Eurachem

*A focus for analytical chemistry in Europe*

# Uncertainty from sampling as a means to improve the quality of sampling – case study with food

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## Background

The content of nutrient and vitamins is strictly regulated in processed cereal-based foods and baby foods for infants and young children (96/5/EC and 98/36/EC).

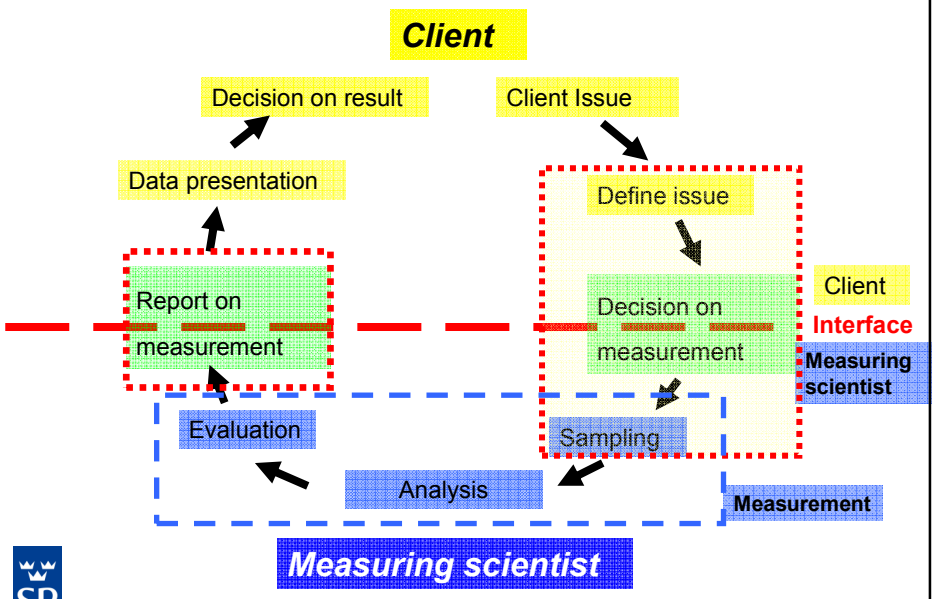
In connection with the surveillance a quite big variance was observed between packages of the same product, even within the same batch. The analytical method used was EN-12823-1 “Foodstuffs – determination of vitamin A by HPLC”

It was therefore recognised a need to determine if the main source of

**measurement uncertainty was due to**

The issue → **sampling or analysis?**

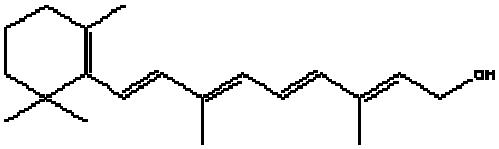
## The measurement cycle



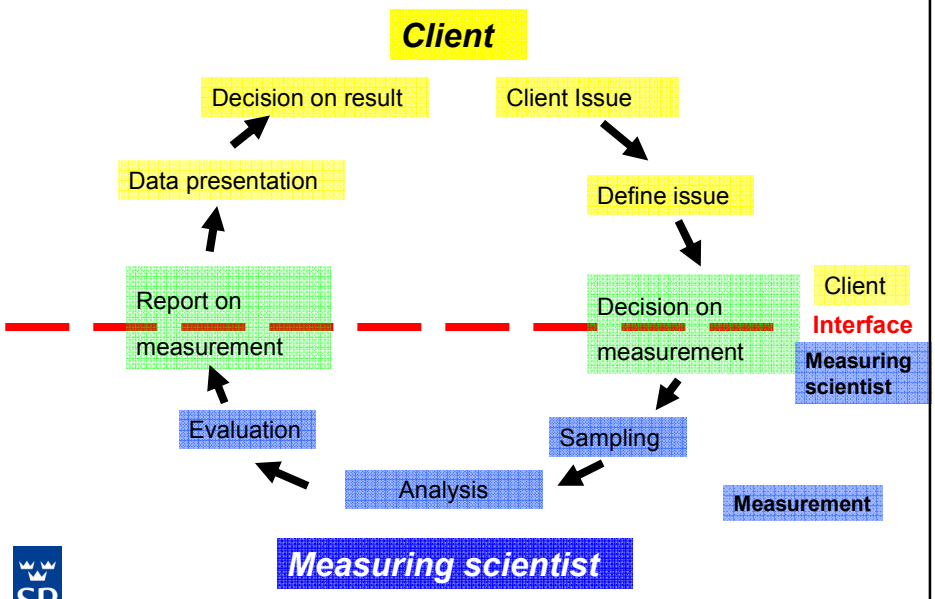



## Decision on measurement

| Measurand | | | |
|---|---|---|---|
| **Analyte & technique** | **Unit** | **Sector & matrix** | **Sampling target** |
| Vitamin A as retinol (trans &cis) HPLC | µg/100 g in powder | Food baby porridge-powder | Produced batch |

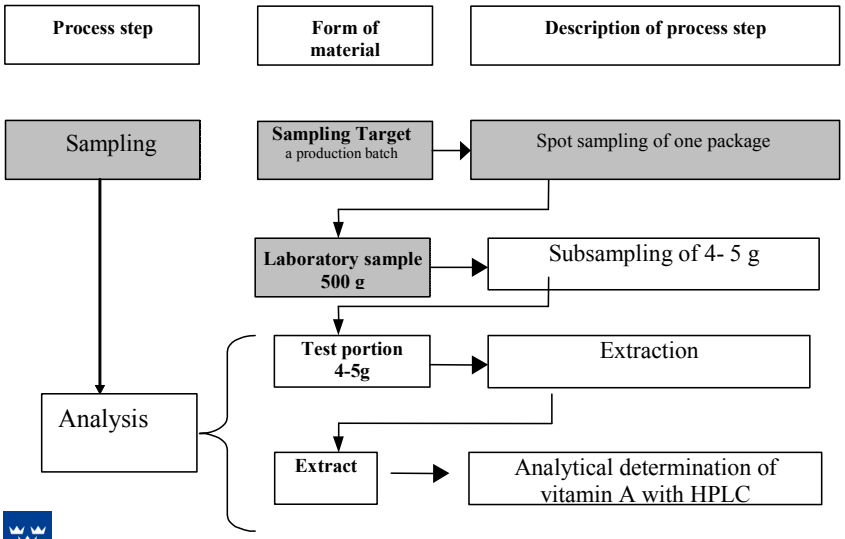


## The measurement cycle






## Sampling and analysis for vitamin A in baby-porridge



## Test on repeatablity

Normal test portion is 4 g

Producer indicated problem with homogeneity!

- Test with 4 g gave a standard deviation of 100 µg/g or 37 % (sampling + analysis)
- Test with 40 g gave an a standard deviation of 37 µg/g or 10 % (sampling + analysis)

Test portion of 40 g was selected!



## Sampling and sampling target

Normally a spot sampling approach

- one sample (one package) of a batch - is used as screening when comparing the content with declared values and legal limits

**One package is taken as representative of a batch**
**Sampling target is the batch**

Sub-sampling in the laboratory

- a mechanical sample divider (Retsch) is used to split the samples.

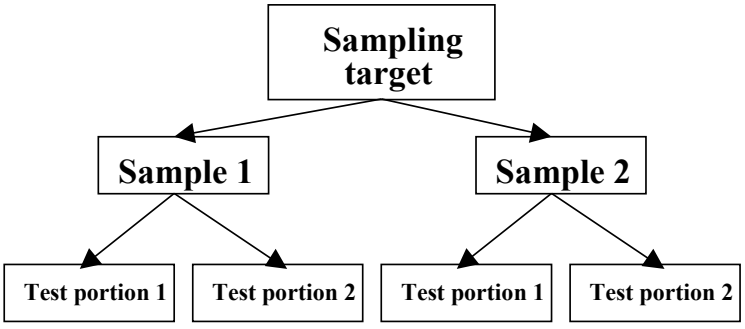
**One test portion of approximately 40 – 50 g**
**is selected for analysis**

## uncertainty in sampling – 10 steps

1. Scope
2. Scenario and sampling target
3. Sampling procedure
4. **Study design – double split replicates**
5. Sample preparation and analysis
6. **Results**
7. Comments
8. Assessment of fitness for purpose
9. Reporting and interpretation
10. Summary



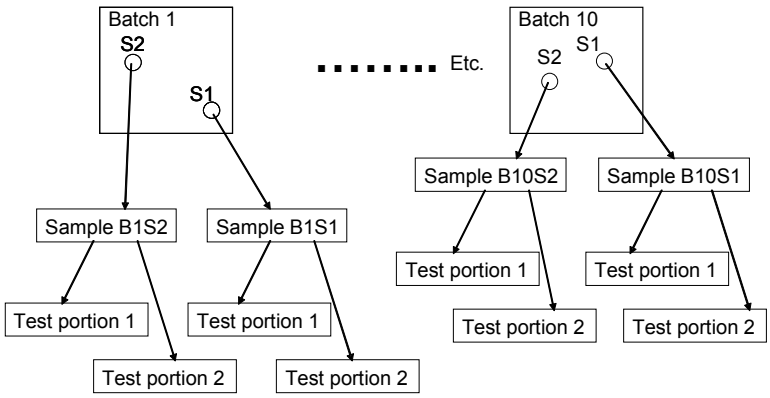
## Replicate design with two split levels




$X_{ijk} = x_{i21}$

sampling target i, sample 2 and test portion 1 for analysis

## Replicate design with two split levels on 10 batches?




$x_{ijk}$=$x_{112}$ is Batch 1, Sample 1, Test sample 2



## 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

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

**Recovery > 99 %**

## Raw data

| 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



## 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 |

## 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** | $= \sqrt{28{,}5^2 - \left(29{,}8/\sqrt{2}\right)^2}$ |



## Expanded uncertainty, U from this study

Expanded uncertainty is given with a confidence interval of 95 %

$$U = 2 \cdot u_c$$

| | s – stand dev µg/100g | RSD[1] % | U relative % |
|---|---|---|---|
| Sampling | 19,1 | 5,5 | 11 |
| Analysis | 29,8 | 8,5 | 17 |
| Measurement | 35,4 | 10,1 | 20 |

[1]RSD % at a level of 350 µg vitamin A/100g

## Comments

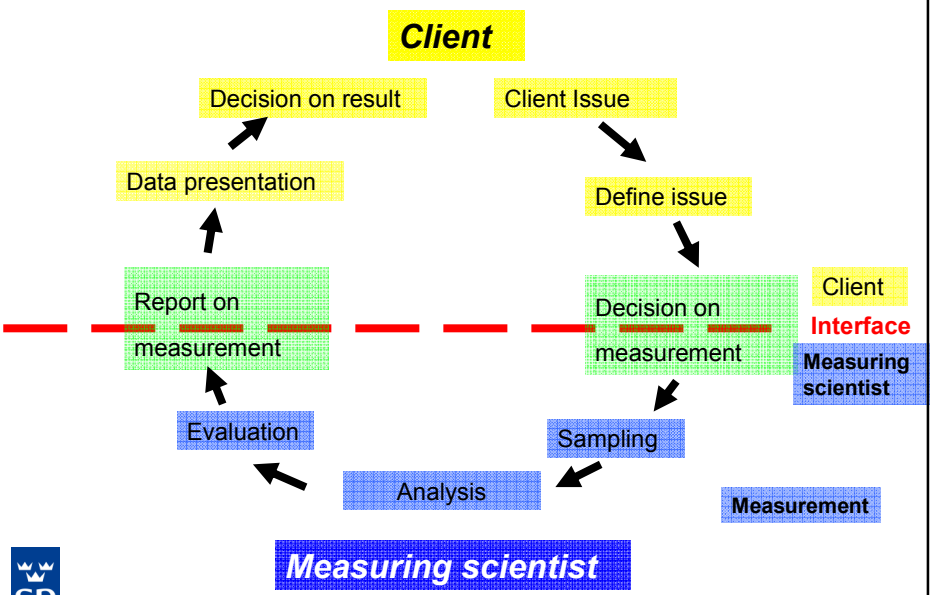
- **Sampling uncertainty lower than analysis**
- **Repeatability higher that reported by laboratory**
- **Measurement uncertainty higher than reported by laboratory**

| Parameter | RSD % | Comment |
|---|---|---|
| Repeatability – this study | 8,5 | Use this value! |
| Repeatability – from laboratory | 6 | |

| Parameter | U % | Comment |
|---|---|---|
| Measurement uncertainty – this study | 20 | Use this value! |
| Analytical uncertainty – from laboratory | 14 | |



## The measurement cycle



## Reporting and interpretation

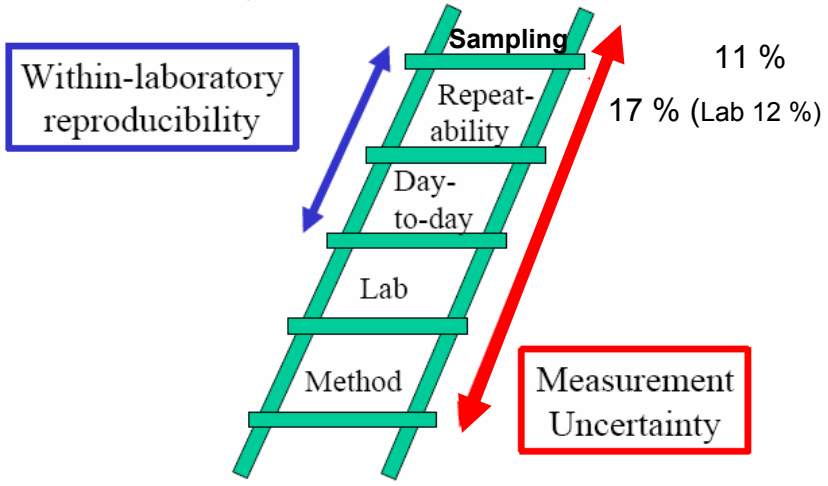
An analytical result can be reported taking test portions of 40 g as e.g.

**300 µg/100 g ± 60 µg/100 g**
**The results is given with an expanded uncertainty (95 % confidence interval, k=2)**

**The uncertainty based on laboratory data would only be ± 47 µg/100 g.**



## Laboratory ladder - baby-porridge with added vitamin A 350 µg/100g – relative uncertainty at 95 % confidence level (k=2)



## Summary

| Expanded Uncertainty | | | Target variability |
|---|---|---|---|
| Sampling | Analytical | Measurement | Typical production variation |
| 11 % | 17 % | 20 % | 16 %<br>(± 2 RSD) |

**Thanks to Astrid Nordbotten**
**from**
**Mattilsynet, Norway…….**



## Conclusion

1. **Replicate design with two split levels is a good generic approach to separate measurement uncertainty into analytical and sampling uncertainty**

2. **Only the random part is estimated for analysis!**
   **Therefore obtain the uncertainty from the laboratory. Use the highest value of analytical uncertainty in this case:**
   **Highest value from this study**
   **Baby-porridge more inhomogeneous with respect to vitamin A**

3. **Only the random part is estimated for sampling:**
   **Comparison with a nominal value**
   **recovery > 99 %**