FAST AND SENSITIVE MICRO SOLID PHASE EXTRACTION METHOD FOR THE ANALYSIS OF STEROID HORMONES

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The presence of endocrine disrupting steroid hormones in the aquatic environment is of worldwide concern. 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 [1]. Estrogens cannot be completely eliminated after a number of specific wastewater treatment processes. Discharge of these effluents into receiving media could result in ppt level concentrations of estrogens in waters [2]. There is an urgent need to develop methods capable to measure very low concentrations of these chemicals at sub ng L⁻¹ levels.

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 different sorbents. However, SPE displays some drawbacks such as multistage operation with time consuming steps, large consumption of solvent and low enrichment factor. Nevertheless, synchronous with modern trends in analytical chemistry towards simplification and miniaturization of sample preparation methods, some modifications must be considered for the SPE method. Miniaturization can be achieved by increasing the interfacial area between the solid adsorbent and sample solution and micro or nano-scale sorbents are used for this purpose.

In the present work, different chain length ionic liquids (IL) were intercalated in the galleries of Montmorillonite (MMT) clay and 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 (µ-SPE) was developed for the LC-MS/MS analysis of Estrone (E1), 17β-estradiol (E2), Estriol (E3) and ethynylestradiol (EE2). The parameters related to the µ-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 and then, selected parameters were optimized by using Box-Behnken Design. Linear calibration plots were obtained for all hormones whose regression coefficients were larger than 0.99. 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⁻¹ for E1, E2, E3 and EE2, respectively. Recovery values were calculated in the range of 86.9 – 97.7 %.

KEYWORDS: Ionic liquids, Montmorillonite, SPE, Estrogenic hormones, LC-MS/MS.

REFERENCES: