Uncertainty estimation from In-House Validation Studies. Determination of Organophosphorus Pesticides in Bread

This is the example A4 of the EURACHEM / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", Second Edition.

Model Equation:

{calculation of the level of pesticide in the sample:

$P_{op} = (I_{op} * c_{ref} * V_{op})/(I_{ref} * Rec * m_{sample}) * F_{hom} * 1e6$

but not used to calculate uncertainty}

{calculation of uncertainty}

$P_{op} = P_{op\ nominal} * f_{repeatability} * f_{bias} * f_{other}$;

List of Quantities:

Quantity	Unit	Definition
P_{op}	mg/kg	Level of pesticide in the sample
$P_{op\ nominal}$	mg/kg	Nominal level of pesticide in the sample
$f_{repeatability}$		Uncertainty contribution covering repeatability
f_{bias}		Uncertainty contribution due to bias (recovery)
f_{other}		Other uncertainty contributions

$P_{op\ nominal}$: Constant
Value: 1.11111111111111

The nominal value of the level of pesticide in the sample is not associated with any uncertainty. A value of 1/0.9 is chosen so that P_{op} will be 1, the the combined uncertainty of the result can be used directly as a relative uncertainty.

$f_{repeatability}$: Type B normal distribution
Value: 1
Expanded Uncertainty: =0.382/sqrt(2)
Coverage Factor: 1

Repeatability has been investigated in a precision study. A number of duplicate tests (same homogenised sample, complete extraction/determination procedure) were performed for typical organophosphorous pesticides found in different bread samples (for data see Table A4.2 in the EURACHEM / CITAC Guide). The normalised difference data (the difference between the duplicate results divided by the mean) provides a measure of the overall run to run variability. To obtain the estimated relative standard uncertainty for single determinations, the standard deviation of the normalised differences is taken and divided by sqrt(2) to correct from a standard deviation for pairwise differences to the standard uncertainty for the single values. This gives an uncertainty of 0.382/sqrt(2) = 0.27.

f_{bias}: Type B normal distribution
Value: 0.9
Expanded Uncertainty: =0.28/sqrt(42)
Coverage Factor: 1

Data from an in-house validation study was used to obtain data on recovery. On 42 spiked bread samples, the mean recovery was 90% with a standard deviation of 28%. The standard uncertainty of the recovery is calculated as the standard deviation of the mean, 0.28/sqrt(42).

f_{other}: Type B normal distribution
Value: 1
Expanded Uncertainty: 0.2
Coverage Factor: 1

This factor includes all other sources of uncertainty not adequately covered by $f_{repeatability}$ and f_{bias}. Due to the design of the precision study, all uncertainty contributions arising from balances and volumetric measurement devices are already covered by $f_{repeatability}$. This leaves only the purity of the reference standard, the possible nonlinearity of the GC response and the sample homogeneity as possible sources of uncertainty. The purity of the reference standard is biven by the manufacturer as 99.53% ±0.06%. Assuming a rectangular distribution, this would be an additional uncertainty of 0.0006/sqrt(3) = 0.00035. This uncertaintiy contribution is so small compared to e.g. the contribution of $f_{repeatability,}$ that it can be safely neglected. Linearity of the response of the GC within the given concentration range is established for the substances under investigation during the validation studies. No allowance is made for nonlinearity. Homogeneity of the bread samples has been estimated on the basis of the sampling method used. A number of feasible pesticide residue distribution scenarios were considered, and a simple binominal statistical distribution used to caluclate the standard uncertainty for the total included in the analysed sample. The scenarios, and the calculated relative standard uncertainties in the amount of pesticide in the final sample, were: Residue distributed on the top surface only: 0.58 (This scenario would arise in the case of decorative additions of whole grains to the surface of the bread) Residue distributed evenly over the surface only: 0.2 Residue distributed evenly throgh the sample, but reduced in concentration by evaporative loss or decomposition close to the surface: 0.05 - 0.10 The second scenario was chosen as the most likely worst case. Therefore an uncertainty of 0.2 was chosen.

Uncertainty Budgets:

P_{op}: Level of pesticide in the sample

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{op\ nominal}$	1.1111111111111 mg/kg					
$f_{repeatability}$	1.0000	0.2701	normal	1.0	0.27 mg/kg	63.3 %
f_{bias}	0.90000	0.04320	normal	1.1	0.048 mg/kg	2.0 %
f_{other}	1.0000	0.2000	normal	1.0	0.20 mg/kg	34.7 %
P_{op}	1.0000 mg/kg	0.3395 mg/kg				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
P_{op}	1.00 mg/kg	0.68 mg/kg	2.00	95% (t-table 95.45%)