Available online at www.sciencedirect.com
SCIENCE DIRECT
Talanta 69 (2006) 835–840
Talanta
www.elsevier.com/locate/talanta

Separation and preconcentration of trace manganese from various samples with Amberlyst 36 column and determination by flame atomic absorption spectrometry

Erdal Kendüzler [a], A. Rehber Türker [b,*], Özcan Yalçınkaya [b]

[a] *Kırşehir Education Faculty, Gazi University, 40100 Kırşehir, Turkey*
[b] *Faculty of Science and Arts, Gazi University, 06500 Ankara, Turkey*

Received 5 August 2005; received in revised form 17 October 2005; accepted 4 November 2005
Available online 15 December 2005

Abstract

This work assesses the potential of a new adsorptive material, Amberlyst 36, for the separation and preconcentration of trace manganese(II) from various media. It is based on the sorption of manganese(II) ions onto a column filled with Amberlyst 36 cation exchange resin, followed by the elution with 5 mL of 3 mol/L nitric acid and determination by flame atomic absorption spectrometry (FAAS) without interference of the matrix. Different factors including pH of sample solution, sample volume, amount of resin, flow rate of sample solution, volume and concentration of eluent, and matrix effects for preconcentration were investigated. Good relative standard deviation (3%) and high recovery (>95%) at 100 μg/L and high enrichment factor (200) and low analytical detection limit (0.245 μg/L) were obtained. The adsorption equilibrium was described well by the Langmuir isotherm model with maximum adsorption capacity of 88 mg/g of manganese on the resin. The method was applied for the manganese determination by FAAS in tap water, commercial natural drinking water, commercial treated drinking water and commercial tea bag sample. The accuracy of the method is confirmed by analyzing the certified reference material (tea leaves GBW 07605). The results demonstrated good agreement with the certified values.

Keywords: Manganese determination; Water analysis; Tea analysis; Preconcentration; Amberlyst 36; Flame atomic absorption spectrometer

1. Introduction

The general trend of the modern analytical chemistry is the elaboration of sample, ecologically safe, sensitive, and selective methods for the determination of trace components combining previous concentration and further determination by physical or physico-chemical methods [1]. Solid-phase extraction (SPE) is a high effective, ecologically safe method for the preconcentration of trace manganese and other metals, which has been developed intensively recent years [2–10]. Metal quantification at low concentration levels (≤μg/L) comprises one of the most considerable targets in analytical chemistry. This interest is demonstrated in different areas such as medicine [11]. In recent years, trace metals are determined in a great variety of environmental (such as water, soil and atmospheric particulate material) and food samples [12,13]. The atomic spectrometry techniques are extensively employed for the quantification of metallic species. Among these techniques, flame atomic absorption spectrometry presents desirable characteristics, such as low costs, operational facilities, high analytical frequency and good selectivity [14]. However, the direct determination of trace metals by this technique is generally difficult because of matrix interference problems and low concentration of metals in samples. These problems can be overcome by using preconcentration and separation procedures before the detection procedure. For this purpose, various preconcentration/separation methods, such as solid-phase extraction [2–10], liquid–liquid extraction [15], cloud-point extraction [16] and liquid membrane [17] have been widely used.

It has been known that manganese in environmental waters is one of the major elements participating in oxidation–reduction process along with carbon, nitrogen, oxygen, sulfur, and iron. Manganese exists mainly in both manganese(II) and manganese(IV) oxidation states in ordinary aqueous environments.

* Corresponding author. Tel.: +90 312 2126030; fax: +90 312 2134513.
E-mail address: aturker@gazi.edu.tr (A.R. Türker).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.11.021

In aqueous environments manganese(IV) is a dominant chemical species, and exists in insoluble forms, such as particulate and colloidal MnO_2. However, manganese(II) ion is rather stable in aqueous environments, which are often linked with water pollution, especially for drinking water [18,19]. Permanganate ion has been rarely found in aqueous environmental system. The greatest parts of dissolved manganese in environmental waters are thought to be manganese(II) ion [3].

In recent years, many papers have been published for the preconcentration of manganese from various samples. Okumura et al. have used Sep-Pak C18 cartridge for in situ solid-phase extraction of manganese as its 4-(2-pyridylazo)resorcinol complex from environmental waters [3]. In that study, water samples were taken into a graduated syringe from all sample sites and the preconcentration was completed in 5 min on sites after sample collection. Then, Sep-Pak C18 cartridge was transported back to the laboratory for elution and determination. Qian et al. [7] have described a method for the separation and determination of Mn(VII)/Mn(II) with crosslinked chitosan. The adsorption rate of crosslinked chitosan for Mn(VII) was quantitative at pH 3, while Mn(II) was not adsorbed. After manganese(II) was oxidized with KIO_4 solution and nitric acid, total manganese was determined by FAAS. Sarmani et al. [9] have developed a method for the preconcentration and separation of trace manganese from natural water samples by complexation with dithiocarbamate followed by adsorption onto C18-solid-phase extraction column. The Mn recovery was good and the selectivity of method was excellent making it possible to detect Mn in the presence of major elements normally found in natural water. Afzali et al. have also developed a flame atomic absorption spectrometry method for the determination of trace amounts of manganese ions after adsorption onto thermal modified kaolinite loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and subsequent desorption with 5.0 mL of 4 mol/L H_2SO_4 [20].

In many preconcentration procedures, such as described above, either a known amount of chelating agent is added to the solution to form the metal chelate or a chelating agent is immobilized on a support of column prior to enrichment procedures. However, in this study, Amberlyst 36 alone has been used as a solid-phase extractor. Any agent was not used as a chelating material or immobilized material. Amberlyst 36 resin has been used before, as catalyst in the reactions of some organic components [21–23]. Yadav and Joshi [21] examined the synthesis of *tert*-amyl methyl ether from *tert*-amyl alcohol and methanol in the presence of a variety of solid acid catalysts. Amberlyst 36 was found to be very effective catalyst in comparison with other solid acids.

The aim of this work is to investigate the use of the Amberlyst 36 as solid-phase extractor for the separation and preconcentration of manganese(II) from aqueous solution. A new solid-phase extractor, Amberlyst 36 which has good physical and chemical properties such as porosity, durability and purity and is resistant in concentrated mineral acids, bases and organic solvents for a long time for manganese determination in drinking waters and tea sample by FAAS was designed. The analytical parameters in order to obtain quantitative recovery have been studied systematically. This procedure was successfully applied to the determination of manganese in drinking water and tea samples.

2. Materials and methods

2.1. Instrumentation

A Philips PU 9285 model flame atomic absorption spectrophotometer, equipped with a manganese hollow-cathode lamp, a deuterium lamp for background corrector and air–acetylene flame as the atomizer, was used for the determination of manganese. The apparatus run under the conditions suggested by the manufacturer, i.e.: lamp current, 9.0 mA; wavelength, 279.5 nm; bandwidth of the slit, 0.5 nm; acetylene flow rate, 1.0 L/min [24]. A Jenway 3010 Model pH meter was used to measure the pH of solutions.

2.2. Reagents and solutions

All reagents were of analytical grade and all solutions were prepared using triple distilled water. The laboratory glassware was kept overnight in a 5% nitric acid solution. Afterwards, it was rinsed thoroughly with water and dried. A stock aqueous solution of manganese (1000 mg/L) was prepared by dissolving 0.4569 g of $Mn(NO_3)_2{\cdot}4H_2O$ (Merck) in 100 mL of water. A working aqueous solution of manganese(II) (10 mg/L) was also prepared from manganese stock solution of 1000 mg/L. An ascorbic acid solution was prepared by dissolving 0.1 g ascorbic acid in 100 mL of triple distilled water. Nitric acid (65%), hydrofluoric acid (48%) and hydrochloric acid (37%) acid were from Merck. Amberlyst 36 (Aldrich) was used after washing with methanol, 1 mol/L HCl solution and water, respectively, and dried for 4 h at 60 °C.

2.3. Collection and preparation of samples

A tap water sample, collected from our laboratory, commercial natural drinking water and commercial treated drinking water were collected from local market in Ankara, Turkey. The samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 μm. The samples were stored in polythene bottles and then acidified with 1.0 mL of concentrated hydrochloric acid per liter of sample. A sample of commercially available tea bag, manufactured in black sea region of Turkey, and one certified reference material (Tea leaves GBW 07605, China) were analyzed. The following mineralization procedure adapted from Krachler et al. [25] was applied to tea samples: a 100 mg of tea samples was taken in a 250 mL PTFE beaker. For dissolution, a minimal volume of 0.05 mol/L nitric acid was added to moisten the sample thoroughly, followed by 10 mL of concentrated nitric acid. The beaker was heated on a hot plate about 3 h. After cooling to room temperature, 2 mL of concentrated hydrofluoric acid were added. Then the contents of the beaker were heated to near dryness. This process was repeated twice by using 5 mL of concentrated nitric acid and 1 mL of concentrated hydrofluoric acid. The resulting solution was transferred into a 25 mL volumetric flask by washing interior

surface of the beaker with small portions of 0.05 mol/L nitric acid and diluted to the mark with water. Then, 5 mL of each of these sample solutions was diluted to 100 mL to decrease the manganese concentration at the working range of the atomic absorption spectrometric method. In addition, ascorbic acid was added to real sample solutions to reduce the manganese ions in higher oxidation states to manganese(II). Finally, the general preconcentration method (Section 2.5) was applied without change.

2.4. Column preparation

The glass column, having a stopcock, was 15 cm length and 0.8 cm internal diameter. A small amount of glass wool was placed at one end of the column in order to hold the certain amount (0.5 mg) of resin. Then, another small glass wool plug was inserted onto the tap of the resin. The bed height of the resin in the column was approximately 1.5 cm. It was washed successively with water, methanol and 1 mol/L hydrochloric acid, respectively. After each use, the resin in the column was washed with water and stored in the column by filling the column with water to above the upper surface of the resin for the next experiment.

2.5. Preconcentration and determination procedure

Proposed preconcentration procedure was tested with model solutions prior to the determination of trace manganese in samples. An aliquot of a solution (50 mL) containing 5 μg of the Mn(II) was placed in a beaker and adjusted to pH 2 by using HCl solution. The column was preconditioned by passing the solution of pH 2 through the column and then, the model solution was passed through the column at a flow rate of 5 mL/min. The adsorbed manganese(II) ions on the column was eluted into a 5 mL calibrated flask by using 5 mL of 3 mol/L nitric acid solution. The eluent was analyzed for the determination of manganese concentration by FAAS. The Amberlyst 36 column has been used repeatedly after washing with 2 mL of 3 mol/L nitric acid solution and triply distilled water, respectively. Using the procedure described above, the recovery of the manganese was calculated from the ratio of the quantities of manganese before and after the enrichment, respectively [26].

3. Results and discussion

In order to obtain the maximum recoveries, a lot of parameters such as pH of sample solution, the type and concentration of elution solution, flow rates of sample solution have been optimized. Interfering affects have also been studied.

3.1. Effect of pH

The first variable optimized was the pH of the sample solution. Because the pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation

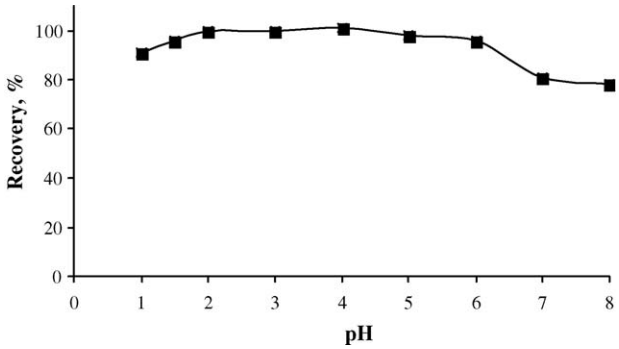

Fig. 1. The effect of pH on the recovery of manganese on a column of Amberlyst 36 (sample volume: 50 mL, amount of manganese: 5 μg, eluent: 5 mL of 3 mol/L nitric acid, flow rate of sample: 5 mL/min).

are strongly influenced by pH, and on the other side, strongly influence the speciation and the biosorption availability of the heavy metals.

The recovery was determined by applying the general sorption procedure by changing the pH of sample solution in the range of 1–8. The sample solutions were adjusted to the desired pH with diluted hydrochloric acid and/or a diluted ammonia solution and passed through the resin. The eluent was then analyzed by FAAS. The results for the recovery of manganese(II) are shown in Fig. 1. Quantitative recoveries (>95%) were obtained at pH range of 1.5–6. pH 2 was selected for subsequent studies. In the literature, manganese was preconcentrated at about neutral pH values [8,9,16,22] which increases precipitation risks. The lower pH values are generally preferred for analyzing real samples, because they are usually dissolved with acids or stored in acidic medium. In addition the precipitation of the some metal ions, an unwanted situation, could be observed at high pH values.

3.2. Effect of amount of resin

The amount of resin is another important parameter that affects the recovery. A quantitative retention is not obtained when the amount of resin is less than optimum value. On the other hand, an excess amount of resin prevents the elution of the retained analyte by a small volume of eluent quantitatively. For this reason, the amounts of resin were optimized. For this purpose, different amounts of Amberlyst 36 (50–800 mg) were studied. Quantitative recoveries of the manganese were obtained at above 300 mg of resin. Therefore, 500 mg of resin has been used for subsequent experiments because of easy elution (not 800 mg) and for obtaining sufficient recovery (not 300 mg) in real samples.

3.3. Desorption

In order to choose a proper eluent for the retained manganese ions, after the extraction of 0.1 μg/mL manganese from water, the manganese ions were stripped with varying concentrations of different eluting agents, such as, HCl, $HClO_4$, HNO_3, ethanol and acetone. The performance of the inorganic

acids was much better than that observed with organic eluents. Quantitative recovery (>95%) has been obtained by using 5 and 10 mL of 3 mol/L nitric acid solution. Therefore, in subsequent experiments, 5 mL of 3 mol/L nitric acid solution among the tested solution was chosen as stripping agent to desorp the manganese.

3.4. Effect of flow rate of sample solution

The flow rate of the sample solution through the column is another important parameter, since it not only affects the recovery of analyte, but also controls the time of analysis. Because a large volume of sample solution is needed in the preconcentration, it is always expected that sample solutions can be passed through the column at a higher flow rate without sacrificing the recoveries. In order to evaluate the effect of flow rate, a set of solutions (50 mL) containing 5 μg Mn(II) was adjusted to the optimum pH value. They were then passed through the column at a flow rate that varied from 0.5 to 5 mL/min adjusted by gravity action. The analyte was desorbed with 5 mL of 3 mol/L nitric acid solution from the resin and determined as mentioned in the recommended procedure (Section 2.5). According to the results, flow rates in the examined range had no significant effect on the recoveries of the manganese. These results indicate that the manganese(II) sorption is very rapid. This fact is a useful feature of the proposed method, because it permits a higher sample throughout. Therefore, the flow rate of 5 mL/min was found to be suitable for optimum loading of the analyte and was used for further studies. Because of the eluent volume is very low the effect of eluent volume has not been studied and 1 mL/min has been selected as an eluent flow rate.

3.5. Effect of sample volume (concentration of analyte)

The influence of the sample volume on recoveries of the manganese was also examined. For this purpose, manganese was preconcentrated from volumes of 50, 100, 250, 500, 750 and 1000 mL of sample solution containing 5 μg manganese by applying the general procedure mentioned above. The recovery of manganese was quantitative (>95%) for all of these sample volumes. By analyzing 5 mL of the final solution after the preconcentration of 1000 mL of sample solution, an enrichment factor of 200, calculated by the method given by Mizuike [26], can be achieved. The time of analysis is the main disadvantage of the proposed method and it is about 3.5 h for 1000 mL of sample volume and 5 mL of eluent. By using the smaller sample volume, the analysis time may be shortened. The preconcentration factor could have been further improved by using larger sample volume and/or smaller eluent volume.

3.6. Influence of interfering species

The effects of potential interferences occurring in drinking water samples on the determination of manganese were investigated using the optimized preconcentration procedure. Metal ions were added individually to a solution as their nitrate or chloride salts, and proposed preconcentration method was applied. The experimental results were given in Table 1. Results show that the most serious interference arises from iron(III). Interference from this ion is probably that it retains strongly on the resin than that of manganese. In order to eliminate the iron interference, 0.1 mol/L NaF solution was added to model solution. By adding NaF, quantitative recovery (>95%) was acquired for Mn(II). However, the concentration of iron in drinking water is normally lower than 5 mg/L [27] and there is no interference at 10-fold of the concentration of manganese. For this reason, NaF was not added to real solutions. As can be seen in Table 1, among the tested other cations no one had serious interfere with the recovery of manganese(II). Therefore, manganese in drink-

Table 1
The effect of some ions on the recovery of manganese (pH: 2, eluent: 5 mL of 3 mol/L nitric acid, flow rate of sample: 5 mL/min, sample volume: 50 mL, concentration of the manganese(II): 0.1 mg/L)

Interfering ions	Concentration (mg/L)	R^a (%)
Na^+	1	98 ± 2
	5	101 ± 1
	25	99 ± 2
	100	98 ± 3
Mg^{2+}	1	99 ± 1
	5	98 ± 3
	25	96 ± 3
	100	98 ± 1
Al^{3+}	1	102 ± 3
	5	98 ± 1
	25	99 ± 1
Zn^{2+}	1	102 ± 2
	5	101 ± 3
	50	98 ± 1
Cu^{2+}	1	97 ± 2
	5	97 ± 1
	25	97 ± 2
Cd^{2+}	1	98 ± 1
	5	100 ± 2
	25	98 ± 1
K^+	1	97 ± 3
	5	99 ± 1
	25	98 ± 1
	100	96 ± 2
Ca^{2+}	1	100 ± 2
	5	99 ± 1
	25	95 ± 2
	100	96 ± 2
Fe^{3+}	1	96 ± 2
	5	98 ± 3
	25	96 ± 3
Fe^{3+} [b]	1	97 ± 2
	5	81 ± 4
	25	32 ± 4
Co^{2+}	1	100 ± 1
	5	98 ± 2
	25	99 ± 1

[a] Mean ± standard deviation for three determinations.
[b] Without masking agent (NaF).

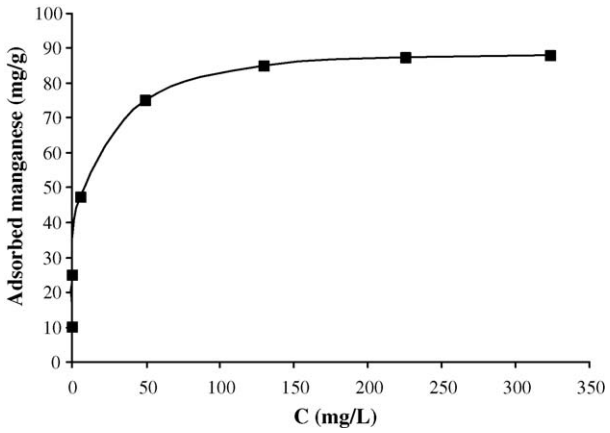

Fig. 2. Adsorption isotherm of Amberlyst 36 for manganese in batch procedure.

ing water can be recovered quantitatively using the proposed procedure.

3.7. Adsorption isotherm and adsorption capacity

The adsorption capacity of the resin was determined by the batch technique [5]. Therefore, the effect of contact (shaking) time on the adsorption of the manganese was evaluated at room temperature (25 ± 1 °C). For this purpose, 50 mL of the model solution (Mn(II): 0.1 μg/mL) and 100 mg of the resin were placed in a flask. The pH of the solution was adjusted to 2 and the flask was shaken with shaker at different time intervals at 200 rpm. The amount of residual manganese(II) in the solution was determined by FAAS after filtration. The data obtained from the adsorption of manganese on the solution showed that a contact time of 60 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time.

The adsorption behaviour of Amberlyst 36 was determined by studying the amount of adsorbed manganese as a function of manganese concentration [5]. Therefore, 50 mL of sample solutions having the manganese the concentrations in the range of 20–500 mg/L at pH 2 were shaken for 60 min with a constant weight (100 mg) of the resin. The profile of the adsorption isotherm of the resin for manganese is shown in Fig. 2, representing the amounts of adsorbed manganese versus the manganese concentration of the supernatant under equilibrium conditions. The analysis of the isotherm data is important in order to develop an equation that accurately represents the results. When the adsorption profile reaches a plateau, a monolayer adsorption is supposed to be established. The data of the isotherm reveal that the adsorption process conforms to the Langmuir model. In Fig. 2, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. A modified Langmuir equation conformed to this kind of adsorption isotherm as represented below

$$\frac{C_E}{Q_E} = \frac{C_E}{Q_0} + \frac{1}{Q_0 b}$$

where C_E is the concentration of manganese(II) in the solution at equilibrium (mg/L), Q_E the amount of sorbed manganese per gram of resin at equilibrium (mg/g), b the "affinity" parameter or Langmuir constant (L/mg) and Q_0 is the "capacity" parameter (mg/g). Based on the linear form of the adsorption isotherm derived from plots of C_E/Q_E versus C_E, the constant Q_0 values were calculated from the slope of the graph. The value of Q_0 is found to be 88 mg/g. The retention capacity of this adsorbent for manganese (88 mg/g) is much higher than the adsorbents already reported in the literatures (1.65 and 6.5 mg/g) [2,28]. The Langmuir constant is 0.2743 L/mg.

3.8. Analytical figures of merit

By using direct aspiration in FAAS without the preconcentration system the linear range for manganese determination was between 0.1 and 5 μg/mL. The calibration equation was $A = 0.004 + 0.113C$, where C is the manganese concentration in μg/mL, and A is the absorbance. Calibration equation calculations are based on the average of triplicate readings for each standard solution.

The recovery of spiked manganese and the precision of the procedure for seven replicates determined as the relative standard deviation of recovery at the optimum conditions given above (amount of manganese, 5 μg; volume of solution, 50 mL; pH, 2; elution solution, 5 mL of 3 mol/L nitric acid; flow rate, 5 mL/min), was in the range of 93–102% and about 3%, respectively.

In order to determine the instrumental detection limit, 50 mL of a blank solution was (triple water) passed through the column and retained manganese was eluted by 50 mL of the elution solution mentioned above. The instrumental detection limit based on three times the standard deviation of the blank ($LOD_i = 3\sigma/m$; where m is the slope of calibration curve) was found to be 49 μg/L for manganese ($N = 20$). The analytical detection limit has been calculated by dividing the instrumental detection limit by the enrichment factor (200 in the present work) [29]. Analytical detection limit (LOD_a) for manganese was 0.245 μg/L. The limit of quantification (LOQ) was calculated as about 0.735 μg/L by considering the three times the LOD value. This manganese concentration cannot be determined directly by flame AAS with sufficient accuracy and precision.

3.9. Validation of the proposed method

In order to evaluate the accuracy of the developed procedure, manganese was determined in standard reference material (Tea leaves GBW 0760). Manganese concentration found as the mean of five determinations at 95% confidence level was 1273 ± 70 μg/g with a relative error of 2.7%. It was found that there is no significant difference between result found by the proposed method and certified value (1240 ± 40 μg/g) according to the t-test. It can be concluded that there is no systematic error in the determination at 95% confidence level.

3.10. Analytical application

Since it was found that the proposed preconcentration method was useful for the preconcentration of trace manganese in the presence of other metal ions, the method was applied to the deter-

Table 2
Determination of manganese in various samples (volume of water samples: 1000 mL, amount of tea sample: 0.2 g) (in μg/L for water samples and in μg/g for tea sample)

Sample	Added	Found $\bar{x} \pm \frac{ts}{\sqrt{N}}$	Relative error (%)
Tap water[a]	–	2.2 ± 0.1	–
	2.0	4.1 ± 0.2	−2.4
Drinking water[b]	–	1.4 ± 0.1	–
	2.0	3.3 ± 0.3	−2.9
Treated water[b]	–	1.1 ± 0.1	–
	2.0	3.2 ± 0.3	+3.2
Tea[b]	–	1050 ± 70	–
	1000	1980 ± 130	−3.4

[a] Mean of seven determinations at 95% confidence level.
[b] Mean of five determinations at 95% confidence level.

mination of manganese (total manganese) in drinking waters and tea samples under optimal experimental conditions. For the determination of total manganese in water samples, ascorbic acid was added to reduce the manganese species to Mn(II) prior to preconcentration procedure. For this purpose, an aliquot of water samples and tea bag sample solutions containing ascorbic acid were passed through the column under the optimum conditions determined experimentally. The accuracy of the method was also checked by measuring the recovery of spiked samples (Table 2). Relative errors, below 5%, demonstrate the applicability of the method and indicate that the proposed method is essentially free from interferences when applied to the analysis of drinking water and tea samples. These results are in agreement with the literature. Tokalıoğlu and Kartal found 912–1295 μg/g manganese in Turkish tea [30].

4. Conclusion

A proposed procedure provides a simple, selective, accurate and precise method for the preconcentration and determination of manganese in large volumes of various sample solutions. The main advantages of the method over the many other solid-phase preconcentration method are permitting to study in a wide range of pH that is no necessity buffer to control the pH values precisely, higher sample volume and not requiring the chelating agent. Amberlyst 36 does not show volume change in operating at wide pH ranges and therefore, easy flow properties and constant flow rates can be maintained. The main disadvantage of the method is duration time. It is about 3.5 h for 1000 mL of sample solution and 5 mL of eluent. Trace manganese in drinking water samples can be effectively preconcentrated to a factor of 200. The column is good enough for manganese determination in matrixes containing interferent ions in high concentrations. The adsorption capacity of Amberlyst 36 for manganese is higher than the adsorbents already reported in the literatures [2,28]. The detection limit achieved was satisfactory for the samples studied, and can be improved by using more sensitive detectors such as ICP–AES and ICP–MS.

References

[1] D. Perez-Bendito, S. Rubio, Environmental Analytical Chemistry, Elsevier, Amsterdam, 1998.
[2] M. Doğutan, H. Filik, R. Apak, Anal. Chim. Acta 485 (2003) 205.
[3] M. Okumura, T. Anate, K. Fujinaga, Y. Seike, Anal. Sci. 18 (2002) 1093.
[4] H. Bağ, A.R. Turker, A. Tunceli, M. Lale, Anal. Sci. 17 (2001) 901.
[5] F. Gode, E. Pehlivan, J. Hazard. Mater. B 100 (2003) 231.
[6] A. Ersoz, R. Say, A. Denizli, Anal. Chim. Acta 502 (2004) 91.
[7] A.X.S. Qian, G.H.F. He, X. Han, Analyst 126 (2001) 239.
[8] S. Baytak, A.R. Türker, Turk. J. Chem. 28 (2004) 243.
[9] S.B. Sarmani, M.P. Abdullah, A.M. Bobaker, J. Radioanal. Nucl. Chem. 259 (2004) 257.
[10] A.M. Starvin, T. Prasada Rao, J. Hazard. Mater. B 113 (2004) 77.
[11] H.A. Mckenzie, L.E. Smythe, Quantitative Trace Analysis of Biological Materials, Elsevier, New York, 1988.
[12] J.E. Fergusson, The Heavy Elements—Chemistry, Impact and Healthy Effects, Pergamon Press, Oxford, 1990.
[13] M.C. Yebra-Biurrum, A. Garcia-Guarrido, Food Chem. 72 (2001) 279.
[14] M.G. Pereira, M.A.Z. Arruda, Microchim. Acta 141 (2003) 115.
[15] Y. Okamoto, Y. Nomura, H. Nakamura, K. Iwamaru, T. Fujiwara, T. Kamamaru, Microchem. J. 65 (2000) 341.
[16] V.O. Doroschuk, S.O. Lelyushok, V.B. Ishchenko, S.A. Kulichenko, Talanta 64 (2004) 853.
[17] L. Soko, L. Chimuka, E. Cukrowska, S. Pole, Anal. Chim. Acta 485 (2003) 25.
[18] J.I. Drever, The Geochemistry of Natural Waters, 3rd ed., Prentice-Hall, New Jersey, 1997.
[19] W. Davison, Earth Sci. Rev. 34 (1993) 119.
[20] D. Afzali, M.A. Taher, A. Mostafavi, S.Z.M. Mobarakeh, Talanta 65 (2005) 476.
[21] G.D. Yadav, A.V. Joshi, Org. Process Res. Dev. 5 (2001) 408.
[22] G.D. Yadav, M.S.M.M. Rahuman, Ultrason. Sonochem. 10 (2003) 135.
[23] G.D. Yadav, H.B. Kulkarni, React. Funct. Polym. 44 (2000) 153.
[24] P.J. Whiteside, B.A. Milner, Atomic Absorption Data Book, Pye Unicam, Cambride, 1984.
[25] M. Krachler, M. Burow, H. Emons, Analyst 125 (1999) 777.
[26] A. Mizuike, Enrichment Techniques for Inorganic Trace Analysis, Springer-Verlag, Berlin, 1983, p. 6.
[27] E. Kenduzler, A.R. Turker, Anal. Sci. 18 (2002) 917.
[28] M.A. Taher, Anal. Sci. 17 (2001) 969.
[29] M.A.A. Akl, I.M.M. Kenawy, R.R. Lasheen, Microchem. J. 78 (2004) 143.
[30] Ş. Tokalıoğlu, Ş. Kartal, Instrum. Sci. Tech. 32 (2004) 387.