Development of a new sequential injection in-line cloud point extraction system for flame atomic absorption spectrometric determination of manganese in food samples

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ABSTRACT

A preconcentration method for manganese determination by sequential injection cloud point extraction with subsequent detection by flame atomic absorption spectrometry (FAAS) has been developed. The enrichment of Mn was performed after a preliminary on-line cloud point extraction and entrapment of manganese-containing surfactant aggregated within a minicolumn packed with cotton. The laboratory-made reagent 4-(5′-bromo-2′-thiazolylazo)orcinol (Br-TAO) and the surfactant Triton X-114 were used for cloud point extraction. The manganese ions were eluted with sulphuric acid solution and directly introduced into the FAAS. Chemical and flow variables affecting the preconcentration were studied. Using a sample volume of 2.80 mL the limit of detection and enrichment factor were calculated to be 0.5 $\mu g\,L^{-1}$ and 14, respectively. The sample frequency is $48\,h^{-1}$, considering a total run cycle of 75 s. The accuracy of the proposed method has been demonstrated by the analysis of the certified reference biological materials rice flour and tomato leaves. The method has been applied to determination of manganese in food samples.

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1. Introduction

Manganese is an essential trace element that can be found in several food items, such as tea, grains, rice, soya beans, eggs, nuts and cereals. This metal is essential for humans and other species of the animal kingdom. Some organisms, such as diatoms, mollusks and sponges, can accumulate manganese. However, excessive levels of manganese are detrimental to the organism. People exposed to very high levels of manganese for long periods of time can develop mental and emotional disturbances and slow and clumsy body movements. Therefore, the determination of trace amounts of manganese in several matrices samples is very important for some areas, such as environmental chemistry and food control [1,2].

Manganese determination at trace levels in real samples is frequently difficult because of low concentration of the metal and matrix interferences. In this manner, the determination generally is associated to preliminary step for enrichment and elimination of interfering species. Several enrichment procedures have been developed for the determination of Mn, involving different analytical techniques such as coprecipitation [3,4], liquid–liquid [5], solid-phase extraction (SPE) [6,7] or cloud-point extraction (CPE) [8–10]. Among the various analytical techniques, CPE has been largely applied in preconcentration procedures due to advantages obtained such as reducing of disposal costs and extraction time, simplicity and achievement of high recoveries. This separation technique has received great attention because of its great potential in separation of toxic solutes from several matrices.

Cloud point extraction has been successfully coupled to on-line systems in order to determine several species in different matrices [11,12]. This combination is advantageous because it eliminates manual operations typical of batch systems, such as heating, centrifugation, cooling, removal of supernatant and dilution. The on-line incorporation of CPE to FIA was reported for the first time for the determination of coproporphyrin in pretreated urine samples [13]. Low levels of mercury(II) have been determined in water samples using a flow injection system involving CPE and spectrophotometric detection [14]. A flow injection on-line micelle-mediated preconcentration and separation procedure was used for ETAAS determination of trace lead in biological samples [15]. A comparison of traditional cloud-point extraction and on-line flow-injection

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cloud-point extraction has been presented in a detailed discussion of several preconcentration conditions for both CPE procedures [16]. The authors highlighted the principal advantages of on-line FI CPE, especially preconcentration factor, extraction efficiency and analysis time. The dye 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) has been used as complexing agent in on-line CPE methodologies for the preconcentration and determination of gadolinium [17], dysprosium [18,19] and iron [19] content in urine samples.

Pyridylazo and thiazolylazo dyes have been used as extractants for various metal ions in different preconcentration methods. The use of these substances in extraction procedures is advantageous duo their great capacity to form insoluble complexes with many metallic substances [20–22]. Several pyridylazo and thiazolylazo reagents have been used for cloud-point extraction of metals. This paper reports the development of a new on-line CPE system with sequential injection for FAAS determination of trace manganese in food samples. A thiazolylazo dye (Br-TAO) has been prepared for the first time for this application. The study of variables affecting the on-line system was followed by application of the procedure in the determination of Mn in food. No reports were found in the literature on CPE on-line systems with sequential injection.

2. Experimental

2.1. Chemicals and reagents

All the reagents were of analytical grade. Deionized water was used to prepare all solutions. The laboratory glassware was kept in dilute nitric acid at least overnight and subsequently washed with deionized water. Manganese stock solution containing $1000 \, \mu g \, mL^{-1}$ was purchased from Merck, Darmstadt, Germany. Working manganese standards of between 5.0 and $100.0 \, \mu g \, L^{-1}$ were prepared on a daily basis by serial dilution from this stock standard. Solutions of the non-ionic surfactant Triton X-114 (Sigma–Aldrich, Milwaukee, USA) were prepared in high purity deionized water. Br-TAO solutions were prepared by dissolving appropriate amounts of 4-(5′-bromo-2′-thiazolylazo)orcinol (Br-TAO) laboratory-prepared in absolute ethanol (Merck). Hydrochloric, nitric and sulphuric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions (Merck). KCl–HCl (3.0), acetate (4.7–6.0), borate (7.0–8.0) and ammonia (8.5–9.2) buffers were used to adjust the sample pH [23]. Sodium carbonate (Vetec, Rio de Janeiro, Brazil), 2-amino-5-bromothiazole (Sigma–Aldrich), sodium nitrite (Vetec), orcinol (Merck) and ethanol (Merck) were used for synthesis of Br-TAO. The accuracy of the method was assessed by analyzing the following certified reference materials (CRM): SRM 1568a rice flour and SRM 1573a tomato leaves from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.2. Instrumentation

A PerkinElmer Instruments (Shelton, USA) model AAnalyst 200 flame atomic absorption spectrometer equipped with an air–acetylene burner was used for absorbance measurements. A manganese hollow cathode lamp (PerkinElmer instruments) was used as the light source at a wavelength of 279.5 nm and operated at 15.0 mA, with a 0.2 nm spectral bandpass. Deuterium lamp background correction was also used. The flame composition was acetylene (flow rate: $2.0 \, L \, min^{-1}$) and air (flow rate: $13.5 \, L \, min^{-1}$). Nebulizer flow rate was $5.0 \, ml \, min^{-1}$. Digestion of food samples and certified reference materials was carried out in a Parr Instrument 4749 (Moline, IL, USA) acid digestion bomb enclosing a chemically inert Teflon sample cup of 23 mL. Infrared spectrum was recorded
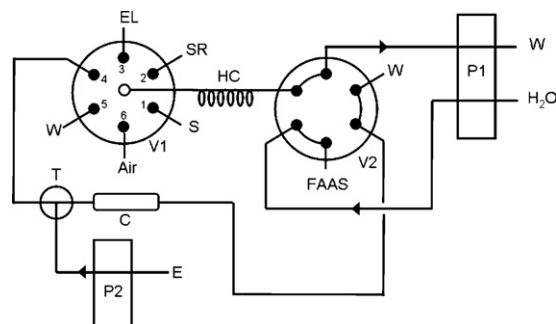

Fig. 1. Schematic diagram of on-line CPE system with sequential injection for FAAS determination of trace manganese. P1 and P2, peristaltic pumps; V1, six-position rotary valve; V2, four-way rotary valve; C, minicolumn packed with cotton; T, T-piece connected to two-way valve; HC, holding coil; S, sample solution; SR, surfactant-reagent solution; EL, electrolyte solution; E, eluent; W, waste.

in an ABB Bomen MB series model MB100 Fourier transform IR spectrometer.

The sequential injection preconcentration system is illustrated in Fig. 1. The SI manifold consists of a Rheodyne (Cotati, USA) model 5011 six-position rotary valve, a Rheodyne model 5041 four-way rotary valve (Cotati, USA) and two multichannel peristaltic pumps model 204 from Millan (Colombo, Brazil) furnished with silicone tubes to delivery the solutions. A T-piece connected to a laboratory-made Teflon two-way valve (T) was inserted into the system. This manually operated valve is open only when P2 is on. A minicolumn manufactured from a PVC tube (3.50 cm length and 0.4 cm i.d.) packed with 100 mg of cotton was also used. All connections of flow system were made using fittings, unions and tees made of plastic and PEEK materials. The manifold was built up with PTFE tube of 0.5 mm bore. All pH measurements were made with a Digimed DM 20 model (Santo Amaro, Brazil) digital pH meter.

2.3. Synthesis of Br-TAO

For Br-TAO preparation, a modified procedure based in the synthesis of similar reagents [20,24] has been performed. 2-Amino-5-bromothiazole (2.0 g) was dissolved in 50 mL of a $6.0 \, mol \, L^{-1}$ hydrochloric acid solution at 0–5 °C. A solution of 0.53 g of sodium nitrite in 20 mL of water was added dropwise. The mixture was stirred and kept at 0–5 °C for 45 min. For coupling, 0.96 g of orcinol was added to 20 mL of $1.0 \, mol \, L^{-1}$ sodium carbonate solution and the mixture was cooled to 0–5 °C. This solution was added dropwise to the above diazotized compound at vigorous stirring. The system was allowed stand overnight in refrigerator at 0–5 °C. The product was filtered and rinsed with cold water. The dark-red precipitate resulting was purified by recrystallization with ethanol and active carbon.

Solubility tests, melting point and IR instrumental techniques have been used for Br-TAO characterization. The solubility of dye was tested and it was found that Br-TAO is soluble in a 5% (w/v) NaOH solution, methanol and ethanol, and insoluble in water. Melting point was determined seven times and varied in the range of 205–207 °C °C. The IR spectrum of the dried product showed bands in the region ranging from 3400 to 3200, 1300 to 1100 and $1050 \, cm^{-1}$ corresponding to –OH, C–O, and –C–N frequencies, respectively. Fig. 2 shows a proposed structure for Br-TAO.

2.4. Operating procedure

The steps of the complete cycle for on-line CPE system with sequential injection for FAAS determination of trace manganese are summarized in Table 1. The analysis procedure started when

Table 1
Sequence steps of a complete measurement cycle for the determination of manganese

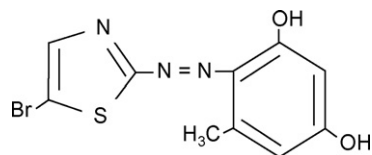| Step	Time (s)	Valve 1 position	Valve 2 position	Pump 1	Pump 2	Action
1	20	1	1	On	Off	Aspirate sample
2	5	2	1	On	Off	Aspirate reagent and surfactant
3	5	3	1	On	Off	Aspirate electrolyte solution
4	30	4	2	On	Off	Propulsion through minicolumn
5	10	5	2	Off	On	Elution and reading washing of holding coil
6	5	6	1	On	Off	Deliver water from holding coil

Fig. 2. Proposed structure for Br-TAO.

the pump 1 (P1) is on, and valve 2 is in position 1. In these conditions, the pump 2 (P2) is turned off and water is carried to FAAS. Firstly, 2800 µL of the sample solution (S), 700 µL of surfactant-reagent solution (SR) and 700 µL of electrolyte solution (EL) were aspirated from ports 1, 2 and 3, respectively, into the holding coil (HC, 200 cm) at a flow rate of 140 µL s^{-1}. When the reaction mixture entered for whole the holding coil, the valves 1 and 2 were simultaneously switched to its 4 and 2 positions, respectively. The reaction mixture was then propelled to the minicolumn (C) through port 4 at a flow rate of 140 µL s^{-1}. After loading, the valve 1 was then switched to position 5. Simultaneously, the pump 2 was turned on and the two-way valve was opened. In this situation, a stream of eluent (E) passes through the minicolumn to release manganese ions directly into the nebulizer of the spectrometer. At the same time, water is dispensed to flow through the holding coil in order to eliminate any loosely adhering concomitants from the tube walls to waste (W). Thereafter, air was aspirated into the holding coil from port 6 in order to deliver the water. The cycle time was 75 s (48 determinations per hour). The transient signal from the detector was recorded as a peak. Peak height values were adopted for quantification, considering that a good precision was achieved within the concentration range studied.

2.5. Samples and sample pre-treatment

Two NIST certified reference biological materials were used for method validation: SRM 1568a (rice flour) and SRM 1573a (tomato leaves). Food samples (rice flour, infant formula and corn flour) were purchased at supermarkets from Jequié, Bahia, Brazil. Approximately 0.10 g for dry sample (food or certified reference biological material) were weighed into PTFE vessels and digested in a mixture of 4.0 mL of 1:1 (v/v) nitric acid solution on a stove. After digestion, the resultant solution was allowed to cool at room temperature. These solutions were adjusted to pH 9.0 with a 10% (w/v) sodium hydroxide and 10 mL of an ammonia buffer solution. The mixtures were finally diluted to final volume by double deionized water. Spiked samples were also prepared in order to calculate the recovery of the digestion procedure. Blanks were prepared in the same way as the samples. The final concentration of Mn in all these samples was in the linear range of the method.

3. Results and discussion

In the optimization of the method, a known amount of manganese (100 µg L^{-1}) has been injected in the system. The parameters potentially influencing the manganese extraction were investigated through the analytical signals.

3.1. Optimisation of chemical variables

The firstly studied parameter was the influence of pH in the cloud point extraction of Mn. The pH of the manganese solution was adjusted by the addition of 10 mL of buffer solution. The pH of buffer solution had been varied in the range of 3.0–10.0. The results are shown in Fig. 3. It can be observed that the analytical signal is maximum at pH 9.0. Therefore, a pH 9.0 (ammonia buffer) manganese solution was used in the following studies.

The addition of electrolytes has been employed as a good alternative in CPE on-line procedures for an efficient preconcentration of hydrophobic substances from an aqueous phase into a non-ionic surfactant phase. The salting-out effect caused by the presence of electrolytes induces the phase separation resulting in a more efficient extraction. The electrolytes Na_2SO_4, NaCl, KCl, K_2SO_4, and KNO_3 were tested as salting-out agents in the proposed CPE system. Best results were provided by NaCl. In this manner, a saturated NaCl solution was used in all subsequent experiments.

The influence of Br-TAO concentration on the cloud point extraction of manganese has also been investigated. Surfactant-reagent solutions (SR) were prepared and the Triton X-114 concentration was fixed at 2.5×10^{-2}% (v/v). Several Br-TAO amounts varying in the range between 3.0×10^{-7} and 1.6×10^{-5} mmol L^{-1} were tested. The analytical signal increases up to a Br-TAO concentration of 3.0×10^{-6} mmol L^{-1} and reaches a maximum value. So a Br-TAO concentration of 1.0×10^{-5} mmol L^{-1} was chosen for further experiments.

The surfactant chosen for cloud point extraction was Triton X-114, which possesses a low cloud-point temperature and high density. In CPE procedures, it is necessary to determine the surfactant concentration for sufficient extraction of target analytes. In this manner, the effect of Triton X-114 concentration on the cloud point extraction of manganese has also been studied. This
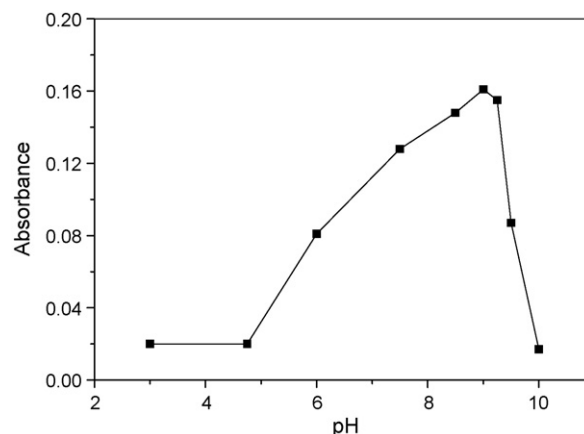

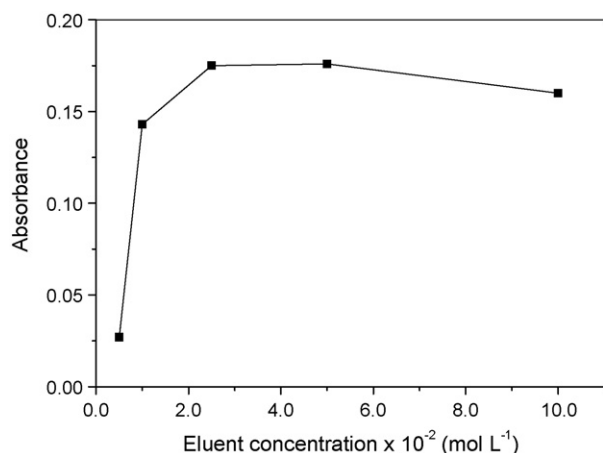**Fig. 3.** Effect of pH on CPE on-line preconcentration of manganese.

Fig. 4. Effect of eluent concentration on CPE on-line preconcentration of manganese.

effect was examined in the range of 1.0×10^{-3} to 2.5×10^{-2}% (v/v). The highest analytical signals for manganese were found in the range between 5.0×10^{-3} and 2.5×10^{-2}% (v/v) surfactant concentrations. A 1.0×10^{-2}% (v/v) Triton X-114 solution was chosen for subsequent work.

After the preconcentration step, an appropriate solvent should be used to remove the manganese-containing surfactant aggregated within the minicolumn. This eluent is also employed to transport the metal ions to FAAS hence the selection of proper eluent is an essential factor determining the analytical signal of manganese. Desorption of the retained manganese from the cotton minicolumn has been investigated. Several synthetic mixtures of varying composition with respect to ethanol and their acid mixtures were employed as eluents to achieve reasonable desorption efficiency and at the same time a favorable analytical signal for manganese. Mixtures containing ethanol were found to be efficient for the elution but these eluents were not able to provide a good analytical signal for manganese. The use of ethanol or water alone resulted in poor elution. Therefore, mixtures containing ethanol were not used as eluent in subsequent experiments. Solutions of hydrochloric, nitric and sulphuric acid presented the best results in terms of elution and response. Sulphuric acid has been chosen for subsequent experiments because this eluent provided more precise results. Different H_2SO_4 concentrations in the range of 5.0×10^{-3} to 1.0×10^{-1} mol L^{-1} were tested for the quantitative elution of manganese ions from the minicolumn. The signals obtained for manganese as a function of sulphuric acid concentration are shown in Fig. 4. The results indicated that the signal for manganese is maximum when the concentration of sulphuric acid is up to 2.5×10^{-2} mol L^{-1}. A 5.0×10^{-2} mol L^{-1} sulphuric acid aqueous solution was used as eluent in all subsequent experiments.

Table 2
Features of the sequential injection on-line CPE preconcentration system for manganese determination (A, absorbance; C, Mn concentration, μg L^{-1})

Enrichment factor	14
Sample consumption (μL)	2800
Consumptive index (mL)	0.20
Sample frequency (h^{-1})	48
Limit of detection (μg L^{-1})	0.5
Limit of quantification (μg L^{-1})	1.7
Linear range (μg L^{-1})	1.7–150.0
Precision (R.S.D.%)	6.3% (50 μg L^{-1}) and 5.4% (100 μg L^{-1})
Calibration function	$A = 5.00 \times 10^{-3} + 2.49 \times 10^{-3}C$

Table 3
Tolerance limits for coexisting ions for determination of manganese (100 μg L^{-1})

Substance	Maximum tolerable amount
Al^{3+}	1.0 mg L^{-1}
Cl$^-$	10.0 g L^{-1}
Co^{2+}	1.0 mg L^{-1}
Cu^{2+}	0.1 mg L^{-1}
Fe^{3+}	1.0 mg L^{-1}
K$^+$	5.0 g L^{-1}
Mg^{2+}	1.0 g L^{-1}
Na$^+$	10.0 g L^{-1}
Ni^{2+}	1.0 mg L^{-1}
Pb^{2+}	0.1 mg L^{-1}
Zn^{2+}	1.0 mg L^{-1}
NO$_3^-$	5.0 g L^{-1}

3.2. Optimization of FI flow conditions

The influence of flow rate of surfactant-rich phase passing through minicolumn has also been investigated. Flow rate values ranging from 75 to 180 μL s^{-1} were tested. The most favorable collecting conditions were achieved when using flow rates in the range from 130 to 155 μL s^{-1}. The flow rate of surfactant-rich phase was fixed at 140 μL s^{-1}. This value was also chosen for aspiration flow rate described in Section 2.4 in order to facilitate the operation.

In the proposed procedure, the eluent flow rate controls the velocity of desorption of manganese from the cotton minicolumn. Experiments were carried out by pumping a 5.0×10^{-2} mol L^{-1} sulphuric acid solution in order to achieve an analytical signal as high as possible. Best results were found within the range of 3.5–7.0 mL min^{-1}. An eluent flow rate of 5.0 mL min^{-1} was selected, which provides good sensitivity and combines aspiration (FAAS) and desorption flow rates.

In order to verify the effect of temperature and incubation time in CPE of manganese, a temperature controlled water-bath has been integrated into the SIA manifold. The holding coil was inserted in the water-bath and the temperature was varied in the range of 30–70 °C. In this experiment, the electrolyte has not been added and the step 3 in Table 1 was modified. At this step, when the reaction mixture entered the holding coil, the flow was stopped for periods from 0 to 60 s. Temperatures exceeding 70 °C were not tested due to the formation of air bubbles. No significant change on analytical signal of manganese was observed if the temperature of holding coil varied from 25 (room temperature) to 70 °C for any incubation time. Therefore, all experiments were carried out at a room temperature of 25 °C and the period for incubation time was suppressed.

After the phase separation, a filtering material should be used in order to retain the micelle phase. Based in previous methodologies [13,17], glass wool, cigarette filter and cotton were tested as filtering material. Best results, in terms of analytical signal and reproducibility, were obtained when cotton was used. The amount of cotton in

Table 4
Results obtained for manganese determination in food samples ($n = 4$)

Sample	Manganese content (μg g^{-1})		R (%)
	Added	Found	
Rice flour	0.0	2.2 ± 0.1	98
	5.0	7.1 ± 0.3	
Infant formula	0.0	6.9 ± 0.3	106
	5.0	12.2 ± 0.5	
Corn flour	0.0	4.3 ± 0.1	104
	5.0	9.5 ± 0.5	

Confidence interval, 95%; R, recovery.

Table 5
A comparison of the analytical features of the present method against some of the on-line preconcentration procedures for Mn with detection by FAAS

Separation technique	EF	f (h^{-1})	V (mL)	LOD (μg L^{-1})	Sample	Reference
SPE	30	10	15	12.0	Natural water	[7]
SPE	26	60	–	1.5	Biological samples	[29]
SPE	47	60	4.2	0.9	Mussel and non-fat milk	[30]
SPE	80	30	7.0	0.5	Seawater	[31]
SPE	21.3	12	2.5	0.8	Urine	[32]
Precipitation	55	–	8	2.0	Biological samples	[33]
			24	1.0		
Precipitation	30	–	150.0	2.6	Water, soil and sediment	[4]
CPE	49.1	–	50.0	0.39	Milk and water	[34]
CPE	20	–	10.0	1.45	Water	[35]
CPE	84	–	70.0	0.60	Saline effluents	[36]
CPE	20	–	100.0	5.0	Water	[37]
CPE	57.6	–	50.0	0.28	Water	[38]
CPE	14	48	2.8	0.5	Food	[This work]

EF, enrichment factor; f, sampling frequency; V, sample volume; LOD, limit of detection; CI, consumption index; SPE, solid-phase extraction; CPE, cloud point extraction.

the minicolumn was varied from 50 to 150 mg. It was found that 100 mg of cotton is sufficient for the maximum analytical signal. The amount of cotton was limited by the backpressure produced by the minicolumn. A cylindrically shaped polyvinyl chloride mini-column (3.50 cm × 4.0 mm id) packed with 100 mg of cotton was then used in further experiments.

3.3. Features of the proposed analytical method

Under the optimal working conditions, the analytical properties of merit obtained for the on-line cloud point extraction system for Mn were summarized in Table 2. Regression curve without preconcentration resulted in the following equation: $A = -2.00 \times 10^{-3} + 1.75 \times 10^{-4}C$ (Mn 50–3000 μg L^{-1}), where A is the absorbance and C is the manganese concentration in solution, in μg L^{-1}. This equation was obtained under optimum conditions of the spectrometer. The relative standard deviation (R.S.D.%, $n = 7$, $C = 1000$ μg L^{-1}) for direct measurement of absorbance is 0.8%.

An enrichment factor of 14 was obtained by aspirating a sample loading volume of 2.8 mL into on-line preconcentration system. Enrichment factor was calculated as the ratio of the slopes of the linear section in calibration graphs for preconcentration and direct aspiration, respectively [25]. Consumptive index (CI) was also calculated. This parameter is defined as the volume of the sample consumed to achieve a unit of EF [25]. It was calculated by the ratio of the sample volume, in milliliters, and EF. The calibration graph for manganese is linear up to 150 μg L^{-1}.

From the calibration curve, the detection limit (LOD) was calculated as LOD = 3(s/m), where s is the standard deviation of 12 measurements of a reagent blank, and m is the slope of the calibration curve. The quantification limit (LOQ) was calculated as LOQ = 10(s/m). From these equations, LOD and LOQ were found to be 0.5 and 1.7 μg L^{-1}, respectively. The precision, assessed as the relative standard deviation of Mn determination was obtained by measuring the analytical signal for seven cycle times at levels of 50 and 100 μg L^{-1} Mn. The R.S.D. obtained were 6.3% (50 μg L^{-1}) and 5.4% (100 μg L^{-1}).

3.4. Effect of foreign ions

To evaluate the interference of co-existing ions on the determination of manganese, solutions of the Mn(II) and a single coexisting ion were prepared. Various kinds of ions were added to the aqueous solution containing 100 μg L^{-1} Mn(II). Manganese was determined by the on-line CPE proposed system. A relative error of less than 5% was considered to be within the range of experimental error. The

NaCl interference was studied without considering the salt amount added as electrolyte. As shown in Table 3, the presence of tested species caused no appreciable interferences in the determination of manganese.

3.5. Analysis of standard reference materials

In order to study the accuracy of the proposed procedure, two standard reference materials were analyzed. The samples were digested by using the dissolution procedure described in section 2.5. The standard rice flour (SRM 1568a) and tomato leaves (SRM 1573a) reference materials have a certified manganese value of 20.0 ± 1.6 and 246 ± 8 μg g^{-1}, respectively. The metal content established by the present procedure (NIST 1568a, 19.3 ± 1.2 μg g^{-1} and NIST 1573a, 239 ± 5 μg g^{-1}) agrees well with the certified values. The results indicate the effectiveness and accuracy of the proposed method.

3.6. Determination of manganese in commercial food samples

The proposed method was applied to the determination of manganese in food samples (rice flour, infant formula and corn flour), collected from supermarkets and street markets in Jequié city, Bahia, Brazil. These samples were subjected to digestion, preconcentration and manganese determination using the proposed procedure. The results are listed in Table 4. The percentage recovery (R) was determined by using the equation: $R = \{100(C_m - C_o)/m\}$. Where C_m is a value of metal in a spiked sample, C_o is a value of metal in a sample and m is the amount of metal spiked. The obtained recoveries were satisfactory for all samples and varied between 98 and 104%. These results demonstrate the applicability of the proposed CPE on-line system in the determination of manganese in food matrices.

4. Conclusion

The proposed on-line sequential injection cloud point extraction system was successfully applied for on-line preconcentration and determination of manganese in food samples by FAAS. This study allowed the development of a new, rapid, easy to use, safe and inexpensive methodology for the determination of trace manganese in food samples. The proposed methodology was compared to a variety of methods for determination of manganese reported recently in the literature. The distinct characteristics are summarized in Table 5. As can be seen from the table, except enrichment factor, the obtained analytical features by the proposed procedure

are comparable to or even better than most of the other methods. The significant features of the proposed method are the sample frequency and the consumptive index obtained by using the on-line system. Other interesting feature is the low sample volume required in this method. Due to good analytical characteristics s the proposed procedure has been demonstrated to be promising for trace element analysis. The wide spectrum of potential methods for inorganic and organic substances make thiazolylazo dyes very promising reagents for analytical purposes, especially in precipitation, cloud point and solid-phase extraction [21]. The use of these reagents in separation systems can result in very interesting and versatile procedures [26–28]. Some studies on this direction are a focus of future work in this laboratory.

Acknowledgements

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