

APPLICATION OF QuEChERS METHOD TO NON-FATTY (vegetables) AND FATTY (milk) BABY FOOD MATRICES

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INTRODUCTION

Presence of pesticide residues in food can negatively affect human health. This stimulates the establishment of legal directives to control their levels through the maximum residue levels (MRLs). Special attention is paid to safety of children and infants, as they represent a vulnerable risk group of the population. Therefore, the European Commission (EC) specified the MRL 10 µg/kg for any individual pesticide in processed cereal-based food and baby food. Also established the prohibition of use of highly toxic pesticides (which have acceptable daily intake values lower than 0.0005 mg/kg body weight) in the production of agricultural products intended for processed cereal-based foods and baby food.

OBJECTIVES

The aim of this work was to explore the possibilities of the simplified procedures of extraction currently used in pesticide residue analysis, in this case with focus on acetonitrile based methods (QuEChERS), here adapted and applied to conventional GC-ECD detector.

The study was made selecting matrices destined for baby food with different characteristics: *Powdered milk, fruits and vegetables* (strawberry, peach, apple, pumpkin and potato) destined for babies and infants foodstuff. Milk is low fatty sample (content of fat 3%) with high water content and organic components, it is a relatively problematic matrix because most of the non-polar lipophilic compounds are found in fatty phase but it is of concern to consider that it is also probable to find in the aqueous phase pesticide compound of different degree of polarity.


A representative list of pesticides of different classes and types was selected, including compounds of high concern for Argentine market like endosulfan (I, II and III), some pyrethroids (cypermethrin, deltamethrin, fenvalerate) and also compound like captan sensible to media conditions.

EXPERIMENTAL PROCEDURE

EXTRACTION METHOD - QuEChERS


MILK

Weigh 1 g of milk sample in a 50 ml falcon tube + 15 ml of water




FRUITS and VEGETABLES


Weigh 15 g of sample in a 50 ml falcon tube




Add 15 ml of acetonitrile with 1% acetic acid




Add 6 g of MgSO₄ anh. and 1.5 g sodium acetate and shake vigorously for 6 minutes




Centrifuge for 5 minutes at 3700 r.p.m.




Take a 1 ml aliquot from supernant and add 250 mg de MgSO₄ anh., 50 mg de PSA and 50 mg de C18




Take a 1 ml aliquot from supernant and add 250 mg de MgSO₄ anh. and 50 mg de PSA



Shake for 20 seconds and centrifuge for 5 minutes at 3700 r.p.m. Take the supernant to a tube for analysis



Dissolve the extract with 1 ml of iso-octane



GC - ECD ANALYSIS

GC-ECD Systems: Hewlett Packard 5890 SERIES II and Varian 3100

Columns: a) HP PAS 1701, 25 m x 0.32 mm id, 0.25 µm film thickness. b) HP PAS 5 25 m x 0.32 mm, 0.52 µm film thickness

Standard Pestanal Riedel-de-Haën (In iso-octane)

RESULTS

LIMITS OF DETECTION, RECOVERY DATA, LINEARITY and MATRIX EFFECT

PESTICIDES	LOD ^a (µg/kg)		RECOVERIES (R.S.D.) (%) ^b (n=6)		LINEARITY ^c LOQ ^d - 200 µg/kg		Matrix Effect ^e
	Milk	F - V ^b	Milk	F - V	Milk	F - V	
Lindane	2	1	74-92 (14)	65-82 (10)	0.9992	0.9973	NS ^f
Aldrin	3	1	68-82 (12)	71-82 (5)	0.9978	0.9990	NS
Endosulfan I	4	2	78-87 (16)	58-83 (9)	0.9968	0.9998	NS
Endosulfan II	4	2	75-86 (16)	74-83 (13)	0.9979	0.9996	NS
Endosulfan III	7	2	85-98 (20)	77-93 (11)	0.9967	0.9984	22
Captan	-	1	-	64-114 (5)	-	0.9995	-
p,p'- DDE	4	1	73-85 (13)	87-112 (5)	0.9991	0.9998	NS
Endrin	4	2	99-105 (17)	74-99 (17)	0.9990	0.9984	NS
Mirex	4	2	101-103 (14)	-	0.9987	-	NS
p,p'- DDT	7	2	89-90 (15)	83-107 (6)	0.9989	0.9977	NS
Oxichlordane	2	1	81-82 (12)	-	0.9992	-	NS
Heptachlor	2	1	73-91 (22)	77-90 (14)	0.9989	0.9999	NS
Heptachlor epox.	-	1	-	87-90 (19)	-	-	-
Clorpyrifos	4	2	70-76 (14)	66-107 (19)	0.9919	0.9999	NS
Clorpirifos, methyl	6	2	64-76 (13)	-	0.9976	-	NS
Diazinon	-	3	-	63-84 (20)	-	0.9872	-
Ethion	8	3	62-65 (19)	-	0.9889	-	25
Fenitrothion	8	2	72-83 (12)	63-84 (20)	0.9963	0.9994	NS
Malathion	15	2	60-79 (11)	61-72 (15)	0.9963	0.9995	39
Folpet	10	3	81-85 (15)	65-97 (7)	0.9953	0.9998	91
Tetrametrina	9	2	54-60 (7)	63-82 (16)	0.9943	0.9943	NS
Fenvalerate	8	2	55-66 (6)	87-91 (5)	0.9931	0.9931	NS
Deltamethrin	5	3	55-66 (10)	88-103 (11)	0.9915	0.9915	NS
Permethrin	10	3	59-70 (7)	92-105 (18)	0.9970	0.9970	NS
Cypermethrin	10	3	51-69 (12)	66-94 (16)	0.9929	0.9929	NS
PCB 52	3	1	52-54 (13)	-	0.9980	-	NS
PCB 138	1	1	51-55 (19)	-	0.9956	-	NS
PCB 153	1	1	51-55 (19)	-	0.9978	-	NS

^a LOD: Limit of detection

^b F - V: Fruits and Vegetables

^c Levels = 7

^d LOQ = 3.3*LOD

^e Average matrix effect (%) calculated at concentration in the middle of calibration range by comparing Average Area in Solvent (AAS) and matrix (AMM)=(AAS-AMM/AAS)x100

^f NS: Not Significant

Matrix effect was not significant for pesticide/fruit and vegetable matrices under study. For the milk validation: Traceability was evaluated by determinations on spiked powdered milk, Reference Material BCR. N° 188 (Commission of the European Communities -Community Bureau of Reference).

APPLICATION TO REAL SAMPLES

The validated method was applied in a pilot monitoring study in Argentina.

MILK

According to SENASA (National Animal Health and Agri-food Quality Service, Argentina) the main pesticides finding in Argentine milk are Endosulfan (I, II and III) and some pyrethroids.

Thirty six samples of different milk powdered commercial brands were collected in different supermarkets.

In this study no positive findings of monitored compounds were detected.

FRUITS AND VEGETABLES

Forty two samples destined to baby food manufacturing processes (peach, apple, pumpkin, potato and strawberry) were analyzed.

Pesticide residues were detected only in two samples (5 %). The compounds detected and the vegetable involved were: a strawberry sample had endosulfan (I and II) and a strawberry sample had captan both below the MRLs.

POWDERED MILK

Samples: 36, from different commercial brands
Positive findings: 0

FRUITS and VEGETABLES

Samples: 42
Positive findings: 2
Pesticides:
Captan (strawberry): 16 ng/g
Endosulfan (strawberry): 4 ng/g



CONCLUSIONS

In general the study showed satisfactory results, which add evidence of the capability of the reduced scale methodology used for extraction and cleanup of pesticide residues, to determine reliably low levels of pesticide residues in fruit and vegetables and in a low fatty sample as powdered milk, using a conventional chromatographic system.

LOD for most compound and matrices were in a range compatible with detection for baby food requirements (MRL 10 µg/kg). Exceptions were observed for several compounds studied (diazinon and malathion in milk).

Further adjustments are needed to lower detection limits of a reduced group of compounds in order to fulfill the requirements for the most demanding regulations.

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