Supporting lnformation

Application of ZIF-8-graphene oxide sponge for solid phase extraction method to the analysis of sex hormones in milk and milk products by high-performance liquid chromatography

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Optimization of SPE conditions

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To evaluate the extraction performance of the ZIF-8-GOS as SPE adsorbent, several SPE conditions were carefully investigated and optimized.

The elution solvent is very important in SPE in order to achieve excellent recovery. Methanol, acetonitrile, acetone, chloromethane, n-Hexane, and a certain proportion of methanol and water were studied. The results show chloromethane has better ability of eluting to two sex hormones (NDL and TTR), while it has no eluting ability to other three sex hormones (E1, E3 and DES). Acetonitrile, acetone and n-Hexane do not elute all sex hormones. Only a certain proportion of methanol and water can elute all analytes. As shown in Fig. S1-a, methanol/water = 60:40 (v/v) has the best recovery.

The volume of elution solvent is a crucial factor to obtain reliable analytical results. To investigate the effect of the extraction recovery, different ratios of methanol to water was used to elute. Fig. S1-b indicates that the maximal recoveries of all analytes are obtained when the elution volume is 1500 μL. Hereby, 1500 μL of methanol/water = 60:40 (v/v) is used for the following experiments.

Addition of salt into aqueous samples can decrease the solubility of nonpolar organic compounds in water, which could increase the distribution coefficient of the analytes to the SPME fiber and thus enhance extraction efficiency. Nevertheless, it could increase the viscosity and density of the solution, and decrease the diffusion rate of the analytes, which is unfavorable to the analytes transferring to the SPE adsorbent. Here, the salt concentration (NaCl, w/w %) was investigated from 0 to 25%. Fig. S1-c shows that there is no significant effect on the recovery when increasing the concentration of NaCl. Based on this, the salt was not added in this study.

Figure S1. The effect of (a) type of elution solvent; (b) the volume of elution solvent; (c) salt effect.

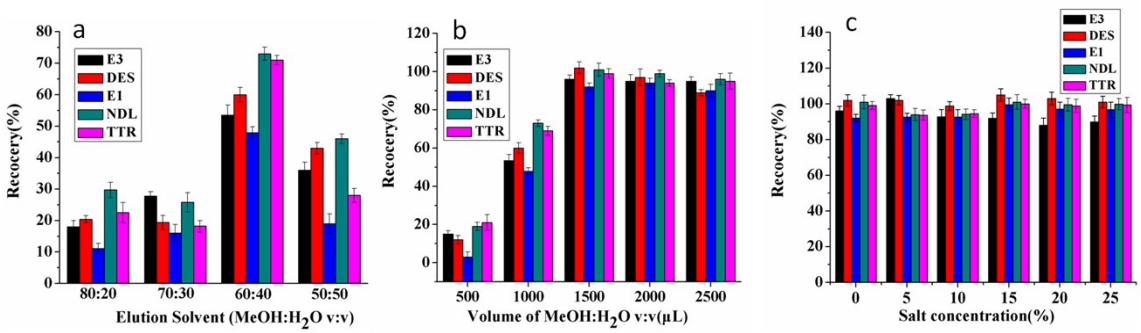


Table S1 Chemical structures of five sex hormones considered in this work.

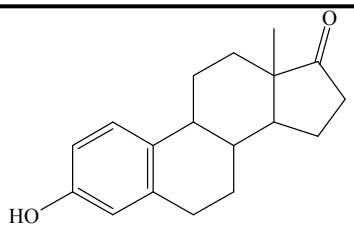
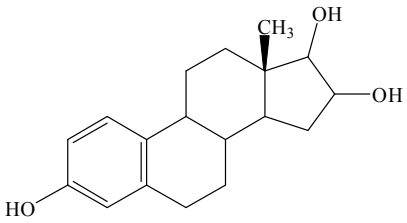
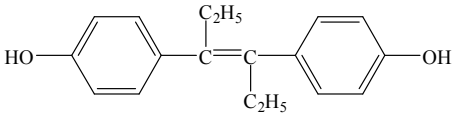
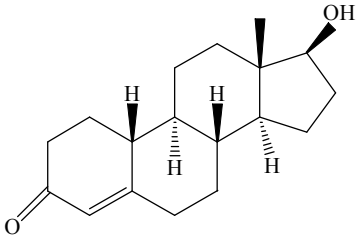
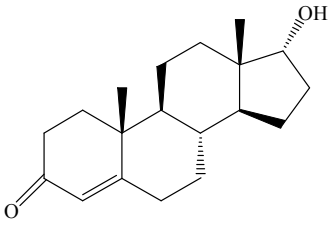
Chemical	CAS Number	Structure	Molecular weight
E1	2440-22-4		225.2
E3	70321-86-7		846.8
DES	3896-11-5		315.8
NDL	3864-99-1		357.9
TTR	25973-55-1		351.5

Table S2 Analytical performance of the proposed method (n = 5).

Analytes	Linear range ($\mu g\ L^{-1}$)	r	Precision (RSD %)		LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)
			Intra-day	Inter-day		
E1	10-3000	0.9998	0.39	1.29	0.52	1.75
E3	10-3000	0.9999	0.29	1.25	2.11	6.97
DES	10-3000	0.9999	0.28	2.07	1.38	4.57
NDL	5-3000	0.9998	0.38	3.86	0.65	2.14
TTR	10-3000	0.9999	0.55	3.34	1.20	3.90