Eurachem Workshop - Uncertainty from sampling and analysis for accredited laboratories

Eurachem

A Eurachem International Workshop
in conjunction with
Eurolab Germany and CITAC.

Date: 19-20 November 2019

Venue: BAM headquarters, Unter den Eichen, Berlin, Germany

ABSTRACTS

BAM

eurolab-Deutschland
Chemische Analytik; Mess- und Prüftechnik e.V.

Uncertainty from sampling and analysis for accredited laboratories

SCIENTIFIC PROGRAMME

Scientific Programme

Day 1: Tuesday 19th November 2019
Introducing uncertainty, and uncertainty from sampling

08:30 – 09:00	*Registration*
09:00 – 09:30	***Welcome and Opening Remarks***
	Welcoming remarks *from Director BAM, and Chairman EUROLAB Germany,*
	Introduction to EURACHEM and its activities *Marina Patriarca (ISS, Italy; Chair of EURACHEM)*
	Introduction to the measurement uncertainty workshop *Steve Ellison (LGC, UK)*
09:30 – 10:30	***Introducing measurement uncertainty***
	Introduction to measurement uncertainty *Wolfhard Wegscheider (Montanuniversitaet Leoben, Austria)*
	Overview of Uncertainty from Sampling (UfS) and the Eurachem Guide (2019). *Mike Ramsey (University of Sussex, UK)*
10:30 – 11:00	*Coffee and Posters*
11:00 – 12:00	***New features in the Eurachem UfS Guide 2nd Edition***
	Expressing uncertainty as an uncertainty factor, and Combining sampling and analytical uncertainty *Mike Ramsey (University of Sussex, UK)*
	Using unbalanced designs to reduce cost of sampling uncertainty estimation *Peter Rostron (UK)*
12:00 – 13:15	*Lunch and Poster time*
13:15 – 13:45	**Applications of UfS estimation across a range of sectors.** *Ariadne Argyraki (University of Athens, Greece)*
13:45 – 15:00	***Parallel discussion sessions***
	Session 1: Applications of Uncertainty from Sampling **Session 2: Methods for evaluating Uncertainty from Sampling**
15:00 – 15:30	*Coffee and Posters*
15:30 – 15:50	***Parallel session summaries***
15:50 – 16:30	***Accreditation perspectives***
	ILAC Guidance on contribution to measurement uncertainty arising from sampling and testing *Erik Oehlenschlaeger (ILAC)*
	The role of accreditation in assuring the quality of sampling *Lawrence Bilham (UKAS)*
16:30 – 16:50	**The way forward for Uncertainty from Sampling.** *Mike Ramsey*
16:50 – 17:00	***Discussion and Close***

Scientific Programme

Day 2: Wednesday 20th November 2019
Evaluation and use of measurement uncertainty

09:00 – 09:45	***Approaches to measurement uncertainty evaluation***
	Eurachem guidance on Measurement Uncertainty - Guides, leaflets and current work *Steve Ellison (LGC, UK)*
	Current approaches to the evaluation of measurement uncertainty in analysis *Vicki Barwick (LGC, UK)*
09:45 – 10:45	***Evaluating uncertainty from validation and QC data***
	MUkit – software for uncertainty from validation and QC according to Nordtest 537 - handling both absolute and relative uncertainty *Teemu Näykki*
	Uncertainty from validation and QC data *Ricardo Bettencourt da Silva (Univ. Lisbon)*
10:45 – 11:15	*Coffee and Posters*
11:15 – 11:45	***Focussing on large uncertainties***
	Uncertainty estimation when the uncertainty is high *Alex Williams*
	Reporting high uncertainty - Asymmetry, Uncertainty Factors and log units *Bertil Magnusson*
11:45 – 12:30	***Conformity assessment***
	Conformity and measurement uncertainty – an introduction *Steve Ellison*
12:00 – 13:45	*Lunch and Poster time*
13:45 – 15:00	***Parallel discussion sessions***
	Session 1: Conformity assessment **Session 2: Handling high uncertainty, asymmetry and bias** **Session 3: Software for MU evaluation**
15:00 – 15:30	*Coffee and Posters*
15:30 – 16:00	***Parallel session summaries***
16:00 – 16:30	**Joint Committee for Guides in Metrology (JCGM) – Current work and future guidance** *Adriaan van der Veen (VSL, NL)*
16:30 – 16:45	***Workshop summary and closing discussion*** *Mike Ramsey and Steve Ellison*
16:45	***CLOSE***

Parallel Sessions

Day 1: 19th November 2019 Introducing uncertainty, and uncertainty from sampling

13:45-15:00

Session 1: Applications **Chair: Ariadne Argyraki**	**Session 2: Methods** **Chair: S. Ellison**
K. Tsimillis, S. Michael. Uncertainty from Sampling: Could the requirements of ISO/IEC 17025:2017 be adopted in medical laboratories? **N. Guigues, B. Lepot, J. Durocher.** Estimation of the measurement uncertainty, including the contribution arising from sampling, of water quality parameters in surface water of the Loire River Basin, France **Dr C. Tiebe, M. E. Bayat, M. Bartholmai.** Uncertainty from sampling of trace explosives amounts and detection by ion mobility spectrometry	**P. Rostron.** Comparing Uncertainty Values – are they really different? **C. Borges, C. Palma, T. Dadamos, R. Bettencourt da Silva.** Evaluation of the sampling uncertainty from the Monte Carlo Simulation of georeferenced information **F. Coimbra.** Uncertainty from sampling in microbiological water analysis
Discussion	**Discussion**

Day 2: Wednesday 20th November 2019. Evaluation and use of measurement uncertainty

13:45-15:00

Session 1: Conformity assessment **Chair: A. Williams**	**Session 2: Handling high uncertainty, asymmetry and bias** **Chair: W. Wegscheider**	**Session 3: Software for MU evaluation** **Chair: B. Magnusson**
I. Kuselman, F. Pennecchi, R. Bettencourt da Silva, D. Brynn Hibbert. Shades of grey in conformity assessment due to measurement uncertainty **R. Bettencourt da Silva, F. Lourenço, D. Brynn Hibbert.** Multivariate and correlated acceptance limits for conformity assessment **R. Bettencourt da Silva.** An introduction to ILAC G8	**S. Uhlig, K. Simon, B. Colson, K Hettwer, K Frost.** Measurement uncertainty in the case of large and heterogeneous variances: A new method for the calculation of asymmetric uncertainty intervals **S. Uhlig, K. Simon, B. Colson, K Hettwer, K Frost** . How to address matrix mismatch bias in the uncertainty budget	**K. Hettwer.** Webtool for taking measurement uncertainty into account in the implementation of the Federal Soil Protection and Contaminated Sites Ordinance **M Koch**. Excel tool for estimation of measurement uncertainty from validation and quality control data according to ISO 11352 **S Ellison.** Measurement uncertainty in R: The metRology package
Discussion	**Discussion**	**Discussion**

Posters

Uncertainty from sampling and analysis for accredited laboratories

PLENARY PRESENTATIONS

Abstracts for oral presentations appear in programme order

Introduction to Measurement Uncertainty

Wolfhard Wegscheider

Montanuniversitaet. General and Analytical Chemistry, Franz-Josef-Strasse 18, Leoben, Leoben 8700, Austria

Abstract

Over the years it was recognized that the expression of quality of analytical results is not a merely statistical exercises, but has to encompass the entire body of knowledge regarding a particular measurement procedure. The underlying idea is that any result of a measurement is underpinned by an interval that describes the credibility and expresses the limits of interpretation of this particular result.

For the effective penetration of this idea into everyday analytical chemistry the Eurachem/CITAC Guide Quantifying Uncertainty in Analytical Measurement conceptually derived from the Guide to the Expression of Uncertainty in Measurement served as a pivotal document since 1995 and is currently available in its 3rd edition. The hands-on approach on seemingly simple laboratory operations to complex measurement issues still guides the laboratories to the essential understanding of a measurement procedure.

It will be shown how this concept is rationalizing any conformity assessement.

In this talk there will be also reference to large components contributing to the combined uncertainty and how this situation is mastered with asymmetric relative uncertainties, a topic central to the 2nd day of the Workshop.

Much emphasis is laid on the Monte Carlo approach as this substitutes easily in complex cases where an analytical solution might not be feasible. The advantages of Monte Carlo will be shown both for results from standard additions and for multivariate calibration where current guidelines and standards lead to inadequate results.

Overview of Uncertainty from Sampling and the Eurachem UfS Guide (2019).

Michael H. Ramsey

School of Life Sciences, University of Sussex, Falmer, Brighton, BN1 9QG, UK

Abstract

The second edition of the Eurachem/CITAC Guide on Measurement Uncertainty arising from Sampling (UfS) [1] was initiated to explain and integrate several recent research developments. The new edition retains the same basic approach and structure as the first edition of 2007, being based on the general concept that primary sampling as the first part of the measurement process, and thus an important contributor to the uncertainty of any measurement value. The two main approaches to estimating UfS, are still based upon either empirical methods or numerical modelling. Six worked examples of both approaches are given across a range of application sectors, including food, animal feed, soil and water. Two of these examples been partially updated to illustrate some of the research developments.

Four main research developments in this area have been included in the second edition. One significant new development is the option of using the Uncertainty Factor as an alternative way to express measurement uncertainty. The upper and lower confidence limits of a measurement value are expressed by multiplying and dividing the measurement value by the uncertainty factor, rather than by the traditional approach of adding and subtracting the uncertainty. This approach is more accurate when the relative expanded uncertainty value is large, typically over 20%, and also where the frequency distribution of the uncertainty is approximately log-normal rather than normal. These two conditions often apply to measurement uncertainty that arises from the sampling process, particularly when the spatial distribution of the analyte in the test material is substantially heterogeneous. The Guide also explains two options for how measurement uncertainty can be calculated by adding the component arising from sampling, expressed as an uncertainty factor, with that arising from chemical analysis, expressed in the traditional way as a relative uncertainty.

A second new development in the methods described in the Guide is the use of an unbalanced experimental design to reduce the cost of estimating UfS by the duplicate method. The first edition of the Guide described the use of a balanced design for the empirical estimation of the measurement uncertainty as a whole, and its two components in the sampling and analytical steps. This balanced design has analytical duplicates on both of the two sample duplicates. The new edition of the Guide stresses the advantage of using an unbalanced design, with an analytical duplicate on only one of the two sample duplicates. This design reduces the extra cost of estimating the uncertainty by 33%.

The third development is a more comprehensive method for the estimation of UfS that uses measurements made in Sampling Proficiency Testing (SPT). In the first edition of the UfS Guide this approach was discussed in theory, but the new edition now refers to the first practical example of the use of SPT data for UfS estimation [2]. In this approach multiple samplers each apply whatever sampling protocol they consider appropriate to achieve the same stated objective for the same sampling target. Using a balanced design across all of the different samplers, it is then possible to include the 'between-sampler' bias in the estimate of UfS, in addition to the components that were previously included. The first practical SPT (concerned the measurement of the moisture content of a 20 ton batch of fresh butter) gave an uncertainty estimate that was factor of 2.2 larger than that from the duplicate method applied to just a single sampler.

The forth development has been the application of UfS estimation to a wider range of measurement types. These include measurements made: (a) *in situ* (e.g. by field sensors without removing a sample) (b) on site (e.g. in a field laboratory on a removed sample) (c) passive measurements of radioactive decay, and (d) at the microscopic scale (e.g. PXRF in mm scale and SIMS at micron scale).

References

1 M H Ramsey, S L R Ellison and P Rostron (eds.) Eurachem/EUROLAB/ CITAC/Nordtest/AMC Guide: *Measurement uncertainty arising from sampling: a guide to methods and approaches.* Second Edition, Eurachem (2019). ISBN (978-0-948926-35-8). Available from http://www.eurachem.org

2 M H Ramsey. B Geelhoed, A P Damant, R Wood (2011) Improved evaluation of measurement uncertainty from sampling by inclusion of between-sampler bias using sampling proficiency testing. Analyst, **136 (7), 1313 – 1321.** DOI:10.1039/C0AN00705F

Expressing uncertainty as an uncertainty factor, and combining sampling and analytical uncertainty

Michael H. Ramsey

School of Life Sciences, University of Sussex, Falmer, Brighton, BN1 9QG, UK

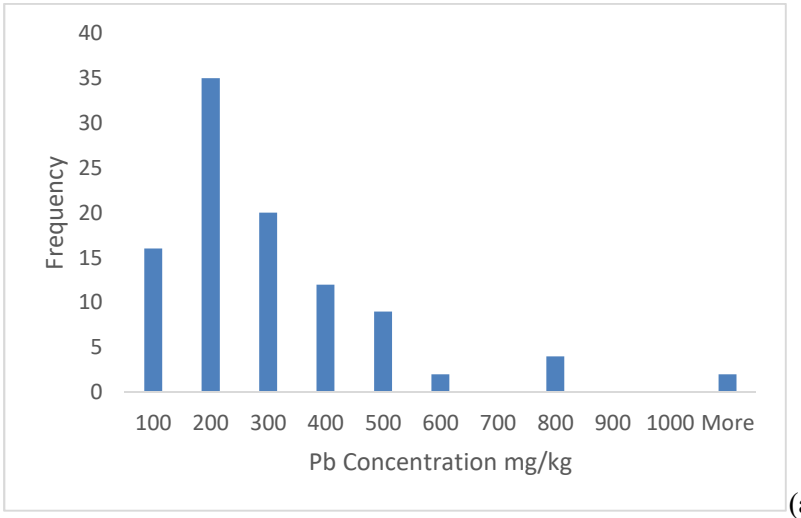
Abstract

The Uncertainty Factor is an alternative way to express measurement uncertainty that is more accurate when the relative expanded uncertainty value is large, typically over 20%, and also where the frequency distribution of the uncertainty is approximately log-normal rather than normal. These two conditions often apply to measurement uncertainty that arises from the sampling process, particularly when the spatial distribution of the analyte in the test material is substantially heterogeneous. The upper and lower confidence limits of a measurement value are expressed by multiplying and dividing the measurement value by the uncertainty factor, rather than by the traditional approach of adding and subtracting the uncertainty.

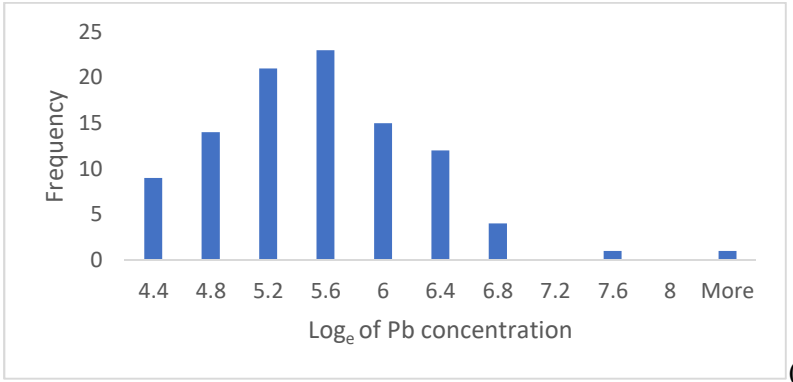
The UfS Guide [1] explains how the expanded uncertainty factor (^{F}U) can be calculated as $^{F}U = \exp(2s_G)$, where s_G is the standard deviation of the log-transformed measurement values. An updated worked example, for Pb-contaminated soil, is provided to show how ^{F}U can be evaluated in practice using the 'duplicate' method. Duplicated Pb analyses are made on duplicated samples taken at 10 of the 100 sampling targets placed in a grid across a contaminated land site in the usual way. However, the natural logarithms of the Pb measurement values are taken before the analysis of variance (ANOVA) is made. This log-transformation is necessary because the frequency distribution of the Pb measurements on the 100 sampling targets is approximately log-normal (Fig 1a), but much closer to normal after the transformation (Fig 1b). The frequency distribution of the measurement uncertainty, as judged by the duplicated samples, is also made closer to normal by this transformation [2].

The results of the ANOVA then give not only the expanded uncertainty factor of the measurement ($^{F}U_{meas}$ = 2.62), but also that arising from the sampling ($^{F}U_{sampling}$ = 2.60) and from the chemical analysis ($^{F}U_{analysis}$ = 1.12). The upper confidence limit of a typical Pb measurement value of 300 mg kg^{-1}, can then be calculated as 784 mg kg^{-1} (300 x 2.62), and the lower confidence limit as 115 mg kg^{-1} (300/2.62). The obvious asymmetry of these confidence limits around the measured value (-185 and +484 mg kg^{-1}) more accurately reflects the skew in the frequency distribution of the uncertainty, than the symmetrical confidence limits (+/- 251 mg kg^{-1}) that can be calculated ignoring this observed asymmetry using ANOVA without log-transformation.

The Guide also explains two options for how measurement uncertainty can be calculated by adding the component arising from sampling, expressed as an uncertainty factor (UF_{samp}), with that arising from chemical analysis, expressed in the traditional way as a relative uncertainty ($U'_{analysis}$). One option is to have both the sampling and analytical uncertainty components calculated and expressed in the log-domain. This happens automatically when ANOVA is performed on log-transformed measurement values. A second option is to assume, for the analytical component, that the relative standard uncertainty ($s'_{analytical}$) is approximately equal to the standard deviation of the natural logarithms ($s_{G,analytical}$). This is an acceptable approximation when the $s'_{analytical} < 0.2$, which is usually the case. The two components can then be added as variances in log-space, as in the first option.



(a)



(b)

Fig 1. Histograms of the Pb measurement values for 100 soil targets shown on (a) the original linear scale, showing positive skew (b) after natural logarithms were taken, showing an approximately normal distribution.

References

1 Ramsey M.H., Ellison S. L. R., and Rostron P.(eds.) (2019) Eurachem/EUROLAB/ CITAC/Nordtest/ AMC Guide: *Measurement uncertainty arising from sampling: a guide to methods and approach,* Second Edition, Eurachem, ISBN 978-0-948926-35-8 http://www.eurachem.org/index.php/publications/guides/musamp

2 Analytical Methods Committee (2019). Why do we need the uncertainty factor? Technical Brief 88, 27. DOI: http://dx.doi.org/10.1039/c9ay90050k Anal. Methods, 2019, 11, 2105–2107 https://pubs.rsc.org/en/content/articlelanding/2019/ay/c9ay90050k#!divAbstract

Using unbalanced designs to reduce cost of sampling uncertainty estimation

Peter Rostron

Formerly of University of Sussex

Abstract

The empirical (top-down) approach to uncertainty estimation depends on acquiring multiple measurements of the sampling targets. The 'Duplicate Method', described in Section 9.4 of the UfS Guide (Ramsey & Ellison, 2007) enables the estimation of the repeatability precision of both the sampling and analytical processes. In its most commonly used 'Balanced Design', two samples are extracted from each sampling target, using the same nominal sampling protocol with permitted variations. Permitted variations reflect a known ambiguity in the sampling protocol and/or the sampling target. Examples might be the spatial precision in defining the sampling point, or heterogeneity of the target analyte in the bulk material (Figure 1).

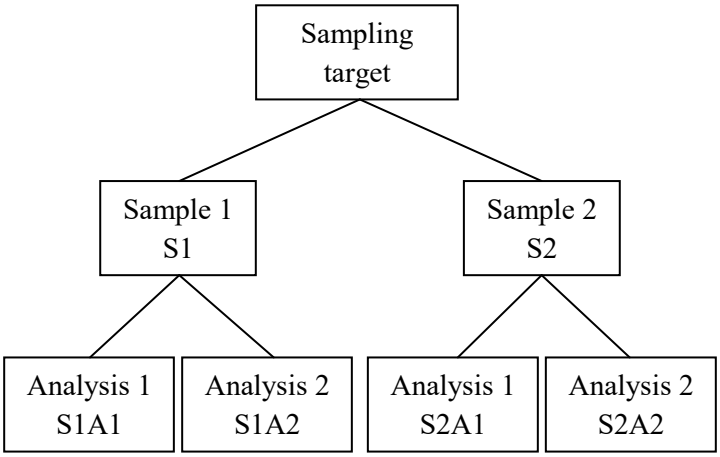


Figure 1 The balanced design method of estimating the repeatability precision of both the sampling and analytical processes using the 'Duplicate Method'(refer to UfS Guide Section 9.4)

Estimates of the different components of repeatability precision (sampling and analytical) can be calculated using ANOVA. An assumption of classical ANOVA is that the distribution of errors within each level of variance approximates to a Gaussian distribution. In practice, it is often the case that a set of otherwise normally distributed measurement values is contaminated by a small number of outlying values. These have a disproportionate effect on the variances calculated using the 'classical' form of ANOVA. In this situation robust methods are able to provide variance estimates that are much closer to the parameters of the assumed underlying normal distributions, and therefore uncertainty estimates that are more representative of the bulk of the data (AMC, 1989a; AMC, 1989b). One practical benefit is that a difference between classical and robust estimates of either the sampling or analytical standard deviations is a clear indication that the data is not normally distributed.

A potential disadvantage of using the empirical approach to uncertainty estimation is the cost of obtaining the additional measurements. It is recommended that 10% of the total number of the sampling targets are subjected to the duplication procedure shown in Figure 1, with a minimum of 8 targets (Lyn *et al*, 2007; Ramsey & Ellison, 2007). This therefore adds (at a minimum) the costs of

acquiring and processing 8 additional samples and performing 24 additional analyses to the overall cost of the investigation.

A cost-saving alternative to the full balanced design shown in Figure 1 is to use an 'unbalanced' design. This method still requires taking a minimum of 8 duplicate samples, but reduces the cost of analysis by only performing duplicated analyses on one of the primary duplicate samples. This is illustrated in Figure 2.

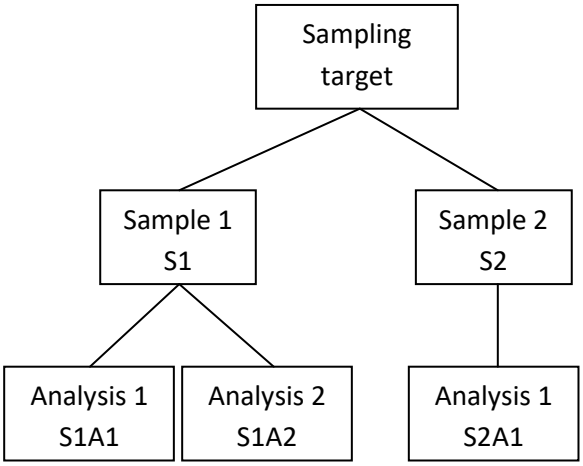


Figure 2 The unbalanced experimental design, where duplicate analyses are performed on the primary sample only (refer to UfS Guide Annex D)

Computer simulation methods have been used to validate the results of the robust ANOVA on the unbalanced design. This was achieved by generating large numbers of simulations of normally distributed data and deliberately introducing 'contamination' by applying differing magnitudes of outlying values. The results produced by the established balanced design were compared with those produced using one simulated analysis of the duplicate sample only. This revealed that the majority of robust estimates of standard deviations from the unbalanced experimental design were within 5% of the estimates from the balanced design, with a maximum difference of 7%. These desk experiments demonstrate that the unbalanced experimental design can be used to obtain robust estimates of uncertainty with a 33% reduction in the additional cost of analysis (Rostron & Ramsey, 2012).

Both balanced and unbalanced robust analysis of variance for a nested experimental design are available as an Excel application (RANOVA2) on the website of the Analytical Methods Committee.

https://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software

References

AMC (1989a) Robust statistics - how not to reject outliers. Part1, basic concepts. Analyst 114:1693-1697

AMC (1989b) Robust statistics - how not to reject outliers. Part2, Inter-Laboratory Trials. Analyst 114:1699-1702

Lyn JA, Ramsey MH, Coad DS, Damant AP, Wood R, Boon KA (2007) The duplicate method of uncertainty estimation: Are eight targets enough? Analyst 132:1147-1152

Ramsey MH, Ellison SLR (eds.) (2007) Measurement uncertainty arising from sampling: a guide to methods and approaches. Eurachem, EUROLAB, CITAC, Nordtest and the RSC Analytical Methods Committee.

Rostron P, Ramsey MH (2012) Cost effective, robust estimation of measurement uncertainty from sampling using unbalanced ANOVA. Accred Qual Assur 17:7–14

ILAC guidance on contribution to Measurement Uncertainty arising from Sampling and Testing

Erik Oehlenschlaeger

DANAK, Skovlunde, Denmark

Abstract

Since ISO/IEC 17025:2017 was issued ILAC has been active in implementing the standard before 30 November 2020. This presentation will provide information about the revision of the guide ILAC G17 for uncertainty in Testing undertaken by The ILAC Accreditation Committee (AIC). The presentation will further address the recent discussions in the AIC about Mesurement Uncertainty arising from sampling.

The Role of Accreditation in Assuring the Quality of Sampling

Lawrence Bilham

United Kingdom Accreditation Service, Staines-upon-Thames, United Kingdom

Abstract

The Role of Accreditation in Assuring the Quality of Sampling

Results of analytical measurements made by a testing laboratory are highly dependent on the sample supplied for analysis. Poor sampling and challenging conditions can lead to unreliable data, potentially leading to problems.

Consistent application of a well-defined sampling protocol by competent staff, with other variables controlled so far as possible are key to quality sampling and working within an accredited system will help ensure this. Accreditation can either be of the organization taking the samples or of a certification body providing certification of the individual person taking the sample.

Accreditation is increasingly being recognised as a valuable tool to verify the technical competence and integrity of organisations offering sampling services, although some sampling activities have been accredited for many years, especially where there is a regulatory requirement for accreditation. In areas where there is no regulatory requirement, the customer may require accreditation, but this relies on their understanding of the many benefits and often comes down to a financial decision.

Accreditation is the formal recognition that an organisation is competent to perform specific activities, (such as sampling) in a reliable, credible and accurate manner. Accreditation ensures that sampling is undertaken impartially, is effective and is assessed by highly professional competent assessors and technical experts in the relevant fields. Accreditation delivers confidence in the sampling performed and it underpins the overall quality of measurement results by ensuring their traceability, comparability, validity and commutability.

The value of accreditation of sampling ultimately lies in the improved reliability of the analytical results generated by the testing laboratory.

Applications of UfS estimation across a range of sectors

Ariadne Argyraki

Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, 15784 Athens, Greece

Abstract

The first edition of the Eurachem/CITAC (The Cooperation on International Traceability in Analytical Chemistry) "Guide on measurement uncertainty arising from sampling" was published in 2007. The Guide introduced methods and approaches for the estimation of the contribution of sampling and sample preparation to measurement uncertainty, as an independent component from the analytical uncertainty. Through the application of the proposed approaches to tackle this issue, a basis for the validation of sampling procedures was defined, regardless the field of investigation (industry, food, environment, etc.).

Since its first edition, the Guide has been cited in over 100 publications including research papers, PhD Theses and regulatory documents, across a range of different sectors including industry, food, and environmental research. In this workshop session, a review of relevant publications is presented with the aim to demonstrate how and to what extent the proposed methodologies have been applied by researchers involved in the measurement process. Furthermore, the presentation provides examples of the Guide being incorporated in ISO documents as well as several technical support regulatory documents related to sampling and analysis of solid and liquid materials.

Both approaches proposed for the evaluation of measurement uncertainty, i.e. by using the "bottom-up" or the "top-down" methods, are included in the reviewed publications. Comparisons of the uncertainty values estimated by the application of both approaches to the same measurement system have also been performed in a few of the reviewed studies, providing information for a more complete estimate of uncertainty. During the session, the criteria for the selection of the appropriate approach for different purposes will be discussed focusing on the critical issues when applying the various approaches.

The way forward for Uncertainty from Sampling.

Michael H. Ramsey

School of Life Sciences, University of Sussex, Falmer, Brighton, BN1 9QG, UK

Abstract

Recent progress in the development and application of research in to Uncertainty from Sampling (UfS) will be used to identify the most effective way forward. Topics will be discussed as a series of issues under three broad categories.

Developing methodology for UfS estimation and reduction, includes utilizing estimation of confidence limits on estimates of UfS (and heterogeneity). This enables the rigorous comparison of UfS values estimated by different methods and for different analytes**.** Similarly, the uncertainty factor is a more reliable way to express U in particular circumstances. In order to achieve fitness-for-purpose (FFP) in measurement including sampling, there is a need to investigate ways of Modifying UfS. Existing approaches (e.g. using the model $s^2 \propto 1/m$) work for some systems but not others, suggesting a need for improved modelling of UfS. Sampling QC procedures also need to be further developed and applied to check whether the conditions present at validation are still present, and whether the estimates of U are still applicable. This is especially the case where subsequent sampling targets are very different (e.g. contaminated land).

New applications of existing UfS methods, and using it to assess fitness for purpose (FFP), are desirable for a wider range of application areas (e.g. gases, particulates, sediments, pharmaceuticals, metals, forensics), and a wider range of measurement situations. More UfS estimation is required for four particular situations: *in situ* measurement techniques (where a sample is not removed), on site measurements (sample removed but analysed on site), passive measurements (e.g. of radioactive decay) and measurements made *in situ* at micro-scale (mm – μm) by microbeam techniques (e.g. PXRF, EPMA, SIMS). Even when the uncertainty of such measurements is high, they can be shown to be fit for some purposes. Including between-sampler bias in estimates of UfS has now been demonstrated using data from Sampling Proficiency Testing (SPT), and needs further development. The extra cost of this approach SPT can be financially justified where there are large adverse consequential costs from underestimation UfS, as in the case evaluation of a potential gold mine. The first example of a database of UfS/UoM estimates for a particular sector (i.e. food), has been used to investigate whether (a) there are typical values that could be used for prediction of UfS (e.g. by regulators) and (b) UfS increases as a function of concentration [1]. This approach could usefully be applied to other sectors for the same purposes. The 'duplicate method' has also been applied to quantify heterogeneity (U_{het}) for microbeam analysis of both powdered and crystaline RMs . In these cases, U_{het} can be added into U of reference value when mass of test portion is small [2,3]

External factors affecting take up of UfS estimation include the limited awareness of many measurement scientists to UfS, which the new UfS Guide aims to address. Regulatory and/or accreditation requirements to estimate UfS can also improve awareness and take-up, as demonstrated by the recent revision to ISO 17025. Cost of estimating UfS is another constraint, but it can be reduced either by use of unbalanced or simple experimental designs. or by an awareness that an appropriate level of UfS can reduce in overall cost to a producer by avoiding adverse effects that can arise from excess uncertainty. Specified systems for making compliance decisions can sometimes exclude UfS (e.g. for food trading) or ignore UfS by assuming samples are 'representative', and therefore that uncertainty only arises from chemical analysis. Better ways need to be found therefore to include UfS in compliance decisions many sectors. The administration and management of the

whole measurement process needs to be reviewed and integrated, by many organisations where it is currently fragmented. One person needs to be responsible for the quality (i.e. uncertainty) arising from the whole process including sampling, sample preparation and analysis. Better education, training and assessment of samplers, via accreditation and/or certification, is essential to improve the quality of sampling to levels that are FFP, rather than perfectly 'representative'. One approach would be to decide on how to regulate UfS, either by setting broad limits (UfS < 20%), or more realistically by identifying case-specific values for each analyte/material, based upon FFP criteria. Users of measurement values, should then be encouraged to use and propagate the UoM (including UfS) values in their interpretation (e.g. in risk assessment, epidemiology, and compliance decisions)

References

1 Ellison, SLR, Ramsey MH, Lawrance P, Stuart B, Minguez J, Walker MJ, (2017) Is measurement uncertainty from sampling related to analyte concentration? Analytical Methods, **9**, 5989-5996. DOI: 10.1039/C7AY00752C. http://pubs.rsc.org/en/content/articlelanding/2017/ay/c7ay00752c#!divAbstract

2 Rostron P. and Ramsey, M.H. (2017) Quantifying heterogeneity of small test portion masses of geological reference materials by PXRF: implications for uncertainty of reference values. Geostandards and Geoanalytical Research, 41, 3, 359-473., DOI: 10.1111/ggr.12162. onlinelibrary.wiley.com/doi/10.1111/ggr.12162/full

3 Ramsey MH and Wiedenbeck M. (2017) Quantifying Isotopic Heterogeneity of Candidate Reference Materials at the Picogram Sampling Scale. Geostandards and Geoanalytical Research, 42,1,5-24, doi: 10.1111/ggr.12198 http://onlinelibrary.wiley.com/doi/10.1111/ggr.12198/full

Eurachem guidance on Measurement Uncertainty - Guides, leaflets and current work

Stephen L R Ellison

LGC Limited, Queens Road, Teddington, TW11 0LY, UK

Abstract

Eurachem began working on guidance for measurement uncertainty in approximately 1993, using draft ISO TAG 4 guidance as a basis for the first edition of the Eurachem Guide on measurement uncertainty for analytical chemistry. This early work culminated in the publication of the first English edition of "Quantifying Uncertainty in Analytical Measurement" (QUAM) in 1995 [1]. This first guide closely paralleled the structure and form of the GUM [2], explaining the principles and focusing on the "law of propagation of uncertainty" that later became known as the "bottom up" approach to uncertainty evaluation [3]. The Guide was accordingly published with the intention of introducing the concepts and enabling analytical laboratories to gather practical experience.

Further research within the Eurachem measurement uncertainty working group, together with experience and feedback gained from further workshops, established both the need and the practicality of using information from method validation and other sources to inform the evaluation of measurement uncertainty. This became particularly apparent as it became clear that direct application of the law of propagation of uncertainty to the simple measurement models in analytical standard methods was prone to understatement of uncertainties in analytical measurement, owing to the dominance of longer-term variations and effects that were hard to capture in a measurement equation. Following further developments in the use of cause-and effect analysis and validation data [4, 5], the working group issued the second edition of QUAM in 2000. The increased focus on use of validation data was welcomed, and the 2nd edition saw broad uptake by laboratories and reference from accreditation agencies world wide [7], with a number of translations becoming available together with a web based implementation. The Second edition remained stable for over a decade.

In the mean time, Eurachem turned to additional topics. With increasing focus on measurement uncertainty by accreditation agencies came a need to consider the use of measurement uncertainty in compliance decisions. To assist, the Eurachem MU Working group prepared guidance on "Use of uncertainty information in compliance assessment" [8], making use of established procedures in other sectors, particularly ASME [9]. Sampling uncertainty was considered sufficiently important to form a separate joint working group with EUROLAB, CITAC, Nordtest and the RSC Analytical Methods Committee. The UfS working group published "Measurement uncertainty arising from sampling" in 2007 [**Error! Reference source not found.**]. Further technical issues included uncertainty near detection limits, and the application of Monte Carlo analysis for uncertainty evaluation; together with guidance on compliance assessment, these topics appeared in the Third Edition of QUAM in 2012 [11].

Another fundamental topic, target measurement uncertainty, was introduced by the 3rd edition of the VIM [12]. Target measurement uncertainty is a maximum admissible uncertainty, and can be used as a criterion to check whether measurement quality quantified by the measurement uncertainty is fit for the intended purpose. Eurachem issued guidance on "Setting and Using Target Uncertainty in Chemical Measurement" in 2015.

Many of these developments were additionally supported by Eurachem Information leaflets; these so far include a basic introduction "Information leaflet for lab customers concerning the quality of

chemical analyses" (2000), "Use of uncertainty information in compliance assessment" (2009), "Using repeated measurements to improve the standard uncertainty" (2015), on the change in uncertainty on averaging, the thorny issue of "Treatment of an observed bias" in uncertainty evaluation (2017) and "Setting target measurement uncertainty" (2018).

Current and future Eurachem work on measurement uncertainty reflects laboratory needs, gaps in technical guidance and international developments. There remains much that can be done to simplify the application of validation data by laboratories; work is ongoing to prepare new and more detailed guidance on using such data. Technical issues include the problem of handling uncorrected bias – still unresolved despite several studies – and the problems associated with large uncertainties and asymmetric distributions. Both topics are currently under consideration by the Eurachem working group. JCGM, the committee responsible for the GUM, is considering a significant restructuring of its guidance on measurement uncertainty, which is expected to include a wider range of approaches including Bayesian statistics for uncertainty evaluation. These developments may result in significant changes to the primary documents on measurement uncertainty for metrology, and are being closely monitored to ensure that Eurachem Guides remain up to date and consistent with international guidance.

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Current approaches to the evaluation of measurement uncertainty

Vicki Barwick

LGC, Queens Road, Teddington, Middlesex TW11 0LY, UK

Testing laboratories may be required to evaluate the measurement uncertainty for results obtained from a large number of methods, which are frequently complex multi-stage procedures. Applying the modelling approach described in the 'GUM' in such situations can be impractical for a number of reasons:

- Difficulty in writing an equation that includes all influence factors – there may be many factors that affect the measurement result but don't appear directly in the calculation of the result;
- Challenges associated with isolating and quantifying individual sources of uncertainty – there may a large number of potential sources of uncertainty which are interrelated and/or poorly understood;
- The process may be too time consuming in a routine testing environment when a 'reasonable estimation' of the uncertainty is all that is required.

Alternative approaches, which make use of method performance data, have therefore been developed. This 'top-down' approach requires data on method 'outputs' (e.g. variation in results obtained from replicating the whole measurement procedure) to estimate the combined effect of a number of sources of uncertainty, as opposed to data on uncertainty introduced by individual influence factors. In testing laboratories such data can generally be obtained from method validation studies and ongoing quality control.

The application of this approach is described in a number of documents [for example 1-4]. This presentation will provide an overview of the different approaches available for evaluating measurement uncertainty, with a focus on the requirements for the top-down approach.

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MUkit – software for uncertainty from validation and QC according to Nordtest 537 [A revised version handling both absolute and relative uncertainty estimation]

Teemu Näykki

Finnish Environment Institute

Abstract

In 2003, Magnusson et al. published the Nordtest technical report TR 537—handbook for estimation of measurement uncertainty in environmental laboratories (revised in 2004, 2011 and 2017 [1]). Its ease of use, reliance on the data available from validation, and quality control have made it popular among routine laboratories. ISO has issued international standard 'Water quality—estimation of measurement uncertainty based on validation and quality control data' [2], which is essentially based on Nordtest TR 537.

The Nordtest handbook describes the estimation of 1) the uncertainty component from within-laboratory reproducibility u_{Rw} (also called intermediate precision), and 2) the uncertainty component due to possible method and laboratory bias u_b. The u_{Rw} reflects the random error component covering method repeatability and day-to-day variation while u_b describes the systematic due to the method and the laboratory. Both of these uncertainty components can be conveniently estimated from quality control and validation data [3], thus significantly reducing the need for performing dedicated experiments for estimating detailed uncertainty contributions and thereby simplifying the uncertainty estimation for routine laboratories [4].

Finnish Environment Institute (SYKE) has developed a computer program MUkit for measurement uncertainty estimation based on quality control and validation data. The approach presented in the software program is based on the calculation methods presented in the Nordtest 537 report. The software is available for download free of charge on the Internet at www.syke.fi/envical and the Nordtest guide can be downloaded from the website: www.nordtest.info

The first version enabled user to carry out the relative measurement uncertainty estimations. In the updated version of MUkit, the user is able to choose the calculation approach between relative and absolute. This is highly needed improvement, since the measurement interval usually has to be divided into several ranges. In the lower concentration range for instrumental methods the absolute measurement uncertainty is usually constant while at higher concentrations the relative uncertainty is constant.

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Top-down uncertainty evaluations – Difficulties and solutions

Ricardo Bettencourt da Silva

Centro de Química Estrutural – Faculdade de Ciências da Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal (rjsilva@fc.ul.pt)

Abstract

Top-down uncertainty evaluations are very popular due to the simplicity of calculations, the fact that it adapts to the information collected during the in-house validation of the measurement procedure and/or tests quality control, and, frequently, the evaluation pragmatism does not drastically overstate the measurement uncertainty. However, these evaluations face some difficulties whose inadequate treatment can lead either to under-estimation or unnecessary overestimation of the measurement uncertainty.

Some of these challenges, and how can be solved, are discussed in this communication, namely:

1) How to develop models of measurement uncertainty variation with the measured quantity;
2) How to evaluate trueness uncertainty for the analysis of samples with different native analyte levels and spiked at different levels;
3) How to deal with relevant systematic effects;
4) How to deal with matrix effects variability.

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Lognormal and Relative Uncertainty - Uncertainty estimation when the uncertainty is high

Alex Williams

Camberley, UK

By using the Monte Carlo method to calculate the uncertainty it is shown that the distribution of values attributed to the measurand is lognormal, when, as is mostly the case, the model equation consists of products of input quantities, that have a positive value. Therefore, the lognormal distribution should be used to calculate the expanded uncertainty U_T from the observed mean m and relative uncertainty u_{rel}, utilizing the formula given by Ramsey and Ellison (1) viz

$$U_T = \frac{\bar{x}}{\sqrt{1+u_{rel}^2}}\left(e^{k\sigma_{ln}} - e^{-k\sigma_{ln}}\right) \text{ where } \sigma_{ln} = \sqrt{\ln(1+u_{rel}^2)}$$

For values of u_{rel} less than 50%, $\sigma_{ln} \approx u_{rel}$ giving $U_T \approx \frac{\bar{x}}{\sqrt{1+u_{rel}^2}}\left(e^{ku_{rel}} - e^{-ku_{rel}}\right)$

With upper and lower limits of $\frac{\bar{x}}{\sqrt{1+u_{rel}^2}}\left(e^{ku_{rel}}\right)$ and $\frac{\bar{x}}{\sqrt{1+u_{rel}^2}}\left(e^{-ku_{rel}}\right)$ respectively.

For values of u_{rel} less than 10%, these limits become $x_u = \bar{x}(1 + k.u_{rel})$ and $x_l = \bar{x}(1 - k.u_{rel})$ i.e.

$x_u = \bar{x} + k.u$ and $x_l = \bar{x} - k.u$ in agreement with current practice for small uncertainties.

Using the lognormal distribution ensures that x_l is always positive, also when the relative uncertainty is constant the exponential terms above are constant and x_u is just a constant multiplied by $\bar{x}$, whereas using a normal distribution the upper limit tends to infinity as ku_{rel} tends to 1, leading to unrealistic values of the upper limit 2

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Reporting high uncertainty
Asymmetric interval, U-factor or log units

Bertil Magnusson[1], Eskil Sahlin[2] and Thomas Svensson[3]

1 – Trollboken AB, Sweden
2 - RISE Research Institutes of Sweden, Sweden
2 – Thomas Svensson Ingenjörsstatistik, Sweden

Abstract

Measurement Uncertainty is a property of a measurement result and is normally given as ± *U*, where *U is* an expanded uncertainty given with a specific coverage probability – usually 95%.

A measurement uncertainty can be given in absolute terms (with the same unit as the unit of the measured value) or in relative terms (for example, as a percentage as in the example below.

Measured value	***Measurement uncertainty, U (95 %)***	
	Absolute	***Relative***
20 µg L^{-1}	2 µg L^{-1}	10 %

In this case the coverage interval is symmetric around the measured value. A symmetric interval is usually preferred and works rather well if the distribution is close to normal and the uncertainty is low – less than 20-30 %.

At higher uncertainties, the assumption of normality becomes questionable. At trace levels, with large relative standard deviation, very high results can become more likely than very low result; symmetry is lost and the distribution can be somewhere between a normal distribution and a log normal distribution.

If the expanded relative uncertainty is > 100 %, then reporting a symmetric interval would indicate that the concentration could be zero even though we are sure that we have detected and measured the analyte. High relative uncertainty can e.g. be due to sampling uncertainty, high heterogeneity in test samples, or measurements performed close to the LOD. Another example is microbiology where there is in many cases a high measurement uncertainty.

The solution proposed here, if the relative uncertainty is high, is to report an asymmetric interval. This is in line with the fact that at high relative uncertainty a log normal distribution is often a better approximation. An asymmetric interval can then be reported using an uncertainty factor which corresponds to a symmetric reported in log units - see example below.

	Measured value	***Measurement uncertainty, U (95 %)***	
		Low value	***High value***
Concentration units	100 µg L^{-1}	100/2 µg L^{-1}	100*2 µg L^{-1}
Log units	2	1.7	2.3

In this presentation the background for reporting asymmetrical intervals will be given with examples from different sectors.

Conformity and measurement uncertainty – an introduction

Stephen L R Ellison

LGC Limited, Queens Road, Teddington, TW11 0LY, UK

Abstract

In order to decide whether a result indicates compliance or non-compliance with a specification, it is necessary to take into account the measurement uncertainty associated with the result. **Figure 1** shows typical scenarios arising when measurement results, for example on the concentration of analyte, are used to assess compliance with an upper specification limit. The vertical lines show the expanded uncertainty $\pm U$ on each result and the associated curve indicates the inferred probability density function for the value of the measurand, showing that there is a larger probability of the value of the measurand lying near the centre of the expanded uncertainty interval than near the ends. Cases i) and iv) are reasonably clear; the measurement results and their uncertainties provide good evidence that the value of the measurand is well above or well below the limit, respectively. In case (ii), however, there is a high probability that the value of the measurand is above the limit, but the limit is nonetheless within the expanded uncertainty interval. Depending on the circumstances, and particularly on the risks associated with making a wrong decision, the probability of an incorrect decision may or may not be sufficiently small to justify a decision of non-compliance. Similarly, in case (iii) the probability that the value of the measurand is below the limit may or may not be sufficient to take the result to justify compliance. Without further information, which has to be based on the risks associated with making a wrong decision, it is not possible to use these two results to make a decision on compliance.

This presentation provides a short introduction to the main issues associated with conformity decisions using measurement results accompanied by measurement uncertainty, with particular attention to the provisions of the Eurachem Guide "Use of uncertainty information in compliance assessment" [8]. This guide makes use of established procedures in other sectors, particularly ASME [9]. In particular, it introduces the concept of "guard bands", illustrated in **Figure 2**, to control risks of incorrect acceptance or incorrect rejection.

The principles are applicable to decisions on compliance with regulatory or manufacturing limits where a decision is made using a measurement result accompanied by information on the uncertainty associated with the result. The problem of assessing conformity where the uncertainty is proportional to the value of the measurand is also considered.

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Figure 1 Assessment of Compliance with an Upper Limit

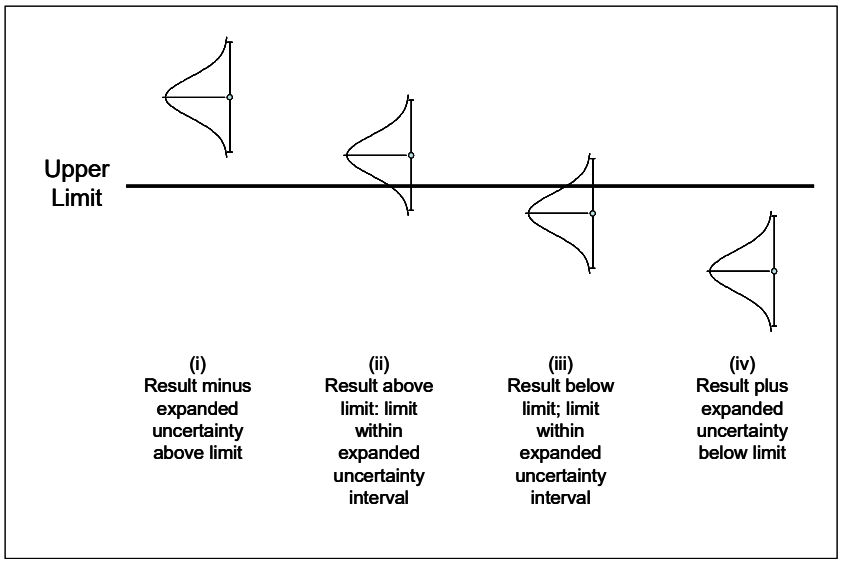

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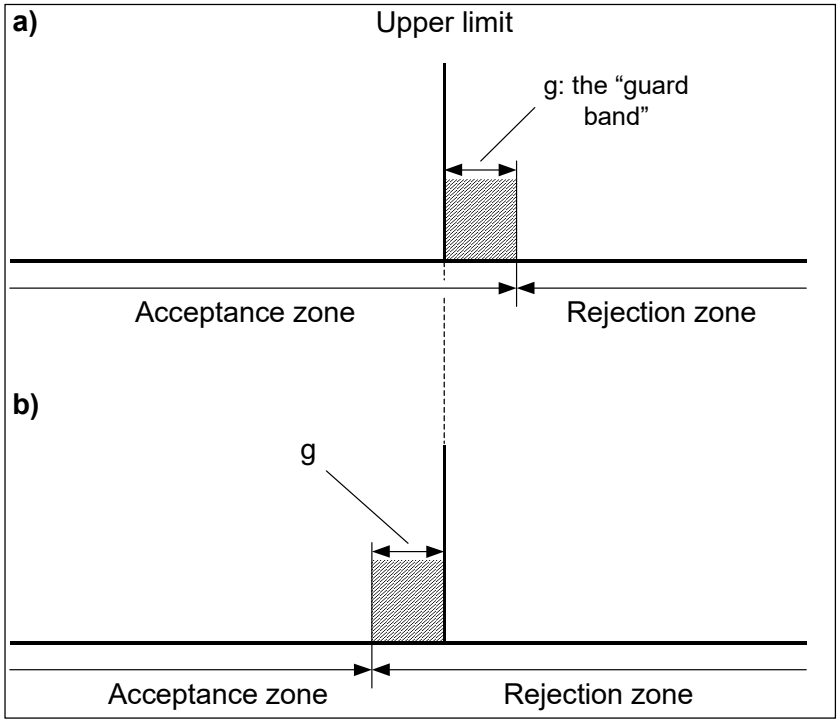
Figure 2 Examples of guard bands.
a) Relaxed acceptance; b) Stringent acceptance



Update on the activities in the Joint Committee on Guides in Metrology regarding the GUM and VIM

Adriaan M.H. van der Veen

Author for correspondence: Adriaan van der Veen, VSL, Delft, Netherlands

Abstract

Working group 1 of the Joint Committee on Guides in Metrology (JCGM-WG1) is responsible for maintaining and developing the "Guide to the expression of Uncertainty in Measurement" (GUM) and the promotion of its use. Working group 2 of the same committee (JCGM-WG2) is responsible for maintaining and developing the International Vocabulary of Metrology (VIM).

In 2014, a committee draft of a revised version of GUM:1995 (JCGM 100) was circulated for review and comment. This revision achieved consistency with GUM Supplement 1 (propagation of distributions using a Monte Carlo method), more attention to the validity of the use of the law of propagation of uncertainty and type A and type B evaluation methods on a comparable (Bayesian) footing. What the revised document did not achieve was the support of the community of users of the current GUM. Reasons for this lack of support included issues with evaluating standard uncertainty for small series of observations (n = 2 and 3), and the necessity to validate the use of the law of propagation of uncertainty when used with non-linear models. Based on the outcome of the first circulation, JCGM-WG1 decided to stop further developing the document.

A new document about the development and use of measurement models has been circulated as committee draft in 2018. Projected as document JCGM 103, it provides extensive guidance on the steps to be taken when developing a measurement model. It explains the specification of the measurand, the development of a ``basic'' model describing the measurement principle and extending such a model to a complete measurement model by including effects arising from the measurement. One clause is devoted to statistical models, which play a role in many data reductions and type A methods for evaluating standard uncertainty.

For the suite of documents maintained by JCGM-WG1, currently issued under the banner "Evaluation of measurement data", a new structure has been proposed. Rather than having GUM:1995 as central point, an introductory document describing the processes involved when evaluating, expressing and using measurement uncertainty will become the entrance point, from which the reader is directed to the document(s) that provides guidance to address a specific problem. The currently issued JCGM-WG1 documents, including GUM:1995 will be taken up in this suite as parts. This New Perspective to the GUM aims at improving the accessibility of the documents and for the future also developing documents specific for targeted audiences with different levels of complexity and presentation. The suite will be issued under the banner "Guide to the expression of Uncertainty in Measurement"

JCGM-WG2 is working on a new edition of the VIM. This new version will use simpler language, take up the annotations developed for the current edition of the VIM (JCGM 200:2012), be electronically searchable, and cover for the first time nominal properties. So far, the VIM has been devoted to quantities only, but in many areas of measurement and testing, qualitative properties, such as DNA-sequences, identity of substances etc. are the principal outcome. The inclusion of terminology related to nominal properties in a substantial manner is therefore a logical step, and implies that the concepts of metrology go beyond just quantities.

Uncertainty from sampling and analysis for accredited laboratories

PARALLEL SESSION PRESENTATIONS

Abstracts for presentations in parallel sessions appear in programme order

Uncertainty from Sampling: Could the requirements of ISO/IEC 17025:2017 be adopted in medical laboratories?

Kyriacos C. Tsimillis[1] and Sappho Michael[2]

[1]*Division of Quality Assurance, Pancyprian Union of Chemists,*
[2]*Ministry of Health, Nicosia, Cyprus*

Abstract

The new ISO/IEC 17025 [1] has introduced a number of new provisions as well as a number of changes to others, already existing. While approaching the end of the transition period for the implementation of the new standard, set for the end November 2020, laboratories try to find their way to adequately address all the new requirements. At the same time accreditation bodies need to ensure their readiness to assess laboratories against the new standard. Last but not least, peer evaluation procedures need to be carried out in a homogeneous way. The inclusion of sampling as a stand-alone laboratory activity, although not expressed in this way, represents one of the main changes compared with the 2005 version of ISO/IEC 17025 [2]. This is reflected in a number of other provisions of the new standard. Among them, the requirement to take into account all contributions that are of significance, including those arising from sampling when evaluating measurement uncertainty is of great importance. In this presentation the requirements referring to sampling and the uncertainty arising from it as applicable are discussed underlining what testing laboratories need to consider. In parallel, a comparison with the ISO 15189 [3] is made with regard to its requirements for sampling. With regard to measurement uncertainty, the said standard is focusing only on contributions arising from the examination phase, thus excluding those arising from the pre-examination processes, including sampling. However, great emphasis is given to the pre-examination processes including patient-collected samples and otherwise collected primary samples and their handling. The existing experience shows that a high percentage of factors contributing to uncertainty are dominant during this phase, thus the measurement result might be compromised. In the case of testing laboratories accredited against ISO/IEC 17025 [1], some approaches addressing the uncertainty from sampling are available [4]. However, these approaches are not applicable in medical laboratories, bearing in mind some inherent difficulties; one of them is that replicate sampling which can be used by testing laboratories [4] is rather unrealistic in the medical sector. Based on the above, it is questionable whether an approach on uncertainty from sampling similar to the one introduced by the new ISO/IEC 17025 [1] could be included in a future revision of ISO 15189 [3].

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4. Eurachem/Eurolab/CITAC/Nordtest/RSC AMC (2019) Uncertainty arising from sampling. A guide to methods and approaches

Estimation of the measurement uncertainty, including the contribution arising from sampling, of water quality parameters in surface water of the Loire River Basin, France

Nathalie GUIGUES (*LNE*) ; Bénédicte LEPOT (*INERIS*) ; Jacky DUROCHER (*AELB*)

Abstract

One of the main objectives of environmental monitoring is to compare measurements to regulatory thresholds. However, this depends strongly on the knowledge of the uncertainty associated with these measurements. The two main contributions of measurement uncertainty are the uncertainty resulting from sampling and that resulting from the analysis. As much as analytical uncertainties tend to be well controlled and well reported, sampling uncertainties are often undescribed and unestimated.

A specific study was designed and carried out at the Loire River Basin in France, in order to:

- estimate the measurement uncertainty, including the contribution of sampling;
- verify that the protocols implemented under the DCE monitoring program for the quality of the surface waters are adequate in relation to the measurement objectives.

The surface waters within the Loire River Basin are characterised by significant variations in concentrations over time and space.

Following the Eurachem/Citac guidance recommendations, the replicate method was selected in order to estimate spatial and temporal variability of surface waters as well as measurement uncertainty. The study was conducted in 2017 under routine and operational conditions with the accreditated laboratories selected by the Loire Bretagne Water Agency. In overall 25 monitoring stations were chosen for estimating the spatial variability and among them 11 monitoring stations were singled out for estimating the temporal variability from April to December. To minimise both the number of analysis and the costs of this study, an unbalanced design was used. As three different teams of samplers were collecting the water samples during the study, a specific test was design to estimate the influence of the sampler on the measurement uncertainty. Finally, robust analysis of variance, by means of RANOVA2 software, was used to calculate the measurement uncertainty.

The results obtained allowed us to demonstrate that the sampling and analysis protocols implemented for water quality monitoring of surface waters were well adapted. These protocols meet the 20% criterion initially stated, i.e. the variability of the measurement process does not impact much the environmental variability.

The expanded measurement uncertainties (k=2) were found to be of the same magnitude or even lower (for major constituent parameters, arsenic and nickel and AMPA), as the analytical uncertainties provided by the laboratories at the concentration levels measured on the River Basin.

However, the results allowed us to pinpoint several issues that should be discussed or investigated. For instance the determination of the sampling contribution to the measurement uncertainty was not possible because the analyses were not carried out under repeatability conditions (in the same analytical batch) but rather under intermediate precision conditions.

Uncertainty from sampling of trace explosives amounts and detection by ion mobility spectrometry

Carlo Tiebe, Mehmet E. Bayat, Matthias Bartholmai

Bundesanstalt für Materialforschung und -prüfung (BAM), 12200 Berlin, Germany

Abstract

Aviation security laws requires aviation security authorities, airport operators and airlines to undertake comprehensive security measures at the airports in order to prevent the danger of possible terrorist threats. Mail and cargo must be screened with listed methods, e. g. x-ray screening, explosive trace detection (ETD), and metal detection equipment (MDE).[1, 2] If a suspicious object has been identified by x-ray, ion mobility spectrometry (IMS) can be used as a fast on-site analytical method orthogonally to x-ray screening to receive further chemical information of particles adhered substances on surfaces of the object prior to departure.[3, 4]

IMS is an analytical method for characterising substances from the velocity of gaseous ions in an electric field and through a supporting gas atmosphere. In the last 25 years, IMS has become a major technology for detection of explosives or chemical agents. The analysis of explosives starts with swab sampling. An operator wipes the surfaces of a suspect object with a sampling pad to collect attached particles. The loaded sampling pad is subsequently thermally desorbed in an ion mobility spectrometer sample inlet for analysis and the operator receives Boolean test results – "Alarm" or "No alarm".[3-5]

Three sampling approaches with four ECAC-certified[6] ETD-devices were performed in this study:

I) liquid evaporation after deposition of a known trace amount of explosive (TNT, RDX, PETN and HMX) in a solution on a sampling swab,
II) manual swab sampling after liquid placement of a known amount of a solved explosive on a 10 cm × 10 cm substrate (aluminium, paper, iron, and polyvinyl chloride – PVC) and solvent evaporation, and
III) manual dry explosive swab sampling after liquid placement of a known amount of a solved explosive on a PTFE- or PTFE coated glass fibre surface and explosive transfer from the PTFE-surface to the investigated substrate.

According the binary regression method[7-10], the functional relation between probability of detection in dependence to a known explosive mass is described with a logit-function:

$$POD = \frac{1}{1 + e^{-A \cdot (m - B)}}$$

where *POD* is the probability of detection (POD) for a known mass of an explosive substance as the ratio of number of "Alarms" to total number of measurements, A (logistic growth rate of the curve) and B (m-value of the sigmoid's midpoint) are estimated parameters by least square method, and m is the explosive mass.

The developed measurement uncertainty model contains and combines quantitative results from weighing, solution and pipetting, and swab sampling and qualitative results – "Alarm" or "No Alarm". Identified uncertainty causes on the POD are dust, deposing solvent effects, and the uncertainty from explosive solvent preparation.

Acknowledgement

The work on which this abstract is based was carried out on behalf of the German Federal Ministery of Transport and Digital Infrastructure under FE-No. 50.0369-2017. The responsibility for the content lies exclusively with the authors.

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Comparing uncertainty values – are they really different?

Peter Rostron

Formerly of University of Sussex

Abstract

Uncertainties arising at different stages of a measurement process can be estimated using Analysis of Variance (ANOVA) on duplicated measurements[1]. The magnitudes of these uncertainties are method dependent and will be different depending on the sampling and analytical methods used. In certain situations it may be useful to be able to compare uncertainties between different methods.

For example, if sampling uncertainty is estimated by two different empirical methods, e.g. using a) the duplicate method; and b) data from a Sampling Proficiency Test, it is important to know if the arithmetic difference between uncertainties is statistically significant. Similar issues arise when comparing values of uncertainty due to analyte heterogeneity, which can also be estimated using the duplicate method. An example will be discussed for candidate reference materials when heterogeneity was estimated using a Portable X-ray Fluorescence (PXRF) instrument set with 2 different beam widths[2].

A defensible answer can be made to these questions if the confidence limits of both the uncertainties can be reliably estimated. If there is no overlap between the confidence intervals, then the uncertainty values can be considered significantly different between methods.

Mathematical approaches to determining confidence intervals of variances estimated by ANOVA exist, however these are based on probability models that assume parametric distributions of data. When it is suspected that the data may be affected by a small proportion of outlying values (i.e. <10%), then the use of robust ANOVA is recommended in the Eurachem guide1. In this situation mathematical methods for determining confidence intervals are not reliable. A potential solution is to use a bootstrapping approach to determine the confidence intervals of the variances of non-parametric data. This computer-intensive approach has been developed for the RANOVA2 program[3] (pending implementation). It has been shown to work well in situations where the number of sampling targets is large or the proportion of outlying values is small.

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Evaluation of the sampling uncertainty from the Monte Carlo Simulation of georeferenced information

Carlos Borges[1], Carla Palma[1], Tony Dadamos[2], Ricardo Bettencourt da Silva[3]

1 - Instituto Hidrográfico, R. Trinas 49, 1249-093 Lisboa, Portugal (Carlos.Borges@hidrografico.pt)

2 – Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trab. São Carlense, São Carlos, Brazil

3 - Centro de Química Estrutural – Faculdade de Ciências da Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal

Abstract

The assessment of the health and trends of a large river or ocean water area is demanding due to their seasonality, heterogeneity and size. All these factors affect the uncertainty of the collected information on the system that is crucial for its interpretation.

If the same area of a river or ocean water, at a specific depth, is assessed in equivalent seasonal conditions, system's heterogeneity is the only preanalytical uncertainty component for assessing system's variation. The system heterogeneity is determined from the analysis of various of their samples.

Many sampling protocols assume samples collected from the studied population are equivalent and interchangeable allowing using simple statistical tools for quantifying system heterogeneity. However, the composition of a river or ocean has concentration gradients resulting from emissions and/or water streams with different composition. Therefore, assuming the interchangeability of samples loses relevant information about the studied system.

This work presents a novel method for the evaluation and optimisation of the sampling uncertainty based on the Monte Carlo simulation of available information of the geographical distribution of studied component concentration. The simulation of system composition considers sample coordinates and sample analysis uncertainties. The system composition simulation allows determining composition distribution required for objectively assessing short- or long-term system trends. These models also allow defining optimal sampling strategies capable of supporting the determination of trends larger than a defined minimum value.

The developed tool was implemented in a used-friendly MS-Excel spreadsheet and successfully applied to study Tagus River and Portuguese maritime areas.

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Uncertainty from sampling in microbiological water analysis

Fátima Marinheiro Coimbra

Relacre – Associação de Laboratórios Acreditados de Portugal, Estrada do Paço do Lumiar Campus do Lumiar Edifício D, 1º Andar, 1649-038 Lisboa, Portugal

e-mail – fcoimbra@adp.pt

Abstract

To meet the requirements of ISO / IEC 17025:2017 laboratories should identify the contributions from different variables to measurement uncertainty. When evaluating measurement uncertainty, all significant contributions, including those arising from sampling, shall be taken into account using appropriate methods of analysis. When the laboratory is also responsible for the sampling activity, reports also shall include information required to evaluate measurement uncertainty for subsequent testing or calibration, where necessary for the interpretation of the results.

The estimation of uncertainty of the measurement of microbiological enumeration methods, for water analysis, shall be carried out according the ISO 29201:2012, combining two components:

- the operational variability (technical uncertainty) which is the combination of all the uncertainties associated with the technical steps of the analytical procedure, and
- the intrinsic variability (distributional uncertainty) which is the unavoidable variation without a cause that is associated with the distribution of particles in the final suspension and in the detection instrument.

In water microbiological enumeration methods the "full" uncertainty of a test result can be estimated only after the final result has been obtained.

Since the publication of the revised ISO/IEC 17025:2017 measurement uncertainty evaluation has expanded its coverage to include sampling uncertainty. According the Portuguese Accreditation Body (IPAC) guideline, OGC001:2018, it is already mandatory to present, on the test reports, the uncertainty for both activities (measure) or the uncertainty of separated activities (sampling + analysis) as it recognized that sampling uncertainty can be significant factor in the final test result obtained from a given sample, including microbiological analysis.

The ISO 29201:2012 - Water Quality – The variability of test results and uncertainty of measurement of microbiological enumeration methods, clearly indicates that uncertainty assessment in this document begins at the time of testing the laboratory sample (analysis), so pre-analytical sampling variance (sampling), at the source, is outside of its scope.

Although the general principles of the Eurachem / CITAC guide: 2019 – Measurement uncertainty arising from sampling, could be apply, it does not specifically address the microbiological sampling. In fact there are currently no presentations specifically on this subject.

This work aims to present a statistical approach for the estimation the relative operational variability of measurement, arising from both sampling and analytical components, for water microbiological enumeration colony counts methods.

In the worked example, sampling and analyses were performed using accredited methods, subject to the required quality assurance and analytical quality control. Ten duplicated water samples C1 and C2

were taken on 10 different days from a natural contaminated well. Each sample C1 and C2 were tested, for Coliform bacteria / Membrane Filtration - ISO 9308-1:2014, in parallel (C1.1 / C1.2; C2.1 / C2.2) by different operators, same batch of consumables and same incubator.

The operational, analytical and measurement, uncertainties were calculated using an approach methodology of the modified global (top-dow), described in ISO 2920:2012 and the operational sampling uncertainty was calculated with the double split design/range statistics.

For comparison, with the same replicate data of the worked example, the random component of the measurement uncertainty and two of its main components (sampling and analytical) were also calculated by analysis of robust variance ANOVA (RANOVA V2).

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Shades of grey in conformity assessment due to measurement uncertainty

Ilya Kuselman[1], Francesca R. Pennecchi[2], Ricardo J. N. B. da Silva[3], D. Brynn Hibbert[4]

[1] *Independent Consultant on Metrology, 4/6 Yarehim St., 7176419 Modiin, Israel*

[2] *Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, 10135 Turin, Italy*

[3] *Centro de Química Estrutural, Faculdade de Ciências da Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal*

[4] *School of Chemistry, UNSW Sydney, Sydney NSW 2052, Australia*

Abstract

Standard specifications for chemical composition of a multicomponent material – a medication, alloy, etc. – are tolerance limits of the actual ('true') concentration or content ci of the i-th component, i = 1, 2, …, n, including main components and impurities or groups of impurities. Conformity assessment of an item (material batch or lot) is based on comparing the measured concentration or content cim with tolerance/specification limits [1]. Since any cim value has associated measurement uncertainty, acceptance limits for measurement results can be used in addition to tolerance limits. In these cases, the decision rules (does the test item conform or not?) are based on comparing the measured property values cim with the acceptance limits. The interval between a tolerance limit and corresponding acceptance limit is the 'grey zone', where probabilities of false decisions on conformity of the item are impermissible. When tolerance limits have been defined by already taking into account measurement uncertainty, acceptance limits and tolerance limits coincide.

Several kinds of risk of a false decision on conformity of an item may be called shades of grey. The probability of accepting a batch of the material, when it should have been rejected, is the 'consumer's risk', whereas the probability of falsely rejecting the batch is the 'producer's risk'. For a specified batch, they are referred to as the 'specific consumer's risk' and the 'specific producer's risk' R^*_{ci}, respectively, for the i-th particular component of the material under control. The risks of incorrect conformity assessment of a batch randomly drawn from a statistical population of such batches are the 'global consumer's risk' and the 'global producer's risk' R_{ci}, as they characterize the material production globally [2]. If a tolerance limit and corresponding acceptance limit coincide, the grey zone collapses, however the risks are still above zero at any measurement result. Thus, there are four shades of grey for each property value of an item – concentration or content of i-th particular component of a material (consumer's and producer's risks, both are specific and global).

A component-by-component evaluation of the risks of a material conformity assessment is not complete in general, as it does not give an answer to the question of the probability of a false decision on conformity of the material as a whole. When conformity assessment for each i-th component of a material is successful (i.e. the particular specific R^*_{ci} or global R_{ci} risks are small enough), the total probability of a false decision concerning the material as a whole (the total specific R^*_{total} or total global R_{total} risk) might still be significant [3].

Hence, there are four kinds of particular risks for each i-th property value (component concentration or content) of a material, and four kinds of total risks. Therefore, for n > 1 components under control one can distinguish 4(n +1) kinds of risks of false decisions – shades of grey. For example, for two components this means - 12, for three components – 16, and for four components – 20 shades of grey.

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Multivariate and correlated acceptance limits for conformity assessment

Ricardo J. N. Bettencourt da Silva[1], Felipe Lourenço[2], D. Brynn Hibbert[3]

[1] *Centro de Química Estrutural, Faculdade de Ciências da Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016, Lisboa, Portugal (rjsilva@fc.ul.pt)*

[2] *Faculdade de Ciências Farmacêuticas (FCF), Universidade de São Paulo (USP), Av. Prof. Lineu Prestes, 580 - Butanta, São Paulo, SP, 05508-000, Brazil*

[3] *School of Chemistry, UNSW Sydney, Sydney, NSW, 2052, Australia*

Abstract

Many industrial products, foodstuffs and environmental samples are checked for values of different chemical parameters against tolerance limits or intervals defined in a specification or legislation. In some cases, the measured values of the different parameters are correlated due to how materials are obtained, chemical constraints and/or due to the simple fact that determinations are performed by multi-analyte procedures that share analytical operations and effects. In these cases, instead of defining an acceptance criterion for each measured value on the tested item separately, based on the respective measurement uncertainty, the multivariate problem should be addressed by defining multivariate criteria. These multivariate criteria are set for a maximum total risk of wrong conformity decisions that is a complex function of all particular risks of the item being rejected by comparing each measured value with its respective limit. Computational tools have been developed to estimate the total specific risk of an item being wrongly considered to conform or not to conform with tolerance limits for various components when the measured values are independent or correlated. However, these tools must be applied for each test to check if the total specific risk is acceptably low. This work presents a tool for setting multivariate acceptance limits applicable to correlated measurements and referenced to a defined total specific risk. The acceptance limits allow the decision about conformity of an item based on the simple comparison of the measured values with the acceptance limits. The acceptance limits are estimated by a user-friendly and iterative tool implemented in a MS-Excel spreadsheet and available as Supplementary Material. This tool is successfully applied to various conformity problems. Acceptance limits based on informative and non-informative prior information are compared for a critical review of the merits and problems associated with Bayesian or frequentist conformity assessments.

Measurement uncertainty in the case of large and heterogeneous variances: A new method for the calculation of asymmetric uncertainty intervals

Uhlig S, Simon K, Colson B, Hettwer K, Frost K

Author for correspondence: Steffen Uhlig, QuoData GmbH, Dresden, Germany

Abstract

A common way to express uncertainty of measurement in chemical trace analysis is the interval y±U, where y denotes the measurement value and U the expanded uncertainty. This approach naturally yields a symmetric interval. However, there are cases where it is not reasonable to work on the assumption of symmetry.

Indeed, the simplest case involves measurement results near natural limits, such as zero or high-purity concentrations. Here, a symmetric uncertainty interval would encompass negative concentration values. Another familiar example is the field of microbiology, or indeed any other field where it is standard practice to log-transform the original (count) data before evaluating measurement uncertainty. Taking the antilog of the limits of the measurement uncertainty intervals will yield an asymmetrical interval in the original count domain.

However, in this talk, the focus lies on a more fundamental issue. Strictly speaking, the assumption of symmetric uncertainty intervals is only admissible if the dispersion of test results remains constant across the concentration levels. If relative standard deviations are low, then this assumption can still be made even if variability between test results does depend on the concentration level. However, as soon as relative standard deviations of, say, 30 % or 40 % are observed, the differences between asymmetric and symmetric intervals are too large to ignore. The theoretical framework within which these distinctions are conveniently drawn will be elucidated on the basis of examples.

How to address matrix mismatch bias in the uncertainty budget

Uhlig S, Simon K, Colson B, Hettwer K, Frost K

Author for correspondence: Steffen Uhlig, QuoData GmbH, Dresden, Germany

Abstract

The Guide to the expression of uncertainty in measurement (GUM) proposes that measurement uncertainty should be calculated on the basis of an equation expressing the relationship between input variables and the measurement result. An alternative approach – described e.g. in EURACHEM/CITAC Guide CG4 and in ISO 21748 – consists in making use of available method validation data. In this approach, there is no "functional relationship" between input variables and the measurement result. Rather, test results are obtained under different measurement conditions, and total observed variation is partitioned into individual components. This approach is often referred to as the top-down approach, while the GUM approach is referred to as the bottom-up approach.

This talk addresses the issue of evaluating measurement uncertainty in the case of a horizontal method across several matrices, applying the top-down approach on in-house data. A simple approach for characterizing variation across matrices consists in spiking the N matrices and obtaining duplicate test results in a single laboratory for each matrix. In this manner, variation between the matrices (matrix bias) can be distinguished from variation within the matrices (repeatability error). In this procedure, the matrix is modelled as a random effect, and the result is a standard deviation characterizing variation across all the matrices included in the specification of the measurand.

Webtool for taking measurement uncertainty into account in the implementation of the Federal Soil Protection and Contaminated Sites Ordinance

Uhlig S, Simon K, Colson B, Hettwer K, Frost K

Author for correspondence: Steffen Uhlig, QuoData GmbH, Dresden, Germany

Abstract

This talk presents the results of an R&D project for the development of a concept for taking measurement uncertainty in account in the implementation of the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung – BBodSchV).

The following measurement uncertainty components are taken into consideration: (1) spatial heterogeneity, (2) systematic deviations during sampling, (3) random deviations during sampling, (4) fundamental variability, (5) systematic deviations of the analysis method, and (6) random analytical deviations. Assessment of contamination levels against given thresholds is made either on the basis of the measurement uncertainty range of an individual test result or on the basis of its evidence level. Both approaches are equivalent, but the determination of the evidence level allows further information to be taken into consideration. The evidence level lies between 0 and 1 and reflects the probability of exceeding a given threshold. A given threshold is considered to be exceeded when the entire measurement uncertainty range of the test result lies above it. This corresponds to an evidence level above 0,95. In this talk, the theoretical framework is illustrated on the basis of concrete examples using the webtool.

Measurement uncertainty in R: The metRology package

Stephen L R Ellison

LGC Limited, Queens Road, Teddington, TW11 0LY, UK

Abstract

R [1] is a powerful, open-source environment for statistics and statistical programming. It can readily be extended by use of "packages"; additional software modules for specific purposes. Packages can be installed on demand from within R itself. Here, we describe some of the features of a package written to support a range of applications in metrology; the package metRology.

The R package metrology [1] provides classes and calculation and plotting functions for metrology applications. The metRology package currently includes functions for:

- Plotting for Key Comparisons (dot-and-bar, consistency);
- Uncertainty evaluation using algebraic or numeric differentiation, with support for correlation;
- Monte Carlo evaluation of uncertainty (including correlation for normally distributed variables);
- Classes and functions for location estimates for metrology comparisons;
- Mandel's *h* and *k* statistics and plots for interlaboratory studies.

This presentation provides a brief “live” introduction to the measurement uncertainty evaluation features. These include implementation of the first-order GUM [2] approach using algebraic differentiation, numerical differentiation using finite difference approaches, including that due to Kragten [4], and a Monte Carlo method.

In addition, the package provides a number of diagnostic tools, including convenient graphical summaries (Figures 1 and 2), to assist in the identification of large contributions to combined uncertainty.

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Figure 1: Example of graphical display of diagnostics for an uncertainty budget using the law of propagation of uncertainty

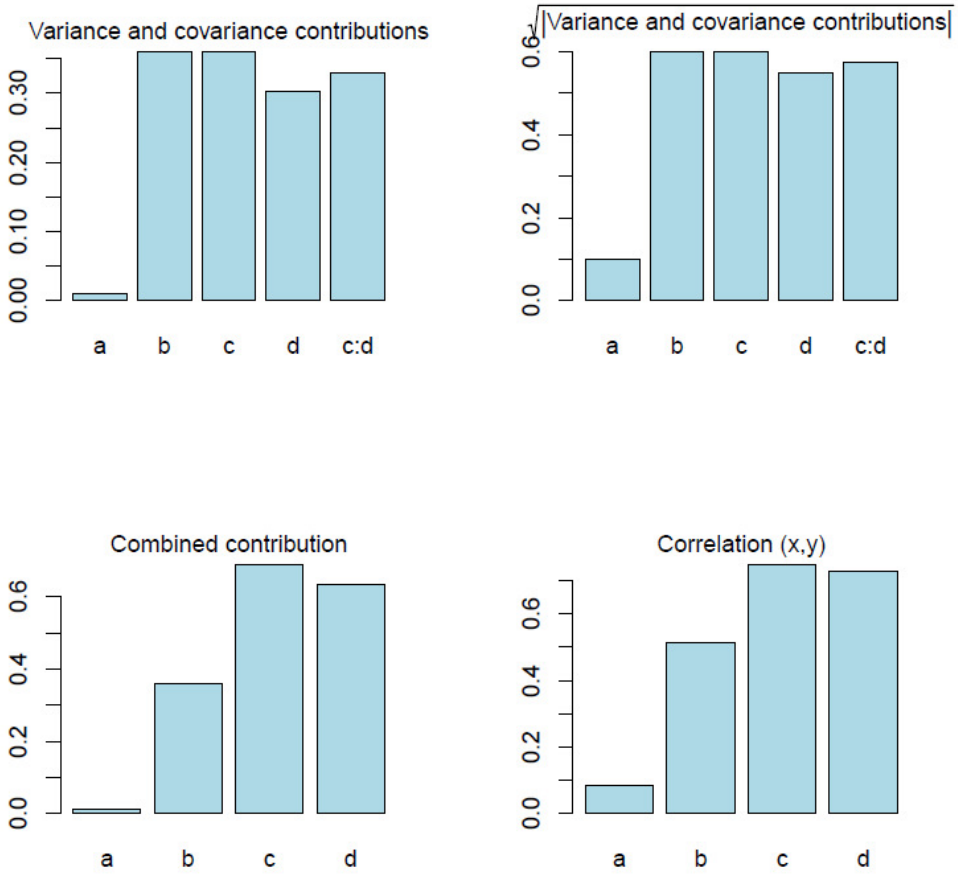
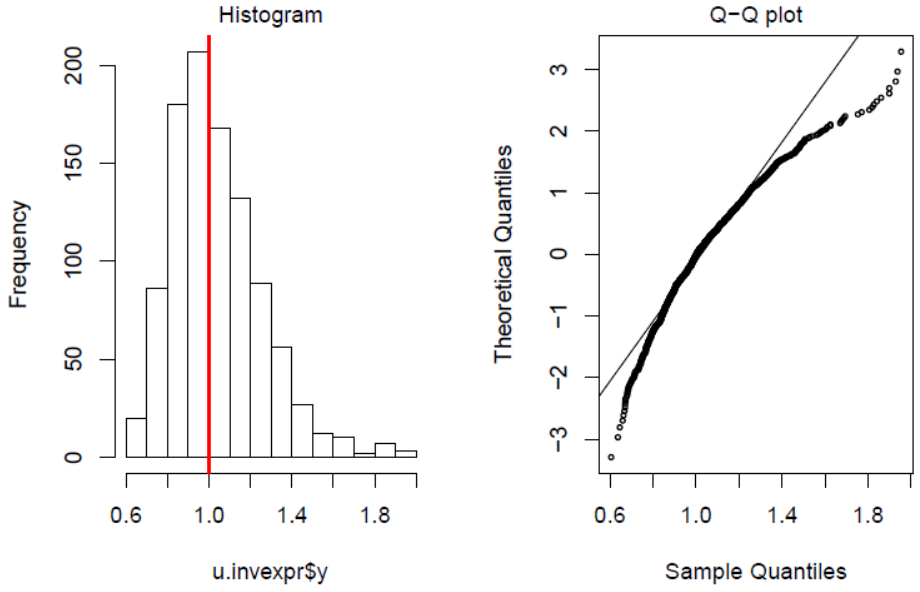


Figure 2: Example of the default plots for uncertainty budget of a simple non-linear function evaluated using Monte Carlo evaluation



Uncertainty from sampling and analysis for accredited laboratories

POSTERS

Abstracts for posters appear in alphabetical order of author for correspondence.

Where a poster is provided in addition to a presentation of the same title, the Abstract is included in programme order in the previous sections and is not repeated here

Accuracy of the dimethylmethylene blue spectrophotometric assay in measuring the amount of encapsulated pentosan polysulfate into nanoparticles

Hanin Abdel-Haq

Istituto Superiore di Sanità, National Center for Drug Research and Evaluation, Rome 00161, Italy

Abstract

Pentosan polysulfate (PPS), a highly sulfated semisynthetic polysaccharide, chemically and structurally resembles glycosaminoglycans (GAGs). Therefore, it was used here the dimethylmethylene blue (DMMB) binding assay, which is a rapid spectrophotometric assay that is widely used to measure sulfated GAGs, to estimate the amount of PPS encapsulated into chitosan-based nanoparticles (NPs). Thus, NPs were prepared by electrostatic interaction between PPS and the polycationic polymer chitosan, under simple and mild conditions. The amount of encapsulated PPS into NPs was quantified either by measuring the free PPS left in the supernatant or by direct measurement of the entrapped PPS into the NPs. The entrapped PPS was released from the NPs by incubation in Tris buffer (20 mM, pH 10) at 37 °C for a maximum of 48 hours and subsequent separation by centrifugation at 16.1 x g for 30 minutes at 22 °C. PPS was detected by the DMMB dye in a linear relationship (R2 = 0.998) at concentration ranges from 0.1 to 1 µg/ml and from 1 to 10 µg/ml. The quantification limit (LOQ) of PPS was ≤ 0.75 µg/ml, which is 10 * standard deviation (SD) of the blank. The drug entrapment efficiency of the NPs was 82.9 ± 0.09 % and 84.1 ± 0.47 % based on the indirect and direct estimation, respectively. This latter result clearly shows that the indirect estimation does not significantly differ from the direct estimation. Additionally, the measurement uncertainty expressed by the relative standard deviation (RSD = 0.1% and 0.6%, respectively) suggests that the DMMB assay is highly reliable in measuring the PPS entrapped amount. The reason of the slightly lower value observed for the indirect estimation, as compared with the direct estimation, is probably due to an overestimation of the unbound PPS whose concentration is too low to be appreciably and correctly estimated. After spiking of known amounts of PPS with chitosan solution, the DMMB assay measured quantities of PPS that were very close to those actual where the percentage difference from actual (accuracy criteria) and %RSD (precision criteria) were lower than 10%. These results are collectively in agreement with previously published data obtained using the capillary zone electrophoresis (CZE) [1]. However, all the uncertainties related to results produced by the DMMB assay are much smaller (10 to 30-fold) than those produced by the CZE, confirming its higher accuracy over other detection assays. On the other hand, sodium levulinate (the unique excipient in the PPS solution) and chitosan neither interacted with the DMMB dye nor interfered with the measurement of the PPS. While, GAGs-positive controls such as dextran and heparin reacted with the DMMB but differently both in quantitative and qualitative terms, with respect to the PPS and to each other.

Overall, the DMMB assay demonstrated to be able to estimate the PPS entrapment efficiency into the NPs with high accuracy both within and between the assay. Moreover, the DMMB dye showed high stability and binding specificity reflected by the absence of any interaction with nonsulfated molecules present in a mixture with the PPS.

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Estimation of sampling uncertainty for concentration of atrazine and desethylatrazin in drinking water wells

Primož Auersperger, Karin Lah

JP VODOVOD KANALIZACIJA SNAGA d.o.o., Vodovodna c. 90, Ljubljana, 1000-Slovenia

Abstract

Nowadays strict legacy demands concerning the EU legal limit 0,1 µg/l for pesticides and their degradation products forced analytical chemists to optimise methods in order to get accurate results at ng/L level. It seems like EU legal limit for pesticides and their degradation products in drinking water will remain the same even though this legal limit is the most rigorous in the world. Since only a few of pollutants are present in groundwater the majority of results will fall in the level below the limit of quantitation (LOQ) and most of them also below the limit of detection (LOD) at ppt and sub-ppt level[1].

Measurement uncertainty of the laboratory analysis is quite well established. However correct estimation of total uncertainty (laboratory + sampling) for the analytical results is a big challenge, connected also to ISO/IEC 17025:2017 accreditation[2]. New edition of Eurachem guide[3] discusses new issues, connected to correct definition of population where there is an estimate for measurement uncertainty of sampling, evaluation of concentration dependency of uncertainty and many tips for better execution of duplicate method experiments. Non-symmetrical distribution (e.g. log normal) is also introduced similar like in microbiological laboratories. Cost for estimation of sampling uncertainty could be one of the most important influences for the implementation. This leads to the question about usefulness of some analytical results where the total uncertainty is too high and therefor significantly influence on interpretation of compliance with specification[4]. There are mostly two possibilities to solve such problem, first one to stop doing such analysis and the second to change sampling plan.

In our work estimation of total uncertainty for analytical results for pesticide atrazine and its degradation product desethylatrazine will be presented. Definition of population will be given as concentration of pesticide in water well on the day of sampling. Contributions to total uncertainty will be partially taken from validation study and partially from "duplicate method" according to Eurachem Guide[3]. Concentration dependency of total uncertainty is presumed from LOD to the upper limit of testing as $U(k=2) = a + b*c_X$, where a and b are predetermined constants and c_X is concentration of pesticide in population.

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Production of IAEA CRMs: Assessment of uncertainty arising from homogeneity of the sample

S. Azemard[1], E. Vassileva[1], A.M. Orani[1], P. Mandjukov[1]

IAEA environment laboratories 4 quai antoine 1er 98000 principality of monaco

Abstract

Since 1960s the International Atomic Energy Agency (IAEA) has been providing help to its member states in the field of data quality and quality assurance. In order to support Member States in their marine monitoring activities, Marine Environment Studies Laboratory (MESL) of the IAEA has produced Certified Reference Materials (CRM's) characterized for trace elements and methylmercury using samples of marine origin - biota and sediments.

A key requirement for any reference material is the equivalence between the various CRM units. Consequently, ISO Guide 17034 [1] requires RM producers to quantify the between-unit variation. Extensive homogeneity tests were carried out on candidate IAEA CRM's in order to estimate the uncertainty contribution coming from the homogeneity of the sample and to ensure its suitability as a certified reference material. The calculation of combined uncertainties of the certified values include the component arising from the heterogeneity of the sample, therefore it is necessary to confirm the obtained final uncertainties on homogeneity arising from within and between units are acceptable for their intended use.

The between-unit homogeneity is evaluated to ensure that the certified values of the CRM are valid for all produced units, within the stated uncertainty. The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected but determines the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit inhomogeneity is necessary to determine the minimum sample intake. In some case the within sample heterogeneity might be significant at the prescribe sample intake and should then be considered in the uncertainty evaluation of homogeneity.

Examples on the developed homogeneity designs as well as data treatment applied for the evaluation of uncertainty arising from sample homogeneity in the latest IAEA candidate CRM's will be shown together with some results for micro homogeneity evaluations.

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Comparison of different strategies for estimation of measurement uncertainty of the total mercury in seawater at the pg kg^{-1} mass fraction levels

S. Azemard[1], E. Vassileva[1], A.M. Orani[1], P. Mandjukov[1]

IAEA environment laboratories 4 quai antoine 1er 98000 principality of monaco

Abstract

In august 2017 Minamata Convention on Mercury entered into force and the countries are required to establish/strengthen the environmental monitoring of mercury and its species in all environmental compartments.

The IAEA Environment Laboratories (IAEA-NAEL) in Monaco acts as the analytical support center for the IAEA Member States' laboratories and are the pillar of the IAEA Quality Assurance program for determination of nuclear and non-nuclear contaminants in the marine environment. In order to assist Member States' laboratories in their monitoring efforts and help in producing comparable and reliable measurement results IAEA NAEL has developed number of recommended monitoring methods for ultra-low-level analysis of total mercury (THg) and methyl mercury (MeHg) in seawater, marine biota and sediments.

An analytical procedure based on hyphenated analytical technique cold-vapor atomic fluorescence spectrometry (CV-AFS), together with improved cleaning and sample processing methods was optimized and validated according to the recommendations of ISO-17025 [1] standard and Eurachem guidelines [2]. Parameters such as LoD, LoQ, recovery, linearity, working range, repeatability and intermediate precision have been carefully evaluated. The traceability of obtained results clearly demonstrated. The estimation of measurement uncertainty was performed according to the requirements of ISO GUM guide [3] and some particular point in this process further investigated.

The evaluation of measurement uncertainty was performed applying different approaches and obtained results were critically evaluated and compared. The BCR 579, Coastal Seawater CRM, used in many monitoring studies for THg in seawater, has an uncertainty on the THg mass fraction of 26% (k=2), which increased the final combined uncertainty for some targeted samples and reference studies.

The modeling approach showed explicitly how the different input parameters affect the final result, and what is their relative contribution to the final combined uncertainty. It is then possible to identify factors affecting the quality of measurement results, and subsequently improve the process, or define some quality control limits.

Evaluation of combined uncertainty according to the approach based on the in-house validation data was performed with the use of available CRMs and with the addition of appropriate standard solutions and the obtained discrepancy was clearly demonstrated.

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EDC-WFD: A project to deliver reliable measurements of estrogens for better monitoring survey and risk assessment

Sophie Lardy-Fontan[1], Christian Piechotta[2], Ester Heath[3], Noora Perkola[4], Stefania Balzamo[5], Paolo De Zorzi[5], Magda Cotman[7], Taner Gokcen[8], Caroline Gardia-Parège[6], Hélène Budzinski[6], Béatrice Lalère[1]

[1] *LNE 1 rue Gaston Boissier 75824 Paris cedex 15 - France*
[2] *BAM – Richard-Willstaetter-Str. 11, 12489 Berlin – Germany*
[3] *JSI Jamova 39, 1000 Ljubljana, Slovenia*
[4] *SYKE, Latokartanonkaari 11, 00790 Helsinki – Finland*
[5] *ISPRA, Via di castel Romano, 100 – Rome – Italy*
[6] *EPOC, UMR 5805 CNRS, University of Bordeaux, 351 cours de la Libération 33405 Talence cedex - France*
[7] *KI / NIC Hajdrihova 19 SI-1000 Ljubljana – Slovenia*
[8] *TUBITAK Ataturk Bulvari 221, TR-06100 Ankara- Turkey"*

Author for correspondence: Stefania Balzamo, ISPRA, Rome, Italy

Abstract

Keywords: estrogens, reliable measurements, comparability, effect based Method, MS based method

Monitoring programs should generate high-quality data on the concentrations of substances and other pollutants in the aquatic environment to enable reliable risk assessment. Furthermore, the need for comparability over space and time is critical for analysis of trends and evaluation of restoration of natural environment. Additionally, research work and exercises at the European level have highlighted that reliable measurements of estrogenic substances at the PNEC level are still challenging to achieve.

The project EDC-WFD "Metrology for monitoring endocrine disrupting compounds under the EU Water Framework Directive" aims to develop traceable analytical methods for determining endocrine disrupting compounds and their effects, with a specific focus on three estrogens of the first watch list (17-beta-estradiol (17βE2), 17-alpha-ethinylestradiol (EE2), and estrone (E1)). Estrogens 17-alpha-estradiol (17□E2) and estriol (E3) will be included to demonstrate the reliability of the developed methods - Mass Spectrometry based method and effect-based methods (EBM) - and to support the requirements of Directive 2013/39/EC, Directive 2009/90/EC and Commission Implementation Decision (EU) 2018/840, hence improving the comparability and compatibility of measurement results within Europe. During the EDC-WFD project four EBM will be deeply investigated in order to improve their rationale use and their support in water quality assessment.

More precisely the objectives of the projects are:

1. Optimise and validate traceable aqueous reference mass spectrometry based methods for the analysis of 5 estrogenic compounds prioritising 3 selected estrogenic compounds 17-beta-estradiol, 17-alpha-ethinylestradiol, and estrone in whole water samples at environmental quality standard (EQS) levels. Methods will have limit of quantification (LOQ) not exceeding 30 % EQS with a measurement uncertainty of ≤50 % at EQS.

2. Evaluate the interaction and partitioning of 5 estrogenic compounds prioritising 3 selected estrogenic compounds 17-beta-estradiol, 17-alpha-ethinylestradiol, and estrone between water samples and suspended particulate matter (SPM) and the capability of developed methods to address the different fractions of matrix (whole water and dissolved concentrations of estrogens).
3. Develop production methods for aqueous reference materials (RM), which are as close as possible to real water samples, with proven homogeneity, short- and long-term stability.
4. Improve the comparability of estrogen measurements with selected Effect-Based Methods (EBM) in whole water samples at EQS level. Methods will have been correctly calibrated and information on uncertainty will be provided.
5. Organise and perform an interlaboratory comparison (ILC) to demonstrate the performance of the developed methods using the reference material (RM) for the selected estrogen substances.
6. Contribute to the work of key European and international standardisation organisations e.g. CEN TC 230 and ISO TC 147 ensuring that the outputs of the project are aligned with needs, communicated quickly to those developing the standards and to those who will use them to support the implementation of directives, and in a form that can be incorporated into the standards at the earliest opportunity

This contribution will present in details the objectives and methods applied within the EDC-WFD project.

Metrologically sound assessment of elemental composition differences in sea cucumber from different origins

Iryna Rehan[1], Carla Palma[1], Vanessa Morgado[1,2], Ricardo Bettencourt da Silva[2]

1 - Instituto Hidrográfico, R. Trinas 49, 1249-093 Lisboa, Portugal

2 - Centro de Química Estrutural – Faculdade de Ciências da Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal (rjsilva@fc.ul.pt)

Abstract

This work describes the metrological evaluation of differences in the elemental composition of sea cucumbers tissues of different species, collected from different types of sea bottoms and from different locations. This work is motivated by the increasing interest for this delicacy and its farming, and for using this animal for monitoring the heath of a habitat.

It was studied five sea cucumber organs/tissues (body wall, muscle, gonads and gut), three species (Holothuria tubulosa, Holothuria forskali and Holothuria arguinensis), two types of sea bottoms (rocky and sandy) and three locations (S1, S2 and S3) in coastal areas close to the city of Setubal, Portugal.

The assessment of differences between levels of total Cd, Cu, Ni and Pb in different sea cucumbers tissues was based on the bottom-up evaluation of the measurement uncertainty supported on Monte Carlo Method combinations of uncertainty components where correlations of uncertainty components was considered.

The compared means of measured values of samples from selected two groups of sea cucumbers were obtained by simulations that considered the sharing of analytical steps and effects that affected the simulated distribution of the difference of the means. The means are considered metrologically different is at least 99 % of difference distribution is below or above zero.

This procedure also allowed to accurately reflect, in this evaluation, the variation of the measurement uncertainty with the measured mass fraction.

For determinations close to the detection limit, the prior information that mass fraction cannot be smaller than zero was considered in a Bayesian assessment of measured values.

This assessment was possible by linking simulated values to a spreadsheet that automatically selects the compared groups of measurement results and combines their values in two means for which is determined the distribution of means difference.

This work illustrates how powerful can be a detailed metrological assessment of complex information when compared to classical statistical evaluations where relevant details are difficult to consider and can be easily omitted such as complex variables correlations, data distribution asymmetry and the variation of the uncertainty with the measurement details.

Little-big issues that testing laboratories are facing when uncertainties are being estimated

Camilo D Aleman C.
Chemist, Ph. D
Mol Labs Ltda
Bogotá, Colombia
quimica@mollabs.com

Immer Mauricio Caicedo G.
Chemical metrologist
Mol Labs Ltda
Bogotá, Colombia
quimiometria@mollabs.com

Abstract

This work puts together and tabulates the frequency of the main issues that analysts are facing in the physicochemical laboratories in the Colombian industry when uncertainties are being estimated[1][2].

Some of the more commons ones are:

- Lack of claritywhen identifying and quantifying sources of uncertainty.
- Quality of training focused on the estimation of physicochemical uncertainties.
- Difficulty in identifying a mathematical model.
- Weaknesses with the mathematical development in chemical related degrees.
- Problems related with the interpretation of guides
- Subjectivity in the estimation of uncertainties procedures used: uncertainties significantly different for the same measurement procedure.

The data was obtained by interviews with analysts from the industrial sector: potabilization plants (aqueducts) , human and pets foods producers, fertilizers and pharmaceutical.

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Uncertainty in fatty acid methyl ester CRM characterization

Camilo D Aleman C.
Chemist, Ph. D
Mol Labs Ltda
Bogotá, Colombia
quimica@mollabs.com

Yolby Milena Rodríguez
Chemist, M.Sc.
Mol Labs Ltda
Bogotá, Colombia
analisis@mollabs.com

Immer Mauricio Caicedo
Chemical metrologist
Mol Labs Ltda
Bogotá, Colombia
quimiometria@mollabs.com

Abstract

This text shows an estimate of the uncertainty of the assigned values of a CRM for fatty acids, quantified by gas chromatography. The procedure is based on the guide CG04 [1]. This included:

a) Uncertainty estimation of the standards solutions, prepared by dilution of a CMR of superior hierarchy, Certificated Reference material of edible vegetable oil. DMR 528a. CENAM, Mexican National Metrology Center;
b) A relevant contribution towards uncertainty estimation is the use of a straight-line calibration function model described in the technical specification ISO 28037 [2], which incorporates uncertainty in both axes: x_i standards solutions and y_i response of the equipment. [Figure 1];
c) The estimation of uncertainties by mass of the test portion;
d) The dilution factors; and
e) The estimation of the contribution to the uncertainty from the homogeneity and stability studies according to the requirements of the ISO 35 Guide [3].

The final result of the CRM production was presented and accredited before EMA (Mexican accreditation entity).

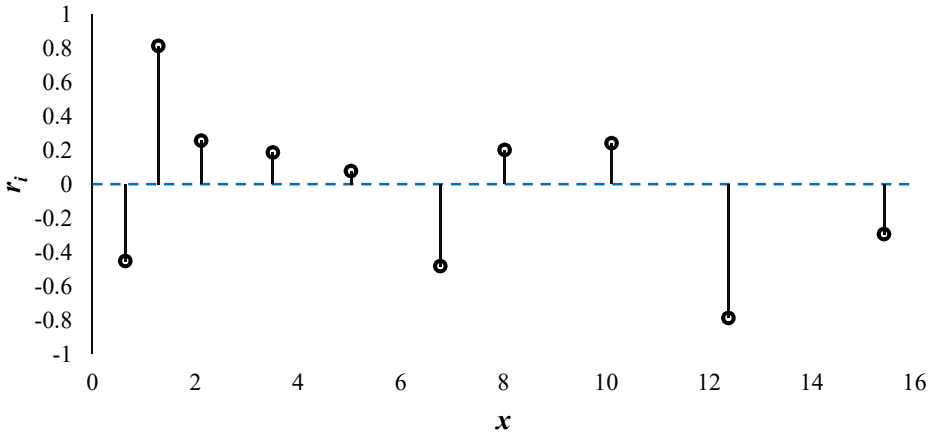

Figure 3- Weighted residuals r_i for quantification of fatty acids (Oleic acid)

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Evaluation of Measurement Uncertainty of a Validated Test Method on Nitrite in Water Supply by UV-Visible Spectrophotometry Equipped with Fiber Optic Probe

Admer Rey C. Dablio, Rodney C. Salazar, Emma D. Tayag

Inorganic Chemistry Section, Chemistry Laboratory, Standards and Testing Division, Industrial Technology Development Institute, Department of Science and Technology, Philippines

Abstract

Nitrite is one of the contaminants monitored in drinking water. The World Health Organization (WHO) has set a guideline value of 3 mg/L to be the maximum concentration safe for human consumption [1]. In the Philippines, an enforceable maximum allowable level of the same value was implemented by the Department of Health (DOH) since 2007 and reflected in the 2017 Philippine National Standard for Drinking Water [2]. With this issue on nitrite in drinking water, testing laboratories in the Philippines offer this testing capability and ensure accurate and reliable test results are given to various stakeholders on drinking water safety through accreditation under ISO/IEC 17025:2017. Measurement results include uncertainty evaluations which ensure reliability of analytical results. In this study, a validated test method for nitrite in water was evaluated. The method used was the colorimetric method based on the Standard Methods for the Examination of Water and Wastewater (SMEWW) Method 4500-NO_2^- [3]. This method used ultraviolet-visible spectrophotometer equipped with fiber optic probe for sample introduction system, instead of the conventional use of cuvettes. The measurement uncertainty evaluation done was based on the GUM approach [4] which utilized an uncertainty budget. Main sources of uncertainty came from volume of the sample solution, volume of standard solutions, purity of the reference standard, and calibration curve. The uncertainty from method and laboratory bias was also evaluated using a certified reference material for nitrite in water supply. A u_{bias} of 4.9 % was obtained for the validated test method. The uncertainty from method precision was evaluated from the intermediate precision conducted by the laboratory from the method validation activities. All standard uncertainties were made relative standard uncertainties before combined standard uncertainty was calculated using the error propagation theory. The combined standard uncertainty was then multiplied to the analytical result to be in the same unit of measure to the measurand. The resulting value is then multiplied to the coverage factor of 2 to get the expanded uncertainty, with stated confidence level of 95%. It was determined that from all the sources of uncertainty identified, the uncertainty from the calibration curve for the instrument calibration done gave the highest contribution.

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The median scaled difference: An outlier-resistant and model-independent indicator of anomalies for Key Comparison data.

S L R Ellison (LGC Limited)

Author for correspondence: S Ellison, LGC, Teddington, United Kingdom

Abstract

A robust pairwise statistic, the pairwise median scaled difference (MSD), has been proposed for the detection of anomalous location/uncertainty pairs in heteroscedastic interlaboratory study data [1]. The statistic provides a simple indication of degree of agreement between a particular laboratory's reported result and those of a majority of other participants in the study. The indicator does not depend on a particular choice of reference value, which is an advantage when there is no independent reference value and in internation key comparison where different reference values estimates can give contradictory indications of the consistency, or otherwise, of a particular laboratory result with the reference value.

The presentation provides a brief description of the MSD indicator and its distribution in the special case of identically distributed independent results. The resistance of the indicator to secondary extreme values – a common problem even in studies of moderate size – will be demonstrated. Simple rules for inspection will be given, and a rigorous interpretation using a simulation method will be shown. The use of the indicator on some typical key and pilot comparison data sets will be demonstrated.

Analysis of microplastics in theory and in practice

C. Goedecke and U. Braun

Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin, Germany

Abstract

Plastics are used in many applications, such as packaging, construction and mobility. Due to their favorable properties like light weight, flexible processing and low costs their production and consequently their input into the environment has increased significantly over the last decades. In the environment, oxidation processes and mechanical abrasion lead to the fragmentation of these plastics into smaller particles, called microplastics (< 5 mm) [1]. To analyze microplastic particles in environmental samples, mainly FTIR or Raman spectroscopic methods are currently applied. These methods provide information about the number, size and shape of the particles but require intensive sample preparation including density separation and enzyme digestion. When using spectroscopic methods, the determination of metrologically traceable microplastic levels is very difficult, e. g. contents in the mg kg^{-1} range, as they are preferred in the regulation. Therefore, we developed a thermoanalytical method, the so-called TED-GC-MS (thermal extraction desorption gas chromatography mass spectrometry), which allows the detection of microplastics in the mg kg^{-1} range with almost no sample preparation in about 2.5 h per measurement. The TED-GC-MS is a two-step analytical method which consists of a thermobalance and a GC-MS system. Up to 50 mg of a solid environmental sample is heated up to 600 °C in a nitrogen atmosphere. During pyrolysis, between 300 and 600 °C polymer-specific decomposition products are evolved and collected on a solid phase adsorber. Afterwards the substances are desorbed, separated and analyzed using the GC-MS [2].

The poster intends to present the theoretical requirements for microplastic analysis and contrast it with the current state of research. Unexpected problems that occur in practice are illustrated and the pretty new method is discussed with regard to quality requirements for well-established methods like LC- or GC-MS.

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A novel nested design approach for estimation of uncertainty arising from sampling in feed

Marios Kostakis, Evangelia Kritikou, Anastasia Koupa, Nikolaos Thomaidis

Author for correspondence: Marios Kostakis, Laboratory of Analytical Chemistry, Chemistry Department, National and Kapodistrian University of Athens, Zographou, Greece

Abstract

In the new version of ISO 17025, sampling is included as a part of laboratory activities with testing and calibration. Laboratories can provide sampling either exclusively or as a part of the method. Moreover, it is clearly stated in the standard that the contribution of uncertainty arising from sampling shall be taken into account. For this reason, there is a concern about the uncertainty of sampling and if it is mandatory for the laboratories to calculate it in any case. As in the measurement of uncertainty of analysis, there are two approaches to estimating uncertainty arising from sampling, the bottom-up and the top-down approach. On the other hand, the difficulties in the measurement of uncertainty arising from sampling are a lot, for instance, the homogeneity of sample or the difficulties of calculation the bias. The scope of this study, firstly, was to propose a novel approach using nested design experiment in order to calculate uncertainty arising from sampling and estimate the parameters that contribute to uncertainty of sampling. Secondly, the aim was to evaluate the method by comparing the results with the other top-down approaches (Range statistics, ANOVA, RANOVA). An already validated method of analysis was used for the determination of content of oxytetracycline in feed (final product) with High Performance Liquid Chromatography with Diode Array Detector (HPLC-DAD). The parameters that were chosen to study were different ways of milling of sample (mill and mortar), particle diameters and lots of production. The calculations took place with the following software: Microsoft EXCEL (range statistics), RANOVA2 EXCEL Workbook for RSC-AMC (ANOVA, RANOVA) and Minitab (nested ANOVA).

Phthalates in tattoo and Permanent Make Up inks: quantification and validation by GC/MS.

C. Leoni[1], C. Majorani[1], C. Abenavoli[1], M. Famele[1], R. Lavalle[1], L. Palleschi[1], C. Ferranti[1], L. Fava[1], R.M. Fidente[1], M.L. Polci[2], S. D'Ilio[1], R. Draisci[1]

[1] *Istituto Superiore di Sanità, Centro nazionale sostanze chimiche, prodotti cosmetici e protezione del consumatore, Rome, Italy*
[2] *Ministero della Salute, Direzione generale della prevenzione sanitaria, Rome, Italy*

Abstract

Over the last few years, the huge diffusion of the practice of tattooing and permanent make-up (PMU) has recently led EU Member States to focus the attention on possible risks for human health that may arise from the use of inks, resulting from an exposure to potentially hazardous substances they may contain. The substances of main concern are aromatic amines, chemical elements, dyes, phthalates, polycyclic aromatic hydrocarbons (IPA) and nitrosamines [1]. Some phthalates are classified as carcinogenic or toxic for reproduction under the regulation (EC) N.1272/2008 (CLP) [2] or are listed in Annex II (banned substances) of the regulation (EC) N.1223/2009 [3] on cosmetics. In 2008, the Council of Europe issued the resolution ResAp (2008)1 [4], that defined requirements and criteria for the evaluation of the safety of tattoos and PMU and drew a list of substances that should not be present in tattoo/PMU inks. A new restriction on substances in tattoo ink and PMU will be published in Annex XVII of the regulation (EC) N. 1907/2006 (REACH) [5].

There are no standard methods or in house validated methods, available at EU level, to be applied in the determination of phthalates in tattoo and PMU inks [6]. Then, the unit of Laboratory for Chemical Safety (Istituto Superiore di Sanità), as a National Reference Laboratory for the implementation of REACH and CLP regulations, carried out the development and in-house validation of an innovative GC-MS method for the quantification of nine phthalates in tattoo inks. The analysed phthalates were: bis(2-methoxyethyl) phthalate (DMEP), benzylbutyl phthalate (BBP), dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), bis(2-ethylhexyl) phthalate (DEHP), dihexyl phthalate (DHXP), di-n-octyl phthalate (DNOP), di-n-pentyl phthalate (DPP), diisopentyl phthalate (DIPP).

Method validation was performed according to requirements of ISO/IEC 17025 [7] and Eurachem Guide "The Fitness for Purpose of Analytical Methods. A Laboratory Guide to Method Validation and Related Topics 2nd" [8]. For all substances of interest, performance characteristics such as, limit of detection (LoD, 0.04 µg/g - 0.12 µg/g), limit of quantification (LoQ, 0.15 µg/g - 0.38 µg/g), working range (3 µg/g - 70 µg/g), intermediate precision (CV %, 2.5 % - 8.4 %), recovery (99 % - 126 %) were assessed. Measurement uncertainty was evaluated using the best available estimate of overall precision and bias (recovery) according to the Eurachem guide "Quantifying uncertainty in analytical measurement (QUAM: 2012)" [9].

In spite of the challenging matrix to be analyzed, the present in-house validated method is found to be accurate and sensitive, furthermore, it allows a fast processing of samples and it is cost-effective which makes it particularly suitable for use in the official controls on tattoo/PMU inks. This method will be a reliable tool in view of the forthcoming REACH restriction that proposes a concentration limit of 0.001% (w/w) for substances classified toxic to reproduction, such as DEHP and DBP.

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CEQAT-DGHS Interlaboratory tests for method validation and measurement uncertainty determination

Peter Lüth[1], Kirstin Frost[2], Lutz Kurth[1], Marcus Malow[1], Heike Michael-Schulz[1], Martin Schmidt[1], Steffen Uhlig[2], Sabine Zakel[3]

[1] *Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin*
[2] *QuoData GmbH, Prellerstraße 14, 01309 Dresden*
[3] *Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig*

Abstract

An explosion in a chemical plant or a fire on a dangerous goods vessel - the reason for such accidents can be numerous. Prevention starts in the laboratory where chemicals are tested for their hazardous properties in order to be able to assess the risks involved in their handling. For this purpose, test methods have been developed and published (see e.g. test methods in [1], [2]). They are applied globally nowadays. Safety experts, manufacturers, suppliers, importers, employers or consumers must be able to rely on the validity of safety-related test methods and on correct test results and assessments in the laboratory.

Interlaboratory tests play a decisive role in assessing the reliability of test results. Participation in interlaboratory tests is not only a crucial element of the quality assurance of laboratories; as such it is explicitly recommended in DIN EN ISO/IEC 17025 [3]. In addition, interlaboratory tests are also used to develop and validate test methods and can be used for the determination of the measurement uncertainty [4], [5].

Interlaboratory tests on different test methods have been performed by Bundesanstalt für Materialforschung und –prüfung (BAM) and Physikalisch-Technische Bundesanstalt (PTB) in collaboration with the QuoData GmbH during the last 10 years. Significant differences between the results of the participating laboratories were observed in all interlaboratory tests. The deviations of the test results were not caused only by laboratory faults but also by deficiencies of the test method (see interlaboratory test reports of the CEQAT-DGHS Centre for quality assurance for testing of dangerous goods and hazardous substances: www.ceqat-dghs.bam.de).

In view of the interlaboratory test results the following conclusions can be drawn:

- To avoid any discrepancy on classification and labelling of chemicals it should become state of the art to use validated test methods and the results accompanied by the measurement uncertainty [6], [7].
- A need for improvement is demonstrated for all examined test methods. Thus, interlaboratory tests shall initially aim at the development, improvement and validation of the test methods (including the determination of the measurement uncertainty) and not on proficiency tests.
- The laboratory management and the practical execution of the tests need to be improved in many laboratories.
- The term "experience of the examiner" must be seen critically: A "long experience with many tests" is not necessarily a guarantee for correct results.

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Determination of the Uncertainty Budgets of the Fluorescence Quantum Yield Values of Certified Standards as New Optical Reference Materials

J. Pauli, C. Würth, A. Güttler, Th. Schneider, U. Resch-Genger

Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Str. 11, 12489 Berlin/D

Abstract

Luminescence techniques are amongst the most commonly used analytical methods in the life and material sciences due to their high sensitivity and their nondestructive and multiparametric character. Photoluminescence signals are, however, affected by wavelength-, polarization- and time-dependent instrument specific effects. [1] This hampers the comparability of fluorescence measurements and calls for simple tools for instrument characterization and the quantification of measured fluorescence intensities. Well characterized fluorescence standards for instrument calibration and performance validation (IPV) can be used also to reference fluorescence signals. Of special importance is the reliable and accurate determination of photoluminescence quantum yields (Φf), that equals the number of emitted per absorbed photons and presents the key performance parameter for emitter efficiency and the comparison of different luminophores. The determination of Φf is typically done with the aid of so-called quantum yield standards with well-known Φf values. These standards can also be applied to evaluate integrating sphere setups, which are increasingly being used for absolute measurements of Φf values. In this respect, division biophotonics of BAM has certificated a set of Φf standards, which absorb and fluorescence in the wavelength range from 350 to 1100 nm [2]. In the following, the route to Φf standards with reliable and traceable Φf values with a complete uncertainty budget will be presented.

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A Statistical approach applied to the Proficiency Test on Plant Protection Products, during 2018.

Angela Santilio[1], Chiara Pompili [1] and Roberto Cammarata[2]

1 Italian National Institute of Health/Department of Environmental and Health, Italy; email: angela.santilio@iss.it
2 Italian National Institute of Health/Direction of Human and Economics resources, Italy; email: roberto.cammarata@iss.it

Abstract

In 2018, the second Proficiency Test (PT) was organized among laboratories all over Europe on plant protection products available on the Italian market. The aim of the trial was to find out the quantity of active ingredient on the different formulation of the plant protection products. Ten Italian laboratories and sixteen ones from the rest of European Union, who routinely deal with pesticides, were invited to participate. Laboratories are not obligated to take part in the PT; all the European and Italian laboratories sent their results. All laboratories obtained data with acceptable values of z-score within the limits, except for three of them who got higher than -3.5 z-score value for the active substances Amisulbrom, one higher than +3.5 z-score value for Dimethomorph and Propiconazole and two for Pirimiphos-Methyl. All the laboratories enjoyed taking part at this trial so another one is planned for the 2020.

The statistical evaluation of the results was performed applying the Jarque-Bera test for the verification of the hypothesis of normality. To use the Jarque-bera test is need to calculate asymmetry and curtosi check. These data are used to verify the acceptability in $\chi 2$ distribution at 95th percentage with the Jarque-Bera formula:

[(GdL^(asymmetry;2)/6)+(GdL1)^(curtosi;2)/(GdL+1)]

After this verification, the z-score values was calculated for each participant in each sample with the following formula:

Zi = 0,6745 * (Xi - Median)/MAD.

Based on the statistical evaluation, for Amisulbron the results obtained are laudable data, in fact most of them are inside the modified z-score range of $-3.5 \leq Z \leq +3.5$, three of them are outliers so outside the range of the modified z-score and one is in a "border line zone" so questionable but still an acceptable value.

For Dimethomorph, the results obtained are valuable data, in fact most of them are inside the z-score range of $-3.5 \leq Z \leq +3.5$ and one of them is completely unacceptable in the positive zone and one is questionable.

For Pirimiphos-methyl, the results obtained are valuable data, in fact most of them are inside the z-score Range of $-3.5 \leq Z \leq +3.5$, two of them are completely unacceptable in in the positive zone and one is questionable.

For Propiconazole, the results obtained are valuable data, in fact most of them are inside the z-score Range of $-3.5 \leq Z \leq +3.5$, one of them is completely unacceptable in the positive zone and two of them are questionable.

The outcome of the ITPT2019 can be considered satisfactory and the third PT organized by Italy.

The participation of the Italian and European laboratories was good. For Italy, ten laboratories were distributed as four in the north, three in the central and two in the south. The European laboratories were sixteen, excluding Italy, distributed as one in the south, eleven in the centre and four in the north of the Continent.

The performance of the laboratories expressed in terms of modified z-score was satisfactory by almost all participants for all substances. For each active substance there are outlier values, and the analysis of Amisulbrom was the most critical.

Almost all of the laboratories used the CIPAC methods for the four compounds or got inspired by the CIPAC method with some modification, for example, without using the internal standard.

One laboratory got 3 outliers of four analysis because it used a multiresidue instrumental method and this one probably has not good performance.

Based on the results it can be concluded that the PT was successfully organized also based on the number of participants.

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Uncertainty of measurement and pesticide residues in vegetable products: application of alternative approaches based on quality control data for multi/single residue methods

Danilo Attard Barbini, Silvana Girolimetti and Patrizia Stefanelli*

Istituto Superiore di Sanità (National Institute of Health), Department Environment and Health. Viale Regina Elena 299, postal code 00161 Rome (Italy)
** Corresponding authors:* patrizia.stefanelli@iss.it

Abstract

It is a requirement under ISO/IEC 17025 that laboratories determine the measurement uncertainty (MU): in the analysis of pesticide residues in food a value of 50 % of expanded MU is associated with analytical result. A prerequisite for the use of the 50% default expanded MU is that the laboratory demonstrates that its own expanded MU is less than this maximum value (1).

Since 2009, a European Standard has been issued for vegetable products describing a method for the analysis of pesticide residues in foods of plant origin such as fruits, vegetables and cereals (2). This quick and easy method, detecting multi analytes in a single extraction, has been collaboratively studied on a large number of commodity/pesticide combinations. Whereas some specific pesticide residues require Single Residue Methods because are not amenable to the Standard method EN 15662:2018. Consequently, we defined a workflow to estimate measurement uncertainty depending on the type of method employed: multi or single residue.

For the first kind of method, the calculation of individual measurement uncertainty (MU) may not always be possible; so an alternative approach was applied estimating a generic MU using data from three different proficiency tests selected for the three main product groups (fruit, vegetable and cereal) defined in the scope of the Standard method in combination of intra – laboratory precision. This approach presents a limitation due to the minimum number of results (31 results) to take into account. This limitation did not permit to apply the same approach in case of a Single Residue Method owing to the limited data of proficiency tests (often less than 31 results) due to the limited pesticide residues / matrix combinations. Therefore, to estimate the MU we applied a specific approach based on internal laboratory quality control for individual pesticides in a specific family group of commodities obtained from routine analysis on real samples. The Flonicamid residue in vegetable products was reported as a case study for Single Residue Method.

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Application of the GUM approach for the evaluation of measurement uncertainty in analytical chemistry on the basis of calibration functions

Uhlig S, Simon K, Colson B, Hettwer K, Frost K

Author for correspondence: Steffen Uhlig, QuoData GmbH, Dresden, Germany

Abstract

In the Guide to the expression of uncertainty in measurement (GUM), the calculations require that a functional relationship between input variables and the measurement result can be established. While, for many physical methods, this is perfectly reasonable requirement, this is not always a practicable approach in analytical chemistry. For this reason, the alternative data-oriented "top-down" approach – in which total observed variation is partitioned into different components – is often resorted to. However, in many cases this approach is not applicable due to incompatibilities between the design of the validation study and the measurand for which measurand uncertainty is being evaluated. In other cases, the precision estimates from the validation can be used, but they must be complemented by estimates from other uncertainty sources, requiring the conduct of further experiments. For this reason, it would be useful to propose a methodology allowing the application of the approach proposed in GUM across a broad range of methods in analytical chemistry.

In this presentation, an application of the GUM approach for analytical chemistry in which the functional relationship is derived from the calibration function is presented. It is shown which quantities are to be considered Type A and Type B, and how the uncertainty of bias correction can be included in the calculation of the combined uncertainty. This approach is first explained on the basis of a relatively simple case: linear calibration by means of an internal standard. However, it is also shown how the methodology works in the more complex case of the calibration of ELISA by means of a four-parameter curve. In particular, it is shown how, in the latter case, measurement uncertainty depends on the concentration.

The EMUE Project – Examples of Measurement Uncertainty Evaluation

Maurice G. Cox, Adriaan M.H. van der Veen, John Greenwood, John Dawkins, Francesca Pennecchi

Author for correspondence: Adriaan van der Veen, VSL, Delft, Netherlands

Abstract

The EMPIR 17NRM05 EMUE Project on "Advancing measurement uncertainty − Comprehensive examples for key international standards" [1] is a 3-years European project, started on July 2018, whose consortium brings together eleven European NMIs and DIs, two accreditation bodies, a public science and technology institute and three unfunded partners (aerospace manufacturer, anti-doping regulator and a large Asian NMI). It aims to promote the harmonised evaluation of measurement uncertainty according to internationally recognised standards and guides across broad disciplines of measurement. Specifically, the project will provide a comprehensive set of new and improved examples to illustrate uncertainty evaluation methods that are in accordance with the GUM and related suite of documents [2]. Some examples will concern traditional metrological areas such as calibration, testing, comparison and conformity assessment; some will relate to the thematic areas of environment, energy, quality of life, industry and society.

The project will deliver the produced examples of and templates for uncertainty evaluation to the Joint Committee for Guides in Metrology (JCGM) and its member organisations (BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML), and to several standards committees and organisations that have expressed a need for such an input. Eurachem, having requested examples to support its guidance documents and activities, is one of the main EMUE stakeholders (participating also in its Stakeholder Advisory Board). As such, it will receive dedicated project output related to applications in the environment sector: that will be used to extend the Eurachem guide on uncertainty arising in sampling [3] and as possible contribution to other Eurachem guides.

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

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