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Fast and simultaneous determination of endocrine disrupting compounds by ultra-high performance liquid chromatography–tandem mass spectrometry

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ABSTRACT

A rapid and sensitive analytical method for the simultaneous determination of thirteen endocrine disruptors (five phthalates, seven parabens, and bisphenol A) in a single chromatographic run has been developed for the first time. The separation method, based on ultra-high performance liquid chromatography (UHPLC), allows the separation of all compounds (including isobaric pairs) in less than 4.1 min. The fast polarity switching mode of the triple quadrupole mass spectrometer used enables the registration of positive (phthalates) and negative (parabens and BPA) ions in the same acquisition run. A Response Surface Methodology was used for the optimization of the method. The optimum elution program starts with 0.2 min in isocratic conditions (79.8% water; 20% acetonitrile, 0.2% ammonium formate 5 mM at pH 10.2), then the content of acetonitrile is linearly increased in 2 min up to 42%, and later up to 98% in 1.1 min. The analytical characteristics of the developed method were satisfactory. The method is robust and showed a linear response with determination coefficients (R^2) higher than 0.991 in the range 5.0–2000 pg on column (or higher) for all the compounds investigated. Instrumental intra- and inter-day precision (expressed as relative standard deviation) were lower than 12% for parabens and bisphenol A, and between 5.9% and 27% for phthalates. Instrumental detection and quantification limits (iLODs and iLOQs) were in the range of medium-high femtograms (270–1300 pg on column for iLODs). Finally, the suitability of the developed method was demonstrated through its application to the analysis of commercial personal care products (shower gels) without any sample treatment, only a simple dilution, being possible to determine the simultaneous presence of phthalates, parabens, and bisphenol A in almost all the gels analyzed.

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1. Introduction

Nowadays, there is a high concern of a number of substances highly widespread in human life with possible endocrine disrupting potential. These endocrine disrupting chemicals (EDCs) include a wide variety of chemical compounds found in several materials commonly used in daily life, such as pesticides, additives or contaminants in food and personal care products. Among these substances, phthalates, parabens, and bisphenol A (BPA) have received special attention in the last years due to their ubiquitous presence in the environment, the clear evidences of their reproductive toxicity, and their estrogenic activity [1–4]. In addition, they are frequently present in personal care products and the safety of such products is a top priority for consumer protection.

Phthalates are commonly found in the cosmetic industry as carriers or solvents [5] while parabens are used as preservatives for their bactericidal and fungicidal properties [6]. Additionally, the presence of both BPA and phthalates in personal care products could be due to both the previous presence of these compounds in the product itself and the migration of the contaminants from the plastic used as packaging. As commented before, the number of studies indicating that phthalates and their metabolites, parabens, and BPA can be toxic has been increased in the last few years. Some of their endocrine-disruptive effects involve fertility and reproductive adverse effects [1–3]. In addition, some of them cause cancer in mammalian animals [4]. This is the reason why, the European Union has published a list of substances prohibited in cosmetics products, which includes dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and diethyl hexyl phthalate (DEHP) [7,8]. Regarding parabens, even when additional human data is needed, the European Parliament with the Regulation 1223/2009/EC [8] establishes a maximum concentration in ready for use

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cosmetic products of 0.4% (as 4-hydroxybenzoic acid) for single parabens or 0.8% (as acid) for mixture of parabens. On the other hand, the Scientific Committee on Consumer Safety has suggested limiting concentrations of 0.19% (w/w) for the sum of the individual concentrations of propylparaben (PP) plus butylparaben (BP) [9]. In addition, Denmark has banned the use of these two parabens in cosmetic products for children under 3 years old [10].

Several analytical methods for the identification and determination of phthalates, parabens, and BPA in personal care products have been published [6,11–24]. For that purpose, separation techniques such as liquid chromatography (LC) [6,12,13,16,21,24], gas chromatography (GC) [11,14,16,17,19–23], and capillary electrophoresis (CE) [15,18] have been used combined with UV, fluorescence, and mass spectrometry (MS) detectors. However, to the best of our knowledge, none of them deals with the separation and quantification of the three groups of compounds in a single chromatographic run using a multi-component method. In addition, the use of ultra-high performance liquid chromatography (UHPLC) is quite scarce in this type of analysis and only one paper [6] reports the use of this technique for the separation of four parabens but using a photometric detection. In this sense, MS detection systems are more common for GC separation methods [11,14,16,17,19,20,22,23] and published LC methods generally employed UV or fluorescence detectors [6,12,13,16,24]. So, the use of triple quadrupole analyzers coupled to UHPLC for the simultaneous determination of these EDCs has not been reported yet.

On the other hand, the chromatographic behavior and sensitivity of these families of compounds are not always satisfactory, and optimization of the instrumental conditions is required. The conventional approaches based on one-factor-at-a-time experiments are very time consuming and usually do not provide good results for LC, because of the high number of degrees of freedom associated with this technique. In particular, in LC methods, there are numerous physicochemical factors that must be adjusted to obtain optimal solutions and to reveal the complex effects of these factors on the quality of the separations. Instead, the use of computer-assisted experimental design in the optimization of chromatographic processes gives much better results since it considers a global maximum including all possible combinations of variables and physicochemical factors that affect LC separations. In fact, the application of these strategies allows chromatographers to develop, optimize and transfer procedures which constitute one of the most commonly analytical activities used at present in laboratories and industries worldwide [25].

In this study, a method based on UHPLC coupled to a triple quadrupole MS analyzer working in multiple reaction monitoring mode (QqQ(MRM)) for the rapid and simultaneous determination of five phthalates, seven parabens, and BPA was developed and applied to the analysis of commercial shower gels.

To the best of our knowledge, this is the first time that an UHPLC-QqQ(MRM) multi-residue method for the simultaneous determination of thirteen EDCs has been presented.

2. Materials and methods

2.1. Reagents, standards, and samples

Native standards of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), diethyl hexyl phthalate (DEHP), methyl paraben (MP), ethyl paraben (EP), n-propyl paraben (nPP), iso-propyl paraben (iPP), n-butyl paraben (nBP), iso-butyl paraben (iPB), benzyl paraben (BzP), and bisphenol A (BPA) were supplied by AccuStandard (New Haven, CT, USA). The isotopically labeled standards DMP-D₄, DEP-D₄, DBP-D₄, BBP-D₄, DEHP-D₄, MP-¹³C₆, nBP-¹³C₆, BPA-¹³C₁₂ were supplied by

Cambridge Isotope Laboratories (Andover, MA, USA).

Water and acetonitrile (ACN), both of LC-MS Ultra CHROMASOLV[®] grade, formic acid, N-methylpyrrolidone and ammonium formate (purity ≥ 99.0%) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Ammonia solution (32% extra pure), acetone, dichloromethane, hexane, and methanol (MeOH) (purity ≥ 99.0%) was purchased from Merck (Darmstadt, Germany). The solvents of LC-MS Ultra CHROMASOLV[®] grade were used for mobile phase and sample preparation and dilution, and the solvents of purity ≥ 99.0% were employed for washing the glassware. Twenty two (n=22) commercially available shower gels were acquired in cosmetic shops and supermarkets in Madrid (Spain).

2.2. Apparatus

All the UHPLC-MS experiments were carried out on a UPLC Acquity[®] system (Waters, Milford, USA), equipped with a quaternary pump, an autosampler, and a column oven, and coupled to a Xevo[®] TQ-S triple quadrupole mass spectrometer (Waters) using an electrospray ionization (ESI) interface.

For MS experiments, nitrogen (99.5% purity) was used as desolvation and cone gases, at 16.7 L min⁻¹ and 2.5 L min⁻¹, respectively, and argon (99.999% purity) was used as collision gas (0.17 mL min⁻¹). ESI source was operating in the fast polarity switching mode. Phthalates were detected in the positive mode, while parabens and BPA were recorded in the negative mode. Optimization and quantitative analysis were carried out in the multiple reaction monitoring (MRM) mode, using two precursor-product ion transition for each compound. As it is common in this type of procedures, the most intense ion of the ESI spectra of each analyte was selected as precursor ion. After that, the two most intense product ions formed at their optimum collision energies were chosen, obtaining the two most abundant precursor-product ion transitions. The most abundant one was used with quantitative purposes and the second most abundant one for confirmatory purposes. These transitions along with their corresponding retention time, polarity, optimized collision energies, cone voltages, and transition ratios are shown in Table 1. The first transition indicated in the table corresponds to the quantitative transition and the second one to the confirmatory transition. The value of dwell time used during the analysis was 0.005 s for all analytes.

The UHPLC experiments were performed on an Acquity UPLC[®] BEH Phenyl column (2.1 mm × 50 mm, 1.7 μm, Waters). A delay column Kinetex C18 (2.1 mm × 30 mm, 1.7 μm, Phenomenex, Torrance, CA, USA) was placed between the LC pump and the injection valve with the purpose of retarding the phthalates coming from the mobile phase [26]. For the optimization process, injections of 5 μL of a mixture of standards (100 pg μL⁻¹) were carried out. The solvent composition for this mixture was adapted to have the same composition as the initial mobile phase used in each LC run. Different elution programs were assayed (see Section 3.2), containing variable percentages of water (eluent A) and acetonitrile (eluent B), and 0.2% of ammonium formate 5 mM (eluent C). Initial percentage of eluent B was maintained for 0.2 min in all experiments, after which the percentage of eluent B was linearly increased to 98%, this value being maintained until complete elution of the compounds was obtained. Then, the program ramped to the original composition and equilibrated for 2 min.

The determinations of pH values were carried out using a Cision BASIC pH-meter that was calibrated using aqueous buffers of pH 4.01, 7.00, and 9.21. Values of pH were taken in aqueous solution.

2.3. Method optimization and analytical characterization

The LC-MS system data acquisition and processing were managed

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