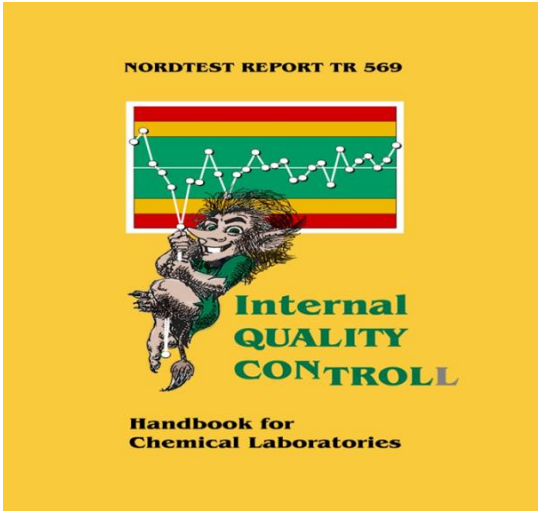
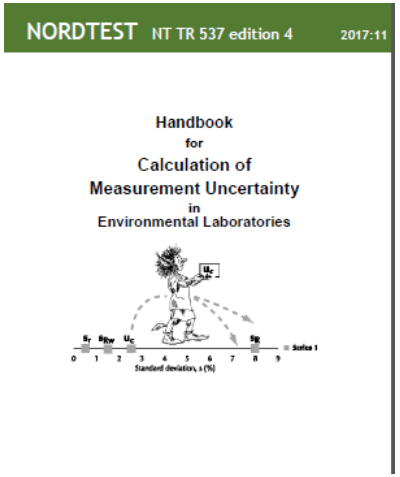
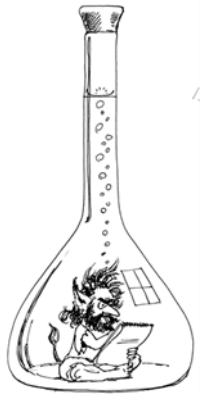
Revised internal Quality Control from NORDTEST

Eurachem workshop 2018 in Dublin on
Data – Quality, Analysis and Integrity





And info on revised measurement uncertainty handbook from Nordtest 2017

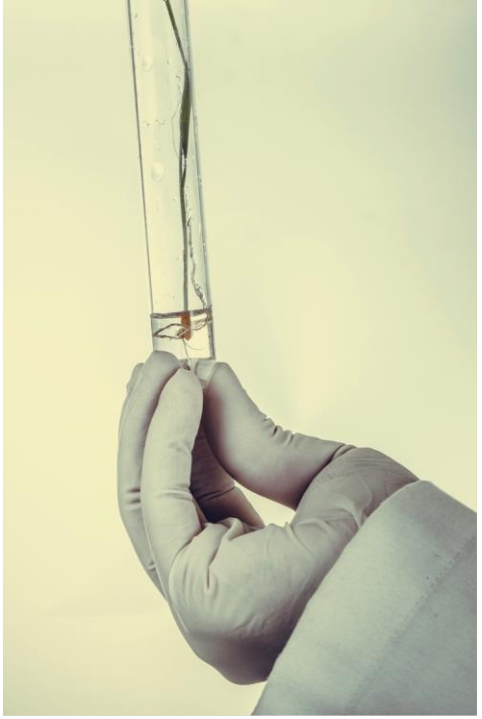


TROLLBOKEN AB

Bertil Magnusson
Research Institutes of Sweden

RESEARCH INSTITUTES OF SWEDEN

Our 2,200 employees support and innovative processes, and our roughly 100 testbeds are instrumental in developing the future-proofing of products, technologies, and services.



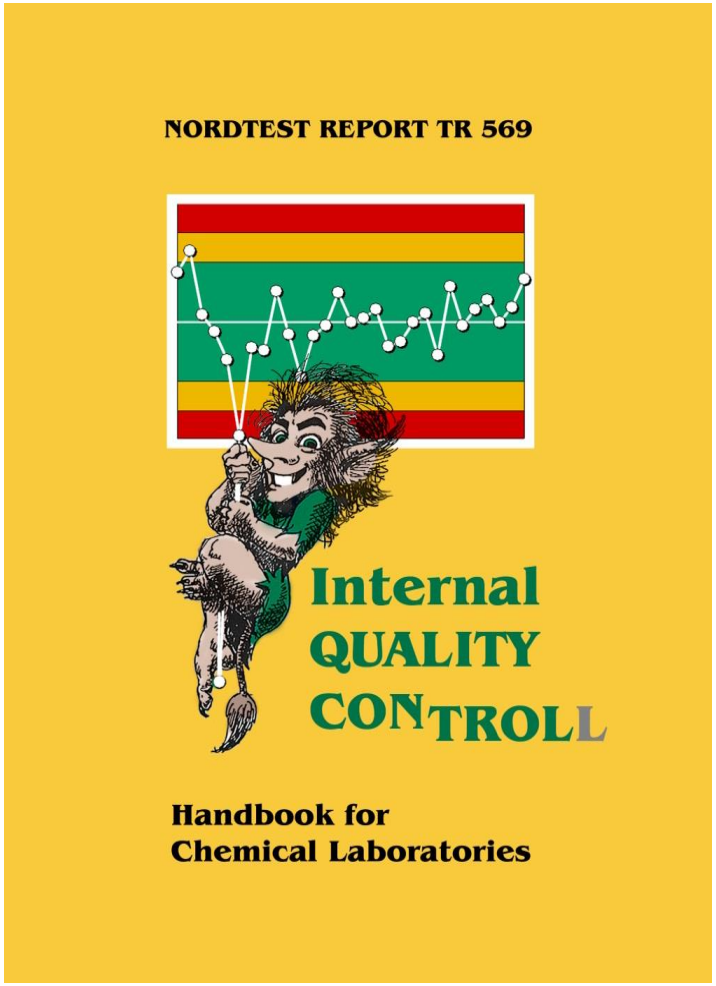
Research Institutes of Sweden

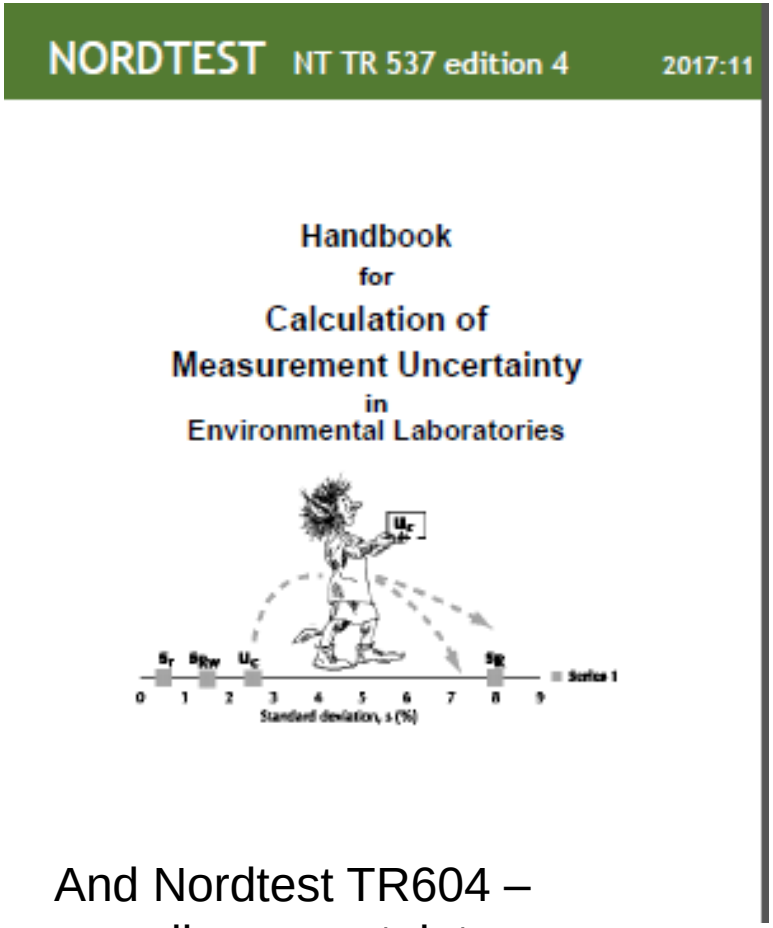
Bioscience and Materials
Chemistry and Materials

Nordtest

The emphasis of Nordtest is to develop, promote and innovate Nordic test methods and pre-normative activity.

Nordtest Handbooks





And Nordtest TR604 – sampling uncertainty…

Downloadable from www.nordtest.info

Authors

Haarald Hovind Norway

Mikael Krysell, Sweden

Irma Makinnen Finland

Ulla Lund, Denmark

And many many analytia chemists…

Terminology in QC

Control sample:

Sample material - test or blank samples, standard solutions

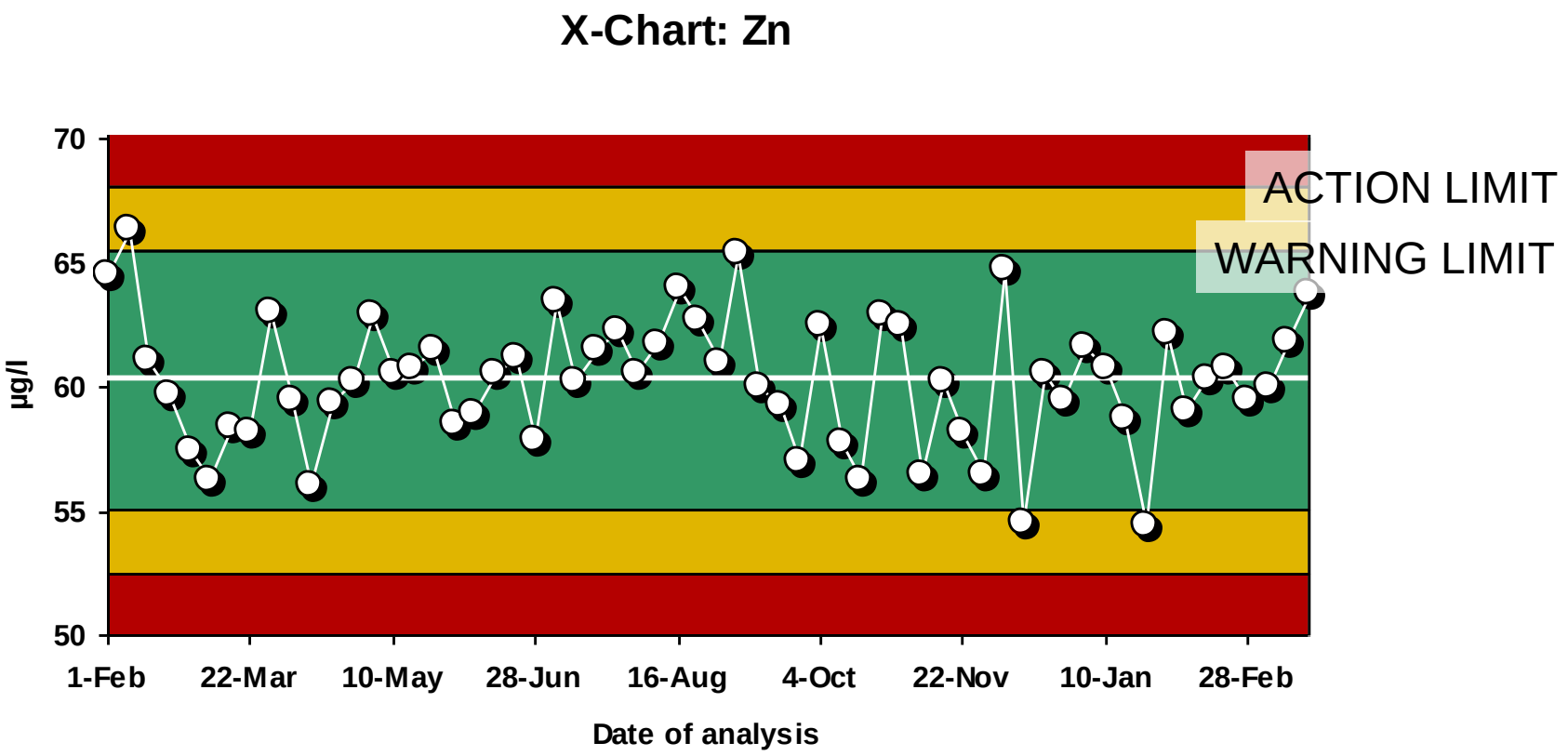
Control value:

Value entered on the control chart

Control limits:

Limits in a control chart (warning and action)

Control chart –
Central line and control limits



Setting up QC

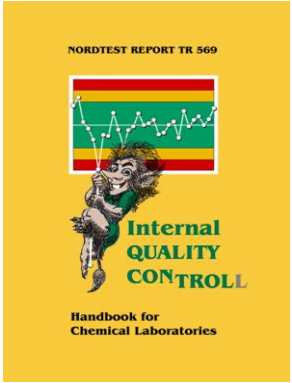
Quality control is not easy to set up…

- Two options
  - Results can be reported
  - Results can not be reported
- When out of control
  - the method should be out of control
    - no problems with the QC sample
    - position of QC sample is crucial in a run
    - QC samples similar to test samples
- QC sample should last for years
- Simple QC rules

Some general recommendations in QC

- Number of replicates - Same for control as for test samples
- Multielement analyses - Target Control Limits
- Control samples similar to test samples
  - a test sample may be better than a reference material
- For wider measuring interval –
  - one low and one high control sample

Nordtest QC revision 2018



More focus on difficult issues:

- target control limits, Chapter 7
- changing of control limits and central line, Chapter 10

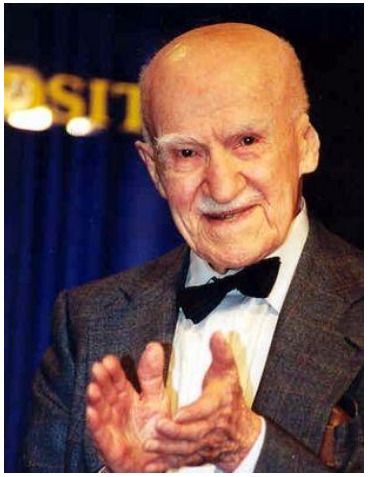
- pooled standard deviation:
  - **is** now more correctly called pooled standard deviation - not combined s,
  - **is** shown in a detailed example with three replicates in every analytical run,
  - is recommended to obtain the standard deviation for range charts - not with a range/factor.

First background to QC

Background
Western Electrical Company 16 May 1924

Shewhart's work pointed out the

- importance of reducing variation in a ***manufacturing process***
- understanding that continual process-adjustment in reaction to non-conformance actually ***increased variation and degraded quality***,
- use of control charts



125 years - special issue in early 2017 on "Advances in the Theory and Application of Statistical Process Control

The gospel of Shewhart and….

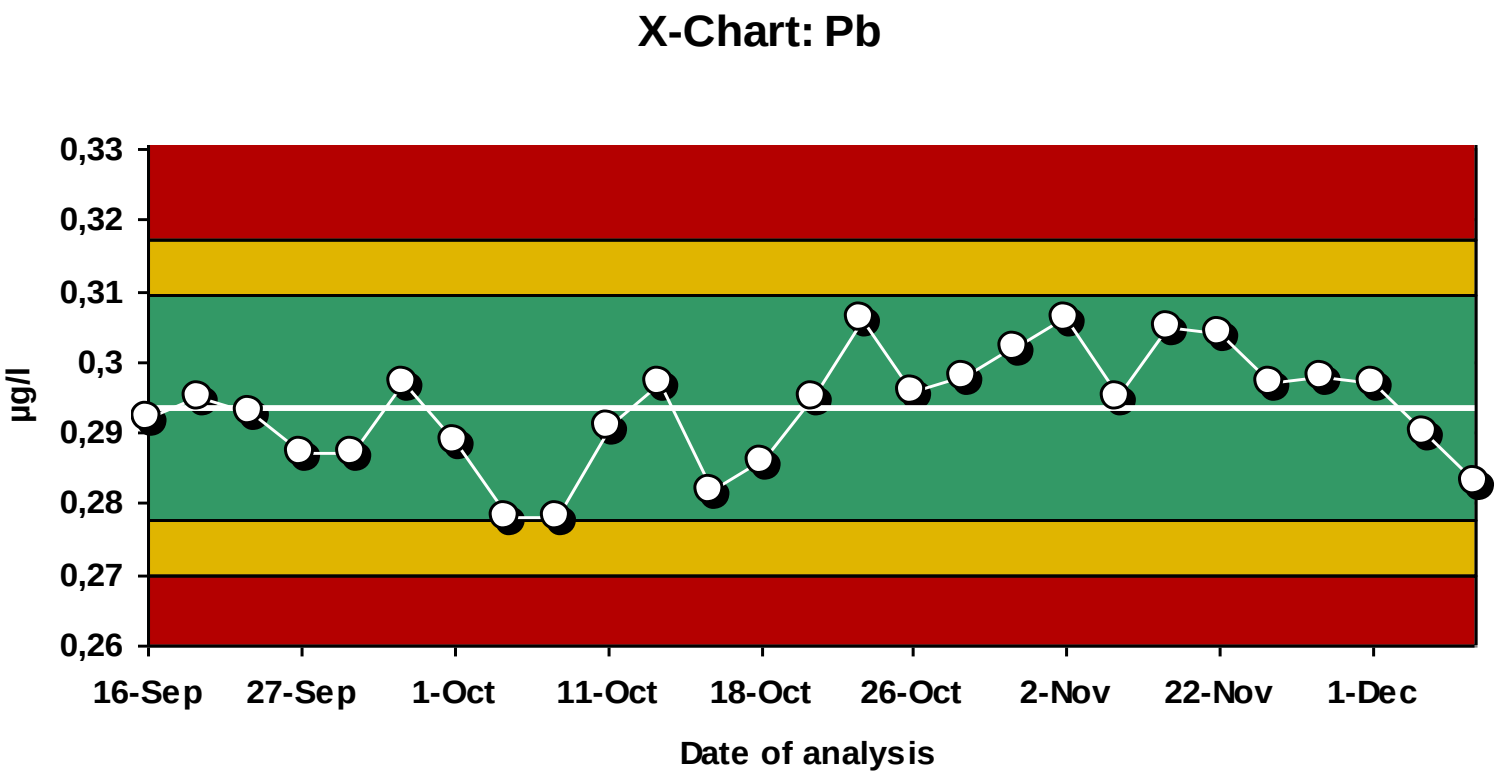
Data have no meaning apart from their context.

In his case production control

Data contain both signal and noise. To be able to extract information, one must separate the signal from the noise within the data.

Example of a standards is ISO 8258 (1991) Shewhart control charts

Is this process in control?
What is the cost of having high content in production?



Nordtest 569: ***All*** *control values within warning limits (green area) are accepted*

Setting the control limits

The control limits can be set:

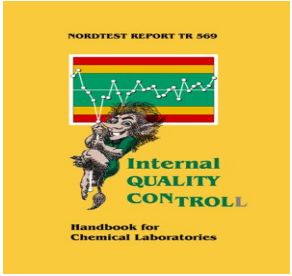
Based on method performance
standard deviation, s_{Rw}, of control values

Statistical control limits

Based on customer requirement the s_{target} is calculated

Target control limits

Nordtest QC revision 2018



More focus on difficult issues:

- **target control limits, Chapter 7**
- **changing of control limits and central line, Chapter 10**
  Note: Changing is generally not recommended
- pooled standard deviation:
  - **is** now more correctly called pooled standard deviation
    - not combined s,
  - **is** shown in a detailed example with three replicates in every analytical run,
  - is recommended to obtain the standard deviation for range charts - not with a range/factor.
  -

Target control limits in this control chart

The requirement

for limit of quantification

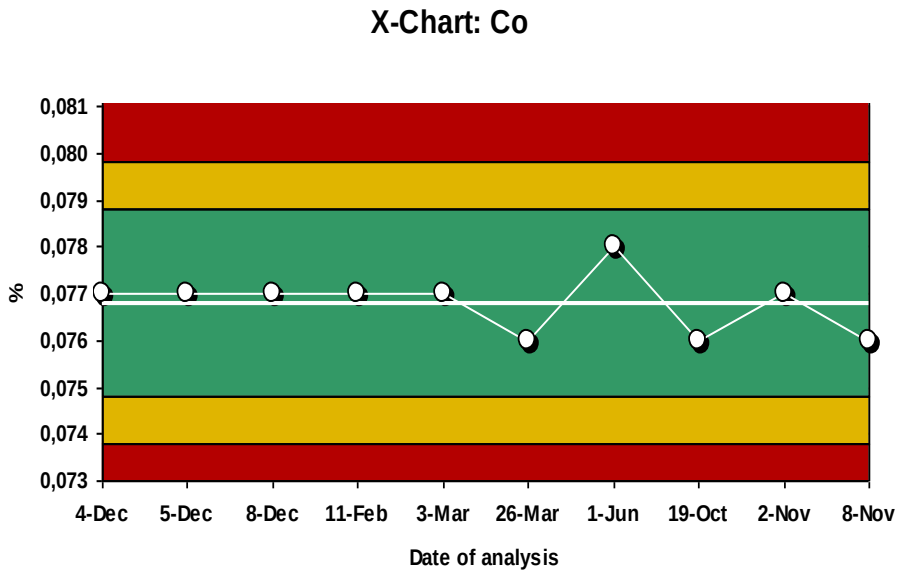
LOQ is 0,01 % Co in steel.

LOQ is often10 s_{Rw}

The target standard deviation *s*

for setting the control limits is

then 0,001 % Co



Example of requirements on s_{Rw}

EC drinking water directive 98/83/EC
at a specific concentration
Within-laboratory reproducibility, 2 s_{Rw} < 10 %

2009/90/EC pointing to the
Water Framework Directive 2000/60/EC
at a specific concentration
LOQ < 30 %

Example of requirements on s_{Rw} from specification

MSA – Measurement System Analysis

s_{Rw} < 1,7 % of tolerance/specification

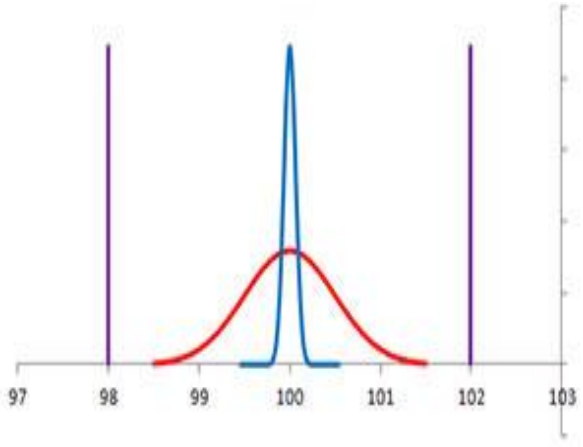
s_{Rw} < 5 % is acceptable

SPC - Statistical Process Control

Capability index, C_p

Acceptable $s_{process}$ < *10 %* of tolerance

Acceptable s_{Rw} < ?



Example of requirements on s_{Rw}

Trollbook – Nordtest Tr 569

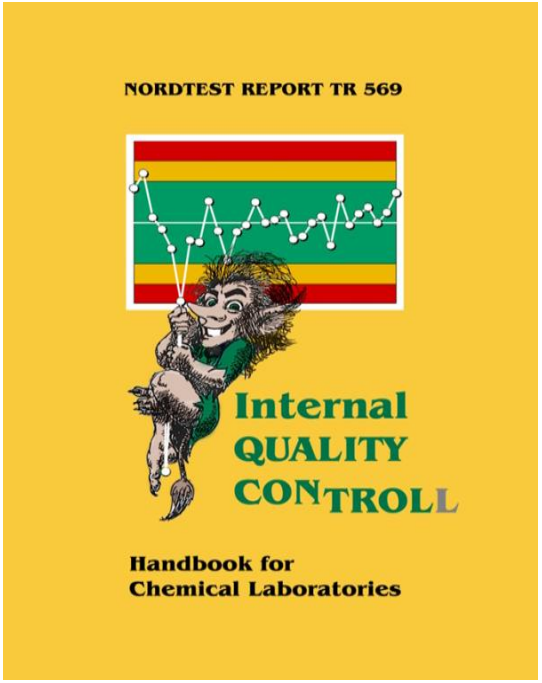
Levels close to LOQ - example 2

Acceptable $s_{Rw} < LOQ/10$

Higher levels – example 1

Target expanded uncertainty is U

Acceptable $s_{Rw} < U/4$



Setting the central line (CL)

Mean central line

The mean value is estimated from control values obtained during a longer time, e.g. a year.

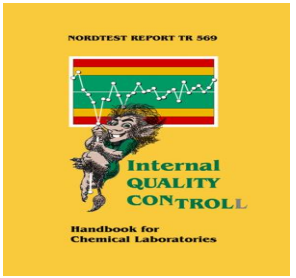
The central line is set to this mean value.

Reference central line

The control sample is a reference material or a well-characterized material.

The central line is set to the nominal value

Nordtest QC revision 2018



More focus on difficult issues:

- target control limits, Chapter 7
- changing of control limits and central line, Chapter 10
  Note: Changing is generally not recommended
- **pooled standard deviation**:
  - **is** now more correctly called pooled standard deviation
    - not combined s,
  - **is** shown in a detailed example with three replicates in every analytical run,
  - is recommended to obtain the standard deviation for range charts - not with a range/factor.
  -

Combined and pooled is not the same

Version 4 says

Combined (pooled) standard deviation (s_C) for several series of analyses.

the standard deviations for k series of analyses with total of $n_1+n_2+\ldots = n_{tot}$ ob

$$s_C = \sqrt{\frac{(n_1 - 1)\cdot s_1^{\,2} + (n_2 - 1)\cdot s_2^{\,2} + \ldots + (n_k - 1)\cdot s_k^{\,2}}{n_{tot} - k}} \qquad 9)$$

Now the text only says Pooled

Pooled standard deviation - repeatability s_r and within- lab reproducibility s_{Rw} from an example with three replicates in ever run

Measurement				Day #				
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
First	7.1	6.9	6.6	6.7	7	7.3	7.1	7
Second	7.1	6.7	6.5	6.5	6.9	7.4	7.1	6.5
Third	7	6.8	6.9	6.6	6.6	7.3	6.9	6.8
	↓	↓	↓	↓	↓	↓	↓	↓
Repeatability								
s	0.058	0.100	0.208	0.100	0.208	0.058	0.115	0.252
s^2	0.003	0.010	0.043	0.010	0.043	0.003	0.013	0.063
s_r	**0.15**							

Within-lab reproducibility		
	s	s^2
	0.226	0.051
	0.342	0.117
	0.226	0.051
s_{Rw}		**0.27**

NOTE – This is a simplified way to estimate s_{Rw} shown in Example 10 giving $s_{Rw} = 0.270$. The correct estimate using ANOVA is 0.272.

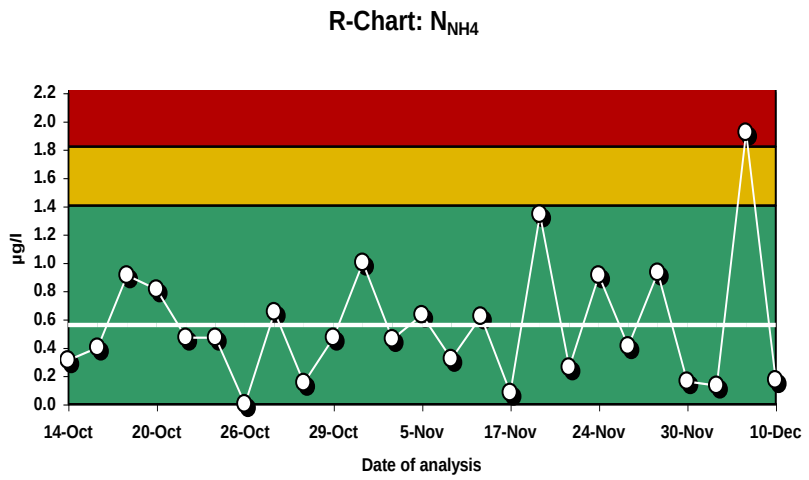
Why the Troll

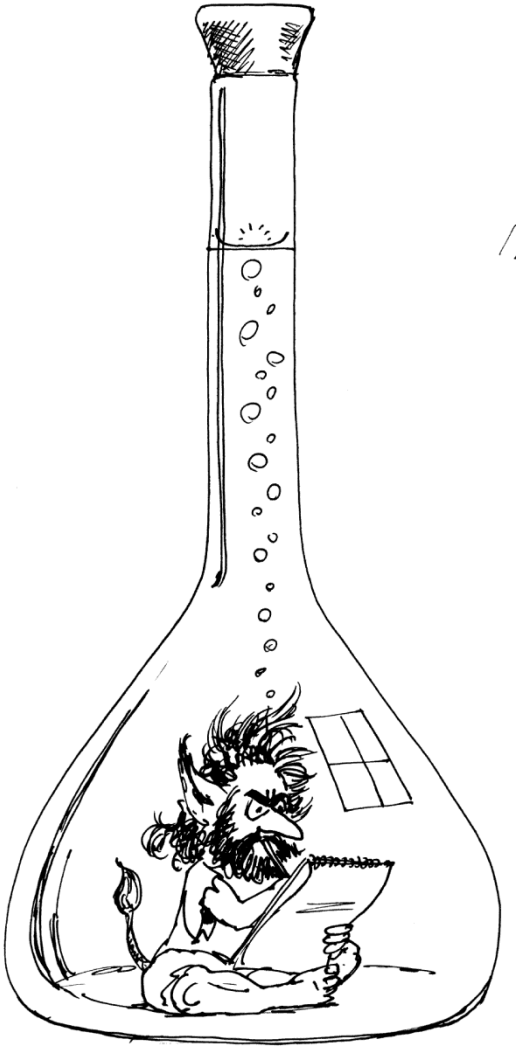
Once upon a time there were a lot of Trolls in the Nordic countries.

They were sometimes pestering us so we have a saying something like

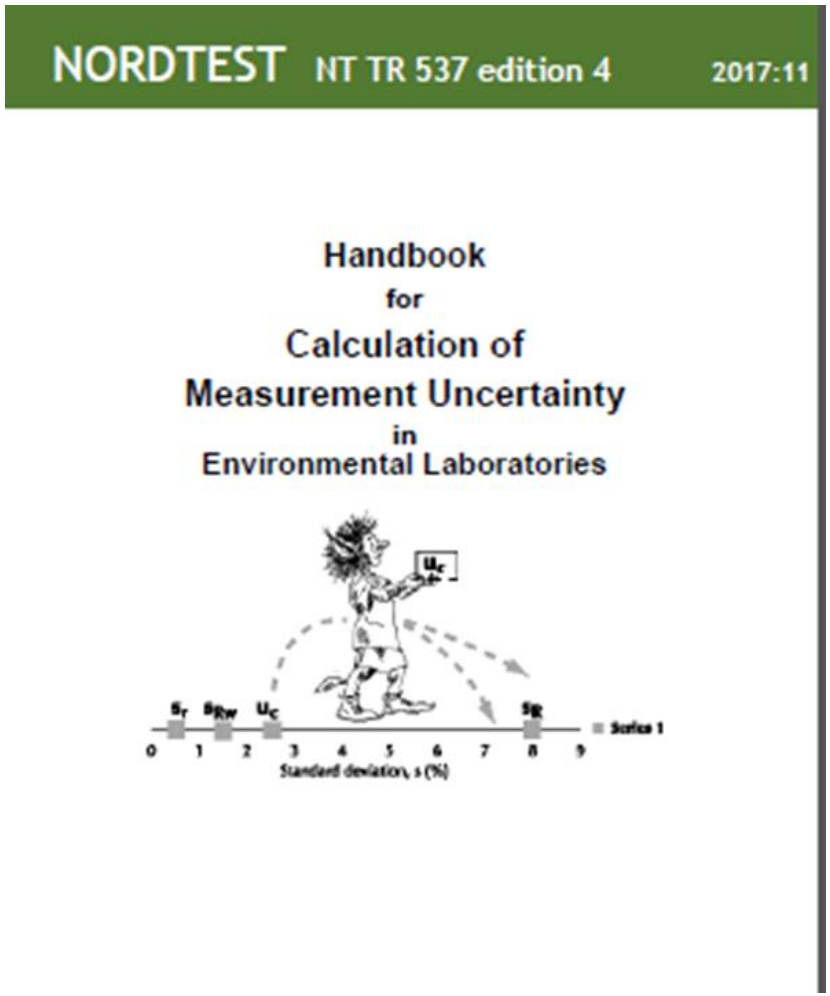
The Troll is up to mischief meaning

there are some odd things going on which we do not understand like a control value in the red area in the control chart





Revised version 2017 of Nordtest 537



Measurement uncertainty (MU) – Nordtest 2017

Major updates are:

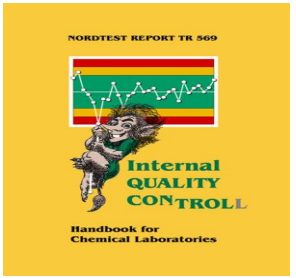
- Uncertainty over the measurement range – a separate section
- Estimating repeatability by a pooled *s* from duplicates
- Use of control chart limits for the s_{Rw} in MU calculations
- Harmonisation with ISO 11352 *Water quality — Estimation of MU based on validation and quality control data.*
- Recommended resources following the Nordtest handbook in detail:
  - software MUkit – freely available software
  - on-line course – a link is given to a course from Tartu University.

Pooled *s* from 50 duplicates – appendix 6 in TR 537

x_1	x_2	Range	*s*
mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
8.90	8.91	-0.01	0.007
8.99	9.01	-0.02	0.014
8.90	8.90	0.00	0.000
9.11	9.12	-0.01	0.007
8.68	8.64	0.04	0.028
		Pooled s	0.0252

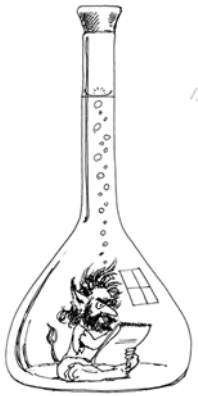
Note only minor difference – with
mean range/1.128 we get an *s* = 0.024

Nordtest QC revision 2018*



More focus on difficult issues:

- target control limits, Chapter 7
- changing of control limits and central line, Chapter 10
  Note: Changing is generally not recommended
- pooled standard deviation:
  - **is** recommended to obtain the standard deviation for range charts - not with a range/factor,
  - **is** now more correctly called pooled standard deviation - not combined s
  - **is** shown in a detailed example with three replicates in every analytical run.
    NOTE: If all results would be used to calculate s_{Rw} a too low estimate will be obtained resulting in too narrow control limits.



*Planned to 1 of July 2018

FAQ on QC and MU
www.trollboken.se