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

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
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
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
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- 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
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- 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
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- 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
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- 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
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- **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)
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- **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
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- **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