Examples of MU estimation

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PROPOSED EXAMPLES TO BE INCLUDED IN THE GUIDELINES ON ESTIMATION OF UNCERTAINTY FOR PESTICIDE RESIDUES

In all the examples the combined relative standard uncertainty (u´) is being calculated.

Then, the coverage factor considered is two (k = 2, with a 95% confidence interval)

Therefore the expanded relative uncertainty (U´) is calculated as:

$$U´ = k \times u´$$

1st Approach

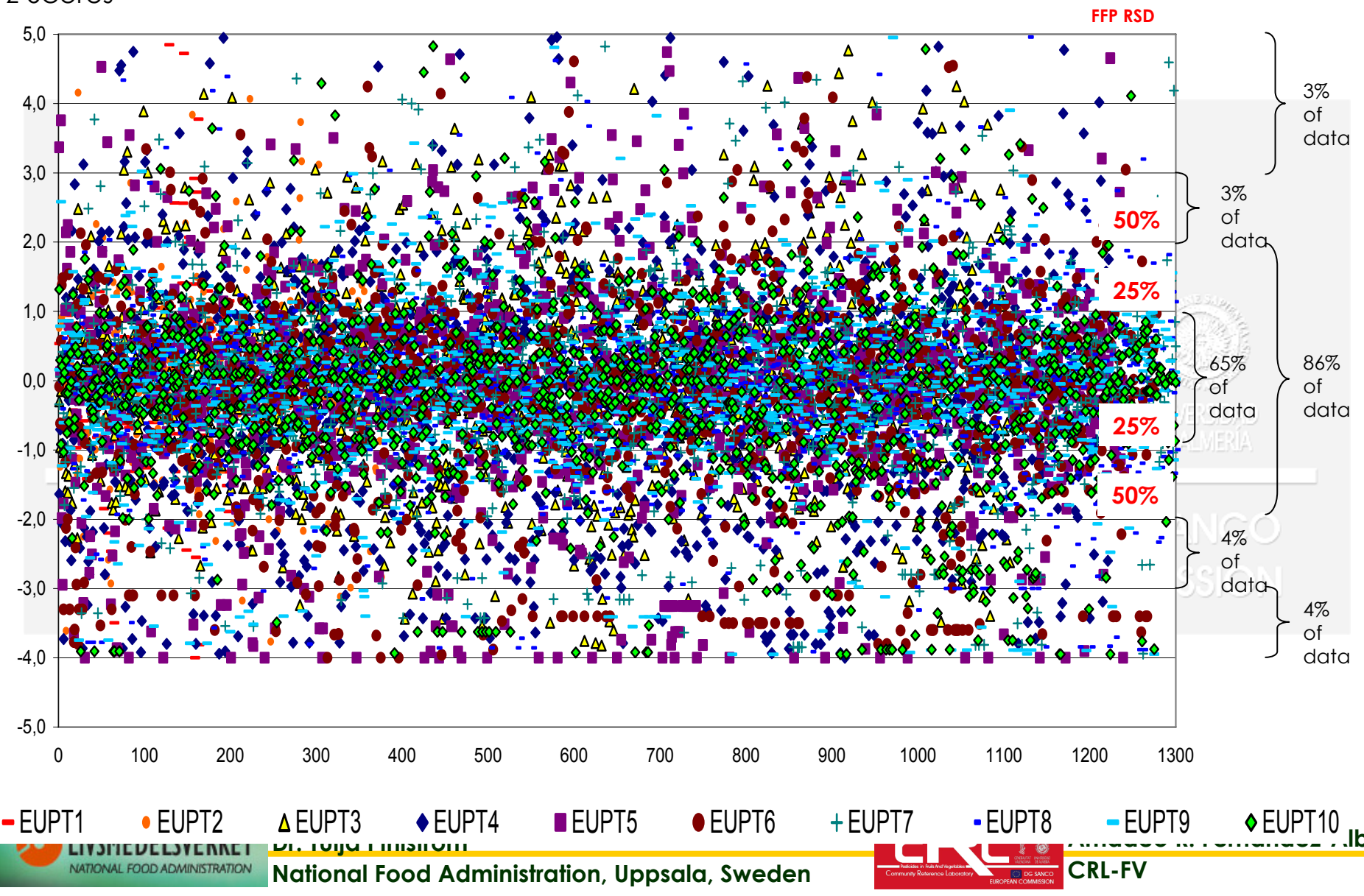
–

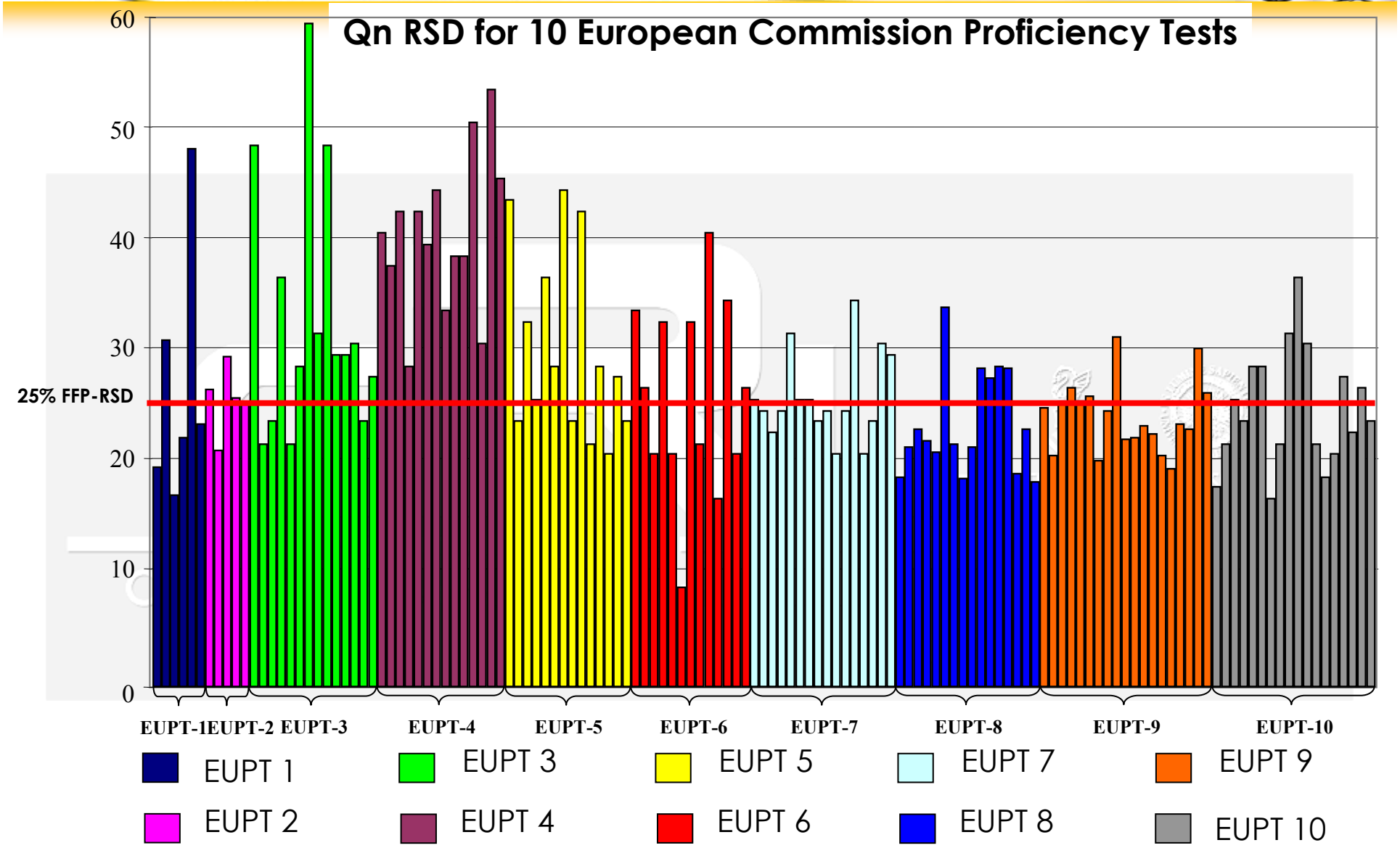
Estimating uncertainty based on PT standards

$$u' = 25\ \%$$

$$U = k * u' = 2 * 25 = 50\%$$

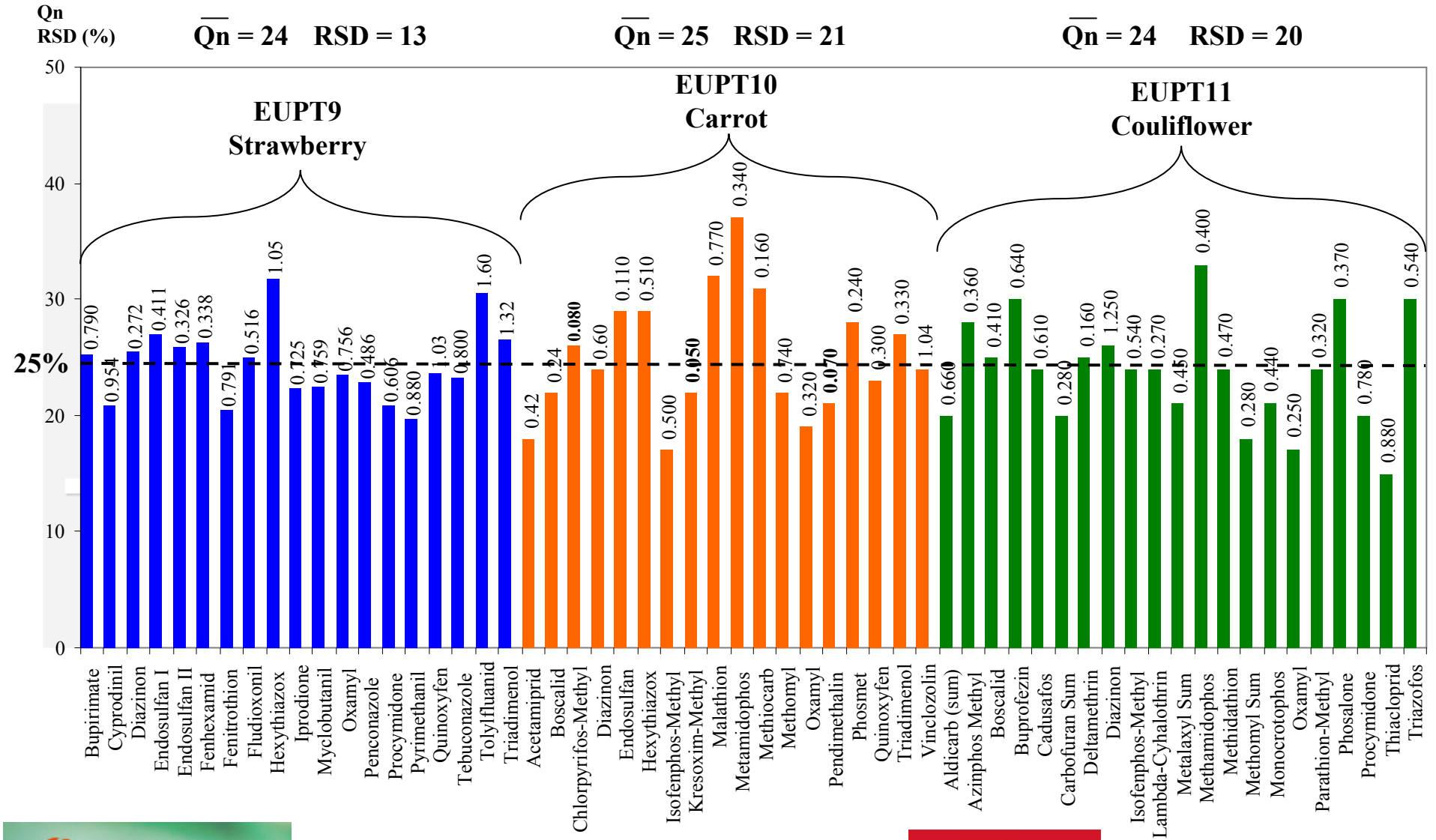
10 EUPT z-Score Results: 12753





Ref.: Medina-Pastor P, Rodriguez-Torreblanca C, Andersson A, Fernandez-Alba A R (2010) Trends in Analytical Chemistry 29:70-83

Qn RSD for EUPT 9 to 11



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2nd Approach

–

Estimating uncertainty based on Horwitz Equation or further modifications

Horwitz

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$$RSD_{Horwitz}\ (\%) = 0.22c^{0.8495}$$

C = 0.01 mg/Kg RSD_H = 32% Lowest MRL

U = k * u´ = 2 * 32 = 64%

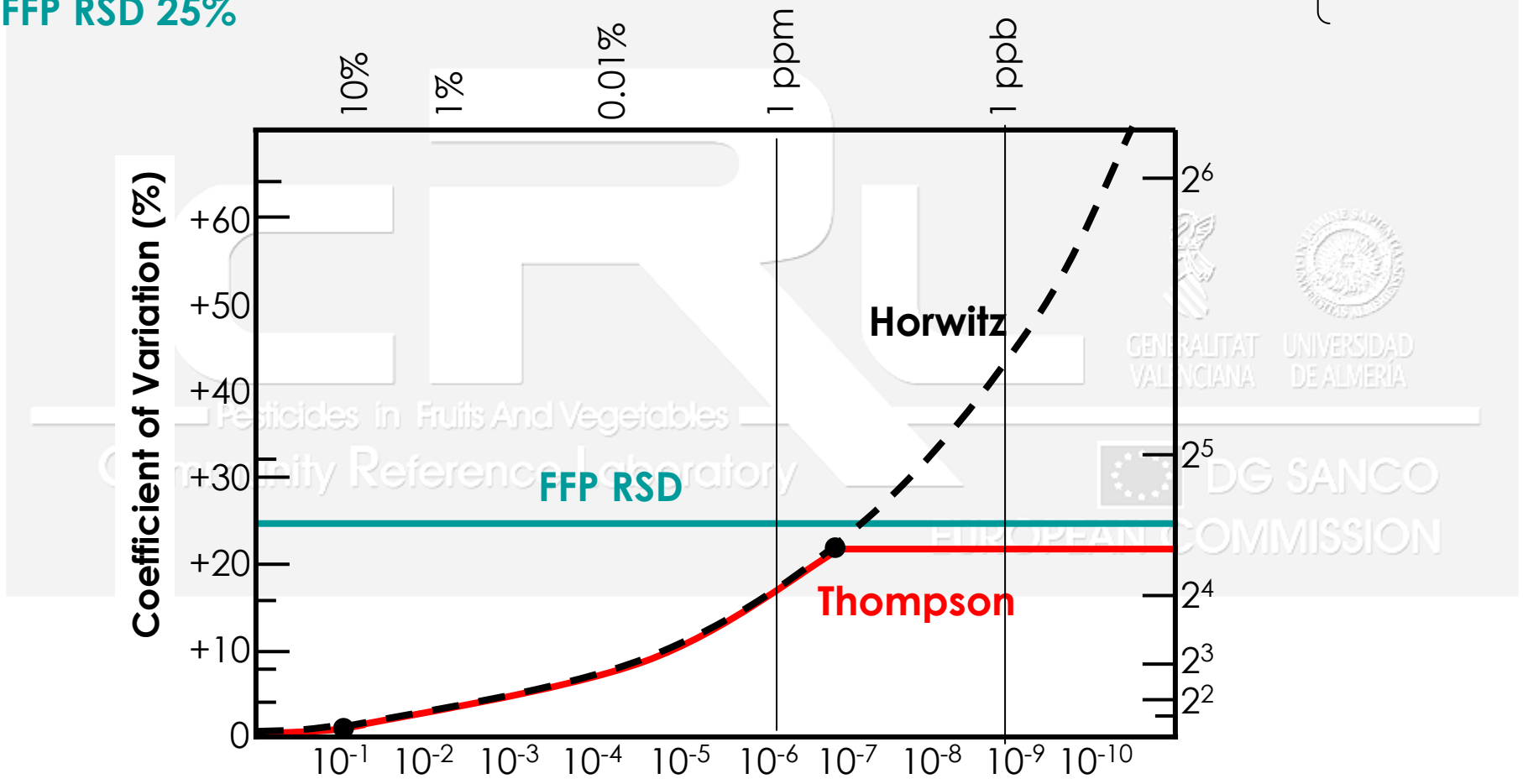
C = 0.05 mg/Kg RSD_H = 25% Average MRL

U = k * u´ = 2 * 25 = 50%

Thompson σ $\begin{cases} 0.22c & \text{if } c<1.2\times10^{-7} \\ 0.22c^{0.8495} & \text{if } 1.2\times10\text{-}7\leq c \leq 0.138 \\ 0.01c^{0.5} & \text{if } c>0.138 \end{cases}$

Horwitz σ $\begin{cases} 0.22c^{0.8495} \end{cases}$

FFP RSD 25%



3rd Approach

–

Estimating uncertainty based only on data from proficiency test participation

PT Data

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Considerations:

- Participation of laboratories at least in 3 proficiency tests; the number of pesticides present in the sample should be taken into account (should be high enough).

- Pesticides considered that are present in the proficiency test should be those in the scope of the laboratory.

- Proficiency test matrix (for the scope of the lab) should be considered too

- Two examples are given, one for GC scope and the other for LC scope for two different laboratories and for matrix with high water content.
- A third example is given for GC and LC together and for two group matrices

Example 1: GC-MS/MS

EUPT3 Cucumber	
Pesticide	(xi – X) / X
Carbendazim	0,071
Deltamethrin	-0,406
Diazinon	0,028
Endosulfan	-0,086
Metalaxyl	-0,175
Permethrin	0,172
Pirimiphos-methyl	0,184
Vinclozolin	-0,174

EUPT5 Lettuce	
Pesticide	(xi – X) / X
Diazinon	-0,052
lambda-Cyhalothrin	0,122
Parathion	0,012
Phosmet	-0,226
Propyzamide	-0,133
Tolclofos-methyl	0,127

EUPT8 Aubergine	
Pesticide	(xi – X) / X
Bifenthrin	-0,047
Bromopropylate	0,069
Carbendazim	-0,004
Chlorpyrifos	-0,050
Cyprodinil	0,011
Diazinon	-0,167
Dichlofluanid	-0,020
Lambda-cyhalothrin	-0,033
Myclobutanil	-0,264
Parathion	1,223
Pirimicarb	-0,159

RSD	0.256
u'	25.6%
U´	51.2%

EUPT10 Carrot	
Pesticide	(xi – X) / X
Chlorpyrifos-methyl	-0,282
Diazinon	-0,317
Endosulfan Sulphate	-0,418
Isofenphos-methyl	-0,126
Phosmet	-0,411
Quinoxifen	-0,181
Vinclozolin	-0,135

EUPT11 Cauliflower	
Pesticide	(xi – X) / X
*Deltamethrin	-0,121
*Diazinon	-0,088
Isofenphos-Methyl	-0,078
*Lambda-Cyhalothrin	-0,207
*Metalaxyl Sum	-0,011
*Parathion-Methyl Sum	-0,134
*Phosalone	0,041
*Procymidone	-0,038

xi = lab. result given for specific pesticide
X = assigned value for specific pesticide

Example 2: LC-MS/MS

EUPT 2 Apple	
Pesticides	(xi – X) / X
Carbendazim	0,325
Thiabendazole	0,358

EUPT 3 Cucumber	
Pesticides	(xi – X) / X
Acephate	0,993
Carbendazim	0,173
Imazalil	0,765
Methamidophos	0,860
Propoxur	0,126

EUPT 4 Orange	
Pesticides	(xi – X) / X
Carbofuran	-0,012
Imazalil	0,221
Omethoate	-0,173

EUPT 5 Lettuce	
Pesticides	(xi – X) / X
Acephate	-0,184
Methiocarb-sulphoxide	-0,084
Omethoate	-0,226

EUPT 6 Tomate	
Pesticides	(xi – X) / X
Dimethoate	0,076
Imazalil	0,162
Imidacloprid	-0,076
Oxydemeton Methyl	0,018
Thiabendazole	0,287

EUPT 7 Grapes	
Pesticides	(xi – X) / X
Acetamiprid	0,014
Carbaryl	-0,040
Dimethoate	0,122
Fenhexamid	0,041
Imidacloprid	0,084
Methomyl	-0,039
Thiabendazole	0,521

EUPT 8 Aubergine	
Pesticides	(xi – X) / X
Acetamiprid	0,153
Carbaryl	0,153
Carbendazim	-0,112
Imazalil	0,129

EUPT 9 Strwaberries	
Pesticides	(xi – X) / X
Bupirimate	0,215
Fenhexamid	0,104
Hexythiazox	0,210
Oxamyl	0,095
Quinoxyfen	0,243
Triadimenol	0,205

EUPT 10 Carrots	
Pesticides	(xi – X) / X
Acetamiprid	0,002
Boscalid	-0,107
Hexythiazox	-0,149
Methamidophos	0,259
Methiocarb -sum	0,459
Methomyl	-0,018
Oxamyl	0,093
Quinoxyfen	-0,255
Triadimenol	-0,036

EUPT 11 Cauliflower	
Pesticides	(xi – X) / X
Aldicarb (sum)	-0,030
Boscalid	-0,159
Methamidophos	-0,187
Methomyl Sum	-0,054
Oxamyl	-0,091
Thiacloprid	-0,146

RSD	0.263
U’	26.3%
U´	52.6%

xi = lab. result given for specific pesticide
X = assigned value for specific pesticide

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EUPT9 Strawberries	
Pesticide	(xi – X) / X
Bupirimate	0,418
Cyprodinil	0,122
Diazinon	0,555
Endosulfan I	0,606
Endosulfan II	0,288
Fenhexamid	0,521
Fenitrothion	0,259
Fludioxonil	0,399
Hexythiazox	0,086
Iprodione	0,342
Myclobutanil	0,296
Oxamyl	-0,083
Penconazole	0,193
Procymidone	0,259
Pyrimethanil	0,085
Quinoxifen	0,117
Tebuconazole	0,288
Tolylfluanid	0,550
Triadimenol	0,515

EUPT10 Carrots	
Pesticide	(xi – X) / X
Acetamiprid	0,193
Boscalid	0,208
Chlorpyrifos-methyl	0,231
Diazinon	0,264
Endosulfan Sulphate	0,089
Hexythiazox	0,289
Isofenphos-methyl	0,361
Kresoxim-methyl	0,120
Malathion SUM	0,402
Methamidophos	-0,315
Methiocarb -sum	0,510
Methomyl	0,031
Oxamyl	0,047
Pendimethalin	0,284
Phosmet	0,343
Quinoxifen	0,379
Triadimenol	0,202
Vinclozolin	0,250

EUPT11 Cauliflower	
Pesticide	(xi – X) / X
Aldicarb Sum	-0,134
Azinphos Methyl	-0,225
Boscalid	-0,191
Buprofezin	-0,009
Cadusafos	-0,141
Carbofuran Sum	0,011
Deltamethrin	0,038
Diazinon	0,248
Isofenphos-Methyl	-0,135
Lambda-Cyhalothrin	0,079
Metalaxyl Sum	0,160
Methamidophos	-0,357
Methidathion	0,771
Methomyl Sum	-0,029
Monocrotophos	-0,106
Oxamyl	-0,046
Parathion-Methyl Sum	0,003
Phosalone	-0,239
Procymidone	-0,004
Thiacloprid	0,138
Triazofos	-0,165

Example 3: GC-MS/MS and LC-MS/MS

RSD	0.245
u'	24.5%
U´	49.0%

xi = lab. result given for specific pesticide
X = assigned value for specific pesticide

Approaches based on a combination of precision & bias

$$U = \sqrt{A^2 + B^2}$$

4th Approach

Estimating uncertainty based on intra-laboratory validation and laboratory bias based on PT data

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

Being:

$u'(R_w)$ = intermediate precision relative standard uncertainty, based on intra-laboratory validation and/or QC data.

$u'(bias)$ = relative standard uncertainty component from method and laboratory bias, based on PT data.

$u'(R_w)$ Comes from reproducibility data (validation data)

Considerations:

- *How many matrices?* at least 2 from the same group

- *How many pesticides from the scope of the method?* At least 20

- *What concentration level?*
  One at least at 0.01 mg/Kg
  A second one at 0.05-0.2mg/Kg

- Number of replicates? at least 5

The **RSD** is calculated from each pesticide **recovery data** and then it is calculated the average of all the RSD of the overall scope.

u'(bias)

Comes from the bias of the laboratory when participating in PTs

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

RMS'_{bias} = root mean square of relative bias values

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

$bias'_i$ = relative bias of PT $_i$ $[x_i - Median_i)/Median_i]$
m = total number of pesticides in all PT schemes

u'(Cref) = average relative standard uncertainty of assigned values

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

S'_{Ri} = inter-laboratory relative standard deviation of PTi (or Qn)
n_i = number of results reported for i pesticides in each PT
m = total number of pesticides in all PT schemes

Example 1: for LC method

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

Reproducibility Data

Recovery Characteristics	Mean Recovery (%)	Standard Deviation SD	Relative Standard Deviation RSD (%)	$u'(R_w)$
127 pesticides LC-MS/MS 0.05mg/Kg Strawberries 5 replicates	100	6	6	0.06

For LC-MS/MS

EUPT No.	Pesticides	[(xi - X)/X]^2
	Carbendazim	0,1059
2	Thiabendazole	0,1279
	Acephate	0,9863
	Carbendazim	0,0301
	Imazalil	0,5847
	Methamidophos	0,7390
3	Propoxur	0,0159
	Carbofuran	0,0001
	Imazalil	0,0489
4	Omethoate	0,0299
	Acephate	0,0339
	Methiocarb-sulf	0,0071
5	Omethoate	0,0510
	Dimethoate	0,0057
	Imazalil	0,0261
	Imidacloprid	0,0057
	Oxydemeton -methyl	0,0003
6	Thiabendazole	0,0822

EUPT No.	Pesticides	[(xi - X)/X]^2
	Acetamiprid	0,0002
	Carbaryl	0,0016
	Dimethoate	0,0150
	Fenhexamid	0,0017
	Imidacloprid	0,0070
	Methomyl	0,0015
7	Thiabendazole	0,2714
	Acetamiprid	0,0234
	Carbaryl	0,0234
	Carbendazim	0,0126
8	Imazalil	0,0166
	Bupirimate	0,0463
	Fenhexamid	0,0107
	Hexythiazox	0,0439
	Oxamyl	0,0091
	Quinoxyfen	0,0589
9	Triadimenol	0,0418

EUPT No.	Pesticides	[(xi - X)/X]^2
	Acetamiprid	0,002
	Boscalid	-0,107
	Hexythiazox	-0,149
	Methamidophos	0,259
	Methiocarb -sum	0,459
	Methomyl	-0,018
	Oxamyl	0,093
	Quinoxyfen	-0,255
10	Triadimenol	-0,036
	Aldicarb (sum)	-0,030
	Boscalid	-0,159
	Methamidophos	-0,187
	Methomyl Sum	-0,054
	Oxamyl	-0,091
11	Thiacloprid	-0,146
	Sum	**3.9461**

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$$\sum(\text{bias}'_i)^2 = 3.9461$$

$$RMS'_{bias} = \sqrt{\frac{\sum(\text{bias}'_i)^2}{m}} \qquad RMS'_{bias} = \sqrt{\frac{3.9461}{50}} = 0.2809$$

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

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

S'_{Ri} = inter-laboratory relative standard deviation of PTi (or Qn)
n_i = number of participants reporting S'_{Ri} results
m = total number of S'_{Ri}

Pesticides	S´ Ri	No Results	√No	S´Ri/ √ n
Carbendazim	0,27	58	7,616	0,035
Thiabendazole	0,26	69	8,307	0,031
Acephate	0,49	69	8,307	0,059
Carbendazim	0,24	75	8,660	0,028
Imazalil	0,60	84	9,165	0,065
Methamidophos	0,49	84	9,165	0,053
Propoxur	0,24	60	7,746	0,031
Carbofuran	0,29	54	7,348	0,039
Imazalil	0,39	68	8,246	0,047
Omethoate	0,54	49	7,000	0,077
Acephate	0,44	78	8,832	0,050
Methiocarb-sul.	0,37	32	5,657	0,065
Omethoate	0,45	61	7,810	0,058
Dimethoate	0,09	114	10,677	0,008
Imazalil	0,41	88	9,381	0,044
Imidacloprid	0,17	52	7,211	0,024
Oxydemeton-me	0,35	42	6,481	0,054
Thiabendazole	0,27	88	9,381	0,029
Acetamiprid	0,26	56	7,483	0,035
Carbaryl	0,25	101	10,050	0,025
Dimethoate	0,32	119	10,909	0,029
Fenhexamid	0,26	89	9,434	0,028
Imidacloprid	0,24	64	8,000	0,030
Methomyl	**0,25**	**71**	**8,426**	**0,030**
Thiabendazole	0,30	104	10,198	0,029

Pesticides	S´ Ri	No Results	√No	S´Ri/ √ n
Acetamiprid	0,19	78	8,832	0,022
Carbaryl	0,21	108	10,392	0,020
Carbendazim	0,34	94	9,695	0,035
Imazalil	0,29	107	10,344	0,028
Bupirimate	0,25	110	10,488	0,024
Fenhexamid	0,26	96	9,798	0,027
Hexythiazox	0,32	71	8,426	0,038
Oxamyl	0,24	111	10,536	0,022
Quinoxyfen	0,24	90	9,487	0,025
Triadimenol	0,27	100	10,000	0,027
Acetamiprid	0,18	85	9,220	0,020
Boscalid	0,22	74	8,602	0,026
Hexythiazox	0,29	80	8,944	0,032
Methamidophos	0,37	103	10,149	0,036
Methiocarb -sum	0,31	65	8,062	0,038
Methomyl	0,22	88	9,381	0,023
Oxamyl	0,19	84	9,165	0,021
Quinoxyfen	0,23	95	9,747	0,024
Triadimenol	0,27	103	10,149	0,027
Aldicarb (sum)	0,20	91	9,539	0,021
Boscalid	0,25	102	10,100	0,025
Methamidophos	0,33	109	10,440	0,032
Methomyl Sum	0,18	84	9,165	0,020
Oxamyl	0,17	89	9,434	0,018
Thiacloprid	0,15	82	9,055	0,017
			Sum	**1.6498**

$$u'(C_{ref}) = \frac{1.6498}{50} = 0.033$$

Because in EUPTs, the assigned value is the median, according to ISO 13528, $u'(C_{ref})$ must be multiplied by a factor of 1.253

$$u'(C_{ref}) = 0.033 * 1.253 = 0.041$$

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

$$u'(bias) = \sqrt{0.2809^2 + 0.041^2} = 0.2840$$

So:

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

$$u' = \sqrt{0.06^2 + 0.284^2} = 0.29 = 0.30$$

$$u' = 0.30$$

$$U = 0.30 * 2 = 0.60$$

Example 2: for GC method

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

Reproducibility Data

Recovery Characteristics	Mean Recovery (%)	Standard Deviation SD	Relative Standard Deviation RSD (%)	$U'(R_w)$
66 pesticides GC-MS/MS 0.05 mg/Kg Peach/Melon 3 replicates	112.9	9.0	8.0	0.08

EUPT No.	Pesticides	[(xi - X)/X]^2
EUPT8	Bifenthrin	0,0022
	Bromopropylate	0,0048
	Chlorpyrifos	0,0025
	Cyprodinil	0,0001
	Diazinon	0,0280
	Dichlofluanid	0,0004
	Lambda-cyhalothrin	0,0011
	Myclobutanil	0,0695
	Parathion	1,4963
	Pirimicarb	0,0253
EUPT9	Bupirimate	0,0458
	Cyprodinil	0,0007
	Diazinon	0,0380
	Endosulfan I	0,0040
	Endosulfan II	0,0191
	Iprodione	0,0018
	Myclobutanil	0,0076
	Procymidone	0,0000
	Pyrimethanil	0,0501
	Quinoxifen	0,0034
	Tebuconazole	0,0000
	Tolylfluanid	0,0066

EUPT No.	Pesticides	[(xi - X)/X]^2
EUPT10	Chlorpyrifos-methyl	0,0796
	Diazinon	0,1003
	Endosulfan Sulphate	0,1746
	Isofenphos-methyl	0,0159
	Phosmet	0,1689
	Quinoxifen	0,0328
	Vinclozolin	0,0181
EUPT11	*Deltamethrin	0,0146
	*Diazinon	0,0077
	Isofenphos-Methyl	0,0060
	*Lambda-Cyhalothrin	0,0428
	*Metalaxyl Sum	0,0001
	*Parathion-Methyl Sum	0,0181
	*Phosalone	0,0017
	*Procymidone	0,0015
	Sum	**2.4900**

$$\sum(bias'_i)^2 = 2.4900$$

$$RMS'_{bias} = \sqrt{\frac{\sum(bias'_i)^2}{m}} \qquad RMS'_{bias} = \sqrt{\frac{2.4900}{37}} = 0.2594$$

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

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

S'_{Ri} = inter-laboratory relative standard deviation of PTi (or Qn)
n_i = number of participants reporting S'_{Ri} results
m = total number of S'_{Ri}

Pesticides	S´ Ri	No Results	√No	S´Ri/ √ n
Bifenthrin	0,233	119	10,909	0,021
Bromopropylate	0,222	125	11,180	0,020
Chlorpyrifos	0,220	127	11,269	0,020
Cyprodinil	0,188	114	10,677	0,018
Diazinon	0,217	127	11,269	0,019
Dichlofluanid	0,289	113	10,630	0,027
Lambda-cyhalothrin	0,289	121	11,000	0,026
Myclobutanil	0,192	114	10,677	0,018
Parathion	0,232	114	10,677	0,022
Pirimicarb	0,184	114	10,677	0,017
Bupirimate	0,253	110	10,488	0,024
Cyprodinil	0,209	115	10,724	0,020
Diazinon	0,260	130	11,402	0,023
Endosulfan I	0,270	124	11,136	0,024
Endosulfan II	0,259	124	11,136	0,023
Iprodione	0,220	117	10,817	0,020
Myclobutanil	0,230	118	10,863	0,021
Procymidone	0,209	129	11,358	0,018
Pyrimethanil	0,197	116	10,770	0,018
Quinoxifen	0,237	90	9,487	0,025
Tebuconazole	0,233	107	10,344	0,023
Tolylfluanid	0,305	118	10,863	0,028
Chlorpyrifos-methyl	0,260	126	11,225	0,023
Diazinon	0,240	125	11,180	0,021

Pesticides	S´ Ri	No Results	√No	S´Ri/ √ n
Endosulfan Sulphate	0,290	110	10,488	0,028
Isofenphos-methyl	0,170	69	8,307	0,020
Phosmet	0,280	95	9,747	0,029
Quinoxyfen	0,230	95	9,747	0,024
Vinclozolin	0,240	124	11,136	0,022
Deltamethrin	0,250	130	11,402	0,022
Diazinon	0,260	144	12,000	0,022
Isofenphos-Methyl	0,240	86	9,274	0,026
Lambda-Cyhalothrin	0,240	138	11,747	0,020
Metalaxyl Sum	0,210	122	11,045	0,019
Parathion-Methyl Sum	0,240	129	11,358	0,021
Phosalone	0,300	136	11,662	0,026
Procymidone	0,200	136	11,662	0,017
			Sum	**1.0976**

$$u'(C_{ref}) = \frac{1.0976}{37} = 0.030$$

Because in EUPT, the assigned value is median, according to ISO 13528, $u'(C_{ref})$ must be multiplied by a factor of 1.253

$$u'(C_{ref}) = 0.030 * 1.253 = 0.037$$

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

$$u'(bias) = \sqrt{0.2594^2 + 0.0371^2} = 0.2621$$

So:

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

$$u' = \sqrt{0.06^2 + 0.262^2} = 0.274 = 0.27$$

$$u' = 0.27$$

$$U = 0.27 * 2 = 0.54$$

5th Approach
–
Estimating uncertainty based on intra-laboratory data (validation data/QC data)

$$U_{c,rel} = \sqrt{\frac{RSD_R^2}{n_m} + U_{mr,REL}^2 + \frac{RSD'^2_R}{n_R}}$$

$\frac{RSD_R^2}{n_m}$ = the relative standard deviation of 5 replicates at different calibration levels, where n_m is the number of replicates.

$U_{mr,REL}^2$ = relative standard deviation uncertainty derive from the use of reference material, volumetric calibration, weighting calibration…; it is considered between 1 and 2%

$\frac{RSD'^2_R}{n_R}$ = is the relative standard deviation of all the recovery data, at different levels, different matrices and different pesticides being n_R the number of data used.

$$u' = \sqrt{(0.05)^2 + (0.01)^2 + (0.11)^2} = 0.12 \quad (\sim 0,\ \sim 0)$$

$$U = 12 * 2 = 24$$

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But this way of calculating it may vary according to internal QC and the sources of error influencing the final results.

Many factors may be neglected and only recovery factors may be taken into account

Example 1

At the beginning of validation it is starts with repeatability experiments:

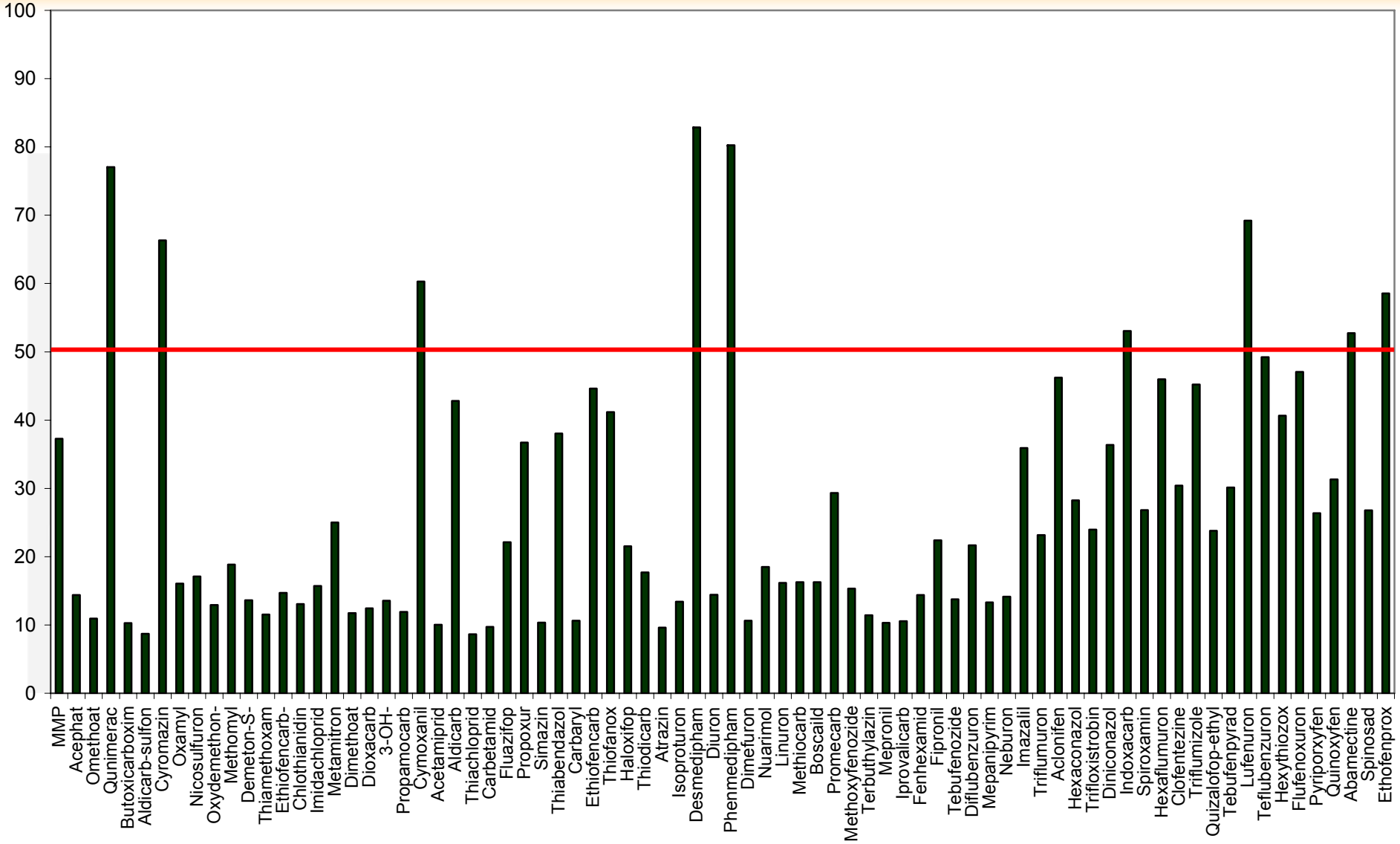
- 5-fold spiking experiments at 0,01 mg/kg
- 5-fold spiking experiments at 0,05 mg/kg
- conditions: same operator, same calibration, same matrix, same level, same day

Continuously data collected from spiking experiments - daily/weekly/monthly/at the end of the year and a control chart is produced.

Based on these reproducibility data (different operator, different calibrations, different matrices, different spiking levels) standard deviation from the mean recoveries (matrix one by one) is calculated and measurement uncertainty is estimated.

The an average MU is calculated and plotted on control chart graphs.

Criterion: < 50%



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Example 2

Recovery Characteristics	Mean Recovery (%)	Standard Deviation SD	Relative Standard Deviation RSD (%)	Expanded MU (U´)
128 pesticides GC-MS/MS Apple/Carrot/Lettuce 3 replicates for 0.05 mg/Kg 5 replicates for 0.01 mg/Kg	88.9	10.8	12.9	25.8
170 pesticides LC-MS/MS Apple/Carrot/Lettuce 3 replicates for 0.05 mg/Kg 5 replicates for 0.01 mg/Kg	89.6	10.9	12.2	24.5

Example 3

Recovery Characteristics	Mean Recovery (%)	Standard Deviation SD	Relative Standard Deviation RSD (%)	Expanded MU (U´)
93 pesticides HPLC-MS/MS 0.01mg/Kg Persimmon/Lettuce/ Artichoke/Green Bean/ QC within 5 months	97.95	15.70	16	32
93 pesticides HPLC-MS/MS 0.01mg/Kg Orange/Grape QC within 5 months	95.81	16.74	17.5	35

Example 4

Recovery Characteristics	Mean Recovery (%)	Standard Deviation SD	Relative Standard Deviation RSD (%)	Expanded MU (U´)
66 pesticides GC-Q-MS 0.5/0.2/0.05mg/Kg Peach/Melon Orange/Grape QC within 5 months	104.6	16.56	14.80	29.6

Uncertainty Estimation Approaches Summary

Approach Number	Combined relative standard uncertainty(%) u´	Expanded relative Uncertainty (%) U´ (k=2,95%)
1	25	50
$2_{Horw.}$	32	64
$2_{Thom.}$	22	44
3	26	52
4	30	60
5	16	32