increases incidence of "false alarms". A further point concerning run length is that it is itself subject to considerable variability. Thus, whilst Average Run Length can be used as a basis for comparing the efficiency of different control systems, the actual number of points plotted before an "out of control" is indicated may vary widely for a given set of experimental conditions.

It has been emphasised by many authors (see ref 5) that too much attention should not be paid to the exact probability levels associated with the action or warning limits. For example, the probability of observing a result outside the 3 standard deviation "action" limits is 0.0027. Given no systematic or increased random error this would correspond to a chance of one in three hundred and seventy of such an event. The validity of the particular value for probability level is dependent on the observations following the Normal distribution - an assumption not always justified particularly when single measurements are made. The significance and value of the action and warning limits

lies in the fact that they have been shown to be useful practical indicators of deviation from controlled conditions. In cases where points have fallen outside, for example, the action limits, it has usually proved fruitful to investigate and minimise sources of error.

SECTION 9 - CUMULATIVE SUM CONTROL CHARTS

In recent years control charts with a somewhat different theoretical basis from the Shewhart chart have been described (7, 8, 9, 10). These charts, known as cumulative sum or Cusum charts are, perhaps, not so widely applicable as the Shewhart chart but may have some advantages in specialised applications.

The basic principle of the most common type of Cusum chart is that a target or expected value is subtracted from the control observation. The resulting value - a deviation from the target - is used to calculate the cumulative sum of the differences from the target level which is then plotted against the serial number of the observation. When the average value of the observation corresponds to the target value the path of the Cusum will lie parallel to the time axis. Deviations of the average from the target value in a positive direction will result in a Cusum which slopes upwards. Similarly, negative deviations will produce a Cusum plot which slopes downwards. The greater the discrepancy between the average value, over any particular time interval, and the target the steeper will be the slope of the Cusum.

The advantage of plotting the results in this way is that changes in the average level over different intervals of time can be easily detected as changes in the slope of the chart. Deviations from a condition of statistical control are, therefore, detected as shifts in slope of the cumulative sum. The significance of the slope of the Cusum plot can be established by the use of a V shaped mask which is placed over the chart (Figure 2). A condition of statistical control is indicated if all points on the plot are contained within the arms of the V. The V-mask is equivalent to the control limits of the Shewhart chart. The

calculation of the angle, θ, of the V-mask and its positioning, d units from the latest point of the chart, are beyond the scope of this document and are described in references 7 and 8.

Cusum charts, by making use of past as well as present control data, can detect departures from a state of statistical control more rapidly than Shewhart charts under certain circumstances. The average run length for a Cusum chart, for the detection of a systematic error which is small in relation to the random error, is shorter than for a Shewhart chart. In cases where larger relative systematic errors (say, of one standard deviation or above) are present the advantage of the Cusum chart over the Shewhart becomes marginal, especially when the complexity of Cusum charts is taken into account.

When Analytical Quality Control effort is limited, the maintenance of Shewhart charts rather than Cusum charts is generally recommended. If additional effort for AQC becomes available, consideration should first be given to the generation of more effective control data. Only where control analyses are already of optimal type and frequency, or where special interest attaches to the detection of systematic errors which are small in relation to the random error, should additional effort be expended on the establishment and maintenance of Cusum charts.

SECTION 10 - QUALITY CONTROL IN SAMPLING

Attention to the quality and effectiveness of sampling procedures is essential if data of adequate accuracy are to be obtained. Many key issues concerning sampling are outside the scope of this report. However there are several important aspects of quality control relating to sampling.

It is necessary to extend any quality assurance measures adopted for the analysis of samples to their collection. A sound approach to quality assurance should cover as many aspects of sampling as possible.

Quality control measures in sampling have three main objectives:

- to provide a way of detecting sampling errors and hence a means of rejecting invalid or misleading data;

- to act as a demonstration that sampling errors have been controlled adequately;

- to indicate the variability of sampling and thereby to give a guide to an important aspect of overall error.

In ensuring the effectiveness of sampling the greatest emphasis should be placed on the choice of sound procedures at the outset. Subsequent activity is then placed on a firm footing.

Apart from general "good practice" aspects of quality assurance in sampling (eg preventive maintenance and checks on the calibration of sampling equipment, provision of written sampling protocols etc), the following quality control measures should be considered and put into practice wherever appropriate:

- the use of field blank samples. These are samples of deionised water which are taken into the field and treated, as far as is possible, in the same way as real samples. For example, the field blanks would be subjected to the same preparatory steps (eg filtration, centrifugation) as real samples and would be preserved and stored in the same way. The exact details of the approach to be followed will vary according to the individual sampling protocol. The guiding principle is that the field blank should be exposed to as many as possible of the potential sources of error which might affect real samples. Field blanks are an invaluable check on sources of sample contamination.

- the use of field check samples. In some situations, eg where sample stability is in question, it is useful to prepare a check sample of known determinand concentration and to treat this in the same way as a

real sample. Such a check sample may be prepared by dividing a sample into two and making a known addition to one portion. The recovery of the added determinand is a check that sample preservation, transport and storage are satisfactory and that undue loss, perhaps by adsorption of determinand or evaporation of volatile components, is adequately controlled.

- laboratory checks on the effectiveness of the cleaning of sample containers. Field blanks give some check that the sample containers are free from important contamination, but more extensive tests should be made before the chosen cleaning procedure can be regarded as acceptable.

- collection and analysis of duplicate samples. This is an invaluable guide to the random error in sample collection and therefore a way of assessing the uncertainty associated with the data.

REFERENCES

1. WILSON A L Approach to Achieving Comparable Analytical Results from a Number of Laboratories. Analyst 104, (1979), p273-289

2. CHEESEMAN R V and WILSON A L Manual on Analytical Quality Control for the Water Industry. Technical Report TR 66, Water Research Centre, 1978.

3. DAVIES O L and GOLDSMITH P L (editors) Statistical methods in Research and Production. 4th Edition revised. Edinburgh, Oliver and Boyd for ICI, 1972.

4. SHEWHART W A Economic Control of the Quality of Manufactured Products. Macmillan, London, 1931.

5. The Application of Statistical Methods of Industrial Standardization and Quality Control. British Standard 600, British Standards Institution, 1935.

6. ASTM Manual on Presentation of Data and Control Chart Analysis STP 150. American Society for Testing and Materials (1976).

7. WOODWARD R H and GOLDSMITH P L Cumulative Sum Techniques. Edinburgh, Oliver and Boyd for ICI, 1964.

8. DEWEY D J and HUNT D T E The Use of Cumulative Sum Charts (Cusum Charts) in Analytical Quality Control. Technical Report TR 174, Water Research Centre, 1982.

9. Data Analysis and Quality Control using Cusum Techniques. British Standard 5703, parts 1 to 4, British Standards Institution, 1982.

10. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY Analytical Quality Control in Water and Wastewater Laboratories. Cinncinnati, Ohio, The Agency, 1972.

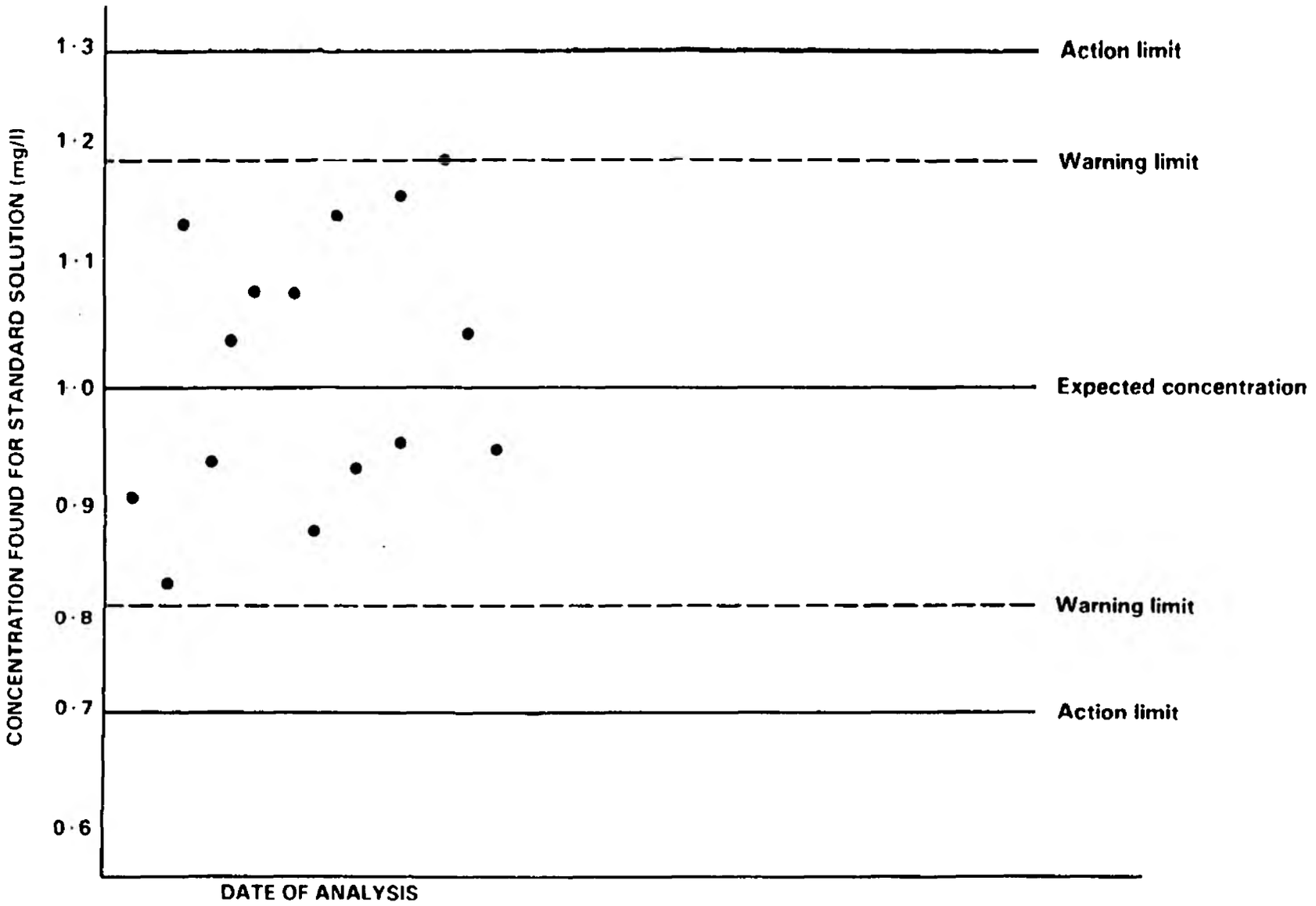


Figure 1
Example of a control chart for a standard solution

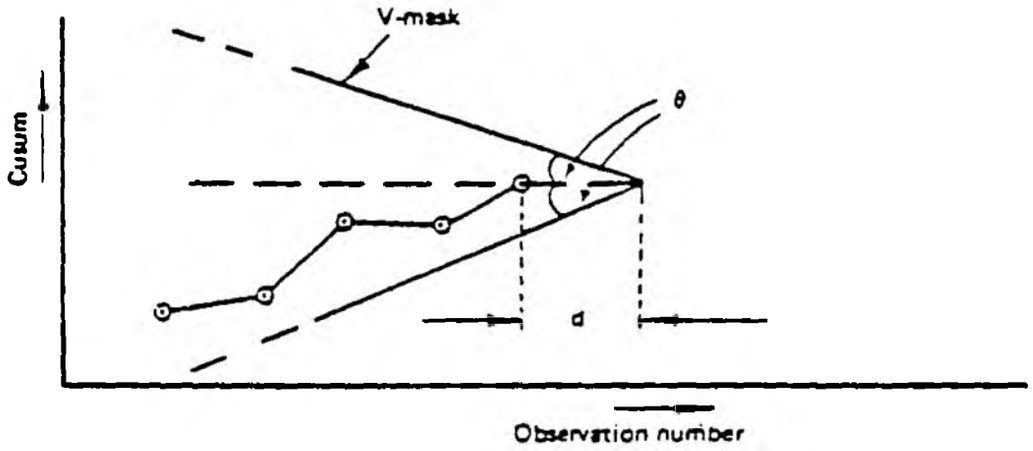


Figure 2 Cusum Chart

APPENDIX A

EXAMPLES OF THE CONSTRUCTION OF SHEWHART CONTROL CHARTS

Example 1a

Suppose that preliminary tests of analytical precision have given an estimate of total standard deviation of 0.1 mg/l (with 10 degrees of freedom) for the analysis of a standard solution of concentration of 1 mg/l, and that it has been decided to analyse a standard of the same concentration in each batch of routine analysis. The control chart would be constructed as in Figure 1. Action and warning limits could be drawn as shown but should be regarded as tentative.

If the first 15 batches of analyses then gave the results for this standard solution of 0.90, 0.82, 1.15, 0.93, 1.05, 1.08, 1.08, 0.87, 1.15, 0.93, 0.94, 1.17, 1.20 , 1.04, 0.94 mg/l, the standard deviation of these results should be calculated and pooled with the estimate already obtained from preliminary tests. The pooled standard deviation should then be used to insert revised action and warning limits. These are shown in Figure 2. Thus, the standard deviation of the above set of results is 0.12 mg/l with 14 degrees of freedom and the pooled estimate is, therefore, 0.11 mg/l with 24 degrees of freedom.

Example 1b

Suppose that the initial estimate of standard deviation for duplicate results is 0.1 mg/l at a concentration of 1.0 mg/l, and that it has been decided to perform duplicate analyses on samples of approximately this concentration in each batch of routine determinations. The standard deviation of the difference between control analyses will be $0.1 \times 2 = 0.14$ mg/l and the chart would then be constructed and the limits revised exactly as in example 1 except that the expected value is zero, and the tentative limits are at 0.28 mg/l (warning) and 0.42 mg/l (action).

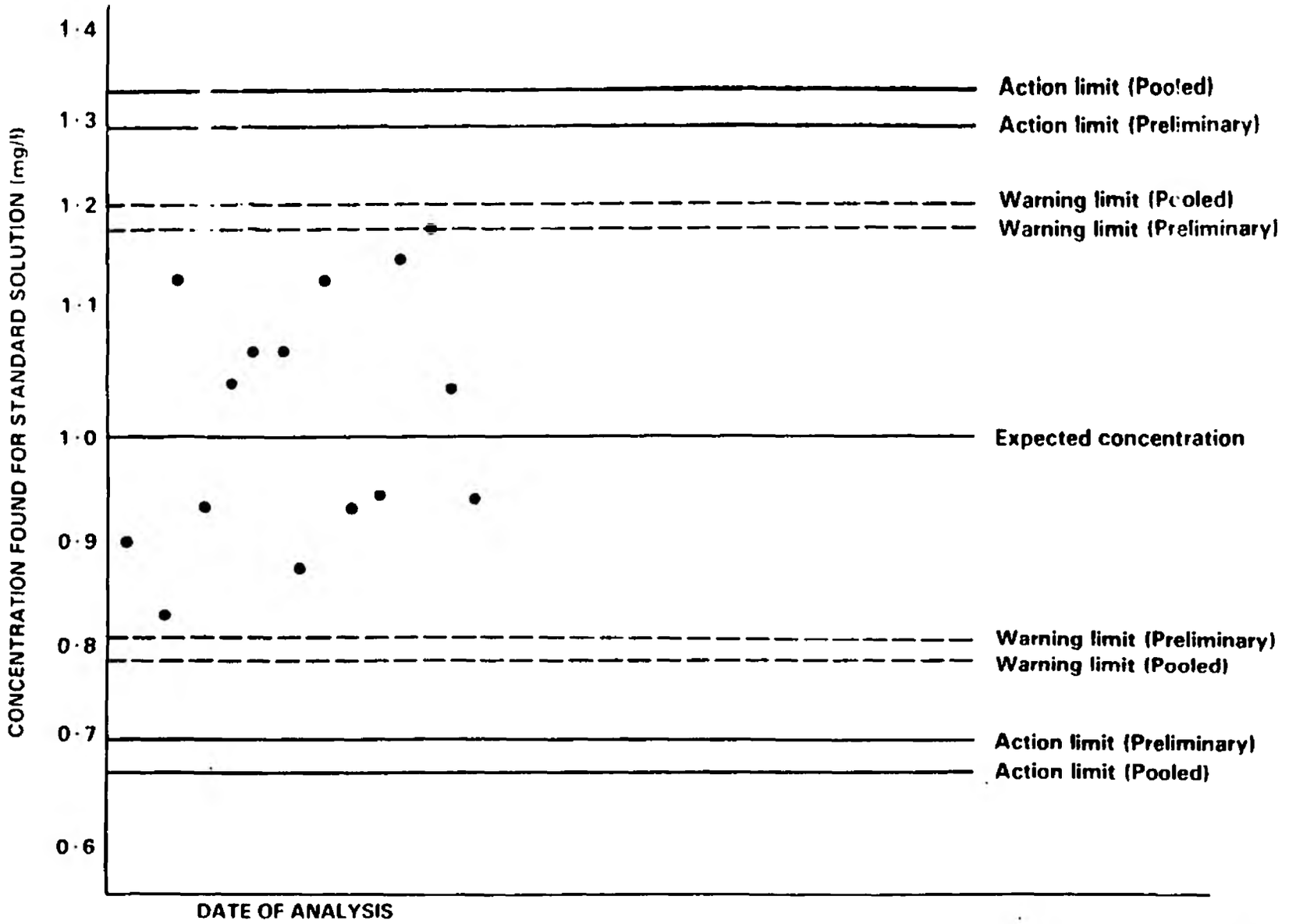


Figure A1.
Example of a control chart for a standard solution

Example 2. Updating Control Charts

This example is intended to illustrate the application of the recommendations relating to updating the limits of a control chart when a change in the precision of analysis is suspected. The case shown is for a moderate change in standard deviation. If a larger change in analytical precision takes place it should be possible to take action sooner than indicated. Conversely, a smaller change in precison will not be detected so readily.

The data plotted in Figure A2 come from the analysis of a control standard for the determination of lead in drinking water. The nominal concentration of the standard was 50 µg Pb/l and the precision target for determinations at this level was that the total standard deviation of results should not be greater than 5% (2.5 µg/l). The chart was established using an initial estimate standard deviation from precision tests. Control data (expressed in µg/l) are summarised below.

	Mean	Total SD
Initial data (from precision tests)	50.2	1.71 (14 degrees of freedom)
First 50 data points	49.9	1.62

Two results were noted as out of control (ie outside ± 2s) for the first 50 points. This is consistent with the expectation that chance variation might cause 5% of observations (ie 2.5 results) to lie outside the 2s limits. The data for the first 50 batches appear to be both in control and of satisfactory precision. (Note that any out of control results, for which on subsequent investigation the cause is identified, were not plotted on the chart since these obviously are not taken from the same population as the "in control" results.)

Inspection of the chart as it progressed from batch 50 onwards revealed that the spread of results appeared to have increased. This is manifest

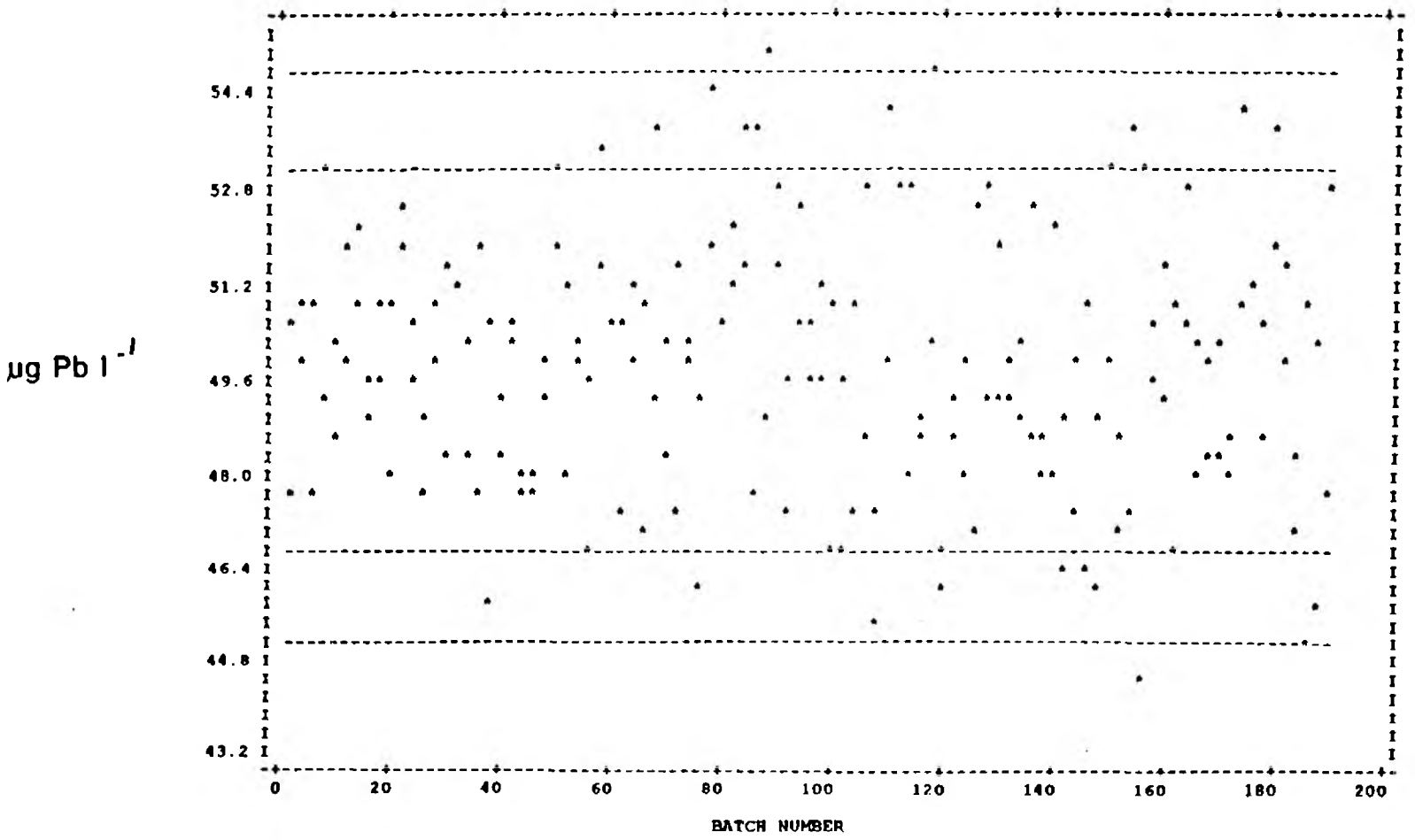


Figure A2. Control chart for lead determination

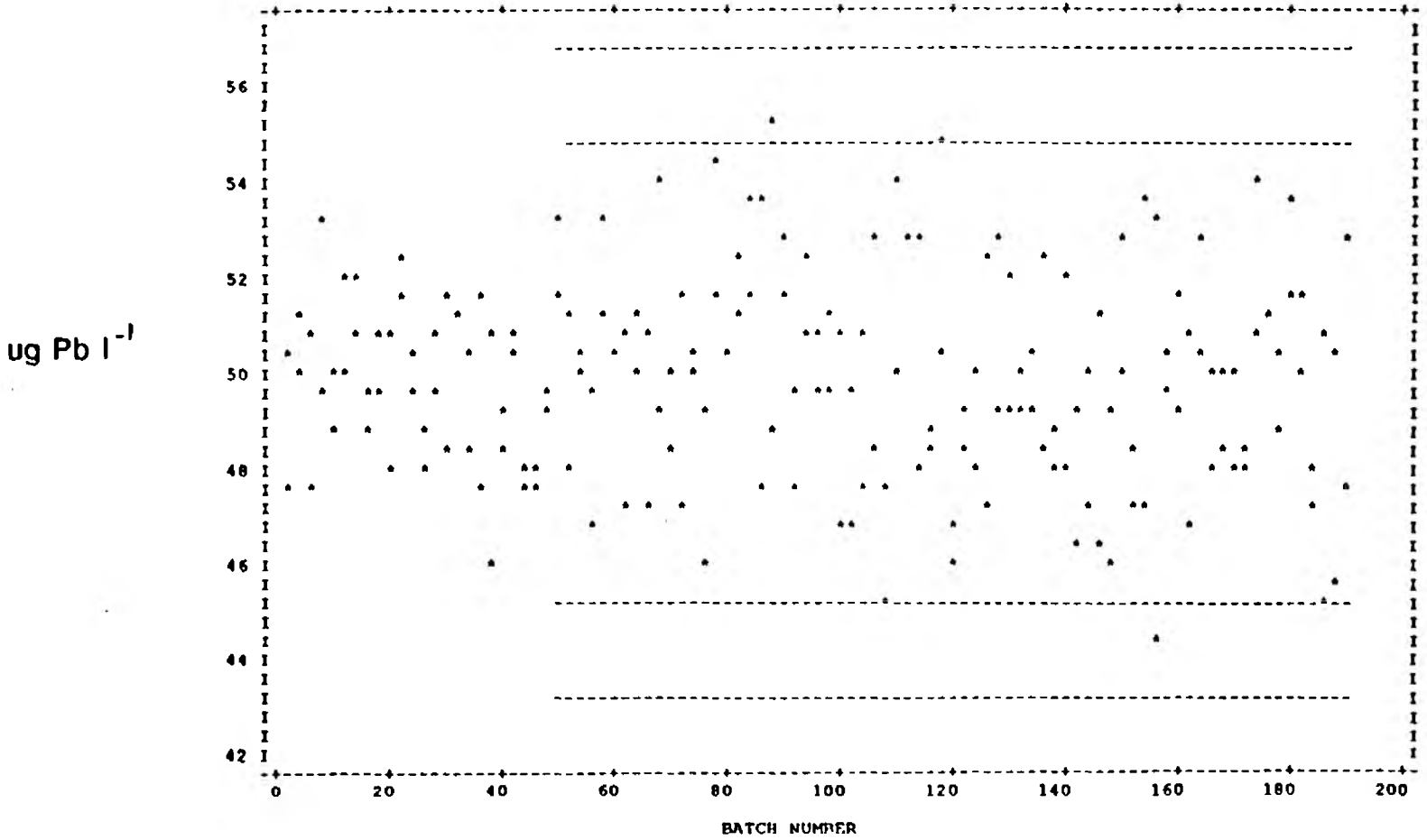


Figure A3. Control chart for lead with revised control limits

in the increase in the numbers of out of control results which appear beyond batch 50. Investigation of the analytical system revealed no clear reason for this. No action was taken until batch 110 when the following parameters were calculated:

		Total SD	Number Non assignable out of control results
Batches 1 to 50	49.9	1.62	2
Batches 1 to 110	50.0	2.00	10
Batches 50 to 110	50.2	2.32	8

Applying the rule that if the number of out of control results (in the last 60 batches) is outside the range 1 to 6 (inclusive), then the control limits should be re-drawn (see page) it appears that by batch 110 we have evidence that the precision has deteriorated. The original control limits no longer were applicable to the analytical system as it was operating at that time. Redrawing the control lines using the estimate obtained from batches 50 to 110 gave the chart shown in Figure A3. This new state of control was maintained for the remaining batches of analysis. Although the precision of the analytical system, despite this unexplained deterioration, did not exceed the maximum of 5% for the whole period under consideration, it is worthwhile examining the performance of the analytical system at other concentrations in the analytical range to ensure that the accuracy achieved still meets the specified requirements.

An alternative approach to detecting this deterioration of precision is to compare the standard deviations of the first 50 data points and the next 60 in an F test.

$$\text{Calculated F value} = \frac{2.32^2}{1.62^2} = 2.05$$

The critical F value from tables, for degrees of freedom of 60 and 50 at the 95% confidence level for a two sided test, is 1.74. The difference

is thus significant. Note that it is not possible to establish the statistical significance of this modest change in standard deviation very much sooner than batch 110. For example, the standard deviation of results for batches 50 to 90 was 2.04. An F test comparing this with the original standard deviation gave a calculated value of:

$$\frac{2.04^2}{1.62^2} = 1.58$$

The tabular value (30 and 50 degrees of freedom, p=0.05 (two sided)) is 1.88 - ie the difference is not shown to be significant at this stage.

Example 3. Control charts - detection of bias

The following example illustrates the effect on a Shewhart control chart of the introduction of of bias into the analytical system. A comparison of Shewhart and Cusum charts is given to show the greater sensitivity to bias of the latter approach.

The data plotted in Figure A4 come from the analysis of an in-house reference sample for the determination of aluminium in treated water. The sample was prepared by repeated determination of the aluminium concentration of a clean water sample of low background aluminium level and a similar matrix composition as the samples of interest. Several different techniques were used to give the concentration as 7.4 ± 1.1 µg/l. This (preserved) sample was then accurately spiked with 200 µg Al/l. The "reference" concentration for the sample was thus 207.4 ± 1.1 µg Al/l. This value was used as the central point of the chart. A standard deviation of 7.94 µg/l (known from previous analyses) was used as the basis for the control limits. This was subsequently confirmed as appropriate to the data by calculation of the standard deviation of results from batches 1 to 60 (7.94 µg/l), 61 to 120 (7.93 µg/l) and batches 121 to 170 (7.31 µg/l). The mean value for the first 60 batches of analysis (207.2 ± 1.0 µg Al/l) confirmed the choice of reference concentration.

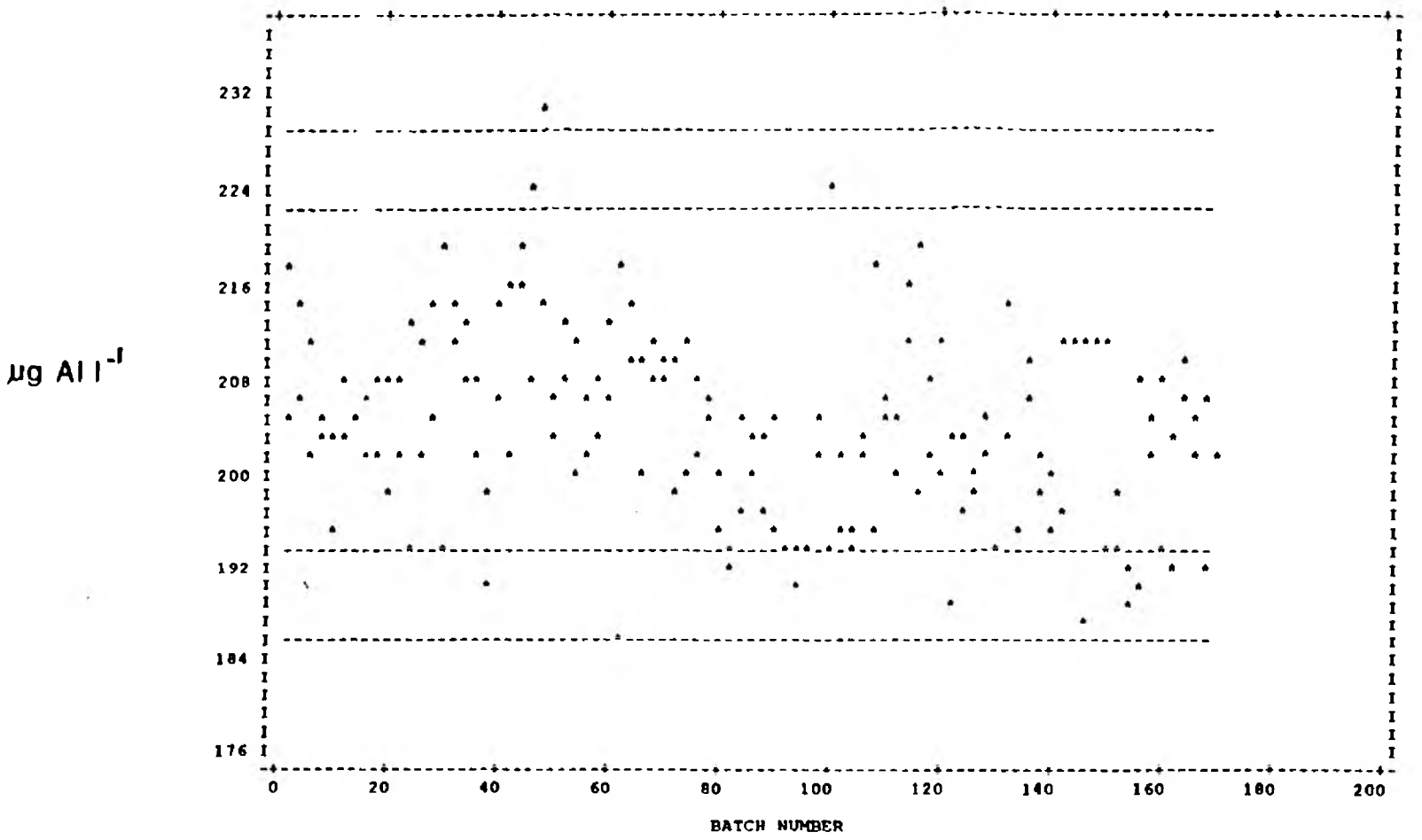


Figure A4. Control chart for aluminium determination in drinking water

An inspection of the chart (Figure A4) might at first reveal only that the analysis is proceeding satisfactorily, though closer examination might suggest that in the second half of the chart there were too many out of control values on the lower side of the mean. This was attributed to a change in the true mean from the reference concentration. The mean result for batches 120 to 170 is 201.1 µg/l with a standard error of 1.0 µg/l. This, given that the uncertainty on original estimate of the reference concentration was of the same size, indicated a statistically significant bias of around 6 µg/l or 3%. It is not clear whether the bias is due to a slow drift in measured values or due to some form of step change in performance. The point at which the bias first appears is also difficult to decide - probably between batches 65 and 85.

Figure A5 shows a plot of the cusum of the difference between the reference concentration of 207.4 µg/l and the measured value for the 170 batches of analysis. Note that the slope of the cusum is the indicator of the level at which aluminium concentrations are being reported. The initial portion of the graph is flat. This indicates that the observed data are of mean near to the reference concentration. (The fact that the mean cusum of this portion is near to zero is not of great importance - there was no early deviation from the reference value.) However, it is clear that something occurred at around batch 80 (from the graph it is possible to say that this change happened between batches 78 and 82). Here the cusum slopes abruptly and consistently downwards. This behaviour corresponds to a step change in the observed results - each new measurement changes the cusum by the same amount, leading to a straight plot. The gradient of this latter part of the cusum gives a measure of the size of the bias intoduced at batch 80. The slope is -600/(170-80) = -6.67 µg/l per measurement, ie the mean has dropped by 6.7 µg/l. This is in good agreement with the estimate from the Shewhart chart.

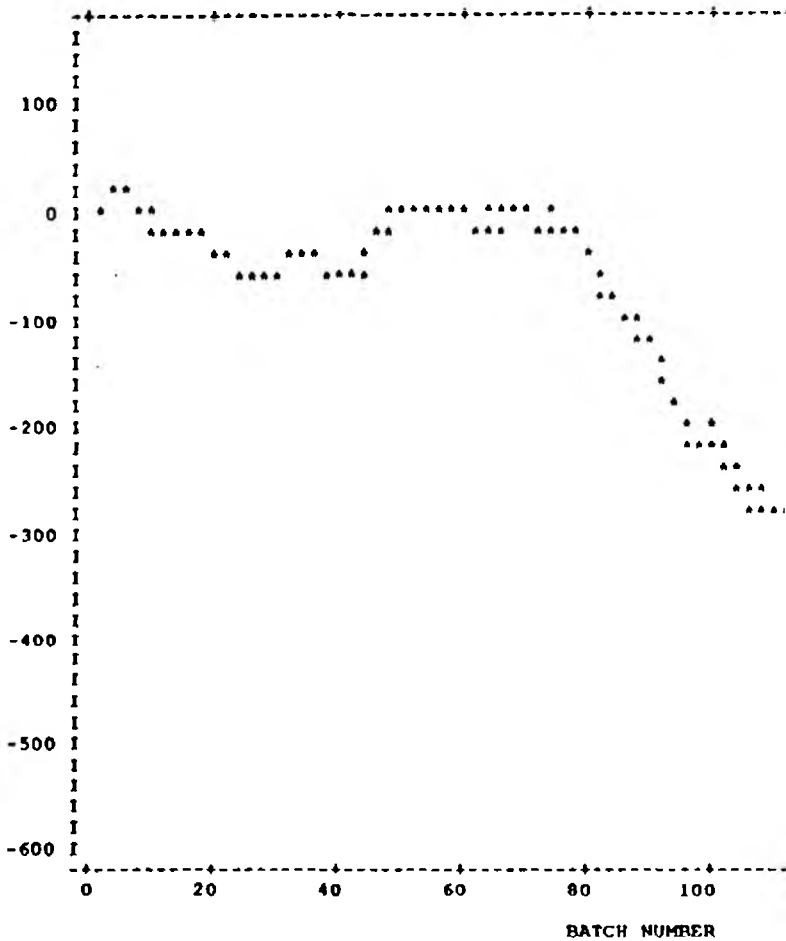
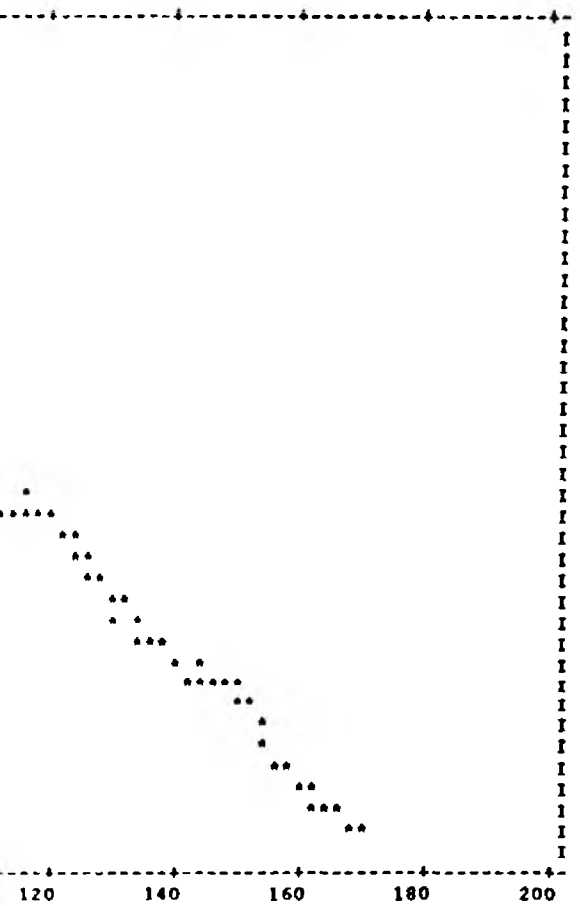


Figure A5. Cusum chart of Al data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