



A comparative study of extractant and chromatographic phases for the rapid and sensitive determination of six phthalates in rainwater samples



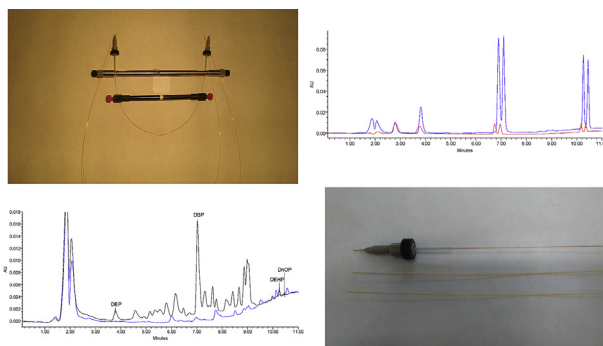
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HIGHLIGHTS

- Six phthalates with different hydrophobicity are separated within 11 min.
- Different extractant phases and other variables of IT-SPME are optimized.
- Blank problems are minimized and controlled.
- Rainfall events with different sampling time and volume are compared.
- Higher concentration of phthalates is found in short-term precipitation events.

GRAPHICAL ABSTRACT



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ABSTRACT

Six phthalic acid esters were determined in rainwater samples, from which a very low sample volume was collected. This method combines on-line in-tube solid-phase microextraction coupled to high-performance liquid chromatography with a diode-array detector. In order to obtain a short analysis time and to reduce the consumption of organic solvents, two chromatographic phases (C18 monolithic and cyanopropyl silica) are compared. Although three critical pairs are found, faster separation, good resolution and lower pressures are achieved using C18 monolithic column. In order to achieve a simple and sensitive method, two commercial capillaries (a porous polymer with divinylbenzene-4-vinylpyridine and a liquid-phase capillary with 95% poly(dimethylsiloxane)-5% poly(diphenylsiloxane)) are tested for the extraction process. Due to great differences of hydrophobicity among the six phthalates, the selection of a modifier is necessary for a good extraction. The best conditions are achieved using 5 mL of sample containing 40% methanol in a 70 cm-long porous polymer capillary. The procedural blanks are controlled and taken into account in the calculation of the detection limits. Except for dimethylphthalate, the method detection limits are in the range from 0.2 to 0.9 ng mL⁻¹ and the inter-day precision is between 5.3% and 12.5%. The recoveries were within the range of 71%–101%. Rainwater samples are analyzed in order to examine the dilution effect and washout of phthalates in the atmosphere. Dibutyl

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phthalate is the predominant phthalate found and di-(2-ethylhexyl) phthalate is detected in all analyzed samples.

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1. Introduction

Phthalates are esters of phthalic acid synthesized by the esterification of this acid with different alcohols. They are a group of industrial chemical compounds with a high production volume, due to their use as plasticizer substances. Phthalates containing shorter alkyl chains are used as film-forming agents, solvents and denaturants, and they can also be found in cosmetics and personal care products. Those with a longer alkyl chain, such as di-2-ethylhexylphthalate (DEHP), are employed for lamination of polyvinyl chloride (PVC) being present in a great variety of products of the daily life (coatings, medical devices, packaging, children toys, etc.). As phthalates are not chemically bonded to polymers, they can migrate, leach or evaporate, ending up in the environment, in food and materials that originally did not contain them. As a result, people are exposed to phthalates throughout their entire life in different ways (ingestion, inhalation and dermal contact) (Ventrice et al., 2013).

Their ubiquity and potential risk for human health and environment as endocrine disruptors make them susceptible to be included in national and international regulations (Ventrice et al., 2013; Heudorf et al., 2007; De Coster and Van Larebeke, 2012; Lin et al., 2003). Concerning European regulation, DEHP is identified as a priority hazardous substance in the field of water policy (Directive, 2013/39/EU). Environmental Quality Standards (EQS) have established an annual average of $1.3 \mu\text{g L}^{-1}$ for DEHP (Directive, 2013/39/EU) in surface waters. Moreover, the US Environmental Protection Agency (EPA) set the maximum admissible concentration (MAC) for this compound in water systems at $6 \mu\text{g L}^{-1}$. Other regulations related to food contact materials (Commission Directive, 2007/19/EC) impose restrictions over several phthalates, including di-*n*-butylphthalate (DBP), benzylbutylphthalate (BBP) and DEHP. In addition, DEHP, BBP and DBP are included among the list of substances subject to authorization as toxic for reproduction in the Regulation 1907/2006 of the European Parliament and of the Council. In the same regulation, it is stated that DEHP, BBP, DBP and di-*n*-octylphthalate (DnOP) have restrictions (limit of concentration 0.1% by weight) in the use of plastic material in toys and childcare articles (Regulation (EC) No 1907/2006).

Rainwater may contain a mixture of organic pollutants, many of them not being characterized yet, and other identified compounds whose concentrations depend on multiple factors (Cottrell et al., 2013; Zuo et al., 2011). The use of rainwater in agriculture or as primary source for drinking water justifies a deeper understanding of this topic (Chakraborty et al., 2016). For some organic micro-pollutants such as aldehydes and polycyclic aromatic hydrocarbons (PAHs), a negative correlation between the levels of pollutant and the volume of sample has been reported. The greatest concentration of pollutant is scavenged in the first collected rainfall volume and the rest, with lower concentration, dilutes the sample (Deng and Zuo, 1999; Taguchi et al., 2012). The scavenging process of the pollutants from aerosols to rainwater, the temporary variations of the pollutant levels and the highest pollutant concentrations reached can be studied by events. However, determination methods usually require relatively large volumes of sample that may not be achieved in short sampling periods.

In addition to this limitation of sample volume, most of the previously reported methods for the determination of phthalates in rainwater involve a lot of tedious and long steps, and high consumption of organic solvents. Miniaturized techniques such as in-tube solid phase microextraction (IT-SPME) can deal with all these limitations. IT-SPME allows the combination of the sample treatment and determination in a single step because it can be easily coupled to liquid chromatography. In addition, it provides a very good sensitivity, selectivity, speed and a very low solvent consumption (Kataoka et al., 2009; Fernández-Amado et al., 2016a). Several methods are able to determine one or two phthalates (DBP and/or DEHP) in environmental matrices using IT-SPME coupled to conventional high performance liquid chromatography (HPLC) (Wen and Feng, 2007; Cháfer-Pericás et al., 2008), capillary liquid chromatography (Muñoz-Ortuño et al., 2014; Jornet-Martínez et al., 2015) or ultra-high performance liquid chromatography (Masiá et al., 2013). A larger number of phthalates are analyzed in other types of matrices: food (Kataoka et al., 2002; Mitani et al., 2004) and medication (Mitani et al., 2003) by IT-SPME in cycle mode. Although the steps of analysis are reduced with respect to classical treatment methods, the analysis time is still long (35 min). In the chromatographic separation using common packed columns, high flows ($1.5\text{--}2.0 \text{ mL min}^{-1}$) are employed, with the consequent high solvent consumption.

In fact, the separation of phthalates by HPLC (coupled or not coupled to IT-SPME) usually takes a long time or needs high flows. The use of a monolithic column allows for the improvement of chromatographic separation because it provides low pressures and very good efficiencies for its porous structure (Zuo, 2014; Núñez et al., 2007; Lim et al., 2004). Monolithic columns have proven their suitability for separation of phthalates by liquid chromatography, both conventional and capillary. Nevertheless, only few phthalates (3–4) were separated in most cases (Núñez et al., 2007; Lim et al., 2004; Su et al., 2010; Jin et al., 2013; Jornet-Martínez et al., 2014), with separation times which may sometimes be long (up to 65 min). When a larger number of phthalates (8) was separated in a short time (8 min), a very high flow up to 10 mL min^{-1} was needed (Nesterenko and Rybalko, 2005). In addition to high pressures (which can lead to a problem with the capillaries when IT-SPME is coupled), high flows imply a high consumption of solvents which is against green chemistry (Jornet-Martínez et al., 2014, 2015; Zhou et al., 2013). One of the trends in analytical chemistry is a reduction of solvent consumption since it implies decreasing of costs, operator exposure to dangerous solvents and generation of toxic residues.

The aim of this work is to develop a rapid (separation in a short time, single-step treatment), sensitive (at ng mL^{-1} concentration level) method for the determination of six EPA phthalates (di-*n*-methyl phthalate (DMP), di-*n*-ethyl phthalate (DEP), DBP, BBP, DEHP and DnOP) in low volume rainwater samples, using simple instrumentation and with low solvent consumption. For this purpose, a comparative study was carried out between different possibilities of the stationary and mobile phases in the chromatographic separation and between capillaries and organic modifiers for the extraction (IT-SPME in-valve mode), in order to achieve a rapid extraction and separation using low flow-rate. In addition, limits of detection and quantitation are usually reported

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