Talanta 160 (2016) 211–216

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Ringer tablet-based ionic liquid phase microextraction: Application in extraction and preconcentration of neonicotinoid insecticides from fruit juice and vegetable samples

Mir Ali Farajzadeh *, Mahdi Bamorowat, Mohammad Reza Afshar Mogaddam

Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form
27 March 2016
Accepted 29 March 2016
Available online 31 March 2016

Keywords:
1–Hexyl–3–methylimidazolium hexafluorophosphate
Ionic liquid
Ringer Tablet
High performance liquid chromatography
Diode array detector

ABSTRACT

An efficient, reliable, sensitive, rapid, and green analytical method for the extraction and determination of neonicotinoid insecticides in aqueous samples has been developed using ionic liquid phase microextraction coupled with high performance liquid chromatography–diode array detector. In this method, a few microliters of 1–hexyl–3–methylimidazolium hexafluorophosphate (as an extractant) is added onto a ringer tablet and it is transferred into a conical test tube containing aqueous phase of the analytes. By manually shaking, the ringer tablet is dissolved and the extractant is released into the aqueous phase as very tiny droplets to provide a cloudy solution. After centrifuging the extracted analytes into ionic liquid are collected at the bottom of a conical test tube. Under the optimum extraction conditions, the method showed low limits of detection and quantification between 0.12 and 0.33 and 0.41 and 1.11 ng mL^{-1}, respectively. Extraction recoveries and enrichment factors were from 66% to 84% and 655% to 843%, respectively. Finally different aqueous samples were successfully analyzed using the proposed method.

1. Introduction

Neonicotinoid insecticides are a relatively new group of active ingredients with novel modes of actions. These insecticides are active against numerous sucking and biting pests and insects including whiteflies, aphides, beetles, and some lepidoptera species [1]. These compounds are the first new class of insecticides introduced in the last 50 years, and they are currently the most widely used insecticides in the world [2]. Neonicotinoids, like nicotine, are nicotinic acetylcholine receptor agonizts. Because most neonicotinoids bond much more strongly to insect neuron receptors than to mammal neuron receptors, these insecticides are selectively more toxic to insects than mammals [3]. These compounds are most commonly used in rice, maize, sunflower, rape, potato, sugar beet, vegetables, and fruits crops [4]. Many countries have formulated strict limits about the neonicotinoids in various matrices. The European Union (EU) legislation has established standards/regulations for the maximum residue limits (MRLs) for neonicotinoid insecticides in different agricultural products. The MRLs for neonicotinoids in fruits, vegetables and cereals are between 0.1 and 1.0 mg kg^{-1} [5]. The accumulation of insecticides in agricultural products is of great concern because plants act as intermediates in the transport of contaminants from soil, water, and air to human and fauna.

Neonicotinoid insecticides are unsuitable for the direct analysis by gas chromatography (GC) due to their low volatility and high polarity [6]. The use of high performance liquid chromatography (HPLC) coupled with various detection systems including ultraviolet [7,8], diode array [9,10], fluorescence [11], and mass spectrometry [12–14] is the preferred choice for neonicotinoid insecticides analysis. Although they are sensitive analytical methods, but neonicotinoids usually are found in very low concentrations in the complex matrices of environmental samples. Therefore, a sample preparation step is still required. A good sample preparation method allows not only the analytes to be preconcentrated but also the other compounds present in the sample matrix to be removed. Liquid–liquid extraction (LLE) [15,16] and solid phase extraction (SPE) [17,18] are the traditional sample pretreatment methods to achieve these objectives. But these conventional methods are tedious, expensive, and time–consuming, and require large amounts of toxic organic solvents and samples. Many efforts have been performed to overcome these drawbacks and to develop efficient, economical, and miniaturized

Abbreviations: AALLME, air–assisted liquid–liquid microextraction; DAD, diode array detector; DLLME, dispersive liquid–liquid microextraction; GC, gas chromatography; LLE, liquid–liquid extraction; LPME, liquid phase microextraction; MS, mass spectrometry; SPE, solid phase extraction; UPLC, ultra high performance liquid chromatography; USAEME, ultrasound–assisted emulsification microextraction; VADLLME, vortex–assisted dispersive liquid–liquid microextraction.

* Corresponding author.
E-mail addresses: mafarajzadeh@yahoo.com, mafarajzadeh@tabrizu.ac.ir (M.A. Farajzadeh).

http://dx.doi.org/10.1016/j.talanta.2016.03.097
0039-9140/

alternatives. Solid phase microextraction (SPME) and liquid phase microextraction (LPME) are mainly developed miniaturized sample preparation techniques. They are easy, fast and solvent–free or with just a little organic solvent consumption. SPME is based on partitioning of the analytes between the sample matrix and fiber coating, and has the advantages of portability and simplicity, however, the fiber is comparatively expensive, fragile, and has a limited lifetime [19]. LPME as a miniaturized sample preparation approach emerged during the mid–to–late 1990s [20,21]. After publication of the first paper on LPME, different modes of LPME, either static or dynamic, have been developed [22–24]. In 2006, Assadi et al. reported a new microextraction technique, which was termed dispersive liquid–liquid microextraction (DLLME) [25]. DLLME is based on a ternary solvent system in which a dispersive solvent disperses an extraction solvent into the sample. The dispersive solvent must be fully miscible with both aqueous sample and extraction phase. The advantages of DLLME method are simplicity of operation, rapidity, low cost, and high extraction recoveries (ERs) and enrichment factors (EFs) [26–30]. The presence of a disperser solvent in aqueous sample solution makes it relatively non–polar and increases the solubility of lipophilic analytes into the aqueous sample solution which leads to relatively low extraction efficiency. To improve the extraction efficiency, ultrasound–assisted emulsification microextraction (USAEME) [31–33], vortex–assisted dispersive liquid–liquid microextraction (VADLLME) [34–36], and air–assisted liquid–liquid microextraction (AALLME) [37,38] have been developed in those an extraction solvent is dispersed into the aqueous sample through continuous ultrasound irradiation, vortexing, or aspiration/dispersing, respectively. Room temperature ionic liquids (RTILs) are a group of organic salts that are liquid at room temperature. They are usually considered environmentally friendly solvents and thus have applications in separation sciences because they have several unique properties, such as low volatility, chemical and thermal stability, and low toxicity. In some studies, RTILs have been used as the extraction solvents instead of organic solvents in LPME in analysis of different analytes in samples [32–34].

The main goal of this study was to resolve the disadvantages of DLLME related to disperser and extraction solvents using an RTIL as an extraction solvent and Ringer tablet as a disperser to develop a green LPME method. In the present work, for the first time, a DLLME method has been developed without consumption of organic disperser solvent for extraction of some neonicotinoid insecticides. It is noted that Ringer tablet is a mixture of several inorganic salts to prepare isotonic diluents for both bacterial cells and bacteriological specimens and it has the following composition: sodium chloride, potassium chloride, calcium chloride, and sodium bicarbonate (2.25, 0.105, 0.12, and 0.05 g, respectively). The influence of various experimental parameters on the performance of the proposed method will be investigated. Then, the analytical figures of the method will be assessed.

2. Materials and methods

2.1. Reagents and standard solutions

The studied neonicotinoid insecticides including imidacloprid, acetamiprid, and thiamethoxam with purity $>98\%$ were kindly provided by GYAH Corporation (Karaj, Iran). RTILs including 1–hexyl–3–methylimidazolium hexafluorophosphate ([HMIM][PF_6]), 1–butyl–3–methylimidazolium hexafluorophosphate ([BMIM][PF_6], and 1–octyl–3–methylimidazolium hexafluorophosphate ([OMIM][PF_6]) tested as the extraction solvents were from Sigma–Aldrich (St. Louis, MO, USA). Ringer tablets were supplied from Merck (Darmstadt, Germany). Analytical grade sodium chloride, hydrochloric acid, and sodium hydroxide were from Merck. HPLC–grade water and acetonitrile were from Caledon (Georgetown, Canada). Individual stock solutions of the target analytes (50 mg L^{-1}) were prepared in acetonitrile and stored in a refrigerator at 4 °C. Fresh working standard solutions with low concentrations were daily prepared by diluting the stock solutions with HPLC–grade water.

2.2. Instrumentation

A Hewlett–Packard 1090–II liquid chromatograph (Palo Alto, CA, USA) equipped with a diode array detector (DAD) was used for separation and determination of the analytes. The separation system was equipped with an auto injector. Separation was carried out on an STR–ODS (II) analytical column (150 × 4.6 mm id., 5 μm particle size) (Shinwa, Kyoto, Japan). Mobile phase was a mixture of acetonitrile: water (30:70, v/v) at a flow rate of 1 mL min^{-1}. Monitoring of the analytes was done at 271 nm for imidacloprid, 253 nm for thiamethoxam, and 244 nm for acetamiprid. Volume of the injected solution into the separation system was 5 μL. ChemStation software was used for data acquisition and processing. A Metrohm 654 pH meter (Metrohm, Herisau, Switzerland) equipped with a glass electrode was used in pH adjustment. A Hettich centrifuge, model D–7200 (Germany) was used for accelerating phase separation.

2.3. Samples

Fruit juice samples available in local supermarkets (Tabriz, Iran) including sour cherry, apple, and strawberry were purchased for analysis. Before analysis all juices were filtered through an Albet DP 414 filter paper (Düren, Germany). Then the filtered juices were diluted at a ratio of 1:2 with HPLC–grade water before analysis. Vegetable samples including lettuce, cucumber, and tomato were prepared from local vendors. These samples were washed with tap water and then with distilled water and crushed using a commercial fruit pulper (Black & Decker, USA) to produce their juices. Then an aliquot of 50 mL of the juices was centrifuged at a rate of 1118*g* for 10 min, and the clear supernatant was diluted at a ratio of 1:5 with HPLC–grade water.

2.4. Microextraction procedure

A 10.0 mL HPLC-grade water spiked with 50 ng mL^{-1} of each analyte or the diluted sample (see Section 2.3) was added to a 15–mL glass test tube with a conical bottom. Then 63 μL of [HMIM][PF_6] as an extraction solvent was added onto a 0.9 g Ringer tablet. After adding the RTIL, it penetrated into the pores of the Ringer tablet and then the tablet was transferred into the aqueous solution. The mixture was shaken manually and the tablet dissolved into the aqueous phase gradually. Dissolving of the Ringer tablet in the aqueous phase led to dispersion of the RTIL in whole parts of the solution and a cloudy solution was produced. During this period the target analytes were extracted into the RTIL. Then the mixture was centrifuged for 4 min at 1118*g* to settle down the RTIL in the bottom of the tube (10 ± 0.5 μL). Whole of the sedimented phase was withdrawn and injected into the separation system for analysis.

2.5. Calculation of EF and ER

The EF is defined as the ratio of the analyte concentration in the sedimented phase (C_{sed}) to the initial concentration of analyte (C_0) in the sample:

$$EF=\frac{C_{sed}}{C_o} \quad (1)$$

C_{sed} is obtained by comparison of the obtained peak areas in