Practical and Valid Approaches for Realistic Estimation of Measurement Uncertainty in Multi-Pesticide Residue Analysis

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Practical and Valid Approaches for Realistic Estimation of Measurement Uncertainty in Multi-Pesticide Residue Analysis

- Introduction
- Uncertainty & "Quality" of Test Results
- GUM Fundamentals
- "Bottom-up" and "top-down" Evaluations
- EURACHEM Guide and CODEX Guidelines
- Draft Revision of the CODEX Guidelines
- Approaches used in EU

Measurement Uncertainty

GUM (BIPM, IEC, IFCC, ISO, IUPAC, OIML)
Guide to the Expression of Uncertainty in Measurement
(ISO, Geneva, 1993 - Revisión 1995)
ISBN: 92-67-10188

"A parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributted to the measurand"

"A non-negative parameter characterising the dispersion of quantity values being attributed to a measurand, based on the infrmation used"

VIM 3 (ISO / IEC Guide 99)
International Vocabulary of Metrology-Basic and general concepts and associated terms
(2007)

Measurement Uncertainty

This parameter may be:

- A standard deviation ***(combined standard uncertainty - u)***
- The width of a confidence interval ***(expanded uncertainty - U)***

Result = Value ± uncertainty

A Realistic Pesticide Residue Test Result

~~0.85 ± 0.01 mg/kg~~

0.85 ± 0.30 mg/kg *(k = 2; 95%)*

from 0.55 to 1.15 mg/kg!

Information leaflet published in 2000 by the "SP-Swedish NTRI" to be delivered to the "laboratory customer" together with the test report

Important information to our customers concerning the quality of measurements

1 Do you use results of chemical analyses as a basis for your decisions and judgements?

Those of us working in accredited laboratories or dealing with issues concerning the quality of measurements, would like to inform you about some important changes concerning the way the results of measurements are presented. These changes make it easier for you as an end-user to make correct decisions.

2 Nobody is perfect!

Results of analyses cannot be perfect! We hope this does not come as a big surprise to you. We use the term measurement uncertainty to describe this lack of perfection.

3 The analytical process

In each step of the analytical work, from sampling to the final measurement, deviations from the true value occur and measurement conditions vary. We take measures and perform controls regularly to assure that these deviations and variations together are small enough to make sure the end result fulfils your requirements. When we don't have full information about all of the steps, e.g. when sampling and initial sample preparation are performed by you as a customer, you can assist us by providing detailed information about how that work was performed. Our experts are ready to advise on all matters regarding sampling. Please contact the laboratory beforehand.

4 Results should be fit-for-the-purpose

The accuracy of the results must of course not be too low nor too high since this would increase the costs. It should be fit for the intended purpose. If you are unsure on what level of accuracy you need, do not hesitate to contact the laboratory.

EMPA · Eurachem – A FOCUS ON ANALYTICAL CHEMISTRY IN EUROPE · eurolab – Organisation for Testing in Europe · EA European co-operation for Accreditation

SP Swedish National Testing and Research Institute
SP Chemistry and Materials Technology
Box 857, SE-501 15 BORÅS, SWEDEN
Telephone + 46 33 16 50 00, Telefax + 46 33 13 55 02, E-mail info@sp.se, Internet www.sp.se

SP INFO 2000:27

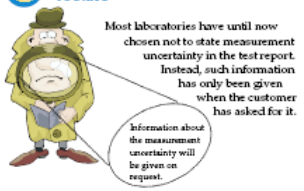
5 Uncertainty and limiting values

Many analyses are made to assure that limiting values are not exceeded. Without information about the measurement uncertainty it may appear to be very easy to make decisions, but these decision may be incorrect, with, e.g. economical consequences when rejecting instead of accepting a product, judicial consequences when returning a verdict of guilty instead of not guilty, or medical consequences when carrying out an unnecessary treatment. There are numerous examples!

A result with and without measurement uncertainty

With a realistic measurement uncertainty the information included in the result becomes much more useful.

6 It will be easier to compare results



In the future, information about the measurement uncertainty will appear more frequently in the test report. It is also possible that you will bump into new and unfamiliar quality terms. This is due to the fact that there are new international guides and standards describing a common and partly new terminology. One of the objectives is to make it easier for you as a customer to compare test results.

7 What could it look like?

When reporting the test result we will give the normal information about what we have measured. When the results are followed by uncertainty statements, they are presented as intervals within which the true values are expected to lie with a certain level of confidence (usually 95%). In the example below the lead content is 1.65 ± 0.15 mmol·kg^{-1}, that is between 1.50 and 1.80. The measurement uncertainty is also often reported relatively, in %.

Total lead content (Pb)	1.65 mmol·kg^{-1}
Measurement uncertainty	0.15 mmol·kg^{-1} (9.1%)

The stated uncertainty is an expanded measurement uncertainty (U). It was obtained by multiplying the combined standard uncertainty u_c with a coverage factor k equal to 2. This corresponds approximately to a 95 % confidence interval.

8 All's well that ends well...

The requirements for a consistent way of reporting test results are increasing. Therefore, those of us involved in measurements are eager to assure ourselves that we understand your needs. You will notice this in your contacts with us before, during and after the test assignment. We hope that you will be satisfied with the final result.

NATURVÅRDSVERKET · FoL · SWEDAC – Styrelsen för ackreditering och teknisk kontroll, Swedish Board for Accreditation and Conformity Assessment · LIVSMEDELSVERKET · VAV

"Based on SP INFO 2000:23, developed by SP and Föreningen Ackrediterade Laboratorier (FoL), in collaboration with the National Food Administration, SWEDAC, the Swedish Environmental Protection Agency and the Swedish Water and Wastewater Association (VAV)."

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A result with and without measurement uncertainty

With a realistic measurement uncertainty the information included in the result becomes much more useful.

6 It will be easier to compare results

Most laboratories have until now chosen not to state measurement uncertainty in the test report. Instead, such information has only been given when the customer has asked for it.

Information about the measurement uncertainty will be given on request.

In the future, information about the measurement uncertainty will appear more frequently in the test report. It is also possible that you will bump into new and unfamiliar quality terms. This is due to the fact that there are new international guides and standards describing a common and partly new terminology. One of the objectives is to make it easier for you as a customer to compare test results.

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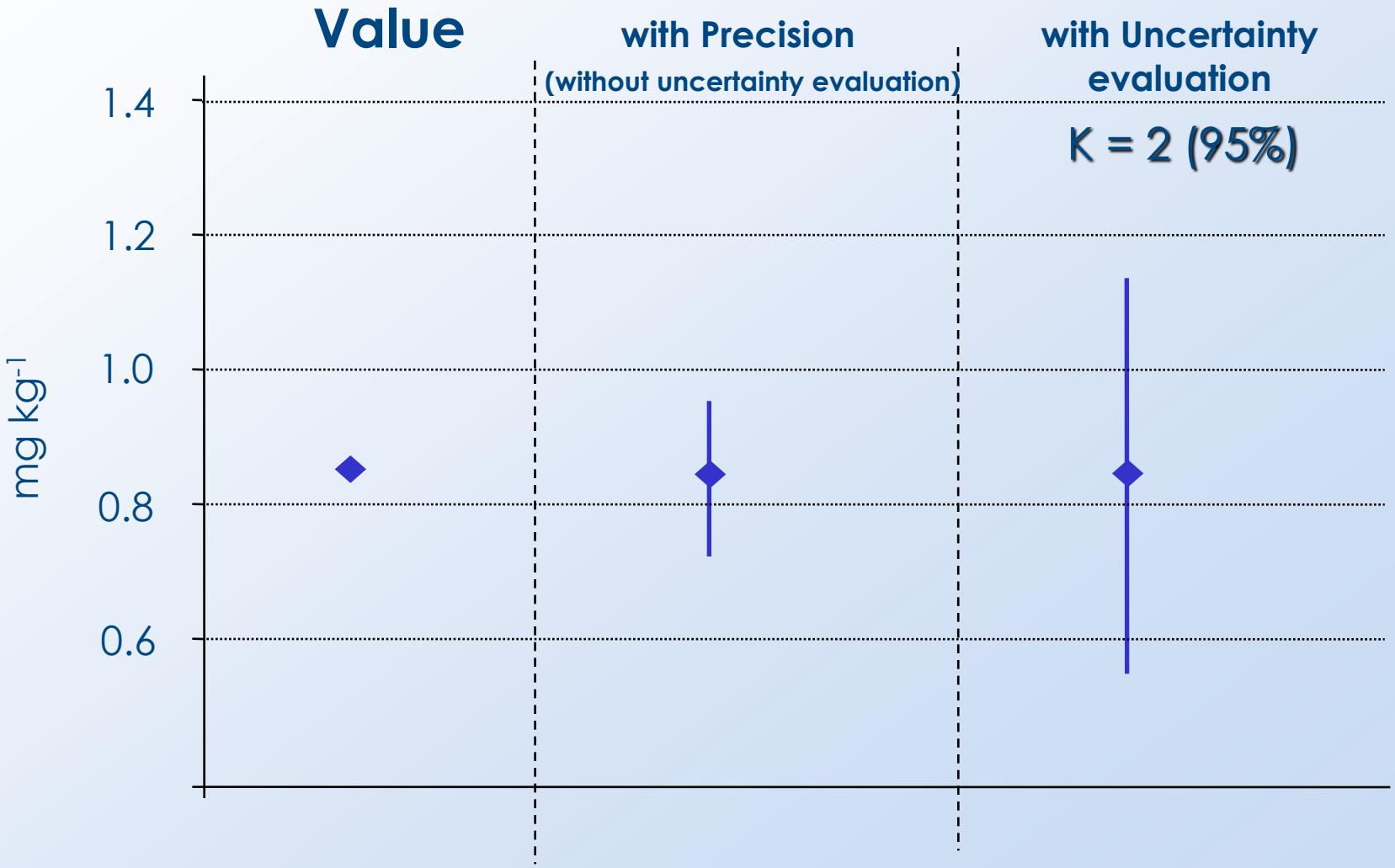
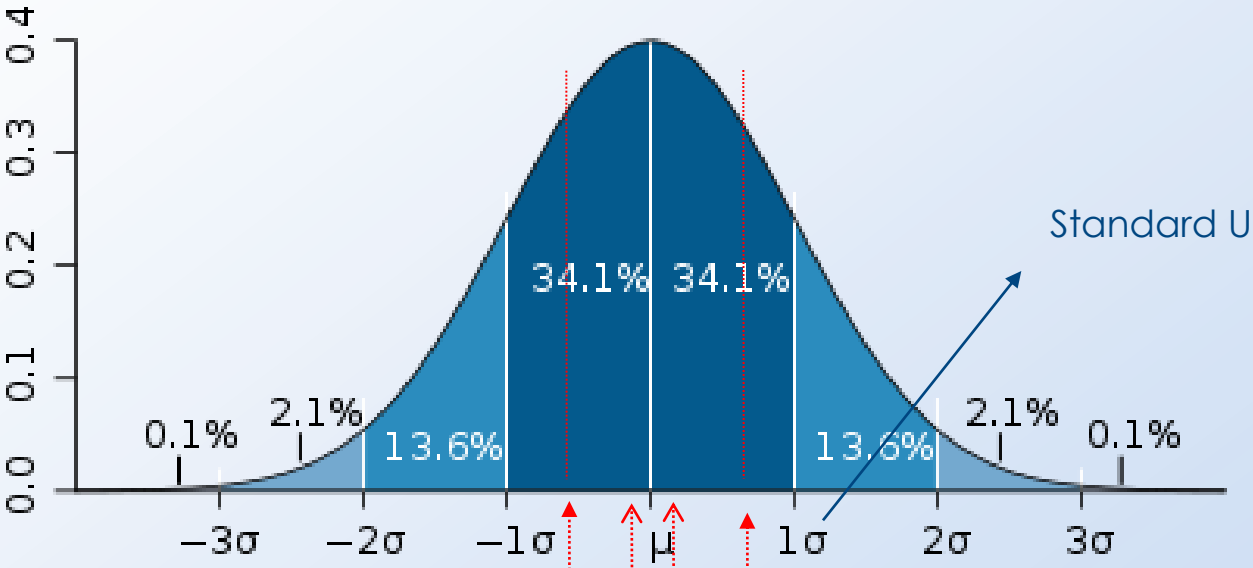
Reporting a Result



"Quality" of ("Confidence" on) the Result



Standard Uncertainty (U_c)

0.85 mg/kg (¿10%?) — 0.845 - 0.854 — **Value**

0.85 ± 0.10 mg/kg (¿50%?) — 0.75 - 0.95 — **with precision**

0.85 ± 0.30 mg/kg *(95%)* — 1.15 - 0.55 — **with uncertainty K=2** ($U = k \times u_c$)

Confidence Level

Reported Result

GUM Fundamentals

GUM (BIPM, IEC, IFCC, ISO, IUPAC, OIML)
Guide to the Expression of Uncertainty in Measurement
(ISO, Geneva, 1993 - Revision 1995)
ISBN: 92-67-10188

- Uncertainty is seen from a positive point of view.
- A realistic uncertainty statement always improve the quality of the result.
- Transparent, simple and standardised procedure for evaluation / expression.
- Type A and Type B evaluations (do not use random and systematic errors!).
- Combined Standard Uncertainty (u_c) / Expanded Uncertainty (U).

Guidelines – Analytical Measurement

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
Quantifying Uncertainty in Analytical Measurement
(2nd Edition, 2000)

NORDTEST Report TR537
Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories (2003)

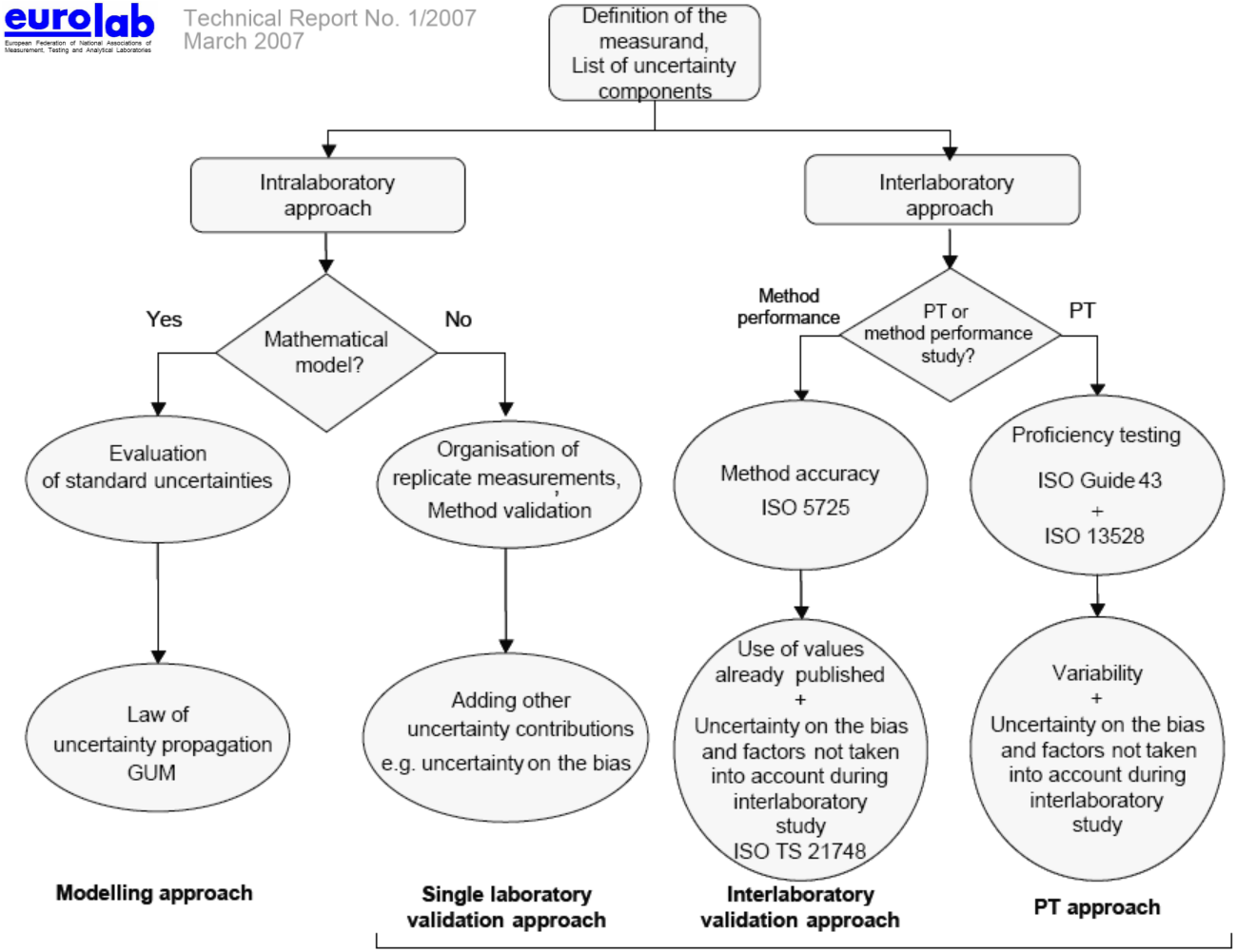
EUROLAB Technical Report No. 1/2006
Guide to the Evaluation of Measurement Uncertainty for Quantitative Test Results
(August 2006)

EUROLAB Technical Report No. 1/2007
Measurement Uncertainty Revisited: Alternative Approaches to Uncertainty Evaluation
(March 2007)

Figure 1: A road map for uncertainty estimation approaches

eurolab
European Federation of National Associations of Measurement, Testing and Analytical Laboratories

Technical Report No. 1/2007
March 2007



Possibilities to Evaluate Uncertainty

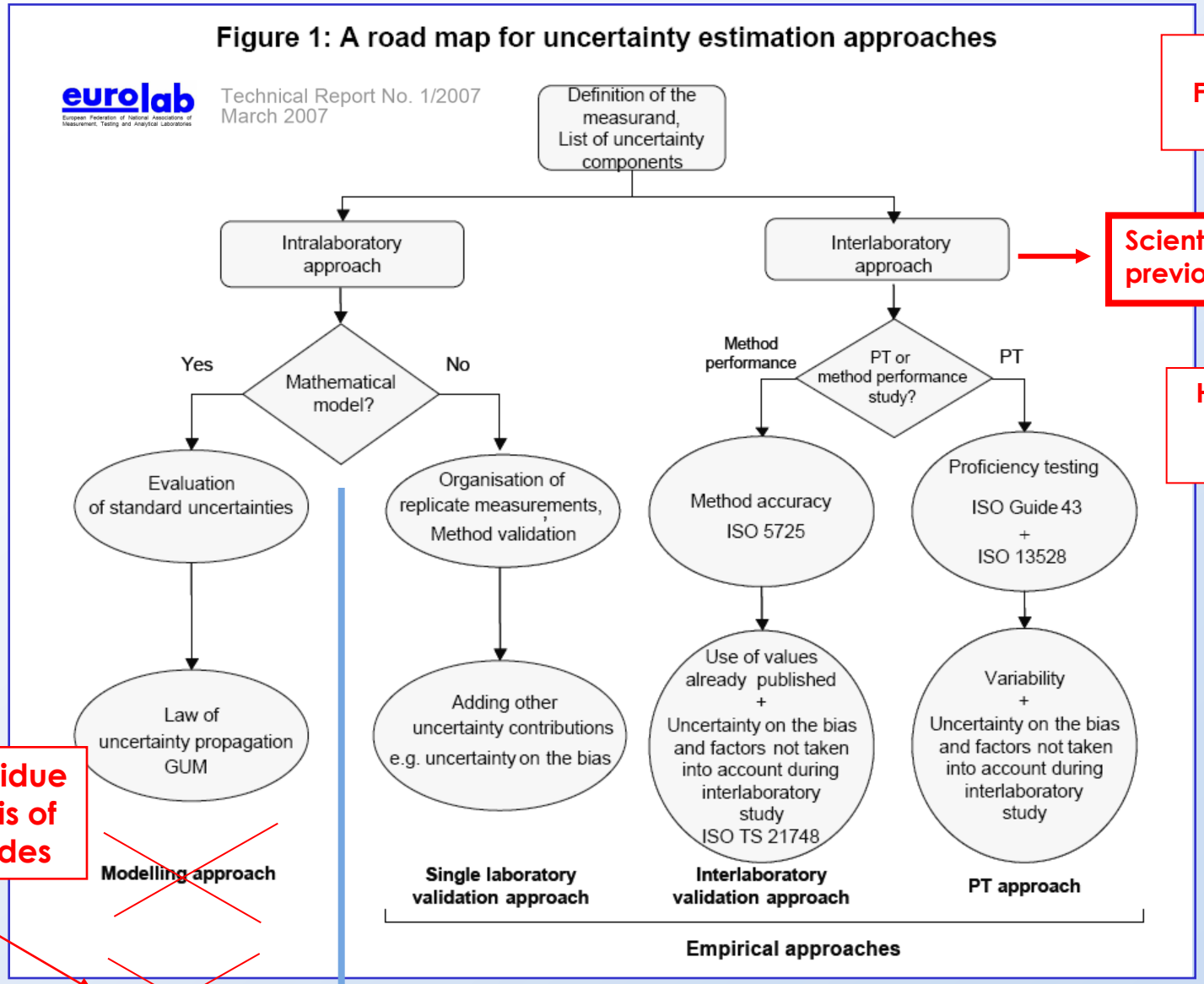
1) Component by component (strict mathematical model)

Impractical for most of the analytical tests

2) Gruping components to obtain the "Overall-Uncertainty", and using information on test method performance from:

- *Validation data*
- *Interlaboratory Studies*
- *Quality Control data*
- *Scientific Judgements from previous experience*

Figure 1: A road map for uncertainty estimation approaches



Default-Fixed Fit-For-Pourpose Value

Scientific judgements previous experience

Horwitz Ecuation concentration -dependent

Multiresidue Analysis of Pesticides

~~bottom-up~~

top-down

Guidelines - Codex Alimentarius

Specific Guidelines for Pesticide Residue Analysis
(Codex Committee on Pesticide Residues - CCPR)

CAC/GL 59-2006
Guidelines on Estimation of Uncertainty of Results

↓

CX/PR 11/43/10
Proposed draft revision of the Guidelines on the estimation of uncertainty of results for the determination of pesticide residues
(Appendix to the Guidelines on Estimation of Uncertainty of Results CAC/GL 59-2006)
(at step 3)

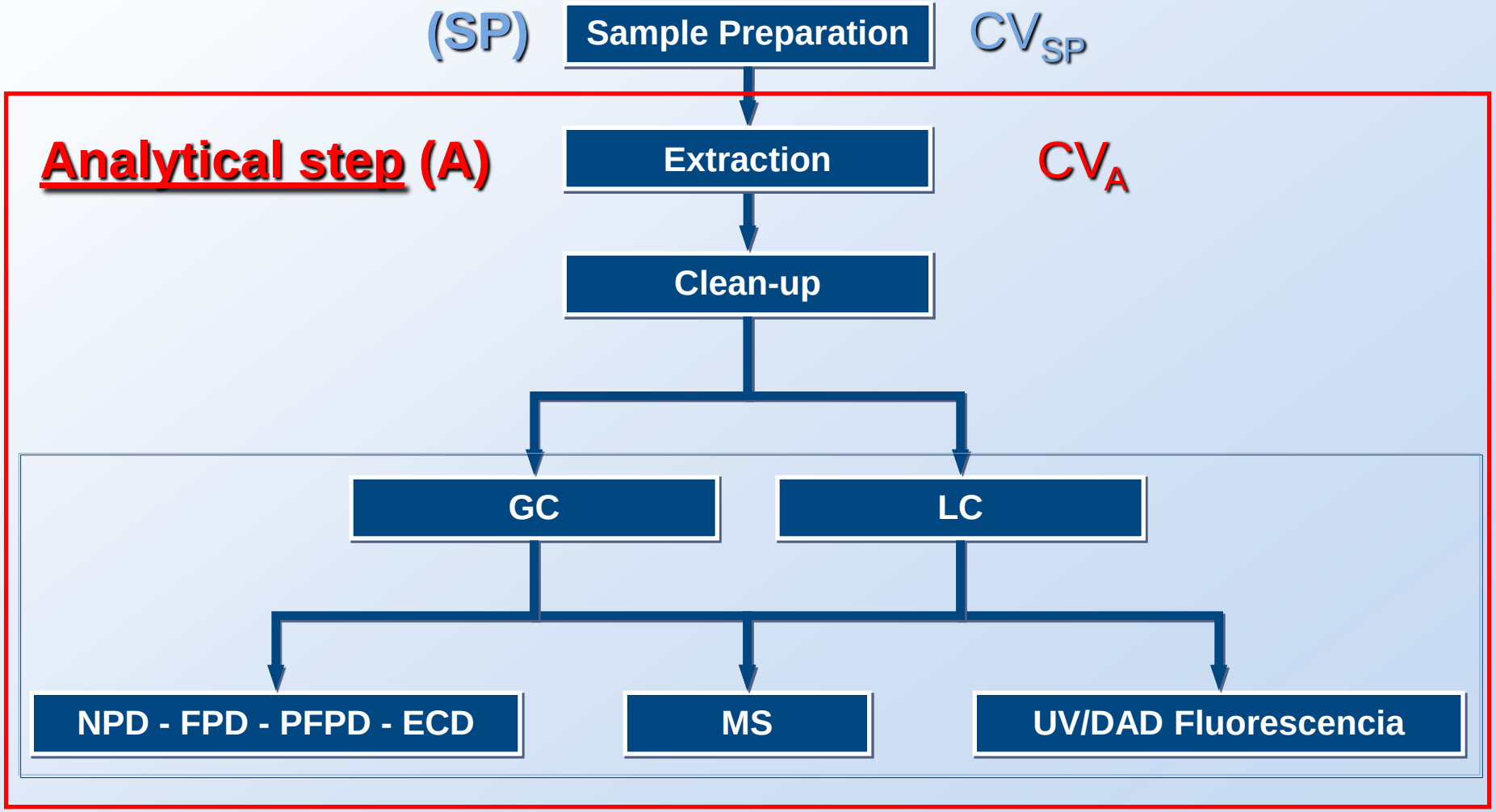
↓ CCPR 43rd Session (Beijing, P.R. China, 4-9 April 2011)

(at step 5/8)

CAC/GL 59-2006

Measurement Uncertainty of the Laboratory

Standard Deviation (S_L) or Relative Standard Deviation (CV_L)



Guidelines - Codex Alimentarius

CAC/GL 59-2006

Guidelines on Estimation of Uncertainty of Results

$$CV_{Res} = \sqrt{CV_S^2 + CV_L^2} \quad \text{and} \quad CV_L = \sqrt{CV_{Sp}^2 + CV_A^2}$$

- Sampling (CV_S)
- Sample Preparation (CV_{SP})
- Analytical step (CV_A)
- Laboratory (CV_L)

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)

$$U_c = \sqrt{U_{hom}^2 + U_{rep}^2 + U_{bias}^2}$$

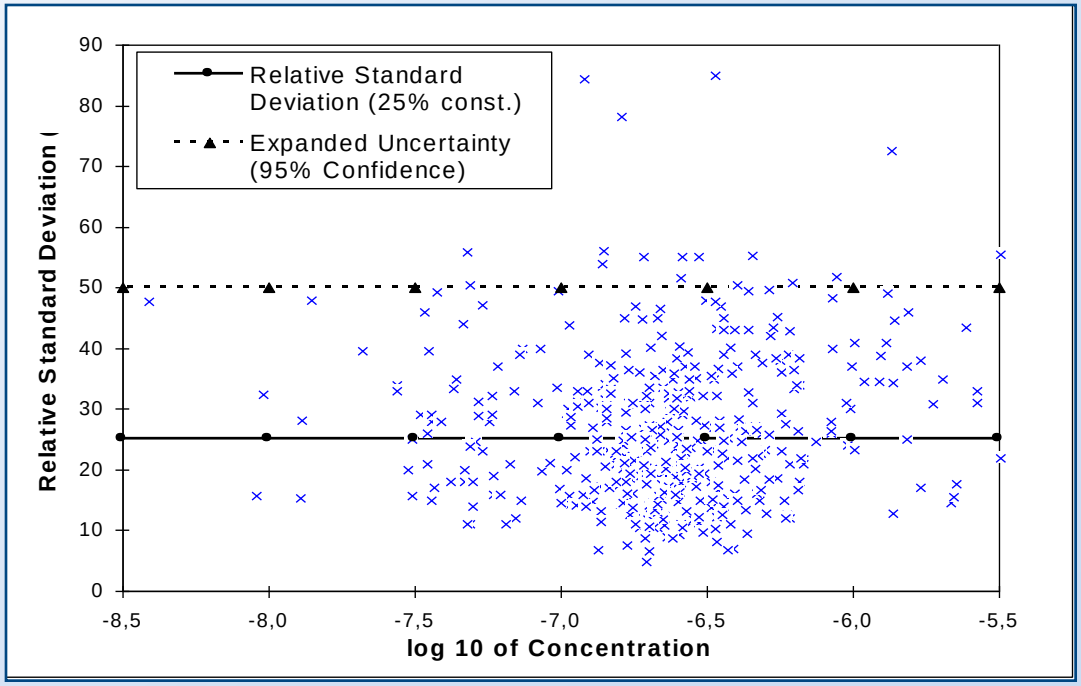
CV_{SP}^2 CV_A^2

CAC / GL 59-2006

Guidelines on Estimation of Uncertainty of Results

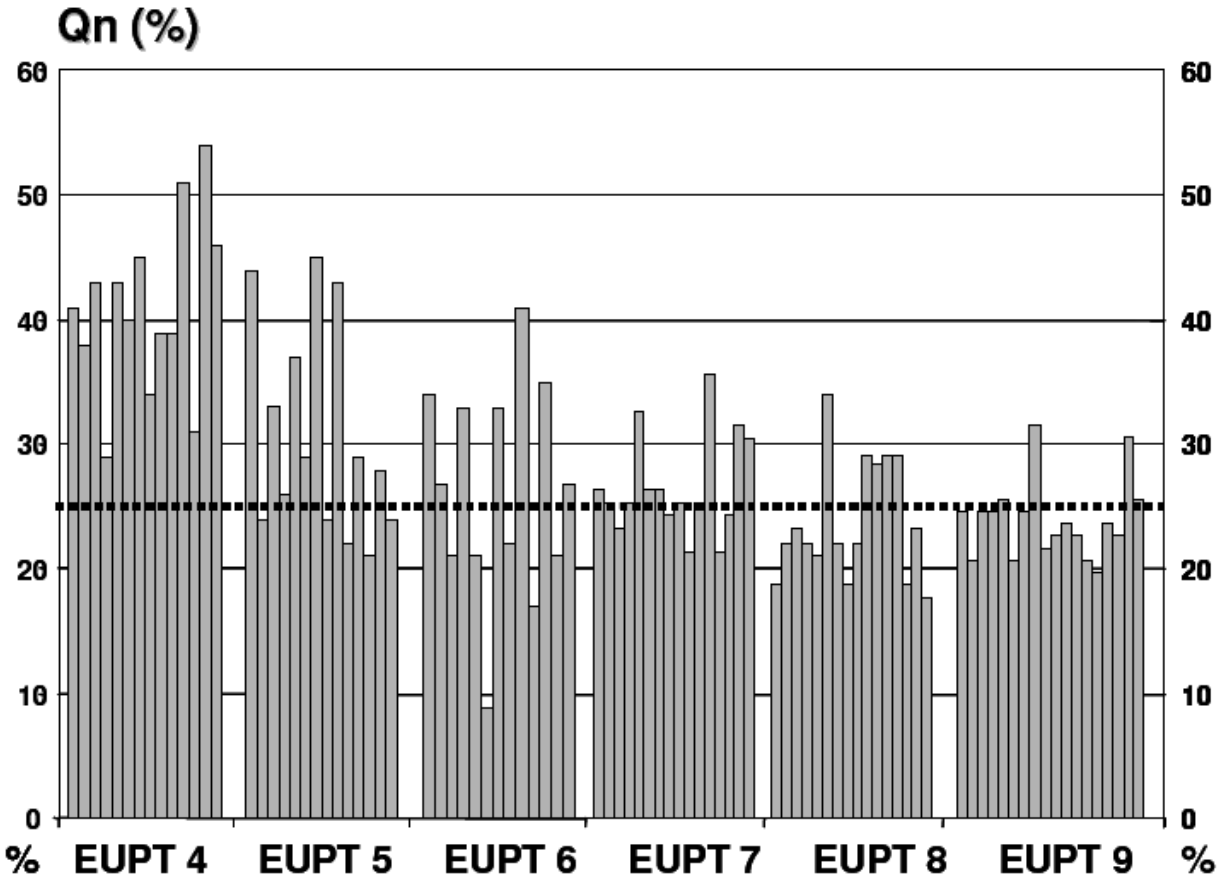
In addition to the estimated uncertainties made by the individual laboratories, regulatory authorities and other risk managers may decide on a default expanded uncertainty of measurements which can be used in judging compliance with MRLs (See section 5) based on between-laboratories reproducibility values. For instance, a 50% expanded uncertainty for CV_L is considered to be a reasonable default value.

Alder et al. (2001) J. AOAC Int. 84, 1569-1578

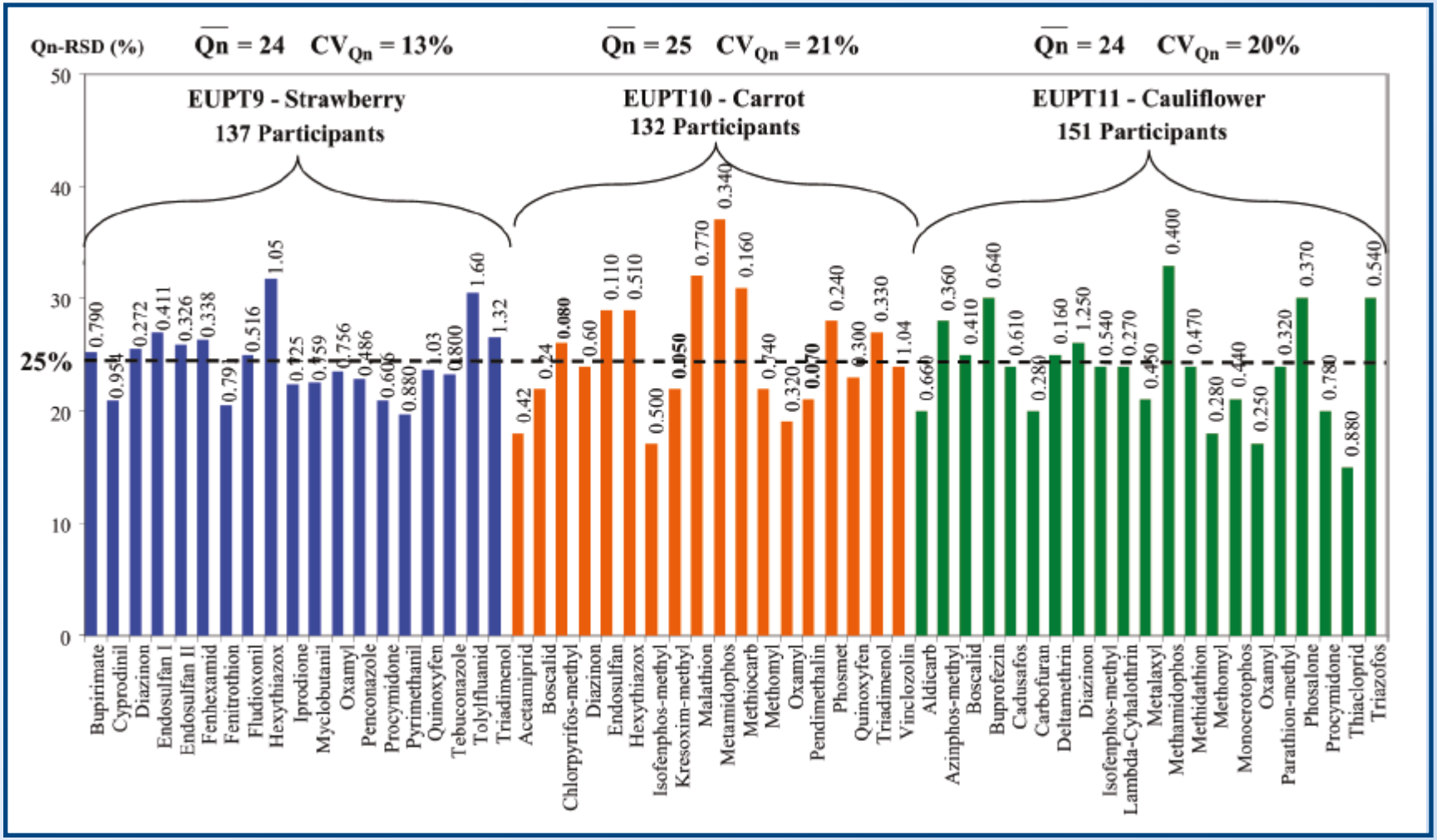


"European Proficiency Tests" EUPT4 – EUPT9

Figure 3



"European Proficiency Tests" EUPT9 – EUPT11



MU estimation based on Horwitz formulas

$$RSD_R = 2^{1-0.5\log c} = 2 * c^{-0.1505}$$

C (kg/kg): i.e., 0.01 mg/kg = 0.00000001 kg/kg

0.01 mg/kg	⇒	32.0 %
0.1 mg/kg	⇒	22.6 %
1 mg/kg	⇒	16.0 %

$$U = k \,.\, RSD_R$$

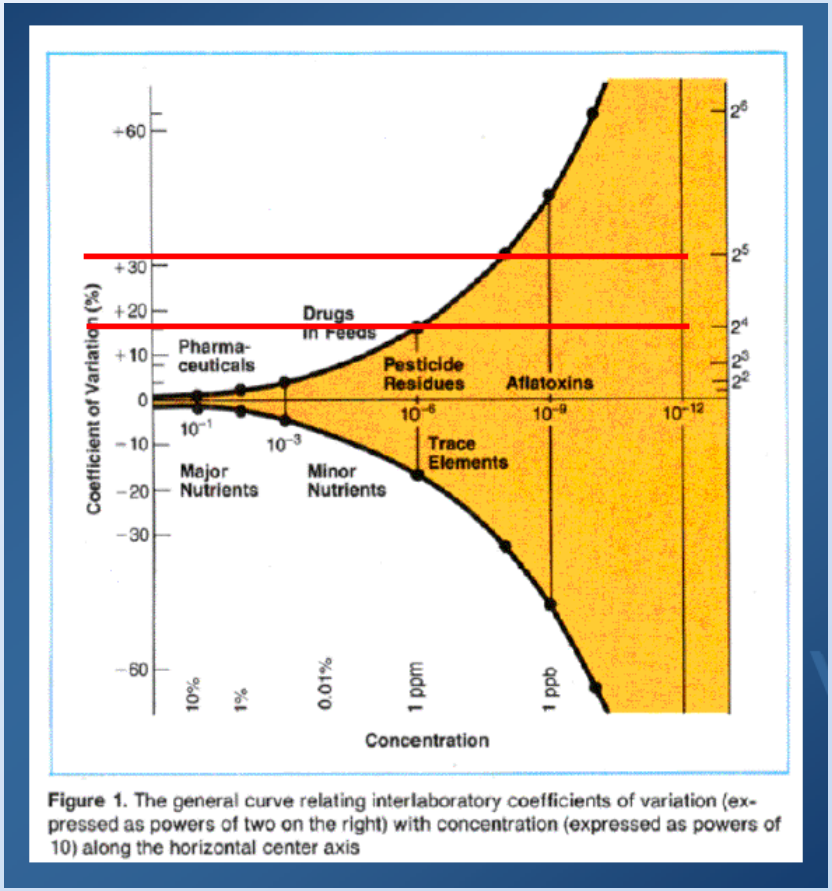


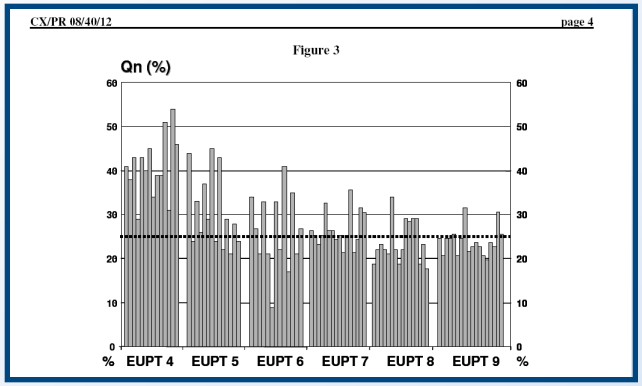
Figure 1. The general curve relating interlaboratory coefficients of variation (expressed as powers of two on the right) with concentration (expressed as powers of 10) along the horizontal center axis

CX/PR 11/43/10

Proposed draft revision of the Guidelines on the estimation of uncertainty of results for the determination of pesticide residues

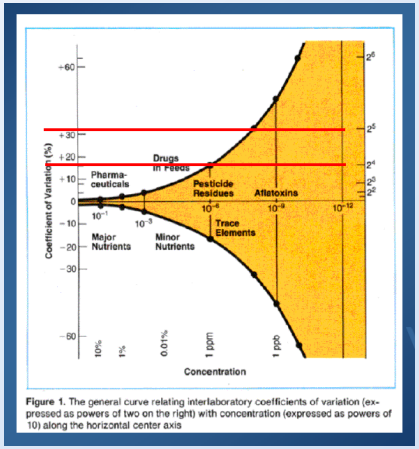
(Appendix to the Guidelines on Estimation of Uncertainty of Results CAC/GL 59-2006)

1



Default-Fixed Value (50% / EU)

2



Concentration-Dependent Formula (HORWITZ)

CX/PR 11/43/10

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(Appendix to the Guidelines on Estimation of Uncertainty of Results CAC/GL 59-2006)

3 Intra-Laboratory Validation/QC/PTs Data

$$u' = (u'_{Rw}{}^2 + u'_{bias}{}^2)^{1/2}$$

Relative intra-laboratory reproducibility SD (QC)

$(\sum(bias)^2/n)^{1/2}$

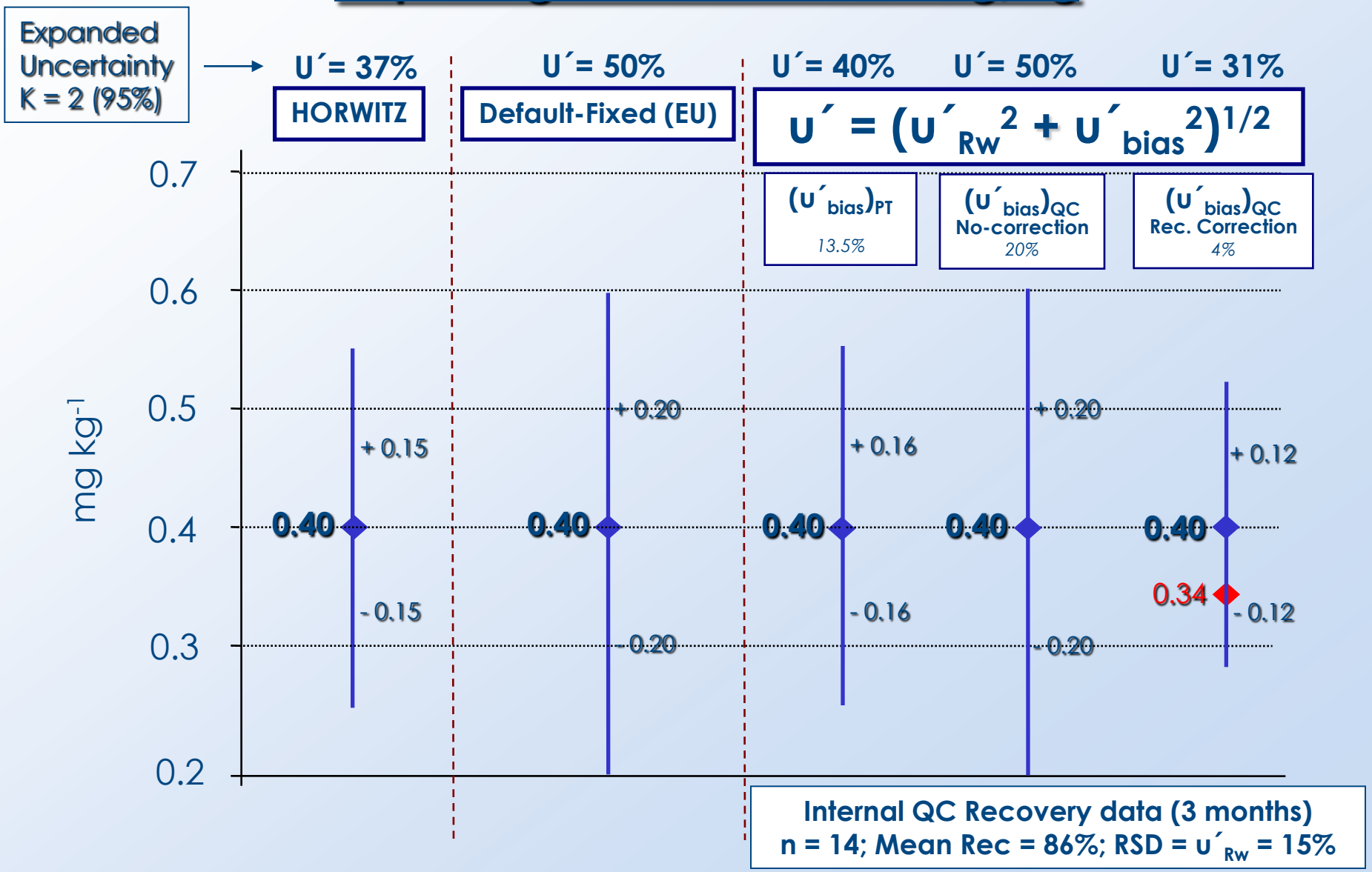
a $(u'_{bias})_{PT}$ → Root Mean Square of relative PTs bias & $u'(C_{ref})_{PT}$

b $(u'_{bias})_{QC}$ *No-correction* → Root Mean Square of relative QC bias & $u'(C_{ref})_{QC}$

c $(u'_{bias})_{QC}$ *Mean Rec. Correction* → $u'(\text{Mean Rec.})_{QC}$ & $u'(C_{ref})_{QC}$

$u'_{Rw} / n^{1/2}$

Reporting a Result of 0.40 mg/kg



1st Comprehensive CRL Survey for Pesticide Residue Laboratories in Europe

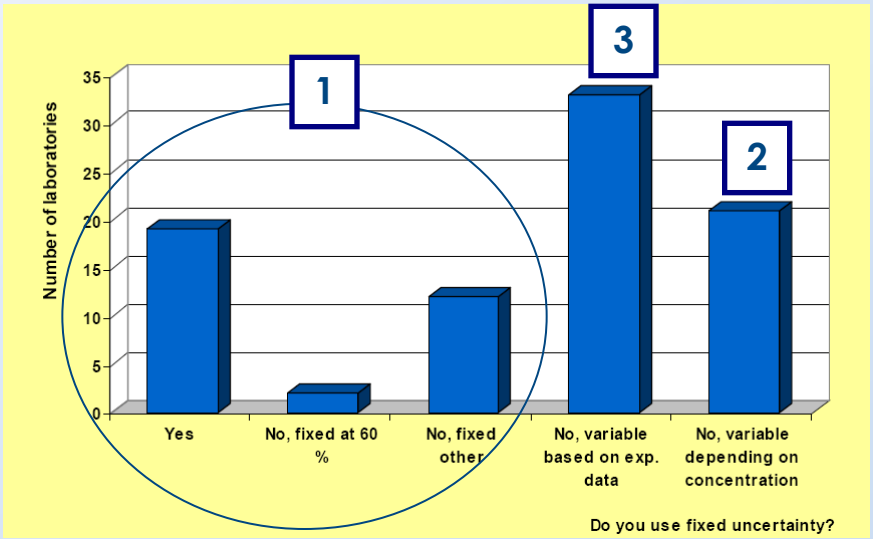
(November 2006 - February 2007)

Community Reference Laboratories for Residues of Pesticides

Single Residue Methods

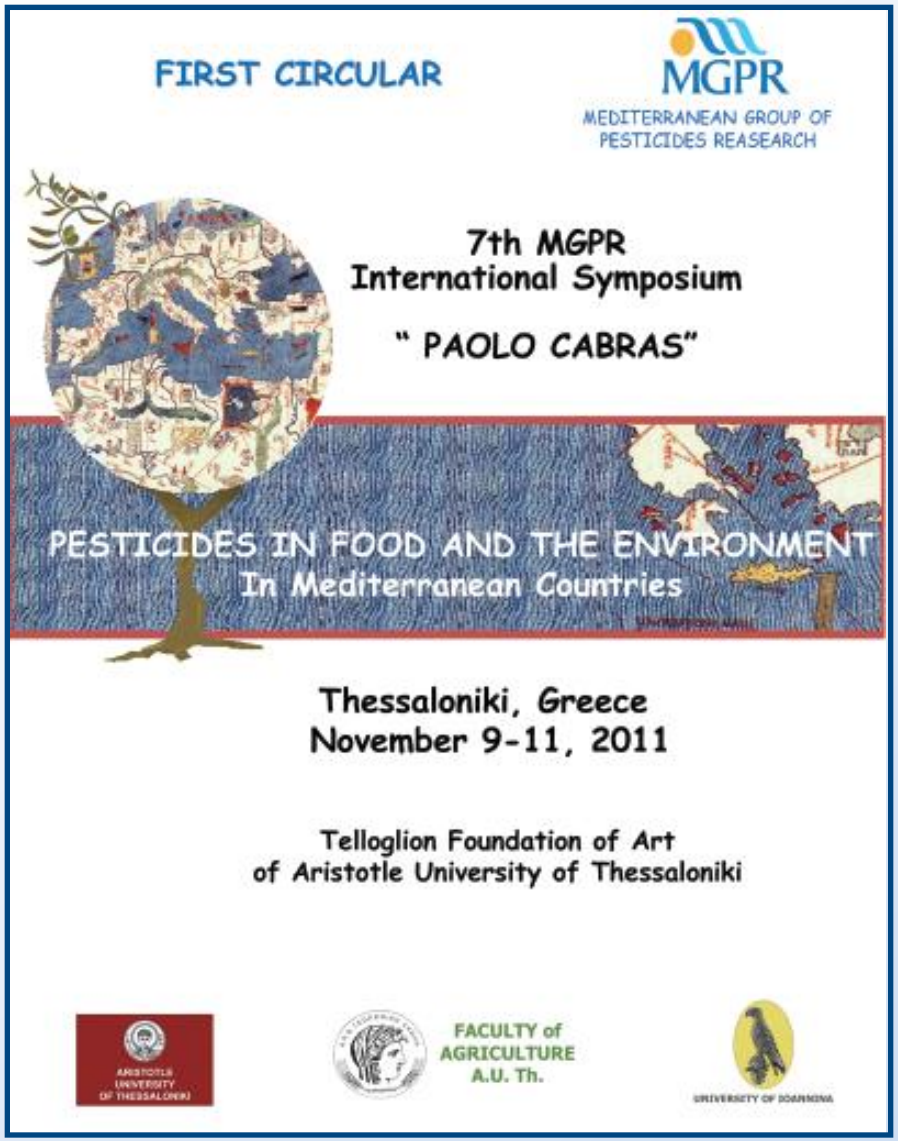
Do you use the fixed uncertainty figure of 50%?

N = 84



1	Default-Fixed Value	38%
2	Concentration-Dependent Formula	24%
3	Intra-Laboratory Validation/QC/PTs Data	38%

- **22 %** Laboratories (**50 %** fixed value)
- **16%** Laboratories (**other** fixed values)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International Symposium
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In Mediterranean Countries
Thessaloniki, Greece
November 9-11, 2011
Telloglion Foundation of Art
of Aristotle University of Thessaloniki
FACULTY of AGRICULTURE A.U. Th.

Many thanks!