CHEMICAL METROLOGY
PROGRESS in GREECE

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on behalf of
EXHM/GCSL-EIM
Chemical Metrology Laboratory
General State Chemical Laboratory, Athens

Chemical Metrology in Greece

Presentation layout

EXHM – chemical metrology

Documentation of CMCs

Reference materials

Proficiency testing

Supporting the State and Society

Hellenic Metrology Institute (EIM)

Hellenic Metrology Institute
E.I.M. – Thessaloniki, 1994

EIM was founded in 1994 as a legal entity under the Ministry of Industry and it is located in Thessaloniki.

EIM in 2013 merged with Accreditation Body (ESYD) and Standardization Body (ELOT) into the umbrella organization, National Quality Infrastructure System (NQIS).

EIM is supervised by the Ministry of Economy, Development & Tourism..

Hellenic Metrology Institute (EIM)

EIM operates the National Laboratories of Greece responsible for the realization of the SI units by the respective national standards, in the following fields:

1. Physical Measurements the Laboratories of Temperature & Humidity, Length & Dimensional Measurements, Acoustics & Vibrations.
2. Mechanical Measurements the Laboratories of Mass, Volume, Flow, Force and Pressure.
3. Electrical Measurements the Laboratories of Electrical Measurements at High Frequencies, Low Frequencies and Time – Frequency.

and has designated

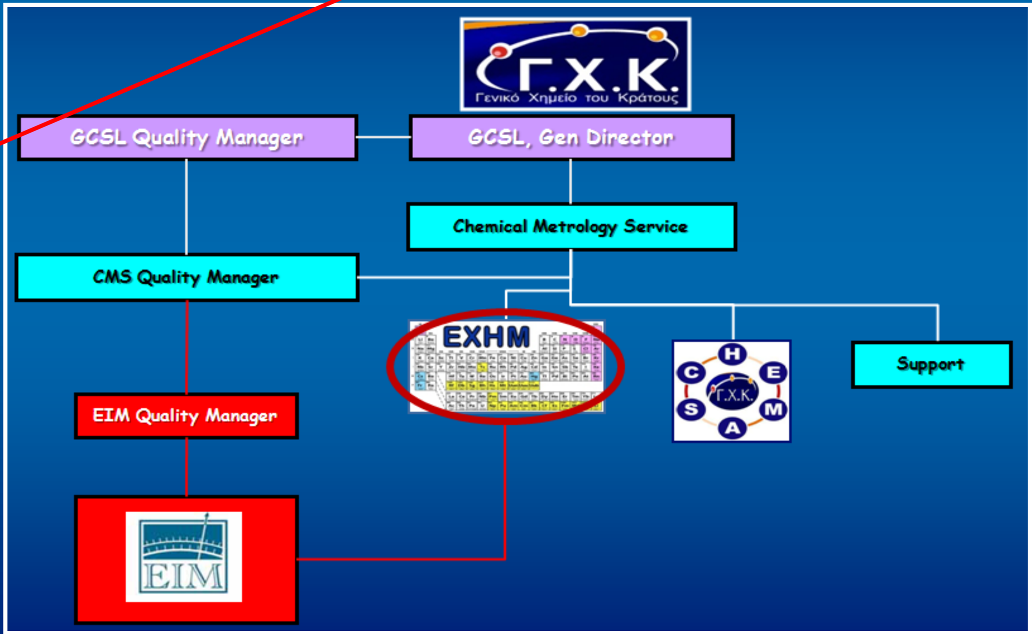
1. IRCL/GAEC-EIM in Athens, in the premises of the Greek Atomic Energy Commission (GAEC) for Nuclear Metrology, and
2. EXHM/GCSL-EIM, in Athens, in the premises of the General Chemistry State Laboratories for Chemistry

Hellenic Metrology Institute
E.I.M. – Thessaloniki, 1994

Εργαστήριο ΧΗμικής Μετρολογίας

CHemical Metrology Laboratory

General State Chemical Laboratory
G.C.S.L. – Athens, 1929

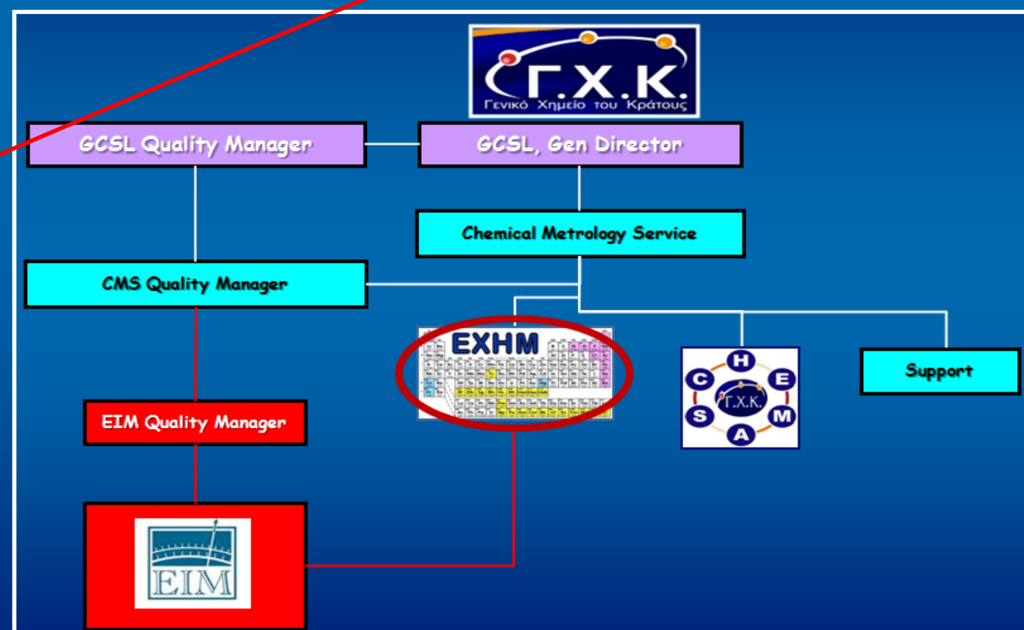


Hellenic Metrology Institute
E.I.M. – Thessaloniki, 1994

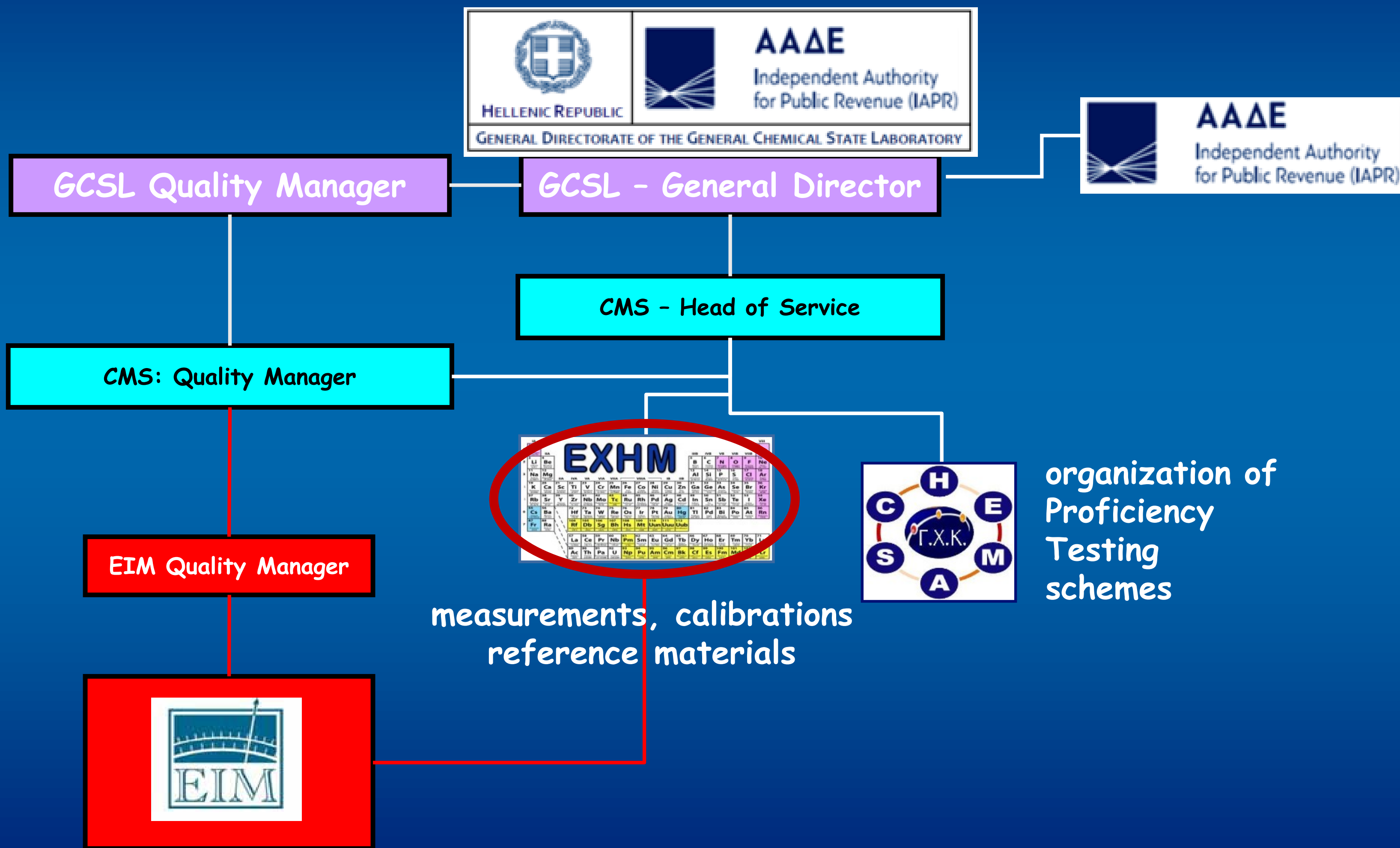
EXHM was established by Greek law (N.3427/2005) in the 5th Athens Chemical Service, the newest GCSL division.

Its main responsibilities and its relationship to EIM are described in detail in Ministerial Decisions 3001148/687 and 3001149/688.

State Chemical Laboratory
G.C.S.L. – Athens, 1929



Chemical Metrology Service – Organization chart



EXHM – major operational milestones

- GCSL installations are renovated in 2005-6 to house EXHM
- the lab was equipped between 2007-2008, partly by funding provided by the 2000-2006 Framework Programme of the European Union (under the "Competitiveness" action)
- was staffed in 2009
- has been providing calibration and testing services to customers since August 2010 as a GCSL section (5th Athens Chemical Service)
- implemented a QMS according to ISO 17025 and ISO 17043 in 2010.
- introduced ISO 17034 compliant clauses and procedures in 2011.
- accredited by ESYD as an interlaboratory testing provider since 2012.
- in 2013 the QMS was submitted to EURAMET TC-Q and was accepted without any revision
- accredited (March 2014) under flexible scope according to ISO/IEC 17025 for tests and calibrations.
- obtained flexible accreditation scope as a PT provider since 2016
- applied for ISO 17034 accreditation in 2016

MRA – Mutual Recognition Arrangement

Reconnaissance mutuelle
des étalons nationaux de mesure
et des certificats d'étalonnage et de mesurage
émis par les laboratoires nationaux de métrologie

Paris, le 14 octobre 1999

Mutual recognition
of national measurement standards
and of calibration and measurement certificates
issued by national metrology institutes

Paris, 14 October 1999

Comité international des poids et mesures

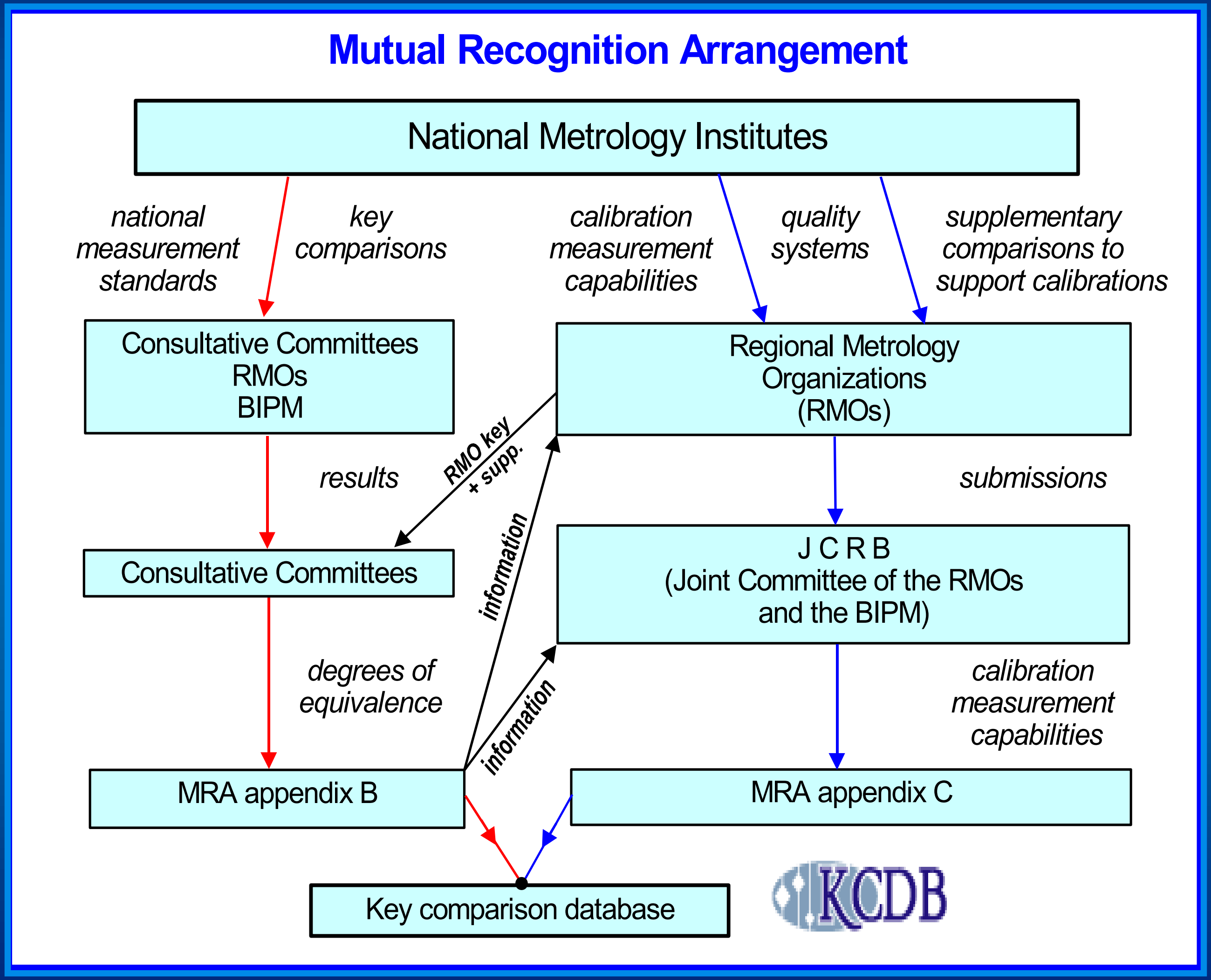
Bureau international des poids et mesures

Organisation intergouvernementale de la Convention du Mètre

purpose

- to define the degree of equivalence between the measurement standards maintained by metrology institutes
- ensure the equivalence of the calibration certificates issued and the reference materials produced by metrology institutes
- the provision of a sound technical base for the development of agreements that support commercial and regulation policies between governments, organizations and/or social groups

World-wide comparability of measurements



Key comparisons

NMI:

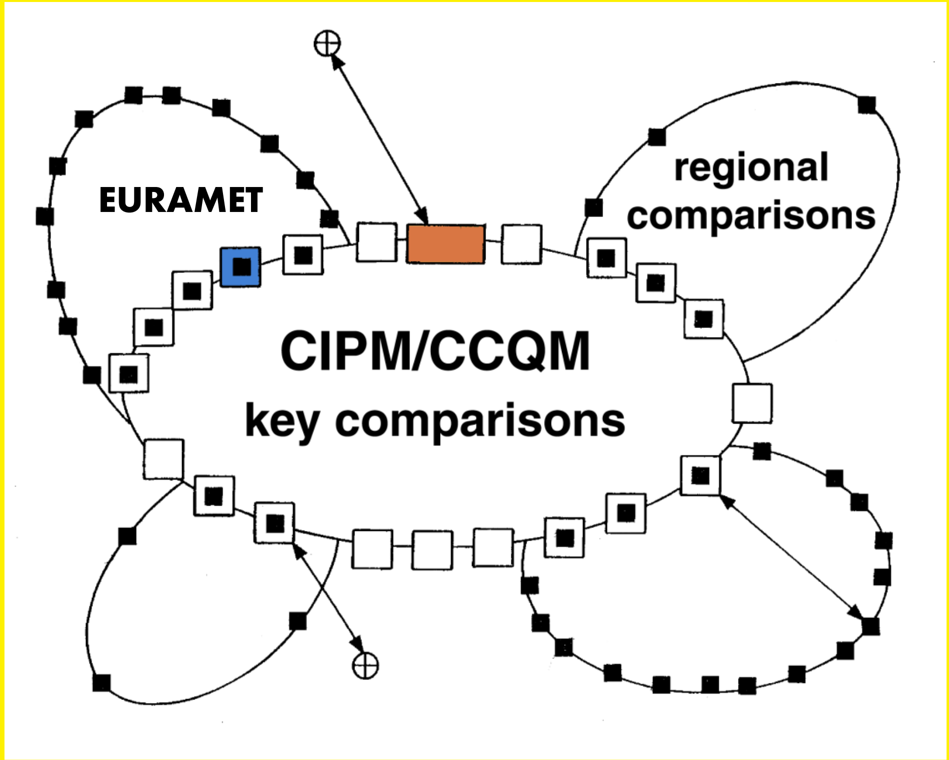
primary measurement systems + devices

primary reference materials

accredited calibration laboratories, reference laboratories

certified reference materials (CRMs)

chemical testing laboratories, which have to demonstrate their traceability
(ISO 17025, ISO 15189)



categories of key comparisons

Track A: model 1 (substances, calibration solutions, matrix materials)

Track B: model 2 (reference materials)

Track C: hot subjects – currents topics

Track D: development of analytical procedures

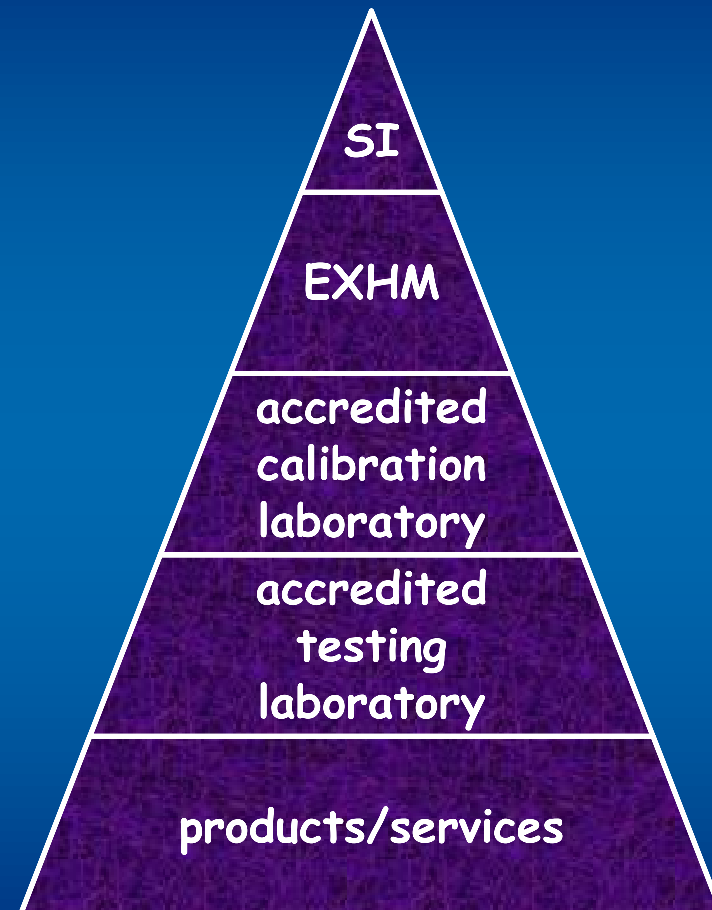
E.XH.M.

traceability

international system of units – (SI)

mol (mole)

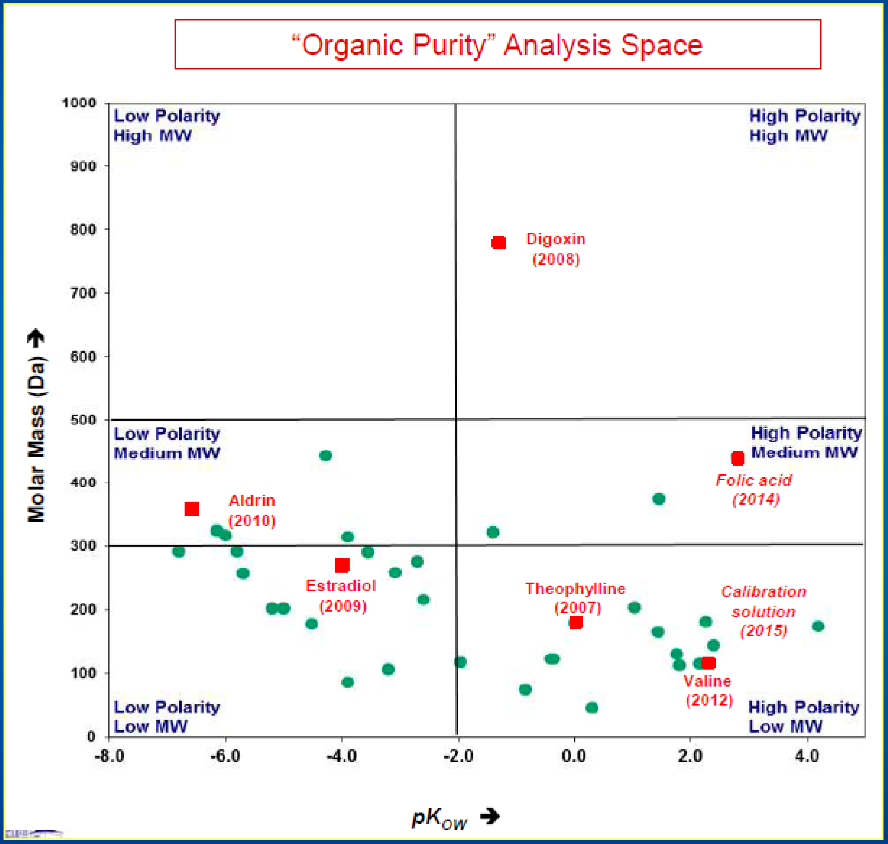
quantity of substance



Responsibilities of EXHM

a) Realization of the SI units by maintaining the national standards.
b) Dissemination of measurement traceability to the metrological system in Greece.
c) Support for the operation of the metrological system in Greece
d) Representation of Greece in international metrology organizations and agreements
e) Promotion of metrological knowledge
f) Operation of calibration laboratories
g) Technical Advisor of the Greek State in issues of metrology

Countless organic compounds



Primary reference methods

- CCQM (1995) : Primary Reference Methods

methods of the highest metrological accuracy, whose procedures can be described comprehensively and be fully understood, and a clear and complete uncertainty statement can be formulated in SI units

- isotope dilution mass spectrometry (IDMS)
- high resolution mass spectrometry (HRMS)
- nuclear magnetic resonance (NMR) spectrometry
- electrochemical methods (e.g. coulometry, voltammetry)
- thermochemical methods
- volumetric methods
- weighing methods

These methods are used for acquiring measurement results that are not related to a measurement standard for quantities of the same category (JCGM, 2008)

Basic equipment

ICP-HRMS

LC-MS/MS AM

GC-IT-MS

FT-Raman

FT-IR

EXHM/ΓΧΚ-EIM: flexible accreditation scope

determination of elements and organic compounds with advanced spectrometric techniques

PRETREATMENT		DETERMINATION		QUANTIFICATION
liquid extraction	→	mass HR balances	→	exact matching
digestion		amount of substance		calibration curve
SPE		LC-MS/MS GC-MSn HR-ICP-MS UV-Vis		standard additions
derivatization				isotope dilution

Special techniques: NMR, KF, HS-IDMS

Chemical Metrology Service – Quality Management System

E.XH.M.

ISO/IEC 17025:2005

- flexible scope
- determination of organic compounds and elements with mass spectrometric techniques with emphasis on isotopic dilution

ISO 17034 (sic)

- design and production of certified reference materials
  (primary calibrators, calibration solutions, matrix materials for contaminants)

S.CHE.M.A.

ISO/IEC 17043:2010

- proficiency testing schemes on:
  foodstuffs
  alcoholic drinks
  environmental samples
  industrial products

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ΕΧΗΜ/ΓΧΚ-ΕΙΜ: accreditation scope

ΕΡΓΑΣΤΗΡΙΟ ΧΗΜΙΚΗΣ ΜΕΤΡΟΛΟΓΙΑΣ
(ΕΧΗΜ/ΓΧΚ-ΕΙΜ)
ΚΑΤΑΛΟΓΟΣ ΔΙΑΠΙΣΤΕΥΜΕΝΩΝ ΔΙΑΔΙΚΑΣΙΩΝ

ομάδες με το ίδιο χρώμα ανήκουν στην ίδια ευέλικτη μέθοδο

χρώμα σε στήλη υποδηλώνει ευελιξία

Α/Α	ΚΩΔΙΚΟΣ	ΚΑΤΕΡΓΑΣΙΑ	ΤΕΧΝΙΚΗ	ΥΠΟΣΤΡΩΜΑ	ΧΑΡΑΚΤΗΡΙΣΤΙΚΑ ΑΝΑΛΥΤΩΝ	ΕΙΔΟΣ ΥΠΟΣΤΡΩΜΑΤΟΣ	ΑΝΑΛΥΤΕΣ	ΝΟΜΙΚΕΣ ΑΠΑΙΤΗΣΕΙΣ	ΑΠΟ	ΕΩΣ
27 01	XTR-LCMS-EM	εκχ. στερεής φάσης	LC-MS/MS	τρόφιμα & ποτά	ρυπαντές/επιμολυντές	γαλακτοκομικά	μελαμίνη	798/2008/ΕΚ	01-07-2012	31-01-2013
27 02	XTR-LCMS-EM	εκχ. υγρού-υγρού	LC-MS/MS	τρόφιμα & ποτά	πρόσθετα	χυμοί και ποτά	βενζοϊκό οξύ	882/2004/ΕΚ	01-07-2012	31-01-2013
27 03	XTR-LCMS-ES	καμία	LC-MS/MS	αλκοόλη και αλκ. υγρά	μετουσιωτικά διαλυτών	αλκοόλη & αλκ. υγρά	BITREX	162/2013/ΕΚ	01-07-2012	31-01-2013
27 04	DIG-ICPMS-ES	καμία	LC-MS/MS	νερά	μέταλλα	πόσιμα & επιφανειακά νερά	Al,As,B,Ba,Cd,Co,Cr,Cu,Fe,Mn,Ni,Pb,Sb,Se,Sn,Zn	ΦΕΚ1977/Β/2011	01-07-2012	31-01-2013
27 05A	XTR-GCMS-ID	εκχ. υγρού-υγρού	GC-IT-MS	αλκοόλη και αλκ. υγρά	μετουσιωτικά διαλυτών	αλκοόλη, αλκ. υγρά	φθαλικοί εστέρες (διμεθυλ, διαιθυλ, δι-ισοβουτυλ, διβουτυλ,	882/2004/ΕΚ	01-07-2012	31-03-2015
27 05A	XTR-GCMS-ID	εκχ. στερεής φάσης	GC-IT-MS	τρόφιμα	ρυπαντές/επιμολυντές	εδώδιμα έλαια	βενζυλβουτυλ, δι(2-αιθυλ)εξυλ, διοκτυλ, διισονονυλ, διισοδεκυλ)	882/2004/ΕΚ	01-07-2012	31-03-2015
27 06	XTR-UVVIS-ECL	εκχ. υγρού-υγρού	UV-Vis	νερά & απόβλητα	μέταλλα	νερά & απόβλητα	εξασθενές χρώμιο	ΦΕΚ1977/Β/2011	01-07-2012	31-03-2015
27 07	1504-LCMS-ECL	μεταναστευση	LC-MS/MS	προσομοιωτές FCM	μη πτητικά οργανικά μόρια	υδατικοί προσομοιωτές	ανιλίνη, 4,4'-μεθυλενοδιανιλίνη, ο-τολουιδίνη	882/2004/ΕΚ	01-07-2012	31-12-2012
27 08A	DIG-ICPMS-SA	χώνευση	HR-ICP-MS	τρόφιμα & ποτά	μέταλλα	τρόφιμα με υψηλή περ. νερού	Pb/Fe/Cu/Cd	333/2007/ΕΚ	01-11-2011	31-12-2012
27 08B	DIG-ICPMS-SA	χώνευση	HR-ICP-MS	τρόφιμα & ποτά	μέταλλα	κρέατα & ψάρια	Fe/Cd	333/2007/ΕΚ	01-11-2011	31-12-2012
27 08Γ	DIG-ICPMS-SA	χώνευση	HR-ICP-MS	τρόφιμα & ποτά	μέταλλα	αιθανόλη	Cu	333/2007/ΕΚ	01-11-2011	31-12-2012
27 08Δ	DIG-ICPMS-SA	χώνευση	HR-ICP-MS	τρόφιμα & ποτά	μέταλλα	τρόφιμα με υψηλά σάκχαρα	Cr	333/2007/ΕΚ	01-11-2011	31-12-2012
27 08Ε	DIG-ICPMS-SA	χώνευση	HR-ICP-MS	τρόφιμα & ποτά	μέταλλα	δημητριακά	Cd, Cr, Cu, Pb	333/2007/ΕΚ	01-11-2011	31-12-2012
27 09	XTR-LCMS-ECL	εκχ. στερεής φάσης	LC-MS/MS	τρόφιμα & ζωοτροφές	μυκοτοξίνες	καλαμπόκι	δεοξυνιβαλενόλη, νιβαλενόλη	401/2006/ΕΚ	01-12-2011	31-03-2012
27 10	XTR-LCMS-ES	εκχ. στερεής φάσης	LC-MS/MS	τρόφιμα ζωικής προέλευσης	μη στεροειδή αντιφλεγμονώδη	κρέας & προϊόντα του	φαινυλοβουταζόνη	657/2002/ΕΚ	01-03-2013	22-03-2013
27 11	GCMS-ID	καμία	GC-IT-MS	αλκοόλη	μετουσιωτικά διαλυτών	αλκοόλη, αλκ. υγρά	μεθυλοαιθυλοκετόνη (MEK)	162/2013/ΕΚ	01-10-2013	30-11-2013
27 12	XTR-LCMS-ES	εκχ. στερεής φάσης	LC-MS/MS	τρόφιμα & ζωοτροφές	μυκοτοξίνες	καρυκεύματα, φυστίκια	αφλατοξίνη B1, B2, G1, G2, ωχρατοξίνη A	401/2006/ΕΚ	01-06-2014	30-12-2014
27 13	XTR-LCMS-EM	εκχ. στερεής φάσης	LC-MS/MS	τρόφιμα & ποτά	ρυπαντές/επιμολυντές	αρτοσκευάσματα, αλεύρι	ακρυλαμίδιο	REC 2013/647/EU	01-04-2014	31-05-2014
27 14	XTR-LCMS-ECL	εκχ. υγρού-υγρού	LC-MS/MS	τρόφιμα & ζωοτροφές	μυκοτοξίνες	φυστίκια κελυφωτά	αφλατοξίνη B1, B2, G1, G2	401/2006/ΕΚ	01-10-2014	31-12-2014
27 15	XTR-LCMS-ECL	εκχ. υγρού-υγρού	LC-MS/MS	τρόφιμα & ζωοτροφές	μη στεροειδή αντιφλεγμονώδη	γάλα	αμινοαντιπυρίνη, 4-μεθυλαμινοαντιπυρίνη, ναπροξένη, δικλοφαινάκη, κετοπροφαίνη, οξυφαινυλβουταζόνη, φαινυλβουταζόνη, μελοξικάμη, φλουνιξίνη, 5-υδροξυφλουνιξίνη, μεφαιναμικό οξύ, τολφαιναμικό οξύ	37/2010/ΕΕ	01-10-2014	31-12-2014
27 16	XTR-LCMS-ECL	εκχ. υγρού-υγρού	LC-MS/MS	τρόφιμα & ζωοτροφές	μη στεροειδή αντιφλεγμονώδη	κρέας	αμινοαντιπυρίνη, 4-μεθυλαμινοαντιπυρίνη, ναπροξένη, δικλοφαινάκη, κετοπροφαίνη, καρπροφαίνη, οξυφαινυλβουταζόνη, φαινυλβουταζόνη, μελοξικάμη, φλουνιξίνη, μεφαιναμικό οξύ, τολφαιναμικό οξύ	37/2010/ΕΕ	01-10-2014	31-12-2014
27 17	XTR-LCMS-ECL	εκχ. υγρού-υγρού	LC-MS/MS	τρόφιμα & ζωοτροφές	μυκοτοξίνες	γάλα	αφλατοξίνη M1	401/2006/ΕΚ	01-10-2014	31-12-2014

LC-MS/MS	τρόφιμα	μη πτητικά οργανικά μόρια
GC-IT-MS	τρόφιμα	πτητικά οργανικά μόρια
LC-MS/MS	προσομοιωτές	μη πτητικά οργανικά μόρια
HR-ICP-MS	τρόφιμα	ανόργανα στοιχεία

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Σελίδα 1 από 1

ΕΚΔΟΣΗ: 5 - ΗΜ/ΝΙΑ: 31.01.2016
ΥΠΕΥΘΥΝΟΣ: Δ27/ΥΠ

ILAC P10 – policy for the traceability of measurement results

ILAC Policy on the Traceability of Measurement Results

ILAC P10:01/2013

ILAC POLICY FOR TRACEABILITY COVERED BY THE ILAC ARRANGEMENT IN CALIBRATION

The general requirement for traceability in ISO/IEC 17025:2005 is:

> *5.6.1 All equipment used for tests and/or calibrations, including equipment for subsidiary measurements (e.g. for environmental conditions) having a significant effect on the accuracy or validity of the result of the test, calibration or sampling shall be calibrated before being put into service.*

It is an obligation of the laboratory to justify the need for calibration. In ISO/IEC 17025:2005, the further traceability requirement for calibration laboratories is:

> *5.6.2.1.1 For calibration laboratories, the programme for calibration of equipment shall be designed and operated so as to ensure that calibrations and measurements made by the laboratory are traceable to the International System of Units (SI) (Système international d'unités).*

For reference standards the traceability requirements of ISO/IEC 17025:2005 are:

> *5.6.3.1 The laboratory shall have a programme and procedure for the calibration of its reference standards. Reference standards shall be calibrated by a body that can provide traceability as described in 5.6.2.1. Such reference standards of measurement held by the laboratory shall be used for calibration only and for no other purpose, unless it can be shown that their performance as reference standards would not be invalidated. Reference standards shall be calibrated before and after any adjustment.*

In order to maintain traceability in calibration programmes, guidance can be found in *ILAC G24:2007* [4] "*Guidelines for the determination of calibration intervals of measuring instruments*.

ILAC P10 – policy for the traceability of measurement results

Clause 5.6.2.1.1 in ISO/IEC 17025:2005 further states that "*When using external calibration services, traceability of measurement shall be assured by the use of calibration services from laboratories that can demonstrate competence, measurement capability and traceability*". For equipment and reference standards that must be calibrated, the ILAC policy is that they shall be calibrated by:

1) An NMI whose service is suitable for the intended need and is covered by the CIPM MRA. Services covered by the CIPM MRA can be viewed in Appendix C of the BIPM KCDB which includes the range and uncertainty for each listed service.
   Note 1: Some NMIs may also indicate that their service is covered by the CIPM MRA by including the CIPM MRA logo on their calibration certificates, however the fixing of the logo is not mandatory and the BIPM KCDB remains the authoritative source of verification.

   Note 2: NMIs from Member States participating in the Metre Convention may take traceability directly from measurements made at the BIPM. The KCDB provides an automatic link to the relevant BIPM calibration services (including the range and uncertainty). Individual calibration certificates issued by the BIPM are also listed.

or

2) An accredited calibration laboratory whose service is suitable for the intended need (i.e, the scope of accreditation specifically covers the appropriate calibration) and the Accreditation Body is covered by the ILAC Arrangement or by Regional Arrangements recognised by ILAC.
   .
   Note: Some calibration laboratories indicate that their service is covered by the ILAC Arrangement by including the ILAC Laboratory Combined MRA mark on the calibration certificate. Alternatively, the accreditation symbol of the accreditation body that is a signatory to the ILAC Arrangement and/or a recognised regional MLA may be included on the calibration certificate. Both of these options may be taken as evidence of traceability.

or

3a) An NMI whose service is suitable for the intended need but not covered by the CIPM MRA. In this case the accreditation body shall establish a policy to ensure that those services meet the relevant criteria for metrological traceability in ISO/IEC 17025:2005.

or

3b) A calibration laboratory whose service is suitable for the intended need but not covered by the ILAC Arrangement or by Regional Arrangements recognised by ILAC. In these cases the accreditation body shall establish a policy to ensure that those services meet the relevant criteria for metrological traceability in ISO/IEC 17025:2005.

Laboratories that have demonstrated traceability of their measurements through the use of calibration services offered according to 1) or 2) above have made use of services that have been subject to relevant peer review or accreditation. In the situation where 3a) or 3b) applies, this is not the case, so these routes should only be applicable when 1) or 2) are not possible for a particular calibration. The laboratory must therefore ensure that appropriate evidence for claimed traceability and measurement uncertainty is available and the accreditation body shall assess this evidence. Further guidance is found in Annex A.

Clause 5.6.2.1.2 of ISO/IEC 17025:2005, states:

> *There are certain calibrations that currently cannot be strictly made in SI units. In these cases calibration shall provide confidence in measurements by establishing traceability to appropriate measurement standards such as:*
> - *the use of certified reference materials provided by a competent supplier to give a reliable physical or chemical characterization of a material;*
> - *the use of specified methods and/or consensus standards that are clearly described and agreed by all parties concerned.*
>
> *Participation in a suitable programme of inter laboratory comparisons is required where possible.*

The ILAC Policy is:

4) Clause 5.6.2.1.2 can only be applied in the case in which the laboratory has demonstrated that the policy 1) to 3) cannot reasonably be met. It is the responsibility of the laboratory to choose a way to satisfy 5.6.2.1.2 and to provide the appropriate evidence. This evidence shall be documented and the documentation shall be assessed by the accreditation body.

traceability

ISO/IEC 17025:2005(E)

5.6 Measurement traceability

5.6.1 General

5.6.2.1 Calibration

5.6.2.1.1 For calibration laboratories, the programme for calibration of equipment shall be designed and operated so as to ensure that calibrations and measurements made by the laboratory are traceable to the International System of Units (SI) (*Système international d'unités*).

A calibration laboratory establishes traceability of its own measurement standards and measuring instruments to the SI by means of an unbroken chain of calibrations or comparisons linking them to relevant primary standards of the SI units of measurement. The link to SI units may be achieved by reference to national measurement standards. National measurement standards may be primary standards, which are primary realizations of the SI units or agreed representations of SI units based on fundamental physical constants, or they may be secondary standards which are standards calibrated by another national metrology institute. When using external calibration services, traceability of measurement shall be assured by the use of calibration services from laboratories that can demonstrate competence, measurement capability and traceability. The calibration certificates issued by these laboratories shall contain the measurement results, including the measurement uncertainty and/or a statement of compliance with an identified metrological specification (see also 5.10.4.2).

5.6.2.2 Testing

5.6.2.2.1 For testing laboratories, the requirements given in 5.6.2.1 apply for measuring and test equipment with measuring functions used, unless it has been established that the associated contribution from the calibration contributes little to the total uncertainty of the test result. When this situation arises, the laboratory shall ensure that the equipment used can provide the uncertainty of measurement needed.

NOTE 4 The term "identified metrological specification" means that it must be clear from the calibration certificate which specification the measurements have been compared with, by including the specification or by giving an unambiguous reference to the specification.

traceability

TECHNICAL REPORT

ISO/TR 16476

First edition
2016-06-01

Reference materials — Establishing and expressing metrological traceability of quantity values assigned to reference materials

Matériaux de référence — Etablissement et expression de la traçabilité métrologique de valeurs assignées à des matériaux de référence

Reference number
ISO/TR 16476:2016(E)

— "Traceability of an RM"

is in common and daily use, it is understood throughout as the traceability of the quantity value assigned to a (certified) reference material.

— "(Analytical) method"

is used in the sense of defining the instrumental implementation of the (most often physical) principle of obtaining, from an appropriately pre-processed and/or transformed object under

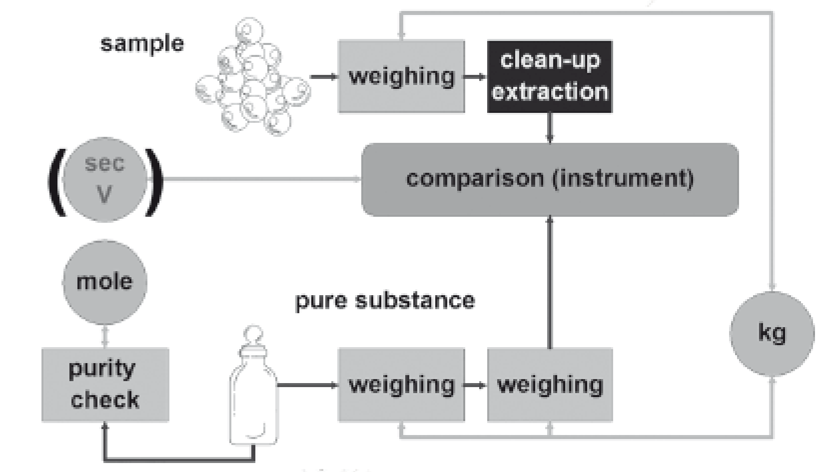
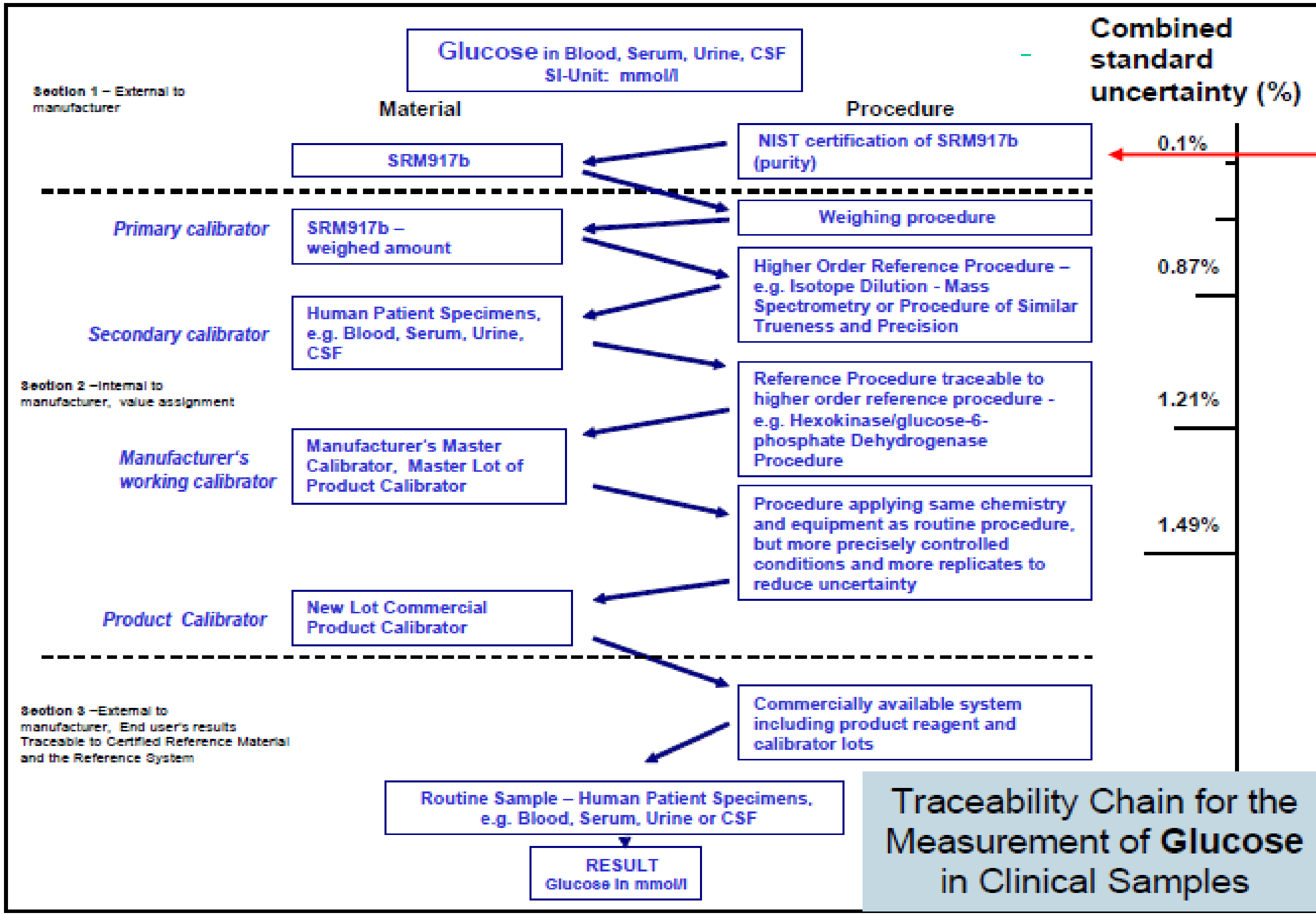


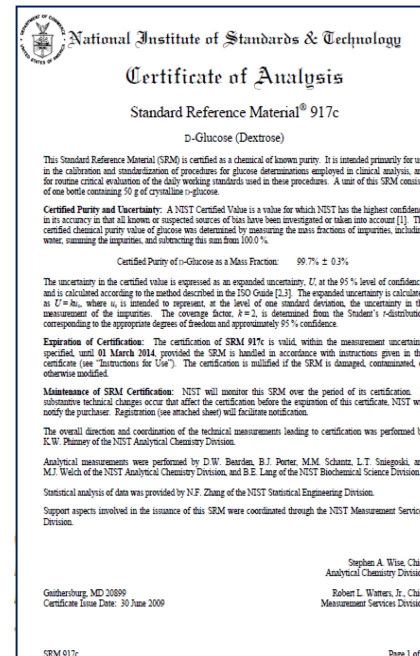
Figure 1 — "Horizontal" traceability network relating the measured quantities in a measurement procedure model to a set of SI units

Traceability chain



Traceability Chain for the Measurement of **Glucose** in Clinical Samples

997 ± 3 mg/g



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 917c

D-Glucose (Dextrose)

This Standard Reference Material (SRM) is certified as a chemical of known purity. It is intended primarily for use in the calibration and standardization of procedures for glucose determinations employed in clinical analysis, and for routine critical evaluation of the daily working standards used in these procedures. A unit of this SRM consists of one bottle containing 50 g of crystalline D-glucose.

Certified Purity and Uncertainty: A NIST Certified Value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. The certified chemical purity value of glucose was determined by measuring the mass fractions of impurities, including water, summing the impurities, and subtracting this sum from 100.0 %.

Certified Purity of D-Glucose as a Mass Fraction: 99.7% ± 0.3%

The uncertainty in the certified value is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the method described in the ISO Guide [2,3]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the uncertainty in the measurement of the impurities. The coverage factor, $k = 2$, is determined from the Student's t-distribution corresponding to the appropriate degrees of freedom and approximately 95 % confidence.

Expiration of Certification: The certification of **SRM 917c** is valid, within the measurement uncertainty specified, until **01 March 2014**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the technical measurements leading to certification was performed by K.W. Phinney of the NIST Analytical Chemistry Division.

Analytical measurements were performed by D.W. Bearden, B.J. Porter, M.M. Schantz, L.T. Sniegoski, and M.J. Welch of the NIST Analytical Chemistry Division, and B.E. Lang of the NIST Biochemical Science Division.

Statistical analysis of data was provided by N.F. Zhang of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 30 June 2009

Robert L. Watters, Jr., Chief
Measurement Services Division

SRM 917c — Page 1 of 2

BIPM-KCDB: key comparisons

Αρχείο Επεξεργασία Προβολή Ιστορικό Σελιδοδείκτες Εργαλεία Βοήθεια

The BIPM key comparison database

kcdb.bipm.org/AppendixB/KCDB_ApB_search_result.asp?search=1&met_idy=2&bra_idy=0&cmt_idy=0&ett_idy_org=0&epo_idy=0&cou_cod

Search

Bureau International des Poids et Mesures

Home | Key and supplementary comparisons | Calibration and Measurement Capabilities - CMCs

Home > Comparisons Search > Results of the search

Key and supplementary comparisons - Results of the search

KCDB

Related links

- KCDB Statistics
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- KCDB Reports
- CIPM MRA
- JCRB
- Find my NMI
- Metrologia

Contact us

- BIPM.KCDB@bipm.org

Search criteria : Amount of Substance, Greece
Your request produced **9** result(s)

List of comparisons

Click on a comparison identifier to view more

Page 1 2

CCQM- K30.1	**Lead in wine 2011 - 2012**
Comparison type, Field	Key comparison in Amount of Substance, Inorganics
Status	**Approved for equivalence,** Results available
CCQM- K100	**Analysis of Copper in Ethanol 2011**
Comparison type, Field	Key comparison in Amount of Substance, Inorganics
Status	**Approved for equivalence,** Results available
CCQM- K103	**Melamine in milk powder 2012**
Comparison type, Field	Key comparison in Amount of Substance, Organics
Status	**Report in progress, Draft B**
CCQM- K107	**Elements and Se speciation in human serum 2013**
Comparison type, Field	Key comparison in Amount of Substance, Inorganics
Status	**Approved for equivalence,** Results available
CCQM- K108	**Determination of arsenic species, total arsenic and cadmium in brown rice flour 2013**
Comparison type, Field	Key comparison in Amount of Substance, Inorganics
Status	**Approved for equivalence,** Results available

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Print this list Top of the page

BIPM - Pavillon de Breteuil F 92312 Sèvres Cedex FRANCE

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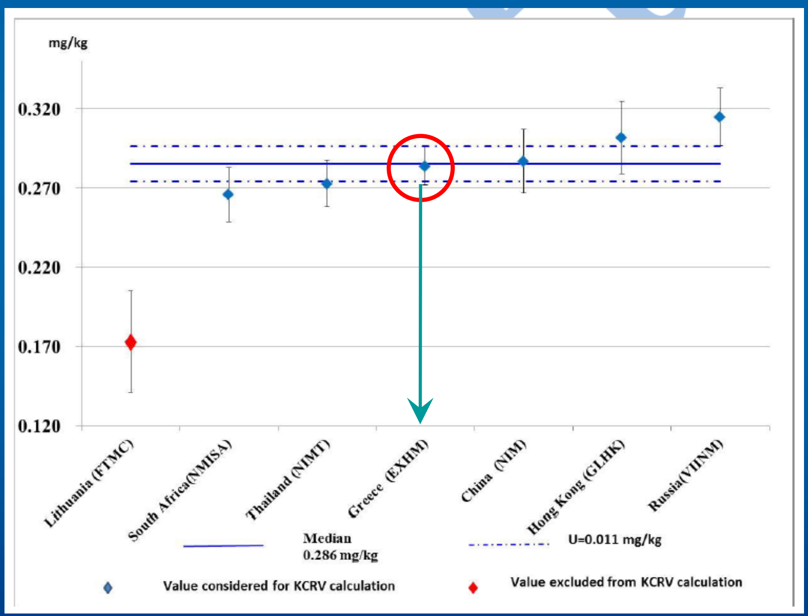
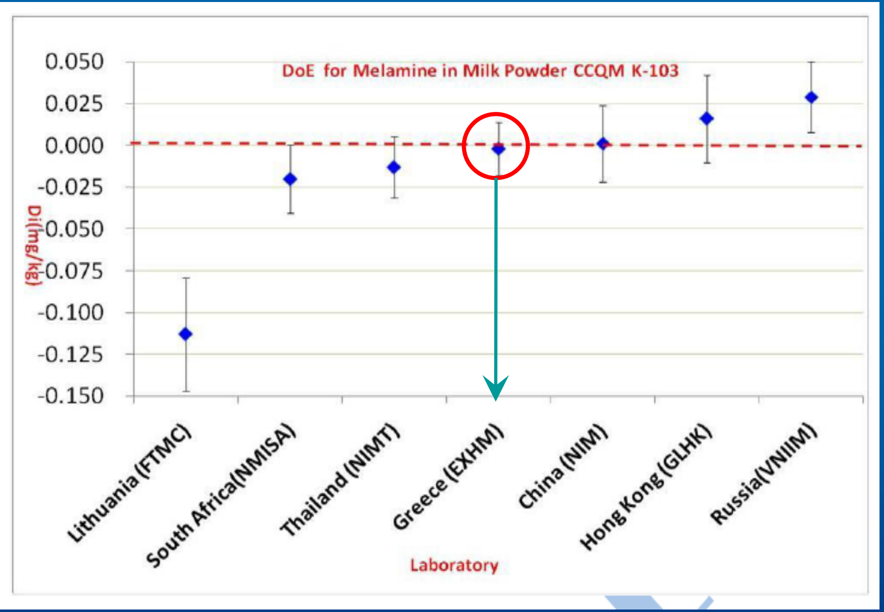
EXHM/ΓΧΚ-EIM CMCs: melamine in milk powder

EXHM 11201	contaminants	milk and milk products	melamine	Mass fraction	0.015	5	mg/kg	3	10	%	2	95%	Yes	Provision of reference value for client materials, PT samples and reference materials	Approved on 19 June 2014





EXHM/ΓΧΚ-EIM CMCs: melamine in milk powder

Hong Kong, China, GL (Government Laboratory)
Complete CMCs in Chemistry for High purity chemicals for Hong Kong, China (.PDF file)

Matrix or material	Analyte or component	Dissemination range of measurement capability		Range of certified values in reference materials	
		Mass fraction in mg/g	Relative expanded uncertainty (k = 2, 95%) in %	Mass fraction in mg/g	Absolute expanded uncertainty (k = 2, 95%) in %
high purity melamine	melamine	950 to 1000	0.5	950 to 1000	0.5

Mechanism(s) for measurement service delivery: CRM GLHK-01-01
Approved on 06 December 2011.
Internal NMI service identifier: GL/GLHK027

Hong Kong, China, GL (Government Laboratory)
Complete CMCs in Chemistry for Food for Hong Kong, China (.PDF file)

Matrix or material	Analyte or component	Dissemination range of measurement capability		Range of certified values in reference materials	
		Mass fraction in mg/kg	Relative expanded uncertainty (k = 2, 95%) in %	Mass fraction in mg/kg	Absolute expanded uncertainty (k = 2, 95%) in mg/kg
milk and milk product	melamine	0.1 to 5	6 to 8	1.15	0.08

Mechanism(s) for measurement service delivery: Certified reference material (GLHK-11-02)
Uncertainty convention 1.
Approved on 19 June 2014.
Internal NMI service identifier: GL/GLHK050

Thailand, NIMT (National Institute of Metrology (Thailand))
Complete CMCs in Chemistry for Food for Thailand (.PDF file)

Greece, EXHM/GCSL-EIM (National Laboratory of Chemical Metrology/GCSL - Hellenic Institute of Metrology)
Complete CMCs in Chemistry for Food for Greece (.PDF file)

Matrix or material	Analyte or component	Dissemination range of measurement capability	
		Mass fraction in mg/kg	Relative expanded uncertainty (k = 2, 95%) in %
milk and milk products	melamine	0.015 to 5	3 to 10

Mechanism(s) for measurement service delivery: Provision of reference value for client materials, PT samples and reference materials
Uncertainty convention 1.
Approved on 19 June 2014.
Internal NMI service identifier: EXHM/GCSL-EIM/EXHM 11201

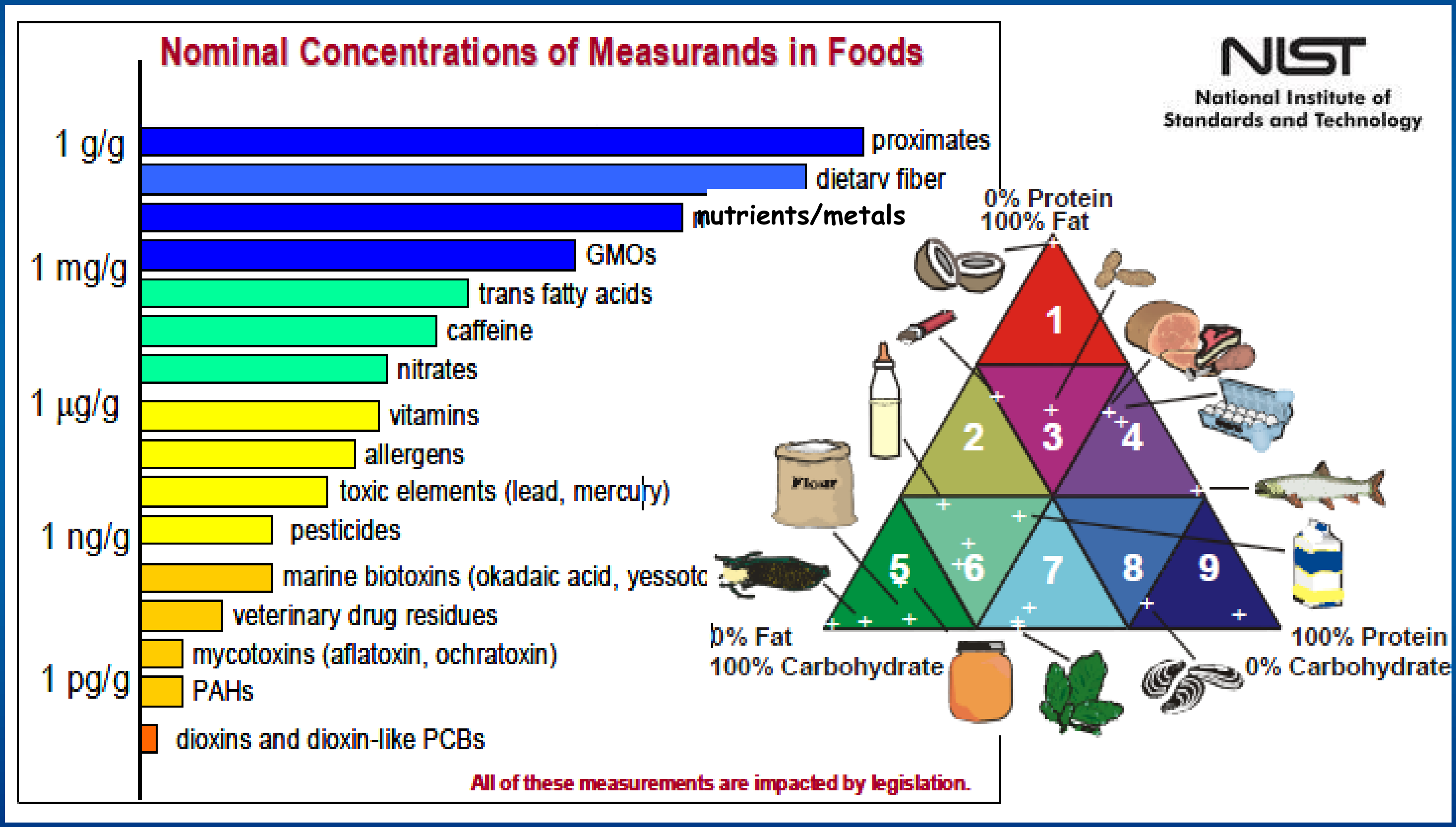
Mechanism(s) for measurement service delivery: Calibration service
Approved on 19 June 2014.
Uncertainty convention 2.

Key comparisons: OAWG plan

Overall Status of OAWG Comparisons

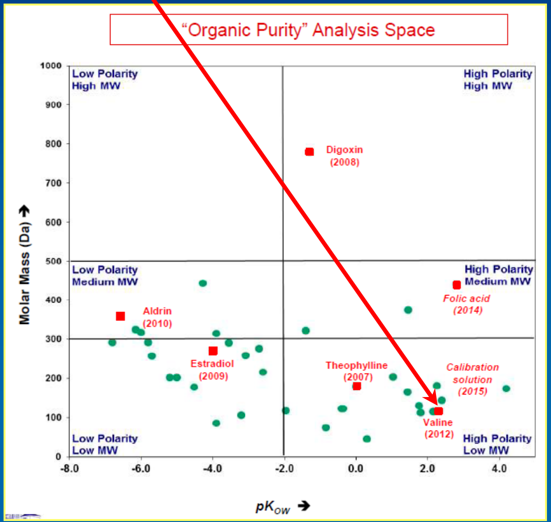
		Agreed by WG	Draft Protocol Distributed	Final Protocol Distributed	Samples Distributed	Measurements complete	Provisional Report	Discussion at WG	Draft A report	Draft B Report	OAWG approval	Report sent to WG chairs	Report on KCDB
	Track A												
K55.a	Organic Purity Assessment - Estradiol												
K55.b	Organic Purity Assessment - Aldrin												
K95	Pesticides in Tea												
K55.c	Organic Purity Assessment - L-Valine												
K102	Brominated Flame Retardants in Sediment												
K95.1	PAHs in tea												
K131	PAHs in organic solution												
K109	Urea-uric acid in serum												
K55.d	Organic Purity Assessment- Folic acid												
K141	Antibiotics in meat												
K78.a	Amino acids in aqueous solution												
K146	PAHs in olive oil												
K148.a	Organic Purity Assessment - Bisphenol A												
	Track B												
K79	Ethanol in Aqueous Solution												
K80	Creatinine in Serum												
K142	Urea-uric acid in serum and plasma												
K147	Niacin in milk powder/infant formula												
	Track C												
K81	Chloramphenicol in Pig Muscle												
K85	Malachite Green in Salmon												
K6.2	Cholesterol in Serum												
K11.2	Glucose in Serum												
K12.2	Creatinine in Serum												
K103	Melamine in Milk												
K104	Avermectin purity												
K126	Carbamazepine in surface water												
K132	Vitamin D in serum												
K133	Phthalates in PVC												
K138	Aflatoxins in fig												
	Track D												
P150	Data acquisition and process in qNMR method												
P150.b	Data acquisition and process in qNMR method												
P164	Human growth hormone in serum												

measurements: infinite combinations of «substances» and «substrates»



year	comparison	subject	analytical technique
2011	AFRIMETS-QM.K27	ethanol in water	GC-IDMS/MS
2012	EURAMET-QM.K12	creatinine in blood serum	LC-IDMS/MS
2012	CCQM-K30.1	heavy metals in wine	HR-ICP-IDMS
2013	CCQM-K100	copper in bioethanol	HR-ICP-IDMS
2013	CCQM-K103	melamine in milk powder	LC-IDMS/MS
2013	CCQM-K55c	purity of organic compunds: valine	MB, qNMR
2013	APMP-QM.S5	heavy metals in fish tissue	HR-ICP-MS
2013	APMP-QM.S6	β-agonists in meat	LC-IDMS/MS
2014	CCQM-K104	purity of organic compunds: avermectin B1a	MB
2014	CCQM-K107	heavy metals in flour	HR-ICP-IDMS
2014	CCQM-K108	heavy metals in blood serum	HR-ICP-IDMS
2015	CCQM-K124	heavy metals in infant formula	HR-ICP-MS
2015	CCQM-K125	heavy metals and hexavalent chromium in potable w	HR-ICP-IDMS
2015	CCQM-K126	carbamazepine in water	LC-IDMS/MS
2015	APMP-QM.S8	preservatives in soy sauce	LC-IDMS/MS
2015	CCQM-P150	purity of organic compunds: dimethylsulfone	qNMR
2016	CCQM-K95.1	PAHs in tea	GC-IDMS/MS
2016	CCQM-K131	calibrants - PAHs in calibration solutions	GC-IDMS/MS
2016	CCQM-K138	aflatoxins in dried figs	LC-IDMS/MS
2016	SIM-QM.K27	ethanol in water	GC-IDMS/MS
2016	SIM-QM.S7	heavy metals in surface water	HR-ICP-IDMS
2017	CCQM-K141	antibiotics in meat	LC-IDMS/MS
2017	CCQM-K78	calibrants - amino acids in calibration solutions	LC-IDMS/MS
2017	CCQM-K55.1a	purity of organic compunds: bisphenol A	MB, qNMR

Key comparison CCQM-K55c: Determination of Valine Purity

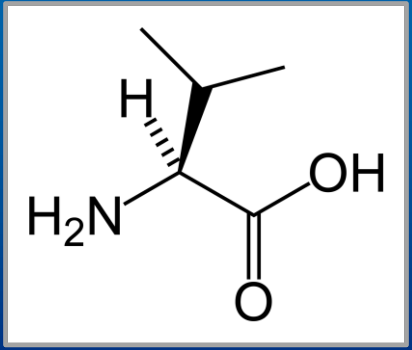


purpose

to demonstrate capability in the estimation of the purity of low molecular weight and high polarity organic compounds and thus the ability to produce primary calibrants for similar materials

two analytical pathways

- 'mass balance' approach (BIPM-NIST)
  - structure-related impurities
  - non-volatile components
  - volatile components
  - water
- quantitative ^{1}H NMR (BAM)



a. mass balance approach

experimental approach:

- related structure impurities

  LC-MS/MS screening for residual amino acids (SIELC Primesep 100)

  determination by standard additions of NIST 2389a

- water content

  Karl Fischer coulometric titration (oven)

- residual organic solvents / volatile matter

  headspace GC-MS

- non-volatiles / inorganics

  ion chromatography for major anions/cations

  HR-ICP-MS for other elements (after mw-assisted acid digestion)

a. mass balance approach

valine mass fraction = 992.5 ± 0.6 mg/g

- related structure impurities: 6.3±0.4 mg/g

  alanine: 2.6 ± 0.2 mg/g

  leucine: 1.8 ± 0.3 mg/g

  isoleucine: 1.9 ± 0.3 mg/g

- water content

  1.2 ± 0.5 mg/g

- residual organic solvents / volatile matter

  not observed (<LOD)

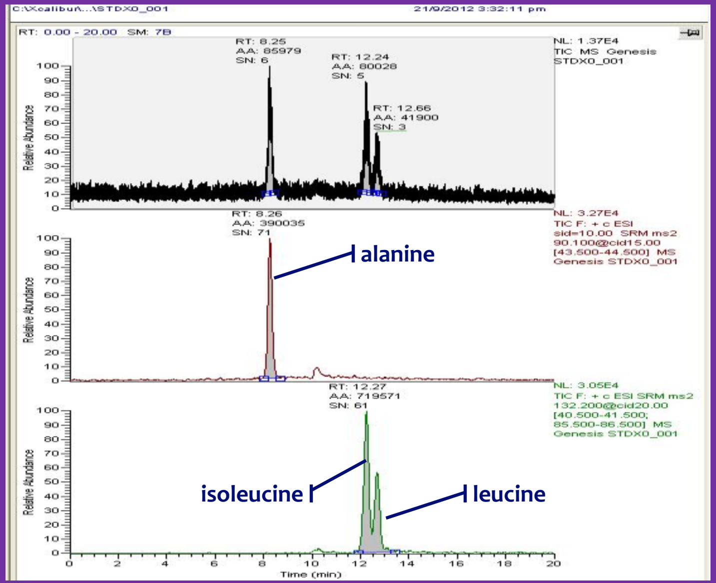
- non-volatiles / inorganics

  <0.1 mg/g

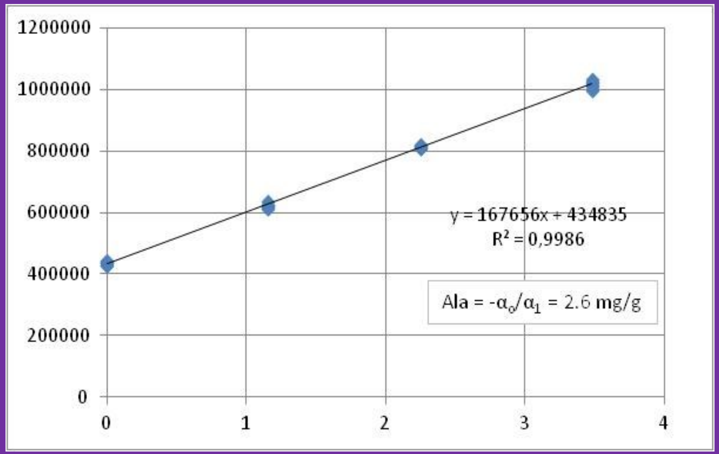
  HR-ICP-MS for other elements
  (after mw-assisted acid digestion)

impurity	S	NH_4	Ca	Fe	Na
μg/g	8,3	7,6	4,6	1,7	1,0

Typical chromatogram



Responce



Amount of Ala added (mg)

a. mass balance approach

$$w_{val} = 1000\ x\ (1 - w_{SRI} - w_{H2O} - w_{vol} - w_{in})$$

uncertainty estimation

- related structure impurities

Ala determination					
uncertainty component	value	units	uncertainty	rel uncertainty	squared RU
regression	2,58	mg	0,0864	3,349E-02	1,121E-03
mass of spike solution	0,090	g	1,312E-05	1,457E-04	2,124E-08
sample mass	0,950	g	4,004E-05	4,214E-05	1,776E-09
spike mass fraction	12,37	μg g^{-1}	0,1900	1,536E-02	2,359E-04
relative standard uncertainty					0,03684
combined standard uncertainty					0,09506
expanded uncertainty (k=2)					0,19011

Leu determination					
uncertainty component	value	units	uncertainty	rel uncertainty	squared RU
regression	1,83	mg	0,1406	7,683E-02	5,903E-03
mass of spike solution	0,090	g	1,312E-05	1,457E-04	2,124E-08
sample mass	0,950	g	4,004E-05	4,214E-05	1,776E-09
spike mass fraction	17,38	μg g^{-1}	0,4090	2,353E-02	5,538E-04
relative standard uncertainty					0,08035
combined standard uncertainty					0,14705
expanded uncertainty (k=2)					0,29410

Ile determination					
uncertainty component	value	units	uncertainty	rel uncertainty	squared RU
regression	1,92	mg	0,1238	6,448E-02	4,158E-03
mass of spike solution	0,090	g	1,312E-05	1,457E-04	2,124E-08
sample mass	0,950	g	4,004E-05	4,214E-05	1,776E-09
spike mass fraction	17,438	μg g^{-1}	0,3810	2,185E-02	4,774E-04
relative standard uncertainty					0,06808
combined standard uncertainty					0,13071
expanded uncertainty (k=2)					0,26143

- water content (KF titration)

KF uncertainty budget					
uncertainty component	value	units	uncertainty	rel uncertainty	squared RU
determination repeatability	1,2	mg g^{-1}	0,2314	1,928E-01	3,718E-02
sample mass	0,0600	g	0,0001	2,030E-03	4,120E-06
relative standard uncertainty					0,19284
combined standard uncertainty					0,23141
expanded uncertainty (k=2)					0,46283

b. qNMR approach: ^{1}H NMR using maleic acid as IS

mass determination:

in-house mass calibration with E1 class standard weights balance capable of 0.1 μg resolution

accurate weighing of sample and internal standard with uncertainties of 0.01%

NMR experiment:

dilution in 99.99% D_2O, T= 300 K

T1 and d1 determination for sample and IS in separate NMR experiments

the NMR spectra were recorded on a Bruker 500 MHz Avance DRX spectrometer

determination of repeatability in six separate NMR experiments

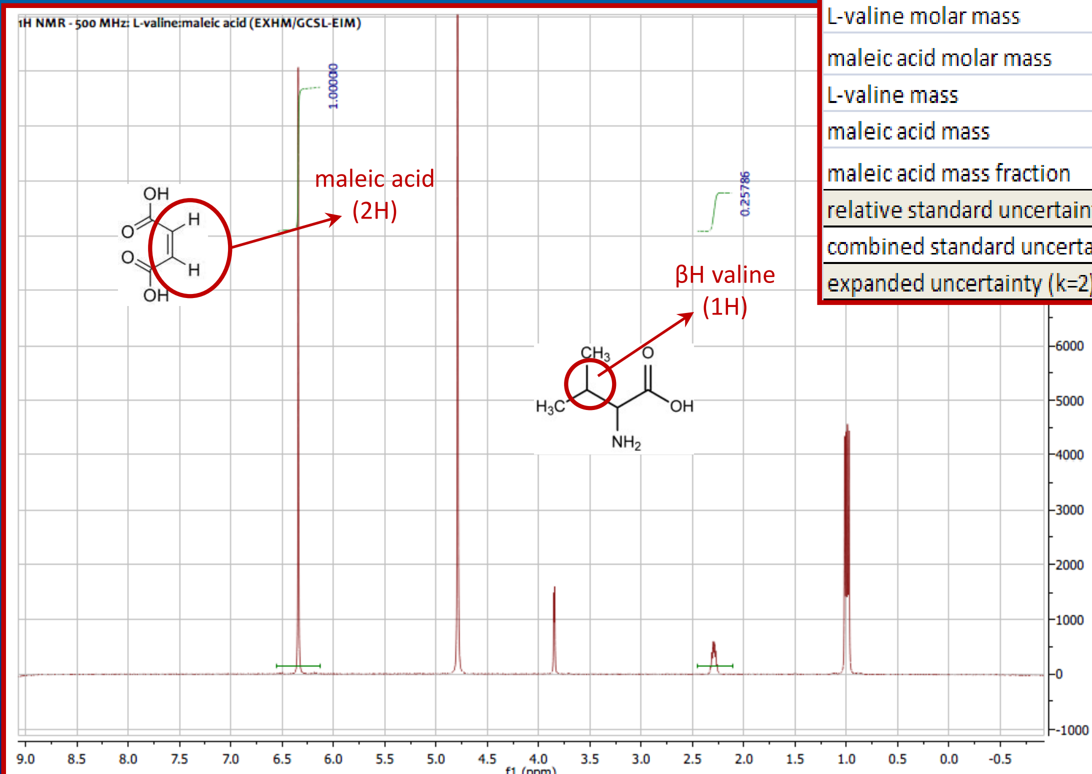
b. qNMR approach

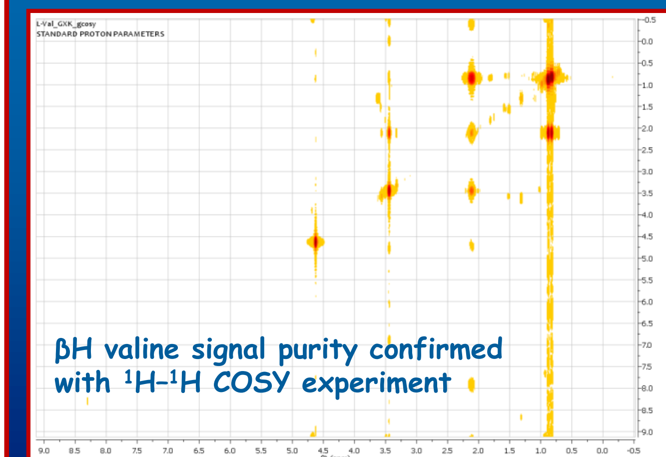
valine mass fraction = 992.0±2.2 mg/g

uncertainty estimation

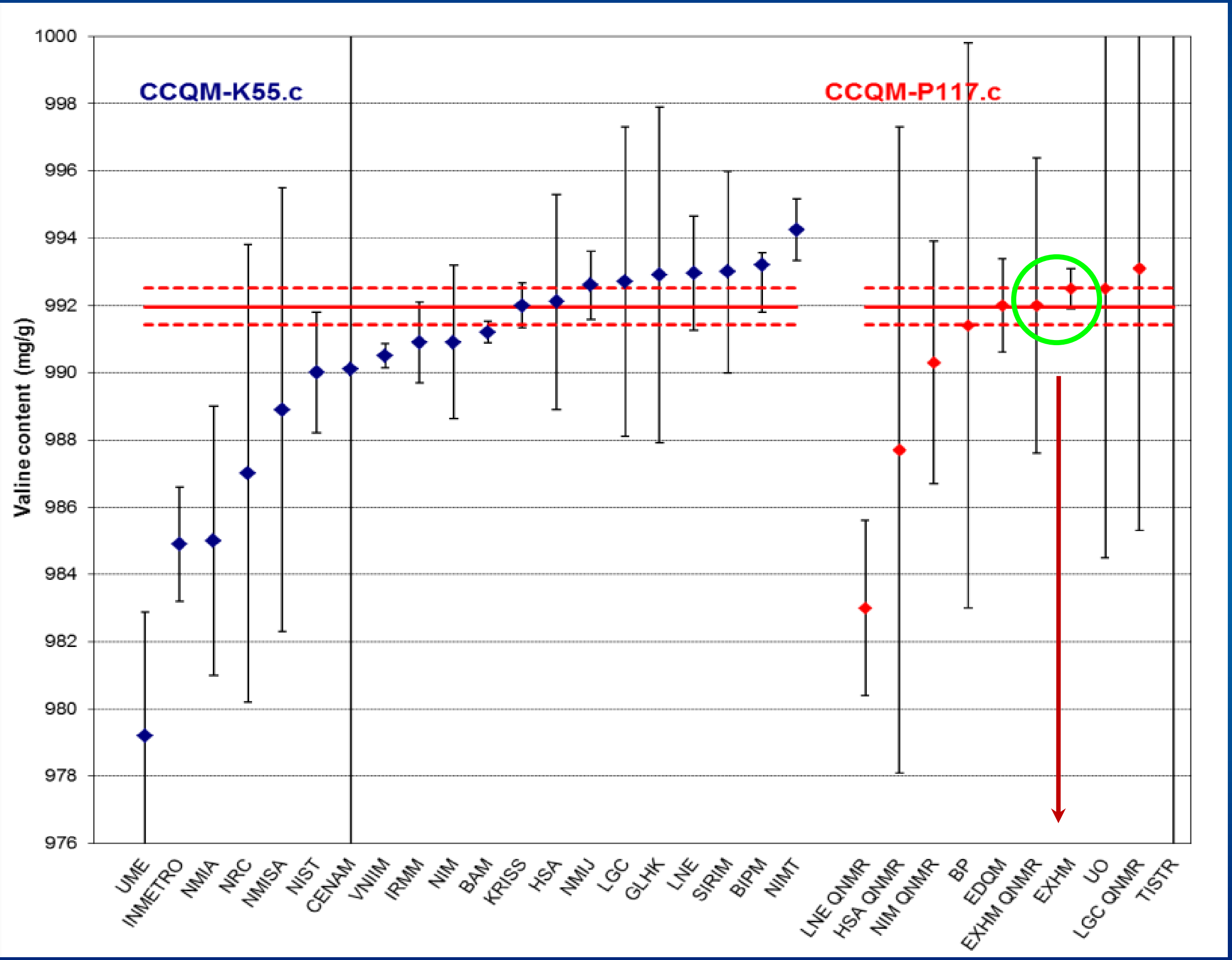
$$w_{val} = \frac{I_{val}}{I_{ma}} \frac{N_{ma}}{N_{val}} \frac{MW_{val}}{MW_{ma}} \frac{m_{ma}}{m_{val}} P_{ma}$$

qNMR uncertainty budget					
uncertainty component	value	units	uncertainty	rel uncertainty	squared RU
integration ratio	0,25786		0,001	2,211E-03	4,886E-06
L-valine molar mass	117,146	g mol^{-1}	0,003	2,561E-05	6,558E-10
maleic acid molar mass	116,072	g mol^{-1}	0,003	2,585E-05	6,680E-10
L-valine mass	10	mg	0,000	3,233E-05	1,045E-09
maleic acid mass	20	mg	0,001	3,182E-05	1,012E-09
maleic acid mass fraction	999,9	mg g^{-1}	0,450	4,500E-04	2,025E-07
relative standard uncertainty					0,00226
combined standard uncertainty					2,23900
expanded uncertainty (k=2)					4,47800





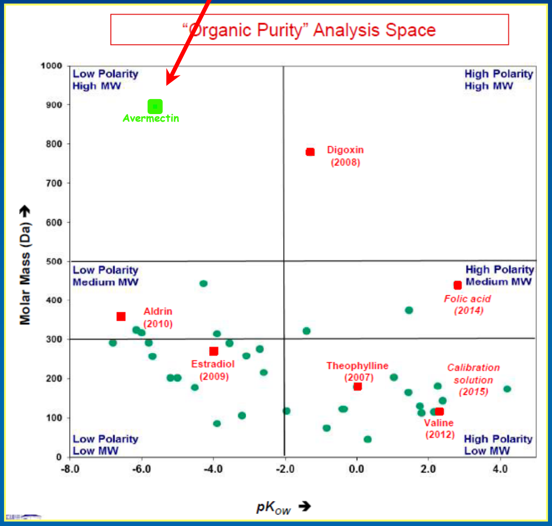
results : valine purity



CCQM.K104: purity determination of avermectin B_{1a}

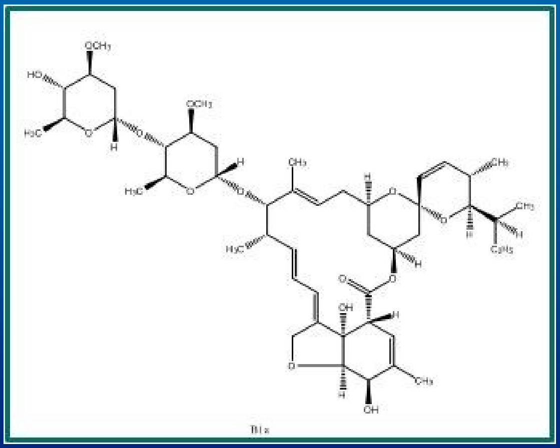
purpose

to document the capability of purity determination of organic compounds with high molecular weight and low polarity and thus characterize calibrants of similar structure



Analytical approach

- Mass balance
  - ➢ structural related impurities
  - ➢ non-volatiles
  - ➢ volatile mater
  - ➢ water



CCQM.K104: purity of avermectin B_{1a}

mass balance approach

experimental procedure:

- **structural related impurities**
  HPLC-UV and LC-MS/MS for identification
  % composition via HPLC UV

- **water**
  Karl Fischer coulometric titration (oven)

- **residual solvents – volatile material**
  GC-FID and/or GC-MS

- **non volatiles / inorganics**
  ion chromatography for main anions/cations
  HR-ICP-MS for other elements

CCQM.K104: purity of avermectin B_{1a}

mass fraction A_{B1a} = 930,3±0,6 mg/g

- Structural related impurities: 47,1 ± 0,3 mg/g

  A_{B1b} : 26,2 ± 0,2 mg/g

  A_{A1a} : 6,2 ± 0,1 mg/g

  A_{A2a} : 4,2 ± 0,1 mg/g

  A_{A1b} : 0,5 ± 0,1 mg/g

  A_{B2a} : 1,6 ± 0,1 mg/g

- water

  20,6 ± 1,0 mg/g

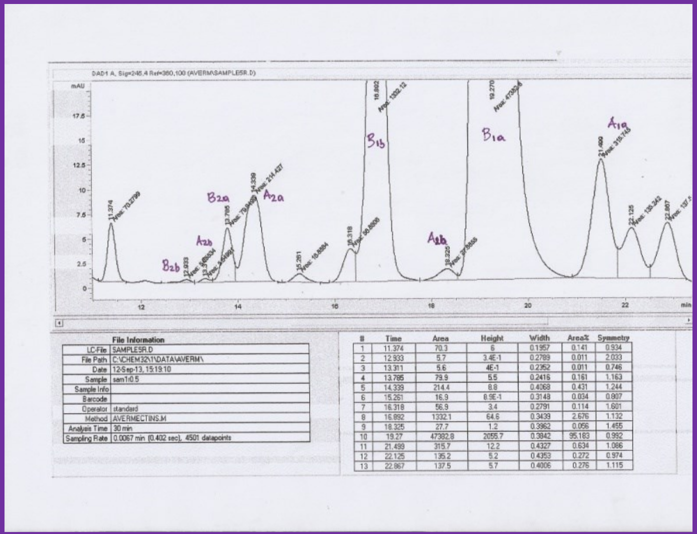
- residual solvents / volatiles

  0,10 ± 0,07 mg/g

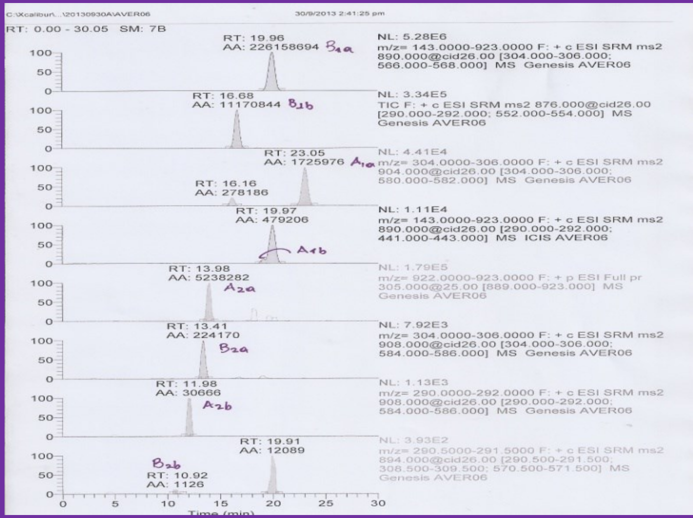
- non volatiles / inorganics

  2,0 ± 0,4 mg/g

χρωματογράφημα LC-UV



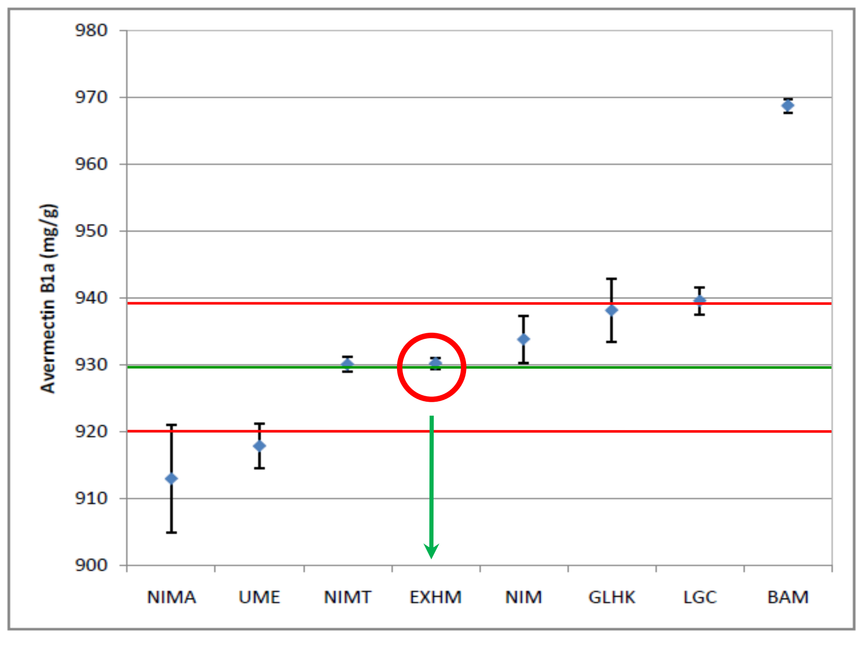
χρωματογράφημα LC-MS/MS

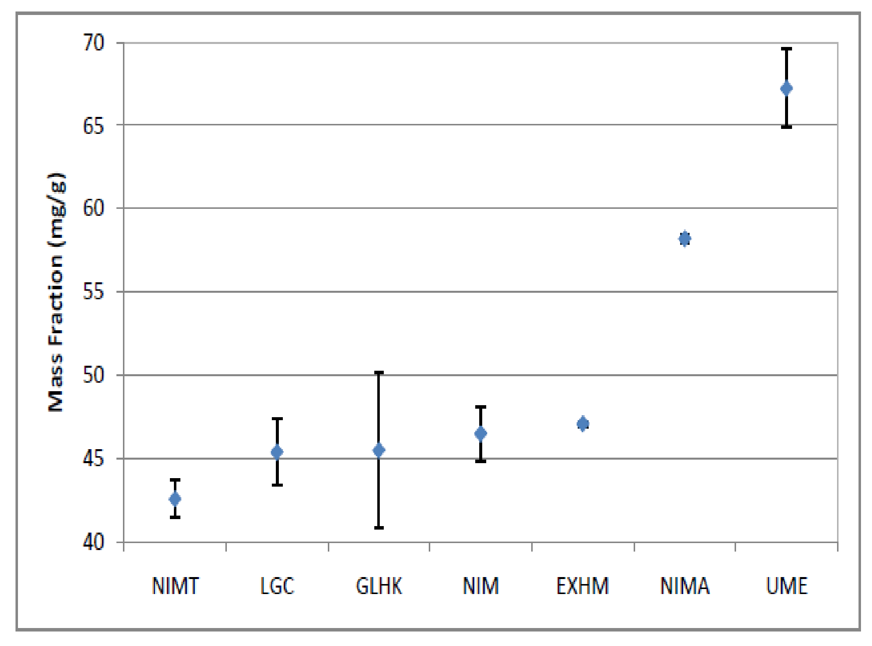


CCQM.K104: purity of avermectin $B_{1\alpha}$

mass fraction $A_{B1\alpha}$= 930,3 ± 1,6 mg/g

structurally related impurities: 47,1±0,3 mg/g

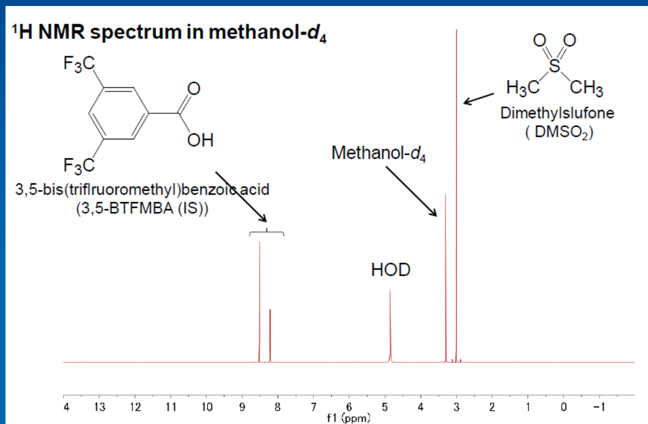




Reference value $A_{B1\alpha}$= 929,0 ± 10,0 mg/g

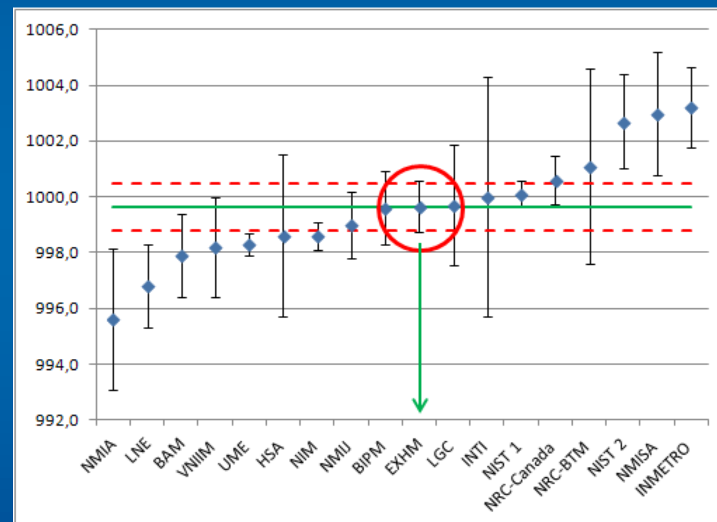
Track D: development of analytical procedures

International comparison on qNMR → CCQM-P150 (NMIJ, LGC, NMIA)



συνιστώσα αβεβαιότητας	τιμή	μονάδα	u_i	u_i/x_i	C_i	C_iu_i	$(C_iu_i)^2$
λήψη & επεξεργασία φάσματος			0,00075		1	0,00075	5,658E-07
προετοιμασία δείγματος			0,00047		1	0,00047	2,216E-07
λόγος σημάτων $DMSO_2$/BTFMBA	0,9984		0,00089	6,790E-04	1001,23	0,88844	7,893E-01
μοριακή μάζα $DMSO_2$	94,135	g mol^{-1}	0,00508	5,398E-05	10,62	0,05396	2,911E-03
μοριακή μάζα BTFMBA	258,117	g mol^{-1}	0,00522	2,024E-05	-3,87	-0,02023	4,092E-04
αριθμός ^{1}H στο μόριο $DSMO_2$	6	nucl/mol	0,00011	1,800E-05	-166,61	-0,01799	3,238E-04
αριθμός ^{1}H στο μόριο BFTMBA	3	nucl/mol	0,00005	1,800E-05	333,21	0,01799	3,238E-04
μάζα $DMSO_2$	7,1	mg	0,00057	8,021E-05	-140,79	-0,08018	6,428E-03
μάζα BTFMBA	39	mg	0,00067	1,717E-05	25,63	0,01716	2,946E-04
συντελεστής διόρθωσης άνωσης	1,00001		0,00000	4,065E-06	999,63	0,00406	1,651E-05
καθαρότητα BTFMBA	999,59	mg g^{-1}	0,26000	2,601E-04	1,00	0,26001	6,761E-02
καθαρότητα $DMSO_2$							**999,642**
συνδυασμένη τυπική αβεβαιότητα							**0,931**
διευρυμένη αβεβαιότητα (k=2,31)							2,152

Reference value from mass balance : 999,64 ± 0,84 mg/g

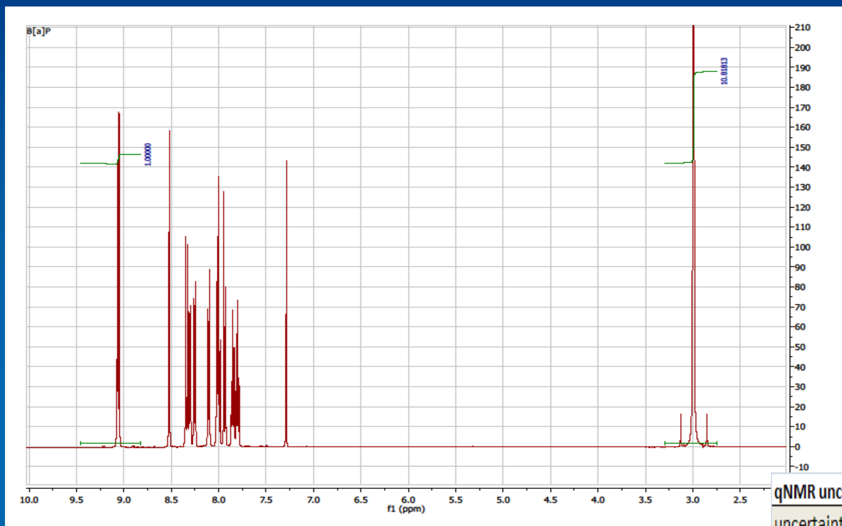


qNMR comparison reference value : 999,69 mg/g

measuring PAHs in tea – linking measurements to SI

or an odyssey in metrological traceability!

Primary calibrant characterization: benzo[a]pyrene purity determination with quantitative ^{1}H NMR



model equation

$$P_A = \frac{I_s}{I_{Std}} \frac{n_{Std}}{n_s} \frac{M_s}{M_{std}} \frac{m_{Std}}{m} P_{std}$$

qNMR uncertainty budget

uncertainty component	value	units	uncertainty	rel uncertainty	Ci	Ciui	squared CiUi
B[a]P integration signal	1,0000		0,0000	0,000E+00	965,658	0,0000	0,000E+00
$DMSO_2$ integration signal	9,5584		0,0092	8,023E-04	-101,028	-0,9295	8,639E-01
B[a]P molar mass	252,3077	g mol^{-1}	0,0045	1,782E-05	3,827	0,0172	2,962E-04
$DMSO_2$ molar mass	94,1354	g mol^{-1}	0,0052	5,548E-05	-10,258	-0,0536	2,871E-03
no of 1H atoms in $DSMO_2$ signal (3,00 ppm)	6	at/int sign	0,0001	1,800E-05	160,943	0,0174	3,021E-04
no of 1H atoms in B[a]P signal (9,06 ppm)	2	at/int sign	0,0000	1,800E-05	-482,829	-0,0174	3,021E-04
B[a]P mass	7,7148	mg	0,0012	1,555E-04	-125,170	-0,1502	2,256E-02
$DMSO_2$ mass	8,8590	mg	0,0012	1,355E-04	109,003	0,1308	1,711E-02
buoyancy correction factor	1,00001		0,0000	4,065E-06	965,647	0,0039	1,541E-05
$DMSO_2$ purity	999,64	mg g^{-1}	0,9124	9,127E-04	0,966	0,8814	7,768E-01
purity value (mg/g)							965,658
combined standard uncertainty (mg/g)							1,298
relative uncertainty (%)							0,134
expanded uncertainty (k=2,31) (mg/kg)							0,310

Calibration solutions preparation and characterization isotope dilution at exact matching

measurement equation

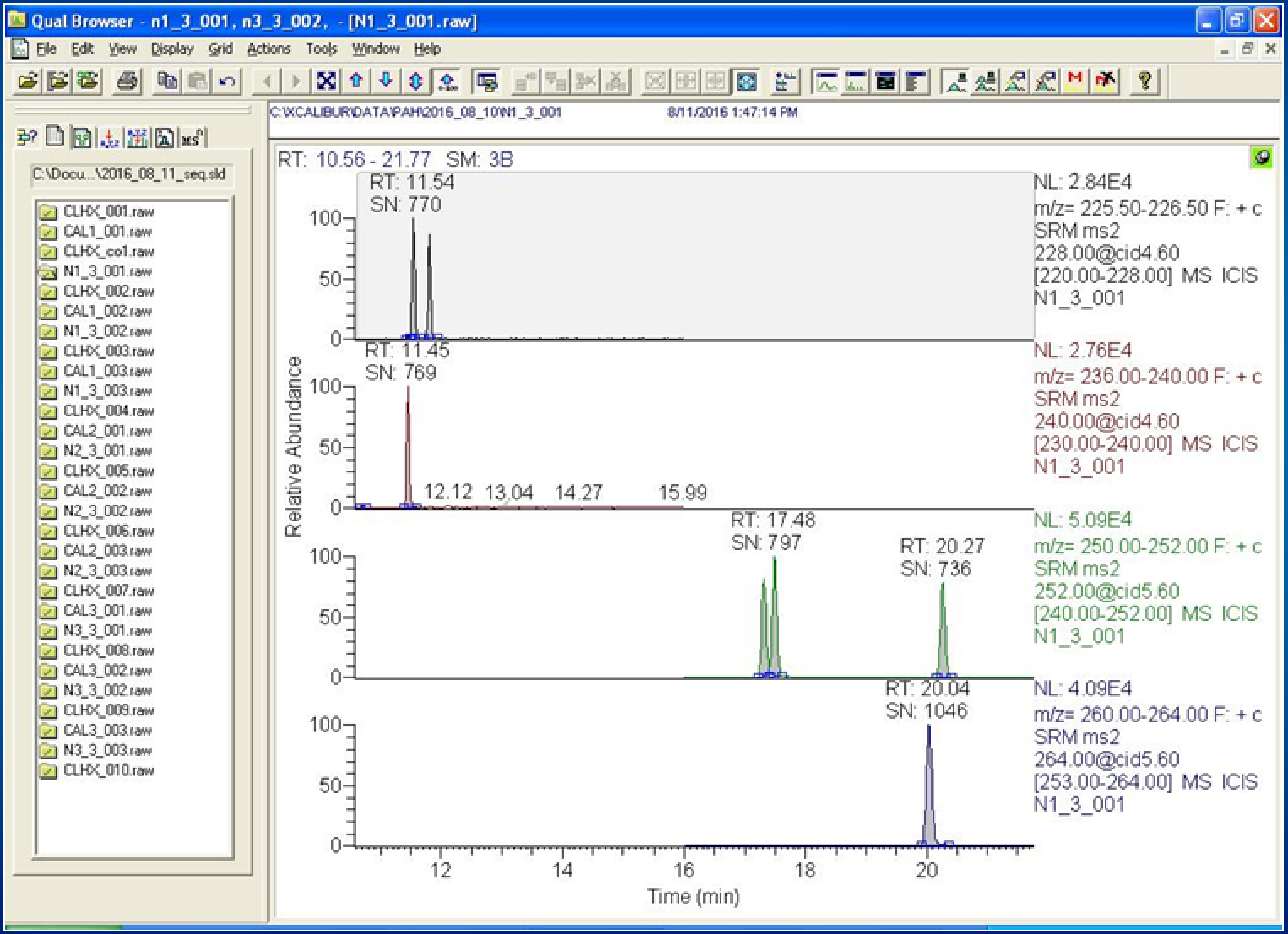
The measurement equation is:

$$w_{A,S} = w_{A,C}\frac{m_{S,dil}}{m_{S,in}} \times \frac{m_{is,S}}{m_{D,S}} \times \frac{m_{A,C}}{m_{is,C}} \times \frac{R_S}{R_C}$$

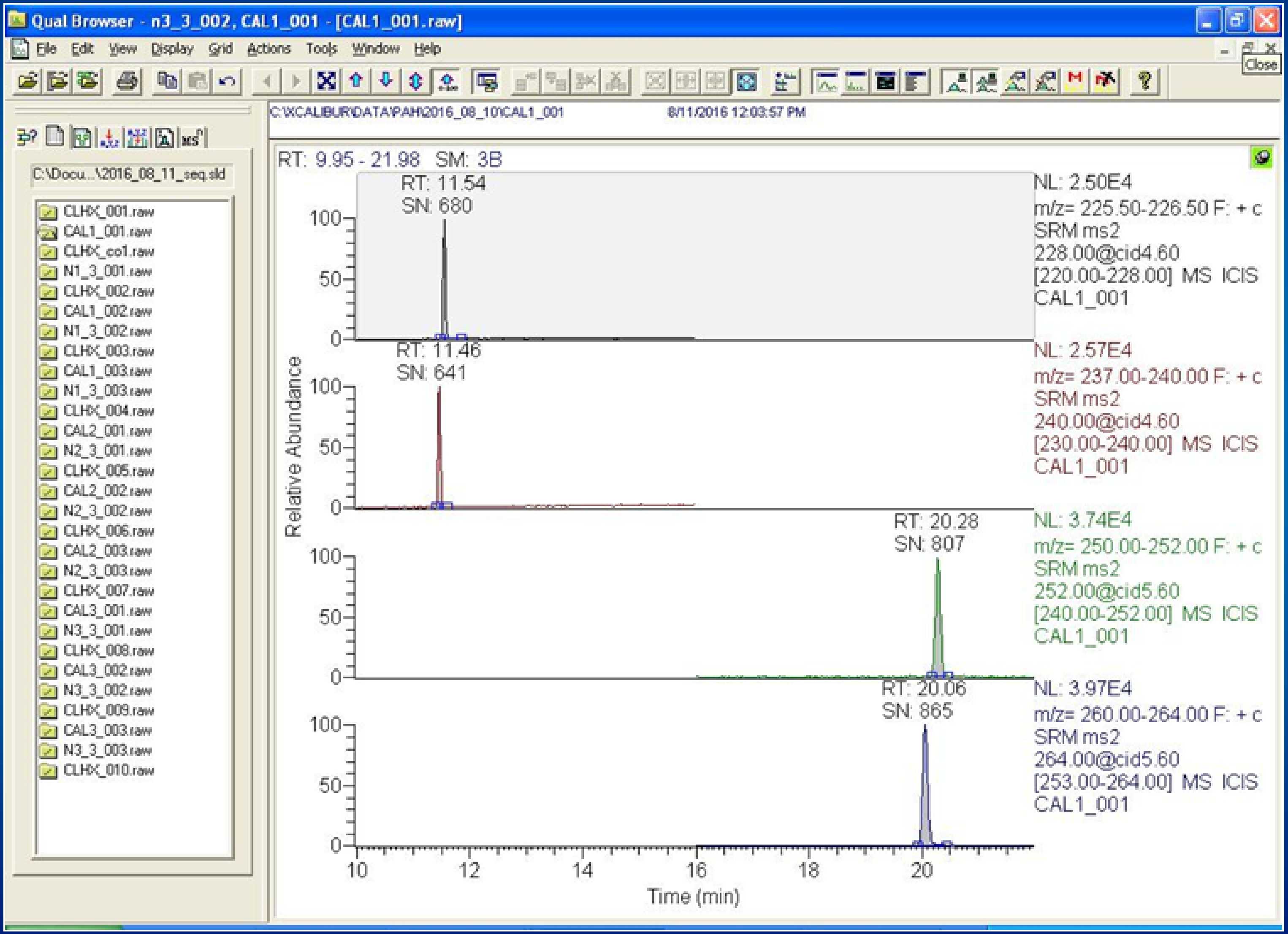
where

$w_{A,S}$	= mass fraction of the analyte (B[a]A or B[a]P) in the sample, (μg/g)
$w_{A,C}$	= mass fraction of the analyte (B[a]A or B[a]P) in the calibration solution, (μg/g)
$m_{S,in}$	= the mass of sample in the diluted sample (g)
$m_{S,dil}$	= the total mass of the diluted sample (g)
$m_{is,S}$	= mass of internal standard solution added to sample blend, (g)
$m_{D,S}$	= mass of diluted test material in sample blend, (g)
$m_{A,C}$	= mass of the analyte (B[a]A or B[a]P) solution added to calibration blend, (g)
$m_{is,C}$	= mass of internal standard solution added to calibration blend, (g)
R_S	= measured peak area ratio of the selected ions in the sample blend
R_C	= measured peak area ratio of the selected ions in the calibration blend

Typical chromatograms – K131 sample + IS



Typical chromatograms: EXHM calibrant + IS



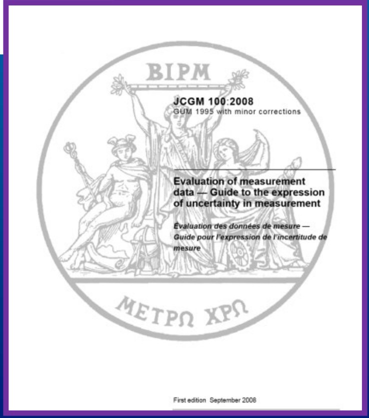
evaluation of uncertainty (JCGM 100:2008)

The equation used to estimate standard uncertainty is:

$$u(w_{BS}) = \sqrt{(s_R)^2 + \sum\left(C_j u(m_i)\right)^2 + \sum\left(C_j u(R_i)\right)^2 + \left(C_j u(w_{MC})\right)^2}$$

where s_R is the standard deviation under reproducibility conditions, n the number of determinations and C_j the sensitivity coefficients associated with each uncertainty component (masses, ion ratios and calibrant concentration). The uncertainty of the peak area ratios was considered to have been included in the estimation of method precision.

Uncertainty estimation was carried out according to JCGM 100: 2008. The standard uncertainties were combined as the sum of the squares of the product of the sensitivity coefficient (obtained by partial differentiation of the measurement equation) and standard uncertainty to give the square of the combined uncertainty. The square root of this value was multiplied by a coverage factor (95% confidence interval) from the t-distribution at the total effective degrees of freedom obtained from the Welch-Satterthwaite equation to give the expanded uncertainty.



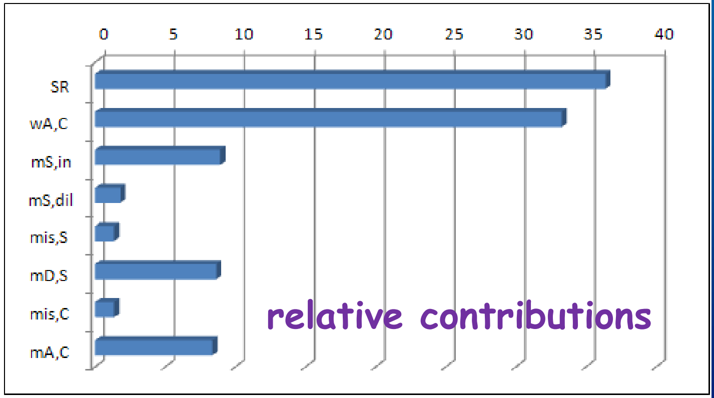
Example – CCQM K131

all calibrants measured against NIST SRM 1647f via IDMS experiments

characterisation and uncertainty budget for B[a]A in EXHM calibrant

uncertainty component (typical values)	symbol	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	S_R	0,646	1,000	0,00480	0,00742	0,0048	0,0000
mass fraction of BaA in the NIST calibration solution, (μg/g)	$w_{A,C}$	5,160	0,125	0,03500	0,01200	0,0044	0,0000
the mass of sample in the diluted NIST sample (g)	$m_{S,in}$	0,1500	-39,161	0,00003	0,00020	-0,0012	0,0000
the total mass of the diluted NIST sample (g)	$m_{S,dil}$	1,5000	3,916	0,00006	0,00004	0,0002	0,0000
mass of BaA-d_{12} solution added to EXHM calibrant, (g)	$m_{is,S}$	0,1600	5,874	0,00003	0,00019	0,0002	0,0000
mass of EXHM calibrant in sample blend, (g)	$m_{D,S}$	0,1450	-37,898	0,00003	0,00019	-0,0011	0,0000
mass of NIST solution added to traceable blend, (g)	$m_{is,C}$	0,1800	5,874	0,00003	0,00022	0,0002	0,0000
mass of BaA-d_{12} solution added to traceable blend, (g)	$m_{A,C}$	0,1600	-36,713	0,00003	0,00019	-0,0011	0,0000
measured peak area ratio of the selected ions in the EXHM calibrant	R_S	0,9990		considered to be included in the			
measured peak area ratio of the selected ions in the traceable blend	R_C	0,9900		estimation of method precision			

result (μg/g)	0,646
combined standard uncertainty (μg/g)	0,007
relative uncertainty (%)	1,05
effective degrees of freedom	20,7
coverage factor	2,09
expanded uncertainty (μg/kg)	0,014



Track comparisons: capability of characterizing calibration solutions

primary analytical method
q ^{1}H NMR

qNMR uncertainty budget							
uncertainty component	value	units	uncertainty	rel uncertainty	Ci	Ciui	squared CiUi
B[a]P integration signal	1,0000		0,0000	0,000E+00	965,658	0,0000	0,000E+00
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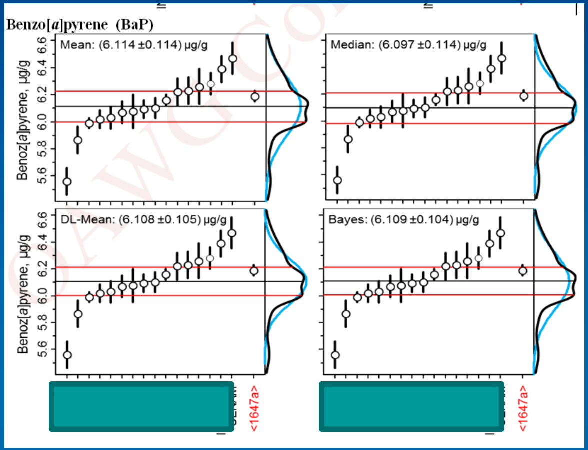
B[a]P molar mass	252,3077	g mol^{-1}	0,0045	1,782E-05	3,827	0,0172	2,962E-04
$DMSO_2$ molar mass	94,1354	g mol^{-1}	0,0052	5,548E-05	-10,258	-0,0536	2,871E-03
no of 1H atoms in $DSMO_2$ signal (3,00 ppm)	6	at/int sign	0,0001	1,800E-05	160,943	0,0174	3,021E-04
no of 1H atoms in B[a]P signal (9,06 ppm)	2	at/int sign	0,0000	1,800E-05	-482,829	-0,0174	3,021E-04
B[a]P mass	7,7148	mg	0,0012	1,555E-04	-125,170	-0,1502	2,256E-02
$DMSO_2$ mass	8,8590	mg	0,0012	1,355E-04	109,003	0,1308	1,711E-02
buoyancy correction factor	1,00001		0,0000	4,065E-06	965,647	0,0039	1,541E-05
$DMSO_2$ purity	999,64	mg g^{-1}	0,9124	9,127E-04	0,966	0,8814	7,768E-01
purity value (mg/g)							965,658
combined standard uncertainty (mg/g)							
relative uncertainty (%)							
expanded uncertainty (k=2,31) (mg/kg)							

$$P_A = \frac{I_s}{I_{Std}} \frac{n_{Std}}{n_s} \frac{M_s}{M_{std}} \frac{m_{Std}}{m} P$$

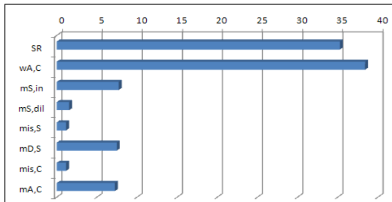
$$w_{A,S} = w_{A,C} \frac{m_{S,in}}{m_{S,dil}} \times \frac{m_{is,S}}{m_{D,S}} \times \frac{m_{A,C}}{m_{is,C}} \times \frac{R_S}{R_C}$$

CCQM-K131: PAHs in solutions



uncertainty component (typical values)	symbol	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	S_R	0,660	1,000	0,00536	0,00812	0,0054	0,0000
mass fraction of BaP in the NIST calibration solution, (µg/g)	$w_{A,C}$	6,220	0,106	0,05500	0,01200	0,0058	0,0000
the mass of sample in the diluted NIST sample (g)	$m_{S,in}$	0,1500	-39,161	0,00003	0,00020	-0,0012	0,0000
the total mass of the diluted NIST sample (g)	$m_{S,dil}$	1,5000	3,916	0,00006	0,00004	0,0002	0,0000
mass of BaP-d_{12} solution added to EXHM calibrant, (g)	$m_{is,S}$	0,1600	5,874	0,00003	0,00019	0,0002	0,0000
mass of EXHM calibrant in sample blend, (g)	$m_{D,S}$	0,1450	-37,898	0,00003	0,00019	-0,0011	0,0000
mass of NIST solution added to traceable blend, (g)	$m_{is,C}$	0,1530	5,874	0,00003	0,00022	0,0002	0,0000
mass of BaP-d_{12} solution added to traceable blend, (g)	$m_{A,C}$	0,1600	-36,713	0,00003	0,00019	-0,0011	0,0000
measured peak area ratio of the selected ions in the EXHM calibrant	R_S	1,0020		considered to be included in the			
measured peak area ratio of the selected ions in the traceable blend	R_C	0,9963		estimation of method precision			

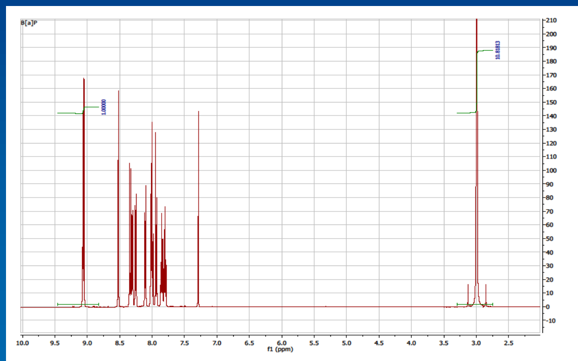
result (µg/g)	0,660
combined standard uncertainty (µg/g)	0,008
relative uncertainty (%)	1,24
effective degrees of freedom	20,3
coverage factor	2,09
expanded uncertainty (µg/kg)	0,017



βαθμονόμηση
ισοτοπική αραίωση σε ακριβή αντιστοίχηση

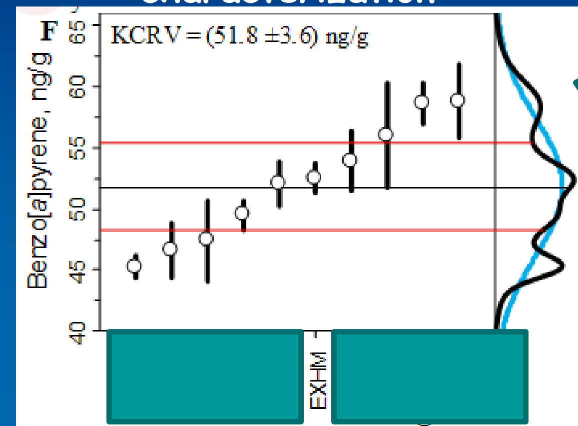
Track A comparisons: capability of characterizing matrix materials

primary characterization method
q ^{1}H NMR

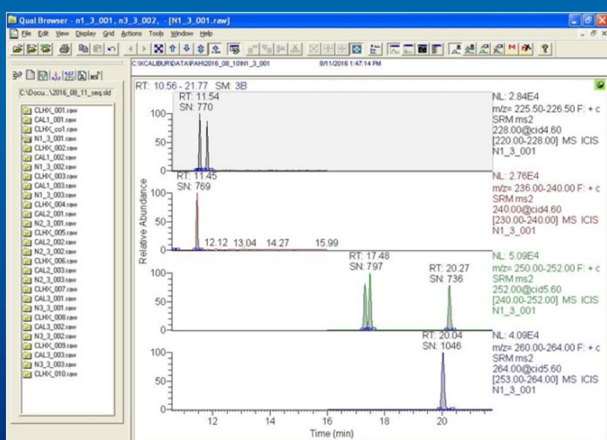


primary calibrant
benzo[a]pyrene

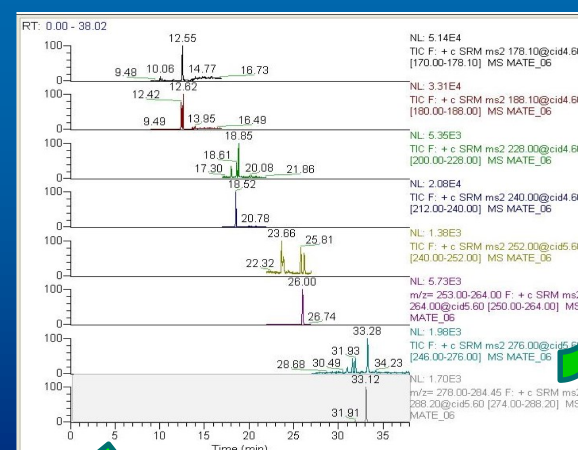
measurement comparison
characterization



CCQM-K95.1: PAHs in tea



secondary calibrant
benzo[a]pyrene calibration solution



calibration
isotope dilution at exact matching

EXHM
CHEMICAL METROLOGY LABORATORY
General Chemical State Laboratory
Hellenic Institute of Metrology
EIM

primary characterization method
q ^{1}H NMR

qNMR uncertainty budget							
uncertainty component	value	units	uncertainty	rel uncertainty	Ci	Ciui	squared CiUi
B[a]P integration signal	1,0000		0,0000	0,000E+00	965,658	0,0000	0,000E+00
$DMSO_2$ integration signal	9,5584		0,0092	8,023E-04	-101,028	-0,9295	8,639E-01
B[a]P molar mass	252,3077	g mol^{-1}	0,0045	1,782E-05	3,827	0,0172	2,962E-04
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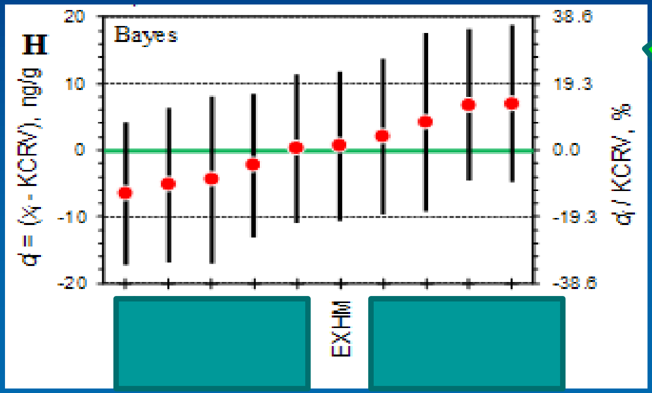
$DMSO_2$ purity	999,64	mg g^{-1}	0,9124	9,127E-04	0,966	0,8814	7,768E-01
purity value (mg/g)							965,658
combined standard uncertainty (mg/g)							1,298
relative uncertainty (%)							0,134
expanded uncertainty (k=2,31) (mg/kg)							0,310

CCQM-K95.1: PAHs in tea
measurement comparison
equivalence



primary calibrant
benzo[a]pyrene

uncertainty component (typical values)	symbol	value	sensitivity coefficient	standard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	S_R	0,660	1,000	0,00536	0,00812	0,0054	0,0000
mass fraction of BaP in the NIST calibration solution, (μg/g)	$w_{A,C}$	6,220	0,106	0,05500	0,01200	0,0058	0,0000
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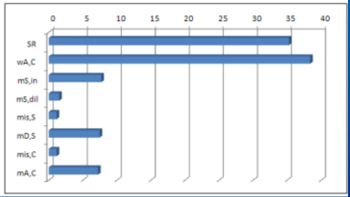
the total mass of the diluted NIST sample (g)	$m_{s,dil}$	1,5000	3,916	0,00006	0,00004	0,0002	0,0000
mass of BaP-d_{12} solution added to EXHM calibrant, (g)	$m_{is,S}$	0,1600	5,874	0,00003	0,00019	0,0002	0,0000
mass of EXHM calibrant in sample blend, (g)	$m_{D,S}$	0,1450	-37,898	0,00003	0,00019	-0,0011	0,0000
mass of NIST solution added to traceable blend, (g)	$m_{is,C}$	0,1530	5,874	0,00003	0,00022	0,0002	0,0000
mass of BaP-d_{12} solution added to traceable blend, (g)	$m_{A,C}$	0,1600	-36,713	0,00003	0,00019	-0,0011	0,0000
measured peak area ratio of the selected ions in the EXHM calibrant	R_S	1,0020		considered to be included in the			
measured peak area ratio of the selected ions in the traceable blend	R_C	0,9963		estimation of method precision			

result (μg/g)	0,660
combined standard uncertainty (μg/g)	0,008
relative uncertainty (%)	1,24
effective degrees of freedom	20,3
coverage factor	2,09
expanded uncertainty (μg/kg)	0,017



uncertainty component	value	sensitivity coefficient	standard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	52,49	1,0000	0,56	0,0107	0,5603	0,3140
mass fraction of B[a]P in the calibration solution, (μg/kg)	643,18	0,0816	11,61	0,0180	0,9473	0,8974
sample moisture content, (g/g)	0,04010	-54,6840	0,00018	0,0044	-0,0098	0,0001
recovery (%)	100,00	-0,5249	0,762	0,0076	-0,4000	0,1600
mass of B[a]P-d_{12} solution added to sample blend, (g)	0,16166	324,7057	0,00007	0,0004	0,0227	0,0005
mass of test material in sample blend, (g)	1,98492	-26,4450	0,00007	0,0000	-0,0019	0,0000
mass of B[a]P solution added to calibration blend, (g)	0,04084	1285,2879	0,00003	0,0007	0,0386	0,0015
mass of B[a]P-d_{12} solution added to calibration blend, (g)	0,04063	-1291,9311	0,00003	0,0007	-0,0388	0,0015
measured peak area ratio of the selected ions in the sample blend	1,0571	49,6558	considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	1,1047	-47,5178	estimation of method precision			

result (ng/g)	52,49
combined standard uncertainty (ng/g)	1,17
relative standard uncertainty (%)	2,23
effective degrees of freedom	20,4
coverage factor	2,00
expanded uncertainty (ng/g)	2,35

$$C_{d,smp} = \frac{1}{Rec} \times \frac{V_{is,smp}\, C_{is,smp}}{m_{d,smp}} \times \frac{V_{d,cal}\, C_{d,cal}}{V_{is,cal}\, C_{is,cal}} \times \frac{R_{smp}}{R_{cal}}$$

secondary calibrant
benzo[a]pyrene calibration solution

calibration
isotope dilution at exact matching

Traceability in reference materials

uncertainty

0,13%
- primary method
- Primary calibrant

0,19%
- weighing and solution preparation
- secondary calibrants

1,24%
- measuring equipment calibration
- measurement at exact matching

2,23%
- analytical determination
- reference material characterization

Results

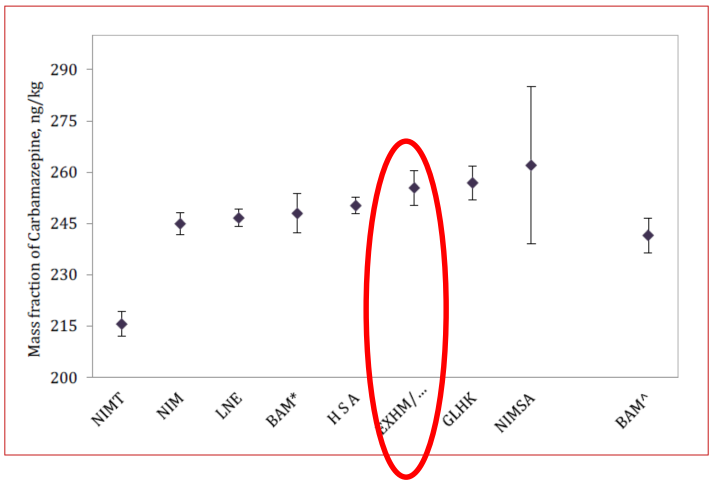
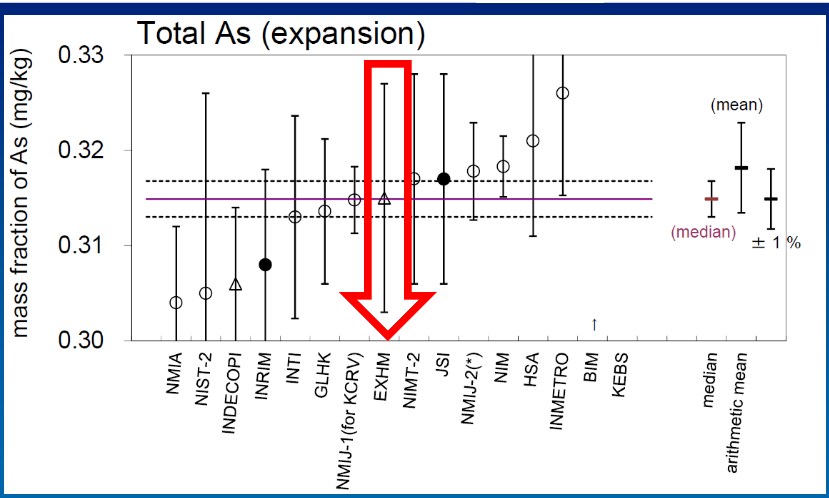
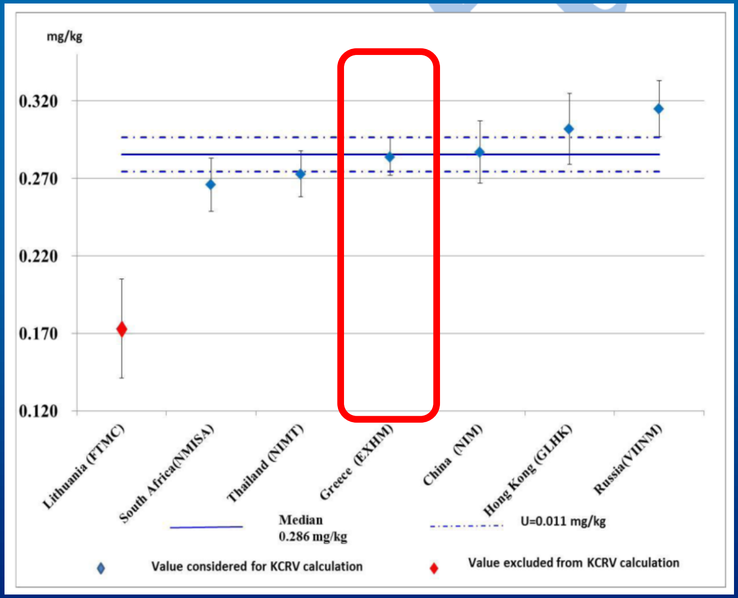


Figure 1: Summary of the participants' result and associated reported standard uncertainties.

CCQM-K126 carbamazepine in surface water



CCQM-K108 As in brown rice flour



CCQM-K103 melamine in milk powder

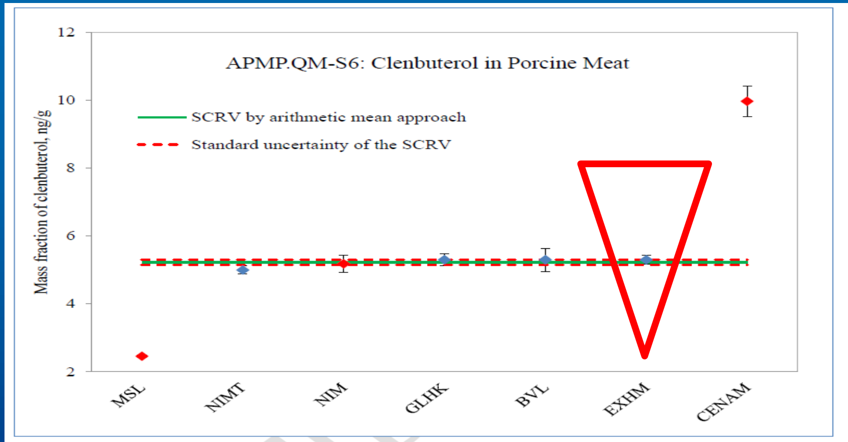


Figure 4: SCRV by arithmetic mean approach (green line) and its standard uncertainty (red dotted line) with participants' results and the associated reported standard uncertainties.

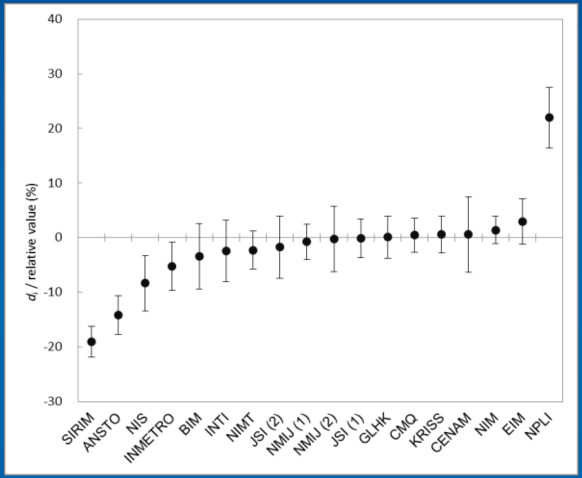
Data included for SCRV calculation
Data excluded from SCRV calculation

APMP-QMS6 clenbuterol in porcine meat

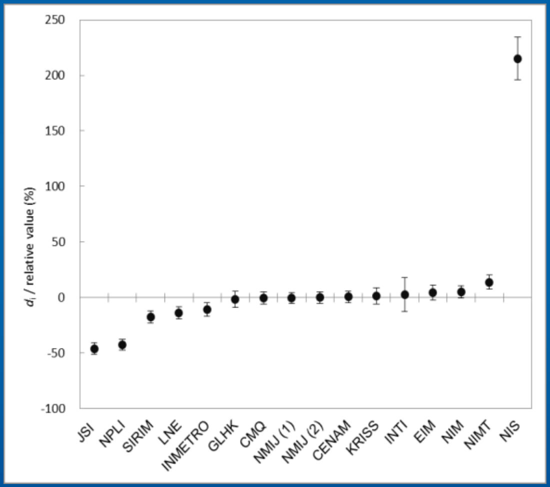
Track A comparisons: matrix materials

Determination of metals

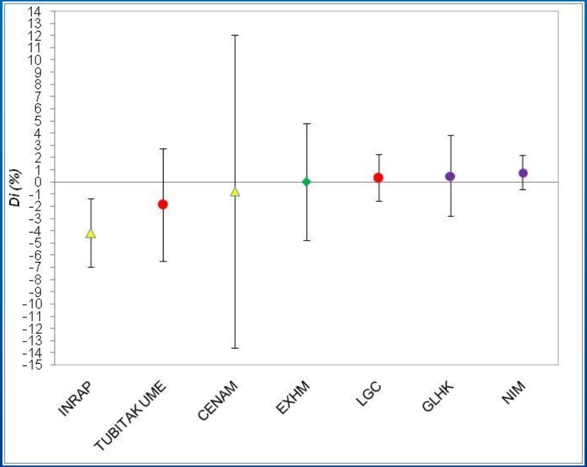
Zn in fishery products



Cd in meat

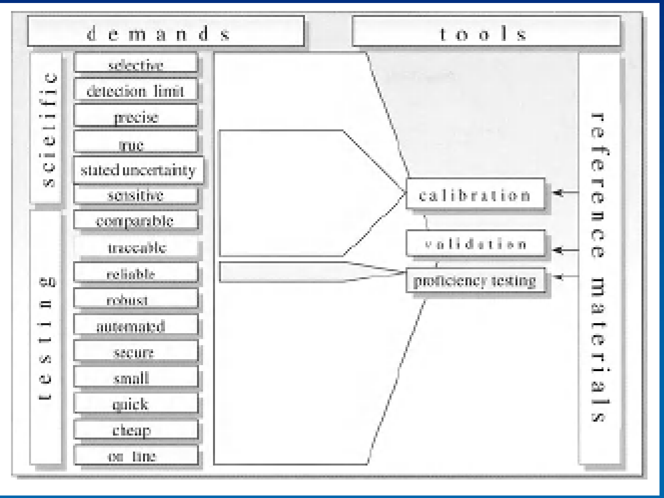


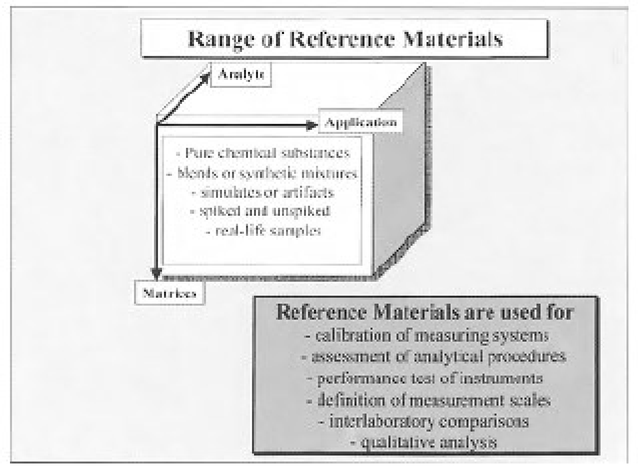
hexavalent Cr in water

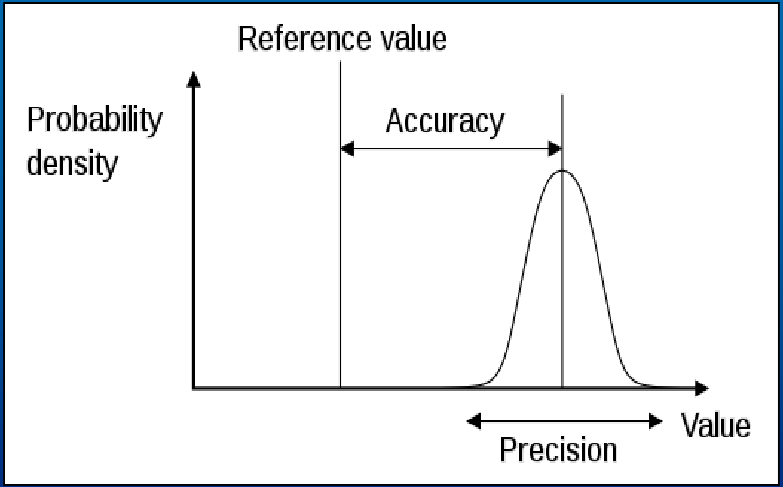


certified reference materials – uses

- trueness / recovery
- calibration
- quality control
- proficiency testing items

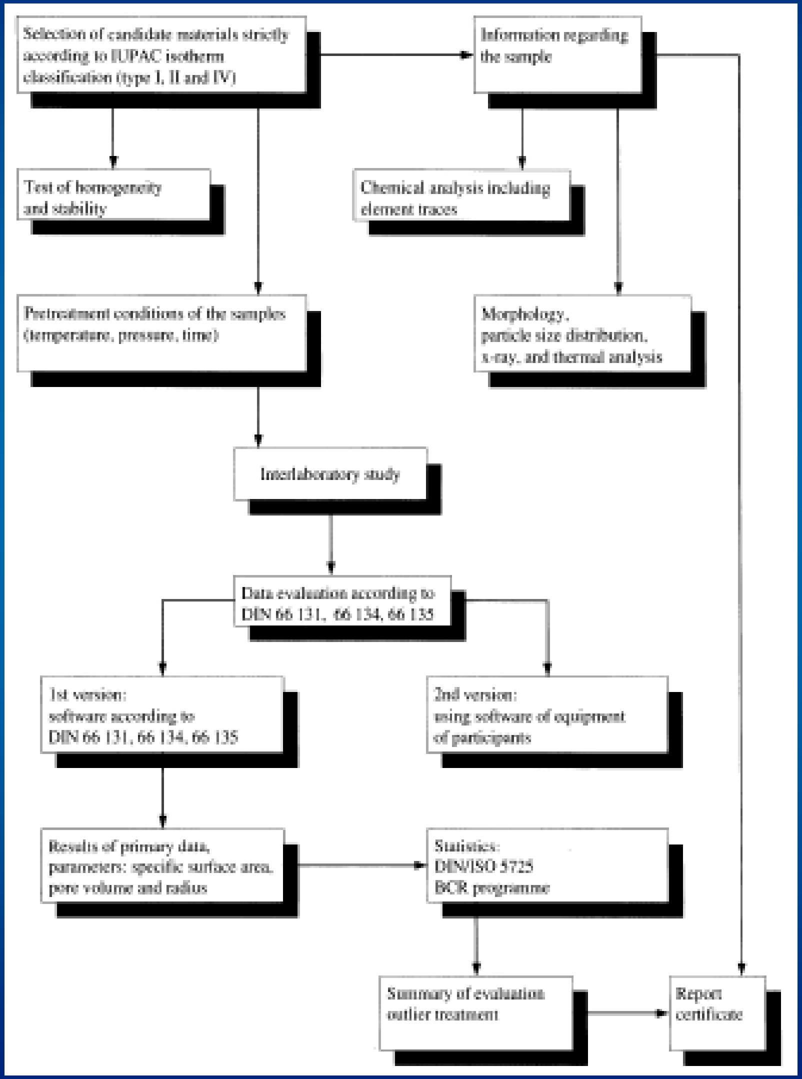




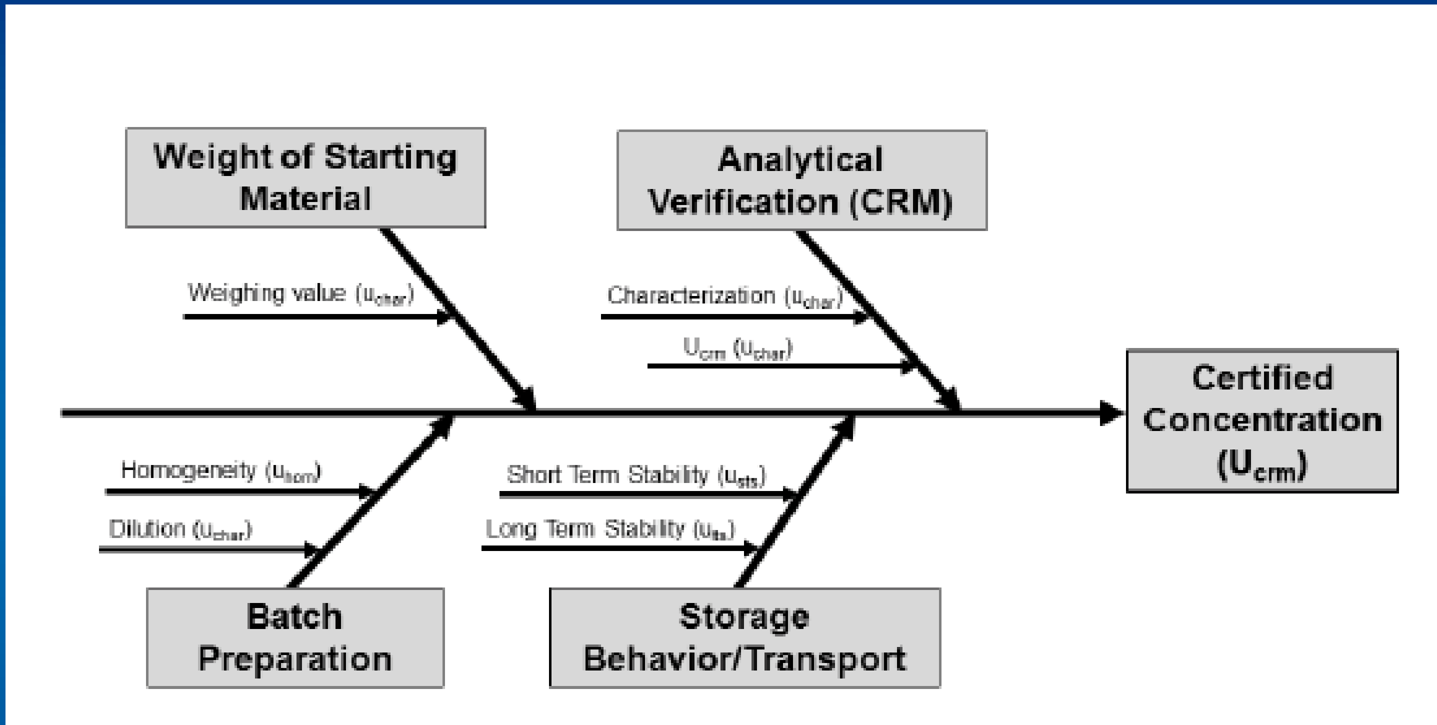


Certified reference materials

- planning
- production
- quality control
- homogeneity
- stability
- characterisation
- uncertainty
- traceability
- certification report
- certificate



reference materials – metrological characterization



$$x_{\mathrm{CRM}} = x_{\mathrm{char}} + \delta x_{\mathrm{bb}} + \delta x_{\mathrm{lts}} + \delta x_{\mathrm{sts}}$$

$$u_{\mathrm{CRM}} = \sqrt{u_{\mathrm{char}}^2 + u_{\mathrm{bb}}^2 + u_{\mathrm{lts}}^2 + u_{\mathrm{sts}}^2}$$

Hellenic CRMs

EXHM
CHEMICAL METROLOGY LABORATORY (EXHM/GCSL-EIM)
GENERAL CHEMICAL STATE LABORATORY - HELLENIC METROLOGY INSTITUTE
CHEMICAL METROLOGY SERVICE, 16 TSOCHA STREET, 115 21 ATHENS, GREECE
tel: +30 210 6479136-8 fax:+30 210 6479114 email: metrology@gcsl.gr
EIM

CERTIFICATE OF ANALYSIS

HRM® - XXXXX "HRM name"

"brief title"		
Measurand	Certified value 1)	Uncertainty 2)
	"property" in "units of measurement"	
"measurand"	"value"	± "meas unc."

1) "brief description of the certification procedure". The certified value is traceable to the SI.

2) Estimated expanded uncertainty *U* with a coverage factor of *k* = "covfact", corresponding to a level of confidence of about "conflev", as defined in the Guide to the expression of uncertainty in measurement (GUM), ISO, 1995. Uncertainty contributions arising from characterisation as well as from homogeneity and stability testing have been taken into account.

The certified properties will be valid for "shelf life" beginning with the dispatch of the material from EXHM; this validity may be extended as further evidence of stability becomes available.
The minimum sample intake is "minamount".

NOTE
Hellenic Reference Material HRM®-XXXX was produced and certified under the responsibility of Εργαστηριο Χημικής Μετρολογίας (EXHM/ΓΧΚ-EIM) according to the principles laid down in the technical guidelines outlined in the Quality Manual, in accordance with the requirements of ISO Guide 34.

It is accepted as an HRM®, Athens, 20xx-xx-xx

Athens, 20xx-xx-xx

EXHM/ΓΧΚ-EIM	ΓΧΚ
Reference Materials	Chemical Metrology Service
(Head of EXHM)	(Head of Chemical Metrology Service)

EXHM
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tel: +30 210 6479136-8 fax:+30 210 6479114 email: metrology@gcsl.gr
EIM

SAMPLE DESCRIPTION

The intended use of reference material HRM®-XXXXX is "xxxxxxxxx".
The material HRM®-xxxx "description".
"Packaging details"
The material is stored at EXHM at "conditions" until dispatch.
The between-bottle homogeneity was evaluated by analysis of variance (ANOVA) on "xx" out of "yy" "packing units" ('zz' replicate analyses per 'packunit'). Extensive stability tests provided sound evidence for a minimum validity of the material as indicated on page 1 of this certificate provided the material is stored according to the instructions given on page 3.
Homogeneity and stability testing are described in detail in the certification report.

PARTICIPANTS

Laboratory	City, Country

ANALYTICAL METHODS USED FOR CERTIFICATION

Pretreatment	Determination

"Comments about methods of analysis with respect to the certified value"
"Traceability from calibration". Remaining systematic between-method biases are sufficiently covered by the allowance made for the intercomparison contribution to the total uncertainty budget. The certified value is traceable to the SI.

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EIM

SAFETY INFORMATION

"Safety info".

INSTRUCTIONS FOR USE

"Handling instructions"
To the best of our knowledge, the stability of the reference material is not affected by limited exposure and handling to ambient temperature during transport and use. However, EXHM cannot be held responsible for any alterations of the material occurring during transportation to, and handling and storage at, the customer's premises, especially of opened samples.

STORAGE

"Storage info".

LEGAL NOTICE

Neither EXHM, not its contractors or any person acting on their behalf:
(a) make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately owned intellectual property rights; or
(b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document save for loss or damage arising solely and directly from EXHM negligence.

TECHNICAL REPORT

A detailed technical report (pdf file or paper copy; in English) describing the production, general characterisation as well as the analytical procedures applied and the treatment of the analytical data during certification of HRM®-xxxxx is available on request from EXHM, HRM Supply of Reference Materials:

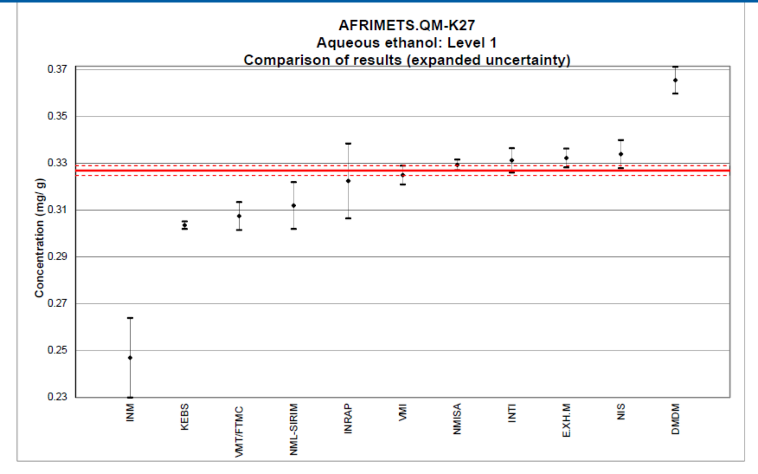
EXHM/ΓΧΚ-EIM, Chemical Metrology Service, 16 Tsocha Street, 115 21 Athens, Greece
www.EXHM.gcsl.gr

Hellenic CRMs

RMs for the calibration of digital pycnometers and alcohol breathing test devices

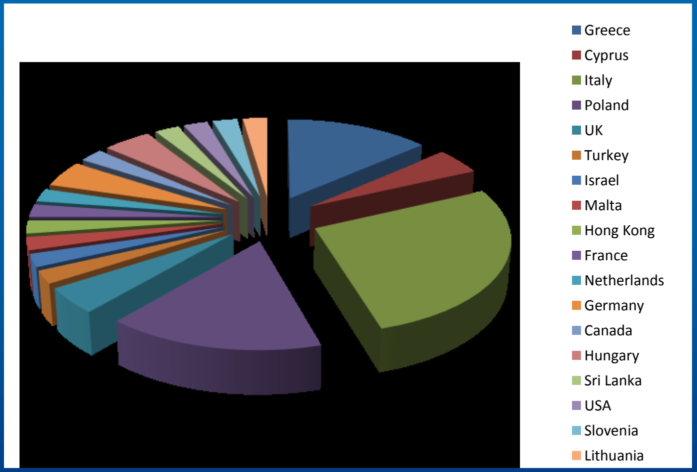
RMs for the calibration of equipment used in mobile labs for fuel control

RMs for the calibration of UV/Vis spectrophotometers



Proficiency testing

- Among the services provided by the Chemical Metrology Service (GCSL)-GREECE are organization of interlaboratory proficiency testing schemes, under the **SCHEMA** logo (**S**cheme for **CHE**mical **M**easurement **A**ssessment).
- more than 15 PTs per year in environmental, industrial and agro-food fields
- is included in the EPTIS database (www.eptis.bam.de)



In SCHEMA PTs 30 08, migration of Cd & Pb from ceramics, more than 50 laboratories participated, the majority of National Reference Laboratories (NRLs) across Europe.

The number of participating laboratories increases in each campaign, in 2017 had over than 400 participants from 40 countries worldwide.

Participation in PTs: purposes and benefits

- documentation of technical competence
- comparative evaluation of performance
- traceability (calibration laboratories)
- benchmarking of measurement uncertainty
- training – gaining experience
- fulfilling the requirements of accreditation bodies
- pointing out, investigating and solving technical problems

evaluation of performance (z-score)

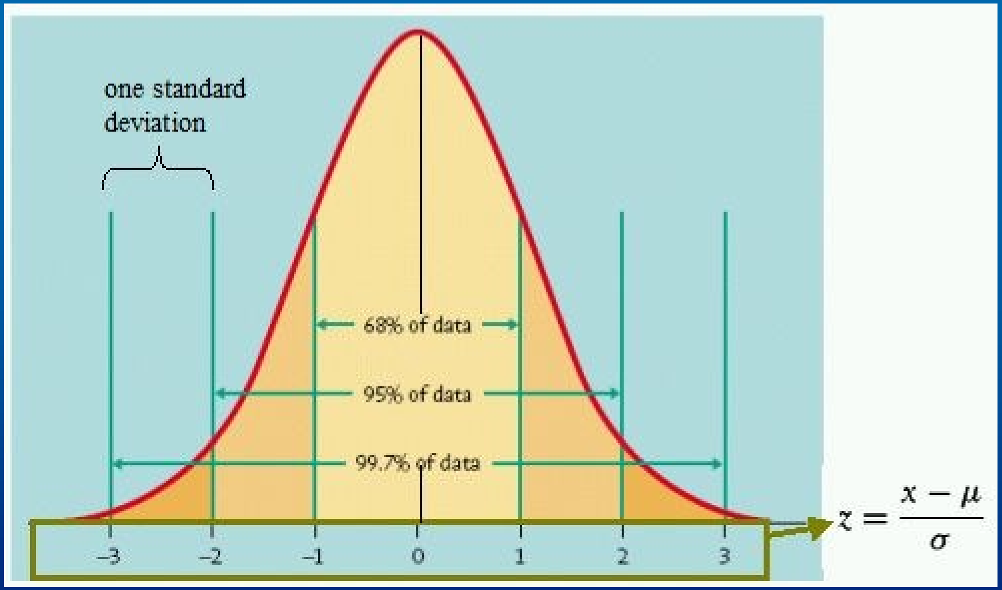
$$z = \frac{x - \hat{X}}{\sigma_p}$$

one-off evaluation

x : laboratory result

$\hat{X}$: assigned value

σ_p : target value of the standard deviation for proficiency assessment



evaluation of performance (z-score)

$$z = \frac{x - \hat{X}}{\sigma_p}$$

one-off evaluation

x : laboratory result

$\hat{X}$: assigned value

σ_p : target value of the standard deviation for proficiency assessment

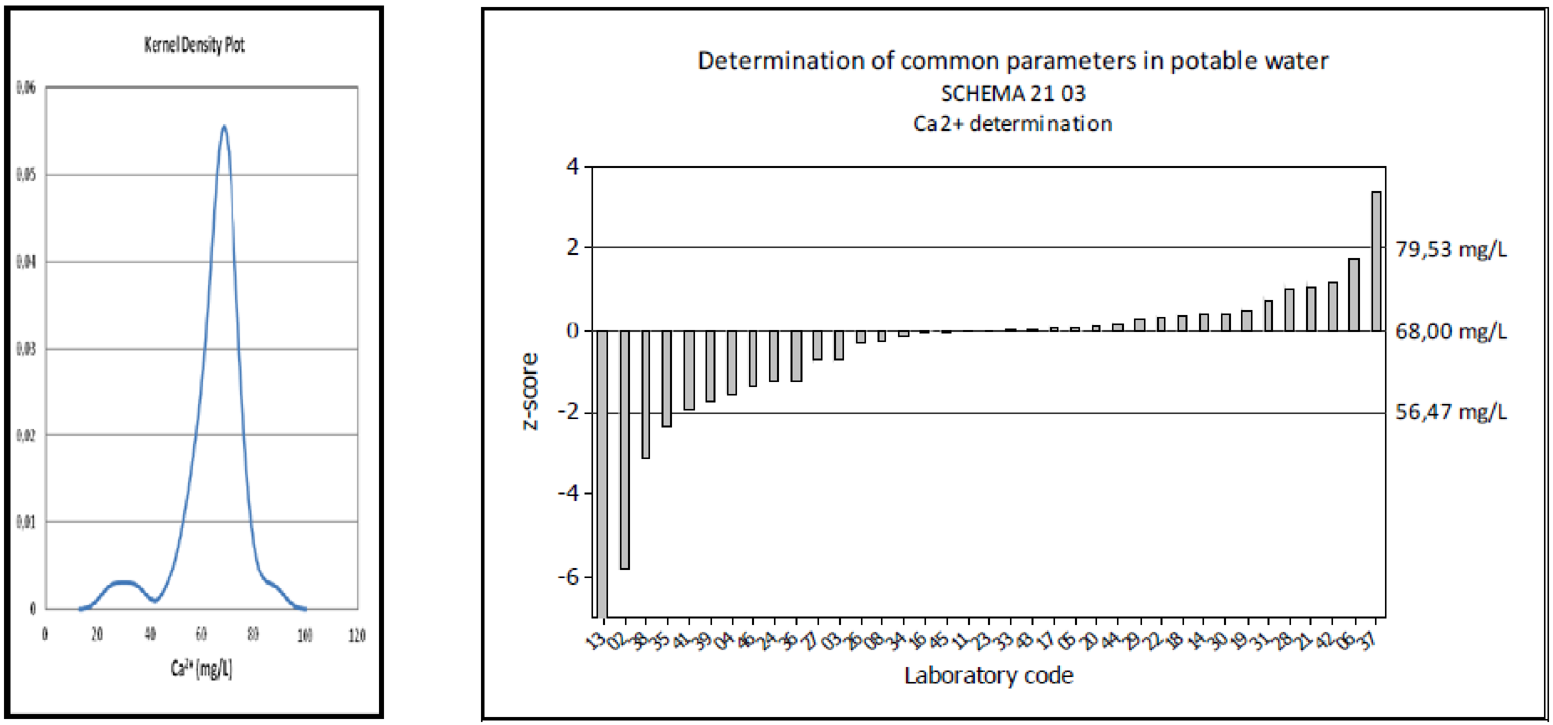
Evaluation using z-scores:

|z| ≤ 2, acceptable or satisfactory,

2<|z|≤3, questionable, triggers a warning signal

|z|>3, unacceptable/unsatisfactory, triggers corrective actions

Proficiency testing



Σχήμα 4. *(A) Πυρηνοδιάγραμμα πυκνότητας (kernel density plot) των αποτελεσμάτων που υπέβαλαν τα εργαστήρια που συμμετείχαν στον προσδιορισμό Ca^{2+} σε πόσιμο νερό και (B) αξιολόγηση της επίδοσης κάθε εργαστηρίου μέσω z-scores.μορφή αναλυτικών προσδιορισμών.*

2016-2017 PT programme

PT code	substrate	parameters	dispatch
SCHEMA 24 06	sewage	pH, total solids, COD, BOD_5, Cr (VI), heavy metals, TSS, TDS	9th-10th 2016
SCHEMA 90 06	edible oils	K_{232}, K_{270}, peroxide value, acidity, FAMEs, FAEs, wax	10th 2016
SCHEMA 12 07	spirit drinks	alcoholic strength, volatile congeners, sugars	10th 2016
SCHEMA 50 07	fuels	density, flash point, CFPP, sulfur, moisture kinematic viscosity, distillation characteristics, Pour Point	11th 2016
SCHEMA 51 08	solid fuels (1/2)	calorific value, moisture, ash, VOCs, content (C, H, N, S)	12th 2016
SCHEMA 70 06	honey	HMF, diastase, conductivity, moisture, sugars, thyme pollen	12th 2016
SCHEMA 13 07	wine	alcoholic strength, acidity (volatile & total), SO_2 (free & total), pH	1st 2017
SCHEMA 21 08	potable water	*anions*: F^-, Cl^-, NO_2^-,NO_3^-, SO_4^{2-} *cations*: Na^+, K^+, Ca^{2+}, Mg^{2+} total hardness, pH, conductivity, alkalinity	1st 2017
SCHEMA 15 03	beer	alcoholic strength, plato, density, fermentation parameters	2nd 2017
SCHEMA 91 04	virgin olive oil	sensory evaluation	2nd 2017
SCHEMA 63 05	flour	pesticide residues, acrylamide	3rd 2017
SCHEMA 60 05	dairy products	moisture, fat, protein, ash, aflatoxin M1	3rd 2017
SCHEMA 200 01	spectrophotometry	**absorbance (AU), wavelength (nm)**	3rd-4th 2017
SCHEMA 22 07	water	heavy metals: e.g. As, Cd, Cr, Pb, Fe, Mn, Al, Ni, Cu	4th 2017
SCHEMA 92 02	olive oil	phthalate esters	5th 2017
SCHEMA 80 04	foostuffs	preservatives (sorbic, benzoic, etc)	5th 2017
SCHEMA 30 08	ceramics	Pb and Cd migration	6th 2017
SCHEMA 62 05	fishery products	histamine, heavy metals	6th 2017
SCHEMA 51 09	solid fuels (2/2)	calorific value, moisture, ash, VOCs, content (C, H, N, S)	6th-7th 2017

EXHM-UVVis-01: comparison in the calibration of UV/Vis spectrophotometers

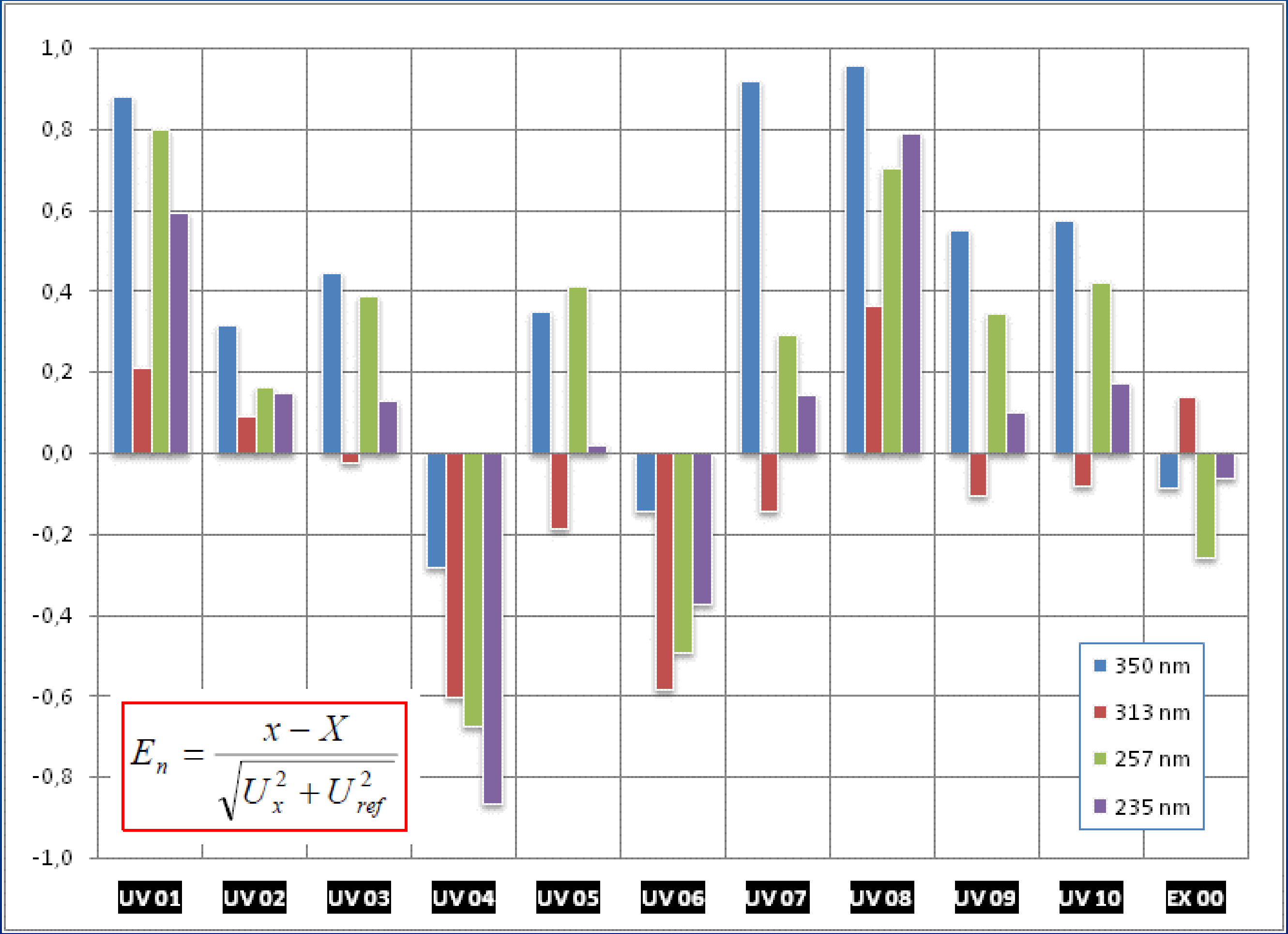
- comparison protocol [ENT 27 01 6.09 01]
- calibration results form [ENT 27 01 6.07 01]
- uncertainty budget form [ENT 27 01 6.07 03]
- performance data form [ENT 27 01 6.07 02]
- traceability of measurement equipment form [ENT 27 01 6.05 02]
- traceability of measurement form [ENT 27 01 6.05 01]
- evaluation questionnaire [ENT 27 01 4.07 01]
- hardware and software manuals (UV-Vis PE Lambda 650 spectrophotometer & UV WinLab)

EXHM-UVVis-01: transfer standard

manufacturer:	Perkin Elmer
model:	Lambda 650
serial number:	650N7020802
readability:	0, 1 mAU – 0,01 nm

En score

calibrations



$$E_n = \frac{x - X}{\sqrt{U_x^2 + U_{ref}^2}}$$

Uncertainty in calibration of spectrophotometers: wavelength

$$E = I - WL_{ref}$$

$$u_E^2 = u_I^2 + u_{WL_{ref}}^2$$

$$I = I_{WL} + \delta I_{digWL} + \delta I_{repWL}$$

Uncertainty in calibration of spectrophotometers: absorbance

$$E = I - A_{ref}$$

$$u_E^2 = u_I^2 + u_{A_{ref}}^2$$

$$I = I_A - I_0 + \delta I_{digA} - \delta I_{dig\,0} + \delta I_{repA} + \delta I_{sl} + \delta I_{wl}$$

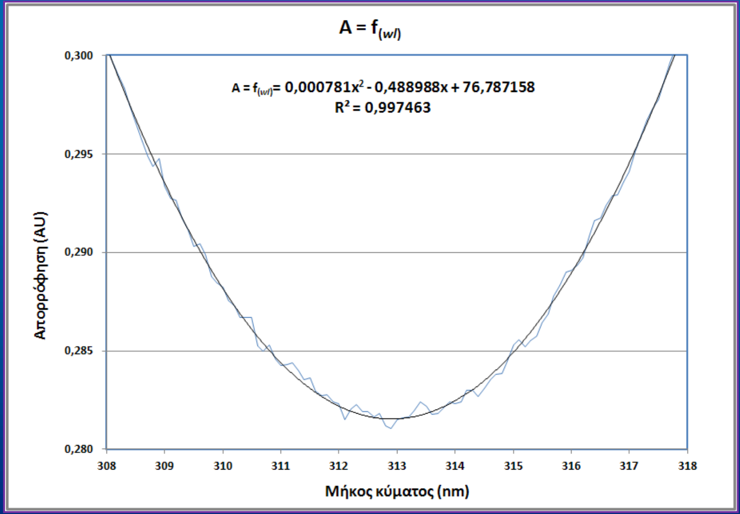
$$A_{ref} = A_N + \delta A_v + \delta A_{op} + \delta A_D + \delta A_T$$

$$f_{(wl)} = m_n wl^n + m_{n-1} wl^{n-1} + \cdots + m_1 wl + m_o$$

$$u_{A,wl}^2 = \frac{\partial f_{wl}}{\partial wl} u_{wl}^2$$

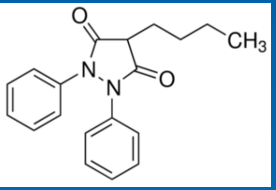
$$\frac{\partial f_{(wl)}}{\partial wl} = n\, m_n wl^{n-1} + (n-1) m_{n-1} wl^{n-2} + \cdots + m_1$$

$$u_{sl} = \frac{\log(1 - r + 10^A \times r)}{\sqrt{3}}$$



EU: horse meat in the food chain (2013) – analytical case

- validation according to Commission Decision 657/2002
- analyte: phenylbutazone
- linearity with matrix-matched standards at five levels
- blank samples spiked at three levels (2,5 – 5 – 7,5 μg/kg)
- determination with LC-ID-MS/MS
- two non-compliant samples out of 36



COMMISSION DECISION

of ►C1 14 August 2002 ◄

implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results

(notified under document number C(2002) 3044)

(Text with EEA relevance)

(2002/657/EC)

(OJ L 221, 17.8.2002, p. 8)

analyte quantification with isotope dilution (ID-LC/MS-MS)

- analyte concentration in the sample

$$C_{d,\text{smp}} = \frac{1}{Rec} \times \frac{V_{is,\text{smp}} \; C_{is,\text{smp}}}{m_{d,\text{smp}}} \times \frac{V_{d,\text{cal}} \; C_{d,\text{cal}}}{V_{is,\text{cal}} \; C_{is,\text{cal}}} \times \frac{R_{\text{smp}}}{R_{\text{cal}}}$$

- recovery

$$Rec = \frac{\bar{m}_{d,\text{obs}}}{m_{d,\text{spk}}} = \frac{\left(\frac{\bar{R}_{smp} - b}{a}\right) C_{is,rec} V_{is,spk}}{V_{d,\text{spk}} \, C_{d,\text{spk}}}$$

- combined

$$C_{d,\text{smp}} = \frac{\alpha \; V_{d,\text{spk}} \, C_{d,\text{spk}}}{(\bar{R}_{smp} - b) C_{is,spk} \; V_{is,spk}} \times \frac{V_{is,\text{smp}} \; C_{is,\text{smp}}}{m_{\text{smp}}} \times \frac{V_{d,\text{cal}} \; C_{d,\text{cal}}}{V_{is,\text{cal}} \; C_{is,\text{cal}}} \times \frac{R_{\text{smp}}}{R_{\text{cal}}}$$

uncertainty

$$\Delta(C_{\text{d,smp}}) = \sqrt{{C_d}^2 \frac{{RSD_R}^2}{n} + \sum_{i=1}^{m} \left(\frac{\partial C_d}{\partial x_i} \Delta_{x_i}\right)^2}$$

ID-LC/MS-MS: uncertainty budget

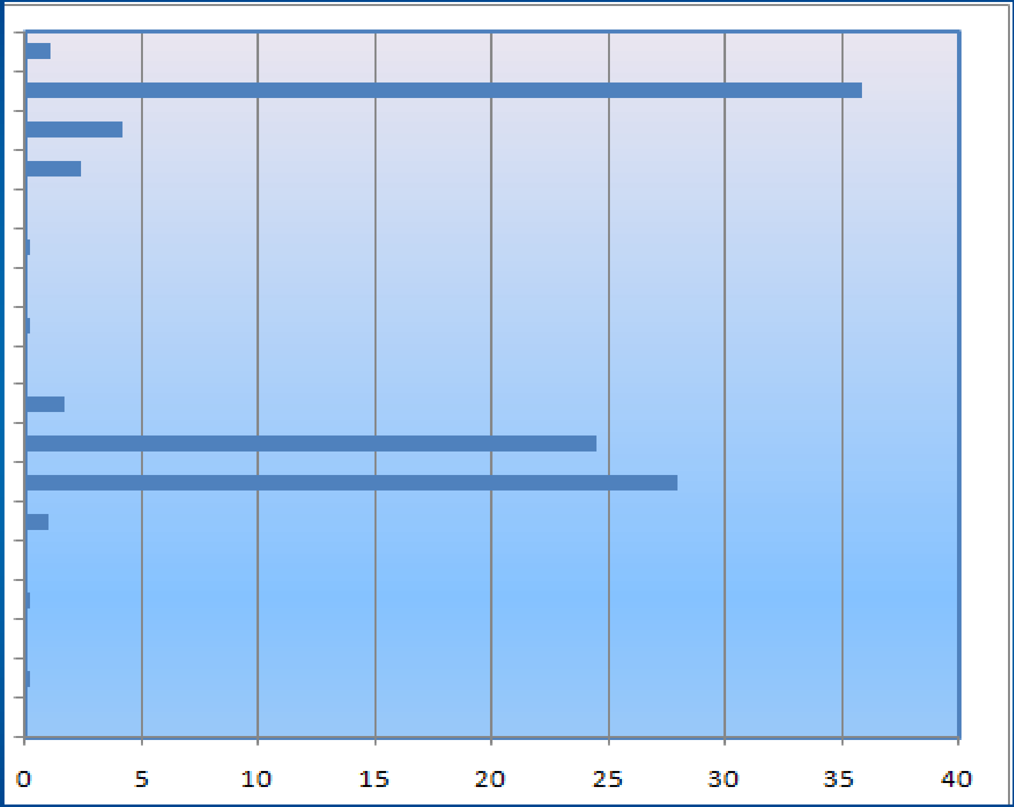
symbol	uncertainty component	value	units	standard uncertainty	relative uncertainty	sensitivity coefficient	$C_i \Delta x_i$	$(C_i \Delta x_i)^2$	contribution (%)	degrees of freedom
	standard error	5,002	μg/kg	0,0353	0,0071	1,0000	0,0353	0,0012	1,0592	35
	reproducibility conditions	5,002	μg/kg	0,2051	0,0410	1,0000	0,2051	0,0421	35,8110	12
Rsmp	analyte/internal standard area ratio in the samle	0,500	-	0,0070	0,0140	10,0041	0,0700	0,0049	4,1755	18
Rcal	analyte/internal standard area ratio in the calibrant	0,496	-	0,0052	0,0105	-10,0859	-0,0526	0,0028	2,360	14
Vd,cal	volume of analyte solution in the calibrant	50	μL	0,1091	0,0022	0,1000	0,0109	0,0001	0,101	∞
Cd,cal	concentration of analyte solution in the calibrant	5	mg/L	0,0165	0,0033	1,0004	0,0165	0,0003	0,232	∞
Vis,cal	volume of IS solution in the calibrant	50	μL	0,1091	0,0022	-0,1000	-0,0109	0,0001	0,101	∞
Cis,cal	concentration of IS solution in the calibrant	5	mg/L	0,0165	0,0033	-1,0004	-0,0165	0,0003	0,232	∞
Vis,smp	volume of IS solution in the sample	100	μL	0,2182	0,0022	0,0500	0,0109	0,0001	0,101	∞
Cis,smp	concentration of IS solution in the sample	0,250	mg/L	0,0022	0,0089	20,0081	0,0444	0,0020	1,678	∞
Rvld	average analyte/IS area ratio in the validation level	0,480	-	0,0187	0,0390	-9,0714	-0,1696	0,0288	24,505	5
a	slope of the calibration curve	0,547	-	0,0198	0,0362	9,1418	0,1812	0,0328	27,945	13
b	intercept of the validation curve	-0,072	-	0,0037	0,0520	9,0714	0,0339	0,0011	0,978	13
Vd,spk	analyte solution volume in the spiking solution	50	μL	0,1091	0,0022	0,1000	0,0109	0,0001	0,101	∞
Cd,spk	analyte solution concentration in the spiking solution	5	mg/L	0,0165	0,0033	1,0004	0,0165	0,0003	0,232	∞
Cis,spk	internal standard solution volume in the spiking solution	50	μL	0,1091	0,0022	-0,1000	-0,0109	0,0001	0,101	∞
Vis,spk	internal standard solution concentration in the spiking solution	5	mg/L	0,0165	0,0033	-1,0004	-0,0165	0,0003	0,232	∞
m	sample mass	5	g	0,0080	0,0016	-1,0004	-0,0080	0,0001	0,055	∞

symbol		value	units
Cd,smp	analyte concentration in the sample	5,002	μg/kg
	combined standard uncertainty	0,343	μg/kg
	relative uncertainty	6,851	(%)
	effective degrees of freedom	34,7	
	k (for 95% confidence level)	2,032	
	expanded uncertainty	0,696	μg/kg

$$C_{d,smp} = \frac{a\, V_{d,spk}\, C_{d,spk}}{\left(\bar{R}_{smp} - b\right) C_{is,spk}\, V_{is,spk}} \times \frac{V_{is,smp}\, C_{is,smp}}{m_{smp}} \times \frac{V_{d,cal}\, C_{d,cal}}{V_{is,cal}\, C_{is,cal}} \times \frac{R_{smp}}{R_{cal}}$$

relative contribution of the uncertainty components

symbol	uncertainty component
	standard error reproducibility conditions
Rsmp	analyte/internal standard area ratio in the samle
Rcal	analyte/internal standard area ratio in the calibrant
Vd,cal	volume of analyte solution in the calibrant
Cd,cal	concentration of analyte solution in the calibrant
Vis,cal	volume of IS solution in the calibrant
Cis,cal	concentration of IS solution in the calibrant
Vis,smp	volume of IS solution in the sample
Cis,smp	concentration of IS solution in the sample
Rvld	average analyte recovery
a	slope of the calibration curve
b	intercept of the validation curve
Vd,spk	analyte solution volume in the spiking solution
Cd,spk	analyte solution concentration in the spiking solution
Cis,spk	internal standard solution volume in the spiking solution
Vis,spk	internal standard solution concentration in the spiking solution
m	sample mass



$$C_{d,\text{smp}} = \frac{\alpha \ V_{d,\text{spk}} C_{d,\text{spk}}}{(\bar{R}_{smp} - b) C_{is,spk} \ V_{is,spk}} \times \frac{V_{is,\text{smp}} \ C_{is,\text{smp}}}{m_{\text{smp}}} \times \frac{V_{d,\text{cal}} \ C_{d,\text{cal}}}{V_{is,\text{cal}} \ C_{is,\text{cal}}} \times \frac{R_{\text{smp}}}{R_{\text{cal}}}$$

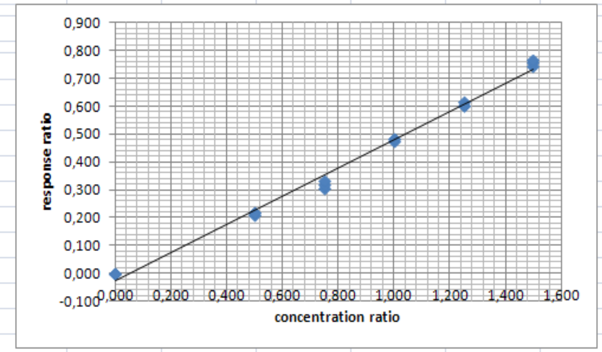
relative contribution of the uncertainty components

Chemical entity			PHENYLBUTAZONE			
calibration curve data (solvent)						
concentration level	residue concentration	in standard concentration	residue response	in standard response	concentration ratio	response ratio
L0_001	0	5			0,000	0,000
L0_002	0	5			0,000	0,000
L1_001	2,50	5	13595520	58000284	0,500	0,234
L1_002	2,50	5	14021069	57872435	0,500	0,242
L2_001	3,75	5	20604795	55437878	0,750	0,372
L2_002	3,75	5	20585495	56720035	0,750	0,363
L3_001	5,00	5	22811948	48302565	1,000	0,472
L3_002	5,00	5	21789129	47407562	1,000	0,460
L4_001	6,25	5	28903437	51656461	1,250	0,560
L4_002	6,25	5	28230301	52539168	1,250	0,537
L5_001	7,50	5	34725391	52833622	1,500	0,657
L5_002	7,50	5	33373269	52566266	1,500	0,635

zero included	
slope	0,4298
intercept	0,0195
RSQ	0,9925
zero excluded	
slope	0,3986
intercept	0,0546
RSQ	0,9903

calibration curve data (matrix matched)						
concentration level	residue concentration	in standard concentration	residue response	in standard response	concentration ratio	response ratio
MM0_001	0	5			0,000	0,000
MM0_002	0	5			0,000	0,000
MM0_003	0	5			0,000	0,000
MM1_001	2,50	5	6132131	29303506	0,500	0,209
MM1_002	2,50	5	6143809	28051383	0,500	0,219
MM1_003	2,50	5	5736678	26233683	0,500	0,219
MM2_001	3,75	5	10076506	32961116	0,750	0,306
MM2_002	3,75	5	10052962	31538455	0,750	0,319
MM2_003	3,75	5	9758642	29455709	0,750	0,331
MM3_001	5,00	5	16789053	35456831	1,000	0,474
MM3_002	5,00	5	16037632	33213672	1,000	0,483
MM3_003	5,00	5	16771708	34781924	1,000	0,482
MM4_001	6,25	5	23861725	38671827	1,250	0,617
MM4_002	6,25	5	24721073	40995360	1,250	0,603
MM4_003	6,25	5	23827627	39607487	1,250	0,602
MM5_001	7,50	5	52371204	70435996	1,500	0,744
MM5_002	7,50	5	56161933	74210160	1,500	0,757
MM5_003	7,50	5	56723505	74113793	1,500	0,765

REGRESSION RESULTS	
zero included	
slope	0,5060
intercept	-0,0257
RSQ	0,9926
zero excluded	
slope	0,5471
intercept	-0,0719
RSQ	0,9949
AVERAGE MATRIX EFFECT	17,73%



REPEATABILITY					
	LEVEL (mg/kg)	AVERAGE (mg/kg)	RECOVERY (%)	SDr (mg/kg)	%RSDr (%)
SET no1	2,50	2,48	99,1	0,24	9,82
	5,00	4,98	99,7	0,20	3,94
	7,50	7,05	94,0	0,44	6,29
SET no2	2,50	2,73	109,3	0,27	9,73
	5,00	5,14	102,7	0,31	6,02
	7,50	6,99	93,1	0,64	9,13
SET no3	2,50	2,55	102,1	0,45	17,49
	5,00	5,05	100,9	0,60	11,83
	7,50	7,12	94,9	0,21	2,91

REPRODUCIBILITY						
LEVEL (mg/kg)	AVERAGE (mg/kg)	RECOVERY (%)	SDr (mg/kg)	%RSDr (%)	UNCRT (mg/kg)	RELEXPU (k=2, %)
2,50	2,53	101,1	0,31	12,09	0,31	24,61
5,00	4,99	99,8	0,44	8,73	0,44	17,57
7,50	7,04	93,8	0,51	7,25	0,51	14,58

CCa	1,138	CCb	1,574

EXHM and the mole metrology market

GCSL laboratories and IAPR
Public service labs (Ministry of Rural Development & Food)
Public utility services (PPC, PEWS, etc)
Greek Army
University laboratories
Hospital and clinical laboratories
Calibration laboratories

around 500 customers