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Traceability, Validation and Measurement Uncertainty in Chemistry: Vol. 3

Practical Examples

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Foreword

Discendo docebis, docendo disces
By learning you will teach; by teaching you will learn
Latin Proverb

Chemical and bio-analytical measurements are omnipresent and often very important in our society. Just think of the quality of the food we eat, the air we breathe, the role of these measurements in health care, in trade and in research. In all these cases, people strive to get reliable data. There is an international standard for assuring the quality of measurement data, namely EN ISO/IEC-17025. It contains particular management as well as technical requirements. These technical requirements are linked to the science behind the measurements, meaning that metrological issues such as traceability, uncertainty and validation are at the heart of this.

So as to provide Life-Long Learning in this area, the TrainMiC® programme [www.trainmic.org] was conceived in 2001 by the Institute for Reference Materials and Measurements of the European Commission Joint Research Centre. First, it addressed the need arising with those countries wanting to enter the EU at that moment. Rather than approaching this training in an anecdotal way and organizing *ad hoc* events, a programme was set up—called TrainMiC®—to create harmonised training material as well as to disseminate knowledge in the various countries via a network of authorised TrainMiC® trainers. Afterwards, the TrainMiC® programme spread to the rest of the EU and Europe's largest Life-Long Learning programme in this area was created. Up to now, 20 national TrainMiC® teams have been set up and more than 9000 people have been trained all across Europe at the end of 2014. Trainers quickly realised the importance of having suitable examples for their training events. They realised soon that creating examples adapted to the various audiences is quite a labour-intensive activity. For this reason, sharing such examples proved to be an attractive proposition. Today, examples are reviewed and then published mainly in an e-collaboration environment which is only available for the authorised trainers. It was decided to publish part of the examples also in the format of a series of books, with a first volume that appeared in 2010, a second one in 2011 and this now being the third volume.

In the meantime, there is a lot of experience in using these examples for training purposes. First and foremost these examples should be seen as a vehicle for problem-based learning. Their intention is not to be a definitive guidance document, explaining a unique way to approach a given problem. Typically, they are used in a classroom context, where small groups of trainees will try to provide answers to the questions raised. It is recommended that they have *group* discussions, because discussion creates learning. Later on, the different groups present the outcome in a session *in plenum*. Also from this, there is learning. The answers provided in the book, are most likely one of the possibilities. As we all know, a lot depends on interpretation.

Brussels, Belgium Philip Taylor

Philip Taylor works for the European Commission Joint Research Centre. As an analytical chemist, he has been involved in many different research areas, techniques and type of activities, ranging from atomic to mass spectrometry, from fundamental constant work to applied industrial analysis, from isotopes to nuclear safeguards, from capacity building to training and teaching.

His current research interests lie in measurement and testing linked to aviation security and detection of CBRNE security threats (Chemical, Biological, Radioactive, Nuclear and Explosives).

There has however been one recurring theme which links up all these areas: how to ensure quality of measurement data. This is very important in the context of ISO/IEC-17025 laboratory accreditation and European Regulations.

For this reason, in 2001 he created a European Training platform for metrology in chemistry (TrainMiC®) involving experts from all across the EU. This was later followed by a teaching initiative, the Euromaster Measurement Science in Chemistry international master programme.

Preface

The publication of the ISO Guide to the Expression of Uncertainty in Measurement in 1993, known as the GUM, has set the ground for the development of metrology in physics, chemistry and biology, in particular, for the generalisation of the evaluation of the uncertainty of routine measurements. This guide, subject to minor revisions in 1995 and 2008, presented the tools and defined the conventions for using the measurement uncertainty concept in the resolution of daily societal problems and demands.

Although this document established a solid base for the development of metrology, the science of measurement, it was only after the publication of the ISO/IEC 17025 Standard in 2000, which imposed the evaluation of the uncertainty of accredited measurements, that GUM started to be used in routine laboratories. Fortunately for chemists, also in 2000, Eurachem published the second edition of a guide for the quantification of measurement uncertainty. The new revision of the guide presented alternatives to the detailed assessment of measurements: the so-called "top-down" approaches. These approaches allow laboratories to apply the GUM principles to routine measurements in chemistry in a cost-effective way. Nowadays, many other guidance documents have been published to help analysts in the evaluation of measurement uncertainty based on Eurachem's pragmatic interpretation of the implementation of GUM principles in chemistry.

The latest revision of the ISO/IEC 17025 standard attracts even more attention to the measurement uncertainty concept by asking laboratories to use it in conformity assessment and in quantifying the risk of wrong conformity decisions.

Nineteen years after important milestones in metrology in chemistry were attained, there is a consensus that accredited laboratories are experienced in "top-down" evaluations of measurement uncertainty. However, most of them are not familiar with the way to define and assess the traceability of measurements in chemistry, in particular, when the specific analytical field has no adequate and stable references for measurements and, therefore, the analysts should be more careful when planning to compare results from different laboratories.

Laboratories not involved in highly regulated analytical fields, such as many of those dedicated to fundamental and applied research, are frequently not aware of the ways to both select references for their measurements and to take information about the measurements' quality in the interpretation of results. The inadequate selection of references for measurements and the underestimation of relevant effects on measurement quality can have severe impacts on the outcomes of the studies undertaken.

Since the state of the art seems to be able to solve most challenges faced by measurements in chemistry, the goal now should be to ensure that this knowledge reaches those who need it.

TrainMiC® Life-Long learning programme has been teaching Metrology in Chemistry successfully since 2001. In 2007, a Portuguese team of 7 authorised trainers was set up and, since then, it has organised 13 courses that trained 211 Portuguese and Brazilian trainees. The courses delivered by the Portuguese team have been extremely appreciated due to the quality of the contents as well as for the demonstrated dedication and competence.

In 2011, during the celebration of the tenth anniversary of the TrainMiC® programme, the Portuguese team was awarded the best Mini-Case elaborated to increase the interactivity between trainers and trainees. This award led to the invitation of a member of the Portuguese team to be the Guest Editor of the third volume of TrainMiC® examples.

The authors of this book of examples wish this document will be useful to many analysts to improve their measurements and keep them alert to the latest developments in this field.

Lisbon, Portugal Ricardo Bettencourt da Silva

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Editors and Contributors

About the Editors

Nineta Hrastelj works as the General Secretary of the European Association for Chemical and Molecular Sciences (EuCheMS). She studied at the University of Ljubljana, Slovenia. Her research topics were horizontal across analytical chemistry, chemometrics and metrology. She is author, co-author or editor of about 250 contributions in research, teaching and related topics of general concern. In the recent years, her expert work is mostly about quality of analytical measurements, where, amongst others, she has been charing the TrainMiC Editorial Board and is a founding member of both, TrainMiC and Measurement Science in Chemistry (previously AcadeMiC) programme of the European Commission JRC.

Ricardo Bettencourt da Silva completed his B.Sc. in chemistry at the Faculty of Sciences of the University of Lisbon (FCUL), his M.Sc. in bromatology at the Faculty of Pharmacy of the University of Lisbon and his Ph.D. in analytical chemistry—metrology in chemistry at FCUL. The last two academic degrees were completed in parallel with his full-time professional experience as analyst, in official, public and private laboratories, of the different inorganic and organic analytes in various types of matrices using classical and instrumental methods of analysis.

This analytical experience was focused on the detailed validation of the measurement procedure, test quality control and evaluation of measurement uncertainty. Since 2002, Ricardo has worked regularly as an assessor of the Portuguese Accreditation Body (IPAC) and as a trainer and consultant for the accreditation of chemical laboratories. In 2009, Ricardo was contracted as a researcher by the Centre for Molecular Sciences and Materials of the Faculty of Sciences of the University of Lisbon where he has been continuing his research work on metrology in chemistry while collaborating in teaching at national and foreign universities. Ricardo's research includes the development of approaches for the detailed evaluation of the uncertainty associated with complex measurements and the assessment of the sources of lack of comparability of measurements in some analytical fields. Ricardo has been a member of the IPAC Accreditation of Chemical Laboratories Working Group since 2006, the Eurachem/CITAC Measurement Uncertainty and Traceability Working Group since 2010, the Portuguese TrainMiC® team since 2008 and the TrainMiC®. Editorial Board since 2010.

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Measurement of Total Reactive Phosphorus in Natural Water by Molecular Spectrophotometry (SMEWW 4500-P D)

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1 Brief Description of the Analytical Procedure

1.1 Introduction

Phosphorus occurs in natural waters almost solely as phosphates. These are classified as free phosphate (orthophosphate), condensed phosphates (pyro-, meta-, and other polyphosphates) and organically bound phosphates.

Various classes of phosphorus compounds can be quantified by molecular spectrophotometry after different sample pre-treatment (Fig. 1).

The free phosphate and some condensed phosphates are quantified by molecular spectrophotometry performed on an untreated aliquot (direct spectrophotometry). This phosphorus compounds fraction is known as "reactive phosphorus" in specific experimental conditions. Most of the condensed phosphates and some organically bound phosphate are also analysed by spectrophotometry after the hydrolysis of the

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sample aliquot with sulphuric acid at boiling water temperature. This phosphorus compounds fraction excluding reactive phosphorus is known as acid-hydrolyzable phosphorus in conditions prescribed by the measurement procedure. Finally, the total phosphorus can be quantified in the samples after more drastic digestion conditions (Fig. 1).

Therefore, the presented analytical procedure does not allow the discrimination of the phosphorus compounds as their chemical classes.

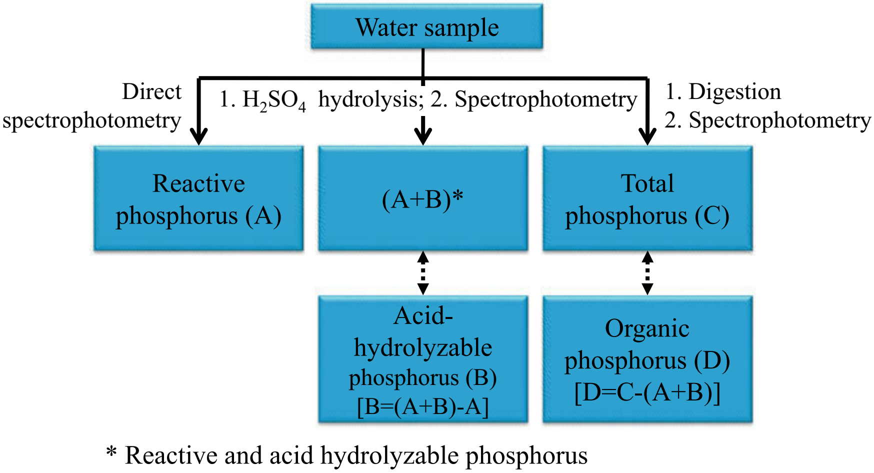

Fig. 1 Steps for the analysis of phosphorus fractions

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