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

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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.

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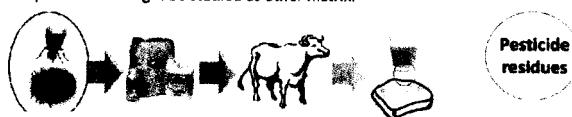
Figure 1: Occurrence of pesticide residues in food of animal origin.

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:

| Chlorfenvinphos | Fipronil | Cypermethrin |
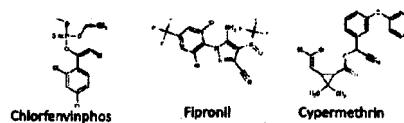
Figure 2: Structural formula of the studied pesticides.

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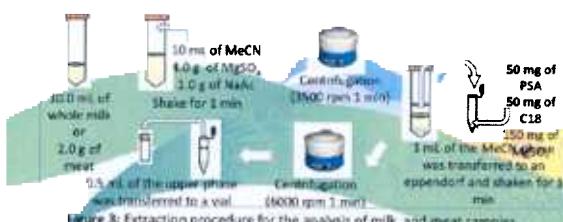
Figure 3: Extraction procedure for the analysis of milk and meat samples.

Extraction procedure: Fat (Figure 4) [3]
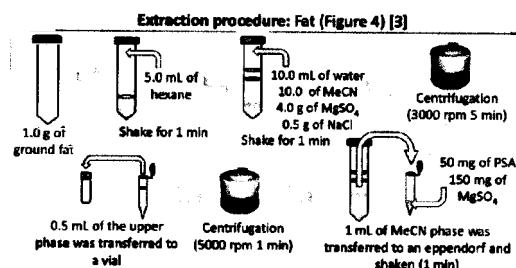
Figure 4: Extraction procedure for the analysis of fat samples.

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 (R²).

	Milk				Fat			
Analytes	Equation	R²	LOD (mg L⁻¹)	LOQ (mg L⁻¹)	Equation	R²	LOD (mg L⁻¹)	LOQ (mg L⁻¹)
Chlorfenvinphos	y = 230502x – 170.27	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 = 170893x + 688.7.7	0.980	0.007	0.020	y = 20651x + 5386.1	0.975	0.05	0.20

	Meat			
Analytes	Equation	R²	LOD (mg L⁻¹)	LOQ (mg L⁻¹)
Chlorfenvinphos	y = 22175x – 521.4	0.9993	0.006	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	120±5	112 ± 22	102 ± 3

Conc. (mg L⁻¹)	Chlorf	Fip	Cyp
0.100	96 ± 1	91 ± 2	79 ± 10
0.200	97 ± 1	86 ± 2	79 ± 10

Conc. (mg kg⁻¹)	Chlorf	Fip	Cyp
0.50	123 ± 12	78 ± 5	92 ± 7
0.70	92 ± 3	88 ± 2	67 ± 8

Chlorf: chlorfenvinphos; fip: fipronil; cyp: cypermethrin

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.

References

[1]Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J. AOAC Int 2003. 86.
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[3]Mastovska, K.; Lehotay, S. J. J. Agric. Food Chem 2006. 54. 7001-7008.

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