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Short communication

On-line in-tube solid phase microextraction-capillary liquid chromatography method for monitoring degradation products of di-(2-ethylhexyl) phthalate in waters

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ABSTRACT

The main di-(2-ethylhexyl) phthalate (DEHP) degradation products, (2-ethylhexyl) phthalate (MEHP), diethyl phthalate (DEP) and dibutyl phthalate (DBP), have been tested. The proposed cost-effective method combines on-line, in-tube solid-phase micro extraction (IT-SPME) in in-valve configuration and capillary liquid chromatography with UV diode array detection (Cap-LC-DAD). Acidification of the samples at pH 3 improved markedly the estimation of MEHP. Aliquots of 4 mL of acidified water samples were directly processed. After sample loading, the analytes were desorbed with the mobile-phase and transferred to the monolithic capillary column. Satisfactory linearity and precision, absence of matrix effect and suitable limits of detection (LODs): 0.005, 0.1, 0.1 and 1.5 μg/L for MEHP, DEP, DEHP and DBP, respectively have been achieved. The main advantages are speed and the reduction of background signal by minimizing sample preparation. Real water samples have been analyzed.

1. Introduction

Phthalate esters are widely used as plasticizers in the manufacture of plastics. Due to their extensive use and possible migration, phthalates are nowadays considered as ubiquitous environmental pollutants. Di-(2-ethylhexyl) phthalate (DEHP) is the most widespread phthalate produced and used. The maximum annual average concentration established for DEHP by Directive 2008/105/CE in surface waters is 1.3 μg/L [1], whereas the US Environmental Protection Agency has set the maximum concentration level for this compound in water systems at 6 μg/L [2].

Numerous studies indicated that DEHP can be degraded in phthalates as (2-ethylhexyl) phthalate (MEHP), diethyl phthalate (DEP) and dibutyl phthalate (DBP) by bacteria and fungi under various environmental conditions [3] as Fig. 1 shows. Recent studies reported that MEHP may be more toxic than DEHP [4–8], nevertheless a vast majority of the proposed methods for phthalates in waters are limited to dialkyl esters [9].

Gas chromatography (GC) coupled to flame ionization detection [4,5,10,11] or mass-spectrometry (MS) [12–16] has been extensively used for phthalates in different matrices. Several LC methods with diode array (DAD) [17,18] or MS detection have been reported [6,19]. The reliability of in-tube solid-phase microextraction (IT-SPME) coupled to capillary liquid chromatography (CapLC) approach has been demonstrated for a variety of organic pollutants by processing on-line between 1 and 4 mL of the samples [20,21]. IT-SPME is a form of SPME, which typically uses a GC capillary column with a proper coating to extract the analytes. In addition, reliability for the determination of DEHP in water samples has been outlined in a recent paper [18]. Contamination during the analysis is a problem commonly encountered in the determination of phthalates at trace levels, resulting in false positive or overestimated results, especially in GC based methods [22,23]. Sample preparation should be as simple as possible to minimize the risk of contamination. Ideally, the employment of extraction solvents, plastics and glassware should be avoided. Liquid chromatographic methods could reduce contamination problems integrating on-line sample processing. With respect to this logic, in-tube solid-phase microextraction (IT-SPME) may be advantageous because sample manipulation can be reduced to a minimum. The employment of the extractive column as the loop of an injection valve (in-valve IT-SPME) can be very useful for the enrichment of organic pollutants. This is due to the fact that when a large volume of sample is passed through the extractive capillary, the analyte is concentrated into the coating.

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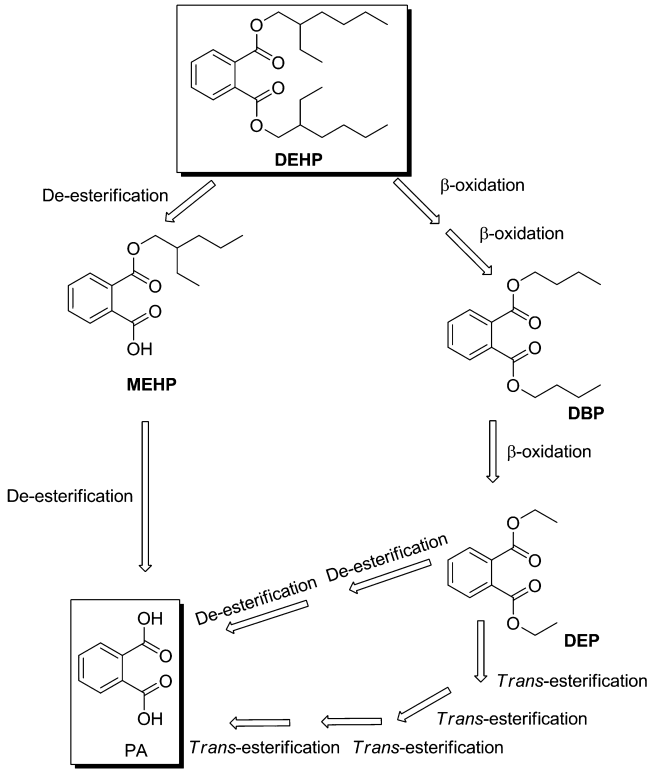

Fig. 1. DEHP biodegradation pathways to obtain phtalates as MEHP, DBP and DEP.

In the present study we have evaluated the possibility of extending the IT-SPME-Cap LC approach to other dialkyl phthalate esters: DEP and DBP, which often are found in waters as degradation product of DEHP and also including the monoalkyl phthalate MEHP. It is proved that acidification of the whole samples was necessary for achieving satisfactory detection limit for MEHP. The main advantages are speed and the reduction of background signal by minimizing sample preparation

2. Experimental

2.1. Reagents and materials

All reagents were of analytical grade. DEHP (99%), DEP (99%) and DBP (99.5%) were purchased from Aldrich (Steinheim, Germany); MEHP (91%) was obtained from Dr. Ehrenstorfer (Ausburg, Germany). Acetonitrile HPLC grade was purchased from Romil (Cambridge, UK). Hydrochloric acid (37%) was purchased from Scharlau (Barcelona, Spain).

Stock standard solutions of the analytes (1 μg/mL) were prepared in acetonitrile. Working solutions were prepared by dilution of the stock solutions with water. All solutions were stored in the dark at 4 °C.

2.2. Apparatus and chromatographic conditions

The capillary chromatographic system used consisted of a binary LC capillary pump (Agilent 100 Series, Waldbronn, Germany) and a UV–vis diode array detector (Agilent 1200 series,) equipped with a 80 nL flow cell. The analytical signal was recorded from 190 to 400 nm, and the chromatograms were monitored at 230 nm The detector was linked to a data system (Agilent, HPLC ChemStation) for data acquisition and calculation.

For the chromatographic separation, an Onyx Monolithic C_{18} column (150 mm × 0.2 mm i.d.) from Phenomenex (Torrance, CA, USA) was used. The mobile-phase was a mixture of acetonitrile/water. In the optimized procedure the initial composition of the mobile phase was acetonitrile-water 30:70 (v/v). The acetonitrile content was linearly increased to reach 100% at min 15. Then, the mobile-phase composition was changed to acetonitrile–water 70:30 (v/v) from 25 min until the end of the run. The mobile phase flow rate was 5 μL/min.

All solvents were filtered through 0.45 mm nylon membranes (Teknokroma, Barcelona, Spain) before use.

2.3. In-tube SPME procedure

For the in-tube SPME procedure, the stainless steel injection loop of a conventional injection valve was replaced by a GC TRB-5 capillary column (Tecknokroma) of 40 cm length and 0.32 mm i.d., coated with 5% diphenyl–95% polydimethylsiloxane (3 μm coating thickness). Capillary connections to the valve were facilitated by the use of 2.5 cm sleeve of 1/16 in. polyether ether ketone (PEEK) tubing and 1/16 in PEEK nuts and ferrules (Teknokroma).

Aliquots of 4 mL of acidified samples at pH = 3 with hydrochloric acid (1 mM), were manually loaded in the extractive column of the IT-SPME device by means of a 1-mL precision syringe (Hamilton, Bonaduz, Switzerland). After sample loading, 50 μL of 1 mM HCl (unless otherwise stated) were flushed through the capillary in order to remove the solution remaining in it (the inner volume of the capillary column was c.a. 32 μL). Finally, the injection valve was manually rotated, so the analytes were desorbed in dynamic mode from the coating of the extractive capillary with the mobile-phase, and sent to the analytical capillary column for separation and detection.

All the experiments were carried out in duplicate and at room temperature.

2.4. Analysis of real water samples

Water samples used in the present study were collected along the coast of the Comunidad Valenciana region (Spain). Washing samples used were obtained by circulating nanopure water through plastic tubings. The samples were stored in dark in brown glass flasks at 4 °C until analysis. Aliquots of 4 mL of the acidified samples were loaded in the IT-SPME and processed as described above. All samples were analyzed in duplicate and at room temperature.

3. Results and discussion

3.1. Chromatographic separation

According to previous studies, the volume of standard solutions processed into the IT-SPME device was 4.0 mL [18]. Different gradient elution programs of acetonitrile/water (see Section 2 for optimum), changes in the pH of the samples and several cleaning solvents before the transfer step to the analytical column, were assayed. Satisfactory results were obtained by acidifying the samples at pH 3 for MEHP (pK_a = 3.08) as the inset of Fig. 2 shows. 50 μL of acidified nanopure water was employed as cleaning solvent chromatograms obtained for a blank (4 mL of nanopure water acidified to pH 3.0) and for standard solutions of the analytes are given in Fig. 2. Under the proposed conditions DBP eluted close to some unknown compounds present in water samples (around 16.7 min), although DBP can be identified through its UV spectra as can be seen in Fig. 2.

3.2. Analytical performance

Table 1 shows relevant analytical parameters of the proposed method. The following criteria for linearity range were applied: