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# A green method for the quantification of plastics-derived endocrine disruptors in beverages by chemometrics-assisted liquid chromatography with simultaneous diode array and fluorescent detection

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## ABSTRACT

The aim of this study was to develop a novel analytical method for the determination of bisphenol A, nonylphenol, octylphenol, diethyl phthalate, dibutyl phthalate and diethylhexyl phthalate, compounds known for their endocrine-disruptor properties, based on liquid chromatography with simultaneous diode array and fluorescent detection. Following the principles of green analytical chemistry, solvent consumption and chromatographic run time were minimized. To deal with the resulting incomplete resolution in the chromatograms, a second-order calibration was proposed. Second-order data (elution time-absorbance wavelength and elution time-fluorescence emission wavelength matrices) were obtained and processed by multivariate curve resolution-alternating least-squares (MCR-ALS). Applying MCR-ALS allowed quantification of the analytes even in the presence of partially overlapped chromatographic and spectral bands among these compounds and the potential interferents. The obtained results from the analysis of beer, wine, soda, juice, water and distilled beverage samples were compared with gas chromatography-mass spectrometry (GC-MS). Limits of detection (LODs) in the range 0.04–0.38 ng mL<sup>-1</sup> were estimated in real samples after a very simple solid-phase extraction. All the samples were found to contain at least three EDs, in concentrations as high as 334 ng mL<sup>-1</sup>.

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## 1. Introduction

According to the International Program on Chemical Safety (IPCS), an endocrine disruptor (ED) is “an exogenous substance or

*Abbreviations:* AJ, apple juice; APs, alkylphenols; BPA, bisphenol A; BSTFA, *N,O*-bis(trimethylsilyl)trifluoroacetamide; Cac, cachaça; ACN, acetonitrile; DAD, diode array detector; DBP, dibutyl phthalate; DEHP, diethylhexyl phthalate; DEP, diethyl phthalate; EDs, endocrine disruptors; EJCRC, elliptical joint confidence region test; FLD, fluorescence detector; GC-MS, gas chromatography-mass spectrometry; IU-PAC, International Union of Pure and Applied Chemistry; LB, lager beer; LC, liquid chromatography; LC-DAD, elution time-absorbance wavelength matrices; LC-FLD, elution time-fluorescence emission wavelength matrices; LOD, limit of detection; LOQ, limit of quantification; LS, lime soda; MCR-ALS, multivariate curve resolution-alternating least-squares; MeOH, methanol; MP, mobile phase; MW, mineral water; nd, not detected; NOAEL, No Observed Adverse Effect Level; NP, nonylphenol; OP, octylphenol; PAEs, phthalate esters; RMSEP, root-mean-square error of prediction; RW, red wine; SB, stout beer; Sch, schnapps; SML, specific migration limit; SPE, solid-phase extraction; TDI, tolerable daily intake; TMCS, trimethylchlorosilane; TW, tonic water; WW, white wine

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mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations” [1]. More than 87,000 compounds of diverse chemical nature and origin are listed as EDs by the U.S. EPA Endocrine Disruptor Screening Program (EDSP), and are classified into several categories: hormones, pharmaceuticals, personal care products, industrial chemicals, pesticides, and combustion byproducts [2]. Phthalate esters (PAEs), alkylphenols (APs) and bisphenol A (BPA) are EDs of particular interest because of their extensive use, mainly in the production of food contact materials, but also in cosmetics, personal care products, medical devices and building materials [3]. In this work some of the most widely spread EDs belonging to these categories are studied, namely, BPA, 4-octylphenol (OP), 4-nonylphenol (NP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and diethylhexyl phthalate (DEHP) (Fig. 1).

PAEs are used as plasticizers in the production of polyethylene, polyvinyl chloride, and other synthetic materials [4]. Since PAEs are not covalently bound to plastics, they can be transferred to the environment, or leak from packing material into food and beverages [5]. On the other hand, APs are derived from the

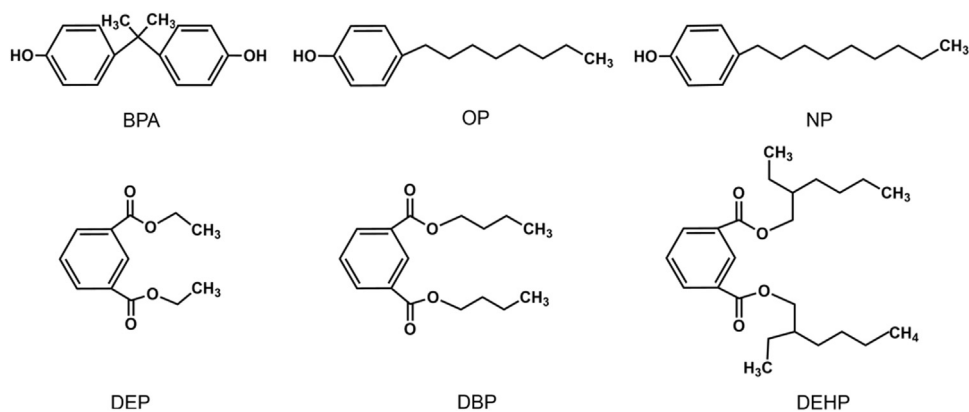


Fig. 1. Structures of the studied EDs.

degradation of alkylphenol ethoxylates, which are surfactants commonly employed in the manufacture of detergents, soaps, paints and other domestic and industrial products [6]. NP is also used as an additive to improve plastic properties [7]. BPA is utilized in the production of epoxy resins, applied as internal coatings of food and beverage cans, and as a monomer in the synthesis of polycarbonate based food contact materials [8].

Several biomonitoring studies have reported a widespread human exposure to PAEs, APs and BPA [9,10]. Even though routes of exposure may vary, diet is always considered the major source of intake [11]. Moreover, the presence of the studied analytes in food and beverages not only represents a health hazard, but also damages product quality, since EDs are a source of carbon for microorganisms that may negatively impact product taste and odour [12]. Therefore, it is essential to develop analytical methods for detecting and quantifying these compounds in a wide variety of food and beverage samples. According to the literature, the most commonly used methods involve liquid chromatography (LC), either equipped with a diode array detector (DAD) or a mass spectrometer [13,14] and gas chromatography-mass spectrometry (GC-MS) [15,16]. Since EDs can be found in beverages at concentrations as low as parts per trillion [17,18] reported methodologies often include a clean-up/preconcentration step prior to instrumental analysis, such as liquid-liquid extraction [19], solid-phase extraction (SPE) [20], and different variants of liquid-liquid micro-extractions [21].

With the purpose of developing a green analytical methodology, i.e. not requiring intense sample pretreatment and minimizing the use of organic solvents [22], a fast and simple method involving a second-order calibration for the quantification of EDs in beverages is here proposed. Analysis was performed through LC with simultaneous measurement of elution time-absorbance wavelength (LC-DAD) and elution time-fluorescent emission wavelength (LC-FLD) second-order data. In this case, instead of pursuing baseline resolution of the analytes, chromatographic conditions were set in order to minimize both solvent usage and experimental time. While dual detection permits the selection of the most appropriate signal for each analyte, second-order calibration enables resolution of overlapping bands and analyte quantification in the presence of interferents. Second-order data was processed by multivariate curve resolution-alternating least-squares (MCR-ALS) [23].

Due to the different chromatographic retention properties of the studied EDs, a simple elution gradient (see below) was applied to shorten the run time. After an easy SPE with C18 membranes, the method was successfully applied to the quantification of the studied plastics-derived EDs in twelve drinks, including beer, wine, soda, juice, water and distilled beverages, and a comparison with a GC-MS method was carried out.

## 2. Experimental

### 2.1. Apparatus

Chromatographic analysis was carried out on an Agilent 1200 liquid chromatograph (Agilent Technologies, Waldbronn, Germany) equipped with a quaternary pump operating at  $1.5 \text{ mL min}^{-1}$ , a fluorescence detector (FLD) irradiating at 226 nm and collecting emission spectra from 295 to 350 nm and a DAD set at a wavelength range from 200 to 300 nm. Both detectors were connected in series, recording absorbance and fluorescence data simultaneously. A Rheodyne injector with a  $20.0 \mu\text{L}$  loop was employed to inject the sample onto a Poroshell 120 EC C18 column ( $4.6 \text{ mm} \times 50 \text{ mm}$ ,  $2.7 \mu\text{m}$  particle size). The data were collected using the software HP ChemStation for LC Rev. HP 1990–1997.

GC-MS was performed using a Shimadzu GC MS-QP2010 Plus gas chromatograph (Kyoto, Japan), equipped with an automatic injector and a Supelco SPB-1 capillary column ( $30 \text{ m} \times 0.25 \text{ mm}$ ,  $d_f$   $0.25 \mu\text{m}$ ). For quantitative determinations, the detector was operated in selected ion-monitoring (SIM) mode. Data acquisition and integration were carried out with the LabSolutions chromatography software.

### 2.2. Reagents and solutions

All reagents were of high-purity grade and used as received. BPA, OP, DEP, DBP and DEHP were purchased from Sigma-Aldrich (St. Louis, MO, USA). NP was provided by Fluka (Buchs, Switzerland). Methanol (MeOH) and acetonitrile (ACN) were obtained from Merck (Darmstadt, Germany) and ethyl acetate by Carlo Erba (Milan, Italy). Ultrapure water was obtained by a Milli Q apparatus (Millipore, Molsheim, France).

MeOH stock solutions of BPA, OP, NP, DEP, DBP and DEHP of about  $1000 \text{ mg L}^{-1}$  were prepared and stored in dark flasks at  $4 \text{ }^\circ\text{C}$ . From these solutions, more diluted MeOH solutions ( $2.00$ – $10.0 \text{ mg L}^{-1}$ ) were obtained.

Empore C18 SPE disks, *N,O*-bis(trimethylsilyl)tri-fluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) were supplied by Supelco (Bellefonte, PA, USA).

PAEs are ubiquitous laboratory contaminants. Therefore, sample contact with plastic materials during storage, transfer and measurements was avoided. All glassware used for the analysis were soaked with a mixture of potassium dichromate, sulfuric acid and water for 24 h, carefully rinsed with tap and Milli-Q water, and finally with methanol. Because of the toxicity of chromium solutions, minimal amounts of the potassium dichromate/sulfuric acid mixture were used. In addition, care was taken in handling the latter mixture, and all rinses were collected for proper disposal.

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