Chapter 6

Control Charts in the Analytical Laboratory

References

1. Manfred Reichenba¨cher l Ju¨rgen W. Einax ,,„Challenges in Analytical Quality Assurance, springer, 2011. Chapter 8
2. Piotr Konieczka and Jacek Namie´snik “Quality Assurance and Quality Control in the Analytical Chemical Laboratory: A Practical Approach, Taylor & Francis Group, 20009. Chapter 1.9
3. W. Funk, V. Dammann, G. Donnevert, Quality Assurance in Analytical Chemistry: Applications in Environmental, Food, and Materials Analysis, Biotechnology, and Medical Engineering”, John Wily, 2007. Chapter 2.6.7

Introduction/Control charts

- For any laboratory that performs a particular activity time and time again, showing the results in a control chart is a good way to monitor the activity and to discover whether a change has caused some deviation in the expected results.
- Walter Shewhart in 1924 designed a chart to indicate whether or not the observed variations in the percent of defective apparatus of a given type are significant; that is, to indicate whether or not the product is satisfactory"
- This was the first control chart, and it has been the basis of statistical quality control ever since
- The data obtained regularly from the QC materials are, in general, evaluated by control charts.
- The user can define warning and action limits on the chart to act as 'alarm bells' when the system is going out of control.
- A control chart is simply a chart on which measured values of whatever is being measured are plotted in time sequence,
- for instance, the successive values obtained from measurement of the quality control sample.
- By plotting this information on a chart, a graph is produced in which the natural fluctuations of the measured value can readily be appreciated.

Introduction/Control charts

- Control charts are extremely valuable in providing a means of monitoring the total performance of the analyst, the instruments, and the test procedure and can be utilized by any laboratory.
- There are a number of different types of control charts but they all illustrate changes over time.
- In the following, Shewhart charts and CuSum charts will be described.

Shewhart Charts

- **It is typically used to monitor day to-day variation of an analytical process.**
- **Measurement value is plotted on the *y-axis against time or successive measurement* on the *x-axis.***
- ***The measurement value on the y-axis may be expressed as* an absolute value or as the difference from the target value.**
- **The QC sample is a sample typical of the samples usually measured by the analytical process, which is stable and available in large quantities.**
- **This QC sample is analyzed at appropriate regular intervals in the sample batches.**

Shewhart Charts

- **As long as the variation in the measured result for the QC sample is acceptable, it is reasonable to assume that the measured results for test samples in those batches are also acceptable.**
- **How do we determine what is acceptable and what is not?**
  - **First of all, the QC sample is measured a number of times (under a variety of conditions which represent normal day-to-day variation).**
  - **The data produced are used to calculate an average or mean value for the QC sample, and the associated standard deviation.**

- **The mean value is frequently used as a 'target' value on the Shewhart chart, i.e. the value to 'aim for'. The standard deviation is used to set action and warning limits on the chart.**

Shewhart Charts

- **Once the chart is set up, day-to-day QC sample results are plotted on the chart and monitored to detect unwanted patterns, such as 'drift' or results lying outside the warning or action limits.**
- **In the Figure below, Shewhart charts have been used to show four types of data:**

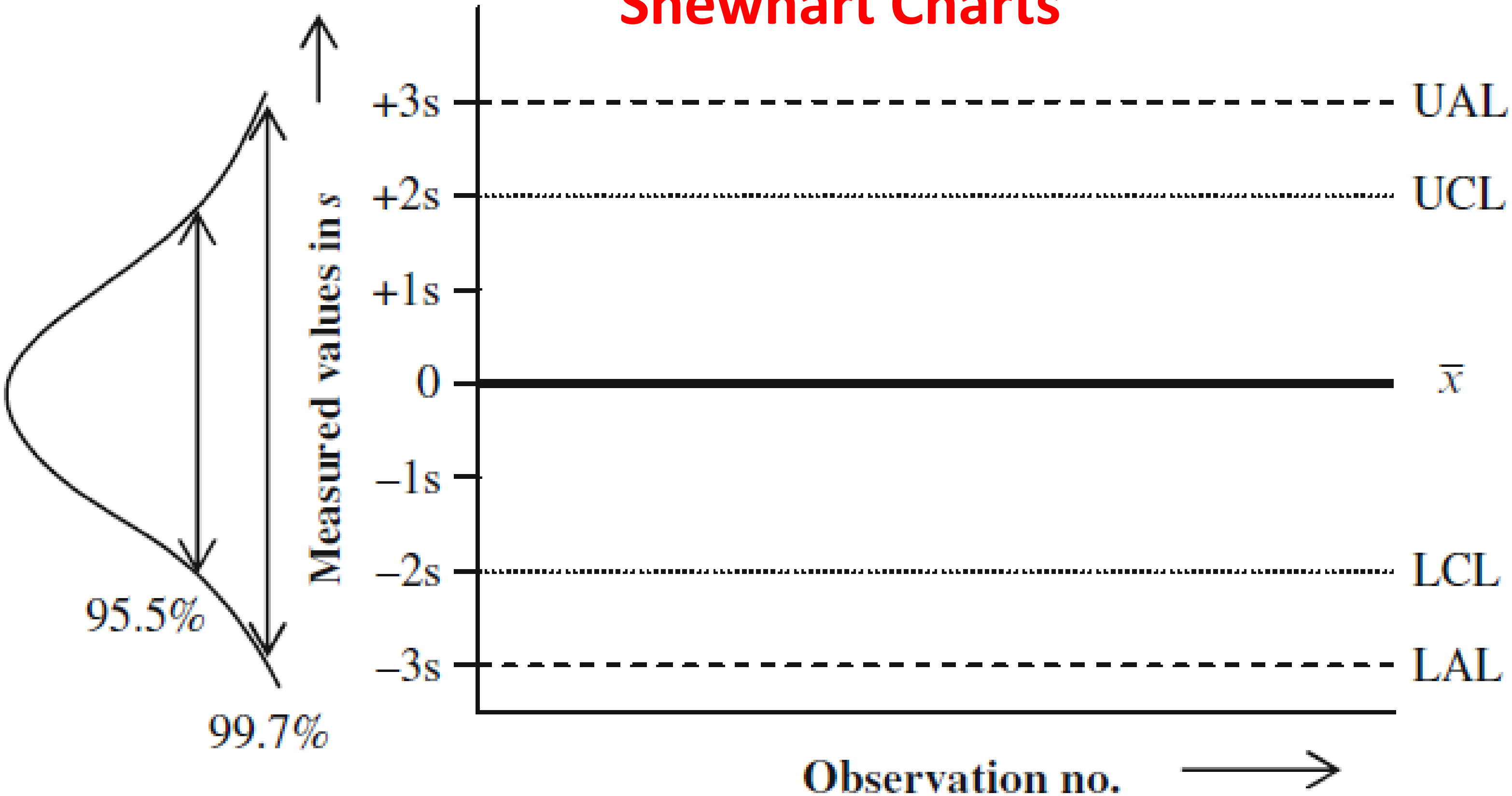
  (a) data subject to normal variation,

  (b) as in (a) but displacement from the target value,

  (c) gradual drift and

  (d) step-change.
- **To keep things simple, action and warning limits have only been included in (a).**

Shewhart Charts



The general pattern of a Shewhart chart and the curve of the normal distribution of the analytical results obtained in the pre-period with the "true" $\bar{x}$ value and the limits at the significance levels P = 95.5% and P = 99.7%; respectively

Shewhart Charts for mean values

- The mean value control chart corresponds to the original form of the Shewhart chart; however, in contrast to industrial product quality control, it is mostly applied to single values in analytical chemistry.
- A mean value control chart serves mainly to validate the precision of an analytical process. Since systematic changes such as trends can also be detected, the accuracy may also be monitored to a limited extent.
- The **central line** of the control chart is **a mean** value around which the measured values obtained by observations vary at random.
- The mean value $\bar{x}$ is the "**true value**" obtained by measurements of an **in-house reference material** or given from **certified referen**

  materials.
- Mostly, the assigned value is obtained in the pre-period, or the **mean of the most recent observations** considered to be under control should be used as the centre line.
- Measured values which lie on the central line are assumed to be **unbiased**.

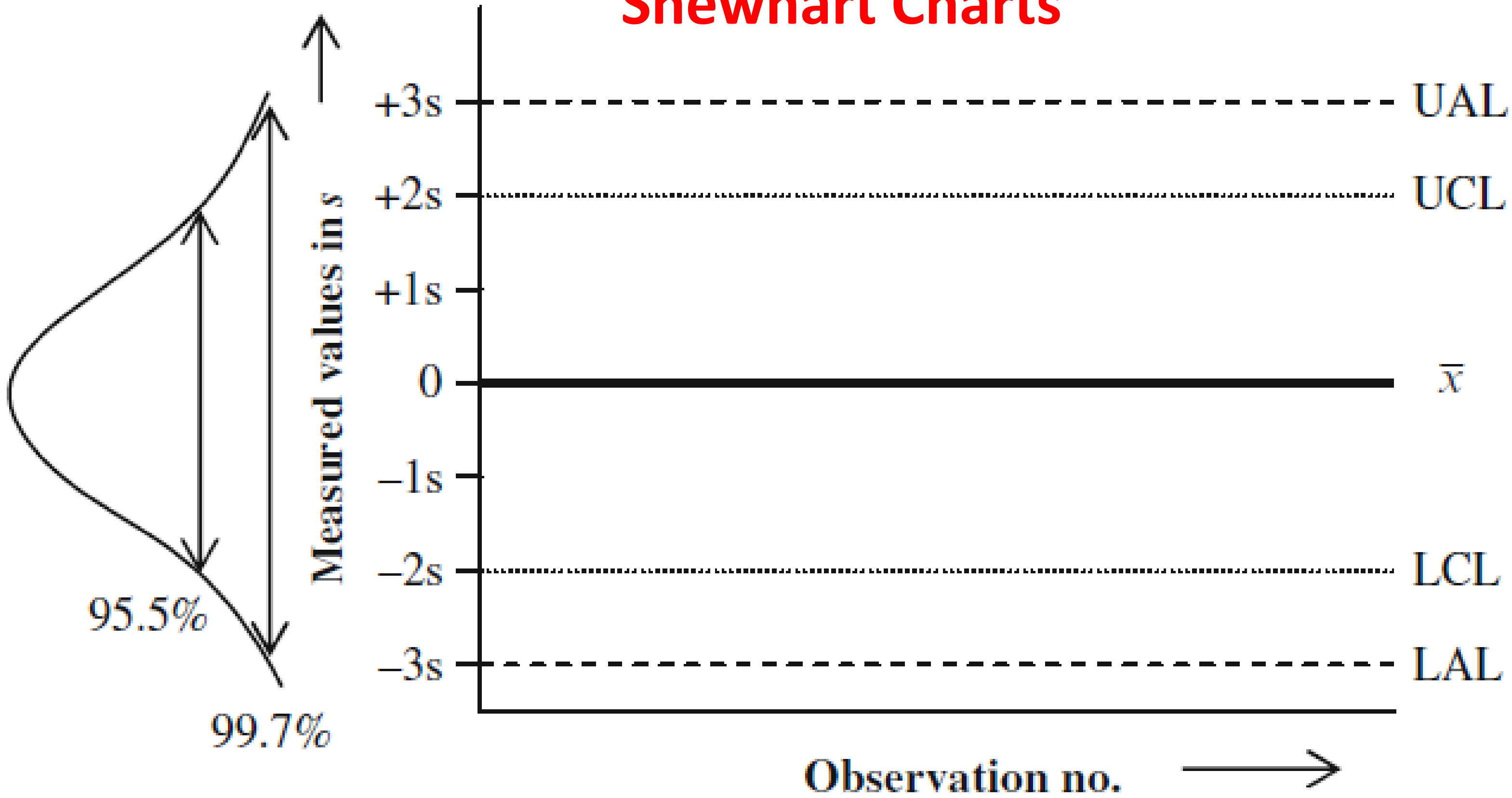
Shewhart Charts for mean values

- Using the mean μ and the standard deviation s obtained, the upper and lower action limit lines UAL and LAL and the upper and lower warning limit lines UWL and LWL, respectively, are constructed, as in the following equations
- Warning limit lines WL: $\boxed{\bar{x} \pm 2 \cdot s}$

Action limit lines AL: $\boxed{\bar{x} \pm 3 \cdot s.}$

- **Note that the warning limit lines are also called control limit lines CL.**
- **In practice, the standard deviation s will be unknown and will have to be estimated from historical data.**
- **On the assumption that the frequency distribution of the measured values follows a normal distribution, the three-sigma (3σ 0r 3s) limits include 99.7% of the area under a normal curve, and the two-sigma (2σ or 2s) lines include 95.5% of the values, as shown in the Fig.**

Shewhart Charts



The general pattern of a Shewhart chart and the curve of the normal distribution of the analytical results obtained in the pre-period with the "true" $\bar{x}$ value and the limits at the significance levels P = 95.5% and P = 99.7%; respectively

In other words:

- **The range of $\pm 2s$ *on either side of the central line covers 95.5% of the area underneath* the curve, i. e. the probability of a "false alarm" in this area is 4.5%, and a single transgression of this limit is tolerated.**
- **The probability of a value exceeding the $\pm$ 3*s limit is 0.3%, i. e., if this occurs, then it is with fair certainty an out-of-control* situation.**
- **During the evaluation of data from the preliminary period, the detection of an out-of-control situation already present in this period indicates that corrective measures are urgently required before routine analysis can begin**

- **A Shewhart control chart constructed according to the Figure given above can be applied as:**
  - **Mean control chart, preferably, for recognition of the precision or trends of an analytical method.**
  - **Blank control chart, for control of reagents and measurement instruments. Note that blank control charts include not analytical results but measured values.**
  - **Recovery control chart, for control of proportional systematic errors caused by the matrix.**
- **We will deal with the mean control chart**

Preparing the control chart

- **Conduct 10–20 measurements for a standard sample.**
- **Calculate the mean x_m *and the standard deviation SD; both values should be* determined for the unbiased series, that is, after the initial rejection of outliers.**
- **Test the hypothesis about a statistically insignificant difference between the obtained mean and the expected value using Student's *t test***
- **If the hypothesis is not rejected, start preparation of the first chart:**

1. **Mark the consecutive numbers of result determinations on the *x-axis of* the graph, and the values of the observed characteristics (the mean) on the *y-axis.***
2. **Mark a central line CL on the graph corresponding to the reference values of the presented characteristic, and two statistically determined control limits, one line on either side of the central line; the upper and lower control limits (UAL and LAL, respectively), or in other words the upper and lower warning limits.**
3. **Both the upper and lower limits on the chart are found within ±3SD from the central line, where SD is the standard deviation of the investigated characteristics.**

- ± 3SD (so-called action limits) show that approximately 99.7% of the values fall in the area bounded by the control lines, provided that the process is statistically ordered.
- The possibility of transgressing the control limits as a result of random incident is insignificantly small; hence, when a point appears outside the control limits ±3SD it is recommended that action be taken on the chart.
- Limits of ±2SD are also marked; however, the occurrence of any value from a sample falling outside these limits is simply warning about a possible transgression of the control limits; therefore, the limits of ±2SD are called warning limits (UWL and LWL).
- Mark the obtained measurement results for 20 consecutive samples as follows:

How to read the measurement results on the chart

- If a determination result is located within the warning limits, it is considered satisfactory.
- The occurrence of results between the warning limits and action limits is also acceptable; however, not more often than two results per 20 determinations.
- If a result for a test sample is found outside the action limits, or seven consecutive results create a trend (decreasing or increasing), calibration should be carried out again.
- There exist three other signs indicating the occurrence of a problem in the analyzed arrangement, namely:

How to read the measurement results on the chart

- **Three consecutive measurement points occurring outside the warning limits, but within the action limits.**
- **Two subsequent measurement points being outside warning limits, but in the interval determined by the action limits, on the same side of the mean value.**
- **Ten consecutive measurement points being found on the same side of the mean value.**
- **The most likely explanation when a point exceeds a control limit is that a systematic error has occurred or the *precision of the measurement has deteriorated.***

Shewhart control charts based on the standard deviation of the mean

- **In some cases the number of replicates appears in the standard deviation of the mean (= σ/ √*n*), *are used to set the acceptable* limits of the graph**
- **The chart is made according to the following steps:**

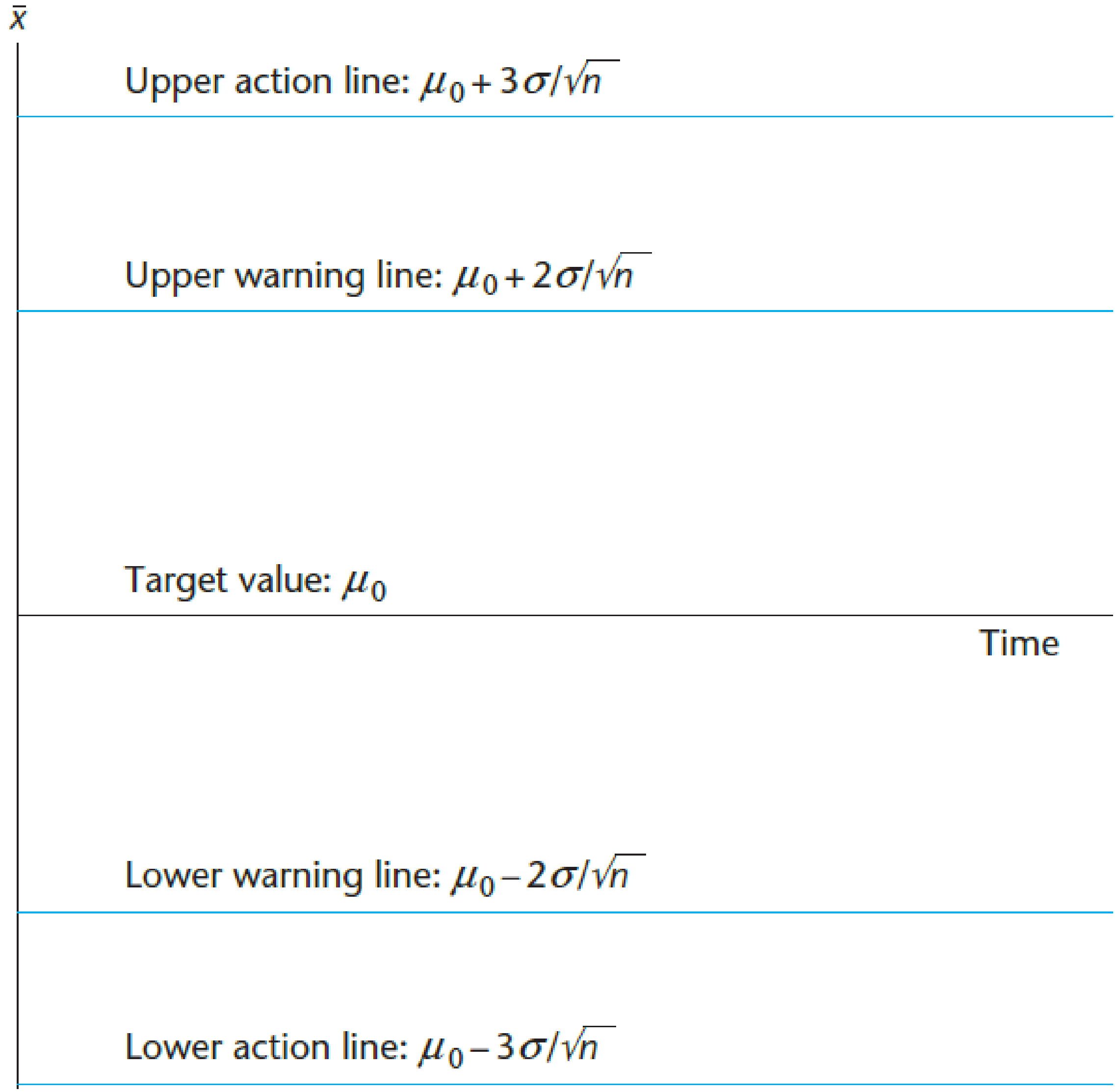
1. Plot the daily mean (x*i) for each of the daily results against day.*

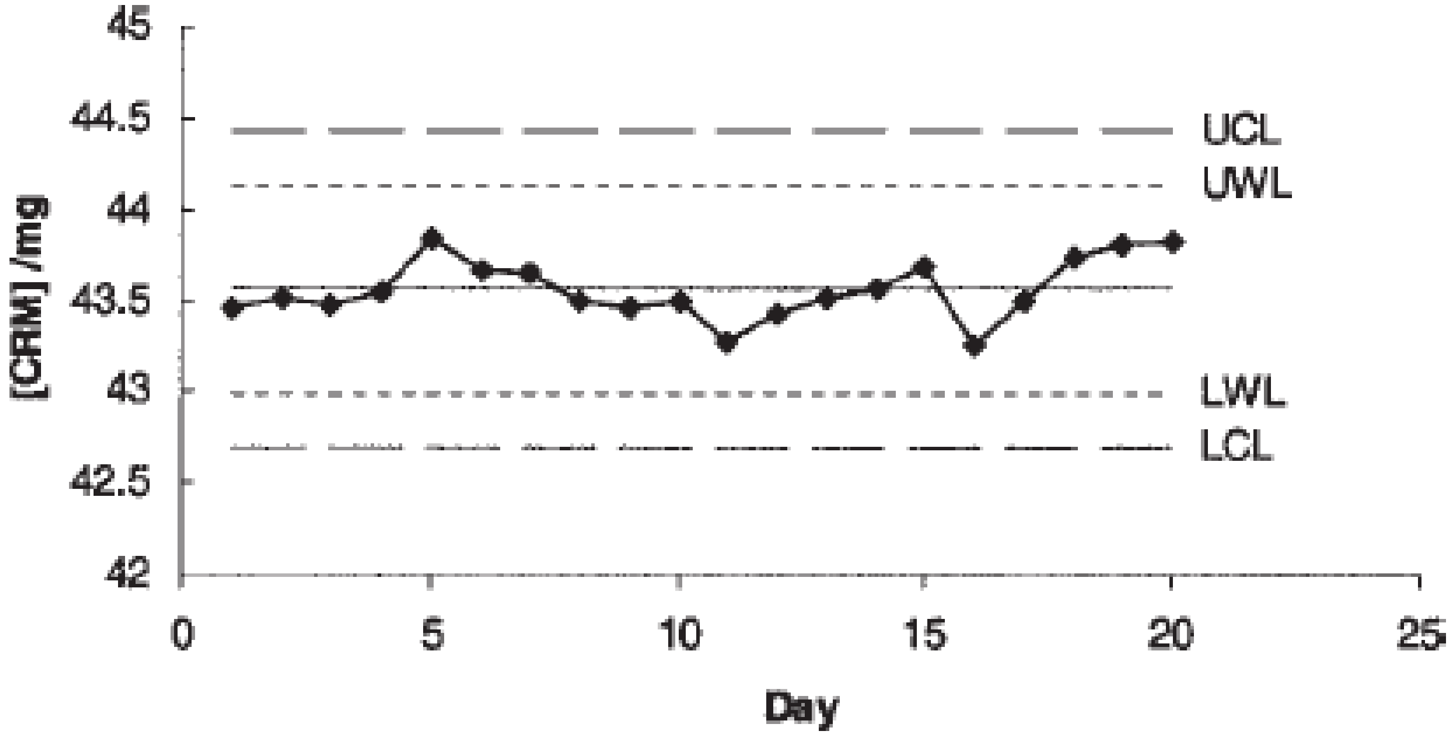
2. Draw a line at the global mean ([).

3. Draw warning lines at [+ 2×*s/√n and [– 2×s/√n.*

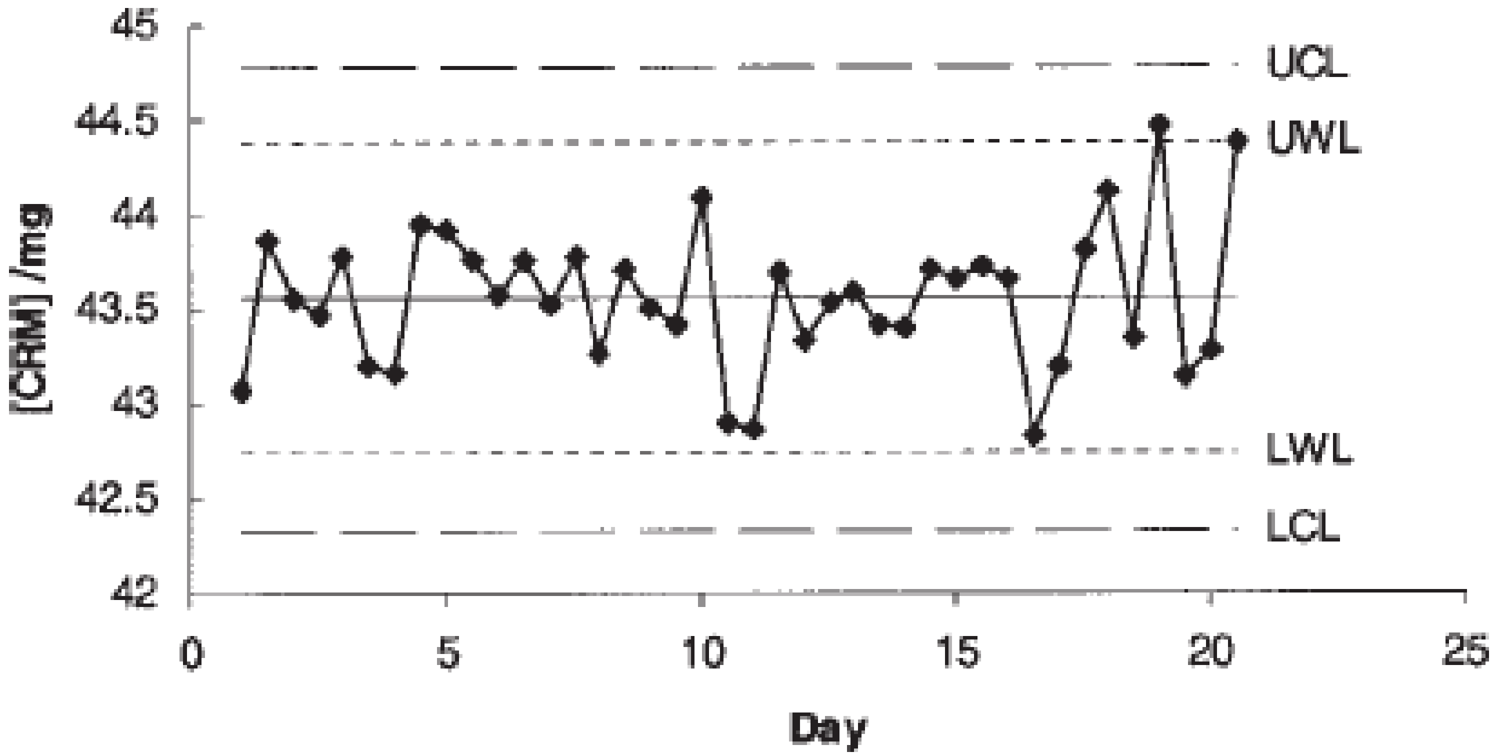
4. Draw action lines at [+ 3×*s/√n and [– 3×s/√n*.

Shewhart chart for mean values/based on standard deviation of the mean





Shewhart means plot of the duplicate analysis of a certified reference material, twice per day for 20 days. Each point is the mean of the day's four results. Warning limits (UWL and LWL) are at the global mean ± 2×*s*/√4 and control (action) limits (UCL and LCL) at the global mean ± 3×*s*/√4, where *s* is the standard deviation of all the data.



Shewhart means plot of the duplicate analysis of a certified reference material, twice per day for 20 days. Each point is the mean of one set of duplicate results. Warning limits (UWL and LWL) are at the global mean ± 2×*s/√2 and control (action) limits (UCL and LCL) at the* global mean ± 3×*s/√2, where s is the standard deviation of all the data*.

Example

Draw a Shewhart chart for the 20 given measurement results obtained for the test samples. Mark the central line, and the warning and action lines.

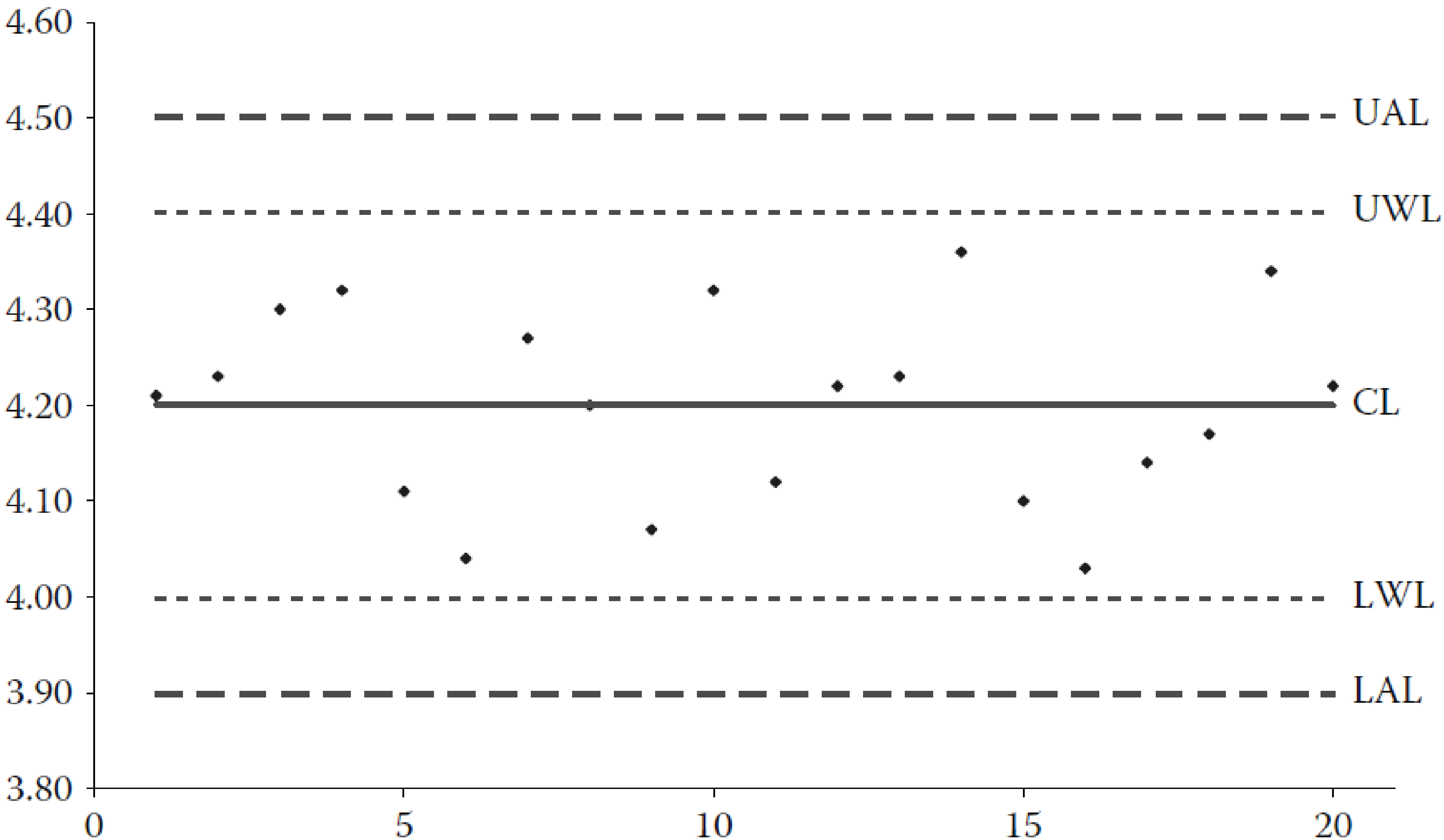
Data: result series:

1	4.21	**11**	4.12
2	4.23	**12**	4.22
3	4.30	**13**	4.23
4	4.32	**14**	4.36
5	4.11	**15**	4.10
6	4.04	**16**	4.03
7	4.27	**17**	4.14
8	4.20	**18**	4.17
9	4.07	**19**	4.34
10	4.32	**20**	4.22

Mean	4.20
SD	0.1005
UAL	4.50
UWL	4.40
LWL	4.00
LAL	3.90

$$\text{UAL and LAL} = \bar{x} \pm 3s$$

$$\text{UWL and LWL} = \bar{x} \pm 2s$$

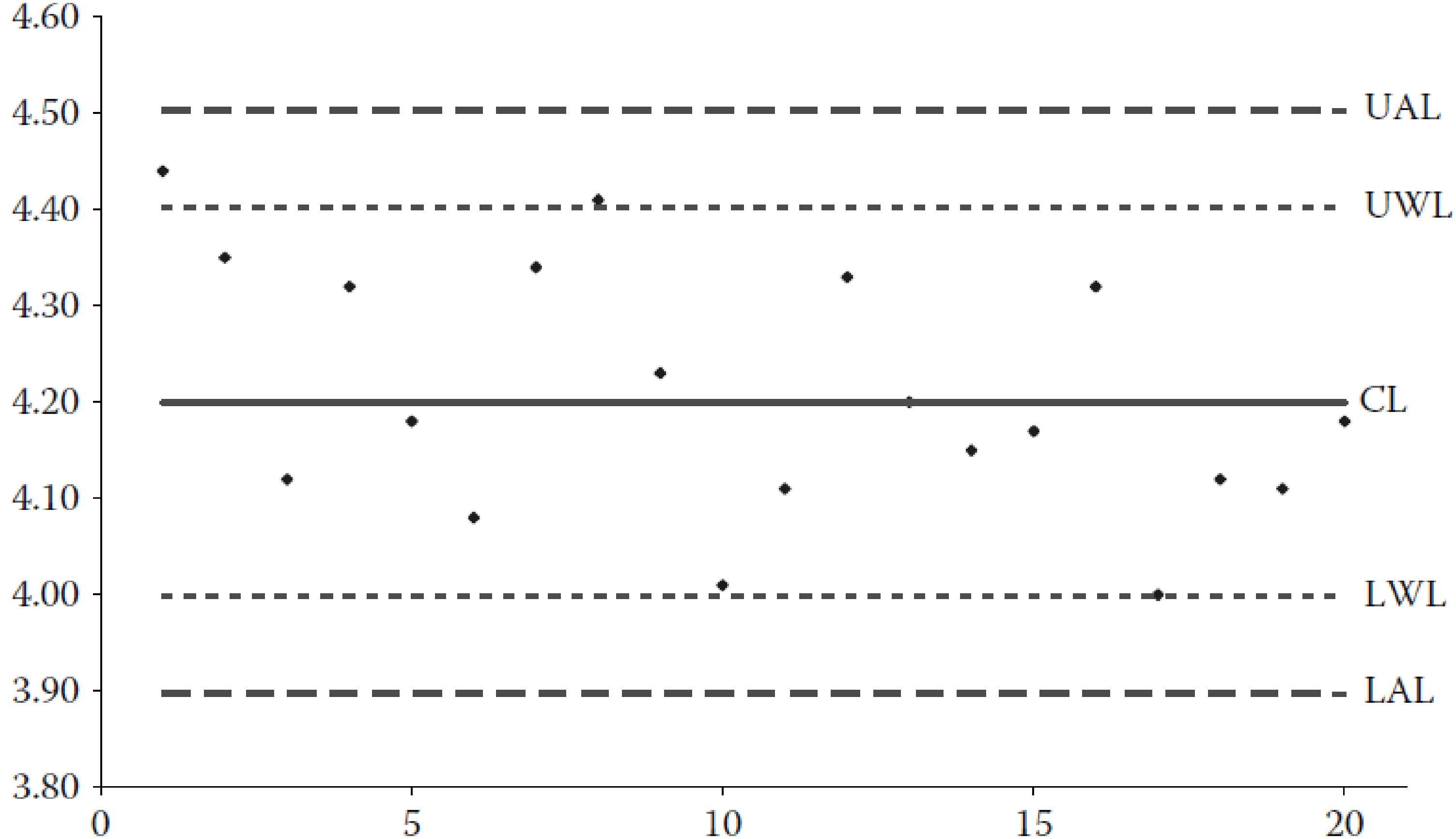

4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
0
5
10
15
20
UAL
UWL
CL
LWL
LAL

Example

Mark the following data from the previous example on the chart.

	Data	Conclusior			
1	4.44	!	**11**	4.11	ok
2	4.35	ok	**12**	4.33	ok
3	4.12	ok	**13**	4.20	ok
4	4.32	ok	**14**	4.15	ok
5	4.18	ok	**15**	4.17	ok
6	4.08	ok	**16**	4.32	ok
7	4.34	ok	**17**	4.00	ok
8	4.41	!	**18**	4.12	ok
9	4.23	ok	**19**	4.11	ok
10	4.01	ok	**20**	4.11	ok

$Mean_1$	4.20
SD_1	0.101
$Mean_2$	4.21
SD_2	0.128
UAL	4.50
UWL	4.40
LWL	4.00
LAL	3.90



4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
0
5
10
15
20
UAL
UWL
CL
LWL
LAL

Example

Draw a new chart based on the data from the previous example.

Solution:

- Values 1 and 8 have been removed from the set of data. The remaining values were used to calculate the means and the standard deviation.
- The variances were compared using the Snedecor's *F test, and then (with variances* not differing in a statistically significant way) the mean were compared using the Student's *t test.*

	Series 1		Series 2
No results, n	20		18
Standard deviation, SD	0.101		0.111
Mean	4.200		4.184
$n/(n-1)SD^2$	0.011		0.013
F		1.22	
$F_{crit(0.05,\ 17,\ 19)}$		1.85	
$F < F_{crit}$			
t		0.456	
$t_{crit(0.05,\ 36)}$		2.031	
$t < t_{crit}$			

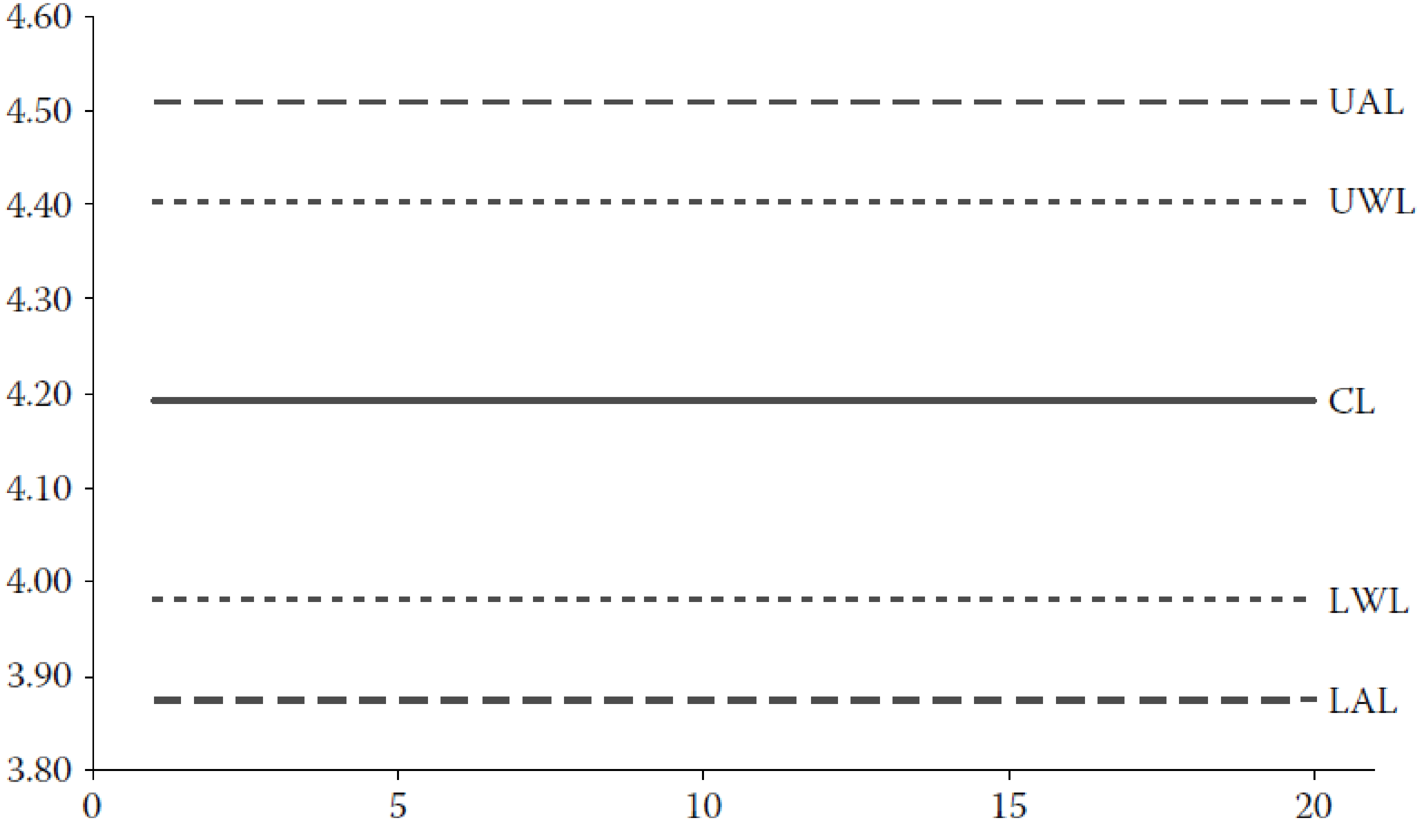
Mean	4.19
SD	0.106
UAL	4.51
UWL	4.40
LWL	3.98
LAL	3.88

$$F = \frac{\frac{n_1}{n_1 - 1} \cdot SD_1^2}{\frac{n_2}{n_2 - 1} \cdot SD_2^2}$$

Student's t test

$$t = \frac{\left(x_{1m} - x_{2m}\right)}{\sqrt{\left(n_1 - 1\right) SD_1^2 + \left(n_2 - 1\right) SD_2^2}} \sqrt{\frac{n_1 n_2 \left(n_1 + n_2 - 2\right)}{n_1 + n_2}}$$

where x_{1m}, x_{2m} denote the means calculated for the two compared sets of results, and SD_1, SD_2 are the standard deviations for the sets of results.


4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
0
5
10
15
20
UAL
UWL
CL
LWL
LAL

How standard deviation is determined?

- When <u>single</u> QC runs are carried out, the standard deviation s is estimated directly from the standard deviation of single results in different runs,
- But when the <u>QC results are averaged by replicates per run</u>, the standard deviation s must be calculated from separate estimation of within- and between-run variances according to the rules of ANOVA calculated by

$$s = \sqrt{s_{\text{bw}}^2 + \frac{s_{\text{in}}^2}{n_j}},$$

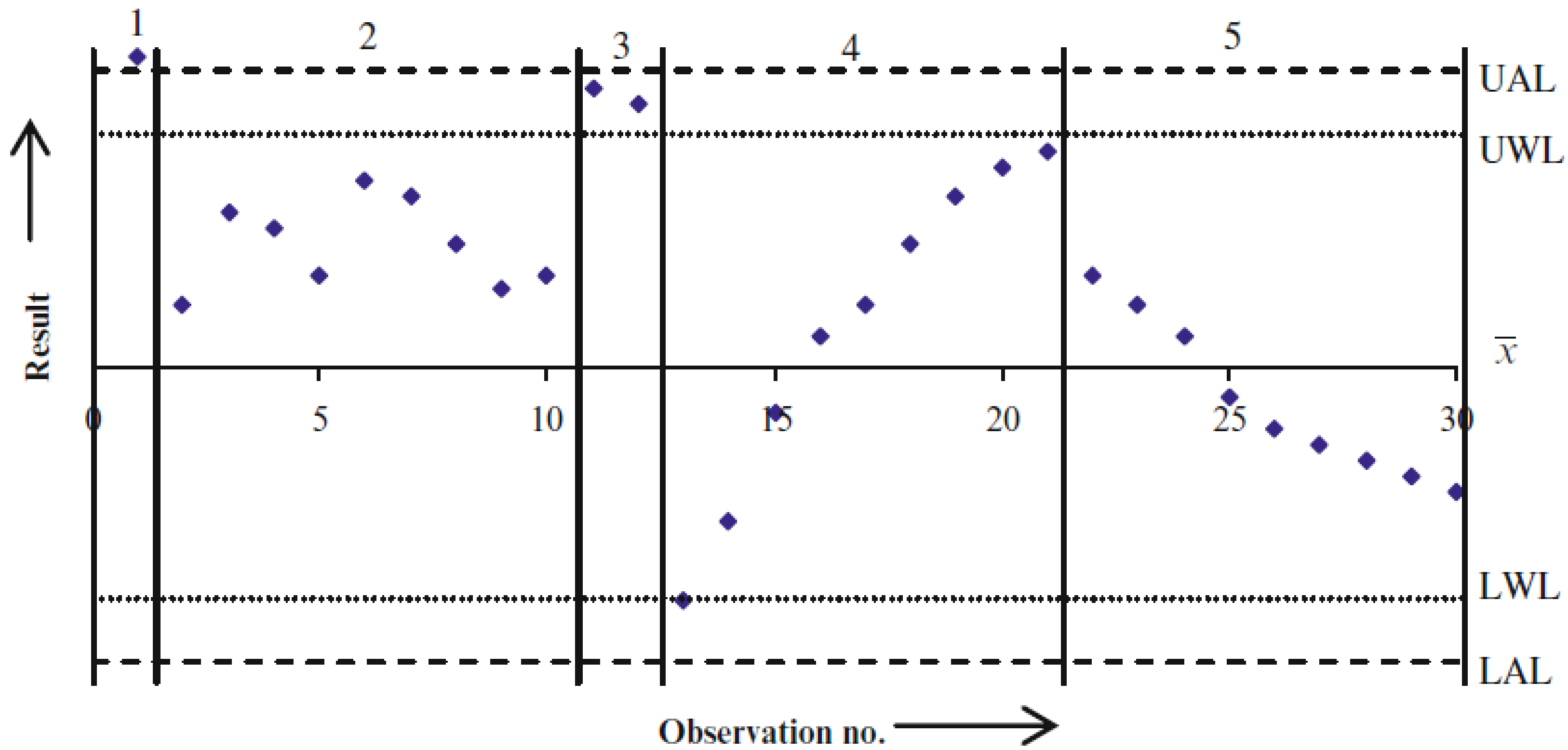
where n_j is the number of the replicates per run, S^2_{bw}, S^2_{in}.

- Finally, the data set used for construction of the control chart has to be inspected to see whether extremely large or small values must be rejected as outliers, because

  such values will distort the charts and make them
  - less sensitive and, therefore, less
  - useful in detecting problems.
- Data obtained by the observations are plotted in chronological order.
- By comparing current data to the limit lines, one can draw conclusions about whether the process variation is consistent (in control) or is unpredictable (out of control):
- affected by special causes of variation. If an out-of-control situation is detected, the measurement process should be stopped, the causes of this variation must be sought and eliminated or changed.

- Besides the out-of-control rules given, there are some additional rules which are illustrated in the Figure below:

1. One measured point lies out of the upper or the lower action line.
2. Nine consecutive measured points lie on one side of the central line.
3. Two consecutive measured points lie outside the warning line.
4. Nine consecutive measured points show an upward trend.
5. Nine consecutive measured points show a downward trend.



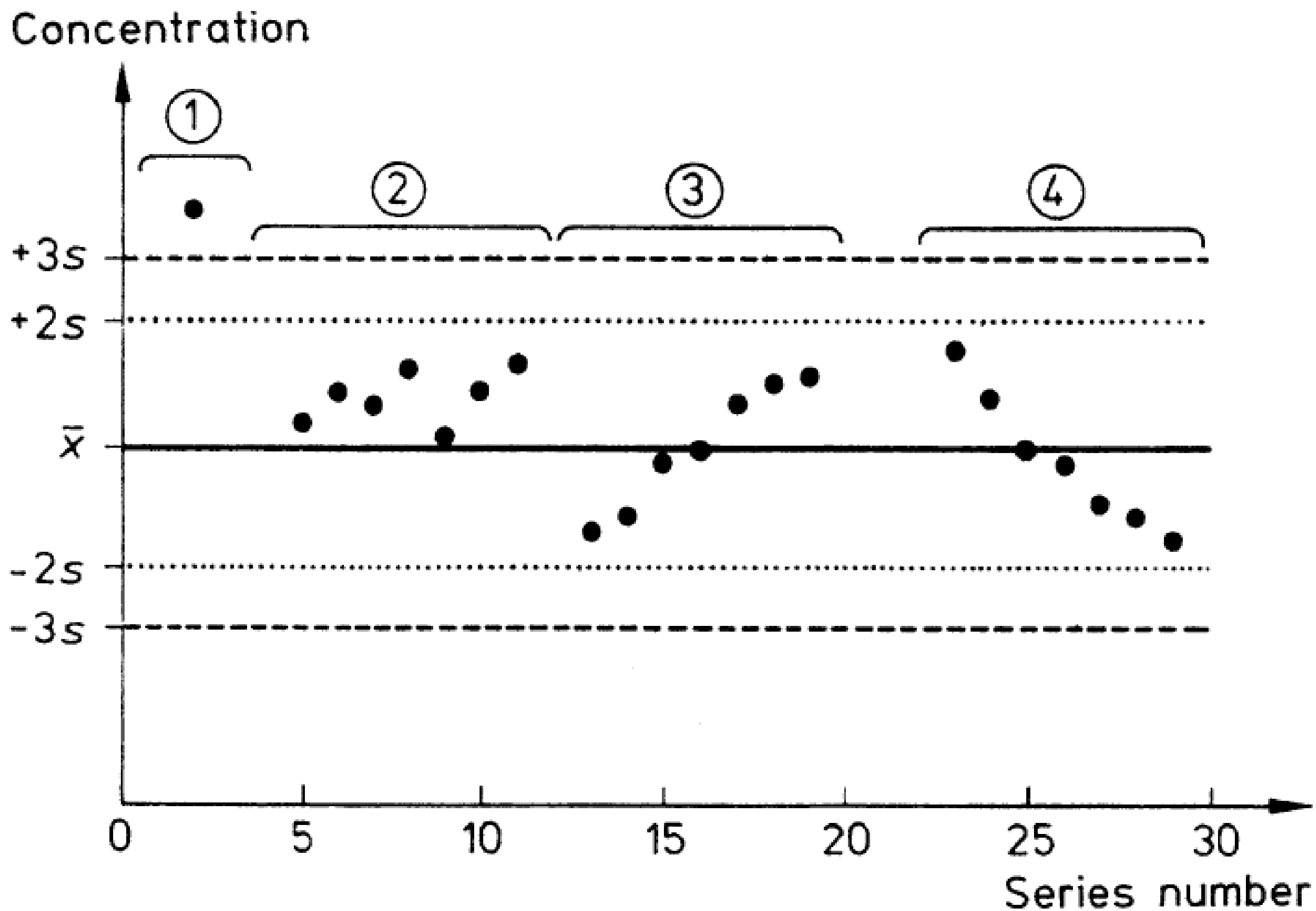
Presentation of some out-of-control situations

A Shewhart control chart constructed according to Fig. 8.2-1 can be applied as:
Mean control chart, preferably, for recognition of the precision or trends of an analytical method

"Out-of-Control" Situations
(Another reference: W. Funk, V. Dammann, G. Donnevert Quality Assurance in Analytical Chemistry

- In addition to the detection of large random errors (gross errors), the control chart should also provide indications of systematic errors or trends in systematic errors.
- The following criteria for out-of-control situations are mentioned in the literature:

1. One value outside of the control limits [29, 56, 109, 117, 179] (no. 1 in Figure 2-10).
2. Seven consecutive values on one side of the central line (no. 2).
3. Seven consecutive values showing an ascending trend (no. 3).
4. Seven consecutive values showing a descending trend (no. 4).
5. Two of three consecutive values outside of the warning limits].
6. Ten of eleven consecutive values on one side of the central line].



Concentration
1
2
3
4
+3s
+2s
$\bar{x}$
-2s
-3s
0
5
10
15
20
25
30
Series number

Conspicuous Entries

- **When evaluating a control chart, one should not only look for out-of-control situations, but should also follow the general progression of the entries on the chart.**
- **Figure 2-11 depicts four examples in which at no time is the process "out of control", but the order of entries suggests influences that are not random.**
- **Action should be taken before the appearance of an out-of-control situation; in cases b), c), and d), out-of-control situations can be expected to arise in the foreseeable future.**

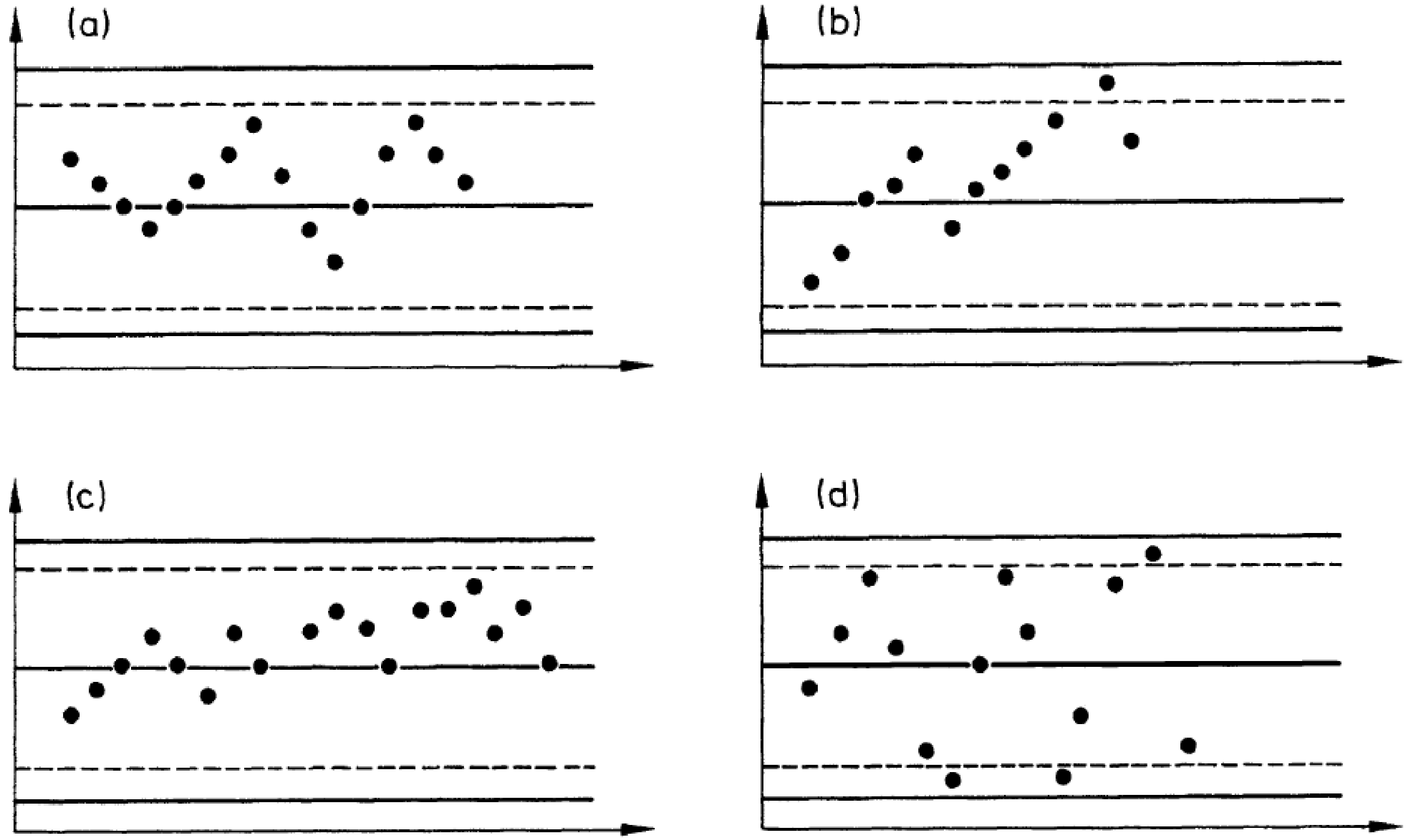


Fig. 2-11 Conspicuous order of entries in a Shewhart chart.

a. cyclical changes (cause: rotation of technician, “Monday” effect, etc.)

b. shift of the mean (cause: technical intervention on the measurement equipment, new reagents, new equipment, disposable articles, etc.)

c. trend (cause: equipment influences, aging of reagents, etc.)

d. many entries close to the control limits (*s enlarged).*

Shewhart Charts for Ranges (R-Charts)
(Precision control charts)

- **Shewhart means chart usually reacts to changes not just in the mean but also to changes in the standard deviation of the results.**
- **While the mean Shewhart chart shows how well mean values of subgroups or single values correlate with the grand average (process mean), it does not provide any information about the distribution of individual results within and between the subgroups.**
- **In contrast, the R-chart (R = range) serves above all the purpose of precision control.**
- **For this, range is defined as the difference between the largest and smallest single results of multiple analyses.**

Shewhart charts for *ranges*
R-Charts

- If a Shewhart chart for mean values suggests that a process is out of control, there are two possible explanations:
- The most obvious is that the process mean has changed: the detection of such changes is the main reason for using control charts in which $\bar{x}$ values are plotted.
- An alternative explanation is that the process mean has remained unchanged but that the variation in the process has increased, i.e. that the action and warning lines are too close together, giving rise to indications that changes in $\bar{x}$ have occurred when in fact they have not.
- Errors of the opposite kind are also possible.

- If the variability of the process has diminished (i.e. improved), then the action and warning lines will be too far apart, perhaps allowing real changes in $\overline{x}$ to go undetected.
- Therefore the variability of the process as well as its mean value must be monitored.
- R-charts are applied for monitoring the analytical precision.
- Analytical precision is concerned with variability between repeated measurements of the same analyte, irrespective of presence or absence of bias.
- The range obtained by replicate measurements within each analytical run is used to control the stability of analytical precision and it thus checks the homogeneity of variances.

Construction of an *R-Chart*

In order to construct an R-chart, the following quantities must be known or calculated:

- **number n of repeated *measurements per subgroup (n_i), at least n = 2*,**
- **number *N of subgroups, series,***
- ***R_i, range of subgroup i,***
- $\bar{R}$ ***, mean value of ranges,***
- ***S^2, variance of the entire measurement,***
- **upper warning limit, UWL,**
- **lower warning limit, LWL,**
- **upper control (action) limit, UCL (UAL)**
- **lower control (action) limit, LCL (LAL).**

- **the ranges, *R_i*, *of all subgroups are determined and combined as* $\bar{R}$ *:***
- ***R_i* = *largest value* – smallest value of a subgroup *i consisting of n single measurements***

$$\bar{R} = \frac{\sum R_i}{N}$$

$\bar{R}$ forms the "central line" of the R-chart

The respective warning and control (action) limits are obtained from the mean range $\bar{R}$ by multiplying it by a factor *D*, which is a function of the number of multiple determinations, *n*, and the significance level:

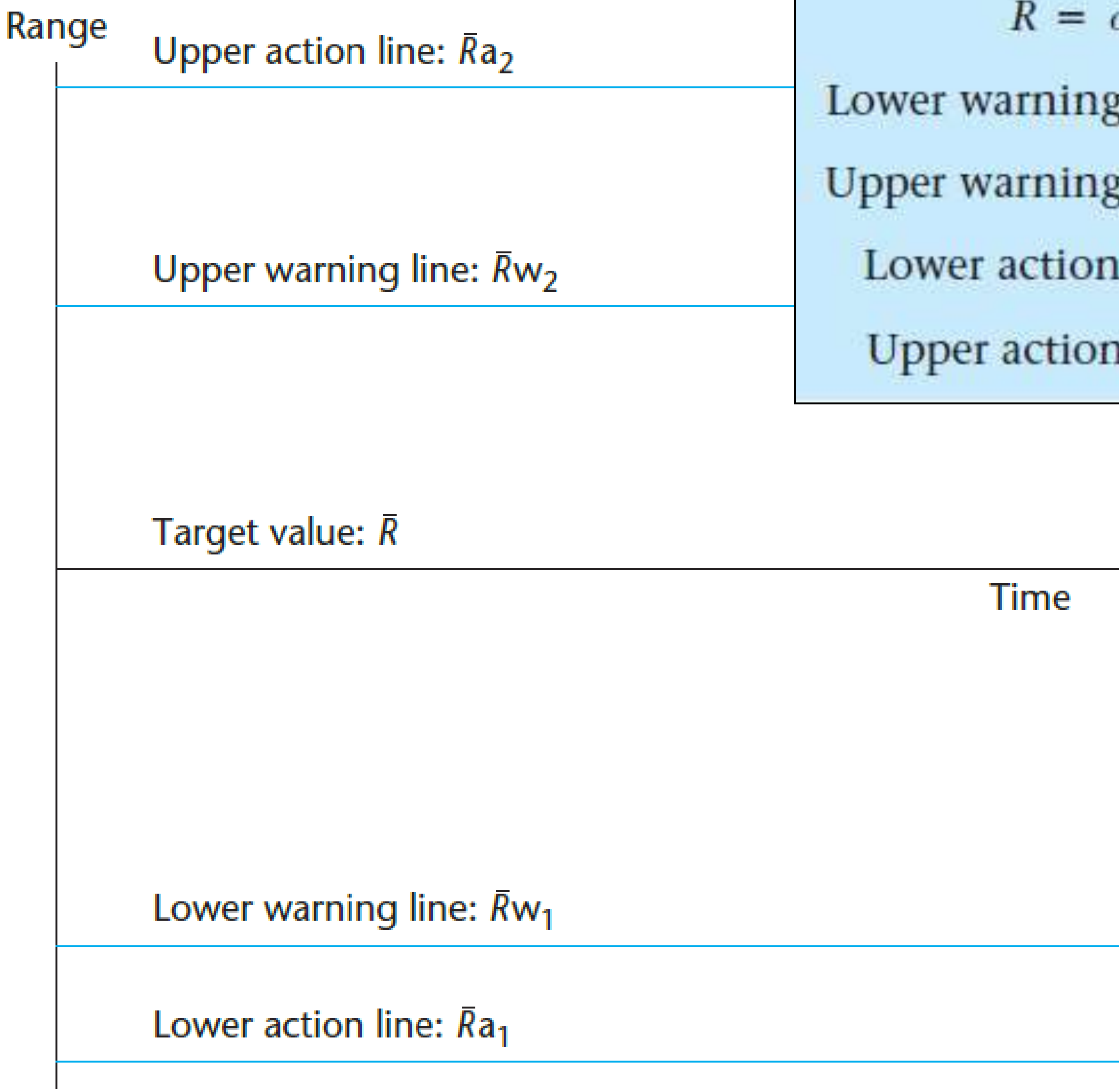
Usually, a Combination 95% and 99,7% confidence Levels are chosen for the action and warning levels

$$\begin{aligned}
\mathrm{LCL} &= D_{\mathrm{Clo}} \cdot \bar{R} \\
\mathrm{UCL} &= D_{\mathrm{Cup}} \cdot \bar{R} \\
\mathrm{LWL} &= D_{\mathrm{Wlo}} \cdot \bar{R} \\
\mathrm{UWL} &= D_{\mathrm{Wup}} \cdot \bar{R}
\end{aligned}$$

Table 2-5 *D*-factors for the calculation of *R*-chart limits.

n	$P = 95\%$ [23]		$P = 99\%$ [23]		$P = 99.7\%$ [3, 4]	
	D_{Wlo}	D_{Wup}	D_{Clo}	D_{Cup}	D_{Clo}	D_{Cup}
2	0.039	2.809	0.008	3.518	0.000	3.267
3	0.179	2.176	0.080	2.614	0.000	2.575
4	0.289	1.935	0.166	2.280	0.000	2.282
5	0.365	1.804	0.239	2.100	0.000	2.115
6	0.421	1.721	0.296	1.986	0.000	2.004
7	0.462	1.662	0.341	1.906	0.076	1.924
8	0.495	0.617	0.378	1.846	0.136	1.864
9	0.522	1.583	0.408	1.798	0.184	1.810
10	0.544	1.555	0.434	1.760	0.223	1.777
11	0.562	1.531	0.456	1.729	0.256	1.744
12	0.578	1.511	0.475	1.702	0.284	1.710
13	0.592	1.494	0.491	1.679	0.308	1.692
14	0.604	1.480	0.506	1.659	0.329	1.671
15	0.615	1.467	0.519	1.642	0.348	1.652
16	0.625	1.455	0.531	1.626	0.364	1.63
17	0.634	1.445	0.542	1.612	0.379	1.621
18	0.642	1.435	0.552	1.599	0.392	1.608
19	0.649	1.427	0.561	1.587	0.404	1.59
20	0.656	1.419	0.569	1.577	0.414	1.58

Shewhart charts for ranges



$$\bar{R} = \sigma d_1$$

$$\text{Lower warning line} = \bar{R}w_1$$

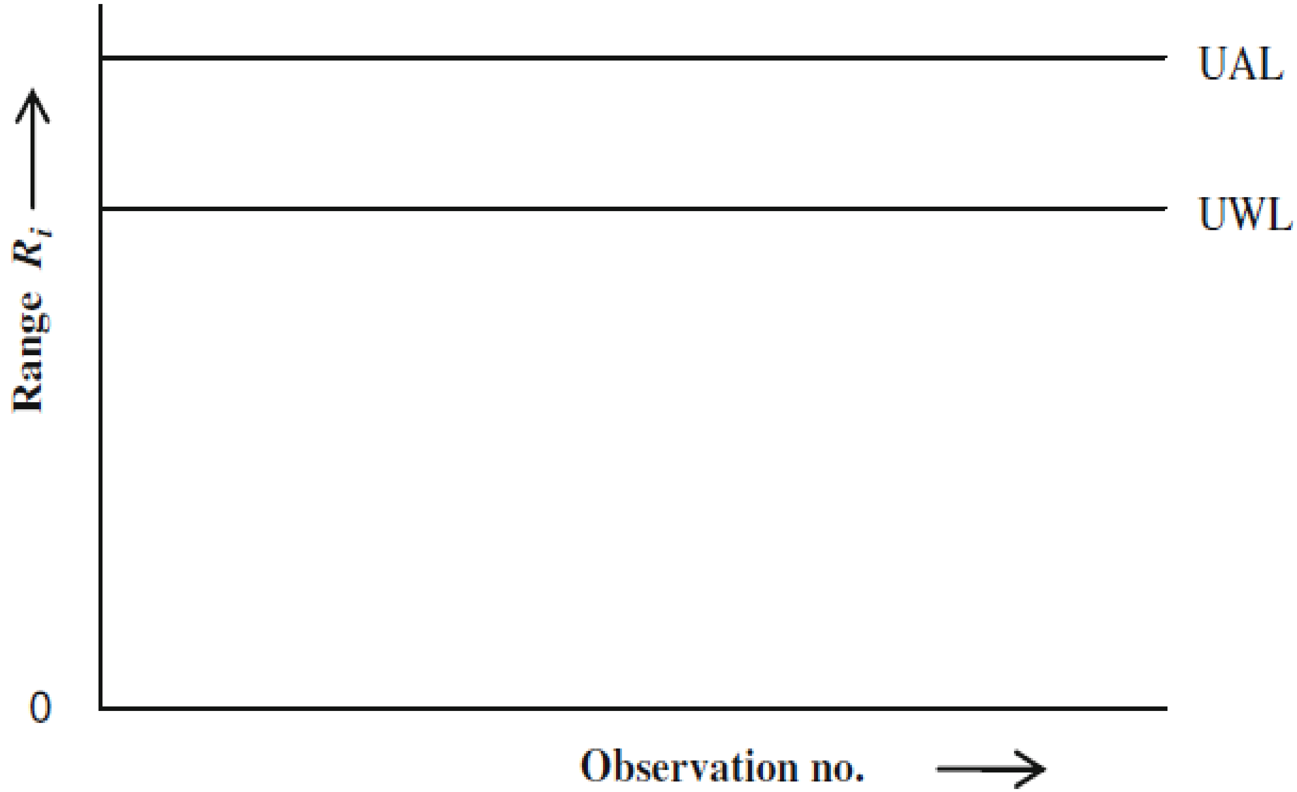
$$\text{Upper warning line} = \bar{R}w_2$$

$$\text{Lower action line} = \bar{R}a_1$$

$$\text{Upper action line} = \bar{R}a_2$$

- It is not always the practice to plot the lower action and warning lines on a control chart for the range, as a reduction in the range is not normally a cause for concern.
- However, as already noted, the variability of a process is one measure of its quality, and a reduction in *R* represents an improvement in quality, the causes of which may be well worth investigating. So plotting both sets of warning and action lines is recommended.

The format of a range chart



In order to construct the limits of the range charts, the ranges Ri of all sub-groups must be determined according to

$$R_i = x_{i,\max} - x_{i,\min},$$

the average range R is calculated by

$$\overline{R} = \frac{\sum R_i}{n}.$$

- **The upper action limit line UAL and upper warning (or control) limit line UWL are obtained by multiplying the average range by tabulated multipliers which are given in Table 8.2-1 for various numbers of replicates n_j .**

Table 8.2-1 D-factors for the calculation of the limits of range charts for nj replicates per run

n_j	D_{WL} $P = 95\%$	D_{AL} $P = 99.7\%$
2	2.809	3.267
3	2.176	2.575
4	1.935	2.282
5	1.804	2.115
6	1.721	2.004
7	1.662	1.924
8	1.617	1.864
9	1.583	1.816
10	1.555	1.777

- **These multipliers DWL and DAL correspond to the two- and three-sigma level, respectively:**

Warning limit lines WL

$$WL = \overline{R} \cdot D_{\mathrm{WL}}$$

Action limit lines AL:

$$AL = \overline{R} \cdot D_{\mathrm{AL}}$$

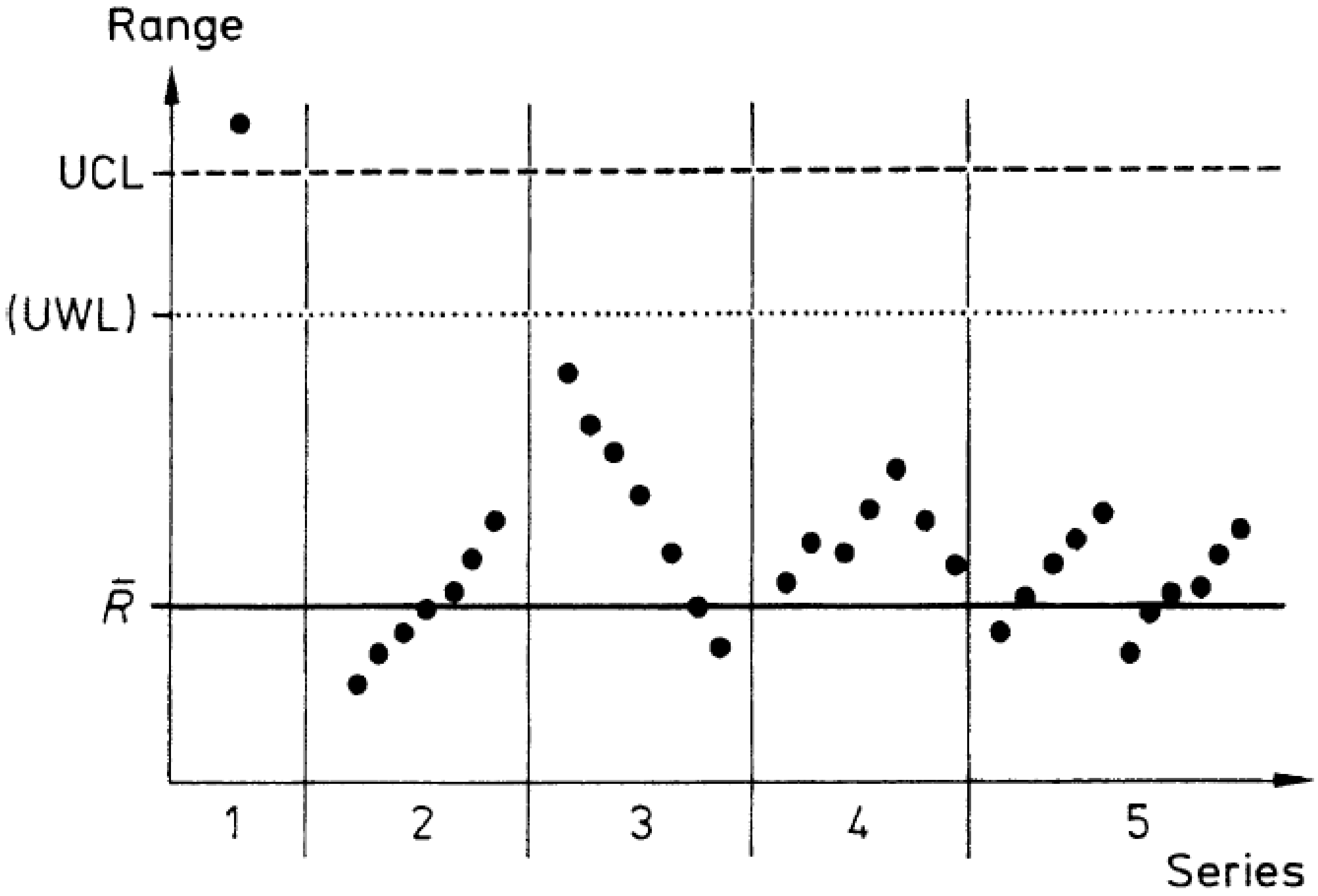
Decision Criteria for *R*-Charts

- **An out-of-control situation exists if**

1. **one R_i value lies above the upper control limit**
2. **one R_i value lies below the lower control limit (valid only if LCL > 0),**
3. **seven consecutive values show an ascending ('2' in the Figure) or descending trend ('3' in the Figure)**
4. **seven consecutive values lie above the range mean, $\overline{R}$ ('4' in the Figure).**

- **So, if just one R_i in the preliminary period lies outside of the upper control limit, all quantities required for the construction of an *R*-chart must be recalculated.**
- **Cyclical movements [ascending ('5' in the Figure) or descending] of the ranges indicate influences resulting from the maintenance schedule of the instruments or aging of the reagents. However, this is not an out-of-control situation.**

Out-of-control situations of R-charts



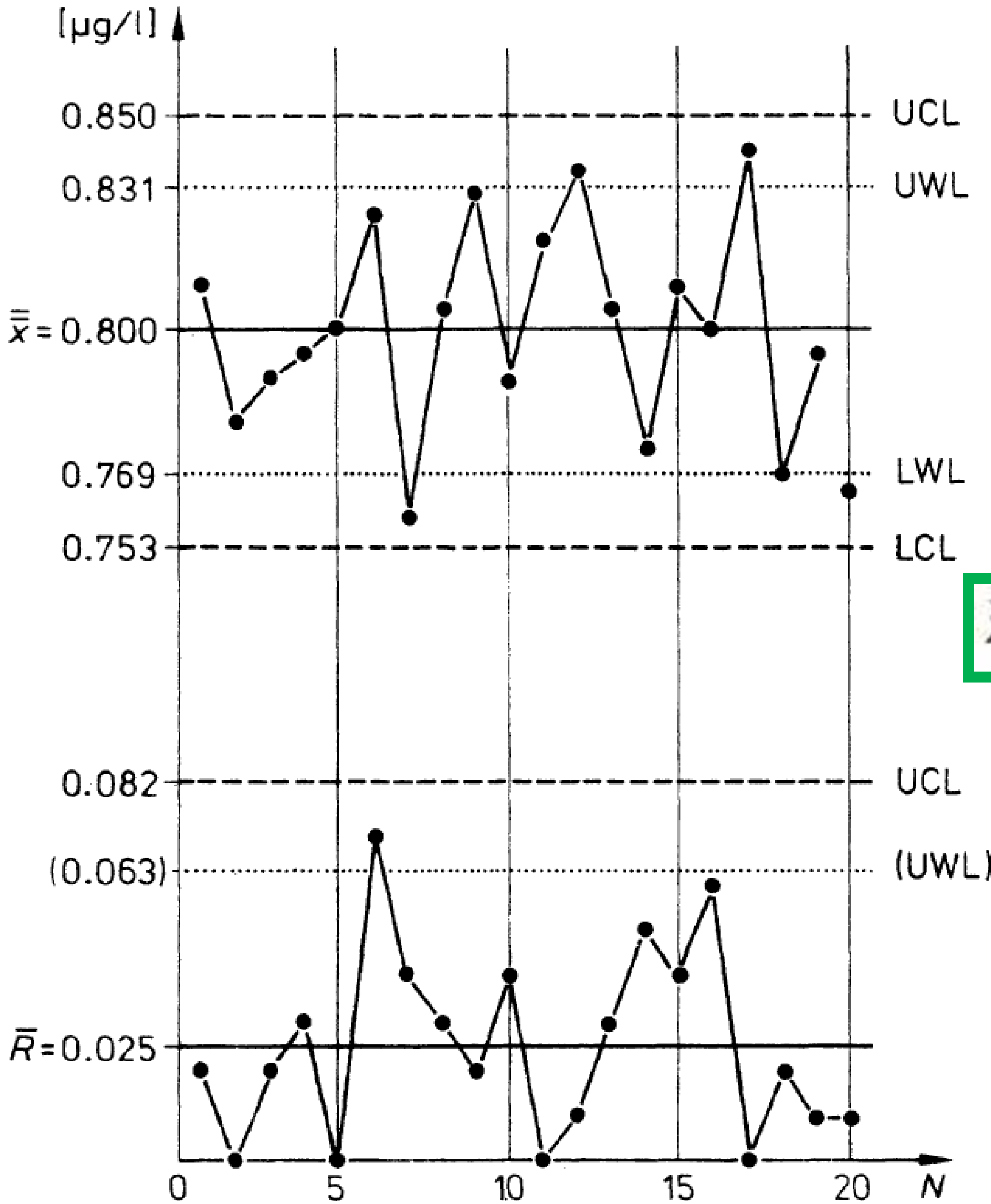
Combination charts

- The $\bar{X}$ *-R combination chart is probably the most useful control chart used in industrial* quality assurance.
- It consists of an $\bar{X}$ *-chart and an R-chart together, arranged* so that the mean value and range for *one given subgroup are positioned* above one another on the graph (see Figure 2-15).
- This process allows different changes to be recorded simultaneously on one chart.
- The $\bar{X}$ -chart reacts sensitively to changes in the mean values of the subgroups; in contrast, the R-chart provides information about too large a distribution within a subgroup
- The primary advantage of this method is that it enables one to decide whether the deviation between subgroups is significantly larger than the deviation within a subgroup.
- In this situation, the R-chart is in control and the $\bar{X}$ -chart indicates "outof- control" situations .
- This occurs frequently with certain chemical processes, indicating insufficiently controlled variables (e. g., temperature).

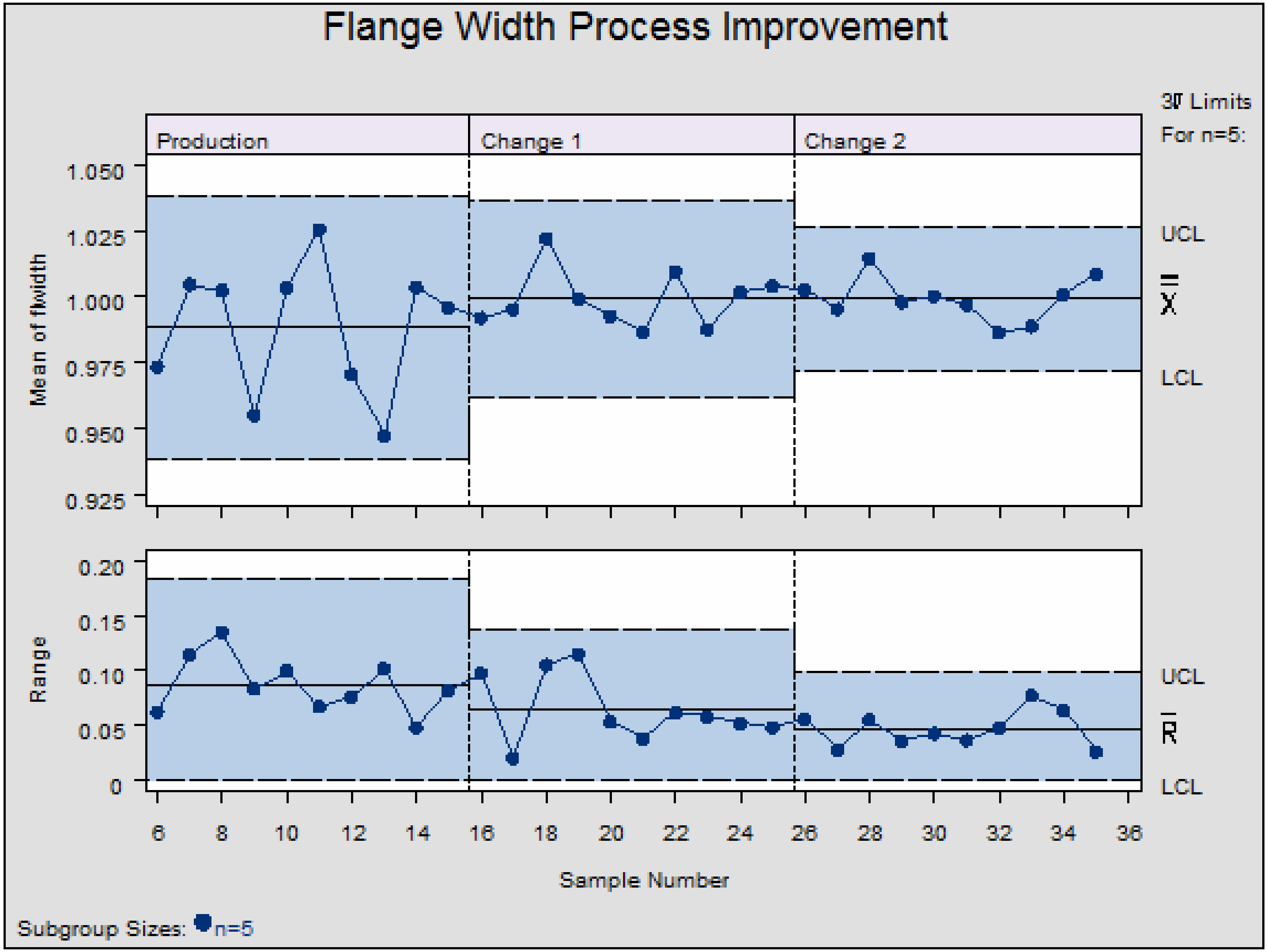
Combination charts

- **If the opposite situation occurs, i. e. the $\bar{X}$ *-chart is in control and the***

  R-chart is **out of control, or if a trend is spotted, this indicates a change in the individual variances**
- **If the mean values tend to always move in the same direction as the range, it could be a "skewed" distribution (the same is true for continuous movement in the opposite direction).**
- **The $\bar{X}$ -R chart only makes sense if the same control sample is used for both range and mean value control. A control sample (synthetic or natural) that remains stable over a long period of time is required.**



$\bar{x}$-R combination chart



Shewhart Control Chart with Multiple Control Limits

Example

- **The performance of a test method for the determination of copper in soil samples by optical emission spectroscopy with inductively coupled plasma (ICP-OES) was monitored by analyzing a quality control material without replicates. The analytical results obtained in the pre-period are given in Table 8.2-2.**
- **The Cu-containing soil sample was used as "in-house reference material" for quality control in routine analysis. The results for the first 35 control measurements are summarized in Table 8.2-3.**

a) Construct a Shewhart mean value control chart with warning and action limits equivalent to the 95.5% and 99.7% confidence limits on the basis of the data set obtained in the pre-period.

(b) Check whether the method is under statistical control at each control point in routine analysis

Table 8.2-2 Analytical results of Cu in a soil sample determined in the pre-period by ICP-OES obtained by single observations

Observation no.	c_{Cu} in mg kg^{-1}	Observation no.	c_{Cu} in mg kg^{-1}
1	24.5	16	24.4
2	24.1	17	23.8
3	26.3	18	23.5
4	22.7	19	22.9
5	23.9	20	24.3
6	24.1	21	24.8
7	30.1	22	24.1
8	23.6	23	24.6
9	23.8	24	24.6
10	24.6	25	24.7
11	22.2	26	24.1
12	23.6	27	24.2
13	23.9	28	23.5
14	24.0	29	22.7
15	24.8	30	24.8

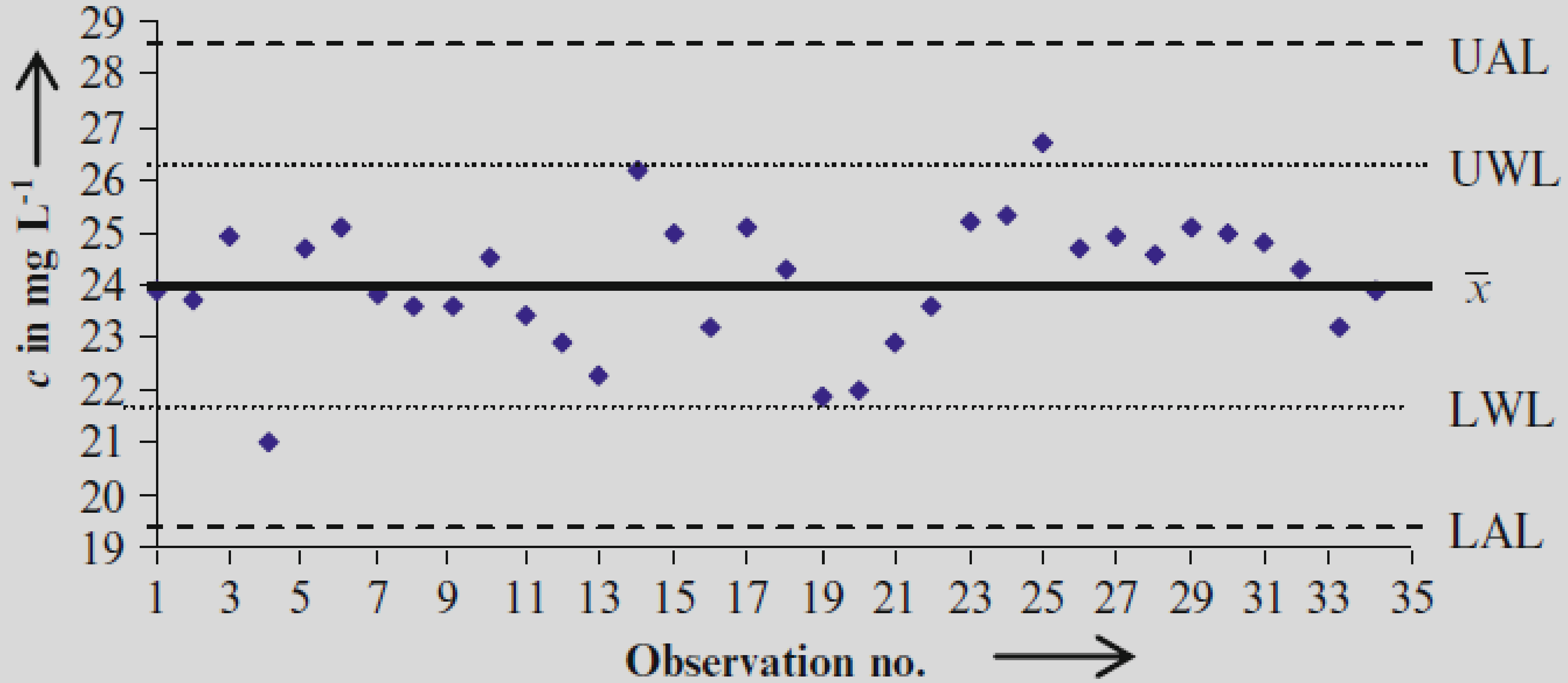
Table 8.2-3 Analytical results of Cu determined by ICP-OES in routine analysis

Observation no.	c_{Cu} in mg kg^{-1}	Observation no.	c_{Cu} in mg kg^{-1}
1	23.9	18	24.3
2	23.7	19	21.9
3	24.9	20	22.0
4	21.0	21	22.9
5	24.7	22	23.6
6	25.1	23	25.2
7	23.8	24	25.3
8	23.6	25	26.7
9	23.6	26	24.7
10	24.5	27	24.9
11	23.4	28	24.6
12	22.9	29	25.1
13	22.3	30	25.0
14	26.2	31	24.8
15	25.0	32	24.3
16	23.2	33	23.2
17	25.1	34	23.9

Solution to Challenge 8.2-1

(a) If the whole data set given in Table 8.2-2 is used for the determination of the standard deviation s the following limits are calculated:

$\bar{x} = 24.24\,\mathrm{mg\,kg^{-1}}$	$s = 1.3594\,\mathrm{mg\,kg^{-1}}$	$\mathrm{UAL} = 28.32\,\mathrm{mg\,kg^{-1}}$
$\mathrm{UWL} = 26.96\,\mathrm{mg\,kg^{-1}}$	$\mathrm{LWL} = 21.52\,\mathrm{mg\,kg^{-1}}$	$\mathrm{LAL} = 20.16\,\mathrm{mg\,kg^{-1}}$



As Fig. 8.2-4 shows, no out-of-control situation can be detected. But are the limits used for the construction of the Shewhart chart valid?

Inspection of the data set in Table 8.2-2 shows that the value of observation no. 7 measured in the pre-period is unusually high, and therefore this value must be detected as an outlier. The Grubbs test must be used because $n = 30$.

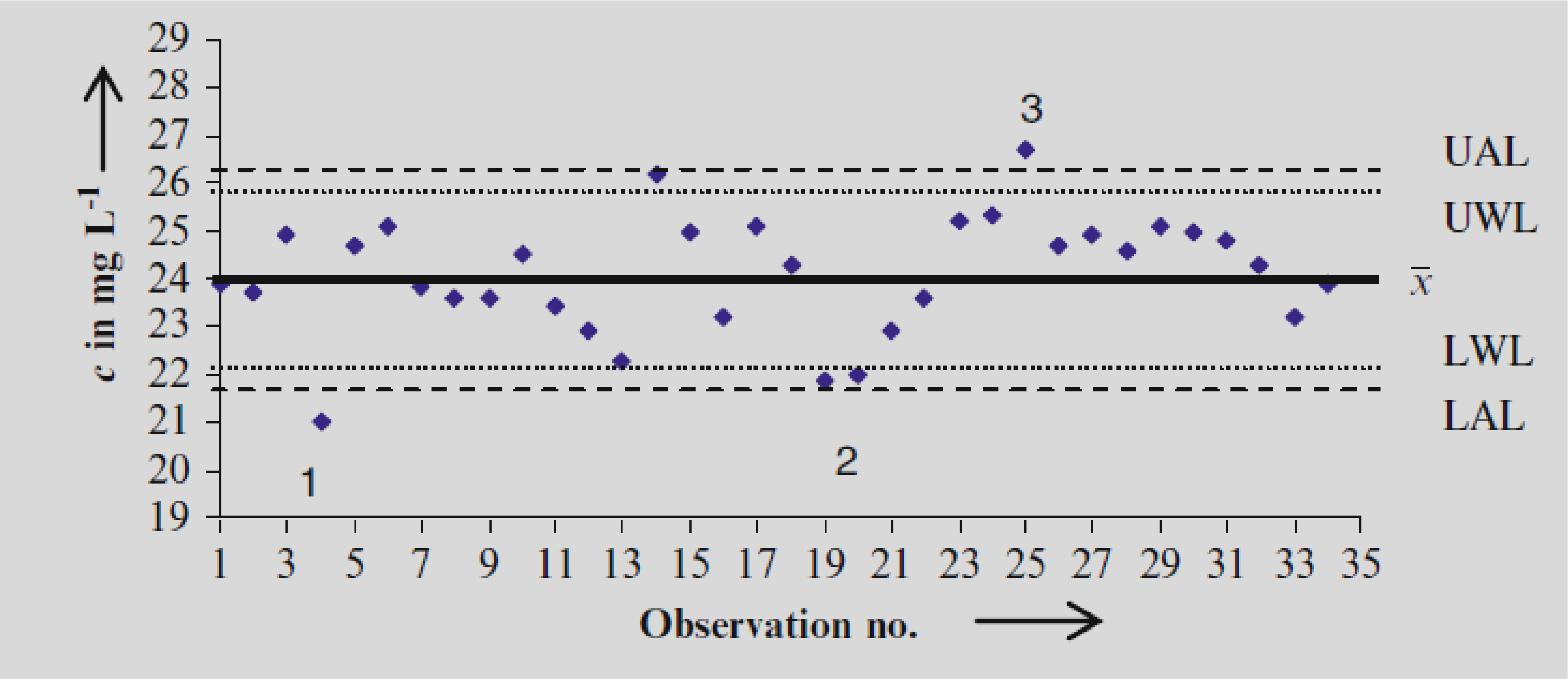
$$\hat{r}_m = \frac{|x^* - \bar{x}|}{s}.$$

The test value calculated according to (3.2.3-2) with $x_{max} = x^* = 30.1$, $x_{min} = 22.2$, and $s = 1.3594$ is $\hat{r}_m = 4.311$ which is greater than the critical value $r_m(P = 95\%, n = 30) = 2.745$. Thus, the measured value for observation no. 7 must be rejected from the data set.

The recalculated limits on the basis of the outlier-free data set are:

$\bar{x} = 24.04\,\mathrm{mg\,kg^{-1}}$	$s = 0.8033\,\mathrm{mg\,kg^{-1}}$	$\mathrm{UAL} = 26.45\,\mathrm{mg\,kg^{-1}}$
$\mathrm{UWL} = 25.64\,\mathrm{mg\,kg^{-1}}$	$\mathrm{LWL} = 22.43\,\mathrm{mg\,kg^{-1}}$	$\mathrm{LAL} = 21.63\,\mathrm{mg\,kg^{-1}}$

$\bar{x} = 24.04\,\mathrm{mg\,kg^{-1}}$	$s = 0.8033\,\mathrm{mg\,kg^{-1}}$	$\mathrm{UAL} = 26.45\,\mathrm{mg\,kg^{-1}}$
$\mathrm{UWL} = 25.64\,\mathrm{mg\,kg^{-1}}$	$\mathrm{LWL} = 22.43\,\mathrm{mg\,kg^{-1}}$	$\mathrm{LAL} = 21.63\,\mathrm{mg\,kg^{-1}}$



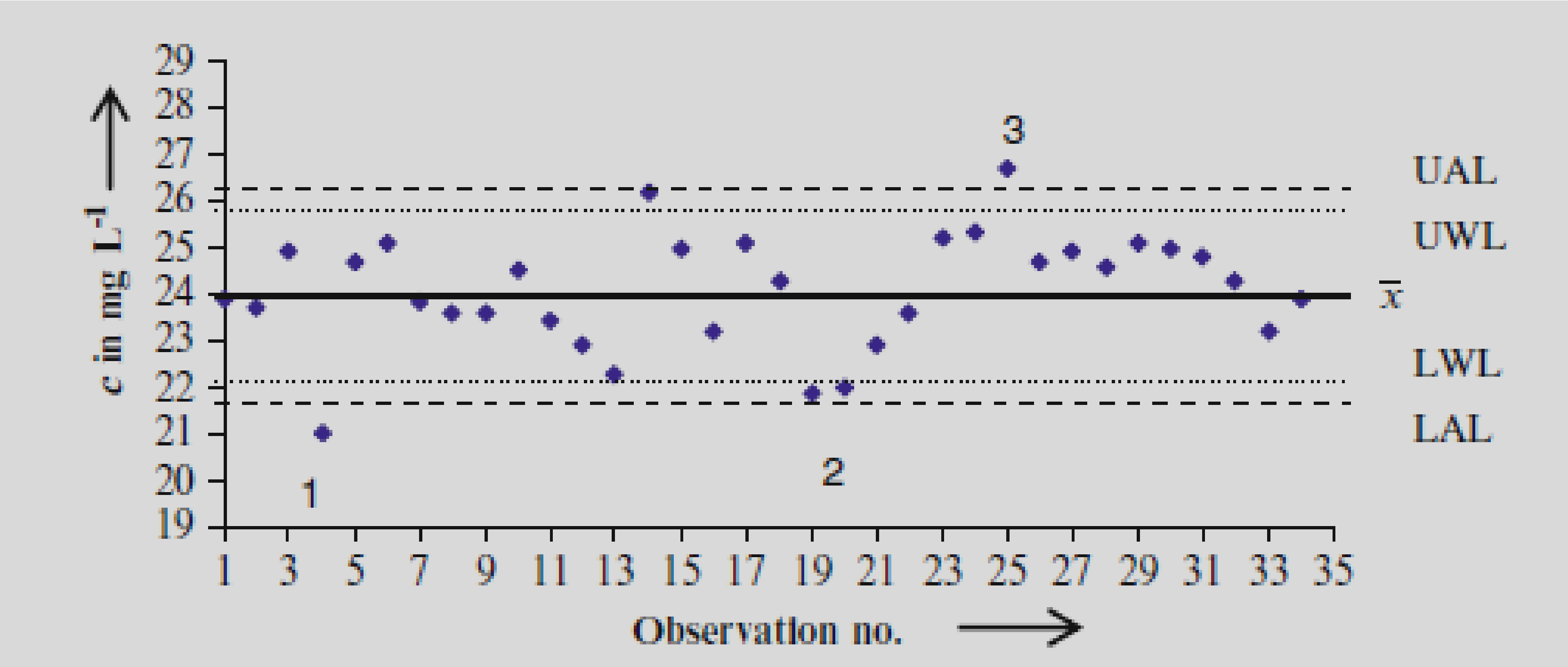


Fig. 8.2-5 Shewhart mean value control chart of the observations given in Table 8.2-3 with the limits calculated by the outlier-free data set from the pre-period listed in Table 8.2-2

The control chart presented in Fig. 8.2-5 shows three out-of-control situations:

1. The value of observation no. 4 lies outside the action limit.
2. Two successive observations (nos. 19 and 20) lie between the control and the action limits.
3. The value of observation no. 25 lies outside the action limit.

Challenge 8.2-1 (continued)

- **This example demonstrates the importance of the evaluation of data used for the determination of the control limits.**
- **Clearly, the determination of the standard deviation used for the calculation of the control limits requires data sets which are normally distributed, which can be checked by the David test (Rapid Test for Normal Distribution (David Test)**

$$\hat{q}_r = \frac{x_{\max} - x_{\min}}{s} .$$

- **Strictly speaking, the test value qr = 5.81 lies outside from the upper value which is 5.26 at the significance level P = 99%, but the difference is only small**

Challenge 8.2-2

Table 8.2-4 presents the results of the determination of the potency assay of a control material of a pharmaceutical product obtained in the pre-period by each three replicates, and the first nine results in routine analysis are given in Table 8.2-5.

(a) Construct the corresponding chart for controlling the mean values! Determine whether the analytical system is under control!
(b) Construct the corresponding chart for controlling of the precision and determine whether the homogeneity of variances is given!

Table 8.2-4 Twelve sets of three replicate potency assay obtained from a control material

Observation no.	c in % (w/w)	Observation no.	c in % (w/w)
1	80.37	7	80.99
	80.95		80.51
	80.81		80.83
2	81.05	8	80.92
	80.74		80.85
	80.99		80.91
3	80.85	9	80.87
	81.09		80.64
	80.96		80.58
4	81.12	10	80.88
	81.05		80.99
	80.92		80.81
5	81.05	11	80.96
	80.91		80.81
	81.18		81.04
6	80.83	12	80.95
	80.63		81.41
	80.97		81.09

Table 8.2-5 The first nine analytical results of three replicates obtained by the quality control in routine analysis

Observation no.	c in % (w/w)	Observation no.	c in % (w/w)
1	80.82	6	80.97
	80.26		81.01
	80.65		81.13
2	80.27	7	81.65
	81.00		81.75
	81.05		81.97
3	80.99	8	80.53
	80.88		80.77
	81.11		80.97
4	80.28	9	81.02
	80.02		81.01
	80.57		81.03
5	80.65		
	80.62		
	80.78		

First, the mean values $\bar{x}_j$ of the i observations of the measured values in the pre-period listed in Table 8.2-7 are checked for normal distribution and outliers.

Average of 3 values

Observation no.	$\bar{x}_j$	$n_j(\bar{x}_j - \bar{\bar{x}})^2$	SS_j
1	80.71	0.11181	0.18320
2	80.93	0.00167	0.05407
3	80.97	0.01214	0.02887
4	81.03	0.04834	0.02060
5	81.05	0.06187	0.03647
6	80.81	0.02598	0.05840
7	80.78	0.04792	0.11947
8	80.89	0.00028	0.00287
9	80.70	0.12779	0.04687
10	80.89	0.00028	0.01647
11	80.94	0.00339	0.02727
12	81.15	0.18294	0.11120
$\bar{\bar{x}}$	80.90		
$\sum n_j(\bar{x}_j - \bar{\bar{x}})^2 = SS_{bw}$	0.62443	$\sum SS_j = SS_{in}$	0.70573
n_i	12	n_j	3
$df_{bw} = n_i - 1$	11	$df_{in} = n_j \cdot n_i - n_i$	24
s^2_{bw}	0.05677	s^2_{in}	0.02941

The test value calculated according to (3.2.1-1) $\hat{q}_r = 3.30$ lies within the critical limits of the David table for $P = 95\%$ and $n = 12$ which are 2.80 and 3.91, and therefore the data can be assumed to be normally distributed.

The intermediate quantities and results given in Table 8.2-6 show that the data set is free of outliers by the Dixon test for $n = 12$. Thus, the whole data set can used to construct the appropriate control charts.

Table 8.2-6 Intermediate quantities and results of the Dixon outlier test on the highest and smallest mean value obtained during the pre-period

Test value	x_1	x_b	x_k	$\hat{Q}$
x_{max}	81.15	81.03	80.71	0.273
x_{min}	80.70	80.78	81.05	0.229

The symbols refer to (3.2.3-1) for $b = 3$ and $k = n–1$. The critical value is $Q(P = 95\%, n = 12) = 0.546$.

$$\hat{Q} = \frac{|x_1^* - x_b|}{|x_1^* - x_k|}$$

a. Because replicates were performed, the standard deviation necessary for the estimation of the control limits according to (8.2-1) and (8.2-2) must be determined by the variance components s2 bw and s2 in according to (8.2-3), which must be obtained by ANOVA. The intermediate quantities and results of ANOVA are listed in Table 8.2-7.

- The standard deviation required for the setup of the Shewhart mean control chart is s = 0.2580% (w/w) calculated according to (8.2-3 using the variances given in Table 8.2-7. The limits of the mean value control charts shown in Fig. 8.2-5 calculated by (8.2-1) and (8.2-2) are:

- Figure 8.2-6 shows the mean value charts for controlling the potency assay of a pharmaceutical drug during routine analysis, constructed with the limit values obtained in the pre-period and the mean values given in Table 8.2-8. Inspection of Fig. 8.2-6 shows an out-of-control situation at observation no. 7. After correction of the problem caused by the preparation of the sample, the analytical system is once more under control, as shown by the measured value of the next observation.

First, the mean values $\bar{x}_j$ of the i observations of the measured values in the pre-period listed in Table 8.2-7 are checked for normal distribution and outliers.

Average of 3 values

Observation no.	$\bar{x}_j$	$n_j(\bar{x}_j - \bar{\bar{x}})^2$	SS_j
1	80.71	0.11181	0.18320
2	80.93	0.00167	0.05407
3	80.97	0.01214	0.02887
4	81.03	0.04834	0.02060
5	81.05	0.06187	0.03647
6	80.81	0.02598	0.05840
7	80.78	0.04792	0.11947
8	80.89	0.00028	0.00287
9	80.70	0.12779	0.04687
10	80.89	0.00028	0.01647
11	80.94	0.00339	0.02727
12	81.15	0.18294	0.11120
$\bar{\bar{x}}$	80.90		
$\sum n_j(\bar{x}_j - \bar{\bar{x}})^2 = SS_{bw}$	0.62443	$\sum SS_j = SS_{in}$	0.70573
n_i	12	n_j	3
$df_{bw} = n_i - 1$	11	$df_{in} = n_j \cdot n_i - n_i$	24
s^2_{bw}	0.05677	s^2_{in}	0.02941

Table 8.2-7 conti

Table 8.2-7 continued

$\bar{x} = 80.90\%$ (w/w)	
UAL = 81.68% (w/w)	UWL = 81.42% (w/w)
LWL = 80.39% (w/w)	LAL = 80.13% (w/w)

(b)

- **The range chart is based on the range values obtained in the pre-periodwhich are given in Table 8.2-9.**
- **The limit values of the range chart calculated according to (8.2-6) and (8.2-7) with the mean value R_i = 0:3042% (w/w),**
  and the D-factors from Table 8.2-1 for n_j = 3 (2.575 and 2.176, respectively are: UAL = 0.783% (w/w) and UWL = 0.662% (w/w).
- **The range chart is shown in Fig. 8.2-7 for the first nine observations in routine analysis with the range values listed in Table 8.2-8.**
- **Observation no. 2 shows an out-of-control situation, because the range value lies outside the upper action line.**
- **After removal of the cause, e.g., exchanging the HPLC injection syringe, the analytical system is again under control.**
- **As the results of this Challenge show, the combination of a mean value and a range chart is appropriate for checking large deviations of the mean, the precision, and also trends in the analytical system**.

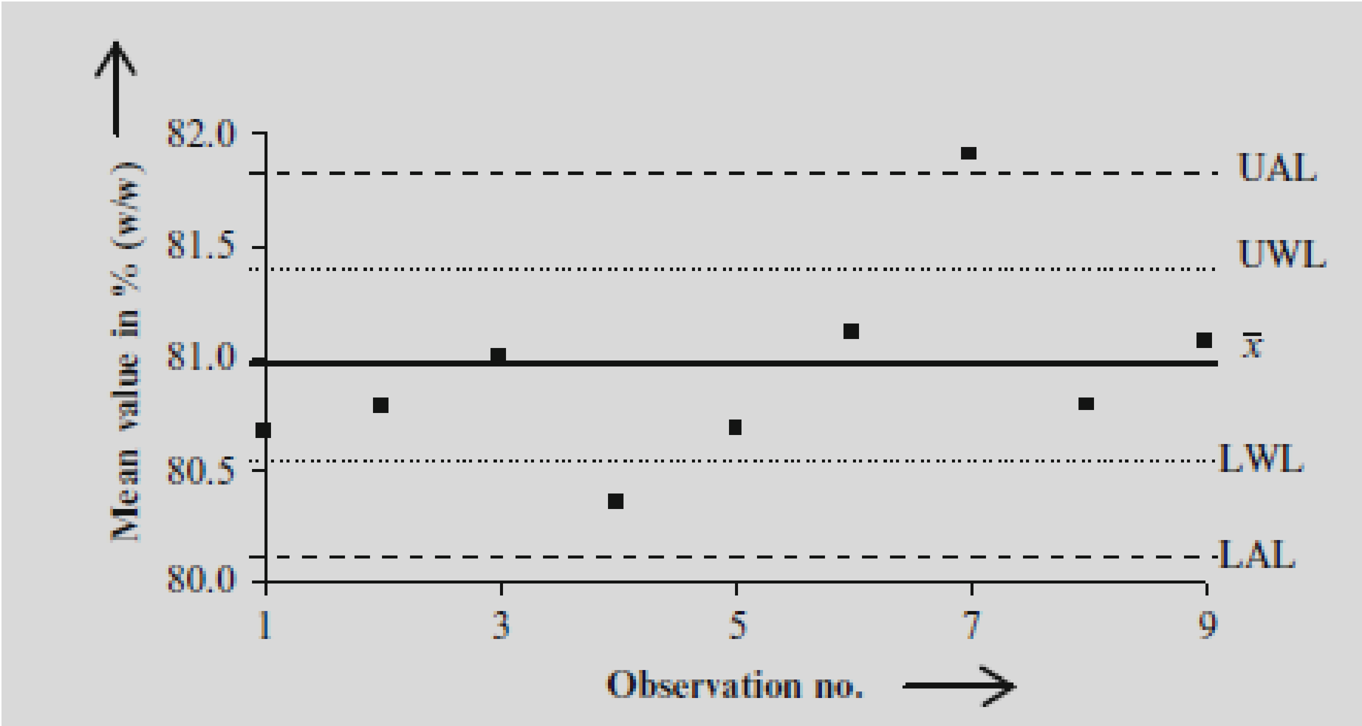


Fig. 8.2-6 Mean value charts for controlling the potency assay of a pharmaceutical drug during routine analysis

Table 8.2-8 The values of the mean and the range of the results given in Table 8.2-5

Observation no.	$\bar{x}_j$	$x_{j,\max}$	$x_{j,\min}$	R_j
1	80.58	80.82	80.26	0.56
2	80.77	81.05	80.27	0.78
3	80.99	81.11	80.88	0.23
4	80.29	80.57	80.02	0.55
5	80.68	80.78	80.62	0.16
6	81.04	81.13	80.97	0.16
7	81.79	81.97	81.65	0.32
8	80.76	80.97	80.53	0.44
9	81.02	81.03	81.01	0.02

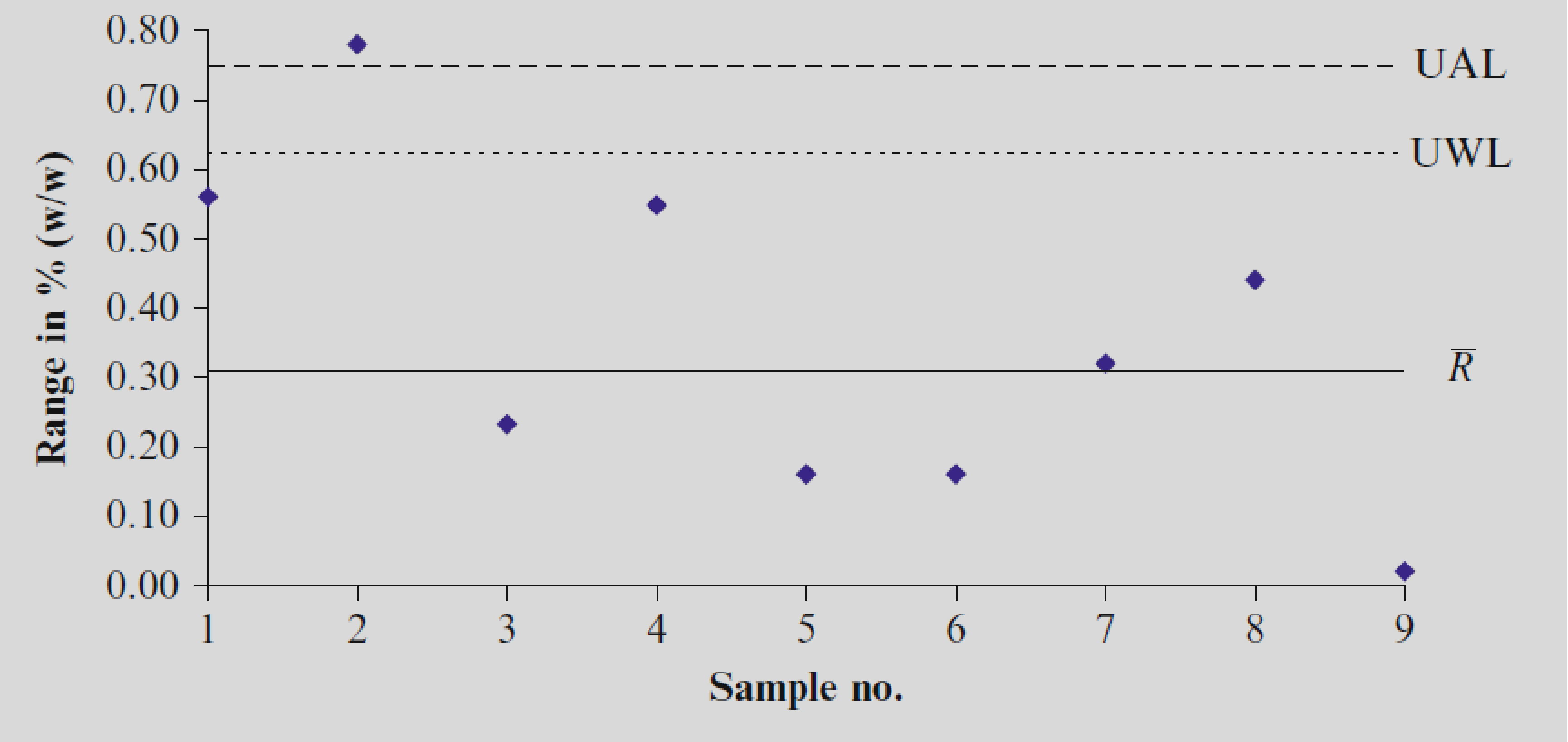


Fig. 8.2-7 Range charts for controlling the potency assay of a pharmaceutical drug during routine analysis

(b)

- **The range chart is based on the range values obtained in the pre-period which are given in Table 8.2-9.**
- **The limit values of the range chart calculated according to (8.2-6) and (8.2-7) with the mean value R_i = 0:3042% (w/w), and the D-factors from Table 8.2-1 for n_j = 3 (2.575 and 2.176, respectively are: UAL = 0.783% (w/w) and UWL = 0.662% (w/w).**

Table 8.2-9 Range values of the data set of Table 8.2-4

Observation no.	x_{max}	x_{min}	R_i
1	80.95	80.37	0.58
2	81.05	80.74	0.31
3	81.09	80.85	0.24
4	81.12	80.92	0.20
5	81.18	80.91	0.27
6	80.97	80.63	0.34
7	80.99	80.51	0.48
8	80.92	80.85	0.07
9	80.87	80.58	0.29
10	80.99	80.81	0.18
11	81.04	80.81	0.23
12	81.41	80.95	0.46

Example

- **Determine the characteristics of the mean and range control charts for a process in which the target value is 57, the process capability is 5, and the sample size is 4.**

- **For the control chart on which mean values will be plotted, the calculation is simple. The warning lines will be at**

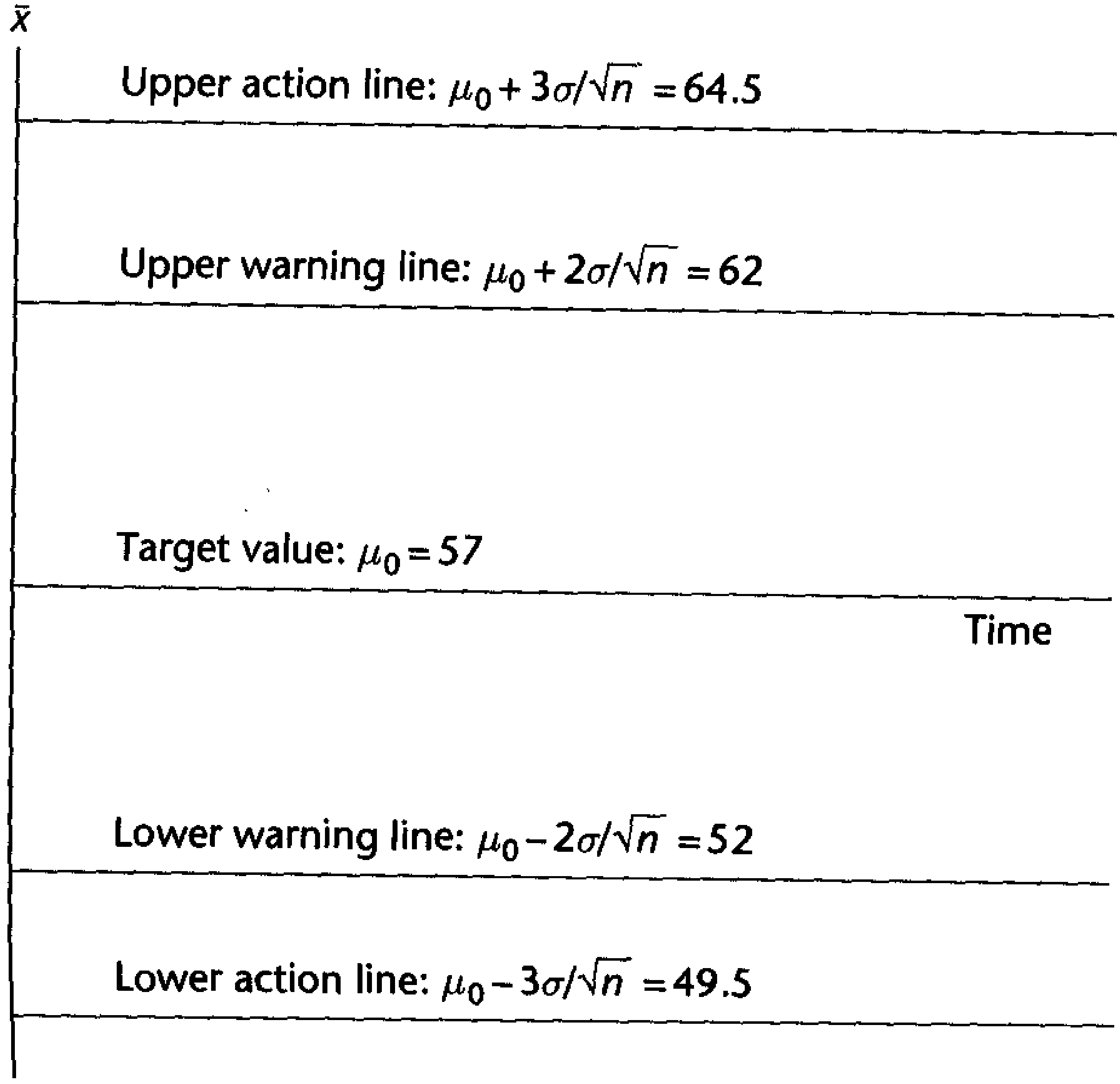
$$\boxed{57 \pm 2 \times 5/\sqrt{4}, \text{ i.e. at } 57 \pm 5,}$$

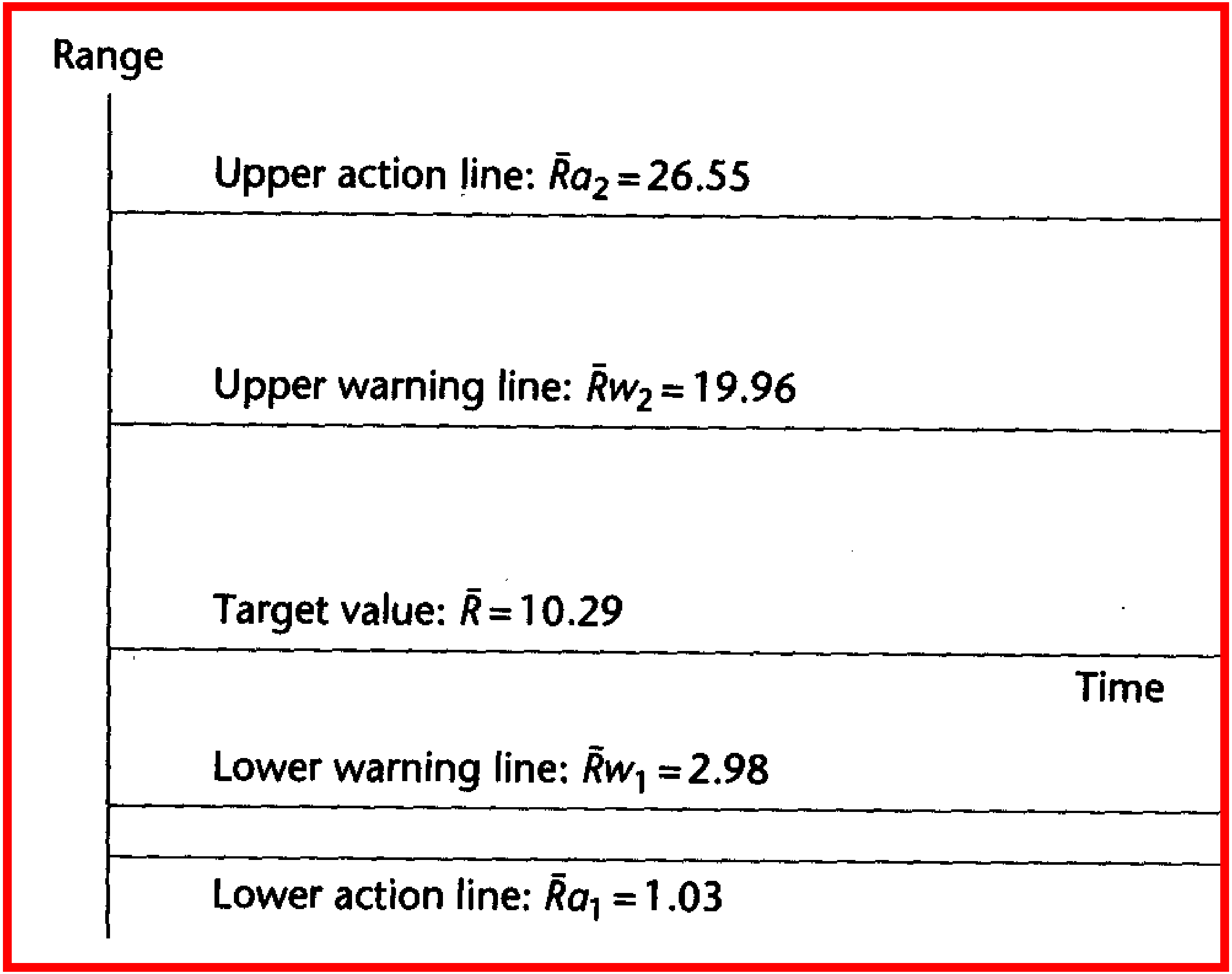
- **The action lines will be at** $\boxed{57 \pm 3 \times 5/\sqrt{4}, \text{ i.e. at } 57 \pm 7.5.}$

- **For the control chart on which ranges are plotted, we must first calculate** $\overline{R}$

- **This gives** $\overline{R}$ **= 5 x 2.059 = 10.29, where the** d_1 **value of 2.059 is taken from statistical tables for** $n = 4$**.**

- **The value of** $\overline{R}$ **is used to determine the lower and upper warning and action lines using equations**
- **The values of** w_1**,** W_2**,** a_1 **and** a_2 **for** $n = 4$ **are 0.29, 1.94, 0.10 and 2.58 respectively, giving on multiplication by 10.29 positions for the four lines of 2.98, 19.96, 1.03 and 26.55 respectively.**


$\bar{x}$
Upper action line: $\mu_0 + 3\sigma/\sqrt{n} = 64.5$
Upper warning line: $\mu_0 + 2\sigma/\sqrt{n} = 62$
Target value: $\mu_0 = 57$
Time
Lower warning line: $\mu_0 - 2\sigma/\sqrt{n} = 52$
Lower action line: $\mu_0 - 3\sigma/\sqrt{n} = 49.5$


Range
Upper action line: $\bar{R}a_2 = 26.55$
Upper warning line: $\bar{R}w_2 = 19.96$
Target value: $\bar{R} = 10.29$
Time
Lower warning line: $\bar{R}w_1 = 2.98$
Lower action line: $\bar{R}a_1 = 1.03$

Example

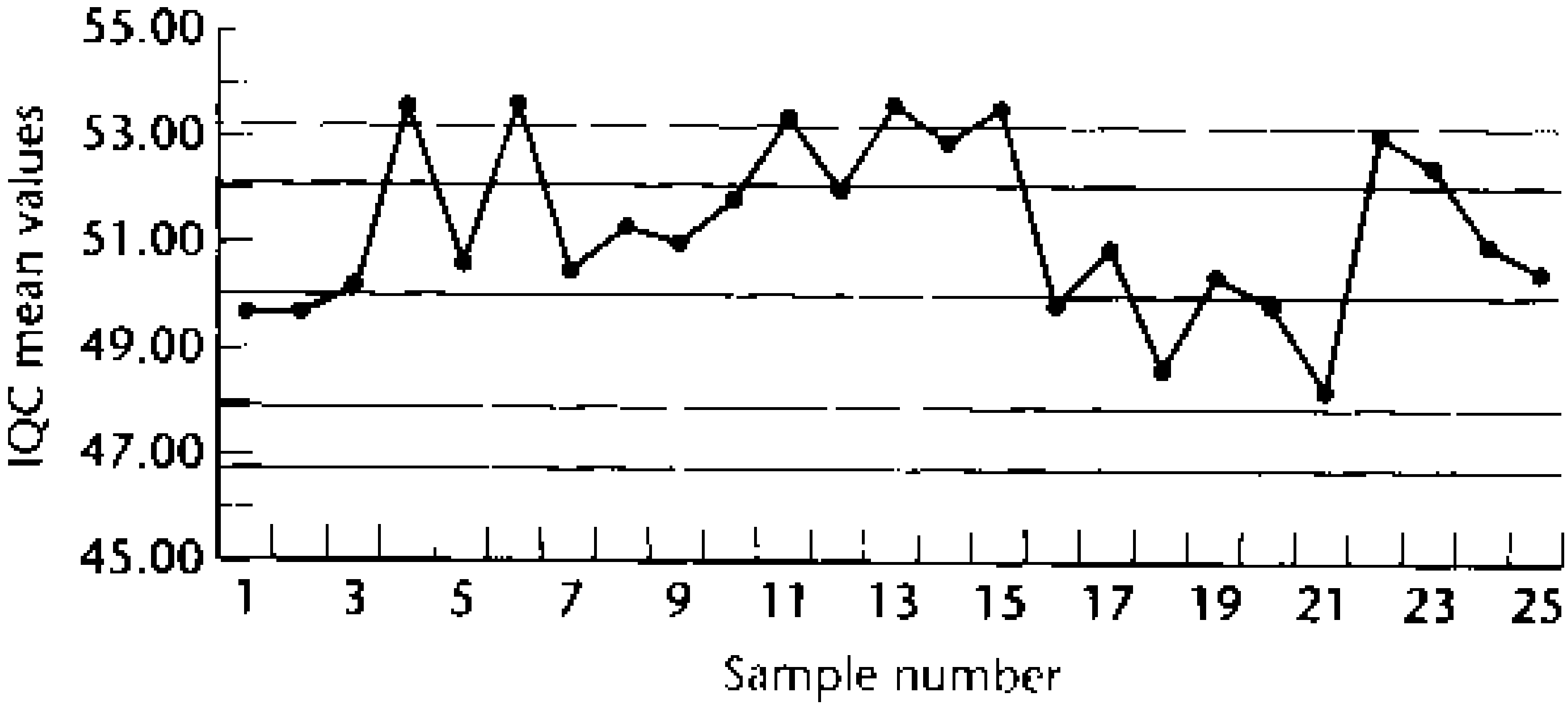
- **An internal quality control standard with an analyte concentration of 50 mg kg^{-1} is analyzed in a laboratory for 25 consecutive days, the sample size being four on each day. The results are given in the Table. Determine the value of $\overline{R}$ and hence plot control charts for the mean and range of the laboratory analyses**

- **When the results are examined there is clearly some evidence that, over the 25-day period of the analyses, the sample means are drifting up and down.**
- **These are the circumstances in which it is important to estimate σ using the method described above.**
- **Using the R-values in the last column of data, $\overline{R}$ is found to be 4.31.**
- **Application of equation (4.4) estimates σ as 4.31/2.059 = 2.09.**
- **The Table also shows that the standard deviation of the 100 measurements, treated as a single sample, is 2.43: because of the drifts in the mean this would be a *significant overestimate of* σ .**

Table 4.2 Excel® Spreadsheet (example)

Sample Number	Sample Values				Chart Mean	Range
	1	2	3	4		
1	48.8	50.8	51.3	47.9	49.70	3.4
2	48.6	50.6	49.3	50.3	49.70	2.0
3	48.2	51.0	49.3	52.1	50.15	3.9
4	54.8	54.6	50.7	53.9	53.50	4.1
5	49.6	54.2	48.3	50.5	50.65	5.9
6	54.8	54.8	52.3	52.5	53.60	2.5
7	49.0	49.4	52.3	51.3	50.50	3.3
8	52.0	49.4	49.7	53.9	51.25	4.5
9	51.0	52.8	49.7	50.5	51.00	3.1
10	51.2	53.4	52.3	50.3	51.80	3.1
11	52.0	54.2	49.9	57.1	53.30	7.2
12	54.6	53.8	51.5	47.9	51.95	6.7
13	52.0	51.7	53.7	56.8	53.55	5.1
14	50.6	50.9	53.9	56.0	52.85	5.4
15	54.2	54.9	52.7	52.2	53.50	2.7
16	48.0	50.3	47.5	53.4	49.80	5.9
17	47.8	51.9	54.3	49.4	50.85	6.5
18	49.4	46.5	47.7	50.8	48.60	4.3
19	48.0	52.5	47.9	53.0	50.35	5.1
20	48.8	47.7	50.5	52.2	49.80	4.5
21	46.6	48.9	50.1	47.4	48.25	3.5
22	54.6	51.1	51.5	54.6	52.95	3.5
23	52.2	52.5	52.9	51.8	52.35	1.1
24	50.8	51.6	49.1	52.3	50.95	3.2
25	53.0	46.6	53.9	48.1	50.40	7.3
			s.d. = 2.43			Mean = 4.31

- **The control chart for the mean is then plotted with the aid of equations (4.9) and (4.10) with**
  - **W = 0.4760,**
  - **A = 0.7505,**
  - **The warning and action lines are at 50 ± 2.05 and 50 ± 3.23 respectively.**
- **The Figure shows the Excel control chart.**
- **This chart shows that the process mean is not yet under control since several of the points fall outside the upper action line.**
- **Similarly, equations (4.5)-(4.8) show that in the control chart for the range the warning lines are at 1.24 and 8.32 and the action lines are at 0.42 and 11.09.**
- **Excel does not automatically produce control charts for ranges, though it does generate charts for standard deviations, which are sometimes used instead of range charts.**
- **However, with one exception, the values of the range in the last column of the Table all lie within the warning lines, indicating that the process variability is under control.**



Shewhart chart for means

- Minitab can be used to produce Shewhart charts for the mean and the range.
- The program calculates a value for $\overline{R}$ directly from the data.
- The Figurebelow shows Minitab charts for the data in the Table.
- Minitab (like some texts) calculates the warning and action lines for the range by approximating the (asymmetrical) distribution of $\overline{R}$ by a normal distribution.
- This is why the positions of these lines differ from those calculated above using equations (4.9) and (4.10).

Cusum (Cumulative sum) charts

- **A cusum chart is a type of control charts (cumulative sum control chart).**
- **It is used to detect small changes from the target mean, T, (between 0-0.5 sigma)**
- **For larger shifts (0.5-2.5), Shewart-type charts are just as good and easier to use.**
- **Cusum charts plot the *cumulative sum of the deviations between each data point (a sample average) and a reference value, T.***
- **Unlike other control charts, one studying a cusum chart will be concerned with the *slope of the plotted line, not just the distance between plotted points and the centerline.***

Cusum Charts
Principle of the Cusum Chart

- **The cumulative sum, *S (cusum), is understood as the sum of the deviations from* a target value.**
- **The target value may, for example, correspond to the mean value of a control sample determined in the preliminary period (pre-period).**
- **This mean value, also known as the reference value, *k, is subtracted from every control analysis result, x_i, and the difference is added to the sum of all previous* differences**

Cumulative sums:

$S_1 = (x_1 - k)$

$S_2 = S_1 + (x_2 - k)$

$S_3 = S_2 + (x_3 - k)$

.

.

$S_N = S_{N-1} + (x_{n} - k) = (\sum x_i) - nk$

CuSum Charts

- **In other words, for a series of measurements x_1, x_2, . . X_n the cumulative sum of differences (CuSum) between the observed value and the target value m is determined using**

$$C_1 = x_1 - \mu$$

$$C_2 = (x_2 - \mu) + (x_1 - \mu) = C_1 + (x_2 - \mu)$$

and so on resulting in (8.3-1):

$$C_i = \sum_{j=1,i} (x_j - \mu).$$

Principle of the Cusum Chart

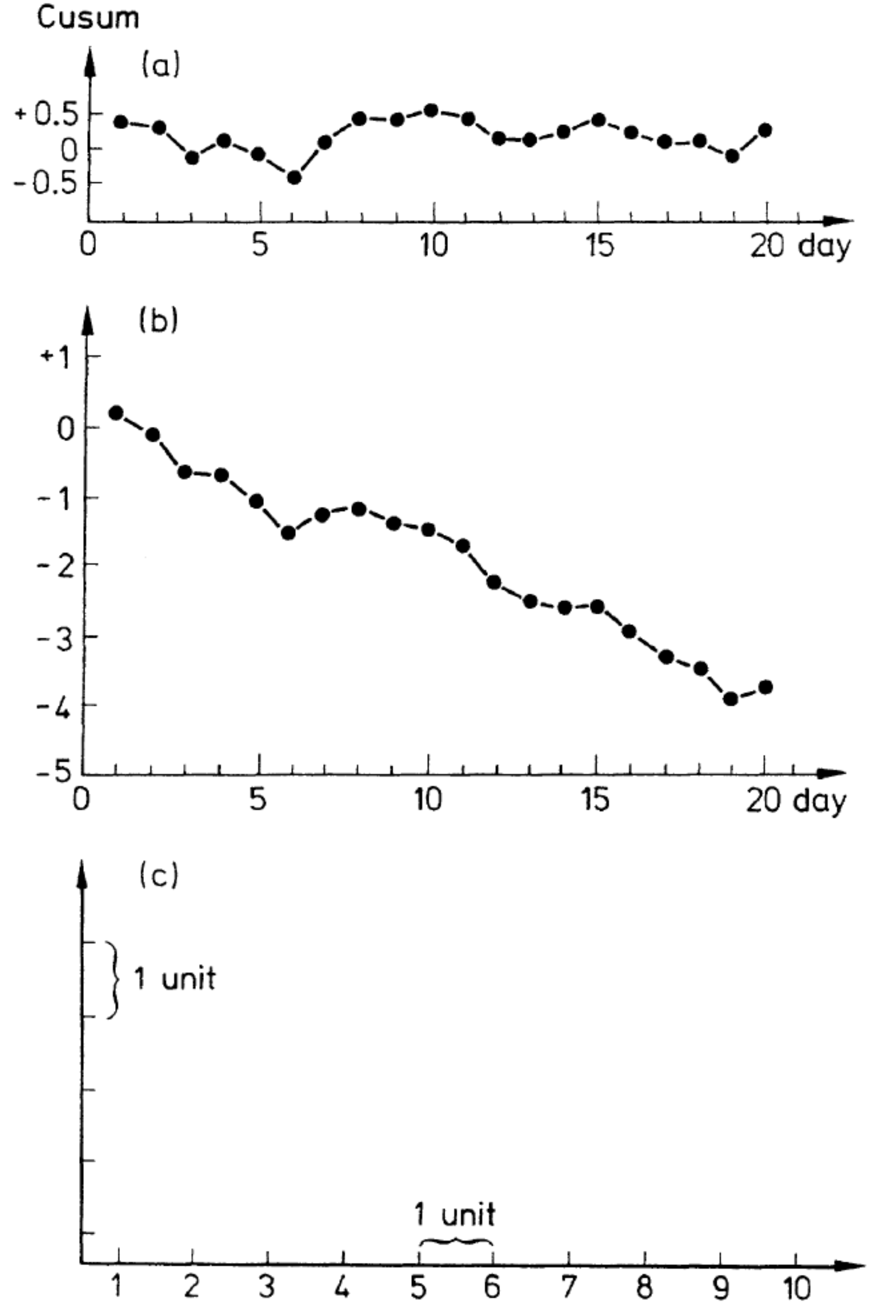
- **The cusum value *S_N (ordinate) is then plotted against the number of observed* results *N (abscissa)* *on a control chart.***
- **To determine an out-of-control situation, the slope of the cusum line is evaluated (see Figure 2-18).**
- **If the process is in control, the results of the control analyses vary randomly around the reference value *k, and the cumulative sums are* distributed around the value 0.**
- **A change in the process leads to**
  - **an increase or decrease in the cumulative sum,**
  - **the slope of the cusum line changes,**
  - **and an out-ofcontrol situation is detected.**

Fig. 2-18 Cusum progression:

a. **cusum progression for a properly chosen reference value k = 6.0,**

b. **cusum progression for an incorrect reference value k = 6.2,**

c. **scale of the cusum axis.**



CuSum Charts

- These values are displayed on a chart such as that in Fig. 8.3-1.
- Both axes are converted to the same scale in units. The scale factor w determines the scaling of the axes. It indicates which CuSum value represents a single unit on the y-axis.
- In general, w, is given in a multiple of the standard deviation w = q X S determined in the pre-period with 1 _ q _ 2. When the CuSum chart is constructed by mean
- values obtained by n analysis, then the standard deviation of the mean sm is used:

Construction of cusum chart

- CUSUM charts are constructed by calculating and plotting a cumulative sum based on the data. Let X1, X2, …, X24 represent 24 data points.
- From this, the cumulative sums S0, S1, …, S24 are calculated. Notice that 24 data points leads to 25 (0 through 24) sums.
- The cumulative sums are calculated as follows:
  1. First calculate the average:

$$\boxed{\overline{X} = \frac{X_1 + X_2 + \ldots + X_{24}}{24}}$$

  2. Start the cumulative sum at zero by setting S0 = 0.
  3. Calculate the other cumulative sums by adding the difference between current value and the average to the previous sum, i.e.:

$$S_i = S_{i-1} + \left(X_i - \overline{X}\right)$$

for i=1,2,…,24.

Example

M	T	M-T	Σ (M-T)
10	10	0	0
11	10	+1	+1
9	10	-1	0
10	10	0	0
12	10	+2	+2
9	10	-1	+1 and so on

- **The cumulative sum is not the cumulative sum of the values. Instead it is the cumulative sum of differences between the values and the average.**
- **Because the average is subtracted from each value, the cumulative sum also ends at zero (S24=0).**

- **How does one interpret a CUSUM chart?**
- **Suppose that during a period of time the values are all above average.**
- **The amounts added to the cumulative sum will be positive and the sum will steadily increase.**
- **A segment of the CUSUM chart with an upward slope indicates a period where the values tend to be above average.**
- **Likewise a segment with a downward slope indicates a period of time where the values tend to be below the average**

Illustration of the cusum charts approach

- An example of the approach is shown in Table 4.3, a series of measurements for which the target value is 80, and $\sigma/\sqrt{n}$ *is* 2.5.
- When the sample means are plotted on a Shewhart chart (Figure 4.6 below) it is clear that from about the ***seventh observation*** onwards a change in the process mean may well have occurred, but all the points remain on or inside the warning lines.
- (Only the lower warning and action lines are shown in the figure.)

Table 4.3 Example data for cusum calculation

Observation number	Sample mean	Sample mean – target value	Cusum
1	82	2	2
2	79	–1	1
3	80	0	1
4	78	–2	–1
5	82	2	1
6	79	–1	0
7	80	0	0
8	79	–1	–1
9	78	–2	–3
10	80	0	–3
11	76	–4	–7
12	77	–3	–10
13	76	–4	–14
14	76	–4	–18
15	75	–5	–23

Figure 4.6 Shewhart chart for Table 4.3 data.

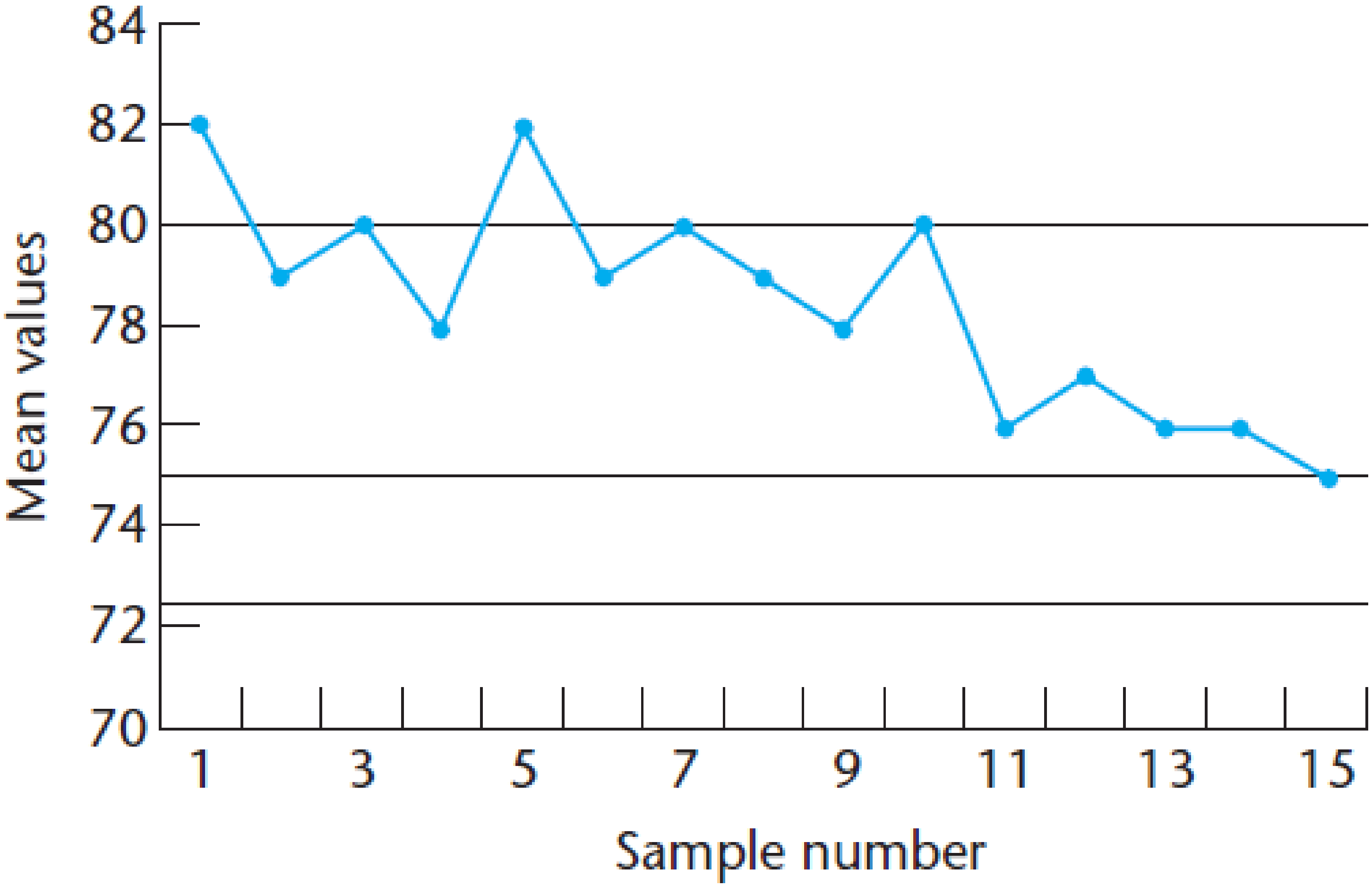
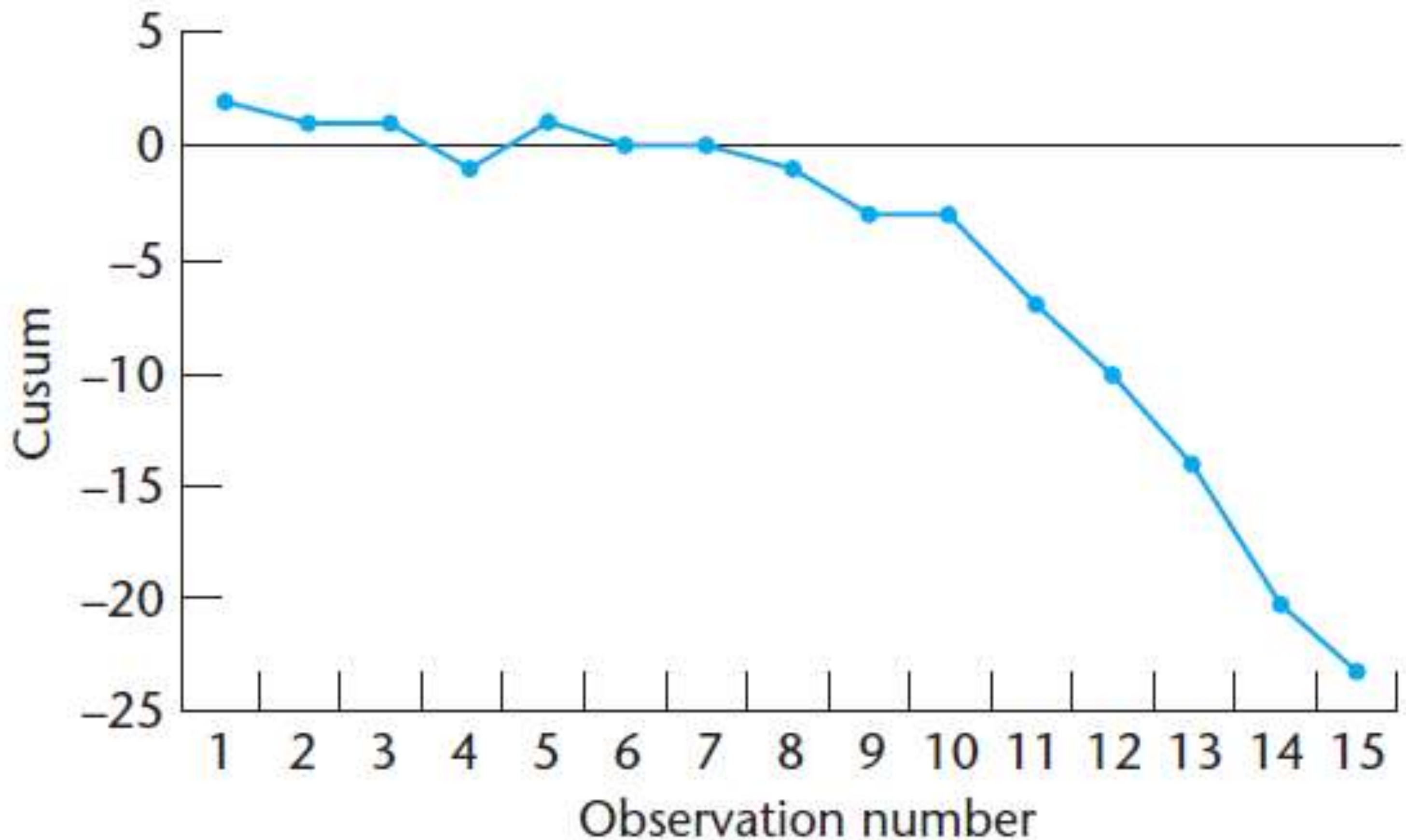


Illustration of the cusum charts approach

- **The calculation of the cusum is shown in the last two columns of the table, which show that the sum of the deviations of the sample means from the target value is carried forward cumulatively, careful attention being paid to the signs of the devia-tions.**
- **If a manufacturing or analytical process is under control, positive and negative deviations from the target value are equally likely and the cusum should oscillate about zero.**
- ***If the process mean changes, the cusum will move away from zero*.**
- **In the example given, the process mean seems to fall after the seventh observation, so the cusum becomes more and more negative. The resulting control chart is shown in Figure 4.7 below.**

Figure 4.7 Cusum chart for Table 4.3 data.

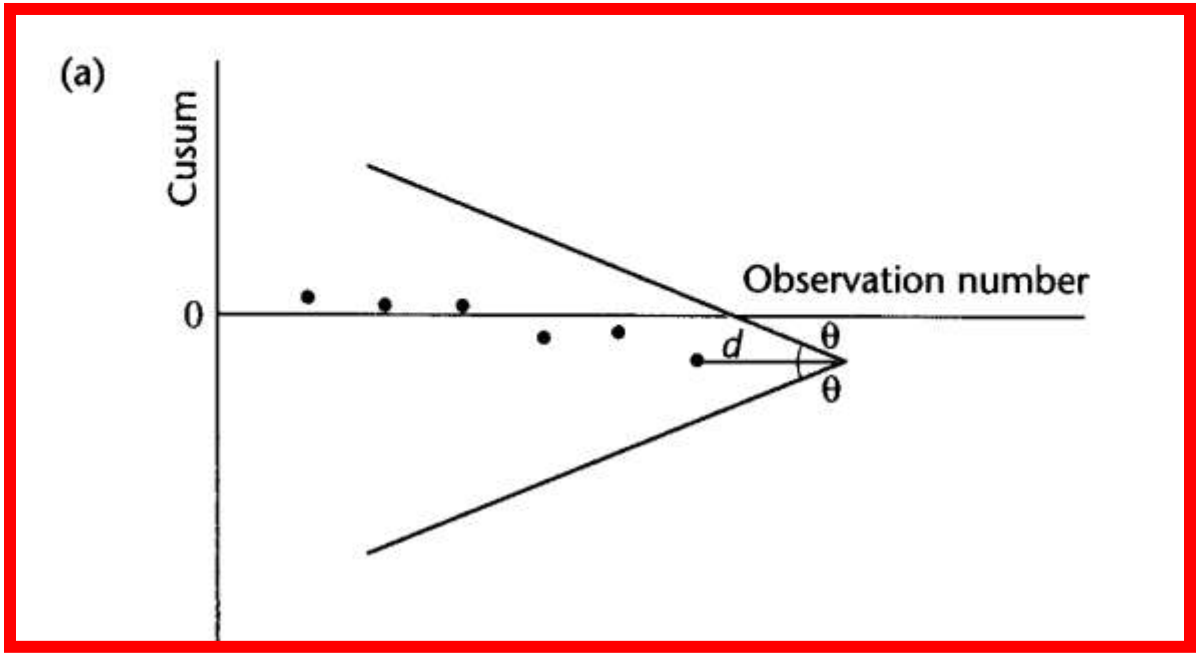


V-mask

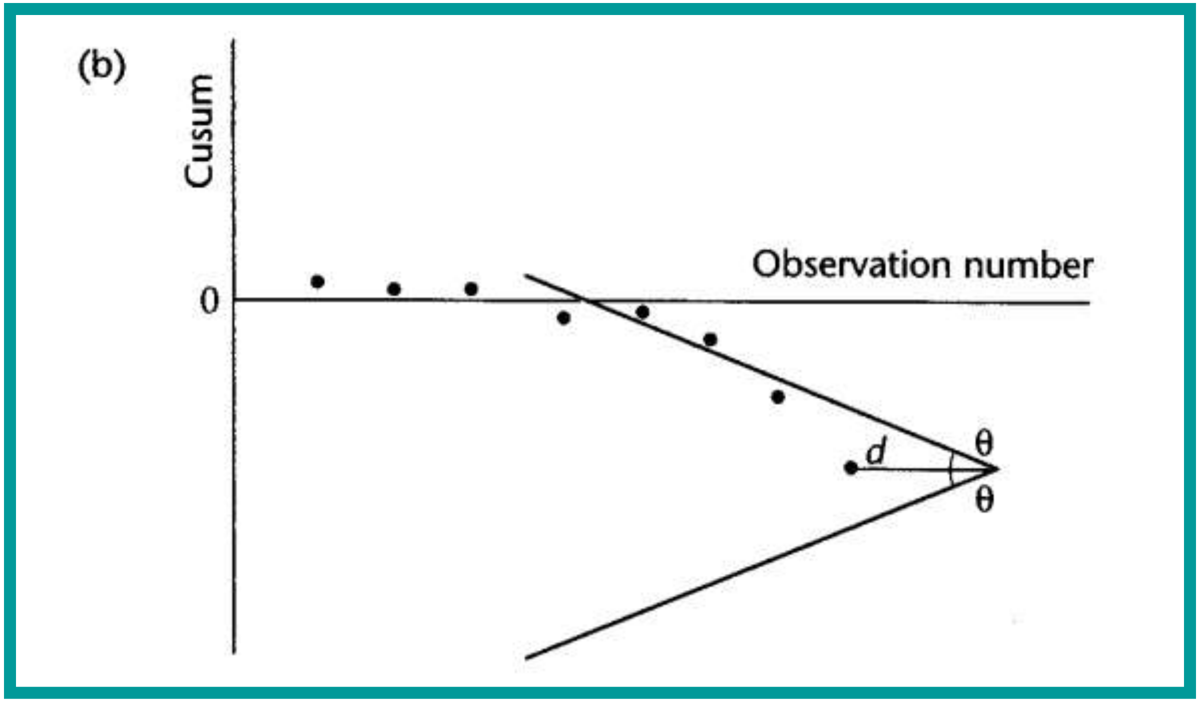
- **Proper interpretation of cusum charts, to show that a genuine change in the process mean has occurred, requires a *V-mask*.**
- **The mask is engraved (imprinted) on a transparent plastic sheet, and is placed over the control chart with its axis of symmetry horizontal and its apex a distance *d* to the right of the last observation (Figure 4.8 below).**

- **If all the points on the chart lie within the arms of the V, then the process is in control (Figure).**
- **The mask is also characterized by tan θ, the tangent of the semi-angle, θ, between the arms of the V.**
- **Values of *d* and tan θ are chosen so that significant changes in the process mean are detected quickly, but false alarms are few.**
- **The unit of *d* is the distance between successive observations.**

Figure 4.8



Use of the V-mask With the process In control



Use of the V-mask With the process out of control

- The value of tan θ used clearly depends on the relative scales of the two axes on the chart: a commonly used convention is to make the distance between successive observations on the x-axis equal to $2\sigma/\sqrt{n}$ on the y-axis.
- In summary, cusum charts have the advantage that they react more quickly than Shewhart charts to a change in the process mean (as Figure 4.7 clearly shows), without increasing the chances of a false alarm.
- The point of the slope change in a cusum chart indicates the point where the process mean has changed, and the value of the slope indicates the size of the change.
- Naturally, if a cusum chart suggests that a change in the process mean has occurred, we must also test for possible changes in σ
- This can be done using a Shewhart chart, but cusum charts for ranges can also be plotted.

Interpretation of cusum chart

CuSum charts cannot be interpreted using warning and action limits as in the interpretation of Shewhart chart, but there are some possibilities for recognizing an out of-control situation:

- **Visual estimation of the slope of the CuSum line. An out-of-control situation can be shown by changes in the slope of the CuSum line.**
- **Numerical criteria.**
- **Use of software packages .**
- **Use of the V-mask as the decision criterion**

Purpose and Applications of the Cusum Chart

- **The cusum chart was introduced into industrial quality assurance by E. S. Page in 1954.**
- **This chart is a further development of the Shewhart chart, whereby single results are no longer entered but instead the summation of the deviations of the single results from a set value.**
- **Therefore, each new entry contains not only information about the current status, but also about past analysis values of the analytical process in question.**
- **In this manner, changes that would not lead to an out-of-control situation on an $\bar{X}$ *-chart* *can be more easily detected.***
- ***This is especially advantageous for processes* with a** large variance

Applications for which cusum technique is suitable

1. **Recognition of a systematic change or shift in the mean value of a process in progress],**
2. **Determination of the order of magnitude by which the mean value has changed.**
3. **Determination of the point in time at which the change occurred.**
4. **Short-term prediction of the future mean value.**

Establishing a Cusum Chart

- **A cusum chart should be dimensioned such that it reacts sensitively to the smallest deviation in the mean value that is seen as important in practice.**
- **This reaction should be reflected in a clearly visible change in the slope of the cusum line.**
- **In the case of an "in-control process", the slope of the line is decisively dependent upon the chosen reference value *k;***
- ***In the case of an "out-of-control process", the***

  clearness of the change in the slope is dependent on the scale of the *y-axis (cusum* axis).
- **Therefore, one must keep in mind not only a correct choice of the referencem value *k, but also of the scale factor, w.***

Choice of the Reference Value *k*

- **If a certified reference material is available for use in quality assurance, then the given standard concentration is equivalent to the reference value *k.***
- ***If this is not* the case, the concentration of the control sample must be determined in a preliminary period (as for an *-chart).***
- ***The estimate of the mean value* should be based on at least 20 analyses.**
- **If the reference value *k is imprecisely determined, then the cusum values do* not fluctuate about the value 0, i. e., the cusum line rises or falls continuously.**
- **An example of this is shown in Figure 2-18**
- **If the "correct" reference value is not chosen, on the one hand the upper or lower limits of the cusum chart may be reached very quickly, but on the otherhand small changes in slope are more difficult to recognize.**

Scale of the *y-Axis (Cusum Axis)*

- **The abscissa and ordinate are first assigned equidistant divisions (each designated as 1 unit).**
- **The scale of the axes is determined by the scale factor, *w*. *This indicates which* cusum value corresponds to a unit on the cusum axis.**
- **Normally, *w is expressed as* "*q number of standard deviations*".**
- ***For this, the standard deviation*** $S = \frac{S'}{\sqrt{n}}$ ***S is determined* from the preliminary period standard deviation *S'***
- **For only one control analysis per series, *s = s'; if the cusum chart is constructed* with mean values from each of *n analyses, then the standard deviation of the* mean values is included in the scale:**

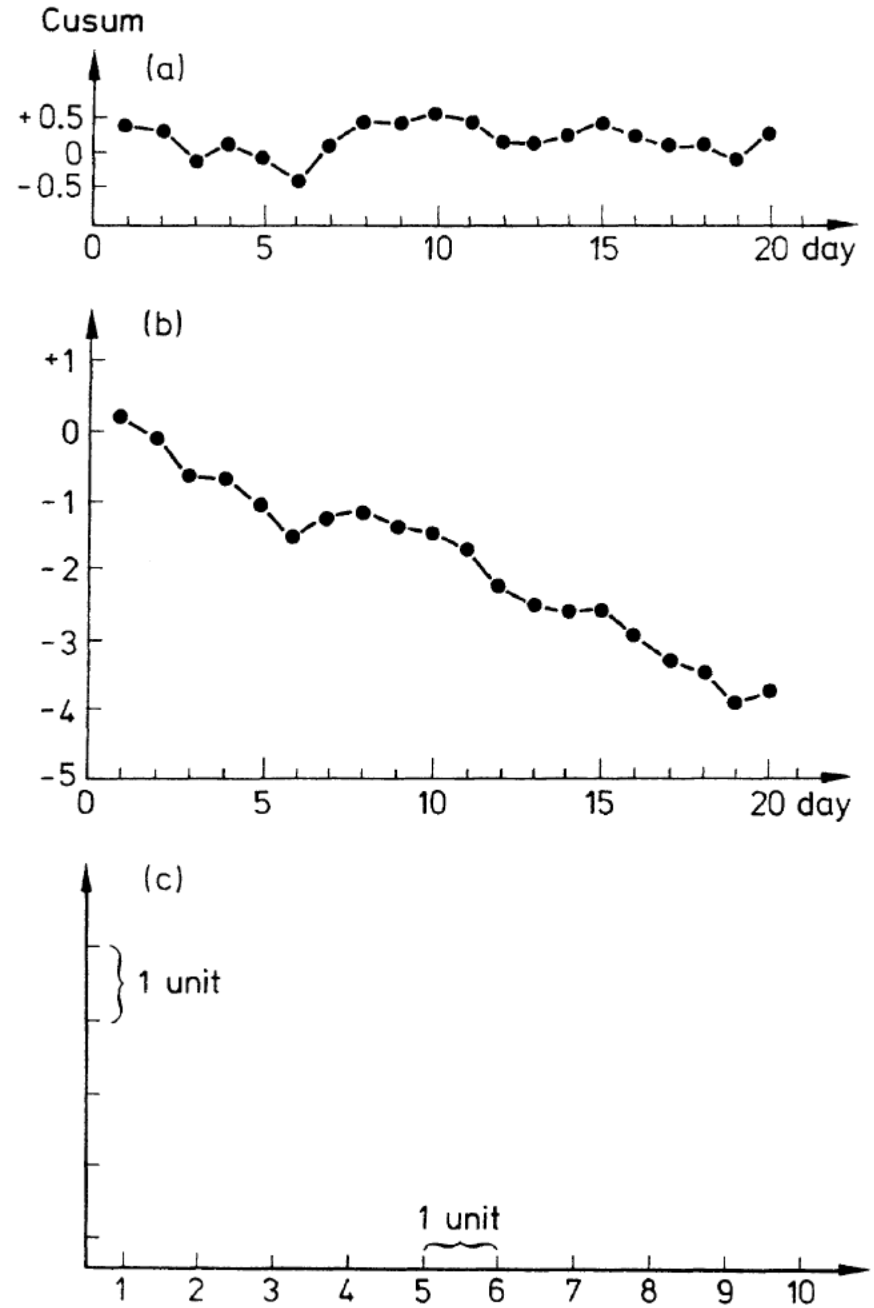
$$S = \frac{S'}{\sqrt{n}}$$

Fig. 2-18 Cusum progression:

a. cusum progression for a properly chosen reference value k = 6.0,

b. cusum progression for an incorrect reference value k = 6.2,

c. scale of the cusum axis.



- **Both the scale of the cusum axis and the correct (or skillful) choice of the reference value contribute to making a cusum chart that is easy to handle.**
- **The cusum axis dimensions should neither be too far apart (see Figure 2-19) nor too close together as a change in the slope is difficult to recognize in both cases.**

- **As an example, the following scale factor was suggested:**

  A factor of w = 2X s (q = 2) to w = 1 X s (q = 1) for use with graphical decision criteria.
- **If the distance between two entries on the *x-axis (e. g., one day) is defined as a* unit, then the same distance on the cusum axis is represented by 2 X *s*.**
- ***The cusum* line rises at 45 if two consecutive values differ by 2 X *s*.**

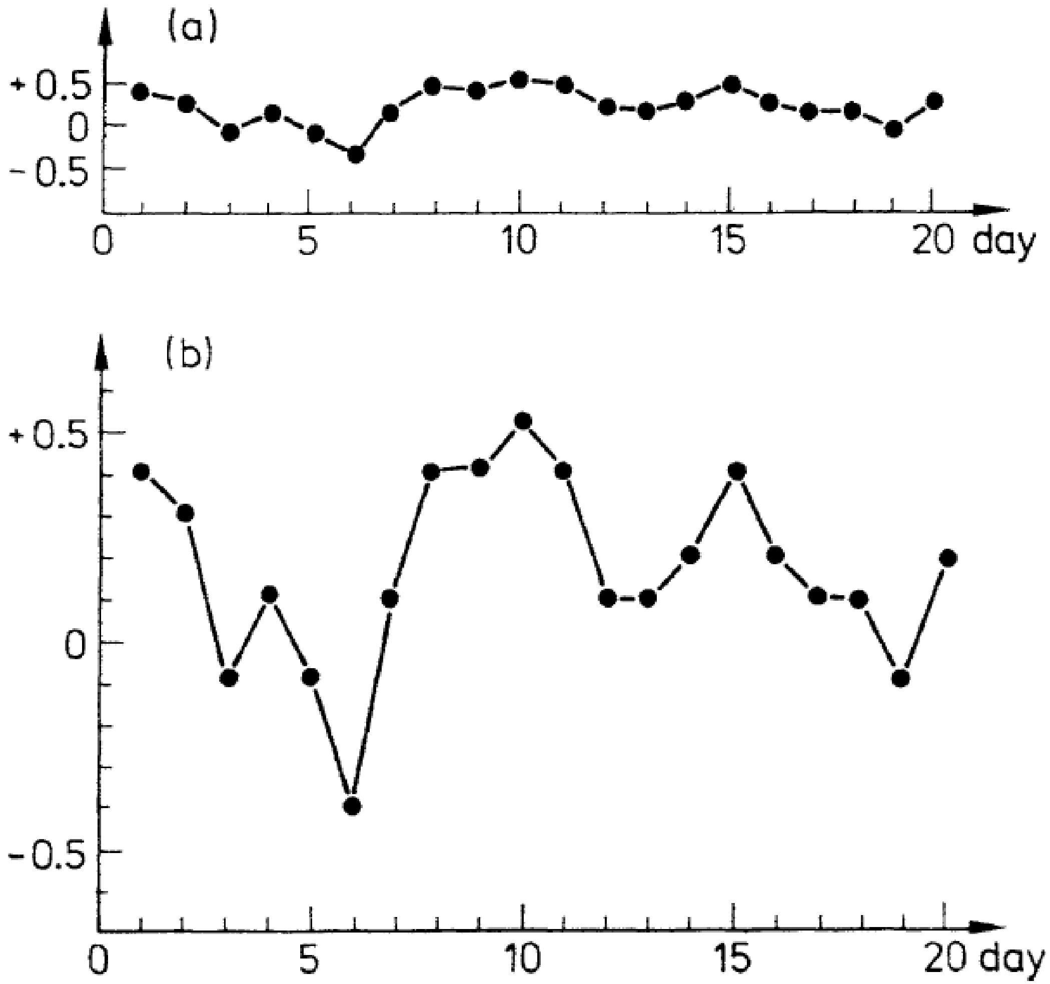


Fig. 2-19 Influence of the cusum axis scale;

a. suitable choice of scale (w = 2s),

b. scale increments too far apart.

Determination of an Out-of-Control Situation

In order to determine an out-of-control situation, there are three decision criteria for cusum charts:

1. **Visual decision criterion.**
2. **The V-mask as decision criterion.**
3. **Numerical decision criterion (this corresponds to the V mask under standardized conditions).**

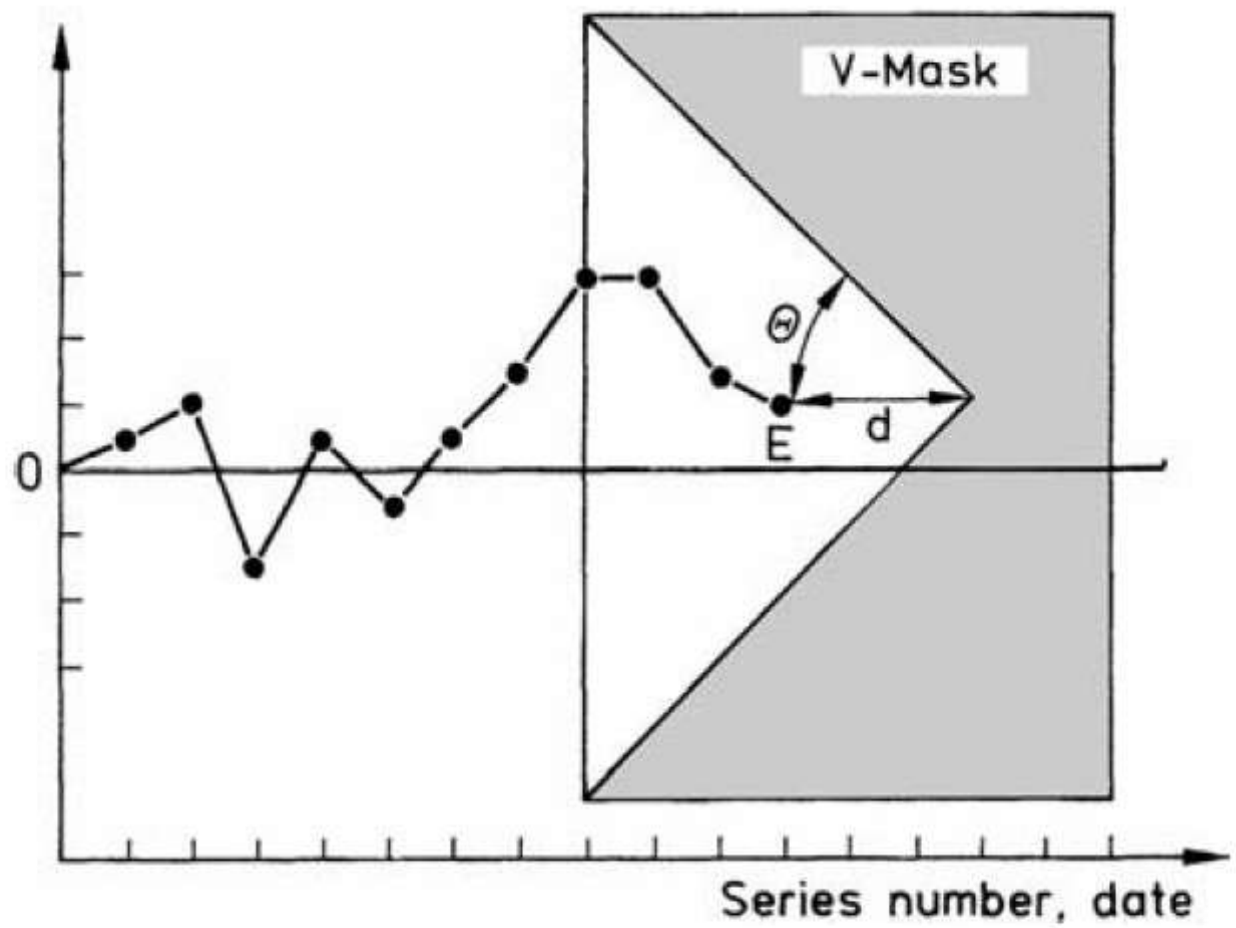
Visual Decision Criterion

- **A deviation of the actual from the required mean value leads to a change in slope.**
- **This change can be easily determined visually if the chart is properly dimensioned and the process is reliable.**
- **However, only slight changes in the cusum progression make a visual interpretation difficult.**
- **In order to make sound decisions, which can be reproduced by others, it is advantageous to use an objective decision criterion.**

V-Mask

- **The V-mask, is a two-sided statistical test that can determine positive and negative deviations from a mean value.**
- **Since it is possible to consider the previous cusum progression, the V-mask technique combines visual interpretation with objective test criteria.**
- **The V-mask is defined by the two parameters *d and* θ *(see Figure 2-20).***

The V-mask parameters d and θ Fig. 2-20



- **The leading distance *d* represents the distance from the vertex of the V-mask to the most recent entry on the chart; *d* is expressed in abscissa units (e. g., days).**
- **θ is the angle between the arms of the mask and the horizontal drawn through the mask vertex.**
- **After establishing these two parameters, the V-mask may be drawn on transparent film or cut out of cardboard**
- **The V-mask is then positioned on the cusum chart at a distance d from the most recent entry, so that the vertex (placed horizontally) points forward.**
- **For each new entry, the mask is shifted so that the point E comes to lie on the new cusum value.**
- **This represents a shifting of one abscissa unit. It should be noted that the V-mask may not turn its vertex around, i. e. the leading distance d remains parallel to the x-axis.**

- **The first cusum value that lies outside of the V-mask indicates the point in time at which the out-of-control situation appeared.**
- **This information can be very helpful when searching for the cause of the error.**
- **If the error is discovered and corrected,**
- **then the cumulative summation begins again at zero.**

- **An out-of-control situation is indicated if the cusum line crosses one of the arms of the V-mask.**
- **The larger the values of θ and d, the more infrequently an out-of-control situation arises.**
- **If the cusum line cuts through the upper arm of the mask, then the mean value has decreased.**
- **The mean value has increased if the line crosses the lower arm (see Figure 2-21).**

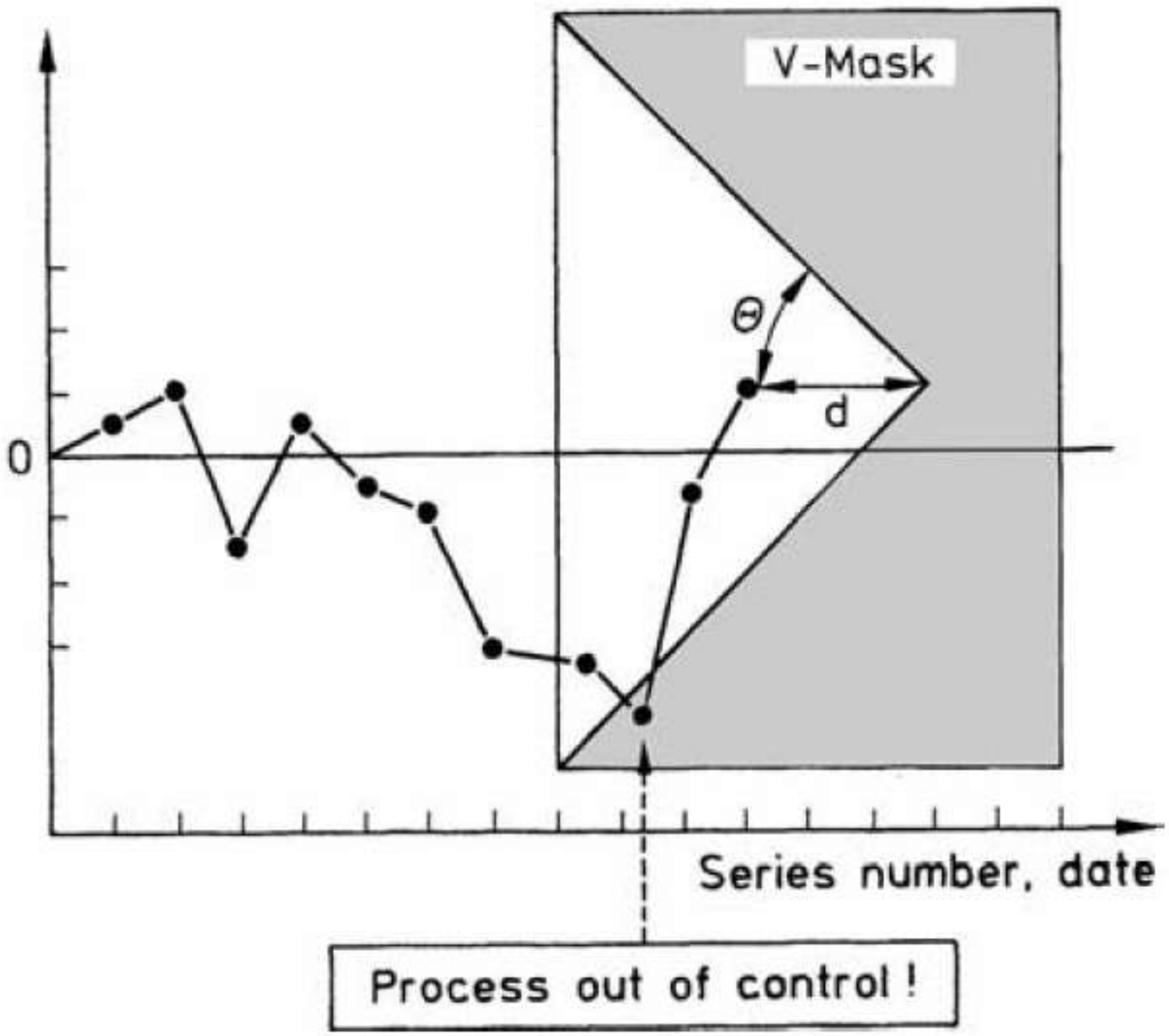


Figure 2-21Ou-of-control situation

Example (Challenge 8.3-1)

In order to control whether the validated ion chromatographic (IC) method for the determination of nitrite-N is fit-for-purpose in routine analysis, a control sample with a content of c = 12.25 mg L^{-1} is analyzed under the same conditions. The results are shown in Table 8.3-1.

(a) Construct a Shewhart chart with warning and action limits for P = 95.5% and P = 99.7%; respectively, and checkwhether an out-of-control situation can be detected.

(b) Construct a CuSum chart and check by a V-mask using the scaling Factor w = 1s and the smallest deviation D = 1.3 X s whether the method can be considered to be under statistical control at P = 99.7%. Compare the result obtained by the Shewhart chart.

Table 8.3-1 Results of controlling the IC method for the determination of nitrite-N in routine analysis using a control sample with c = 12:25 mg L

Observation no.	c in mg L^{-1}	Observation no.	c in mg L^{-1}
1	12.28	11	12.34
2	12.37	12	12.17
3	12.00	13	12.34
4	12.23	14	12.35
5	12.38	15	11.89
6	12.18	16	12.12
7	12.01	17	12.18
8	12.23	18	12.20
9	12.33	19	12.09
10	12.38	20	12.15

Solution to Challenge 8.3-1

(a) The standard deviation of the results given in Table 8.3-1 is s = 0.140 mgL^{-1} and the mean value is $\bar{x}$ = 12.21 mgL^{-1}

- Warning limits (WL) calculated as $\mu \pm 2s$ = 12.21 $\pm$ 0.28 mg L^{-1} are 12.49 mgL^{-1} and 11.93 mg L^{-1}
- Action limits (AL) calculated as $\mu \pm 2s$ =12.21 $\pm$ 0.42 mg L^{-1}are

  12.63 mg L^{-1} and 11.79 mg L^{-1}
- The Shewhart chart is shown in Fig. 8.3-3.
- According to the Shewhart chart, no out-of-control condition can be detected.
- The measured value of observation no. 15 lies indeed outside the lower warning line, but inside the action line. Because the next measured value is again inside the warning line no out-of-control situation is present at observation no. 15.

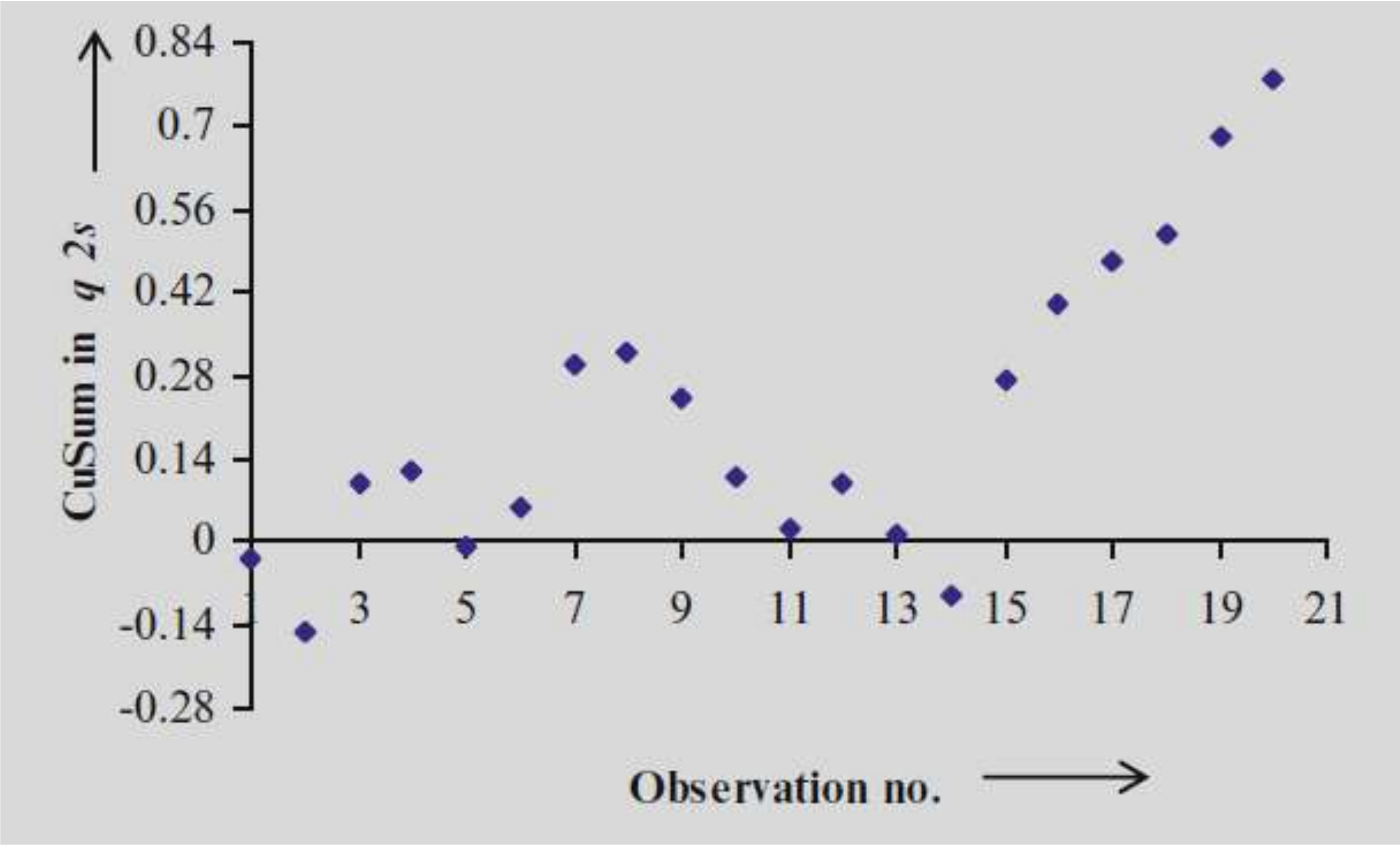


Fig. 8.3-4 CuSum chart for the data given in Table 8.3-2

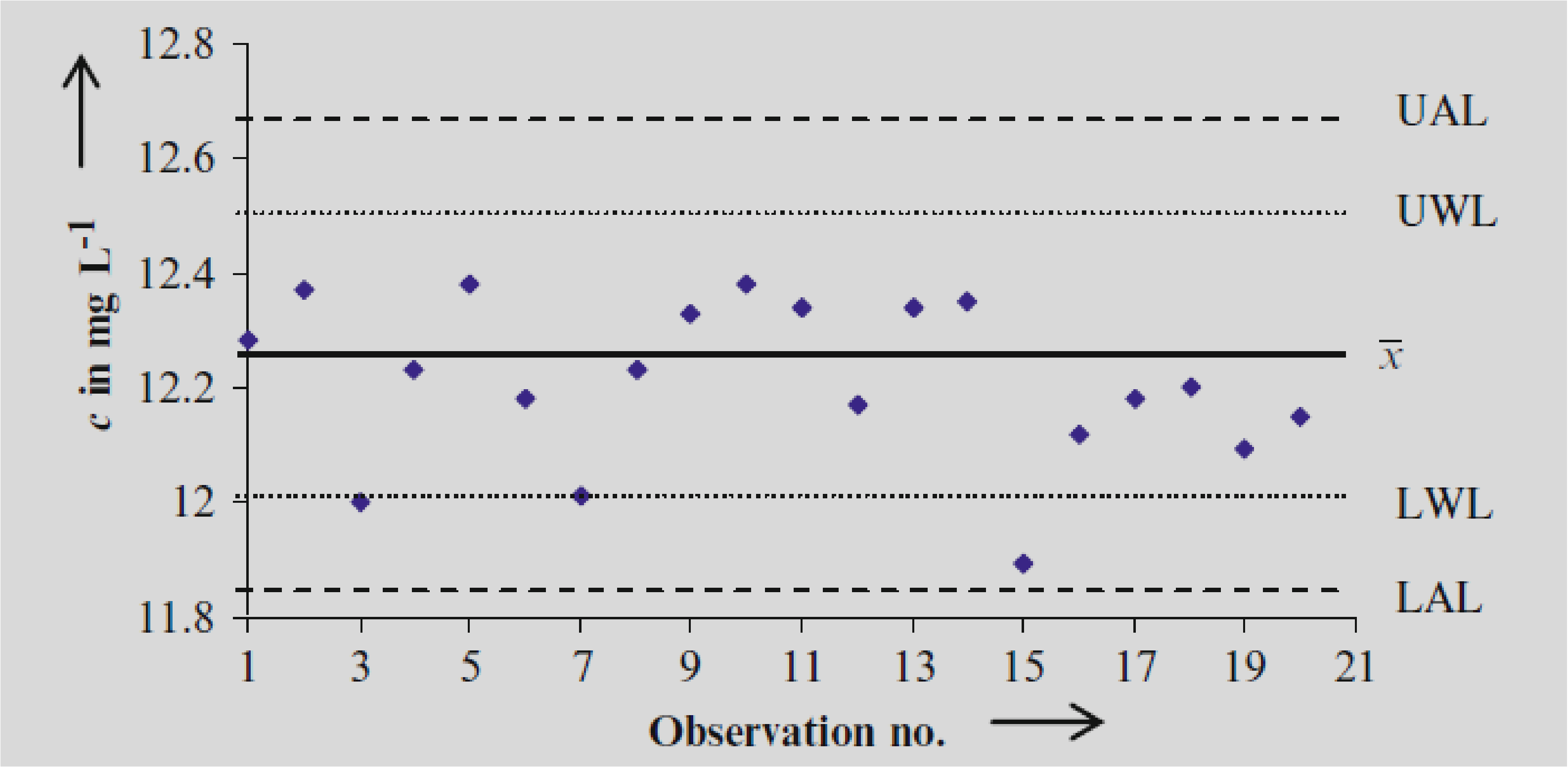


Fig. 8.3-3 Shewhart chart constructed from data in Table 8.3-1

b. The CuSum-values calculated according to (8.3-1) are summarized in Table 8.3-2 and the CuSum chart is shown in Fig. 8.3-4.

$$C_i = \sum_{j=1,i} (x_j - \mu). \qquad (8.3\text{-}1)$$

- In order to check for an out-of-control situation, the V-mask must be constructed using the parameters:

l. Standard error of the mean s_m = 0:03133 mg L^{-1} which is calculated by (8.3-2) from the results given in Table 8.3-1.

$$s_{\mathrm{m}} = \frac{s}{\sqrt{n}}. \qquad (8.3\text{-}2)$$

2. The scaling factor given as w = 1XS.

3. The smallest deviation D = 1.5XS.

Table 8.3-2 Calculation of the cumulative sum (CuSum) for the data given in Table 8.3-1

Observation no.	$\mu - x_i$	C_i	Observation no.	$\mu - x_i$	C_i
1	−0.03	−0.03	11	−0.09	0.02
2	−0.12	−0.15	12	0.08	0.10
3	0.25	0.10	13	−0.09	0.01
4	0.02	0.12	14	−0.10	−0.09
5	−0.13	−0.01	15	0.36	0.27
6	0.07	0.06	16	0.13	0.40
7	0.24	0.30	17	0.07	0.47
8	0.02	0.32	18	0.05	0.52
9	−0.08	0.24	19	0.16	0.68
10	−0.13	0.11	20	0.10	0.78

Calculation of the angle θ :

$$\theta = \arctan\left(\frac{D}{2w}\right) = \arctan\left(\frac{1.5}{2}\right) = 0.6435 \quad (8.3\text{-}5)$$

$$\theta = 36.87^\circ.$$

Calculation of the distance d in the V-mask:

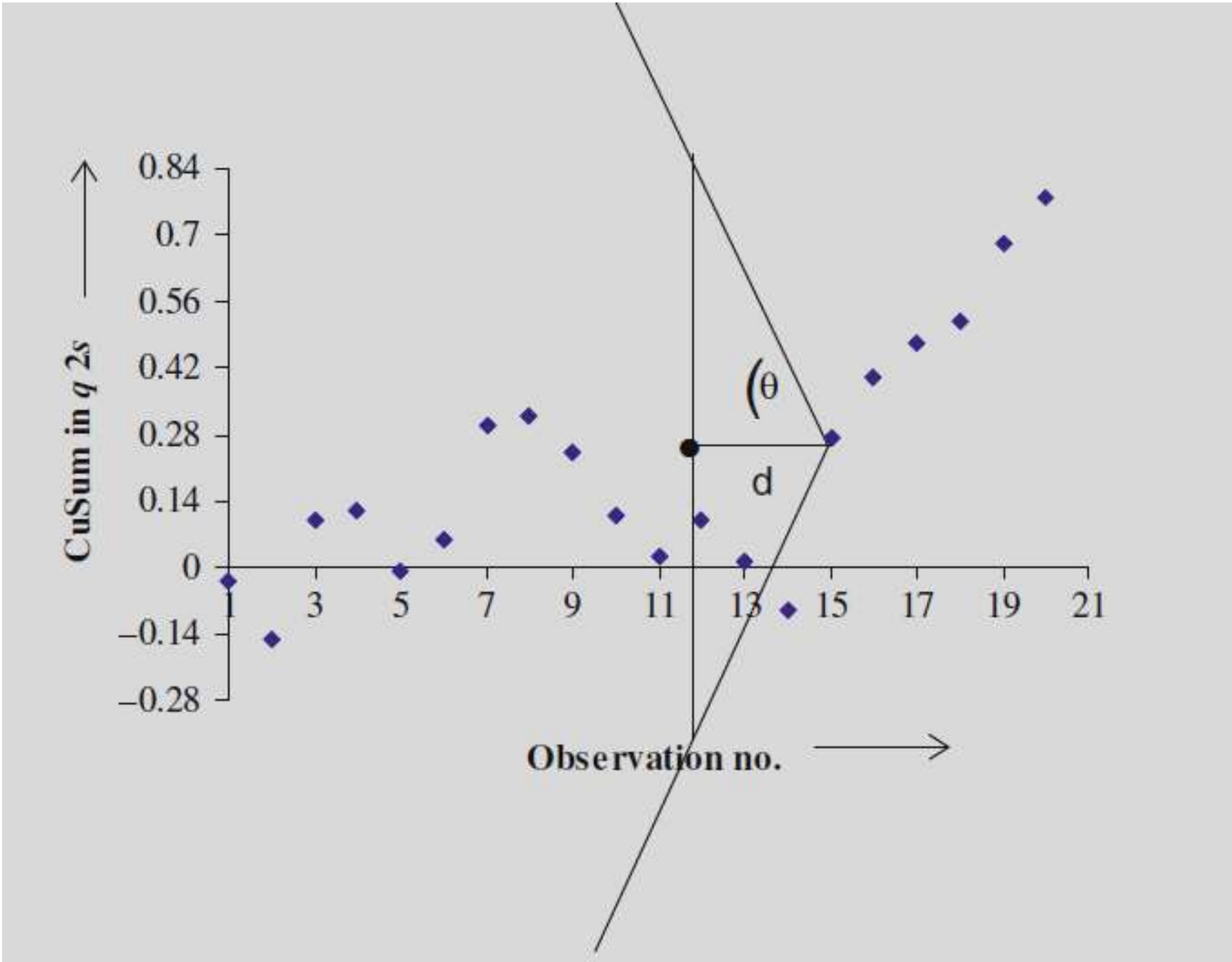
$$d = \frac{-2 \cdot s^2}{D^2} \cdot \ln\alpha = \frac{-2}{1.3^2} \cdot \ln 0.027 = 4.25 \text{ units.} \quad (8.3\text{-}6)$$

- **The V-mask constructed with y = 37 and d =4.3 units overlies observation no. 15.**
- **As Fig. 8.3-5 shows, observation no. 14 falls outside the lower arm of the V-mask, indicating an upward shift which is manifest at observation point 15.**
- **Note that the Shewhart mean chart does not show any out-of-control situation.**
- **This demonstrates the higher sensitivity of the CuSum chart in comparison with the Shewhart mean value chart.**
- **The relative merits of different chart types when applied to detect gross errors, shifts in mean, and shifts in variability are summarized in Table 8.3-3.**

Table 8.3-3 Relative merits of different chart types when applied to detect changes in the first column

Cause of change	Chart type		
	Mean	Range	CuSum
Gross error	+++	++	+
Shifts in mean	++		+++
Shifts in variability		+++	

+ suitable, ++ very suitable, +++ especially suitable for recognizing out-of-control situations



0.84
0.7
0.56
0.42
0.28
0.14
0
–0.14
–0.28
CuSum in q 2s
1
3
5
7
9
11
13
15
17
19
21
θ
d
Observation no.