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Agroscope

Estimation of Measurement Uncertainty for Phys.-Chem. Parameters based on Proficiency Test Results

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Introduction

- National control labs have to be accredited according to ISO/IEC 17025
- ISO/IEC 17025 requires an estimation of the measurement uncertainty for each analytical method.

- 5.4.6.2 Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement. In certain cases the nature of the test method may preclude rigorous, metrologically and statistically valid, calculation of uncertainty of measurement. In these cases the laboratory shall at least attempt to identify all the components of uncertainty and make a reasonable estimation, and shall ensure that the form of reporting of the result does not give a wrong impression of the uncertainty. Reasonable estimation shall be based on knowledge of the performance of the method and on the measurement scope and shall make use of, for example, previous experience and validation data. (ISO/IEC 17025:2005)

QUAM 2012 (Chapter 7.6 and 7.8)

- For Collaborative Study or for Proficiency Testing
- 7.6.3. ……. the **reproducibility standard deviation s_R**, adjusted for concentration if necessary, may be used as the **combined standard uncertainty**.
  - If methods operating within their defined scope
  - If the contributions from any remaining sources have been shown to be negligible
    (Most probable for MT phys.-chem. Test)
- *QUAM:2012.P1*
  Quantifying Uncertainty in Analytical Measurement, EURACHEM / CITAC Guide CG 4, Third Edition

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CIPAC Methods

Analytical methods with collaborative trial:

- **Repeatability r:** e.g. 3 g/kg at 177 to 179 g/kg
- **Reproducibility R:** e.g. 5 g/kg at 177 to 179 g/kg

MT-Methods

There is usually no validation information in the method

→ labs have to evaluate/validate the methods themselves

Nowadays, accreditation auditors want to see at least an estimation of the measurement uncertainty and a determination of the laboratory reproducibility for phys.- chem. tests!!

Typically Points of a Validation

- **Linearity (r) of MT method** → not possible to measure; often the graduation of the glassware defines linearity
- **Repeatability of MT method** → can be determined with suitable samples (e.g. 6 determinations)
- **Accuracy (recovery) of MT method** → recovery cannot be measured; accuracy can be derived from proficiency tests
- **Specificity of MT method** → MT methods are standardized methods
- **Reproducibility of MT method** → with proficiency tests and interlaboratory trials

Missed/Rare Information's for MT Methods

- Certified Control Samples not available
- Only a few proficiency tests (e.g. FASFC)
- Some MT-Methods are done by only a few labs – limited comparison of results
- Not all MT-Methods are well standardized. Especially visual observations are prone to be interpreted very differently from lab to lab

FASFC = Federal Agency for the Safety of The Food Chain, Gembloux, Belgium

Our Solution

We use the following elements for the **estimation of the measurement uncertainty**

- Results from PT's 2008 – 2017 (FASFC Gembloux, participants 11 – 24 labs)
- Six determinations of suitable samples
- Validation data in the MT method, if available
- Organize an interlaboratory comparison (2 – 3 labs), if no results from PTs are available

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Absolute or Relative Measurement Uncertainty?

Agroscope applies:

- Absolute uncertainty – for pH-determination
- Relative uncertainty – for most other MT-Tests

- There is little data so far available to support the decision whether uncertainty of a MT-method should be expressed in an absolute or a relative manner. (Uncertainty based on relative standard deviation or on standard deviation)

Density

Mettler Toledo Densito 30PX (source mt.com)
Measurement principle: Oscillating body method

Density: Proficiency Tests 2008 - 2017

- 2017
  Mean: 1.0799 g/ml; Min. 1.0752 g/ml ; Max. 1.0818 g/ml
  SD 0.001 **RSD 0.09 %**
- 2015
  Mean: 1.1098 g/ml; Min. 1.0955 g/ml; Max. 1.1209 g/ml
  SD 0.009 **RSD 0.80 %**
- 2012
  Mean: 1.0914 g/ml; Min. 1.0753 g/ml; Max. 1.1000 g/ml
  SD 0.005 **RSD 0.46 %**
- 2010
  Mean: 1.03 g/ml; Min. 1.0091 g/ml; Max. 1.0540 g/ml
  SD 0.009 **RSD 0.87 %**
- 2008
  Mean: 1.204 g/ml; Min. 1.1413 g/ml Max. 1.2061 g/ml
  SD 0.002 **RSD 0.13 %**

Density

Optimistic case

RSD 0.09 %	mu (2 * RSD) =	± 0.18 %

Realistic case

RSD 0.46 %	mu (2 * RSD) =	± 0.9 %

Worst case

RSD 0.87 %	mu (2 * RSD) =	± 1.7 %
	mu (2 * RSD) =	**± 1.0 %**

Remarks: mu = measurement uncertainty

Suspensibility MT 184

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MT 184 – Proficiency Tests 2012 - 2015

- **2015 (Triadimenol)**
  Mean 100.2 %; Min. 95.6 % Max. 101.6 %
  SD 1.1 %; **RSD 1.1 %**
- **2014 (Deltamethrin)**
  Mean 92.7 %; Min. 86.4 % Max. 99.2 %
  SD 5.3 %; **RSD 5.8 %**
- **2012 (Azoxystrobin)**
  Mean 99.3 %; Min. 95.1 % Max. 100.7 % (106 %)
  SD 0.8 %; **RSD 0.8 %**

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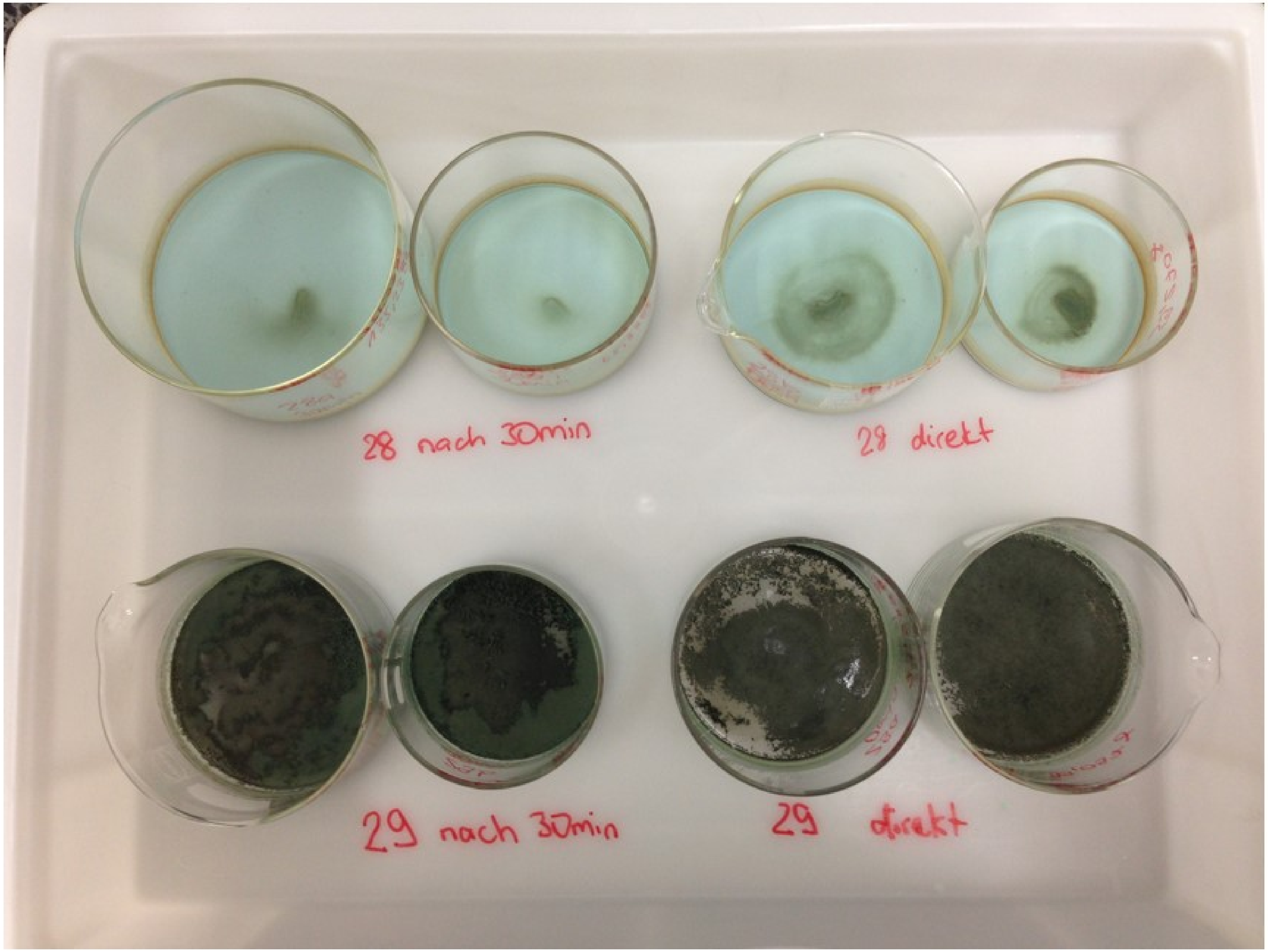
MT 184 – Proficiency Tests 2010 - 2011

- **2011 (Pyraclostrobin)**
  Mean: 75.1 %; Min. 40.3 % Max. 98.9 %
  SD 19.7 %; **RSD 26.3 %**
- **2011 (Pyraclostrobin) - reevaluation (gravimetric)**
  Mean: 79.8 %; Min. 70.6 % Max. 89.1 %
  SD 2.9 %; **RSD 3.6 %**
- **2010 (Cypermethrin)**
  Mean: 99.3 %; Min. 97.5 % Max. 101 %
  SD 1.1 %; **RSD 1.1 %**
  with outliers: Mean 99.3 %; Min. 69.0 % Max. 110 %
  SD 9.2 %; **RSD 9.3 %**

MT 184 Gravimetric Determination



Suspensibility MT 184

Optimistic case

RSD 0.82 %	mu (2 * RSD) =	± 1.6 %
RSD 1.13 %	mu (2 * RSD) =	± 2.2 %

Realistic case

RSD 3.62 %	mu (2 * RSD) =	± 7.2 %

Worst case

RSD 9.26 %	mu (2 * RSD) =	± 18.5 %
RSD 26.3 %	mu (2 * RSD) =	± 52.5 %

mu (2 * RSD) = ± 8 %

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Persistent Foam MT 47.3

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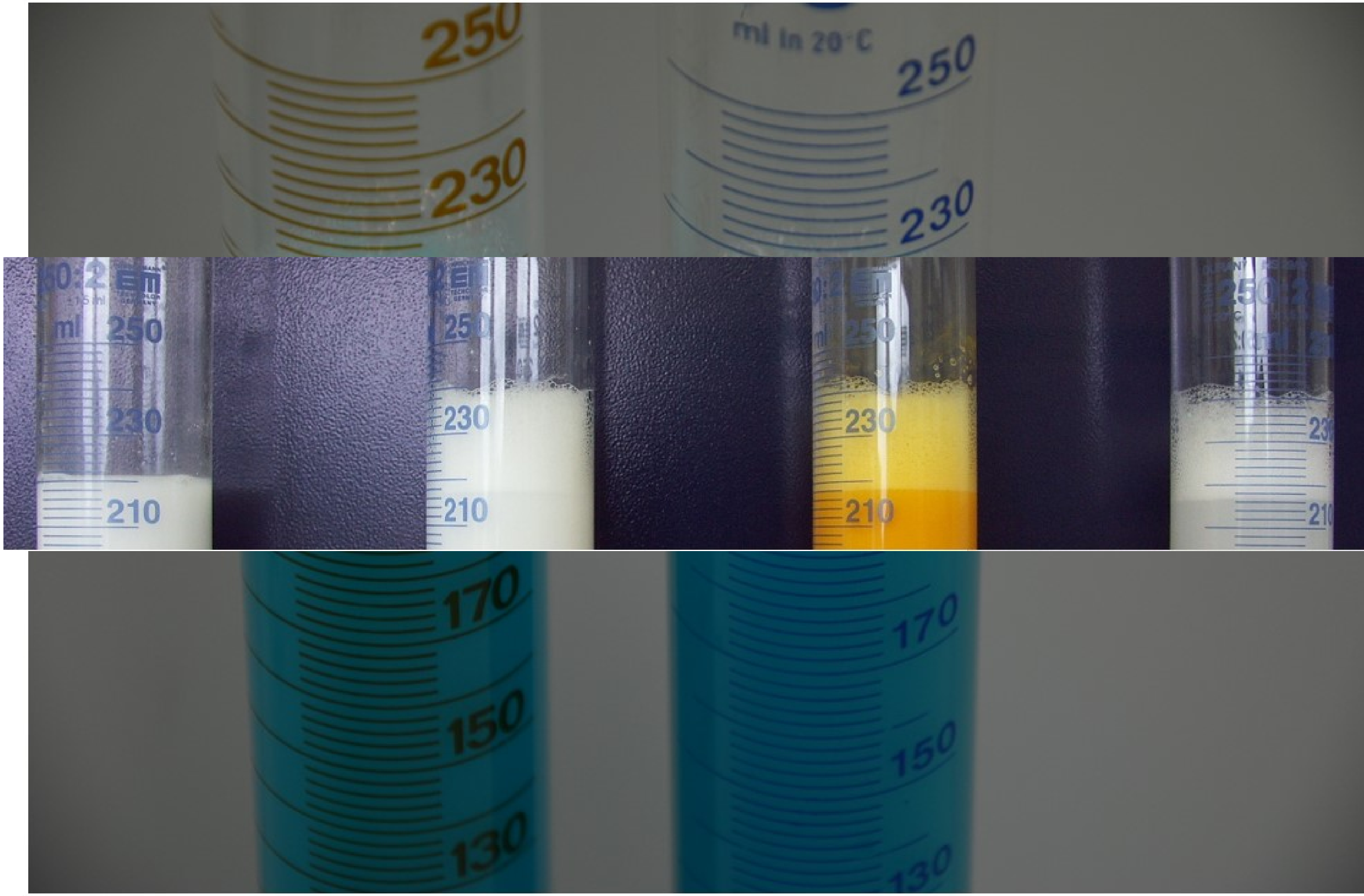

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Persistent Foam Proficiency Tests

- 2017
- Mean 15 ml; SD 3.93; **RSD 25.76 %**
- 2015
  Mean 17 ml; SD 6.65; **RSD 40.3 %**
- 2014
  Mean 26 ml; SD 11.92; **RSD 46.2 %**
- 2012
  Mean 3 ml; SD 2.22; **RSD 75.5 %**
- 2010
  Mean 17 ml; SD 4.7; **RSD 27.3 %**
- 2010
  Mean 28 ml; SD 10.1; **RSD 36.9 %**

Persistent foam

- **realistic case ?**
  RSD 27.3% mu (2 * RSD) = ± 55 %

- **Agroscope**
  - EC with 8 ml foam
    - repeatability: RSD (n = 6) 30 % / SD 2.4 ml
  - EC with **66 ml** foam
    - repeatability: RSD (n = 6) **3.5 %**

± 25 % (at > 8 ml)
± 2 ml (at < 8 ml)

Wet Sieve Test (MT 185)

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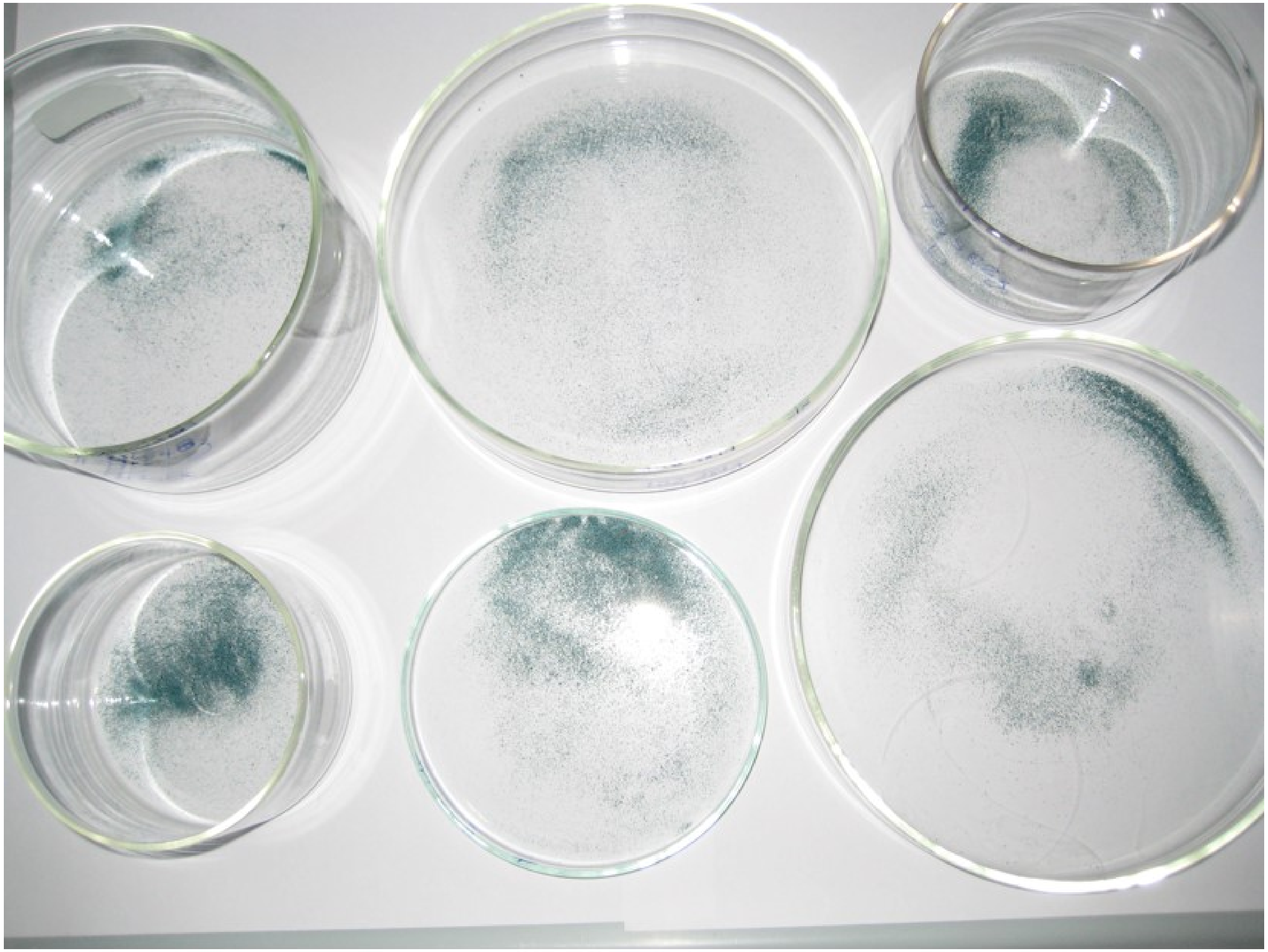
Wet Sieve Test – Gravimetric Determination (n = 6)



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- 2015
  Mean 0.015 % ; Min. 0 %; Max. 0.10 %
  no statis[illegible] eval. possible
- 2014
  Min [illegible] 5 %
  no s[illegible]
- 2012
  Mean 0.01 [illegible] 02 %
  SD 0.008 [illegible]
- 2011
  Mea[illegible] 0 %; [illegible]
  SD 0.[illegible] **90%**
- 2010
  Mean 0.01 %; Min. 0 %; Max. 0.03 %
  SD 0.011; **RSD 110%**

Wet Sieve Test

Problem: Very Low Residues in Prof Tests

Agroscope:
repeatability: RSD (n = 6) 16.0 % (residue 0.45 %)

Estimation: mu (2 * RSD) = ± 30.0 %

Interlaboratory comparison (2016, 2 labs)
Lab A: 0.42 %; Lab B: 0.44 % → RSD_R (n=2): 2.8 %
→ Accuracy is good

Wetting of Wettable Powders (MT 53.3)

Wetting of wettable powders

- 2014
  Min. 0 min; [illegible] 1.07 min[illegible]bers of results 17
  No statisti[illegible]
  * outlier
- 2011
  Min. 0 min[illegible]rs of results 17
  No statistica[illegible] possib[illegible]

- **Agroscope (2013):**
  reproducibility: RSD (n = 6) 29.7 % (mean 28.8 s)
  → **mu (2 * RSD) = ± 50.0 %**

Interlaboratory comparison (2016, 2 labs)

Lab A: 27 s; Lab B: 30 s → RSD_R (n=2): 6.9 %

→ Accuracy is good

Dustiness of Granular Products (MT 171)

Dustiness

- **Problem: No PT results**

- **Agroscope (2013):**
  repeatability: RSD (n = 6) 16.9 % (mean 21.3 mg)
  RSD (n = 6) **20.5 %** (mean 3.5 mg)

- **Interlaboratory comparison (2016, 2 labs)**
  Lab A: 19.0 mg; Lab B: 23.3 mg → RSD_R (n=2): 14 %
  Lab A: 6.0 mg; Lab B: 7.4 mg → RSD_R (n=2): 15 %
  → Accuracy is good

→ mu (2 * RSD) = ± 40.0 %

Conclusion
Estimation of Uncertainty

- The estimation of measurement uncertainty of phys.-chem. methods is not well established
- Usually MT-Methods give no information about uncertainty
- Results from proficiency tests, as the annual FASFC trial, are an excellent basis to estimate uncertainty.
  However only results can be used that have a useful distribution around the mean value (NOT 100 %, NOT 0 mg).
- If there are no proficiency tests available, accuracy and reproducibility can be tested with 1 or 2 other labs that analyse the same samples.
- Preferentially samples with test results in the range of the tolerance value should be used since those are most relevant.

Thank you for your attention

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