A Multiresidue Method for Quantitation and Screening of Pesticide Residues in Baby Food Using LC-MS/MS

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ABSTRACT

Purpose: Develop a multiresidue method for pesticides quantitation and screening in baby food using LC-MS/MS

Methods: Chromatographic separation was performed on a Thermo Scientific™ Vanquish™ Flex UHPLC system using a Thermo Scientific™ Accucore™ aQ C18 column

Mass spectrometric analysis was performed on a Thermo Scientific™ TSQ Quantis™ Triple Quadrupole mass spectrometer

Data processing was performed with the Thermo Scientific™ TraceFinder™ software

Results: The method provides robust, accurate, reproducible and sensitive quantitation of pesticide residues in baby food matrices

INTRODUCTION

A large number of pesticide residues is used worldwide in food products for preventing, destroying or controlling pest activity. Therefore, for consumer protection, regulatory agencies have established maximum residue levels (MRLs). For baby food products MRLs are even lower[1,2] compared to other food commodities, and therefore, sensitive analytical methods that allow simultaneous analysis of a large number of pesticides in challenging matrices are required. We have developed a multiresidue method for the analysis of pesticide residues in baby food using a triple quadrupole mass spectrometer, coupled to a UHPLC system. The 15-min method allows for pesticide quantitation and screening at low concentration levels (ppb) which are required for baby food.[1,2]

MATERIALS AND METHODS

Sample Preparation

Baby food was obtained from a local retail store. Samples were extracted using a QuEChERS extraction kit. Briefly 10g of sample was weighed and 10ml of ACN was added. The mixture was shaken followed by addition of salts from a pre-prepared QuEChERs extraction mix and then shaken again. Followed centrifugation the supernatant was collected. Matrix-matched standards were prepared by spiking the pesticide standards (225 pesticides) into the extracted matrices at concentration levels ranging from 0.05 to 200 ppb. QC samples were prepared by spiking the pesticide standards at concentrations of 0.5 ppb, 1.5 ppb and 12.5 ppb.

Liquid Chromatography

Chromatographic separation was performed on a Vanquish Flex UHPLC system using an Accucore aQ C18 column (100 × 2.1 mm, 2.6 µm). Mobile phase A consisted of 100% water containing 5mM ammonium formate and 0.1% formic acid. Mobile phase B consisted of 100 % methanol, 5mM ammonium formate and 0.1% formic acid. The flow rate was 300 µl/min and the column temperature was set at 25 °C. Analysis time was 15 min including 3 min equilibration time. Injection sample volume was 2 ul. The LC gradient is shown in Table 1.

Table 1. LC gradient

Time	Flow (ml/min)	% B
0.00	0.300	2.0
1.00	0.300	2.0
2.00	0.300	50.0
9.00	0.300	98.0
12.00	0.300	98.0
12.10	0.300	2.0
15.00	0.300	2.0

Mass Spectrometry

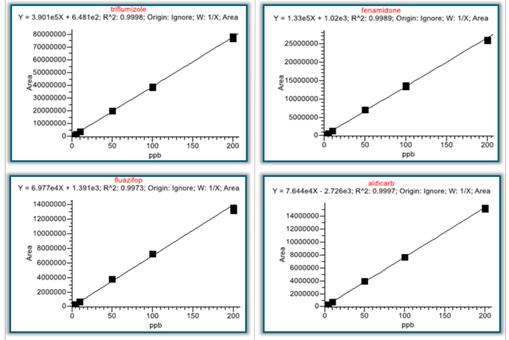
Mass spectrometric analysis was performed on a TSQ Quantis Triple Quadrupole mass spectrometer. The TSQ Quantis Triple Quadrupole mass spectrometer was operated in timed-SRM mode with polarity switching. The SRM conditions were optimized in an automated way using the Compound Optimization tool by direct infusion of each analyte.

Data Acquisition and Processing

TraceFinder software was used for data acquisition, data processing, data review and reporting. LOQ levels were determined as the lowest calibration levels for which % CV, % RSD and % Difference were at or below 15% and ion ratio was within the calculated average ion ratio.

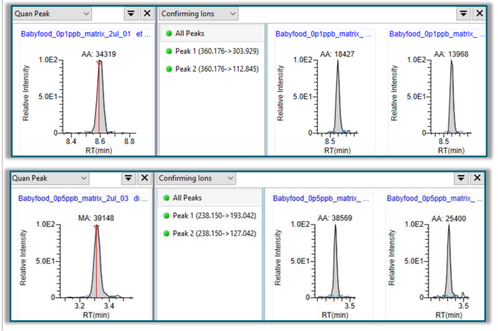
RESULTS

Figure 1. Representative calibration curves



Calibration curves for triflumizole, fenamidone, fluazifop and aldicarb. Calibration ranges were from 0.1 to 200 ppb for triflumizole and fenamidone and from 0.5 to 200 ppb for fluazifop and aldicarb.

Figure 2. Examples of quantifier and qualifier ions at LOQ levels



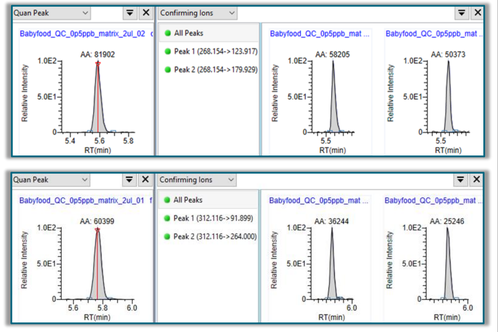
Data is shown for etoxazol at 0.1 ppb (upper panel) and dicrotophos at 0.5 ppb (lower panel)

Table 2. Obtained % Diff, % RSD and % CV at LOQ levels for representative pesticide residues

Pesticide Residue	LOQ (ppb)	% Diff Injection 1	% Diff Injection 2	% Diff Injection 3	% RSD	% CV
Aldicarb	0.5	7.14	-5.23	11.80	8.42	9.03
Cadusofos	0.5	3.65	-7.93	3.38	6.63	6.51
Carbofuran	0.5	10.36	4.18	3.23	3.65	3.94
Diazinon	0.1	-5.40	-8.62	-2.60	3.19	3.43
Dicrotophos	0.5	-3.89	-4.07	-3.76	0.16	0.17
Dimethachlor	0.5	3.61	-1.97	-1.17	3.01	3.01
Disulfoton-sulfoxide	0.5	1.96	4.65	1.69	1.59	1.66
Edifenphos	0.5	-3.82	5.23	8.38	6.13	6.13
Ethion	0.05	9.32	6.88	10.14	1.56	1.75
Fenazaquin	0.1	-11.71	-5.87	-7.72	3.26	3.01
Fenpyroximate	0.5	8.30	-1.75	1.77	4.96	4.68
Flufenacet	0.5	-7.86	-3.60	-2.86	2.84	2.76
Haloxyfop-methyl	0.5	-1.11	-4.32	-1.88	1.72	1.67
Monocrotophos	0.5	-3.17	1.82	-6.85	4.47	4.23
Norflurazon	0.1	7.29	2.85	2.52	2.55	2.83
Pencycuron	0.1	4.33	9.30	4.33	2.70	3.32
Primicarb	0.1	9.53	10.03	8.56	0.69	0.78
Prochloraz	0.5	-2.46	1.13	4.23	3.32	2.92
Propoxur	0.5	-1.62	4.80	4.48	3.53	2.99
Quinoxyphen	0.1	-5.78	8.84	-4.61	8.16	9.37
Triazophos	0.1	3.40	-4.65	6.59	5.69	5.50
Tricyclazole	0.05	1.93	9.73	10.40	4.39	5.27

The % Diff represents the difference between the calculated amount and the expected amount, divided by the expected amount. % RSD is based on the calculated amount and % CV is based on the peak areas.

Figure 3. Examples of quantifier and qualifier ions for the QC samples



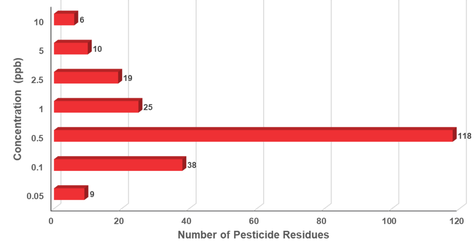
Data is shown for etoxazol (upper panel) and dicrotophos (lower panel) at 0.5 ppb

Table 3. Obtained % Diff, % RSD and % CV for QC samples at concentration levels of 0.5 ppb, 1.5 ppb and 12.5 ppb

Pesticide Residue	Concentration (ppb)	% Diff Injection 1	% Diff Injection 2	% Diff Injection 3	% RSD	% CV
Diphenamid	0.5	-8.30	-11.43	9.08	1.80	1.86
	1.5	-5.79	-3.29	-3.20	1.53	1.55
	12.5	0.48	1.69	0.78	0.63	0.63
Fluopicolide	0.5	3.66	2.87	9.13	3.24	3.62
	1.5	-3.26	2.41	-7.22	4.97	5.01
	12.5	2.52	3.92	1.84	1.04	1.02
trans-Permethrin	0.5	4.08	0.29	2.36	1.86	1.58
	1.5	3.52	1.94	2.42	0.79	0.75
	12.5	2.64	7.04	1.39	2.86	2.85
Tebufenpyrad	0.5	-5.25	-0.69	-8.87	4.31	4.35
	1.5	0.61	-2.28	-3.78	2.27	2.27
	12.5	5.56	4.25	5.21	0.65	0.64

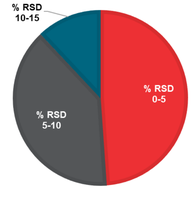
The % Diff represents the difference between the calculated amount and the expected amount, divided by the expected amount. % RSD is based on the calculated amount and % CV is based on the peak areas.

Figure 4. Obtained LOQ levels per number of analytes



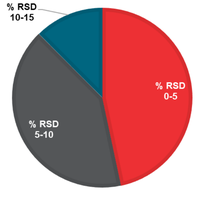
LOQ levels were at or below 1 ppb for 84% of the pesticide residue tested.

Figure 5. Obtained % CV at LOQ levels



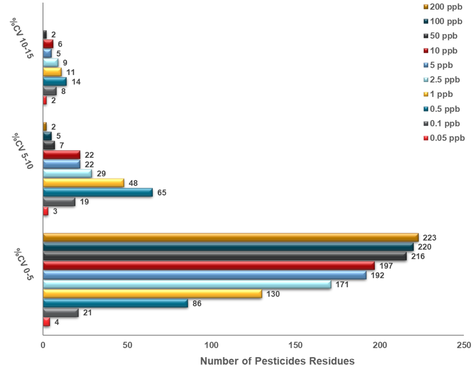
Obtained % CV values at LOQ levels were within 10% for 88% of all pesticides tested

Figure 6. Obtained % RSD at LOQ levels



Obtained % RSD values at LOQ levels were within 10% for 88% of all pesticides tested

Figure 7. Obtained % CV at all calibration levels for all pesticides residues tested



Obtained % CV were within 5% for the vast majority of all pesticide residues tested at calibration levels ranging from 0.05 ppb to 200 ppb

CONCLUSIONS

We have developed a multiresidue LC-MS/MS method for screening and quantitation of pesticide residues in baby food

The TSQ Quantis Triple Quadrupole mass spectrometer delivers sensitive, confident, accurate and reproducible quantitation

LOQ levels for 84% of the pesticide residues tested were at or below 1 ppb

Obtained % CV and % RSD at LOQ levels were within 10% for the vast majority (88%) of all pesticide residues tested

REFERENCES

1. Commission Directive 2006/141/EC.
2. Commission Directive 2006/125/EC

TRADEMARKS/LICENSING

PO65520-EN0519S

ThermoFisher SCIENTIFIC