Application of QuEChERS Method and Gas Chromatography - Mass Spectrometry for the analysis of cypermethrin, fipronil and chlorfenvinphos residues in cattle's milk, meat, and fat - Brondi S.H.G.[1], Macedo A.N.[2], Nogueira A.R.A.[1*]

1 - Embrapa Pecuária Sudeste, São Carlos, SP - Brazil
2 - Universidade Federal de São Carlos, São Carlos, SP - Brazil
*poster presenter: anarita@cppse.embrapa.br

The presence of chemical contaminants in food is a major concern worldwide, especially of pesticides used for cattle disease. However, in animal origin foods, the quality can be endangered due to the presence of contaminants, especially of cypermethrin, fipronil and chlorfenvinphos, which are used in Brazil to treat cattle. Methods for monitoring contaminants should be rapid, use few reagents in small amounts, be specific, and be sensitive. Anastassiades *et al.* (2003) developed an approach which they dubbed quick, easy, cheap, effective, rugged, and safe (QuEChERS). The aim of this study was to evaluate QuEChERS method in combination with gas chromatography-mass spectrometry for the determination of cypermethrin, fipronil and chlorfenvinphos residues in cattle's milk, meat, and fat. Milk and meat were analyzed by mixing the pesticide with the sample in a centrifuge tube. Acetonitrile, $MgSO_4$, and NaCl were added and the mixture was centrifuged. An aliquot of the extract was mixed with primary secondary amine, C18, and $MgSO_4$ for dispersive SPE. The mixture was centrifuged and the supernatant was analyzed. Fat sample was analyzed under similar procedures and hexane was used. The oven temperature program was set at 100°C - 12°C min^{-1} - 190°C - 32°C min^{-1} - 270°C (4 min) and the mass spectrometry was operated in the selected ion monitoring (SIM) mode. The quantification limits were below 0.020 mg kg^{-1}, and it was possible to analyze cypermethrin, fipronil and chlorfenvinphos in low concentrations. The methods resulted in extracts that contained the target pesticides, with recovery values within the Brazilian legislation requirements.

Key-words: QuEChERS method, gas-chromatography, pesticides

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Silvia Helena Govoni Brondi[1], Adriana Nori Macedo[2], Ana Rita de Araujo Nogueira[1*]
[1]Embrapa Pecuária Sudeste, São CarlosSP, Brazil; [2]Departamento de Química, Universidade Federal de São Carlos, S.Carlos SP, Brazil.
*anarita@cppse.embrapa.br

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Introduction

Milk and beef are highlighted as widely consumed food of animal origin, so it is important to develop methods for the analysis of pesticide residues in such matrices. Moreover, beef is often consumed together with fat, which has different composition and might be studied as other matrix.

Figure 1: Occurrence of pesticide residues in food of animal origin.

Objectives

Application of modified QuEChERS methods for the analysis of fipronil, chlorfenvinphos, and cypermethrin in bovine milk, meat, and fat samples, using gas chromatography-mass spectrometry (GC-MS).

Experimental

Analytes:

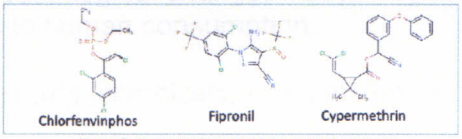

Figure 2: Structural formula of the studied pesticides.

Chromatographic analisys: GC-MS, QP 2010 (Shimadzu)

- Capillary column DB-5 (30 m x 0.25 mm x 0.1 µm)
- Injector, interface and ion source temperature: 250 ºC
- Column temperature program:
  100 ºC – 12 ºC min^{-1} – 190 ºC – 32 ºC min^{-1} – 270 ºC (4 min)
- Carrier gas: helium (0.75 mL min^{-1})
- Injection volume: 1 µL
- Injection mode: splitless
- SIM selected ions (Table 1)

Extraction procedure: Milk and Meat (Figure 3) [1,2]

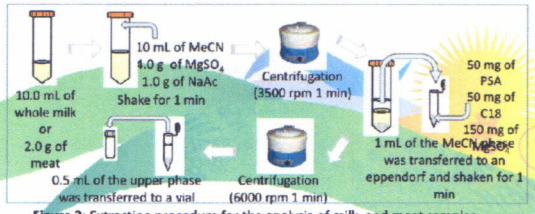

Figure 3: Extraction procedure for the analysis of milk and meat samples.

Extraction procedure: Fat (Figure 4) [3]

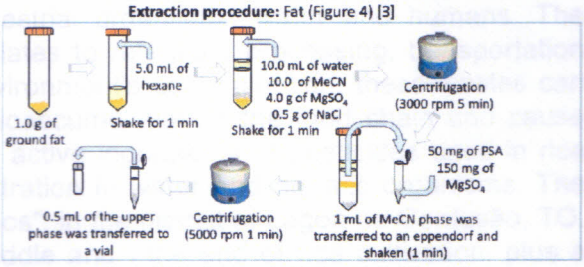

Figure 4: Extraction procedure for the analysis of fat samples.

Results and discusion

Table 1: SIM selected ions.

Analytes	Ions (m/z)
Chlorfenvinphos	267
Fipronil	351
Cypermethrin	181

Table 2: Calibration curve equation and determination coefficient (R^2).

Analytes	Milk				Fat			
	Equation	R^2	LOD (mg L^{-1})	LOQ (mg L^{-1})	Equation	R^2	LOD (mg L^{-1})	LOQ (mg L^{-1})
Chlorfenvinphos	y = 230602x - 176.27	0.994	0.007	0.020	y = 25673x + 2408.4	0.976	0.05	0.20
Fipronil	y = 55951x - 44.315	0.990	0.003	0.010	y = 9460.5x + 639.98	0.979	0.03	0.10
Cypermethrin	y = 178893x + 6887.7	0.980	0.007	0.020	y = 20651x + 5386.1	0.975	0.05	0.10

Analytes	Meat			
	Equation	R^2	LOD (mg L^{-1})	LOQ (mg L^{-1})
Chlorfenvinphos	y = 22175x - 521.4	0.9993	0.005	0.020
Fipronil	y = 138751x – 1002.3	0.9974	0.003	0.010
Cypermethrin	y = 170171x + 3883.6	0.9966	0.002	0.020

Table 3: Recovery and RSD.

Conc. (mg kg^{-1})	Chlorf	Fip	Cyp
0.10	117±0.9	81 ± 27	111 ± 0.4
0.20	129±5	112 ± 22	102 ± 3

Chlorf: chlorfenvinphos; fip: fipronil; cyp: cypermethrin

Conc. (mg L^{-1})	Chlorf	Fip	Cyp	Conc. (mg kg^{-1})	Chlorf	Fip	Cyp
0.100	98 ± 1	91 ± 2	79 ± 10	0.50	123 ± 12	78 ± 5	92 ± 7
0.200	97 ± 1	86 ± 2	79 ± 10	0.70	92 ± 3	88 ± 2	67 ± 8

Conclusion

The modifications of the method QuEChERS studied in this work were efficient for the analysis of pesticides in bovine meat, fat and milk, which are very complex matrices. They presented acceptable linearity, recovery and RSD.

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