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Vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction for the determination of carbamates in juices by micellar electrokinetic chromatography tandem mass spectrometry

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ABSTRACT

A new method based on vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction has been developed for the extraction of carbamate pesticides in juice samples prior to their determination by micellar electrokinetic chromatography coupled to tandem mass spectrometry. This sample treatment allowed the satisfactory extraction and the extract clean-up of 25 carbamates from different fruit and vegetal juices (banana, tomato, and peach). In this study, the addition of ammonium perfluorooctanoate in the aqueous sample in combination with vortex agitation, provided very clean extracts with short extraction times. Under optimized conditions, recoveries of the proposed method for these pesticides from fortified juice samples ranged from 81% to 104%, with relative standard deviations lower than 15%. Limits of quantification were between 2.3 μg kg^{-1} and 4.7 μg kg^{-1}, showing the high sensitivity of this fast and simple method.

1. Introduction

Pesticides are often found at higher concentrations in the peel of the fruit than in its juice; however, in the production of some types of juices (e.g., peach or tomato) the entire fruit is squeezed without removing the peel. Therefore, the concentration of pesticide residues in juices should be monitored strictly to ensure food safety [1]. In this sense, pesticide content in different food and feed commodities is controlled by European Union (EU), which has established a maximum residue level (MRL) of 10 μg kg^{-1} for processed food, as juices [2,3]. Among the different families of pesticides, carbamates (CRB) are extensively used for agricultural activities, making it possible to find residues in fruit juices [4]. This kind of pesticides have an anticholinesterase activity, so their presence in foods could have adverse health effects such as headache, vomiting, abdominal cramps, uncontrolled urination or defecation [5,6].

Usually, chromatographic methods have been used for the determination of pesticides (including CRB) in food and beverages, which have been compiled in recent reviews [1,7]. Moreover, liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) is the technique of choice for most of the recent applications for determination of pesticides [8], including CRB in juices [9].

Instead, the use of capillary electrophoresis (CE) has been less explored, especially for the determination of CRB, as most of them are neutral compounds in a wide range of pH [10,11], making the use of micellar electrokinetic chromatography (MEKC) mandatory [12–15]. Thus, sweeping-MEKC–UV/vis has been previously proposed for the determination of some CRB pesticide in different

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Abbreviations: ALD, aldicarb; ALDSFN, aldicarb-sulfone; APFO, ammonium perfluorooctanoate; ASL, asulam; BGE, background electrolyte; BTH, benthiocarb; BY, benomyl; CAR, carbaryl; CBZ, carbendazim; CE, capillary electrophoresis; CF, carbofuran; 3-CF, carbofuran-3-hydroxy; CMC, critical micellar concentration; CRB, carbamate; DETH, diethofencarb; DLLME, dispersive liquid–liquid microextraction; ESI, electrospray; ETH, ethiofencarb; ETHSFX, ethiofencarb-sulfoxide; EU, European Union; FEN, fenobucarb; FNX, fenoxycarb; FURA, furathiocarb; HF-LPME, hollow-fiber LPME; IPA, 2-propanol; ISO, isoprocarb; IT, ion trap; LC, liquid chromatography; LLE, liquid–liquid extraction; LOD, limit of detection; LOQ, limit of quantification; LPME, liquid phase microextraction; ME, matrix effect; MeCN, acetonitrile; MEKC, micellar electrokinetic chromatography; MeOH, methanol; MRL, maximum residue level; MRM, multiple reaction monitoring; MS, mass spectrometry; MS/MS, tandem mass spectrometry; MTH, methiocarb; MTY, methomyl; NP, napropamid; PIR, pirimicarb; PIRDES, pirimicarb-desmethyl; PR, promecarb; PRM, propamocarb; PX, propoxur; PY, pyraclostrobin; SDME, single-drop microextraction; SDS, sodium dodecyl sulfate; SPE, solid phase extraction; SPME, solid phase micro-extraction; VALLME, vortex-assisted liquid–liquid microextraction; VSLLME, vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction

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types of fruits and juices using sodium dodecyl sulfate (SDS) as micellar medium [16]. Nevertheless, CE coupled to tandem mass spectrometry (MS/MS) is a very appropriate technique for the determination of pesticides in different food commodities, because it provides higher sensitivity than UV/vis, and of its capability for unambiguous evidences for pesticide identification and quantification at trace levels, being a useful tool in food safety [17]. However, the direct coupling of MEKC with MS requires the use of alternative pseudo-stationary phases as, for instance, the (semi) volatile surfactant ammonium perfluorooctanoate (APFO) instead of the common surfactants, as SDS [18–21]. It should be highlighted that by using APFO similar results to standard systems based on SDS have been obtained, with exceptional results regarding its high compatibility with MS [18]. This approach has been reported for the determination of CRBs in waters [22,23].

Another key point in pesticide determination is the sample treatment. Frequently, it is based on solid phase extraction (SPE), liquid–liquid extraction (LLE) or solid phase micro-extraction (SPME) [24], although during the last decade QuEChERS has emerged as the treatment preferred for pesticide determination [25]. In this sense, several methods have been reported for the determination of CRBs in juice samples, based on SPE [26], LLE [27] and QuEChERS [28,29]. However, recently, different strategies based on liquid phase microextraction (LPME) techniques have been proposed for simplifying sample treatment and preconcentration for pesticide residue determination. LPME can be classified into three main groups: single-drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME), and hollow-fiber LPME (HF-LPME), that with different variations have given rise to new sample treatments [30,31], that have been recently proposed for CRB determination in juices [16,32–35].

We will focus on DLLME, whose principles, applications, advantages and disadvantages have been exhaustively commented on several reviews [36–38], and one of its variations named vortex-assisted liquid–liquid microextraction (VALLME). In VALLME the dispersion of the extraction solvent into the aqueous solution is achieved by vortex mixing without any dispersant solvent [39]. However, it was observed that the extraction time in VALLME was quite long, because the mass-transfer efficiency between sample and extraction organic solvent was slower than in DLLME [40,41]. The addition of a surfactant as an emulsifier to enhance the speed of the mass-transfer from aqueous samples to the extraction solvent was then proposed, showing that the use of surfactants below their critical micellar concentration (CMC) enhances the dispersion of the water-immiscible phase into the aqueous phase. This fact is because the generated emulsion reduces the interfacial tension between organic solvent and water by adsorbing at the liquid–liquid interface, thus increasing the dispersion. This methodology was named vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction (VSLLME), and thanks to the combination of agitation by vortex and surfactant, shorter extraction times than VALLME were achieved [42–44].

The aim of this work was to develop and validate an analytical method for the determination of 25 CRB pesticides in different juices using VSLLME extraction and MEKC–MS/MS, which is not yet documented in the literature. VSLLME was optimized by means of an experimental design. The method was validated for different kinds of juice samples, such as banana, peach and tomato juice, achieving limits of quantification (LOQs) below 10 $\mu g\,kg^{-1}$ (the MRL established for processed samples by current EU legislation) and MRLs established for the product commodities used for obtaining these juices [2].

2. Material and methods

2.1. Chemicals and reagents

Water, methanol (MeOH) and 2-propanol (IPA) (LC–MS Chromasolv grade) were supplied from Fluka Analytical (Steinheim, Germany). APFO at pH 9.0 was prepared with perfluorooctanoic acid 96% (Sigma-Aldrich; St. Louis, MO, USA) and ammonium hydroxide (Panreac-Química; Barcelona, Spain). Tween 80 and triton X-114 were obtained from Panreac-Química (Barcelona, Spain). Chloroform, tetrachloromethane, dibromomethane and formic acid were obtained from Sigma-Aldrich.

Pestanal grade analytical standards of carbendazim (CBZ), benomyl (BY), methomyl (MTY), asulam (ASL), aldicarb-sulfone (ALDSFN), ethiofencarb-sulfoxide (ETHSFX), carbofuran-3-hydroxy (3-CF), carbaryl (CAR), aldicarb (ALD), carbofuran (CF), propoxur (PX), methiocarb (MTH), isoprocarb (ISO), ethiofencarb (ETH), promecarb (PR), fenobucarb (FEN), pirimicarb-desmethyl (PIRDES), diethofencarb (DETH), pirimicarb (PIR), benthiocarb (BTH), fenoxycarb (FNX), napropamid (NP), propamocarb (PRM), pyraclostrobin (PY) and furathiocarb (FURA) were supplied by Fluka. Individual stock standard solutions of each compound were prepared by dissolving accurately weighed amounts in MeOH and stored in the dark at 4 °C. They were stable for at least 4 months. Working standard solutions containing all the CRBs were freshly prepared by proper dilution of the stock standard solutions with MeOH.

Nylon syringe filters, 0.22 μm × 13 mm (Agela Technologies, New York, USA), were used for filtration of the sample extracts before injection into the MEKC–MS/MS system.

2.2. Instrumentation

MEKC experiments were carried out with an HP^{3D} CE instrument (Agilent Technologies, Waldbronn, Germany). The coaxial sheath liquid sprayer was supplied by Agilent Technologies. MS was performed using an Agilent 1100 Series LC/MSD SL mass spectrometer equipped with electrospray (ESI) ionization and an ion trap (IT) analyzer. MS spectrometer was controlled by a PC running the Esquire software 4.1 from Bruker Daltonics (Bremen, Germany).

The StatGraphics Plus Software 5.1 (Statistical Graphics Rockville; MD, USA) was used to generate the experimental designs and data processing.

Vortex agitator (Genie 2 model from Scientific Industries; Bohemia, NY, USA), pH-meter (Crison model pH 2000; Barcelona, Spain) with a resolution of ± 0.01 pH unit, a centrifuge (Universal 320 model from Hettich; Leipzig, Germany) and a nitrogen evaporator (System EVA-EC from VLM GmbH, Bielefeld, Germany) were also used.

2.3. MEKC procedure

Separation was carried out in a bare fused-silica capillary (90 cm total length, 50 μm ID, 375 μm OD) from Polymicro Technologies (Phoenix, AZ, USA). The electrophoretic separation was achieved using a voltage of 23 kV (positive mode). The background electrolyte (BGE) was an aqueous solution of 100 mM perfluorooctanoic acid adjusted to pH 9.0 with 15 M ammonium hydroxide. The temperature of the capillary was kept constant at 24 °C. The sample was hydrodynamically injected for 30 s at 50 mbar. In order to improve the sensitivity for some CRBs, the sample solvent was 75 mM APFO at pH 9.0, less concentrated than the BGE, providing a small stacking effect and allowing on-line preconcentration [22,45].

Before the first use, the capillary was conditioned by flushing with 1 M NaOH (10 min at 25 °C), water (10 min) and finally with