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Determination of Pesticide Residues in Foods for Infant and Follow-on Infant Formula by LC-MS/MS and GC-MS/MS Methods

Miroslava Kuzniarová^{1,2}, Milena Dömötörová¹, Martina Micháliková¹

- ¹ Public Health Authority of the Slovak Republic, National Reference Centre for Pesticide Residues, Trnavská street 52, 826 45 Bratislava, Slovak Republic, miroslava.kuzniarova@uvzsr.sk
- ² Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 **Bratislava, Slovak Republic**

INTRODUCTION & AIM

The National Reference Centre for Pesticide Residues of the Public Health Authority of the Slovak Republic has developed, validated and implemented methods for the determination of over 200 pesticides in baby food. High-performance liquid and gas chromatography with tandem mass spectrometric detection (LC-MS/MS, GC-MS/MS) and gas chromatography with electron capture degtector (GC-ECD) were used to analyze the final sample extracts. Baby food samples were pretreated using the QuEChERS method. Before using the methods for the determination of pesticides, various validation parameters were checked for each pesticide residue according to the SANTE document from 2011. The determination of selected pesticides is accredited by the Slovak National Accreditation Service (with accreditation under STN EN ISO/IEC 17025:2018.). The accuracy of the methods is verified at least once every five years by participating in international comparative tests. Our laboratory achieves satisfactory results in the tests..

LC METHOD

Details about LC-MS/MS (QTRAP) method

Optimized LC conditions:

Column: Kinetex® 2.6 µm Polar C18 100 Å,

100 × 2.1 mm

Column temperature: 30 °C Injection volume: 4, 6 uL

Autosampler temperature: 15 °C

Mobile phase A: 0.1% Formic acid in Methanol Mobile phase B: 0.1% Formic acid in deionized

water

Run time: 22 min (12.6 min)

Flow rate: 0.25 mL/min

Gradient elution:

0.00	5	95	
5.20	45	55	
10.70	95	5	
11.80	95	5	
15.00	100	0	
15.10	100	0	
22.00	5	95	

Time (min) MP A (%) MP B (%)

Optimized MS/MS conditions:

Scan type: Scheduled MRM (Multiple Reaction Monitoring) Target cycle time: 1 s Ion source: Electrospray Ionization (ESI) Curtain gas (CUR): 40 psi Collision gas (CAD): Medium

Ion spray voltage (IS): 4500 (5500) V Ion source temperature (TEM): 400 °C Ion source gas 1 (GS1): 50 psi

Ion source gas 2 (GS2): 50 psi Entrance potential (EP): 10 V

Time (min) MP A (%) MP B (%)

0.00	5	95	
1.33	5	95	
2.20	60	40	
5.00	95	5	
7.50	95	5	
7.51	100	0	
9.50	100	0	
9.60	5	95	
12.60	5	95	

GC METHODS

Details about GC-MS/MS (IT) method Capillary column: 5% phenyl-methylpolysiloxane

stationary phase, 30 m × 0.25 mm i.d., 0.25 um film thickness, equipped with a 10 m guard column

GC Conditions

Oven temperature program:

Ramp Rate (°C/	min) Temp. (°C) H	old Time (min)
_	75	3.5
20	190	0
2	220	0

300

Injector temperature program:

Ramp Rate (°C/min) Temp. (°C) Hold Time (min) 80 200 280 32.5 80

Carrier gas: Helium, constant flow at 1 mL/min

Injection volume: 7 µL

MS/MS Conditions:

Ion trap temperature: 220 °C Transfer line temperature: 270 °C Manifold temperature: 50 °C Ionization mode: EI (Electron Ionization)

Details about GC-ECD method

Capillary column: 100% dimethylpolysiloxane stationary phase, 60 m \times 0.25 mm i.d., 0.25 μ m film thickness

Primary GC Conditions:

Oven temperature program:

Ramp Rate (°C/m	nin) Temp.(°C)	Hold Time (min)
-	60	1
15	100	0
10	160	0
2.5	275	10

Injection mode: Splitless Injector temperature: 250 °C Detector temperature: 330 °C Carrier gas: Helium, constant flow at 1 mL/min Make-up gas: Nitrogen, constant flow at 30 mL/min Injection volume: 1 µL



QuEChERS SAMPLE PRE-TREATMENT

Mix. 1: 8:2:2:1 (MgSO₄ (coarse) : NaCl : Na₃Cit·2H₂O : Na₂HCit·1.5H₂O). 6.5 g of Mix. 1 is added to 10 mL ACN.

Mix. 2: 6:1 (MgSO₄ (fine) : PSA). 1.05 g of Mix. 2 is added to 6 ml of extract

Mix. 3: 34.2:1.8:6 (MgSO₄ (fine) : GCB : PSA). 1.05 g of Mix. 3 is added to 6 ml of extract. Mix. 4: 4:1 (MgSO₄ (coarse): NaCl). 5 g of Mix. 4 is

added to 6 ml of extract. Mix. 5: 4:1 (MgSO₄: NaCl). For one analytical

sample 5 g of Mix. 5 is added.

Mix. 6: 1:4 (NaCl: MgSO₄ (fine)). 2 g of Mix. 6 is added to 5 ml of extract.

QuEChERS - Basic Method: Sample preparation for pesticide analysis with extract clean-up using Mix. 2.

QuEChERS with GCB: Sample preparation for pesticide analysis in matrices with high carotenoid or chlorophyll content, with extract clean-up using Mix. 3.

QuEChERS acidified with H2SO4: Acidified method QuECHERS with 100 mL H₂SO₄ for Chlorotalonil, with extract clean-up using Mix. 4.

A-QuEChERS (QuA): Acidified method QuEChERS (10 mL 1% HCOOH in ACN), with extract clean-up using Mix. 5.

QuEChERS for matrices with high fat content:

Sample preparation for pesticide analysis in matrices with high fat content, with extract clean-up using Mix. 6.







Procedure of QuEChERS (basic method or GCB)

(5 g powdered sample + 10-20 mL H₂O, let stand for 10 min) or (10 g liquid sample)















RESULTS & DISCUSSION

Analytical methods validated for a broad spectrum of over 200 pesticide active substances and metabolites in various infant food matrices, including fruit and vegetable purees, milk-based formulas, cereal products, and foods for special medical purposes. All baby food tested in recent years met pesticide safety standards.

In terms of selectivity and specificity, the blank response and the ratio of quantitation and qualification ions in the sample were not allowed to exceed 30%. In terms of linearity, deviations from the calibration line were allowed to be 20% and changes in response at calibration levels measured before and after the sample sequence had to be within 30%. In terms of accuracy, the accepted recovery is in the range of 60-140%, the residue reproducibility is within 20% and the measurement uncertainty is within 50%. I C-MS/MS (A 197 partricida activa substance/matabolita ± A GC-MS/MS (IT) (A 36 +

2,4"-DDT	2,4"-DDD	Bifenthrin	Pyrazophos	Acephate	Cyantraniliprole	Etoxazole	Flufenacet	Linuron	Penthiopyrad	Spirotetramat	Triticonazole
A'-Dicofol	2.4'-DDE	Bromorropylate	Pyriproxyfen	Acetamirrid	Cvazofamid	Famoxadone	Flufenexuron	Lufenuron	Phenthoate	Spiroxamine	2.4-D
4.4'-DDD	2.4'-Dicofol	Cyprodinil	Ouinoxyfen	Aclonifen	Cyflufenamid	Fenamidone	Fluoricolide	Malaccon	Phorate sulfone	Sulfoxaflor	BYI08330-enol
4,4"-DDE	4,4'-Dicofol	Desmethylpirimicarb	Tebuconazole	Aldicarb-sulfone	Cymoxanil	Fenamiphos	Fluopyram	Malathion	Phosalone	Tebuconazole	Desmethyl chlorovnifos-meti
4,4 '-DDT	Acrinathrin	Diphenylamine	Tefluthrin	Aldicarb-sulfoxide	Cyproconazole	Fenamiphos-sulfone	Fluquinconazole	Mandipropamid	Phosmet	Tebufenozide	Disulfoton
Aldrin	Bifenthrin	Ethion	Tetraconazole	Ametoctradin	Cyprodinil	Fenamiphos- sulfoxide	Flusilazole	Mecarbam	Phosmet-oxon	Tebufenpyrad	Dodine
alpha-Endosulfan	Captan	Fipronil	Tolclofos-methyl	Azinphos-methyl	Demeton-S-methyl	Fenarimol		Mepanipyrim	Phosphamidon	Teflubenzuron	Emameetin benzoute Bla
alpha-HCH	delta-HCH	Fipronil-desulfinyl	Vinclozolin	Azoxystrobin	Demeton-S-methyl- sulfone	Fenazaquin		Metaflumizone	Phoxim	Terbufos	Fentin
beta-Endosulfan	Epoxiconazole	Fipronil-sulfone	2-Phenylphenol	Bifenthrin	Demeton-S-methyl- sulfoxide	Fenbuconazole	Fluxapyroxad	Metalaxyl	Pirimicarb	Terbufos-sulfone	Fluazifop-P
beta-HCH	Fipronil	Flusilazole	2,4'- DDT	Bitertanol	Desmethylpirimicarb	Fenhexamid	hydrochloride	Metconazole	Pirimiphos-methyl	Terbufos-sulfoxide	Haloxy fop
Cyfluthrin	Fipronil-desulfinyl	Chlorfenapyr	Chlorpeopham	Bixafen	Diszinon	Fenoxyearb		Methamidophos	Profenofos	Terbuthylazine	Haloxyfop-2- ethoxyethyl
Cypermethrin	Fipronil-sulfone	Chlorfenvinphos	Chlorpyrifos	Boscalid	Diethofencarb	Fenpropathrin	Hexaconazole	Methidathion	Prochloraz	Tetraconazole	Haloxy fop-methy
Deltamethrin	Fluquinconazole	Chlorobenzilate	Cypermethrin	Bromuconazole	Difenoconazole	Fenpropidin	Hexythiazox	Methiocarb	Propamocarb	Tetramethrin	Haloxyfop-R
Dicofol	Folpet	Isofenphos-methyl	Diazinon	BTS 44595	Diflubenzuron	Fenpropimorph	Chlorantranilipeole	Methiocarb- sulfoxide	Propargite	Thiabendazole	Haloxyfop-R- methyl
Dieldrin	Chlorothalonil	Kresoxim-methyl	EtoSenprox	BTS 44596	Dichloflusnid	Fenpyrazamine	Chlorfenvinphos	Metolachlor	Propiconazole	Thiacloprid	Methomyl
Endosulfan-sulfate	Chlorpyrifos-methyl	Metalaxyl	Etoxazole	Bupirimate	Dichlorvos	Fenpyroximate	Chlorpeopham	Metrafenone	Propyzamide	Thiamethoxam	Methoxyfenozide
Endrin	Isocarbophos	Methacrifos	Fenitrothion	Buprofezin	Dimethoate	Fensulfothion	Chlorpyrifos	Metribuzin	Proquinazid	Thiophanate-methyl	Pyridalyl
gama-HCH	Isoprothiolane	Nitrofen	Fenpropidin	BY108330- ketohydroxy	Dinethonorph	Fensulfothion-exon	Chlorpyrifos-methyl	Monocrotophos	Prosulfocarb	Tolclofos-methyl	Spinetoram
НСВ	Metolachlor	Oxadixyl	Fenvalerate/ Esfenvalerate	BY108330- monohydroxy	Diniconazole	Fensulfothion-exon- sulfone	Imazalil	Myclobatanil	Prothioconazole- desthio	Tolylfluanid	Spinosyn A
Heptachlor	Metribuzin	Parathion-methyl	Fludioxonil	Cadusafos	Disulfoton	Fensulfothion- sulfone	Imidaclopeid	Omethoate	Prothiophos	Triadimefon	Spinosyn D
Heptachlorepoxid- cis	Nitrofen	Penconazole	Heptachlor-endo- epoxide	Carbaryl	Disulfoton-sulfone	Fenthion	Indoxacarb	Oxadixyl	Pyraclostrobin	Triadimenol	Terbufos
Heptachlorepoxid- trans	Penconazole	Pendimethalin	Isocarbophos	Carbendazim	Disulfoton-sulfoxide	Fenthion-oxon	Iprodione	Oxamyl	Pyrazophos	Triazophos	Thiodicarb
Chlordane-cis	Pyridaben	Phenthoute	Procymidone	Carbofuran	DMST	Fenthion-oxon- sulfone	Iprovalicarb	Paclobutrazol	Pyridaben	Tricyclazole	TNFA
Chlordane-oxy	Spirodiclofen	Pirimicarb	Pyridaben	Carbofuran-3- hydroxy	EPN	Fenthion-oxon- sulfoxide	Isofenphos-methyl	Paraoxon-methyl	Pyrimethanil	Trifloxystrobin	
Chlordane-trans	Spiromesifen	Pirimicarb-desmethyl	Resmethrin	Carboxin	Epoxiconazole	Fenthion-sulfoxide	Isoprothiolane	Parathion-ethyl	Pyriproxyten	Triflumizole	1
Lambda-cyhalothrin	tau-Fluvalinate	Propiconazole	Terbufos-sulfone	Clofentezine	Ethion	Floricamid	Soproteron	Penc onazo le	Quinoxyfen	Triflumizole, FM-6-	
Metoxychlor	Tetradifon	Propyzamide	Tetradifon	Clomazone	Ethirimol	Fluzzifop-P-butyl	Sopyrazam	Pencycuron	Resmethrin	Triflumuron	1
Permethrin	Tolylfleanid	Prothiophos	Trifluralin	Clothianidin	Ethorrophos	Fludioxonil	Kresoxim-methyl	Pendimethalin	Spiromesifen	Trichlorfon	1

Table 1. Pesticides active subtance or metabolite analysed by GC-ECD, GC-MS/MS (IT) and LC-MS/MS, A – acredited, N - Nonacredited

CONCLUSION

The results of official pesticide control and European monitoring in baby food carried out over the last 10 years indicate the safety of baby food, in terms of pesticide content, and none of the tested samples exceeded the permitted limit

FUTURE WORK

The goal of the NRC RP is to expand the range of controlled pesticides and to apply new equipment GC-MS/MS (TQ) to routine analysis.