UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

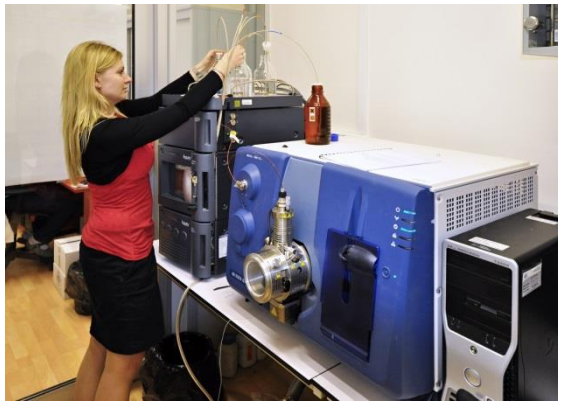
EUCHINASAFE
中欧食品安全

Quality Assurance / Quality Control in residue analysis

Vladimír Kocourek

Prague, 2022

FACULTY OF
FOOD AND BIOCHEMICAL TECHNOLOGY
UCT PRAGUE

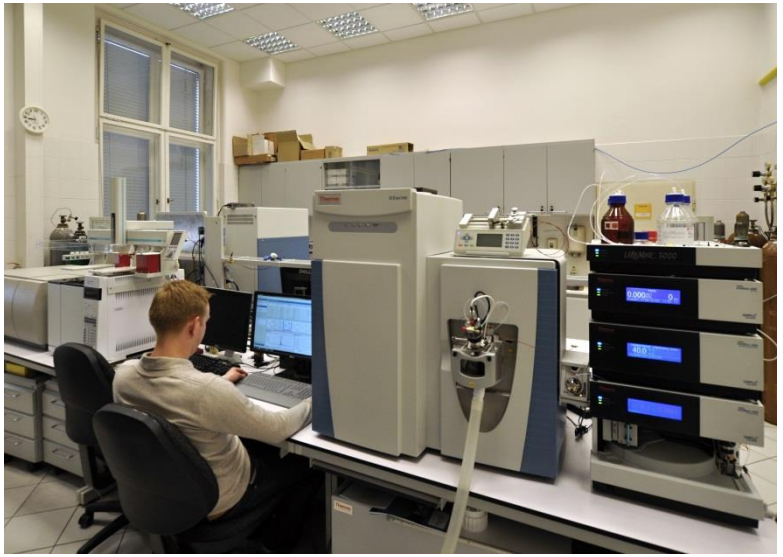


MRM: 532 pesticides and metabolites

GC amenable: 203

LC amenable: 449

GC/LC (overlap): 120



Regulation (EU) 2017/625 on official controls and other official activities performed to ensure the application of food and feed law

Designation of the official laboratory:

The competent authorities shall designate official laboratories to carry out the laboratory analyses on samples taken for official controls and other official activities

…providing that this Laboratory:

- has the expertise, equipment and infrastructure required to carry out analyses,
- has a sufficient number of qualified, trained and experienced staff;
- ensures that all tasks are performed impartially and free from any conflict of interest, and…

….**operates in accordance with the standard EN ISO/IEC 17025** and is accredited in accordance with that standard by a national accreditation body and the scope of the accreditation of an official laboratory includes relevant analytical methods. *Flexible scope is defined and supported*.

Accreditation of testing laboratory (EN ISO/IEC 17025:2017)

DESIGNATION of the official testing laboratory according to the regulation (EU) 2017/625:

CZECH AGRICULTURE AND FOOD INSPECTION AUTHORITY

STÁTNÍ ZEMĚDĚLSKÁ A POTRAVINÁŘSKÁ INSPEKCE
ÚSTŘEDNÍ INSPEKTORÁT
Květná 15, 603 00 Brno tel.: 543 540 201
e-mail: epodatelna@szpi.gov.cz, ID datové schránky: avraiqg

Čj.: SZPI/AM921-83/2019

Státní zemědělská a potravinářská inspekce (dále jen SZPI) v souladu s ustanovením § 3 odst. 3 písm. n) zákona č. 146/2002 Sb., o Státní zemědělské a potravinářské inspekci a o změně některých souvisejících zákonů, ve znění pozdějších předpisů, ve spojení s čl. 37 odst. 1 nařízení (EU) 2017/625 v platném znění (dále jen „nařízení o úředních kontrolách“)

určuje

Vysokou školu chemicko-technologickou v Praze

Metrologická a zkušební laboratoř VŠCHT Praha
se sídlem Technická 1903/3, 166 28 Praha 6 - Dejvice, IČ 60461373

jako úřední laboratoř č. 15
(dále také „laboratoř“)

k provádění laboratorních analýz, testů a diagnostiky vzorků odebraných při úředních kontrolách a jiných úředních činnostech.

Úkoly, které laboratoř provádí jakožto úřední laboratoř:

1. Příprava vzorků, provádění laboratorních analýz, testů a diagnostiky a uchovávání vzorků odebraných SZPI (včetně vzorků pro druhé odborné stanovisko a rozhodčích vzorků).
2. Vyjádření výsledků, vyhodnocení, interpretace a odborných stanovisek provedených zkoušek.

ilac-MRA

NÁRODNÍ AKREDITAČNÍ ORGÁN

EA MLA Signatory
Český institut pro akreditaci, o.p.s.
Olšanská 54/3, 130 00 Praha 3

issues

according to section 16 of Act No. 22/1997 Coll., on technical requirements for products, as amended

CERTIFICATE OF ACCREDITATION

No. **192/2019**

Vysoká škola chemicko-technologická v Praze
with registered office Technická 1905/5, 166 28 Praha 6, Dejvice, Company Registration No. 60461373

to the Testing Laboratory No. **1316.2**
Metrological and Testing laboratory

Scope of accreditation:

Chemical analysis of food including beverages and food supplements, food and pharmaceutical raw materials and products, feedstuffs, chemical preparations, biological materials of human, plant and animal origin, environmental components and forensic samples including addictive substances to the extent as specified in the appendix to this Certificate.

This Certificate of Accreditation is a proof of Accreditation issued on the basis of assessment of fulfillment of the accreditation criteria in accordance with

ČSN EN ISO/IEC 17025:2018

In its activities performed within the scope and for the period of validity of this Certificate, the Body is entitled to refer to this Certificate, provided that the accreditation is not suspended and the Body meets the specified accreditation requirements in accordance with the relevant regulations applicable to the activity of an accredited Conformity Assessment Body.

This Certificate of Accreditation replaces, to the full extent, Certificate No.: 202/2018 of 18. 4. 2018, or any administrative acts building upon it.

The Certificate of Accreditation is valid until: **29. 4. 2024**

Prague: 29. 4. 2019

Český institut pro akreditaci, o.p.s. -2-

Jiří Růžička
Director
Czech Accreditation Institute
Public Service Company

Flexible scope of accreditation: pesticides

EUROPEAN ACCREDITATION

Publication Reference **EA-4/22 G: 2018**

EA Guidance on Accreditation of Pesticide Residues Analysis in Food and Feed

Flexible scope of accreditation

„If a laboratory develops new testing methods or modifies them, it requires a sound technical understanding of the techniques used. This competence can be acquired, e.g. by participation in suitable research projects or developing projects, in projects for the development or standardisation of test method etc.“

- ✓ **Flexibility concerning object/matrix/sample**

  changes with respect to various matrices within a product area (e.g. LC-MS method which is extended from determination of mycotoxins in cereals and bakery products for the determination of mycotoxins in herbal food supplements).

- ✓ **Flexibility concerning parameters/components/analytes**

  changes with respect to parameters (e.g. the extension of DON determination in cereals to other mycotoxins in cereals by LC-MS method) .

- ✓ **Flexibility concerning the performance of the method**

  changes in the performance of the method for a given matrix type and a given analyte (e.g. the modification of measuring range and uncertainty).

- ✓ **Flexibility concerning the method**

  This means flexibility which allows adoption of methods that are equivalent to methods already covered by accreditation (e.g. new method based on the same measuring principle).

Analytical method for decision making

Defining the task → Selection of method → Sample handling → Analytical procedure measuring → Calibration a Calculation → Data processing → Interpretation, Presentation

Ask before you get started analysis:

- ✓ **Why do I test ?**
- ✓ **What is the commodity/matrix I have to test ?**
- ✓ **What is the pesticide I have to test for ?**
- ✓ **What kind of result do I need (*quantitative, semi-quantitative or qualitative*) ?**
- ✓ **How much time do I have to get a result?**
- ✓ **What infrastructure/equipment do I have?**
- ✓ **What happens with the results?**
- ✓ **How do I test (method / procedure selection) ?**

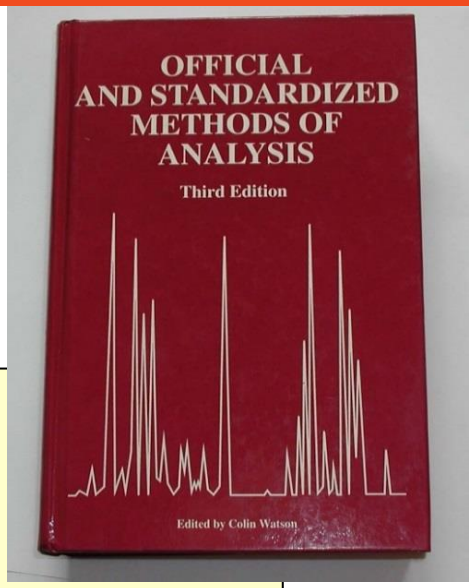
Analytical measurements should be „fit-for-purpose“

UCT PRAGUE

QUALITY ASSURANCE (QA) prerequisits:

- QMS documented and reviewed
- laboratory environment and facilities are suitable
- educated and trained personnel
- specifications for reagents, and reference materials (RMs)
- equipment maintained and calibrated
- procedures for sample handling
- documented and validated methods
- evaluation of measurement uncertainty
- internal quality control procedures - QC
- participation in proficiency testing (PT)
- procedures for checking and reporting results
- procedures for implementing preventive and corrective actions
- internal quality audit and review procedures

Choice of Method



Consider a „standard method“ if available – as this will save on development time.

However the method must be checked to prove that it’s suitable for laboratory/situation. Modification may well be required.

EU general approach:

! …not to establish a specific method of analysis but to establish performance criteria with which the method of analysis used for official control has to comply.

In selecting a method we shall consider:

- sample type (matrix) and size,
- type of data required (qualitative/quantitative ?),
- expected concentration level(s) of analyte(s),
- precision & accuracy required, confirmation ?
- likely interferences,
- number & frequency of samples delivered,
- response time, economy,….

Regulation (EU) 2017/625 on official controls and other official activities performed to ensure the application of food and feed law

Methods used for sampling and analyses shall comply with EU performance criteria.

According to the suitability for their specific needs, official laboratories shall prefer **EN, ISO**, (or other internationally recognized) standards or relevant **methods recommended by the EURLs**.

Methods of analysis which are **applicable uniformly to various groups of commodities** should be given preference over methods which apply only to individual commodities.

In situations where methods of analysis can only be validated within a single laboratory, those **methods should be validated in accordance with internationally accepted protocols or guidelines**.

The repeatability and reproducibility shall be expressed in an internationally recognised form, e.g. the 95 % confidence intervals as defined by ISO 5725 'Accuracy (trueness and precision) of measurement'

EN standards (example)

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15662

May 2018

ICS 67.050

Supersedes EN 15662:2008

English Version

Foods of plant origin - Multimethod for the determination of pesticide residues using GC- and LC-based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE - Modular QuEChERS-method

Aliments d'origine végétale - Multiméthode de détermination des résidus de pesticides par analyse CG et CL après extraction/partition avec de l'acétonitrile et purification par SPE dispersive - Méthode modulaire

Pflanzliche Lebensmittel - Multiverfahren zur Bestimmung von Pestizidrückständen mit GC und LC nach Acetonitril-Extraktion/Verteilung und Reinigung mit dispersiver SPE - Modulares QuEChERS-Verfahren

European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

Quick Method for the Analysis of Highly Polar Pesticides in Food Involving Extraction with Acidified Methanol and LC- or IC-MS/MS Measurement

I. Food of Plant Origin (QuPPe-PO-Method)

Version 12 (22.07.2021, Document History, see page **98**)

Check for latest version of this Method under www.quppe.eu ; older versions: obsolete versions

Authors: M. Anastassiades; A.-K. Wachtler; D. I. Kolberg; E. Eichhorn; H. Marks; A. Benkenstein; S. Zechmann; D. Mack; C. Wildgrube; A. Barth; I. Sigalov; S. Görlich; D. Dörk; G. Cerchia

EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL-SRM)

Contact: CVUA Stuttgart, Schaflandstr. 3/2, DE-70736 Fellbach, Germany, www.eurl-pesticides.eu; EURL@cvuas.bwl.de

UCT PRAGUE

WHAT IS VALIDATION?

- **Validation is a process, within which the method is demonstrated to be suitable for its purpose. It documents methods performance !**

- **During validation process, methods Performance characteristics are estimated.**

- **Validation documents, that the methods performance characteristics are capable of producing results in line with the needs of the analytical problem.**

Is it possible to detect pesticide residues at regulation levels using the method ?

Is it possible to correctly quantify the amount of residues in apple/orange/… ?

…

- **Validation procedure (protocol) is related to a particular analyte and matrix**

Applicability

There are six method validation principles:

Analytical measurements should be made to satisfy an agreed requirement („fit-for-purpose“)

Analytical measurements should be made using the equipment and instruments which have been verified and calibrated to ensure traceability

Analytical measurements made in one location should be consistent with those elsewhere

Staff making analytical measurements should be both qualified and competent to undertake the task (transparently)

Laboratory should have well defined quality control and quality assurance procedures

There should be an independent assessment of the technical performance of the laboratory

UCT PRAGUE

VALIDATION

VALIDATION PARAMETERS

- PRECISION
- TRUENESS

→ ACCURACY

Where possible, the validation of in-house validated methods shall include a certified reference material.

- RANGE & LINEARITY
- LIMIT OF DETECTION & LIMIT OF QUANTIFICATION
- SPECIFITY & SELECTIVITY
- RUGGEDNESS

TRUENESS

HOW TO ESTIMATE TRUENESS (RECOVERY)

(Certified) Reference materials are not available…

BLANK SAMPLE IS AVAILABLE

$$\text{MEAN RECOVERY (\%)} = \frac{\text{MEAN VALUE}}{\text{ADDED AMOUNT}} \cdot 100$$

- **Recovery values can be both below or above 100%**
- **Recoveries between 80 and 120 are usually acceptable.**

Recovery → Trueness if mean value: $n \rightarrow \infty$; but in practice: $n \geq 5$

UCT PRAGUE

PRECISION

PRECISION is related to RANDOM ERRORS

- Component of measurement error that - in replicate measurements - varies in an unpredictable manner
- Random error = error - systematic error
- Correction of random error can not be done

Some sources of random errors:

- Methods (procedure, calibration,...)
- Laboratory (facility, environment)
- Equipment and materials / reagents / calibrants
- Personnel
- Time

PRECISION

- **PRECISION represents random errors of a set of replicate measurements**
- **PRECISION is calculated as a (relative) standard deviation of replicate measurements σ_x**
- **Less precision is reflected by a larger standard deviation**
- **Precision depends critically on the conditions ! REPEATABILITY and REPRODUCIBILITY conditions are particular sets of extreme conditions.**

...nothing to do with true or reference value !

PRECISION

REPEATABILITY AND REPRODUCIBILITY

Repeatability: a set of conditions that includes

- the same measurement, procedure, operators, same measuring system, operating conditions and location, and replicate measurements on the same or similar objects over a short period of time

Reproducibility: a set of conditions that includes

- different locations, operators, measuring systems, or even methods on the same or similar objects.

Intermediate precision (*intra-laboratory reproducibility*):

- the same laboratory, method, procedure but within an extended period of time - may include new calibrations, calibrants, operators, measuring systems, etc.

PRECISION

INCREASING NUMBER OF CONSIDERED RANDOM ERROR SOURCES

REPEATABILITY		INTRA-LABORATORY REPEATABILITY		REPRODUCIBILITY	
SAMPLE:	SAME	SAMPLE:	SAME	SAMPLE:	SAME
OPERATOR:	SAME	OPERATOR:	DIFFERENT	OPERATOR:	DIFFERENT
INSTRUMENT:	SAME	INSTRUMENT:	SAME / DIFF.	INSTRUMENT:	DIFFERENT
TIME PERIOD:	SHORT	TIME PERIOD:	LONG	TIME PERIOD:	LONG
CALIBRATION:	SAME	CALIBRATION:	DIFFERENT	CALIBRATION:	DIFFERENT
LAB:	SAME	LAB:	SAME	LAB:	DIFFERENT

- Precision value is related to a certain analyte and concentration level

Reproducibility (s_R)

Two sources of variability:

s_r^2 intra-laboratory variation

s_L^2 inter-laboratory variation

William Horwitz
(1918-2006)

$$s_R^2 = \sigma_r^2 + \sigma_L^2$$

How to estimate s_R (and, consequently R):

1. **reproducibility standard deviation s_R requires a special interlaboratory comparison** (see ISO 5725-3)
2. **estimation from Horwitz equation based on concentration level**

…the RSD_R can be expressed as a function of the concentration …

PRECISION

REPRODUCIBILITY - HORWITZ

Relative standard deviation – variation coefficient:

- **lower concentration of analyte → increasing RSD**
- nature of analyte, matrix, analytical method etc.: less important – even can be ignored !

$$RSD = 2^{(1- 0.5*\log X)}$$

X is an analyte concentration expressed as a mass ratio

Method performance criteria: Reg. 401/2006/EC

(a) Performance criteria for aflatoxins

Criterion	Concentration Range	Recommended Value	Maximum permitted Value
Blanks	All	Negligible	—
Recovery — Aflatoxin M1	0,01-0,05 mg/kg	60 to 120 %	
	> 0,05 mg/kg	70 to 110 %	
Recovery-Aflatoxins B_1, B_2, G_1, G_2	< 1,0 mg/kg	50 to 120 %	
	1-10 mg/kg	70 to 110 %	
	> 10 mg/kg	80 to 110 %	
Reproducibility RSD_R	All	As derived from Horwitz Equation (*) (**)	2 × value derived from Horwitz Equation (*) (**)

Repeatability RSD_r may be calculated as 0,66 times Reproducibility RSD_R at the concentration of interest.

UCT PRAGUE

Method performance criteria: Reg. 401/2006/EC

Performance criteria for deoxynivalenol

Level µg/kg	Deoxynivalenol		
	RSD_r %	RSD_R %	Recovery %
> 100-≤ 500	≤ 20	≤ 40	60 to 110
> 500	≤ 20	≤ 40	70 to 120

(b) Performance criteria for ochratoxin A

Level µg/kg	Ochratoxin A		
	RSD_r %	RSD_R %	Recovery %
< 1	≤ 40	≤ 60	50 to 120
≥ 1	≤ 20	≤ 30	70 to 110

Method performance criteria: Reg. 401/2006/EC

Performance criteria for zearalenone

Level µg/kg	Zearalenone		
	RSD_r %	RSD_R %	Recovery %
≤ 50	≤ 40	≤ 50	60 to 120
> 50	≤ 25	≤ 40	70 to 120

Performance criteria for Fumonisin B_1 and B_2 individually

Level µg/kg	Fumonisin B_1 and B_2 individually		
	RSD_r %	RSD_R %	Recovery %
≤ 500	≤ 30	≤ 60	60 to 120
> 500	≤ 20	≤ 30	70 to 110

Performance criteria for T-2 and HT-2 toxin individually

Level µg/kg	T-2 and HT-2 toxin individually		
	RSD_r %	RSD_R %	Recovery %
15-250	≤ 30	≤ 50	60 to 130
> 250	≤ 25	≤ 40	60 to 130

UCT PRAGUE

PRECISION

INCREASING NUMBER OF CONSIDERED RANDOM ERROR SOURCES

REPEATABILITY

INTRA-LABORATORY REPEATABILITY

REPRODUCIBILITY

- **Repeated analyses of a sample containing analyte(s) at:**
  - **level close to expected concentration in analyzed matrix**
  - **level close to regulatory limit (MRL)**
  - **low level close to limit of quantification of the method (LOQ)**
- **Appropriate number of repeats: 8 – 15 (at least 5)**
- **Calculated as standard deviation or relative standard deviation (RSD)**

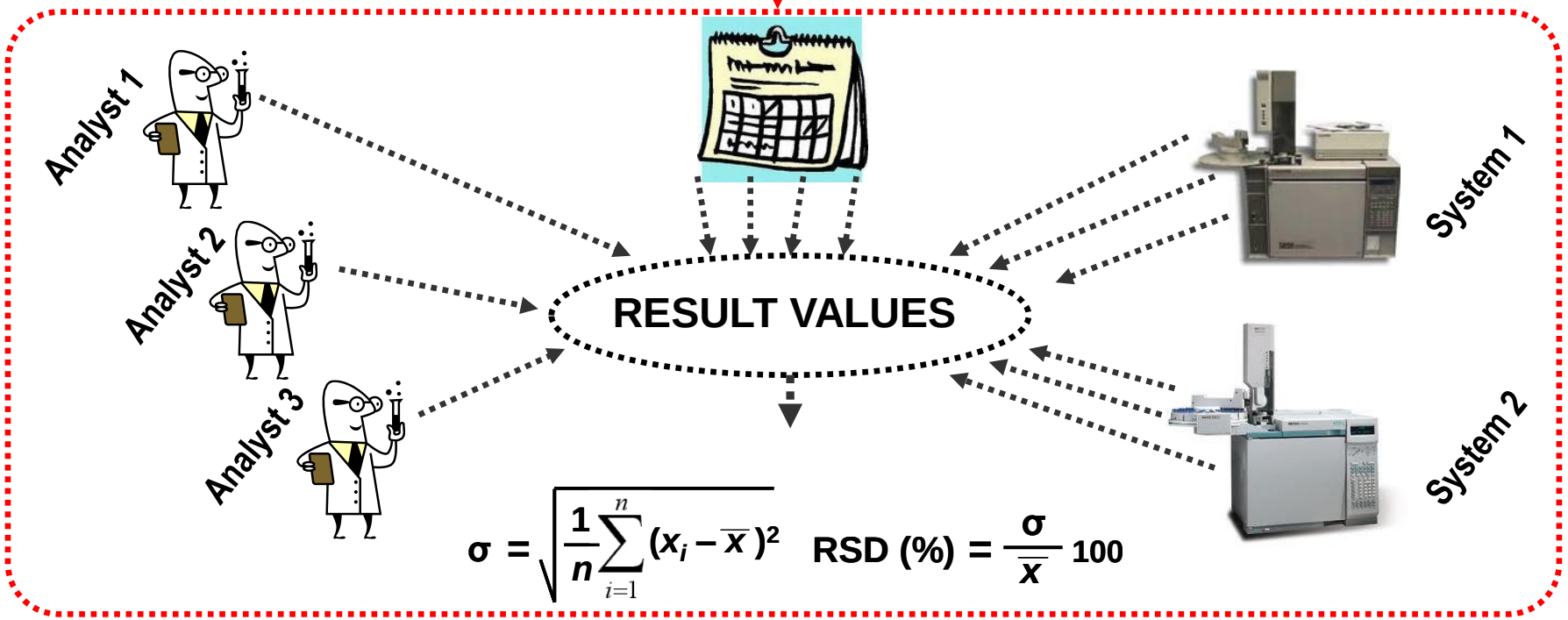
PRECISION

INCREASING NUMBER OF CONSIDERED RANDOM ERROR SOURCES

REPEATABILITY

INTRA-LABORATORY REPEATABILITY

REPRODUCIBILITY



$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2} \qquad \text{RSD (\%)} = \frac{\sigma}{\bar{x}}\,100$$

UCT PRAGUE

PRECISION

INCREASING NUMBER OF CONSIDERED RANDOM ERROR SOURCES

REPEATABILITY

INTRA-LABORATORY REPEATABILITY

REPRODUCIBILITY

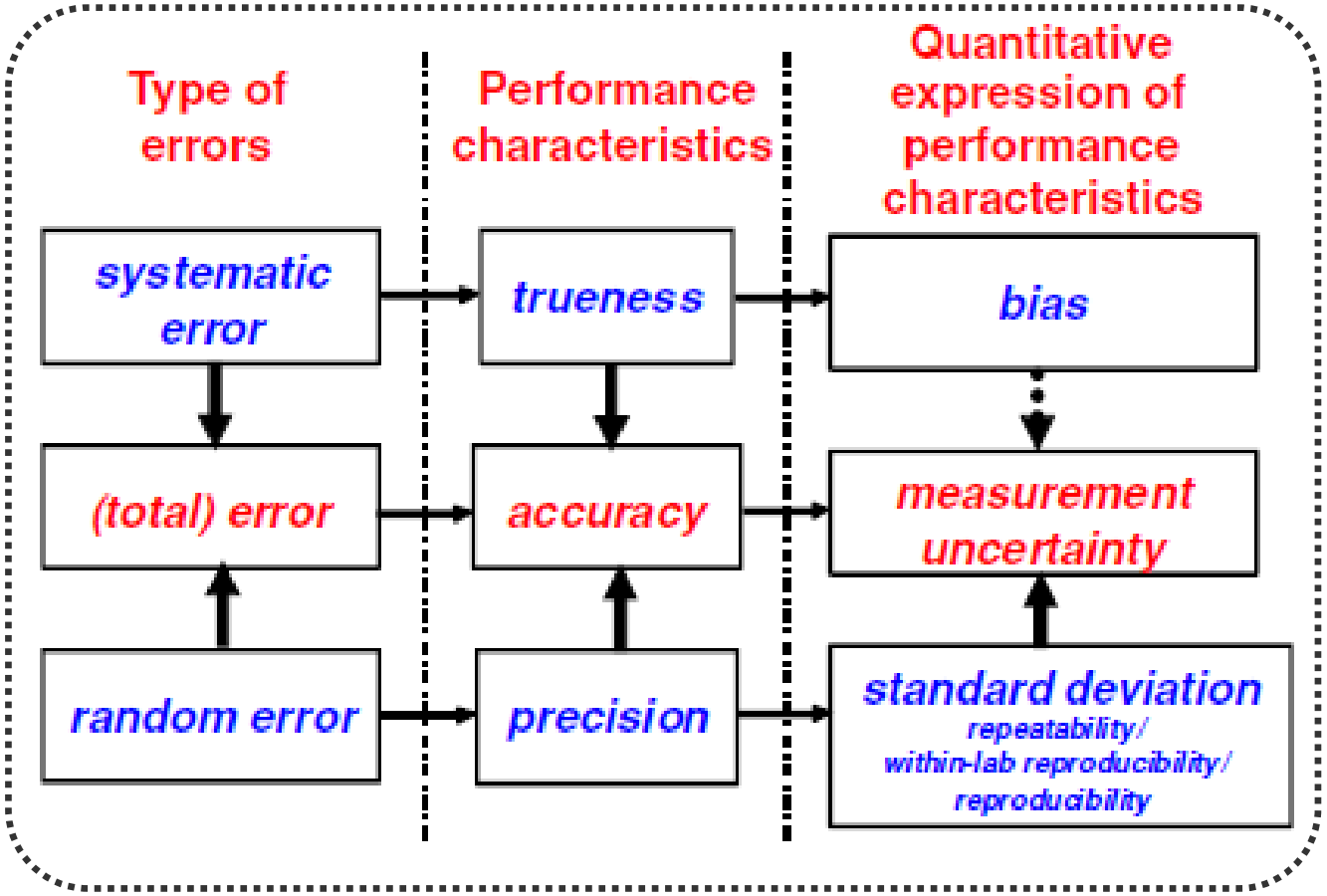
- **Can be estimated within an inter-laboratory study…**

…however…

- **inter-laboratory study is time-demanding and costly**
- **it is problematic to find sufficient number of competent laboratories**
- **in multi residue analysis it is almost impossible to perform this kind of study for all analytes / matrices / concentration levels**

TRUENESS AND PRECISION = ACCURACY

RELATIONSHIPS BETWEEN TYPE OF ERROR, RELATED CHARACTERISTICS AND THEIR QUANTITATIVE EXPRESSION



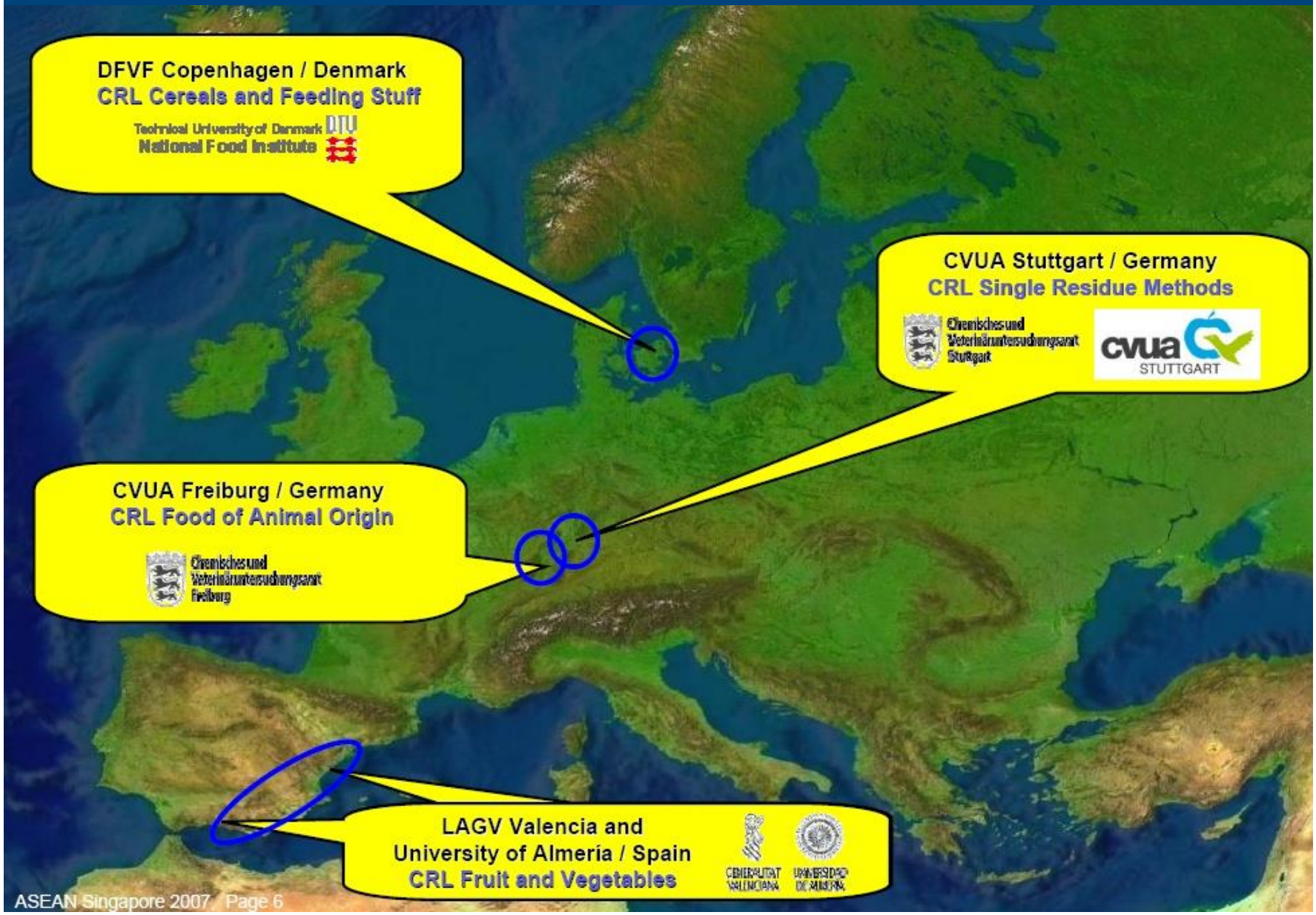
QUALITY CONTROL (QC)

QC procedures relate to ensuring the quality of results obtained for specific samples or sets of samples and include

ANALYSIS OF QC SAMPLES

- ✓ analysis of **measurement standards (including RMs)**
- ✓ analysis of **blind samples**
- ✓ analysis of **sample blanks and reagent blanks**
- ✓ analysis of **spiked samples**
- ✓ analysis in **duplicate / replicate**
- ✓ **use of QC charts to monitor trends**
- ✓ **participation in proficiency testing (PT) and EQC schemes**

Location of the 4 EURLs for Pesticides



EU RLs for pesticide residues

https://www.eurl-pesticides.eu

You are here: Home

EURL Portal | EURL for Fruits and Vegetables | EURL for Cereals and Feeding Stuff | EURL for Food of Animal Origin | EURL for Single Residue Methods

Topics

General Info
- DG SANTE
- About EURLs
- RASFF
- Control Programs

AQC Procedures
- AQC Documents
- AQC Panel

Proficiency Tests
- About EUPTs
- General Protocol
- Annual EUPT-Calendars
- EUPT-FV24
- EUPT-FV23
- EUPT-FV-SM14
- EUPT-FV-SM13
- EUPT-FV-SC04
- EUPT-CF16
- EUPT-CF15
- EUPT-AO17
- EUPT-AO16
- EUPT-SRM17

Workshops
- Workshop Overview

Library
- News Archive
- Pilot Monitoring Studies *new*
- Surveys
- List of Methods
- Sources of Standards

Latest News

07-02-2022 | EURL-AO
Quantification method for analysis of pesticide residues in milk and dairy products using GC-MS/MS
Validation report

04-02-2022 | EURL-SRM
Analysis of Meptyldinocap by QuEChERS followed by alkaline hydrolysis and LC-MS/MS measurement
A simple and sensitive method for the analysis of Meptyldinocap and 2,4-DNOP is presented, either individually or as a sum, following transformation of Meptyldinocap to 2,4-DNOP under alkaline conditions. The procedure involves QuEChERS or QuOil extraction and LC- MS/MS measurement in ESI negative mode either directly or after alkaline hydrolysis.

04-02-2022 | EURL-SRM
Analysis of the Folpet degradant Phthalimide and the Captan degradant Tetrahydrophthalimide by QuEChERS and LC-MS/MS
A new simple and highly sensitive method for the analysis of PI and THPI was developed based on QuEChERS extraction and LC-MS/MS using ESI positive mode.

31-01-2022 | EURL-SRM
Intermediate analytical observations as regards of the analysis of Propineb as Propylenediamine following reductive cleavage with HCl/SnCl2 and measurement via ion-pair LC-MS/MS
A method for the analysis of propineb residues was developed which starts with the traditional reductive cleavage with HCl/SnCl2 to CS2 and 1,2-diamonopropane (PDA), followed by a QuEChERS-like step under alkaline conditions and measurement via ion-pair LC-MS/MS

05-01-2022 | EURL-CF
Workshop 2022
Workshop dates for 2022

04-01-2022 | EURL-AO
Validation and determination of pesticide residues in (offal and) fish samples
Validation and monitoring report

31-12-2021 | EURL-FV
EUPT-FV-SM14
European Proficiency Test in Fruits and Vegetables Screening Method 14

22-12-2021 | EURL-AO
EUPT AO-17 Website
17th EU Proficiency Test on Pesticides - Rape Seed Oil Test Material

Quicklinks

- EURL-DataPool
- EU-MRLs Database (COM)
- EU-Legisl. on MRLs (COM)
- EU-Legisl. on PPPs (COM)
- RASFF Portal DB (COM)
- CIRCA BC Login
- How to Use CIRCA BC
- EURL Method Finder List

Pesticide residues: (official) analysis

ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED

Document Nº SANTE/12682 /2019 **Implemented by 01/01/2020**

UCT PRAGUE

ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED

Document No. DG SANTE/12682/2019, *implemented by 01/01/20*

Coordinators:

Tuija Pihlström	Swedish Food Agency, SFA, Uppsala, Sweden
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Ralf Lippold	EURL-AO, CVUA Freiburg, Freiburg, Germany
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Advisory Board:

André de Kok	Wageningen Food Safety Research, Wageningen, The Netherlands
Finbarr O´Regan	Pesticide Control Laboratory, DAFM, Kildare, Ireland
Patrizia Pelosi	Natonal Institute of Health, ISS, Rome, Italy
Antonio Valverde	University of Almería, Almería, Spain
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Hans Mol	Wageningen Food Safety Research, Wageningen, The Netherlands
Magnus Jezussek	LGL, Erlangen, Germany

UCT PRAGUE

ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED

Document No. DG SANTE/12682/2019, *implemented by January 2020*

Document is intended for laboratories involved in official control of pesticide residues in food and feed in the European Union. The document supports the validity of data reported within official controls and used for checking compliance with MRLs or assessment of consumer exposure to pesticides.

The key objectives are to:

- ✓ provide a harmonized, cost-effective quality assurance and quality control system in the EU
- ✓ ensure the quality and comparability of analytical results
- ✓ ensure that acceptable accuracy is achieved
- ✓ ensure that false positives or false negatives are avoided
- ✓ support compliance with, and specific implementation of ISO/IEC 17025 (accreditation standard)

This document is complementary and integral to the requirements in ISO/IEC 17025:2017 !

SANTE/12682/2019 - topics

A. *Introduction and legal background*

B. Sampling, transport, and storage of laboratory samples

- **Sampling**
- **Transport**
- **Traceability**
- **Storage**

C. Sample analysis

- **sample preparation and processing (extraction, clean-up, concentration,...)**
- **chromatographic separation and determination**
- **calibration and quantification, data processing**
- **on-going method performance verification during routine analysis (IQC)**
- **screening methods**
- **proficiency testing (EQC)**

SANTE/12682/2019 - topics

D. Identification of analytes, confirmation; criteria (MS)

E. Reporting results

- calculation and expression of results
- correction for recovery
- rounding of data
- qualifying results with measurement uncertainty
- interpretation of results for enforcement purposes

F. Standards, calibration standard solutions

- identity, purity, and storage of reference standards
- preparation, use and storage of stock solutions and working standards
- testing and replacement of standards

G. Analytical method validation and performance criteria

- method performance acceptability criteria: quantitative / screening methods

H. Additional recommendations: contamination / interference

Sample preparation

- The recovery of incurred residues can be lower than the recovery obtained from the analysis of spiked samples.
- To improve the extraction efficiency of low moisture commodities (cereals, dried fruits), addition of water to the samples prior to extraction is recommended.
- Where the MRL residue definition of a pesticide includes salts, it is important that the salts are dissociated by the analytical method used. (the addition of water, a change of pH may also be necessary).
- Where the residue definition includes esters or conjugates that cannot be analysed directly, the analytical method should involve a hydrolysis step.
- To avoid losses during evaporation steps the temperature should be kept as low as is practicable. A small volume of a high boiling point solvent may be used as a “keeper”.
- Analyte stability in extracts should be evaluated during method validation.
- All sample preparation and processing procedures should be undertaken within the shortest time practicable to minimise sample decay and pesticide losses.

Separation and identification of analytes

Sample extracts are normally analysed using capillary GC and/or HPLC (UPLC) coupled to MS for the identification and quantification of pesticides

Selective detectors for GC (ECD, FPD, PFPD, NPD) and LC (DAD, fluorescence) are less widely used as they offer only limited specificity. Their use, even in combination with different polarity columns, does not provide unambiguous identification !

Chromatographic separation:

- 1st peak should have RT ≥ 2 x RT_0 (matching dead volume),
- difference between RT of standard a RT of analyte ≤ 0.1 min (GC i LC)
- shodu lze ověřit přídavkem analytu, jehož přítomnost se předpokládá, případně lze využít isotopově značený interní standard (IL-IS)

Identification of analytes is generally based on:

- retention times (RT),
- characteristic ions (m/z)
- poměru intenzit iontů (m/z)

Identification of analytes, confirmation

Mass spectrometry:

- **based on MS-spectra** (incl. full scan)
- **based on selected ions: suitable for residue analysis.**

Guidance for identification based on MS spectra is limited to some recommendations whereas for identification based on selected ions more detailed criteria are provided.

Identification based on MS-spectra:

- Laboratories that use spectral matching for identification need to set their own criteria and demonstrate these are fit-for-purpose.
- Reference spectra for the analyte should be generated using the same instruments and conditions used for analysis of the samples.
- Subtraction of background spektra, deconvolution - *to be described*.
- Whenever background correction is used, this must be applied uniformly throughout the batch and should be clearly recorded.

Identification of analytes, confirmation

Identification based on selected ions:

- Molecular ions, (de)protonated molecules or adduct ions are highly characteristic for the analyte and should be included in the identification procedure whenever possible.
- In practice, the choice of ions for identification may change depending on background interferences.
- For determination of the reference ion ratio, responses outside the linear range should be excluded.
- Ion ratios in unit mass resolution MS/MS have shown to be consistent and should not deviate more than 30 % (relative) from the reference value.
- Larger tolerances may lead to a higher percentage of FP results. Similarly, if the tolerances are decreased, then the likelihood of FN will increase.
- For HRMS, the variability of ion ratios is not only affected by S/N of the peaks in the extracted ion chromatograms, but may also be affected by the way fragment ions are generated, and by matrix - matching ion ratios are not necessary.

Identification of analytes, confirmation

Different types and modes of mass spectrometric detectors provide different degrees of selectivity, which relates to the confidence in identification (Table 3):

MS detector/Characteristics		Acquisition	Requirements for identification	
Resolution	Typical systems (examples)		minimum number of ions	other
Unit mass resolution	Single MS quadrupole, ion trap, TOF	full scan, limited m/z range, SIM	3 ions	S/N ≥ 3[d] Analyte peaks from both product ions in the extracted ion chromatograms must fully overlap. Ion ratio from sample extracts should be within **±30 % (relative)** of average of calibration standards from same sequence
	MS/MS triple quadrupole, ion trap, Q-trap, Q-TOF, Q-Orbitrap	selected or multiple reaction monitoring (SRM, MRM), mass resolution for precursor-ion isolation equal to or better than unit mass resolution	2 product ions	
Accurate mass measurement	High resolution MS: (Q-)TOF (Q-)Orbitrap FT-ICR-MS sector MS	full scan, limited m/z range, SIM, fragmentation with or without precursor-ion selection, or combinations thereof	2 ions with mass accuracy ≤ 5 ppm[a, b, c]	S/N ≥ 3[d] Analyte peaks from precursor and/or product ion(s) in the extracted ion chromatograms must fully overlap. Ion ratio: see D12

[a] preferably including the molecular ion, (de)protonated molecule or adduct ion
[b] including at least one fragment ion
[c] < 1 mDa for m/z < 200
[d] in case noise is absent, a signal should be present in at least 5 subsequent scans

Identification of analytes, confirmation

EURACHEM/CITAC Guide:
Assessment of the performance and uncertainty in qualitative chemical analysis *(AQA – 04/2020)*

Qualitative criteria such as the presence or absence of a particular feature...

„When only positive results are subject to confirmation because false positive results are particularly harmful, the negative results are assumed to be correct. This assumption may be incorrect but without confirmation the analyst will never know !!! The point here is that, in order to calculate a false positive rate, it is necessary to know the number of true negatives.“

Table 3. Minimum number of analyses to find one or more false result.

	Confidence level	
False result rate	95%	99%
0.5 %	598	919
1 %	299	459
5 %	59	90

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Confirmation of results

Confirmatory analysis is required if:

- the initial analysis does not provide unambiguous identification, or
- does not meet the requirements for quantitative analysis, or
- MRL is exceeded.

This may involve re-analysis of the extract or the sample. In cases where a MRL is exceeded, a confirmatory analysis of another analytical portion is always required.

For unusual pesticide/matrix combinations, a confirmatory analysis is also recommended.

The use of different determination techniques and/or confirmation of results by an independent expert laboratory will provide further supporting evidence.

Reporting results

The results from the individual analytes measured must always be reported and their concentrations expressed in **mg/kg**.

Where the residue definition includes more than one analyte, the respective sum of analytes must be calculated.

For quantitative methods, residues of analytes below the RL must be reported as < RL mg/kg (RL ≈ LOQ).

Where screening methods are used and a pesticide is not detected, the result must be reported as < SDL mg/kg (SDL ≈ LOD).

Where the same homogenised sample is analysed by two techniques, the result should be that obtained using the technique which is considered to be the most accurate.

QC: In case there are two replicates the relative difference of the individual results should not exceed 30 % of the mean. *Close to the RL, the variation may be higher and additional caution is required in deciding whether or not this limit has been exceeded.*

Reporting results: correction for recovery

As a practical approach, residues results do not have to be adjusted for recovery when the mean recovery is within the range of 80-120 % and the default expanded measurement uncertainty of 50 % is not exceeded.

In case of recovery correction, the mean recovery obtained during initial validation, the mean recovery obtained during on-going validation, or the (mean) recovery obtained for spiked samples analysed with the real samples.

In case of lack of information on the suitability of a mean recovery % to be used for recovery correction, alternative approaches to account for recovery losses may be considered to avoid the need for recovery correction, e.g.:

- the use of standard addition before extraction,
- addition of an isotopically labelled internal standard (IL-IS)
- procedural calibration (*spiking a series of blank test portions with different amounts of analyte, prior to extraction*).

Reporting results: rounding

Result:* *UNIFORMITY – CONSISTENCY – SIGNIFICANCE

Rounding to significant figures should be done after the calculation of the result

- **results** at or above the RL but <10 mg/kg: round to 2 significant figures,
- **results ≥10 mg/kg** may be rounded to 3 significant figures or to a whole number,
- **RL (LOQ)** should be rounded to 1 significant figure at <10 mg/kg and 2 significant figures at ≥10 mg/kg.
- **Expanded uncertainty** should be calculated using rounded value of result (!) and rounded according to above mentioned rules,

Additional significant figures may be recorded for the purpose of statistical analysis, monitoring of dietary exposure and when reporting results for proficiency tests.

Reporting results for enforcement: rounding

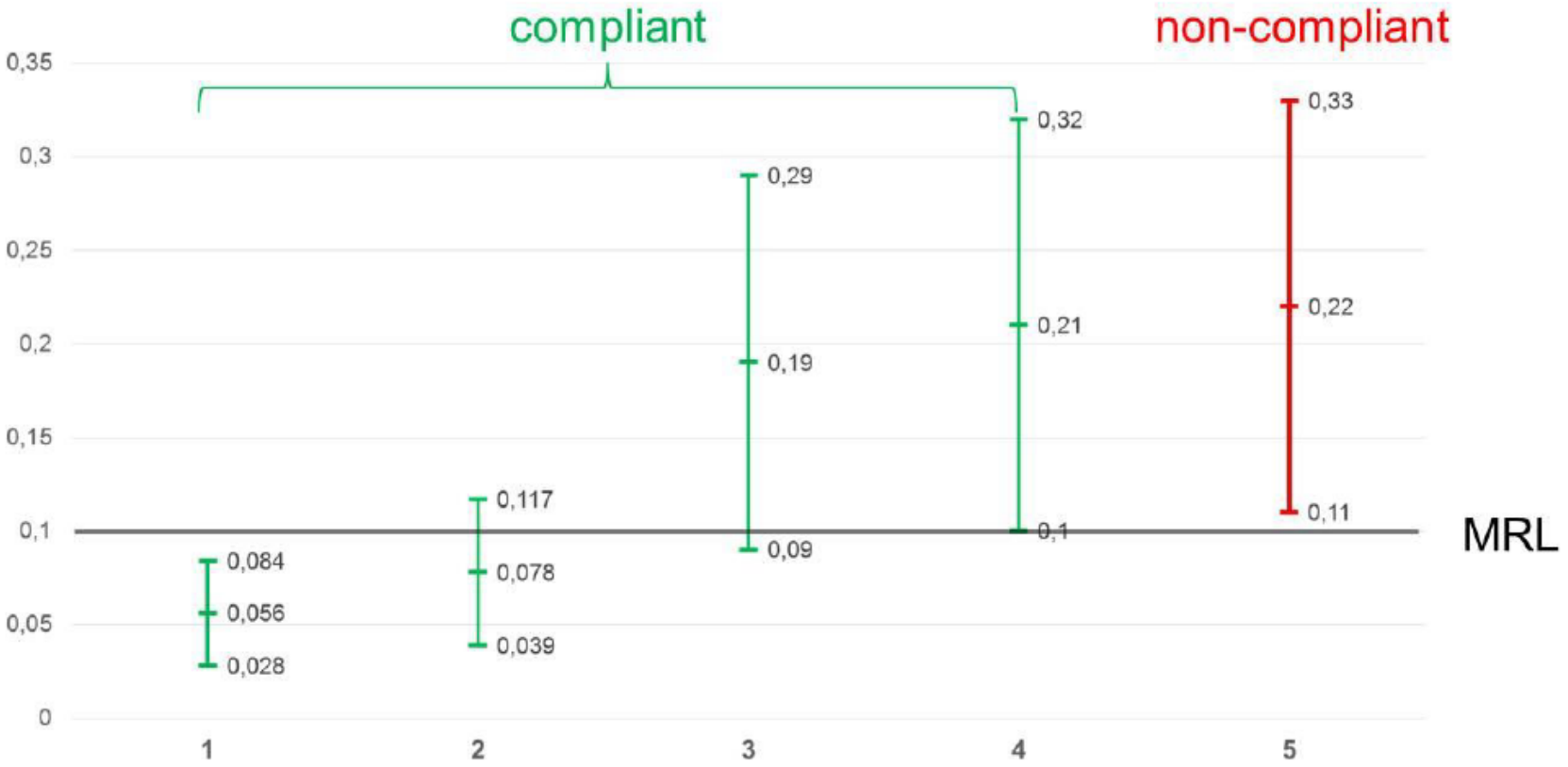
Example:

Analytical result = **0.02454705 mg/kg**

Rounded to 2 significant figures: 0.025 mg/kg

Expanded uncertainty (50 % for official control) = 0.025 / 2 = 0.0125 mg/kg (0.013)

Result in the Test report: **0.025 ± 0.013 mg/kg**



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Reporting results: rounding

No.	Primary result (mg/kg)	Rounded result (mg/kg)	Primary value for the Expanded Uncertainty (mg/kg)	Rounded value of the Expanded Uncertainty (mg/kg)	**Reported result** (mg/kg)	Result plus Expanded Uncertainty (mg/kg)	Result minus Expanded Uncertainty (mg/kg)	MRL (mg/kg)	Interpretation
1	0.05**5**97	0.056	± 0.02**8**	± 0.028	0.056 ± 0.028	0.084	0.028	0.1	Result plus expanded uncertainty <MRL; Compliant
2	0.07**8**43	0.078	± 0.03**9**	± 0.039	0.078 ± 0.039	0.117	0.039	0.1	Result < MRL; Compliant
3	0.1**9**43	0.19	± 0.0**9**5	± 0.10	0.19 ± 0.10	0.29	0.09	0.1	Result> MRL; Compliant due to the uncertainty interval
4	0.21**3**4	0.21	± 0.1**0**5	± 0.11	0.21 ± 0.11	0.32	0.10	0.1	Result > MRL; Compliant due to the uncertainty interval
5	0.21**6**8	0.22	± 0.1**1**0	± 0.11	0.22 ± 0.11	0.33	0.11	0.1	Result minus expanded uncertainty >MRL; Non-compliant

UCT PRAGUE

Reporting LOQ for complex residue definitions

EUROPEAN COMMISSION
HEALTH & FOOD SAFETY DIRECTORATE-GENERAL

Pesticides and biocides

SANCO/12574/2014
30/11-01/12 2015 rev. 5(1)

Working document on the summing up of LOQs in case of complex residue definitions.

Application date: 1 January 2017

$$LOQ\ (legal\ RD) = LOQc1 * CF_1 + LOQc2 * CF_2 + LOQc3 * CF_3$$

Příklad výpočtu LOQ pro porovnání s MRL:

MRL for Aldicarb (sum of aldicarb, its sulfoxide and its sulfone, expressed as aldicarb) on oranges: 0.02* mg/kg

Aldicarb LOQ=0.006 mg/kg, CF_{MW}=1

Aldicarb sulfone LOQ= 0.006 mg/kg, CF_{MW}=0.85

Aldicarb sulfoxide LOQ= 0.006 mg/kg, CF_{MW}= 0.92

Sensitivity check (to be checked by the lab): sum of individual LOQs (taking into account CF) of 0.017 mg/kg ≤ MRL 0.02*mg/kg ⇒ OK

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Expanded uncertainty: calculation (E7-E11)

„*Top-down*“ approach generally recommended for pesticide residues (and mycotoxins)

- ✓ is mostly based on the use of intra-laboratory QC data for individual pesticides in a commodity group;
- ✓ proficiency test results can provide an important indication of the contribution of the inter- laboratory bias to the MU of an individual laboratory.

$$u' = \sqrt{u'(bias)^2 + u'(precision)^2}$$

$$u'(bias) = \sqrt{mean_{bias}^2 + SD.P_{bias}^2}$$ → (stdev.p in Excel)

$$u' = \sqrt{mean_{bias}^2 + SD.P_{bias}^2 + RSD_{wR}^2}$$

u'(precision) = RSD_{wR}

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Calculation of uncertainty from QC data (spike) *example*

Pirimiphos-methyl: QC samples - "blank" matrix spiked at 0.05 mg/kg.

QC spike (mg/kg):

Date	0,050	Result (mg/kg)	Rel. bias (%)		
10.01.20	apple	0.0509	2%		
26.01.20	pear	0.0453	-9%		
04.02.20	lettuce	0.0583	17%		
08.02.20	cauliflower	0.0408	-18%		
22.02.20	tomatoes	0.0447	-11%		
28.02.20	onion	0.0495	-1%		
05.03.20	green beans	0.0466	-7%		
06.03.20	carrot	0.0522	4%		
12.03.20	leek	0.0559	12%		
17.03.20	apple	0.0511	2%		
19.03.20	cauliflower	0.0448	-10%		
22.03.20	apple	0.0513	3%		
	N (min 8 !)	12			
	Mean	0.0493			
	SD.P-bias (smodch.p) (%)		0.09657		
	Standard dev. measured (stdeva) (mg/kg)	0.0050			
	RSDwR (%)	10.233%			
	u (bias) (%)		**9.277%**	standard uncertainty - bias	
	u (precision) = RSDwR (%)	**10.23%**		standard uncertainty - precisior	
	u (combined)	**13.81%**		combined standard uncertainty	
	U (expanded) = 2.u (combined)	**27.61%**		expanded uncertainty (k=2)	
	U (uncorrected result)	**28%**			
	Recovery used for correction	*98.57%*			
	u (bias) (%)	*2.95%*			
	U (corrected result)	***21.3%***			

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Interpretation of results for enforcement purposes

A default expanded MU of 50 % (corresponding to a 95 % confidence level and a coverage factor of 2) has been calculated from EU proficiency tests.

This **50 % value** covers the inter-laboratory variability between the European laboratories and **is recommended to be used by regulatory authorities in cases of enforcement decisions** (MRL- exceedances).

- *A prerequisite for the use of the 50 % default expanded MU is that the laboratory must demonstrate that its own expanded MU is less than 50 %* (*typically about 35 - 45 %)*.
- *For results obtained with single-residue methods, particularly if stable isotopically labelled internal standards have been used, lower expanded MU can be justified.*
- **For official food control,** compliance with the MRL is checked by assuming that **the MRL is exceeded if the measured value exceeds the MRL by more than the expanded uncertainty:**

$$x - U > MRL$$

Pesticide standards

Standards should be of **known purity** and must be assigned with a unique identification code and recorded in a way that ensures full **traceability** – e.g. **source of supply, lot number, date of receipt** and place / history of storage.

Standards should be stored at low temperature, with light and moisture excluded, i.e. under conditions that minimise the rate of degradation.

Under such conditions, the supplier's expiry date, which is often based on less stringent storage conditions, may be replaced (as appropriate for each standard), by a date **allowing for storage up to 10 years**.

Standard may be retained and a **new expiry date may be allocated,** only providing that it is checked and its purity is shown to remain acceptable**.**

For screening purposes only, the standards and derived solutions may be used after the expiry date, providing that the RL can be achieved.

Pesticide standards

When preparing stock standards of “pure” standards of analytes and internal standards, the identity and mass of the “pure” standard and the identity and amount of the solvent must be recorded. The solvent(s) must be appropriate to the analyte (solubility, no reaction) and method of analysis. Moisture must be excluded during equilibration of the “pure” standard to room temperature before use and concentrations must be corrected for the purity of the “pure” standard.

Not less than 10 mg of the “pure” standard should be weighed using a 5 decimal place balance. The ambient temperature should be that at which the glassware is calibrated, otherwise preparation of the standard should be based on solvent - mass measurement.

Existing stock and working solutions may be tested against newly prepared solutions by comparing the detector responses obtained from appropriate dilutions of individual standards or mixtures of standards.

The means from at least 5 replicate measurements for each of two solutions (old and new) should not differ by more than ± 10 %. *The mean from the new solution is taken to be 100 %.*

Pesticide working (calibration) standards

When preparing working standards, a record must be kept of the identity and amount of all solutions and solvents employed.

Septum closures are particularly prone to evaporation losses - in addition to being a potential source of contamination - and should be replaced as soon as practicable after piercing, if solutions are to be retained.

Following equilibration to room temperature, solutions must be re-mixed and a check made to ensure that the analyte has remained in solution, especially where solubility at low temperatures is limited.

For suspensions (e.g. dithiocarbamates) and solutions of highly volatile fumigants that should be prepared freshly, the concentration of the analyte solution should be compared with a second solution made independently at the same time.

Calibration: pesticide residues

Responses used to quantify residues must be within the dynamic range of the detector.

Extracts containing high-level analytes may be diluted to bring them within the calibrated range !

Validation of analytical methods shall include determination of recovery at the proposed reporting limit.

Calibration by interpolation between two levels is acceptable providing the difference between the 2 levels is not greater than a factor of 10 and providing the response factors of both calibration standards are within acceptable limits. **The response factor of such bracketing calibration standards at each level should not differ by more than 20 %** .

Single-level calibration may provide more accurate results than multi-level calibration if the detector response is variable with time. **When single-level calibration is employed, the sample response should be within ± 20 % of the calibration standard response if the MRL is exceeded.**

The potential for matrix effects to occur should be assessed at method validation. If the techniques used are not inherently free from such effects, calibration should be **matrix-matched** routinely.

Where a calibration standard is a mixture of isomers, etc., of the analyte, detector response generally may be assumed to be similar, on a molar basis, for each component.

Contamination & interference: pesticide residues

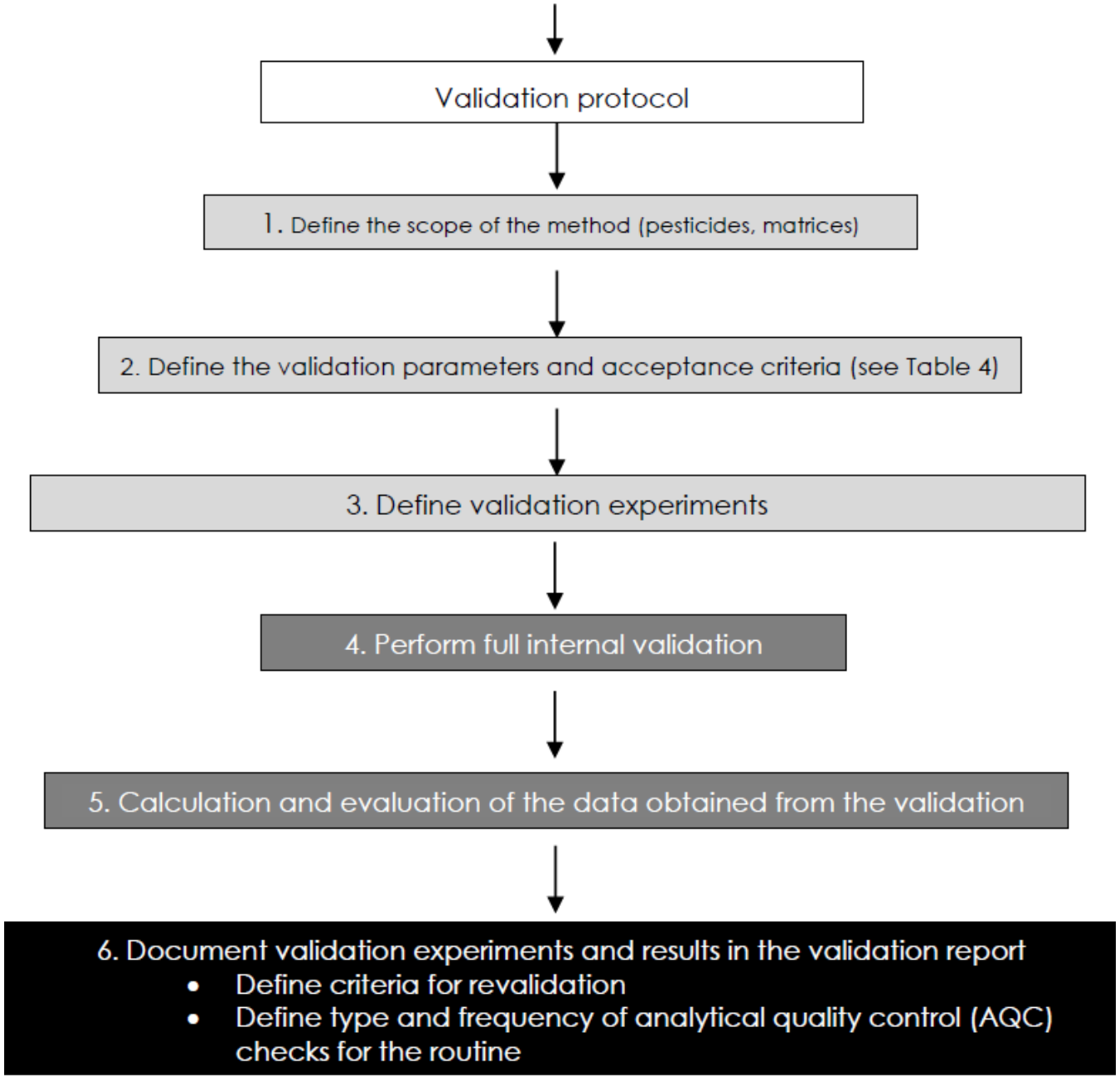
Samples must be separated from each other, and from other sources of potential contamination, during transit to, and storage at, the laboratory.

Volumetric equipment, such as flasks, pipettes and syringes must be cleaned scrupulously, especially for re-use. As far as practicable, separate glassware, etc., should be allocated to standards and sample extracts, in order to avoid cross-contamination.

Equipment, containers, solvents (including water), reagents, etc., should be checked as sources of possible interference. *Rubber and plastic items (e.g. seals, protective gloves, wash bottles) and lubricants are frequent sources.*

Vial seals should be PTFE-lined. Extracts should be kept out of contact with seals by keeping vials upright. Vial seals may have to be replaced quickly after piercing, if re-analysis of the extracts is necessary. Analysis of reagent blanks should identify sources of interference in the equipment or materials used.

INITIAL VALIDATION PLAN FOR QUANTITATIVE METHODS



Initial method validation: experimental

A typical example of the experimental set up of a validation is:

Sample set (sub-samples from 1 homogenised sample):

- Reagent blank
- 1 blank (non-spiked) sample
- 5 spiked samples at target LOQ
- 5 spiked samples at 2-10x target LOQ

Instrumental sample sequence:

- Calibration standards
- Reagent blank
- Blank sample
- 5 spiked samples at target LOQ
- 5 spiked samples at 2-10 x target LOQ
- Calibration standards

ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED

Document No. DG SANTE/12682/2019, *implemented by January 2020*

Parameter	What/How	Criterion
Linearity	Linearity check from five levels	deviation of back-calculated conc. from true conc. ≤± 20 %
Matrix effect	Comparison of response from solvent standards and matrix-matched standards	(≤ 20 %) → cal.
LOQ	Lowest spike level meeting the identification and method performance criteria for recovery and precision	≤ MRL
Specificity	Response in reagent blank and control samples	< 30 % of RL (LOQ)
Trueness (bias)	Average recovery for spike levels tested	70-120 %
Precision (RSD_r)	Repeatability RSD_r for spike levels tested	≤ 20 %
Precision (RSD_{wR})	Within-laboratory reproducibility, derived from on-going method validation / verification	≤ 20 %
Ion ratio	Check compliance with identification requirements for MS techniques	*Table 3*
Retention time	(both GC and LC)	± 0.1 min.

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Proficiency testing (PT)

Regular participation in proficiency testing (also known as external quality assessment, EQA) is a recognised way for a laboratory to monitor its performance against both its own requirements and the norm of peer laboratories.

PT helps to highlight variation between laboratories (reproducibility), and systematic errors (bias).

Accreditation bodies strongly encourage laboratories to participate in PT as an integral part of their quality management.
In certain instances, accreditation bodies may specify participation in a particular PT scheme as a requirement for accreditation.

It is important to monitor PT results as part of the QC procedures and take action as necessary.

- ✓ Requirements for the competence of PT providers are described in ISO/IEC 17043,
- ✓ Selection, use and interpretation of PT schemes: see Eurachem Guide on www.eurachem.org

Proficiency testing (PT)

The standard **ISO/IEC 17025:2017** establishes in sub-clause 7.7.2:

The laboratory shall monitor its performance by comparison with results of other laboratories. This monitoring shall include, either or both of the following:

a) participation in proficiency testing (providers that meet ISO/IEC 17043 are considered to be competent)

b) participation in interlaboratory comparisons other than proficiency testing.

$$z_i = \frac{(x_i - x_{pt})}{\sigma_{\text{pt}}}$$

$$\zeta = \frac{x - \hat{X}}{\sqrt{u_x{}^2 + uX^2}}$$

Proficiency testing (PT)

EURLs responsible for pesticide residues in food and feed annually organize EUPTs.

EUPTs are directed to all National Reference Laboratories (NRLs) and all Official Laboratories (OfLs) in the EU Member States.

Laboratories outside this EURL/NRL/OfL-Network may be allowed to participate on a case-by-case basis.

Participating laboratories will be provided with an assessment of their analytical performance and the reliability of their data.

EURL

European Union Reference Laboratory for Residues of Pesticides
Pesticides in Cereals and Feedingstuff

CERTIFICATE OF PARTICIPATION

This is to certify that the following institution

Metrological and Testing laboratory, University of Chemistry and Technolo

Praha, Czech Republic

participated in proficiency test

EUPT-CF14

(Lab Code: 92)

European Union Proficiency Test on Incurred and Spiked Pesticide Residues in Rice

June 2020

This laboratory analysed for **100** % of the mandatory compounds (**164** out of 164 and **32** out of 38 voluntary compounds)
Additionally, the laboratory detected and quantified **100** % of the compounds in the Test Item.
Accordingly, the laboratory achieved the following qualification:
Category **A** AZ²: **0.5 Good**

Mette Erecius Poulse
(Head of EURL-CF)

EURL

European Union Reference Laboratory for Residues of Pesticides
Pesticides in Cereals and Feedingstuff

EUPT-CF14: Proficiency Test on Incurred and Spiked Pesticide Residues in Rice

General Information:

Organizer: European Union Reference Laboratory on Cereals and Feedingstuff (EURL-CF), DTU National Food Institute, Denmark
Test Material: Rice Kernels with Incurred and Spiked Pesticide Residues (see below)
Participating lab: **Metrological and Testing laboratory, University of Chemistry and Technology, Praha, Czech Republic**
Lab-Code: **92**

Reported results: (The detailed laboratory performance is documented in the final report)

Analytes	Assigned value, mg/kg	Your results, mg/kg	Your z-scores	Classification	Total No. of results *)	Acceptable results |z-score| ≤ 2 *)	Questionable results 2 < |z-score| < 3 *)	Unacceptable results |z-score| ≥ 3 *)
Acephate	0.048	0.055	0.6	Acceptable	119	91%	2%	8%
Acetamiprid	0.070	0.100	1.4	Acceptable	128	94%	4%	2%
Azoxystrobin	0.305	0.370	0.8	Acceptable	138	95%	1%	4%
Buprofezin	0.054	0.050	-0.1	Acceptable	135	96%	2%	2%
Carbendazim	0.046	0.046	-0.1	Acceptable	124	88%	6%	6%
Carbofuran	0.057	0.070	1.0	Acceptable	126	93%	2%	5%
Cyproconazole	0.068	0.089	1.2	Acceptable	135	95%	2%	3%
Dichlorvos	0.015	0.014	-0.2	Acceptable	133	71%	5%	25%
Difenoconazole	0.048	0.048	0.0	Acceptable	139	95%	1%	4%
Hexaconazole	0.090	0.100	0.4	Acceptable	134	94%	1%	4%
Imidacloprid	0.068	0.073	0.2	Acceptable	127	92%	3%	5%
Isoprothiolane	0.405	0.504	1.0	Acceptable	122	95%	2%	3%
Metalaxyl	0.073	0.067	-0.3	Acceptable	131	95%	3%	2%
Profenofos	0.205	0.268	1.2	Acceptable	132	92%	4%	4%
Pyriproxyfen	0.152	0.173	0.5	Acceptable	129	94%	5%	2%
Thiamethoxam	0.053	0.059	0.4	Acceptable	125	95%	2%	2%
DDE-pp **)	0.035	0.035	0.0	Acceptable	127	90%	6%	5%
Endrin-ketone **)	0.036				55	62%	4%	35%
Oxathiapiprolin **)	0.050				39	79%	0%	21%

EUROPEAN ACCREDITATION

Publication Reference **EA-4/21 INF: 2018**

Guidelines for the assessment of the appropriateness of small interlaboratory comparisons within the process of laboratory accreditation

…this document is not intended as a substitute to ISO/IEC 17043 !

- The use of an assigned value based on an external reference should be preferred over an assigned value based on participants results;
- Assigned value may stem from a suitable CRM or measurements performed by expert laboratories.
- Zeta-scores may also be used, preferably in combination with z scores.

Reasons for laboratories to organise or participate in a small ILC – for example:

✓there is no suitable PT scheme available, for example in fields with fast technical developments, or where such measurements are very advanced or or in fields with few laboratories performing very specific measurements;

✓participation in a PT scheme would not be appropriate if it poses an unreasonable burden to the laboratory;

✓the low number of existing laboratories in the sector.

In such cases, a laboratory or a small group of laboratories may decide to organise an ILC among themselves (2-7 laboratories)

Small interlaboratory comparison (ILC) - example

Within the frame of EU-China-Safe project the University of Chemistry and Technology Prague (Czech Republic) in collaboration with Queens University, Belfast and China National Center for Food Safety Risk Assessment (CFSA) have organized the
Inter-laboratory Comparison Study (ILC) on pesticide residues in green tea

The aim of this ILC was to obtain information regarding the quality, accuracy and comparability of pesticide residues data in food reported within the framework of EU and China laboratories implementing multidetection LC-MS based method for pesticide residues analysis in food matrix developed within this project.

Assigned value was set for each analyte. A fit-for-purpose relative target standard deviation (σFFP) of 25 % was chosen to calculate the target standard deviations (σ) as well as the z-scores for the individual pesticides.

Test material (green tea spiked with pesticides) was dispatched in July 2021, ILC results reported in October 2021.

6 laboratories from China and 1 laboratory from EU participated in this ILC study.

Small interlaboratory comparison (ILC) - example

The evaluation and scoring of the results of the participating laboratories was based on z-scores and false positive (FP) or false negative (FN) rate.

analyte	assigned value (X_a) [mg/kg]	number of scores $\|z\| \leq 2.0$	total number of analytes	% $\|z\| \leq 2.0$	number of False Negative
Chlorpyrifos (ethyl)	0.119	5	7	71 %	1
Dimethoate	0.068	7	7	100 %	-
Dinotefuran	0.056	7	7	100 %	-
Fenpropimorph	0.079	6	7	86 %	1
Imidacloprid	0.047	6	7	86 %	1
Malathion	0.107	6	7	86 %	-
Pirimiphos-methyl	0.138	6	7	86 %	-
Pyridaben	0.081	6	7	86 %	-
Tolfenpyrad	0.077	6	7	86 %	-

Total number of False Positive results: 3

Total number of False Negative results: 3

Thanks for Attention

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