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One-pot synthesized functionalized mesoporous silica as a reversed-phase sorbent for solid-phase extraction of endocrine disrupting compounds in milks

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ABSTRACT

A new procedure for the determination of 12 naturally occurring hormones and some related synthetic chemicals in milk, commonly used as growth promoters in cattle, is reported. The method is based on liquid–liquid extraction followed by solid-phase extraction (SPE) using a new one-pot synthesized ordered mesoporous silica (of the SBA-15 type) functionalized with octadecyl groups (denoted as SBA-15-C_{18}-CO) as reversed-phase sorbent. The analytes were eluted with methanol and then submitted to HPLC with diode array detection. Under optimal conditions, the method quantification limit for the analytes ranged from 0.023 to 1.36 μg/mL. The sorbent afforded the extraction of estrone, 17β-estradiol, estriol, progesterone, hexestrol, diethylstilbestrol, 4-androstene-3,17-dione, ethinylestradiol, 17α-methyltestosterone, nandrolone, prednisolone and testosterone with mean recoveries ranging from 72% to 105% (except for diethylstilbestrol) with RSD < 11%. These results were comparable and, in some cases, even better than those obtained with other extraction methods, therefore SBA-15-C_{18}-CO mesoporous silica possess a high potential as a reversed-phase sorbent for SPE of the 12 mentioned endocrine disrupting compounds in milk samples.

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1. Introduction

Endocrine disruptors are exogeneous substances that modify the function of the endocrine system and, consequently, they cause adverse effects in humans' health [1]. Endocrine-disrupting chemicals (EDCs) have been associated with altered reproductive function in males and females, increased incidence of breast cancer, abnormal growth patterns and neurodevelopmental delays, as well as changes in immune function. Several studies have reported that EDCs can adversely affect humans [2,3]. An increasing broad spectrum of compounds, both natural and synthetic can be considered EDCs, such as pesticides, plasticizers, polycyclic aromatic hydrocarbons and hormones [4]. Steroid hormones are illegally administered to animals as growth promoters in order to gain weight faster and increase milk production. These compounds which can be carcinogenic even at very low levels are listed within Group A in Annex I of the Council Directive 96/22/EC (Group A: substances having anabolic effect and unauthorized substances) [5]. For Group A substances, "zero tolerance" is established by EU, except for melengestrol acetate which maximum residue limit (MRL) has been set at 1 μg/kg in cow fat. Growth promoters can pass from the blood stream and can be finally excreted in milk by the mammary gland.

As milk and dairy products are major constituents of human diets, the consumption of these products could be considered an important source of these dangerous substances for the humans [6]. For these reasons, it is very important to develop multi-residue methods to determine the levels of these compounds in milks. Most of the methods published in the literature use HPLC–MS [6–10] or GC–MS [11–13] for the determination of steroid hormones in milk. The studies about separation of steroid hormones by HPLC–DAD are quite limited. However, due to its simplicity, this technique is usually employed as a starting point for the evaluation of new methodologies in sample preparation [14–16].

Current trends in sample treatment are focused on the synthesis of new materials and their application as sorbents in solid phase

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extraction (SPE) or other techniques such as matrix solid phase dispersion (MSPD), molecular imprinted solid phase extraction (MISPE), etc. In this sense, ordered mesoporous silicas are promising materials because of their desirable characteristics: (a) highly ordered and size-controlled mesoporous structures, (b) extremely high surface areas and large pore volumes, (c) very good thermal and chemical stability and (d) high flexibility in functionalization to enable the introduction of hydrophilic, hydrophobic, polar as well as charged functional moieties on surface. For all these reasons, mesoporous silicas are presented as a good alternative to classical sorbents, such as amorphous silica and polymeric materials [17,18]. A variety of hybrid ordered mesoporous silica (MCM-41, SBA-15, MSU, PMOs, etc.) SPE sorbents have been explored for the determination of inorganic (heavy metals) and organic (pesticides, hormones, etc.) contaminants in different samples [16–22]. In general, a common theme of these funtionalization strategies was attachment of the organic moiety by the post-synthesis (or grafting) method. However, organically modified ordered mesoporous silicas can also be prepared by co-condensation (or one-pot) method, in such a way that the organic functionalities project into the pores. In this strategy, since the organic functionalities are direct components of the silica matrix, pore blocking is not a problem. Furthermore, the organic units are generally more homogeneously distributed than in materials synthesized with the grafting process [17].

In any case, hybrid mesoporous silicas remain scarcely used owing to their unknown potential for extracting many emerging contaminants (especially from complex matrices such as foods). The main objective of this study was therefore to assess the potential of SBA-15 type mesoporous silica, synthesized and functionalized by co-condensation procedure with octadecyl groups (denoted as SBA-15-C_{18}-CO), as an SPE sorbent for preconcentrating the endocrine disrupting compounds estrone (E1), 17β-estradiol (17β-E2), estriol (E3), progesterone (P), hexestrol (HEX), diethylstilbestrol (DES), 4-androstene-3,17-dione (AND), ethinylestradiol (EE2), 17α-methyltestosterone (17α-MT), nandrolone (NAN), prednisolone (PRED) and testosterone (T) from milks prior to their determination by HPLC–DAD. To our knowledge, no application of this type of material to the extraction of 12 steroid hormones as model analytes from complex food matrices has to date been reported.

2. Experimental

2.1. Reagents and materials

Tetraethylorthosilicate (TEOS) 98% (M = 208.33 g/mol, d = 0.934 g/mL), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO20PO70EO20, Pluronic 123, M_{av} = 5800 g/mol, d = 1.019 g/mL), cetyltrimethylammonium bromide (CTAB) 98%, (M = 364.46 g/mol), octadecylsilane (OTES) 97% (M = 284.61 g/mol, d = 0.795 g/mL), E1, 17β-E2, E3, P, HEX and DES were purchased from Sigma–Aldrich (St. Louis, MO, USA). AND, EE2, 17α-MT, NAN, PRED and T were purchased from Fluka (Busch, Switzerland). Ethanol absolute was purchased from SDS (Peypin, France). Hydrochloride acid 35% (M = 36.45 g/mol, d = 1.19 g/mL) was purchased for Panreac (Castellar del Vallès, Barcelona, Spain). HPLC-grade solvents acetonitrile (ACN) and methanol (MeOH) were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Standard solutions

Stock standard solutions of 4000 mg/L were prepared by diluting in MeOH adequate amounts of each compound and stored at −20 °C. Working solutions were prepared at various concentrations by appropriate dilution of the stock solution in MeOH (0.5–150 mg/L). All working solutions were filtered through a 0.45 μm pore size nylon filter membrane before analysis. Water (resistance 18.2 MΩ cm) was obtained from a Millipore Milli-Q-System (Billerica, MA, USA).

2.3. Milk samples

Whole and skimmed UHT cow milks have been used. These samples were bought in a commercial market in Madrid (Spain) and frozen in individual fractions at −20 °C until analysis.

2.4. Synthesis of SBA-15-C_{18}-CO

12 g of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) was dissolved in 361 g of water and 375 g of 2.0 M HCl solution with stirring at room temperature. After 22 mL of TEOS was added to that homogeneous solution with stirring at room temperature. The resulting mixture was stirred at 40 °C for 3 h for prehydrolysis, and then 4.15 g of OTES was slowly added into the solution. The resulting mixture was stirred at 40 °C for 20 h and then transferred into a polypropylene bottle and reacted under static condition at 50 °C for 2 h and 90 °C for 24 h. The solid product was recovered by filtration, washed with water, and dried at room temperature overnight. The template was removed from the synthesized material by refluxing in ethanol: H_2O (95:5, v/v) for 24 h. Finally, the material was dried at 50 °C for 24 h. The synthesized material was characterized by X-ray diffraction (XRD), N_2 gas adsorption–desorption isotherms, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA).

2.5. Sample extraction procedure

1 g of spiked milk was mixed with 2 mL of 0.2 M acetate buffer (pH 5.2) and it was shaken before adding 2.5 mL of MeOH. The mixture was vortexed for 1 min and then it was centrifuged at 4000 rpm for 5 min. The supernatant was taken and water was added until a final volume of 25 mL was obtained. This extract was purified by SPE. To prepare the SPE cartridges, 100 mg of SBA-15-C_{18}-CO were packed into a 6 mL syringe type cartridge (65 mm length, 11 mm diameter) plugged with porous PTFE disks at both ends. To prevent the material lost during sample loading, a 0.45 μm pore size nylon filter membrane was also inserted at the bottom of the mesoporous silica bed. In all instances conditioning of the cartridges was accomplished by passing 1 × 3 mL MeOH and 1 × 1 mL Milli-Q water at a flow rate of 1 mL/min. After sample extract loading (25 mL) cartridges were dried with a Supelco Visiprep™ DL solid phase extraction vacuum manifold 12 port model (Sigma Aldrich, St. Louis, MO, USA) connected to a vacuum pump at 7.6 psi. Once the entire extract was loaded, the stationary phase was washed with 1 × 5 mL Milli-Q water to remove interferences. Finally, elution of the analytes was performed by passing 1 × 2 mL MeOH at a flow rate of 0.5 mL/min. In all cases, the corresponding extracts were evaporated and re-dissolved with 150 μL of MeOH (preconcentration factor = 6.7) for subsequent analysis in the HPLC–DAD system.

2.6. Chromatographic analysis

HPLC analyses were performed on a Varian ProStar chromatographic system (Varian Ibérica, Madrid, Spain). The system consisted of a 230 ProStar ternary pump, a ProStar 410 autosampler with a six-port injection valve equipped with a 20 μL injection loop (Rheodyne), a photodiode array detector DAD 335 ProStar UV–vis detector and a PC-based data acquisition system Varian Star Workstation.

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