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# Use of oleic-acid functionalized nanoparticles for the magnetic solid-phase microextraction of alkylphenols in fruit juices using liquid chromatography-tandem mass spectrometry



Pilar Viñas, Marta Pastor-Belda, Aitor Torres, Natalia Campillo, Manuel Hernández-Córdoba\*

Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, E-30100 Murcia, Spain

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## ABSTRACT

Magnetic nanoparticles of cobalt ferrite with oleic acid as the surfactant (CoFe<sub>2</sub>O<sub>4</sub>/oleic acid) were used as sorbent material for the determination of alkylphenols in fruit juices. High sensitivity and specificity were achieved by liquid chromatography and detection using both diode-array (DAD) and electrospray-ion trap-tandem mass spectrometry (ESI-IT-MS/MS) in the selected reaction monitoring (SRM) mode of the negative fragment ions for alkylphenols (APs) and in positive mode for ethoxylate APs (APEOs). The optimized conditions for the different variables influencing the magnetic separation procedure were: mass of magnetic nanoparticles, 50 mg, juice volume, 10 mL diluted to 25 mL with water, pH 6, stirring for 10 min at room temperature, separation with an external neodymium magnet, desorption with 3 mL of methanol and orbital shaking for 5 min. The enriched organic phase was evaporated and reconstituted with 100  $\mu$ L acetonitrile before injecting 30  $\mu$ L into a liquid chromatograph with a mobile phase composed of acetonitrile/0.1% (v/v) formic acid under gradient elution. Quantification limits were in the range 3.6 to 125 ng mL<sup>-1</sup>. The recoveries obtained were in the 91–119% range, with RSDs lower than 14%. The ESI-MS/MS spectra permitted the correct identification of both APs and APEOs in the fruit juice samples.

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## 1. Introduction

Magnetic solid-phase extraction (MSPE) is a new procedure for the preconcentration of target analytes from large volumes of liquids. The technique [1,2] is based on the use of magnetic or magnetizable materials which are appropriate adsorbents of organic molecules from samples and consists of several simple steps, including the binding of analytes to magnetic nanoparticles (MNPs), separation from the sample using a magnetic field and the elution of target compounds [3]. The dispersion of MNPs into the solution improves the adsorption of the analytes due to the large surface area between extractant and sample. The technique can be classified as a particular type of dispersive solid-phase extraction (DSPE) [4] or dispersive microsolid-phase extraction (D $\mu$ SPE) [5]. The paramagnetic properties of these particles allow their easy isolation in solution since they can be attracted with the aid of an external magnetic field. Thus, suspended magnetic particles

tagged with analytes can be removed from large sample volumes using a magnet while their isolation and purification are easier and faster than when other procedures are used [6]. The technique is advantageous for biological samples with complex matrices, as the analytes bound to magnetic materials can be easily and selectively removed from the sample. Another possibility is the combination of D $\mu$ SPE with stir-bar-sorptive extraction (SBSE) in a new approach termed stir-bar-sorptive-dispersive microextraction (SBS D $\mu$ E) [7]. After magnetic separation, analytical techniques such as liquid chromatography (LC) or gas chromatography (GC) can be applied [3].

MNPs represent one of the most promising materials in analytical nanotechnology since they can be easily isolated from the matrix by using an external magnetic field. The advantages over SPE sorbents include large surface areas, high extraction efficiencies and the need for lower amounts of organic solvents [5]. The simplicity of obtaining MNPs in large quantity allows a wide range of potential applications in environmental, biological and food analysis. Moreover, MNPs can be reused or recycled [8]. There are various magnetic materials which are based on ferromagnetic

\* Corresponding author.

E-mail address: [hcordoba@um.es](mailto:hcordoba@um.es) (M. Hernández-Córdoba).

metal elements, including iron, cobalt and nickel. Pure inorganic magnetic particles compose the core of the magnetic material but are prone to the formation of large aggregates resulting in changes of their magnetic properties. Moreover, their lack of selectivity makes them unsuitable for samples with complex matrices. In the case of biological applications, MNPs can be bio-functionalized with hydrophobic groups [3], coating their surface with organic molecules (such as polymer or surfactant), thus improving their chemical stability, preventing their oxidation and providing specific functionalities like selectivity [8,9].

Alkylphenols (APs) and alkylphenol ethoxylates (APEOs) are incorporated in epoxy resins in plastics and rubber. They are, for example, used in tap water pipes, from which they can be released, resulting important contaminants in the environment, especially in waters [10]. The use of industrial and waste waters for irrigation purposes may lead to the presence of these compounds as food contaminants, especially in fruits and vegetables. The exposure route for these chemicals in humans is mainly through water, although there is also some exposure through soil and foods [11,12]. These chemicals are considered as environmentally persistent contaminants, and are classified as endocrine disrupting chemicals (EDCs) [13], so are subject to EU controls [14].

Miniaturized solid-phase sample preparation methods offer environmentally friendly analytical procedures with increased analysis speed. Miniaturized techniques for APs include solid-phase microextraction (SPME) [15–18] and stir-bar-sorptive extraction (SBSE) [19,20], mostly in water samples. After extraction, the analysis of APs and APEOs [21] can be performed by LC, a technique which does not require derivatization and can be used for polar and high-molecular-weight APs [16,17,22–42].

Synthesized MNPs graphene sheets [43] and silica-MNPs [44] have been proposed as supports for hemimicelles/admicelles for SPE of APs from environmental water samples. The main disadvantage of these sorbents is that they disrupt surfactant aggregates during analyte elution, which produces extracts containing high surfactant concentrations that may suppress ionization in mass spectrometry (MS) [5].

The procedure described here involves the use of magnetic nanoparticles of cobalt ferrite, with oleic acid as the surfactant (CoFe<sub>2</sub>O<sub>4</sub>/oleic acid), for the determination of the APs 4-*tert*-butylphenol (TBP), 4-pentylphenol (PP), 4-hexylphenol (HP), 4-*tert*-octylphenol (TOP), octylphenol (OP), 4-nonylphenol (NP), and the APEOs, 4-*tert*-octylphenol monoethoxylate (TOP<sub>1</sub>EO), 4-*tert*-octylphenol diethoxylate (TOP<sub>2</sub>EO), 4-nonylphenol monoethoxylate (NP<sub>1</sub>EO) and 4-nonylphenol diethoxylate (NP<sub>2</sub>EO) in fruit juices, using LC with both diode array detection (DAD) and electrospray ion trap-tandem mass spectrometry (ESI-IT-MS/MS). Benzo(k)fluoranthene (BkF) was used as the surrogate standard.

## 2. Experimental

### 2.1. Reagents and samples

Chromatographic quality acetonitrile, ethanol, methanol and acetone were obtained from Sigma (St. Louis, MO, USA). The water used was previously purified in a Milli-Q system (Millipore, Bedford, MA, USA). Analytical standards of TBP, PP and HP were obtained from Sigma; TOP and OP from Supelco (Bellefonte, PA, USA); NP, TOP<sub>1</sub>EO, TOP<sub>2</sub>EO, NP<sub>1</sub>EO and NP<sub>2</sub>EO, from Fluka (Buchs, Switzerland). Stock solutions of APs containing 400 µg mL<sup>-1</sup> of each component were prepared in methanol and stored in amber vials at -20 °C. Working standard solutions were prepared daily in methanol and stored at 4 °C. For APEOs, stock solutions containing 10 or 50 µg mL<sup>-1</sup> of each component were diluted in methanol and stored at 4 °C. Benzo(k)fluoranthene, obtained from

Sigma, was used as surrogate standard. Other reagents were sodium chloride, formic acid, iron (III) chloride, cobalt (II) chloride, sodium hydroxide (Merck, Darmstadt, Germany) and oleic acid (Fluka) (Buchs, Switzerland).

APs are contaminants in many products commonly found in the laboratory and so plastics must be avoided and glassware must be carefully cleaned by rinsing with distilled water and then with acetone before drying in an oven at around 180 °C. In our case, blanks were run for each series of samples.

Five different commercially obtained fruit juices (orange, pineapple, apple, peach and grapefruit) were analyzed immediately after opening. All the samples were in tetra brick packages and maintained at ambient temperature.

For the recovery studies, 10 mL aliquots of the fruit juice diluted to 25 mL with water were fortified by adding different volumes of a standard solution containing the APs, leading to fortification levels in the 16–200 ng mL<sup>-1</sup> range (400 ng mL<sup>-1</sup> for TBP), depending on the compound, and spiked at 80 ng mL<sup>-1</sup> with a solution of BkF (surrogate standard). The fortified samples were homogenized for 5 min and left to stand for 1 h at room temperature to distribute the analytes evenly and to allow them to interact with the matrix, before carrying out the analyses. The fortification procedure was applied to two samples (pineapple and grapefruit juices).

### 2.2. Instrumentation

The LC system consisted of an Agilent 1100 (Agilent, Waldbronn, Germany) quaternary pump operating at room temperature with a flow-rate of 0.4 mL min<sup>-1</sup>. The diode-array detector operated at 225 nm. The UV-vis spectra, recorded in the 200–600 nm range, were used for the tentative identification of APs at the corresponding retention times. The ion trap mass spectrometer (Agilent XCT Plus) was equipped with an electrospray ionization (ESI) source. Data were collected in negative mode for APs and in positive mode for APEOs by scanning at *m/z* 50–450 range in ultrascan mode using a nebulizer gas pressure of 45 psi; a drying gas flow of 10 L min<sup>-1</sup> and a drying gas temperature of 350 °C. The surrogate standard BkF can be detected in both ionization modes. Other operation parameters were: ICC, 200000/20 ms; capillary voltage, 3500 V; cap exit, 102.3 V; skimmer voltage, 40 V; octapole 1 DC, 12 V; octapole 2 DC, 1.7 V; octapole RF, 152.1 V and trap drive 36.7. The parameters were optimized using a mass calibrating solution, ESI tuning solution Agilent G2431A, using two reference compounds with 118.1 and 322.1 *m/z*. Table 1 shows data for the ESI-IT-MS/MS settings in selected reaction monitoring (SRM) mode. An Eclipse XDB-C18 (5 cm × 0.46 cm × 5 µm) analytical column (Agilent) was used. The mobile phase was a mixture of acetonitrile and 0.1% (v/v) formic acid, operating under gradient elution with the optimized program being: an isocratic step with 55:45 acetonitrile:formic acid (v/v) for 3.5 min; a linear gradient to 70:30 (v/v) in 0.5 min, which was held for 1.5 min; a linear gradient to 80:20 (v/v) in 1.5 min, which was held for 13 min. Finally, the initial conditions were re-established in 1 min and held for 10 min. The flow-rate was 0.4 mL min<sup>-1</sup>. Injection (30 µL) was performed using an autosampler and vials of 2 mL capacity provided with 250 µL microinserts with polymeric feet were used.

Solutions were stored in 2 or 10 mL amber glass vials. To filter the extracts, Nylon filters (0.45 µm) (Teknokroma, Barcelona, Spain) were used. An EBA 20 (Hettich, Tuttlingen, Germany) centrifuge was used at a speed near to the maximum supported by the conical glass tubes, 3000 rpm. An IKA-KS 130 Basic orbital agitator was also used. MNPs were dried at 100 °C using a drying oven. A rotatory evaporator (BÜCHI Labortechnik AG, Flawil, Switzerland) was also used.

Permanent magnets composed of Nd-Fe-B were supplied by

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