

# Extracting syringe for extraction of phthalate esters in aqueous environmental samples

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## Abstract

The use of the extracting syringe (ESy), a fully automated membrane-based extraction technique, for analysis of phthalate esters in complex aqueous samples has been investigated. The ESy, working as an autosampler that combines the extraction process and injection into the gas chromatograph (GC) in one single step, is placed on top of the GC equipped with a flame ionisation detector. The aqueous samples are loaded in a tray and automatically extracted by employing microporous membrane liquid–liquid extraction principle. After the extraction, the extract is directly injected into the GC's programmable temperature vapourisation injector. Six different phthalate esters were used as model compounds. Four extraction solvents were tested and the addition of sample organic modifier was examined.

Toluene was the optimal solvent to use for extraction. Due to the large variation in polarity of phthalate esters, 50% methanol as organic modifier had to be added to the samples so as to extract the most nonpolar phthalate esters; di-2-ethylhexylphthalate and di-*n*-octylphthalate, whereas the other four relatively polar phthalate esters were extracted from unmodified samples. No significant difference between extraction of river water, leachate water from a landfill and reagent water was noted, except for minor deviations. The extraction time was 20 min for extraction of a 1-mL sample, resulting in a good linearity for all aqueous media investigated, good enrichment factors (54–110 folds) and low LOD values (0.2–10 ng mL<sup>-1</sup>) and relative standard deviation (%R.S.D.; 0.9–3.7%).

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## 1. Introduction

The international awareness of the impact of endocrine disrupting compounds on wellbeing of man and their far-reaching polluting effects on the environment has been markedly observed in the last few years. The phthalic acid diesters (phthalate esters) are classified among these compounds as they have been reported for their endocrine disrupting activity in humans and animals [1,2]. The physicochemical properties of phthalate esters make their use as plasticizers in the manufacturing of PVC resins, cellulose, clothes, adhesives, medical products and food packaging of indispensable value for the industry [3]. Because of the tremendous production and use of products containing phthalate esters, the products are directly or indirectly disposed

into the environment. As phthalate esters are physically blended into the products, they are easily leached into the environment (i.e. biota and ecosystem) and food products, causing pollution. Phthalate esters are known as widespread contaminants [1–3]. The environmental pollution of phthalates has been found in surface water, ground water, drinking water, wastewater, sediments and air samples at ng mL<sup>-1</sup> levels [4–9].

Accordingly, for phthalate esters analysis at trace levels in complex matrixes, such as water samples, developing fast and reliable analytical protocols is basically of significant importance for monitoring phthalate ester-contaminated samples. In this context, the most frequently adapted extraction techniques available today are liquid–liquid extraction (LLE) and solid-phase extraction (SPE). The drawbacks of using these techniques are pretty much known, and thus have urged the scientists to quest for new innovative sample preparation procedures. Subsequently, the attempts for miniaturisation of LLE [10–15] and modifications of SPE [5,6,16,17] have never been

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ceased, aiming at new modified approaches that are believed to offer good alternatives for fast analysis, and overcome the disadvantages of the often used procedures. Since its invention in 1990, solid-phase micro-extraction (SPME) [18] has become a workhorse in sample handling methodologies, in spite of being an equilibrium extraction (i.e. non-exhaustive extraction). An updated modification of SPME has lately been emerged, with a technique called stir bar sorptive extraction (SBSE) [9,19,20], where an exhaustive extraction can be reached due to the possibility of using a larger amount of the extracting phase (i.e. polydimethylsiloxane (PDMS)) than in SPME.

In the literature, a plethora of publications have been cited on phthalate esters analysis in aqueous media, based on LLE [7,8,21], SPE [4,21–25] and SPME [26–31]. In addition, SBSE [9] has also been utilised as pre-concentration procedure for determination of phthalate esters in air samples.

Coupling SPME to high performance liquid chromatography (HPLC) has been tried and was first pioneered by Pawliszyn et al., with a technique named In-Tube SPME [32–38], but this combination has been accompanied with some difficulties in preparing the SPME/HPLC-interface. Therefore, another emerging development of the In-Tube SPME coupled to the HPLC system has been focused on and applied for phthalate esters analysis in water samples, namely the “fibre-in-tube SPE”, “wire-in-tube SPE” and “fibre-in-tube SPME” [5,6,39] techniques.

Other attractive and alternative protocols in sample preparation are based on application of membrane technology in analytical chemistry [40,41], due to the fact that this technology provides miniaturised and automated setups for extraction and analysis, which are deemed plausible scenarios in order to circumvent the demerits of the traditional extraction procedures. The most frequently used membrane extraction procedures in quantitative analysis are either based on flat-sheet or hollow-fibre membranes. The flat-sheet based methodologies are the supported liquid membrane (SLM) and microporous membrane liquid–liquid extraction (MMLLE) [40–44]. The hollow-fibre membranes are also being utilised, such as membrane extraction with a sorbent interface (MESI), which can be employed for analysis of volatile organic compounds [45,46]. The two extraction techniques, MMLLE and SLM, can also be performed by using hollow-fibres with a technique known as liquid-phase micro-extraction (LPME) [47], and by manipulating the chemistries in the lumen and outside environment of the hollow-fibre as well as in the fibre’s pores.

MMLLE, which was employed in our current study, is considered as a micro-LLE carried out on the two sides of a flat-sheet microporous membrane, which acts as phase separator of the organic and aqueous phases. In MMLLE, the aqueous sample is exposed on one side of the membrane and the extracting water-immiscible solvent is kept either stagnant or flowing on the other side of the membrane and also fills the membrane pores. In addition to the on-line coupling of the flat-sheet MMLLE with HPLC [48–50], MMLLE has also been connected on-line with GC [51–54].

In a recent study, a hollow-fibre based LPME procedure was compared to SPME for phthalate esters analysis in water samples

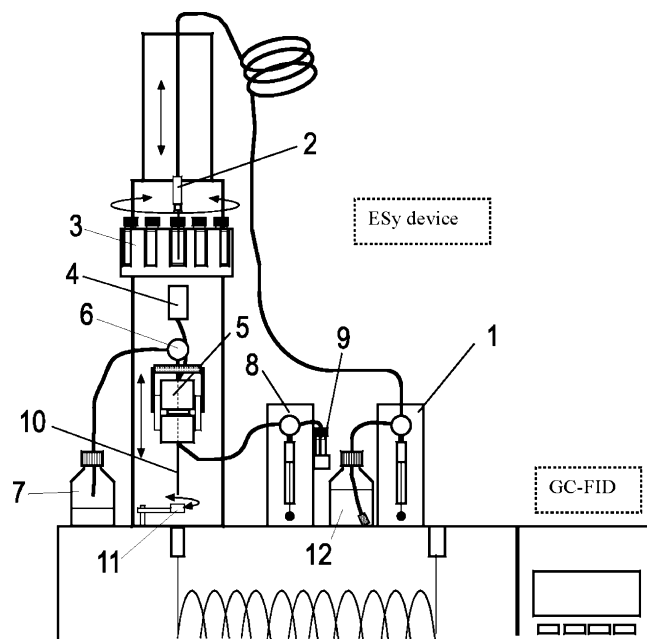


Fig. 1. The ESy autosampler prototype. The parts numbered are: sample pump (1), sample pipette (2), sample tray (3), pipette needle port (4), extraction card holder; called card guard (CG) (5), waste valve (6), waste bottle (7), solvent pump (8), 4-mL solvent vial (9), GC needle (10), solvent cup (11) and washing fluid (12). For details see text.

[55], where LPME has shown comparable results to SPME with the advantage of no carry-over of analytes. In the same study, different phthalate esters were detected in tap water and bottled mineral water, and found in quantities of  $0.05\text{--}1.04\ \mu\text{g L}^{-1}$  and  $0.08\text{--}0.87\ \mu\text{g L}^{-1}$  using LPME and SPME, respectively.

We have been encouraged by the early obtained results of our new innovative technique [56–58], based on a fully automated and on-line micro-MMLLE-GC setup, which has been called extracting syringe (ESy) (upper part of Fig. 1). This new technique has been exploited in two configurations; the first one was developed for bioanalysis and based on a hollow-fibre membrane [56], and the second was utilised for environmental analysis and based on a flat-sheet membrane [57,58].

In this study, we are presenting the potential of the ESy for phthalate esters analysis in aqueous media. Various parameters, such as extraction solvent, sample organic modifier, extraction repeatability, enrichment factors and limit of detection (LOD), and method application for analysis of real-world complex water samples were all of utmost interest.

## 2. Experimental

### 2.1. Chemicals and standards

Toluene, xylene and isooctane (SupraSolv), methanol and acetonitrile (Lichrosolv) were all purchased from Merck (Darmstadt, Germany). Cyclohexane was obtained from Riedel-deHaen (Seeize, Germany). Purification of reagent water was carried out by a Milli-Q/RO4 unit (Millipore, Bedford, MA).

Two different EPA standard mixtures, containing six phthalate esters; dimethyl-phthalate (DMP), diethylphthalate (DEP),

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