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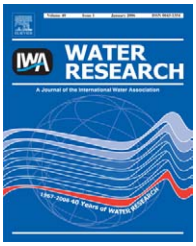

# Considerations on ultra-trace analysis of phthalates in drinking water

*P. Serôdio*[a], *J.M.F. Nogueira*[a,b,*]

[a]*Chemistry and Biochemistry Department, Faculty of Sciences, University of Lisbon, Campo Grande Ed. C8, 1749-016, Lisbon, Portugal*
[b]*Center for Molecular Sciences and Materials, Faculty of Sciences, University of Lisbon, Campo Grande Ed. C8, 1749-016, Lisbon, Portugal*

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ABSTRACT

Stir bar sorptive extraction with liquid desorption followed by large volume injection and capillary gas chromatography coupled to mass spectrometry (SBSE-LD/LVI-GC–MS), had been applied for the determination of ultra-traces of seven-phthalates (dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, butyl benzyl phthalate, bis(2-ethylhexyl) adipate, bis(2-ethylhexyl) phthalate and bis(1-octyl) phthalate) in drinking water samples, which are included in the priority lists set by several international regulatory organizations.

Instrumental calibration under the selected-ion monitoring mode acquisition (LVI-GC–MS(SIM)), experimental parameters that could affect the SBSE-LD efficiency, as well as, the control of the contamination profile are fully discussed. Throughout systematic assays on 30 mL water samples spiked at the 0.40 μg/L level, it had been established that stir bars coated with 47 μL of polydimethylsiloxane, an equilibrium time of 60 min (1000 rpm) and methanol as back extraction solvent, allowed the best analytical performance to monitor phthalates in water matrices. From the data obtained, good accuracy and a remarkable reproducibility (< 14.8%) were attained, providing experimental recovery data in agreement with the theoretical equilibrium described by the octanol–water partition coefficients ($K_{PDMS/W} \approx K_{O/W}$), with the exception of bis(2-ethylhexyl) adipate, bis(2-ethylhexyl) phthalate and bis(1-octyl) phthalate, for which lower yields were measured. Additionally, a remarkable linear dynamic range between 25 and 2000 ng/L ($r^2 > 0.99$) and low detection limits (3–40 ng/L) were also achieved for the seven-phthalates studied. The application of the present method to monitor phthalates in tap and bottled mineral water samples, allowed convenient selectivity and high sensitivity up to 1.0 μg/L level, using the standard addition methodology. The proposed method showed to be feasible and sensitive with a low sample volume requirement to monitor phthalates in drinking water matrices at the ultra-trace level, in compliance with international regulatory directives on water quality.

## 1. Introduction

Phthalate esters, commonly known as phthalates and bis(2-ethylhexyl) adipate are synthetic compounds widely used as polymer additives in plastics, particularly polyvinyl chloride, but also in rubber, cellulose and styrene production, to improve their softness and flexibility. They are present in many consumer products including children toys, cosmetics, personal care products, blood bags, organic solvents, packaging, paper coatings, insecticides, decorating and building

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[*] *Corresponding author.* Chemistry and Biochemistry Department, Faculty of Sciences, University of Lisbon, Campo Grande Ed. C8, 1749-016, Lisbon, Portugal. Tel.: +351 217500899; fax: +351 217500088.
E-mail address: nogueira@fc.ul.pt (J.M.F. Nogueira).

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products, etc. (Agency for Toxic Substances and Disease Registry, 1995, 1997, 2001, 2002; David et al., 2001). Nowadays, due to large and widespread use, phthalates are considered as ubiquitous environmental pollutants. Since their physical rather than chemical incorporation in the polymeric matrix, phthalates easily migrate into foods, beverages and drinking water from the packaging or bottling material or manufacturing processes, being ingested and absorbed into the body, as well as during blood transfusions from PVC blood bags (Balafas et al., 1999; Wahl et al., 1999; European Chemical Bureau, 2000). Although the highest levels tend to be found in fatty foods, such as milk and dairy products, fish, meat and vegetable oils, the presence of phthalates in surface, ground and drinking waters can occur at trace levels, linked to discharges from rubber and chemical plants, landfill, urban and industrial wastewater treatment plants, and municipal incineration stations, widely scattering the potential risk for human exposure (David et al., 2003). An increasing social concern has been aroused to the adverse effects on public health caused by phthalates, which are suspected to be endocrine disrupting chemicals exhibiting carcinogenic action (Hoyer, 2001; McKee et al., 2004). Due to their potential risks for human health and environment, several phthalates has been listed as priority substances by many national and international regulatory organizations. The European Union (EU) published a candidate list of substances with evidence or potential endocrine disrupting action, which includes di-*n*-butyl phthalate, butylbenzyl phthalate and di-2-ethylhexyl phthalate (DEHP). Since DEHP is the most widespread phthalate produced and used, it was incorporated in the list of priority substances in the field of water policy established by EU and the World Health Organization (WHO), has established a guideline value of 8.0 μg/L in fresh and drinking waters (EU Council, 2001; World Health Organization, 2003). The United States Environmental Protection Agency (USEPA) under the Safe Drinking Water Act, regulate DEHP and bis(2-ethylhexyl) adipate by means of National Primary Drinking Water Regulations. The maximum contaminant levels had been set at 6.0 μg/L and 0.4 mg/L, respectively. Simultaneously, USEPA advises closely screening of phthalates in drinking water at concentrations above 0.6 μg/L (USEPA, 1991). While USEPA analytical procedures have been implemented to monitor phthalates in drinking, municipal and industrial waters, no specific methods have been purposed by the EU directives (EU Council, 2001; US EPA, 1980, 1994). Capillary gas chromatography (GC) with flame ionization (FID), electron capture (ECD) or mass spectrometry (MS) detection, and high performance liquid chromatography with diode-array and tandem mass spectrometry detection prior to sample preparation methodologies for enrichment, i.e. liquid–liquid extraction (LLE) and solid-phase extraction (SPE), have been purposed for the determination of phthalates in several types of matrices such as water (Peñalver et al., 2000, 2001; Luks-Betlej et al., 2001; Cortazar et al., 2002), milk (Calafat et al., 2004), urine (Silva et al., 2004), serum (Takatori et al., 2004), plastics (Li et al., 2004), packaging materials (Balafas et al., 1999), PVC toys and childcare articles (Earls et al., 2003). USEPA methods 506, 606 and 8061A, used by dedicated routine laboratories are specific for phthalate analysis in different types of water matrices, using LLE or SPE followed by GC–FID, GC–ECD or GC–MS (US EPA, 1995, 1996, 2001). Nevertheless, the use of 1 L of water sample and even though 20 mL of total volume of organic solvents minimum are actually nonsense towards the common contamination problems involved, neither practical nor environmental friendly and therefore, difficult to justify nowadays. In the last decade, solid-phase microextraction (SPME) has becoming a popular solventless method for sample preparation by its simplicity and had been successfully applied on the analysis of phthalates in water matrices (Peñalver et al., 2000, 2001, Luks-Betlej et al., 2001; Cortazar et al., 2002; Prokupková et al., 2002; Polo et al., 2005). Meanwhile, a more recent solventless method, stir bar sorptive extraction (SBSE), allowing a higher performance and presents the advantage of a much higher amount of polymer available, i.e. polydimethylsiloxane (PDMS), which results in higher sample capacity, recovery and sensitivity improvement by a factor of 100–1000 than SPME, decreasing the detection limits at the sub-ng/L level (Baltussen et al., 1999, 2002). The theory and the enrichment process is similar to that of SPME based on PDMS sorption, which the efficiency of analyte partitioning between the polymeric phase and water, at the equilibrium, can be predicted by the octanol–water partitioning coefficients ($K_{\mathrm{PDMS/W}} \approx K_{\mathrm{O/W}}$) (Baltussen et al., 1999). For phthalate analysis in particular, SBSE with liquid desorption (LD) seems to be a more suitable stripping process, avoiding the usual contaminations coming from the PDMS of the stir bar during the conventional thermal desorption, offering additional interesting features such as cost-effectiveness, the opportunity for method development and/or possible reanalysis, which had been successfully applied to monitor several classes of priority pollutants in water matrices (Popp et al., 2001; León et al., 2003; Serôdio and Nogueira, 2004, 2005; Garcia-Falcon et al., 2004). In the present contribution, stir bar sorptive extraction with liquid desorption followed by large volume injection and capillary gas chromatography coupled to mass spectrometry (SBSE-LD/LVI-GC–MS), is purposed for ultra-trace analysis of phthalates in drinking water samples. The performance of the method is evaluated in terms of accuracy, linearity, precision, and limits of detection, for which systematic studies were carried out in order to foresee the most important parameters that could affect the SBSE-LD efficiency. Finally, under the standard addition methodology, tap and bottled mineral water matrices were monitorised in compliance with international regulatory directives on water quality.

## 2. Materials and methods

### 2.1. Reagents and chemicals

EPA 525 Update Phthalate Esters Mix (500 μg/mL each in methanol) including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis(2-ethylhexyl) adipate (DEHA), bis(2-ethylhexyl) phthalate (DEHP) and neat certified bis(1-octyl) phthalate (BOP) (96.4%; Lot: 9141X, no.36938) standard were purchased from Supelco (Bellefonte, PA, USA). HPLC-grade ethyl acetate (99.8%), methanol (MeOH, 99.9%), acetonitrile