A practicable way to set up and to use control charts

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Set up a new analytical method

• Working range (lowest and highest sample concentration?)
• Needed precision of the method (limiting values?)
• Calibration of the instrument with (matrix adapted) standards (linear, quadratic?)
• LOD, LOQ, maximum acceptable LOQ
• CRM, ring-test samples (deviation from the reference content, recovery, spike)…….
New analytical method

• The new method is working *today* with the
  – required accuracy of the mean (trueness)
  – required precision
But what is tomorrow....?

Control charts **check** the quality of your method over a longer period and allows you to **adjust** your method – if needed!
Types of control charts

• X-Chart / Mean-Chart
• Blank Chart
• R-Chart / Range Chart
• Recovery Chart
• ……..
Properties of a control sample

- Similar matrix like your sample
- Similar analyt concentration
- Available over a longer period
- Stability of the sample
- Homogenity of the sample
- No contamination effects from bottle material
- No losses of the analyt or contamination during taking of subsamples
Examples for control samples (for a mean chart)

• **Deposition**
  – Mineral water
  – Synthetic sample

• **Foliage and Litterfall**
  – Old ringtest material
  – (Standard) Reference material

• **Soil**
  – Old ringtest material
  – (Standard) Reference material
## Types of control samples

<table>
<thead>
<tr>
<th>Sample material</th>
<th>Trueness</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>No</td>
<td>Yes (Mean-Chart)</td>
</tr>
<tr>
<td>Blank</td>
<td>Yes (Blank-Chart)</td>
<td>Yes</td>
</tr>
<tr>
<td>Real sample</td>
<td>No</td>
<td>Yes (Range-Chart)</td>
</tr>
<tr>
<td>Real sample + Spike</td>
<td>Yes (Recovery-Chart)</td>
<td>No</td>
</tr>
<tr>
<td>Synth. Sample</td>
<td>Yes (same matrix effects like in real samples)</td>
<td>Yes</td>
</tr>
<tr>
<td>Ringtest material</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>(Standard) Reference Material</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
You can’t check the trueness of your method, if you use a calibration standard as control sample or if you prepare the control sample and calibration standards out of the same material!
„Standard“
20cm

„QC Sample“
= same ruler
like above
20cm
"Standard“ 20cm

"QC Sample“ 20cm
A good rule of thumb is for starting a control chart, use a reference material (ring test sample); central line is the nominal value and the action limit is equal (or a little bit lower than) the maximum tolerable limit (see ringtest reports).
Example for target control limits

- Reference material: $6 \pm 0.2 \text{ mg Ca/g}$

“Nominal value”
Example for target control limits

- Reference material: 6 ± 0.2 mg Ca/g
- Max. tolerable limit (high): 10% for Ca

“Requirement on the analytical quality”
Example for target control limits

- Reference material: $6 \pm 0.2 \text{ mg Ca/g}$
- Max. tolerable limit (high): 10% for Ca

$\rightarrow$ Central line 6 mg Ca/g
$\rightarrow$ „Action limit“ $\pm 10\% = \text{max. } 5.4 - 6.6$
$\rightarrow$ better use 5.5 – 6.5 mg Ca/g

You had to measure this sample over a longer period on different days, different reagents and with different calibrations,… (> 25 repetitions).
X-Chart / Mean-Chart

- $\bar{x} \pm 3s$ (99.7%)
- $\bar{x} \pm 2s$ (95.4%)

Analytical result
Statistic control limits

- Reference material: 6 ± 0.2 mg Ca/g
- Your standard deviation: 0.1 mg Ca/g

→ Central line: your average 5.9 mg Ca/g
   
   (Your average = nominal concentration of reference material?)

→ Warning limit ± 2s (± 0.2 mg Ca/g)

→ Action limit ± 3s (± 0.3 mg Ca/g)

These statistic control limits should be smaller than the target control limits!
Statistic control limits

KEEP IN MIND - Statistic limits mean:

• 3 values of 1000 are outside of the action limits

• 46 values of 1000 are outside of the warning limits
X-Chart / Mean-Chart

Date of analysis

Upper action limit
Upper warning limit
Mean value
Lower warning limit
Lower action limit

1-Feb 1-Mar 29-Mar 26-Apr 24-May 21-Jun 19-Jul 16-Aug
In control situations

• The control value is within the warning limits

• The control value is between warning and action limit and the two previous control values were within warning limits
Analytical run

S0-S2  Standard solutions
BL     Blank samples
QC     Quality Control samples
T1...  Test samples

Calibration OK Samples OK
Out of control situations

• The control value is outside the action limits

• The control value is between the warning and the action limit and at least one of the two previous control values is also between warning and action limit
Out of control situations – what to do now?

• Analyze some more (at least two) control samples

• Remedial actions have to be taken to find and eliminate the cause(s) of error
  – Check the calibration
  – Check the standards and reagents
  – Exchange of vessels? ….

The problem and the solution should be documented. Analyses which have been carried out since the last acceptable control value was obtained must be repeated.
Analytical run

Samples Not ok
Analytical run

Samples OK Samples OK
Out of control situations – what to do now?

• Analyse more control samples
• Due the decrease before: check the reagents/standards
• Re-analyze all samples from the last acceptable control value till now
• Documented problem and solution!
• How avoid errors like this in future?
Out of control situations – what to do now?

- Analyse more control samples
- Due the increase: Exchange of vessels? Contamination?
- Re-analyze all samples from the last acceptable control value till now
- Documented problem and solution!
- How avoid errors like this in future?
In control but out of statistical control situations

- Seven control values in consecutive order gradually increasing or decreasing
- 10 out of 11 consecutive control values are lying on the same side of the central line
In control but out of statistical control situations

- 10 out of 11 consecutive control values are lying on the same side of the central line
- Change of the standard sample batch
In control but out of statistical control situations

• In this case the analyst can report the analytical results but a problem may be developing

• Important trends should be discovered as early as possible

• Each laboratory has to decide in the quality manually how to treat these trends
Multielement methods & control charts

KEEP IN MIND - Statistic limits mean, if you analyse 20 elements with ICP:

• 60 results of 1000 samples are outside of the action limits

• 920 results of 1000 samples are outside of the warning limits
Multielement methods & control charts

• Using target control limits
• Or wider (statistical) limits for those analytes that are less important

Otherwise very often one result is out of control and making ordinary daily interpretation very unpractical!
Additional reporting is needed!

- For interpretation of the results of the control charts
- To find reasons for out of control situations
- To avoid errors in future
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- For interpretation of the results of the control charts
- To find reasons for out of control situations
- To avoid errors in future

- Value below action limit
- Too old reagent (stable only for one week)
- Write an opening date on the reagent bottle
Long-term evaluation of quality control data

- What is the quality (random and systematic effects) currently in the laboratory?
- Has the quality significantly changed over time?
- Are control limits and central line in the control chart still optimal for detecting out of control situations?
Other uses of quality control data and control charts

- Measurement uncertainty
- Method validation
- Method comparison
- Estimation of limit of detection
- Person comparison or qualification
- Evaluation of proficiency tests
- Environmental parameters and similar checks
NORDTEST REPORT TR 569

Internal Quality Control

Handbook for Chemical Laboratories
...after the 5th „Labheads“ meeting you know how to **ADJUST** your method!

Thank you for your attention!