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Negative corona discharge-ion mobility spectrometry as a detection system for low density extraction solvent-based dispersive liquid–liquid microextraction

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ABSTRACT

This paper deals with a method based on negative corona discharge ionization ion mobility spectrometry (NCD-IMS) for the analysis of ethion (as an organophosphorus pesticide). The negative ions such as O_2^- and NO_x^- were eliminated from the background spectrum to increase the instrument sensitivity. The method was used to specify the sample extracted via dispersive liquid–liquid microextraction (DLLME) based on low density extraction solvent. The ion mobility spectrum of ethion in the negative mode and the reduced mobility value for its ion peak are firstly reported and compared with those of the positive mode. In order to combine the low density solvent DLLME directly with NCD-IMS, cyclohexane was selected as the extraction solvent, helping us to have a direct injection up to 20 μL solution, without any signal interference. The method was exhaustively validated in terms of sensitivity, enrichment factor, relative recovery, and repeatability. The linear dynamic range of 0.2–100.0 μg L^{-1}, detection limit of 0.075 μg L^{-1}, and the relative standard deviation (RSD) of about 5% were obtained for the analysis of ethion through this method. The average recoveries were calculated about 68% and 92% for the grape juice and underground water, respectively. Finally, some real samples were analyzed and the feasibility of the proposed method was successfully verified by the efficient extraction of the analyte using DLLME before the analysis by NCD-IMS.

1. Introduction

Organophosphorus pesticides (opps) are widely used as insecticides and acaricides for increasing agricultural productivity. These compounds are harmful to human health because they act on the central nervous system. As the opps compounds have long half-lives, their residues can remain in surface water, groundwater, soil and agricultural products [1]. Therefore, development of an analytical method with high accuracy and sensitivity for the determination of these compounds' residues is necessary. In this regard, various preparation methods such as liquid–liquid extraction (LLE) [2], solid-phase extraction (SPE) [3], solid-phase microextraction (SPME) [4] and single-drop microextraction (SDME) [5] have been utilized for the analysis of opps pesticides in various matrices. In LLE method, in addition to several tedious steps of preparation and extraction, a large amount of hazardous and toxic organic solvents has to be used. These disadvantages make the environment pollution require a long time to achieve the equilibrium, and cause loss of sample at each step [6]. In SPE method, though the time and solvent volume needed are comparatively less than in LLE method, the SPE method, nevertheless, requires toxic organic solvents for the elution step [7]. The next method, namely, SPME method suffers from a variety of drawbacks including high cost, short lifetime and fragile extractive fibers, and sample carry–over effect [8]. Also, the SDME methods impose some limitations such as the need for fast stirring speed, instability of hanging drop, and possibility of dissolving of the drop during the extraction process [9]. To overcome some of these problems, dispersive liquid–liquid microextraction (DLLME) method was firstly developed by Rezaee et al. in 2006 [10]. The major advantages of this method are low time and cost, simplicity of operation, high recovery, high enrichment factor (EF), and low consumption of organic solvents [11]. These advantages are luring the scientists into using this method for the extraction and preconcentration of a wide variety of pesticides from different environmental and foodstuff samples. In this method, a cloudy solution is formed when an appropriate mixture of extraction and dispersive solvent is injected into an aqueous sample. This cloudy solution results from tiny droplets of extraction solvent dispersed into the aqueous sample. In order to take out the analyte from aqueous phase with a high potential, the extraction solvent must be soluble

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in the dispersive solvent while having a very low solubility in water. After centrifuging, tiny droplets of extraction solvent containing analyte can be collected in lower or upper aqueous phase, based on the density, and then separated from the aqueous phase. Only some solvents which have a higher density than water can form a cloudy solution in DLLME technique [12]. Typically, in this case, chlorinated solvents such as chloroform, tetrachloromethane, chlorobenzene and tetrachloroethane are used as the extraction solvents. These solvents are very toxic and hazardous to humans and environment. In addition, chlorinated solvents have a very high electron affinity and therefore produce a strong signal using analytical apparatus in the negative mode such as gas chromatography-electron capture detector (GC-ECD) or mass spectrometry (MS). In fact, as the solvent signal may overlap with some analyte peaks, the DLLME–GC-ECD technique cannot be used to extract and measure the opps pesticides. To overcome these problems, Farajzadeh et al. [13] used some solvents lighter than water as the extraction solvent, for the first time. In DLLME based on the low density extraction solvents, all the treatment steps except the steps after centrifuging are the same as those in the technique with solvents heavier than water. Unlike the heavy solvents, low density extraction solvent droplets were delivered on the surface of the aqueous phase. For collection of the extracted phase, some special extraction tubes were designed and developed for DLLME procedure [12–14].

In DLLME technique, the collected organic phase can be monitored using several methods such as GC with different detectors [13–15] or high performance liquid chromatography (HPLC) with various detectors [16,17]. However, these methods are very laborious and require a long run time for separation in a column [18]. In addition, HPLC methods require expensive solvents in the elution step. Very recently [19], we have described the feasibility of corona discharge ion mobility spectrometry (CD-IMS) in the positive mode as a detection system for DLLME extraction procedure. Based on the obtained results, it was concluded that IMS could be used as a very fast and sensitive method with no vacuum required for the analysis of analytes extracted by DLLME. However, in some cases it is necessary to develop the negative corona discharge ion mobility spectrometry (NCD-IMS) for the analysis of some chemical compounds with more sensitivity compared with positive the mode. In this regard, some problems such as limitations on selection of extraction solvent must be considered.

Considering the discussions above, the objective of this work is to develop the application of CD-IMS in the negative mode as a detection system for DLLME method based on low-density extraction solvent. The ethion compound (as anorganophosphorus pesticide) was extracted by DLLME procedure and the collected phase was directly injected into the NCD-IMS. Some parameters affecting the extraction efficiency such as type and volume of extraction solvent, type and volume of dispersive solvent, salt addition and pH effect were studied. The proposed method was applied to determine ethion residue in the grape juice and groundwater samples.

2. Experimental section

2.1. Instrumentation

The corona discharge ionization ion mobility spectrometer (CD-IMS) used for this research was designed and constructed at Isfahan University of Technology, described in detail previously [19]. In this work, however, the design of the ionization source was changed and a novel design of point-in-cylinder geometry was used to establish the corona discharge without interferences of negative ions such as NO_X^-. The details of this newly designed CD-IMS in negative mode have been presented in an Iranian patent [20]. Table 1 summarizes the negative CD-IMS operating conditions under which the mobility spectra were taken.

Table 1
Typical operating conditions of NCD-IMS during the experimental runs.

Operating parameters	Setting
Needle voltage	−2.7 kV
Target electrode voltage	−8.0 kV
Drift field	400 V cm^{-1}
Temperature of injector	200 °C
Temperature of cell	150 °C
Drift gas flow (N_2, 99.999%)	800 mL min^{-1}
Carrier gas flow (N_2, 99.999%)	400 mL min^{-1}
Drift tube length	11 cm
Shutter grid pulse	0.3 ms
Number of IMS averages	25
Number of points per ion mobility spectrum	500

2.2. Standard solutions and reagents

Ethion (99% purity) was obtained from Accustandard Company, USA. All the reagents used in this study such as cyclohexane, toluene, n-hexane, methanol, acetone and acetonitrile were HPLC grade prepared from Merck Company, Germany. The stock standard solutions were prepared in methanol with the concentration of 1000 mg L^{-1}. The standard working solutions with required concentrations were daily prepared by dilution of the stock solution using deionized water.

2.3. Sample preparation

Prior to carrying out the extraction using DLLME method, some sample pretreatment steps must be accomplished due to the solid matrix of sample grape. In this work, the sample was washed with water to remove the surface contaminants. Afterward, it was homogenized by a blender and then 1.000 g of the homogenized sample was accurately weighed and transferred into a 10-mL test tube. 100 μL of aqueous standard solution of ethion (1000 μg L^{-1}) was spiked to the sample and was diluted with 9 mL deionized water. Before DLLME procedure, the pesticide in the matrix was spread out from sample by heated water. For doing that, the test tube was heated at 70 °C for 60 min in steam bath. Coagulation of fibers could occur in the sample matrix during the warming of aqueous solution, increasing the extraction efficiency. The test tube was centrifuged at 3000 rpm for 15 min, helping us to separate fibers and other insoluble solid particles. Finally, 5 mL of supernatant solution was transferred into the extraction vessel.

2.4. DLLME procedure

DLLME procedure was carried out for 5 mL ethion aqueous solution transferred into the extraction vessel designed for low density extraction solvent. The extraction vessel used in this work was designed previously by Farajzadeh et. al [13]. The bottom of the extraction vessel was closed by a septum. 0.5 mL methanol (as dispersive solvent) containing 40 μL cyclohexane (as extraction solvent) was rapidly injected into the solution using 2-mL syringe, resulting a cloudy solution. The cloudy solution was centrifuged for 5 min at 3000 rpm for separating the organic phase from aqueous phase. In this DLLME procedure, organic phase containing the extracted analyte was collected on the upper aqueous phase due to the lower density of cyclohexane. In the next step, 2 mL deionized water was gently injected into the extraction vessel through the septum, helping us to transfer the organic phase into the narrow neck of the extraction vessel. This results in simple collection of the organic phase by a 25-μL microsyringe. Finally,