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Development of dispersive liquid–liquid microextraction technique using ternary solvents mixture followed by heating for the rapid and sensitive analysis of phthalate esters and di(2-ethylhexyl) adipate

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ABSTRACT

In this study, for the first time, a dispersive liquid–liquid microextraction technique using a ternary solvent mixture is reported. In order to extract five phthalate esters and di(2-ethylhexyl) adipate with different polarities from aqueous samples, a simplex centroid experimental design method was used to select an optimal mixture of ternary solvents prior to gas chromatographyflame ionization detection. In this work, dimethyl formamide as a disperser solvent containing dichloromethane, chloroform, and carbon tetrachloride as a ternary extraction solvent mixture is injected into sample solution and a cloudy solution is formed. After centrifuging, 250 μL of the obtained sedimented phase was transferred into another tube and 5 μL DMF was added to it. Then, the tube was heated in a water bath at 75 °C for 5 min in order to evaporate the main portion of the extraction solvents. Finally, 2 μL of the remained phase is injected into the separation system. Under the optimum extraction conditions, the method shows wide linear ranges and low limits of detection and quantification between 0.03-0.15 and 0.09-0.55 μg L^{-1}, respectively. Enrichment factors and extraction recoveries are in the ranges of 980–4500 and 20–90%, respectively. The method is successfully applied in the determination of the target analytes in mineral water, soda, lemon juice, vinegar, dough, and yogurt packed in plastic packages.

1. Introduction

Phthalic acid esters commonly referred to as phthalate esters (PEs), along with di(2-ethylhexyl) adipate (DEHA) are chemical compounds that are widely used since they improve the softness and flexibility of plastics. These compounds have come to the attention of governments and the public in recent years because of their use as plasticizers in consumer products, medical devices, children's toys, and various kinds of packaging [1,2]. As PEs and DEHA are not chemically bound to plastics, they can be released from the plastic into the environment [3]. Food samples contaminated with PEs and DEHA have been also reported under microwave irradiation due to use of plastics as food containers or in food packaging and food wrap [4,5]. Due to widespread use of the mentioned compounds, they are considered as ubiquitous environmental pollutants [6–8]. They may have adverse effects on human health. They can be considered as endocrine disrupting compounds by means of their carcinogenic action [9]. In order to assess the health risk from the potential exposures to plasticizers, it requires a simple, fast and reliable analytical method to determine the extent of PEs and DEHA migration from the plastic materials into samples.

In order to determine trace levels of PEs and DEHA in food samples, an extraction and preconcentration step is often required prior to their analysis by gas chromatography (GC) [10] or liquid chromatography (LC) [11–13]. Several sample preparation methods have been developed for the analysis of target analytes such as liquid–liquid extraction (LLE) [14–16], cloud point extraction (CPE) [17], solid-phase extraction (SPE) [18–22], solid-phase microextraction (SPME) [23–26], dispersive solid-phase extraction (DSPE) [27], liquid-phase microextraction (LPME) [28,29], dispersive liquid–liquid microextraction (DLLME) [30–32], ultrasound-assisted DLLME [33,34], and automated-DLLME [35].

Selecting a suitable extraction solvent is critical in all solvent extraction methods. A good extraction solvent should have a strong solubility capability for the compounds of interest. One of the main objectives in a sensitive analysis is to obtain the enrichment factors (EFs) as high as possible to earn low limit of detection (LODs).

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This goal is usually accomplished by changing the type of extraction solvent because it is the factor which influences the EFs strongly. On the other hand, components having different polarities existing in a sample cannot be extracted efficiently by a single solvent. To overcome this problem, different liquid–liquid equilibrium of ternary solvent systems in extraction of different compounds has been investigated [36,37]. As the carbon number of alkyl group in PEs increases, the polarity of them decreases. So, polarities of different PEs used in this study are not the same and all PEs as well as DEHA cannot be extracted efficiently by an extraction solvent.

The goal of this study was to develop an efficient extraction method in order to achieve the maximum EFs and low LODs for all target analytes with different polarities. In this study, a sensitive analytical method is proposed based on extraction and preconcentration of some PEs and DEHA by DLLME using a ternary solvents mixture followed by heating. In order to use the different abilities of various solvents in extraction of analytes, a ternary solvents mixture including solvents with different polarities is utilized. Simplex centroid experimental design is used to select the optimal solvents mixture for an efficient extraction of the analytes. The simplex centroid experimental design is one of the mixture designs. Most chemists represent their experimental conditions in a mixture space, which corresponds to all possible allowed proportions of components that add up to 100%. A three components mixture can be represented by a triangle. Points within this triangle represent possible mixtures [38]. In this study, for the first time, this technique is successfully applied for the extraction/preconcentration of the selected PEs and DEHA from different aqueous samples. Separation and detection of the enriched analytes are carried out using GC equipped with flame ionization detection (FID) or mass spectrometry (MS).

2. Materials and methods

2.1. Chemicals and solutions

Dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), di-*n*-butyl phthalate (DNBP), di(2-ethylhexyl) phthalate (DEHP), and DEHA were purchased from Sigma–Aldrich (Louis, USA). Organic solvents such as acetone, dimethyl formamide (DMF), acetonitrile, dimethyl sulfoxide (DMSO), methanol, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) were purchased from Merck (Darmstadt, Germany). Sodium hydroxide and sodium chloride (analytical-reagent grade, Mojallali, Iran) were used for pH adjustment and ionic strength, respectively. De-ionized water was obtained from Ghazi Company (Tabriz, Iran). The selected compounds in this study are found in most environments even in de-ionized water which is contaminated from its plastic container (Fig. 4h). In order to establish a sensitive analytical method, preparation of a clean blank in which the analytes' contents are below their LODs of the method is necessary. For this purpose, 2 L NaOH (0.1 M) solution prepared in de-ionized water was refluxed for 1 h and then distilled. 100 mL of first fraction was discarded and the following 1 L was collected in a glass bottle. This water (blank water) was used for the preparation of aqueous solutions throughout the study. GC–FID chromatograms of de-ionized water and blank water illustrated in Fig. 4 indicate efficiency of the procedure for preparation of blank water.

A standard solution of analytes (250 mg L^{-1}, each analyte) was prepared by dissolving an appropriate amount of each analyte in DMF. This solution was injected directly into the separation system each day (three times) for quality control and the obtained peak areas were used in the calculation of EFs and extraction recoveries (ERs). Also, a stock solution of analytes was prepared in acetone at a concentration of 250 mg L^{-1} (each analyte). This solution was prepared weekly to spike the samples or to obtain the optimum experimental conditions.

2.2. Samples

All analyzed samples including mineral water, soda, lemon juice, vinegar, dough (a savory yogurt-based beverage), and yogurt were purchased from local supermarkets (Tabriz, Iran). Vinegar, lemon juice, and dough samples filtered through a filter paper (ALBET, DP 135 125, Barcelona, Spain) and were diluted at ratios of 1:5, 1:20, and 1:40, respectively, with blank water before being used. The soda sample was analyzed after diluting with blank water at a ratio of 1:10 without filtration. Since the observed matrix effect was various in different real samples, so, in order to reduce the matrix effect, different dilution ratios were selected in the cases of various samples. The yogurt sample (12 g) was poured into 200 mL blank water, homogenized, and then filtered through the filter paper before being analyzed. The mineral water was analyzed immediately after opening without filtration or dilution. It should be noticed that pH of all analyzed samples were adjusted at 7 ± 1 before analysis using 0.1 M HCl or NaOH solutions.

2.3. Apparatus

A Shimadzu gas chromatograph (GC-2014, Tokyo, Japan) equipped with a split/splitless injector system, and an FID was used for separation and determination of the analytes. Helium (99.999%, Gulf Cryo, United Arab Emirates) was used as the carrier gas at a constant linear velocity of 30 cm s^{-1}. Separation was carried out on an SPB-1 capillary column (100% dimethyl siloxane, 30 m × 0.25 mm i.d., and film thickness 0.25 μm) (Supelco, Bellefonte, USA). The oven temperature was programmed as follows: initial temperature 90 °C (held 2 min), ramped at 20 °C min^{-1} to 190 °C, then at 10 °C min^{-1} to 210 °C, finally at 15 °C min^{-1} to 290 °C and held at 290 °C for 3 min. The total time for one GC run was about 17 min. The injector and FID temperatures were maintained at 300 °C. Hydrogen gas was generated with a hydrogen generator (OPGU-1500S, Shimadzu, Japan) for FID at a flow rate of 40 mL min^{-1}. The flow rate of air for FID was 300 mL min^{-1}. Make up gas (helium) flow rate was 30 mL min^{-1}. GC–MS analysis was carried out on an Agilent 7890A gas chromatograph with a 5975C mass-selective detector (Agilent Technologies, CA, USA). The separation was carried out on an HP-5 MS capillary column (30 m × 0.25 mm i.d., and film thickness 0.25 μm). Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}.

2.4. Extraction procedure

A 50 mL of standard solution (50 μg L^{-1} of each analyte) or sample was placed into a glass test tube with conic bottom. A 2.0 mL DMF (disperser solvent), containing 122 μL CH_2Cl_2, 404 μL $CHCl_3$, and 44 μL CCl_4 (extraction solvents) was injected rapidly into the sample solution using a syringe. A cloudy solution (resulted from the dispersion of fine droplets of the extraction solvents into the aqueous sample) was formed. In this step, the analytes were extracted into the fine droplets. After centrifuging for 4 min at 4000 rpm, the extraction solvents were sedimented in the bottom of the tube (about 270 μL). A 250 μL of the sedimented phase was transferred into another test tube and 5 μL DMF was added to it. Then, the tube was placed in a water bath at 75 ± 1 °C for 5 ± 0.5 min to evaporate the main portion of the extraction solvents. It should be noted that boiling points of the studied solvents are low (39.6, 61.2, and 76.7 °C for CH_2Cl_2, $CHCl_3$, and carbon tetrachloride, respectively) and the heating temperature (75 °C) was selected according to boiling points of these solvents. So, the analytes were concentrated into DMF (b.p. 152 °C). The volume of remained phase