


Using MOOCs for teaching analytical chemistry: experience at University of Tartu

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sisu.ut.ee/measurement

I. Leito, I. Helm, L. Jalukse. *Anal Bioanal Chem* (2015) 407:1277–1281

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Massive Open Online Courses

- Term coined in 2008
 - by D. Cormier and G. Siemens
- MOOCs were hailed as the **future of higher education**
 - 2012: „Year of the MOOC“ by NYT
- Since then, a lot of criticism
 - insufficient interaction between teachers and students, low course completion rates, etc
 - It is acknowledged that MOOCs **were originally overhyped**

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MOOCs: still very promising



MOOCs are approximately here

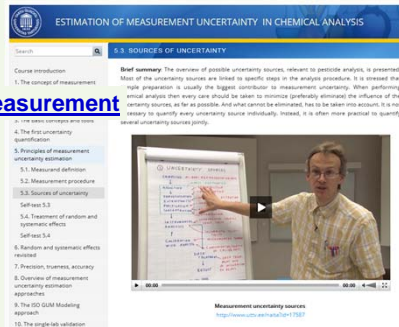
„Gartner Hype Cycle“ by Jeremy Kemp at Wikipedia. Licensed under CC BY-SA 3.0 via Wikimedia Commons

- MOOCs have **undoubted advantages**
- Offered by many leading universities
- Offered by many online providers
 - Coursera, edX, Udacity, ...

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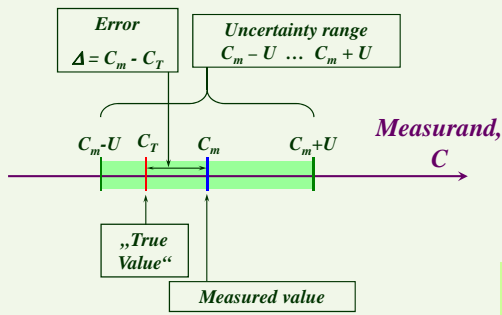
On-line course: Estimation of measurement uncertainty in chemical analysis

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Value, error and uncertainty



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Measurement result

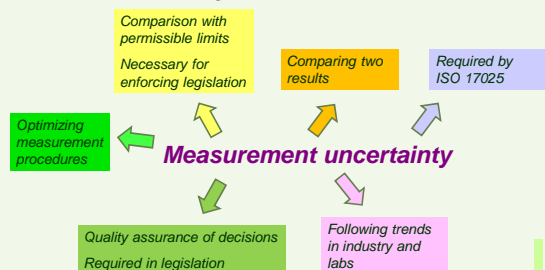
- This way of writing:

The benzene content of a fuel is
 $C_{\text{benzene}} = (32 \pm 6) \text{ mg/kg}, k = 2, \text{norm.}$

Estimate of measurement uncertainty
- Is a **measurement result** and means the following:
 - The true content of benzene in the fuel is in the range of 26 ... 38 mg/kg with the approximate probability 95%
 - The “± 6 mg/kg” is the **measurement uncertainty**
 - It is the expanded uncertainty

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Why do we need measurement uncertainty estimates?



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Measurement uncertainty in Chemistry

- „Notoriously difficult“ ← In practice: often underestimated uncertainties
- Needs:
 - In-depth understanding of the particular chemical analysis procedure: physical-chemical principles, influencing factors
 - Knowledge and skills in mathematics (random quantities, distribution functions, ...)
- Chemical analysis usually cannot be modeled well

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Teaching measurement uncertainty

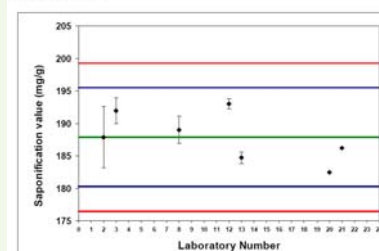
- Very difficult ← It is usually taught at the level of basics but difficulties emerge first of all with practical applications
- Usually taught in connection with analytical chemistry
- Many guideline materials and courses
- Most of them stop exactly at the moment when it starts getting interesting and useful

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Consequences?

Figure 6. Results of Participants with Self-declared Uncertainties and z-Score Boundaries,* SAPV Measurement.



*The consensus value (mean as average) is denoted by the solid green line. The dotted green line denotes the median consensus value. The z-boundaries are denoted by blue lines. The 2 σ boundaries are denoted by red lines.

EstOil-5 Final report, 2009
<http://www.ut.ee/katsekoda/ILC/>

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Our goal

- Web-based teaching material for
 - Independent learning to estimate measurement uncertainty in real-life situations
 - On-line reference point of explanations of concepts and approaches
 - Support for auditorial teaching of metrology in chemistry at UT
 - Offering as MOOCs
- Required previous knowledge
 - General analytical chemistry knowledge

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Course contents

- Theoretical basis as well as practical skills
- Detailed and example-based treatment
 - Modeling (ISO GUM)
 - Within-lab validation (Nordtest)
- Close to 50 short video lectures
 - Supplemented by textual explanations and downloadable slides and calculation files
- Numerous tests and calculation exercises
 - Understanding of main concepts
 - Calculation exercises from real life situations
 - Feedback is given

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ESTIMATION OF MEASUREMENT UNCERTAINTY IN CHEMICAL ANALYSIS

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6.3. SOURCES OF UNCERTAINTY

Brief summary: The overview of possible uncertainty sources, relevant to pesticide analysis, is presented. Most of the uncertainty sources are linked to specific steps in the analysis procedure. It is stressed that sample preparation is usually the biggest contributor to measurement uncertainty. When performing chemical analysis then every care should be taken to minimize (previously eliminated) the influence of the uncertainty sources, as far as possible. And what cannot be eliminated, has to be taken into account. It is not necessary to quantify every uncertainty source individually. Instead, it is often more practical to quantify several uncertainty sources jointly.

Measurement uncertainty sources

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Step 3 – Uncertainty sources

Uncertainty sources in general
http://www.utlu.ee/mehata?id=17638

Step 3 – Uncertainty sources

Sampling
Sample preparation
Analysis

Uncertainty sources: one by one
http://www.utlu.ee/mehata?id=17639

The following schemes list the main uncertainty sources in chemical analysis and comment on the presence or absence of the respective uncertainty sources in our case. (1)

Step 3 – Uncertainty sources

- Sampling
- Sample non-representativeness

The result is expressed for sample; sampling is not included

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ESTIMATION OF MEASUREMENT UNCERTAINTY IN CHEMICAL ANALYSIS

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5.1. MEASURAND DEFINITION

Brief summary: The first principle of measurement uncertainty is: the measurand must be correctly and unambiguously defined. The importance of measurand definition is explained on the example of pesticide determination in oranges.

Defining the measurand
http://www.utlu.ee/mehata?id=17355

Defining the measurand in the case of pesticide determination in oranges is not trivial. On one hand it is important to define whether the result is applied to a single orange or few oranges that were taken as the sample or whether it is applied to the whole lot of oranges. On the other hand, orange is not a homogenous analysis object. Pesticides are applied on orange surfaces, not inside. At the same time pesticide can diffuse from the orange peel to the inside. So, a number of different possibilities exist: whole orange, whole peel,

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2. THE ORIGIN OF MEASUREMENT UNCERTAINTY

Brief summary: Explanation, on the example of pipetting, where measurement uncertainty comes from. The concept of **uncertainty sources** – effects that cause the deviation of the measured value from the true value – is introduced. The main uncertainty sources of pipetting are introduced and explained: repeatability, calibration, temperature effect. Explanation of random and systematic effects is given. The concept of **repeatability** is introduced.

The first video demonstrates how pipetting with a classical volumetric pipette is done and explains where the uncertainty of the pipetted volume comes from.

Why measurement results have uncertainty? The concept of uncertainty source explained on the example of pipetting

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Calculating the combined standard uncertainty
http://www.utlu.ee/mehata?id=17721

Numerical calculation of the uncertainty components: the Krageri method
http://www.utlu.ee/mehata?id=17721

The initial XLS file (i.e. containing only the data but not the calculations) used in this example and the XLS file containing the also the combined standard uncertainty (and expanded uncertainty) calculation according to the Krageri's approach can be downloaded from here:

- uncertainty_of_photometric_nh4_determination_krageri_initial.xls 49 KB
- uncertainty_of_photometric_nh4_determination_krageri_solved.xls 52 KB

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10.4. SINGLE-LAB VALIDATION APPROACH: ROADMAP

Roadmap:

Possible bias: $w(Cr_{ref})$ from certificates

Possible bias: $w(Cr_{ref}) = \frac{w(Cr_{ref})}{\sqrt{R}}$

Combined standard uncertainty: $u_c = \sqrt{u_{bias}^2 + u_{rand}^2}$

Roadmap:

Possible bias: $w(Cr_{ref}) = \frac{w(Cr_{ref})}{\sqrt{R}}$

Combined standard uncertainty: $u_c = \sqrt{u_{bias}^2 + u_{rand}^2}$

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ESTIMATION OF MEASUREMENT UNCERTAINTY IN CHEMICAL ANALYSIS

14 TESTS AND EXERCISES

This section contains a compilation of all the tests and exercises of this course.

- The concept of measurement uncertainty (MU) - Self test 1
- The origin of measurement uncertainty - Self test 2
- The normal distribution - Self test 3.1
- Mean, standard deviation and standard uncertainty - Self test 3.2
- Standard deviation of the mean - Self test 3.3
- Rectangular and triangular distributions - Self test 3.3.1
- The Student distribution - Self test 3.4
- Quantifying uncertainty components - Self test 4.1
- Random and systematic effects needed - Self test 4.2
- Looking at the obtained uncertainty - Self test 4.3
- Expanded uncertainty - Self test 4.4
- Presenting measurement results - Self test 4.5
- Sources of uncertainty - Self test 5.1
- Treatment of random and systematic effects - Self test 5.4
- Random and systematic effects needed - Self test 5.5
- Precision, trueness, accuracy - Self test 7
- Overview of measurement uncertainty estimation approaches - Self test 8
- Standard uncertainties of the input quantities - Self test 9.1
- The ISO GUM Modeling approach - Self test 9.2, 9.3, and Self test 9.4
- Uncertainty component accounting for random effects - Self test 10.1
- Uncertainty component accounting for systematic effects - Self test 10.2
- Determination of acrylamide in snacks by LC-MS - Self test 10.3, 10.4 and Self test 10.5
- Comparison of the approaches - Self test 11

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1. The concept of measurement uncertainty (MU)

2. The origin of measurement uncertainty

3. The basic concepts and tools

4. The first uncertainty quantification

5. Principles of measurement uncertainty estimation

6. Random and systematic effects needed

7. Precision, trueness, accuracy

8. Overview of measurement uncertainty estimation approaches

9. The ISO GUM Modeling approach

10. The single-lab validation approach

10.1. Principles

10.2. Uncertainty component accounting for random effects

Self test 10.2

10.3. Uncertainty component accounting for systematic effects

Self test 10.3

10.4. Roadmap

10.5. Determination of

A laboratory wants to estimate the measurement uncertainty of protein content determination in different foods. For this protein content in a control sample of smoked sausage was determined repeatedly during a time period of almost one year. Every day when this smoked sausage was analysed only one parallel measurement was made. The following results were obtained:

| Week | Result (g/100g) |
|------|-----------------|
| 1 | 26.5 |
| 2 | 26.5 |
| 3 | 26.5 |
| 4 | 26.5 |
| 5 | 26.5 |
| 6 | 26.5 |
| 7 | 26.5 |
| 8 | 26.5 |
| 9 | 26.5 |
| 10 | 26.5 |
| 11 | 26.5 |
| 12 | 26.5 |
| 13 | 26.5 |
| 14 | 26.5 |
| 15 | 26.5 |
| 16 | 26.5 |
| 17 | 26.5 |
| 18 | 26.5 |
| 19 | 26.5 |
| 20 | 26.5 |
| 21 | 26.5 |
| 22 | 26.5 |
| 23 | 26.5 |
| 24 | 26.5 |
| 25 | 26.5 |
| 26 | 26.5 |
| 27 | 26.5 |
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| 31 | 26.5 |
| 32 | 26.5 |
| 33 | 26.5 |
| 34 | 26.5 |
| 35 | 26.5 |
| 36 | 26.5 |
| 37 | 26.5 |
| 38 | 26.5 |
| 39 | 26.5 |
| 40 | 26.5 |
| 41 | 26.5 |
| 42 | 26.5 |
| 43 | 26.5 |
| 44 | 26.5 |
| 45 | 26.5 |
| 46 | 26.5 |
| 47 | 26.5 |
| 48 | 26.5 |
| 49 | 26.5 |
| 50 | 26.5 |

In addition the laboratory analysed two certified reference materials: Ham with protein content (19.6 ± 0.6) g/100g (n=2, norm) and cheese with protein content (28.3 ± 0.7) g/100g (n=2, norm). The laboratory has carried out four bias determinations with the following results (each found value is found as a mean from a number of parallel measurements):

| Reference value (g/100g) | Found value (g/100g) |
|--------------------------|----------------------|
| 26.3 | 26.9 |
| 26.3 | 27.2 |
| 19.6 | 20.1 |
| 19.6 | 20.4 |

Please calculate the combined standard uncertainty of the protein determination procedure (please give 1 or 2 decimals). Absolute uncertainties can be used in this case.

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9.2. Step 3 - Model equation

9.3. Step 4 - Uncertainty estimation

9.4. Step 4 - Value of the input quantities

9.5. Step 5 - Standard uncertainties of the input quantities

Self test 9.5

9.6. Step 6 - Value of the output quantity

9.7. Step 7 - Combined standard uncertainty

9.8. Step 8 - Expanded uncertainty

9.9. Step 9 - Looking at the obtained uncertainty

Self test 9.9

10. The single-lab validation approach

11. Comparison of the approaches

12. Comparing measurement results

13. Additional materials and case studies

14. Tests and Exercises

Please refresh!

This standard uncertainty takes into account the repeatability of the pipetting and transfer steps of the procedure.

Feedback: Since sample preparation was performed only once it is not included in the repeatability. The remaining steps are included.

If the indicator is subjective and a systematic over-estimation occurs as a result then this standard deviation does not take it into account.

Feedback: Such a situation is a systematic effect (both within day and in the long term) and it cannot be accounted for by repeatability (which takes into account only effects that are random within day).

If the organic bases that cause toxicity are sensitive compounds and partially decompose during sample preparation, preparation of solution or during titration then this standard uncertainty takes this decomposition into account.

Feedback: Decomposition always involves a systematic effect. This effect cannot be taken into account by repeatability standard deviation. Decomposition can (and usually should) in addition also have a random component - for different replicate titrations the amount of decomposed analyte is different. This effect is taken into account by repeatability. So, if the compounds are unstable then one usually sees that repeatability standard deviation gets higher. However, the risk effect is still there. So, if one suspects that the standard deviation fully includes the uncertainty due to analyte instability then the uncertainty will be underestimated.

This standard uncertainty takes into account the overall repeatability of all steps of the procedure (sample preparation, pipetting, titration).

Feedback: Since sample preparation was performed only once it is not included in the repeatability. The remaining steps are included.

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Platforms

- Course contents: sisu.ut.ee
- Admin, forums, knowledge evaluation: moodle.ut.ee

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MOOC: UT Moodle Environment

ESTIMATION OF MEASUREMENT UNCERTAINTY IN CHEMICAL ANALYSIS

Week 1 3-8, March

The concept and origin of measurement uncertainty

This section discusses the concept of measurement uncertainty and its estimation. It explains the origin of measurement uncertainty and its estimation. It also discusses the concept of measurement uncertainty and its estimation. It explains the origin of measurement uncertainty and its estimation. It also discusses the concept of measurement uncertainty and its estimation.

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Divided into 6 weeks

- The **concept** and **origin** of measurement uncertainty
- The basic **concepts** and **tools**
- The **first uncertainty quantification**
 - On the example of pipetting
- The **principles** of measurement uncertainty estimation (random and systematic effects and definitions for precision, trueness, accuracy)
- Overview of the measurement uncertainty estimation **approaches**. The ISO GUM **modeling approach**
 - On the example of photometric determination of NH_4^+
- The single lab **validation approach**. Comparison of different approaches. Comparing measurement results.
 - On the example of LC-MS determination of acrylamide

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Weeks in Moodle

Week 2 10-16. March

The second presents the most basic concepts and how to perform operations on measurement systems. This, the essence of metrology, is the foundation for the rest of the course. The most important function for a measurement system is its ability to provide information on the quality of the measured quantity. This is done by comparing the measured value with a reference value. The reference value is the value of the measured quantity in a certain state, which is usually the value of the measured quantity in a certain state. The reference value is the value of the measured quantity in a certain state, which is usually the value of the measured quantity in a certain state. The reference value is the value of the measured quantity in a certain state, which is usually the value of the measured quantity in a certain state.

Week 3 17-23. March

The next uncertainty quantification. The uncertainty quantification is the process of determining the uncertainty of a measurement. This is done by comparing the measured value with a reference value. The reference value is the value of the measured quantity in a certain state, which is usually the value of the measured quantity in a certain state. The reference value is the value of the measured quantity in a certain state, which is usually the value of the measured quantity in a certain state.

„Easy“ Test

Estimation of Measurement Uncertainty in Chemical Analysis (P2AV.TK.652)

1. The measurement is a random variable with a normal distribution. The mean value is 10.0 and the standard deviation is 0.2. The measurement is 10.1. What is the probability that the measurement is between 9.8 and 10.4?

2. The measurement is a random variable with a normal distribution. The mean value is 10.0 and the standard deviation is 0.2. The measurement is 10.1. What is the probability that the measurement is between 9.8 and 10.4?

3. The measurement is a random variable with a normal distribution. The mean value is 10.0 and the standard deviation is 0.2. The measurement is 10.1. What is the probability that the measurement is between 9.8 and 10.4?

„Difficult“ Test

Estimation of Measurement Uncertainty in Chemical Analysis (P2AV.TK.652)


1. The measurement is a random variable with a normal distribution. The mean value is 10.0 and the standard deviation is 0.2. The measurement is 10.1. What is the probability that the measurement is between 9.8 and 10.4?

2. The measurement is a random variable with a normal distribution. The mean value is 10.0 and the standard deviation is 0.2. The measurement is 10.1. What is the probability that the measurement is between 9.8 and 10.4?

3. The measurement is a random variable with a normal distribution. The mean value is 10.0 and the standard deviation is 0.2. The measurement is 10.1. What is the probability that the measurement is between 9.8 and 10.4?

MOOC: Spring 2014 edition

270 participants from 40 countries!



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High participation activity

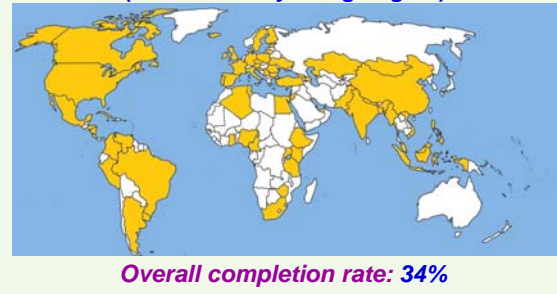
- More than 300 posts to the forums
- Constant counseling by our team

| Discussion | Started by | Replies | Unread | Last post |
|------------|------------------|---------|--------|----------------------------|
| Week 1 | Isabelle Brabant | 4 | 0 | Wed, 10 Apr 2014, 9:32 PM |
| Week 2 | Isabelle Brabant | 9 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Thanks | Karine Marlet | 13 | 0 | Tue, 15 Apr 2014, 10:50 AM |
| Week 3 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 4 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 5 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 6 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 7 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 8 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 9 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 10 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 11 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 12 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 13 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 14 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 15 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 16 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 17 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 18 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 19 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |
| Week 20 | Isabelle Brabant | 1 | 0 | Wed, 10 Apr 2014, 9:30 AM |

Overall completion rate: 52%
Completion rate of those who started: 67%

MOOC: Spring 2015 edition

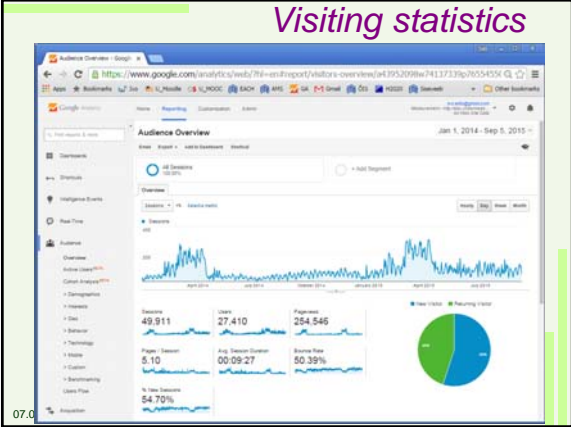
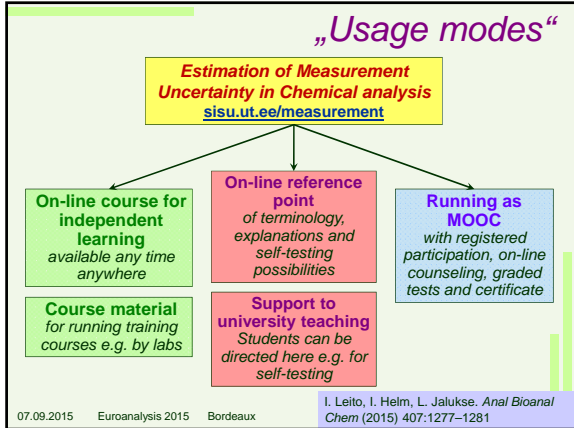
489 participants from 70 countries (Forum activity still going on)



Overall completion rate: 34%
Completion rate of those who started: 60%

MOOCs vs „traditional“ teaching I. Leito, I. Helm, L. Jalukse
Anal Bioanal Chem (2015)
407:1277–1281

| Aspect | Conventional university course | Practitioner training (short) course | MOOC |
|---|--------------------------------|--|---------------|
| Interaction between students and teachers | Direct | Direct | Remote |
| Possibility to deliver the course simultaneously to many participants | Low | Low | High |
| Level of self-discipline needed from participants | Average | Average | High |
| Time constraints, time to “digest” the knowledge | Not a problem | Serious time constraints | Not a problem |
| Possibility of independent homework | Possible | Usually impossible | Possible |
| Possibility of hands-on problem-solving | Possible | Possible (within the time constraints) | Possible |
| Possibility of teamwork | Possible | Possible (within the time constraints) | Not easy |
| Possibility of experimental work | Easy | Possible, but not easy | Not possible |
| Possibility of working with participants of uneven level or preparation | Difficult but doable | Difficult | Possible |
| Possibilities of meaningful assessment of obtained knowledge | Wide possibilities | Difficult | Possible |
| Danger of cheating during knowledge assessment | Can be made low | Can be made low | Can be high |
| Costs of setting up the course ^a | Medium | Medium | Medium |
| Costs of running the course ^b | High | High | Low |
| Travel and accommodation costs | Can be high | Can be high | None |



Many thanks to the team!

Materials development

- Lauri Jalukse
- Irja Helm

Video

- Enno Kaasik

Web design, study administration

- Triin Marandi
- Lehti Pilt
- Esta Pilt

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Thank you for your attention!

MOOC – Third edition: Spring 2016
Registration will open in the beginning of 2016

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