Journal of Chromatography A, 1456 (2016) 58–67

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

# Synthesis of mimic molecularly imprinted ordered mesoporous silica adsorbent by thermally reversible semicovalent approach for pipette-tip solid-phase extraction-liquid chromatography fluorescence determination of estradiol in milk

Lu Wang[a], Hongyuan Yan[a,*], Chunliu Yang[a], Zan Li[a], Fengxia Qiao[b,*]

[a] Key Laboratory of Medicinal Chemistry and Molecular Diagnosis, Department of Preventive Medicine and Health Management, Hebei University, Baoding, 071002, China
[b] Department of Biochemistry, Baoding University, Baoding, 071002, China

ARTICLE INFO

*Article history:*
Received 22 January 2016
Received in revised form 22 March 2016
Accepted 2 June 2016
Available online 4 June 2016

*Keywords:*
Mimic molecular imprinting
Ordered mesoporous silica
Pipette-tip solid-phase extraction
Estradiol
Milk samples

ABSTRACT

A mimic molecularly imprinted ordered mesoporous silica (MIOMS) adsorbent was prepared utilizing a thermally reversible semicovalent approach. The thermally reversible covalent template-monomer complex was firstly synthesized by employing 4,4′-sulfonyldiphenol (BPS) and (3-isocyanatopropyl) triethoxysilane (ICPTES) as template and monomer, respectively. The template-monomer complex was incorporated into ordered mesoporous silica via a simple self-assembly process. The adsorption experiment illustrated that the imprint-removed silica (MIOMS-ir) had higher special recognition ability (250 $\mu g\,g^{-1}$) for estradiol (E2) than the non-imprinted silica (NIOMS-ir) (25 $\mu g\,g^{-1}$). MIOMS-ir was applied as an adsorbent in pipette-tip solid-phase extraction (PT-SPE) coupled with liquid chromatography-fluorescence detector (LC-FLD) for determination of E2 in milk samples. Under the optimized conditions, only 3 mg of the adsorbent, 0.3 mL of water as washing solvent, and 0.5 mL of acetonitrile-acetic acid (96:4, v/v) as elution solvent were used in the pretreatment procedure of milk samples. Good calibration linearity was obtained in a range of 25 ng $L^{-1}$ to 1000 ng $L^{-1}$, and the recoveries at three spiked levels were ranged from 95.4% to 107.0% with relative standard deviations (RSDs) $\leq$3.1% (n = 3). The proposed MIOMS-ir-PT-SPE-LC-FLD method combined the advantages of PT-SPE and ordered mesoporous material such as ease assembly, low cost, high extraction efficiency and large specific surface area, so it is a potential pretreatment strategy for the extraction and determination of E2 in complex milk samples.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Estradiol (E2) (Fig. 1) is a natural estrogen and one of the endocrine disrupting chemicals. It can promote animal growth, improve lean meat proportion of livestock, and increase milk yield by improving the milk secretion of animals. Therefore, it is widely used in the livestock and poultry industry [1]. It is reported that most of milk is produced from pregnant cows in modern dairy industry, so the content of estradiol in commercial milk shows a sustained growth [2]. However, low concentration of E2 can cause the disequilibrium of the humoral and cellular immunity, resulting in many pathological changes in reproductive, immune, cardiovascular and nerve system [3]. Meanwhile, milk products occupy an important position in human diet structure [4–7]. So the development of a simple and sensitive strategy for rapid determination of E2, especially at low level, is of great importance. Because of trace level of analytes and a large number of interfering substances originating from sample matrices, highly-efficient pretreatment techniques are required prior to further instrumental analysis [8].

For isolation of E2 and purification of milk samples, several preparation procedures have been developed mainly including solid-phase extraction (SPE) [9], solid phase microextraction (SPME) [10], liquid-liquid extraction (LLE) [11], and matrix solid-phase dispersion (MSPD) [12]. Each of these methods has its advantages, but some drawbacks exist in these strategies. LLE and SPME possess high enrichment ability and low organic solvent consumption, but they suffer from low recovery and reproducibility. MSPD is a simple and efficient sample-pretreatment method, but

* Corresponding authors.
*E-mail address:* yanhy@hbu.edu.cn (H. Yan).

http://dx.doi.org/10.1016/j.chroma.2016.06.010
0021-9673/© 2016 Elsevier B.V. All rights reserved.

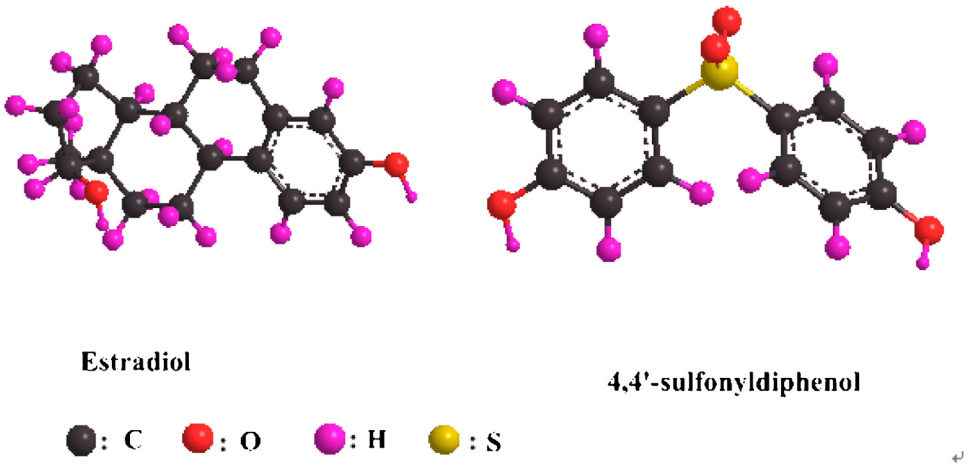


**Fig. 1.** Structures of estradiol and 4,4′-sulfonyldiphenol.

time-consuming purification processes are usually required when it pretreating high-fat samples. Among various available methods, solid-phase extraction (SPE) technique is most widely used as the clean-up and preconcentration step of estrogens [9,13]. However, larger quantities of adsorbent and organic solvents are needed in common SPE to satisfy the requirements of instrumental analysis and handle suitable sample volumes. Recently, miniaturized SPE (mini-SPE) has been proposed, the mini-tip cartridge has many advantages such as small bed volume, low consumption of adsorbent, low solvent consumption, ease of operation, time efficiency, and versatility [14,15]. However, the common shortage of conventional SPE adsorbents is lack of special selectivity resulting in the co-extraction of matrix components, which interferes the quantitative analysis of analytes.

Molecular imprinting is proved to be a useful technique to build selective recognition sites in stable polymers in various areas of analytical chemistry, and it is also an attractive method for the preparation of selective adsorbents in recent years [16]. Until now, there are some studies of molecularly imprinted polymers on estradiol have been reported [17–19]. Currently, there are three strategies, namely covalent, non-covalent and semicovalent imprinting, for preparing molecularly imprinted materials [20]. Among the three strategies, semicovalent imprinting method combines the advantages of covalent and non-covalent strategies ensuring that the functional monomer residues are present only in the imprinted cavities, and thus greatly reduces the non-specific binding sites as well as makes the molecular imprinting polymers rapidly take up target molecules via the non-covalent interactions [21]. To date, most of the researches of semicovalent imprinting methods have focused on employing a target analyte as a template to achieve high selectivity, but serious template leakage happens in the followed SPE procedure [22–25], which significantly affects the results of quantification determination of the analytes. [26]. The applications of molecularly imprinted polymers, especially for SPE applications, were focused on organic polymers which have advantages such as good chemical stability and reusability [27–29]. However, organic polymers are easy to swell or shrink when they exposed to organic solvents [24]. Silica adsorbents exhibits minimal swelling in the presence of organic solvents and shows excellent thermal stability [22]. Moreover, mesoporous silica such as MCM-41 [30,31], SBA-15 [32–34], could guarantee high binding capacity and good site accessibility for target molecules because of their uniform ordered structure, high specific surface area, and large pore volume. Recently, the research of mesoporous silica combined molecular imprinting technique has been applied to the recognition of heavy metal ions [35,36], but the reports about the preparation of ordered mesoporous silica materials combined with mimic molecular imprinting techniques for the recognition of small molecules are few, especially for E2.

A mimic semicovalent molecularly imprinted ordered mesoporous silica adsorbent was designed in this study to solve the problem of template leakage, create well-defined imprinted sites, achieve rapid target molecule interaction and be applied to pipette-tip solid-phase extraction (PT-SPE) of E2 from milk samples. 4,4′-Sulfonyldiphenol, one of the endocrine disrupting chemicals, was chosen as the mimic template molecule in order to forbid the influence of template leakage for the determination of estradiol [37], because it has two hydroxyl as much as E2 and it keeps the two hexatomic rings of E2. Therefore, they have the similar adsorption mechanism. And from the results, by using 4,4′-sulfonyldiphenol as template, the presented method has high extraction efficiency. This method combines the large specific surface area and high adsorption capacity of ordered mesoporous silica with the advantages of PT-SPE such as easy self-assembly, low cost, and high extraction efficiency.

## 2. Materials and methods

### 2.1. Chemicals and materials

Diethylstilbestrol, estradiol (E2), sulfamethoxazole, 4,4′-sulfonyldiphenol, (3-isocyanatopropyl) triethoxysilane (ICPTES), indole-3-acetic acid, cyanazine, and tetraethoxysilane (TEOS) were purchased from Aladdin Chem. Co. Ltd. (Shanghai, China). $P_{123}$ ($P_{123}$, Mn ~5800 g $mol^{-1}$) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile was supplied by Xingke High Purity Solvents Co. Ltd. (Shanghai, China). NaCl, hydrochloric and ethanol were obtained from Tianyi Chemical Co. Ltd. (Tianjin, China). Tetrahydrofuran (THF) was purchased from Tianjin Fuchen Chemical Co. Ltd. (Tianjin, China). The adsorbent materials HLB, $NH_2$, $C_{18}$ and $SiO_2$ were supplied by Varian Co. Ltd. (Palo Alto, CA, USA). All the other reagents used in the experiment were of the highest grade available and all used water was double-deionized and filtered with 0.45-μm filter membrane.

### 2.2. Apparatus and chromatographic conditions

HPLC analysis was performed using a LC-20A system equipped with two LC-20AT Solvent Delivery Units and a RF-20A fluorescence detector (Shimadzu, Kyoto, Japan). A LC-solution workstation (Shimadzu, Kyoto, Japan) was used to control the system and also for data processing. The analytical column (250 mm × 4.6 mm, Pro-

Download English Version:

https://daneshyari.com/en/article/1198721

Download Persian Version:

https://daneshyari.com/article/1198721

Daneshyari.com