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ORIGINAL ARTICLE

Determination of Trace Amount of Manganese in Water Samples by Micro-funnel Magnetic Stirring-assisted Liquid Phase Microextraction Technique

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KEYWORDS

Micro-funnel magnetic stirring-assisted liquid phase Microextraction;
Manganese;
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ABSTRACT: In this study, trace amounts of manganese ions were extracted using a sensitive, selective, rapid, and simple micro-funnel magnetic stirring-assisted liquid phase microextraction (MF-MSA-LPME) method and determined by flame atomic absorption spectrometry (FAAS). 1-(2-Thiazolylazo)-2-naphthol((TAN) and 1-octanol were chosen as chelating agent and extraction solvent, respectively. The effective parameters on extraction efficiency such as type and volume of extraction solvent, pH of sample solution, ligand concentration, extraction time, and ion strength were investigated and optimized. Under the optimum form, limit of detection (LOD), relative standard deviation, and the enrichment factor were 0.16 µg L^{-1}, 2.9%, and 252, respectively. The calibration graph was linear over the range of 1-120 µg L^{-1} with correlation of coefficient r^2 = 0.995.The proposed method could successfully determine trace amounts of manganese ions in the real water samples with good accuracy and validity.

INTRODUCTION

Manganese (Mn) is a key element for the appropriate function of several enzymes and plays essential roles in the nervous system, function of brain, and the bone growth. However, excessive intake of manganese in body can lead to lesions, headache, psychotic behavior, drowsiness, and other illnesses. So, manganese is an important element from an environmental perspective [1] and accurate determination of trace amounts of manganese in environmental samples is important and requires simple and sensitive instruments. On the other hand, due to low concentration and matrix effects, the determination of trace amounts of manganese in real samples is difficult. Although atomic spectrometric methods are powerful analytical tools for the determination of elements at a trace level in environmental samples, preconcentration techniques combined with AAS are still required. Several sample preparation methods have been used for the determination of trace amounts of manganese from various matrices, including co-precipitation [2], solid phase extraction (SPE) [3-5], liquid liquid extraction (LLE) [6], and cloud point extraction (CPE) [7]. However, these methods are relatively expensive, time-consuming and in some cases require a large amount of hazardous and expensive organic solvent. Recently, dispersive liquid-liquid microextraction (DLLME), a new mode of LPME, was introduced. This method has many advantages, including high enrichment factor, simplicity, ease of operation, low sample volume, low cost, and low consumption of organic solvents [8, 9]. But one of the serious drawbacks of DLLME is that the extraction solvents are limited only to chlorinated solvents, which have higher density than water. Therefore, recently, several modified DLLME methods have been developed

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using low-density solvents and different extraction devices [10-14]. However, a common problem with these methods is the difficulty of withdrawing very little amounts of extraction solvents from the sample solution surface. Therefore bell-shaped extraction device assisted liquid liquid microextraction (BSED–LLME), was introduced by Radomir Cabala et.al. based on applying a low density organic solvent due to avoidance of the drawback mentioned above, [15].

In our previous study, [16] we reported a micro-funnel magnetic stirring-assisted dispersive liquid phase microextraction technique for determination of 3-chloro-4-(dichloromethyl)-5-hydroxy-2 (5H)-furanone in aqueous samples by GC-ECD.

The aim of this study is to introduce a modified micro-funnel device for extraction of trace amounts of manganese and its determination using flame atomic absorption spectroscopy method. A homemade micro-funnel vessel is applied for the microextraction procedure by collecting the organic solvent in narrow neck glass tube. Unlike the DLLME method, extraction was carried out without the use of disperser solvent and centrifugation step. Finally, the upper organic phase was easily removed and injected to flame atomic absorption spectroscopy (FAAS) system.

MATERIALS AND METHODS

Reagents

All reagents were applied in analytical grade. Analytical grade of manganese nitrate and nitrate salts of other cations (all from Merck, Darmstadt, Germany) were available in the highest purity. Double-distilled water was used throughout the experiment. The glassware was kept in a 5% (v/v) nitric acid solution overnight and washed afterwards with double-distilled water. Working solutions of Mn at µg L^{-1} level were prepared daily by diluting a 1000 µg L^{-1} stock solution. The pH of sample solutions was adjusted using hydrochloric acid and ammonia. 1-undecanol, 1-decanol, 1-dodecanol, and 1-octanol were purchased (all from Merck, Darmstadt, Germany) as extraction solvents. 1-(2-Thiazolylazo)-2-naphthol (TAN) solution, as the chelating agent, was prepared by dissolving the appropriate amount of TAN (Merck, Darmstadt, Germany) in 1-octanol.

Instrumentation

Manganese was determined using a Shimadzu flame atomic absorption spectrophotometer (AA-680) equipped with a deuterium lamp for the background correction of an air–acetylene burner. A manganese hollow cathode lamp (analytical wavelength 279.5 nm) from Hamamatsu, Photonic Co. Ltd, L233 series was employed as the radiation source. Acetylene and air flow rates were 1.8 and 8 L min^{-1}, respectively. All pH measurements were carried out by a pH meter model Metrohm Lab-827. The sample solution was stirred using Magnetic stirrer (IKA RH basic 2, Germany). A homemade microfunnel vessel was applied for extraction process.

General procedure

A schematic procedure of the MF-MSA-LLME is shown in Figure 1. A total volume of 50 mL solution containing 100 µg L^{-1} of manganese ions and $NaNO_3$ (0.2 % w/v) was adjusted to a pH of 9. Afterwards, the prepared solution was poured in a cylindrical glass vial (13 cm height and 28 mm i.d.). 200 µL of TAN solution (500 µg in n-octanol) was lightly injected on the top-center surface of the sample solution by a 250 µL Hamilton syringe (Figure 1a). The micro funnel cap was placed on the cylindrical vial and the mixture was vigorously stirred at 1200 rpm for 7.5 min. As a result, a cloudy solution is formed due to the dispersion of many fine droplets of n-octanol in sample solution. Therefore, the species were extracted into the fine droplets (Figure 1b). Afterwards, the magnetic stirrer was stopped and the solution was kept immobilized for one minute (Figure 1c). Accordingly, the emulsified fine droplets of the extraction phase were collected on the top of the solution (Figure 1d). Then the organic phase was moved to the capillary tube of micro-funnel by injecting a few milliliters of double distilled water into the vial through the rubber cap, which holds the micro-funnel and the glass tube together (Figure 1e). Finally, the organic phase was manually removed by microsyringe, transferred into the eppendorf vial, diluted with 300 µL of methanol (Figure 1f), and introduced into the flame atomic absorption spectrometer for analysis.

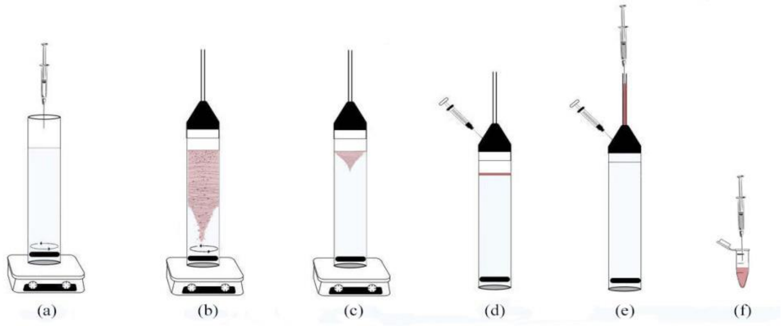

Figure 1. General process of MF-MSA-LLME for (a)–(f).

Sample preparation

Different water samples were collected from different parts of Arak, Iran (river water of Hossein Abad, mineral water of Sarband Mountain, tap water, and well water of different parts of the city). These water samples were filtered using 0.45 µm micropore membranes, adjusted to the a pH of 9, and stored in glass containers at 4°C.

RESULTS AND DISCUSSION

The important parameters affecting the proposed microextraction procedure include: type and volume of extraction solvent, pH of sample solution, ligand concentration, extraction time, and effect of salt. These parameters were investigated and optimized by one factor at a time method.

Effect of type and volume of extraction solvent

In this proposed method, extraction solvent has lower density than water, immiscibility with aqueous phase, and the extraction capability of target analyte. For this purpose, 1-undecanol, 1-dodecanol, 1-decanol, and n-octanol were tested. The result demonstrated that n-octanol has the highest extraction efficiency for the extraction of manganese. Therefore, n-octanol was selected as the proper extracting solvent for further experiments. The effect of volume of the extracting solvent was also studied in the range of 75-350 µL. The results (Figure 2) showed that by increasing the volume of solvent above 200 µL, the extraction efficiency decreased. Thus, in the subsequent experiments, 200 µL was chosen as the optimum volume of the extraction solvent.

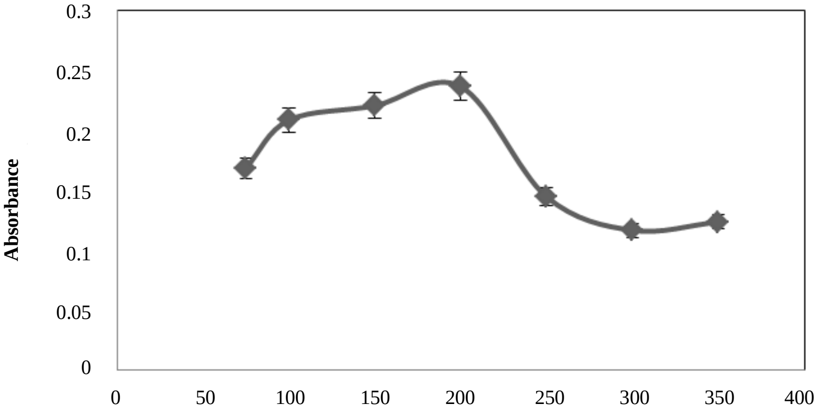

Figure 2. Effect of extraction solvent volume on the MF-MSA-LPME procedure. Conditions for extraction: concentration of manganese: 20 µg L^{-1}, pH: 9, $NaNO_3$ concentration 0.2% w/v, extracting: TAN solution (500 µg in n-octanol), extraction time: 7.5 min.

The effect of pH of sample solution

The pH of aqueous solution plays a critical role in the formation of Mn^{2+}–TAN complex and the extraction of manganese. So, the effect of pH was investigated within the pH range of 5-12. The illustrated results in Figure 3 show that the maximum analytical signal was achieved at pH 9.0. Hence, the pH value of 9.0 was used for subsequent experiments.

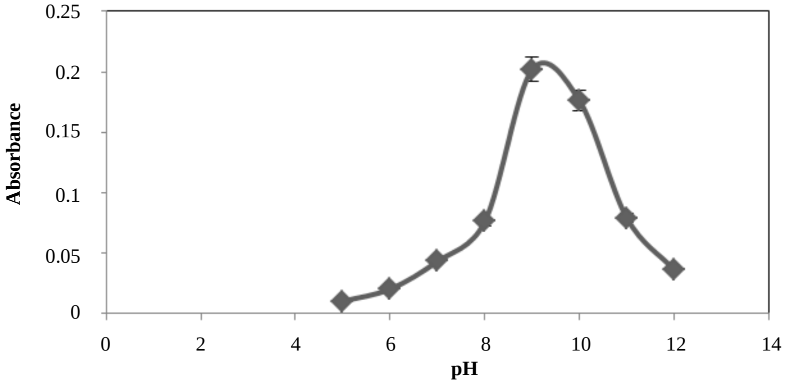

Figure 3. Effect of pH of sample solution on the MF-MSA-LLME procedure. Conditions for extraction: concentration of manganese: 20 µg L^{-1}, $NaNO_3$ concentration 0.2% w/v, extracting: 200 µL TAN solution (500 µg in n-octanol), extraction time: 7.5 min**.**

Effect of TAN concentration

The effect of TAN concentration on the extraction of manganese ions was investigated using the proposed MF-MSA-LLME method at different concentrations of TAN in the extraction solvent. The results indicated that by increasing TAN concentration to 500µg, the extraction efficiency increased, and then, remained more or less constant (Figure 4). So, the TAN concentration of 200 µg was chosen as the optimum amount of ligand for further studies.

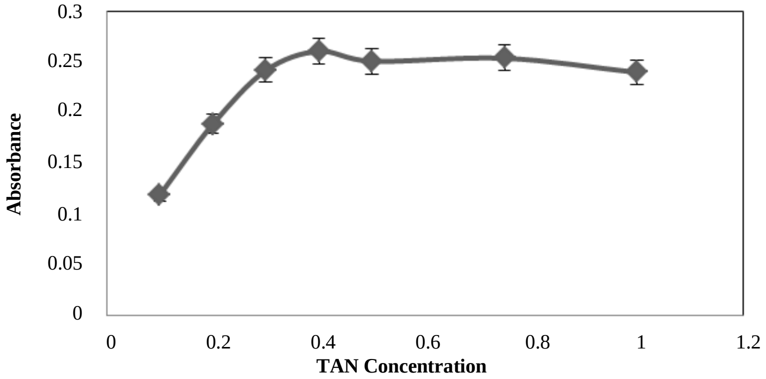

Figure 4. Effect of the TAN concentration on the MF-MSA-LLME procedure. Conditions for extraction: concentration of manganese: 20 µg L^{-1}, pH: 9, $NaNO_3$ concentration 0.2% w/v, extracting: 200 µL TAN solution (µg in n-octanol), extraction time: 7.5 min**.**

Extraction time

In MF-MSA-LLME, the interval time between the introduction of the extraction solvent (n-octanol including 500 µg of ligand) and the end of stirring step was defined as the extraction time. The effect of extraction time was examined over the range of 0.5 to 13 minute under optimal values obtained from the parameters studied above. As can be seen in Figure 5, the signals of Mn increase along with increasing the extraction time up to 7.5 min. Thus, 7.5 min was selected as the extraction time for further investigation.

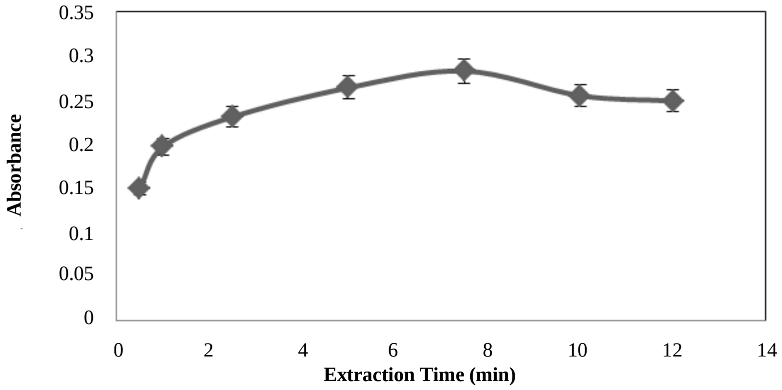

Figure 5. Effect of extraction time on the MF-MSA-LLME procedure. Conditions for extraction: concentration of manganese: 20 µg L^{-1}, pH: 9, $NaNO_3$ concentration 0.2% w/v, extracting: 200 µL TAN solution (500 µg in n-octanol).

Effect of salt

The influence of ionic strength on the extraction recovery was evaluated by adding various amounts of $NaNO_3$ (0–2% w⁄v) to sample solution. The results showed that the extraction efficiency was increased by increasing $NaNO_3$ concentration up to 0. 2%, and then, remained constant (Figure 6). Therefore, 0.2% of $NaNO_3$ concentration was applied for subsequent studies.

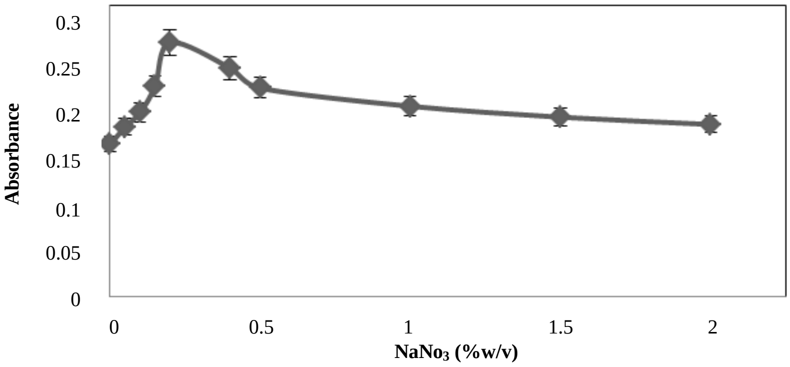

Figure 6. Effect of salt on the MF-MSA-LLME procedure. Conditions for extraction: concentration of manganese: 20 µg L^{-1}, pH: 9, extracting: 200 µL TAN solution (500µg in n-octanol), extraction time: 7.5 min**.**

Interference effect of foreign ions

In order to study the effect of other metal ions in the MF-MSA-LLME method, a total volume of 50 mL of sample solution containing 20 µg L^{-1} of Mn was prepared in the presence of different amounts of other ions and treated according to the recommended procedure. The tolerance limit was set as the concentration of added ion that caused ±5% relative error in the determination Mn. Table 1 displays the tolerance limits of the interference ions. The results demonstrate that most of the cations and anions did not seriously interfere with the extraction and determination of manganese using the proposed method.

Table 1. Effect of foreign ions on the recovery of 20 µg L^{-1} Mn (II) using MF-MSA-LLME.

Ions	Tolerance limits (µg L^{-1})
K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}	1000
Ni^{2+}, Zn^{2+}	500
Pb^{+2}, Cd^{2+}	250
Ag^+, Co^{2+}	150
Cu^{2+}, Pd^{2+}	100
Fe^{2+}, Cr^{3+}	50

Figures of Merit

The analytical characteristics of the proposed method, including linear dynamic range (LDR), limit of detection (LOD), reproducibility, correlation coefficient, and enhancement factor (EF) were analyzed under the optimum conditions and the results are summarized in Table 2. The calibration graph was linear in the range of 1 to 120 µg L^{-1} of manganese. The regression equation for the calibration curve after MF-MSA-LLME was $A=11.477\ C_{Mn}–0.0.056$ with a correlation coefficient (r^2) of 0.995. The LOD of the method for determination of Mn(II) was determined to be 3Sb/m, where "S_b" is standard deviation of the blank signals for seven replicates, and "m" is calibration curve's slope of the MF-MSA-LPME method, which was equal to 0.16 µg L^{-1}. The relative standard deviation (RSD) for seven replicate measurements of 20 µg L^{-1} Mn (II) was 2.9 %. Enrichment factor (EF) was about 252, which was calculated from the slope ratio of the calibration curves for manganese determination with (11.477) and without (0.0455) MF-MSA-LPME.

Table 2. Analytical characteristics of the proposed method for determination of Mn (II)

Parameter	Value
Regression equation before extraction	$A = 0.0455\ C_{Mn} – 0.0056$
Regression equation after extraction	$A = 11.477\ C_{Mn} – 0.0506$
Linear range (µg L^{-1})	1-120
Correlation coefficient (r^2)	0.995
Enhancement Factor	252
RSD (%) (n=7, Mn^{2+}concentration=20 µg L^{-1})	2.9
LOD (µg L^{-1}) (n=7)	0.16

Analysis of real samples

The developed MF-MSA-LLME procedure method was applied to determine manganese (II) in environmental water samples (river water of Hossein Abad, mineral water of Sarband Mountain, tap water and well water of different parts of the city). Results and the recovery for spiked samples are listed in Table 3**.** The accuracy of the method was studied using the analysis of the samples spiked with the predefined amount of manganese. As can be seen, the relative recoveries of manganese from the mentioned water samples were between 94.50 and 108.27 %. These results indicated that the matrices of these water samples have little effect on the extraction efficiency of manganese using MF-MSA-LLME method.

Table 3. Analytical results of Mn (II) in environmental water samples

Sample	Mn added (µg L^{-1})	Found (µg L^{-1})[a]	Recovery (%)
Tap water	0	N.D [b]	-
	20	21.41 ± 0.76	107.05
	40	42.56 ± 0.57	106.40
Well water	0	ND	-
	20	19.82 ± 0.12	99.10
	40	43.31 ± 0.24	108.27
Mineral water	0	N.D	-
	20	19.94 ± 0.98	99.70
	40	41.76 ± 0.88	104.40
River water	0	N.D	-
	20	18.9 ± 0.99	94.50
	40	40.97 ± 0.91	102.42

[a] Mean value of three replicate determination ± standard deviation (n = 3), [b] Not. Detection

Comparison of MF-MSA-LPME with the other methods

The results of the comparison made between the present method and other reported methods in terms of preconcentration and determination of manganese are summarized in Table 4. As can be concluded from Table 4, the present method has a low LOD, good enrichment factor, and good RSD, and these characteristics are comparable to or even better than most of the other reported methods. The results clearly show that the developed MF-MSA-LLME is sensitive, precise, and accurate for the determination of Mn(II) in different real samples.

Table 4. Comparison of analytical characteristics of the proposed method with some published methods for determination of manganese by FAAS.

Method	LOD (μg L^{-1})[a]	EF/PF[b]	RSD (%)	Linear range (μg L^{-1})	Ref.
SPE	2.6	225	3	20-310	[5]
SPE-SFODME[c]	0.57	81	3.57	1.90-400	[17]
LL-USAEME[d]	0.5	9.51	2.9	2−850	[18]
DLLME	3	50	3.3	10-200	[19]
IL-DLLME[e]	0.52	82.6	3.3	2–100	[20]
MF-MSA-LPME	0.16	252	2.9	1−120	This work

[a] Limit of detection, [b] EF: enhancement factor; PF: preconcentration factor,[c] Solid-phase extraction combined with solidified floating organic drop microextraction, [d] ligandless-ultrasound-assisted emulsification microextraction ,[e] Ionic liquid based dispersive liquid liquid microextraction

CONCLUSIONS

In this study, we introduced a novel, effective, and sensitive MF-MSA-LLME method by the application of home-designed extraction tube device coupled with flame atomic absorption spectrometry for the preconcentration and determination of manganese in water samples. The use of modified microfunnel system as a suitable technique for easy extraction solvent withdrawal has a unique applicability to this method. The developed method was successfully applied without using disperser solvent and centrifugation step. This method has advantages such as low cost, low toxicity, rapidity, good enhancement factor, low LOD, and high sensitivity and selectivity. The proposed method could successfully determine trace amounts of manganese ions in the real water samples with satisfactory results.

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