Eurachem

Scientific Workshop in Connection with Eurachem General Assembly 2022

QUALITY ASSURANCE CHALLENGES OF MEASUREMENTS FROM FIELD TO LABORATORY WITH A FOCUS ON ISO/IEC 17025:2017 REQUIREMENTS

Online Workshop

16-18 May 2022

Book of Abstracts

Organized and hosted by:

Georgian Laboratory Association

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Scientific Workshop in Connection with Eurachem General Assembly 2022

"Quality Assurance Challenges of Measurements from Field to Laboratory with a Focus on ISO/IEC 17025:2017 Requirements", 16-18 May 2022

Hosted and organized by: Georgian Laboratory Association (GeLab) – Tbilisi, Georgia

Foreword

The international scientific workshop on “Quality assurance challenges of Measurements from field to Laboratory with a focus on ISO/IEC 17025:2017 requirements” is organized in connection with Eurachem General Assembly 2022 and hosted by Georgian Laboratory Association (GeLab) in Tbilisi, Georgia. The workshop is organized as an online event and offers participants a unique opportunity to network, and share experiences in the field of quality assurance in field and laboratory measurement.

The workshop is held over three days, from 16 to 18 May 2022 and includes 6 sessions with lecture and poster presentations. In addition to the main sessions, 2 parallel sessions are planned each day focusing on actual topics related to selection and use of certified reference materials, proficiency testing, uncertainty and compliance assessment, and validation of sampling procedures.

The lectures and posters cover a wide range of issues from different spheres of studies and provide insights into existing challenges, as well as offer solutions in order to assure quality from field sampling to laboratory analysis.

We would like to express our gratitude to the chairpersons, speakers and attendees for their invaluable contribution to the success of the scientific workshop.

We are grateful to our sponsors for their support in organising the workshop.

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Scientific Workshop Program

16 May 2022 - Monday

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13:00 – 13:10 (GMT+4) 11:00 – 11:10 (CEST)	Opening remarks	**Nino Manvelidze,** GeLab/NTA of UNIDO-GQSP in Georgia **Cong WU,** Industrial Development Officer of UNIDO
Session 1. *Session Chair:* ***Isabelle Vercruysse*** *(Belgium)*		
13:10 – 13:25 (GMT+4) 11:10 – 11:25 (CEST)	Eurachem – a focus for analytical chemistry in Europe	**Vicki Barwick** (UK), Eurachem Chair
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13:50 – 14:15 (GMT+4) 11:50 – 12:15 (CEST)	Revision of Eurachem Guides in relation to ISO/IEC 17025 - Developments in the revision of ISO 15189	**Kyriacos Tsimillis, Sappho Michael** (Cyprus)
14:15 – 14:45 (GMT+4) 12:15 – 12:45 (CEST)	LUNCH BREAK	
Session 2. *Session Chair:* ***David Milde*** *(Czech Republic)*		
14:45 – 15:10 (GMT+4) 12:45 – 13:10 (CEST)	Proficiency Testing (PT) – a tool to improve laboratory performance	**Brian Brookman** (UK)
15:10 – 15:30 (GMT+4) 13:10 – 13:30 (CEST)	Quality control activities in microbiological food testing including PT tests and the relevant interpretations	**Turkan Abbasova** (Azerbaijan)
15:30 – 15:45 (GMT+4) 13:30 – 13:45 (CEST)	**POSTER SESSION**	
	Poster 01. Total risk assessment in oil spill source identification using normalised methods requirements	**Ana Catarina Rocha** (Portugal)
	Poster 02. Sampling plan impact on the microbiological assessment of raw milk cheese	**Sophi Meladze** (Georgia)
	Poster 03. Sampling rules for the determination of organic compounds in water (drinking, underground and surface water)	**Natalia Niniashvili** (Georgia)
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	WG 1.1. Selection and use of certified reference materials	**Marina Patriarca** (Italy)
	WG 1.2. Proficiency Testing	**Brian Brookman** (UK)
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13:25 – 13:50 (GMT+4) 11:25 – 11:50 (CEST)	Use of measurement uncertainty in compliance assessment	**Stephen Ellison** (UK)
13:50 – 14:15 (GMT+4) 11:50 – 12:15 (CEST)	Evaluating uncertainty for microbiological methods (approach in ISO 29201:2012 Water quality — The variability of test results and the uncertainty of measurement of microbiological enumeration methods)	**Bertil Magnusson** (Sweden)
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Session 4. *Session Chair:* ***Tamar Sachaneli*** *(Georgia)*		
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	Poster 04**.** Evaluation of the correlation of oceanic water parameters unmasked by representative sampling and sample analysis uncertainty	**Carlos Borges** (Portugal)
	Poster 05**.** Evaluation of the uncertainty of microplastics quantification in sediments: a bottom-up assessment	**Vanessa Morgado** (Portugal)
	Poster 06**.** Evaluation of measurement uncertainty by sampling on the example of determination of an active phosphorus compound in the soil in accordance with the requirements of ISO/IEC 17025:2017	**Ketevan Jibladze** (Georgia)
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15:10 – 15:40 (CEST)	

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13:25 – 13:50 (GMT+4) 11:25 – 11:50 (CEST)	Overview of uncertainty from sampling	**Mike Ramsey** (UK)
13:50 – 14:10 (GMT+4) 11:50 – 12:10 (CEST)	Difficulties of sampling petroleum products in non-standard conditions	**Teo Khuchua** (Georgia)
14:10 – 14:30 (GMT+4) 12:10 – 12:30 (CEST)	Sampling technique of graphene oxide-based nano metal composites and their influence on pathogenic microorganisms	**Giorgi Kvartskhava, Tamar Sachaneli** (Georgia)
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Session 6. *Session Chair:* ***Elina Bakradze*** *(Georgia)*		
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	Poster 08. Surface water and soil sampling for arsenic content determination	**Sophio Khmiadashvili** (Georgia)
	Poster 09. Impact of soil sampling on phosphorus determination results	**Nino Shagidze** (Georgia)
	Poster 10. Assuring the quality on field and laboratory measurements in the context of the risk-based approach of ISO17025:2017	**Aristos Loucaides** (Cyprus)
15:40 – 16:40 (GMT+4) 13:40 – 14:40 (CEST)	**PARALLEL BREAKOUT SESSIONS**	
	WG 2.1. Uncertainty & compliance assessment	**Stephen Ellison** (UK), **Bertil Magnusson** (Sweden)
	WG 2.2. Validation of sampling procedures	**Lorens Sibbesen** (Denmark), **Mike Ramsey** (UK)
16:40 – 16:45 (GMT+4) 14:40 – 14:45 (CEST)	SHORT BREAK	
16:45 – 17:05 (GMT+4) 14:45 - 15:05 (CEST)	Feedback from breakout sessions	

17:05 – 17:20 (GMT+4) 15:05 – 15:20 (CEST)	Closing of Day 3 Closing of the Scientific Workshop

Lecture Abstracts

Eurachem – A focus for analytical chemistry in Europe

Vicki Barwick

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Keywords: traceability, metrology, quality assurance, guidance

Established in 1989, the aim of Eurachem is to provide a focus for analytical chemistry and quality-related issues in Europe. The main objectives are establishing a system for the international traceability of chemical measurement results and the promotion of good quality practices. Eurachem currently has 35 member countries plus the European Commission, and is effectively a 'network of networks'. A requirement of membership is the establishment of a national Eurachem network which supports the dissemination of Eurachem's aims and outputs.

Eurachem also has liaison arrangements with a number of European and international organisations. In 2021 new Memorandums of Understanding were agreed with Eurolab, NMKL (Nordic Committee on Food Analysis) and the Europe Section of AOAC International. Other liaisons include: the Technical Committee for Metrology in Chemistry (TC-MC) within Euramet; European Cooperation for Accreditation (EA); European Chemical Society-Division of Analytical Chemistry (EuChemS-DAC); Cooperation on International Traceability in Analytical Chemistry (CITAC); International Laboratory Accreditation Cooperation (ILAC); Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM); International Union of Pure and Applied Chemistry (IUPAC); the CODEX Alimentarius Commission (via its Committee on methods of Analysis and Sampling); Joint Committee on Traceability in Laboratory Medicine (JCTLM) and the ISO Reference Materials Committee (ISO/TC334).

Eurachem produces authoritative guidance to support laboratories in ensuring measurement quality throughout the measurement cycle. Historically the focus was mainly on the analysis part of the cycle, with guides covering metrological traceability, method validation, measurement uncertainty and proficiency testing. However, Eurachem guides also cover other aspects of the measurement cycle, including sampling and interpretation of results against limits. All guides are available free of charge from the Eurachem website and translations of a number of guides are available [1].

In addition to the development and publication of guidance documents, a key Eurachem activity is the organization of conferences and workshops on quality assurance issues. Since 2010 Eurachem has organized over 20 workshops and training events, with truly international audiences.

This presentation will provide an overview of Eurachem's aims and activities.

References

[1] https://www.eurachem.org/index.php/publications

Activities of the Eurachem Education and Training Working Group

David Milde

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Keywords: education, training, Eurachem guides, reading list

This talk will introduce the Eurachem Education and Training Working Group (ET WG), its previous activities, current working programme, and strategy for near future. The ET WG has been established and will operate in accordance with the Eurachem Memorandum of Understanding. The group attempts to have representatives from each of the member states. Regarding previous activities, the working group organized or supported several Eurachem workshops focused on quality assurance in general or, e.g., internal quality control.

The working group members developed the following two guides: Eurachem/CITAC 'Guide to Quality in Analytical Chemistry: An aid to accreditation' [1] and Eurachem Guide 'Terminology in Analytical Measurement: Introduction to VIM 3' (TAM) [2]. Both are currently under revision and were translated into several languages. In addition to the guides, two information leaflets were prepared. One entitled 'You talk, we understand – The way out of the tower of Babel' provides an introduction to terminology in measurements and promotes TAM guide. The other one published shortly after edition of the revised ISO/IEC 17025 called 'ISO/IEC 17025:2017 - A New Accreditation Standard' gives a quick overview of the main changes in the 2017 edition of the standard. The development and maintenance of a reading list to support teaching and training of metrology in chemistry and quality assurance is another ongoing task of the ET WG. This reading list is freely accessible on Eurachem website.

The summary of activities and near future programme of the ET WG is shown in the following points:

- Collate and evaluate information on the state of education and training in analytical science in member states with respect to the development of teaching aids and training materials.
- Contribute to the development and delivery of education and training in chemical metrology and quality assurance by producing freely available materials such as the above-mentioned Eurachem guides and leaflets.
- Organise workshops on metrology in chemistry and support other Eurachem workshops.
- Collaborate with other interested organisations such as EuCheMS, Eurolab, TrainMiC, and the UK Chemical and Biological Metrology programme.

References

[1] Barwick, V. (Ed.), 2016. Eurachem/CITAC Guide: Guide to Quality in Analytical Chemistry: An Aid to Accreditation (3rd ed.). ISBN 978-0-948926-32-7. Available from www.eurachem.org

[2] Barwick, V., Prichard, E. (Eds.), 2011. Eurachem Guide: Terminology in Analytical Measurement – Introduction to VIM 3. ISBN 978-0-948926-29-7. Available from www.eurachem.org.

Revision of Eurachem Guides in relation to ISO/IEC 17025 - Developments in the revision of ISO 15189

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Keywords: Eurachem guides, risk-based thinking, uncertainty from sampling, information management

Eurachem provides important support to laboratories mainly via publications and training. All aspects referring to the competence of laboratories are addressed in guides drafted by thematic Working Groups. Some of the challenges of ISO/IEC 17025 [1] e.g. uncertainty from sampling, statements of conformity have already been addressed in existing guides; however, some of the additional requirements as well as the new philosophy introduced by the said standard made it necessary to revise two guides, namely those dealing with analytical and microbiological laboratories respectively [2,3]. Two task force groups are still working; in the meantime, a leaflet was prepared [4] to provide a comprehensive picture of what is changing in the life of laboratories with the new ISO/IEC 17025. This presentation describes the main elements of this revision. Further to this, the presentation provides a comprehensive description of the ISO/DIS 15189 [5]. The text is structured in a way similar to that of ISO/IEC 17025 and other standards in ISO/IEC 17000 series for the competence of conformity assessment bodies. Main changes introduced in ISO/IEC 17025 are also made to ISO 15189; these refer to the risk-based thinking linked with opportunities, terminology (distinction between “shall”, “should”, “may” and “can”), metrological traceability, control of data and information technology. The alternative of implementing a quality management system e.g. in accordance with ISO 9001 to meet specified requirements of ISO 15189 is also provided. The document contains the requirements for point-of-care testing (POCT) thus superseding ISO 22870 [6]. Further to the alignment with ISO/IEC 17025, ISO 15189 has to address the specific needs of medical laboratories and the objective of promoting the welfare of the patients. To this end, there is a number of particular requirements. Contrary to ISO/IEC 17025, sampling is not meant to be a stand-alone activity. On the other hand, uncertainty arising from sampling remains a challenge of how to be taken on board [7].

References

[1] ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories
[2] V. Barwick (Ed), Eurachem/CITAC Guide: Guide to Quality in Analytical Chemistry: An Aid to Accreditation (3rd ed. 2016). ISBN 978-0-948926-32-7. www.eurachem.org
[3] Eleftheriadou, M. and Tsimillis, K.C. (Eds), Eurachem guide: Accreditation for Microbiological Laboratories, Second edition (2013), ISBN: 978-91-87017-92-6. www.eurachem.org
[4] Eurachem leaflet (2018) A new ISO/IEC 17025 for laboratories. www.eurachem.org
[5] ISO DIS 15189 Medical laboratories – Requirements for quality and competence
[6] ISO 22870 (2016) Point-of-care-testing – Requirements for quality and competence
[7] Tsimillis, K.C. and Michael, S., 2022. Uncertainty from sampling: Could the requirements of ISO/IEC 17025 (2017) be adopted in Medical Laboratories? DOI: 10.4018/IJRQEH.2

Proficiency Testing (PT) – a tool to improve laboratory performance

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Keywords: proficiency, validity, improvement

A regular independent assessment of the technical performance of a laboratory is necessary to assure the validity of measurement results and should form part of an overall quality strategy. A well-established approach to achieve this independent assessment is for a laboratory to participate in proficiency testing (PT) schemes. The important role of PT is well recognised in the international laboratory competency standards, ISO/IEC 17025 [1] and ISO 15189 [2].

The primary aim of PT is to provide the infrastructure for a laboratory to monitor and improve the quality of its routine analytical measurements. A PT scheme provides laboratories with a framework for obtaining a regular external and independent assessment of their performance. PT not only addresses the measurement phase in the measurement cycle, but it also plays an important role in addressing the pre-analytical and post-analytical phases.

To maximise the benefits of PT participation it is essential that the laboratory selects the most appropriate PT scheme, that those selected are used appropriately, and that they understand how to correctly interpret their PT results. To support laboratories in these important aspects of their PT participation, Eurachem has developed a guide on the 'Selection, Use and Interpretation of Proficiency Testing (PT) Schemes' [3]. This presentation will provide an overview of the guide, highlighting some of the key aspects to support laboratories in establishing their PT participation plan.

By participating in appropriate PT schemes, a laboratory can gain many benefits; the use of PT should be much wider than the basic statement of whether the laboratory is competent or not. The Eurachem PT guide explores how laboratories can benefit from participation in PT schemes in various ways. A good overview on how a PT provider evaluates the performance of the laboratory participating is given along with guidance on how the laboratory should interpret their PT results, both in terms of performance in a particular PT round and in terms of reviewing longer term performance over multiple PT rounds.

One of the key selection criteria for the laboratory to consider when choosing the most appropriate PT scheme in which to participate is the competency of the PT provider, and as such, if they comply with the international standard ISO/IEC 17043 [4], which is currently being revised.

In conclusion, participating in PT schemes is an essential requirement for any laboratory wishing to ensure and demonstrate the validity of their analytical measurements. Key to this is establishing a participation strategy, selecting the most appropriate PT schemes in which to participate and correctly interpret their PT results. The recently revised Eurachem PT guide provides valuable advice to assist the laboratory in doing this, and the international standard ISO/IEC 17043 provides the framework for assessing the competency of the providers of such PT schemes.

References

[1] ISO/IEC 17025:2017*, General requirements for the competence of testing and calibration laboratories*, ISO, Geneva

[2] ISO 15189:2012, *Medical laboratories – Requirements for quality and competence*, ISO, Geneva
[3] B. Brookman and I. Mann (eds.) *Eurachem Guide: Selection, Use and Interpretation of Proficiency Testing (PT) Schemes (3rd ed. 2021)*. Available from www.eurachem.org
[4] ISO/IEC 17043:2010, *Conformity assessment – General requirements for proficiency testing*, ISO, Geneva

Quality control activities in microbiological food testing including PT tests and the relevant interpretations

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Keywords: quality control, microbiological analysis, food testing

Microbiological food analyses are based on biological, biochemical, molecular methods for the detection, identification or enumeration of microorganisms in food. Each day many laboratories carry out thousands of microbiological analyses of food and water in order to control the critical control points of HACCP plan for the production, final product and raw material quality and compliance with the legal requirements. To meet those specific needs, a proper method should be selected. Moreover, preference shall be given to the standard test method, if it exists in that specific area. In order to comply with the fitness for purpose, the methods should be validated or verified. Following verification of the method performance criteria, proper internal or external quality control tools should be selected to systematically monitor and evaluate the daily work. Internal quality control consists of all the procedures undertaken by a laboratory for the continuous evaluation of its work in order to ensure the consistency of results day-to-day and their conformity with the defined criteria. The quality control procedures in food microbiological testing laboratories include use of spiked samples contaminated with reference culture, checking the linearity of dilutions, assessing repeatability and reproducibility of the method during routine analysis, checking replicate counting.

This presentation aims at explaining the quality control tools for food microbiological testing laboratory with given examples in addition to the statistical tools for the evaluation of the results.

Quality control in microbiological analysis - validation, measurement uncertainty in quantitative and qualitative analysis, PT tests, Verification quality control analyses.

Validation for qualitative analysis in microbiological testing – limit of detection (LOD), precision, specificity, sensitivity.

Validation of quantitate microbiological testing - repeatability, reproducibility, trueness, recovery.

External quality control of proficiency test: - There are many proficiency tests designed for microbiological analysis. However, when choosing a PT scheme close attention should be paid to ISO/IEC Guide 43-1 (Proficiency testing by interlaboratory comparisons – Part 1: Development and operation of proficiency testing schemes) and ILAC G13:2000 (Guidelines for the requirements for the competence of the providers of proficiency testing schemes) requirements and instructions related to test method, matrix, and work range in current laboratory.

Conclusion: to give reliable results for microbiological analysis, the laboratory should apply both internal and external quality control programmes. Depending on the obtained results, all possibilities which can influence the test result should be reset.

References

[1] EA-4/10 Accreditation in Microbiological Laboratories
[2] NMKL Report 5: Quality Assurance Guidelines for Microbiological Laboratories

Assessment of performance and uncertainty in qualitative chemical analysis: The Eurachem/CITAC Guide

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[2] Faculdade de Ciências, Universidade de Lisboa, Portugal

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Keywords: qualitative analysis, validation, uncertainty

Many chemical analyses are strictly qualitative, providing no numerical value, and many quantitative analysis procedures involve a prior demanding confirmation of the presence of the species to be quantified. Those analyses only play their role properly if the qualitative analysis is sufficiently reliable for the purpose.

This communication presents the recently published Eurachem/CITAC guide on the assessment of performance and uncertainty in qualitative chemical analysis [1].

The guide presents some useful tools to describe the performance of qualitative analytical methods, show that qualitative analysis methods are valid, and that reported qualitative results are sufficiently reliable to support definitive conclusions on the tested item.

The guide defines qualitative analysis as “classification (of the tested item) according to specified criteria” typically in one of two classes, such as the presence or non-presence of a chemical species above a detection limit.

While classification can depend on qualitative or quantitative criteria, or on both, analytical performance for qualitative analysis procedures can be reported as a contingency table with the probability of true or false classifications. Such a table can be used to provide a range of different metrics that describe the performance of an analytical procedure, and can also be used as the basis for expressions of confidence (“uncertainty”) in a qualitative analytical result.

The guide discusses the difficulty of quantifying the performance of a highly selective qualitative analysis method and, in cases where qualitative determinations rely on quantitative criteria, shows how modelling or simulation of quantitative indications can be used to characterise the performance of qualitative analysis.

The document also discusses how the uncertainty of qualitative analysis results can be reported and presents some examples of assessing the performance and uncertainty in chemical and biochemical analysis.

References

[1] R. B. Silva, S. Ellison (Ed.), 2021. Assessment of performance and uncertainty in qualitative chemical analysis. Eurachem. (wwww.eurachem.org)

Use of measurement uncertainty in compliance assessment

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Keywords: measurement uncertainty; conformity assessment; decision rules

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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. The treatment of measurement uncertainty in compliance decisions involves the establishment of a 'decision rule' that states how measurement uncertainty should be used in coming to a decision. Depending on the circumstances, and particularly on the risks associated with making an incorrect decision, the decision rule may be different in different circumstances.

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" [1]. This guide makes use of established procedures in other sectors, particularly ASME [2]. In particular, it introduces the concept of "guard bands" – regions that, with the permitted limits, define a range of acceptable values for a measurement result. This can be used 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.

References

[1] S L R Ellison and A Williams (Eds). Eurachem/CITAC guide: Use of uncertainty information in compliance assessment. (First Edition) (2007). Available from https://www.eurachem.org.

[2] ASME B89.7.3.1-2001 Guidelines for Decision Rules: considering Measurement Uncertainty in Determining Conformance with Specifications.

Evaluating uncertainty for microbiological methods (According to ISO 29201 Water quality — The variability of test results and the uncertainty of measurement of microbiological enumeration methods)

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Keywords: microbiology, uncertainty

In microbiology the main uncertainty components for the analytical uncertainty for a sample delivered to the laboratory, u_{anal}, are according to ISO 29201.

- u_o – operational (technical) uncertainty due to the use of the technical procedure;
- u_d – distributional (Poisson) uncertainty or intrinsic variability due to taking a test portion of a laboratory sample. Note: Normally a test portion is taken from the laboratory sample but in the case the *whole* laboratory sample[1] is used for analysis u_d is set to zero;
- u_{conf} – increase in the distributional uncertainty due to result from confirmation;

Additional uncertainty contributions for solids and viscous fluids according to ISO 19036.

- u_{matrix} – uncertainty arising from imperfect mixing of the laboratory sample. Mainly relevant for solids and viscous liquids. Provided that the whole laboratory sample can be made homogeneous, u_{matrix} can be set to 0.10 $\log_{10}$ CFU/g (≈ 23%) according to section 6.2 in ISO 19036.

Additional uncertainty from sampling:

u_{samp} – uncertainty due to sampling is considered in Annex D.

The scope also gives information on reporting:

- CFU < 10; summary of proposed reporting in ISO standards
- CFU ≥ 10; relative uncertainty in % or asymmetric intervals

[1] Laboratory sample is “Sample prepared for sending to the laboratory and intended for inspection or testing”, from ISO 19036.

Method validation – overview of accreditation requirements

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Keywords: method validation, valid methods, accreditation requirements, laboratory responsibility

The concept "Method Validation" was appearing in the analytical societies during the 90s, but it didn't become a formal (formulated) requirement for accreditation until the emergence of the new ISO/IEC standard 17025 "*General requirements for the competence of testing and calibration laboratories*" in 1999. Validity of the methods applied in analytical laboratories (i.e., reliability and fitness for the purpose of their application) has though been discussed for decades, and the understanding of the concept – and how it can be achieved – is still developing. This is of course dictated by the technological development within analytical chemistry – but also by the changes in political approaches to the mechanisms of conformity assessment. Hence, there has also been some changes in the requirements for method validation from the first issue in 1999 to the present 2017-version of the conformity assessment standard ISO/IEC 17025 [1] - the common basis for accreditation of laboratories.

Eurachem issued its first guideline on the subject in 1998, "*The Fitness for Purpose of Analytical Methods. A Laboratory Guide to Method Validation and Related Topics*" and a revised version was issued in 2014 [2]. Right now, intensive work is carried out towards a 3rd revised version, and as it can be seen the focus in the guidance is on 'The Fitness for Purpose" which is actually the key point talking about method validation (or valid methods), which is very much in line with the approach in the ISO/IEC 17025:2017

This presentation will give an overview of the development in requirements on method validation for accredited laboratories to comply with, but it will also be pointing forward to new challenges (e.g., related to the sampling preceding the testing in the laboratory, use of non-targeted methods etc.) in relation to ensuring the application of valid analytical methods in the analytical laboratories – now and in the future.

References

[1] ISO/IEC 17025:2017, "General requirements for the competence of testing and calibration laboratories", ISO Geneva 2017.
[2] B. Magnusson and U. Örnemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from www.eurachem.org.

Planning method validation studies

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Keywords: validation, planning, documentation

Method validation should be carried out according to a documented procedure. Planning is therefore an essential step of the validation process. Although the requirements for a validation plan may be stated in sectoral guidelines, and national accreditation bodies may specify minimum requirements, it is generally left to the laboratory to devise a suitable plan to meet its particular requirements. Eurachem has published guidance on method validation planning and reporting as a supplement [1] to the guide 'The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics' [2]. The keys issues to consider when planning a validation study are outlined below:

- The method to be validated: A written procedure (such as a standard operating procedure) describing the method to be evaluated should be available.
- Critical steps in the method and instrument requirements: Be familiar with the method and aware of any critical steps that require particular attention.
- Extent of the validation: Decide which performance characteristics (e.g. precision, bias, limit of detection) need to be studied and the level of replication required.
- Performance criteria: Decide the criteria against which the chosen performance characteristics will be assessed (e.g. target values for precision, bias, limit of detection).
- Experimental design and order of evaluation of performance characteristics: Choose suitable experimental designs to maximise the information obtained.
- Materials to be analysed: Identify appropriate materials for evaluating different performance characteristics (e.g. certified reference materials (CRMs), spiked samples and test samples.
- Evaluation of the data and assessment of fitness for purpose: Include details of how the data will be evaluated, including any statistical parameters that will be calculated from the data and any statistical tests that will be applied.

The supplement [1] provides an example of a planning document which laboratories can use as the basis of their own plan. The plan is structured in such a way that when the experimental work has been completed, it can be easily converted into a validation report.

References

[1] V. Barwick (ed.), Planning and Reporting Method Validation Studies – Supplement to Eurachem Guide on the Fitness for Purpose of Analytical Methods (2019). Available from www.eurachem.org.

[2] B. Magnusson and U. Örnemark (eds.), Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics (2nd ed., 2014), ISBN 978-91-87461-59-0. Available from www.eurachem.org.

Validation and uncertainty estimation of HPLC method combined with ultrasound-assisted extraction procedure for quantitative determination of hesperidin obtained from citrus peel

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Keywords: validation, hesperidin, measurement uncertainty, extraction, HPLC

Citrus waste material represents a low-cost and rich source of valuable bioactive compounds such as essential oil (mostly composed of d-limonene), beta-carotene, hesperidin and pectin. Hesperidin ($C_{28}H_{34}O_{15}$) is the most abundant bioflavonoid in citrus peel and has potential benefits in the prevention of many diseases [1].

The aim of this study was to validate a new, effective, selective, specific and reproducible method obtained with a combination of the high-yield sequential stepwise ultrasound-assisted extraction (UAE) procedure and analytical procedure for quantitative determination of hesperidin in the dry extracted product and the citrus waste - tangerine peel.

The tangerine waste material was dried using the laboratory drying standard procedure [1]. The two-stage sequential UAE was carried out in the controlled temperature (30±2ºC) conditions under ultrasonication by ultrasound power at 25 kHz. The chromatographic analysis was performed using LC-20AD Prominence Shimadzu HPLC System (Japan) and the HPLC column - Agilent SB-C18 4.6×250 mm, 5 µm (USA) with an isocratic elution of mobile phase. The external standard method was used for quantification of hesperidin. The proposed method was validated with respect to the following validation parameters: robustness, system suitability test, specificity, linearity-range, precision, accuracy, sensitivity, limits of quantification (LOQ) and detection (LOD). A design of experiments by Placket-Burman approach was used for the robustness study of the combined method and the critical factors were selected based on the risk assessment. The measurement uncertainty of the proposed method was evaluated based on the four-step process using the combination of two appropriate - bottom-up and top-down approaches using the method validation data.

The LOD and LOQ of the analytical procedure were 0.00001 mg/mL and 0.000025 mg/mL, respectively. The calibration curve (0.000025-0.5 mg/mL) is linear and the square of correlation coefficient is equal to 0.99992. The determined average amount of hesperidin in the dry citrus peel samples is equal to 35.36 ± 3.14 mg/g (k=2, 95% level of confidence). The mean recovery of the combined method is 91.48 %. The purity of the dry extracted product of hesperidin is not less than 90 %. The research results confirm that the proposed method is validated and can be used for quantitative estimation of hesperidin in the dry citrus peel as a starting material of the citrus waste reprocessing manufacture.

References

[1] Tsitsagi, M., Ebralidze, K., Chkhaidze, M., Rubashvili, I. and Tsitsishvili. V. 2018. Sequential Extraction of Bioactive Compounds from Tangerine (Citrus Unshiu) Peel. Annals of Agrarian Science, 16(2), pp.236-241.

ISO/IEC 17025:2017 requirements for in-house methods and sampling errors during the validation process by GC-MS

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Keyword: method validation, sampling errors, in-house methods

ISO 17025 requires the laboratories to use appropriate methods that meet the needs of the client. If non-standard methods are to be used, obtaining confirmation from the client is mandatory, and methods should be fully validated and documented. Documented in-house (own) methods of a laboratory are subject to a high-level validation. Method validation and verification provides objective evidence that a method fits its aim, meaning that the particular requirements for a specific intended use are fulfilled [1]. During the validation numerous relevant overall performance indicators are applied such as selectivity, specificity, accuracy, precision, linearity, range, limit of detection (LOD), limit of quantification (LOQ), ruggedness, and robustness. Those can lead to various types of errors, including, as follows: errors in procedure, measurement errors, transcription errors, conversion and calculation errors [2,3]. Actually, analytical measurement errors are divided into two categories – systematic (or determinate) and random (or indeterminate) errors [3].

In its turn, sampling errors are statistical errors that arise in case sample does not represent the whole population. Determination of sampling errors that impact the data variation should be given an important consideration in food expertise. It is recommended to dissociate analytical method validation from validation of the sampling methods to reduce the risk of erroneous results. Sampling errors may greatly influence validation data, lead to incorrect conclusions, impact trends, add variation or significantly affect data accuracy and precision in other ways. Sampling errors include sample definition, sample collection, and sample handling [4].

References

[1] ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories
[2] Tuija Pihlström Amadeo R. Fernández-Alba, Miguel, Carmen Ferrer Amate, Mette Erecius Poulsen, Ralf Lippold, 2019, Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed, SANTE/2017/11813.
[3] J. N. Miller and J. C. Miller 2018. Statistics and Chemometrics for Analytical Chemistry. Harlow, England: Pearson.
[4] Patricia L. Smith, 2011. Sampling Errors in Validation, Journal of Validation Technology.

From field to laboratory for scientific research (Challenges related to sampling and transportation)

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Keywords: sampling, qualitative analysis, reliability

Sampling plays an important role in laboratory analysis. Qualitative representative samples provide a correct assessment in chemical and microbiological analysis for various parameters. Using proper sampling procedures, proper equipment, and safe systems helps reduce the risk of incorrect results.

The method of sampling for analysis is determined to some extent by the state of the aggregation of test sample - gas, liquid, or solid. For example, in the determination of trace elements, the problem of sampling is often combined with the problem of contamination, and to some extent depends on the homogeneity of the samples. The quality of the control of the chemical composition of the analysed samples largely depends also on the methods of sampling. Since the measurement of the composition of a laboratory sample during control, as a rule, is preceded by experimental operations of sampling and sample preparation, their error significantly affects the reliability of the control results.

Proper Sampling and preparation of samples is one of the important steps for a good laboratory analysis. The result of the study, its accuracy and reliability depend not only on modern equipment and experienced specialists, but also on compliance with the requirements for sampling. Errors in sampling technology can distort the results of laboratory tests, or make them completely unfeasible. For example, the main problem in assessing the content of mycotoxins in measured products is the uneven distribution of these substances in products, especially in whole grains. Different parts of the same batch may contain different concentrations of mycotoxins.

Each object of study has its own rules for sampling, which are prescribed in regulatory documents. Methods and conditions for sampling air, soil, water, waste, food and feed products, etc. have been developed. There are also international sampling standards.

Sampling conditions for different types of analyses also differ. For example, sampling for microbiological analysis implies that the sample must contain only those microorganisms that are present in the medium under study, so that they are preserved until the beginning of the analysis itself, and that no other microorganisms enter the sample. And the conditions for sampling for chemical analysis should be such that no foreign substances get into the sample and that the chemical elements contained in it remain intact and do not enter into any chemical reactions.

So, the general principles of sampling are: 1) the sample must reflect the place of sampling; 2) the sample must reflect the conditions of its selection; 3) the sample must be stored and delivered to the laboratory under such conditions that the composition of the studied components and the properties of the analysed sample remain unchanged; 4) the sample must be taken in the volume that corresponds to the research methodology and is sufficient for analysis.

Based on the foregoing, a competent and professional approach to sampling is extremely important. In this area, there are official rules that include, in addition to sampling, requirements for transportation, preparation for storage, and safety. Their strict observance minimizes the errors of the results, helps chemists and biologists to cope with their tasks - to see the real picture of the quality of the analysed sample.

Evaluation of the measurement uncertainty based on in-house validation data

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Keywords: measurement uncertainty, method validation, top-down evaluations

Measurement uncertainty can be evaluated from a detailed assessment of all the individual uncertainty components separately or by quantifying uncertainty components with equivalent nature combined. Alternatively, precision and trueness studies conducted during method validation can be used to quantify between-days random effects, and systematic effects kept constant during precision studies, respectively.

This simplified way of evaluating the measurement uncertainty can be designated “top-down based on in-house method validation data”, being popular for not requiring the complex dissection of the measurement in individual uncertainty components. This approach is applied regardless of the complexity of the analytical method, for scopes known to be associated with equivalent measurement performance. For methods applicable to a large number of matrices associated with significantly different measurement performance, parallel uncertainty evaluations for different matrices classes can be required.

However, due to the simplicity of algorithms used, frequently some challenges associated with these uncertainty evaluations are overlooked, such as: (1) how measurement uncertainty varies with the concentration; (2) how measurement precision increases with replicate analysis; (3) the impact of sample heterogeneity on the measurement uncertainty; (4) how results from the analysis of various reference materials can be used to quantify systematic effects and (5) how correcting or not correcting results for observed bias impacts on the uncertainty.

This communication summarises the progress of the Measurement Uncertainty and Traceability working group on developing guidance for the “top-down evaluation of the measurement uncertainty based on in-house method validation”.

Overview of uncertainty from sampling

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Keywords: measurement uncertainty, sampling, duplicate method

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It is now widely accepted that the measurement process begins at the moment that the primary sample is taken, rather than when the laboratory sample arrives at the laboratory. Consequently, the uncertainty of a measurement value (MU) needs to include the contributions from all stages in the measurement process, including the sampling and physical sample preparation. Guidance on the estimation of measurement uncertainty arising from sampling (UfS) has been published by Eurachem/CITAC [1]. This issue has recently acquired greater urgency as the inclusion of UfS in estimates of MU is now required for accreditation of laboratories to ISO/EC 17025, according to the most recent documentation [2]. This talk aims to give an overview of UfS, how it arises, and how it can be estimated, primarily using examples taken from the Eurachem UfS Guide [1].

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] ISO/IEC 17025:2017 – General requirements for the competence of testing and calibration laboratories

Difficulties of sampling petroleum products in nonstandard conditions

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Keywords: sampling, petroleum products, non-standard conditions

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According to Paragraph 7.6 of the international standard “ISO 17025-2017/2018, General requirements for the competence of testing and calibration laboratories”, laboratories shall identify the contributions to measurement uncertainty. When evaluating measurement uncertainty, all contributions that are of significance, including those arising from sampling, shall be taken into account using appropriate methods of analysis. Where the test method precludes rigorous evaluation of measurement uncertainty, an estimation shall be made based on an understanding of the theoretical principles or practical experience of the performance of the method.

Nonstandard sampling procedures described in this report are summarized by practical example of nonstandard condition.

Petroleum products sampling is a procedure, by which representative samples of petroleum products are obtained for subsequent analysis. Sampling rules are set out in standard procedures and their maintenance is one of essential requirement, especially for arbitration.

In some cases, due to engineering and technical difficulties representative samples of petroleum products cannot be obtained in accordance with the standard procedures. In this case, the client is notified and once his/her consent is obtained, an optimal method of representative sampling shall be identified. This will reduce risks that could negatively impact final results.

References

[1] ASTM D 4057-19, Standard Practice for Manual Sampling of Petroleum and Petroleum Products.
[2] GOST 2517-12. Petroleum and petroleum products, Methods of sampling.
[3] GOST 31873-2012. Petroleum and petroleum products. Methods of manual sampling

Sampling technique of graphene oxide-based nano metal composites and their influence on pathogenic microorganisms

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Keywords: sampling technique, nano metal composites, pathogenic microorganisms

Over the last years, the food industry has been developing the use of nanomaterials because of their specific nanoscale properties. The risk of bacterial attacks has grown enormously in the food sector. This increasing risk stimulates scientists to develop new antibacterial nanoparticle substances that have no side effects and are easy to implement. There is a variety of metal NPs which have received great attention due to their unique antimicrobial properties, strong cytotoxicity towards a broad range of microorganisms. The active biocide substances improve the quality of the food, extend shelf life, and prevent or delay spoilage [1,2].

In this study, the antibacterial activity of synthesized graphene oxide composites - rGO-Ag, rGO-Cu, rGO-TiO_2 [3] was studied against indicator bacterial strains. Microbial cultures of *P. aeruginosa, B. subtillis, and E. faecalis* were used for the experiments. The standardized broth cultures of test microorganisms were incubated with different concentrations of GO nanocomposites (20,40 µg/mL) in saline at 37°C for 24 h to evaluate the antimicrobial effect. Samples were homogenized before and after microbial inoculation. As controls, bacteria were incubated with fresh, diluted TSB (1:10). The colony-forming units (CFU) were counted from each plate and the antibacterial activity was expressed as a function of cell viability loss.

The results demonstrated that, depending on the homogenization of the sample, rGO-AgNP exhibited significant antibacterial activity compared to rGO-Cu, and rGO-TiO2. All nanocomposites fully inhibited the growth of *Enterococcus faecalis* significantly reduced *P.aeruginosa, Bacillus subtillis* growth at 2 and 24 h in a time-dependent way compared to the respective time controls.

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References

[1] Carbone, M., Donia, D. T., Sabbatella, G., Antiochia, R., 2016. Silver nanoparticles in polymeric matrices for fresh food packaging. Journal of King Saud University – Science, 28, 4, pp. 273-279.

[2] Jacobs, A., Renaudina, G., Forestier, C., Nedelec, J., Descamps, S., 2020. Biological properties of copper-doped biomaterials for orthopedic applications: A review of antibacterial, angiogenic and osteogenic aspects, Acta Biomaterialia, 117, pp. 21–39.

[3] Dundua, T., Sachaneli, T., Kvartskhava, G., Gamkrelidze, N., Meladze, S., Sarajishvili, K., Japharidze, M., 2021. Preparation of graphene oxide composites containing nanosized silver, copper, and titanium oxide and study of their biocidal properties. *6th International Conference "Nanotechnology" (GTU nano 2021)*, Tbilisi, Georgia.

Impact of soil sampling on results of laboratory analysis

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Keywords: soil sampling, soil organic carbon, measurement uncertainty, uncertainty from sampling

Sampling is of particular importance during soil analysis as it has a large impact on the final results, as it may be the largest source of errors. Proper sampling and suitability of the sampling method with the purpose of the study are essential in making the right assessment. Significantly different compositions can be obtained due to soil heterogeneity when using different sampling strategies on the same site. Soil heterogeneity can be a result of site-specific characteristics, which should be taken into account prior to the selection of sampling strategy. High variability of soil properties is a function of a high degree of variability in the soil-forming factors, which leads to the formation of soil and influences its spatial distribution [1]. Based on the development of a certain soil, sometimes, it may become more homogenous due to the destruction of soil genetic horizons by erosion processes or through cultivation on arable land. Studies indicate, that among soil-forming factors topography is one of the best predictors of soil conditions [2]. Besides that, the sampling design should consider the variability of soil property itself as some properties of soil tend to have much higher variability than others [3].

Considering heterogeneity of soil and a high degree of variability of certain soil properties, it is essential to assess the impact of sampling on measurement results. In the current study, we estimated measurement uncertainty using robust analysis of variance (RANOVA) [3] on the example of organic carbon content in black soils from arable lands of Eastern Georgia. The study showed that sampling has a considerable contribution to the measurement uncertainty with a total variance of 28.3%, and an expanded relative uncertainty of 17.7 %, while the percentage variance from the analysis was 7.8%, and expanded relative uncertainty – 9.3%. Obtained values underline the importance of sampling and its impact on the final results of the measurement should not be underestimated.

References

[1] McBratney, A. and Minasny, B., 2007. On measuring pedodiversity. Geoderma, 141(1-2), pp.149-154.
[2] Hartemink, A.E., Zhang, Y., Bockheim, J.G., Curi, N., Silva, S.H.G., Grauer-Gray, J., Lowe, D.J. and Krasilnikov, P., 2020. Soil horizon variation: A review. *Advances in Agronomy*, *160*(1), pp.125-185.
[3] Carter, M.R. and Gregorich E.G. (2008). Soil sampling and methods of analysis. Boca Raton (Fla.): CRC Press, Cop.
[4] Eurachem/EUROLAB/CITAC/Nordtest/ AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches, M. H. Ramsey, S. L. R. Ellison and P. Rostron, Eurachem, Second edn, 2019, ISBN (978-0-948926-35-8), available from http://www.eurachem.org.

Poster Abstracts

Total risk assessment in oil spill source identification using normalised methods requirements

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Keywords: oil spill identification, Monte Carlo simulation, compositional match, true and false result rate, total risk

1. Introduction

Oil spills and refined products are a widespread problem and lead to high costs for society at economic and environmental levels. National laws and international conventions (*e.g.*, MARPOL 73/78) establish systems for the management of infractions and compensations. However, objective and reliable pieces of evidence are needed in order to assign liability at the judicial level. Chemical analysis has been a valuable support for judicial investigations. These analyses are performed on samples collected in the spill and suspected source(s) of its origin and require a sufficiently comprehensive and solid characterisation of the chemical composition of the samples. Oil spill source identification is based on the distinct relative content of hydrocarbons in crude oil and its derivatives. These products differ in chemical compositions due to the different conditions of oil formation and oil refining processes. Thus, these products have unique compositional characteristics, namely fingerprint, allowing the differentiation among their types and origins [1].

During the last five decades, forensic laboratories have developed and optimised analytical methodologies capable of identifying oil spill sources with a high level of objectivity and reliability. The methods use gas chromatography, *e.g.*, Gas Chromatography-Mass Spectrometry (GC-MS), to provide an extensive characterisation of the oils fingerprint allied to conventional and/or multivariate statistical methods for data processing and interpretation. Ratios between chromatographic signals of specific components, *i.e.*, diagnostic ratios (DR), have been widely used to distinguish oils and refined products and identify the source of an oil spill. Depending on the product type, a set of DR is defined to characterise the fingerprint of the product. The equivalence between a set of relevant DR, observed for the spill and suspected source samples, indicates sample composition equivalence and allows the identification of the spill origin. The most common approaches to compare DR observed in a spill, and suspected source samples are based on Student's t statistics and a maximum relative difference of 14% [2-4]. The Nordtest method suggests the triplicate analysis of samples and the comparison of DR using Student's t statistics (S-t), which assumes that the probability distributions of DR follow the normal distribution [2]. In contrast, the CEN 15522-2 methodology, revised in 2020 and submitted for publication as a reference standard (prEN 15522-2), suggests the analysis of duplicate samples and uses a single criterion (SC) for evaluating DR equivalence [3, 4]. This approach for DR comparison relies on empirical knowledge that experts have acquired over the years, assuming a most probable analysis dispersion (relative standard deviation of 5%). However, the chromatographic signals that define the DR have specific dispersion and correlation,

responsible for deviations to the normality of their probability distributions [5]. Therefore, if inadequate assumptions or approximations are considered, erroneous assessments can be made about the equivalence of DR and, consequently, about the fingerprints equivalence of compared samples. The development of approaches for results interpretation based on statistical methods that better describe the reality of the variables under study is essential to ensure identification quality. This work compares the two mentioned common approaches for the assessment of DR equivalence, *i.e.*, S-t and SC, with a developed alternative approach based on the accurate simulation of correlated chromatographic signals using the Monte Carlo Method (MCM). The comparison among the three approaches consisted in defining criteria for DR comparison and quantifying the probability of true acceptance and false rejection of compositional equivalence between two samples (*i.e.*, total risk).

2. Methodology

In this study, it was developed a tool based on DR values simulator developed by Rocha *et al.* (2022) to estimate the confidence limits for DR comparison, as well as the probability of the true acceptance and false rejection of the compositional equivalence between samples. The tool is more flexible than the previous one regarding replicates numbers and considers the DR set defined by the recent prEN15522-2 method [4]. The tool allows the selection of the DR set depending on product type, the replicate analysis of both samples, and two possible DR formats (*A/(A+B)* and *A/B*). The confidence limits for DR comparison and the total risks of true acceptance of fingerprint equivalence were estimated for MCM, S-t, and SC approaches. Twenty-nine chromatographic signals were used to determine 22 DR, simulated simultaneously.

An extract of crude oils was analysed by GC-MS to estimate the dispersion and the correlation of the chromatographic signals used for MCM simulation. The S-t and SC approaches were compared with MCM simulations following the conditions indicated in each method. For S-t *vs* MCM were considered triplicate analysis for each sample, and the DR were calculated using *A/(A+B)* format [2]. On the other hand, for SC *vs* MCM were considered duplicate analyses for each sample and the DR were determined using *A/B* format [3, 4]. One hundred thousand simulations are performed for each chromatographic signal, generating 100 000 values of each ratio used to define the MCM confidence limits for the DR comparison. An additional set of 10 000 values of each ratio was obtained to assess the DR equivalence using the limits estimated (S-t, SC and MCM). This set of 10 000 results $\times$ 22 DR is used to estimate the total risks of true acceptance of fingerprint equivalence between samples.

3. Conclusions

The developed tool was successfully applied to assess the fingerprint equivalence between two samples using 22 DR to characterise each sample. The limits defined for the MCM approach were, in general, wider than the limits defined for S-t and SC approaches in this study. These differences impact on the total risk of true acceptance of composition equivalence between samples, showing lower total risks for the S-t and SC approaches than the MCM approach. The innovative and flexible tool developed proved to be very suitable for oil fingerprint comparison. The MCM approach describes exactly the probability distribution of the DR adapting to the statistical complexity of this variable. Therefore, this approach is more adequate for DR comparison and to estimate the quality of the identifications than the common S-t and SC approaches.

References

[1] Wang, Z.; Fingas, M; Page, D.S. Oil spill identification. *J. Chromatogr. A* 1999, *843*, 369-411. doi: 10.1016/S0021-9673(99)00120-X
[2] Daling, P.S.; Faksness, L.G.; Hansen, A.B.; Stout, S.A. Improved and standardised methodology for oil spill fingerprinting. *Environ. Forensics* 2002, *3*, 263-278. doi: 10.1006/enfo.2002.0099
[3] European Committee for Standardization (2012). Oil spill identification - Waterborn petroleum and petroleum products - Part 2: Analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses. Brussels Studies Institute. Brussels:Belgium. 138 p. (Ref. CEN/TR 15522-2:2012:E)
[4] European Committee for Standardization (2020). Oil spill identification - Waterborn petroleum and petroleum products - Part 2: Analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses. Brussels Studies Institute. Brussels:Belgium. 194 p. (Ref. prEN 15522-2:2020 E.)
[5] Rocha, A.C.; Palma, C.; Bettencourt da Silva, R.J.N. (2022). Development and validation of statistically sound criteria for the match of unweathered GC-MS fingerprints in oil spill forensics. Chemosphere, 289, 133085.

Sampling plan impact on the microbiological assessment of raw milk cheese

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Keywords: raw milk cheese, sampling plan, Escherichia coli, Enterococcus faecalis, Total Viable Count

1. Introduction

The traditional Georgian cheese 'Imeruli Kveli' is produced from cow milk to which 20 % of buffalo or goat milk can be added. It is produced in the Imereti region (Western Georgia) and most of the manufacture is based on the artisanal process of rennet curd made from raw milk [1].

Microbial variability in the production environment is particularly important for fermented foods, which rely on the action of microorganisms for their production. Many modern fermentation practices employ starter cultures as a means of standardizing the fermentation process. In the production, Imeruli Kveli producers don't use starter cultures. The cheese made from milk that has not undergone heat treatment may represent a food safety concern, especially pathogenic bacteria, such as *E. coli* and *Enterococcus faecalis* which enter the food by way of the raw ingredients or the food processing environment and change quality in the finished product [2].

A primary goal of modern cheese manufacturing is consistent product quality. One aspect of product quality that remains poorly understood is the variability of pathogenic microbial subpopulations due to temporal or facility changes within cheese production environments. Therefore, our aim was to quantify this variability by measuring by days and the storage condition in the cheese microbiome changes.

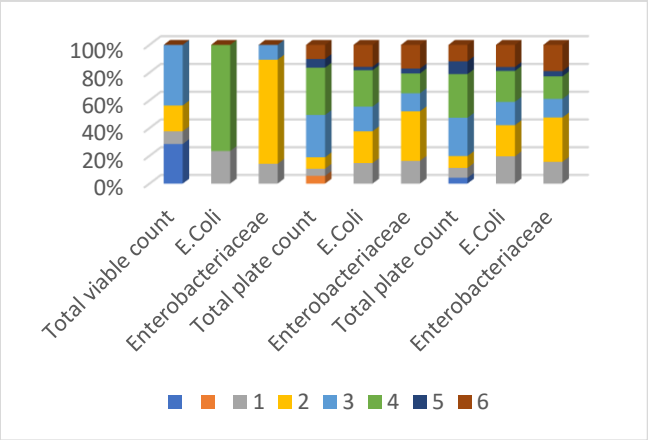
2. Methodology

Six cheese samples were prepared under laboratory conditions following the production steps described in the PGI document [1]. The samples were stored in different conditions: in the refrigerator, at room temperature, and in brine. The microbiological indicators of each sample were monitored at each relevant manufacturing step: in raw milk, fresh cheese, and fermented cheese. Detection and enumeration of targeted microorganisms in the samples Total Viable Counts, *Enterobacteriaceae,* and *Escherichia coli* were monitored by standard culture method. [3,4,5].

3. Results and discussion

The results of milk examination resulted positive for *Enterobacteriaceae*, and among these, *E. coli* was evidenced.

Chart 1. Total bacterial count, *Enterobacteriaceae,* and *E. coli* counts in cheese samples



Results of Total Viable Counts, *Enterobacteriaceae,* and *E. coli* enumeration showed that temperature has a consistent effect on the inactivation rate of all microorganisms. Brined cheeses have lower pH and much higher undissociated lactic acid levels and lower pathogen rates were observed. Results of *Enterobacteriaceae* and *E. coli* enumeration showed a bad hygienic level in all samples tested.

4. Conclusion

In Georgia, traditional cheese-making processes are carried out in small and artisanal enterprises closely linked to the area of origin. Since the traditional method of cheese production technology involves the use of raw milk, it continues to be a concern because small enterprises cannot be controlled properly. This study provides an overview of the behaviour of microorganisms during the artisanal production of Georgian fermented cheese Imeruli Kveli. The obtained data point to a potential hazard of microbial growth in an early stage of milk and curd fermentation, which is incorporated into this manufacturing method. Therefore, it is necessary to know the relations between microbiological quality and safety data and artisanal manufacturing conditions, including the efficacy of critical process steps. Estimation of uncertainty of quantitative determinations derived by the cultivation of microorganisms is required to get more accurate results.

References

[1] www.sakpatenti.gov.ge
[2] Fox, P. F., Guinee, T. P., Cogan, T. M., McSweeney, P. L. H. 2017. “Microbiology of cheese ripening,” in Fundamentals of Cheese Science. Boston, MA: Springer US. pp. 333–390.
[3] ISO 6887-5. Microbiology of food and animal feeding stuffs. Preparation of test samples, initial suspension and decimal dilutions for microbiological examination. In Part 5: Specific Rules for the Preparation of Milk and Milk Products; International Organization of Standardization (ISO): Geneva, Switzerland, 2010; pp. 1–12.
[4] ISO 4833-1. Microbiology of food chain. Horizontal method for the enumeration of microorganisms. In Part 1: Colony Count at 30 Degrees C by the Pour Plate Technique; International Organization of Standardization (ISO): Geneva, Switzerland, 2014; pp. 1–16.
[5] ISO 21528. Microbiology of the food chain —Horizontal method for the detection and enumeration of Enterobacteriaceae —Part 1: Detection of Enterobacteriaceae; Part 2: Colony-count technique; International Organization of Standardization (ISO): Geneva, Switzerland, 2014, pp. 1–15.

Sampling rules for the determination of organic compounds in water (drinking, underground and surface water)

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Keywords: water, total petroleum hydrocarbons (TPH), pesticides, organic compounds

1. Introduction

Following the rules of any kind of sampling is a necessary prerequisite for obtaining reliable analysis results from any type of water supply source. We will focus on the sampling rules required to determine organic compounds. Different indicators are monitored; however, we will focus on taking the sample needed to determine organic compounds which requires many different types of analyses [1].

Sampling is associated with a variety of problems, such as:

- Selection of sampling device.
- Minimization of possible contamination of test water.
- Strict observance of transportation and storage conditions [2].

2. Methodology

Water sampling should be undertaken by using different types of devices such as bathometer, automated devices, special clamp and so on. We will focus on the sampling required for the determination of organic compounds (Total petroleum hydrocarbons; Pesticides), the determination of which requires many different types of analysis.

3. Results

Methods of storage and conservation of samples					
Name of the indicator	Material of utensils used for sampling and storage	Storage and conservation methods	Maximum recommended shelf life	Maximum recommended shelf life	Note
Total petroleum hydrocarbons	glass	Extraction and cooling to 2-5^{0}C	24 hours	Laboratory	The dish should be washed with an extractant before sampling
Pesticides	glass	Add the extractant used for extraction according to the cooling method to 2-5ºC	5 days	Laboratory	After sampling, the extractant is rapidly added or extracted at the site of sampling

4. Discussion

Monitoring of water bodies includes monitoring of surface waters (rivers, lakes, reservoirs), coastal waters, wastewater. In order to get the right results, it is necessary not only to perform the relevant analysis correctly, but also to follow the rules of water sampling first.

References

[1] Technical regulation of sanitary rules for water sampling. Resolution of the Government of Georgia N26. January 3, 2014. Tbilisi
[2] Fomin G.S. inspection of chemical, bacteriological and radiation safety according to international standards. 2010. Moscow

Evaluation of the correlation of oceanic water parameters unmasked by representative sampling and sample analysis uncertainty

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Keywords: correlation, sampling uncertainty, marine environment, Monte Carlo Method

1. Introduction

Oceanic water masses present some features that distinguish them from transitional or freshwaters. These features are conservative oceanographic parameters like temperature and salinity. Previous studies suggest the existence of relationships/correlations between nutrients and some of these conservative parameters, e.g. [1]. However, the determination of this correlation is affected and can be masked by system heterogeneity and measurement uncertainty. This masking will be larger when large and heterogeneous systems are studied.

This work describes a tool to estimate the correlation between the values of a pair of parameters estimated from a large environmental area where the impact of system heterogeneity, sampling uncertainty and sample analysis uncertainty in the assessment is considered. The uncertainty of "representative" sampling was estimated from the Monte Carlo simulation of georeferenced information affected by analytical uncertainty [2-3]. It was assessed the correlations between total oxidized nitrogen, NO_x, and temperature, *t*, distinguishable regardless of system heterogeneity and analytical uncertainty.

2. Materials and Methods

Water from an area of the Portuguese Continental Platform was sampled during two field surveys: October 2018 and May 2019. The sampling stations were located on a grid between 40.12º N and 40.46º N and 8.96º W and 9.30º W at a distance of 5 nautical miles between them. In each sampling occasion, samples of 4 L to 5 L along with temperature data were collected at 25 m depth, using an Idronaut CTD/Rosette system equipped with 8 L Niskin bottles. Samples were preserved according to validated procedures until analysis.

The determinations were performed by Segmented Flow Analysis using previously validated methods. The previously developed tool was used to obtain estimates of concentration distribution with uncertainty for the several measurands by application of the Single Sampling (SS) modelling strategy. Details regarding both the determinations and the modelling strategy can be found elsewhere [2].

The total uncertainty associated with the measurement was calculated by combining the pertaining sampling uncertainty with the analytical uncertainty.

Uncertainty components are combined as relative standard uncertainties (s'_r, s'_I and u'_T) above two times the Limit of Quantification. When observed distribution deviates significantly from normality, uncertainty components are combined by the Monte Carlo Method.

The quantification of the correlation between NO_x and *t* was performed by Pearson's correlation

coefficient, *r*. Each simulated pair of NO_x and *t* values was obtained for the same GPS coordinates avoiding losing or reducing observed correlation from system heterogeneity. It was assumed that data correlation is meaningful if the calculated *r* is greater than the tabulated *r* value (r_{crit}) for a significance level, *p*, of 0.05 (i.e., for a 95% confidence level).

3. Results

Table 1 presents the results of the Monte Carlo simulations of the concentration of NO_x (µmol L^{-1}) and *t* (ºC) in the two studied occasions affected by the respective uncertainty for the SS strategy. Figure 1 presents the results of correlation, *r*, for the selected pair of variables on the same occasions, along with the dataset dimension, *n*, and the respective graphic representation of the datasets. The "minus" sign indicates a (significant) negative correlation, with NO_x decreasing with an increasing *t*.

Table 1. Simulated uncertainty of the measurement of NO_x and *t*, from random sampling, in the studied area for 95% confidence level on two sampling occasions and relevant uncertainty components. (§ - Value obtained by the Monte Carlo Method; Analytical components of uncertainty are, for NOx: s'_I = 1.21% (Oct2018), s'_I = 6.10% (May2019) and u'_T = 3.09%). (results reported with one or three significant figures)

Parameter	October 2018				May 2019			
	Mean §	**s'_S (%) §**	**s'_r (%)**	**U' (%)**	**Mean §**	**s'_S (%) §**	**s'_r (%)**	**U' (%)**
NO_x / µmol L^{-1}	1.18	34.9	1.02	70.0	0.789	57.0	4.61	115
t / ºC	16.7	1.60	0.009	3.19	16.7	1.60	0.009	3.21

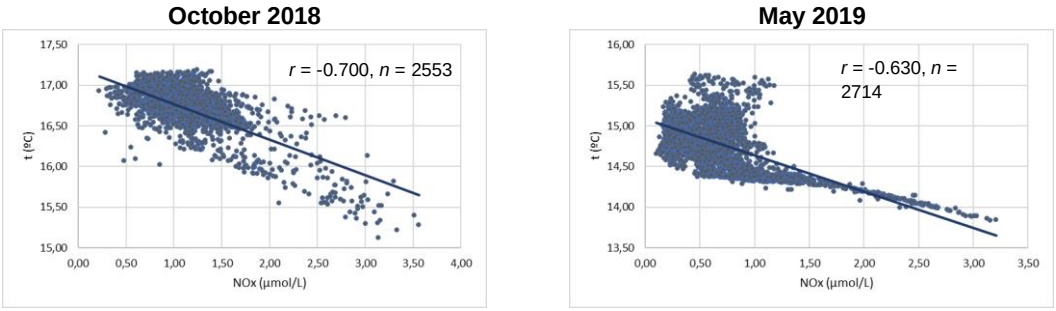

Figure 1. Correlations between NO_x and *t* for the two sampling occasions (r_{crit} ≈ 0.40 for n = 2500).

4. Discussion and Conclusions

Analysing the main features of Table 1, the relative expanded uncertainty associated with NO_x is 1 to 2 orders of magnitude higher than that of *t*. Also, for both variables, the total uncertainty main contributor is the uncertainty arising from sampling (>90% in some cases).

A detailed analysis of the graphs presented in Figure 1 allows us to check the existence, of an agglomerate of points at lower concentrations of NO_x. This agglomerate was more evident in May 2019. The stronger temperature stratification expected in the western Iberian coast in May, responsible for more homogeneous masses of water at the same depth when compared with more heterogeneous water masses in October, can explain a somewhat weaker correlation between studied parameters than the one determined for October 2018. A more heterogeneous water mass masks temperature and NO_x correlation.

Nevertheless, although for the case here presented, the correlation is slightly affected by system heterogeneity, it can be stated that it is still meaningful.

Acknowledgments

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References

[1] Iwata, T.; Shinomura, Y.; Natori, Y.; Igarashi, Y.; Sohrin, R.; Suzuki, Y. *J. Oceanogr.*, **2005**, 61, 721-732.
[2] Borges, C.; Palma, C.; Silva, R. B. *Anal. Chem.* **2019**, 91, 5698–5705.
[3] Borges, C.; Palma, C.; Dadamos, T.; Bettencourt da Silva, R.J.N. *Chemosphere*, **2021**, 263, 128036.

Evaluation of the uncertainty of microplastics quantification in sediments: a bottom-up assessment

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Keywords: microplastics; micro-ATR-FTIR; bottom-up approach; uncertainty; validation

1. Framework

The concern with the contamination of the environment with micro(plastics) is very trending nowadays due to the fact that this material is ubiquitous.

Plastic production reached over 368 million tonnes worldwide and 57.9 million tonnes in Europe in 2019 [1,2] due to its wide application. Actual statistics point that more than 60% of the global composition of marine litter is plastic and about 1.15 to 2.41 million tons of plastic are dumped into oceans every year from rivers [3,4].

The awareness of this threat to the environment and human health attracted the scientific community to the monitoring of microplastics contamination in several aquatic systems and matrices, namely, surface water, column water, seafloor sediment, and beaches.

The monitoring of the level and trends of the contamination by microplastics is essential to determine the relevance and potential sources of this contamination necessary to define strategies to reduce it. The contamination is classified regarding microplastics' physical-chemical properties. The impact of microplastics in open ocean, rivers, estuarine areas, and coastal regions compartments is only possible to understand if this contamination is characterized adequately and objectively.

2. Synopsis

This work presents the first bottom-up evaluation of the uncertainty of microplastics contamination quantification in sediments from four Portuguese inland waters, namely Ria de Aveiro, Ria Formosa, Mira and Mondego rivers.

Sediment samples were prepared according to the following procedure: (i) Sediment sieving to isolate sediment matter with the size range of microplastics; (ii) Weighing sieved sediment; (iii) Digesting the aliquot using peroxide hydrogen (H_2O_2); (iv) Separating the lighter microparticles from the densest matter of the samples using a saturated solution of sodium chloride (NaCl); (v) Filtrating the NaCl solution above the settled matter to a adequate filter; (vi) Storing filters in closed Petri dishes. The suspicious microparticles on the filters were analysed under a stereomicroscope for the identification of their physical characteristics. The chemical analysis was performed by the Perkin Elmer spectrometer Spotlight 200i Microscope System or by the PerkinElmer Spectrum Two FTIR (Fourier transform infrared spectroscopy) [5].

The bottom-up evaluation of the uncertainty of microplastics contamination quantification involved the identification and quantification of systematic and random effects affecting laboratory analysis. The

uncertainty components affecting particles counting were modelled by the Poisson-Lognormal distribution using inputs estimated from duplicate sediment analysis and the analysis of sediments spiked with microparticles. The Monte Carlo Method was used to combine the uncertainty from particles counting with the uncertainty from the determination of the dry mass of the analytical portion. The developed methodology was implemented in a user-friendly MS-Excel spreadsheet used to simulate the probability distribution function of the estimate of the measurand. Distribution percentiles were used to define confidence intervals that encloses the true value of the contamination with a defined probability.

Results demonstrated the ubiquitous presence of microplastics in all studied inland waters, reaching up to 969 microplastics per kg^{-1} associated with an uncertainty interval of [361; 2932] kg^{-1}. After the comparison of the contamination of sediment samples collected in various Portuguese inland waters, it was concluded that several samples had metrologically different contamination for 99% confidence level.

Acknowledgements

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References

[1] Birley, A.W.; Heath, R.J.; Scott, M.J. Plastics Materials, Properties and Applications. Springer Science+Business Media, New York (1988).
[2] PlasticsEurope Association of Plastics Manufactures, 2019. Plastics – the Facts 2020 An analysis of European plastics production, demand and waste data. Available from http://www.plasticseurope.org.
[3] Lebreton, L.; van der µZwet, J.; Damsteeg, J.; Slat, B.; Andrady, A.; Reisser, J., 2017. River plastic emissions to the world's oceans. Nature Communications, 8, 15611.
[4] Tekman, M.B.; Gutow, L.; Macario, A.; Haas, A.; Walter, A.; Bergmann, M. Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung. Litterbase. Online portal for marine litter available from: https://litterbase.awi.de/.
[5] Morgado, V.; Palma, C.; Bettencourt da Silva, R.J.N., 2021. Validated spreadsheet for the identification of PE, PET, PP and PS microplastics by micro-ATR-FTIR spectra with known uncertainty. Talanta, 234, 1222624. DOI 10.1016/j.talanta.2021.122624.

Evaluation of measurement uncertainty by sampling on the example of determination of an active phosphorus compound in the soil in accordance with the requirements of ISO/IEC 17025:2017

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Keywords: uncertainty, sample preparation, phosphorus, soil

1. Introduction

Uncertainty of measurement is the most important general parameter of characteristic of measurement quality and has a great influence on decisions that is made based on measurement results. Methods for estimating the uncertainty of the sampling process are insufficient. In order to make the right decision based on the measurement results, it is necessary to take the uncertainty into account, which is associated with the sampling process when assessing uncertainty. We developed an estimate of the total uncertainty of the measurement, and the uncertainty of the individual components by using a model approach and an example approach to determine the mobile phosphorus compound in the soil.

2. Methodology

Sampling scheme was drawn up: 20 samples were taken per hectare from a depth of 30 cm using a soil auger; Factors affecting the measurement were identified and could be related to sampling tools, sampling error, soil moisture, or soil sample lost from the sampling device. Since these factors are difficult to determine individually, they are generally referred to as the "depth effect"; shredding and distribution during sample preparation reduce the amount of soil sample. We have a cause-and-effect diagram of the measurement process. Samples were taken by conical and quartering methods, air dried and drilled through a hole <2 mm in diameter [1]. Determination of the phosphorus mobile compound was performed by the Oniani method (modified by Cinao) [2].

3. Results and discussion

The plot was divided into nine squares (A, B, C x 1, 2, 3) and five squares ("crosswise" across the plot), which are selected with five separate samples. The result of the measurement was determined by the arithmetic mean of the results of 5 separate samples. The concentration of the mobile compounds of the phosphorus measured in the five squares is: A1 - 500 mln^{-1}; A3 – 498 mln^{-1}; B2 – 502 mln^{-1}; C1 – 500 mln^{-1}; C3 – 498 mln^{-1}. Xscr = X ana – 500 mln^{-1}; ssqr – 2 mln^{-1} (0,4%). Standard deviation between measurement values (ssqr between samples have taken from a single quadratic. $u_{b\text{-}loc}= s_{sqr}/\sqrt{n_{b\text{-}loc}}$=0,179%. A special experiment was conducted to detect the total effect of the "depth effect" factors. Samples from 35 cm deep were taken in five "test squares". Segments 25-30 cm and 30-35 cm were separated from them and then the selected segments were combined from different squares. The uncertainty caused by the ''depth effect“ was estimated by the content of phosphorus below and above the nominal depth in the soil layers (c_-, c_+). In particular, the phosphorus content is: c_- (25-30 см) - 350 mln^{-1}; c_+ (30-35 см) – 335

mln^{-1}. The upper and lower limits were estimated: x_+ - 485 mln^{-1}; x_- - 517 mln^{-1}; Δx_- 32 mln^{-1}. Standard uncertainty u_{depth} = 9,25. When we are distributing the samples, we follow the initial samples 2 to 7 times by the method of conjugation and quartering, the mean standard deviation is -1.2. u_{dry} =0,6%). The standard uncertainty of input type A is $u_A(x_i)$ tp (v)/kp=1,085. Determined input values: sampling between sampling sites; sampling strategy; depth; sample splitting; drying; The standard uncertainty of the measuring utensils, used tools, reagents and the type of probability distribution; uncertainty budget [3], [4]. Extended uncertainty of the mass fraction of the mobile compounds of phosphorus in the soil U = 20,33.

The result of the measurement is 500 ± 20.33 mln^{-1}.

4. Conclusion

The result obtained meets the requirements of the standard.

References

[1] Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches: M H Ramsey and S L R Ellison (Eds): translation of the first edition, 2007 – Kyiv.: LLC "Yurka Liubchenka", 2015. – 156 p**.**

[2] GOST 26206-91 Soils. Determination of mobile compounds of phosphorus and potassium by Oniani method modified by CINAO.

[3] Miller, J., Miller, J. and Miller, R., 2018. Statistics and chemometrics for analytical chemistry. Harlow, England: Pearson.

[4] Williams, A., Ellison, S., Berglund, M., Haesselbarth, W., Hedegaard, K., Kaarls, R., Mnsson, M., Rösslein, M., Stephany, R., Veen, A., Wegscheider, W., Wiel, H., Wood, R., Rong, P., Salit, M., Squirrell, A., Yasuda, K., Johnson, R., Lee, J., Mowrey, D., Regge, P., Fajgelj, A. and Galsworthy, D., 2000. Quantifying uncertainty in analytical measurement. London: Eurachem.

Water sampling process at city of Batumi Chaisubani water supply headwork from surface sources and centralized water supply system, quality research and evaluation of results (from water supply source to customer)

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Keywords: drinking water quality, source of water supply, water disinfection, residual free chlorine

1. Introduction

The centralized water supply system of LLC “Batumi Water” is supplied with both: surface water and groundwater. Surface water sources are the following rivers: water of Chakvi; Koroli and its left tributary – river Lecha.

City Batumi Chaisubani’s centralized water supply system consists of: water intake structures of the rivers Korolistkali and Lecha, water treatment plant of Chaisubani (headwork of Chaisubani), repository reservoir of drinking water (Injalo, Salibauri and Todogauri).

To ensure safe, continuous and reliable supply of drinking water to customers from water supply of Chaisubani, the following was conducted: field, laboratory and cameral (office) works. The aim of this work was to conduct water sampling at city Batumi Chaisubani water supply headwork from surface sources and centralized water supply system, undertake quality research and evaluate the results.

2. Methodology

Existing literature, normative documents in force in the country were reviewed as well as potential sources of pollution were identified. A group of specialists involved in sampling was formed to carry out the planned work. They developed water sampling plan from surface and centralized water supply systems, also from water catchment system. Surface and drinking water sampling points were selected for fieldwork. Water samples were taken in accordance with the requirements of the legislation [3]. The list of organoleptic, physico-chemical, microbiological and parasitological parameters to be tested in the surface source of water supply and drinking water of centralized water supply has been determined according to the normative documents [1, 3]. Research methods and quantities of samples required for the study were selected. Defined parameters (temperature, pH, turbidity, dissolved oxygen, TDS, Residual Free Chlorine, etc.) [4] were measured at the time of sampling on the spot and a list of indicators that require sample pre-conservation with appropriate preservatives.

Containers meeting the requirements of ISO standards were prepared for water sampling.

Portable tools were prepared prior to the start of the excavation work. The appropriate devices were calibrated on-site before sampling. The relevant information was entered (sample number, research parameter, date of sampling, etc.) on the waterproof labels used for marking the bottles,

Some sort of problematic issues arose during the sampling: 1. The normative document [3] provides guideline for taking of test water samples from the water supply source up to 100 meters upstream and 100 meters downstream. When taking water samples from a surface water supply source, this was not possible due to the geographical location (narrow valley, difficult terrain), which was mentioned in the water sampling act [2]; 2. Due to the changing climatic condition of the city of Batumi, there was a sudden change in the weather. At the scheduled time of sampling, the high turbidity of the water was determined due to which the field work was postponed until the improvement of the weather. 3. Two field brigades were involved in the study to ensure the timely transportation of microbiological samples. One was taking samples while the other was transporting the aforementioned.

Laboratory test were performed at Ltd “Scientifical-Research Institute of Sanitary, Hygiene and Medical Ecology”, Laboratory Research Centre of the Ministry of Agriculture of the Autonomous Republic of Adjara and LLC “Batumi Water”- Chemical and Microbiological Laboratory.

During the field works, Korolistskali and Lecha river samples were taken from the Chaisubani headwork’s water intake structures arranged on rivers. Water flows from the Chaisubani headworks to the water treatment plant, where it goes through the treatment stages. The treated drinking water from the Chaisubani headworks flows into the Injalo, Salibauri and Todogauri reservoirs, from where it is distributed to the city of Batumi through water supply network in different districts. Samples of drinking water entering and leaving the reservoirs were taken from the inlet and outlet pipes of the tanks installed on the reservoirs.

3. Results and discussion

The water of the river Korilistavi and Lecha, taken from the Chaisubani headwaters, belongs to low mineralized waters. The surveyed indicators comply with the existing normative requirements [3]. The treated drinking water entering and leaving the Chaisubani water supply reservoirs belongs to the soft mineralized, hydrocarbonate-calcium type soft water. The defined organoleptic, microbiological, physico-chemical, radiological and parasitological parameters comply with the requirements of the "Technical Regulation of Drinking Water".

4. Conclusion

According to the research results, the study indicated that the waters of the Korolistskali and Lecha rivers belong to the low mineralized waters. The impact of supply reservoirs on the quality of water leaving the reservoirs was not revealed. The quality of water from all storage reservoirs complies with the requirements of the "Technical Regulation of Drinking Water" [1].

The water quality of City of Batumi Chaisubani water pipeline is harmless for the health of the population, complies with the established norms and ensures safe, uninterrupted and reliable supply of drinking water to consumers.

References

[1] "Technical Regulation of Drinking Water" approved by the Resolution of the Government of Georgia N 58 of January 15, 2014.

[2] "Rules of Procedure for Disinfection of Central and Local Water Supply Drinking Water with Chlorine and Disinfection of Water Supply Facilities" approved by the Resolution N62 of the Government of Georgia of January 15, 2014.
[3] “Technical Regulation on Surface Water Pollution of Georgia”. approved by the Resolution N425 of the Government of Georgia of December 31, 2013.
[4] Guidelines for Drinking-water Quality FOURTH EDITION, 2017. pp. 66; 68; 147; 205; 224; 228; 240.

Surface water and soil sampling for arsenic content determination

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Keywords: sampling, arsenic, environment water, soil

1. Introduction

Sampling is considered to be a crucial step in the analysis of inorganic compounds in the environment. This article describes field sampling techniques and provides detailed step-by-step procedures for the collection and preservation of all major environmental matrices (water and soil). The aim is to signify the importance of sampling to the overall analytical procedure. Finally, quality control issues to be considered in environmental sampling are given.

2. Methodology

The sampling procedure includes the following: the preparation of containers, collection of samples, preservation of samples, identification of containers and recording of the sample and environmental conditions of collection for traceability purposes.

For chemical analysis of arsenic, the detailed procedures for specific collection, preservation and storage procedures have been documented based on the Georgian legislation: 1) for water - Decree of the Government of Georgia №26 (dated January 3, 2014 Tbilisi) on “Approval of the Sanitary Rules of Water Sampling"; 2) for soil - Decree 38/N of the Minister of Labor, Health and Social Affairs of Georgia dated February 24, 2003; 3) also depending the reference standard – (i) ISO 5667-3:2018 Water quality -- Sampling -- Part 3: Preservation and handling of water samples and (ii) Standard Methods for the Examination of water and wastewater, 23rd Edition.

The set of sampling bottles, types and volumes for each individual test must be detailed in the Sample collection / Reception record.

3. Results and discussion

The water samples were taken from the rivers: Sokhurtula, Kajiani, Lukhuni at the entrance to the Uravi Village, and near the confluence with the Rioni river.

All soil samples for the analysis were collected (20-25 cm) depth using sterile materials in hermetic plastic 50 ml flasks, transported to the laboratory at 4°C, and stored at - 20°C.

Soil samples were taken in the village Uravi, near the sarcophagus, near the ruined building of the factory and factory area.

The arsenic content in the water samples taken from the rivers did not exceed the maximum permissible concentration.

As for the soil, in comparison with the maximum permissible concentrations approved in Georgia, arsenic content in all the taken soil samples was above the norm.

4. Conclusions

This study highlighted that:

For any chemical analysis, the most important step is sampling and sample preparation. The purity of the sample should be ensured before taking a measurement to obtain the optimum results. Otherwise, the results will be always affected at least to a certain extent.

In the Ambrolauri region of Georgia, after the plants producing arsenic concentrate were closed in the 90s, plant premises were demolished and drums with arsenic waste material remained scattered around openly for some years.

In the past, the Ministry of Environment took several efforts to initiate discussions on the issue with different line ministries, scientific institutions, NGOs, other experts as well as with local population to develop and implement effective measures.

The study shows that nowadays the situation has improved in comparison with the previous years as high concentration of arsenic in surface waters has not been observed;

In soils there was fixed the exceedance of permissible concentrations but still situation is better than it was in previous years.

References

[1] Georgian legislation for water - Decree of the Government of Georgia №26 January 3, 2014 Tbilisi on Approval of the "Sanitary Rules of Water Sampling";
[2] Decree 38/N Approved by the Minister of Labour, Health and Social Affairs of Georgia on 24 February 2003;
[3] Reference standard – (i) ISO 5667-3:2018 Water quality -- Sampling -- Part 3: Preservation and handling of water samples and (ii) Standard Methods for the Examination of water and wastewater, 23rd Edition.

Impact of soil sampling on phosphorus determination results

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Keywords: soil, phosphorus, chemical analysis

1. Introduction

Soil is a special natural body, transient between living and non-living nature. Its fertility is one of the main factors for plant life. Phosphorus composition is a significant parameter among the chemical characteristics of soil, as it is one of the main nutritional elements of plant, playing a principal role in metabolism [1].

Low concentration of phosphorus in a liquid fraction of the soil limits its uptake by plant. Lack of the element destroys interchange of energy and metabolism in plant; the period of maturation is prolonged, quality of the production falls, leaves change their colour and grow slowly [1].

The aim of the project was to study the concentration of phosphorus in different type soils and to select the corresponding method for the element determination according to soil type; as well as to set replicate experiments for the evaluation of method accuracy; to determine the relation between sampling, processing and final results [2].

2. Experimental methods

Soil samples from different sites of Georgia were selected for the experiment. Phosphorus was determined after Olsen and Machigin. Applied methods differ by the preparation of soil extracts, which depends on the soil type. In the case of acid soils, the solution of sodium bicarbonate was used for extraction, while for alkali soils – ammonium carbonate. Phosphorus in extracts was revealed by the ammonium molybdate. The optical density of the received blue colour solution was measured at 700nm wave length [3, 4].

3. Results and discussion

Content of phosphorus was different in various types of soils. Tables 1 and 2 demonstrate that phosphorus concentration in the upper layers of soil was higher compared to lower ones. The pH played a significant role as well since it regulates the ions concentration in a liquid fraction of soil, affects the phosphorus retention, and correspondingly its existence in the soil.

Table 1: Phosphorus determination in the soil after Machigin

Sample	1		2		3		4		5	
Depth of a layer (cm)	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40
pH	7.76	7.86	7.88	8.03	7.88	8.15	7.70	7.85	7.88	7.70
P_2O_5 (mg/100 g)	6.09	2.97	2.95	0.99	1.74	1.22	2.02	1.74	2.87	2.06

Table 2: Phosphorus determination in the soil after Olsen

Sample	1		2		3		4		5	
Depth of a layer (cm)	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40
pH	6.41	6.59	6.01	5.97	5.02	4.74	5.69	5.83	5.50	5.29
P_2O_5 (mg/100 g)	19.06	16.28	10.72	9.14	9.36	6.38	13.50	13.24	15.66	10.78

4. Conclusion

The reliability of the obtained results depends on many other parameters. One of the important factors is right sampling in field conditions and laboratory processing in accordance with the relevant standard.

The investigation of the influence of environmental conditions on the accuracy of analysis and final results is planned in future.

References

[1] Henry D. Foth.1990. Fundamentals of Soil Science. Michigan State University;
[2] Ganesh S., Fahmida Khan, Ahmed M. K., Velavendan P., Pandeyand N. K. Kamachi Mudali U.2012. Spectrophotometric determination of trace amounts of phosphate in water and soil. Water Science & Technology, 66(12):2653-8;
[3] Determination of mobile compounds of phosphorus and potassium by Machigin method modified by CINAO. GOST 26205-91;
[4] Agrochemical methods of soil research. Publishing house "Nauka" M. 1975. pages 146–150 (in Russian).

Assuring the quality on field and laboratory measurements in the context of the risk-based approach of ISO17025:2017

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1. Introduction

The advent of the latest edition of the accreditation standard has been pushing labs towards more realistic approaches in relation to risk appraisal and risk management. Field sampling as well as in-situ measurements, in particular, require good perception of risk, in the overall context of assuring the quality of sampling protocols, sample integrity, transportation conditions and analytical results.

2. Methodology

While under normal circumstances, most site measurements can be repeated and verified under laboratory conditions, it is seldom the case that specific measurements, that need to be carried out on-site, cannot be replicated or verified in the lab, and they form at the same time an integral part of the interpretation of the in-lab acquired results.

In other instances, observations carried in-situ dictate the sampling protocol to be applied and also the actual testing methods to be followed in the lab. All of the above issues will be considered with detailed reference to real-life in-situ and laboratory-acquired data, stemming out of the 30+ years' experience of our lab.

It is worth mentioning that additional quality assurance requirements that have been imposed in the context of the recent pandemic will also be examined.

3. Results and Discussion

Gathered data from different sampling and testing scenario will be analysed on the basis of a risk-based approach and appropriate decision rules and guidelines will be put forward. It is highlighted that the risk factor will be examined both from the side of the lab as well as from the side of the customer.

4. Conclusion

In view of the above, it becomes evident that testing laboratories involved in sampling must have an excellent understanding of the customer processes. This is critical in obtaining the right sample, from the right point, at the right time, especially in the context of failure investigations and crisis management in general.

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