Electronic Supplementary Material

Preparation of ionic liquid-modified SiO₂@Fe₃O₄ nanocomposite as a magnetic sorbent for use in solid phase extraction of zinc(II) ions from milk and water samples

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Effect of the nano-sorbent amount and extraction time

In order to obtain quantitative extraction of the analyte, the influence of the amount of nanosorbent on recovery was studied in the range of 10–100 mg. A test solution of 150 mL of sample including 5 ng mL⁻¹Zn(II) ions was employed. As shown in Fig. 1S, the quantitative recovery of Zn(II) ion was obtained within the range of 50–100 mg of the nano-sorbent. From these results, 50 mg of the nano-sorbent was used in all further experiments.

The extraction recovery was studied at time intervals in the range of 1–20 min. It was observed that after 10 min the recoveries of the Zn(II) ions exhibited no obvious variation (Fig. 2S). Thus, the extraction time of 10 min was selected for further studies.



Fig. 1S: Effect of amount of the adsorbent on the adsorption of Zn(II) ions by $Fe_3O_4@SiO_2@IL$ nano-sorbent. Utilized conditions: sample volume: 150.0 mL, Zn(II) ions concentration: 5 ng mL⁻¹, pH: 9, extraction time :10 min, elution condition: 1.5 mL of the 0.5 mol L⁻¹ of HNO₃ in ethanol, desorption time: 4 min.



Fig. 2S: Effect of extraction time on the adsorption of Zn(II) ions by Fe₃O₄@SiO₂@IL nanosorbent. Utilized conditions: sample volume: 150.0 mL, Zn(II) ions concentration: 5 ng mL⁻¹, pH: 9, amount of the nanosorbent: 50.0 mg, elution condition: 1.5 mL of the 0.5 mol L⁻¹ of HNO₃ in ethanol, desorption time: 4 min.

Sample volume and pre-concentration factor

An important parameter to control solid-phase extraction of real samples is the sample volume. For this purpose, 10, 25.0, 50.0, 100.0, 150.0, 200.0 and 250.0 mL of sample solutions containing 1.5 µg of Zn(II) ions were studied. Based on the obtained results that are given in Fig. 3S, recovery of Zn(II) ions was found to be quantitative when sample volume was chosen between 10.0 and 150.0 mL. Above 150.0 mL, the recovery decreased for the analyte. So, by analyzing 1.5 mL of the final solution after the pre-concentration of 150.0 mL of sample solution, an enrichment factor was found as 100.



Fig. 38: Effect of sample volume on the adsorption of Zn(II) ions by $Fe_3O_4@SiO_2@IL$ nanosorbent. Utilized conditions: Zn(II) ions concentration: 5 ng mL^{-1} , pH: 9, amount of the nanosorbent: 50.0 mg, extraction time :10 min, elution condition: 1.5 mL of the 0.5 mol L^{-1} of HNO₃ in ethanol, desorption time: 4 min.

Calibration graph

A calibration graph was constructed in the optimum solid-phase extraction and detection conditions. The calibration graph was linear between 0.5 and 15 ng mL⁻¹ concentration range with a correlation coefficient of 0.9994 applying the pre-concentration procedure (Fig. 4S). The calibration equation is $A = 0.05 C_{Zn(II)} + 0.04$, where $C_{Zn(II)}$ is the concentration of Zn(II) ions in ng mL⁻¹. The limit of detection (LOD) and limit of quantification (LOQ) of this method, defined as $3S_b/m$, and $10S_b/m$ (where S_b is the standard deviation of six replicate measurements of the blank and *m* is the slope of the calibration curve) were 0.17 and 0.5 ng mL⁻¹, respectively.



Fig. 4S: Calibration graph for solid-phase extraction and determination of Zn. Utilized conditions: sample volume: 150.0 mL, Zn(II) ions concentration: 5 ng mL⁻¹, pH: 9, PAN concentration 4.0 μ mol L⁻¹, amount of the nanosorbent: 50.0 mg, extraction time :10 min, elution condition: 1.5 mL of the 0.5 mol L⁻¹ of HNO₃ in ethanol, desorption time: 5 min.