



# Ionic liquid intercalated clay sorbents for micro solid phase extraction of steroid hormones from water samples with analysis by liquid chromatography–tandem mass spectrometry



Can Aftafa<sup>a</sup>, Füsün Okçu Pelit<sup>a,\*</sup>, Esra Evrim Yalçinkaya<sup>a</sup>, Hayati Turkmen<sup>a</sup>, İlgi Kapdan<sup>b</sup>, F. Nil Ertaş<sup>a</sup>

<sup>a</sup> Ege University, Faculty of Science, Department of Chemistry, 35100 Bornova, İzmir, Turkey

<sup>b</sup> Dokuz Eylül University, Faculty of Engineering, Department of Environmental Engineering, Buca, İzmir, Turkey

## ARTICLE INFO

### Article history:

Received 12 June 2014

Received in revised form 24 July 2014

Accepted 30 July 2014

Available online 4 August 2014

### Keywords:

Ionic liquids  
Montmorillonite  
Solid phase extraction  
Endocrine disruptors  
Estrogenic hormones  
LC–MS/MS

## ABSTRACT

Clay material plays an important role in the transport and retention of many compounds in the soil, therefore, clay based sorbents are promising alternatives for selective sorption of organic pollutants. In the present work, different chain length ionic liquids (ILs) namely, 1-methyl-3-octyl-imidazolium bromide, 1-methyl-3-undecyl-imidazolium bromide and 1-methyl-3-octadecyl-imidazolium bromide were intercalated in the galleries of montmorillonite (MMT) clay. Then, this novel nanofiller surface was utilized in micro extraction of estrogenic hormones for the first time. A fast procedure where sonication-assisted emulsification microextraction combined with vortex assisted micro-solid phase extraction ( $\mu$ -SPE) was developed for the LC–MS/MS analysis of estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3) and ethynylestradiol (EE2). The parameters related to the  $\mu$ -SPE procedure namely; pH, sorbent amount, extraction solvent type and volume, sonication and vortex time, sample volume and salt effect on the extraction efficiency were screened by applying Plackett–Burmann design. The selected parameters were then optimized by using Box–Behnken design. The method was validated for the determination of estrogenic hormone residues in river water samples. Linear calibration plots were obtained for all hormones whose regression coefficients were larger than 0.98. RSD values were found less than 10% for three levels of concentration. LOD levels were calculated as; 0.012, 0.062, 0.018 and 0.693 ng L<sup>-1</sup> for E1, E2, E3 and EE2, respectively. Recovery values were calculated in the range of 86.9–97.7%. Considering large sample volumes required for attaining low limits of these hormones, present method provides an ease for analyst as 10 mL of the sample is adequate for achieving the same sensitivity.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

The presence of endocrine disrupting steroid hormones in the aquatic environment is of worldwide concern [1]. The risks derived from the discharging of municipal waste water from the treatment plants containing estrogenic hormones have been pointed out in various monitoring programs. Steroid hormones are considered as the future candidates in the list of European Community Water Framework Directives to be monitored in surface water [2]. Natural steroid estrogenic hormones, estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3) secreted by humans and animals, and the synthetic ethynylestradiol (EE2) used by women were identified as

having the highest endocrine disrupting potential [3] since they are causing feminization of male and sexually immature fish [4], hermaphroditism and decreased fertility in wildlife [5].

Estrogens cannot be completely eliminated after a number of specific waste water treatment processes. Discharge of these effluents into receiving media could result in ppt level concentrations of estrogens in river [6], surface water [7–9], ground water [10] and hence in drinking water [11]. For this reason, there is an urgent need to develop methods capable to measure very low concentrations of these chemicals at sub ng L<sup>-1</sup> levels.

Several analytical methods have been developed to identify and quantify these substances in water samples. Gas chromatographic techniques by using mass spectrometric detector GC–MS [12–14], and tandem mass spectrometric detectors (MS/MS) were only applied after a derivatization step for the volatilization of the hormones [8]. However, liquid chromatographic techniques coupled

\* Corresponding author. Tel.: +90 232 3115447; fax: +90 232 3888264.  
E-mail address: [fusun.okcu@ege.edu.tr](mailto:fusun.okcu@ege.edu.tr) (F.O. Pelit).

to diode array [15], fluorescence [16], MS [17–19] and MS/MS detector systems have been widely used for the determination of estrogens in recent years [20–23].

Although chromatographic techniques provide powerful separation for multiresidue analysis in complex matrices, sample preparation method chosen prior to the analysis constitutes a critical step for the sensitivity and selectivity of the method. Solid phase extraction (SPE) is an efficient method for improving the clean-up of the samples and high preconcentration factors can be reached by this means. In hormone analysis, classical SPE methodology was applied by utilizing  $C_{18}$  bonded silica [6,23–26], polymeric [27] and graphitized carbon black [9] sorbents.

Synchronous with modern trends in analytical chemistry toward simplification and miniaturization of sample preparation methods, some modifications can be encountered for the SPE method [28]. Miniaturization can be achieved by reducing the solvent volumes and increasing the interfacial area between the solid adsorbent and sample solution and micro or nano-scale sorbents are used for this purpose [29–31].

In addition to the common adsorbents used in SPE, clay based sorbents are potentially useful materials for the adsorption of environmental pollutants due to their unique polarity, pore-size distribution, and high surface areas [32]. Considering their important role in the transport and retention of organic compounds in the soil, intercalated clays can be utilized as selective sorbents for organic pollutants.

Other micro extraction techniques like stir bar sorptive extraction (SBSE) [33], solid phase microextraction (SPME) [34,35], dispersive liquid–liquid microextraction (DLLME) using either solvents [36] or ionic liquids (ILs) [37] were also applied for hormone analysis in water samples. In recent years, studies were focused on modification of ILs on different nano scale supports to produce alternative surfaces for effective separation [38].

Cationic nanoclays such as sodium montmorillonite (MMT-Na) provides an alternative support as the exchange of its interlayer sodium cations with long alkyl chains based on quaternary ammonium salts with halides. Thus, functional nanofillers such as MMT clay treated with ILs to impart organophilic properties has been the topic of recent publications [39–41]. By this means, the increased basal spacing of nanoclay improves the attraction of organic analytes for nanocomposite applications.

In this study; different chain length ionic liquids namely, 1-methyl-3-octyl-imidazolium bromide, 1-methyl-3-undecyl-imidazolium bromide and 1-methyl-3-octadecyl-imidazolium bromide were intercalated in the galleries of MMT clay. The polar structure of MMT was intercalated with hydrophobic ILs (IL-MMT) and this novel material was utilized as a sorbent in micro extraction of four estrogenic hormones: estrone (E1),  $17\beta$ -estradiol (E2), estriol (E3) and ethynylestradiol (EE2). The dispersion of nano IL-MMT materials was maintained by sonication-assisted emulsification combined with vortex assisted micro-solid phase extraction ( $\mu$ -SPE) system for the determination of targeted steroid hormones for the first time. This method provides a rapid and selective separation of the targeted hormones in water samples followed by sensitive determination inherited from LC–MS/MS system.

Optimization is usually achieved in a traditional trial and error method, studying each factor separately or more recently, using a statistical method based on the use of an experimental design. Latter methodology provides more information about any interaction between these factors and the number of experiments required can also be reduced by this means. Use of response surface methodology (RSM) will enable the evaluation of the effects of several factors, as well as the interactions between them, and Plackett–Burmann design followed by Box–Behnken design have been successfully employed in optimizing the extraction conditions.

## 2. Experimental

### 2.1. Chemicals and reagents

All the reagents used were of analytical grade. The hormones E1, E2, E3 and EE2, were purchased from Sigma–Aldrich (St. Quentin Fallavier, France). The degree of purity was at least 98% for all the steroids and they were used without any further purification. Individual stock solutions at  $200 \text{ mg L}^{-1}$  were prepared in acetonitrile and working solutions were prepared by diluting suitable aliquots of each individual solutions in acetonitrile/purified water (28/72, v/v). HPLC grade acetonitrile, n-hexane, cyclohexane, toluene and ethyl acetate and reagent grade sodium hydroxide, ammonia and acetic acid were obtained from Merck (Darmstadt, Germany).

Sodium montmorillonite,  $\text{Na}^+$ -MMT, a hydrated aluminum silicate with sodium as the predominant exchangeable cation (trade name: Cloisite<sup>™</sup>-Na<sup>+</sup>, Southern Clay Products) is a powder with typical particle size of less than  $2 \mu\text{m}$ ; it was used for the ion exchange modification with the ILs. 1-Methyl-3-octyl-imidazolium bromide [ $C_8\text{mimBr}$ ], 1-methyl-3-undecyl-imidazolium bromide [ $C_{12}\text{mimBr}$ ] and 1-methyl-3-octadecyl-imidazolium bromide [ $C_{18}\text{mimBr}$ ] ionic liquids were synthesized according to the literature [42]. The measurements were made at ambient laboratory temperature and all the solutions were allowed to attain this temperature prior to their measurement.

### 2.2. Apparatus

The extraction procedure was carried out by using an ultrasonic water bath purchased from (Elma E100H Elmasonic) and IKA MS3 Digital vortex stirrer was used for vortex mixing. A Beckman Coulter Allegra X15R centrifuge was used for precipitation process. Aqueous solutions were prepared with ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) from a MilliPore Milli-Q Gradient water purification system (Saint-Quentin-en-Yvelines, France).

LC–MS/MS measurements were performed by using Thermo TSQ Quantum Access Max Triple Quadruple MS (Les Ulis, France) equipped with a degasser, a binary pump, an autosampler and a column oven. For data processing, Xcalibur software from ThermoFinnigan was used. A Hypersil gold analytical column C18 ( $2.1 \text{ mm} \times 50 \text{ mm}/1.9 \mu\text{m}$  particle size) was used. The column oven temperature was set to  $25^\circ\text{C}$  and injection volume was set to  $25 \mu\text{L}$  in full loop mode. Samples were analyzed in negative mode by using selected reaction monitoring (SRM) mode.

Former study of our group includes optimization of instrumental parameters by Box–Behnken design [43] for the analysis of E1, E2, E3 and EE2 standard mixture. The main parameters studied were; mobile phase composition and flow rate, interphase parameters namely; collision energy, collision gas pressure, spray voltage, sheath gas pressure, ion sweep gas pressure, auxiliary gas pressure, vaporizer temperature and capillary temperature. Optimum conditions determined were given below: isocratic elution program was applied with  $137 \mu\text{L min}^{-1}$  flow rate. The mobile phase was composed of 44% acetonitrile, 3% 0.20 M ammonia solution and 53% water. Precursor (Parent mass) and product ion masses as well as the individual declustering potential and collision energy voltages of each steroid are shown in Table 1. Interface conditions were as follows; sheath gas pressure: 33 arb, ion sweep gas pressure: 0.4 arb, auxiliary gas pressure: 17 arb, collision gas pressure: 1.9, interface capillary temperature:  $254^\circ\text{C}$ , vaporizer temperature:  $352^\circ\text{C}$  and spray voltage was chosen as 2740 V.

### 2.3. Synthesis of IL-MMT sorbents

The modified clay has been prepared by a cation exchange method, which is a reaction between the sodium cations of MMT

Download English Version:

<https://daneshyari.com/en/article/1199284>

Download Persian Version:

<https://daneshyari.com/article/1199284>

[Daneshyari.com](https://daneshyari.com)