Statens tilsyn for planter, fisk, dyr og næringsmidler

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Measurement Uncertainty in Sampling – Example of a practical approach

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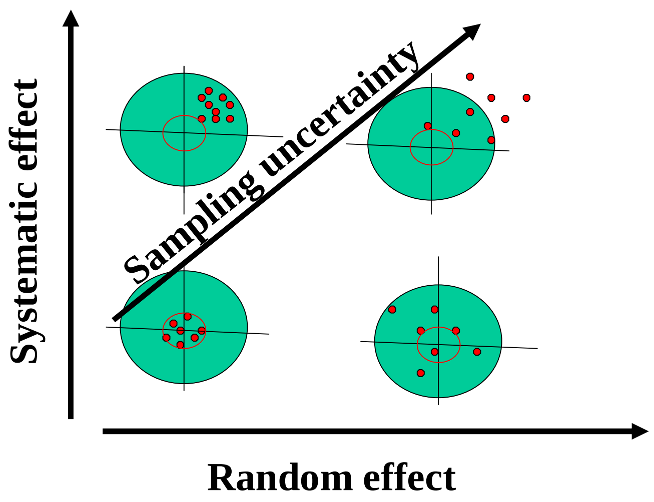
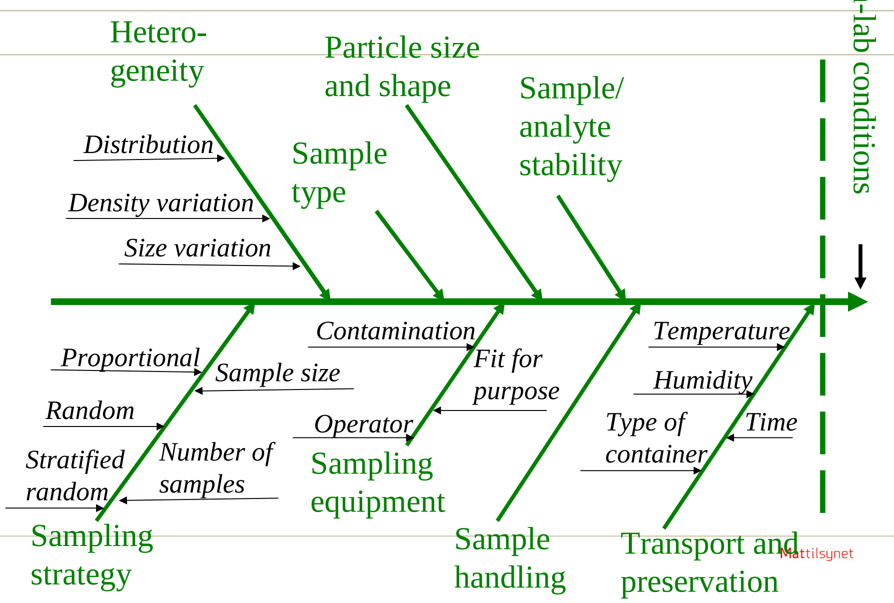
Systematic and random effects on sampling uncertainty



Cause-effect (fish-bone) diagram - ***examples*** of possible sources contributing to the uncertainty



Uncertainty contribution to systematic and random effects

	Random *(precision)*	***Systematic*** *(bias)*
Analysis	Analytical variability - including sample splitting/preparation and handling (combined contribution of random effects)	Analytical bias (combined effect of bias sources)
Sampling	Sampling variability (dominated by heterogeneity and operator variations)	Sampling bias (combined effect of selection bias, operator bias etc.)

Background of a NordTest[1] project

- In connection with the surveillance of baby foods (cereal based baby porridge, powder) a too big variance in the vitamin A (retinol) content was observed between packages of the same product, even within the same batch. (The analytical method used was EN-12823-1 “Foodstuffs – determination of vitamin A by HPLC”)
- It was therefore recognised a need to determine **if** the main source of ***measurement uncertainty was due to***
  - ***Sampling??***
  - ***Analysis??***

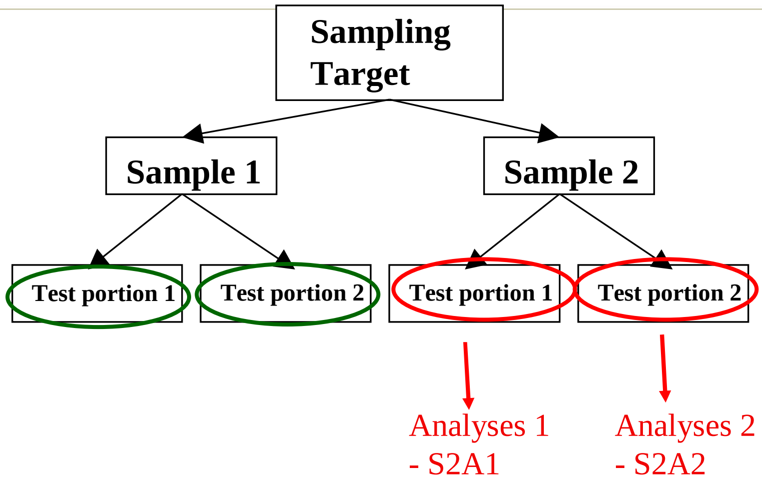
1) The NordTest guide TR 604 can be downloaded from http://www.nordicinnovation.net/nordtestfiler/tr604.pdf

Case study: Estimation of measurement uncertainty when analysing retinol in (cereal based) baby porridge powder

- Estimation by using a practical design – the empirical duplicate method (nested design)
- Estimation by using ANOVA[1] and RANGE statistics
- Look at effects of the test portion size on the uncertainty (40 g and 4 g test portions - Analytical method EN-12823-1). Subsampling in the laboratory by using a mechanical sample divider (Retsch)

1) Analysis of variance = ANOVA

Replicate design with two split levels



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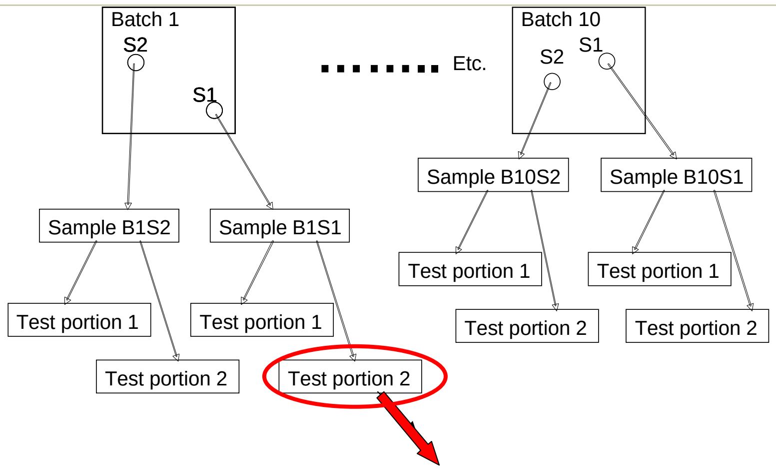
Replicate design with two split levels on 10 batches



B1-S1A2 = Batch 1, Sample 1, Test portion 2

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Comments on the design

Duplication of the sampling

Drawback

- **Only random part of uncertainty evaluated**

Benefits

- **Simple and generic design**

$$s^2_{\text{measurement}} = s^2_{\text{sampling}} + s^2_{\text{analysis}}$$

Systematic part **– (*Not treated today*)**

- **Nominal value “known” - 349 µg/100 g (retinol)**
- **Mean value obtained compared with nominal value**

Recovery > 99 %

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Test on measurement repeatablity (sampling + analysis)

Normal test portion is 2 – 10 g (EN-12823-1)

Producer indicated problem with homogeneity!

Case study shows:

- **Test portion of 4 g gave a standard deviation of 37 % (sampling + analysis)**

- **Test portion of 40 g gave a standard deviation of 10 % (sampling + analysis)**

Test portion of 40 g should be selected!

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Results, 40 g test portion – validation study

Batch	S1A1	S1A2	S2A1	S2A2
B1	402	325	361	351
B2	382	319	349	362
B3	332	291	397	348
B4	280	278	358	321
B5	370	409	378	460
B6	344	318	381	392
B7	297	333	341	315
B8	336	320	292	306
B9	372	353	332	337
B10	407	361	322	382

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ANOVA-calculation using ROBAN[1] (University of Newcastle, Imperial College and University of Sussex)

CLASSICAL ANOVA RESULTS – baby porridge, 40 g test sample

Mean = 347,85001
Standard Deviation (Total) = 39,733311

	Sampling	Analysis
	--------	--------
Sums of Squares	14231	16595
Standard Deviation	***17,2***	***28,8***
Percentage Variance	18,8	52,6

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1) http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/

ANOVA-calculation using ROBAN

Baby porridge, 40 g test sample

ROBUST ANOVA RESULTS:

Mean = 346,01602
Standard Deviation (Total) = 41,312828

	Sampling	Analysis	Measurement
	--------	----------	-----------
Standard Deviation	**21,217979**	**30,456478**	37,118725
Percentage Variance	26,377777	54,348744	80,726523
Relative Uncertainty (% at 95% confidence)	**12,26416**	**17,604085**	**21,454917**

Classical ANOVA

	Sampling	Analysis
Standard Deviation	17.2	28.8

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Range calculation (performed by Bertil Magnusson, SP)

Sample 1				Sample 2				Range
x_{i11}	x_{i12}	Range	Mean	x_{i21}	x_{i22}	Range	Mean	Measurement
402	325	77	363.5	361	351	10	356	7.5
382	319	63	350.5	349	362	13	355.5	5
332	291	41	311.5	397	348	49	372.5	61
280	278	2	279	358	321	37	339.5	60.5
370	409	39	389.5	378	460	82	419	29.5
344	318	26	331	381	392	11	386.5	55.5
297	333	36	315	341	315	26	328	13
336	320	16	328	292	306	14	299	29
372	353	19	362.5	332	337	5	334.5	28
407	361	46	384	322	382	60	352	32
		36.5				30.7		**32,1**

Mean range for analysis is 33,6 μg/100 g

Mean range for measurement

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Range results – Analysis (n=1)

Parameter	Vitamin A µg/100g	Comment
Mean range from duplicates	**33,6**	
Stand dev. estimated from range	**29,8**	***s* = range/1.128**

Results – Measurement (n=2)

Parameter	Vitamin A µg/100g	Comment
Mean range from –duplicates	**32,1**	
Standard dev. estimated from range	**28,5**	**s = range/1.128**

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Results - Sampling

$$s_{sampling} = \sqrt{s^2_{measurement} - s^2_{analysis}}$$

Parameter	Vitamin A µg/100g	Comment
Measurement standard dev.	**28,5**	**Measurement (sampling + analytical, n=2)**
Analysis – standard dev.	**29,8**	**Analytical part (n=1)**
Sampling– standard dev.	19,1	$= \sqrt{28{,}5^2 - \left(29{,}8/\sqrt{2}\right)^2}$

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Comparison between different methods of calculating the measurement uncertainty – case study Vitamin A in baby porridge

	s_{anal}	RSD_{anal}	s_{sampl}	RSD_{samp}	s_{meas}	RSD_{meas}
	µg/ 100 g	%	µg/ 100g	%	µg/ 100g	%
Range	30	8.6	19	5.5	35	10
ANOVA	29	8.3	17	5.0	34	10
Robust ANOVA	31	8.8	21	6.1	37	11

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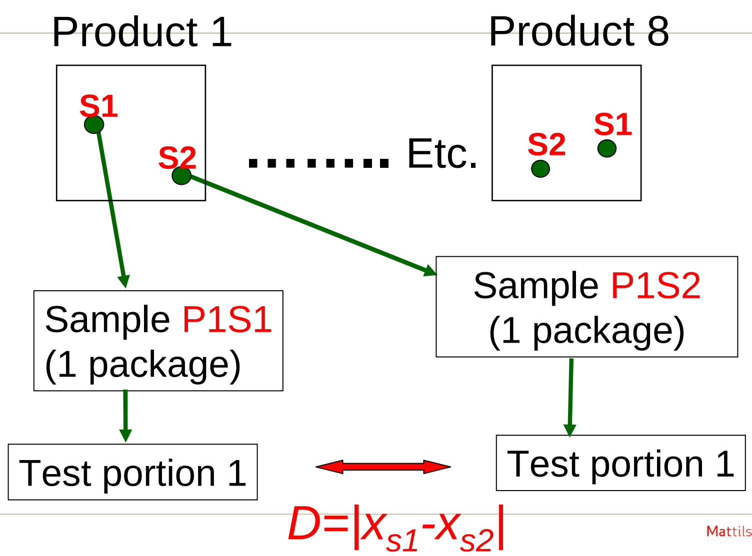
Design: Quality control (QC)



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Calculation of Limits and Central line in Control chart - baby porridge

The calculation are based upon the result from the validation study: RSD(%)= $u_{measurement}$ = 9,7%

Central line: $C_l = 1,128*9,7\%$
Warning limit: $L_w = 2,83*9,7\%$
Action limit: $L_a = 3,69*9,7\%$

Fore each product, calculate

$$d(\%) = (D/\bar{x})*100\% \qquad (D=|x_{s1}-x_{s2}|)$$

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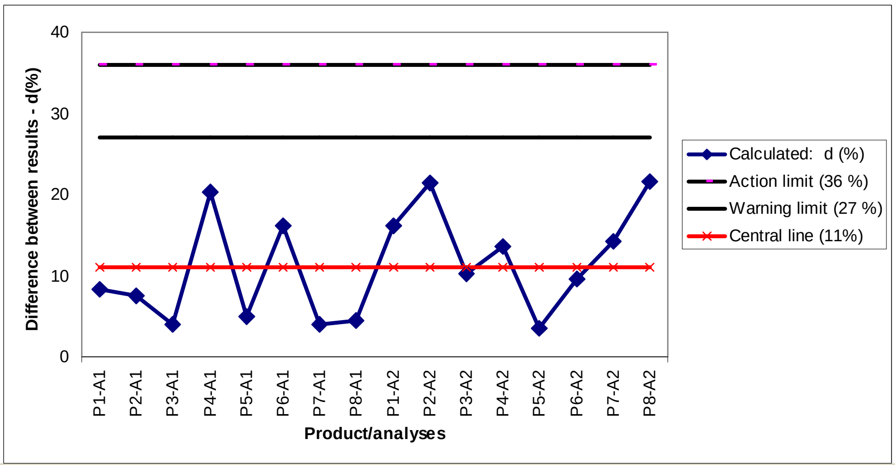
Control chart, QC analyses of vitamin A in baby porridge containing cereals and fruits



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Case study: Nitrate in lettuce in green house.
Study performed by J. Lyn (FSA, UK) and co-workers.
See example in the EuraChem Guide[1] on UFS

'W' Sampling Design for Lettuce

Duplicate is equally likely interpretation of 'W' design

1) Can be downloaded from http://www.eurachem.org/

University of Sussex

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Case study lettuce: Data set

SAMPLE TARGET	S1A1	S1A2	S2A1	S2A2
A	3898	4139	4466	4693
B	3910	3993	4201	4126
C	5708	5903	4061	3782
D	5028	4754	5450	5416
E	4640	4401	4248	4191
F	5182	5023	4662	4839
G	3028	3224	3023	2901
H	3966	4283	4131	3788

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Comparison between different methods of calculating the uncertainty – case study “Nitrate in green house lettuce”

	s_{anal}	RSD_{anal}	s_{sampl}	RSD_{samp}	s_{meas}	RSD_{meas}
	mg/kg	%	mg/kg	%	mg/kg	%
Range	167	3,8	448	10	478	11
ANOVA	148	3,4	518	12	539	12
Robust ANOVA	168	4	319	7	361	8

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Estimation of measurement uncertainty by using a double split design

Different ways of estimating sampling uncertainty give similar results.

If there are outliers in the data sets use

- **Robust ANOVA**
- **Perform outliers test**

The double split design is a simple and generic design, but only the random part of uncertainty is estimated.

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