Magnetic solid phase extraction with CoFe₂O₄/oleic acid nanoparticles coupled to gas chromatography-mass spectrometry for the determination of alkylphenols in baby foods

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ABSTRACT

Magnetic solid phase extraction (MSPE) with cobalt ferrite nanoparticles coated with oleic acid is described for the determination of alkylphenols (APs), 4-tert-butylphenol (TBP), 4-pentylphenol (PP), 4-hexylphenol (HP), 4-tert-octylphenol (TOP), 4-n-octylphenol (OP) and 4-nonylphenol (NP) in baby foods using gas chromatography with mass spectrometry (GC–MS). Prior to MSPE, the sample was treated with trichloroacetic acid, and the APs derivatized with acetic anhydride. Parameters affecting the extraction efficiency: amount of magnetic nanoparticles, extraction time and desorption conditions, were optimized. The enriched phase obtained was evaporated to dryness and the residue reconstituted in 50 μL of methanol, 1 μL of which was injected into the GC–MS. Samples were quantified applying matrix-matched calibration and using 2-chloro-5-bromoanisole as surrogate standard. The analysis of 0.5 g of sample provided detection limits in the 0.4–1.7 ng g⁻¹ range. Some samples contained APs at levels of between 3 ng g⁻¹ for HP and 122 ng g⁻¹ for TOP.

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1. Introduction

Alkylphenols (APs) are a group of environmentally persistent contaminants used in the production of surfactants and as stabilizers of different types of resins (Mezcua et al., 2012). These compounds are considered as endocrine disrupting chemicals (EDCs), especially the xenoestrogens nonylphenol (NP) and octylphenol (OP) (Capriotti et al., 2013; Kudłak & Namieśnik, 2008). Some foods may contain these pollutants because of contamination from raw materials or during the food-making process (Mezcua et al., 2012). The presence of APs in certain packaging materials can be another reason for the APs appearance in food, the migration from the packages has been previously demonstrated (Cacho, Campillo, Viñas, & Hernández-Córdoba, 2012; Fasano, Cirillo, Esposito, & Lacorte, 2015; Fernandes, Rose, & Charlton, 2008).

Food safety is a relevant subject for many governments (Capriotti et al., 2013), with special attention to foods consumed in the first years of life. Sensitive, selective and reliable analytical methods are needed to address these concerns. In this respect, the analysis of food samples for their AP content has been carried out using gas chromatography (GC) for the high sensitivity achieved (Ademollo, Ferrara, Delise, Fabietti, & Funari, 2008; Cacho et al., 2012; Fasano et al., 2015; Fernandes et al., 2008; Ferrara, Ademollo, Delise, Fabietti, & Funari, 2008; Li, Cheng, & Ding, 2008; Lu, Wu, Stoffella, & Wilson, 2013; Meier, Klungsøyr, Boitsov, Eide, & Svardal, 2005; Raecker, Thiele, Boehme, & Guenther, 2011), and liquid chromatography (LC) (Carabias-Martínez, Rodríguez-Gonzalo, & Revilla-Ruiz, 2006; Chen, Wang, Gwo, & Chen, 2012; Ferrer et al., 2011; Niu, Zhang, Wu, & Shao, 2012; Rodríguez-Gonzalo, García-Gómez, & Carabias-Martínez, 2010; Shao, Han, Tu, & Huang, 2007; Viñas, López-García, Bravo-Bravo, Briceño, & Hernández-Córdoba, 2012). Most of the chromatographic methods developed to date use mass spectrometry (MS) as the detection system. The complexity of foods and the low expected concentrations of APs mean that suitable sample preparation techniques must be applied prior to analytical measurement. The extraction of APs from solid food matrices into organic solvents has been carried out by solid-liquid extraction (SLE) (Ferrara et al., 2008; Meier et al., 2005), sometimes aided by ultrasonication (Guenther et al., 2002; Lu et al., 2013; Niu, Zhang, et al., 2012), steam distillation (Guenther et al., 2002; Li et al., 2008), pressurized liquid extraction (PLE) (Carabias-Martínez et al., 2006; Ferrer et al., 2011) or matrix solid phase dispersion (MSPD) (Chen et al., 2012; Shao et al., 2007). Prior to chromatographic analysis, sample extracts or liquid samples are usually submitted to clean-up steps, using classic liquid-liquid extraction (LLE), solid-phase extraction (SPE) (Carabias-Martínez

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et al., 2006; Lu et al., 2013; Niu, Zhang, et al., 2012; Shao et al., 2007), or gel permeation (Meier et al., 2005). Chen et al. (2012) proposed disk-type SPE as an alternative to the classic SPE for AP determination in fish. In addition, QuEChERS methodology has also been applied for this purpose in packed food (Fasano et al., 2015).

Microextraction techniques were developed with the aim to match the guidelines of green analytical chemistry, decreasing sample preparation time and the consumption of toxic organic solvents. In this sense, APs have been preconcentrated from liquid foods and liquid extracts obtained from solid samples by solid-phase microextraction (SPME) (Kataoka, Ise, & Narimatsu, 2002) and stir bar sorptive extraction (SBSE) (Cacho et al., 2012). This latter technique has also been applied in the analysis of animal feed (Liu et al., 2012).

The use of magnetic nanoparticles (MNPs) as sorbents has been successfully applied for the preconcentration different types of analyte from a wide range of sample matrices (Aguilar-Arteaga, Rodriguez, & Barrado, 2010; He, Huang, Wang, Zhang, & Li, 2014; Hu, He, & Chen, 2015; Ríos, Zougagh, & Bouri, 2013), in a technique named as magnetic solid phase extraction (MSPE). The increase of the contact surface between analyte and adsorbent in MSPE technique improves the extraction efficiencies, compared with traditional SPE. Besides, in MSPE the volume of organic solvent in the desorption step is lower than in SPE due to the dispersion of the particles. The procedure involves the dispersion of MNPs into the sample solution and, after adsorption of the analytes, an external magnetic field is applied to isolate the enriched MNPs, while the solution is discarded. Finally, the target compounds can be eluted from the magnetized sorbent with a small quantity of an adequate solvent to be analyzed. The determination of APs has been attempted by MSPE, using different types of MNPs, the most commonly used being magnetite (Fe_3O_4), with different protecting surfaces to avoid oxidation which also act as sorbents, such as surfactants (Ju, Yang, & Liu, 2015; Zhao, Shi, Cai, & Mou, 2008), silica (Zhao, Shi, Wang, Cai, & Jiang, 2008), silica and C18 (Alcudia-León, Lucena, Cárdenas, & Valcárcel, 2013) and carbon based materials (Liu, Feng, Wang, Wu, & Wang, 2014; Liu et al., 2012; Niu, Wang, Zhang, Meng, & Cai, 2012; Rao, Cai, Yin, Long, & Zhang, 2014). Komarek and coworkers proposed commonly used magnetized chromatographic stationary phases for APs isolation (Komarek et al., 2008). Most of the MSPE methods applied for AP determination focus on the analysis of waters (Alcudia-León et al., 2013; Ju et al., 2015; Liu et al., 2014; Liu et al., 2012; Niu, Wang, et al., 2012; Rao et al., 2014; Zhao, Shi, Cai, et al., 2008; Zhao, Shi, Wang, et al., 2008), and only one method has been applied to honey peach juice analysis (Komarek et al., 2008). Fe_3O_4 MNPs functionalized with tetraethylenepentamine have been used to remove phospholipids from blood samples before AP determination (Zhao et al., 2013).

Different properties, such as hardness, high coercivity, moderate magnetization and high physical and chemical stability, make cobalt ferrite an attractive magnetic material to be used in the production of MNPs (Maaz, Mumtaz, Hasanain, & Ceylan, 2007). Moreover, in order to protect cobalt ferrite nanoparticles from atmospheric oxygen, avoiding their oxidation, and also to prevent their agglomeration, the particles are usually coated and dispersed in tetradecyl-trimethyl-ammonium bromide or oleic acid. In this paper, cobalt ferrite coated with oleic acid nanoparticles are used in MSPE procedure. Up to date, this type of nanoparticle has been used for GC (Benedé, Chisvert, Giokas, & Salvador, 2016; Román, Chisvert, & Canals, 2011) and LC analysis (Benedé, Chisvert, Giokas, & Salvador, 2014; Viñas, Pastor-Belda, Torres, Campillo, & Hernández-Córdoba, 2016). This paper describes a new application of cobalt ferrite nanoparticles coated with oleic acid for the determination of the non-ionic surfactants, 4-tert-butylphenol (TBP), 4-pentylphenol (PP), 4-hexylphenol (HP), 4-tert-octylphenol (TOP),

4-octylphenol (OP) and 4-nonylphenol (NP), in different types of baby food using GC with mass spectrometry (MS).

2. Experimental

2.1. Reagents

4-tert-butylphenol (TBP, 99%), 4-pentylphenol (PP, 98%), 4-hexylphenol (HP, 98%), 4-nonylphenol (NP, 99.9%), 4-n-octylphenol (OP), 4-tert-octylphenol (TOP, 99.9%) and 5-bromo-2-chloroanisole (surrogate standard) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Individual stock solutions of the compounds (500 µg mL^{-1}) were prepared using HPLC grade methanol as solvent and stored in darkness at $-20\,°C$. Working standard solutions were freshly prepared in methanol and stored at $4\,°C$.

Iron (III) chloride hexahydrate (97%) and oleic acid (90%), acetic anhydride, anhydrous potassium phosphate, potassium hydrogen phosphate, trichloroacetic acid (TCA, 99%) and sodium hydroxide were also purchased from Sigma-Aldrich. Cobalt (II) chloride hexahydrate pure was provided by Acros (New York, USA) Methanol, acetonitrile, ethanol and acetone were obtained from J.T. Baker (Deventer, Netherlands). The water used was previously purified in a Milli-Q system (Millipore, Bedford, MA, USA). The carrier gas used for GC was helium (Air Liquide, Madrid, Spain).

2.2. Instrumentation

An Agilent 6890N (Agilent, Waldbronn, Germany) gas chromatograph provided with a split-splitless injector port was used. The injection port was held at $240\,°C$ in the splitless mode. The GC temperature was programmed as follows: start temperature $80\,°C$ (held 0.5 min) and increased to $180\,°C$ at $20\,°C\,min^{-1}$ (held 3 min) and then to $240\,°C$ at $40\,°C\,min^{-1}$ (held 7 min). A VF-23 ms (Agilent) capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness), with a highly substituted cyanopropyl low-bleed stationary phase, was used with helium as carrier gas (1 mL min^{-1}). An Agilent 5973 quadrupole mass selective spectrometer was used and the ionization was carried out in the electron ionization (EI) mode (70 eV). The temperatures of the ion source and the transfer line were 230 and $250\,°C$, respectively. The analytes were quantified under the selected ion monitoring (SIM) mode using the target ion (Table 1). Identification was confirmed by comparing the retention time and relevant MS-spectra, more specifically the qualifier-to-target ion ratios, with those obtained in the injection of pure standards.

An Unicen 21 (TQTech, Shenzhen, China) centrifuge, an orbital agitator IKA KS 130 Basic (IKA, Staufen Germany) and a rotatory evaporator (BÜCHI Labortechnik AG, Flawil, Switzerland) were used in the sample treatment. Permanent magnets composed of Nd-Fe-B (3 × 1 × 1 cm) (Supermagnete, Gottmadingen, Germany) were used to separate the nanoparticles from the solutions, which were filtered through 0.45 µm Nylon filters (Agilent). An ultrasonic processor UP 200 H (Dr. Hielscher, Teltow, Germany), with an effective output of 200 W in liquid media equipped with a titanium sonotrode (7 mm i.d.) was used to desorb the analytes from magnetic nanoparticles, working for 1.5 min, applying 90 cycles of a duration of 0.8 s per cycle and 140 µm amplitude.

2.3. Synthesis of cobalt ferrite coated with oleic acid nanoparticles

The procedure proposed by Maaz et al. was used to synthesize the oleic acid coated magnetic nanoparticles. The co-precipitation of Co^{2+}/Fe^{3+} salts was carried out under alkaline conditions. One hundred milliliters of 0.4 M iron chloride and 100 mL 0.2 M cobalt