Recent developments in measurement uncertainty

Lisbon, 6-7 June 2011
Dear Colleagues,

The Faculty of Sciences of the University of Lisbon, Eurachem-Portugal and RELACRE (Portuguese Association of Accredited Laboratories) have the honour of organizing the Workshop “Recent Developments in Measurement Uncertainty” promoted by the Eurachem/CITAC Measurement Uncertainty and Traceability Working Group.

This workshop, held at the Museum of Science of the University of Lisbon on the 6-7 June 2011, provides an excellent opportunity to present work performed on Metrology in Chemistry and to be updated with the latest developments in evaluation of the quality of measurements. The diversity of analytical fields covered in the presentations and the impact of the developments in Metrology in Chemistry on the management of key issues in developed societies, highlight the importance of the discussions promoted in this event.

This workshop also celebrates the XVIth anniversary of the first edition of the most cited document of Metrology in Chemistry, the Eurachem/CITAC guide “Quantifying Uncertainty in Analytical Measurements”, through the presentation and discussion of a draft of its third edition.

The Journal of Accreditation and Quality Assurance sponsors this workshop through the publication of a topical issue with a selection of papers presented at the event. Participants are kindly invited to submit their work.

The Organizing Committee warmly welcomes all participants, gratefully acknowledges their presence and wishes them a profitable and pleasant time during the entire Workshop, from both scientific and social points of view.

All best wishes,

Ricardo Bettencourt da Silva
Workshop secretary

[Signature]
## DAY 1: 6 JUNE 2011

### MEASUREMENT UNCERTAINTY AND TRACEABILITY

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15:00-15:30 Coffee Break

**15:30-17:00 Breakouts in parallel sections**

Session A: COMPLIANCE  
Chair: Bertil Magnusson

*Wilfried Hinrichs*: A probabilistic approach to assessing the compliance of concrete regarding the content of dissolved chloride in its components

Session B: TRACEABILITY  
Chair: Ricardo Bettencourt da Silva

*Francesca Rolle*: Metrological traceability for benzo[a]pyrene quantification in airborne particulate matter

17:00-17:30 Feedback from breakouts

17:45 Visit to the Museum

19:30 Dinner – Restaurant "O Forcado"
DAY 2: 7 JUNE 2011

**NUMERICAL APPROACHES, SOFTWARE EVALUATION AND FUTURE DIRECTIONS**

Session: **NUMERICAL METHODS**
Chair: Bertil Magnusson

09:00-09:30 Steve Ellison - Monte Carlo evaluation, Kragten and numerical derivative methods

09:30-10:00 Matthias Roesslein - GUM/Supplement 1 - Numeriacal implementation

10:00-12:00 Poster Section including Coffee Break

12:00-13:00 Lunch

Session: **NUMERICAL METHODS CONTINUED**
Chair: Maire Walsh

13:00-13:15 Introduction to breakouts

13:15-14:30 Breakouts in parallel sections

Session C: **NUMERICAL METHODS**
Chair: Matthias Roesslein

Pedro Salgueiro - Metrological assessment of internal standard technique for quality control of GC-MS determinations for arson detection

Session D: **UNCERTAINTY AND DETECTION LIMITS**
Chair: Steve Ellison

Rudolf Schneider - Uncertainty in measurement with Immunoassays

14:30-15:00 Coffee Break

Session: Future Directions
Chair: Maire Walsh

15:00-15:30 Adriaan van der Veen: Revision of the Guide to the expression of uncertainty in measurement

15:30-15:50 Katy Klauenberg: Bayesian uncertainty analysis of an international ELISA comparability study

15:50-16:30 **CLOSING DISCUSSION**
INVITED LECTURES
Measurement uncertainty - a Résumé

Alex Williams

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There have been many developments in measurement uncertainty since the first EURACHEM guide was published in 1993. The purpose of this presentation is to give a résumé of these developments together with an overview of the topics that will be discussed in this workshop. I will start first with discussion of the measurement process, which will lead naturally on to traceability and measurement uncertainty. Then I will discuss how uncertainty is evaluated, dealing briefly with the evaluation of the individual components including the use numerical techniques for combining the individual components and also the use data from validation studies. This will be followed by a description of the use of measurement uncertainty in the assessment of compliance with a specification or regulation.
The new draft Eurachem Guide for Measurement Uncertainty:  
a summary of structure and changes

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The first edition of the EURACHEM Guide for “Quantifying Uncertainty in Analytical Measurement” was published in 1995 based on the ISO Guide to the Expression of Uncertainty in Measurement. The second edition, published in 2000, was prepared in the light of practical experience of uncertainty estimation in chemistry laboratories. The second edition stressed that the procedures introduced by a laboratory to estimate its measurement uncertainty should be integrated with existing quality assurance measures, including method validation studies, since these measures frequently provide much of the information required to evaluate the measurement uncertainty. The guide therefore provides explicitly for the use of validation and related data in the construction of uncertainty estimates.

The new third edition retains the features of the second edition and adds information based on developments in uncertainty estimation and use since 2000. The additional material provides improved guidance on the expression of uncertainty near zero, new guidance on the use of Monte Carlo methods for uncertainty evaluation, improved guidance on the use of Proficiency Testing data and improved guidance on the assessment of compliance of results with measurement uncertainty.

In this presentation, the structure of the revised Guide will be discussed with particular emphasis on the new sections.
Uncertainty and compliance assessment

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In order to utilise a result to decide whether it indicates compliance or non-compliance with a specification, it is necessary to take into account the measurement uncertainty. In 2007 a EURACHEM/CITAC guide was presented, *Use of uncertainty information in compliance assessment* focusing on decisions on compliance with regulatory or manufacturing limits.

The guide points out that the key to the assessment of compliance is the concept of decision rules. These rules give a prescription for the acceptance or rejection of a test result for a sample based on the measurement result, its uncertainty and the limits, taking into account the acceptable level of the probability of making a wrong decision. On the basis of the decision rule, a guard band is calculated. Using the permitted limit and the guard band an acceptance zone and a rejection zone are determined, such that if the measurement result lies in the acceptance zone the test result is declared compliant and if in the rejection zone it is declared noncompliant. The point between these zones is called the decision limit.

This presentation discusses the relevant information needed for reliable compliance assessment of a test result. An example is presented for blood alcohol with an upper regulatory limit of 0.2 mg/g for the concentration (mass fraction) of blood alcohol for a driver. Here the decision rule focuses on a very low probability of a false positive result. Using this decision rule the guard band is added to the permitted limit giving a decision limit higher than the regulatory limit.
Uncertainty and metrological traceability

Ricardo J. N. Bettencourt da Silva

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The metrological traceability concept is intimately related with the measurement uncertainty one since involves the definition of the reference for measurements. The link between the measurement reference and the measurement itself can be supported on the use of standards of different metrological levels for which the value is estimated from comparisons performed with known uncertainty. The used standards represent the link of this chain of comparisons, known as metrological traceability chain, and their strength is quantified by the measurement uncertainty. The way laboratories define the traceability of their measurements is by selecting and properly using the reference for the measurements. This reference must be adequate for the intended use of measurements and can vary from a local reference (ex. sample of raw material from a factory that is known to perform well) to an international and long-term stable reference (ex. SI units).

This presentation discuss how relevant the metrological traceability chain concept is for the intended use of the measurement and how the traceability chain should be defined before measurement procedure validation and uncertainty evaluation.
Monte Carlo evaluation, Kragten and Numerical derivative methods

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The revised edition of the EURACHEM Guide for “Quantifying Uncertainty in Analytical Measurement” provides guidance on two numerical methods of evaluating measurement uncertainty; the spreadsheet-based method originally proposed by Kragten\(^1\) and the use of Monte Carlo methods for uncertainty evaluation as described, for example, in JCGM Guide 101:2008. These approaches provide alternatives to the algebraic differentiation of the measurement model proposed in the ISO Guide to the Expression of Uncertainty in measurement.

In this presentation, strategies for the numerical estimation of uncertainty are reviewed and the strengths and weaknesses of each in different circumstances are compared.

The meaning of a measurement result without an indication of the confidence is rather limited. A useful measure of the confidence that can be placed on a measurement is measurement uncertainty. Measurement uncertainty is defined as a parameter that characterizes the dispersion of the values that could reasonably be attributed to the result of a measurement. The dispersion of the measurement result follows from the dispersion of the different quantities influencing the measurement. The available and relevant information about the influence quantities can be described via probability density functions. The propagation of them through the measurement model yields again a probability density function representing the state of knowledge about the outcome of the measurement. This probability density function can be used to calculate a parameter representing the measurement uncertainty. An appropriate way to propagate probability density functions through an arbitrary measurement model is based on the Monte Carlo method. As this method is computationally intensive, it is necessary to implement it in an adequate way. This talk elaborates some of the computational aspects of the Monte Carlo method. The results of this elaboration are realized in the software tool MUSE. The tool is open source (GPL V3) and can be downloaded for free at http://sourceforge.net/projects/freemuse/files/.
Revision of the Guide to the expression of uncertainty in measurement

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Since its publication in 1993 the Guide to the expression of uncertainty in measurement (GUM) has become the authoritative document concerning the evaluation and expression of measurement uncertainty in many areas, but especially physics, chemistry and microbiology. The measurement community has made vast investments in implementing the GUM. In various areas and sectors such as calibration, analytical chemistry, microbiology and reference material production, guides or guidelines have been developed on how to implement the GUM given the specific needs and constraints. Working Group 1 of the Joint Committee on Guides in Metrology (JCGM WG1) has started the revision of the core document. The paper gives an overview of the plans and the progress made so far.
Oral Communications
Use of measurement uncertainty in testing a drug substance

Jane Weitzel

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The vision for metrology at the United States Pharmacopeia (USP) is for international recognition, harmonization and official acceptance of all USP reference standards as well as having cutting-edge Reference Standards, including Certified Reference Materials which are based on sound, scientific, metrological principles, such as Measurement Uncertainty. This paper will demonstrate the use of Measurement Uncertainty (MU) in method validation, routine method use, and reporting data for an assay and impurities test of a pharmaceutical Drug Substance.

Pharmaceutical manufacturing companies are required to test the Drug Substance, DS, used in their drug products. In this example, the DS is a USP compendial substance so there is a monograph containing a method to determine the concentration of the impurities and to determine whether the DS meets the assay specification of 98.0% to 102.0%. The USP monograph only listed two impurities, but there are two additional known impurities. A new method was developed and validated following the requirements in USP <1225> because the USP method did not separate all the four known impurities. The MU was initially estimated using the data from the method validation. This estimation of the MU identified that the validation design was not optimal for estimating the MU; however, the MU estimate is usable.

The MU estimate determined that the method was fit for use with one replicate, avoiding the expense of duplicate analyses. The MU estimate was used to set up decision rules for comparing test data to the assay and impurity specifications. The information from the MU estimate was used to monitor the routine use of the method using control charts that assess accuracy and precision of each run based upon actual method performance capability.

Validation of measurement uncertainty: total hardness in drinking and natural waters as a case study

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In the field of water policy, the degree of total hardness is one of the assessment indicators for the water quality intended for human consumption\textsuperscript{1}. It is required to establish environmental quality standards values of some metals, as is the case of cadmium and its compounds in surface waters\textsuperscript{2} and total zinc and dissolved copper in surface waters for aquaculture - fish waters\textsuperscript{3}, since this parameter affects bioavailability of metals\textsuperscript{2}.

Measurement uncertainty of analytical results is a requirement for accreditation of testing laboratories\textsuperscript{4}. An increasing on publications concerning this subject over the last decades, led to a very important accomplishment for chemical laboratories. However, some caution and critical mass towards the recent willingness to avoid the opposite: some oversimplification and generalization on this subject.

Reporting uncertainty of a measurement result plays an important role on compliance with specified requirements, either by customers or regulation bodies, however few work has been done regarding fit-for-intended-use of measurement uncertainty itself. Despite of regulations requirements, as in national and european legislation, which establishes performance characteristics of methods\textsuperscript{1} and limit values\textsuperscript{2}, no target measurement uncertainty associated to the analytical results has been suggested.

In this work total hardness determination was carried out using complexometric titration with ethylenediamine tetraacetic acid (EDTA), based on APHA Method 2340 C\textsuperscript{5}. Measurement uncertainty was estimated by distinct approaches, namely modeling approach considering the GUM uncertainty framework based on the law of propagation of uncertainty and an empirical approach in which two models were considered: single-laboratory validation and quality control data and interlaboratory comparisons (ILC)/proficiency testing (PT) reports.

The suitability of each model was critically evaluated by using both target precision and trueness requirements for quality of surface water and groundwater intended for the abstraction of drinking water, regulated by Decree-Law n° 236/98 of 1 of August\textsuperscript{3} and Decree-Law n° 306/2007 of 27 of August\textsuperscript{1}.

It was found that the results obtained by different models in the range [100-500] mg L\textsuperscript{-1} were far below the results of the uncertainty expected. For the analytical method used and the ILC's data presented, we can conclude that the collaborative approach (as well as intralaboratory approach) is a valid alternative since reference values were used.

Indoor air quality: Measurement uncertainty as a tool for the anion - cation balance acceptance criteria

Maria Trancoso\textsuperscript{a}, Ana Sousa\textsuperscript{a}, Filomena Mouro\textsuperscript{a}, Maria C. Freitas\textsuperscript{b}, Susana Almeida\textsuperscript{b}, Nuno Canha\textsuperscript{b}

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In recent years, the indoor air quality has been studied more frequently due to an increasing concern within the scientific community on the effects of indoor air quality upon health. The indoor air quality studies of schools has a large impact in both health and educational performance of children since they constitute a sensitive group with higher risk than adults, particularly vulnerable to pollutants due to their undeveloped airways.

A total of 14 basic schools located in Lisbon city, Portugal, were selected for sampling the total particulate matter (TPM) by passive deposition into polycarbonate filters and to assess the indoor air quality. Compared to automatic samplers, this passive sampling method represents an easier and cheaper way to assess several indoor air quality environments with no interference in the classroom activities. The procedure was performed on four different campaigns during 2009-2010. The filter loads were measured by gravimetry with a 0.1 µg sensitivity balance and, afterwards, the TPM water soluble ions content was assessed by ionic chromatography (Cl\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, PO\textsubscript{4}\textsuperscript{3-} and SO\textsubscript{4}\textsuperscript{2-}); flame absorption (Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+}) and indophenol-blue spectrophotometry for NH\textsubscript{4}\textsuperscript{+}.

Nowadays is well-recognized that the quality of results depends on the use of validated methods as much as metrological traceability and measurement uncertainty. In this work each measurement uncertainty was evaluated using an intralaboratorial modelling approach, evaluating standard uncertainties associated with each or grouped individual input parameters and combining them using the law of propagation of uncertainties. The anion - cation balances were assessed taking into account the acceptance criteria for the percentage difference defined from the measurement uncertainties.
Uncertainty evaluation model for a practical approach in the
certification of CRM: Performing certification and
homogeneity test simultaneously

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The basic model $x_{\text{CRM}} = x_{\text{char}} + \delta x_{\text{bb}} + \delta x_{\text{sts}} + \delta x_{\text{ilts}}$ in the ISO Guide 35 for the
evaluation of uncertainty is reviewed. In the basic model, the authors of the Guide
assume that the homogeneity and stability studies are designed in such a way that the
values of the error terms are zero, but their uncertainties are not. As the
recommendations of Guide 35\(^1\) are treated as mandatory by many accreditation bodies
offering RM producer accreditation in accordance with Guide 34\(^2\), many RM producers
implement measurement models to evaluate those uncertainties separately. Those
models sometimes require too excessive works, and are impractical due to technical or
just economic reasons. We propose a revised model in which a single method is
employed in the characterization, homogeneity and stability studies. In this model, at
least 10 bottles is selected and one subsample from each bottle is measured by a single
method for certification and assessment of homogeneity. It is shown that it is not
necessary to evaluate the uncertainty due to the between-bottle inhomogeneity $\mu_{\text{bb}}$
separately. The $\mu_{\text{bb}}$ is shown to be one of the uncertainty components of the certified
value $x_{\text{char}}$, because $x_{\text{char}}$ is the mean value of selected bottles.\(^3\) Application of this model
to the certification of a few CRMs\(^4\) will be also presented.

certification, ISO, Geneva, Switzerland.
Switzerland.
The use of measurement uncertainty in an operating mine

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There are many analysis-based decisions made on a daily basis in an operating mine and measurement uncertainty plays a role in all of them. The first decision is whether a block of mined material should be sent to the mill for processing or to the waste dump since it is below the cutoff grade. Other decisions are made during the operation of the mill. Is the level of the mineral of interest too high in the mill tails? If so, adjustments to the concentrator operations will have to be made. Is there an acceptable mass balance between the ore entering the mill as compared to that reporting to the concentrate plus that in the mill tails (waste stream)? If not, was the sampling process for the different streams a problem or is it an analytical problem? A final critical analysis is made when the concentrate from the mill is sold. Concerns here are associated with the concentration of the element of interest to decide the monetary value of a shipment. There can also be the level of minor constituents of the concentrate that might be paid for (gold in a copper concentrate for example) or that might be charged for as a penalty element (arsenic often is considered a penalty element) above a negotiated or decreed level. In each of these instances, it is important to have a reliable estimate of the uncertainty of the measurement (including the contribution of sampling variability) so that decisions can be made with some level of confidence. This paper will look at these considerations using data from an operating mine to illustrate the importance of the estimation of measurement uncertainty in an operating mine.
Metrologically-related out-of-specification test results

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Out-of-specification (OOS) test results are results that fall outside the specification or regulatory limits, or other established acceptance criteria. After identification of an OOS test result it is important to determine its root causes: to avoid any repetition of the situation when appearance of a next OOS test result is possible or even inevitable.

The FDA Guidance (2006) formulates general/organizational rules for that including production review, additional laboratory testing, reporting testing results and concluding the investigation of the OOS test result. A metrological approach to investigating OOS test results is under development by joint IUPAC/CITAC project 2008-030-1.

Any OOS test result can indicate an analyte concentration in the product/environment violating the specification limit, or be caused by measurement/metrological problems, i.e., be metrologically-related. When an OOS test result differs from the specification limit in the measurement uncertainty range, it is considered as metrologically-related.

Investigation of OOS test results based on the metrological concepts should include: 1) assessment of validation data of the analytical method; 2) evaluation of the measurement uncertainty taking into account the validation data; 3) assessment of the relevant metrological traceability chains; and 4) assessment of consumer’s and producer’s risks caused by the measurement uncertainty.

An example of such investigation of OOS test results of mass concentration of total suspended particulates in air is demonstrated. As a case, when a test result is multi-component one, data of results of pesticide residue testing in tomatoes are studied. Another example is provided for investigating influence of metrologically-related OOS test results on long-term stability study of some pharmaceutical products.
A probabilistic approach to assessing the compliance of concrete regarding the content of dissolved chloride in its components

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A major factor influencing the durability of steel-armed concrete is the protection against corrosion which often occurs through an attack by dissolved chlorides. The chlorides both migrate into the concrete from the environment and they are introduced through the components into the concrete, i.e. mainly cement, aggregates, water and additives. That is why the soluble chloride contents of all components are limited and subject to an assessment of compliance.

EN 206-1 limits the input of soluble chlorides in the production of concrete by summing up the individual limiting values of all components. It is also possible to sum up the particular measurement values, if available. The first method tends to produce unrealistic results and the second one disregards the variances of the dissolved chlorides in the components and the measurement uncertainty. In contrast to these deterministic procedures our proposed communication would explain a more realistic probabilistic approach: The mass content of dissolved chlorides is defined as the sum of gamma-distributed parameters of each component. The variances around the mean values are influenced by the spread of Cl⁻ contents in the materials as well as by the specific measurement uncertainty. The measurement uncertainty data are taken from the test procedures for the particular components, i.e. for example, from EN 196-2 for cement and EN 1744-1 for aggregates and from effects on the measurement uncertainty due to sampling procedures.

For pre-stressed concrete the maximum content of Cl⁻ is limited to 0.10%. It is in no way an exception that in cements the mean value of Cl⁻ is about 0.07% with a standard deviation of 0.02% and 0.01% due to the measurement. On the basis of the deterministic approach that would automatically trigger a decision for cement with a significant lower Cl⁻ content. However, in our model we would come up with a set of probabilities of conformity which could be used to find further options. Another example is a decision on the application of recycled aggregates with usually higher levels of dissolved chloride contents for less sophisticated purposes.

Having arrived at a probability density function for a specific concrete design it is possible to calculate the producer’s and the user’s conformity risks. The measurement uncertainty budgets of the respective test procedures would be one out of some possibilities for controlling these risks.
Metrological traceability for benzo[a]pyrene quantification in airborne particulate matter

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Airborne particulate matter (PM) represents one of the most important sources of urban pollution due to its physical and chemical properties. There is a great concern for PM dangerous effects on human health because fine particles can deeply penetrate into the respiratory system, carrying the contaminants adsorbed on their surface. Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds that originate from incomplete combustion of organic matter and can be adsorbed on PM. PAHs have a particular chemical structure, with at least two condensed benzene rings, that is related to their harmful effects on health. For this reason the International Agency for Research on Cancer classified PAHs as potential carcinogenic agents and benzo[a]pyrene (BaP) as carcinogenic to humans (group 1)\(^1\). The international regulations\(^2,3\) require the monitoring of PM and PAHs levels in ambient air by means of standard methods. In particular BaP is assumed as a toxicity marker for the whole PAHs class and its target value is established\(^3\).

In this framework, a metrological traceable procedure for the quantification of BaP in airborne PM was developed at INRIM, starting from the standard method prescribed by the European legislation for this contaminant\(^4\). The identification and quantification of BaP in PM samples were carried out by gas-chromatography coupled with mass-spectrometry (GS-MS). Metrological traceability was established in all the procedure steps, after performing the method validation. Suitable CRMs were used to validate the analytical method and to calibrate the GC-MS. Uncertainty evaluation was performed following the GUM approach, identifying and taking into account all the relevant sources deriving from the whole procedure steps. Metrological traceability is particularly necessary in analytical fields connected with human health as the accuracy and the comparability of results of measurements performed in different laboratories and times is fundamental. This condition represents the basis to support the planning of preventive actions to reduce PAHs levels in atmosphere and also to guarantee the reliability of epidemiological studies.

Metrological assessment of internal standard technique for quality control of GC-MS determinations for arson detection

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The qualitative evaluation of the use of accelerants in arson by the ASTM E 1412-07 standard\textsuperscript{1} involves the concentration of the volatile fraction of debris into activated charcoal strips (ACS) at defined temperature and time, the solvent extraction of the concentrated compounds from ACS and the evaluation of extracts by GC-MS according to ASTM E 1618-10 standard\textsuperscript{2}. The variability of the performance of the analysis of some microliters of extract by GC demands the monitoring of measurement performance by the internal standard technique. Since the internal standard adsorption into ACS significantly varies with the amount of previously retained compounds, the standard has to be added after charcoal strips removing from the extracts. A strategy for the addition of internal standards to solvent extracts from debris, involving the gravimetric control of the volume of solvent mixtures with several composition using models of the volumic mass variation with composition was developed. The adequacy of the developed strategy for the control of the repeatability of GC-MS measurements was metrologically checked using the numerical Kragten method\textsuperscript{3} for uncertainty components combination. This numerical method successfully handled 21 input quantities since the linear assumption of the variation of the output quantity with the input quantities uncertainty is valid. The developed quality control strategy proved to be valid after performed adjustments in relevant analytical steps and further supported the control of the sample preparation performance and debris conservation by using two additional internal standards. This work illustrated how metrology can be used to develop and validate strategies for the control of qualitative forensic assessments supported by GC-MS determinations.

Uncertainty in measurement with Immunoassays

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Immunoassays are invaluable analytical tools in biochemical and medical research and in clinical diagnostics. They have also gained a certain share in supporting screening and monitoring programs of environmentally relevant compounds and of contaminants in food. In the latter areas most applications require the assessment of the uncertainty of the result measured. Yet there is still consensus missing on how to assess precision and accuracy, measurement ranges and detection limits and how immunoassays should be validated.

We have been working with ELISAs for carbamazepine,\textsuperscript{1} caffeine,\textsuperscript{2} and estrogen hormones.\textsuperscript{3} Benefits obtained by using robust statistics, adapted calibration strategies, practical estimates for the limit of detection, precision profiles, power curves and control charts will be demonstrated. A thorough assessment of temperature influence on uncertainty has been carried out which underlines the importance of this major factor – across several different immunoassay formats. The assessment of uncertainty in measurement with immunoassays should follow a straightforward Design of Experiment approach for which we have developed elements of a potential guide.

In the talk results from BAM's ongoing struggle to enhance quality assurance with environmental immunoassays are presented.


Bayesian uncertainty analysis of an international ELISA comparability study

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Immunoassays are biochemical tests applied to measure even very low concentrations of substance using the highly specific bindings between an antibody and its antigen. Immunoassays thus have a wide range of applications, e.g. to detect the presence of an infection, of hormones or drugs. This work focuses on an Enzyme-Linked ImmunoSorbent Assay, called sandwich ELISA, which allows detection of antigens by ‘sandwiching’ them between two antibodies and labelling one type of antibody with an enzyme to generate a detectable signal (e.g. fluorescence).\textsuperscript{1}

ELISAs typically involve a high number of protocol steps, each susceptible to perturbations. A recent publication\textsuperscript{2} has highlighted the variability in concentration estimates in the scope of an international comparability study. Some laboratories estimated an average concentration twice as high as other laboratories. But little is published on the uncertainties of individual laboratory estimates. Decisions which are based on plausible ranges of measurements (such as credible intervals) are generally superior to those solely based on point estimates (such as the mean). Reliable uncertainties are thus vital – and not only in metrology.

Because of limitations of metrological guidelines to express measurement uncertainty (GUM (S1)\textsuperscript{3}), we have developed a Bayesian framework to rigorously quantify the uncertainty in ELISA concentration estimates. This framework encompasses simultaneous calibration of a nonlinear model and estimation of the unknown concentration from a set of fluorescence measurements. The resulting Bayesian uncertainties of individual ELISAs and laboratory estimates are considerably larger than previously reported uncertainties in Ref. 2. The average concentrations we estimate differ from the ones estimated by each study participant. In general, this leads to different conclusions about the comparability study. In particular, the inter- and intra-laboratory consistency is increased, and repeatability problems occur for fewer laboratories.

POSTERS
Validation and measurement uncertainty for GMO analysis

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Commercialization of GMO’s is strictly regulated in the European Union following Directive 2001/18/EC¹ and Regulations (EC) N° 1829/2003² and (EC) N° 1830/2003³. To be able to comply with these regulations, detection and quantification of GM events in food and feed samples are necessary. Therefore, the EU-RL⁴ validates quantitative real-time PCR methods which have to be adopted by the enforcement laboratories. These laboratories need to show the good functioning of the methods by performing an in-house validation.

Method validation consists in the first place of the assessment of a number of method acceptance parameters such as applicability, practicability, PCR efficiency, linearity, limit of detection and quantification, and repeatability⁵. Additionally, the measurement uncertainty for each method needs to be calculated. This parameter gives an estimate of the variability of the quantitative analytical results. Once the different parameters are assessed and agree with the set criteria, a validation dossier can be established. Subsequently, the method can be declared fit for purpose and can be used in the laboratory for the quantification of the GM event in food and feed samples.

In routine analysis, real-life food and feed samples such as cornflakes, noodles, flour, shreet, milk,… are tested for the presence of GM events. The outcome of each quantification experiment needs to be reported as measurement result and its uncertainty⁶. This allows deciding whether the analytical result falls within the specifications for food and feed control as laid down in the GMO regulations. The authors will present the different steps addressed in the validation process and the calculation of the measurement uncertainty. To this purpose, the results for a specific GM event that was validated in the laboratory and is used in routine analysis will be used.

4. EU Reference Laboratory for GM food and feed: http://gmo-crl.jrc.ec.europa.eu/
Gas analyzers for stationary sources emission gases are complex measuring instruments, with wide possibilities of continuous measurements of gas emissions. These instruments, depending on the number of measuring cells, are capable of measuring concentrations of number of gases (CO, O₂, SO₂, NO, NO₂, NOₓ). Gas sampling is performed with the measuring probe, and depending on the instrument's sensors, smaller or larger concentrations of gases can be measured.

For the purpose of control of gaseous emissions from stationary sources, it is necessary that calibration of these instruments is done by competent entities. Measurement uncertainty plays a significant role in reporting the results of gas concentration measurements.

The first PT scheme in Serbia for accredited laboratories for calibration of gas analysers for stationary sources emissions was organized by Directorate of Measures and Precious Metals, Serbia (DMPM) as a pilot laboratory in cooperation with Accreditation Board of Serbia, with the aim of proving competence of laboratories in this field. There was one accredited laboratory participating in this PT scheme, and the object of calibration was a new instrument, provided by the producer of gas analysers.

The calibration of the measuring instrument was done with the traditional method of introducing the Certified Reference Materials CRMs – gas mixtures with different NO and NO₂ concentrations from the high pressure cylinders to the analyser. Calibration of an instrument at DMPM was conducted in different measuring points from the ones used for calibration at the accredited laboratory. The calibration curve obtained at DMPM was used as a reference, and by the means of interpolation and extrapolation for the measuring points of the accredited laboratory, the En score was calculated (according ISO 17043), as a classification of accredited laboratory’s performance. The measurement uncertainty of gas analysers calibration was calculated in accordance with the „Guide to the expression of uncertainty in measurement“ and all relevant uncertainty sources were considered.
Uncertainty associated to the analysis of pesticide residues using several approaches: a case study

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Measurement uncertainty is a quantitative indicator of the confidence in the analytical data and describes the range around a reported or experimental result within which the true value can be expected to lie within a defined probability. Several approaches can be used to estimate the measurement uncertainty associated to the analysis of pesticide residues: a) top-down approach where the estimation can be based on default values, the main ways include the Horwitz equation or fit-for-purpose relative standard deviation (FFP-RSD); b) bottom-up approach where the estimation is function of the uncertainty sources. As regards bottom-up approach, we have investigated the following contributions: weight of sample, calibration solutions, final volume of sample and intermediate repeatability studies. The commodity/residue combination selected in this study was celery / tau-fluvalinate pesticide. Tau-fluvalinate is a broad-spectrum insecticide in the pyrethroid class of pesticides. The Maximum Residue Limit (MRL) of tau-fluvalinate in celery has been set at 0.01 mg/kg. The presented work compares the uncertainty estimated by experimental data using repeated analysis (n = 10) of a real sample and a spiked sample. We have analysed samples of celery containing residues of the pesticide tau-fluvalinate at about 0.1 – 0.5 mg/kg; another sample of celery found free (at 0.01mg/kg) from residues of the investigated pesticide was fortified at a concentration level near the value found in the incurred samples and analysed in 10 replicates. The quantification of tau-fluvalinate residues in celery was performed by QuEChERS method (acetonitrile extraction/partitioning and dispersive SPE cleanup) followed by LC-MS/MS(QQQ) determination.
Uncertainty of lead in foods with internal control data:  
ISO 21748 approach and Monte Carlo

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One of the simplest approaches for estimating uncertainty in trials, is the one used in the ISO 21748:2010\textsuperscript{1} standard, where repeatability, reproducibility and trueness data are used for its calculation. This paper compares a systematic approach to this\textsuperscript{2}, based on the use of internal control data in terms of recovery tests, compared to those obtained by the Monte Carlo probabilistic method\textsuperscript{3}. Both methods were applied to the routine laboratory samples for two years for the analysis of lead in foods by Inductively coupled plasma atomic emission spectrometry (AES-ICP)).

The practical application of both methods was performed using spreadsheets (Excel \textregistered and Open Office) of easy access for any laboratory, and results obtained showed different, though comparable, values of uncertainty. The results were validated the following year when a better match was found between the experimental values and the results obtained by the Monte Carlo method.

The presented results show the possibility of applying these methodologies to analytical trials when using routine samples that also includes the variability of matrix and analyte through recovery trials.

2. NT Techn report 537.
Examples of the use of experimental design based validation data for measurement uncertainty estimation: Determination of chloramphenicol in urine and muscle

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All laboratories accredited according to ISO 17025 shall have and shall apply procedures to estimate the uncertainty of measurement. The EURACHEM/CITAC guide for quantifying uncertainty in analytical measurement suggests two principally different approaches: 1) the classical GUM approach ("bottom up", determination of MU for every single source of error/uncertainty); 2) “top down”-approach (determination of MU for combined contributions of error/uncertainty sources, based on validation data). The EURL in Berlin uses an approach which combines data from a matrix comprehensive in house validation (based on an experimental plan using the software “OptiVal/InterVal Plus”), with data of a bottom up approach (for those sources of uncertainty, which are not covered by the validation data).

The approach is discussed on the basis of two validation experiments: The determinations of chloramphenicol in plasma and in urine for the control of this compound in food according to Council Directive 96/23/EC. Experimental validation plans were created using potentially relevant influencing factors (e.g. cartridges, storage times, lots of chemicals, species) with the software “OptiVal/InterVal Plus”. Validation was done according to the experimental plan with spiked matrix samples; provided that the factors were chosen correctly the resulting data should reflect the uncertainty of the method. So far the uncertainty of the concentration of the spiking solution is not covered by the experimental plan and has to be included in the calculation of the total uncertainty. The uncertainty of the spiking solution was estimated with a bottom up approach and entered in the software; finally a combined total uncertainty is calculated. This total uncertainty is reported concentration dependent; in addition contributions of the other sources (e.g. repeatability, run, matrix) to the total uncertainty can be estimated. Especially the contribution of the matrix to the uncertainty is difficult to estimate with other approaches. Anyhow, the validation data show that – depending on the method – its contribution cannot be neglected.
The evaluation of measurement uncertainties has been widely applied to the calibration of measurement instruments whereas its application to tests is a recent phenomenon. The generalization of the evaluation of measurement uncertainties to tests has been a gradual process, in line with changes in the requirements of the normative framework that regulates the accreditation of tests laboratories and also as the perceived good practices have evolved. The mere identification of the relevant sources of uncertainty was followed by the requirement to provide a simplified estimate of the measurement uncertainty and it is now an accepted requirement to properly evaluate the expanded measurement uncertainty associated with the test.

This is certainly the case in chemical metrology where the evaluation of measurement uncertainty applies for each chemical parameter being studied. Therefore, it is relevant to compare different approaches commonly used in chemical laboratories to evaluate measurement uncertainties, and to validate these procedures with an accepted validation tool as specified in the Supplement 1 to the GUM. Among common features in chemical metrology, the use of linear regression and the comparison between quantities expressed in the form of ratios are very common and need to be properly evaluated.

Input uncertainties associated with each pair of quantities and eventual correlations in the linear regression data need to be taken into consideration, to adequately evaluate the uncertainty associated with this step, and the ratios require also proper validation as the relative values of uncertainties in the numerator and denominator may greatly influence the final value of measurement uncertainty.

In this work the evaluation of measurement uncertainty will be applied to the determination of phenols in a water sample using an analytical method of molecular absorption. A comparison will try to be established among three different approaches for the evaluation of uncertainties, namely data validation (internal and external quality control), GUM and Monte Carlo.

1. NP EN ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories.
Reducing uncertainty in the density determination of liquids: Application of the substitution method in oscillation-type densimetry

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Density, $\rho$, is defined as the mass per unit volume of a fluid or a solid, and depends, in general, on both temperature and pressure. It is a property of extreme importance, routinely applied in the control of industrial processes, but also used in fields such as biomedical diagnostics, fiscal control and basic research. The uncertainty requirement in a density measurement depends on its specific application and can vary from better than 0.1 % to 1 %1.

In the Laboratory of Properties of Liquids of the Portuguese Institute for Quality, density determination of liquid samples can be performed with an oscillation-type density meter DMA 5000 (Anton Paar). The uncertainty budget, previously established2, comprises four major uncertainty components: the uncertainty associated with the measurements repeatability, the uncertainty due to the density meter resolution, the uncertainty related to the density meter calibration, which depends on the uncertainty of the Certified Reference Materials used, and the uncertainty of the temperature and pressure measurement of the sample inside the measuring cell. Uncertainties between 0.03 and 0.06 kg/m$^3$ are usually attainable with this procedure2.

The use of the substitution method in oscillation-type densimetry allows the reducing of the uncertainty, since the only uncertainty components that are significant are the uncertainty associated with the repeatability of the measurements and the uncertainty of the material used as reference standard in the substitution method, all other uncertainty components are consider negligible. With this procedure uncertainties of 0.002 kg/m$^3$ have been reported for aqueous samples3.

In this work, the substitution method was applied for density determination of several liquid samples and its uncertainty compared with the uncertainty obtained using the non-substitution procedure.

A novel approach to include the uncertainty associated with the standard in the model equation of gravimetric standard addition experiments

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Standard addition is applied to liquid samples or solutions of solid samples in case of complex matrices and low concentrations, if external calibration methods provide wrong results (due to different sensitivities in the sample and calibration solution) and if the method of isotopic dilution is too tedious and expensive or impossible (monoisotopic analytes).

The standard addition can be performed by volumetric or gravimetric sample preparation. As the volumetric sample preparation causes a loss of accuracy by demanding simplifying preconditions, a model equation for gravimetric standard addition experiments was set up. To reduce the contribution to the measurement uncertainty caused by signal drifts and fluctuation, an internal standard was additionally used. The gravimetric equation was accordingly modified and successfully tested in international key comparisons.

A new approach to include the uncertainty associated with the standard directly into the model equation was presented. Overcoming the limitations of this latest approach, a new model equation was derived from the equations in and . Using this novel equation and the ordinary least squares algorithm for the regression line yielded also a new formula for the associated measurement uncertainty. For the first time this uncertainty accounts directly for the uncertainty associated with the standard.

In the presentation the derivation of the new model equation and the resulting associated measurement uncertainty will be shown for gravimetric standard addition experiments both with and without an internal standard.


The research within this EURAMET joint research project receives funding from the European Community’s Seventh Framework Programme, ERA-NET Plus, under Grant Agreement No. 217257.
Sampling uncertainty on arable fields estimated by different methods

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On 3 fields of arable land, different sampling procedures were evaluated with regard to sampling uncertainty of average mass fractions (i.e. the measurand) for 15 analytes, obtained from composite samples. Three different approaches to estimate sampling uncertainty were compared:

1. Reference sampling (RS) (systematic sampling, about 200 increments)
2. Collaborative trial (CT) (X-path, totally 20 increments, 18 samplers)
3. Proficiency test (PT) (sampling protocol of own choice, in duplicate)

The poster summarizes values estimated from these experiments for some nutritional and toxic elements:

- \textit{point selection standard deviations} as a measure of variance in the scale of sampling locations ("points") from the RS,
- \textit{reproducibility standard deviations} for the CT and the PT,
- deviations from the reference value (i.e. \textit{bias}),
- \textit{uncertainty contributions} arising from sampler and the sampling process ("within fields") and from analysis,
- \textit{combined standard uncertainties} from sampling and analysis.

From these data some conclusions are drawn\textsuperscript{1,2}:

For a reliable estimation of the sampling uncertainty by a modelling approach (RS), errors in increment materialization, splitting and mechanical sample preparation must be considered. For the applied sampling protocol (CT) the uncertainty contribution from sampling generally is in the same range as the uncertainty contribution from analysis; while the uncertainty contribution from the sampler mostly is comparatively small (PT). Generally, only in a few cases significant bias due to large-scale heterogeneity in the mean value of the CT and PT are observed. Consequently, it can be concluded that even a relatively simple X-path is sufficient in most cases to cover the area of arable fields.

Recovery correction and its impact on measurement uncertainty: Data from QuEChERS verifications

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Although on the agenda for more than a decade\textsuperscript{1,2}, the questions whether and how to correct results of pesticide analyses for recoveries are still not finally settled. This work is using data from within-laboratory verifications of the QuEChERS method for a total of 552 pesticides analyzed by LC-MS/MS and GC-MS according to the SANCO criteria\textsuperscript{3}. Model calculations are done for individual pesticides to estimate whether recovery correction is advisable, and how the measurement uncertainty is influenced.

Improving comparability of analytical results with practical software for estimating measurement uncertainty

Teemu Näykki, Atte Virtanen, Ivo Leito

Finnish Environment Institute (SYKE) is the metrological designated institute for chemical analyses from water environment and the national environmental reference laboratory. Its duties include arranging proficiency tests for environmental laboratories. SYKE has noticed that measurement uncertainties reported by laboratories and their success in the proficiency tests are inconsistent and laboratories generally report the uncertainties lower than their success indicates. Furthermore the deviation of the uncertainty estimates is high\(^1\).

SYKE is actively developing practical tools for environmental laboratories to reduce measurement uncertainty and improve the quality and traceability of analytical results. One of tasks under development is the practical software for estimating measurement uncertainty in environmental laboratories. The development of the software gives possibility to improve the quality and reliability of information collected from the waters, as the analysis results obtained in different laboratories are more comparable. By increased quality less erroneous interpretations and decisions are made from the state of the environment.

Measurement uncertainty calculations performed by software are based on the guidance of NORDTEST Technical Report 537\(^2\). By the software public and commercial environmental testing laboratories may better manage measurement uncertainty evaluations of the analytical results. The software which is under development allows laboratories straightforwardly calculate the measurement uncertainty using the results of quality control samples, routine samples duplicates and proficiency test results. If laboratories participate in proficiency tests arranged by SYKE, they may fluently use the results of proficiency tests to estimate their method bias. According to plan both the user interface and the web service will be implemented using Microsoft's tools and the .NET environment.

The long term development of the uncertainty estimations will be monitored and the estimations are compared before and after the use of the software. SYKE is seeking interested participants as pilot laboratories for testing the software before publishing it in autumn 2011.

Determination of uranium in fucus (*vesiculosus*) by using Isotope Dilution High Resolution Inductively Coupled Plasma Mass Spectrometry (ID HR ICP-MS)

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Fucus (*vesiculosus*), seaweed originated from Baltic Sea (54°57'N, 11°59'E) was selected as IAEA candidate reference material for uranium in marine environment studies. The sample is expected to have high anthropogenic concentrations of radionuclides coming from the accident in Chernobyl.

An analytical method based on isotope dilution single detector inductively coupled plasma magnetic sector mass spectrometry (ID-ICP-SMS) and applied as a primary method of measurements to the specific case of the certification of U mass fraction in fucus matrix is proposed.

The developed analytical procedure was validated in three complementary ways. First, all major sources of uncertainty were identified and propagated together following the ISO/GUM guidelines. Second, this quality was controlled with a matrix matching CRM and third the ID-ICP-MS result for the uranium mass fraction was compared with result received with Alfa spectrometry method. Detailed uncertainty budgets are presented for both methodologies and the major uncertainty sources discussed.
Evaluation of uncertainty of feed additives measurement in feedingstuffs and premixtures using data from proficiency testing

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An interlaboratory experimental approach based on data from proficiency testing (PT) was applied in order to estimate the uncertainty of some feed additive measurement (vitamin A and E, copper, lysine, methionine, threonine) in feedingstuffs and premixtures. Several PTs have been organized in the years 2005-2010 by national reference laboratories for feed additives from Hungary and Poland. Results obtained by the National Laboratory for Feedingstuffs in these PTs were applied to bias ($b$) calculation as the measure of trueness. Instead of bias the experimental approach to estimating standard uncertainty ($u$) took into account within-laboratory reproducibility ($s_w$) as the criterion of measurement precision. Following formulas presented below and published in Eurolab Technical Report¹ and Nordtest Handbook² were taken into account.

$$u = \sqrt{s_w^2 + b^2} \quad b = \sqrt{\Delta^2 + u_{pr}^2 + \frac{s_{pr}^2}{n}} \quad \Delta = \frac{\sum (bias_i)^2}{n}$$

Within-laboratory reproducibilities ($s_w$) were calculated on the basis of control cards (copper), from the range between two replications (amino acids) or were obtained from validation studies (vitamin A and E). Obtained results were summarised in the following Table.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Feed</th>
<th>$s_w$ (%)</th>
<th>bias (%)</th>
<th>$u$ (%)</th>
<th>$U = 2 \cdot u$ (%)</th>
<th>$U$ (%) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin A</td>
<td>Feedingstuffs</td>
<td>4.0</td>
<td>12.4</td>
<td>13.1</td>
<td>26.2</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>Premixtures</td>
<td>2.0</td>
<td>7.2</td>
<td>7.5</td>
<td>15.0</td>
<td>11.8</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>Feedingstuffs</td>
<td>2.0</td>
<td>9.0</td>
<td>9.1</td>
<td>18.2</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>Premixtures</td>
<td>1.0</td>
<td>6.1</td>
<td>6.4</td>
<td>12.8</td>
<td>8.2</td>
</tr>
<tr>
<td>Copper</td>
<td>Feedingstuffs</td>
<td>3.5</td>
<td>4.6</td>
<td>5.8</td>
<td>11.6</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Premixtures</td>
<td>2.7</td>
<td>4.6</td>
<td>5.3</td>
<td>10.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Lysine</td>
<td>Feedingstuffs</td>
<td>3.1</td>
<td>3.6</td>
<td>4.7</td>
<td>9.2</td>
<td>7.9</td>
</tr>
<tr>
<td>Methionine</td>
<td>Feedingstuffs</td>
<td>5.3</td>
<td>5.4</td>
<td>7.6</td>
<td>15.2</td>
<td>9.0</td>
</tr>
<tr>
<td>Threonine</td>
<td>Feedingstuffs</td>
<td>2.7</td>
<td>5.8</td>
<td>6.4</td>
<td>12.8</td>
<td>8.6</td>
</tr>
</tbody>
</table>

* Expanded uncertainty for the Horrat value $H=1$ calculated from the Horwitz’ formula $\text{RSD}_R = 2 \cdot c^{-0.15}; U (\%) = 2 \cdot \text{RSD}_R$ (accepted Horrat value $0.5 < H < 2$)

Obtained expanded uncertainties may be applied to test result interpretation and in assessment of compliance with rules concerning feed additives, especially permissible tolerances recommended in Commission Regulation 939/2010.

Evaluation of sampling uncertainty of loose material

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The paper offers a simple method of sampling uncertainty evaluation of loose material, using the example of analyzing mineral components in feedingstuffs. The essence of the proposal lies in separating two components of results’ variability, analytical variability of a method (repeatability) and technical variability corresponding with the inhomogeneity of the analyzed material. Variability of study results for a mineral component in incremental samples, expressed as variation coefficient \( CV_m(\%) \), depends on method repeatability \( CV_r(\%) \) and inhomogeneity \( CV_h(\%) \), in compliance with the Gauss’ law of error propagation:

\[
CV_m = \sqrt{CV_r^2 + CV_h^2} \quad [1] \quad \text{where} \quad CV_h = \sqrt{CV_m^2 - CV_r^2} \quad [2]
\]

Inhomogeneity \( CV_h(\%) \) calculated from the formula [2] may be applied as the measure of sampling standard uncertainty for a batch of the analyzed material when the sampling method has been adjusted to the requirements or to legal recommendations. Analytical variability \( CV_r \) was calculated from the range of duplicate analyses, following Nordtest Handbook\textsuperscript{1}. Taking into account the above assumptions, sampling uncertainty of feed mixture was calculated for chlorides, calcium, zinc and copper determination. Series of ten incremental samples were taken from the analyzed feedingstuffs batch. In each series mass of the incremental sample was 50, 100, 150, 200 or 250 g. It was assessed that the mass of the incremental sample and physicochemical form of mineral component (salt, oxide, degree of fineness) affects sampling uncertainty. In the case of an incremental samples with the mass of 100 g, inhomogeneity \( CV_h(\%) \) as the measure of standard sampling uncertainty for determination the content of chlorides (added as NaCl), calcium (CaCO\textsubscript{3}), zinc (ZnO) and copper (CuSO\textsubscript{4} \cdot 5 H\textsubscript{2}O) amounted to 3.25%, 3.16%, 4.45% and 9.54%, respectively. Expanded sampling uncertainty \((U = 2 \cdot CV_h)\) calculated for zinc (8.9%) and copper (19.1%) in the feed mixture remained within the range of acceptable technical tolerance (up to 20%) for these feed additives at the feed mixture level, recommended in Commission Regulation 939/2010.

Uncertainty of total mercury and histamine determinations in fishery and aquaculture products

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In recent years, according to ISO 17025, it became mandatory the quantification of uncertainty associated to the results of methods. Thus, the laboratories of INRB, IP / L-IPIMAR, which are already accredited by the Portuguese Institute for Accreditation (IPAC), have optimising the uncertainties measurement of validated analytical methods. The first approach for the calculation was done using the step-by-step methodology, but at present, the laboratories have a history of data on quality control and results from proficiency tests, that allows them to use such information in the measurement of uncertainties. The aim of this work is to present the methodology used to calculate the uncertainty of total mercury and histamine determinations in fishery and aquaculture products.

For total mercury the within-laboratory reproducibility is combined with the laboratory bias. Within-laboratory reproducibility standard deviation of relative differences between samples of a given concentration range has been used. Two ranges of concentrations for both total mercury and histamine determinations are employed. With regard to bias, different components have been applied: for total mercury, regular analysis of a certified reference material (CRM) and interlaboratory comparisons in what concerns histamine.

These uncertainties are expressed as $U$, the combined expanded measurement uncertainty, using a coverage factor $k = 2$, providing a level of confidence of approximately 95\%.
Assessment and application of measurement uncertainty in the official control monitoring of biotoxins in shellfish

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Shellfish, such as mussels and oysters, may periodically accumulate harmful toxins. These are derived from marine phytoplankton and their accumulation in shellfish flesh can result in illness following consumption of contaminated molluscs. To ensure consumer protection, monitoring of toxins in shellfish is a statutory requirement in Europe. The three major classes of marine biotoxins regularly monitored in the UK are amnesic shellfish poisoning (ASP), paralytic shellfish poisoning (PSP) and the lipophilic toxins, classically known as diarrhetic shellfish poisoning (DSP). Toxin levels determined in UK shellfish are compared to the maximum permitted levels specified by European legislation, enabling decisions to be made on the opening or closure of shellfish harvesting areas or recall of contaminated products. For many years, the reference methods for detecting PSP and DSP toxins have been a quantitative and qualitative mouse bioassay (MBA) respectively. Such methods have provided a degree of health protection for many years but little is known about their actual performance. With the more recent availability and validation of alternative instrumental methodologies for PSP and DSP detection, full method performance characteristics have now been determined for a wide range of toxins in a variety of shellfish species. This has enabled a thorough assessment of measurement uncertainty (MU).

Protocols followed for the assessment of MU will be described for each of the three toxin classes. These follow as closely as possible the guidance described by the Eurachem/CITAC guide for quantifying uncertainty in analytical measurement. However, the degree of complexity associated with these calculations varies depending on the number of individual analytes, the use of toxicity equivalence factors (TEFs) and the availability of data on the effects of inter and intra-species matrix variability. Similarly, methods for assessing the total values of MU to be applied to the final toxicity results vary depending on the nature of the regulatory limits and the format in which the toxin results are reported.

A final complication is the consideration on how MU should be used in the context of public health and enforcement; the toxicity results generated by Cefas being used by the competent authority to determine whether shellfish are safe to harvest or whether shellfish already placed on the market should be recalled. The current approach taken by Cefas and the UK Food Standards Agency for each of the major toxin classes will be discussed.
Estimation of between-bottle homogeneity from complete composition data

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In the preparation of synthetic mixtures as proficiency testing material, often the between-bottle homogeneity needs be assessed as part of the assignment of reference values to the batch. The composition of synthetic mixtures is often expressed in terms of mass or amount–of–substance fractions of all components present. The existing modelling of between-bottle homogeneity studies is augmented in order to deal with the mathematical particularities of total composition measurements. The augmented model allows reducing the scatter in the measurement results. The estimates obtained for the between-bottle homogeneity and repeatability standard deviation are freed from scatter common to all components, and not caused by effects in the preparation process. In particular for the bulk component, the estimates give a much better impression of the between-bottle homogeneity of the batch.
Uncertainty estimation to evaluate the performance of a combustion system

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In the last decade, the development of practical approaches to estimate the uncertainty of measurements in chemical analysis, enforced by the increased number of publications and other scientific papers in this area currently allow laboratories to more reliably uncertainties without spending too much time and human or economic resources. However, the estimation of uncertainty of any measurement is still greatly correlated with the requirements of ISO17025, which obliges the accredited laboratories to adequately estimate the uncertainty. It is very common that scientific publications, in the areas as energy or environment, present results which can define the way of an investigation without estimate the uncertainty of a measurement.

In currently investigation the estimation of uncertainties was applied to evaluate the performance of a mass balance of ashes and elements in a combustion system. In the combustion system at LNEG, the fuel used as input gives rise to four output streams: bottom ashes, ashes from both 1\textsuperscript{st} cyclone and 2\textsuperscript{nd} cyclone and fly ash. If operating conditions are well controlled, including gaseous emissions, the mass output (ash or element) collected, i.e., the sum of four ash streams must be equal to the fuel input (ash or element) in the system. Experimentally this is often achieved if uncertainties associated with the evaluation of mass of fuel input, fuel heterogeneity, mass of ash (bottom ash, cyclones and fly ash), fuel ash content and uncounted unburned matter were correctly estimated. For elemental recovery ratio the uncertainty of analytical concentration determinations should also be included.

In this work, the evaluation of uncertainties was under taken using data of internal quality control and proficiency testing. The internal quality control allows the evaluation of the precision of analytical method and the use of duplicates of sample permits the inclusion of its heterogeneity. The streams of ashes were treated in independent control charts because ashes from different streams had varying heterogeneity and consequently different precision. The trueness was evaluated using data from several proficiency tests; the interlaboratorial samples were used as reference materials. Bias with statistical meaning was included.

Only with the uncertainty estimation it is possible to make a reliable evaluation of the mass balance and in most of the cases, mass balance closures different from 100\% can be justified by uncertainties. The differences between fuel matrix, coal and biomass, were evidenced by the dimension of the uncertainty associated with the ash recovery ratio.
Measurement uncertainty in tracing the value of absorbance in calibration of biochemical analyzers

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Biochemical analyzers, which work on principles of absorption spectrophotometry, became most widely present in medical biochemical laboratories. Construction of these devices in most cases doesn't allow calibration by usual methods, using ND filters as standards. From this reason, it was necessary to develop suitable method, i.e. to create a solution which could be, regarding its characteristics, used as a mean of comparison, for methods of calibration of biochemical analyzers. In this paper, the metrological characterization of solutions is presented, and the measuring uncertainty of methods used for calibration is estimated. The method that is developed provides metrological traceability to primary spectrophotometric standard.

The spectral characteristic (an influence of radiation wavelength and spectral bandwidth) of colored solutions, time stability of transmittance/absorbance value which they reproduce and temperature influence were identified as basic metrological characteristics that are important for their use and classification. All the measurements, including those for metrological characterization of the solutions, and calibration measurements of the solutions in comparison methods, are performed at primary spectrophotometric system.

Overall measurement uncertainty of the calibration of biochemical analyzers by method of comparison using colored solutions as means of comparison, is evaluated from measurement uncertainty of primary spectrophotometric system, reproducibility of measurements (which is expressed as stability of the spectral transmission value of the reference solutions), and uncertainty components due to influential parameters (bandwidth, temperature). Careful interpretation of spectrophotometric data, evaluation of influential parameters and correction of systematic errors wherever possible was the tool for proving that the results are at the level of uncertainty that can meet requirements in calibration of biochemical analyzers.
Uncertainties from linear least squares calibration

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With the recent publication of the ISO/TS 28037 Technical Specification\(^1\), “Determination and use of straight-line calibration functions”, it seems to be the time to update the corresponding part of the EURACHEM/CITAC Guide ”Quantifying Uncertainty in Analytical Measurement” Second Edition\(^2\). Indeed, in the E.3 part of the Guide, “Uncertainties from linear least squares calibration”, it may be more pedagogical to introduce the uncertainty estimation of the predicted quantity from the measured response by means of the calibration function instead of only using the variability in the observed quantity. More precisely, the uncertainty measurement consists of components that are not only evaluated by type A evaluation, as displayed in the EURACHEM/CITAC Guide Second Edition E.3.1 to E.3.5 parts, but also by type B evaluation. That is to say, the uncertainty measurement is based on means other that statistical distributions of the quantity values. Therefore, this approach would enable to avoid misinterpretation of the Guide or mistakes like those found in some ISO Standards\(^3\) dealing with evaluating uncertainties when using linear least square calibration.

Once the expression of uncertainty from linear squares calibration was exhibited evidencing the type A and type B evaluations, this work displays examples from the refractometry of the glucose aqueous solutions. Indeed, from the refractive index measurement of these solutions, international tables\(^4\) of correspondence between refractive index and volume or mass fractions may be used to deduce the values of the latter quantities of the solutions. In this way, glucose mass fractions and ethanol potential volume fractions are estimated with associated uncertainties from the linear least square calibration function deduced by the international tables. In a first step, due to the small magnitude of the uncertainty values found in the tables, their data can be considered as un-weighted, giving a simple uncertainty expression. By the same token, the result obtained from the un-weighted approximation can be regarded also as a particular case of the weighted data approach that this work displays, in agreement with the ISO/TS 28037 Technical Specification. Anyway, it is the most realistic model that is preferentially used for the refractometers calibration procedure.

4. OIML R 124 Refractometers for the measurement of the sugar content of grape must (1997).
A new primary cell for electrolytic conductivity measurements of ultrapure water

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The measurement of electrolytic conductivity of aqueous solutions is of great importance in many fields of science and technology (pharmaceutical, biotechnology, food, health care, environment, semiconductor, and power generation industries). It is typically employed for monitoring water quality. As a sum parameter, it allows to obtain information about ionic contaminants in liquid samples: by definition, in ultrapure water only hydronium ($\text{H}_3\text{O}^+$) and hydroxide ($\text{OH}^-$) ions are in solution, in concentration given by the water dissociation constant. The characterization of ultrapure water through reliable and accurate electrolytic conductivity measurements allows its use as a reference for the analysis of physical and chemical properties of solutions.

A new primary cell for ultrapure water measurements has been developed at I.N.Ri.M.: it is composed of two half-cells with Pt round and planar electrodes connected to current and potential terminals (used for resistance measurements). The two half-cells can be linked with or without a central section, allowing a differential measurement of resistance and minimizing the effects due to the electrode manufacturing faults. The traceability to the International System of Units of the electrolytic conductivity values is achieved by measurements of resistance and length. Moreover, a valve pipeline placed on each half-cell permits measurements with the sample flowing. The main advantage of this cell regards the ability to carry out measurements of solutions with very low electrolytic conductivity values due to the removable section size, and the possibility to use the flow system which prevents the solution contamination.

A set of conductivity measurements on a solution of 500 $\mu$S/cm have been carried out in order to compare the measurement capability of this cell with respect to the previous reference standard one and a relative uncertainty of about 0.2% has been calculated. Moreover, preliminary measurements with the flow circuit on a 10 $\mu$S/cm solution are in progress also to test the material contamination.
Development of metrological models for the quantitative or semi-quantitative GC-MS assessment of the compliance of tear gas weapons with legislation

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The tear gases are the most widely used non-lethal weapons, both by security forces and by the general public. One type of these weapons is the pepper spray, whose active principle is capsaicin (from \textit{oleoresin capsicum}). This is the only self-defense aerosol allowed in Portugal, where capsaicin concentration must be below 5% (Decreto-Lei 17/2009, 6\textsuperscript{th} of May). Due this legal requirement it is necessary to assure result quality by using a valid measurement procedure.

The cost effective evaluation of the compliance of self defence weapons with legislation involves the use of two measurement procedures with increasing quantitative capability. Samples are first assessed by a semi-quantitative measurement procedure based on single-point GC-MS calibration. Whenever the semi-quantitative measurement uncertainty makes evaluation inconclusive, the quantitative evaluation of sample compliance using multi-point GC-MS calibration is performed.

This work aims at developing performance metrological models of both measurement procedures and defining metrologically sound criteria for samples compliance evaluations. The developed models include the evaluation of the impact of instrumental performance, sample dilution and standards preparation on measurement uncertainty. A strategy for the estimation of the reference substances purity is also presented.
Uncertainty calculation in Dynamic Generation of primary gas mixtures

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Dynamic Generation processes follow the international standard ISO 6145 and include techniques to produce toxic gases in air at concentrations equivalent to those found currently in ambient air and workplace environments. The production of these gases is normally designated by Standard atmospheres. Preparation of gas mixtures at the low-concentration (ppb) can be achieved through the application of permeation techniques (ISO 6145-10). This technique is used for reactive unstable mixtures in low concentrations. The composition of gas mixtures is certified by analytical methods such as Chemiluminescence and Fluorescence. The choice of these systems presents some advantages comparing to the static system. Being dynamic, the system allows the composition to be balanced with the carrier system, preventing adsorption losses in the walls of the apparatus. Another advantage is the possibility to modify the ratio of compound/carrier gas during the preparation process.

The production of reference gas mixtures of environmental pollutants is an area that has been widely developed in recent years at the Instituto Português da Qualidade (IPQ) to ensure traceability at national level of the amount of pollutants present in the air.

In this work, emphasis is given to the technique of dynamic generation of gas mixtures of nitrogen dioxide (NO₂) and sulfur dioxide (SO₂), in 10⁻⁹ mol/mol range. These gases are indicators of air quality and are found in atmosphere in molar fraction close to nmol/mol order of magnitude.

This communication describes the uncertainty calculation in dynamic generation process. The uncertainties have been calculated in accordance with GUM - Guide to the expression of uncertainty in measurement. The uncertainty sources have been estimated and the combined uncertainty of the measurements was calculated. The expanded uncertainty is expressed by the combined uncertainty of measuring multiplied by the expansion factor (k) in order to correspond to a confidence interval of approximately 95%.

Development of a detailed measurement model for the assessment of atmospheric aerosols water soluble fraction by Ion Chromatography

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Air composition is known to have a relevant impact on public health, on the environment and on meteorology and climate. The chemical characterization of air gaseous and aerosol fraction is used to monitor risks from exposition to polluted air and to develop air transport and climate models. Air is appropriately sampled, and aerosols are collected in conveniently chosen filters, kept and treated according to the planned strategy. The ionic composition of the water soluble fraction of aerosols, assessed by Ion Chromatography, IC, is particularly useful to estimate the mineral composition of aerosols of both natural and anthropogenic origins.

The reliability of conclusions about the systems under study depends on the quality of the measurement results.

The assessment of trends in air composition must be supported on measurement results traced to a common reference and reported with measurement uncertainty. In this work, a metrological model has been developed for the determination of ion composition of the atmospheric aerosols water soluble fraction according to an operationally defined measurement procedure. The uncertainty associated with the results is evaluated by the Differential Approach1. The metrological relevance of individual analytical steps and effects has been identified. The uncertainty budget is divided in the extraction, extract dilution and ionic chromatography quantification components.

1) Since no reference materials of urban aerosols were used, a strategy for assessing the performance of the extraction step was developed based on the following definitions and assumptions: The bias associated with the measurement procedure is, by definition, zero;

2) IC determinations can be affected by a relevant bias;

3) The impact of controlled and uncontrolled experimental parameters on water extraction variability can be estimated in intralaboratory environment.

The evaluation of the extraction step involved the estimation of the intermediate precision from duplicate analysis of pooled urban aerosol samples prepared from real samples to ensure homogeneity. The uncertainty associated with the preparation of duplicate filters was considered.

Analytical measurement uncertainty of food carotenoid determination

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INTRODUCTION. Carotenoid determination in food is a complex analytical process involving several mass transfer steps (extraction, evaporation, saponification, etc.). For consistent interpretation of an analytical method result it is necessary to evaluate the confidence that can be placed in it; this can be provided by the quantification of its accuracy (trueness and precision) in the form of a measurement uncertainty estimate. The Guide to the expression of Uncertainty in Measurement issued by the International Organization for Standardization1 establishes rules for evaluating and expressing uncertainty. Although it is a very powerful tool2, it is even more complex when analytical methods include mass transfer steps that lack descriptive models for the behaviour of the analyte in the analytical system. The guide was interpreted for analytical chemistry by EURACHEM, whose second edition3 already includes the possibility of using interlaboratory information and also the use of information obtained from analytical methods in-house validation. MATERIAL AND METHODS. Analytical measurement uncertainty was estimated based on intralaboratory data, studies of precision and analytical process performance, and on contribution of standard stock solution concentration not covered by precision data (bottom-up approach). After estimation of all sources of uncertainty the combined standard uncertainty (u c) was calculated according to their laws of combination3. The expanded uncertainty (U c) was calculated as U c = k u c, where k is the coverage factor3. This methodology was applied to different food matrices of fruits and vegetables. RESULTS. Relative measurement expanded uncertainty was mainly between 0.10-0.31, higher values were found for measurements near instrumental quantification limits (ex. 0.75 for β-cryptoxanthin, and 0.99 for lutein, in pear) or when sample chromatograms presented interferences with the analyte peak (ex. 0.44 for α-carotene in orange). Lower relative measurement expanded uncertainty values (0.028-0.13) were obtained for food matrices not requiring the saponification step. Trueness studies showed good laboratory performance. CONCLUSIONS. Analytical measurement uncertainty of food carotenoid determination was 10-30% of the final result in the great majority of cases. The saponification step should be avoided if food carotenoids are not present in the ester form. Carotenoid values included in Food Composition Data Bases should be expressed taking into account the measurement uncertainty, to give correct information on data accuracy.

Quantifying Uncertainty in Determination of Polysaccharides in Glicoconjugate Vaccines

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As Italian OMCL (Official Medicines Control Laboratories), Istituto Superiore di Sanità provides analytical capability for the AIFA (Agenzia Italiana del Farmaco) not only in the area of Official Control Authority of Batch Release but also in a number of activities including testing of chemicals and biologicals drugs sampled for defects, recalls, complaints, etc. In this context, Bacterial Vaccines Unit, in accordance to UNI CEI EN ISO/IEC 17025 has quantified uncertainty in determination of polysaccharides in glicoconjugate vaccines. For an anti meningococcal type c Vaccine, quantification uncertainty in determination of sialic acid concentration by a chromatographic method (HPAEC - PAD) was calculated from validation data of two different substances: a pure Men C polysaccharide and a glicoconjugate vaccine as Men C-CRM detectable at levels between 0.1 µg/mL and 2 µg/mL. Uncertainty sources were identified, analysed and grouped in three main components: precision, bias and other components not included in the previous two. Precision component was investigated performing, for each substance, 2 determinations per analytical session in 6 different days. Bias component was investigated using 6 spiked samples during the in house validation study because no Certified Reference Material was available; other components were considered negligible.

The final results were expressed as expanded relative uncertainty.
Measurement Uncertainty of Assigned Reference Values for UV/VIS Absorption Spectrophotometer Measurement Standards

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Performance evaluation and qualification of ultraviolet and visible molecular absorption spectrophotometers is a critical task for regulatory compliance in the life science industry because it is a necessary requirement preceding method validation. The various performance parameters of a spectrophotometer are usually tested using dedicated reference material standards that are certified for a specific parameter such as resolution, stray radiant energy (stray light), wavelength accuracy, and photometric accuracy and linearity. The certification of reference material standards for evaluating the accuracy of the photometric scale in a meaningful way is challenging because of the non-SI nature of the metrological traceability pathways. This applies equally with respect to the certification of new photometric reference material standards and to the recertification of the measurement standards after field use of typically one to two years.

A modern approach, with increased scientific rigor, to the estimation of measurement uncertainty of the assigned photometric reference values using the modified GUM is discussed. The various budget components that are relevant to the characterization of photometric reference materials are described, and the experimental results for representative certification and recertification analyses are presented. Many of the different budget components are estimated by Type B evaluation which generally requires sufficient expertise and insightful experience to avoid under-estimation of the measurement uncertainties.
Detailed Evaluation of the Uncertainty for the Determination of Chemical Oxygen Demand in wastewater

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Chemical oxygen demand (COD) is one of the most relevant chemical parameters for the characterisation of wastewaters before (influent) and after (effluent) treatment in order to monitor its quality and compliance with the law¹.

Reliable COD values are important for protecting the environment and to guarantee the economical sustainability of the treatment facility.

In this work the potassium dichromate open reflux method² was validated by studying the parameters of its quantitative performance. Models for the metrological performance of the determination of COD in wastewater were developed aiming at producing detailed estimates of the uncertainty associated with results obtained in a Portuguese Wastewater Treatment Plant.

A detailed assessment of the measurement uncertainty, using the differential approach³, allowed the quantification of individual uncertainty components, aiming at introducing strategies for reducing both measurement uncertainty and cost of analysis. The developed metrological model was validated through the analysis of samples from proficiency tests.

Results show the variation of percentage contributions of uncertainty components with the COD value and proved that the measurement procedure is fit for the assessment of compliance of wastewaters with Directive 91/271/EEC¹.

Chemical Oxygen Demand -
evaluation of interferences and measurement uncertainty

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The determination of the Chemical Oxygen Demand (COD) in industrial wastewaters requires a detailed study of the presence of interfering compounds that can significantly affect the estimation of the target oxidability of the sample. Whenever, the oxidability of the organic matter of the wastewater is the goal of the analysis, the elimination of oxidants from the matrix is determinant. The elimination of interferences is performed during method development and subsequently validated through a detailed study of the measurement performance.

The reliability of results depends on an adequate definition of the measurements traceability and on a proper validation of the measurement procedure that includes the evaluation of the measurement uncertainty. In this work, the uncertainty was estimated using the top-down approach based on intralaboratory validation data, namely the measurement trueness and precision\(^1\).

Results show that the measurement, including the evaluated uncertainty, is fit for the assessment of the compliance of industrial wastewaters with the legislation\(^2\).

This work highlights the need for a detailed understanding of the sample matrix and a careful measurement procedure development before measurement validation and uncertainty evaluation.

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