

Introduction

Milk is one of the most complete food for humans, because it contains nutrients required for growth and development of newborns. However, milk quality can be endangered due to the presence of contaminants, especially of cypermethrin pesticide, which is widely used in Brazil to treat lactating dairy cows, mainly against ticks, flies, lice and dermatobia.

Methods for monitoring veterinary drugs, for example pesticide residues, should be rapid, have small number of analytical steps, use few reagents in small amounts, be specific, and be sensitive enough to enable detection at very low levels.

Anastassiades *et al.* [1] developed an approach which they dubbed quick, easy, cheap, effective, rugged, and safe (QuEChERS). It presents several advantages over most of the traditional extraction techniques, according to Lehotay [2]: high recoveries are achieved for a wide polarity and volatility range of pesticides, very accurate results, solvent usage and waste are very small, high sample throughput, a single person can perform the method without much training or technical skill, the method is quite rugged, of low cost and labor, and few materials and glassware are needed.



Objective

The aim of this study was to evaluate QuEChERS method in combination with gas chromatography-mass spectrometry (GC-MS) for the determination of cypermethrin residue in bovine milk.

Experimental

Extraction technique: QuEChERS Method (Figure 1) - (1,2) weigh a 10 g milk; (3) add cypermethrin; (4,5) add 10 mL of MeCN, 4 g of MgSO₄ and 1 g of NaCl in each tube, and centrifuge at 3000 rpm for 1 min; (6,7,8) transfer 1 mL of MeCN extract to a 1.5 mL minicentrifuge tube for dispersive SPE using 50 mg of PSA + 50 mg of C18 + 150 mg of MgSO₄; (9) mix the extract, and centrifuge at 6000 rpm for 1 min; (10,11,12) transfer 0.5 mL of the supernatant to an autosampler vial for analysis by GC-MS.

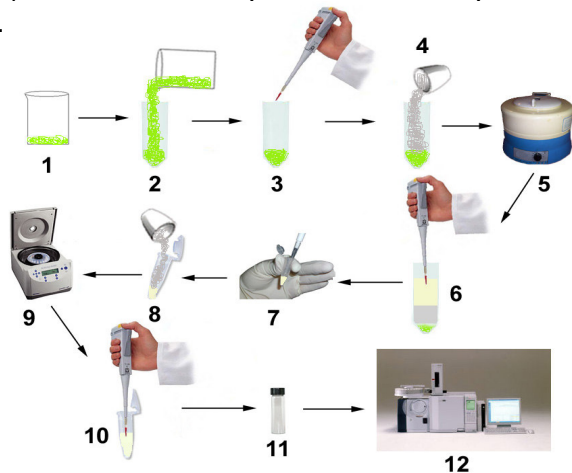


Figure 1: QuEChERS Method

GC-MS analyses

Cypermethrin was determined by gas chromatography coupled to mass spectrometry using a QP 2010 GC-MS from Shimadzu (Kyoto, Japan), equipped with a mass selective detector (MSD) and 30 m DB-5 capillary column, with an internal diameter of 0.25 mm and 0.1 µm film thickness.

The analytical conditions: temperature of injector: 250°C, temperature of the interface: 250°C, helium used as carrier gas, splitless injection, and oven program: 150°C - 15°C min⁻¹ - 270°C (7 min).

Selected ions (m/z) for cypermethrin: 163, 165, 181



Results and Discussion

The method developed resulted in extracts that contained the target analyte (Figure 2), with recovery values within the ANVISA [3] requirements, from 70% to 120%, with relative standard deviations below 20%. Detection and quantification limits were 0.025 and 0.075 mg kg⁻¹, respectively. It is possible to analyze cypermethrin in milk below the maximum residue limit of 0.10 mg kg⁻¹.

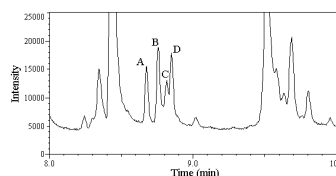


Figure 2: GC-MS chromatogram of cypermethrin (A, B, C, D) obtained after QuEChERS method was applied, in the concentration of 0.1 mg kg⁻¹ in milk.

The method was applied to milk samples from cows submitted to the treatment with cypermethrin, and it was registered residue in 0.2 mg kg⁻¹ concentration, which is superior than the maximum residue limits (LMRs) (Figure 3).

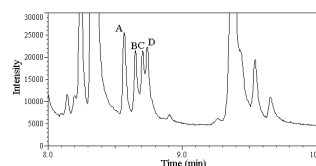


Figure 3: GC-MS chromatogram of sample milk from cow submitted to the treatment with cypermethrin. A, B, C, D = cypermethrin pesticide

Conclusion

The proposed method is rapid and inexpensive, and reduces consumption of organic solvents, which are toxic to health and to the environment. The method may be used as a screening procedure for analysis of cypermethrin residue in milk.

References

- [1] Anastassiades, M.; Lehotay, S.J.; Stajnbaher, D.; Schenk, F.J. *J. AOAC Internacional*, 2003, 86, 412-431.
- [2] Lehotay, S.J. In *Methods in Biotechnology*. Vidal, J.L.M.; Frenich, A.G. (eds). Humana Press, Totowa, NJ, 2005, 239-261.
- [3] ANVISA, 2006. <http://e-legis.bvs.br/leisref/public/showAct.php?id=25129>

