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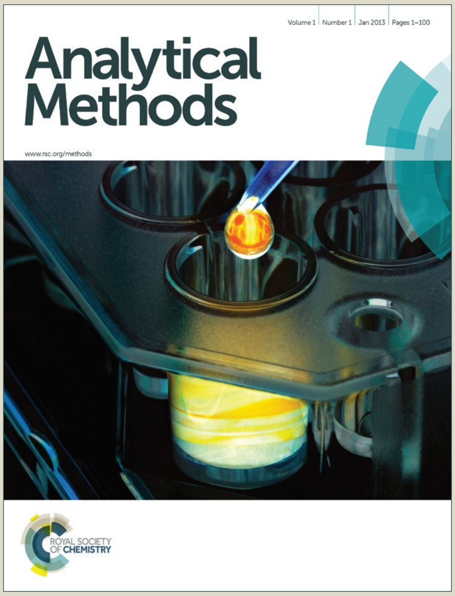

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Ultrasound-assisted cloud point extraction of manganese, zinc and tin from digested food samples for their determination by FAAS

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Abstract

The current study is focused on determination of the trace levels of manganese, zinc and tin in the wet acid digested foods by flame atomic absorption spectrometry (FAAS) after preconcentration with ultrasound assisted-cloud point extraction (UA-CPE). The preconcentration procedure is making use of the 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one (Quercetin) as chelating agent, the cationic surfactant cetyltrimethylammonium bromide (CTAB) as counter ion, the non-ionic surfactant polyoxyethylenesorbitan monolaurate (Tween 20) as extracting agent, and of acidic methanol as the diluting agent. The significant analytical parameters were optimized, and the selected values were pH of 4.0, chelating agent concentration of 8.5 μmol L^{-1}, cationic and nonionic surfactant concentrations of 30 μmol L^{-1} and 0.5% w/v), sample volume of 10 mL, equilibrium temperature of 60 ^{o}C, incubation time of 15 min and diluting agent amount of 1.25 mL, respectively. At optimum conditions, the detection limits for manganese, zinc and tin were 0.34, 0.15 and 0.7 μg L^{-1} with sensitivity enhancement factors of 116, 175 and 153, respectively. The precision was evaluated as relative standard deviations (RSDs %) for solution containing 15 μg L^{-1} of Mn(II), 40 μg L^{-1} of Zn(II), and 20 μg L^{-1} of Sn(II), and was found to be 2.3, 2.0 and 2.5 % (n: 5), respectively. The accuracy of the method was evaluated by analysis of standard reference materials (SRMs) and through recovery rates from spiked aqueous samples. The obtained results were statistically in good agreement with the certified values at 95 % confidence limit, in which the recoveries for target analytes varied in the range of 95.6–104.2 %. The method was successfully applied to the analysis of manganese, zinc and tin contents of various food samples, which are generally of plant origin, including black and green tea after dry ashing and wet digestion steps.

Keyword: Manganese, Zinc, Tin, Ultrasound assisted-cloud point extraction, Flame Atomic Absorption Spectrometry, Foods/Vegetables

1. Introduction

Zinc is an essential element in the nutrition of animals including human beings. [1,2] It acts as a co-factor innumerous of enzymes and plays an important role in protein synthesis and cell division. It exerts a crucial influence on maintenance of cell membrane stability and function of immune system. On the other hand, zinc can be toxic when exposures exceed physiological needs. After single or short-term exposure to concentrations of zinc in water and beverages between 1.0 and 2.5 mg L^{-1}, poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhea are reported. [3] Manganese is an inorganic nutrient involved in many important enzymes and/or proteins and thereby in many physiological functions of the organism. Intake varies greatly, depending mainly on the consumption of rich sources, such as unrefined cereals, green leafy vegetables, and tea. The usual intake of this mineral is 2–5 mg day^{-1} with absorption of 5–10 %. Deficiency signs include poor reproductive performance, growth retardation, congenital malformations in offspring, abnormal function of bone and cartilage and impaired glucose tolerance. [4] Manganese levels in foods have been determined in order to define more clearly human dietary requirements or levels of absorption of manganese from the diet. [5] The acute toxicity of inorganic tin is manifested as gastric irritation, nausea, vomiting and abdominal discomfort. Inorganic tin salts are poorly absorbed by the gastrointestinal tract and rapidly excreted. Nevertheless, there are several case reports of gastric irritation and vomiting in humans consuming canned foods or beverages, particularly sour fruit products packaged in tinplate cans and containing high levels of tin. Especially, canned food represent the main source of human exposure to tin. The maximum level of tin in canned foods is 200 mg kg^{-1} for canned foods other than beverages and 100 mg kg-^{1} for canned beverages, including fruit and vegetable juices. [6] Taking all these facts into consideration, the determinations of the metal ions in various foods and vegetables have now become an important analytical task.

Several coupled techniques such as inductively coupled plasma optical emission spectrometry (ICP OES),[7,8] inductively coupled plasma mass spectrometry (ICP-MS),[9,10] high resolution magnetic sector field inductively coupled mass spectrometry (HR-ICP-MS),[11] electrothermal atomic absorption spectrometry (ETAAS),[12,13] high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS),[14] hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES)[15] and inductively coupled plasma optical emission spectrometry (ICP OES)[16,17] are presented for the determination of trace metals with sufficient sensitivity. But these techniques have various types of inherent interferences arising from molecular interference ions (needs the use of reaction or collision cells to destroy their interference effects) as well as spectral line overlap (resulted from other matrix components) and background radiation (often encountered in Ca-rich samples). Moreover, all these interferences need the use of high resolution, cool plasma, low-pressure ICP discharges, alternative ICP discharges such as He, mixed gas (He-Ar, N_2-Ar), matrix alteration through elimination of S- and Cl-containing reagents, chromatography and solvent extraction lead to increase in the cost of the analysis. The monitoring of zinc and manganese including nontoxic tin in food is extremely important to ensure adequate intake of these essential and nonessential nutrients. Moreover, it is very important to be able to determine trace elements essential to human diet in several matrices. [18] The techniques involving atomic absorption spectrometry are widely used for the quantification of elements. Among these techniques, flame atomic absorption spectrometry (FAAS) in place of ETAAS, in which the latter is sensitive, but narrow concentration range, prone to interferences, poor precision, expensive, tedious and time-consuming due to long furnace program, presents interesting characteristics, because of the relative speed of analysis, robustness of equipment, low cost, ease of operation, high analytical frequency and good selectivity. [19-21] However, the direct determination of trace metals by this technique is often hampered due to the low concentration of metals in the samples. These problems can be overcome using a separation or preconcentration procedure before the detection. [22] Thus, various methods of separation and preconcentration have been used, such as solid-phase extraction (SPE), liquid– liquid extraction (LLE), cloud-point extraction (CPE), co-precipitation, electro-analytical deposition and ion exchange (IE). The use of micellar systems such as cloud point extraction (CPE) with and without ultrasound induction for separation and preconcentration has recently attracted considerable attention mainly because it is in agreement with the "green chemistry" principles. Green chemistry can be defined as those procedures for decreasing or eliminating the use or generation of toxic substances for human health and for the environment. [23] The CPE (or UA-CPE for fast and efficient mass transfer) is a green method for the following reasons: (a) it uses as an extractor media diluted solutions of the surfactants that are inexpensive, resulting in the economy of reagents and generation of few laboratory residues; and (b) surfactants are not toxic, not volatile, and not easily flammable, unlike organic solvents used in the LLE.[24-26]

In the current study, the experimental conditions for the extraction and quantitative recoveries of Mn(II), Zn(II), and Sn(II) into micellar phase of polyoxyethylenesorbitan monolaurate (Tween 20) at pH 4.0 have been investigated prior to their FAAS determinations. For this purpose, the main variables affecting complex formation and extraction efficiency were optimized in detail. Then, the proposed method was successfully applied to separation/preconcentration and determination of the analytes from various food samples.

2. Materials and Methods

2.1. Instrumentation

The determinations of target metals were performed on a Shimadzu AAS-6300 model flame atomic absorption spectrometer with hollow cathode lamp and equipped with a deuterium background correction. The conditions for determination of target metals is given in Table 1. The pH values were measured using a digital pH meter (Selecta-2001 plus, Barcelano, Spain) supplied with a glass-calomel electrode. A centrifuge (Hettich universal 320 model, Darmstadt, Germany) was used to speed up the phase separationA programmable ultrasonic bath (UCP-10 model, Seoul, Korea) was used for incubation with temperature ranging from 0 to 80 °C and ultrasound frequency of 40 kHz at power of 300 watt.

2.2. Reagents, standard solutions and samples

Ultra-pure water (resistivity of 18.2 MΩ cm) obtained by a Labconco water purification system (Kansas City, USA) was used throughout this study. All glass wares, pipettes and plastic tubes were cleaned by soaking in 5.0 % (v/v) HNO_3 solution during one day, later were rinsed five times with ultra-pure water before starting of experiment. The standard solutions of Mn(II) and Zn(II) at μg L^{-1} levels used for calibration were prepared daily by diluting a 1000 mg L^{-1} metal stock solutions purchased from Merck (Darmstadt, Germany) with 0.2 mol L^{-1} HNO_3 solution immediately before use. The stock solution of 1000 mg L^{-1} Sn(II) was prepared by dissolving 1.94 g of $SnCl_2 \times 2H_2O$ supplied by Merck (Darmstadt, Germany) (98 % (w/w) in 2.0 mol L^{-1} HCl solution while heating, and then completing to 1000 mL with water. The calibration solutions of Sn(II) at μg L^{-1} levels were obtained daily by stepwise dilution of stock solution with water. A 50 mmol L^{-1} 2-(3,4-dihydroxyphenyl)-

3,5,7-trihydroxy-4H-chromen-4-one (Quercetin) solution (Sigma) was prepared by dissolution of the chelating agent in ethanol-water mixture (1:4 ratio, v/v). All ionic and nonionic surfactants, cetyltrimethylammonium bromide (CTAB, 1.0×10^{-3} mol L^{-1}) and polyoxyethylenesorbitan monolaurate (Tween 20, 5.0 % (v/v)), obtained from Sigma, were prepared by dissolving appropriate amounts of surfactant in 100 mL volumetric flask. The pH of the sample solutions was adjusted with universal Britton-Robinson (BR) (0.04 mol L^{-1}, pH 4.0) buffer solution.

Foods (corn flakes, rice noodles, butter cookies, brown rice, dried apricot, dried apple, walnut, almond, oatmeal and cashew), vegetables (radish, cowslip, mushroom, mint, tomato, spinach and garlic) and tea samples (green tea, black tea) were collected from local markets (Sivas, Turkey) to evaluate the applicability of the method. For accuracy studies, two standard reference materials (SRMs) supplied from National Institute of Standards and Techology (Gaithersburg, MD, USA) were analyzed: SRM 2385 Slurried spinach and SRM 1548a Typical diet.

2.3. Sampling, preparation of samples to analysis

Sample preparation steps of the foods and vegetables for nonvolatile manganese and zinc are as follows. Initially, vegetable samples were cleaned with tap water and ultra-pure water. The foods (15 g) and vegetables (25 g) were dried at a temperature of 110 ^{o}C for 24 h. The dried samples were ground or homogenized using an agate homogenizer to reduce the particle size and stored in polyethylene bottles until analysis. All the dried and homogenized samples (1.5 g) were transferred into silica crucibles with lid. The silica crucibles were then placed to furnace for heating of 2.5 h at 450-500 ^{o}C. The possible volatilization losses without the use of any ashing aid can be further minimized if the ashing temperature is attained using a slow ramp in a series of mineralization stages at different times and temperatures in a programmable electric oven (90-250 °C, 450 °C, 450-100 °C). In this context, tin was not included into digestion step due to form insoluble refractory compounds during dry ashing. After this period, the residues were cooled to room temperature, treated with 12 mL of mixture of 2.0 mol L^{-1} HNO_3 and 1.0 mol L^{-1} H_2O_2 (3:1, v/v) as ashing aids to prevent the volatilization of the analytes and also to speed up the ashing process, and again kept in a furnace for 1 h at the same temperature to ensure a complete acid mixture oxidation of the organic matrix. After cooling again, the final residues were transferred into Erlenmeyer flasks, treated with 10 mL of mixture of 1.0 mol L^{-1} HCl and 0.2 mol L^{-1} $HClO_4$ (3:2, v/v) and evaporated to fumes on a hot plate.[27] Then, the solutions were left to cool down.

Sample preparation steps of the foods and vegetables for tin as a metal forming volatile or insoluble refractory compounds are as follows: In a similar way, vegetable samples were initially cleaned with tap water and ultra-pure water. The foods (15 g) and vegetables (25 g) were dried at a temperature of 110 ^{o}C for 24 h. The dried samples were ground and/or homogenized using an agate homogenizer to reduce the particle size and stored in polyethylene bottles until analysis. In order to avoid risk of transformation of Sn(II) to Sn(IV) and the dangers of possible volatilization losses, tartaric acid, 0.05 mol L^{-1} as both reductant and protective was added to the dried and homogenized samples of about 1.5 g before acid extraction. Then, 20 mL of mixture of 65 % (w/w) HNO_3 and 30 % (w/w) H_2O_2 and 3 mol L^{-1} $HClO_4$ (2:1:1, v/v) added to the beaker using a graduated pipette, and was completed to 100 mL with the water. The resulting mixtures were allowed to decompose on heating plates at 125 ^{o}C for about 2 h in a hood. Then, the solution was left to cool down.

The next steps are common to each analyte. The following operations were performed. After cooling to room temperature, the mixtures were transferred to centrifuge tubes of 50 mL, then centrifuged for 5 min at 4000 rpm, and finally filtered through membrane filter with 0.45 µm pore size (Sartorius, Germany). The pH of the digested samples was adjusted to 4.0±0.1 by using diluted NaOH solution (2.0 mol L^{-1}) or buffer solution. Then, the UA-CPE procedure given in Section 2.4 was applied by taking 10 mL of the pretreated samples. The manganese, zinc and tin amounts in the samples were determined via FAAS using the standard addition method to suppress the possible matrix effect. In a similar way, at least one blank solution including SRMs (0.2 g) was run for each sample in order to evaluate analyte contamination by reagents used.

2.4. The procedure

For UA-CPE procedure under optimum conditions, 10 mL aliquots of the pretreated sample or calibration standard solutions containing Mn(II), Zn(II) and Sn(II) (in the range of 1–70, 0.8-125 and 2.5-190 μg L^{-1}, respectively) and 30 μL of 50 mmol L^{-1} Quercetin were added and adjusted to pH 4.0 using 0.7 mL of 0.04 mol L^{-1} BR buffer in a centrifuge tube of 50 mL with conical bottom. Then, 425 μL of 1.0×10^{-3} mol L^{-1} CTAB and 5 mL of 5.0 % (v/v) Tween 20 were sequentially added, and the volume of the solution was completed to 50 mL with water. Later, the resulting mixture was maintained at 60 ^{o}C for 15 min in the ultrasonic bath for heating to the cloud point of Tween 20 under ultrasound power (300 W, 40 kHz). The mixture was centrifuged for 10 min at 4000 rpm, and then cooled in an ice-bath for 5 min to facilitate phase separation. After that, the aqueous phase was easily decanted. The surfactant-rich phase was completed to 1.25 mL with methanol solution containing 0.1 mol L^{-1} HNO_3 to decrease the viscosity and to facilitate the mass transfer rate using a vortex agitator, and then the manganese, zinc and tin contents were readily determined by FAAS. Moreover, to determine possible signal contributions that may come from the reagents used, the same procedure was in parallel applied into the reagent blanks. A negligible blank signal contribution with mean value of 3.8×10^{-3} was individually obtained from three replicate measurements of the spiked and unspiked samples of Mn(II), Zn(II) and Sn(II) at levels of 10, 15 and 25 μg L^{-1}.

3. Results and Discussion

The effect of the reagents (pH, sample volume, type of solvent, Quercetin, CTAB and Tween 20 concentrations) and experimental conditions (ultrasoond power, equilibrium temperature and time) on the absorbance of Mn(II), Zn(II) and Sn(II) ions were investigated by the univariate method, varying each parameter one-by-one holding fixed the remaining, in order to take into account the sensitivity and precision of the analytical measurements. Due to familiarity and ease to use, the univariate method is widely used in optimization step to obtain maximum efficiency of analytical methods. All experiments were carried out in triplicate for optimization of the each variable. The standard concentrations of manganese, zinc and tin, so as to fall in to the range of linearity, were fixed at levels of 10, 15 and 25 µg L^{-1} during the optimization, respectively.

3.1. Effect of pH and buffer volume

One of the most important factors in the UA-CPE procedure for quantitative absorbance of analyte ions is the pH of the aqueous phase. The reaction between analyte ions and the Quercetin as chelating agent in presence of CTAB and Tween 20 can be affected by changes of pH value. Also, the extraction of Mn(II), Zn(II) and Sn(II) ions by Tween 20 micelles generally occurs after the formation of a complex with enough hydrophobicity. In order to test the effect of pH on the absorbance of analyte ions, a series of sample solutions of Mn(II), Zn(II) and Sn(II) were adjusted to different pH values ranging from 2.5 to 8.0 by using universal Britton-Robinson (0.04 mol L^{-1}) buffer solution and performed according to the proposed procedure. The results of the study are shown in Figs 1(a). Generally, the absorbance of analyte ions increased up to pH 4.0. After this pH value, all the absorbances of Mn(II), Zn(II) and Sn(II) ions have been almost remained constant with a slight decrease in slope. However, the sharper decrease in absorbance of Zn(II) may be due to its hydrolysis in terms of amphoteric nature, so as to give stable hydroxo complexes, $Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ with –logβ values of 9.07, 15.34, 27.18 and 39.58 depending on increasing pH.[28] Thus, a pH value of 4.0 was employed as optimal for the ensuing investigations.

The effect of buffer volume added to the analytical solution on the absorbances of analyte ions was investigated in volume of 0.1-2.0 mL according to the suggested procedure. As can be seen from Figs. 1(b), the absorbance for each analyte was maximum when 0.7 mL of BR buffer solution at 0.04 mol L^{-1} was added to a final volume of 50 mL of test solution. In range of 0.7-2.0 mL, the absorbance for each analyte was gradually decreased. Therefore, an aliquot of 0.7 mL of the BR buffer solution at pH 4.0 was employed as optimal for the ensuing investigations..

3.2. Effect of chelating agent concentration

2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one (Quercetin), which is a highly reagent flavonol with pK_a values changing within the range of 5.7-9.0 [29-34], acts as bi and/or tridentate ligand and can form very stable complexes with metal ions (so as to give ML or ML_2 complexes at stoichiometric ratios of 1:1 or 1:2) through hydroxyl oxygen atom of phenyl and one of the keto group oxygen atoms. Quercetin complexes of Mn(II), Zn(II) and Sn(II) can be easily interacted with hydrophobic and hydrophilic etoxy moities of CTAB and Tween 20 respectively, and these interactions increase extraction of them. To determine the concentration of Quercetin required for quantitative absorbances of Mn(II), Zn(II) and Sn(II) ions, the procedure was applied to the Quercetin concentrations ranging from 2 to 40 µmol L^{-1}. As could be seen from Figs. 2(a), the absorbance of the analyte ions increased with increasing concentration of the Quercetin up to 30 µmol L^{-1}, and gradually decreased in range 30-40 µmol L^{-1}. The resulting concentration value is enough for the preconcentration of analyte ions, which can be found in low levels in food and vegetable samples. Consequently, a Quercetin concentration of 30 µmol L^{-1} was employed as optimal for the ensuing investigations..

3.3. Effect of CTAB concentration

The cationic surfactant, CTAB as both a sensitivity enhancement auxiliary ligand and counter ion was used to obtain hydrophobic complex of the Mn(II), Zn(II) and Sn(II) ions in presence of Quercetin at pH 4.0. The effect of the CTAB concentration on the absorbance of analyte ions was investigated in the range of 1.5-15 μmol L^{-1} keeping other conditions constant, in order to find the optimal CTAB concentration for the extraction of analyte ions in the model solutions. From the results observed in Figs 2(b), the best absorbance for all the target analyte ions was obtained at CTAB concentration of 8.5 μmol L^{-1}. At higher concentrations than 8.5 μmol L^{-1}, the absorbance gradually decreased. Therefore, a CTAB concentration of 8.5 μmol L^{-1} was employed as optimal for the ensuing investigations.

3.4. Effect of Tween 20 concentration

In this study, the nonionic surfactant, Tween 20 as extracting agent was used to extract complexes of the target analyte ions into the micellar phase of Tween 20. In this context, the effect of Tween 20 concentration on the absorbance of analyte ions was investigated by passing 50 mL of a model solution containing various amounts of the Tween 20 in range of 0.1-1.0 % (v/v). The results are shown in Figs 3(a). The obtained results showed that by increasing Tween 20 concentration up to 0.5 % (v/v) depending on the increasing of hydrophobic micelles, absorbance slowly increased, and remained constant at higher concentrations than 0.5 % (v/v) for the each analyte ions. Therefore, a Tween 20 concentration 0.5 % (v/v) was chosen as optimal for the ensuing investigations.

3.5. Effects of equilibration temperature and time

Equilibration temperature is an important parameter affecting to formation of micelles for this extraction procedure. Determination of optimum equilibrium temperature is necessary to complete extraction of metal complexes to into micellar phase of Tween 20. Thus, the absorbance dependence of metal complexes on equilibration temperature was investigated in range of 30–80 ^{o}C under optimized reagents conditions and ultrasound effect (40 kHz at 300 watt) in Figs 4(a). The results showed that an equilibration temperature of 60 ^{o}C was adequate to achieve the best absorbance for each metal complex. Ultrasound effect is an important stage at which the formation of micelles becomes well dispersed into the aqueous solution. The equilibration time was defined as the time between the addition of the Tween 20 and the end of sonication. Thus, the effect of equilibration time on the absorbance of the each analyte was investigated in the range of 5-30 min under ultrasound power in Figs 4(b). It was observed that after 15 min, the absorbance of the each metal ion had not shown a significant change. Consequently, an equilibration time of 15 min was employed as optimal for the ensuing investigations..

3.6. Effect of sample volume

The target metal ions are generally found at lower concentrations than the detection limit of FAAS in real samples. To explore the possibility of preconcentration of each analyte from different sample volumes, the effect of the sample volume on the absorbance of metal ions was investigated in range of 5-40 mL under optimal reagent conditions. The results are shown at Figs. 3(b). The absorbance of all metal ions was not almost affected by sample volume up to a volume of 25 mL with gradually a decrease in range of 25-40 mL. However, a slight signal fluctuation was observed in range of 10-25 mL for only Zn(II) ions. Therefore, a sample volume of 10 mL was concluded to be enough for analysis of real samples. Because the quantitative recovery values (>95%) were obtained at 10 mL for Zn(II) and 25 mL for Mn(II)/Sn(II) ions, the preconcentration factor was found to be 8 and 20 by the ratio of the sample volume for each metal ion (10 and 25 mL) to the surfactant-rich phase volume (1.25 mL), respectively. In the present study, because UA-CPE process is performed in a centrifuge tube of 50 mL, the highest possible preconcentration factor was found to be 40 from ratio of aqueous phase volume (50 mL) to surfactant rich phase volume (1.25 mL).

3.7. Effect of diluting agent

The obtained surfactant-rich phase after the UA-CPE is relatively viscous and low volume for determination of the metal ions by FAAS. Thus, thisphase must be diluted prior to its analysis by FAAS. For this purpose, several organic solvents such as methanol, ethanol, acidic methanol, acidic ethanol, acetonitrile and tetrahydrofuran (THF) were evaluated to select the diluting agent which can dissolve the surfactant-rich phase entirely and provide the best absorbance. A series of aqueous solutions were investigated using 1.25 mL of each solvent. From the results, the maximum absorbance as a measure of analytical sensitivity, m/s (in which m and s are slope of calibration curve and standard deviation respectively) from calibration data obtained for three replicate measurements of each metal ion at 10, 20 and 30 μg L^{-1} by FAAS after UA-CPE was obtained using 0.1 mol L^{-1} HNO_3 in methanol. For smaller volumes from 1.25 mL, the reproducibility of the absorbance of metal ions was very poor, whereas for higher volumes, there was a decrease in the absorbance of metal ions due to excess dilution. Therefore, a volume of 1.25 mL was found to be suitable for extractive preconcentration.

3.8. Matrix effect

The matrix effect is one of the main problems for determination of metal ions in real samples. To overcome this problem, after the optimization of all the variables that affect the experimental design, the interference effects of some anions and cations that can be potentially found in the real samples were individually investigated depending on increasing concentration of interfering ion in the range of 5-1000 tolerance limits for each ions. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding ±5.0 % in the determination of each metal ion of 50 μg L^{-1}. The results of the study showed that metal ions such as K^+, Cr^{3+}, Fe^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Ag^+, Co^{2+} and Ba^{2+} anions such as PO_4^{3-}, Cl^-, thiourea, citrate and Br^- could be tolerated up to 500-1000 fold mass ratio. On the other hand, metal ions such as Mo^{6+}, Al^{3+}, Pb^{2+}, Cd^{2+} and Hg^{2+} and anions such as $Cr_2O_7^{2-}$, CN^- and NO_2^- can be tolerated up to 100-500-fold mass ratios. As it is understood from the results, the method possesses a reasonably high tolerance limit for the foreign ions. Consequently, the method can be successfully applied for the extraction and determination of the metal ions from real samples.

4. Analytical figures of merit

The analytical figures of the proposed method were obtained by applying 50 mL of the model solutions under the optimum conditions. In the present study, the limit of detection (LOD) for each metal ion is defined as $3S_{blank}/m$ (where m is the slope of the calibration curve and S_{blank} is the standard deviation for twelve replicate measurements of blank) are 0.34, 0.15 and 0.7 μg L^{-1} for Mn(II), Zn(II) and Sn(II) respectively. The limit of quantification (LOQ) ($10S_{blank}/m$) is described as the minimum amount of analyte that can be accurately and precisely measured. The LOQs of Mn(II), Zn(II) and Sn(II) are found 1.17, 0.45 and 2.3 μg L^{-1}, respectively. The sensitivity enhancement factors are defined as the ratio between the slopes of the calibration curves obtained with and without preconcentration, calculated as 116, 175 and 153 for Mn(II), Zn(II) and Sn(II), respectively. The precision was evaluated as relative standard deviations (RSDs %) for five replicate measurements of a solution containing 15 μg L^{-1} of Mn(II), 40 μg L^{-1} of Zn(II), and 20 μg L^{-1} of Sn(II), was found to be 2.3, 2.0 and 2.5 %, respectively. The analytical figures for each metal ion including process with and without preconcentration are also listed in Table 2.

A comparison of the analytical features of the procedure with those of previously published methods in literature for the target metal ions is shown in Table 3. As it is understood from the results, the proposed procedure offers comparable results in terms of analytical features (such as linearity range, LOD, LOQ, accuracy, precision, and sensitivity enhancement factor) along with simple, low cost, sensitive, accurate, reliable and quick determination of trace multi elements. Due to the provided features (reasonable sensitivity, low cost, a low LOD, wide linearity range, accuracy, reliability, and relatively eco-friendly process when considered extraction step), the proposed UA-CPE/FAAS method can be recommended as a suitable alternative to sensitive, but expensive analytical techniques such as ICP-MS, GF-AAS and ICP-OES for determination of trace levels of manganese, zinc and tin in the foods and vegetables. Moreover, GF-AAS or ETAAS requires (i) very clean reagents to avoid blank problems (ii) expert user in his/her area (iii) expensive background correction instruments (like Zeeman) besides contamination from matrix modifiers and interaction of graphite furnace with sample, so as to cause signal fluctuation.

5. The method accuracy and analytical applications

The method accuracy was evaluated by analysis of two SRMs as well as recovery studies from spiked samples. The analysis results of five replicate measurements by FAAS after preconcentration with UA-CPE are shown in Table 4. According to the analysis results of SRMs, the recoveries of the target metal ions were nearly quantitative with a lower RSD than 5.6 %, and the values found for each analyte (with experimental t-value ranging from 1.56 to 2.61) were statistically in good agreement with the certified values of SRMs (with tabulated t-value of 2.78) at 95 % confidence limit.

In order to assess the applicability of the method to analysis of the target metal ions in the selected foods and vegetables, aliquots 10 mL of the samples prepared as given in Section 2.3 were analyzed using the standard addition method under the optimum conditions. The results obtained for the foods and vegetables are given in Table 5(a) and in Table 5(b), respectively. The recoveries of Mn(II), Zn(II) and Sn(II) for the foods samples were found to be higher than 95.6 % with a lower RSD than 3.5 %, respectively. In a similar way, the recoveries of

Mn(II), Zn(II) and Sn(II) for the vegetable samples were found to be higher than 95.8 % with a lower RSD than 2.6 %, respectively. As is understood from the results, the UA-CPE process is safely applied successfully to the preconcentration and determination of the target metal ions from different sample matrices with consistent results.

6. Conclusions

In the current study, a new analytical method for the determination of trace amounts of manganese, zinc and tin in food matrices is described using UA-CPE combined with FAAS. In this study, Quercetin chosen as chelating agent in presence of CTAB at pH 4.0 is for the first time reported for preconcentration and determination of the target metal ions using the UA-CPE. The advantages of the UA-CPE procedure compared to other preconcentration procedures such as liquid-liquid extraction and co-precipitation can be summarized as follows: (a) simplicity, low cost, non-pollution, high recoveries, and high sensitivity enhancement factors; (b) by combination of UA-CPE with FAAS, lower detection limits obtained. (c) Tools used in the proposed procedure including dry ashing step can be usually found in almost every analytical research laboratories. The results of this study clearly show that the use of the proposed UA-CPE/FAAS method is very effective for preconcentration, accurate and reliable determination of trace amounts of manganese, zinc and tin in the selected food matrices.

Compliance with ethics requirements

Authors have no financial relationship with the organization that sponsored the research.

Conflict of interest

Authors declare that he has no conflict of interest.

Ethical approval

This article does not contain any studies with human or animal subjects.

Informed consent

On behalf of other authors, informed consent was obtained from all individual participants included in the study.

References

1. L.A. Brunborg, K. Julshamn, R. Nortvedt and L. Frøyland, Food Chem, 2006, **96**, 524–531.

2. R.J.V. Saun, Small Ruminant Res,2005, **61**, 153–164.

3. M. Hernick and C.A. Fierke, Arch. Biochem. Biophys, 2005, **443**, 71–84.

4. Commission Regulation (EC) No 1881/2006 of 20 December 2006, Setting maximum levels for certain contaminants in foodstuffs. Official Journal of European Communities L 364:5–24.

5. S.B. GoldhaberRegul. Toxicol. Pharm, 2003, **38**, 232–242.

6. U. Tinggi, C. Reilly and C. Patterson, Food Chem, 1997, **60**,123–128.

7. H.E. Feiding, L.I. Huachang and F.E.N.G. Xianjin, Chinese J Inorg Chem, 2011, **2,** 009.

8. D.E.N.G. Quan-dao, X.U. Guang, L.I.N. Guan-chun, L.I.U. Jian-fa and L.I.U. Ling-zhi, Metallurgical Analysis, 2011, **1,** 009.

9. I. Trandafir, V. Nour and M.E. Ionica, Pol J Environ Stud, 2012, **21(3),** 749-754.

10. D.V. Biller and K.W. Bruland, Marine Chem, 2012, **130,** 12-20.

11. A. Milne, W. Landing, M. Bizimis and P. Morton, Anal Chim Acta, 2010, **665(2),** 200-207.

12. A. Baysal, M. Ozcan and S. Akman, Food Chem. Toxicol, 2011, **49(6)**, 1399-1403.

13. P. Olmedo, A. Pla, A.F. Hernández, O. López-Guarnido, L. Rodrigo and F. Gil, Anal Chim Acta, 2010, **659(1),** 60-67.

14. L.S. Nunes, J.T. Barbosa, A.P. Fernandes, V.A. Lemos, W.N. Santos, M.G.A. Korn and L. Teixeira, Food Chem, 2011, **127(2),** 780-783.

15. P. Pohl and P. Jamroz, J. Anal. At. Spectrom, 2011, **26(7),** 1317-1337.

16. H. Sereshti, V. Khojeh and S. Samadi, Talanta, 2011, **83(3),** 885-890.

17. I. Aydin, U. Yuksel, R. Guzel, B. Ziyadanogullari and F. Aydin, At. Spectrosc, 2010, **31(2)**, 67.

18. J.G. Ibanez, A. Carreon-Alvarez, M. Barcena-Soto and M. Casillas, J. Food Compos. Anal, 2008, **21**, 672– 683.

19. E.G.P. da Silva, V. Hatje, W.N.L. dos Santos, L.M. Costa, A.R.A. Nogueira and S.L.C. Ferreira, J. Food Compos. Anal, 2008, **21**, 259– 263.

20. B. Welz and M. Sperling, Atomic Absorption Spectrometry. Wiley-VCH, Weinheim, Germany, 1999.

21. S.L.C. Ferreira, A.S. Souza, G.C. Brandao, H.S. Ferreira, W.N.L. dos Santos, M.F. Pimentel and M.G.R. Vale, Talanta, 2008, **74**, 699–702.

22. V. Camel, Spectrochim. Acta, Part B, 2003, **58**, 1177–1233.

23. P.T. Anastas, Critical Reviews of Analytical Chemistry, 1999, **29**, 167–175.

24. M.A. Bezerra, M.A. Zezzi Arruda and S.L. Costa Ferreira, Appl. Spectrosc. Rev, 2005, **40**, 269–299.

25. C. Bosch Ojeda, andF. Sanchez Rojas, Anal Bioanal Chem, 2009, **394**, 759–782.

26. K. Pytlakowska, V. Kozik and M. Dabioch, Talanta, (2013, **110**, 202-228.

27. I.O. Akinyele and O.S. Shokunbi, Food Chem, 2015, **173**, 682-684.

28. M.R. Hutcheson, M.D. Engelmann and I.F. Cheng, BioMetals, 2005, **18,** 43–51.

29. Š. Ramešová, R. Sokolová , I. Degano, J. Bulíčková, J.Žabka and M. Gál, Anal Bioanal Chem, 2012, **402(2),** 975-982.

30. M. Musialik, R. Kuzmicz, T.S. Pawlowski and G. Litwinienko, J. Org. Chem, 2009, **74(7),** 2699–2709.

31. Y. Zheng, I.S. Haworth, Z. Zuo, M.S.S. Chow and A.H.L. Chow, J. Pharm. Sci, 2005, **94(5),** 1079–1089.

32. G.M. Escandar and L.F. Sala, Can. J. Chem, 1991, **69(12),** 1994–2001.

33. I.G. Zenkevich and S.V. Guschina, J. Anal. Chem, 2010, **65(4),** 371–375.

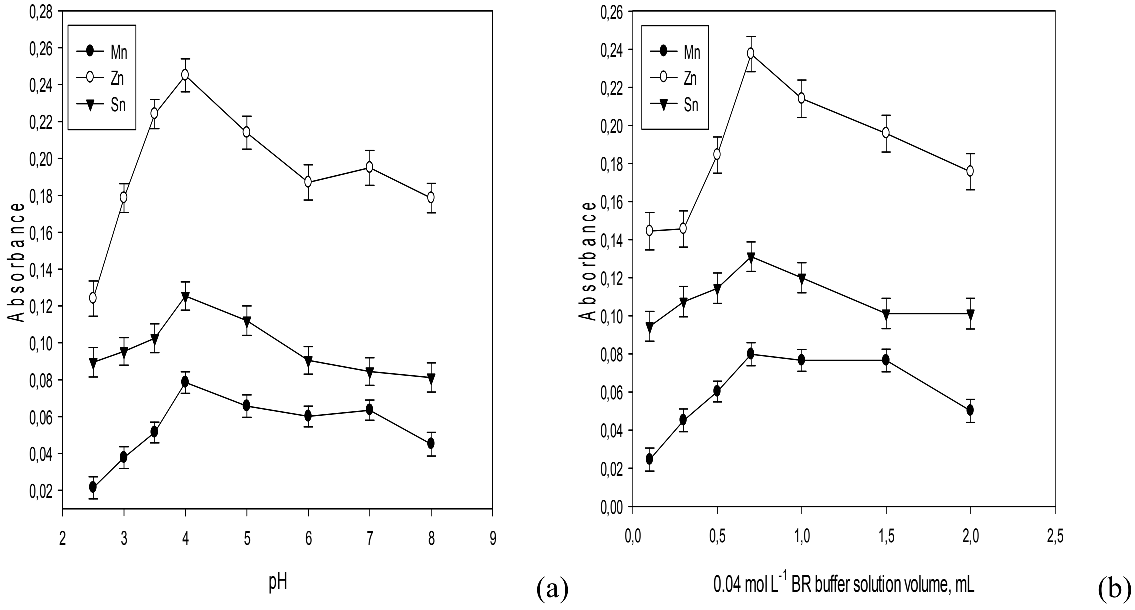
34. A.M.O. Brett andM.E. Ghica, Electroanal,, 2003, **15,** 1745–1750.

35. K. Boutakhrit, M. Crisci, F. Bolle and J. Van Loco, Food Addit Contam A, 2011, **28(2),** 173-179.

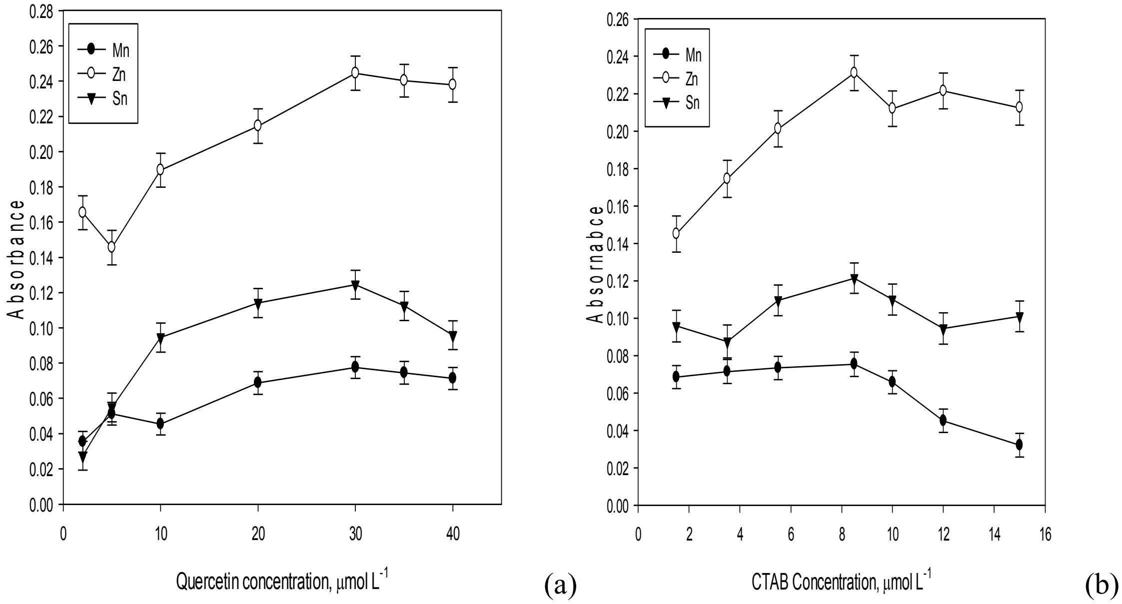
36. Z. Hongxing and R. Yu-Kui, J. Chem, 2011, **8(2),** 782-786.

37. L.S. Nunes, J.T. Barbosa, A.P. Fernandes, V.A. Lemos, W.N. Dos Santos, M.G.A. Korn and L.S. Teixeira, Food Chem, 2011, **127(2),** 780-783.

38. L. Ranjbar, Y. Yamini, A. Saleh, S. Seidi and Faraji, M. MicrochimActa, 2012, **177(1-2),** 119-127.

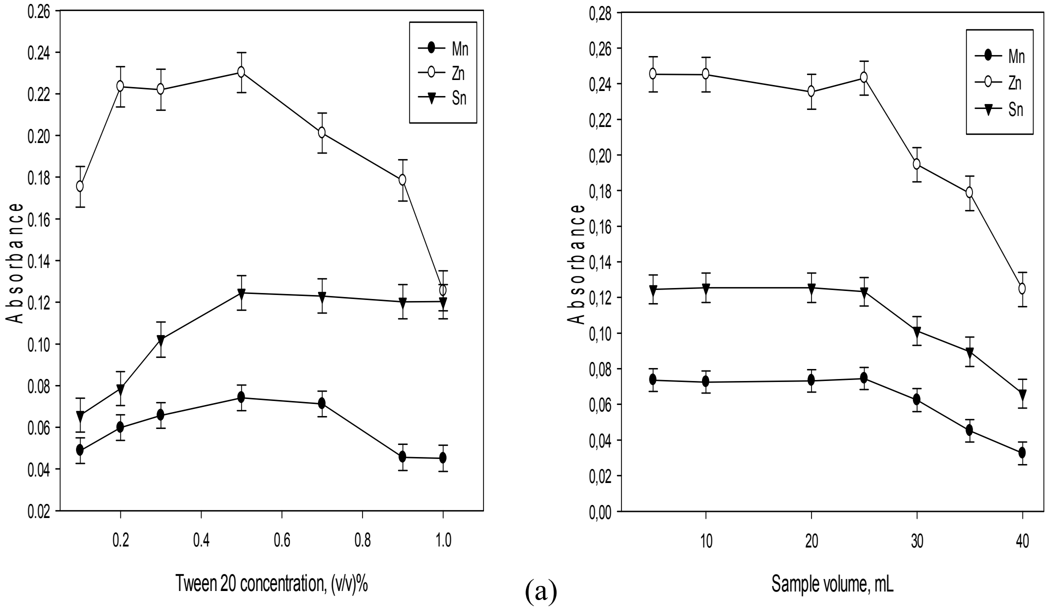


Figures 1 Effect of (a) pH and (b) buffer volume on the absorbance of the target metal ions. The optimum experimental conditions were as indicated in Section 2.4.



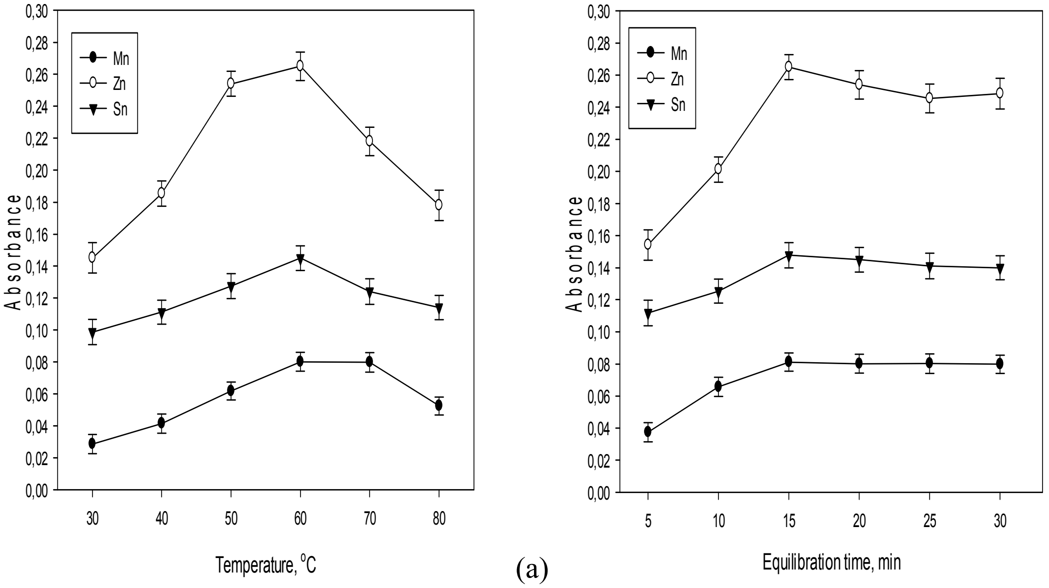
(a) (b)

Figures 2 Effect of (a) Quercetin and (b) CTAB concentrations on the absorbance of the target metal ions. The optimum experimental conditions were as indicated in Section 2.4.



(a) (b)

Figures 3 Effect of (a) Tween 20 concentration and (b) sample volume on the absorbance of the target metal ions. The optimum experimental conditions were as indicated in Section 2.4.



(a) (b)

Figure 4 Effect of (a) equlibration temperature and (b) time on the absorbance of the target metal ions. The optimum experimental conditions were as indicated in Section 2.4.

Table 1 Parameters and operating conditions for the determination of target metals using the FAAS

Parameters	Mn	Zn	Sn
Wavelength (nm)	279.5	213.9	286.3
Lamp current (mA)	10	10	8
Spectral bandwidth (nm)	0.2	0.5	0.2
Burner height (mm)	7	7	9
Air/acetylene flow rates (L min^{-1})	15/2	15/2	15/3

Table 2 Analytical figures of merit obtained for the target metals under the optimum conditions

Analytical features	After preconcentration			Before preconcentration		
	Mn	Zn	Sn	Mn	Zn	Sn
Slope	9.3×10^{-3}	1.38×10^{-2}	5.7×10^{-3}	8.02×10^{-5}	7.89×10^{-5}	3.73×10^{-5}
Intercept	7.0×10^{-4}	9.5×10^{-3}	1.2×10^{-3}	4.5×10^{-3}	7.6×10^{3}	11.5×10^{-2}
Correlation coefficient (r^2)	0.9945	0.9982	0.9973	0.9938	0.9945	0.9956
Linear range (μg L^{-1})	1.0-70	0.8-125	2.5-190	40-1200	35-1200	76-1500
Detection limit (μg L^{-1})	0.34	0.15	0.7	11.4	10.5	22.8
Limit of quantification (μg L^{-1})	1.17	0.45	2.3	38	35	76
RSD %	2.3	2.0	2.5	2.6	3.2	2.8
Recovery %	97.2	102.8	96.9	96.5	101.3	97.5
Sensitivity enhancement factor	116	175	153	-	-	-

Table 3 Comparison of the proposed UA-CPE/FAAS method with the other methods reported in the literature

Sample	Technique	Linear range (µg L^{-1})			LOD (µg L^{-1})			EF			RSD (%)			References
		Mn	Zn	Sn	Mn	Zn	Sn	Mn	Zn	Sn	Mn	Zn	Sn	
Foods	FAAS	2-310	1–300	-	2.6	1.5	-	27	39	-	3.0	2.3	-	29
Foods	ICP OES	-	-	500–5000	-	-	200	-	-	-	-	-	11.3	35
Corn Seeds	ICP-MS	-	-	-	4.40	15.03	0.36	-	-	-	4.18	1.88	13.08	36
Vegetables	HR-CS FAAS	-	-	-	-	58	-	-	-	-	-	5-11	-	37
Environmental samples	ICP OES	0.75-200	5-200	-	0.1	0.1	-	102	86	-	6.0	4.5	-	38
Foods and vegetables	FAAS	1.0-70	0.8-125	2.5-190	0.34	0.15	0.7	116	175	153	2.3	2.0	2.5	This work

LOD: Detection limit, EF: Sensitivity enhancement factor, RSD: Relative standard deviation

FAAS: Flame atomic absorption spectrometry

ICP OES: Inductively coupled plasma optical emission spectrometry

ICP-MS: Inductively- coupled-plasma mass spectrometry

HR-CS FAAS: High-resolution continuum source flame atomic absorption spectrometry

ICP-OES: Inductively coupled plasma optical emission spectrometry

Table 4 The analysis results of target analyte ions in SRMs after application of proposed method (n: 5)

SRMs	Mn (µg kg^{-1})				Zn (µg kg^{-1})				Sn (µg kg^{-1})			
	Added	Found	RDS %	Student t-test	Added	Found	RDS %	Student t-test	Added	Found	RDS %	Student t-test
[a]SRM 1548a	-	5.6±0.2	3.6	1.68	-	23.9±0.8	3.3	1.96	-	16.5±0.6	3.6	2.61
Typical diet	20	25.3±0.8	3.2	-	10	33.8±1.2	3.5	-	10	26.6±0.9	3.4	-
[b]SRM 2385	-	35.4±2.0	5.6	1.56	-	8.6±0.3	3.5	1.71	-	-	-	-
Slurried spinach	5	40.3±1.8	4.5	-	15	23.3±0.7	3.0	-	-	-	-	-

[a]Certified values (1000 fold-diluted) are 5.75±0.17, 24.6 ±1.79 and 17.2±2.57 µg kg^{-1} for Mn, Zn and Sn, respectively

[b]Certified values are 36.8±3.0 (10 fold-diluted) and 8.37±0.37 µg kg^{-1} for Mn and Zn, respectively

[b]The tabulated t-value is 2.78 for four degrees of freedom at 95 % confidence level

Table 5(a) The analysis results of target metal ions extracted and preconcentrated from food samples (n: 3)

Sample	Added ($\mu g\ kg^{-1}$)			Found ($\mu g\ kg^{-1}$)			RSD (%)		
	Mn	Zn	Sn	Mn	Zn	Sn	Mn	Zn	Sn
Corn flakes	-	-	-	11.8	2.1	5.6	2.1	2.7	1.8
	15	20	25	26.2	21.5	30.1	1.7	2.4	1.6
Rice noodles	-	-	-	4.3	15.9	9.2	1.9	2.9	2.1
	15	20	25	18.4	35.2	33.8	1.5	2.8	1.8
Butter cookies	-	-	-	39.1	6.4	15.7	1.7	3.5	2.9
	15	20	25	52.4	26.8	40.3	1.5	3.0	2.5
Brown rice	-	-	-	8.5	10.2	17.3	1.4	2.4	3.1
	15	20	25	22.8	29.3	41.2	1.1	2.1	2.7
Dried apricot	-	-	-	3.2	2.7	4.4	2.0	2.5	1.9
	15	20	25	17.5	22.1	28.8	1.8	2.0	1.6
Dried apple	-	-	-	1.8	3.1	6.7	2.5	1.9	2.4
	15	20	25	17.1	23.7	30.9	2.2	1.7	2.2
Walnut	-	-	-	19.4	8.7	10.3	1.5	2.6	2.5
	15	20	25	35.3	28.0	34.8	1.1	2.3	1.9
Almond	-	-	-	22.5	15.6	6.9	1.8	2.8	2.7
	15	20	25	36.8	36.8	31.6	1.5	2.5	2.3
Oatmeal	-	-	-	10.3	4.8	11.2	2.3	2.9	1.8
	15	20	25	25.7	24.4	35.2	1.9	2.7	1.5
Cashew	-	-	-	33.7	14.2	4.1	2.2	1.8	2.1
	15	20	25	47.8	33.5	28.3	1.7	1.5	1.7

Table 5(b) The analysis results of target metal ions extracted and preconcentrated from vegetable samples (n: 3)

Sample	Added (μg kg^{-1})			Found (μg kg^{-1})			RSD (%)		
	Mn	Zn	Sn	Mn	Zn	Sn	Mn	Zn	Sn
Radish	-	-	-	25.8	16.1	14.7	1.7	2.3	1.9
	15	20	25	40.1	36.8	39.1	1.5	2.0	1.6
Cowslip	-	-	-	39.2	25.6	8.5	1.4	2.5	1.8
	15	20	25	54.6	44.4	32.7	1.2	2.2	1.7
Mushroom	-	-	-	22.1	33.5	6.8	1.9	1.7	2.2
	15	20	25	36.2	54.4	32.4	1.6	1.5	1.9
Green tea	-	-	-	13.5	41.2	15.4	1.7	1.8	2.6
	15	20	25	29.0	60.1	38.9	1.3	1.4	2.1
Black tea	-	-	-	10.2	33.6	20.7	1.5	1.9	2.4
	15	20	25	24.7	51.9	43.8	1.3	1.6	2.2
Mint	-	-	-	6.5	12.8	9.2	1.4	2.2	1.8
	15	20	25	21.8	33.3	33.4	1.1	2.0	1.5
Tomato	-	-	-	8.4	27.6	2.8	1.6	1.7	1.7
	15	20	25	22.9	47.0	28.1	1.2	1.3	1.4
Spinach	-	-	-	35.8	55.2	3.6	1.8	1.8	1.9
	15	20	25	49.9	72.5	27.9	1.5	1.4	1.7
Garlic	-	-	-	17.5	8.7	5.1	1.4	2.1	2.4
	15	20	25	31.8	27.8	30.8	1.2	1.8	2.0

Graphical Abstract