Updates on Testing of Pesticide Residues in Food

29 October 2015

Food Testing – Pesticide Residues

- **Previous briefs available on websites of**
  - **Government Laboratory**
  - **Centre for Food Safety**

http://www.govtlab.gov.hk/

http://www.cfs.gov.hk/

Pesticide Residues in Food

- To avoid common mistakes in calculations
- To improve ruggedness of the analytical method
- To speed-up the result reporting cycle

Pesticide Residues in Food

- To avoid common mistakes in calculations
- Residue definition, MRL, Reporting Limit (RL)
- Portion of samples for laboratory analysis
- Data integration
- Quantitative Calibration
- Measurement Uncertainty

Pesticide Residues in Food

- **To avoid common mistakes in calculations**

- **Residue definition, MRL, Reporting Limit (RL)**
- **Portion of samples for laboratory analysis**

***Portion of Commodities to which CODEX Maximum Residue Limits Apply and which is Analyzed*, CAC/GL 41-1993 (Revision 1993, Amendment 2010), CODEX Alimentarius, 2010.**

➔ **Refer to previous presentation files for examples of calculation involved**

Data integration – Indoxacarb as Example

- **What is Indoxacarb ?**
- **ISO 1750 Amendment 3 (1981) ➔ Indoxacarb is the S-isomer, the only stereoisomer (CAS 173584-44-6, DPX-KN128)**
- **Residue study data uses:**
- **DPX-MP062 (3 + 1 of S + R isomer)**
- **DPX-JW062 (1 : 1 of S : R isomer)**
- **Consider any possible R / S isomer separation in GC or LC**
- **Consider the isomer ratio of reference standard / sample**
- **Consider the residue definition: Sum of indoxacarb and its R enantiomer**
- **Consider detector response factor of S- and R- isomers**
- **Consider PAM, JMPR and CODEX publications**
- **➔ Integrate peaks from all isomeric components**

Quantitative Calibration - Overview

- Multi-level Calibration – Linear Regression
- Multi-level Calibration – Relative Response Factor (RRF)
- Multi-level Calibration – Standard Addition
- Bracketing – by interpolation between two levels
- Single-level Calibration

Plotting concentration of target analyte with …

- Analyte Area
- Area Ratio from analyte / internal standard (IS)

➔Linearity of the plot / calculation

➔Relative or absolute acceptable calibration range

- SANCO/12571/2013
- ISO 11095:1996 – Linear Calibration Using Reference Materials

Matrix-matched Calibration

- Compensate matrix effect measured as detector response
- Matrix co-elution during chromatographic separation
- Ion-source effects

Solution-based Calibration

- Select relatively "interference free" m/z or SRM
- Ion-ratio of target analyte should be similar among:

  Solution-based <> Sample extract <> Matrix-matched
- Some analytes have less than three reliable MRM in some matrices-detector combinations

Procedural Standard Calibration

- Method dependent

→ e.g. Analytes require derivatisation before analysis

Compensation by adding Internal Standard vs "Matrix-Cal"

- **Isotopically labelled internal standard**

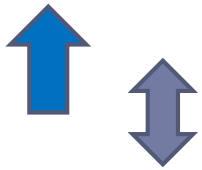
→ **Compensates matrix effect within sample extract, improve method performance (recovery, repeatability)**

→ **Insufficient clean-up / chromatographic separation would widen the RRT between labelled IS and native analyte**

- **Matrix-based calibration**

→ **Compensates matrix effect between sample and standard extract**

- **Other internal standard**



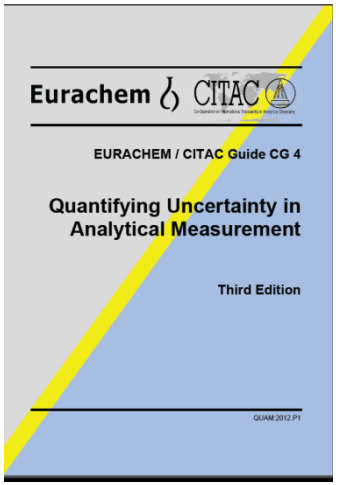
→ **IS and analyte may respond differently**

Measurement Uncertainty - Overview

Type A – Statistics

Type B – From other information

IUPAC



Measurement Uncertainty – Reference Documents

EU - Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed, SANCO/12571/2013

- Paragraphs E8 – E15

➔ Within-lab data

➔ "Inter-laboratory bias", evaluated by PT results

➔ Prerequisite to use of default MU (50%)

➔ Reporting limit vs lowest spike level

- Appendix C – Worked examples on MU estimation

➔ Participation of EUPT

➔ Within-lab data

Measurement Uncertainty – Reference Documents

CODEX - Guidelines on Estimation of Uncertainty of Results, CAC/GL 59-2006 (Amendment 2011)

- Approaches –

➔ EUPT participation ➔ 20-25% RSD from EUPTs ➔50% (k=2)

➔ Precision data – Horwitz approach

➔ Precision data – Inter-laboratory (collaboration / PT studies)

➔ In-house validation (including PT)

- Worked examples in Annex

Pesticide Residues in Food

- To improve ruggedness of the analytical method
  - Homogeneity of laboratory sub-sampling

➔ Suitable blender & food processor

  - Benefits:

➔ Blend all sample "in one go"

➔ Shorter blending time, avoid degradation of analytes

➔ Improve within-lab repeatability

Pesticide Residues in Food

- To improve ruggedness of the analytical method

- Clean-up materials

➔ dispersive SPE for GC and LC analysis

➔ SPE for GC analysis

➔ Choice of extraction solvent and pH

- Examples of International published methods

➔ EURL : http://www.eurl-pesticides.eu/

➔ USA : CLG-PST5, USDA method

➔ AOAC : 2007.1, Official Methods of Analysis

➔ GB, BS, Japan, CODEX... etc

Pesticide Residues in Food

- To improve ruggedness of the analytical method

- Automation of laborious steps

➔ Example: vertical shaker

- Benefits:

➔ Reproducible shaking conditions

➔ Avoid degradation of acid sensitive analytes

➔ Improve work efficiency:
Batch shaking of extraction and clean-up tubes

Pesticide Residues in Food

- To speed-up the result reporting cycle
- Maximize the analytes in multi-residue analysis
- Group-up analytical methods
- Screening → Confirmation → Quantitation
- Chromatographic run time
- Detector selection

Pesticide Residues in Food

- To speed-up the result reporting cycle
- Maximize the analytes in multi-residue analysis
- Group-up analytical methods

➔ Minimize number of injection and release instrument time

- Screening → Confirmation → Quantitation

➔ Most of the reported values are "Not Detected"

➔ Quantitative analysis of results below Reporting Limit (RL)

Pesticide Residues in Food

- To speed-up the result reporting cycle
- Detector selection
  - Limitation of traditional detectors, such as GC-ECD / FPD / PFPD / NPD and LC-DAD / FLD
  - "Limited specificity"
  - "Does not provide unambiguous identification"
  - Refer to paragraph C13 of SANCO/12571/2013

Pesticide Residues in Food

- To speed-up the result reporting cycle
- Fast GC / LC separation
- Detector selection - MS/MS, TOF, Orbitrap
- Benefits:

➔ Maximize the analyte per chromatographic run

➔ Remove matrix interferences

➔ Reduce repeating sample preparation and injections for confirmation

Thank You