Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Chromatography A, 1071 (2005) 67–70
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Short communication

Residue analysis of organophosphorus pesticides in animal matrices by dual column capillary gas chromatography with nitrogen–phosphorus detection

Giampiero Pagliuca*, Teresa Gazzotti, Elisa Zironi, Patrizia Sticca

Department of Veterinary Public Health and Animal Pathology, Food Hygiene and Technology Section, Alma Mater Studiorum, University of Bologna, Via Tolara di Sopra, 50 I 40064 Ozzano Emilia, BO, Italy

Abstract

Organophosphorus pesticides (OPPs) were determined in matrices of animal origin by dual column capillary gas chromatography using nitrogen–phosphorus detection (NPD). This method was tested on cow milk and on liver and muscle of wild boar. The isolation of these pesticides was performed by liquid partition followed by cleanup with solid phase cartridge (SPE C18), after extraction from the matrix. The analytes identification was obtained by comparing the retention times in two columns with different polarity. The quantification of each OPP was obtained using parathion-ethyl as internal standard. The method was developed in a UNI EN ISO 9001:2000 certified laboratory. The recovery, investigated by analyzing samples spiked at 5, 10 and 50 ppb, ranged from 59 to 117% in milk, from 60 to 81% in liver and from 68 to 76% in muscle. The limit of quantification (LOQ) and limit of detection (LOD) were, respectively, 5 and 1 ppb for each compound and allowed quantifying the residues below the legal limits.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Organophosphorus pesticides; Solid phase extraction; Animal matrices

1. Introduction

Organophosphorus pesticide (OPPs), mainly used as insecticides, are esters of phosphoric acid with different substituents.

These compounds, even if they are less persistent in the environment than the organochlorine pesticides, can be accumulated along the food chain and may therefore represent a risk for human health.

Animals can accumulate such substances from contaminated feed and water or from insecticide practices in stables. Therefore, an indirect source of OPPs can be represented by animal-derived products [1–4].

The presence of fat in these matrices could interfere with the analytes isolation and determination [1].

In this study acephate, chlorpyriphos, chlorpyriphos-methyl, diazinon, methamidophos, methidation, phorate, pirimiphos-methyl were determined in cow milk and chlorpyriphos and dimethoate in liver and muscle of wild boar.

The isolation of these pesticides was performed by liquid partition followed by cleanup with solid phase cartridge, after the extraction from the matrix [1,2,4,5].

The samples were analyzed by dual column capillary gas chromatography using nitrogen–phosphorus detection (NPD). The GLC separations were carried out under the same programmed conditions by a single injection (splitless mode), allowing to achieve the separation of nine OPPs in both columns.

2. Experimental

Solvents were for pesticides residue analysis.

The standard pesticides were obtained from Dr. Ehrenstorfer, Augsburg, Germany.

* Corresponding author. Tel.: +39 051 2097 323; fax: +39 051 2097 323.
E-mail address: pagliuca@vet.unibo.it (G. Pagliuca).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.08.142

2.1. Sample preparation

2.1.1. Cow milk samples

Twenty grams of milk, warmed to 20 °C, were extracted with 25 mL of acetone:acetonitrile (1:4), mixing gently the sample and the solvent with a magnetic stirrer, and allowed to stand for 20 min. The sample was afterwards shaken for 30 s and then centrifuged at 4000 rpm for 5 min.

The liquid phase was decanted in a flask, then the milk solid was collected and redissolved in 2 mL of water. After the addition of 20 mL of acetone:acetonitrile (1:4), the sample was mixed again and re-extracted as before. The liquid phase was joined to the previous one. The extraction was repeated a third time. The liquid phases were shaken with 50 mL of dichloromethane in a separatory funnel and was allowed for phases to separate. The dichloromethane phase was collected while the remaining acetone:acetonitrile phase was extracted two additional times with 50 mL of dichloromethane.

The three dichloromethane extracts were gathered up and dried over anhydrous sodium sulphate for 30 min, filtered on filter paper and carried to dryness on a rotary evaporator. The sample was dissolved in 1 mL of acetonitrile and loaded on SPE C18 Monofunctional cartridge (500 mg/3 mL Phenomenex) which was previously conditioned with 5 mL of acetonitrile. The flask was then washed with other 2 mL of acetonitrile and 1 mL of 2-propanol.

The resulting 4 mL were concentrated to dryness and redissolved in 200 μL of acetone.

2.1.2. Wild boar samples

Ten grams of liver or muscle were homogenized with an Ultraturrax apparatus and extracted, stirring for 10 min with 15 mL of acetone:acetonitrile (1:4). After filtration, the extraction procedure was repeated twice. The organic phases were extracted by partitioning with 30 mL of dichloromethane: the extraction was repeated three times. The extracted solution after drying over anhydrous sodium sulphate was purified as previously described through the SPE cartridge using 3 mL of acetonitrile.

2.2. Instrumentation

All analyses were performed on a HRGC Mega 28560, equipped with two NPDs (nitrogen–phosphorus detector)

Two columns were used: Zebron ZB-5 (30 m × 0.32 mm i.d., 0.25 μm d.f.) and Zebron ZB-50 (30 m × 0.32 mm i.d., 0.25 μm d.f.). Zebron ZB-5 has a non-polar phase (5% phenyl–95% dimethylpolysiloxane) whether Zebron ZB-50 has a polar phase (50% phenyl–50% dimethylpolysiloxane). The columns were both connected to the injector by a glass dual column adapter, in order to split the sample mixture.

The samples were injected into the GLC system in splittless mode (30 s). Temperature of injector was set to 260 °C. The NPD system used nitrogen as make up gas and a temperature set point of 290 °C. Helium (1 cc/min) was used as carrier gas.

2.2.1. Cow milk samples

The chromatographic temperature program was first rated from 100 to 130 °C at 5 °C/min, then this temperature was maintained for 10 min, then a second rate of 5 °C/min up to 220 °C followed, then this temperature was maintained for 7 min, and finally a third rate at 6 °C/min to 274 °C followed. GC analysis time was 50 min.

2.2.2. Wild boar samples

The chromatographic temperature program was first rated from 130 to 220 °C at 7 °C/min, then this temperature was maintained for 7 min, then a second rate of 5 °C/min up to 235 °C followed. GC analysis time was 30 min.

2.3. Quantification

The quantification of each OPP was performed using parathion-ethyl as internal standard (I.S.). Before extraction, 1 mL of 0.2 ppm parathion-ethyl standard solution in acetone was added to samples.

3. Results and discussion

The OPPs studied were chosen according to the information available on their use in Italy and considering their attitude to bio-accumulate in animal tissues and animal-derived products.

The single step of SPE C18 Monofunctional clean-up showed satisfying recoveries and allowed to process more samples at the same time.

The analyte identifications were obtained by comparing the retention times in the two columns with different polarity (Fig. 1) and the reported programmed conditions were chosen to avoid the interference of the matrix. For instance, in muscle and liver analyses, the initial temperature and the gradient were increased to separate dimethoate from a matrix related peak (Figs. 2 and 3).

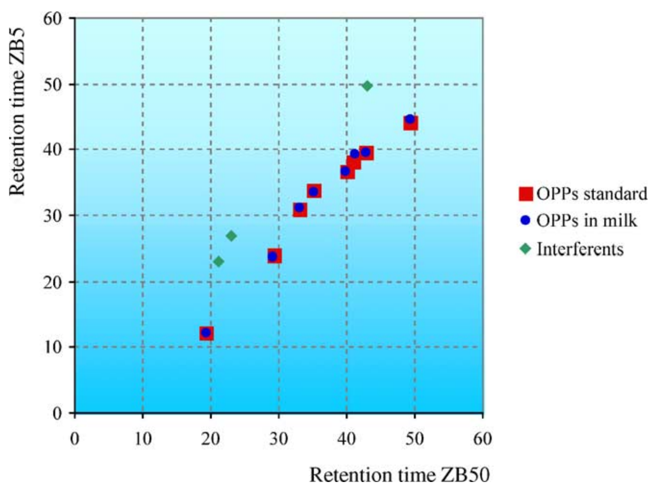

Fig. 1. Comparison between the retention times of analytes and interferents in ZB50 and ZB5 columns.

Download English Version:

https://daneshyari.com/en/article/9749179

Download Persian Version:

https://daneshyari.com/article/9749179

Daneshyari.com