Determination of Pesticide Residues in Rice-Based Baby Food using GC-MS/MS with APGC™ after Extraction and Clean Up using QuEChERS

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INTRODUCTION

In Europe, specific maximum residue levels (MRLs) were set for food intended for infants and young children. Commission Directive 2006/125/EC specifically applies to processed cereal-based foods and baby foods for infants and young children and Commission Delegated Regulation (EU) 2021/1041 amending Delegated Regulation (EU) 2016/127 deals with the requirements for pesticides in infant formulae and follow-on formulae.[1,2] Following the precautionary principle, the legal limits for these types of food products were set at very low levels. In general, the default MRL of 0.01 mg/kg is applicable but more severe limitations were set for pesticides or metabolites of pesticides with an ADI lower that 0.0005 mg/kg body weight per day. Certain pesticides have MRLs listed at lower concentration (0.004 - 0.008 mg/kg) and others should not be used at all in agricultural production intended for infant formula and baby food. These analytes need to be tested down to a reporting limit of at least 0.003 mg/kg which can be analytical challenging. The objective of this study was to demonstrate the performance of a method for the determination of residues of pesticides and their metabolites, at concentrations suitable for checking MRL compliance in baby foods and lower, using GC-MS/MS with APGC on Xevo™ TQ-XS.

For more information on the ionization mechanism for APGC please read our white paper (LINK).

METHODS

Sample preparation

A QuEChERS extraction protocol was used for sample extraction with dSPE clean-up. In brief 5 g of infant food sample was added to a 50 mL falcon tube. It was hydrated, 10 mL of acetonitrile was added and shaken vigorously by hand for 1 minute. The QuEChERS salts were added (4g $MgSO_4$, 1 g NaCl, 1g Na_3 citrate dihydrate and 0.5 g Na_2H citrate sesquihydrate) and shaken. The sample was centrifuged and then frozen overnight. Then 6 mL was taken and 900 mg $MgSO_4$ and 150 mg PSA was added and the tube shaken. The sample was centrifuged, then formic acid was added and the extract diluted 1:1 with acetonitrile ready for injection onto the GC-MS/MS. [3]

The 2 spike levels used for the validation batch were 0.0005 and 0.001 mg/kg with 5 replicates at each level.

Instrument methods

GC Conditions:	Conditions previously published (LINK)
MS System:	Xevo™ TQ-XS Mass Spectrometer
Source Type	APGC 2.0 with water as a modifier
Source Temp	150ºC
Transfer line temp:	280ºC
Corona current:	2.0 µA
Auxiliary gas flow:	200 L/hr
Cone gas flow:	265 L/hr

RESULTS AND DISCUSSION

The sensitivity of the method was evaluated by assessment of the response of the matrix-matched standards at the lowest concentration prepared (0.0003 mg/kg or 0.3 µg/kg) for 166 pesticides. Results for 2-phenylphenol were discounted due to a detected residue in the blank. Of the remaining 165 analytes all but one could be detected at 0.0003 mg/kg. The limit of detection for thiometon was 0.005 mg/kg. Figure 1 shows chromatograms for a selection of priority pesticides in baby food in the 0.0005 mg/kg matrix matched standard, which demonstrates the sensitivity of this method.

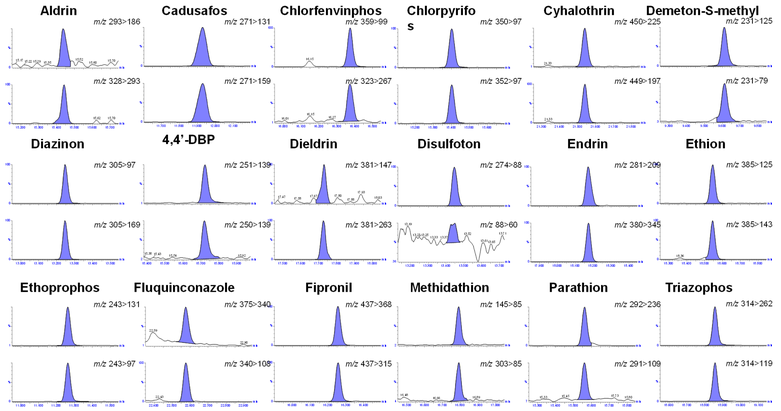

Figure 1. Chromatograms from the analysis of a selection of priority pesticides in the baby food matrix-matched standard at 0.0005 mg/kg

The lowest calibration level for each analyte was established by evaluation of the bracketed calibration graph. Of the 165 pesticides in the method 96% exhibited residuals within ± 20% SANTE tolerance and 95% had r^2 values >0.98.[4]

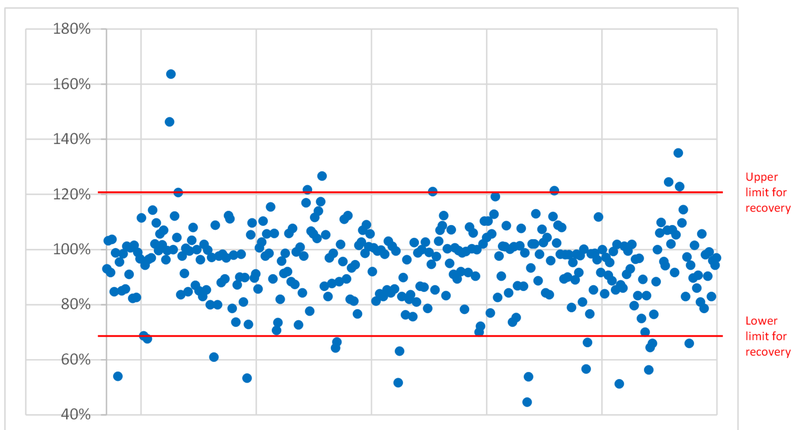

Figure 2. Summary of the recoveries (%) from the analysis of spiked baby food.

Identification criteria, retention time and ion ratios, were calculated. All pesticides' retention times were within the ± 0.1 min from the calibration reference standard. Ion ratios were assessed against the average from the calibration standards and 94% were within ± 30% tolerance.

The spiked samples recoveries were assessed against the SANTE guidelines where the average recovery for each spike level tested should be between 70 -120%. For the lower spike level 90% of pesticides were within this tolerance and 92% at the higher spiking levels. Figure 2 displays a summary of the recovery results obtained.

The repeatability (RSDr) of the method was assessed against the SANTE guideline values of RSDr should be ≤ 20%. At 0.0005 mg/kg (0.5 µg/kg) 96% of the pesticides were within this tolerance. At the higher spike level of 0.001 mg/kg (1 µg/kg) all the analytes exhibited values for RSDr ≤ 20%. Figure 3 displays a summary of this information.

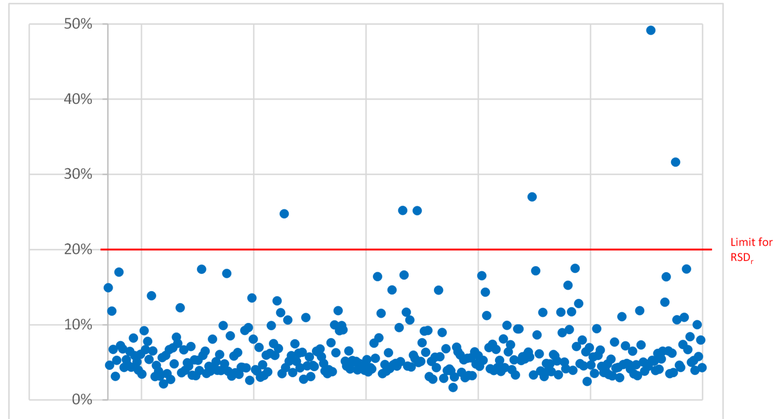

Figure 3. Summary of the repeatability (% RSD_r) from the analysis of spiked baby food

CONCLUSION

The method exhibited very high sensitivity (instrument LODs typically ≤ 0.0003 mg/kg) without the need for solvent exchange, PTV or large volume injection.

The method was successfully validated according the SANTE guidelines, presenting results for 166 pesticides in rice-based baby food. The results from analysis of the spikes at 0.0005 and 0.001 mg/kg showed that 91 % and 98 % of the analytes were within the required tolerances for recovery and repeatability, respectively.

References

1. Commission Directive 2006/125/EC of 5 December 2006 on processed cereal-based foods and baby foods for infants
2. Commission Delegated Regulation (EU) 2021/1041 of 16 April 2021 amending Delegated Regulation (EU) 2016/127 as regards the requirements on pesticides in infant formula and follow-on formula. *OJ L* 225, 25.6.2021, p. 4–6d young children. *OJ L* 339, 6.12.2006, p. 16–35
3. EURL-CF. Validation Report 31A. Determination of pesticide residues in rice based babyfood by LC-MS/MS and GC-MS/MS (QuEChERS method), 2019
4. Document No. SANTE/11313/2021. Guidance Document on Analytical Quality, Control, and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed. 2019.

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