Combination of cloud point extraction and flame atomic absorption spectrometry for preconcentration and determination of nickel and manganese ions in water and food samples

Çiğdem Arpa Şahin*, Melis Efeçınar, Nuray Şatıroğlu

Hacettepe University, Chemistry Department, 06800, Beytepe, Ankara, Turkey

ABSTRACT

A simple, rapid, inexpensive, and nonpolluting cloud point extraction (CPE) technique has been improved for the preconcentration and determination of nickel and manganese. After complexation with p-nitrophenylazoresorcinol (Magneson I), the analytes could be competitively extracted in a surfactant octylphenoxy polyethoxyethanol (Triton X-114), prior to determination by flame atomic absorption spectrometry (FAAS). The effects of experimental conditions such as pH, concentration of chelating agent and surfactant, equilibration temperature and time on CPE were studied. Under the optimum conditions, preconcentration of a 25 mL sample solution permitted the detection of 2.7 ng mL^{-1} Ni^{2+} and 2.9 ng mL^{-1} Mn^{2+} with enrichment factors of 17 and 19 for Ni^{2+} and Mn^{2+}, respectively. The developed method was applied to the determination of trace nickel and manganese in water and food samples with satisfactory results.

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1. Introduction

Nickel is the metal component of the enzyme urease and is considered to be essential for plants and some domestic animals. More attention has been paid on the toxicity of nickel in low concentration, the fact that nickel can cause an allergic reaction and that certain nickel compounds may be carcinogenic [1–3]. Manganese is necessary for the proper function of several enzymes and is an essential micro-nutrient for the function of the brain, nervous system and normal bone growth. It optimizes enzyme and membrane transport functions [4–6]. Similar to other essential metals, both excess and deficiency of manganese in the body can cause serious impairment of vital physiological and biochemical processes, excessive intake can cause lesions, headache, psychotic behavior, drowsiness and other related symptoms and/or diseases [7–9]. Therefore, it is important from an analytical point of view to develop sensitive and economical methods for determination of trace amounts of nickel and manganese [10,11]. The use of micellar systems such as CPE for separation and preconcentration has attracted considerable attention in the last few years 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 [12]. CPE 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 liquid–liquid extraction [13,14].

CPE consist of three simple steps: (1) solubilization of the analytes in the micellar aggregates; (2) clouding; (3) phase separation for analysis. When a surfactant solution is heated over a critical temperature, the solution easily separates into two distinct phases: one contains a surfactant at a concentration below, or equal to, a critical micelle concentration; the other is a surfactant-rich phase. The hydrophobic compounds initially present in the solution and bound to the micelles are extracted to the surfactant-rich phase. This phenomenon is observed, in particular, for polyoxyethylene surfactants and can be attributed to the two ethylene oxide segments in the micelle that repel each other at low temperature when they are hydrated and attract each other when the temperature increases owing to the dehydration.

Numerous organic reagents such as PAN, PAR, DDTC and TAN have been used for the CPE of nickel and manganese [15,16]. In analytical chemistry, azo reagents have been widely used as chelating agent to selective and sensitive determination of metals. The complex formation reactions between Magneson I and nickel and manganese are very fast and the selectivity of Magneson I is

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* Corresponding author. Tel.: +90 312 2977967; fax: +90 312 2992163.
E-mail address: carpa@hacettepe.edu.tr (Ç. Arpa Şahin).

enhanced by suitable selection of pH. Even so, according our knowledge, the use of Magneson I for preconcentration has not been reported before.

In the present work a simple, selective and sensitive CPE method for preconcentration and determination of nickel and manganese ions in various real samples using Magneson I as selective and sensitized complexing agent and Triton X-114 as surfactant in basic media was established.

2. Experimental

2.1. Apparatus

A Perkin-Elmer Model Analyst 800 Atomic Absorption Spectrophotometer equipped with deuterium back ground correction and air-acetylene burner was used for Ni and Mn measurements in both surfactant-rich and poor phase. Nickel and manganese hollow cathode lamps were used as radiation source. The most sensitive wavelengths (nm) and lamp currents (mA) used for the determination of the analytes were as follows: Ni 232.0 and 25, and Mn 279.5 and 20 respectively. Slit widths were 0.2 nm. All of the absorbance measurements were carried out in air/acetylene flame at flow rates of 17 and 2.0 L min^{-1}. The nebulizer flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal by aspirating a solution containing the analyte in methanol containing 0.1 mol L^{-1} nitric acid. A Fisher Scientific Accumet Model 15 pH meter was used to measure pH values. A Clifton Model NE1-22 thermostatic bath, maintained at the desired temperature, was used for cloud point temperature experiments. A Hettich, EBA 21 model centrifuge was used to accelerate the phase separation.

2.2. Reagents

All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.1 MΩ cm) obtained from a Barnstead, Nanopure Diamond purification system. Stock solutions were prepared from appropriate amounts of the respective nitrates (E. Merck, Darmstadt, Germany) as 1000 mg/L in deionized water, and diluted daily for obtaining working solutions prior to use. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with deionized water. The non-ionic surfactant Triton X-114 (Sigma–Aldrich, Milwaukee, USA) was used without further purification. A 0.1% (w/v) Magneson I solution was prepared by dissolving appropriate amount of Magneson I obtained from Sigma–Aldrich in ethanol. A buffer solution of pH 11.5 was prepared by using Sodium hydrogen orthophosphate (E. Merck) and Sodium hydroxide (E. Merck) at appropriate concentrations. Nitric acid (E. Merck), methanol (E. Merck) and sodium chloride (E. Merck) were used. Laboratory glassware was kept overnight in 10% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in dust free environment. The following certified reference waters were used for method validation: Surface water SPS-SW1 and SPS-SW2 were obtained from Spectrapure Standards, Norway.

2.3. Samples and sample pretreatment

Tomato paste, hazelnut, multi grain bread, white bread, spinach, lettuce and cabbage samples were purchased from local supermarkets at Ankara in Turkey. First, spinach, lettuce and cabbage samples were cleaned with tap water and double distilled water. Then, these samples, tomato paste and bread samples were dried at 110 °C. Each of the dried varieties of samples and hazelnut samples were ground to reduce particle size and then thoroughly mixed to ensure homogeneity samples individually. Masses of 500 mg of tomato paste, hazelnut, multi grain bread, white bread, spinach,

Table 1
Optimum conditions for the CPE of nickel and manganese ions.

Optimum conditions for CPE of Ni and Mn	Value
Concentration of chelating agent	0.1% (w/v)
Concentration of surfactant	0.1% (v/v)
pH range	11.5–12.0
Equilibrium temperature (°C)	70
Equilibrium time (min)	40
Centrifugation rate (rpm)	6000
Centrifugation time (min)	5
Diluent	0.1 mol L^{-1} HNO$_3$ in ethanol

lettuce and cabbage were transferred into separate 250 mL beakers and 5 mL of 0.5 mol L^{-1} nitric acid was added to moisten the samples thoroughly. This was followed by adding 10 mL of concentrated nitric acid and heating on a hot plate (130 °C) for 3 h. After cooling to room temperature, 5 mL of concentrated perchloric acid was added drop wise. The beaker was heated gently until completion of sample decomposition resulting in a clear solution. This was left to cool down and then was transferred into a 100 mL volumetric flask by rinsing the interior of the beaker with small portions of 0.1 mol L^{-1} nitric acid and the solution was filled to the mark with the same acid [17].

2.4. CPE procedure

For the CPE, aliquots of 25 mL of the standard or sample solution containing analyte ion (5–200 ng mL^{-1}), 2 mL of phosphate buffer solution (pH 11.5), 1 mL of NaCl solution (0.2 mol L^{-1}), 1 mL of 0.1% (w/v) Magneson I solution and 1 mL of 0.1% (v/v) Triton X-114 solution were placed in a graduated centrifuge tube. This solution was heated at 70 °C for 40 min in the thermostatic bath for equilibration and then separation of two phases was achieved by centrifugation for 5 min at 6000 rpm. The mixture was cooled in an ice bath to increase the viscosity of the surfactant-rich phase, and the supernatant aqueous phase was carefully removed with a pipette. The micellar phase was treated with 1 mL 0.1 mol L^{-1} HNO$_3$ in ethanol in order to reduce its viscosity and facilitate sample handling. The final solution was introduced to the flame by conventional aspiration.

3. Results and discussion

The optimum conditions for CPE method for preconcentration and determination of nickel and manganese ions were examined and the selected values are presented in Table 1.

3.1. Effect of pH

pH plays a unique role on metal-chelate formation and subsequent extraction [18–21]. Separation of metal ions by cloud point method involves the prior formation of a complex with sufficient hydrophobicity to be extracted in to the small volume of surfactant-rich phase. Extraction recovery depends on the pH at which complex formation occurs. In order to find optimum pH, the effect of pH in the range 3–13 on the complex formation reactions was investigated. Fig. 1 shows the effect of pH on the extraction of the Ni^{2+} and Mn^{2+} complexes. As can be seen in Fig. 1, a pH value of around 11.5 found to be the optimum for the quantitative extraction of Magneson I-nickel and Magneson I-manganese complexes.

3.2. Effect of Magneson I concentration

Magneson I is a phenylazo compound which acts as a ligand. It complexes the metal ions through the azo-nitrogen atom, the
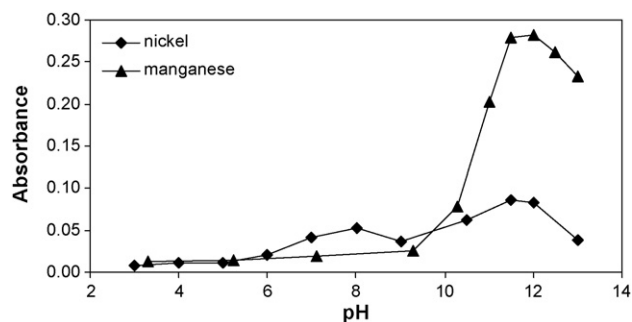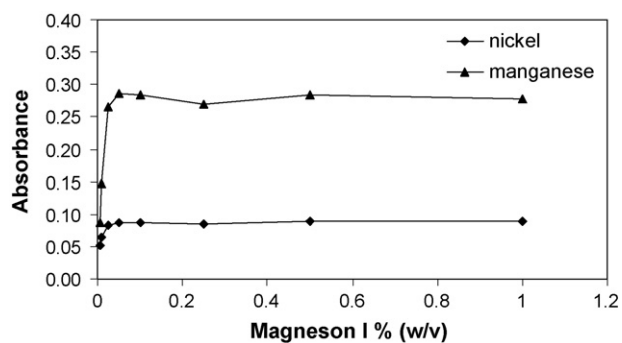
Fig. 1. Influence of the pH on CPE of nickel and manganese. Sample, 25 mL, 200 ng mL^{-1}; surfactant, 0.1% Triton X-114; ligand, 0.1% Magneson I; dilution solvent, 0.1 mol L^{-1} HNO$_3$ in ethanol; equilibration temperature, 70 °C; equilibration time, 40 min.

amino-nitrogen atom, and o-hydroxyl group. In order to study the influence of Magneson I concentration on analytical response for nickel and manganese, different concentrations of the Magneson I in the range of 5×10^{-3}–1.00% (w/v) were used, and general procedure was applied. The absorbances as a function of the concentration of Magneson I were shown in Fig. 2. As can be seen CPE efficiency increased rapidly as the concentration of Magneson I increased from 5×10^{-3}% to 5×10^{-2}%, then kept almost constant with further increase in the Magneson I concentration up to 1.00%. Therefore, Magneson I concentration of 5×10^{-2}% was chosen for subsequent experiments.

3.3. Effect of Triton X-114 concentration

The amount of Triton X-114 not only affected the extraction efficiency, but also the volume of surfactant-rich phase. A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{org}/V_{aqueous}$), thus improving its concentration factor. [22]. There is a narrow range within which easy separation, maximum extraction efficiency and analytical signal are accomplished. The variation of the analytical signal of Ni^{2+} and Mn^{2+} within the Triton X-114 concentration range of 0.05–1% (v/v) was examined (Fig. 3). Quantitative extraction was observed when the Triton X-114 concentration was higher than 0.10% (v/v). At lower concentrations, the extraction efficiency of complex is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. With increase of Triton X-114 concentration above 0.20% (v/v) the signals decrease because of the increment in the volumes and the viscosity of the surfactant phase, leading to poor sensitivity [23]. So, a concentration of 0.1% (v/v) was chosen as the optimum Triton X-114 concentration in order to achieve the highest possible extraction efficiency.

Fig. 2. Influence of Magneson I on CPE of nickel and manganese. Sample, 25 mL, 200 ng mL^{-1}; surfactant, 0.1% Triton X-114; pH 11.5; dilution solvent, 0.1 mol L^{-1} HNO$_3$ in ethanol; equilibration temperature, 70 °C; equilibration time, 40 min.
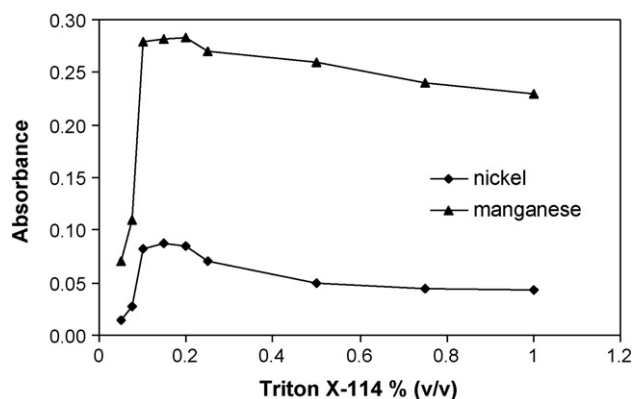
Fig. 3. Influence of Triton X-114 concentration on CPE of nickel and manganese. Sample, 25 mL, 200 ng mL^{-1} pH 11.5; ligand, 0.1% Magneson I; dilution solvent, 0.1 mol L^{-1} HNO$_3$ in ethanol; equilibration temperature, 70 °C; equilibration time, 40 min.

3.4. Effects of the equilibrium temperature and time

When temperature increases, the system is further away from the cloud point, causing the nonionic surfactant to be less water soluble. To achieve easy phase separation, optimal equilibration temperature and incubation time are necessary to complete extraction. The effect of the equilibration temperature and time was studied with a range of 20–80 °C and 5–60 min respectively. It was found that an equilibration temperature of 70 °C and a time of 40 min were adequate to achieve quantitative extraction.

3.5. Effect of viscosity

In order to facilitate the sample introduction in FAAS nebulizer, it was necessary to decrease the surfactant-rich phase viscosity. Different solvents such as acetone, ethanol, methanol and acidic solutions of ethanol and methanol were tried in order to select the one producing the optimal results regarding sensitivity. The best result was obtained for acidic solution of ethanol. A volume of 1 mL of ethanol solution containing 0.1 mol L^{-1} nitric acid was added to the surfactant-rich phase after separation. This amount of ethanol was chosen to ensure a sufficient volume of sample for conventional aspiration. For smaller volumes, the reproducibility of the signals was very poor, whereas for higher volumes, there was a decrease in the signal due to dilution.

3.6. Effect of ionic strength

For the investigating the influence of ionic strength on performance of CPE, various experiments were performed by adding different amount of NaCl (0.005–0.05 mol L^{-1}). Other experimental conditions were kept constant. The results showed that ionic strength has no significant effect on the enrichment factor. Thus ionic strength was kept constant at 0.01 mol L^{-1} with sodium chloride.

3.7. Interferences

The effect of foreign ions on the determination of Ni^{2+} and Mn^{2+} by the proposed method was investigated by measuring the absorbance of the solutions containing 200 ng mL^{-1} of each metal ion in the presence of various amounts of other ions. The tolerance limit was defined as the concentration of added ion that caused less than ±5% relative error in the determination of Ni^{2+} and Mn^{2+}. The maximum tolerances of the investigated cations and anions are

Table 2
Effect of interferent ions on preconcentration of 200 ng mL^{-1} nickel and manganese.

Ions	Metal to interferent ratio (w/w)	
	Ni	Mn
Al^{3+}	1:1000	1:500
Fe^{3+}	1:10	1:50
Cr^{3+}	1:10	1:10
Zn^{2+}	1:10	1:50
Cd^{2+}	1:100	1:500
Co^{2+}	1:50	1:500
Cu^{2+}	1:500	1:1000
Pb^{2+}	1:500	1:1000
Mn^{2+}	1:500	–
Ni^{2+}	–	1:500
Mg^{2+}	1:500	1:500
Na^+	1:5000	1:5000
CO_3^{2-}	1:500	1:1000
SCN^-	1:500	1:1000
NO_3^-	1:500	1:500
Cl^-	1:5000	1:5000

Table 3
Analytical characteristics of the method.

Parameter	Analytical feature	
	Ni	Mn
Enrichment factor	19	17
Sample volume, mL	25	25
Limit of detection, ng mL^{-1} (3s)	2.7	2.9
Limit of quantification, ng mL^{-1} (10s)	9.0	9.7
Precision (200 ng mL^{-1}, n = 10) RSD (%)	1.8	1.3
Linear range, ng mL^{-1}	10–400	10–400

given in Table 2. Ni^{2+} and Mn^{2+} recoveries were nearly quantitative in the presence of other ions.

3.8. Analytical features

The calibration graphs were linear in the range of 10–400 ng mL^{-1} nickel and 10–400 ng mL^{-1} manganese under the optimum conditions of general procedure. The regression equations for nickel and manganese determination were $A = 4.31 \times 10^{-4}C + 8.87 \times 10^{-4}$ and $A = 1.46 \times 10^{-3}C + 7.78 \times 10^{-3}$, respectively, where A is the absorbance and C is the metal concentration in solution (ng mL^{-1}). The correlation coefficient of the calibration curve equations was higher than 0.990 for all elements, which indicates that a good linear regression was established between the absorbances and the concentrations. The equation obtained by direct aspiration in FAAS without the preconcentration procedure, the linear equation for nickel (1000–4000) was $A = 2.23 \times 10^{-5}C + 2.00 \times 10^{-4}$ ($R^2 = 0.99$) and for manganese (500–2000) was $A = 8.48 \times 10^{-5}C + 1.15 \times 10^{-3}$ ($R^2 = 1.00$). The preconcentration factor for Ni^{2+} and Mn^{2+} calculated by dividing the aqueous phase volume to the final volume of preconcentrated phase was 17, while the enhancement factor as the ratio of slope of calibration curve of the analytes after preconcentration to that prior preconcentration was and enhancement factor were 19 and 17 for Ni^{2+} and Mn^{2+} respectively.

The precision of the method, calculated as the relative standard deviation of ten independent measurements carried out 200 ng mL^{-1} nickel or manganese. The limit of detection (LOD) is defined as the concentration equivalent to three times the standard deviation of 10 measurements of the blank [24] and is the lowest analyte concentration that produces a response detectable above the noise level of the system. The limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured. LOQ, defined as ten times the standard deviation of the blank (n = 10). Table 3 gives the analytical features of the method.

Table 4
Determination of analyte ions in certified reference materials using proposed methodology (n = 4).

Ion	Certified (µg L^{-1})	Found (µg L^{-1})	RSD %	Recovery %
SP-SW1				
Ni	10	10.1	1.2	101.0
Mn	10	9.76	1.1	97.6
SP-SW2				
Ni	50	50.4	0.9	100.8
Mn	50	49.3	1.3	98.6

Table 5
Determination of analyte ions in tap water and some real food samples using proposed methodology (n = 4).

Sample	Added (µg g^{-1})	Found (µg g^{-1})	Recovery %
Tap water			
Ni	0	n.d[a]	–
	5	4.8 ± 0.1	96.6
	10	9.7 ± 0.3	97.1
	50	51.3 ± 1.3	102.7
Mn	0	12.1 ± 0.8	–
	5	16.6 ± 0.8	97.4
	10	21.4 ± 0.2	96.7
	50	64.7 ± 1.1	104.2
Tomato paste			
Ni	0	n.d	–
	10	9.4 ± 1.4	94.0
	20	19.2 ± 0.8	96.0
Mn	0	n.d	–
	10	9.95 ± 1.1	99.5
	20	19.6 ± 0.7	98.0
Hazelnut			
Ni	0	n.d	–
	10	10.2 ± 0.6	102.0
	20	19.7 ± 1.2	98.5
Mn	0	83.0 ± 1.0	–
	10	93.5 ± 1.2	105.0
Multi grain bread			
Ni	0	2.4 ± 0.8	–
	10	12.5 ± 0.6	101.0
Mn	0	28.4 ± 1.1	–
	10	38.2 ± 1.3	98.0
White bread			
Ni	0	2.7 ± 0.7	–
	10	12.5 ± 0.9	98.0
Mn	0	4.4 ± 1.0	–
	10	15.0 ± 1.1	106.0
Spinach			
Ni	0	2.8 ± 1.4	–
	10	13.0 ± 0.9	102.0
Mn	0	39.6 ± 1.5	–
	10	49.8 ± 1.2	102.0
Lettuce			
Ni	0	n.d	–
	10	10.5 ± 0.7	105.0
	20	20.3 ± 1.3	101.5
Mn	0	24.0 ± 1.0	–
	10	34.4 ± 1.0	104.0
Cabbage			
Ni	0	15.3 ± 1.3	–
	10	25.8 ± 0.8	105.0
Mn	0	46.9 ± 1.2	–
	10	57.3 ± 1.5	104.0

[a] Not detected

Table 6
Comparison of the characteristic data between recent published CPE methods and presented method.

Reagent	Surfactant	Element	Sample volume (mL)	EF[a]/PF[b]	LOD[c] (μg L^{-1})	Sample	Reference
Me-BTABr	Triton X-114	Ni	10	23	1.1	Water	[25]
APDC	Triton X-114	Ni	10	20	11.0	Water	[26]
PAN	Triton X-114	Ni	10	25	6.0	Water	[27]
PAN	Triton X-114	Mn	50	49.1	0.39	Milk	[28]
1-nitroso-2-naphthol	PONPE 7.5	Ni	10	29	1.09	Water	[29]
PHBI	Triton X-114	Ni	15	30	2.1	Biological and environmental	[30]
PAR	OP-7	Mn	100	20	5	Water	[15]
Ligandless	Tween-80	Ni	5-10	10	1.1	Water, food, pharmaceutical	[31]
Dithizone	Triton X-114	Ni	10	39	1.2	Water	[32]
PMBP	Triton X-100	Mn	10	20	1.45	Water	[33]
TAR	Triton X-114	Mn	70	84	0.60	Saline effluents of a petroleum refinery	[34]
TAN	Triton X-114	Mn	50	57.6	0.28	Water	[35]
IYPMI	Triton X-114	Ni	15	39	2.1	Biological, soil and blood	[36]
Magneson I	Triton X-114	Ni	25	17	2.7	Water and food	This study
		Mn	25	19	2.9		

[a] Enrichment factor
[b] Preconcentration factor
[c] Limit of detection

3.9. Accuracy of the method

In order to validate the proposed method, recovery experiments were carried out by certified reference materials SPS-SW1 (Surface water) and SPS-SW2 (Surface water). Results are the average of three replicates. As Table 4 indicates there is a good agreement between the obtained results and the known values. The recoveries are close to 100% and indicate that the proposed system was helpful for the determination of Ni^{2+} and Mn^{2+} in the real samples.

3.10. Determination of nickel and manganese in real samples

The proposed method was applied to the determination of nickel and manganese in tap water (Beytepe, Ankara, Turkey) and food samples (tomato paste, hazelnut, multi grain bread, white bread, spinach, lettuce and cabbage). These samples were subjected to preconcentration and metal ions determination using the proposed procedure. The results are given in Table 5. The percentage recovery (R) was calculated by using the equation: $R = \{100(C_m - C_0)/m\}$. Where C_m is a value of metal in a spiked sample, C_0 is a value of metal in a sample and m is the amount of metal spiked [25]. The obtained recoveries were reasonable for trace nickel and manganese analysis in food matrices, in a range of 94–106%.

4. Conclusion

The reagent Magneson I was successfully employed in a CPE procedure for determination of nickel and manganese in food samples by FAAS. This study offers a simple, rapid, inexpensive, and non-polluting technique for the preconcentration and determination of trace metals. Triton X-114 is of relatively low-cost and toxicity. Magneson I is a very stable, and fairly selective complexing reagent. The surfactant-rich phase can be directly introduced into the nebulizer of a flame atomic absorption spectrometer by dilution with acidified ethanol. The proposed preconcentration method allows nickel and manganese determination in food samples at μg kg^{-1} levels. Table 6 gives the comparison of the proposed method with other CPE methods for determination of nickel and manganese in the literature. The obtained detection limits by the proposed procedure are comparable to most of those reported in the literature. Due to good analytical characteristics, the proposed CPE procedure has been demonstrated to be very interesting for trace nickel and manganese analysis [15,25–36].

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