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Pushing the Boundaries of Pesticide Residue Analysis in Baby Food through Enhanced Sensitivity GC-MS/MS Technology

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ABSTRACT

Pesticides are widely used in food production and to control and manage various pests. The detection, quantification, and confirmation of pesticide residue in food at trace levels requires sensitive, selective and robust analytical instrumentation.

With ever increasing pressure to analyze contaminants at very low levels in greater number of samples and with shorter turnaround times, laboratories seek continuous improvements in analytical instrumentation to increase productivity and minimize downtime.

This study describes optimized sample extraction and analysis for multi-residue pesticides analysis in baby food using superior sensitivity on a Thermo Scientific™ GC-MS/MS system. Accurate and sensitive detection, quantification, and identification of pesticides in baby foods is of particular importance as babies are more vulnerable to adverse health effects from these chemicals. In this work, various commercially available fruit and vegetables based baby-food samples were subjected to an optimized QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction method to isolate the pesticide residue using acetonitrile as the final extraction solvent. Direct analysis of extracts in acetonitrile is desired to avoid the need for solvent exchange to a more GC amenable solvent. The QuEChERS extracts were then analyzed for pesticide residue content using a fast targeted timed-SRM method for >200 pesticides including priority pesticides. The performance of the method was assessed and various analytical parameters investigated. The data presented in this study demonstrates unprecedented method performance from sample preparation to sensitive and robust GC-MS/MS analysis in addition to automated data processing and reporting capabilities.

INTRODUCTION

The detection and subsequent quantification of pesticide residues and other chemical residues and contaminants is of paramount importance, especially when the food stuff is intended to be consumed by infants or young children.

In the European Union (EU), the maximum residue level (MRL) for the majority of pesticide-commodity combinations is set at the default level of 10 µg/kg.[1–3] However, a small number of pesticides and their metabolites may allow infants and young children (under worst-case intake conditions) to exceed the acceptable daily intake (ADI) values. The EU has therefore established LoD MRLs, between 3-8 µg/kg for a number of specific pesticides prohibited in baby foods.[4] The use of GC-MS/MS for the detection and identification of residues of prohibited compounds, in compliance with the residue definitions, have proved challenging, especially when the diverse composition of multi-ingredient baby foods are taken into account. Also the increased levels of selectivity and sensitivity provided by triple quadrupole instruments compared to single quadrupole instruments enabled analysts to adopt faster, less specific sample extraction procedures. The QuEChERS procedure has become the standard approach for sample preparation in many laboratories because of an improvement in productivity.[5]

In this study, the quantitative performance of the Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system with AEI source was assessed for the analysis of >200 pesticides in baby food at very low concentrations (as low as 0.025 µg/kg). A complete evaluation of method performance include: Sample preparation, overall method suitability measured from pesticides recoveries, selectivity, sensitivity, linearity and long term robustness.

MATERIALS AND METHODS

To test the linearity and dynamic range of the system, post-spiked carrot/potato and apple/pear baby food samples were prepared using the citrate buffered QuEChERS protocol using Thermo Scientific™ HyperSep™ dispersive solid phase extraction (dSPE) products. Immediately after dSPE clean up the final extracts (1 g sample/mL of acetonitrile) were acidified with 5% formic acid in acetonitrile and were spiked with a mixture of 211 pesticides (including internal standard) at 14 concentrations spanning a range of 0.025–250 µg/kg. Robustness was tested using repeat injections of samples (carrot/potato) spiked at the 10 µg/kg level. For method evaluation, pre-spiked carrot/potato and apple/pear/banana baby food samples were each prepared at 1.0, 2.5 and 10.0 µg/kg (n = 6 for each concentration).

RESULTS

The experiments described here evaluate the sample preparation procedure and the quantitative performance of the TSQ 9000 GC-MS/MS system with Advanced Electron Ion (AEI) source for the analysis of pesticides in baby food matrices. Pesticide recoveries were obtained from the extracts performed on the samples spiked before extraction. All detected compounds, at the three spiking levels in both matrices satisfied all SANTE requirements.[3] More than 98% of the target pesticide residues had recoveries between 70–120% and at the 10 µg/kg spiking level with only one pesticide displaying a precision >20% (anthraquinone in carrot/potato). An example of the recovery and precision data is displayed in Figure 1.

Table 1. Gas Chromatograph and Mass Spectrometer instrument parameters.

TRACE 1310 GC Parameters	
Injection Volume (µL):	1
Liner:	Siltek™ six baffle PTV liner (P/N 453T2120)
Inlet (°C):	70
Carrier Gas, (mL/min):	He, 1.2
Inlet Mode:	Splitless (split flow 50mL/min after 2 min)
Column:	TraceGOLD™ TG-5SilMS with SafeGuard (30m × 0.25mm, 0.25µm- with 5m integrated guard column - P/N 26096-1425)

PTV Parameters:		Rate (°C/s)	Temp (°C)	Time (min)	Flow (mL/min)
	Injection	—	70	0.10	—
	Transfer	5.0	300	2.00	—
	Cleaning	14.5	320	5.00	75.0

Oven Program:	Temperature				
	Ramp	RT (min)	Rate (°C/min)	Target Temp (°C)	Hold Time (min)
	Initial	0	—	40	1.50
	1	1.5	25.0	90	1.50
	2	5	25.0	180	0.00
	3	8.6	5.0	280	0.00
	Final	28.6	10.0	300	5.00
	Run Time	35.6	—	—	—

TSQ 900 Mass Spectrometer Parameters	
Transfer Line (°C):	250
Ionization Type:	EI
Ion Source (°C):	320
Acquisition Mode:	Timed SRM
Tuning Parameters:	AEI Smart Tune
Collision Gas and Pressure (psi):	Argon at 70
Peak Width (Da):	0.7 (both Q1 and Q3)

Figure 1. Recovery and precision data for apple/pear/banana extractions (n=6) at a concentration of 10 µg/kg. Error bars show one standard deviation.

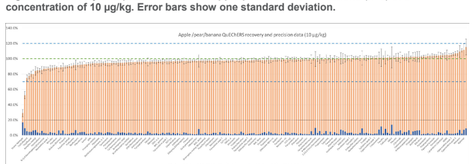


Figure 2. Example (A – dichlobenil, B – dieldrin, and C – deltamethrin) chromatographic peaks showing the lowest detectable matrix matched carrot/potato standard which meets SANTE requirements.

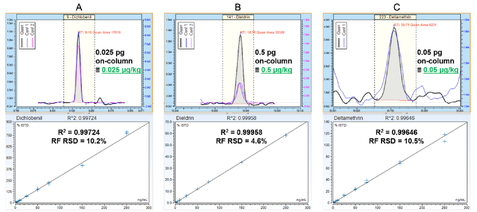
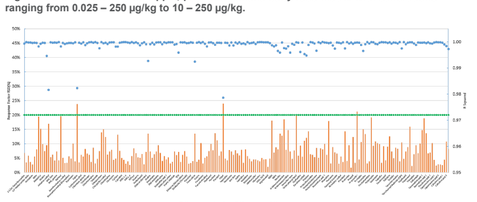


Figure 2 shows the lowest detectable standard for dichlobenil, dieldrin and deltamethrin which satisfies SANTE requirements. The MRLs are 10 µg/kg, 3 µg/kg* and 10 µg/kg respectively. Calibration curves show duplicate injection at 14 discrete levels ranging from 0.025 to 250 pg on column. *Dieldrin is classed as a prohibited pesticide and 3 µg/kg considered to be the current limit of quantification, but is subject to regular review.[4]

Compound linearity was assessed by injecting matrix matched standards in the range of 0.025 to 250 µg/kg in duplicate for both carrot/potato and apple/pear/banana. Both sets of linearity data showed R^2 > 0.990 and RF % RSDs of <20% for over 96% of component peaks indicating excellent linear response.

Figure 3. Calibration data for Apple, pear and banana baby food matrix with calibrations ranging from 0.025 – 250 µg/kg to 10 – 250 µg/kg.



System sensitivity, defined as instrumental detection limits (IDLs) was determined experimentally by performing n=10 replicates of the lowest matrix matched standard of carrot and potato that met all SANTE criteria. Calculations of IDLs were them made using one-tailed student t-test at the 99% confidence interval for the corresponding degrees of freedom and taking into account the concentration and absolute peak area %RSD for each compound (Figures 3 and 4).

Figure 4. Example quantification SRM overlays of cadusafos and chlorbenzilate injected at the lowest level that met all SANTE criteria. Annotated are on column concentration, % RSD derived from absolute peak area response and calculated IDLs.

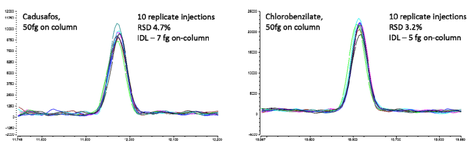
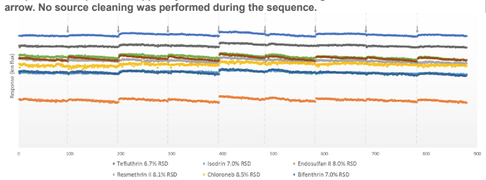


Figure 5. Plot showing the calculated IDLs for all pesticides. IDLs ranged from ~5 fg (chlorobenzilate) to ~2.0 pg (bioallethrin) with >95% of compounds showing an IDL of less than 500 fg on column (equivalent to 0.5 µg/kg in sample extract – carrot/potato).

Figure 6. Robustness data showing almost 900 sequential injections of carrot/potato matrix sample extract spiked at 10 ppb. Injector maintenance and tuning intervals are marked with an arrow. No source cleaning was performed during the sequence.



The TSQ 9000 AEI system was setup as described in Table 1. After an initial source cleaning, repeat injections of a sample extract (1g/mL carrot and potato) spiked at the default MRL (10 µg/kg) were made. Extracts resulting from the QuEChERS methodology contain a lot of undesirable matrix co-extracted components which can easily contaminate the GC inlet, the chromatographic column and the MS ion source. In order to test the robustness of the AEI ion source only, after every ~100 sample injections, the PTV liner was replaced along with the injector septum, approximately 10 cm trimmed from the guard column followed by automatic tuning of the system using the Smart Tune feature. Smart tune uses the MS parameters established during the initial tuning on a clean source and intelligently assess the performance of the system, only re-tuning when MS performance has been compromised. No additional maintenance was performed.

CONCLUSIONS

In this work it has been demonstrated that by using QuEChERS with Thermo Scientific HyperSep dispersive solid phase extraction (dSPE) and a direct injection of acetonitrile extracts, the TSQ 9000 AEI system delivers outstanding quantitative performance for low level pesticide residue analysis in baby food.

- Direct analysis of acetonitrile extracts using an optimized PTV injection.
- QuEChERS extraction and subsequent clean-up of over 200 pesticides from replicate analysis (n=6 at three concentrations) of each of two sample matrices, demonstrating excellent accuracy (recovery) and precision.
- Accurate, quantitative analysis of over 200 pesticides over up to 5 orders of magnitude (0.025 – 250 µg/kg), showing outstanding LODs and linear responses.
- Source robustness displayed over ~900 consecutive injections of sample matrix (1 g/mL).
- High sensitivity providing the real possibility to dilute the sample extract, thus limiting matrix contamination and system maintenance, leading to a potential increase in laboratory productivity.

REFERENCES

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