Determination of Pesticides Residues in Baby Food

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Outline

- Introduction
- Challenges: methods, instrumentation
- Proficiency tests
- Conclusions

Introduction

Infants and young children are vulnerable group:

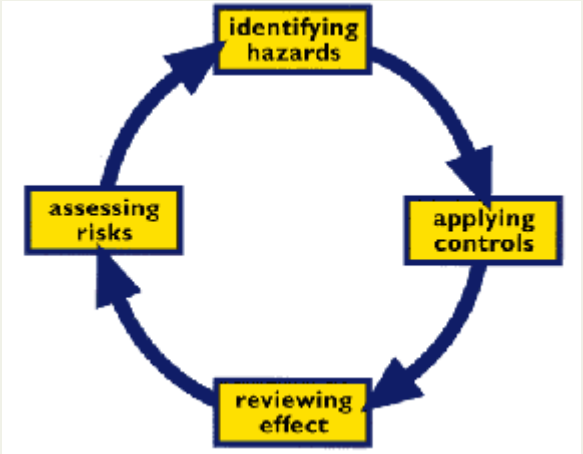
- **Relative food intake to body weight is the higher**
- **Diet is less varied**
- **Developing internal organs and central nervous system**

Increased chances of exposure

Risk assessment

- **Interest in collecting pesticide residue data at concentrations as low as possible to assess exposure**

- **Exposure assessment when <LOQ**
  - **Assume values of zero (under-estimates exposure)**
  - **Assume levels are at LOQ (over-estimates exposure)**



Legislation

- 1999/50/EC: MRL = 0.01 mg/kg for all pesticides

- 2006/141/EC Infant formulae and follow-on formulae
- 2006/125/EC baby food
  - Specific MRLs for selected substances
  - Banned list LOQ ≤ 0.003 mg/kg

- 2015 REVIEW AND RECOMMENDATION
- Co-ordinated programme?

Current Legislation

PESTICIDES WHICH SHALL NOT BE USED IN AGRICULTURAL PRODUCTION INTENDED FOR THE PRODUCTION OF PROCESSED CEREAL-BASED FOODS AND BABY FOODS

Table 1

Chemical name of the substance (residue definition)
Disulfoton (sum of disulfoton, disulfoton sulfoxide and disulfoton sulfone expressed as disulfoton)
Fensulfothion (sum of fensulfothion, its oxygen analogue and their sulfones, expressed as fensulfothion)
Fentin, expressed as triphenyltin cation
Haloxyfop (sum of haloxyfop, its salts and esters including conjugates, expressed as haloxyfop)
Heptachlor and *trans*-heptachlor epoxide, expressed as heptachlor
Hexachlorobenzene
Nitrofen
Omethoate
Terbufos (sum of terbufos, its sulfoxide and sulfone, expressed as terbufos)

Table 2

Chemical name of the substance
Aldrin and dieldrin, expressed as dieldrin
Endrin

SPECIFIC MAXIMUM RESIDUE LEVELS OF PESTICIDES OR METABOLITES OF PESTICIDES IN PROCESSED CEREAL-BASED FOODS AND BABY FOODS

Chemical name of the substance	Maximum residue level (mg/kg)
Cadusafos	0,006
Demeton-S-methyl/demeton-S-methyl sulfone/oxydemeton-methyl (individually or combined, expressed as demeton-S-methyl)	0,006
Ethoprophos	0,008
Fipronil (sum of fipronil and fipronil-desulfinyl, expressed as fipronil)	0,004
Propineb/propylenethiourea (sum of propineb and propylenethiourea)	0,006

Challenges

Availability of standards & methods

Suppression / sensitivity (certain compounds / matrices)

Carry-over, instrument maintenance and utilisation

Matrix-matching, AQC

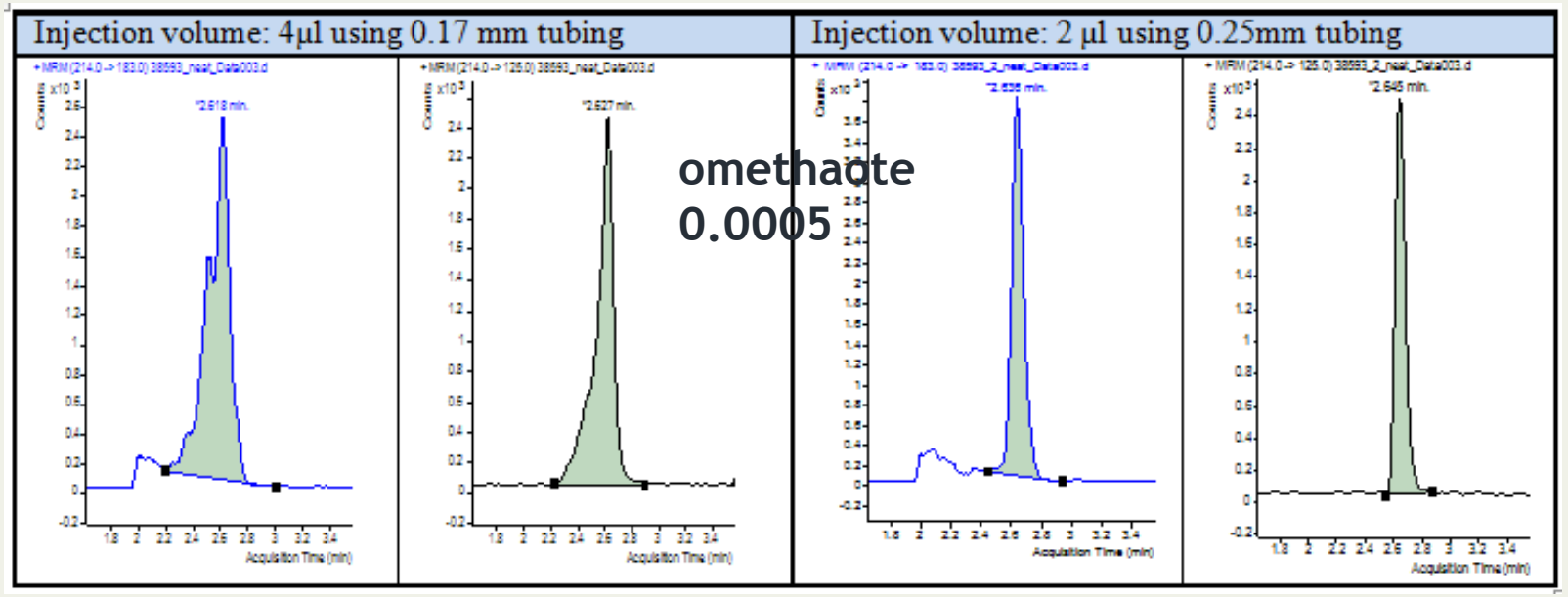
Cost / effort

Practical solutions

- Modified existing methods or new methods
- Use of over-spiking and/or ILIS
- intensive clean-up
- 7 LC-MS and 3 GC-MS based methods

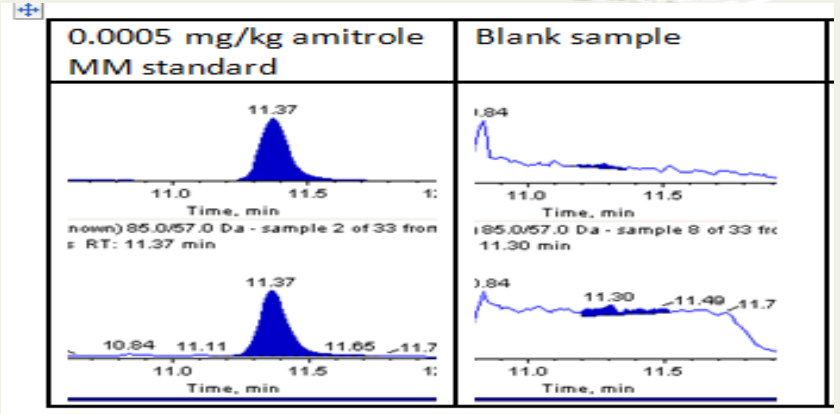
Methods

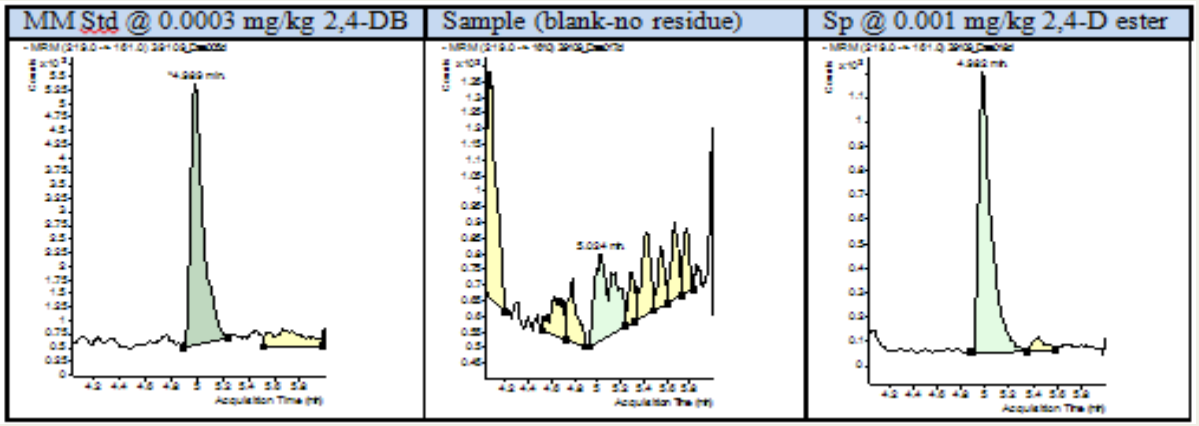
- Two LC-MS/MS MRM runs
- QuEChERS (with C_{18} clean-up)
- LC-MS/MS system flushed with phosphoric acid
- Extra solvent injections to minimise carryover
- Optimised injection conditions to improved peak



Methods

- Five LC-MS/MS SRM runs
  - amitrole
  - ETU, PTU
  - diquat
  - glyphosate, glufosinate and related compounds
  - acidic herbicides





Methods

- **GC-MS/MS: 2 MRM, 1SRM**

1. Miniaturised ethyl acetate, concentration & HPGPC

2. QuEChERS / solvent exchange / HPGPC clean-up / dSPE PSA, C_{18}, carbon

  - **Clean-up & backflush**
    - ✓ **Removal of high-boiling matrix material**
    - ✓ **Prevention of contamination of MS ion source: reduced maintenance**
    - ✓ **Improved spectral quality**
    - ✓ **Robust chromatography: more consistent retention times and peak shapes**
    - ✓ **Extended column life-time**

- **SRM for the analysis of dithiocarbamates**

Results

- 108 priority analytes
  Validated at 0.3 µg/kg - 1 µg/kg (0.0003-0.001 mg/kg)
- 193 other compounds
  Validated at 1 µg/kg (0.001 mg/kg)
- Multiple residues were detected in nearly all of the samples
- None of the residues were above the current MRLs

Results (EU 2012)

EFSA reported:1,520 baby food samples

- 91.6 % were free of measurable residues
- 7.8 % detectable residues below the MRL
- 0.6% MRL exceedances

Pirimiphos-methyl
BACs, DDAC
Carbendazim
Azoxystrobin
Ethoprophos
Chlorpyrifos-methyl
Chlormequat
Dichlorvos
Fluazifop-P-butyl

Results

UK National Monitoring data 2002-2014 (over 1000 samples)

Residues Detected

BACs, DDAC
Chlormequat
Chlorpropham
Diphenylamine
ETU
Fluazifop-P
Pirimiphos-methyl

Participation in Proficiency Tests

- Requirement for accreditation
- Mandatory for official laboratories
- Limited number of PTs for baby food

Issues faced by PT organisers

- Some pesticides degrade during preparation
- The robust mean needs to be significantly greater than MRRL (LoQ)
- Labs unable to meet MRRL
- Poor standard deviation
- Difficult to carry out statistical analyses
  - When robust mean is close to LOQ
- Number of participants is relatively low

Conclusions

- Decreasing LOQs - detect banned pesticides at very low concentrations
- Improved exposure estimates & risk assessment
- Challenging for labs (methods, experience, instruments, AQC)
- Number of reported pesticide residues increase dramatically
- Social impact: consumers concern, media

Acknowledgements

Richard Fussell
Mike Hetmanski
Monica Garcia Lopez

FAPAS
Chemical Residues Directorate

Happy & Healthy babies

Thank You for your attention