Magnetic Solid Phase Extraction Using Ionic Liquid Coated Magnetic Core Fe₃O₄@SiO₂ Nanoparticles Followed by UV Spectrophotometry for Separation/Analysis of Safranine T in Food

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Abstract: Hydrophobic ionic liquids (IL) 1-octyl-3-methylimidazole hexafluorophosphate ([OMIM] PF₆) coated Fe₃O₄@SiO₂ nanoparticles was employed in magnetic solid phase extraction (MSPE) method coupled with ultraviolet visible spectrophotometry for the analysis of safranine T (ST). The results showed that safranine T was adsorbed fast by Fe₃O₄@SiO₂@[OMIM] PF₆ and eluted by ethanol. Different parameters, such as; pH, temperature, ionic strength, eluent type, volume and temperature were studied. This method introduced wide linear range of 15-350 ng mL⁻¹, the correlation coefficient was 0.9991, the equations of calibration graph was A (absorbance) = 0.04+0.13c (μg mL⁻¹), the detection limit was 0.37 ng mL⁻¹ (RSD = 5.1%). The current method could be applied for the analysis of ST in food samples with satisfactory results.

Keywords: Safranine T, Ionic Liquid Loaded Magnetic Nanoparticles, Magnetic Solid Phase Extraction, UV- Spectrophotometry

1. Introduction

Magnetic solid phase extraction (MSPE) was that, it is a process depends on using magnetic sorbents for separation of various analytes in different volume of the sample [1] in MSPE procedures. The magnetic absorbent was mixed with sample and the analyte was absorbed by magnetic sorbents. The analyte magnetic sorbents were then separated from the sample by using an external magnetic field, after being eluted by a perfect eluent [2].

Safranine T (ST) is a type of alkali industrial dye or stain (Figure 1), that could be used in different dyeing manuf acturies [3]. ST was also known as food additives [4], however, in many food manuf acturies ST was illegally used to improve the properties of food products [5], so introducing a simple and fast method for the separation of ST in dietary products is very important. The well-known techniques for ST separation were performed by using high performance liquid chromatography (HPLC), UV–visible spectrophotometry and the fluorescence method depend on calixarene derivatives. However, UV–visible spectrophotometry has good properties of easy operation and low-cost of analysis.

MSPE has been used in widely in many analysis fields such as food, environmental and biological analysis [6, 7]. Nowadays, scientists are focusing on the use of Fe₃O₄ nanoparticles (NPs) as MSPE absorbent with special functional groups change to measure the amount of the target analytes. Various materials were applied in Fe₃O₄NPs modification. Some scientists selected poly aniline coated Fe₃O₄ (PANIs/Fe₃O₄) as sorbents for MSPE fluoroquinolones in honey samples [8]. Pardasani et al. used multi-walled carbon nano-tube functionalized Fe₃O₄ (MWCNT/ Fe₃O₄) as sorbents for dispersive SPE of nerve agents from water [9].
Ionic liquid (IL), are a type of organic salts possess special physicochemical properties, like good stability and hydrophobic properties [10]. Many studies have described the utilization of IL through SPE [11, 12]. Ionic liquids coated MNPs were used as an adsorbent in separation of aromatic hydrocarbons in water [13]. Fe$_3$O$_4$@IL@methyl orange NPs were used for separation of PAHs in water [14]. However, it has not been reported to separate or extract ST with Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$.

In this work, MSPE sorbents (Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$) were prepared, these sorbents have the property of the ionic liquids and (MNPs). When compared other studies, these MSPE sorbents provides a rapid, and efficient sample preparation process, which enables the treatment of large volume samples in a short period of time [15]. E$_{safranin}$% on Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ showed a higher extraction efficiency, which was attributed to hydrophobicity of ionic liquids. Therefore, Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ was applied. Anew method of MSPE accompanied with UV-spectrophotometry for ST separation from food samples was applied. The Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ can be used repeatedly for 10 times.

2. Experimental Section

2.1. Equipment and Reagents

Infrared spectra was measured with a Bruker Tensor 27 spectrometer (Bruker Company, Germany). Samples were pressed into potassium bromide (KBr) pellets and recorded at the frequencies from 4000 to 400 cm$^{-1}$ with resolution of 4 cm$^{-1}$. UV-2550 spectrophotometer (Shimadzu Corporation, Japan) was used.

2.2. Chemicals and Reagents

All chemicals and reagents were at least of analytical reagent grade, unless otherwise stated. Safranine T standards were obtained from the Sigma-Aldrich (Shanghai, China). A standard stock solution was prepared by dissolving 10.0 mg of each standard in 100 mL of ethanol and stored in dark at 4°C. N-methylimidazole (Darui Fine Chemicals, Shanghai, China), tetraethyl orthosilicate (TEOS), KPF$_6$, FeCl$_3$, (NH$_4$)$_2$Fe(SO$_4$)$_2$, ethanol, acetone, methylene chloride (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).

2.3. Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ MNPs Preparation

The hydrophobic ionic liquid, 1-octyl-3-methylimidazole hexafluoro- phosphate ([OMIM] PF$_6$) was prepared according to literature [16, 17]. Fe$_3$O$_4$ MNPs were prepared by conventional co-precipitation method [18, 19]. First, FeCl$_3$ (3.30 g) was dissolved in deionized water (80 mL) followed by addition of polyethylene glycol (40 mL, 10%, w/w) and of (NH$_4$)$_2$Fe(SO$_4$)$_2$ (4.23 g) in water solution under stirring. Then ammonium hydroxide (8 mL, 26.5%, w/w) was added rapidly under vigorous stirring. The resultant solution was stirred (3000 r min$^{-1}$) at 80°C for 60 min. After cooling to room temperature, the obtained Fe$_3$O$_4$ precipitate was collected by an external magnetic field, washed with deionized water five times and dried at 60°C for 12 h in vacuum.

The preparation of Fe$_3$O$_4$@SiO$_2$ was done according to literature. Fe$_3$O$_4$ (1.0 g) were dissolved in 200 mL of the ethanol and 50 mL of deionized water by sonication for 15 min, and then 4 mL ammonium hydroxide and 6 mL TEOS were added sequentially. The mixture was reacted for 6 h at 60°C under a continuous stirring. The resultant product was collected by an external magnetic field, and rinsed with deionized water and ethanol for six times thoroughly, and then dried in vacuum to obtain Fe$_3$O$_4$@SiO$_2$.

IL functionalized MNPs Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ (Figure 2) were prepared according to process detailed in literature [20]. A 4.00 g of [OMIM] PF$_6$ was dissolved in 60.0 mL acetone, and then 3.00 g Fe$_3$O$_4$@SiO$_2$ nanoparticles were added. Stir the mixture inside the fume hood until the acetone completely evaporated. The obtained Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ functionalized material was washed with methylene chloride and dried at 60°C under vacuum for 12 h. The solid was carefully grinded into powders, which were Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ MNPs [21].

2.4. Extraction Procedure

The extraction procedure was done as follow, 10.0 mL of the working solution or aqueous sample and 0.05 g of Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$-MNPs were transferred into a centrifuge tube, and the solution in the tube was subsequently shaken for 15 min at room temperature. Then, Fe$_3$O$_4$@SiO$_2$@ILs with adsorbed target ST was separated from the solution by an external magnetic field. The supernatant ST was analyzed using UV-2550-vis spectrophotometer at 246 nm.

2.5. Determination of the Isoelectric Point

Isoelectric point (IEP) shows the density of charge on metal oxide (Fe$_3$O$_4$) along with the pH level, which is a predominant factor for adsorption of analyte. When the (Fe$_3$O$_4$) surface is negative, the pH value will be above the IEP and vise versa [22].

2.6. Sample Preparation

20.0 g of 4 different manufactured tomato sauces were
weighted in 4 beakers, dissolved in 40.0 mL of ethanol + 1.0 mL of ammonia. Then 0.4 mL of The resultant clear solution from each type of tomato sauces was added to 1.5 g of IL [OMIM] PF$_6$, then 2.0 mL of NaCl 15% were added to each test tubes (10.0 mL) from 4 different types of samples.

3. Results and Discussion

3.1. Characterization of Fe$_3$O$_4$@SiO$_2$@ILs MNPs

3.1.1. FTIR Characterization

The infra red spectra of Fe$_3$O$_4$ (curve a), Fe$_3$O$_4$@SiO$_2$ (curve b) and Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ (curve c) were illustrated in Figure 2. A. Compared curves of a and b, the peak at 1630 cm$^{-1}$ was due the propriety of Si-O-Si, then the peak at 750 cm$^{-1}$ might be attributed to the silanol groups (Si-OH) of silica, for FTIR spectra of Fe$_3$O$_4$@SiO$_2$, the peak at 550 cm$^{-1}$ was significantly reduced. But in the Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$, the peak at wave numbers 750 and 1360 cm$^{-1}$ were due to P-F stretching vibration of imidazole ring in [OMIM] PF$_6$-MNPs, which showed that Ionic liquid (IL) was well immobilized on the surface of the magnetic nanoparticles (Fe$_3$O$_4$@SiO$_2$).

3.1.2. Characterization by Scanning Electron Microscope (SEM)

The microscopic morphological structures which applied by SEM to differentiate and compare the external features of Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ were shown in Figure 3, the SEM micrographs of Fe$_3$O$_4$@SiO$_2$ (A) and Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ (B). Comparing (A) with (B), Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ (B) showed a spongy, and coarse surface while Fe$_3$O$_4$@SiO$_2$ (A) showed a layer shape surface, with brightness and availability of macro pores. The modification of Fe$_3$O$_4$ MNPs made the ionic liquid, Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ surface changed.

3.1.3. Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) revealed the weight loss process of the material, which indicated the difference between the Fe$_3$O$_4$@SiO$_2$ (a) and Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ (b). In this work, TGA was conducted in a nitrogen atmosphere, and the heating rate employed was 5°C min$^{-1}$ all cases from 25 to 1000°C (Figure 4). The experimental results could be concluded that (1) the Fe$_3$O$_4$@SiO$_2$ (a) showed a mass loss of about 2.7% after heating to 240°C corresponding to the water content; (2) for the Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ (b), an additional weight loss of 6.6% was observed from 240 to 750°C due to the decomposition of ILs in addition to 2.7% after heating to 240°C. This observation suggested that the ILs [OMIM] PF$_6$ had been coated on the surface of Fe$_3$O$_4$@SiO$_2$.

3.2. Adsorption Process

3.2.1. Efficiency of Extraction of Various MNPs

The efficiency of extraction for ST ($E_{\text{safranine} %}$) by Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$, IL and Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ were evaluated in Figure 5. D. it was summarized as follows: (1) the priority of $E_{\text{safranine} %}$ was like this: Fe$_3$O$_4$ < Fe$_3$O$_4$@SiO$_2$ < IL ([OMIM] PF$_6$) < Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ within similar conditions; (2) ($E_{\text{safranine} %}$) on Fe$_3$O$_4$ was less than the other MNPs, because the ($E_{\text{safranine} %}$) possess IL hydrophobicity; (3) ($E_{\text{safranine} %}$) was higher when IL chain loaded and ($E_{\text{safranine} %}$) on Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ showed the best efficiency of extraction, so, this compound was applied in the current work.

![Figure 2. Infrared spectra (a) Fe$_3$O$_4$ (b) Fe$_3$O$_4$@SiO$_2$ (c) Fe$_3$O$_4$@SiO$_2@$IL (OMIM) PF$_6$.](image)

![Figure 3. SEM micrographs of (A) Fe$_3$O$_4$@SiO$_2$ and (B) Fe$_3$O$_4$@SiO$_2@$IL.](image)
Figure 4. TGA curves of (a) Fe₃O₄@SiO₂ and (b) Fe₃O₄@SiO₂@[OMIM] PF₆.

Figure 5. Extraction efficiency of Fe₃O₄, Fe₃O₄@SiO₂, IL and Fe₃O₄@SiO₂@IL ([OMIM] PF₆) for safranine T.

3.2.2. pH Value

The pH value is not only affecting the existing ST but also can change the density of the negative charge on the Fe₃O₄@SiO₂@[OMIM] PF₆ MNPs surface. Thus, it was necessary to investigate the pH value effect which was varied between "3.0 and 13.0" by Fe₃O₄ and Fe₃O₄@SiO₂@[OMIM] PF₆. Figure 6) the extraction efficiency for ST reached the maximum value at pH 7.0. According to the zeta potential of Fe₃O₄@SiO₂@[OMIM] PF₆ MNPs shown in (Figure 7), its particles have isoelectric point at pH 7.0, which was also the maximum extraction efficiency for ST. It illustrated that the main effect of ST on Fe₃O₄@SiO₂@[OMIM] PF₆ MNPs was the hydrophobic effect of ionic liquid. Therefore pH 7.0 was chosen.

Figure 6. Effect of pH on extraction efficiency of safranin T by Fe₃O₄ and Fe₃O₄@SiO₂@IL ([OMIM] PF₆) (cc0 =4.0 µg mL⁻¹).

Figure 7. Zeta potential of Fe₃O₄@SiO₂@IL MNPs.

3.2.3. Extraction Temperature

The extraction efficiency of ST, on Fe₃O₄@SiO₂@[OMIM] PF₆ at various temperatures (0.10-60.0°C) were investigated. The efficiency of extraction of ST by Fe₃O₄@SiO₂@[OMIM] PF₆ was higher, the extraction was exothermic when temperature increases, the analytes will be desorbed [23], the highest extraction efficiency was found at 40°C. Therefore, experiments were done at 40°C. Figure 8.

Figure 8. Effect of temperature on extraction efficiency (cc0 =4.0 µg mL⁻¹).

3.2.4. Ionic Strength

The extraction efficiency of ST increased with the NaCl concentration above 25% because of the NaCl salting effect [24]. In addition to this, the hydrophobic attraction was higher when NaCl concentration was high. and adsorption efficiency decreasing when NaCl was above 25%, which attributed to increasing of sample viscosity because it decreases the transference of ST from the bulk sample to the extractant [25]. Therefore, 25% (w/v) of NaCl was selected.

3.2.5. Sample Volume

The extraction efficiency of ST varied with the increase of sample amount. The amount of the sample increased from 10.0 mL to 90.0 mL. The efficiency of adsorption of ST was above 94% from 10.0 to 80.0 mL and went down slightly when sample amount was higher than 80.0 mL. Therefore the sample volume 80.0 mL was selected.

3.2.6. Adsorption Time

The extraction process was finished in 15.0 min., the adsorption efficiency remained almost stable (85.0%) along with increasing time, so 15.0 min was selected as the extraction time for ST. (Figure 9).
3.3. Adsorption Capacity

The capacity of adsorption is known as highest volume of ST which extracted by one gram of the Fe₃O₄@SiO₂@[OMIM] PF₆ MNPs. The capacity of adsorption for ST by this MNPs was studied. When the ST amount was 50.0 µg mL⁻¹, and it reached the highest value. Therefore it was found to be 15.34 mg g⁻¹ for Fe₃O₄@SiO₂@[OMIM] PF₆. (Figure 10).

3.4. Elution Process

3.4.1. Eluent Type

Various eluents were studied in this work, their elution efficiency was ordered as follow: ethanol > methanol > cetyltrimethyl ammonium bromide (CTAB) > sodium dodecyl sulfonate (SDS) > NaOH (0.1 mol. L⁻¹) > HCl (0.1 mol. L⁻¹). So ethanol was selected. (Figure 11)

The effect ethanol volume on the elution efficiency of ST was studied. The finding showed that it was higher than 98% when ethanol amount was 4.0 mL, so the volume 4.0 mL was selected for the eluent.

3.4.2. Elution Time

The elution process was finished in 10.0 min, elution efficiency did not changed until it reached 85% thereafter. Elution time of 10.0 min was selected for ST elution.

3.4.3. Elution Temperature

Elution efficiency for ST at various temperatures (5–60°C) was observed, which was increased with increasing temperature from below 15°C. Then it was higher than 85% and decreased from 20 to 60°C. Therefore, 15°C was selected.

3.5. The Reusability of Fe₃O₄@SiO₂@[OMIM] PF₆

In order to investigate the recycling of the Fe₃O₄@SiO₂@[OMIM] PF₆, they were washed with 2.0 mL ethanol two times after any MSPE run and assembled with ILs. and subsequently assembled with IL. Each re-prepared adsorbent was used for MSPE. The experimental results were shown in (Figure 12) with no loss of the sorption capacity occurred after ten times of recycling. These results indicated that the self-assembly did not influence the stability of the Fe₃O₄@SiO₂@[OMIM] PF₆ MNPs for reusability.

3.6. Evaluation of Interferents

The effect of interferents which food samples may contain...
on separation of ST in the availability of interferents was investigated. The limit of tolerance for different interferents were found as follow, SO$_4^{2-}$, NO$_3$ was 500, Citrate was 250, Br$^-$, glucose was 100, Zn$^{2+}$, Cu$^{2+}$ was 50, Bright yellow, sunset yellow, Rhodamine B was 20 and for Allura red, congo red, was 10. The results showed that most of the foreign material in samples had no interference in ST separation.

3.7. Analytical Performance of the Method

Under optimum conditions described above, The proposed method introduced wide linearity within the concentration range of 15-350 ng mL$^{-1}$. With a correlation coefficient of 0.9991, the equations of calibration graph was $A = 0.04 + 0.13c$ (µg mL$^{-1}$). The detection limit, was 0.37ng mL$^{-1}$ (RSD = 5.1%). The pre-concentration factor, defined as the quotient of volume before absorption and after elution, was 10-fold.

3.8. Separation of ST in Food Samples

This method was introduced to separate the ST amounts in different types of tomato sauces samples. The amounts of ST in tomato sauces were measured up to the national standard. To further verify the viability of the method, recovery experiments were carried out, the results were ranged from 97.5% to 101.2%, which was satisfactory (Table 1).

Table 1. The recoveries of safranine T in different of tomato sauce samples (n=3).

| Sample       | Added / mg. kg$^{-1}$ | Found / mg. kg$^{-1}$ | Recovery |
|--------------|-----------------------|-----------------------|----------|
| Tomato sauce A | 0.00                  | ND                    | —        |
|              | 2.00                  | 1.95$^1$              | 97.5%    |
|              | 4.00                  | 3.99                  | 99.8%    |
|              | 8.00$^1$              | 8.04                  | 100.5%   |
| Tomato sauce B | 0.00                  | ND                    | —        |
|              | 2.00                  | 0.98                  | 98.7%    |
|              | 4.00                  | 4.85                  | 100.2%   |
|              | 8.00                  | 9.67                  | 99.3%    |
| Tomato sauce C | 0.00                  | ND                    | —        |
|              | 2.00                  | 1.99                  | 99.5%    |
|              | 4.00                  | 4.05                  | 101.2%   |
|              | 8.00                  | 7.88                  | 98.5%    |
| Tomato sauce D | 0.00                  | ND                    | —        |
|              | 2.00                  | 1.97                  | 98.3%    |
|              | 4.00                  | 4.01                  | 100.3%   |
|              | 8.00                  | 7.90                  | 98.7%    |

3.9. Comparison with Other Methods

In (Table 2) the linear range and the limit of detection for separation of ST in real samples was listed. This method had LOD similar to the ultra performance liquid chromatography-tandem mass spectrometry UPLC-MS/MS method. However, UPLC-MS/MS needs complicated tools, using toxic eluents, intensive preparation of sample process and professional technicians. Compared with other reported methods, the method adopted is better than the UPLC-MS/MS method of rapidity, satisfactory linear range and limit of detection.

4. Conclusion

In this work, Fe$_3$O$_4$@SiO$_2$@[OMIM] PF$_6$ was synthesized as MSPE adsorbent coupled with UV-visible spectrophotometry to separate ST in food samples. ILS as possible environmentally friendly solvent can obtain good extraction efficiency. The magnetic separation greatly improved the separation rate and reduced the analysis time. This introduced method for the separation of Safranine T from real samples was proved to be simpler, faster, lower cost and satisfactory.

Table 2. Comparison with the results in other literatures.

| Method                  | LR (ng/m L$^{-1}$) | LOD (ng/mL$^{-1}$) | Ref      |
|------------------------|--------------------|--------------------|----------|
| HPLC fluorescence      | 1000 - 5000        | 4                  | [26]     |
| UPLC-MS/MS             | 10 - 500           | 0.7                | [27]     |
| Fluorescence           | 100 - 4000         | 34                 | [28]     |
| MSPE / UV spectrophotometry | 15 – 350        | 0.37               | This method |

References

[1] Ding X P, Tang D B, Li T, Wang S F& Zhou, YY. (2011). A novel spectrofluorometric method for the determination of methiocarb using an amphiphilic p-sulfonatocalix [4] arene. Spectrochim. Acta, PartA. 81:44–47.
[2] Liu Q, Shi J B, Wang T, Guo F, Liu L H & Jiang G B.(2012) Hemimicelles/admicelles supported on magnetic graphene sheets for enhanced magnetic solid-phase extraction, J.Chromatogr.A.1257:1–8.
[3] Kirsch P, Fleig I, Frentzel-Beyme R, Gembardt C, Steinborn J, Thiess A M., et al. (1978) Ar-beitsmed. Sozialmed. Priventivmed, 13:1-28.
[4] Ministry of Health of the People's Republic of China (2008) The China National Standardization Management Committee: Hygienic standards for uses of food additives (GB2760-2007). Standards Press of China.
[5] IARC. Monographs on the evaluation of carcinogenic risk to humans. (1987)118:1–42.
[6] Jiang H M, Yang T, Wang Y H, Lian H Z, & Hu X. (2013) Magnetic solid-phase extraction combined with graphite furnace atomic absorption spectrometry for speciation of Cr (III) and Cr (VI) in environmental waters. Talanta, 116: 361–367.
[7] Mashhadizadeh MH & Amoli-Diva Pourghazi M K. (2013) Magnetic nanoparticles solid phase extraction for determination of ochratoxin A in cereals using high-performance liquid chromatography with fluorescence detection, J. Chromatogr. A. 1320: 17–26.
[8] Rastkari N, Ahmadkhaniha R. (2013) Magnetic solid-phase extraction based onmagnetic multi-walled carbon nanotubes for the determination of phthalatemonoesters in urine samples, J. Chromatogr. A. 1286: 22–28.
[9] Galan-Cano F, Alcudia-Leon Mdel C, Lucena R, Cardenas S, VarcarcelM. (2013) Dispersive micro-solid phase extraction with ionic liquid-modified silica for the determination of organophosphate pesticides in water by ultra performance liquid chromatography, Microchem. J. 106: 311-317.
[10] Dupont, J, de Souza RF, Suarez PAZ. (2002) Ionic liquid (molten salt) phase organo- metallic catalysis, Chem. Rev. 102: 3667–3692.

[11] Liu X D, Yu Y J, Zhao M Y, Zhang H Y, Li Y, & Duan G L. (2014) Solid phase extraction using magnetic core mesoporous shell microspheres with C18-modified interior pore-walls for residue analysis of cephalosporins in milk by LC-MS/MS. Food Chem. 150: 206–212.

[12] Vidal L, Riekkola ML & Canals A. (2012) Ionic liquid-modified materials for solid-phase extraction and separation, Anal. Chim. Acta, 715: 19–41.

[13] Fontanals N, Borrull F & Marcé RM. (2012) Ionic liquids in solid-phase extraction, Trends Anal. Chem. 41: 15–26.

[14] Gao Q, Zheng H B, Luo D, Ding J, & Feng Y Q. (2012) Facile synthesis of magnetic one-dimensional polyaniline and its application in magnetic solid phase extraction for fluoroquinolones in honey samples. Anal. Chim. Acta 720: 57–62.

[15] Pardasani D, Kanaujia PK, Purohit A K, Shrivastava A R, Dubey DK. (2011) Magnetic multi-walled carbon nanotubes assisted dispersive solid phase extraction of nerve agents and their markers from muddy water. Talanta, 86: 248–255.

[16] Dzyuba SV, & Bartsch RA. (2001) Efficient synthesis of 1-alkyl (aralkyl)-3-methyl (ethyl) imidazolium halids: precursors for room-temperature ionic liquids. Journal of Heteroc. Chem. 38: 265–268.

[17] Tokuda H, Hayamizu K, Ishii K, Susan MABH, Tsuzuki S, Hayamizu K, & Watanabe M. (2004) Physicochemical properties and structures of room temperature ionic liquids. 1. variation of anionic species. J. Physic. Chem. B. 108: 16593–16600.

[18] Hong RY, Zhang S Z, Han Y P, Li HZ, Ding J, & Zheng Y. (2006) Preparation, characterization and application of bilayer surfactant-stabilized ferrofluids. Powder Technol. 170: 1–11.

[19] Hou YH, Han XY, Chen J, Li Z L, Chen XC, & Gai, LG. (2013) Isolation of PCR-ready genomic DNA from Aspergillus niger cells with Fe3O4/SiO2 microspheres. Sep. Purif. Technol. 116: 101–106.

[20] Zhao X, Shi Y, Wang T, Cai Y & Jiang G. (2008) Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples J. Chromatogr. A. 1188: 140–147.

[21] Chen, J. P., & Zhu, X. S. (2015) Ionic liquid coated magnetic core/shell Fe3O4@SiO2 nanoparticles for the separation/analysis of linuron in food samples Spectrochimica Acta Part A: 137. 456–462.

[22] Dang GF, Ma XG, & Zhou JP. (2012) Preparation of Silica-coated Magnetic Nanomaterials Modified with ionic liquid and its application in detection of trace cadmium ion in water. Chin. J. Instrumen. Anal. 7: 823–827.

[23] Ho TD, Canestraro AJ & Anderson JL. (2011) Ionic liquids in solid-phase microextraction: a review, Anal. Chim. Acta. 695: 18-43.

[24] Hu YQ, Guo T, Ye X S, Li Q, Guo M, Liu H N, & Wu Z J. (2013) Dye adsorption by resins: Effect of ionic strength on hydrophobic and electrostatic interactions. Chem. Eng. J. 228: 392-397.

[25] Ho T D, Cole W T S, Augusto F, & Anderson J L. (2013) Insight into the extraction mechanism of polymeric ionic liquid sorbent coatings in solid-phase microextraction. J. of Chromatogr. A. 1298: 146-151.

[26] He S K. (2009). Determination of safranine T in food by high performance liquid chromatography. Fujian Analysis & Testing; 2: 9–11.

[27] Zheng X Y. (2009) Determination of safranine T in foods by ultra performance liquid chromatography-tandem mass spectrometry. J. Fuzhou Univ. 37, 752–755.

[28] Wang WJ, Zhu X S & Yan CG. (2013) Determination of safranine T in food samples by CTAB sensitized fluorescence quenching method of the derivatives of calix [4] arene Food Chem. 141: 2207-2212.