Seminario Internacional - INTI
"Validación de Métodos, Control de Calidad y Estimación de la Incertidumbre de Medición Aplicable al Análisis Multirresiduos de Plaguicidas"

Buenos Aires (Argentina), 16-17 Junio 2009

Evaluación de la Incertidumbre en el Análisis de Residuos de Plaguicidas

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Grupo Residuos de Plaguicidas
Universidad de Almería

Evaluación de la Incertidumbre en el Análisis de Residuos de Plaguicidas

- Bibliografía
- Incertidumbre de Medida
- Conceptos Básicos de la GUM
- Evaluaciones “down-top” y “top-down”
- Guía EURACHEM y Directrices Codex
- Propuestas de Nuevas Directrices Codex
- Incertidumbre y LMRs

Documento de Referencia

GUM (BIPM, IEC, IFCC, ISO, IUPAC, OIML)
Guía para la Expresión de la Incertidumbre de Medida
(ISO, Ginebra, 1993 – Revisión 1995)
ISBN: 92-67-10188

Todas las directrices o recomendaciones específicas en cualquier campo para la evaluación de la incertidumbre de medida tendrán que ser compatibles con la GUM

Acreditación e Incertidumbre

ISO/IEC 17025

Requisitos Generales relativos a la Competencia de los Laboratorios de Ensayo y Calibración

(1999 – Revisión 2005)

Especifica requisitos detallados en relación a la incertidumbre de medida y como debe ésta indicarse en los informes de ensayo

Directrices – Entidades de Acreditación

ILAC-G17:2002

Introducing the Concept of Uncertainty of Measurement in Testing in Association with the Application of the Standard ISO/IEC 17025

EA-4/16

Guidelines on the Expression of Uncertainty in Quantitative Testing

(Rev. 00, December 2003)

G-ENAC-09

Guía para la Expresión de la Incertidumbre en los Ensayos Cuantitativos (traducción literal de EA-4/16)

(Rev. 1, Julio 2005)

Directrices – Análisis Químicos

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

EURACHEM / CITAC Guide
***Use of Uncertainty Information in Compliance* Assessment**
(1st Edition, 2007)

EUROLAB Technical Report No. 1/2002
Measurement Uncertainty in Testing
(June 2002)

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)

Directrices - Codex Alimentarius

Generales para los Análisis Químicos

(Codex Committee on Methods of Analysis and sampling - CCMAS)

CAC / GL 54-2004

Directrices sobre la Incertidumbre de Medida

Directrices - Codex Alimentarius

Específicas para el Análisis de Residuos de Plaguicidas

(Codex Committee on Pesticide Residues - CCPR)

CAC / GL 59-2006

Directrices sobre la Estimación de la Incertidumbre de los Resultados

ALINORM 09/32/24 (Appendix X)

Proposed draft revision of the Guidelines on the estimation of uncertainty of results for the determination of pesticide residues (CAC/GL 59-2006) at step 3

Definición ISO - GUM de Incertidumbre de Medida

'Parámetro asociado al resultado de una medida, que caracteriza la dispersión de los valores que pueden atribuirse razonablemente al mesurando'

Este parámetro puede ser:

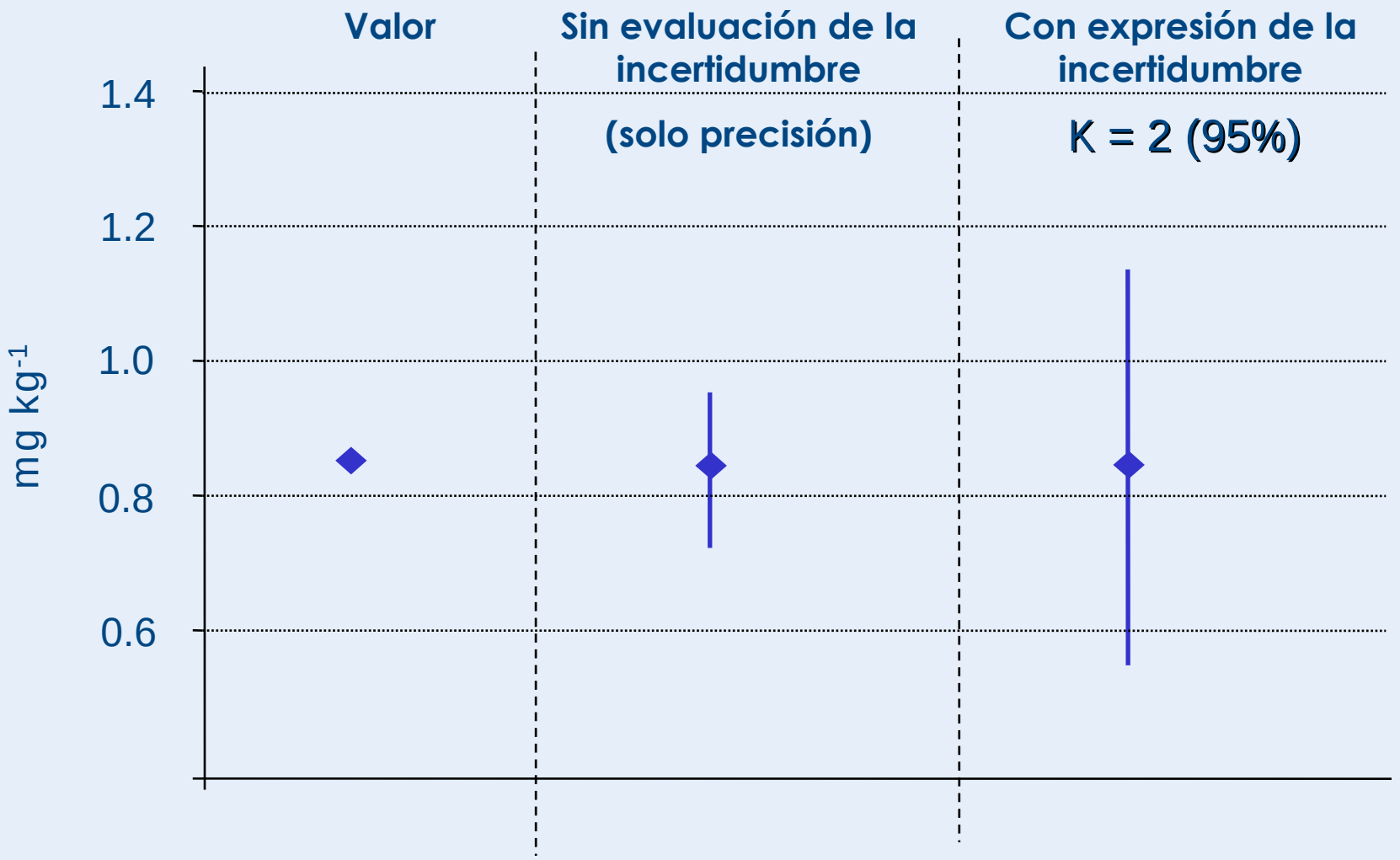
- una desviación estándar ***(incertidumbre estandar combinada)***
- una parte de un intervalo indicando un cierto nivel de confianza ***(incertidumbre expandida)***

Resultado = Valor ± incertidumbre

0.85 ± 0.30 mg/kg *(k = 2; 95%)*

¡entre 1.15 y 0.55 mg/kg!

Formas de Expresar un Resultado



Folleto informativo publicado en el año 2000 por el "SP-Swedish NTRI" para ser entregado a los clientes de los laboratorios junto a los informes de ensayo

Important information to our customers concerning the quality of measurements

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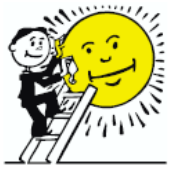
Those of us working in accredited laboratories or dealing with issues concerning the quality of measurements, would like to inform you about some important changes concerning the way the results of measurements are presented. These changes make it easier for you as an end-user to make correct decisions.

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 FOR ANALYTICAL CHEMISTRY IN EUROPE · eurolab – Organization 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 PROVNING · FORSKNING

SPINFO 2000:27

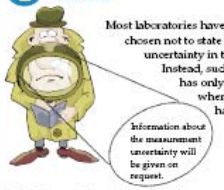
5 Uncertainty and limiting values

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



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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%)

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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.

NATUR VÅRDS VERKET · FoL · SWEDAC – 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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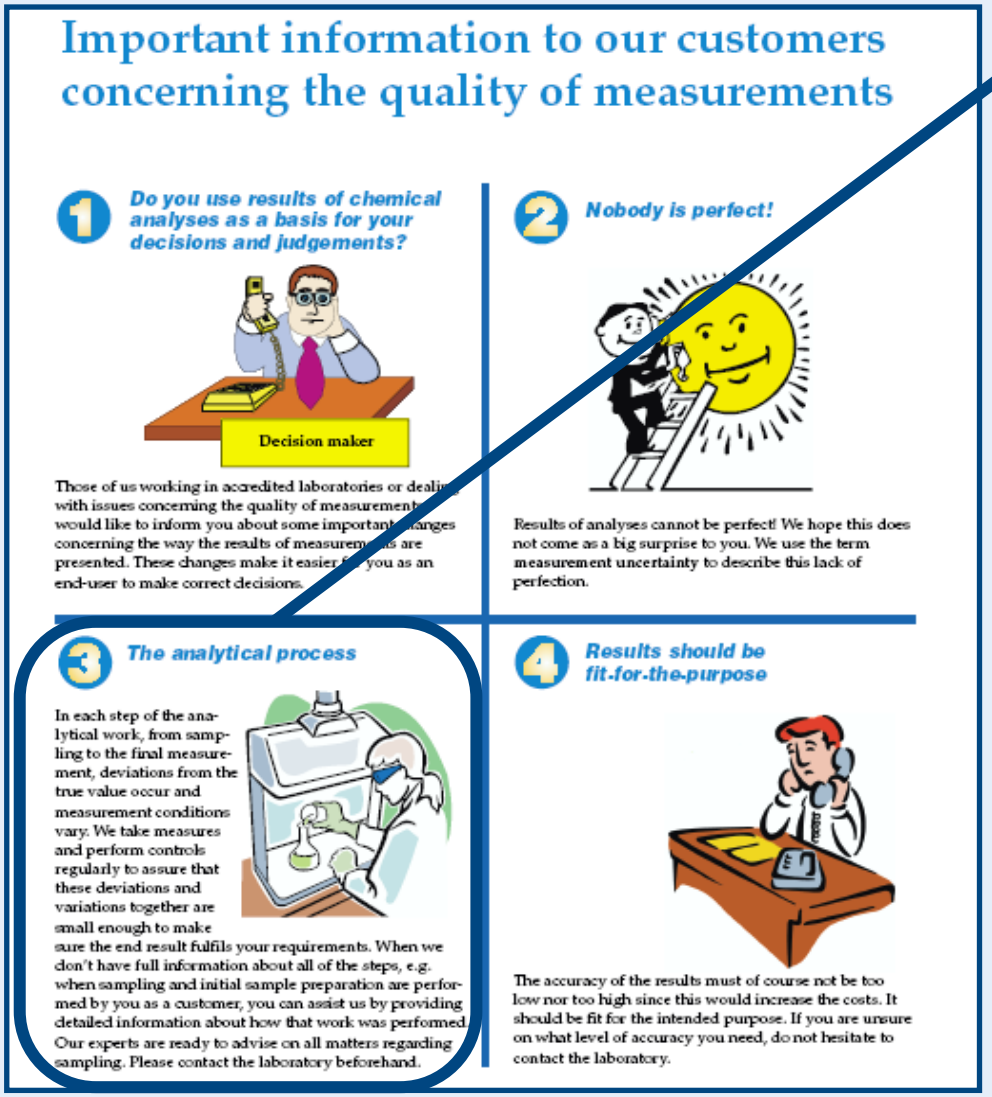
Los resultados de los análisis no pueden ser perfectos....

Utilizamos el término: "Incertidumbre de Medida" para describir esta falta de perfección.



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En cada etapa del trabajo analítico, desde el muestreo hasta la medida final, ocurren desviaciones del valor verdadero y las condiciones de medida varían.

Nosotros tomamos medidas y realizamos controles regularmente para conseguir que estas desviaciones y variaciones juntas sean suficientemente pequeñas para asegurar que el resultado final se ajuste a sus necesidades.....

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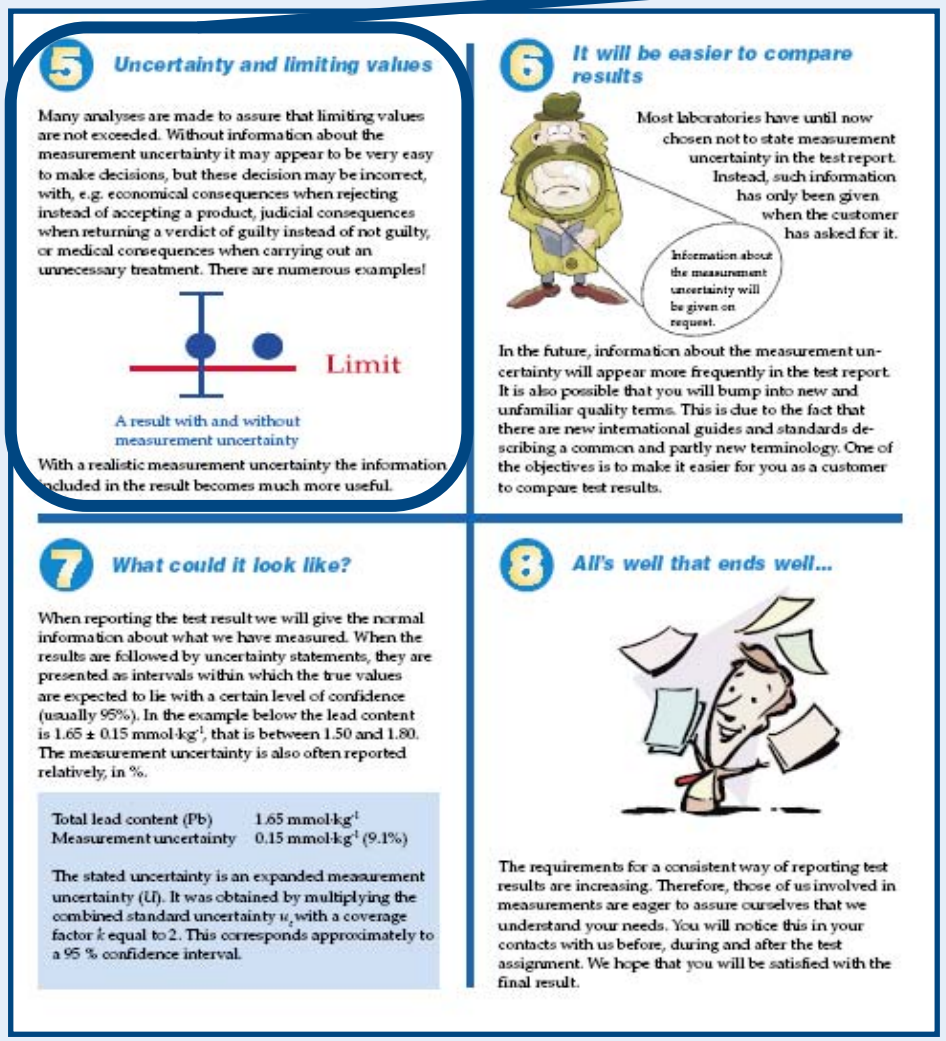
La Exactitud de los resultados no debe ser, por supuesto, demasiado baja, pero tampoco demasiado alta, ya que ésto incrementaría los costes.

Debería ajustarse al propósito perseguido.

Si no está seguro del nivel de exactitud que necesita, no dude en contactar con el laboratorio.



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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

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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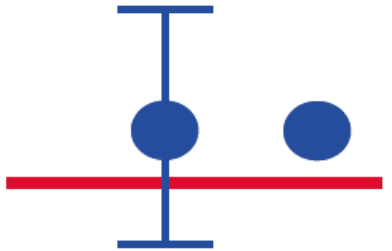
Muchos análisis se realizan para asegurar que no se superan unos valores límite.

Sin información sobre la Incertidumbre de Medida puede parecer muy fácil el tomar decisiones, pero estas decisiones pueden ser incorrectas....

Con una Incertidumbre de Medida realista la información incluida en el resultado se hace mucho más útil.



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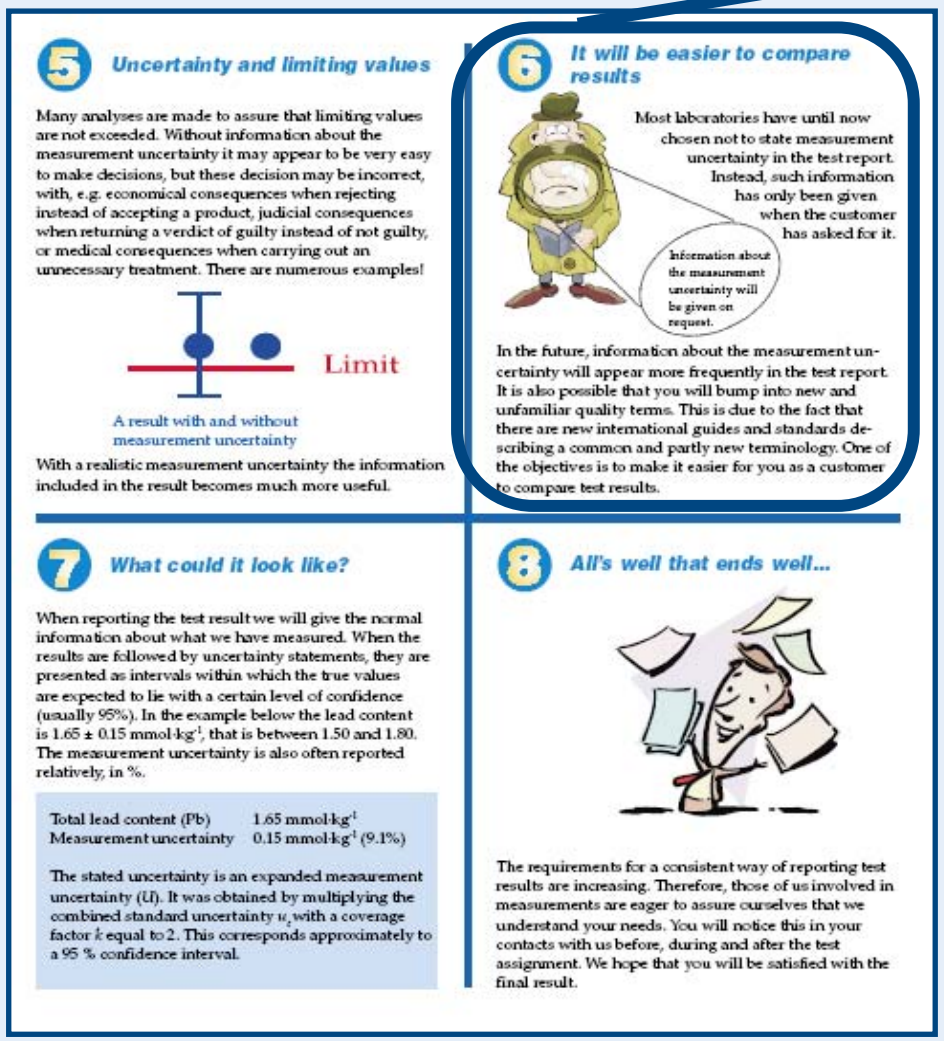

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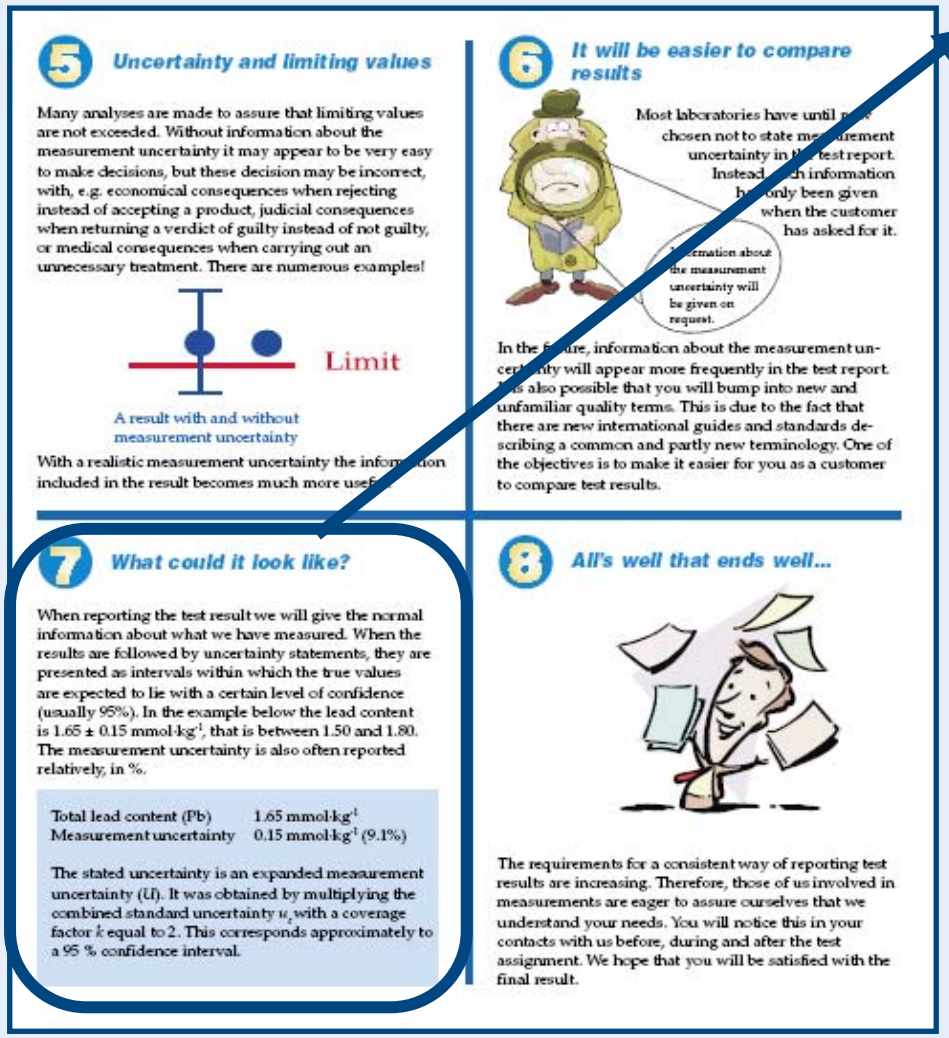
Hasta ahora, la mayoría de los laboratorios han elegido el no indicar la Incertidumbre de Medida en el informe de ensayo.

En su lugar, dicha información únicamente se da al cliente cuando éste la pide.

En el futuro, la información sobre la Incertidumbre de Medida aparecerá mas frecuentemente en el informe de ensayo.... nuevas guías y estándares internacionales....

Uno de los objetivos es el hacerle al cliente más fácil la comparación de los resultados de los ensayos.



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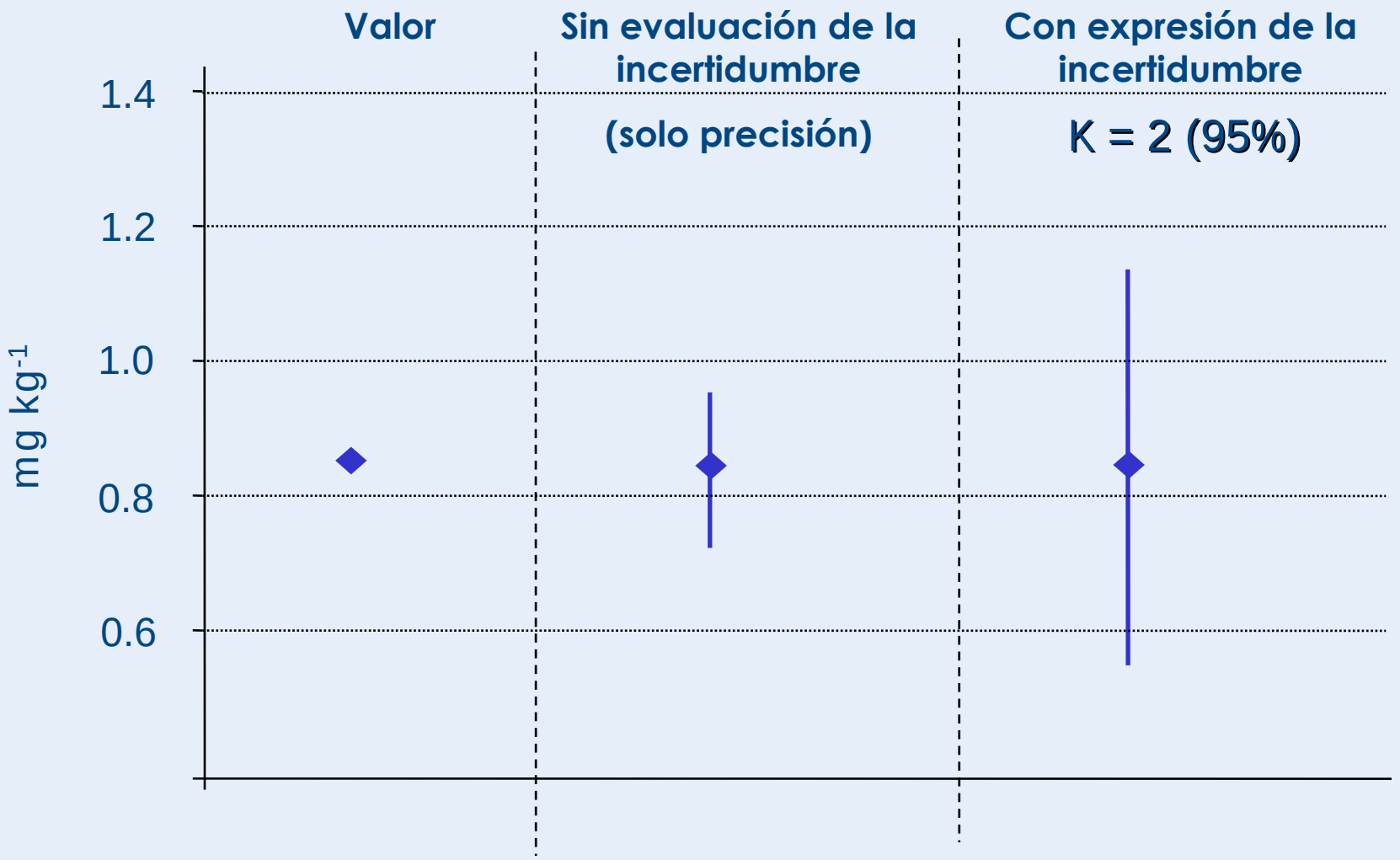
A la hora de presentar los resultados de ensayo daremos la información normal sobre lo que hemos medido. Cuando los resultados van seguidos por indicaciones de la Incertidumbre, éstos se presentan como intervalos en los que se espera se encuentren los valores verdaderos con un determinado nivel de confianza (usualmente 95%).

Contenido en Plomo:
1.65 ± 0.15 mmol/kg (entre 1.50 y 1.80)

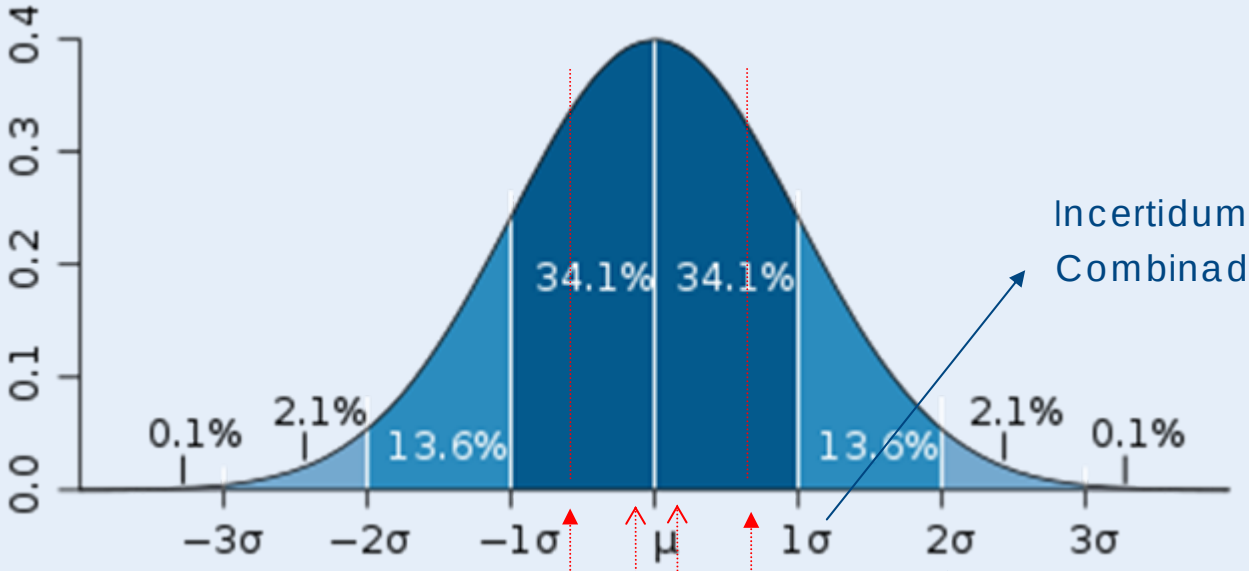
Incertidumbre de Medida Expandida (U)
Incertidumbre Estándar Combinada (u_c)
Factor de Cobertura (k)
(k = 2 aprox. 95% nivel de confianza)

$U = k \times u_c$

Formas de Expresar un Resultado



"Calidad" del Resultado



Incertidumbre Estándar Combinada (u_c)

0.85 mg/kg (¿10%?) — Valor

0.845 - 0.854

0.85 ± 0.10 mg/kg (¿50%?) — con precisión

0.75 - 0.95

0.85 ± 0.30 mg/kg *(95%)* — con incertidumbre K=2 ($U = k \times u_c$)

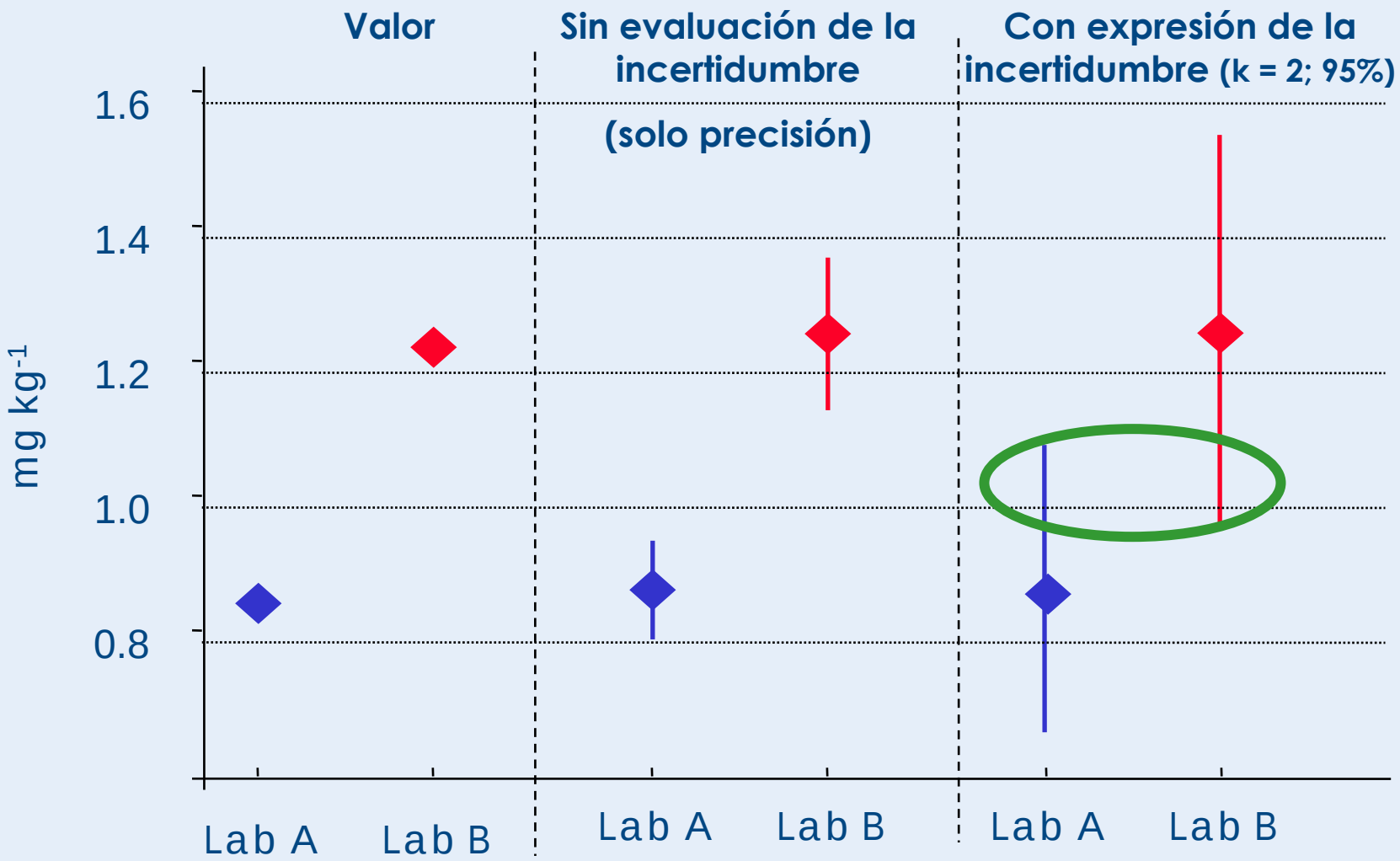
1.15 - 0.55

Conceptos básicos en la GUM

GUM (BIPM, IEC, IFCC, ISO, IUPAC, OIML)
Guía para la Expresión de la Incertidumbre de Medida
(ISO, Ginebra, 1993 – Revisión 1995)
ISBN: 92-67-10188

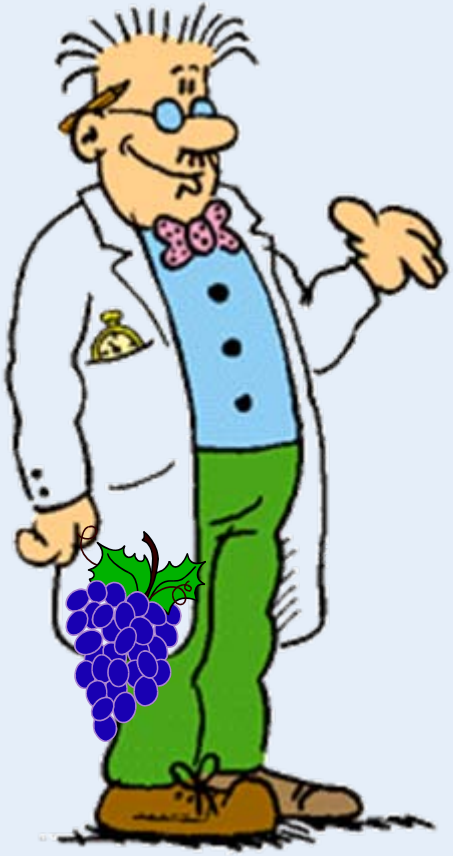
- Apreciación de la incertidumbre como un aspecto siempre positivo
- Aporta calidad al resultado, sea ésta grande o pequeña
- Se consideran todas las magnitudes que pueden influir en el mensurando
- Procedimiento simple y estandarizado de evaluación y expresión
- Evaluaciones Tipo A y Tipo B (no usa errores aleatorios y sistemáticos)
- Incertidumbre Estándar Combinada (u_c) / Incertidumbre Expandida (U)

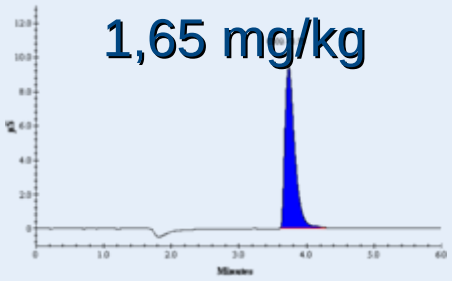
¿Son estos resultados diferentes?



¿Resultado Violativo o no Violativo?

Resultado = 1,65 ± 0,82 mg/kg ***(k = 2; 95%)***





Procedimiento de Evaluación - GUM

- Definir el Mensurando

- Desarrollo del Modelo de Medida (magnitudes, ecuación, diagrama causa-efecto, ...)

- Identificar todas las posibles fuentes de incertidumbre

- Estimar el valor de las magnitudes que influyen en el mensurando

- Evaluar incertidumbre estándar asociada a cada magnitud ($u_i = SD_i$)

- Calcular el valor del mensurando (ecuación modelo)

- Combinar las u_i (ley de propagación: $u_c = (u_1^2 + u_2^2 + u_3^2 + ...)^{1/2}$

- Calcular e informar la incertidumbre expandida ($U = k \times u_c$)

  k = Factor de Cobertura (distribución; nivel de confianza)

  Usualmente *k* = 2 (distribución normal; ≈ 95%)

Factores que pueden contribuir a la Incertidumbre de Medida

- Toma, Manejo, Almacenamiento de la Muestra
- Preparación de la Muestra Analítica
- Propiedades del Objeto Analizado
- Condiciones Ambientales
- Patrones y Materiales de Referencia
- Métodos y Equipos
- Operador
- Corrección de Resultados (efectos sistemáticos)
- etc.

¿Cómo evaluar las muchas componentes de la Incertidumbre de Medida?

Componente por componente

(mathematical / modelling / "down-top" approach)

Inviable para ensayos analíticos complicados

De forma global, agrupando muchas componentes

(empirical / "top-down" approaches)

Datos de Validación / Control de Calidad

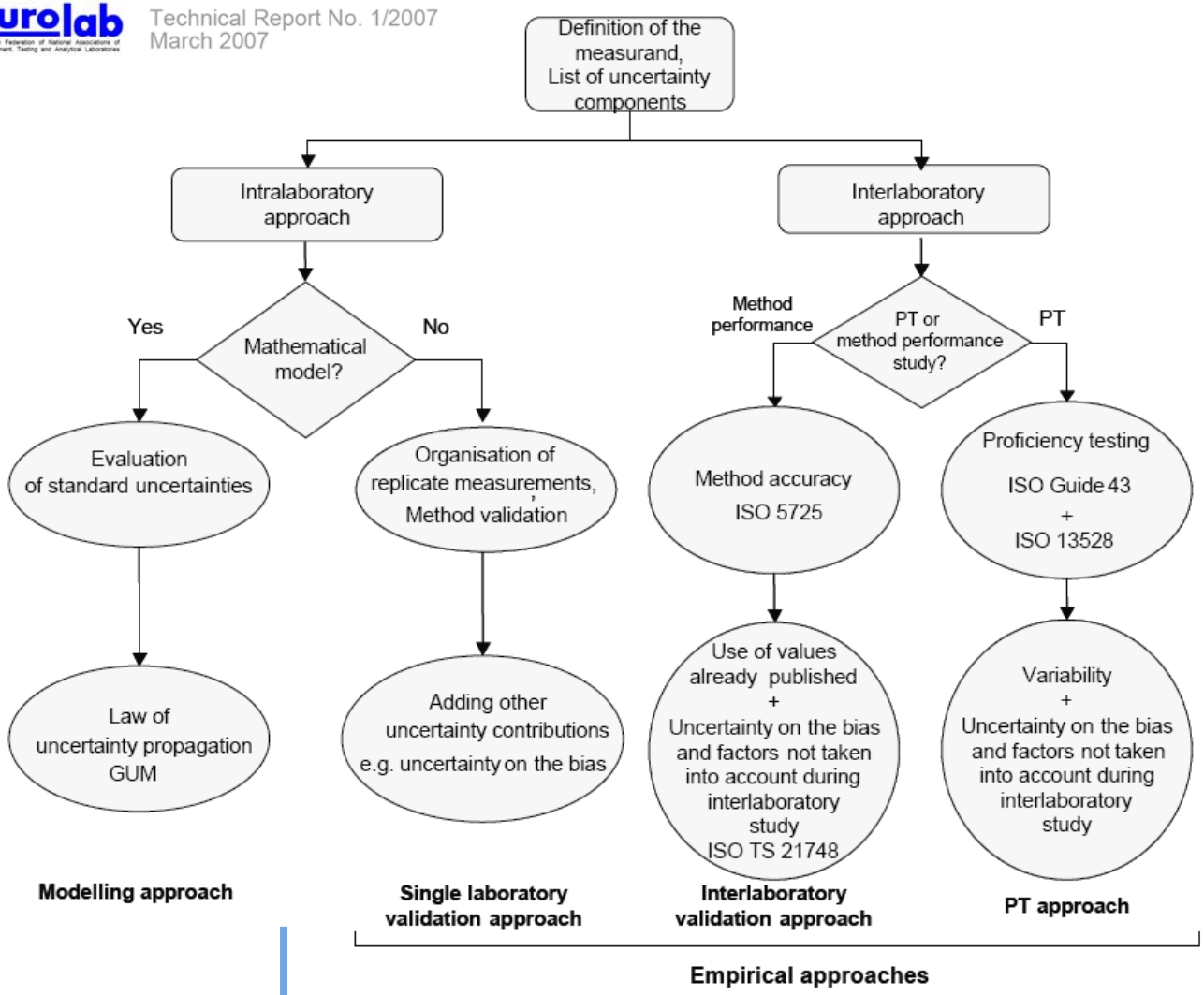
Estudios de Intercomparación

Ensayos de Aptitud (PTs)

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



down-top

top-down

Análisis Multi-Residuos de Pesticidas

COMPLICADOS / ELEVADA INCERTIDUMBRE

- Gran influencia de la destreza del analista,
- y del estado de mantenimiento de los equipos.
- Respuesta de los equipos variable con el tiempo.
- "Efecto Matriz" imprevisible.
- Interferencias imprevisibles (matriz, reactivos, etc.).
- Inexistencia de "Materiales de Referencia".
- Gran número de combinaciones pesticida/matriz.

Figure 1: A road map for uncertainty estimation approaches

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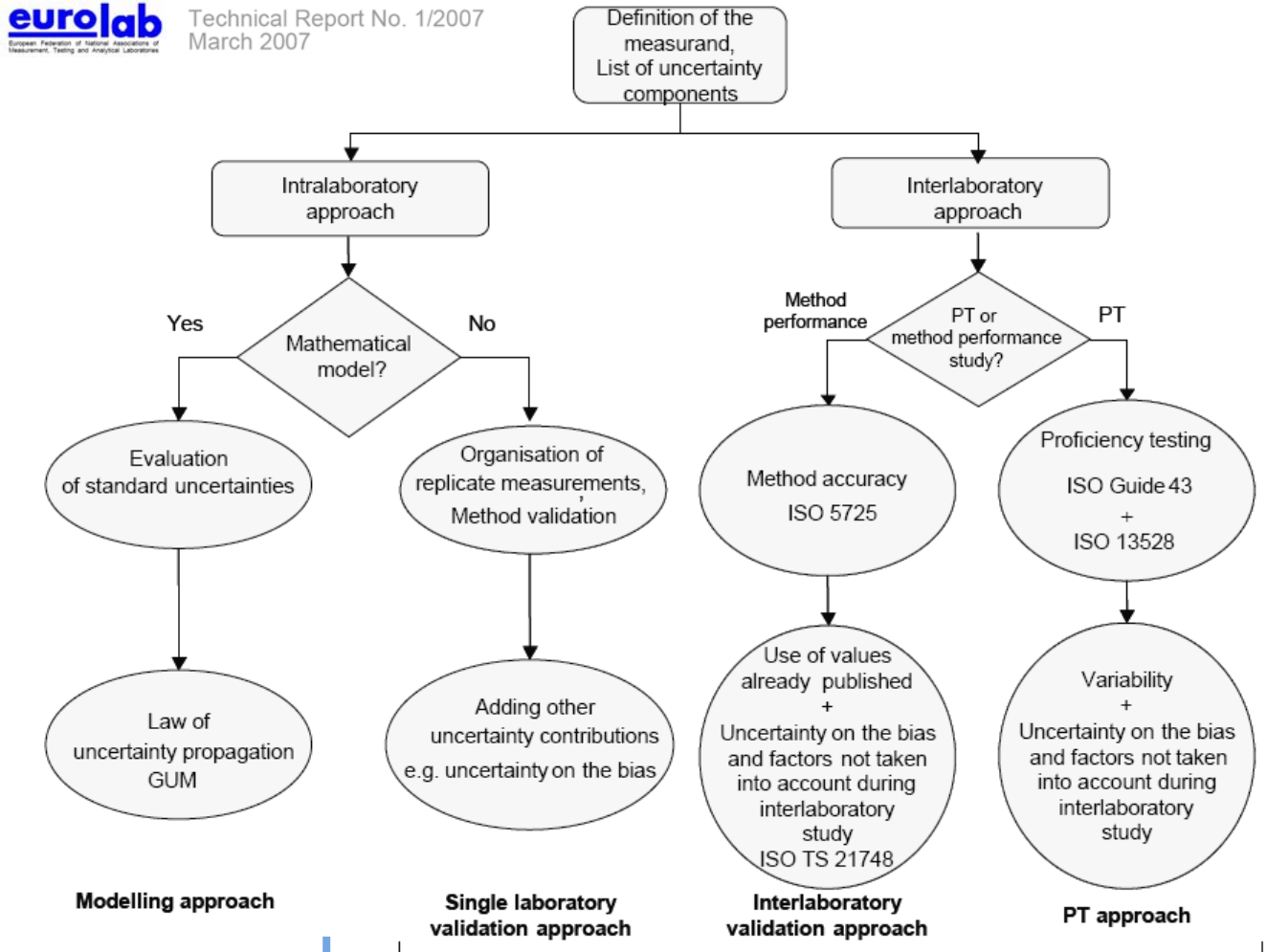

Análisis Multirresiduos de Pesticidas

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top-down

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)

Quantifying Uncertainty in Analytical Measurement

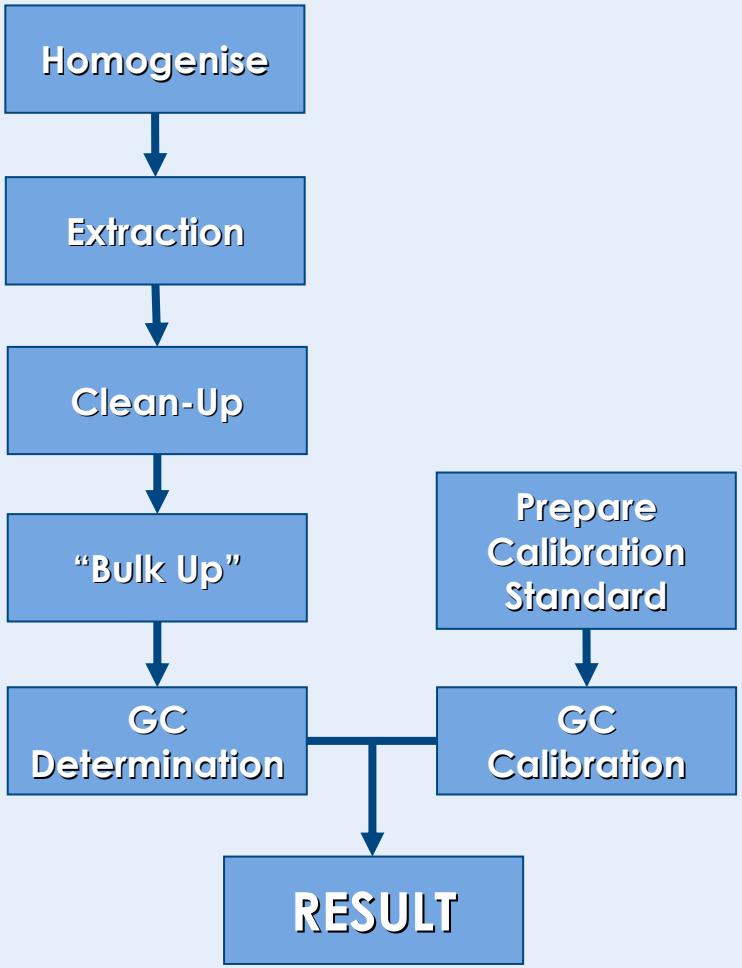
(2nd Edition, 2000)

Ejemplo de evaluación de la Incertidumbre a partir de estudios de validación "in-house": (Example A4)

Determinación de Plaguicidas Organofosforados en Pan

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
(Example A4)

Organophosphorus Pesticides Analysis



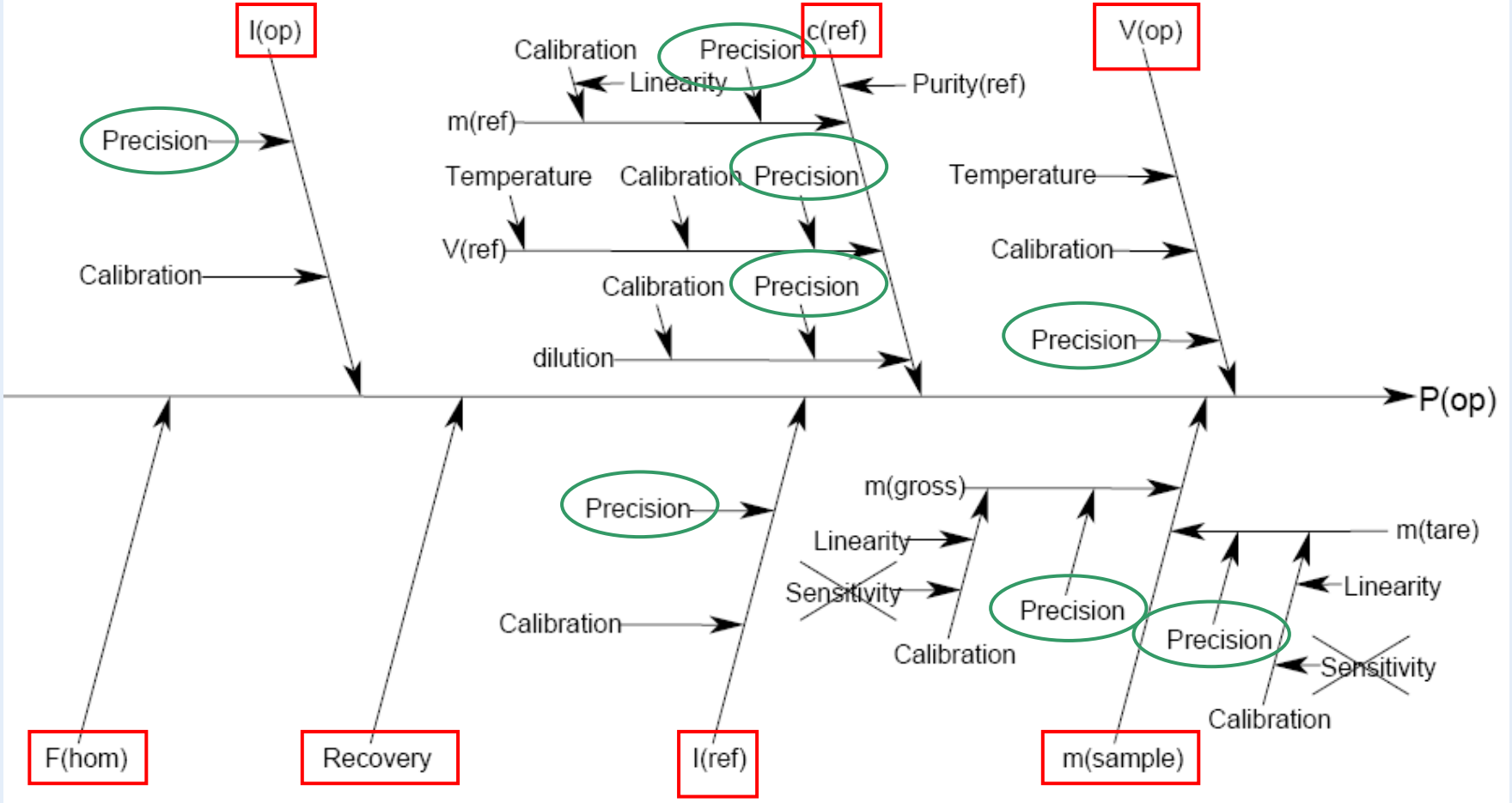
Measurand:

$$P_{op} = \frac{I_{op} \bullet c_{ref} \bullet V_{op}}{I_{ref} \bullet Rec \bullet m_{sample}} \bullet F_{hom} \; mg \; kg^{-1}$$

- P_{op}: Level of pesticide in the sample (mg kg^{-1})
- I_{op}: Peak intensity of the sample extract
- c_{ref}: Mass concentration of the reference standard (µg ml^{-1})
- V_{op}: Final volume of the extract (ml)
- I_{ref}: Peak intensity of the reference standard
- **Rec:** Recovery
- M_{sample}: Mass of the investigated sub-sample (g)
- F_{hom}: Correction factor for sample inhomogeneity

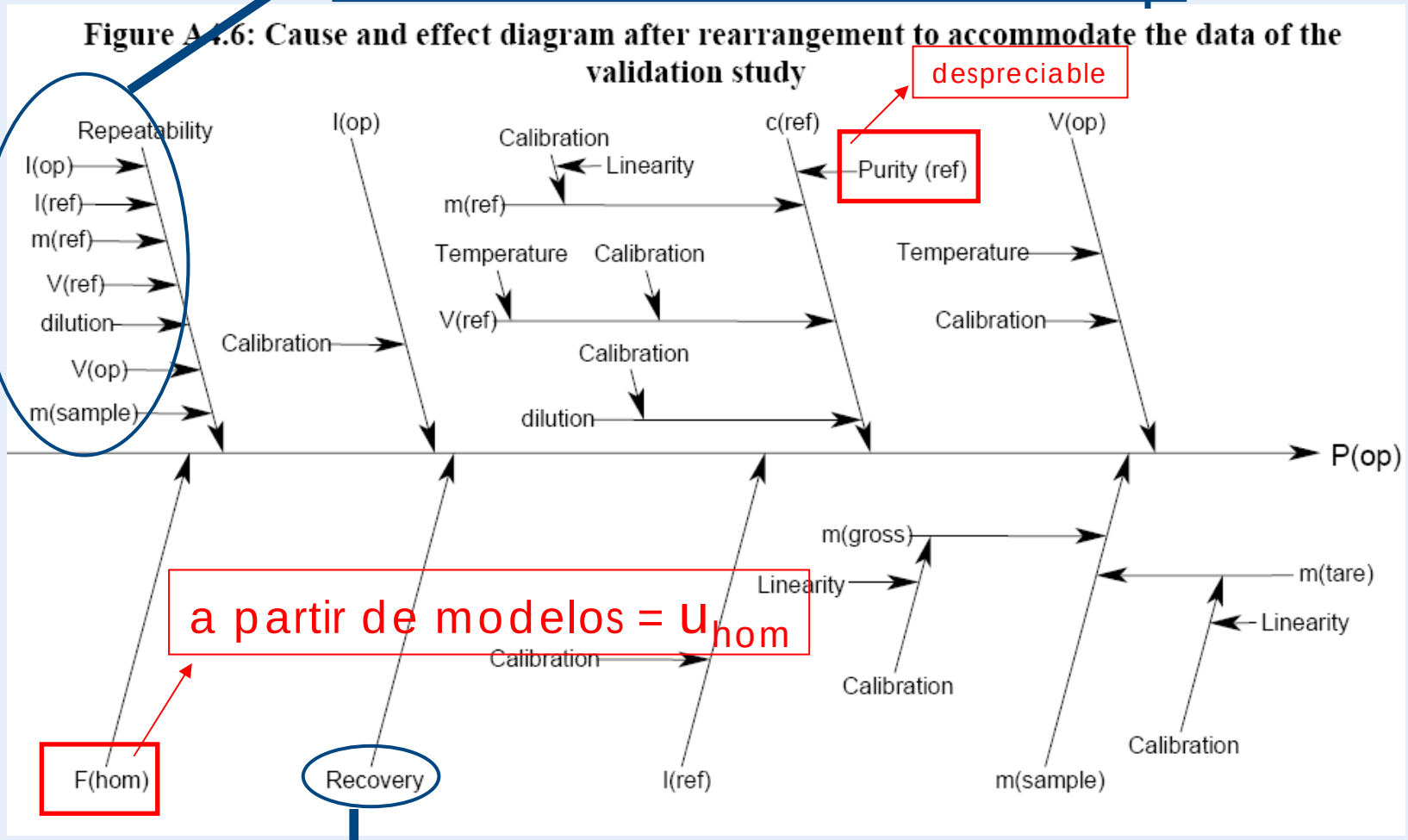
EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
(Example A4)

Figure A4.5: Cause and effect diagram with added main branch for sample inhomogeneity



EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
(Example A4)

Estudio precisión (Validación) = u_{rep}



Estudio sesgo-recuperación (Validación) = u_{rec}

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
(Example A4)

s = 0.382

Table A4.2: Results of duplicate pesticide analysis (in bread)

Residue	D1 [mg kg^{-1}]	D2 [mg kg^{-1}]	Mean [mg kg^{-1}]	Difference D1-D2	Difference/ mean
Malathion	1.30	1.30	1.30	0.00	0.000
Malathion	1.30	0.90	1.10	0.40	0.364
Malathion	0.57	0.53	0.55	0.04	0.073
Malathion	0.16	0.26	0.21	-0.10	-0.476
Malathion	0.65	0.58	0.62	0.07	0.114
Pirimiphos Methyl	0.04	0.04	0.04	0.00	0.000
Chlorpyrifos Methyl	0.08	0.09	0.085	-0.01	-0.118
Pirimiphos Methyl	0.02	0.02	0.02	0.00	0.000
Chlorpyrifos Methyl	0.01	0.02	0.015	-0.01	-0.667
Pirimiphos Methyl	0.02	0.01	0.015	0.01	0.667
Chlorpyrifos Methyl	0.03	0.02	0.025	0.01	0.400
Chlorpyrifos Methyl	0.04	0.06	0.05	-0.02	-0.400
Pirimiphos Methyl	0.07	0.08	0.75	-0.10	-0.133
Chlorpyrifos Methyl	0.01	0.01	0.10	0.00	0.000
Pirimiphos Methyl	0.06	0.03	0.045	0.03	0.667

Estudio precisión

$$u_{rep} = 0.382 / 2^{1/2} = 0.27$$

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
(Example A4)

Table A4.3: Results of pesticide recovery studies

Substrate	Residue Type	Conc. [mg kg^{-1}]	N[1)]	Mean [2)] [%]	s [2)] [%]
Waste Oil	PCB	10.0	8	84	9
Butter	OC	0.65	33	109	12
Compound Animal Feed I	OC	0.325	100	90	9
Animal & Vegetable Fats I	OC	0.33	34	102	24
Brassicas 1987	OC	0.32	32	104	18
Bread	OP	0.13	42	90	28
Rusks	OP	0.13	30	84	27
Meat & Bone Feeds	OC	0.325	8	95	12
Maize Gluten Feeds	OC	0.325	9	92	9
Rape Feed I	OC	0.325	11	89	13
Wheat Feed I	OC	0.325	25	88	9
Soya Feed I	OC	0.325	13	85	19
Barley Feed I	OC	0.325	9	84	22

(1) The number of experiments carried out

(2) The mean and sample standard deviation s are given as percentage recoveries.

$$u_{rec} = 0.28 / 42^{1/2} = 0.043$$

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)
(Example A4)

Patrón: 99.53% ± 0.06%
u_{ref} = 0.0006/$3^{1/2}$ *(distribución rectangular)*
u_{ref} = 0.00035 = DESPRECIABLE

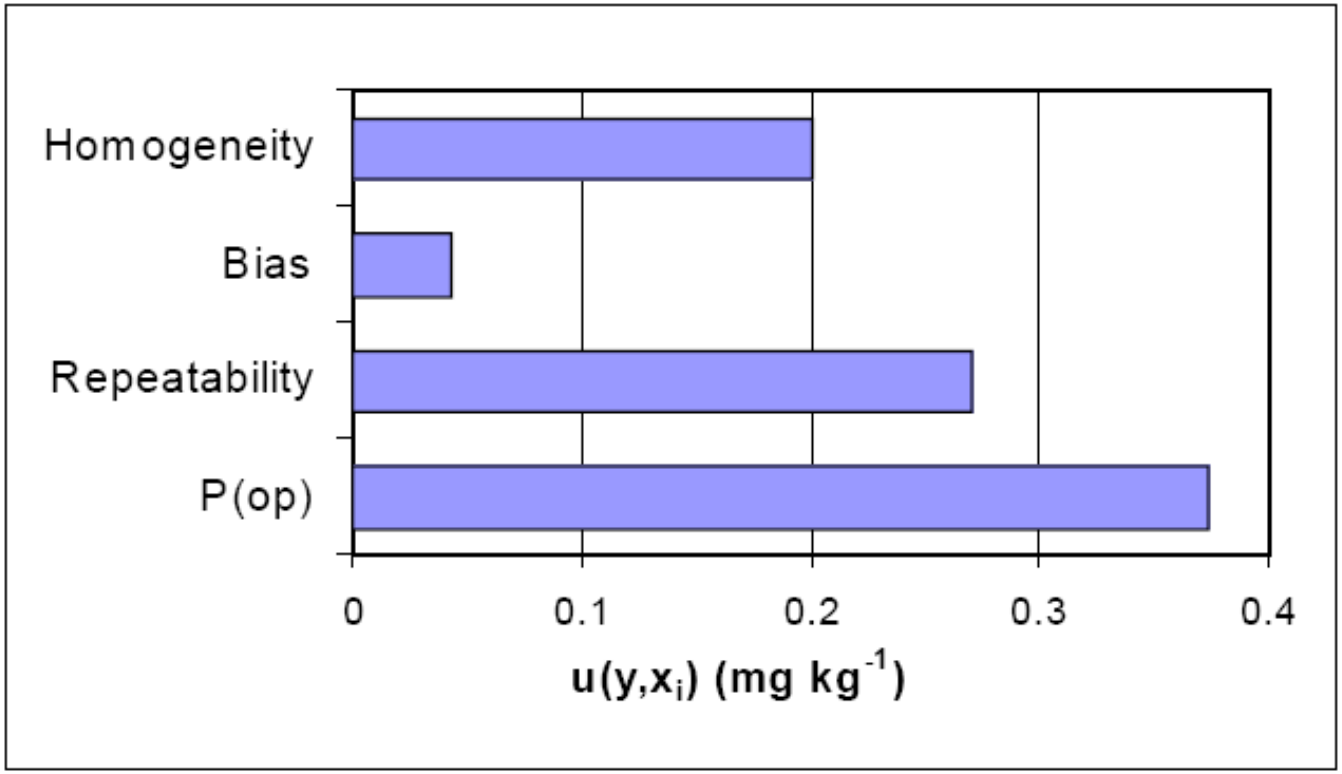
Table A4.4: Uncertainties in pesticide analysis

Description	Value x	Standard uncertainty $u(x)$	Relative standard uncertainty $u(x)$	Remark
Repeatability(1)	1.0	0.27	0.27	Duplicate tests of different types of samples
Bias (*Rec*) (2)	0.9	0.043	0.048	Spiked samples
Other sources (3) (Homogeneity)	1.0	0.2	0.2	Estimations founded on model assumptions
P_{op}	- -	**0.373**	0.34	

$$u_c = \sqrt{u_{hom}^2 + u_{rep}^2 + u_{rec}^2}$$

- Preparación muestra analítica (hom)
- Precisión (rep)
- Sesgo-Bias (rec)

Figure A4.8: Uncertainties in pesticide analysis



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

- Preparación muestra analítica
- Precisión
- Sesgo

Directrices - Codex Alimentarius

Específicas para el Análisis de Residuos de Plaguicidas

CAC / GL 59-2006

Directrices sobre la Estimación de la Incertidumbre de los Resultados

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)

Quantifying Uncertainty in Analytical Measurement

(2nd Edition, 2000) (Example A4)

Análisis Multirresiduos (Plaguicidas/Vegetales)

Incertidumbre de Medida de un Laboratorio:

Desviación Estándar (S_L) ó Desviación Estandar Relativa (CV_L)

CAC / GL 59-2006

Cuadro 1: Fuentes de error en la preparación de la porción de prueba

	Fuentes de errores sistemáticos	Fuentes de errores aleatorios
Preparación de la muestra	La porción de muestra por analizar (muestra analítica) puede elegirse incorrectamente	La muestra analítica está en contacto con otras porciones de la muestra y es contaminada por ésta
		El enjuagado y lavado se efectúan en distinta medida; tallos y piedras pueden eliminarse diferentemente
Procesamiento de la muestra (S_{Sp})	Descomposición del analito durante el procesamiento de la muestra, contaminación cruzada de las muestras	Falta de homogeneidad del analito en unidades individuales de la muestra analítica
		Falta de homogeneidad del analito en la muestra analítica molida/picada
		Variación de temperatura durante el proceso de homogenización
		La textura (madurez) de los materiales de la planta afecta a la eficiencia del proceso de homogenización

CAC / GL 59-2006

Cuadro 2: Fuentes de errores en el análisis (S_A):

	Fuentes de errores sistemáticos	Fuentes de errores aleatorios
Extracción / limpieza	Recuperación incompleta del analito	Variación de la composición (p.ej. contenido de agua, grasa y de azúcar) de los materiales de muestra tomados de un producto
	Interferencia de materiales extraídos simultáneamente (carga del adsorbente)	Temperatura y composición de la muestra/matriz soluble
Determinación cuantitativa	Interferencia de los compuestos extraídos simultáneamente	Variación del volumen nominal de los mecanismos dentro de los intervalos de tolerancia permitidos
	Pureza incorrecta del patrón analítico	Precisión y linealidad de balances
	Mediciones desviadas del peso/volumen	Reacciones de derivación incompletas y variables
	Sesgo del operador al leer instrumentos y equipo análogos	Cambio de las condiciones del entorno-laboratorio durante el análisis
	Determinación de sustancia que no es originaria de la muestra (p.ej. contaminación del material de envasado)	Condiciones de detección, cromatográficas y de inyección variables, (efecto matriz, inactividad del sistema, respuesta del detector, variación de señal a ruido, etc.)
	Determinación de sustancia que difiere de la definición de residuo	Efectos del operador (falta de atención)
	Calibración desviada	Calibración

CAC / GL 59-2006

Incertidumbre de Medida

$$S_{Res} = \sqrt{S_S^2 + (S_{Sp}^2 + S_A^2)} \; ; \; S_{Res} = \sqrt{S_S^2 + S_L^2}$$

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

Muestreo (CV_S)

Preparación Muestra (CV_{SP})
Etapa Analítica (CV_A)
Laboratorio (CV_L)

Reproducibilidad Intra-laboratorio

CAC / GL 59-2006

Incertidumbre de Medida

Procesamiento de la muestra Incluye la operación física realizada para homogeneizar la muestra analítica y el submuestreo, pero excluye la descomposición y evaporación de analitos. CV_{SP}	Varía en gran medida dependiendo de la matriz de muestra y el equipo. No puede darse ningún valor típico. Los analistas tienen que intentar mantenerlos[c] por debajo del 8-10%.	Puede verse influido por el equipo utilizado para picar/homogeneizar la muestra y la matriz de muestra, pero es independiente del analito.
Análisis Incluye todos los procedimientos realizados desde el punto de fijar las porciones de prueba. CV_A	Dentro de la reproductibilidad de laboratorio: 16-53% para concentraciones de 1µg/kg a 1 mg/kg[c]. La media entre reproductibilidad de laboratorios dentro de 0,001-10 mg/kg: 25%[d]	El CV_A típico puede determinarse adecuadamente partiendo de estudios de recuperación realizados con varias combinaciones de plaguicidas -productos en días diferentes y durante el uso del método.

Preparación Muestra (CV_{SP})

Etapa Analítica (CV_A)

Laboratorio (CV_L)

$$CV_L = \sqrt{CV_{Sp}^2 + CV_A^2}$$

CAC / GL 59-2006

Directrices - Codex Alimentarius

CAC / GL 59-2006

Directrices sobre la Estimación de la Incertidumbre de los Resultados

$$CV_L = \sqrt{CV_{Sp}^2 + CV_A^2}$$

¡Evaluar la incertidumbre mediante estudios de validación y control de calidad sobre una gama representativa de analitos y matrices!

CAC / GL 59-2006

Guidelines - Codex Alimentarius

CAC/GL 59-2006

Directrices sobre la Estimación de la Incertidumbre de los Resultados

$$CV_L = \sqrt{CV_{Sp}^2 + CV_A^2}$$

Incorporar la incertidumbre asociada a la recuperación cuando el resultado se ha corregido en cuanto a recuperación (u_{bias})

$$u_c = \sqrt{u_{hom}^2 + u_{rep}^2 + u_{bias}^2}$$

EURACHEM / CITAC Guide CG 4 (QUAM:2000.1)

¿Cuántas evaluaciones de incertidumbre (validaciones) han de hacerse en un laboratorio?

Incertidumbre depende de	*Si*	*No*	*Max.*	*Total*
Analitos	X		800	800
Matrices	X		25	20,000
Concentración	X		3	60,000
Métodos		X		60,000
Laboratorios		X		60,000

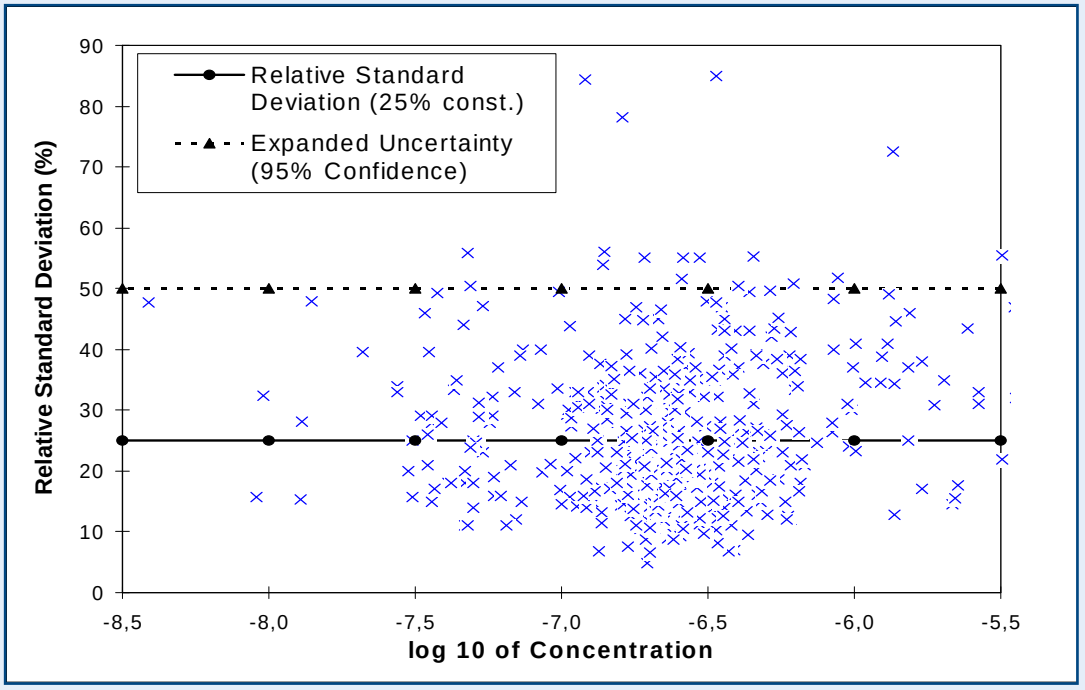
CAC / GL 59-2006

CAC / GL 59-2006

Directrices sobre la Estimación de la Incertidumbre de los Resultados

Además de las incertidumbres estimadas por laboratorios individuales, las autoridades de control y demás gestores de riesgos pueden decidir sobre una incertidumbre expandida por defecto de las mediciones que puede utilizarse para estimar el cumplimiento de los LMR (véase la sección 5) a partir de valores de reproductibilidad entre laboratorios. Por ejemplo, una incertidumbre expandida del 50% para CV_L se considera que es un valor por defecto razonable.

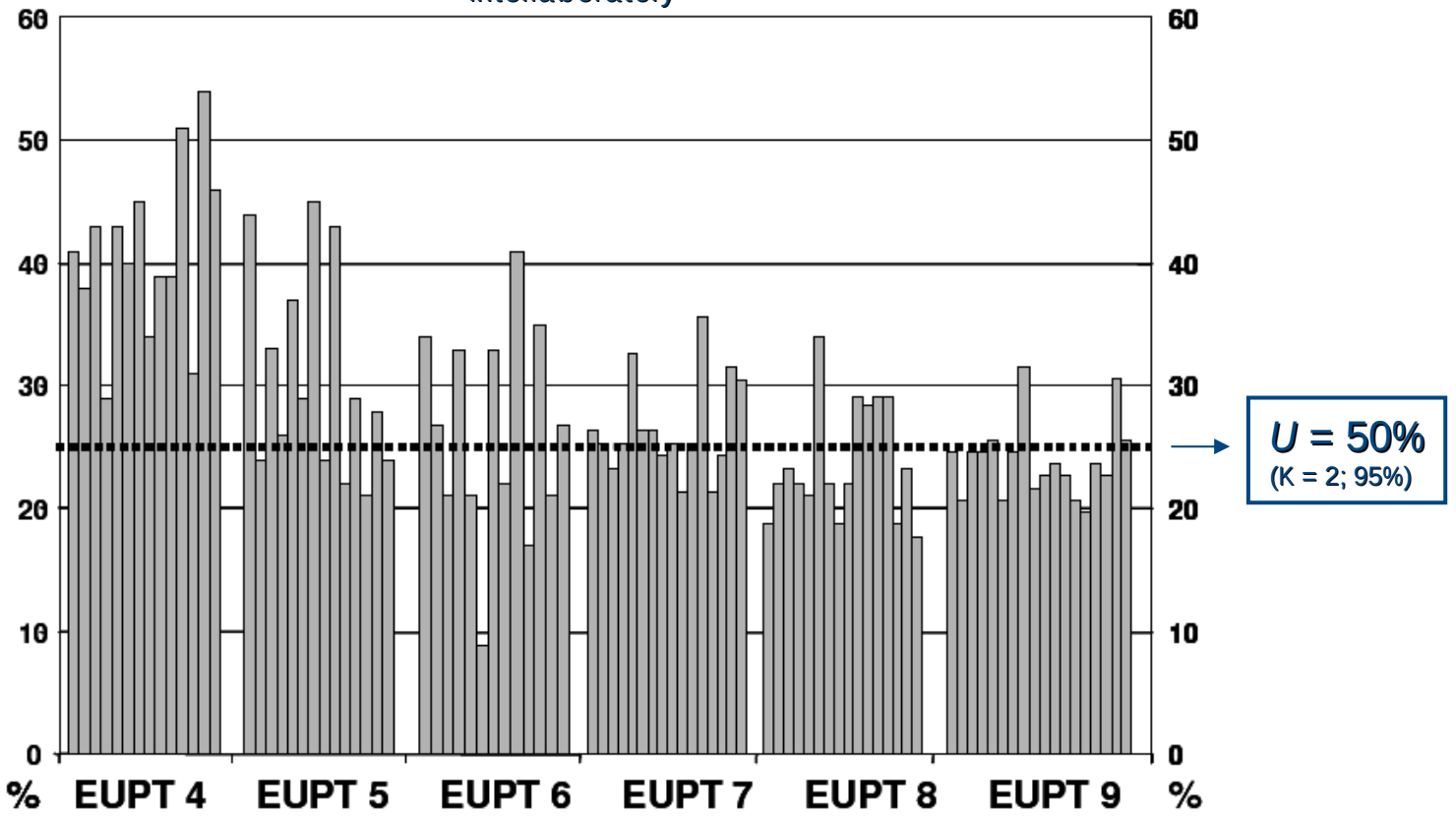
Alder et al. (2001) J. AOAC Int. 84, 1569-1578



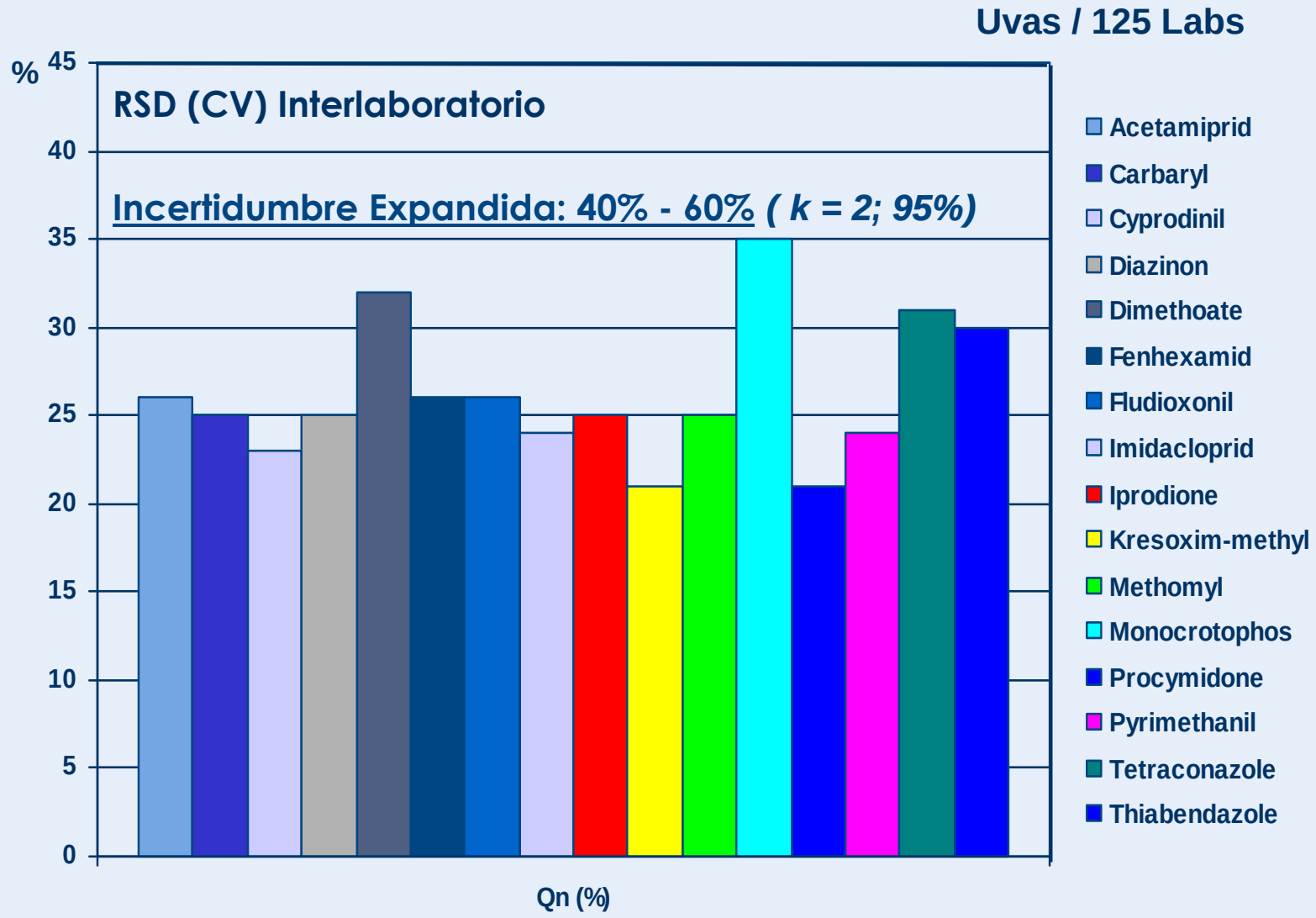
"European Proficiency Tests" EUPT4 – EUPT9

Figure 3

Qn (%) = Robust $RSD_{Interlaboratory}$ = *u* (relative standard uncertainty)



"Proficiency Test" Europeo EUPT-07 (2005)



Codex Alimentarius

Desarrollo de Nuevas Directrices

Específicas para el Análisis de Residuos de Plaguicidas

ALINORM 08/31/24 (Appendix IX)

Project Document: Proposal for new work on the revision and extension of Guidelines CAC/GL 59-2006

CX/PR 08/40/5 y *CX/PR 09/41/5*

Discussion paper on the estimation of Uncertainty of Results for the determination of pesticide residues prepared by IAEA

↓

ALINORM 09/32/24 (Appendix X)

Proposed draft revision of the Guidelines on the estimation of uncertainty of results for the determination of pesticide residues (CAC/GL 59-2006) at step 3

ALINORM 09/32/24: APPENDIX X

codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

JOINT OFFICE: Viale delle Terme di Caracalla 00153 ROME Tel: 39 06 57051 www.codexalimentarius.net Email: codex@fao.org Facsimile: 39 06 5705 4593

ALINORM 09/32/24

JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX ALIMENTARIUS COMMISSION

Thirty-second Session
Rome, Italy, 29 June - 4 July 2009

REPORT OF THE FORTY-FIRST SESSION OF THE CODEX COMMITTEE ON PESTICIDE RESIDUES

Beijing, China, 20 – 25 April 2009

APPENDIX X

PROPOSED DRAFT REVISION OF THE GUIDELINES ON THE ESTIMATION OF UNCERTAINTY OF RESULTS FOR THE DETERMINATION OF PESTICIDE RESIDUES (CAC/RCP 59-2006) AT STEP 3

Directrices sobre estimación de la incertidumbre a partir de:

- Resultados de participación en PTs *(NORDTEST approach)*

[7] NORDTEST Report TR 537, HANDBOOK FOR CALCULATION OF MEASUREMENT UNCERTAINTY IN ENVIRONMENTAL LABORATORIES, EDITION 2

- Otras "top-down/empirical approaches"
  - i) Ecuación de Horwitz
  - ii) Un valor por defecto y generalizado (*U* = 50%) *(EU approach)*

[5] Document N° SANCO/2007/3131 - METHOD VALIDATION AND QUALITY CONTROL FOR PESTICIDE RESIDUE ANALYSIS IN FOOD AND FEED (www.crl-pesticides.eu)

Estimación de la incertidumbre a partir de PTs:

1) ***Reproducibilidad intra-laboratorio (validación/QC)***

2) **Sesgo del laboratorio-método (resultados obtenidos en al menos 6 diferentes PTs con matrices y plaguicidas incluidos en el alcance del método**

ALINORM 09/32/24: APPENDIX X

$$U' = k * u'$$

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

(Validation/QC data)

where:

$$u'(bias) = \sqrt{RMS'_{bias}{}^2 + u'(C_{ref})^2}$$

and:

$$RMS'_{bias} = \sqrt{\frac{\sum (bias'_i)^2}{m}}$$

and:

$$u'(C_{ref}) = \frac{\sum_i \frac{S'_{Ri}}{\sqrt{n_i}}}{m}$$

U'	=	expanded relative uncertainty
k	=	coverage factor
u'	=	combined relative standard uncertainty
$u'(R_W)$	=	intermediate precision relative standard uncertainty
u'(bias)	=	relative standard uncertainty component from method and laboratory bias, based on PT data
RMS'_{bias}	=	root mean square of relative bias values
$bias'_i$	=	relative bias of PT i [obtained result$_i$ – assigned value$_i$)/assigned value$_i$]
$u'(C_{ref})$	=	average relative standard uncertainty of assigned values
S'_{Ri}	=	interlaboratory relative standard deviation of PT i
n_i	=	number of participants in PT i
m		total number of PT schemes

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Validation/QC data (average RSD intralab-reproducibilities)

Ejemplo Estimación de la incertidumbre a partir de PTs

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

$$u'(bias) = \sqrt{RMS'_{bias}{}^2 + u'(C_{ref})^2}$$

and:

$$RMS'_{bias} = \sqrt{\frac{\sum (bias'_i)^2}{m}}$$

and:

$$u'(C_{ref}) = \frac{\sum_i \frac{S'_{Ri}}{\sqrt{n_i}}}{m}$$

2.4.1 Estimating u(bias) – the uncertainty component from method & lab bias

Uncertainty component for the uncertainty of the assigned value PT providers increasingly report uncertainties for their assigned values. If the provider reports an uncertainty, use the uncertainty estimate supplied.	
Step	**Example**
Find the interlaboratory standard deviations, s_R, for all laboratories participating in the exercises.	The s_R has been on average 9 % in six exercises. Mean number of participants = 12
Calculate the uncertainty of the assigned value, $u(C_{ref})$ Note 1	$u(C_{ref}) = \frac{s_R}{\sqrt{n}} = \frac{9}{\sqrt{12}} = 2.6\ \%$

Note 1: If the assigned value is a median value the equation will, following the principles of ISO 13528 [12], be $u(C_{ref}) = 1.253 \cdot s_R / \sqrt{n}$.

Uncertainty component for laboratory and method bias for a specific laboratory	
Step	**Example**
Obtain the laboratory's deviations from the assigned value for at least six PT rounds	The relative bias has been 2 %, 7 %, -2 %, 3 %, 6 % and 5 %.
Quantify the components	RMS_{bias} = 4.6 %, $u(C_{ref})$ = 2.6 %
Calculate uncertainty component arising from method and laboratory bias, u(bias)	$u(bias) = \sqrt{RMS_{bias}{}^2 + u(C_{ref})^2} = \sqrt{4.6^2 + 2.6^2} = 5.3\%$

[1] The use of an RMS value is equivalent to an estimated standard deviation around an assumed value of bias equal to zero. This implies that the RMS value takes into account both the bias and the variation of bias.

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Table 1: Laboratory estimates of uncertainty

Sample type	Analyte[Note 1]	Estimated uncertainty (RSD[Note 2])
Fruit and vegetable	Multiple organochlorine pesticides	0.17 (17%)
Meat product (kidney fat)	Multiple organochlorine pesticides	0.18 (18%)

Note 1: "Analyte" = chemical material of interest. The corresponding measurand is the analyte concentration, usually expressed as a mass fraction.

Note 2: Expressed as a relative standard deviation

* Strictly, the mean RSD is biased slightly low, but across a wide range of materials and analytes, the relative standard deviations are sufficiently consistent to make more rigorous treatment unnecessary in this case.

Validation/QC data: u (R_w)

EXAMPLE 9: PESTICIDE RESIDUES IN FOODSTUFFS

Sector	Measurand / Matrix	Technique	Approaches for	
			estimation	verification
Food chain	Organochlorine pesticides and PCBs	Gas chromatography / Mass spectrometric detection (GC-MS)	Single laboratory validation data	PT performance

Table 2: PT results for pesticides in food matrices (source: FAPAS reports [1])

Round	Material	Pesticide	Assigned value x_{ref} ug kg^{-1}	Laboratory value x_i ug kg^{-1}	Difference (x_i-x_{ref}) ug kg^{-1}	Relative difference (x_i-x_{ref}) / x_{ref}
1	HVO*	heptachlor	64.6	58	-6.6	-0.10
1	HVO	PCB 101	35.4	32	-3.4	-0.10
1	HVO	PCB 52	25.9	23	-2.9	-0.11
1	HVO	p,p'-DDT	65.5	68	2.5	0.04
2	Milk powder	*cis*-chlordane	32.3	38	5.7	0.18
2	Milk powder	γ-HCH	41	47	6	0.15
2	Milk powder	p,p'-DDE	36	36	0	0.00
2	Milk powder	*trans*-chlordane	38.5	40	1.5	0.04
3	Chicken	β-HCH	31.8	55	23.2	0.73
3	Chicken	p,p'-DDE	34.8	37	2.2	0.06
3	Chicken	*trans*-heptachlor epoxide	50	45	-5	-0.10
4	HVO	γ-HCH	39.6	41	1.4	0.04
4	HVO	oxychlordane	44.2	45	0.8	0.02
4	HVO	trans-chlordane	64.6	65	0.4	0.01
5	HVO	aldrin	41.4	35	-6.4	-0.15
5	HVO	α-endosulfan	40.6	34	-6.6	-0.16
5	HVO	PCB 101	41.3	35	-6.3	-0.15
5	HVO	quintozene	52.4	NA		
6	Milk powder	dieldrin	32.9	37	4.1	0.12
6	Milk powder	γ-HCH	45.5	56	10.5	0.23
6	Milk powder	o,p'-DDT	49.1	54	4.9	0.10
6	Milk powder	PCB 52	37.8	45	7.2	0.19
7	Chicken	α-HCH	30.5	28.6	-1.9	-0.06
7	Chicken	α-endosulfan	37.2	29.4	-7.8	-0.21
7	Chicken	pp'-DDT	41.8	31.4	-10.4	-0.25
8	Vegetable oil	γ-HCH	33.7	30.8	-2.9	-0.09
8	Vegetable oil	oxychlordane	41.6	36.4	-5.2	-0.13
8	Vegetable oil	PCB 101	46.8	38.1	-8.7	-0.19
8	Vegetable oil	PCB 118	44.5	32	-12.5	-0.28
8	Vegetable oil	PCB 138	62.1	49.8	-12.3	-0.20
8	Vegetable oil	PCB 153	52.6	38.6	-14	-0.27
8	Vegetable oil	PCB 180	52.3	37.8	-14.5	-0.28
8	Vegetable oil	PCB 28	26.9	21.1	-5.8	-0.22
8	Vegetable oil	PCB 52	34.1	27.9	-6.2	-0.18

*HVO = hydrogenated vegetable oil

$$U = k * u = \sqrt{u(R_W)^2 + u(bias)^2}$$

$$u(bias) = \sqrt{RMS_{bias}^{\ 2} + u(C_{ref})^2}$$ = 0.16 (16 %)

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$ = 0.16 (16 %)

$$u(C_{ref}) = \frac{S_R}{\sqrt{n}}$$ = 0.20/10 (2 %)

- Media de 100 labs
- 20% de media de la RSD-interlabs

u = 24%

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Los datos de los PTs también pueden formar, por sí mismos, la base para una estimación de la incertidumbre

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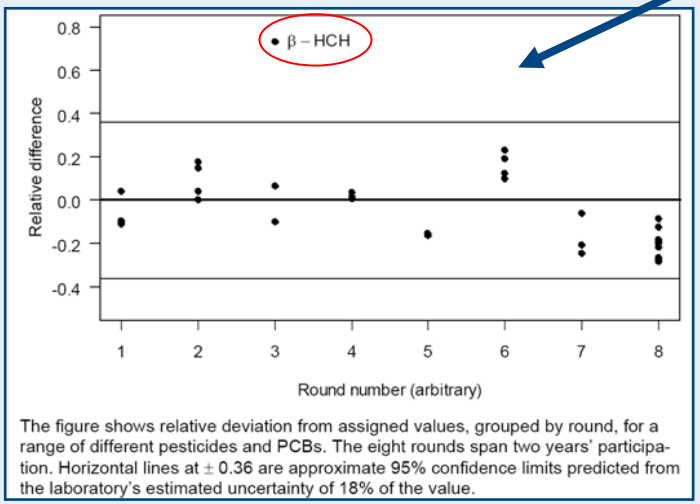
U (%) ~ Desviación estándar de las diferencias relativas

EXAMPLE 9: PESTICIDE RESIDUES IN FOODSTUFFS

Sector	Measurand / Matrix	Technique	Approaches for	
			estimation	verification
Food chain	Organochlorine pesticides and PCBs	Gas chromatography / Mass spectrometric detection (GC-MS)	Single laboratory validation data	PT performance

Table 1: Laboratory estimates of uncertainty

Sample type	Analyte[Note 1]	Estimated uncertainty (RSD[Note 2])
Fruit and vegetable	Multiple organochlorine pesticides	0.17 (17%)
Meat product (kidney fat)	Multiple organochlorine pesticides	0.18 (18%)



The figure shows relative deviation from assigned values, grouped by round, for a range of different pesticides and PCBs. The eight rounds span two years' participation. Horizontal lines at ± 0.36 are approximate 95% confidence limits predicted from the laboratory's estimated uncertainty of 18% of the value.

S = 15 %

Table 2: PT results for pesticides in food matrices (source: FAPAS reports [1])

Round	Material	Pesticide	Assigned value x_{ref} ug kg^{-1}	Laboratory value x_i ug kg^{-1}	Difference (x_i-x_{ref}) ug kg^{-1}	Relative difference $(x_i-x_{ref}) / x_{ref}$
1	HVO*	heptachlor	64.6	58	-6.6	-0.10
1	HVO	PCB 101	35.4	32	-3.4	-0.10
1	HVO	PCB 52	25.9	23	-2.9	-0.11
1	HVO	p,p'-DDT	65.5	68	2.5	0.04
2	Milk powder	*cis*-chlordane	32.3	38	5.7	0.18
2	Milk powder	γ-HCH	41	47	6	0.15
2	Milk powder	p,p'-DDE	36	36	0	0.00
2	Milk powder	*trans*-chlordane	38.5	40	1.5	0.04
3	Chicken	β-HCH	31.8	55	23.2	0.73
3	Chicken	p,p'-DDE	34.8	37	2.2	0.06
3	Chicken	*trans*-heptachlor epoxide	50	45	-5	-0.10
4	HVO	γ-HCH	39.6	41	1.4	0.04
4	HVO	oxychlordane	44.2	45	0.8	0.02
4	HVO	trans-chlordane	64.6	65	0.4	0.01
5	HVO	aldrin	41.4	35	-6.4	-0.15
5	HVO	α-endosulfan	40.6	34	-6.6	-0.16
5	HVO	PCB 101	41.3	35	-6.3	-0.15
5	HVO	quintozene	52.4	NA		
6	Milk powder	dieldrin	32.9	37	4.1	0.12
6	Milk powder	γ-HCH	45.5	56	10.5	0.23
6	Milk powder	o,p'-DDT	49.1	54	4.9	0.10
6	Milk powder	PCB 52	37.8	45	7.2	0.19
7	Chicken	α-HCH	30.5	28.6	-1.9	-0.06
7	Chicken	α-endosulfan	37.2	29.4	-7.8	-0.21
7	Chicken	pp'-DDT	41.8	31.4	-10.4	-0.25
8	Vegetable oil	γ-HCH	33.7	30.8	-2.9	-0.09
8	Vegetable oil	oxychlordane	41.6	36.4	-5.2	-0.13
8	Vegetable oil	PCB 101	46.8	38.1	-8.7	-0.19
8	Vegetable oil	PCB 118	44.5	32	-12.5	-0.28
8	Vegetable oil	PCB 138	62.1	49.8	-12.3	-0.20
8	Vegetable oil	PCB 153	52.6	38.6	-14	-0.27
8	Vegetable oil	PCB 180	52.3	37.8	-14.5	-0.28
8	Vegetable oil	PCB 28	26.9	21.1	-5.8	-0.22
8	Vegetable oil	PCB 52	34.1	27.9	-6.2	-0.18

*HVO = hydrogenated vegetable oil

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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 %

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

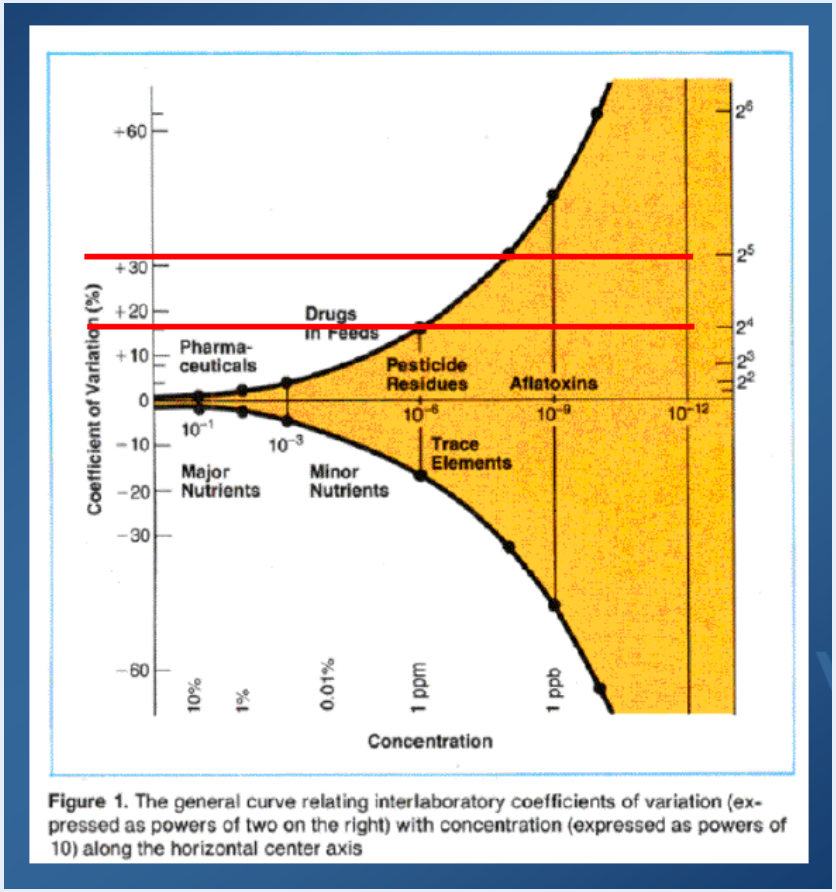

Figure 1. The general curve relating interlaboratory coefficients of variation (expressed as powers of two on the right) with concentration (expressed as powers of 10) along the horizontal center axis

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21. As is an emerging practice in the EC and elsewhere already, empirical top-down estimation of ±50% MU could complement a mathematically stringent bottom-up calculation model if the respective empirical quality criteria are met. Alternatively the Horwitz formula approach of estimating concentration-dependent MU based on the evaluation of results of interlaboratory collaborative tests could be applied as well. However, the laboratory must prove the applicability of this uncertainty value to their measurements.

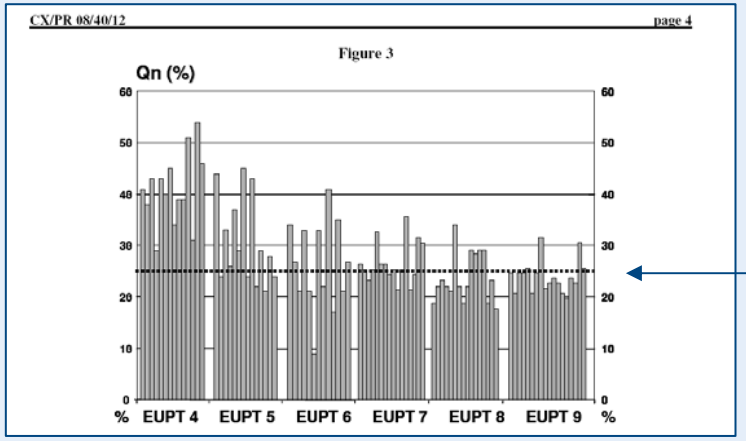
20. Applying a PT-based simplified ±50% MU approach should only be used by individual laboratories if the following analytical performance and quality criteria can be demonstrated:

(a) Within-laboratory SD smaller than the between-laboratories SD.

(b) Successful participation in PT schemes (z-score ≤|2| for 95%, z-score ≤|3| for not more than 5% of the values).

(c) Small bias from method and/or laboratory recovery tests.

(d) Verification of analytical performance by regularly analysing suitable reference material, if available.



U = 50%
(K = 2; 95%)

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Utilización de los PTs para "Verificar" la Incertidumbre estimada mediante otras aproximaciones

$$\zeta = \frac{x - x_a}{\sqrt{u(x)^2 + u(x_a)^2}}$$

Valor absoluto entre 0 y 2 → **Correcta**

Valor absoluto > 2 → **Infraestimada**

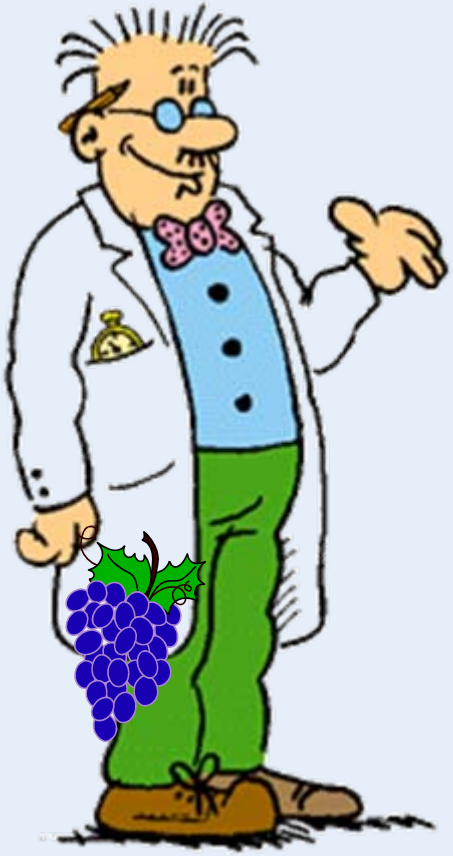
with:

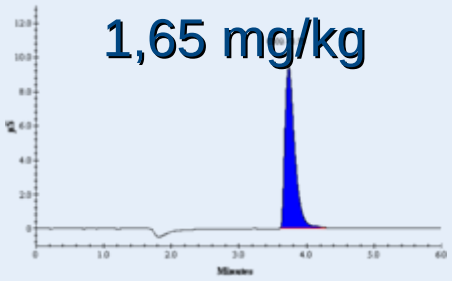
x	=	laboratory result
x_a	=	assigned value
u(x)	=	standard uncertainty of laboratory results
$u(x_a)$	=	standard uncertainty of assigned values

Uncertainties are considered correct if |ζ| is in the range 0 to 2; underestimated if |ζ| is frequently over 2.

¿Resultado Violativo o no Violativo?

Resultado = 1,65 ± 0,82 mg/kg ***(k = 2; 95%)***





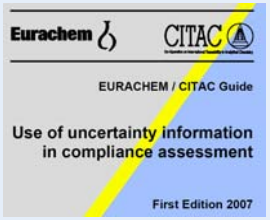
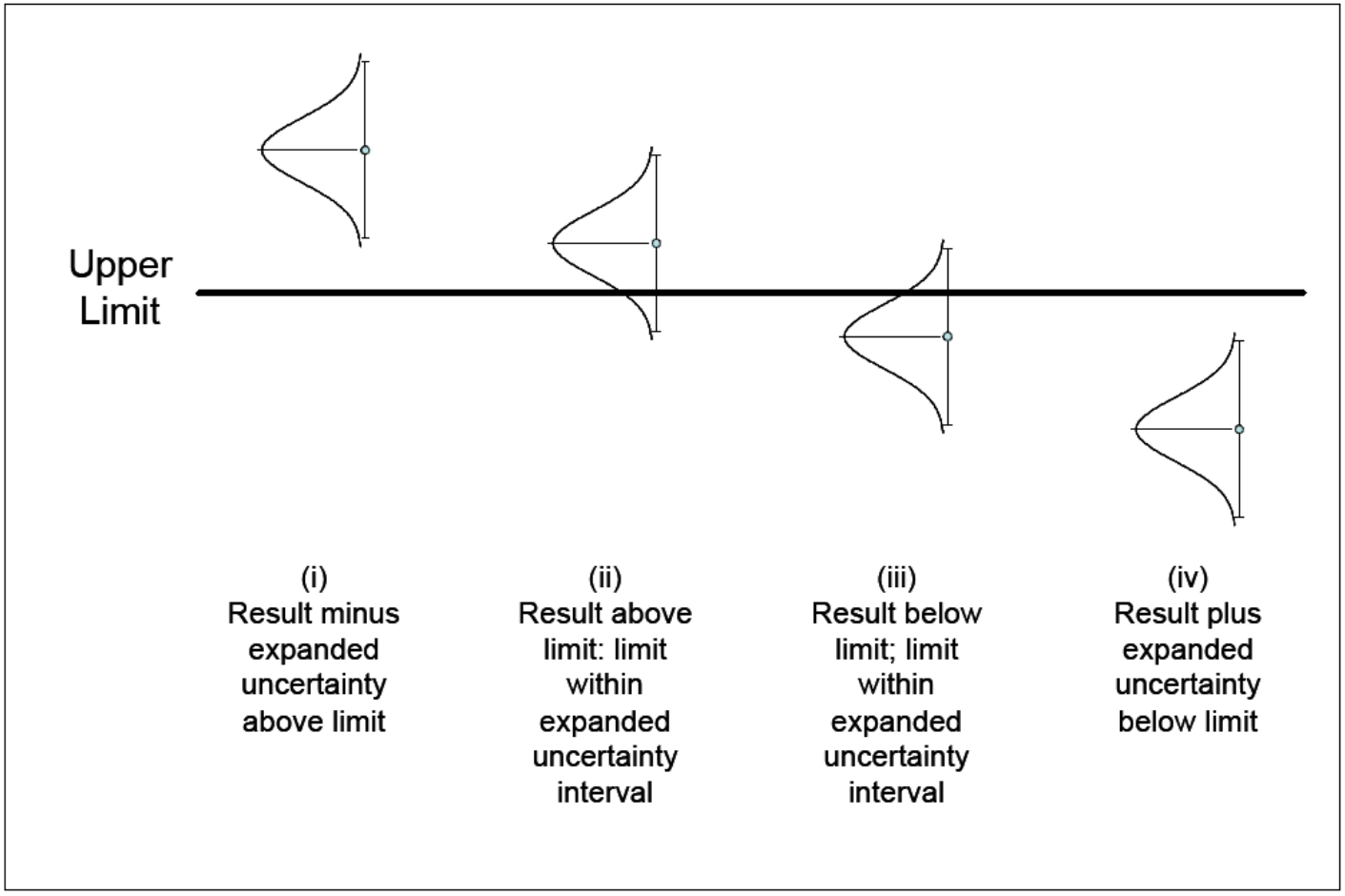
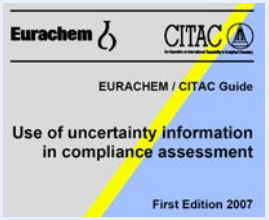


Figure 1 Assessment of Compliance with an Upper Limit





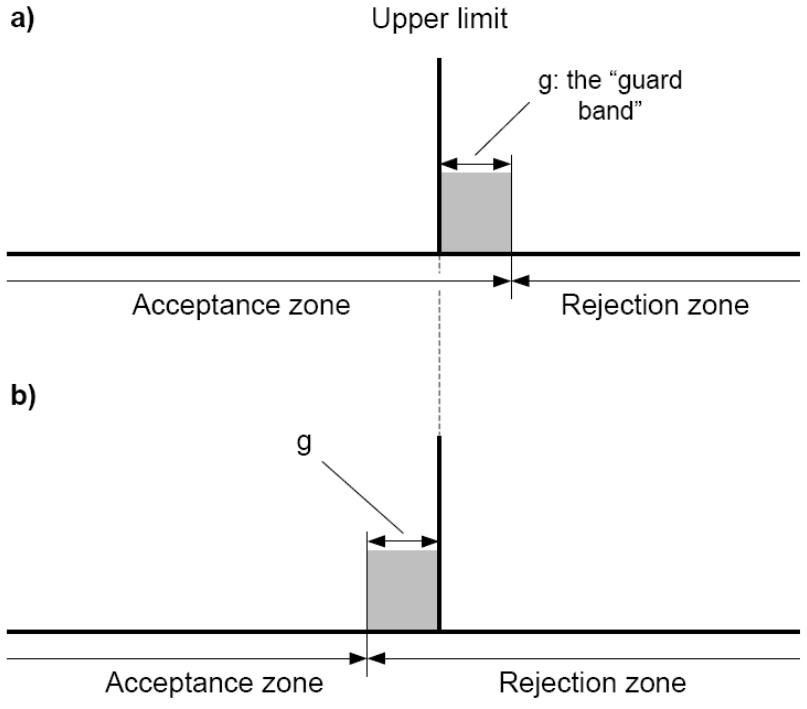
4. Decision rules and Acceptance zones

The key to the assessment of compliance is the concept of "Decision rules". These rules give a prescription for the acceptance or rejection of a product based on the measurement result, its uncertainty and the specification limit or limits, taking into account the acceptable level of the probability of making a wrong decision. On the basis of the Decision rules, an "Acceptance zone" and a "Rejection zone" are determined, such that if the measurement result lies in the acceptance zone the product is declared compliant and if in the rejection zone it is declared non-compliant.

a) High confidence of correct rejection →

b) High confidence of correct acceptance →

Figure 2: Acceptance and Rejection zones for an Upper Limit



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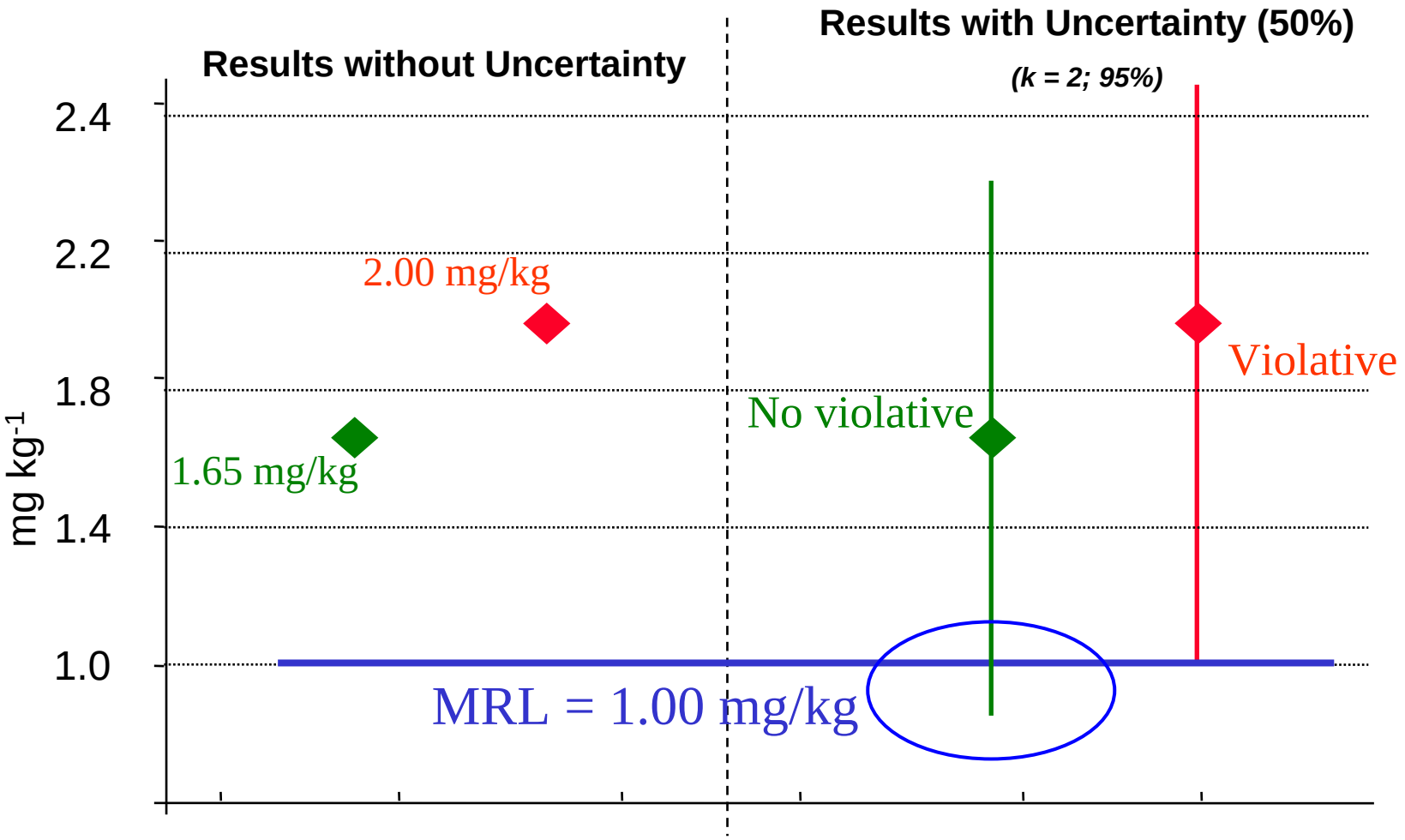

Con una Incertidumbre expandida del 50%
un resultado (X) será violativo cuando X > 2 MRL