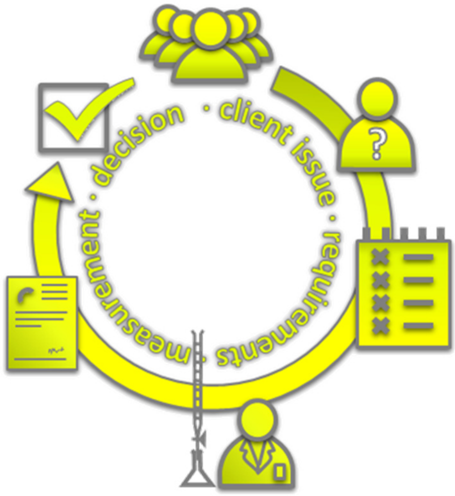
Eurachem

A Focus for Analytical Chemistry in Europe
25th anniversary

WORKSHOP ON QUALITY IN ANALYTICAL MEASUREMENTS

FROM SPECIFICATION TO DECISION



BOOK OF ABSTRACTS

LISBON, 19-21 MAY 2014

http/eurachem2014.fc.ul.pt

WELCOME MESSAGE

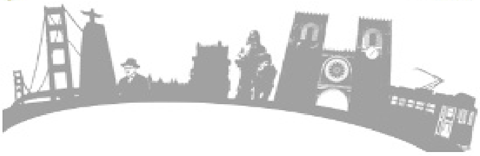
Dear Colleagues,

On the occasion of the celebrations of the 25th anniversary of Eurachem, the "Measurement Uncertainty and Traceability" Working Group, with the collaboration of the Working Groups on "Method Validation", "Proficiency Testing", and "Education and Training" of this network, are organising a workshop on "Quality in Analytical Measurements: From specification to decision". This event will discuss the most relevant features of the measurement process, starting from the identification of the analytical problem to the final decision on measurement result. The measurement process also involves defining quality requirements for measurements, the development and validation of measurements meeting these requirements, the production and reporting of measurements with uncertainty, and the interpretation of the analytical information. Measurement adequacy for an intended use relies on measurement traceability and uncertainty. Although not being part of the measurement process itself, analyst training, laboratory proficiency testing and management requirements of the quality assurance program, are relevant for the success of the measurement.

The Workshop will begin with the presentation of the history and achievements of Eurachem, which has played a relevant role in understanding and improving the measurement process in chemistry, and will close with possible challenges for metrology in chemistry. In between the most relevant steps and supports of the measurement process will be discussed, focussing on the identification of knowledge gaps, lack of the materialisation of adequate units, or on the adequate application of available measurement supports. All these topics will be introduced and some Case Studies presented before breakout sessions, giving participants the opportunity to identify problems and discuss their solutions.

Wishing this event becomes a pleasant and rewarding opportunity for all participants who can this way contribute to Eurachem's Activity Plan for the coming years,

Ricardo Bettencourt da Silva
Workshop Secretary



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B. Brookman
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SCIENTIFIC PROGRAM

Monday, May 19
The measurement cycle: Part I

8:00	Registration	
9:00	Welcome Sub-Director of FCUL, Prof. Dr. José Rebordão Eurachem Chair, Bertil Magnusson Eurachem-Portugal, Ricardo Bettencourt da Silva RELACRE President, Álvaro Ribeiro	
Session:	**Eurachem 25th Anniversary** **The measurement cycle** Chair: B. Magnusson	
9:15	Eurachem – how it began	A. Williams
9:30	What Eurachem has achieved	M. Walsh
9:50	The measurement cycle	W. Wegscheider
10:20	Coffee	
Session:	**Setting requirements for measurement validation** Chair: M. F. Camões	
10:50	Setting the measurement requirement	R. B. Silva
11:20	Method validation and verification	L. Sibbesen
11:50	JRC contribution to the fitness for purpose of analytical methods for food and feed matrices	F. Cordeiro
12:10	Assessment of the determination of total sulphur in fertilisers by ICP-OES	M. J. Nunes
12:30	Lunch	
Session:	**Bias evaluation and proficiency testing** Chair: M. Walsh	
13:30	Recovery/ bias evaluation	I. Leito
14:00	Proficiency Testing (PT) – a tool to improve laboratory performance	B. Brookman
14:30	Use of interlaboratory study to better define the characteristics of dispersion of results in natural gas analyses	E. Basset

14:50	Assessing a New Approach (Triple A-Classification) to Evaluate Performance-Underperformance of Laboratories Participating in the EU Proficiency Tests for Multi-residue Analysis of Pesticides in Fruits and Vegetables	A. Valverde
15:10	Tea	
15:40	Parallel breakout sessions on: 1) Setting the measurement requirement (Chair: R. B. Silva) 2) Method validation and verification (Chair: M. Patriarca) 3) Challenges in recovery/bias evaluation (Chair: D. Milde)	
17:10	Report back from the breakout sessions	
17:55	**Closing**	
18:15	-	
19:15	**Workshop dinner – Mundial Hotel**	

Tuesday, May 20
The measurement cycle: Part II

Session:	**Measurement traceability and uncertainty** Chair: A. Williams	
9:00	Traceability in chemical analysis – Are we ready to deliver?	H. Emons
9:30	Uncertainty evaluation for analysis and sampling	S. Ellison
10:00	Specifications and traceability in the pharmaceutical industry	K. Byrialsen
10:20	Estimation of measurement uncertainty in the fluorometric determination of ammoniacal nitrogen in seawater by continuous flow analysis (CFA)	I. Claramunt
10:40	Coffee	
Session:	**Compliance assessment** Chair: W. Wegscheider	
11:10	Reporting the result and assessment of compliance	B. Magnusson
11:40	NMIJ Analytical Skill-Upgrade Training Program	K. Chiba
12:00	Quality assurance of chemical analysis: classification, modeling and quantification of human errors	I. Kuselman
12:20	Lunch	
13:20	Poster session	
14:50	Tea	
15:20	Parallel breakout sessions on:	
	1) Challenges in uncertainty evaluation (Chair: A. Williams)	
	2) Traceability and use of reference materials (Chair: S. Ellison)	
	3) Use of uncertainty in assessment of compliance (Chair: J. Engman)	
16:50	Report back from the breakout sessions	
17:35	**Closing**	

Wednesday, May 21
Underpinning the measurement cycle

Session: **Quality Assurance and Training**
Chair: P. De Bièvre

9:00	QA/QC to underpin the measurement cycle	P. Bianco
9:30	Key skills for the analytical scientist: Assessing competence in the laboratory	V. Barwick
10:00	Courses of Study and Interest-based Subjects	M. F. Camões
10:20	Training needs to understand Quality Assurance	K. Tsimillis
10:40	Coffee	
11:10	Where next	M. F. Camões
11:30	Where next: Three parallel discussions about the same topic 1) Group I (Chair: M. Suchanek) 2) Group II (Chair: B. Magnusson) 3) Group III (Chair: W. Wegscheider)	
12:15	Report back from Breakout Sessions	
12:45	**Closing** Rector of the University of Lisbon, Prof. Dr. José Cruz Serra Coordinator of CCMM-FCUL, Prof. Dr. Carlos Nieto de Castro Eurachem Chair, Bertil Magnunsson Eurachem-Portugal Ricardo Bettencourt da Silva RELACRE President, Álvaro Ribeiro	
13:00	Lunch	

EURACHEM 25th ANNIVERSARY – THE MEASUREMENT CYCLE

INVITED LECTURES

Eurachem – how it began

Alex Williams

Chairman EURACHEM/CITAC Measurement Traceability and Uncertainty WG;
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A personal recollection of the events that enable me to propose the setting up of a network called Eurachem and the subsequent discussions within Europe, which developed the proposal, defined its objectives and set out its framework of operation.

IL – 2

What Eurachem has achieved

Máire C. Walsh

Eurachem Chairperson Nov 1995 – May 1998; email – mcwalsh@iol.ie

Eurachem's achievements over the past 25 years will be evaluated against the Memorandum of Understanding (MoU) signed in 1990 and its implementation through the various Strategic Plans. Current Plan 2013-2017 is available at www.eurachem.org

Section 2 of the MoU deals with the strategies aims and objectives and 2.1 states; "The aim of EURACHEM is to provide a forum for European laboratories and other organisations to promote the adoption of common principles of valid analytical measurement and collaboration on the various tasks required to achieve mutual acceptability of test data".

The Mission Statement as outlined in the Strategic Plan is;

- To promote best practice in chemical measurements and in measurements where chemistry is coupled with other disciplines.
- To develop strategies which will cater for new and emerging analytical technologies.
- To address the needs and expectations of the analytical community in the 21st century.

The measurement cycle

Wolfhard Wegscheider

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Despite the long standing tradition in analytical chemistry of upholding the role and prime importance of quality aspects, recent observations on results in proficiency testing and real samples suggest that the reliable achievement of acceptable quality can still not be taken for granted. It is likely that the reasons for this sobering finding are complex, not easily spottable and even harder to avoid. A logically structured approach with great potential is a closer examination of the customers´ needs by mapping them onto the performance characteristics of the anticipated analytical procedure. This may be regarded as a "*measurement cycle*" if it is followed up to the actual usage of measurement results in the decision process of the customer.

Such a cycle can be regarded as a specific implementation of section 4.4.1 of ISO 17025.

This activity undoubtedly adds to the complexity (and cost!) of the data generation business, but is being regarded useful for sensitive results in environments where great risks are involved with wrong decisions (cf.[1] for a discussion in the health sciences).

The formal means to arrive at more reliable decisions is to reduce the size of the guard band where no decisions can realistically be made[2]. This is accomplished by a reduction of measurement uncertainty through optimization of a procedure or by even resorting to an alternative measurement principle coupled with an improvement of robustness. The "old" knowledge[3, Fig. 3] that precision must be controlled prior to the control of bias is complemented in quality-by-design approaches by the notion that the factors influencing precision are not necessarily those that influence bias[4]. This leads to robust design methodology[5]. The potential impact of these principles on analytical quality[6] will be discussed.

1. F.D. Lasky, R.B. Boser, Clin. Chem. 43 (1997) 866-872.
2. Eurachem/CITAC Guide, Use of uncertainty information in compliance assessment, S.L.R. Ellison and A. Williams, eds., 2007.
3. J.K. Taylor, Anal. Chem. 55/6 (1983) 600A-608A.
4. G. Taguchi, Introduction to Quality Engineering, Unipub/Kraus Intern. Publications, White Plains, NY, 1986.
5. M. Arvidsson, I. Gremyr, Qual. Reliab. Engng. Int. 24 (2008) 23-35.
6. F.G. Vogt, A.S. Kord, J. Pharm. Sci. 100 (2011) 797-812.

SETTING REQUIREMENTS FOR MEASUREMENT VALIDATION

INVITED LECTURES

Setting the measurement requirement

Ricardo Bettencourt da Silva

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Measurements in chemistry are performed for a variety of reasons ranging from compliance assessment, distinguishing analysed items or characterising a new material. The assessment of the compliance of a silver alloy with a specification, the assessment of the distribution of a drug in organs of a test animal or the characterisation of a meteor, are some of such examples. In all these cases measurements must be fit for the intended use. The quality of a measurement traceable to an adequate reference, is quantified by its uncertainty. Therefore, the decision of measurement adequacy involves checking if uncertainty magnitude is smaller than a target value: target measurement uncertainty: "measurement uncertainty specified as an upper limit and decided on the basis of the intended use of measurement results"[1]. For instance, if differences of more than 10% must be distinguished in the concentration of a drug in test animal organs, measurement results must be reported with a relative standard uncertainty not larger than 2.4% (i.e. 10%/4.2[2]). The target measurement uncertainty should be set as part of defining the measurement requirement and be a reference both for procedure validation and for subsequent measurements.

In order to guarantee the successful comparison of the estimated and target measurement uncertainties, adequate target values of other performance parameters, determined prior to the measurement uncertainty, should be set.

Some analytical fields have target values of these performance parameters defined, while others just define target measurement uncertainty since relevant uncertainty components are not reflected in conventional performance parameters.

This communication presents some examples where target measurement uncertainty has not been set previously and suggests how this can be defined based, on decision rules, on target values of some performance data, on performance data of measurements known to be fit-for-intended used, on the magnitude of trends or differences to be distinguished and on target values of equivalent or related analytical problems. It is also discussed how the variability of uncertainty estimation should be considered in the comparison of estimated and target measurement uncertainties.

1. JCGM, *International Vocabulary of Metrology—Basic and General Concepts and Associated Terms (VIM)*, 3rd Ed., BIPM, France, **2008**.
2. R. Bettencourt da Silva, *Water* 5 **(2013)** 1279-1302.

IL – 5

Method Validation and Verification

Lorens P. Sibbesen

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Performing analytical measurements is probably something done many times every minute somewhere around the world. It is typically done in a laboratory by analytical professionals on behalf of some clients/customers who need information on the composition or content of some material for the sake of making a decision related to the material.

Clients/customers (mostly) don't know much about analytical methods

- what they can be used for
- how they should be performed to give reliable results
- that the results always has some (sometime even significant) uncertainty to it
- that there may be alternative methods for the same task (…and these may even give different results!)
- etc.

and they may become rather frustrated once they realize how much their decisions (AND the consequences of making the wrong decisions!) rely on confidence in the actual laboratory performing the analytical measurements for them!

Sometimes it is a question of "Blind Faith" from the side of the clients/customers!

On other occasions they may wonder about results being different from time to time – or from laboratory to laboratory!

It is therefore crucial, that the laboratories are in good contact with their clients/customers to clarify the actual expectations/requirements – and that they based on this can provide "objective evidence" that the method performed can give reliable results for the analytical task handled in the laboratory.

Method Validation or Verification is one of the very important tools (but not the only one!) for providing the "objective evidence" for convincing the client/customer, that the method chosen for the task can…

- be applied on the samples delivered to the laboratory
- handle the expected levels of component(s) (analytes) in the samples (low or high)
- give the same results (on similar samples) over time – and when applied in a different laboratory

This may be rather complicated in many situations where issues like interference problems, very low levels of analytes, limited performance of instrumentation etc. etc. is the case.

The Eurachem Guide “Fitness for Purpose of Analytical Methods” - which will be out in it’s second revised version this year - is dealing with all these issues and giving good guidance on how the laboratory can provide the objective evidence through method validation or verification.

ORAL COMMUNICATIONS

JRC contribution to the fitness for purpose of analytical methods for food and feed matrices

Fernando Cordeiro, Ioannis Fiamegkos, Piotr Robouch, Beatriz de la Calle

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There is an increased need for the development and validation of analytical methods to assure measurement reliability at more challenging maximum legal limits for contaminants in foodstuffs.

The International Measurement Evaluation Programme (IMEP®), a non-commercial proficiency testing provider, supports the European legislation, the harmonisation of analytical measurements and the improvement of the analytical capabilities of laboratories by organising interlaboratory comparison exercises, aimed to validate methods of analysis (collaborative studies, CTs). To fulfil these commitments IMEP follows international guidelines (ISO and AOAC INT.).

Examples will be presented, all leading to international standards (either ISO or EN) ultimately demonstrating the fulfilment of the requirements towards the guidelines and the reliability of the data analysis.

- IMEP-25: in support to Directive 98/83/EC (Drinking Water Directive) on the determination of dissolved bromate.[1] The outcome of this CT was adopted as ISO 11206.
- IMEP-32: in support to Directive 2002/32/EC on the determination of inorganic arsenic in animal feed of marine origin.[2] The outcome of this CT was adopted as EN 16278.
- IMEP-115: in support to EC Regulations 1881/2006 and 882/2004 on the determination of methylmercury in seafood[3] The Technical Committee 275 of the European Committee for Standardisation (CEN) agreed to formally standardise the method, which will become a European Standard.
- IMEP-41: In support to EC Regulation 1881/2006 on the determination of inorganic arsenic in food (2014).

1. ISO 11206: 2011 - Water quality - Determination of dissolved bromate - Method using ion chromatography and post column reaction.
   Determination of Dissolved Bromate in Drinking Water by Ion Chromatography and Post Column Reaction: Interlaboratory Study, F. Cordeiro, P. Robouch, F. Schmitz, M.B. de la Calle, *J. of AOAC INT.*, Vol. 94, N° 5 (2011) p. 1592-1600.
2. EN 16278:2012 - Animal feeding stuffs - Determination of inorganic arsenic by hydride generation atomic absorption spectrometry (HG-AAS) after microwave extraction and separation by solid phase extraction (SPE).
3. IMEP-115: Determination of methylmercury in seafood by elemental mercury analysis. A collaborative study. F. Cordeiro, J. Calderón, S. Gonçalves, M. H. Lourenço, P. Robouch, H. Emteborg, P. Conneely, M-F. Tumba-Tshilumba, B. De la Calle, J. of AOAC INT., Vol. 97, N° 2 (2014) p.

OC – 2

Assesment of the determination of total sulfur in fertilisers by ICP-OES

M. João Nunes, M. João Moura

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email - mjoao.nunes@iniav.pt, email - mjoao.moura@iniav.pt

The fertiliser European market complies with the regulation (EC) nº 2003/2003.[1] It determines at Community level the designation, definition and composition of certain fertilisers (EC fertilisers). This regulation stipulates the rules for chemical fertiliser type, composition and the specific analytical methods used in the determination of nutrients pertaining to the classification of different fertiliser types.
This work presents a strategy for assessing the performance of the determination of total sulfur present in fertilisers extractable by boiling in diluted hydrochloric acid in the form of sulfates following EN 15960 standard[2] and quantification by inductively coupled plasma with optical emission spectrometry (ICP-OES).[3]
The measurement procedure validation involves checking the adequacy of the linear weighted regression model for the calibration of the ICP-OES, the determination of the limit of quantification, the assessment of measurement repeatability, intermediate precision and trueness, and the evaluation of the measurement uncertainty using the differential approach.[4] This validation was carried out using reference materials of different types of fertilisers. A rigorous quality control of the measurement is essential to ensure that compliance decision is reliable.[5] Subsequently to measurement procedure validation, test quality control is implemented. The measurement performance is assessed by checking the metrological compatibility of known and measured concentration of control standards and reference materials considering respective uncertainties.[6]

1. Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers, Official Journal L 304, (2003), P. 0001-0194, Annex IV.
2. EN 15960:2011, Fertilizers — Extraction of total calcium, total magnesium, total sodium and total sulfur in the forms of sulfates. European Committee for Standardization. Brussels.
3. EN 15749:2009 – Fertilizers - Determination of sulfates content using three different methods. Method B specifies the method using inductively coupled plasma optical spectrometry (ICP-OES). European Committee for Standardization. Brussels.
4. A. G. Correia, R. J. N. Bettencourt da Silva, F. Pedra, M. J. Nunes, Accreditation and Quality Assurance 19 (2014) 87-97.
5. Eurachem, CITAC, Use of uncertainty information in compliance assessment, 1st edn. 2007.
6. JCGM, International vocabulary of metrology—basic and general concepts and associated terms (VIM), JCGM 200 (2008) (www.bipm.org/vim).

POSTERS

Accuracy in niacin quantification in food matrices, by an RP-HPLC method

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This work intended to evaluate accuracy of niacin quantification in food matrices, by an RP-HPLC method, in order to validate it for four different food groups: legumes, grains, dairy products and fish.

The analytical method was a RP-HPLC with fluorometric detection, based on EN 15652:2009. Samples (1 to 10 g) were submitted to an acid hydrolysis with 0.1mol/l HCl for 30 min in an autoclave at 121ºC. After filtration, 50 µl of the solutions, were injected and separated at 37 ºC on a HPLC system. The stationary phase was the Fortis C18 5 µm (150 x 4,6 mm) column and the mobile phase consisted of 0.07 mol/l phosphate buffer, 0.075 mol/l hydrogen peroxide and 5x10-6 mol/l copper sulphate, at a 1 ml/min flow rate. Excitation and emission wavelengths were 322 nm and 380 nm, respectively. Quantification was made with five external standards. Results were expressed in mg/100 g.

To evaluate precision, at least one matrix of each food group was chosen: roasted peanuts, canned green peas, wheat bran, powder milk and canned tuna. Method trueness was assessed by testing five different reference materials from FAPAS and NIST. Each FAPAS sample 2160, 2166, 2172, 2176 (Breakfast Cereals) were tested once over a period of 14 months and, NIST 1849 (Infant/Adult Formula) was tested twice in the same period.

In the precision study, the five matrices were tested in triplicate in four different days. Repeatability and intermediate precision standard deviations (Sr and SPi) were calculated, for each matrix, trough ANOVA ($p < 0.05$). Repeatability and Intermediate precision limits; r and Pi were calculated using the following formulas: $r = 2.8 * S_r$ and $Pi = 2.8 * S_{Pi}$. Trueness was evaluated from the z-scores obtained.

The obtained mean, Sr and SPi (mg/100 g) were respectively 13.4/0.52/1.25 (peanuts), 0.59/0.02/0.05 (green peas), 18.2/0.23/0.78 (wheat bran), 0.73/0.02/0.06 (powder milk) and 9.5/0.24/0.60 (tuna).

The r and Pi values ranged from 0.05 to 1.46, and from 0.14 to 3.50, respectively.

All the │z-scores│ obtained for FAPAS samples were <1 and, the │z-scores│obtained for NIST reference material were both <2.

The repeatability data obtained in this study, for niacin in different food matrices were in accordance with the ones presented in the method standard EN 15652:2009. Trueness evaluation using breakfast cereals and formulas revealed a good method/laboratory performance. Accuracy evaluation, using representative matrices and niacin contents, showed the method suitable to its purpose and fit to be submitted to accreditation by an external entity.

P – 2

Method validation of heavy metals such as arsenic, lead and cadmium in meat and meat products by inductively coupled plasma-mass spectrometry

Turkan Abbasova, Saida Kamalova, Aydan Hamidullazade, Sevil Hasanova

State Committee for Standardization, Metrology and Patent the Republic of the Azerbaijan Experimental Testing Centre AzTEST Food and Agricultural Products Testing Laboratory, Baku;
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Heavy metals may cause significant diseases in central nervous system, reduce the mental health, damage the blood composition, and affect the normal functions of vital organs. Therefore the main task of our laboratory is to analyze and detect the trace and toxic elements in human consumed food. The NMKL method used at the laboratory was recognised by international accreditation body for validation arsenic (As), cadmium (Cd) and lead (Pb) in meat and meat products. The method is based on the determination of trace metals by inductively coupled plasma-mass spectrophotometer after pressure digestion. Sample is firstly digested in a microwave oven with an aid of nitric acid and 30% hydrogen peroxide. Digested sample, which is diluted with deionised water to the known volume, is nebulised and aerosol transferred to a high frequency inductively coupled plasma. The high temperature of plasma is used to dry the aerosol and to atomise and ionise the elements. The ions are extracted from the plasma and transferred to mass spectrophotometer where the ions are separated by their mass/charge ratio. The quantification of elements was based on calibration curves constructed for each batch of analysis. Calibration standard solutions were prepared at five concentration levels covering the concentration range of the analyzed samples. For validation studies, meat sample (meat paste) were spiked at four levels of As, Pb, and Cd that at least covers their estimated limit of quantification level, maximum residue level (MRL), and 0.25-5 times of MRLs. These units depend from traces (As, Cd, Pb). Two specialists being familiar with the method performed the validation during several days. The work was distributed between them, thus, the precision data reflects the within laboratory reproducibility. Altogether 85 samples were analyzed. The experimental results revealed that the relative standard deviations for repeatability (RSDr) and for reproducibility (RSD_R) are ranged from 0, 89% to 8,85% and 4.96% to 12.06% respectively. Average recoveries are above 102, 53%, except for lead with the average recoveries of 93, 66% at its limit of quantification level. For monitoring the validity of the method, the laboratory participated into proficiency test the results are within the acceptable Z score. The uncertainty of the analytical result has been estimated by using validation data^2 and combined relative standard uncertainty is ranged from 0, 05 to 0.13. As a result, recoveries, RSDr, and RSD_R values for each element were within the

acceptable range according to the criteria specified in 2002/657/EC EU Regulation[3] and the original method.[1]

Keywords: trace metals, ICP-MS, method validation and uncertainty estimation

1. Nordic Committee on Food Analysis. 2007. Trace Elements-As, Cd, Hg, Pb and other elements. Determination by ICP-MS after pressure digestion. No:186.
2. Barwick, V.J., and Ellison, S.L. R. 2000. Development and Harmonization of Uncertainty Principles, Part (d): Protocol for uncertainty evaluation from validation data.
3. Commission Regulation (EC) No 337/2007 of 28 May 2007 laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzopyrene in foodstuffs.

Uncertainty sources at the determination of limit of detection and limit of quantification in gas chromatography and comprehensive two dimensional gas chromatography

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LOD and LOQ are two fundamental elements of method validation that define the limitations of an analytical method.[1-3]

The IUPAC[2] defines LOD and LOQ as the concentration, c_L, or the quantity, q_L, derived from the smallest measure, x_L, that can be detected or quantified with reasonable certainty for a given analytical procedure.

The x_L is obtained using equation:

$$x_L = \overline{x}_{bi} + k \times s_{bi}$$

where $\overline{x}_{bi}$ is the mean of the blank, s_{bi} is the standard deviation of the blank, and k is a numerical factor chosen according to the confidence level desired.[3]

The IUPAC recommends to apply $k = 3$ and $k = 10$ for the calculation of LOD and LOQ, respectively.[2] Conversion of measurement units, x_L, to concentration, c_L, is performed by calibration.

This contribution discusses procedures to estimate LOD and LOQ for undecane separated by one dimensional and comprehensive two dimen-sional gas chromatography. LOD and LOQ were estimated from blank signals obtained at equal chromatographic conditions as used for the separation of undecane. Analysis ToolPak, Microsoft Excel (2010) was used to perform statistical evaluation of blank chromatograms.

One dimensional gas chromatography

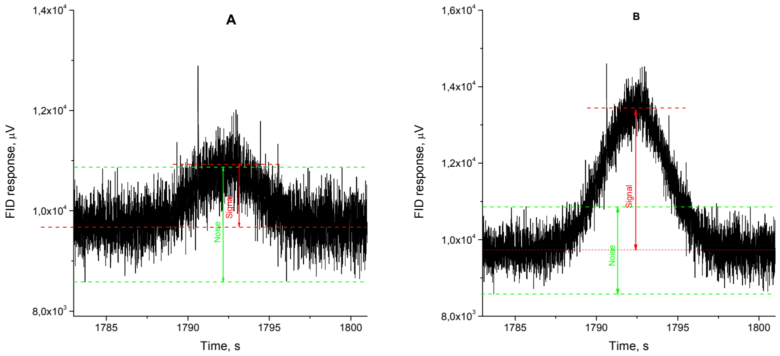

Figure 1. GC-FID records of simulated chromatograms with addition of $3 \times s_{bi}$ (A) and $10 \times s_{bi}$ (B) to the blank.

Comprehensive two dimensional gas chromatography

In this method, two columns of different selectivity are coupled in series. Very small fractions of the effluent from the first column are continuously focused via a modulator and narrow fractions are separated on the second column. Through modulation, peak eluting from the second column are much thinner that those eluted from the first column.

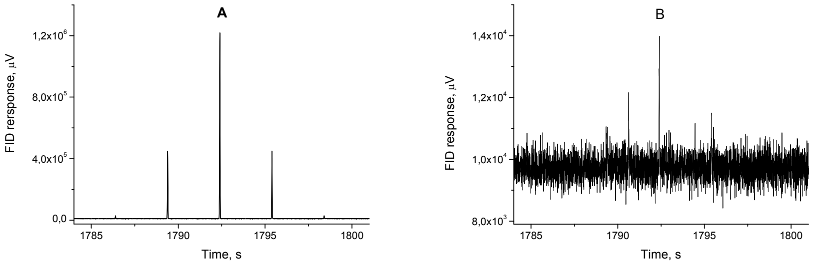

Figure 2. Pattern of 2D peaks of undecane for 3 seconds modulation time (A) and simulated chromatogram with addition of 10×s_{bi} (B) portions of undecane highest peak to the blank.

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contract No APVV-0797–11.

1. S. L. R. Ellison, A. Williams, Quantifying Uncertainty in Analytical Measurement, Third Edition, Discussion Draft 1, EURACHEM/CITAC Guide, 2011.
2. IUPAC, Pure & Appl. Chem., 67 (1995) 1699–1723.
3. ISO 11843-1, Capability of detection. Part 1: Terms and definitions. ISO, Genève 1997.

Validation of copper and mercury in marine sediments

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The validation of an analytical method is the statistical treatment from which it is possible to determine if a method complies with the quality parameters required by the laboratory. Therefore the methods should be evaluated as well as tested to confirm that it is suitable for the intended purpose. Thus, the purpose of this work is to validate two trace elements - Copper (Cu) and Mercury (Hg) in marine sediments. These two metals had a distinct treatment. The Cu study was based on the microwave digestion of the samples and quantification of the elements by Atomic Absorption Spectroscopy (AAS) analysis; in the case of Hg, the samples were analyzed and quantified directly with DMA analyzer.

Quantification of Cu and Hg was performed with calibration curves which were constructed using standard solutions for Cu and certified reference materials for Hg.

Several parameters have been taken into account and evaluated for the validation of the methods, namely: working range, linearity, sensitivity, detection limits, precision (repeatability and reproducibility) and accuracy tests.

The estimation of measurement uncertainty was done with two components: precision component (precision of duplicates) and accuracy component (inter-laboratory studies).

Therefore, the proposed methods passed in a satisfactory way the validation parameters considered and could be used to evaluate Cu and Hg in marine sediments. Both of the methods have been accredited by the Portuguese Institute of accreditation (IPAC).

P – 5

Comparison of pressurised liquid extraction and soxhlet extraction for the determination of organic pollutants in marine sediments

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In these work here was to evaluate the efficiency of the extraction conditions in Pressurised liquid extraction (PLE) and compared to traditional Soxhlet extraction for the determination of chlorinated pollutants PCBs and HCB in sediment sample. Polychlorinated biphenyls (PCBs) and the Organoclorine Pesticides (OCPs) mainly have been produced in large volumes, during production use and disposal, these have entered the environment, there were stable as could undergo long-range transportation by atmospheric transport or stream pathway in which they were drained into lakes and seas, and accumulated in the sediment. In these work sediment samples from different areas has extracted with PLE using n-hexane/acetone (1:1, v/v; two cycles) and were compared to Soxhlet extraction (reference method) using *n*- hexane/acetone (1:1, v/v; 16h). The concentrations of 7 indicator PCBs the CBs 28, 52, 101, 118, 138, 153,1 80 and the pesticide Hexachlorobenzene (HCB) were compared.

The methodology demand a clean-up in order to remove co-extracted substances like lipids, fatty acids or sulphur.

After that step a silica gel column was used to fractionate the extracts. The first fraction containing PCBs are eluted from the column by a non-polar solvent (*n*-hexane), the second fraction containing de OCPs was eluted with solvent mixture n-hexane/diethyl ether (85:15, v/v). Both fractions were concentrated solvent exchanged to iso-octane and final volume was adjusted to 1 mL. PCBs e OCPs were analysed using a gas cromatograph equipped with an electron-capture detector (ECD).

The statistic analysis of the Least-Squares Method reveals a linear relationship between the measured response Y- Concentration of analytes in Tested Method (PLE) and the X-Concentration of analytes in Reference Method. The results of the more accurate method (Soxhlet extraction) were placing as an independent variable. To evaluate the results obtained by the methods, two conditions were verified: 1) the range associated with the straight line intercept contained zero and the range associated with the slope line had the 1 value.

Establishment of a model to estimate the uncertainties associated to the measurement of atmospheric pollutants in a crude refinery

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The follow up of environmental processes leads to obtaining results which quality of measurements is a requirement rarely explained. However important decisions of environmental management, social and political, with direct impact in populations, are made supported by these results. The validation of a measurement, to support the decision, is impossible without the knowledge of the uncertainty associated to the result itself. It is the uncertainty that defines the quality of the result.

This work is intended to contribute to the improvement of Pollution Control in Galp Energy's Refinery in Sines through the establishment of a model to calculate the uncertainties associated to the contents of pollutant measured. In this study were used the measured values of the pollutants sulphur dioxide, nitrogen oxides and particles monitored.

After characterization of the measure equipment, it was made a statistical study to the values measured by the three gas analysers during one year and it was determined the model of calculation of the uncertainty value associated to each one of the measures.

To evaluate the uncertainty ir air measurements, was used the procedure described in ASTM Standard D7440–08, involving the specification of the measurement process, the identification of the uncertainty sources, the calculation of the combined uncertainty and the calculation of the expanded uncertainty.

The values associated to the respective uncertainty were critically compared with the limits imposed by the environmental license of the Company.

The determination of the uncertainty associated to the results of the gaseous effluents of this installation reinforces the credibility of the measured values, the commitment to the continuous improvement of the quality of the processes, products and services, of the environmental performance and of the safety of people and goods, as a contribution to the sustainable development of this Company.

P – 7

Performance of the method EN 12396-1 - with the introduction of minor modifications - versus the criteria of SANCO 12571/2013 for quantitative determinations

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The spectrophotometric method based on EN 12396-1:1998 standard[1] continues to be widely used in routine test laboratories for the quantification of total dithiocarbamates (DTCs) in vegetable food, expressed as disulfide carbon released during the analysis. The procedure described on this European Standard leads to unsatisfying limit of quantification (LoQ) values for several commodities, since it corresponds to 5-10 times their Maximum Residue Limits (MRL) set up in the European Union[2], taking values as low as 0.05 mg/kg. Therefore, in an attempt to reduce the LoQ, two major modifications were introduced to the method: decreasing the lower calibration level down to one order of magnitude and using spectrophotometric cells with 2 cm of pathway, instead of 1 cm. The document SANCO 12571/2013[3] is focused on the determination of pesticide residues in food by mass spectrometry coupled to chromatography techniques but the same criteria of quantitative validation were here used to evaluate the performance of the present spectrophotometric method. The assessment of linearity, working range, intermediate precision, trueness, selectivity, sensitivity, limit of quantification and uncertainty were based on results of different commodities, spiked with thiram at several concentration levels. The compliance of these performance parameters with the requirements of SANCO document was proved. The accuracy was also evaluated by the participation in three proficiency tests, with acceptable results. The uncertainty was estimated by the supra-analytical approach[4-5] at the several levels of fortification, the expanded value being consistent with the maximum of 50%, which was set by EFSA for checking the infractions to MRL.

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2. http://ec.europa.eu/sanco_pesticides
3. Document SANCO/12571/2013 of the European Commission, Health & Consumer Protection Directorate-General, 2013.
4. EURACHEM/CITAC Guide CG4, Quantifying uncertainty in analytical measurement, 3nd edition, 2012.
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Validation of nickel quantitative analysis using ICP-OES with an ultrasonic nebulizer

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A crucial step in water quality risk management is search and analysis of hazards in water, which sets the basis for improving the knowledge of water quality. In order to comply with the requirements of the EU Drinking Water Directive (DWD) (98/83/CE) and the Water Framework Directive (2000/60/CE; 2013/39/EU) as regards to priority substances in water, Águas do Algarve laboratory decided to implement an validate a methodology for analysis of priority substances in water, in particular Nickel. This work describes the implementation and validation of an analytical method by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with an Ultrasonic Nebulizer for the quantitative analysis of the referred priority substance in drinking, surface and groundwater. Generally, a major advantage of performing quantitative analysis by ICP-OES is the fact that sequence multi-elemental analysis can be accomplished with the rapid achievement of results.

Method accreditation, based on the standard ISO/IEC 17025, was attained for Nickel and other parameters. Thus, method's implementation and validation was carried out and an estimation of measurement uncertainty was calculated. Additionally, external and internal quality control was implemented, in routine, for all methods.

Requirements for the implementation of Nickel quantitative analysis by ICP-OES with an Ultrasonic Nebulizer were followed[1-3]: definition/optimization of the specified conditions for each method; definition of the working range; initial selection of wavelength (where applicable) and evaluation of possible spectral interferences (when applicable). Characterizing parameters to validate the analytical methods included: a) Specificity/Selectivity; b) Range of work[4]; c) Linearity[4]; d) Thresholds of the analytical test method (Limit of detection (LOD) and limit of quantification (LOQ)); e) Sensitivity (constant across the range); f) Study of possible spectral interferences (Spike recovery); g) Precision (standard deviation); h) Trueness (based on proficiency testing and reference materials data) and i) Uncertainty (based on quality control data)[5];.

As a conclusion, the selected methodology was shown to be a good option for detection and quantification of Nickel associated with low uncertainties, as required by the DWD and Water Framework Directive. Furthermore, limits of detection for the metal in water were adequate for water monitoring and the method was shown to be adequate for drinking, surface and groundwater.

1. International Organization for Standardization. Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) - ISO 11885, 2007.
2. U.S. Environmental Protection Agency. Determination of metals and trace elements in water and wastes by inductively coupled plasma – Atomic emission spectrometry - METHOD 200.7, 1994.
3. American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation (WEF). Standard Methods for Examination of Water and WasteWater. 22nd Edition. APHA, AWWA & WEF, Washington DC. 2012.
4. International Organization for Standardization. Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function - ISO 8466-1. 1990.
5. International Organization for Standardization. Water quality – Estimation of measurement uncertainty based on validation and quality control data - ISO 11352. 2012.

Environmentally friendly matrix effect matching evaluation for the major elements in solid biofuel characterization by atomic absorption spectrometry

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The thermo-chemical conversion of biomass has become increasingly important, from the last decade, due to the need to reduce CO_2 emissions and to increase renewable energy sources. Currently, the use of biomass already has a strong economic environmental and social impact.

The biomass source can be very different whereby biomass characterization is a crucial task allowing the prediction and prevention of problems associated with biofuel burning. Major elements (Al, Ca, Mg, Na, K, Fe, Si and Mn) determined by flame atomic absorption spectrometry (FAAS) requires preliminary procedures to convert the solid sample into a solution destroying either organic matter or inert matrix. In this work grinded biofuels (under 0.25 mm) were decomposed following EN 15290:2011 and closed vessels microwave assisted extraction, under controlled conditions of temperature and pressure. A mixture of H_2O_2-HNO_3-HF was used in a first step and then boric acid was added for HF complexation. This procedure leads to an efficiently dissolution, because H_2O_2 - HNO_3 mixture ensures the organic matter destruction and HF dissolves the alumosilicate matrix; the recovery of each element without loss of volatile species; minimization of contamination; increasing of measurement precision and technician safety. However, resilient matrix effects on the elemental determination by FAAS were noticed due to HF-H_3BO_3 mixture and calibration by standard addition did not compensate constant deviations.

Matching calibration standards with the same reagents and applying the same procedures used for samples could compensate for matrix effects that influence analytical response, but high quantities of toxic reagents must be used.

In this work the need of a fluoboric-boric acid matrix matching was studied using one way ANOVA tests. No significance differences were obtained for Si, Al, Fe and Mn among of seven groups of mixtures of nitric acid and blank reagent in proportions from 0 to 100 %, because the calculated values were lower than the critical value, $F_{6,14}=2.84$ ($P=0.05$). For Ca, Mg, Na and K significance differences were obtained. All samples were analysed using a dilution factor of ten since the mass fractions quite exceed the analytical dynamic ranges. The calibration solutions were prepared using the reagent blank in the same proportion.

The procedure was validated using the standard reference material 1573a, tomato leaves, purchased from National Institute of Standards and Technology. Recoveries within 1±0.1 were obtained.

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BIAS EVALUATION AND PROFICIENCY TESTING

INVITED LECTURES

Recovery/bias evaluation

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In very broad terms the effects affecting measurement results can be divided into random and systematic. Estimation of random effects – evaluation of precision – is relatively straightforward and can be done by repeating measurements using a suitable experimental design. Estimation of systematic effects – evaluation of bias[1,2] – is much more difficult. Firstly, a fundamental requirement for bias determination is availability of a reliable reference value, carried by a sample/material, with suitable analyte-matrix-concentration combination. Secondly, bias may or may not be present, but any measurement result is influenced by random effects. So, bias determination has to be carried out in such a way that bias is separated from precision, which is easy in theory, but often not so easy in practice.

The presentation will discuss the definition and meaning of bias, sources of bias in chemical analysis, the difficulties that occur when evaluating bias and ways to overcome them. Explanations of principles and approaches are supplemented by practical examples.

1. International vocabulary of metrology – Basic and general concepts and associated terms (VIM), 3rd ed, JCGM 200:2012.
2. B. Magnusson, S. L. R. Ellison, Anal. Bioanal. Chem. 390 (2008), 201-213.

IL – 7

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

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Measurements undertaken by laboratories are made for a variety of reasons but all are carried out in order to make decisions about the item under examination. Such decisions can significantly impact on important issues such as compliance, trade, safety and health to name just a few. Reliable decisions can only be taken if the measurements are also reliable; in other words they are fit for the purpose for which they are intended. An appropriate quality assurance system within a laboratory is a key element in ensuring fit-for-purpose analysis leading to reliable decisions.

There are a range of important quality activities; such as method validation, instrument calibration, staff training, and internal quality control that establish an appropriate quality assurance system within a laboratory. A range of products such as reference materials and traceable standards are available to support such activities. However, none of these activities or products provides an independent assessment of the laboratory's output i.e. they do no validate the final measurement result. The only quality tool available for this purpose is proficiency testing.

Participation in proficiency testing provides a laboratory the infrastructure to monitor and improve the quality of its routine analytical measurements. In addition it provides a range of other benefits including a demonstration of the competence of a laboratory to its customers, regulators and accreditation body. To maximise these benefits it is essential that the laboratory implements an appropriate PT participation strategy and selects PT schemes that are fit for their purpose.

The presentation will explore further the purpose, different types and benefits of PT, along with establishing a PT participation plan and selecting appropriate PT schemes in which to participate. Some of reasons for unsatisfactory PT performance will also be considered. The presentation will conclude by reviewing some of the work in the field of proficiency testing that has been conducted by Eurachem over the past twenty five years.

ORAL COMMUNICATIONS

Use of interlaboratory study to better define the characteristics of dispersion of results in natural gas analyses

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Presented by *Basset, E.*

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The aim of this study was to define and estimate rigorously the dispersion characteristics of the gas calorific value measurement in France.

Measurement of natural gas calorific value is done routinely throughout the transmission system and at its interface with other gas operators such as LNG terminals, underground storages, distribution networks and gas producers. To do so, process gas chromatographs continuously analyze the major components of natural gas which consist of: nitrogen, carbon dioxide, and saturated hydrocarbons from methane through n-pentane. They also analyze the C6+ fraction consisting of the sum of all hydrocarbons heavier than hexane.

To have a global overview of the state of the art of major components analysis within the GDF SUEZ group, a proficiency testing scheme has been carried out by the CRIGEN (GDF SUEZ Gas and Sustainable Energies Research Center). The collaborative study involved 23 laboratories expected to be representative of the population of laboratories among GDF SUEZ operators GRTgaz, Storengy and Elengy. A laboratory is, in this case, a combination of an operator and a chromatographic instrument. The instruments come from three different manufacturers. Each of the laboratories conducting the study was sent a gas cylinder containing the exact same unknown blend of major components. Following analysis, the laboratories sent "raw data" results (peak areas and concentrations) back to the CRIGEN who made the necessary calculations for the assay.

The use of statistical tools, especially the analysis of variance (ANOVA) helped improve the knowledge of the characteristics of the dispersion of results in the gas chromatographic method for quantitative analysis of natural gas and for measurement of gas calorific value. The interlaboratory study enabled the CRIGEN to recover information on several levels. The first point of comparison, based on statistical exploitation, was the repeatability. Under this criteria all of the effects of the uncontrolled factors that correspond to the intrinsic performances of the chromatographic devices are gathered. The second point of comparison was the reproducibility and the determination of the factors that have a significant influence on the result. The third point of comparison was the determination of the testing laboratories' accuracy.

Finally, the Proficiency Testing Scheme allowed for the evaluation of the measurement uncertainties for natural gas composition for this type of equipment and improved the knowledge of calorific value uncertainty in operating conditions.

Assessing a new approach (triple A-classification) to evaluate performance-underperformance of laboratories participating in the EU proficiency tests for multi-residue analysis of pesticides in fruits and vegetables

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Since 2004, European official laboratories analysing pesticide residues in fruits and vegetables are being classified into just two groups or categories (A and B) taking into account the results obtained in the EU Proficiency Test for multi-residue analysis of pesticides in fruits and vegetables (EUPT-FV). Those laboratories that detect at least 90 % of the pesticides present in the Test Item and reported no false positives are considered to have a "sufficient scope" and are classified into Category A. In order to obtain a more informative laboratory classification, a new three-dimensional (XYZ) , classification with three categories (A, B or C) within each dimension, has been proposed. With this new approach, laboratories would be evaluated taking into account the percentage of "detected" pesticides (dimension X: scope), the percentage of "acceptable" z-scores (dimension Y: performance), and the number of false positives (dimension Z: false positives). The borderline criteria for establishing categories A, B and C in scope (X) and performance (Y) are 90% and 50%, but those laboratories classified as C in scope can only be classified as B or C in performance, the borderline criteria being in this case 90%. Finally, laboratories are classified as A, B or C in the third dimension when they report none, one, or more than one false positive, respectively. This new evaluation approach has been checked by using the results obtained in the EUPTs organised by the EU Reference Laboratory for Pesticides in Fruits and Vegetables (EURL-FV) in last two years. In 2012, the Test Item (pears homogenate) contained 17 pesticides, 154 laboratories (from EU, Iceland, Norway, Switzerland, Serbia, and Turkey) reported at least one result, and the most frequent laboratory categories were AAA (50.5 %), BAA (14%), CBA (12%) and BBA (6%). That year, 55% of the laboratories were classified into the old "Category A", being this percentage equivalent to the sum of the AAA (50.5%), ABA (4.5%) and ACA (0%) new categories.

POSTERS

Monitoring laboratory performance over time from proficiency testing by interlaboratory comparisons

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Proficiency testing by interlaboratory comparisons is used to determine the individual performance of a laboratory for a specific test or measurement and to monitor the continuing performance of laboratories.

Monitoring PT performance over time allows to identify potential problems related to random and systematics errors.

Participation in interlaboratory comparison tests (IEC), is a requirement of the accreditation bodies either for granting laboratory accreditation by EN ISO/IEC 17025:2005 as external quality control.

In this work laboratory performance trend over time for moisture in general analysis sample (EN 14774-3:2009), ash content (EN 14775:2009) and volatile matter (EN 15148:2009) in different biomass sources purchased by WEPAL, BIMEP program was evaluated from 2011 to 2013, for 18 samples. The following parameters were used: individual *z*-scores; the rescaled sum *z*-scores parameter, *RSZ*; the sum squared *z*-scores, *SSZ* and *J*-scores [1, 2].

For moisture in general analysis sample and volatile matter all $|z\text{-score}| \leq 2$ while for ash content two scores (not in sequence) within $2 < |z\text{-score}| < 3$ were obtained.

No trends over time were detected, for all parameters, since $RSZ \leq 2$ and $SSZ < \chi^2_{18}$ distribution (χ^2_{18} =28.9) and cumulative *J*-scores<8 and it was not necessary to trigger any investigation procedure.

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2. S. L. R. Ellison, V.J. Barwick, T, J. Farrant, , Practical Statistics for the Analytical Scienstist. A Bench Guide, 2 nd Edition, RSCPublishing, Cambridge, 2009.

P – 11

European proficiency tests for fruit and vegetables from 1996 to 2013 – History and main achievements

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European Proficiency Tests in Fruits and Vegetables (EUPT-FV) date back to 1996, when they were organised for the first time by the National Food Administration in Uppsala, Sweden. Since 2006 the European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables (EURL-FV) in Almería, Spain, has organised them on behalf of the European Commission, Health & Consumer Protection Directorate-General (DG-SANCO). The collection of information during the past years (EUPT-FV01 to EUPT-FV15) involving European official laboratories for pesticide residue control has generated an important database of more than 23000 pesticide residue results using Multi-residue Methods (MRMs), and has led to very valuable achievements in areas such as test sample preparation, data dispersion and statistical evaluation; as well as giving an overview as to the effectiveness of Proficiency Tests as an important tool in the development of quality control results in food control laboratories. In this work, a historical overview, as well as a selection of the main achievements obtained, are explained and documented.

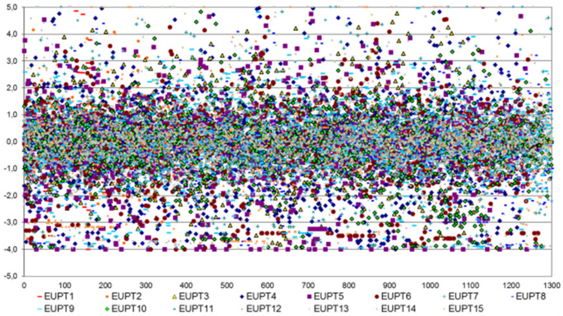

Figure 1. z-Score for 15 EUPT results.

Achieving lower z-scores: evaluation of z-score results along the uncertainty range of a sample

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Proficiency testing by inter-laboratory comparisons, to evaluate performances and the validation of analytical methods, is mandatory and an essential tool of improvement in the accreditation environmental of official laboratories.[1] Good performances are demonstrated when lower z-scores are obtained, more specifically when achieved z-scores below 2 ($z<2$).

Usually, when quantifying a certain substance, it is expected to be performed more than one assay in order to obtain a range of results, assuming the mean value as the best approach. However, in methods with high uncertainty there is a significant probability this can lead to fail the proficiency test.

In our statistical study we show the importance of taking into account the error susceptibility along the range of possible results. To better understand that, z-scores were calculated for several values that could be obtained in a simulated proficiency test. It was concluded that, if the real concentration is in the lower bound of the reported range, it will have a very smaller tolerance to error than if it is in the higher bound. These findings suggests that a lower value inside the range of results should be reported in order obtain acceptable z-scores at any concentration inside the uncertainty of the sample.

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MEASUREMENT TRACEABILITY AND UNCERTAINTY

INVITED LECTURES

Traceability in chemical analysis – Are we ready to deliver?

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Chemical analysis has to provide reliable information for decision making. This may include data for scientific research, industrial production processes, healthcare diagnostics, regulatory control and many other activities. The analytical information has to be relevant for answering the question-of-interest and comparable to other data. Therefore, appropriate metrological traceability of measurement results on properly chosen measurands is a fundamental prerequisite. However, establishing and communicating metrological traceability in the course of a chemical analysis is usually much more demanding than for measurement results of several of the 'more straightforward' physical parameters such as mass or time. This results not only from the huge number of chemical species and their analytically relevant atomic/molecular environment (matrix) which could be present in the samples-of-interest, but also from species transformations in the measurement process and other phenomena.

The presentation will discuss achievements and current limitations regarding the implementation of the concept 'metrological traceability' for chemical measurement results. Aspects such as the interplay between qualitative and quantitative analysis and structural changes of the measurement target during the analytical process will be considered as well as the relevance of starting and reference points of traceability chains for decision making and the adequate realisation of measurement scales. Obviously, the corresponding Eurachem guide will be included in the reflections.

IL – 9

Uncertainty evaluation for analysis and sampling

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The EURACHEM Guide for “Quantifying Uncertainty in Analytical Measurement”, now in its 3rd edition, deals primarily with uncertainties arising from sample preparation and measurement in the laboratory. The Guide stresses that the procedures introduced by a laboratory to estimate its measurement uncertainty should be integrated with existing quality assurance measures, including method validation studies, since these measures frequently provide much of the information required to evaluate the measurement uncertainty. The guide therefore provides explicitly for the use of validation and related data in the construction of uncertainty estimates. The third edition, published in 2012, added information based on developments in uncertainty estimation and use since 2000. It includes improved guidance on the expression of uncertainty near zero, new guidance on the use of Monte Carlo methods for uncertainty evaluation, improved guidance on the use of Proficiency Testing data and improved guidance on the assessment of compliance of results with measurement uncertainty.

The topic of uncertainty arising from sampling is considered in detail in a separate Eurachem Guide, published in 2007. This guidance acknowledges that sampling contributes to uncertainty in some circumstances, and provides simple and economical experimental approaches for estimating the variability due to particular sampling plans. In addition it includes examples of these approaches and of approaches based on a detailed analysis of contributions to uncertainty.

In this presentation, the development and principles of these two Guides will be reviewed with particular emphasis on recent developments.

ORAL COMMUNICATIONS

Specifications and traceability in the pharmaceutical industry

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The specifications for a protein drug product are defined during the development phase for the product. These specifications are approved by the health authorities in the region where the drug product is marketed. The approved product specifications are an agreement made between the authorities and the manufacturer and must be fulfilled when the drug product is analysed. Therefore, it is important to know the relevant sources of variation that will contribute to variation of the results from the analyses.

During development and the first years of commercial production pharmaceutical manufacurers often establish in-house reference materials to be used for analysis of the drug product. The manufacturer is able to estimate and control the uncertainty contributions related to the production process, the product stability, the analytical procedure, and the value assigned to in-house reference standards.

If a regional authority chooses to publish an official specification for the product (called a Pharmacopoeial monograph) a pharmacopoeial reference material is also established. At that time point, the analytical results for the drug product must be traceable to the pharmacopoeial reference material. Over time, several regional pharmacopoeial monographs and related reference materials are likely to be issued. The manufacturer is then expected to demonstrate traceability to all regional pharmacopoeial reference materials where the drug product is marketed. The assigned value for pharmacopoeial protein reference materials is typically stated without information on the associated uncertainty. Therefore, the manufacturer is expected to operate with several traceability chains that are not linked. When a reference material batch is replaced a shift may occur in the analytical results due to the new assigned value for the reference material. The missing uncertainty information can in these situations make control of traceability complicated.

The ideal solution will be establishment of harmonized monographs and reference materials with stated uncertainty. If this is not implemented a worst case scenario would be that if a patient travels between the different regions the medicine from the same manufacturer could have different contents of active substances even though the same content is stated on the label.

OC – 6

Estimation of measurement uncertainty in the fluorometric determination of ammoniacal nitrogen in seawater by continuous flow analysis (CFA)

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Nitrogen is the most important limiting nutrient for the growth of autotrophic organisms in coastal and oceanic environments. Molecular nitrogen (N_2), nitrate (NO_3), nitrite (NO_2) and ammoniacal nitrogen (NH_3-NH_4^+) are the main chemical forms of inorganic nitrogen. The last three forms are the so-called dissolved inorganic nitrogen (DIN).[1] The ammoniacal nitrogen is the mixture of ammonia (NH_3) and its ionized form, the ammonium (NH_4^+), which in seawater pH conditions (approx. 8) is mainly composed of ammonium (95%).[2] The molecular nitrogen is the most abundant chemical form, although the majority of the autotrophic organisms are not able to fix it and prefer nitrate and ammonium as their nitrogen source. The ammonium is assimilated more easily than the nitrate but is toxic in high concentrations in ammonia form.[3] The DIN, as a central element in coastal and oceanic biogeochemical cycles, is one of the compounds measured for the physico-chemical quality indices established by the Water Framework Directive 2000/60/EC[4] and one of the characteristics to be measured in the Marine Strategy Framework Directive 2008/56/EC.[5]

Nitrates and nitrites standard method for continuous flow analysis[6] can be utilized in seawater easily, however, the indophenol blue method for the ammoniacal nitrogen[7] suffers severe interferences in salt waters. For this reason, alternative methods to determinate ammoniacal nitrogen in seawater have been proposed based on the fluorescence presented by the reaction product of ammonium and orthophtaldialdehyde (OPA).[8] In this work, an estimation of the measurement uncertainty in the determination of ammoniacal nitrogen in seawater by continuous flow analysis based on the alternative fluorescence spectroscopy method proposed by Kerouel and Aminot (1997)[8] in the range of 7-70 µg/L NH_3-N was carried out by means of a global model of uncertainty quantification. The model takes into account the contributions of the bias and the intermediate precision from validation data[9] and is intended to be applicable for routine laboratories which do not possess the time or the resources to develop the Guide to the expression of Uncertainty in Measurement (GUM)[10] approach strictly. The expanded uncertainty calculated did not exceed 5%, except next to the lower limit where it reached 13%.

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POSTERS

Estimation of the minimal preanalytical uncertainty

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Background: We sought a model to estimate preanalytical uncertainty of blood samples.

Materials and methods*:* We collected blood into 2 RST tubes and 2 SST tubes from each arm of 20 individuals. Optimal preanalytical handling of the blood samples included a loosely-fastened tourniquet, wide bore needles, recommended clotting time and centrifugation speed, and minimal storage before analysis. The serum samples were analysed on Roche Modular. We used linear mixed-effects models to estimate the between-venipuncture SD, the preanalytical SD, the measurement repeatability SD, systematic differences between the tubes and between venipunctures.

Results: For LDH the preanalytical SD (3.2 U/L, 95% CI 2.8–3.7) was significantly higher than the SD for measurement repeatability (1.9 U/L, 95% CI 1.7–2.1). For potassium both the preanalytical SD (0.092 mmol/L, 95% CI 0.080–0.11) and the between-venipuncture SD (0.075 mmol/L, 95% CI 0.048–0.12) were significantly higher than the SD of measurement repeatability SD (0.031 mmol/L, 95% CI 0.028–0.035). For glucose the between-venipuncture SD (0.20 mmol/L, 95% CI 0.14–0.27) was significantly higher than the preanalytical SD (0.07 mmol/L, 95% CI 0.06–0.08), and the measurement repeatability SD (0.057 mmol/L, 95% CI 0.051–0.064). No significant systematic differences were found between venipunctures. Statistically significant mean differences were seen between SST tubes and RST tubes for 7 of the 15 analytes.

Conclusions: The linear mixed-effects model is useful to determine the minimal preanalytical uncertainty, which is inevitable even when the samples are handled optimally.

M.S. Sylte, T. Wentzel-Larsen, B.J. Bolann, *Clin Chem* 56 **(2010)**1329-35.

P – 14

COMAR – the international database for certified reference materials

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The usefulness of reference materials (RMs) and certified reference materials (CRMs) is beyond question. RMs play an important role in materials testing and especially in chemical analysis because they provide "measurement benchmarks" and ensure reliability and comparability of measurements. In addition; CRMs establish traceability. Not surprisingly; therefore the use of RMs is a basic requirement of quality control and quality management (e.g. ISO/IEC 17025). The permanent problem potential RMs users are faced with is to find out the proper RM needed.

The international database for certified reference materials COMAR has been developed to assist analytical and testing laboratories to address this problem. COMAR provides information on available CRMs and helps labs to find out the CRM needed. COMAR is the only database specialized in certified reference materials, covering a broad application scope and including producers from all over the world.

Access to COMAR is free of charge for any user worldwide via internet: http://www.comar.bam.de. New users are first requested to register online.

COMAR provides the following possibilities for CRM search:

COMAR is maintained by appointed coding centres (COMAR partners), which co-operate on a voluntary basis. Presently there are 21 COMAR partners, all are renowned national or international metrological institutes well experienced in CRM production.

COMAR contains information on some 10 000 CRMs of more than 200 producers in 24 countries. The critical point of every database is maintaining the provided formation up-to-date. The COMAR central secretariat at BAM supports the COMAR partners, but the COMAR partners (COMAR coding centres) are responsible for the update of RM information of selected producers in their countries.

The demand for information about available CRMs is still growing, not surprisingly also the number of COMAR users. The number of registered users has permanently been growing and has now reached some 20 300 from more than 100 countries worldwide. On average there are about 500 user logins and about 2 500 downloaded search results monthly. So COMAR is well accepted by the reference materials community.

The poster will summarize key points on COMAR related to the data management, main search possibilities, RM information provided and the current amount of CRM data contained.

Quantification of FAMEs in biodiesel: flame ionization detection vs. isotope dilution mass spectrometry

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Critical properties of biodiesel are directly connected to their most abundant compounds: fatty acid methyl esters (FAMEs). A deeper knowledge of the FAME composition can be used as a tool to anticipate the characteristics of a given biodiesel or improve some of its properties.[1]

Gas chromatography (GC) coupled to flame ionisation detector (FID) remains as the most frequently used method for the analysis of FAMEs. Nonetheless, the sensitivity and selectivity of mass spectrometry (MS) methods advocate an enhanced role for GC-MS in FAME analysis which is particularly advantageous in complex samples, where spectrometric confirmation of analytes is advisable. Within MS, isotope dilution mass spectrometry (IDMS) has the potential of being a calibration method for achieving high accuracy. IDMS offers different calibration strategies according the degree of accuracy required.[2]

To assess the utility of GC-IDMS methods for FAME quantification in biodiesel, a comparative study of GC-FID and two different GC-IDMS methods (calibration by graphical method and exact signal matching) has been conducted and the quantitative results compared. The performance of both GC-IDMS approaches was in agreement with that of GC-FID. These results confirm that GC-IDMS is a good alternative to GC-FID for FAME analysis. This study also confirms the differences in the degree of accuracy which can be achieved according to the calibration approach selected. While the graphical method calibration yields uncertainty values comparable to those obtained by GC-FID, the exact matching approach provides uncertainty values 50% lower than the ones obtained by the other methods.

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P – 16

Implementing VIM3 calibration in some analytical chemistry laboratories

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From its definition in the newest edition of the International Vocabulary of Metrology (VIM3)[1], calibration does not only consist on establishing a correspondence between reference values (from standards, very often) and indications (from measuring instrument under calibration). The calibration consists also of a second step that uses the first step relation to deduce the measurement result from indication, which has a series of consequences. The first consequence is the increasing importance given to modelling in metrology and calibration, in particular. This consequence is associated with requirements[2] such as the choice of the interval where the model is valid, an estimation of the validity of the model and a way to estimate the associated uncertainty to the measured value, as uncertainty is an essential component of the measurement result. Based on the ISO/TS 28037 Technical Specification[3], "Determination and use of straight-line calibration functions", it is the objective of this communication to exemplify the new concept and definition of calibration for some analytical chemistry Laboratories, with the affine function, a very simple case of calibration function.

More particularly, this communication intends to display an implementation of the new definition of calibration in some Analytical Chemistry Laboratories of IPQ: Refractometry, the Liquids Proprieties, pH and Spectrophotometry. IPQ stands for the Portuguese Institute for Quality, the National Metrology Institute of Portugal.

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Uncertainty from sample preparation in laboratory on the example of various feeds

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A way of uncertainty calculation from test sample preparation in laboratory was presented on the example of various feeds. Laboratory samples were divided randomly (riffle divider) on 6 test samples of about 100 g each and grinded.

The essence of the proposal lies in separating two components of results' variability expressed as coefficient of variation CV_p (%): analytical variability CV_a (repeatability) and technical variability CV_h corresponding with the inhomogeneity of a feed component. The law of Gauss' error propagation was used. Analytical variability CV_r was calculated from the range of duplicate analyses on the basis of Nordtest TR 537.[1] For calculation following formulas were used:

$$CV_p = \sqrt{CV_h^{\,2} + CV_a^{\,2}} \qquad CV_h = \sqrt{CV_p^{\,2} - CV_a^{\,2}} \qquad u_{s+h} = \sqrt{u_s^{\,2} + CV_h^{\,2}}$$

It was assumed that technical variability CV_h is the component of standard measurement uncertainty from sample preparation in the uncertainty budget u_{s+h} . Expanded uncertainty U_{s+h} for coverage factor k=2 (P=95%) was calculated in the simple way: $U_{s+h} = u_{s+h}\ 2$. Results of uncertainty calculation (%) are given in the Table (n=6).

Feed component	Loose feed		Granulated feed		Premixture without grinding* Ø=416 μm		Premixture grinded* Ø=260 μm	
	U	U_{s+h}	U	U_{s+h}	U	U_{s+h}	U	U_{s+h}
Protein	3.0	4.3	4.0	4.8	nd	nd	nd	nd
Calcium	10.0	12.4	10.0	10.2	10.0	14.8	10.0	10.0
Chloride	8.4	10.3	9.7	9.7	nd	nd	nd	nd
Iron	nd	nd	15.0	15.8	10.0	14.2	10.0	10.4
Zink	15	18.1	15.0	15.8	10.0	22.8	10.0	12,6
Copper	nd	nd	20.0	23.2	10.0	22.4	10.0	11.8
Selenium	15.0	28.0	15.0	16.0	nd	nd	nd	nd
Vitamin A	19.4	31.1	27.5	28.0	nd	nd	nd	nd
Vitamin E	13.1	13.1	17.1	20.4	nd	nd	nd	nd

U – expanded uncertainty (k=2) according to GUM; U_{s+h} – expended uncertainty (k=2) with uncertainty from sample preparation; nd – not determined; Ø – mean particle diameter; * premixtures with homogeneity confirmed by chloride testing

Calculated uncertainties with uncertainties from sample preparation for loose feed and no grinded premixture were higher of 21% up to 128% than uncertainties of the analytical procedure and measurement, calculated according to GUM[2] during validation of a method. Generally, in the case of granulated feed mixture, the obtained uncertainties were similar. Grinding of premixture resulted in decreasing measurement uncertainties. Uncertainty from sample preparation should be taken into account in the uncertainty budget of a test method, especially in the case of inhomogeneity of the materials analysed. Furthermore, laboratory should check characteristics of tested materials (especially homogeneity) and use proper divider and grinding mill for sample preparation, as this step has been shown to be one of the largest sources of laboratory errors, in some cases much larger than analytical procedure.[3]

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The prospect of the *TILSAM* method regarding customer needs and benefits in view of existing gas CMCs

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Metrological traceability is a highly demanded quality for more and more measurement results. Measurements on gases, as, e.g., those of natural or biogas mixtures, exhaust gases or gaseous pollutants emitted into the atmosphere play an enormous role in our daily life and in economics. Providing traceability to those measurement results is an essential task for most national metrology institutes (NMIs) worldwide. Demanding traceability is under the responsibility of many decision making authorities on the other hand. Customers, as such, e.g., users of gas analysers in industry are looking for the most economic way to fulfil the demanded quality requirements on measurement results to be reported. Any analytical measurement capability and any method have to find a position in this context regarding usability, applicability and costs.

Current practice in gas analysis is that traceability is provided by means of primary or certified reference gas standards, highest-quality gas mixtures owned and disseminated by NMIs. The NMIs' capabilities to provide traceability for gaseous compounds are listed in the so called CMC list (CMC = calibration and measurement capability) hosted by the BIPM.[1] Any traceable measurement result in the field finally has undergone a (lengthy chain of) comparison(s) to a primary reference gas mixture held by a NMI. Any gas analyzer, in order to yield traceable measurement results, has to be calibrated by a reference gas mixture, which itself has been calibrated by such a primary reference gas mixture.

The comparably new method of traceable infrared laser-spectrometric amount fraction measurement (*TILSAM*)[2], an innovative approach to provide traceability by an instrument and not by a reference gas, seeks to establish itself among the other existing methods in gas analysis[3-5]. Instrumentation based on the *TILSAM* method could complement existing gas standards in future in situations where portable, cylinder-based gas standards are not applicable or even not available, e.g. for reactive or sticky molecules. A *TILSAM* instrumentation would serve the purpose probing a molecule-specific transition and relying only on molecular line data[6] and physical measurands like total gas pressure and gas temperature. Metrology studies on CO_2 and other gaseous compounds as well as on H_2O vapour revealed already some of the potential of the method as being compared to reference or even primary standards.

In our presentation we will demonstrate the merits of this approach as a primary method directly applied (PMDA)[7] and compare it to existing methodologies. We discuss its potentials in gas metrology regarding quality figures of measurement results and provision of traceability to field measurements as well as its impact and benefits to specific field applications in industry or science, as e.g., those of environmental sensing. Possible draw backs and limitations will have to be balanced with the pros as well. We discuss the prospects and limitations of this methodology.

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3. Gas metrology by calibration-free infrared laser-spectrometry as a potential primary method. EUROMET project 934; from http://www.euramet.org.
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Variability of uncertainty associated to heavy metals determination in urban soils

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Soil is an essential non-renewable resource in Earth providing support, food and water to humans and other living beings communities. It is essential to the environment and society that soil functions and its quality are maintained. Nowadays soil quality has declined in the countryside due to the use of pesticides and agrochemicals as well as in the cities due to their intense growth. Atmospheric pollution can also be considered a threat to soils' quality as air pollutants settle in soils.

Studies of soil pollution in several sites of Lisbon have been conducted by our group throughout the last decade. These studies have a renewed importance due to the spreading of urban gardening activities over different areas in the city. A critical factor for the soil quality is for instance the heavy metals content which can contaminate the vegetables and therefore have negative effects on urban farmers' health. The quality of analytical results is crucial to have confidence in them so that they can be used by the city administration to decide whether to use those soils as urban gardens or not.

In this work, we present the evaluation of uncertainty associated to the determination by graphite furnace atomic absorption spectrometry (GFAAS), of lead, nickel, cadmium and chromium in the urban soils of Lisbon.[1] We describe the applied methodology for the optimization of the analytical procedures for each metal in order to minimize the associated uncertainty.

We used three composite samples per site and per year associated to a blank sample determination. The uncertainty for each metal in each local is evaluated during the sampling period of 10 years and the evolution analysed regarding the timeline.

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P – 20

Measurement quality in the determination of iron content in ore

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LKAB has the largest underground iron ore mine in the world and exports mainly fines and specialized pellets suitable for blast furnaces. There is a high demand of quality control during the whole production process and a variety of chemical and physical analyses are carried out to ensure top quality.

This study is focused on the last and most valuable analysis in the whole production chain; the determination of iron concentration in the final product. Sampling is done with automatic samplers (Figure 1) straight from the conveyor belts loading the ships in the ports of Narvik, Norway and Luleå, Sweden. This is to ensure the sample is representative for the exact load going to the customer.

The sample is sent to the LKAB chemical laboratory in Kiruna, Sweden, where it is analysed with XRF and a wet chemistry method involving titration with potassium dichromate. The maximum difference allowed between the XRF analysis and the titration is 0.1 %. The total iron ore content ranges normally from 66 - 71 %.

The calibrations on the XRF is made with lithium borate beads of internal standards, taken from the whole production chain and validation is made with 25 different certified reference materials. The beads are made with M4 gas fluxers from Claisse, and with every sample from freight ships there is also a reference sample done to ensure a proper melting process. The iron content is not measured but instead calculated. This calculation involves the total sum of measured oxides, a correction for sodium and sulphur and also a constant for yearly average of trace metals.

For the titration there is also a reference material analysed to make sure the sample preparation was made correctly. Both with XRF and titration double samples are made and if it is less than 0.1 % difference a mean value is calculated and then compared to the other method where the limit of difference also is 0.1 %.

For both LKAB and our customers the results from the CSIRO round robin tests six times a year are an important indication of how well the measurement of iron and other oxides go.

The measurement uncertainty is calculated based on the round robin tests, daily analysis of control samples, the difference between two different methods and repeatability comes from the double samples. The results from 2012-2013 gave an absolute uncertainty of 0.059 % for iron concentration.

Validation of the quantification of Mitragynine in Kratom by HPLC-DAD

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Mitragynine is the most abundant indole alkaloid present in *Mitragyna speciosa* Korth (Rubiaceae family), an endemic plant from Southeast Asia marketed in Europe as Kratom (dried leaves or as an extract). This alkaloid, besides being a chemical marker for *M. speciosa*, showed a strong antinociceptive effect and yet, acts like a psychostimulant. The consumption of these vegetable products is dangerous due to the psychotropic effects of their alkaloids. The content of these natural products varies according to geographical region and season. The vegetal material processing can also play a relevant role in composition variability.

This work presents the validation of the quantification of mitragynine in kratom by HPLC-DAD, after a solid-liquid extraction, to allow studying the contents of this alkaloid in commercialised products. This variability is relevant to evaluate the consumption risk.

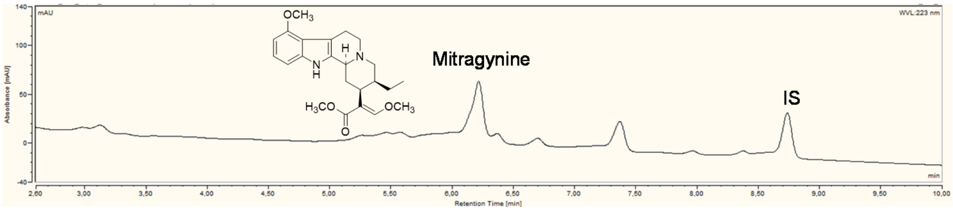

Figure 1 – HPLC chromatogram profile of Kratom samples.

The validation involved studying the performance of the analytical steps separately and combining their uncertainty using Monte Carlo simulations.

The uncertainty associated with gravimetric and volumetric steps was assessed through Monte Carlo simulations of components described in the Eurachem/CITAC guide[1]. The instrumental quantification was assessed through Monte Carlo simulations of signals taking into account models of the variation of signal precision with the mass concentration of the analyte and the correlation of operations and effects involved in calibrators preparations, and using the non-parametric Theil's regression method. The uncertainty associated with the extraction step was assessed comparing the observed dispersion of the results from the extraction and re-extraction of mitragynine from kratom samples with the simulated from all the other analytical steps. Therefore the extractability of the analyte was assessed from samples with incurred analyte. This evaluation strategy is the Monte Carlo version of the differential approach for the evaluation of the measurement uncertainty[2].

The defined relative target standard uncertainty, u'^{tg}, is 2.4% since it was intended to be discriminated differences of mitragynine mass fraction in samples larger than 10% (u'^{tg} =10%/4.24)[3].

Mitragynine measurements are fit for the intended use in the studied mass fraction range, 0.08-5 % (w/w), since presented relative standard uncertainties between 1.6-2.4%. The analysed kratom products present mitragynine mass fraction between 1.2-2.7% (w/w).

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Validation of the quantification of Cathinones in "plant feeders" by ^{1}H qNMR

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Cathinone, the main active principle of the plant *Catha edulis*, has been used as a prototype for the development of several synthetic derivatives that quickly came to market of legal drugs. These *designer drugs* are intentionally marketed as alternatives to illegal ones, aiming to circumvent drug legislation. The astonishing rate, at which new *designer drugs* appear, makes their impact on user's health unpredictable. Therefore it is extremely important to know the composition of these products. Those cathinones are normally sold in Europe as *plant feeders*. Previously we identified, by GC-MS and NMR, 19 psychoactive compounds in 27 *plant feeders* which showed hepatotoxic effects.[1]

This work reports the validation of the quantification of various cathinones in several synthetic drugs by ^{1}H qNMR using maleic acid as internal standard. The measurement procedures were subsequently applied to the characterisation of several *plant feeders* purchased in Portuguese *smart shops*.

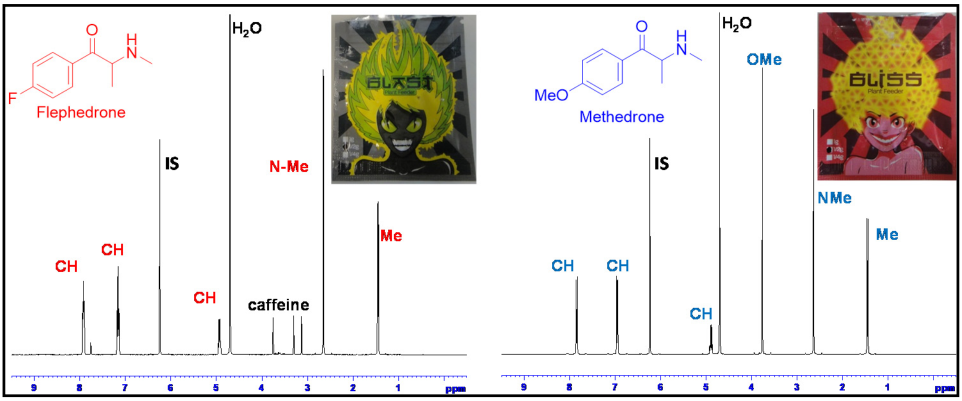

Figure 1 – ^{1}H NMR spectra of the *plant feeders* Blast and Bliss showing the signals of flephedrone, methedrone, caffeine and IS (maleic acid).

The validation of these quantifications involved studying the performance of all analytical steps individually, the determination of the uncertainty of the reference value and the combination of these information using the uncertainty propagation.[2,3] The linearity assumption of the uncertainty propagation law was tested by the differences of uncertainty estimated by the numerical Kragten method using either positive or negative increments.[3,4]

The uncertainty associated with gravimetric and volumetric steps was estimated as suggested by the Eurachem/CITAC guide.[3] Models of the repeatability of the NMR signals were used to estimate the variability of the instrumental signal. The linearity of the NMR response was tested by the metrological compatibility[5] of the results using signals at different chemical shifts.

The target relative standard uncertainty[5] of these determinations is 2.8% since differences in the composition of products of more than 10% are required to be distinguished.[6]

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Optimisation of the efficiency gain quantification of the catalytic photodegradation of methylene blue

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Some endocrine disruptors, such as active substances and metabolites of some medicines or preservatives of personal-care products are known to be concentrating in the environment due to the inefficiency of wastewater treatment plants to remove these residues. There are cases in which photodegradation with UV-light or from sunlight radiation can be successfully applied. Nevertheless, available technologies are, in many cases, not feasible due to the energy requirements or duration of relevant residues reduction.

Some catalysts, mainly semiconductor nanomaterials, have been developed to improve the efficiency of such processes.[1]

The new technologies are first assessed in the laboratory for some pollutants or photodegradation markers and, if proved efficient, applied to more complex systems.

This work presents a strategy to develop reliable detailed models of the determination of the efficiency gain of the catalytic photodegradation of methylene blue. Methylene blue was chosen since it is a very popular compound for assessing and comparing the efficiency of photocatalytic degradation processes. These models are used to guarantee the reporting of the photocatalytic gain with uncertainty, to allow the comparison of results of different tests performed in the same or different laboratories, and to minimise determination uncertainty. A smaller uncertainty of the catalytic gain allows the reliable distinguishing of smaller efficiency improvements. The long term use of only slightly improved catalytic solutions can drive to relevant economic benefits.

The determination of methylene blue, performed spectrophotometrically at 660 nm, was assessed between 0.3 and 30 mg L^{-1}.

The applicability of the linear unweighted regression model in this range was assessed namely, the linearity of the variation of the instrumental signal with mass concentration, the homogeneity of the variance of the instrumental signal and the negligible uncertainty of the ratio of the concentration of any pair of calibrators considering the instrumental signal repeatability.[2]

The uncertainty was evaluated using the so called “bottom-up” approach.

The developed model allows the minimisation of the estimated catalytic gain uncertainty.

This work is applicable to the determination of the efficiency gain when using or not using a catalyst, or when using different catalysts in the photodegradation of methylene blue in the same experimental conditions (i.e. reactor design, lamp irradiation power, temperature, pH and dissolved oxygen content). The impact of a specific experimental condition in the efficiency gain can also be assessed using the developed tool.

Acknowledgements

This work was supported by Fundação para a Ciência e Tecnologia (FCT) under project PEst-OE/QUI/UI0612/2014 and PEst-OE/QUI/UI0536/2014.

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A comparison study on the uncertainty evaluation for the determination of total nitrogen, using ISO 11352 and other alternative approaches

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One of the important indicators of the water quality is the quantity of inorganic substances it contains. These can be evaluated using different analytical methods, such as Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Nitrogen (TN). Since the determination of COD is the least environmental friendly, the combination of the TOC and TN are generally being accepted as the best methods.

To determine Total Nitrogen (TN) a sample is injected in the reactor at a temperature of 750-950 ºC in the presence of a catalyst where all the chemically connected nitrogen is converted into nitrite oxide NO. An air flux or oxygen conveys the oxidation products to the chemiluminescense detector where the nitrite oxide reacts with the nitrogen to form excited NO_2*. The rapid decay of NO_2* emits light which is in turn measured in photomultiplier tube. The electrical signal of the photomultiplier tube is then amplified and transmitted to a computer for data treatment.

The test also involves the determination of Nitrate + Nitrite from the injection of the sample into the reactor. These are converted into nitrite oxide, to be determined by chemiluminescense as in the total nitrogen procedure.

The procedure resumed above involves a number of intermediate calculations in order to determine the final quantities required. These quantities entail the estimation of an expanded uncertainty for the measurand, resulting from many sources of input uncertainties, during the overall process of determination. They include precision, reproducibility, reference materials, interlaboratory comparisons, among others.

This work aims to compare and discuss the different methods available to evaluate the measurement uncertainty associated with this typical test of water quality assessment. International standard ISO 11352:2012 exemplifies the estimation of measurement uncertainty based on (a) reference material; (b) proficiency tests; (c) quality control sample and recovery experiments. It will be attempted to establish a comparison between these approaches and the conventional ISO-GUM approach and a Monte Carlo method.

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Assessment of the compatibility of mean activity coefficients estimated experimentally and by Pitzer equations

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Calibration of pH meters covering the most useful range of pH values is usually performed with pH buffer reference solutions of low ionic strength, I (below 0.1 mol dm^{-3}). For pH measurements in seawater matrix (I = 0.7 mol dm^{-3}) calibration buffers with high ionic strength are required; ongoing research on the development of pH buffer solutions in a seawater-like matrix will establish values of primary pH reference buffers for appropriate calibrating solutions.

The Harned cell (platinized, or palladized, platinum based hydrogen gas electrode, indicator of hydrogen ions, and a silver-silver chloride electrode, indicator of chloride ions, without transference working under potentiometric conditions), in association with the Nernst equation, is the basis of the primary method for pH assignment to reference pH buffer solutions.

Experimental measurements of potential have been planned according to a consistent sequence of acidic aqueous electrolyte solutions of increasing complexity, progressively approaching seawater composition. High complexity introduces deviations from ideal behaviour that reflect upon activity values, a, significantly different from concentration, m, $a = \gamma\ m$, where activity coefficients, γ, become significantly different from 1. In ionic solutions, mean activity coefficients, $\gamma_{\pm} = (\gamma_{+}\ .\ \gamma_{-})^{1/2}$, can be experimentally assessed.

Values of $\gamma_{\pm}$ obtained experimentally were compared with those calculated from the semi-empirical Pitzer model equations which describe the non-ideal behaviour of electrolyte solutions by taking into account electrostatic and short-range forces.

In this work, mean activity coefficients estimated experimentally and by Pitzer models were compared considering uncertainty quantified for both estimations using the numerical Kragten and Monte Carlo methods. The mean activity coefficients vary approximately linearly with relevant input quantities ranges proving the adequacy of the combination of uncertainty components using the Kragten method. The experimental and theoretical estimates are metrologically compatible for 95% confidence level.

COMPLIANCE ASSESSMENT

INVITED LECTURES

Reporting the result and assessment of compliance

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Reporting results and assessment of compliance is the last part of the measurement cycle starting with the client issue and ending with a decision on the result.

Reporting results

In order to have good quality the results need to be reported accurately, clearly, unambiguously and objectively, and in accordance with any specific instructions in the test methods. Important information in the test report for the quality of the result is

- What have been measured
    - A detailed definition of the measurand including the sample, the test item

    Example: *mass fraction of total Cd in mg/kg in a* ***certain soil batch*** *reported on dry mass basis (105 °C, 2h)*
- The sampling target – laboratory sample or ?
- To follow general ISO recommendations for reporting
- Report correct number of significant figures
- Info about quality/accreditation and method/procedure

Compliance assessment

In addition to a detailed reported result we need for compliance assessment:

- External or internal specification/legal limit etc
- Decision rule

Dependent on the client issue different parameters to describe the measurement quality is required for compliance assessment. For example:

- Compliance with a legal limit or an external specification
    - $\mathbf{u_c}$ combined standard measurement uncertainty is required,
- Compliance in production – client issue: is my process stable?
    - $\mathbf{s_{Rw}}$ is required where s_{Rw} is the intermediate precision, the within laboratory reproducibility standard deviation
- Comparison in research – is there any difference between sample A and treated sample B analysed at the same time
    - $\mathbf{s_r}$ **is required** where s_r is the repeatability standard deviation

The oral contribution will describe the important issues for clear reporting and give examples on compliance assessment in legal area (blood alcohol), product testing (EU toy directive) and environmental testing (sludge from water purification plants).

ORAL COMMUNICATIONS

NMIJ analytical skill-upgrade training program

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National Metrology Institute of Japan (NMIJ) has been conducting **NMIJ Analytical Skill-Upgrade Program** in order to disseminate the metrological traceability, the uncertainty and the quality control of analysis into the chemical analysis field. The program consists of a proficiency test (PT), a comprehensive review of the test results and a seminar on technical methods and procedures. The PT is carried out based on the En values in which the reference values are provided by NMIJ, although the results are also evaluated with the Z-score. The participants are required to write the detailed report on their experimental procedures used, although they use their favourite methods to analyse the test samples. The reported analytical procedures are reviewed carefully and some of them are repeated by us in some case. We evaluate the analytical procedures as well as analytical results of each participant, since the comprehensive review of their own analytical procedures is thought to be very effective for them to understand the traceability and the uncertainty. The correlation between the analytical processes and the results of all participants are analysed, too. Based on the comprehensive review, the technical seminar is held.

In recent 5 years, NMIJ provided more than 10 Programs. The targets of the Program were the heavy metals (Cd, As, Cu *etc.*) in rice[1], the pesticides in rice and vegetables, the water analysis, and so on. Some of the programs were also carried out in Thailand and Mexico under the collaboration with TISTER and CENAM, respectively.

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OC – 8

Quality assurance of chemical analysis: classification, modeling and quantification of human errors

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Human errors in chemical analysis may lead to atypical test results, in particular out-of-specification test results that fall outside established specifications in the pharmaceutical industry, or do not comply with regulatory, legislation or specification limits in other industries and fields, such as environmental and food analysis. Inside the limits or at their absence (e.g., for an environmental object or a new material) errors may also lead to incorrect evaluation of the tested properties. Therefore, study of human errors is necessary in any field of analytical chemistry and required from any laboratory seeking accreditation. Such a study includes classification, modeling and quantification of human errors. The classification distinguishes commission errors (mistakes and violations) and omission errors (lapses and slips) by different scenarios at different stages of the analysis. A Swiss cheese model is used for characterization of the errors interaction with a laboratory quality system. A new technique for quantification of human errors in chemical analysis, based on expert knowledge and experience, is discussed. Two examples of the human error classification, modeling and quantification using this technique, developed recently and discussed also in the lecture, are for: 1) pH measurements of groundwater, and 2) multi-residue analysis of pesticides in fruits and vegetables.

POSTERS

Uncertainty associated with the measurement of mineral micropollutants in natural waters and in waste waters: differences observed between analytical methods during proficiency testing schemes

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Proficiency testing schemes show that the state of the analytical technique does not always meet the needs of precision expected from laboratories for the sanitary control or the police of waters.

Indeed, the extent of the doubt zone observed around the regulation values[1] is sometimes such that one can have doubts about the efficiency of risk management for the concerned parameters.

The measurements of metals and trace metalloids in superficial continental waters, in waters intended for human consumption and in waste waters follow this fact. Some are reliable, others are less reliable.

In order to draw up a state if the situation, but also in order to explore the possibilities of improvement, the large quantity of data collected by the provider of proficiency testing schemes AGLAE was re-processed method by method[2]. This study, conducted jointly by AGLAE and the University of Lille 1, enabled to highlight significant differences.

Between others, ICP-MS was confirmed as globally more reproducible (at the interlaboratory scale) than the other methods usually used (AAS-thermal, AAS-flame, etc.); including at the lowest concentration levels.

The poster aims at:

- On the one hand showing the major tendency for some mineral micropollutants,
- on the other hand seeing to what extent[3] the widespread use of one analytical technique would enable to better meet the regulation.

1. zone in which the risk to misclassify a sample is high = high risk to classify the sample as 'compliant' whereas it is not, or conversely classify it as 'non-compliant' whereas it is
2. originally, data are mainly processed all methods combined
3. except economic considerations

P – 27

Evaluation of performance of handheld XRF analyzer and possibilities for use in quantitative assessment

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During several years the IKEA group has used handheld X-ray fluorescence analyzers (XRF) to prevent non-compliant materials in IKEA products. This instrument facilitates non destructive testing in short time period and with low cost. The method is often regarded as semi quantitative and the measurement uncertainty can be high. Therefore the results are normally considered to be preliminary.

IKEA chemical requirements specify limit values to be met, the test methods to be used and the frequency of testing. The verifying methods for test of elemental composition are almost exclusively methods that include complete digestion of the sample followed by a spectroscopic detection. These methods are performed at chemical laboratories and require several days from dispatch of sample until test results are finalized. These results normally have low measurement uncertainty.

With the handheld XRF instruments a large number of samples of relevant materials can be tested. These portable analyzers can be equipped with a customized set up of calibrations for different materials. Examples of prioritized materials and chemical risks are heavy metals and halogens in polymeric materials. Also the instrument can be used to check metal alloy composition. In this study, instruments calibrated for analysis of *e.g.* Co, Mn, Fe, Ni, Cr and Cu in metal samples and *e.g.* Br, Cl, Cr, Fe and Sb in polymeric samples are evaluated.

Results from a recently performed XRF-proficiency test including more than twelve instruments at different locations are summarized. These results together with method validation data and method comparisons are used to evaluate the possibilities to use results obtained with the handheld XRF for compliance assessment. Examples including a few materials and elements of interest are given. With a robust test and assessment strategy taking into account the demonstrated measurement uncertainty it can be possible that the direct XRF method can be used in compliance assessment without violating fulfilment of chemical requirements.

QUALITY ASSURANCE AND TRAINING

INVITED LECTURES

IL – 11

QA/QC to underpin the measurement cycle

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IL – 12

Key skills for the analytical scientist: Assessing competence in the laboratory

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A laboratory stands or falls by the expertise and competence of its staff. Effective training of laboratory staff is therefore an essential step in ensuring the quality of measurement results. Standards such as ISO/IEC 17025[1] and ISO 15189[2] require laboratories to ensure and demonstrate the competence of their staff. There is also a requirement to have in place procedures for identifying training needs, for providing suitable training and for assessing the effectiveness of the training.

It is important that training addresses the complete measurement cycle, that staff understand the significance of each step, and are aware of the procedures in place within the laboratory. Experience shows that issues arise not only in relation to practical laboratory skills, but also in the broader understanding of the importance of quality assurance (for example, why QC materials are analysed, following up 'out of spec' measurements and appreciating the importance of following standard operating procedures *without deviation!*).

This presentation will discuss the current accreditation requirements, where in the measurement cycle skills gaps tend to arise, how these gaps can be identified, and how competence can be assessed and monitored.

1. ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories.
2. ISO 15189, Medical laboratories — Requirements for quality and competence

Where next

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At the beginning there was a will, there was an objective, but there was no path. EURACHEM made the path by walking, one step at a time first, several steps later. As we progressed, some routes were consolidated and new ones were opened. We know how it began, which challenges were faced, what was achieved.

We know where we are, we know who we are and the Future comes next; what will be will be. We are informed enough to issue some educated guesses; we can enroll in some conjectures and, no doubt, we will be surprised by some unexpected, unforeseen and decisive breakthrough.

Whatever the circumstances, the key for success always lays on hardworking and dedicated people, learning and teaching, doing research, networking.

Examples will be given of standing issues, ongoing work, short-term and long-term perspectives of what needs to be done.

ORAL COMMUNICATIONS

Courses of study and interest-based subjects

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"Lifelong learning is being recognized by traditional colleges and universities as valid in addition to degree attainment…. The institutions produce educated citizens who buy goods and services in the community and the education facilities and personnel generate economic activity during the operations and institutional activities. Similar to health facilities, educational institutions are among the top employers in many cities and towns of the world. Whether brick-and-mortar institutions or on-line schools, there is a great economic impact worldwide from learning, including lifelong learning, for all age groups. Some learning is accomplished in segments or interest categories and can still be valuable to the individual and community. The economic impact of educational institutions at all levels will continue to be significant into the future as formal courses of study continue and interest-based subjects are pursued…. [http://en.wikipedia.org/wiki//Lifelong_learning]".

The above statement can be applied to the history of teaching and learning Quality in Analytical Chemistry. The awareness to the need for organized action can be traced back on time to some situations that identified gaps in regular school education.

For logistic reasons of various kinds, the European Union was the forum by excellence and European institutions were in a position that enabled them to take lead in the implementation of opportunities for education and training at all levels. EURACHEM was pioneer, others followed acting at local, national, regional and international levels.

This is the case of the consortium of nine European universities that, for the past seven years has put up and implemented the Euromaster Programme Measurement Science in Chemistry [http://www.msc-euromaster.eu/]; the consortium is a cooperation of universities jointly delivering a common programme on Measurement Science in Chemistry. The aim is to offer an education in Measurement Science which enables students to build those competence and skills which are needed to be able to obtain reliable results in chemical and bio-analysis.

The recently well succeeded reapplication for the Eurolabel® awarded by the European Chemistry Thematic Network, ECTN, [http://ectn-assoc.cpe.fr/association/index.htm] was an opportunity for revision of the scope, aims, procedures and achievements, which will be presented.

OC – 10

Training needs to understand quality assurance

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Quality Assurance is defined as part of quality management focused on providing confidence that quality requirements will be fulfilled[1] other parts being quality planning, quality control and quality improvement. These terms are of interest/applicable and of (decisive) importance to all activities of economic interest with regard to products, services and procedures including conformity assessment activities. Quality assurance is of importance not only for a particular activity but also for activities linked with it; this may include supplies, manufacture, marketing, conformity assessment, accreditation, competent authorities, customers. The presentation is focused on the training needs referring to specific aspects of interest to the main parties involved in each case. Based on the experience gained within the Cyprus Accreditation Body, the presentation gives examples illustrating the importance of training and awareness for the understanding of various aspects of quality assurance by all parties, to the extent needed so that they know what they are looking for, how compliance with requirements is documented and how an assessment of compliance is confirmed. The presentation is focused on laboratories and interrelated activities with reference to the requirements of accreditation and certification standards applicable in each case[2-4]. Common understanding of basic aspects of quality assurance and their use as tools in a common technical language require training and awareness at all levels so that quality assurance helps the expectations and the overall quality and economic goals of the society to be met. This is how quality culture is created and enhanced.

1. ISO 9000 (2005): Quality management systems-Fundamentals and vocabulary
2. ISO/IEC 17025 (2005): General requirements for the competence of testing and calibration laboratories
3. ISO 15189 (2012): Medical laboratories-Requirements for quality and competence
4. ISO 9001 (2008): Quality management systems-Requirements

POSTERS

The quality system and metrology in chemistry: HR University training

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This work portrays the proactivity of teachers, students and private sector represented by partner companies, in teaching Metrology in Chemistry at University. Teaching is based on methods described in the literature[1,2] and others, searching innovation and improvement of university learning[3]. One of the first goals of the presented teaching strategy is to reduce the deterministic view of the world followed by the Brazilian academy, specially in courses in the fields of the exact sciences, in training human resources, HR[4], while increasing the probabilistic view. The study of Quality and Metrology in Chemistry, initiated during graduation and continued in post-graduation, associated to the evidence that these topics are part of everyday life increased the awareness[5] to the need for the dissemination of these concepts. The developed innovative teaching programme aims at producing human resources properly educated in developing quality systems, through bringing teachers and students together, sharing experiences and discussing approaches and perspectives. Since the study began in 1999 the results obtained are highly satisfactory, namely on what concerns:

1- Promotion of cooperation between faculty members, thus mitigating academic isolation;

2- Convergence of working methods between the university and the private sector;

3- Integration of students treated as equal active agents in work teams;

4- Training HR properly inserted in Quality Systems and Chemical Metrology culture;

5- Supporting the private sector with human resources that can disseminate knowledge and implement actions on Quality and Metrology in Chemistry.

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5. P. R. Villa de Paula, O. Hojo, C. C. M. Santos, J. P. Batistuti, F. L. Fertonani, 5to. Congreso Iberoamericano de Quimica Analitica, Universidad de la Republica, Montivideo, Uruguay, 2012.

TrainMiC® a steadily growing and sustainable learning community

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TrainMiC® is a life-long learning programme providing European-wide, harmonised training in metrology in chemistry and the training focusses on how to interpret the metrological requirements of the ISO/IEC-17025 for chemical and bio-analytical measurements across different sectors (environment, food, consumer protection, etc.). It was created in 2001, originally in response to supporting countries in EU accession. Shortly afterwards, it became operational in many other countries and today even beyond the EU.

Its modus operandi is that of a *Community of Practice*, and its members collaborate both face-to-face as well as virtually via an e-collaboration platform. The programme operates via a network of about 90 authorised trainers who have signed a JRC licence agreement. Although the JRC-IRMM manages the programme, TrainMiC® is based on devolution and federating resources of various individuals and organisations. There have been close to 9000 participants in training events, most of which have been organised locally by national teams. For this purpose, training material was translated in 14 different languages.

The programme has become a sustainable platform for technical and scientific harmonisation opening the way to collaboration across Europe and beyond.

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FACULDADE · DE · CIÊNCIAS UNIVERSIDADE · DE · LISBOA

RELACRE
ASSOCIAÇÃO DE LABORATÓRIOS
ACREDITADOS DE PORTUGAL