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Combination of dispersive liquid–liquid microextraction and solid–phase microextraction: An efficient hyphenated sample preparation method

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ABSTRACT

Two well-known microextraction methods, dispersive liquid–liquid microextraction (DLLME) and solid–phase microextraction (SPME), were combined, resulting in as an encouraging method. The method, named DLLME–SPME, was performed based on total vaporization technique. For the DLLME step, 1,1,2,2-tetrachloroethane and acetonitrile were used as extraction and disperser solvents, respectively. Halloysite nanotubes–titanium dioxide was used as the fiber coating in the SPME step. The method was applied for the extraction of diazinon and parathion (as the test compounds) in environmental water samples and fruit juices, and gas chromatography–corona discharge ion mobility spectrometry was used as the determination apparatus. Desorption temperature and time, extraction temperature and time, and the volume of the extracting solvent in the DLLME step were optimized as the effective parameters on the extraction efficiency. The relative standard deviations (RSDs) of intra-day were found to be 4–7% and 6–8% for diazinon and parathion, respectively. Also, the RSDs of inter-day were 7–9% and 8–10% for diazinon and parathion, respectively. The limits of quantification and detection were obtained to be 0.015 and 0.005 $\mu g\,L^{-1}$ for diazinon, and 0.020 and 0.007 $\mu g\,L^{-1}$ for parathion. A good linearity range (r^2 □ 0.993) was obtained in the range of 0.015–3.000 and 0.020–3.000 $\mu g\,L^{-1}$ for diazinon and parathion, respectively. The high enrichment factors were obtained as 3150 and 2965 for diazinon and parathion, respectively. This method showed high sensitivity with good recovery values (between 87 and 99%) for the extraction of target analytes in the real samples. Overall, the results revealed that the developed DLLME–SPME method had better extraction efficiency than DLLME and SPME alone.

1. Introduction

The analysis of compounds at ultra-trace level encouraged the researchers to develop new sample preparation methods in the separation science. In the last two decades, several microextraction methods have been introduced for the sample preparation and preconcentration of various organic and inorganic analytes. Basically, microextraction methods are divided in two general categories: i) sorbent-based techniques such as solid–phase extraction (SPE) [1], micro solid–phase extraction (μ-SPE) [2], stir–bar sorptive extraction [3], and solid–phase microextraction (SPME) [4]; and ii) solvent-based methods such as single–drop microextraction [5], hollow–fiber liquid–phase microextraction [6], and dispersive liquid–liquid microextraction (DLLME) [7].

SPME was introduced by Pawliszyn and co-workers in 1990 [4]. In this method, the analyte is extracted by a sorbent coated on a fiber. Based on the vapor pressure of the target analytes, SPME can be applied in the headspace or immersion mode. The main advantages of SPME include simplicity, the feature of being solvent-free, high enrichment factor, capability of the analysis of analytes in different types of matrices (gas, liquid and solid), in vivo sampling and easy automation. The polarity of the fiber coating can be a quasi-selective parameter for the extraction of polar, semi-polar and non-polar compounds. Therefore, the choice of sorbent phase can offer selectivity in this method. On the other hand, SPME has a few considerable limitations; for example, there are limited polar-sorbent coatings for the extraction of polar analytes [8]; also the addition of salt, existence of non-volatile particles, the use of the organic solvent, and acidic or basic solution may damage the fiber coating. Further, the partitioning of the analyte among the sample, headspace and fiber coating can affect the extraction efficiency [9,10]. In complex matrices (e.g. foodstuff and biological samples),

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the macro molecules and other particles are immobilized on the surface of the fiber coating. This effect lead to damaging the coating structure and/or loss of some adsorption sites on the fiber coating, finally decreasing the extraction efficiency. Despite the above mentioned limitations, the high recovery in complex matrices with low relative standard deviation (RSD) can be regarded as the important features that make SPME a favorable method in analytical chemistry.

Dispersive liquid–liquid microextraction as a high-performance technique was introduced by Assadi and co-workers in 2006 [7]. Briefly, in this method, a low volume of extraction and disperser solvents is mixed and rapidly injected into an aqueous sample. A cloudy solution is formed and then the solution is centrifuged. So, analytes are extracted with small volume of the extraction solvent. High enrichment factor and clean-up efficiency, short extraction time and easy performance are the main advantages of this method. Based on the density of the solvent extraction, DLLME can be performed using both low-density and high-density solvents [11,12]. Besides the good advantages, DLLME is suffering from some limitations. The matrix effect and the use of toxic solvents are the main drawbacks of DLLME; the particles or non-volatile compounds can be introduced into the analytical instrument by liquid injection, resulting in instrumental malefaction. Additionally, after the centrifuge step, the collected extraction solvent is about 10–50 μL and just a portion of it (~1 μL) can be injected to the detection system. This results in a considerable reduction of sensitivity, thereby making analysis more challenging, especially in ultra-trace scales in complex samples. Generally, most studies in the field of sample preparation have been published annually with the subjects of DLLME and SPME. According to the privileges and capabilities of the two described methods, it can be of interest to have the advantages of both methods together, as a novel designed method, while their drawbacks can be lessened. To promote the extraction and clean-up capability of the sample preparation step, a few combined methods such as solid–liquid phase microextraction (SLME) and combination of DLLME with SPE and μ-SPE as sorbent-based extraction techniques have been previously reported for the extraction of different compounds in various samples [13–15]. SLME has advantages like high enrichment factor, easy performance, feature of being no memory effect and no stripping of the coating. However, this method suffers from the limitations for the selection of solid sorbent and analysis of high volatile compounds. Also, the main benefits of DLLME with SPE and μ-SPE are high enrichment factor and high clean up capability. But, the challenges of two mentioned methods are use of large sample and solvent volumes, multi-step procedure and need the vacuum. More importantly, using the large volumes of toxic organic solvents are risky and unfriendly for the environment. Therefore, it is desirable to develop a combined method to obtain a better extraction efficiency with green aspects.

The aim of this study was combining the DLLME and SPME techniques as a new powerful hyphenated sample preparation method to improve the extraction efficiency. The combined method (DLLME–SPME) has a higher selectivity (related to DLLME) because of using the solid-sorbent in SPME step, and higher clean-up capability (related to SPME) by performing the DLLME procedure before the SPME step. By total vaporization procedure, the partitioning between the liquid sample and headspace is eliminated, and analyte will be totally existence at the headspace. Also, we have no problematic liquid direct injection. Diazinon and parathion as organophosphorus pesticides (OPPs) were selected as the model compounds. Halloysite nanotubes–titanium dioxide (HNT–TiO_2) fiber was used for SPME experiments. Gas chromatography–corona discharge ion mobility spectrometry (GC–CD–IMS) was also applied for the separation and quantification of the extracted analytes. The effective parameters on the extraction efficiency, such as collected solvent volume in the DLLME procedure, extraction temperature and extraction time in SPME step, were investigated and optimized. The feasibility and performance of the present method were evaluated in environmental and wastewater samples.

Table 1
Instrumental parameters for CD–IMS.

Parameter	Setting
Needle voltage	11.70 kV
Target electrode voltage	9.00 kV
Drift field	500 V cm^{-1}
Drift gas flow (N_2)	700 mL min^{-1}
Make-up gas flow (N_2)	20 mL min^{-1}
Drift tube temperature	200 °C
Shutter grid pulse	0.2 ms
Number of IMS averages	25
Number of points per ion mobility spectrum	500

2. Experimental

2.1. Chemicals and materials

Diazinon was purchased from Accustandard, Inc. (New Haven, USA). Parathion, halloysite nanotubes and titanium isopropoxide (TTIP) were obtained from Sigma-Aldrich (St. Louis, USA). 1,1,2,2-tetrachloroethane (1,1,2,2-TCE) (99%), tetraethoxysilane (TEOS), isopropyl alcohol, nitric acid (HNO_3), hydrochloric acid (HCl), methanol (HPLC grade) and sodium chloride (NaCl) (99.5%) were purchased from Merck (Darmstadt, Germany). Methyltrimethoxysilane (MTMOS) was supplied by Fluka (Buchs, Switzerland). Acetonitrile (ACN) was purchased from Caledon Laboratories (Georgetown, ON, Canada). Ethanol was purchased from Bidestan Co. (Qazvin, Iran). Pure water was prepared by OES (Overseas Equipment & Services) water purification system (OK, USA). Stock standard solutions of diazinon and parathion (1000 mg L^{-1}) were produced in methanol. A mixture of standard working solutions with the concentration of 10 mg L^{-1} was prepared. Working standard solutions were prepared by appropriate stepwise dilution of the standard mixture solution using pure water daily.

2.2. Instrumentation

The GC–CD–IMS used for this research was designed and constructed at Isfahan University of Technology. The instrumental details of CD–IMS have been described previously [16]. The main parts of CD–IMS are a cell equipped with the corona discharge needle, two high voltage power supplies, a pulse generator, an analog to digital converter and a computer. The instrumental conditions of the IMS in this research are tabulated in Table 1.

The GC was carried out using a Shimadzu (model 14A, Kyoto, Japan) fitted with a split/splitless injector. GC separation was performed with a capillary column (Agilent, HP-5, 30 m by 0.32 mm i.d., and 0.5-μm film thickness, Palo Alto, CA, USA). Nitrogen was used as the carrier gas and set at 1 mL min^{-1}. The temperatures of the injector and detector (IMS) were set at 260 and 200 °C, respectively. The column was held at the initial temperature of 70 °C for 1 min, and this was followed by a linear thermal gradient of 15 °C min^{-1} to 220 °C (held for 1 min), resulting in a run time of 12 min.

2.3. SPME fiber preparation

The SPME fiber used in this research had been developed previously at our research group [17]. In the first step, for the preparation of HNTs–TiO_2 heteroarchitecture, a solution of 0.5-mL of TTIP, 7.5-mL of isopropyl alcohol and 22.5-mL of HNO_3 2 mol L^{-1} was prepared and stirred at room temperature for 1 h to form a homogenous solution. After that, the solution was diluted to 125 mL by

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