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Automatic in-tube SPME and fast liquid chromatography: A cost-effective method for the estimation of dibuthyl and di-2-ethylhexyl phthalates in environmental water samples

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ABSTRACT

A 80-cm length commercially available capillary coated with 95% polydimethylsiloxane and 5% polydiphenylsiloxane (TBR-5) was employed to carry out on-line extraction and preconcentration of dibuthyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) in the chromatographic system. The coated capillary was placed between the sample injection loop and the injection needle of an autosampler. Variables affecting the automatic in-tube solid-phase microextraction (SPME) were optimized. A Genesis C_{18} (5 cm × 4.6 mm i.d., 4 μm particle size) was employed as analytical column. The achieved limits of detection by use of diode array detection were 1 and 2.5 $\mu g L^{-1}$, respectively. The proposed conditions have been applied to determine those compounds at low ppb levels ($\leq$250 $\mu g L^{-1}$) in aqueous samples. No matrix effect was found, and recoveries between 85 and 115% were obtained. The precision of the method was good, and the achieved intra- and inter-day variation coefficients were between 5 and 20%. The analysis time per sample was 20 min and any off-line pretreatment of the samples was needed. The taken sample volume was 100 μL. Data on the application of the described method to the analysis of different water samples are presented.

1. Introduction

Phthalates esters are synthetic compounds used as polymer additives in plastics, rubber, cellulose and styrene production [1]. They are present in many consumer products, such as children toys, cosmetics, personal care products, blood bags, organic solvents, packaging, paper coatings and insecticides [2]. Due to the widespread use of phthalates, they are considered as ubiquitous environmental pollutants [3–5]. The phthalates can have adverse effects on human health, although it has not been demonstrated, they can be considered as endocrine disrupting compounds by means of their carcinogenic action [6]. The European Union has published a list of priority substances with a potential endocrine disrupting action, which includes di-*n*-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP). As DEHP is the most widely used phthalate, it was incorporated in the list of priority substances in the field of water policy by the EU and the World Health Organization (WHO) was given the guideline value at 8.0 $\mu g L^{-1}$ in fresh and drinking waters [7,8]. No specific methods have been established by the EU directives, however, USEPA directive proposed the method 8061A (dated on

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December 1996) dedicated to the phthalate analysis in different types of water matrices [9]. This method uses 1 L of water sample and because of it is based on gas chromatography (GC) with electron capture detection (ECD), compound identification should be supported by at least one additional qualitative technique. Instructions for that action were done in the 8061A method description and also it is indicated that alternatively, GC/MS (mass spectrometry) could be used for compound confirmation.

The determination of phthalates in water samples generally requires a preconcentration technique, such as liquid–liquid extraction [10,11] or solid-phase extraction (SPE) [9,12], followed by gas chromatography (GC) [13] or liquid chromatography (LC) [14]. These sample preparations often result in high blank values due to phthalates present in chemical and plastic accessories [15]. The use of solid-phase microextraction (SPME) provides extraction and preconcentration in one step, besides this is a solvent-free extraction technique. This sample preparation method has been used for the determination of phthalates, in some works it was coupled to LC [16–18] or to GC [19]. A study about the comparison of different fibers was presented in order to develop an optimized SPME method for the most common phthalates [20], the best results were obtained with the polydimethylsiloxane–divinylbenzene fiber. The stir bar sorptive extraction (SBSE) [21] and liquid-phase microextraction [22] were also applied for the determination of phthalates in water. Because of phthalates are present in the analytical laboratory, scrupulous cleaning and design of quality control procedures must ensure analytical results free of systematic errors and false positives. However, Kayali et al. [18] confirmed the difficulties to determine DEHP at trace levels by SPME-GC due to the blanks presented variable significant intensities. These authors proposed an on-fiber SPME-HPLC method which requires 500 mL of sample extracting the analytes for 30 min.

In-tube SPME is a relatively new microextraction technique, which can be easily coupled to LC for the analysis of less volatile and thermally labile compounds [23–27]. This technique uses a coated open capillary as the SPME device. In previous works, phthalate esters were determined by in-tube SPME coupled to LC and photodiode array detection (DAD) system in food samples [28], in liquid medicines [29] and in water samples [30]. In this latter work the in-tube SPME system needed two valves, two syringe pumps, a LC pump and a UV/vis conventional detector. Moreover, for the real sample analysis, the extraction capillary had to be modified for extracting the analyte at a lower concentration. A stainless wire was inserted into the DB-17 capillary, so that the phase ratio would be smaller than that of the in-tube capillary only, 20 min was proposed as extraction time and 160 μL of sample was processed. The detection limits achieved were 0.2 and 30 $\mu g L^{-1}$ for DBP and DEHP, respectively. Limited linear calibration ranges (0.2–5 $\mu g L^{-1}$ given for DBP) were achieved. Paper [30] proposes as a better option in fiber in-tube SPME instead of in-tube SPME.

Nowadays, the general tendency is to simplify the sample preparation, to diminish the sample volume needed, the number of off-line steps and the amount of solvents employed. In this sense, we report a new automatic procedure free of systematic error for estimation DBP and DEHP in water samples based on a simple in-tube SPME method with a commercial unmodified capillary column using a conventional liquid chromatograph with an autosampler. No preprocessing of the sample is needed and 100 μL was used as taken sample volume. To our knowledge, there are not published methods which carry out an automated in-tube SPME procedure to determine phthalates in water samples. On the other hand, the paper increases the applicability of in-tube SPME-fast HPLC and improves the figures of merit achieved by other published methods for the analytes.

2. Experimental

2.1. Apparatus

The chromatographic system used consisted of a quaternary pump (Hewlett-Packard 1100 Series) equipped with a high-pressure six-port valve (Rheodyne model 7725), an on-line degasser and an autosampler (Hewlett-Packard 1050 Series). All the components of the system were linked with fused silica tubing (500 μm i.d.). A photodiode array detector (DAD, Hewlett-Packard, 1040 M Series II) was coupled to a data system (Agilent, HPLC ChemStation) for data acquisition and calculation. The signal was registered in the DAD detector and it was monitored at 230 nm. The corresponding spectra were also saved.

2.2. Reagents and solutions

All the reagents were of analytical grade. Dibutyl phthalate, di(2-ethylhexyl) phthalate, dimethyl phthalate and diethyl phthalate were obtained from Sigma–Aldrich (Steinheim, Germany). Triazines (simazine, atrazine, propazine, ametryn, prometryn, terbutryn) were obtained from Sigma (St. Louis, MO, USA). Organophosphorous compounds (fensulfothion, fenamiphos, fenitrothion, malathion, parathion, chlorfenvinphos, fenthion, fonofos, chlorpyrifos, trifluraline) and volatile organic compounds (benzene, toluene, chlorobenzene, ethylbenzene, *m*,*p*-xylene, *o*-xylene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Acetonitrile and methanol were of HPLC grade (Scharlau, Barcelona, Spain).

Stock standard solutions of phthalates (10 $\mu g mL^{-1}$) were prepared in acetonitrile. Working solutions of these compounds were prepared by dilution of the stock solutions with water. The concentrations measured for establishing the calibration graphs are: 3, 12.5, 25 (three replicates), 100 (three replicates) and 250 $\mu g L^{-1}$ for DBP and 7.5, 12,5, 25 (three replicates), 100 (three replicates) and 250 $\mu g L^{-1}$ for DEHP. Water was deionized and filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain). All solutions were stored in the dark at ambient temperature.

2.3. Columns, mobile phases and chromatographic conditions

A Genesis C18 (5 cm × 4.6 mm i.d., 4 μm particle diameter) (Jones Chromatography, Mid Glamorgan, United Kingdom) col-