A Novel Method Using Solid-Phase Extraction with Slotted Quartz Tube Atomic Absorption Spectrometry for the Determination of Manganese in Walnut Samples

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Mn\(^{2+}\) was separated and preconcentrated using both solid-phase extraction (SPE) and a slotted quartz tube (SQT), and detected by a flame atomic absorption spectrometry (FAAS) system. Firstly, Mn\(^{2+}\) was retained on a column filled with Amberlite CG-120 resin, and then retained Mn\(^{2+}\) ions on the Amberlite CG-120 resin eluted with 5 mL of 4 mol/L HNO\(_3\). This part was called the “first preconcentration step”. Furthermore, to determine the Mn\(^{2+}\) in a walnut sample, the SQT device was also used after the separation and preconcentration of Mn\(^{2+}\) from the Amberlite CG-120 resin so as to further improve the sensitivity of system. This part was called the “second preconcentration step” in this study. The enrichment factor and limit of detection values were found to be 360 fold and 0.22 μg/L, in turn, after a two-step preconcentration method. The good accuracy of method was confirmed with the use of standard reference material (spinach leaves, NIST-1570a).

Keywords Manganese, two-step preconcentration method, solid-phase extraction, slotted quartz tube, atomic-absorption spectrometry

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Introduction

Manganese (Mn) is an essential element for both humans and other animals. This element plays important roles in the nervous system, brain functions and the growth of bones; it also affects enzymatic reactions.\(^1\) During a deficiency of Mn, there may be some unwanted effects, such as poor reproductive performance, congenital malformations in offspring, growth retardation, abnormal function for bones, and impaired glucose tolerance. On the contrary, in the case of a surplus of Mn, depression effect, excessive sleeping, hallucinations, neurological disorders, over-flow of the liver and DNA mutations may emerge.\(^2\) It may be received in the body with a variety of foods, which are tea, grains, rice, soya beans, eggs, nuts and cereals. Therefore, the determination of sub levels of Mn in the food samples is a very important issue.\(^3\)

In order to determine the concentration of Mn\(^{2+}\) in the real samples, various analytical detection techniques have been employed, such as flame atomic-absorption spectrometry (FAAS),\(^4\) inductively coupled plasma-optical emission spectrometry (ICP-OES),\(^5\) high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS)\(^6\) and electrothermal atomic-absorption spectrometry (ETAAS).\(^7\) Among them, FAAS is currently an employed popular technique for trace-element determination because of its low cost, speed, ease of operation, and selectivity.\(^8\) On the other hand, a direct determination of some elements in the real samples by FAAS is often difficult because of the fact that real samples can contain low concentrations of elements. Because of this, separation and/or preconcentration steps should be applied before the detection step of elements by FAAS.\(^9\)

Several separation and preconcentration methods have been used for the Mn\(^{2+}\) detection, such as cloud-point extraction (CPE),\(^10\) liquid-liquid microextraction (DLLME),\(^11\) and solid-phase extraction (SPE).\(^12\) Among them, SPE is the most common method as the separation and preconcentration of elements by researchers, owing to the high enrichment factor, the ability to combine with different detection techniques, low cost and low consumption of organic solvents.\(^13\) Several reports have appeared concerning solid-phase extraction sorbents for the separation and preconcentration of Mn\(^{2+}\); such as Amberlyst 36 resin,\(^14\) modified amberlite XAD resin,\(^15\) polyhydroxyl-polyurethane foam (PPF),\(^16\) Diaion SP-850 resin.\(^17\)

In addition to the extraction methods explained above, used to increase the sensitivity of FAAS, there have also been different methods to improve the sensitivity of FAAS: the slotted quartz tube (SQT), Delves’ microsampling cup, electrothermal atomizers for AAS and chemical vapor generation.\(^18\) Among them, an attempt was made by Watling, who suggested the use of the slotted quartz tube (SQT) together with FAAS. This method provides a sensitivity increment of around 2 and 5 fold, which depends on the elements.\(^19\)

In the present study, Mn\(^{2+}\) was enriched by a two-step preconcentration method. During the first step, the solid-phase extraction method with Amberlite CG-120 resin was used to separate and preconcentrate Mn\(^{2+}\). Amberlite CG-120 is categorized as the strong cation-exchanger resin. The functional

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groups of this resin are the Na⁺ form and sulfonic acid groups. It’s optimum pH condition for adsorption is among -0.4 - 10.20. In this stage, some important analytical parameters, such as the pH effect, sample flow rate and its volume, the elution flow rate and its volume and the amount of adsorbent on the recovery of the Mn²⁺ were optimized. In the case of the second step, the SQT device was also used together with the FAAS method after the separation and preconcentration of Mn²⁺ from the Amberlite CG-120 resin so as to improve the sensitivity of the system further for the determination of Mn²⁺ in walnut samples. To the best of our knowledge, there have been no studies reported in the literature to preconcentrate Mn²⁺ using two-step preconcentration methods, which are solid-phase extraction and using the SQT device, respectively.

**Experimental**

**Apparatus**

A flame atomic-absorption spectrophotometer (ATI UNICAM 939 Model) equipped with a deuterium lamp for a background corrector, a Mn hollow-cathode lamp (lamp current, 12.0 mA; wavelength, 279.5 nm; bandwidth of the slit, 0.5 nm), an air/ acetylene flame (acetylene flow rate, 9.0 L/min) as the atomizer and a slotted quartz tube with two slots (length of the slotted quartz tube, 12 cm; top slot of the slotted quartz tube, 4 cm; the below slot of slotted quartz tube, 5 cm) was used for the determination of Mn²⁺. A pH meter (Thermo Orion 3 Stars General procedure for the sorption of Mn²⁺ on the column until the next experiment. The SQT device was also used together with the FAAS method after the separation and preconcentration of Mn²⁺ from the Amberlite CG-120 resin so as to improve the sensitivity of the system further for the determination of Mn²⁺ in walnut samples. To the best of our knowledge, there have been no studies reported in the literature to preconcentrate Mn²⁺ using two-step preconcentration methods, which are solid-phase extraction and using the SQT device, respectively.

**Reagents**

In this study, all reagents were of analytical grade. An 18 MΩ cm⁻¹ deionized water purification system (PURIS purification system Expe-UP Series) was used in all experiments. The laboratory glassware was cleaned with 5% nitric acid. Afterwards, it was rinsed thoroughly with deionized water, and then dried. HNO₃, 65% (w/w), was supplied from Merck and HCl, 37% (w/w), was supplied from Riedel-de Haen.

**The preparation of the Mn²⁺ solution**

A stock aqueous solution of Mn²⁺ (1000 mg/L) was prepared by dissolving 0.13 g of MnSO₄·H₂O supplied from Sigma-Aldrich in 100 mL of water. A working aqueous solution of Mn²⁺ was also prepared from the above-mentioned stock solution by necessary dilution.

**Column preparation**

Firstly, a small amount of glass wool was placed at one end of the column (length of column, 15 cm; internal diameter of column, 0.8 cm). Afterwards, 300 mg of Amberlite CG-120 resin was added on it. Then, another piece of glass wool was placed back onto the Amberlite CG-120 resin. A solid-phase extractor, Amberlite CG-120 resin, was employed after washing with ethanol, a 1 mol/L HCl solution, 1 mol/L HNO₃ and water, respectively. Finally, after each usage, the column was stored by filling the water from the upper surface of the Amberlite CG-120 resin until the next experiment.

**Collection and preparation of samples**

In this study, the determination of Mn²⁺ was achieved for both standard reference materials (spinach leaves-NIST 1570a) and walnut samples. The walnut samples obtained from the local market were grown in Burdur, Turkey. Then, 0.1 g of walnut sample was placed into a teflon container. After this, 1.0 mL of concentrated HNO₃ was added. This container was sealed tightly, and then positioned in the carousel of a microwave oven. The temperature reached 200°C from room temperature for 15 min escalation at a certain speed. The temperature was kept constant for 15 min at 200°C, and thawing process was terminated. The cooling process was associated around 15 min. After that dissolved walnut samples were transported to a 100-mL flask and completed by 18 MΩ cm⁻¹ deionized water up to 100 mL. In addition, a 0.15-g standard reference material (spinach leaves-NIST 1570a) was digested by adding of 2 mL of HNO₃ on it using a microwave oven digestion system that employed the same program as explained above.

**Results and Discussion**

In this study, some experimental parameters in the first preconcentration step, which was Amberlite CG-120 resin, were optimized to obtain quantitative recoveries for Mn²⁺ detection. These parameters were the pH, concentration and type of eluent, eluent and sample flow rate, sample volume and amount of sorbent. Then, some other experimental parameters in the second preconcentration step, which involved the SQT device, such as the observation height i.e. the distance between the top of the burner head and SQT device and the acetylene flow rate; these optimized to find their optimum values.

**Effect of the pH**

The first optimization parameters based on the recovery of Mn²⁺ on the adsorbent involved the pH values. The recovery values were found by changing the pH of the solutions in the range of between 1 and 5 values. The results for the recovery of Mn²⁺ based on the pH values are shown in Fig. 1. Good quantitative recoveries were obtained for Mn²⁺ at over the wide pH range of 1 – 3 values. In principle, since real samples are usually dissolved in acidified solutions, and components of sample were not precipitated acidified solutions, pH 1 was selected as being the optimum value for subsequent experiment instead of higher pH values.

**Effect of the amount of Amberlite CG-120 resin**

The effect of the amount of Amberlite CG-120 resin is another important parameter concerning the adsorption of Mn²⁺ on the resin. For this reason, the effects of different amounts of Amberlite CG-120 resin varied from 0 to 0.5 g for the Mn²⁺
adsorption were investigated. Quantitative recovery was obtained from 0.05 to 0.3 g. In real samples applications, some ions in the samples may adsorb on the resin instead of the Mn$^{2+}$ determined. Thus, the adsorption capacity for Mn$^{2+}$ decreased by time lower than 0.3 g resin was used. Therefore, 0.3 g of Amberlite CG-120 resin was chosen as the optimum value used for subsequent experiments for Mn$^{2+}$ detection.

The effect of type and volume of the eluent

Different eluting agents, such as 2 mol/L HNO$_3$, 2 mol/L HCl, 2 mol/L HClO$_4$, ethanol and acetone, were tried for the elution of Mn$^{2+}$ on the Amberlite CG-120 resin. Quantitative recovery has been obtained using 10 mL of 2 mol/L HNO$_3$. After that, univariate optimization has been again applied to find the exact optimum concentration and volume of HNO$_3$ solutions. To do this, various concentrations of HNO$_3$ of between 0.1 and 4.0 mol/L for both 5 and 10 mL volumes of HNO$_3$ have been investigated, respectively. Quantitative recovery has been obtained by using 5 mL of 4 mol/L HNO$_3$ solutions. Thus, 5 mL of a 4 mol/L HNO$_3$ solution was employed as the eluent solution for subsequent experiments.

Effect of the flow rate of sample and eluent solution

The flow rates of the sample and eluent solutions are the most significant parameters for controlling the time of studies. After 25 mL solution containing 5 μg Mn$^{2+}$ had adjusted to the optimum pH value explained above, this solution was passed through the column at a flow rate varied from 0.25 to 5 mL/min, adjusted by gravity action, as shown in Fig. 2. A quantitative recovery was obtained from 0.25 to 1 mL/min. A flow rate of 1 mL/min was chosen as the best flow rate of the sample solution to save time. Additionally, an eluent solution was also passed through the Amberlite CG-120 resin at different flow rates, ranging from 0.25 to 2 mL/min, as shown in Fig. 3. A flow rate of 0.5 mL/min was chosen as the eluent flow rate based on the higher quantitative recovery.

Effect of the sample volume

In order to reach the highest preconcentration factor for Mn$^{2+}$ detection, the sample volume is a crucial parameter. Therefore, the influences of the sample volume on the recovery of Mn$^{2+}$ were also investigated. To do this, volumes of 25, 50, 100, 250, 500, 750 and 1000 mL of the sample solutions were passed through the Amberlite CG-120 column, respectively. The results, based on the recovery of Mn$^{2+}$, are shown in Fig. 4 for all of these sample volumes. As shown in Fig. 4, quantitative recovery for Mn$^{2+}$ detection was observed from 25 to 750 mL. By the time that the sample and eluent volumes were chosen to be 750 and 5 mL, in turn, an enrichment factor was found to be 150 fold.
at a lower flow rate, optimization has no significant effect on the Mn²⁺ signal. The absorbance value was found to be approximately 0.050 at a 1.1 mL/min acetylene flow rate. On the other hand, the absorbance value increased with an increase in the acetylene flow rate. The optimum acetylene flow rate was chosen to be the 0.8 mL/min. Moreover, the effect of the observation height i.e., the distance between the top of the burner head and the SQT device, was also investigated as the Mn²⁺ signal varied from 0.7 to 1.0 cm. The optimum observation height was found to be 0.9 cm, since the signal of 1 mg/L Mn²⁺ was reduced at lower and higher values than this optimum value.

Matrix effect

In real samples applications, some ions affect the analyte signal to be determined as positively and/or negatively, which is called as matrix effects. Therefore, the matrix effect was also investigated in this study. For this purpose, different cation ions prepared from the salts of Cl⁻, NO₃⁻, SO₄²⁻ ions were added individually to a solution of 25 mL containing 5 μg Mn²⁺, and then the proposed preconcentration method was applied. The results revealed that there were no important matrix effects on the Mn²⁺ signal using this suggested method, except that the Ca²⁺ ion at especially the higher concentration given in Table 1. Furthermore, additional experiments were also performed to decide whether the major elements (K⁺ and Mg²⁺) are adsorbed on the column or not. The experimental results revealed that 90% of K⁺ and 91% of Mg²⁺ in the dissolved walnut samples had not been adsorbed on the column. Afterwards, the adsorbed K⁺ and Mg²⁺ on the column had been obtained by 5 mL of 4 mol/L HNO₃ and then the washing solutions. As a result, there has been no memory effect observed for K⁺ and Mg²⁺.

Slotted quartz tube (SQT) optimizations

FAAS united with a SQT device was used for improving the sensitivity further in this study. Some of the analytical parameters, such as observation height i.e., the distance between the top of the burner head and the SQT device and acetylene flow rate were optimized. This part was called as the second preconcentration step for Mn²⁺ detection in this suggested study. In addition, the effect of the acetylene flow rate varied from 0.8 to 1.1 L/min was also investigated for the Mn²⁺ signal. The absorbance value for a 1 mg/L Mn²⁺ solution was found to be approximately 0.050 at a 1.1 mL/min acetylene flow rate. On the other hand, the absorbance value increased upon decreasing the acetylene flow rates; the absorbance value was found to be 0.095 at a flow rate of 0.8 mL/min. Because the flame goes out at a lower flow rate, optimization has not been achieved at a flow rate lower than 0.8 mL/min. Therefore, the optimum acetylene flow rate was chosen to be 0.8 mL/min. Moreover, the effect of the observation height i.e., the distance between the top of the burner head and the SQT device, was also investigated as the Mn²⁺ signal varied from 0.7 to 1.0 cm. The optimum observation height was found to be 0.9 cm, since the signal of 1 mg/L Mn²⁺ was reduced at lower and higher values than this optimum value.

Validation of the proposed method

The accuracy of the method was evaluated by determining Mn²⁺ in a certified reference material, “spinach leaves, NIST-1570a”. The Mn²⁺ value was determined in the certified reference material, and found to be 75.7 ± 5.2 μg/kg, which is in good agreement with the certified value of 75.9 ± 1.9 μg/kg, based on three replicate measurements at the 95% confidence level in which relative standard deviation (RSD) was found to be 3%.

Analytical application

The developed two-step preconcentration method was also applied for determining Mn²⁺ in walnut samples under the optimum experimental conditions. The accuracy of the method was also checked by measuring the recovery of spiked Mn²⁺ on the walnut samples as well, as shown in Table 2. During this experiment, firstly 0.1 g of the walnut samples were digested using microwave oven and then Mn²⁺ concentration was determined in these walnut samples, and found to be 160 ± 15 mg/kg. After that, 16 and 36 μg of Mn²⁺ were added in turn on the 0.1 g of walnut samples and the developed method was applied. The recovery value was calculated, and found to be 95 and 89% for Mn²⁺ determination, respectively.

Table 1 Effect of some ions on the recovery of Mn²⁺

| Ion (mg L⁻¹) | Conc./mg L⁻¹ | Mn²⁺, R% | Ion (mg L⁻¹) | Conc./mg L⁻¹ | Mn²⁺, R% |
|-------------|--------------|---------|-------------|--------------|---------|
| Na⁺         | 1            | 91      | Fe³⁺        | 1            | 98      |
|             | 5            | 89      |             | 5            | 94      |
|             | 50           | 100     |             | 50           | 89      |
| K⁺          | 1            | 90      | Zn²⁺        | 1            | 97      |
|             | 5            | 89      |             | 5            | 97      |
|             | 50           | 90      |             | 50           | 94      |
| Mg²⁺        | 1            | 85      | Co²⁺        | 1            | 94      |
|             | 5            | 87      |             | 5            | 89      |
|             | 50           | 89      |             | 50           | 80      |
| Ca²⁺        | 1            | 89      | Al³⁺        | 1            | 98      |
|             | 5            | 90      |             | 5            | 93      |
|             | 50           | 95      |             | 50           | 92      |
|             | 100          | 87      |             | 100          | 87      |
|             | 250          | 71      |             | 250          | 71      |
|             | 500          | 53      |             | 500          | 53      |

pH, 1; sample volume, 25 mL; eluent volume, 5 mL 4 mol/L HNO₃; amount of Mn²⁺, 5 μg; flow rate of sample, 1 mL/min; flow rate of eluent, 0.5 mL/min; resin amount, 300 mg.

Table 2 Determination of Mn²⁺ in a real sample (amount of walnut sample, 0.1 g)

| Sample | Added Mn²⁺/mg kg⁻¹ | Found/mg kg⁻¹ | RSD, % |
|--------|--------------------|---------------|--------|
| Walnut | —                  | 160 ± 15      | 9      |
|        | 160                | 305 ± 6       | 2      |
|        | 360                | 467 ± 24      | 5      |

a. Mean of five determinations.

Analytical figures of merit

The LOD value was obtained using both Amberlite CG-120 resin and the SQT device together, which is called a two-step preconcentration method. The LOD was found to be 0.22 μg/L using this preconcentration method (N = 25). In order to perform this experiment, 100 mL of a 4.0 mol/L HNO₃ solution (blank solution) was passed through Amberlite CG-120 resin. Afterwards, the retained Mn²⁺ in a blank solution on the Amberlite CG-120 resin was eluted by 100 mL of 4 mol/L of HNO₃. In this part of the study, there was no enrichment on the Amberlite CG-120 resin due to the fact that both of the volumes of the passed solution through the Amberlite CG-120 resin and the eluent solution were the same. Then, this eluent was used for determining the LOD (3σ) by SQT-FAAS. The linear range for FAAS and SQT-FAAS were found to be between 0.5 and 5.0 mg/L, and between 0.2 and 5.0 mg/L, respectively. Additionally, the linear equations for FAAS and SQT-FAAS, in turn, were found to be y = 0.0683x – 0.0031 and y = 0.1663x – 0.0138. Upon comparing the slopes of calibration plots without and with SQT, a 2.4-fold sensitivity enrichment was obtained. In addition, upon using only the Amberlite CG-120 resin, called first preconcentration step, a 150-fold enrichment was obtained, as explained above. Therefore, the total enrichment factor for Mn²⁺ was found to be 360 fold using a two-step preconcentration method.

The accuracy of the method was evaluated by determining Mn²⁺ in a certified reference material, “spinach leaves, NIST-1570a”. The Mn²⁺ value was determined in the certified reference material, and found to be 75.7 ± 5.2 μg/kg, which is in good agreement with the certified value of 75.9 ± 1.9 μg/kg, based on three replicate measurements at the 95% confidence level in which relative standard deviation (RSD) was found to be 3%.

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Conclusions

In conclusion, the developed two-step preconcentration method provides a simple, accurate and precise method for the preconcentration and determination of Mn$^{2+}$ ions. One of the most important parts in this study is that there is no necessity to use buffer solutions and a chelating agent for the separation and preconcentration of Mn$^{2+}$. In the solid-phase extraction step, Mn$^{2+}$ in walnut samples is preconcentrated as a factor of 360 fold in the developed two-step preconcentration method. Moreover, the Amberlite CG-120 resin is very effective for Mn$^{2+}$ determination in matrixes containing some matrix ions at the level of high concentrations. It has been found that the analytical performance of this method is comparable with the other preconcentration methods found in the literature summarized given in Table 3.

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Table 3 Comparison of the analytical performance of this proposed method and different preconcentration methods in the literature

| Study | pH | LOD/ \( \text{mg L}^{-1} \) | Enhancement factor | Resin type | Sample volume/ mL | Measuring instrument | Reference |
|-------|----|-----------------|-------------------|------------|------------------|---------------------|-----------|
| 1     | 9  | 0.26            | 24.7              | Amberlite XAD-4 | 30               | FAAS                | 21        |
| 2     | 6  | 0.15            | 325               | Graphene oxide | 1300             | FAAS                | 22        |
| 3     | 5  | 0.19            | 100               | Polyurethane foam | 1000             | FAAS                | 23        |
| 4     | 8  | 0.10            | 100               | Amberlite XAD-2010 | 500              | FAAS                | 24        |
| 5     | 10.5 | 0.88         | 45.6 n-Dodecyl trimethylammonium bromide | 10 | FAAS | 1 |
| 6     | 9  | 0.60            | 697               | Magnetic multi-wall carbon nanotube | 50-150 | FAAS | 4 |
| This study | 1 | 0.22           | 360               | Amberlite CG-120 | 750              | SQT-FAAS            | —         |