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Simultaneous in situ derivatization and ultrasound-assisted dispersive magnetic solid phase extraction for thiamine determination by spectrofluorimetry

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ABSTRACT

A simple and rapid method for the simultaneous in situ derivatizaion, preconcentration and extraction of thiamine (vitamin B_1) as a model analyte was developed by a novel quantitative method, namely ultrasound-assisted dispersive magnetic solid phase extraction spectrofluorimetry (USA-DMSPE-FL) from different real samples. This method consists of sample preparation, in situ derivatization, exhaustive extraction and clean up by a single process. High extraction efficiency and in situ derivatization in a short period of time is the main advantages of this procedure. For this purpose, the reusable magnetic multi-wall carbon nanotube (MMWCNT) nanocomposite was used as an adsorbent for preconcentration and determination of thiamine. Thiamine was, simultaneously, in situ derivatized as thiochrome by potassium hexacyanoferrate (III) and adsorbed on MMWCNT in an ultrasonic water bath. The MMWCNTs were then collected using an external magnetic field. Subsequently, the extracted thiochrome was washed from the surface of the adsorbent and determined by spectrofluorimetry.

The developed method, which has been analytically characterized under its optimal operating conditions, allows the detection of the analyte in the samples with method detection limits of 0.37 μg L^{-1}. The repeatability of the method, expressed as the relative standard deviation (RSD, $n=6$), varies between 2.0% and 4.8% in different real samples, while the enhancement factor is 197. The proposed procedure has been applied for the determination of thiamine in biological (serum and urine), pharmaceutical (multivitamin tablet and B complex syrup) and foodstuff samples (cereal, wheat flour, banana and honey) with the good recoveries in the range from 90% to 105%.

1. Introduction

Thiamine (vitamin B_1), a water-soluble vitamin, is a biologically and pharmaceutically important compound. It is necessary for carbohydrate metabolism, the maintenance of normal neural activity and prevention and treatment of beriberi disease: pregnant women, infants, adolescents, and especially, elderly people are the groups at risk of hypovitaminosis of vitamin B_1 [1]. Thiamine is very important to the brain, particularly in terms of emotional health and well being, and also is useful for focus and concentration. There have been suggestions that thiamine may have a beneficial effect in treating Alzheimer's disease [2].

A wide variety of analytical techniques are available for the determination of thiamine in pharmaceutical preparations, biological and food samples, including spectrophotometry [3], spectrofluorimetry [4,5], fluorimetry [6,7], turbidimetry [8], electrochemical methods [9–11], high performance liquid chromatography [12] and capillary electrophoresis [13]. In most cases, thiamine and its phosphoric esters are analyzed after oxidation to a strongly fluorescent derivative (thiochrome) using potassium hexacyanoferrate in alkaline conditions [14].

Spectrofluorimetric methods are the most commonly used techniques and continue to enjoy wide popularity. The common availability of the instrumentation, the simplicity of procedures, sensitivity, speed, precision and accuracy of the technique still make spectrofluorimetric methods attractive. The analytical advantages of the application of fluorescence to thiamine determination are its proper selectivity, sensitivity and wide dynamic range.

Nevertheless, some of the reported methods for the determination of thiamine are time-consuming, tedious or insensitive. HPLC methods are widely combined with a pre- or post-column derivatization which takes too much time, and using toxic reagent is a common practice in these methods. In addition, the levels of thiamine in some real samples are lower than detection limit of

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these techniques. Thus, the clinical investigations of thiamine in pharmaceutical and biological samples require sensitive, simple and inexpensive analytical methods without time-consuming steps prior to analysis. However, most of these methods are relatively expensive and are not accurately reliable for the determination of trace amounts of thiamine. Also, due to matrix effects and low concentrations of thiamine in different samples, using separation and pre-concentration steps are still necessary, and a couple of them with simple and less expensive determination techniques such as spectrofluorimetry is very attractive.

Several methods have been proposed for separation and preconcentration of trace amounts of thiamine such as dispersive liquid–liquid microextraction (DLLME) [2,15], cloud point extraction (CPE) [16], liquid–liquid extraction (LLE) and solid-phase extraction (SPE) [2,15,17–19]. Among these techniques, the SPE procedures are considered superior to the other procedures for their simplicity, capability to eliminate undesirable matrix components, and their ability to achieve higher enrichment factors [20].

Carbon nanotubes (CNTs) have been nominated as a solid phase extractant for various inorganic and organic compounds/elements at trace levels. Without any doubt the use of CNTs in SPE is among the most important applications of these materials in analytical science. Their use is based on CNTs properties suitable for SPE, like their ability to establish π–π interactions as well as excellent Van der Waals interactions with other molecules, in particular with hydrophobic ones. They also possess a large surface area, especially on the outside and interstitial spaces within nanotubes bundles. Their chemical, mechanical and thermal stability should also be considered [21]. This combination of physicochemical properties makes CNT a very attractive choice for solid phase extraction (SPE).

However, due to their hydrophobic nature and nano-size, carbon nanotubes tend to aggregate and produce resistance against liquid flow when used as SPE adsorbent. This material behavior makes the SPE procedure inefficient, especially when aqueous solvents containing suspended particles are used [22]. To solve this problem, CNTs have been modified with magnetic particles by a chemical process, which were further used as adsorbents of magnetic solid-phase extraction (MSPE) [23,24]. The prepared magnetic CNT can be well dispersed in water and easily separated from the medium with the help of a magnet [25].

An interesting approach in sample preparation is to couple ultrasound-assisted extraction (UAE) (Both US-assisted solid–liquid extraction and liquid–liquid extraction) with other extraction techniques to take the most of both procedures in order to achieve good extraction yields, with lower solvent consumption, and be cost effective [26]. It is well-known that ultrasound is a powerful aid in the acceleration of various steps, such as homogenizing and mass transferring between immiscible phases, in the processes of separation and extraction [27]. Moreover, in our work US dramatically increases dispersion of MMWCNT that leads to lower consumption of the adsorbent which could obtain high extraction efficiency and extraction equilibrium in a very short time. This technique overcomes the problems of pre- or post-column derivatization which takes too much time and using toxic reagent in HPLC. To our knowledge, this is the first time UAE and DMSPE are used with in situ derivatization simultaneously.

This paper describes a sensitive and reliable method for the determination of thiamine as thiochrome using ultrasound-assisted dispersive magnetic solid phase extraction spectrofluorimetry (USA-DMSPE-FL). To this aim, we report the use of MMWCNT nanocomposite for the preconcentration and determination of thiamine that was simultaneously derivatized as thiochrome and adsorbed on MMWCNT in an ultrasonic water bath. The MMWCNTs were then collected using an external magnetic field. Subsequently, the extracted thiamine was washed from the surface of the adsorbent and determined by spectrofluorimetry. This methodology has not been applied previously in the in situ derivatization, extraction and determination of thiamine in different type of real samples: pharmaceuticals (B complex syrup and multivitamin tablet), biological samples (urine and serum) and foodstuffs (wheat flour, cereal, honey and banana).

2. Experimental

2.1. Chemicals and materials

MMWCNT nanocomposite was prepared according to our previous study [28]. All chemicals used were of analytical-reagent grade. All aqueous solutions were prepared using ultra pure Milli-Q purification system. Thiamine hydrochloride stock standard solution (1000 mg L^{-1}) was prepared by dissolving the required amount of vitamin (Fluka, Buchs, Switzerland) in ultra pure water. This solution, stored in the dark at 4 °C, was stable for at least four weeks. Working solutions of lower concentrations were prepared daily from the above stock solution as required. A 5000 mg L^{-1} solution of ferricyanide was prepared by dissolving appropriate amount of potassium hexacyanoferrate (III) (Merck, Darmstadt, Germany) in sodium hydroxide solution. Other reagents including ammonium ferric sulfate, ammonium ferrous sulfate, ammonium hydroxide, sodium hydroxide, 1-propanol and hydrochloric acid were purchased from Merck. The pH of solutions was adjusted by 1 mol L^{-1} NaOH solution.

2.2. Apparatus

All fluorescence measurements were made using a Perkin-Elmer LS 50 spectrofluorimeter equipped with xenon discharge lamp and quartz cell. Instrument excitation and emission slits both were adjusted to 15 nm. A 40 kHz and 0.138 kW ultrasonic water bath with temperature control (Tecno-Gaz SpA, Italy) was used. The pH of solutions was determined and adjusted using a pH meter model 823 Metrohm with a combined glass–calomel electrode. Magnetic separation was done with a strong magnet with 1 T magnetic fields including the dimensions of the magnet employed ($10 \times 3 \times 2$ mm^3). An adjustable sampler (100–1000 μL) was prepared from Eppendorf (Hamburg, Germany).

2.3. Sample preparation

2.3.1. Pharmaceutical formulations

2.3.1.1. Multivitamin tablet. For extraction and determination of vitamin B_1 from the multivitamin tablet sample, an appropriate amount (equivalent to 1.5 mg thiamine for vitamin B_1) of powdered sample was accurately weighed into a 100 mL volumetric flask, and 10 mL of 0.1 mol L^{-1} HCl solution was added, and then diluted to the mark with water. After sonication for 20 min, the insoluble residue was filtered off through a 0.45 μm cellulose acetate filter. The filtrate was diluted step-wise with ultra pure water to a concentration of about 5 mg L^{-1} thiamine for determinations.

2.3.1.2. B complex syrup. An aliquot of 250 μL (equivalent to 0.25 mg thiamine for multiple vitamin B syrup) was measured into a 50 mL volumetric flask, and 10 mL of 0.1 mol L^{-1} HCl solution added; then diluted to the mark with ultra pure water to a concentration of about 5 mg L^{-1} thiamine for determinations and the analysis was followed up as indicated in the procedure.

2.3.2. Biological samples

2.3.2.1. Spiked human urine samples. Urine samples, obtained from two healthy volunteers, were collected and integrated. An aliquot of 10 mL from this mixture were placed in graduate centrifuge tubes. This solution was centrifuged for 5 min at 5000 rpm and

2 mL of supernatant was transferred into a new test tube and stored frozen until assays. Aliquots of centrifuged human urine sample (200 μL) were spiked with different amounts of thiamine (50 and 80 μg L^{-1}) and the analysis was followed up as indicated in the procedure.

2.3.2.2. Spiked human serum samples. Serum samples obtained from Dr. Shariati hospital (Tehran, Iran). Serum samples were spiked with 20 and 40 μg L^{-1} of thiamine and the analysis was followed up as indicated in the procedure.

2.3.3. Food stuff samples

2.3.3.1. Cereal. 1.0 g of cereal that was purchased from a local supermarket was grounded and mixed with 0.1 mol L^{-1} HCl solution. After integrating for 15 min, the mixture was centrifuged for 10 min at 5000 rpm, and the supernatant was filtered through a 0.45 μm cellulose acetate filter and diluted up to 10 mL with ultra pure water.

2.3.3.2. Wheat flour. 1.0 g of wheat flour was mixed with 0.1 mol L^{-1} HCl solution for 20 min. Then, the mixture was centrifuged for 10 min at 5000 rpm, and the supernatant was filtered through a 0.45 μm cellulose acetate filter and diluted up to 10 mL with ultra pure water.

2.3.3.3. Banana. 3.0 g of banana was weighed and cut into small pieces and extracted with 0.1 mol L^{-1} HCl solution in water bath at a suitable temperature and time period. The mixture was centrifuged for 5 min at 5000 rpm, and the supernatant was filtered through a 0.45 μm cellulose acetate filter and diluted up to 10 mL with ultra pure water.

2.3.3.4. Honey. The honey sample was prepared by weighing 2.0 g and diluting up to 10 mL with ultra pure water.

2.4. USA-DMSPE-FL procedure

48 mL of sample solutions containing 50 μg L^{-1} of thiamine were taken in a 50 mL conical capped tube. The vial was immersed into an ultrasonic water bath. The ultrasonic water bath was switched on and 200 μL of potassium hexacyanoferrate (III) solution (5000 mg L^{-1}) in 4% w/v NaOH as derivatizing agent and 1 mL of MMWCNT suspension (containing 4 mg of the adsorbent in ultra pure water) were dispersed into the sample solution simultaneously and final volume of the solutions was adjusted at 50 mL using deionized water. After a 3 min sonication at 40 kHz of ultrasonic frequency and 0.138 kW of power at 25 ± 3 °C, the extracted thiochrome was treated with a magnet to separate the MMWCNT nanocomposite adsorbents from the solution. After about 30 s, the solution became limpid and the supernatant solution was completely decanted. 1 mL of 1-propanol (eluent solution) was added to the isolated adsorbent and the obtained mixture was agitated and again exposed on the strong magnet and the clear solution of eluent was removed using a sampler and injected into a quartz cell. Subsequently, the cell was located in spectrofluorimeter to obtain related spectra. The fluorescence intensity was measured at 438 nm with the excitation wavelength set at 365 nm.

3. Results and discussion

3.1. Influence of pH

The oxidation of thiamine to thiochrome is a very efficient, simple, and fast derivatization reaction, giving a highly fluorescent derivative. An alkaline medium is needed for the reaction, and the pH effect was studied in the 6–13 range potassium hexacyanoferrate/sodium hydroxide solution. The sensitivity continuously increased up to pH 11 and after that, remained constant. Thus pH 11 was chosen for further studies and solutions were subjected to the USA-DMSPE and spectrofluorimetric determination. So, the pH adjustment was not carried out by using buffer systems and the addition of proper amount of OH^- is sufficient for adjustment of pH and achievement of higher analytical signal.

3.2. Influence of the addition of NaCl

The impact of ionic strength on extraction efficiency and subsequent measurement was evaluated by adding different amounts of NaCl (0–3% (w/v)). Other experimental conditions were kept constant. Based on the results obtained in this study salt addition has no significant and beneficial effect on the analytical signals. Therefore, no salt was added in the subsequent experiments.

3.3. Influence of amount of MMWCNT

In comparison with the traditional adsorbents (microsized sorbents), CNTs offer a significantly higher surface area to volume ratio. Thus, satisfactory results can be achieved with fewer amounts of CNTs. Also, insufficient amount of adsorbent will cause the breakthrough of the analytes whereas higher amounts will increase the cost and time of the analytical procedure. Higher amounts of adsorbent material may also adversely affect the final signal strength if the back extraction (elution) of the analytes from sorbet is not quantitative. In order to examine the essence of the adsorbent, 3–10 mg of the MMWCNTs was added to 50 mL of the sample solution. The obtained results showed that by increasing the sorbent amounts from 4 up to 10 mg fluorescence intensity remained constant. So, a 4 mg of the MMWCNTs was selected for all subsequent experiments for both ions.

3.4. Influence of derivatizing agent and sodium hydroxide concentrations

The experiments revealed that the concentration of oxidizing species $K_3Fe(CN)_6$ in the reagent solution had a critical influence on fluorescence intensity. The influence of ferricyanide concentration was studied from 10 to 50 mg L^{-1}. The signals sharply increased with the increase of $K_3Fe(CN)_6$ concentration from 10 to 20 mg L^{-1}, after which the intensity of signals gradually declined. The decline in intensity may be due to the rate of thiochrome decomposition reaction at higher concentrations. Thus, in the following experiment concentration of 20 mg L^{-1} was selected.

Oxidation of thiamine to thiochrome by $K_3Fe(CN)_6$ requires a strong alkaline medium. It was found in the present study that the fluorescence intensity was rapidly increased with the increase of sodium hydroxide concentration in the range 0–4% (w/v), after which the increase rate was gradually slowed down, and the signal finally leveled off at the 4% (w/v) concentration. So, a compromise concentration (4% w/v) for sodium hydroxide in the reagent solution was adopted.

3.5. Influence of extraction time

For studying effect of extraction time on fluorescence intensity of the thiamine, the extraction times were varied in the range of 1–8 min. It was observed that after 3 min, the fluorescence intensity of the thiamine had no significant variation. Therefore, the extraction time of 3 min was selected for further studies.

3.6. Influence of sample volume

In SPE, the sample volume is determined by typical concentrations of potential analytes and degree to which they will need to be concentrated from the sample prior to analysis. It also depends upon the detection limits and the linear range of the instrument used for the analysis. In order to obtain a higher enhancement factor, a larger volume of sample solution is required. Due to the magnetically assisted separation of the adsorbent (MMWCNT), it is possible to collect the adsorbent from larger volumes of the sample solution. Thus the extraction of 50 $\mu g\,L^{-1}$ of thiamine from different volumes of water samples ranging from 50 to 200 mL were investigated. Thiamine was quantitatively recovered in the sample volume range of 50–150 mL.

3.7. Influence of desorption conditions

In order to choose the best solvent for desorption of the thiamine from MMWCNT surface, different eluents were selected and their elution efficiencies were investigated. As it can be seen in Fig. 1, desorption ability for 1-propanol was superior to that of the other eluents (in comparison between 1- propanol and methanol, 1-propanol was chosen because of its less toxicity). Therefore, it was used as eluent in further experiments. Also, for selecting the optimal volume of the eluent for quantitative desorption of thiamine, a minimum volume that we could use in spectroflourimetry was 1 mL. At higher volumes of the eluent, the fluorescence intensity of the thiamine decreased due to dilution effect. So, 1 mL of eluent was applied in the subsequent experiments.

The effect of desorption time on the recovery of vitamin B_1 was investigated in the range of 1–3 min, and no significant effect was observed when the time of desorption was greater than 2 min. Therefore, the time of 2 min that was sufficient for quantitative desorption of the vitamin from adsorbent was selected for the subsequent experiments.

3.8. Interference studies

In order to assess the possible analytical applications of the proposed method, the effect of concomitant species on the determination of thiamine in real samples was examined. Samples containing a fixed concentration of thiamine (50 $\mu g\,L^{-1}$) and various excess amounts of the foreign species were subjected to the proposed method. The study was focused on some common drugs, excipients and some compounds abundant in the chosen real samples. The tolerance ratio of each foreign substance was taken as the largest amount yielding an error in the determination of the analyte not exceeding 5% (Table 1).

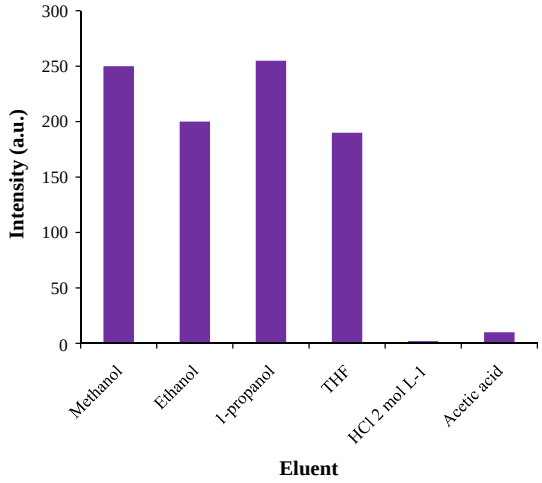

Fig. 1. Selection of type of eluent. pH = 11.0, concentration of thiamine: 50 $\mu g\,L^{-1}$, extraction time = 3 min.

Table 1
Effects of interfering ions on preconcentration and determination of 50 $\mu g\,L^{-1}$ of thiamine.

Interference	Interference to thiamine ratio (w/w)
Saccharose, glucose,lactose, fructose	400
Ascorbic acid	1000
Urea	300
Citrate	100
Pyridoxine	700
Biotin	500
Na^+, K^+, Ca^{+2}, Mg^{+2}	1000

3.9. Regeneration experiments

The regeneration of the adsorbent is a key factor in improving process economics. The repeated availability of MMWCNT through many cycles of sorption/desorption was investigated to evaluate the application potential of this material in the preconcentration and determination of thiamine. MMWCNT can be regenerated by 1-propanol/water and reused for ten successive SPE processes. At higher cycles, fluorescence intensity may be due to losing or dissolving some amounts of the adsorbent during the successive steps.

3.10. Quantitative analysis

To evaluate practical applicability of the proposed USA-DMSPE-FL technique, linearity, relative standard deviations (RSDs), limits of detection, and preconcentration factor (PF) were investigated by extraction of thiamine from different real samples under the optimal conditions. The calibration curve for thiamine was linear from 1.0–500 $\mu g\,L^{-1}$ with the coefficient of determination (R^2) of 0.998 and equation of $I = 1.154C\,(\pm 0.02) - 11.45\,(\pm 3.58)$. The limit of detection (LOD) based on $3S_b/m$ definition (where m is the slope of the calibration curve and S_b is the standard deviation of six blank measurements) was 0.37 $\mu g\,L^{-1}$. Relative standard deviations (RSDs %) of the method for determination of thiamine was 2.0% (six replicates measurements at 50 $\mu g\,L^{-1}$). The enhancement factor was achieved higher than 150 as expected value and calculated as the ratio between the slopes of the calibration curves after and before extraction, which was about 197 ($V = 150$ mL). This was due to effect of 1-propanol that enhanced the intensity of thiochrome.

3.11. Application of the proposed method to real samples

In order to evaluate the reliability and analytical applicability of the proposed method for analysis of different matrices, the optimized method was applied for the determination of vitamin B_1 in some real samples. The results of extraction of vitamin B_1 from pharmaceutical, biological and foodstuff samples are tabulated in Table 2.

3.11.1. Extraction of thiamine from pharmaceutical formulations

Following the procedure above described, the proposed method was applied to assay thiamine in pharmaceutical preparations (B complex syrup and multivitamin tablet). According to Table 2, the results obtained by the current method agreed well with the labeled values of vitamin B_1 for multivitamin tablet, and B complex syrup.

3.11.2. Determination of thiamine in spiked human urine and serum

The proposed method was also applied with preliminary success to the determination of the vitamin in human urine and serum. Urine and serum samples were collected from two volunteers as described under Section 2.3.2. Aliquots of 200 μL urine samples were spiked into two different concentrations of thiamine at 50 and 80 μg L^{-1} and 20 and 40 μg L^{-1} for serum samples and recovery experiments were conducted for these samples as well.

Table 2
Determinathin of thiamine in pharmaceutical formulations, foodstuffs and spiked biological samples with the proposed method.

Sample	Thiamine added (μg L^{-1})	Thiamine found (μg L^{-1})	Recovery (%)	RSD (%)	)Thiamine (μg g^{-1})
Food ($n=3$)					
Cereal	0	13.0	–	2.7	6.5
	10.0	22.1	96.3	3.1	–
Wheat flour	0	2.45	–	2.4	1.2
	10.0	13.10	105.2	3.7	–
Banana	0	4.6	–	2.0	0.8
	10.0	13.3	91.1	2.9	–
Honey	0	3.46	–	4.8	0.87
	10.0	13.40	99.5	3.8	–
Biological ($n=5$)					
Human urine	50.0	45.1	90.2	4.5	–
	80.0	73.9	92.3	2.3	
Human serum	20.0	22.4	101.8	2.5	–
	40.0	41.5	103.7	2.9	
Pharmaceutical ($n=5$)	Labeled amount	Determined amount (mean ± SD)	Recovery (%)		
Multivitamin tablet (mg/tablet)	1.5	1.41 ± 0.06	94.0		
B complex syrup (mg in 5 mL)	5.0	4.78 ± 0.16	95.6		

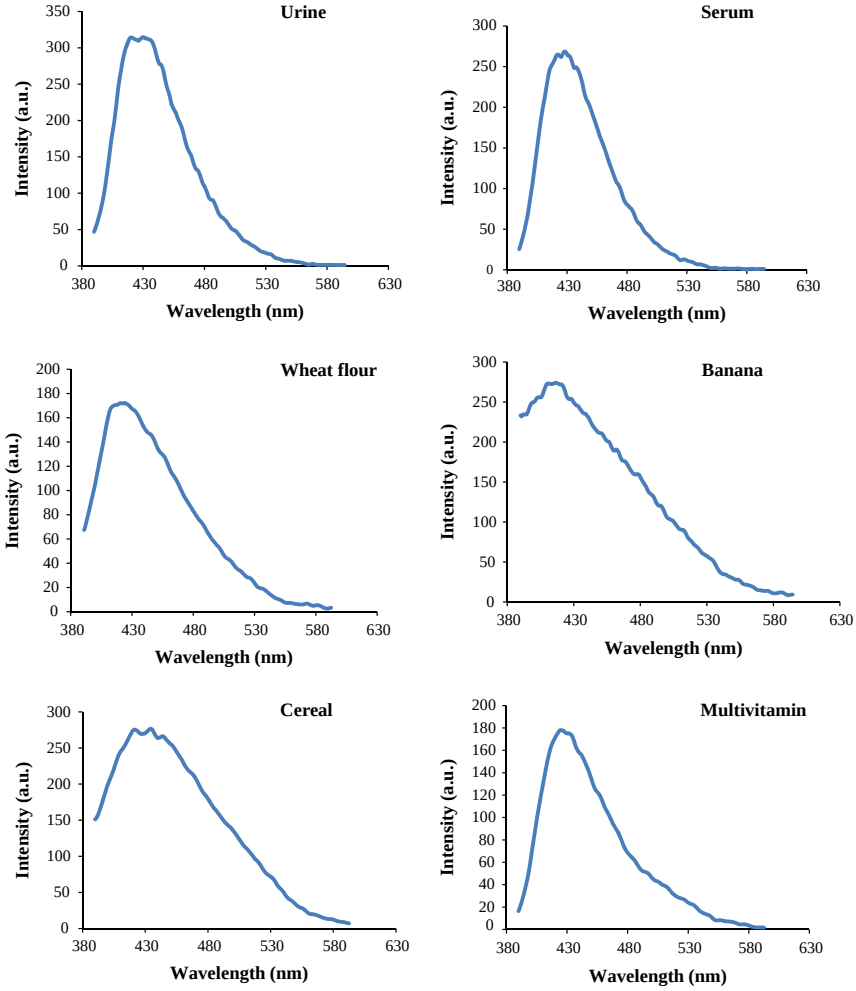

Fig. 2. Elution profiles obtained for different real samples by USA-DMSFE-FL. λ_{ex}: 365 nm, slit width 15 nm; λ_{em}: 430 nm, slit width 15 nm. For urine, serum and multivitamin, emission slit width is 7 nm. 50 μg L^{-1} spiked urine sample, 20 μg L^{-1} spiked serum samples and non-spiked samples of cereal, banana, wheat flour and multivitamin.

Table 3
Comparison of the proposed method with some of the methods reported in the literature for extraction and determination of thiamine.

Method	Sample species	LOD ($\mu g\ L^{-1}$)	LDR ($\mu g\ L^{-1}$)	RSD (%)	Ref.
FI-FL	Drug	1.8	5–280, 30–2000	1.9, 2.4	[29]
CZE-CL	Plasma, urine, saliva	50–100	100–200,000	1.8–4.0	[13]
HPLC-FL	Plasma, erythrocyte, urine	0.2	–	1.1–7.6	[30]
DLLME-Spectrofluorimetry	Drug, urine	0.06	0.2–100	3.0	[2]
DLLME-HPLC-FL	Food	0.09	1.0–10	3.2	[15]
HPLC-FL	Food	0.34	2.0–800	2.0–3.0	[31]
HPLC-CLD-UV	Food	9.2	22–8200	<7.3	[32]
SPE-HPLC-FL	Serum	1.6	25–500	3.4–12.7	[33]
USA-DMSPE-FL	Drug, urine, serum, food	0.37	1.0–500	2.0	This work

CZE: capillary zone electrophoresis, FI: flow injection, HPLC: high performance liquid chromatography, CLD: coulometric detector, SPE: solid phase extraction, CL: chemiluminescence, FL: fluorescence, DLLME: dispersive liquid–liquid microextraction.

Due to the high sensitivity of the proposed method and the consequent possibility of diluting largely the sample, no interference was found despite the presence of a very complex matrix of the samples (Table 2).

3.11.3. *Determination of thiamine in foodstuff samples*

Finally, samples of different types of foods rich in thiamine as cereal, honey, wheat flour and banana were analyzed. To test the accuracy of the proposed method, four different foods were fortified and analyzed by the optimized method, taking into account the known analyte contents of these samples. The results for thiamine are presented in Table 2.

The results of analysis of real samples showed that the development method can be reliably used for the determination of thiamine in different matrices (Fig. 2).

3.12. *Comparison of the proposed method with other methods*

Table 3 provides a comparison between the characteristics of the proposed method with those that were reported recently in the literature for the determination of vitamin B_1 in different real samples. As can be seen, sensitivity and precision of the current method are comparable to or even better than some of them, which use very sensitive separation methods such as HPLC. All the results reveal that the optimized method is not only a good sample preconcentration technique, but also an excellent sample clean up procedure that can be used for the trace analysis of thiamine in different and complicated matrices such as biological and food samples. Also, the proposed MMWCNT based DSPE has some advantages in comparison with other applied extraction methods such as SPE, including lower consumption of adsorbent and eluting organic solvents and shorter extraction times.

4. Conclusion

The aim of the present research was to develop an efficient method for simultaneous in situ derivatization, extraction and determination of trace amounts of thiamine in biological, pharmaceutical and foodstuff samples. Due to the complexity of the matrices which include vitamin B_1 and low concentration of this vitamin in these samples, direct determination of vitamin B_1 by analytical instrumentations does not contribute to satisfactory results. So, it is essential to apply a sample preparation and preconcentration step prior to final analysis.

The magnetic multi wall carbon nanotube nanocomposite with high magnetism was used as sorbent for preconcentration and determination of thiamine. The magnetic separation greatly improved the separation rate while avoided the time-consuming column passing or filtration operation. Easy regeneration is another property of MMWCNTs, and the experiments have proved that these adsorbents can be reused for ten times on average without the obvious reduction of recovery after wash/clean procedures.

The results further demonstrated that the proposed USA-DMSPE-FL method has good precision, linearity, and accuracy over the investigated concentration range. Likewise, the proposed method provides a simple, fast, sensitive and selective with little consumption of organic solvent and adsorbent for extraction and determination of vitamin B_1. Furthermore, there is a possibility of extraction of vitamin B_1 from large volumes of sample and therefore the sample diluting and decrease of matrix effects are possible.

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