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Full Length Research Paper

Determination of residues of deltaméthrin in wheat and potato by HPLC

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Residues of deltamethrin, a pyrethroid insecticide commonly used to protect stored grains, have been determined in wheat and potato by high -performance liquid chromatography with UV detection at 233 nm after extraction by chloroform and a silica gel clean-up. Recoveries from fortified samples spiked with 1 ppm of deltamethrin exceeded 75% for both products. The control carried out on imported products showed the presence of this insecticide that sometimes exceeded the maximum limits of residues authorized by the OMS/FAO (0.10 ppm in potatoes and 1.00 in wheat).

Key words: deltamethrin, residues, wheat, potato, HPLC

INTRODUCTION

The quality of the human being food is at the present time a major concern of the modern world. It implies several fields, among them treatments with pesticides. In fact, the use of the agricultural pesticides turned out to be a need throughout the whole world, and this since antiquity, certain species of insects being able to be indirectly harmful for the man while attacking the cultures. This is why it is essential to protect the cultures and harvests using chemicals which thus contribute to improve the quality, the quantity and the conservation.

However, it was recognized that the subsequent residues of those pesticides are a clear factor of pollution of food and of the biological chains. For the human being, this can involve toxic effects that can even be mutagenic and/or carcinogenic.

Our attention was focused on deltamethrin [(S)-∝-cyano-3-henoxybenzyle cis-(1R, 3R)-2, 2-dimethyl-3-(2, 2-dibomovinyl) cyclopropanecarboxylate], which is regarded as the leader of the family of synthetic pyrethroid insecticides. It is commonly sold around the world; it is moreover imported and used in Algeria. Its usages have been largely developed since its first appearance on the market. Conceived initially for the fight anti - depredators in full field, it is presently the most used insecticide for the conservation of grains in the silos (Dikshit, 2000) and potato (Fidalgo et al., 2000). Its domestic use is larger and larger (against cockroaches, flies and other insects). Mosquito nets impregnated with synthetic pyrethroid (among them deltamethrin) constitute at the present time an essential tool of intervention for the fight against paludism in the south of the Sahara in Africa (Darriet et al., 2000). It is also largely used in veterinary medicine as acaricide to fight against animal infestations by *Rhipicephalus sanguineus* (Estrada-Peña, 2005) or like acaricide and scabicide (Pavan et al., 1999).

The analysis of residues of this insecticide must be required in food because it is suspected to be endocrine-disrupting (Xue and Xu, 2006).

Various methods have been described in the literature for the extraction and the determination of residues of deltamethrin in plants, fruits and other food products. They are all based on an extraction with organic solvents, a purification on silica gel column, alumina or florisil and an analysis by gas chromatography (GC) or high performance liquid chromatography (HPLC) with traditional detectors such as the electron capture detector or UV visibledetector (Haddad et al., 1989; Venant et al., 1990; Navickiene et al., 1998; Pavan et al., 1999; Cai et al. 2002). Detection by mass spectrometry is used for the determination of the residues of this pesticide in oils (Lamiri et al., 1999; Sanchez et al., 2006) and in blood (Ramesh and Ravi,

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2004). An enzyme-linked immunosorbent assay (ELISA) is also used to determine deltamethrin residues in milk (Lee et al., 2003). Some authors used the solid phase extraction to determine a group of pesticides (including deltamethrin) in water (Lopez-Blanco et al., 2006), or a microwave assisted extraction of some pyrethroid insecticides from soil (Esteva-Turrillas et al., 2004). Others reported purification by gel permeation chromatography of deltamethrin extracts in olive oil (Sanchez et al., 2006).

Algeria is the largest importer of wheat in the world and the importation of potatoes also became a practice to conpensate for the deficits recorded in the local market.

The aim of this work is to develop a method for the determination of deltamethrin residues in wheat and potato (two products of everyday consumption in our country) by adapting a method described in the literature by Baker and Bottomley (1982)

Materials and methods

An HPLC (Gilson, Middleton, USA) composed of : a monopiston pump (model 302), a manometric module (model 802), a Rheodyne Inc Model 7125 injector fitteed with a 20 µl loop of, a variable wavelength ultraviolet detector (model Holochrome), and a stainless-steel column (250 x 4.6 mm i.d.) packed with 5 µm Ultrasphere ODS (Beckman, Galway, Ireland). The chromatograms were recorded using a computing integrator (L.C.I. 100, Perkin – Elmer, Kuesnacht, Switzerland). A rotary-evaporator (VV micro, Heidolph, Heizbad, Germany), a Sorvall Omni-mixer (Ivan Sorvall Inc., Newington, USA), a magnetic stirrer (Jouan, Saint-Mazaire, France), a buchner for vacuum filtration, a Pyrex column with Teflon taps (30 x 1 cm i.d.), Whatman n°. 3 filter-papers

Reagents

Methanol and acetonitrile (HPLC grade); chloroform, hexane, dichloromethane, anhydrous sodium sulphate and silica gel (70 to 230 mesh A.S.T.M.) activated at 130°C during 10 hours (pesticide grade) were obtained from Merck (Darmstadt, Germany). Bi-distilled water was obtained in the laboratory using an Fisons' apparatus (Ecublens, Switzerland). Deltamethrin pesticide reference standard (98 % of purity) was gracefully provided by Roussel – Uclaf (Paris, France).

Extraction of deltamethrin residues

25 grams of sample were crushed or cutted in small pieces (according to the nature of the food) and transferred in a beaker (150 ml) with anhydrous sodium sulphate (20g) and chloroform (100 ml), and next the mixture was homogenised by a simple agitation during 5 minutes. The solvent was decanted on a Buchner funnel under suction using a Whatman n°. 3 filter-paper. The operation was repeated with 50 ml of chloroform. The beaker was washed with 2 portions of 15 ml of chloroform and the washings was used to rinse the residue in the Buchner funnel. The filtrate was transfered in a separating funnel of 500 ml and the flask of the buchner was washed with 2 portions of 50 ml of bi - distilled water which were added to the separating funnel. The aqueous phase was discarded and the chloroformic phase was dried by passing it through 15 g of anhydrous sodium sulphate in a glass column (of 300 mm length and 10 mm diameter). The chloroform extract was then concentrated to 5 ml by using a rotary-evaporator under reduced pressure with the water-bath at 40°C

Purification

By using a Pasteur pipette, the chloroform extract was transferred on to 5 g of silica gel column that has been activated at 130°C during 10 hours and slurry packed in hexane. The solution was let to pass. The flask of the rotary-evaporator was rinsed with two portions of 10 ml of hexane which were also transfered in the column and let to pass; the eluate was discarded and the process was repeated with 25 ml of hexane - dichloromethane (4+1), which was also discarded. Finally the column was eluted with 60 ml of dichloromethane which was collected. The dichloromethane was removed using the rotary-evaporator at 40°C. The dry residue is dissolved with 10 ml of acetonitrile (or methanol or hexane). It is then ready to be analysed.

Analytical method

A suitable volume (20µl) of the extract was injected into the column and eluted with a mobile phase: acetonitrile - water (92:8) V/V at a flow rate of 0.85 ml/min. For detection, an absorption wavelength of 233 nm was employed. Figure 1 shows the chromatograms of 1 µg/ml of a deltamethrin solution in the mentioned conditions. With this method, the sensitivity of the detector for deltamethrin was found to be 0.02 µg/ml, which leads to a minimal detectable quantity of 0.4 ng, (at a 90% confidence degree) and a linearity range between 0.8 ng and 60 ng

RESULTS AND DISCUSSION

To test the performances of this method of extraction - purification, we have chosen samples of wheat and potato produced in Algeria. We carried out two analyses respecttively: one after addition of a known quantity of deltamethrin (fortified sample) and the other without addition of deltamethrin (blank sample). The analysis was repeated twenty times in order to evaluate the reproductibility of the method. The quantities of deltamethrin added were 1 mg/kg (quantities which are close to the ones recommendded by the manufacturer). The fortified sample is left at rest during one hour before starting the operation of extraction - purification. The residue obtained after this operation was analysed by HPLC.

Analysis of the blank samples (not fortified) of wheat and potato after the procedure of extraction–purification indicates the absence of a peak at the time of retention of deltamethrin. Under the already quoted chromatographic conditions this peak is well resolved compared to the close peaks in the fortified samples (a typical chromatogram is presented on Figure 2).

The present method of extraction - purification gave very good recovery results (Table 1); the calculated coefficients of variation are all lower than 6 % indicating a very good reproductibility. The poorer result obtained with potato could be explained by a greater loss by vaporization at the time of the pesticide introduction.

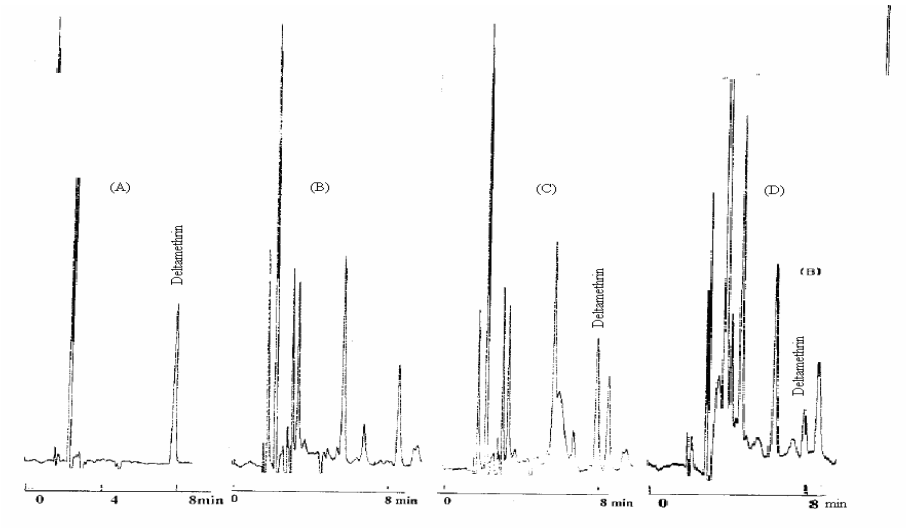

Figure 1: Chromatograms of extract of (A) standard deltamethrin (20 ng), (B) wheat not fortified, (C) wheat fortified with 1 mg/kg of deltamethrin and (D) wheat of importation. Injection of 20 µl, mobile phase: acetonitrile - water (92:8) V/V at a flow rate of 0.85 ml/min; detection, 233 nm.

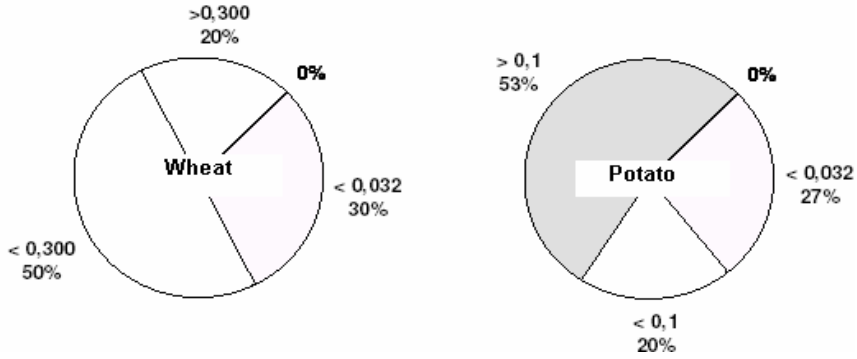

Figure 2. Chart of deltamethrin residues (in mg/kg) in wheat and potato of importation.

Table 1. Recovery of the deltamethrin from fortified samples (Fortification level = 1 mg/kg, number of replicates =20).

	Wheat	Potato
Recovery (%)	85.80	76.40
Standard deviation	0.023	0.021
Coefficient of variation (%)	2.68	2.75

We took wheat and potato samples of importation at the level of the Algiers harbour. The extracted and purified residues were analysed by HPLC. A typical chromatogram is presented in Figure 1.

The results obtained are represented on Figure 2 and confirmed the use of deltamethrin by the exporters of wheat and potato. If the residue proportions in wheat are much lower than the L.M.R. fixed by the O.M.S. / F.A.O. (1 mg/kg), on the other hand those found in potato are higher than the L.M.R. (0.1 mg/kg.) for the majority of them.

CONCLUSION

The method of extraction - purification that we have adapted and tested and that consists of an extraction with chloroform followed by purification on activated silica gel appears to be completely satisfactory since it leads to deltamethrin recoveries higher than 75%.

The use of deltamethrin in the stored food products by the exporters was largely confirmed by the found results. The residues found in potato exceeding the standards, push us to conclude that a strict control of the imported food products is essential in order to protect the consumers.

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