

Determination of trace amounts of manganese in water samples by flame atomic absorption spectrometry after dispersive liquid-liquid microextraction

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Dispersive liquid-liquid microextraction was combined with flame atomic absorption spectrometry for the determination of manganese in water samples. 1-(2-Pyridylazo)-2-naphthol (PAN), chloroform and ethanol were used as chelating agent, extraction solvent and disperser solvent, respectively. In this extraction method, a mixture of 500 μL ethanol (disperser solvent) and 100 μL chloroform (extraction solvent) was rapidly injected by syringe into the water sample containing manganese ions and 4×10^{-4} mol L^{-1} 1-(2-pyridylazo)-2-naphthol (PAN) (chelating agent). Thereby, a cloudy solution was formed. After centrifugation (5 min at 4000 rpm), the droplets of the cloud were settled at the bottom of the conical test tube (70 ± 2 μL). The settled phase was separated using a micro-syringe and diluted to 100 μL with ethanol. A microsample introduction system was employed for the nebulization of a micro-volume of the diluted solution into FAAS. Some effective parameters on extraction and complex formation, such as extraction and disperser solvent type and their volume, extraction time, salt effect, pH and concentration of the chelating agent, were optimized. Under the optimum conditions, an enrichment factor (EF) of 50 was obtained from only 5 mL of water sample. The calibration graph was linear in the range of 10–200 ng mL^{-1} with limit of detection (LOD) of 3.0 ng mL^{-1} . The relative standard deviation (R.S.D.) for ten replicate measurements of 50 ng mL^{-1} of manganese was 3.3 %. The method was successfully applied for the extraction and determination of manganese in some natural water samples.

Keywords: Dispersive liquid-liquid microextraction, Preconcentration, Manganese, Water sample, FAAS.

INTRODUCTION

Manganese is a necessity for the proper function of several enzymes and is an essential micro-nutrient for the function of the brain, nervous system and normal bone growth. It is present in large quantities in various steel materials as a hardening agent. It also finds application in pharmaceutical preparations. However, excessive intake can cause lesions, headache, psychotic behavior, drowsiness and other related symptoms and/or diseases. Thus manganese is an important element from the environmental perspective [1]. In general, concentrations of manganese in fresh waters [2] are within the range from 0.02 to 130 ng mL^{-1} . Therefore, the determination of this metal as Mn^{2+} ion often requires a method offering low detection limits. Although atomic spectrometric methods are powerful analytical tools for the determination of trace elements in environmental samples, preconcentration techniques combined with AAS are still necessary [3]. Liquid-liquid extraction (LLE) [4-6], solid phase extraction (SPE) [7-17] and cloud point extraction (CPE) [18-21] have been widely used for the preconcentration of manganese from water samples prior to its determination by flame atomic absorption spectrometry. However, that technique is rather

time-consuming and requires a large amount of sample. Separation and preconcentration based on dispersive liquid-liquid microextraction (DLLME) offer a convenient alternative to more conventional extraction methods [22]. This is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with other extraction methods. In this method, the appropriate mixture of extraction solvent and disperser solvent is rapidly injected by syringe into aqueous samples containing the analytes. Thereby, a cloudy solution is formed. In fact, the cloudy state is due to the formation of fine droplets of extraction solvent dispersed in the sample solution. Then, this cloudy solution is centrifuged and the fine droplets are settled at the bottom of a conical test tube. The determination of the analytes in the settled phase can be performed by instrumental analysis. In this extraction method, any component originally present in the solution that interacts with the fine droplets of extraction solvent directly or after previous derivatization reaction can be extracted from the initial solution and concentrated in the small volume of the settled phase. The advantages of DLLME method are simplicity of operation, rapidity, low cost, high recovery and enrichment factor. The dispersive liquid-liquid extraction methodology has been used to separate and preconcentrate organic compounds prior to their

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determination with chromatographic methods [23-25]. The DLLME has also been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes [26-27].

In the present work we report on the results obtained in a study of the dispersive liquid-liquid microextraction of manganese after the formation of a complex with PAN, with subsequent analysis by flame atomic absorption spectrometry using microsample introduction. The proposed method was also applied to the determination of manganese in water samples.

EXPERIMENTAL

Apparatus

A Thermo M series (Model: M5) flame atomic absorption spectrometer was utilized, equipped with a 50 mm burner head, deuterium background correction and air-acetylene flame. A manganese hollow cathode lamp (Thermo Scientific S51214) was used as radiation source, operated at 15 mA with a monochromator spectral bandpass of 0.1 nm. For manganese detection, the wavelength was set at the 232.0 nm resonance line. The acetylene and the air-flow rates were 0.8 and 10.0 L min⁻¹, respectively. The Centurion Scientific centrifuge (Model K240R, Arundel, UK) was used to accelerate the phase separation. The pH values were measured with a Metrohm pH-meter (Model: 691, Herisau, Switzerland), supplied with a glass-combined electrode.

Reagents and solutions

All reagents used were of analytical grade. All solutions were prepared with ultra pure water. The manganese stock solution (1000.0 mg L⁻¹) was prepared by dissolving appropriate amounts of Mn(NO₃)₂ in ultra pure water. Working solutions were prepared from the stock solution by serial dilutions with ultra pure water. Chloroform, carbon tetrachloride, chlorobenzene, acetone, methanol and ethanol were of analytical grade from Merck (Darmstadt, Germany). A 1 × 10⁻² mol L⁻¹ solution of 1-(2-pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) was prepared by dissolving an appropriate amount of PAN in acetone. This solution was kept in a dark place at room temperature. A stock standard ammonia/ammonium chloride buffer solution (0.1 mol L⁻¹, pH 10.0) was prepared by dissolving an appropriate amount of ammonia in ultra pure water and neutralizing to pH 10.0 with hydrochloric acid. The pipettes and vessels used for trace analysis were kept in 10%

nitric acid for at least 24 h and subsequently washed four times with ultra pure water before use.

Dispersive Liquid-Liquid Microextraction Procedure

5.0 mL of ultra pure water was placed in a 10 mL screw cap glass test tube with conical bottom and spiked at levels of 10-200 ng mL⁻¹ of manganese. Then 0.2 mL of 1.0 × 10⁻² mol L⁻¹ of PAN (as chelating agent) was added to this solution and the pH of the solution was adjusted by adding ammonia / ammonium chloride buffer solution (1.0 × 10⁻³ mol L⁻¹, pH 10.0). Then a mixture of 500 µL of ethanol (as disperser solvent) and 100 µL of chloroform (as extraction solvent) was injected rapidly into the sample solution by using 1.0-mL syringe, and the mixture was gently shaken. A cloudy solution (water, ethanol and chloroform) was formed in the test tube. In this step, manganese ions were extracted into the fine droplets of chloroform. The mixture was then centrifuged for 5 min at 4000 rpm. After this process, the dispersed fine droplets of chloroform were settled at the bottom of the conical test tube (70 ± 2 µL). The settled phase was separated using a micro-syringe, diluted to 100 µl with ethanol and then injected into the microsample introduction (discrete nebulization) system of FAAS.

RESULTS AND DISCUSSION

In this research, DLLME combined with FAAS was developed for determination of manganese in water samples. In order to obtain a high recovery and a high enrichment factor, the effects of different parameters on the complexation and extraction conditions such as pH, concentration of buffer and chelating agent, kind of extraction and disperser solvent and their volumes, extraction time and salt addition, were optimized. In order to study the mentioned parameters, extraction recovery and enrichment factor were calculated by equations (1) and (2), respectively.

$$EF = C_{\text{sed}} / C_0 \quad (1)$$

where EF, C_{sed} and C₀ are the enrichment factor, concentration of analyte in the sedimented phase and initial concentration of analyte in the aqueous sample, respectively.

$$R \% = [(C_{\text{sed}} \times V_{\text{sed}}) / (C_0 \times V_{\text{aq}})] \times 100 = [(EF \times V_{\text{sed}}) / V_{\text{aq}}] \times 100 \quad (2)$$

where R %, V_{sed} and V_{aq} are the extraction recovery, volume of sedimented phase and volume of aqueous sample, respectively. These parameters are known except C_{sed}. Calculation of C_{sed} was done by direct injection of a standard solution of Mn-

PAN complex in chloroform with concentration in the range of 0.5-10 $\mu\text{g mL}^{-1}$ to FAAS.

Effect of pH

The separation of metal ions by dispersive liquid-liquid microextraction involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of sedimented phase, thus achieving the desired preconcentration. The pH value plays a unique role in metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of manganese from water samples was studied within the pH range of 2-12 by addition of NaOH or HCl. The results are illustrated in Figure 1. According to these results, the pH of 10.0 was chosen for the extraction.

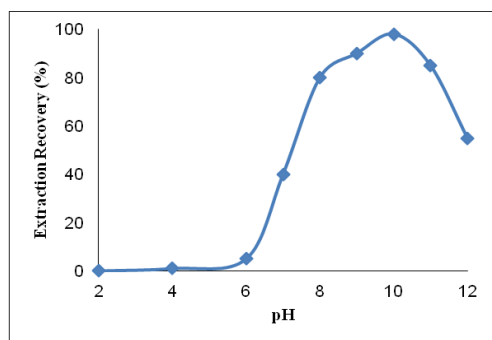


Fig. 1. Effect of pH on the extraction recovery of manganese by DLLME. Extraction conditions: water sample volume, 5.0 mL; disperser solvent (ethanol) volume, 500 μL ; extraction solvent (CHCl_3), 100 μL ; PAN concentration, $4.0 \times 10^{-4} \text{ mol L}^{-1}$, concentration of manganese, $50 \mu\text{g L}^{-1}$.

Effect of PAN concentration

Dispersive liquid-liquid microextraction of 0.25 μg of manganese using PAN from 5.0 mL sample solutions was conducted by varying the concentration of PAN. The extraction recovery for Mn (II) as a function of the concentration of chelating agent is shown in Figure 2. The recovery increases up to a PAN concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ and reaches near quantitative extraction efficiency. A concentration of $4.0 \times 10^{-4} \text{ mol L}^{-1}$ of PAN was chosen to account for other extractable species that might potentially interfere with the assaying of Mn (II).

Effect of Type and Volume of Extraction Solvent

Careful attention should be paid to the selection of the extraction solvent. It should have higher density than water, extraction capability for the compounds of interest and low solubility in water. Chloroform, carbon tetrachloride and

chlorobenzene were compared in the extraction of manganese. A series of sample solutions were studied by using 500 μL ethanol and different volumes of extraction solvent to achieve 70 μL volume of sedimented phase. Thereby, 100, 80 and 80 μL of chloroform, carbon tetrachloride and chlorobenzene, respectively, were used. The results revealed that chloroform has the highest extraction efficiency (98.5 %) in comparison with carbon tetrachloride (32.0 %) and chlorobenzene (76.0 %). Hence, chloroform was chosen as extraction solvent.

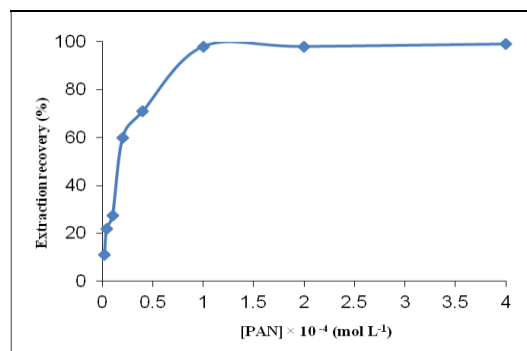


Fig. 2. Effect of PAN concentration on the extraction recovery of manganese by DLLME. Extraction conditions: water sample volume, 5.0 mL; disperser solvent (ethanol) volume, 500 μL ; extraction solvent (CHCl_3), 100 μL ; concentration of manganese, $50 \mu\text{g L}^{-1}$; pH = 10.0.

To examine the effect of the extraction solvent volume, solutions containing different volumes of chloroform were subjected to the same DLLME procedure. The experimental conditions were fixed and included the use of 500 μL ethanol containing different volumes of chloroform. Figure 3 shows the curve of extraction recovery *versus* volume of the extraction solvent (chloroform). According to Figure 3, the extraction recovery increases up to

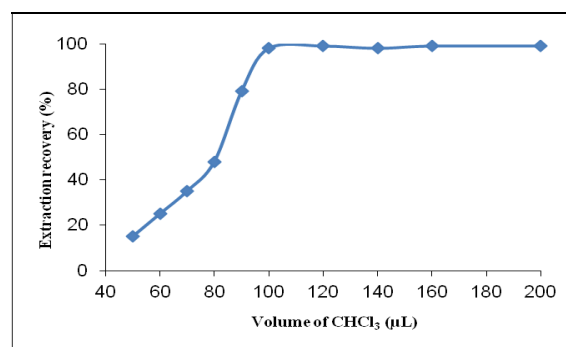


Fig. 3. Effect of the volume of extraction solvent (CHCl_3) on the extraction recovery of manganese by DLLME. Extraction conditions: water sample volume, 5.0 mL; disperser solvent (ethanol) volume, 500 μL ; PAN concentration, $4.0 \times 10^{-4} \text{ mol L}^{-1}$; concentration of manganese, $50 \mu\text{g L}^{-1}$; pH= 10.0.

100 μL of chloroform and then remains constant. Thus, 100 μL of chloroform was chosen as the optimum amount.

Effect of Type and Volume of Disperser Solvent

The main criterion for selection of the disperser solvent is its miscibility in both the extraction solvent and the aqueous sample. For this purpose, different solvents such as acetone, ethanol and methanol were tested. A series of sample solutions were studied by using 500 μL of each disperser solvent containing 100 μL of chloroform (extraction solvent). The results showed the best extraction recovery when ethanol was used. Thus, ethanol was selected as a disperser solvent.

Investigation of the effect of different volumes of ethanol (disperser solvent) on the extraction recovery would be very rough, because the variation of the volume of ethanol makes change in the volume of settled phase at constant volume of chloroform (extraction solvent). Thereby, to achieve a constant volume of the settled phase (70 μL) the volumes of ethanol and chloroform were changed simultaneously. The experimental conditions were fixed and included the use of different volumes of ethanol, 300, 400, 500, 600, 700, 800, 900, 1000, 1200 and 1500 μL containing 90, 95, 100, 105, 110, 115, 120, 125, 135 and 150 μL of chloroform, respectively. Under these conditions, the volume of the sedimented phase was constant ($70 \pm 2 \mu\text{L}$). Figure 4 shows the curve of extraction recovery *versus* volume of the disperser solvent (ethanol). The results show that there was no considerable variation of the extraction recovery between 400 and 800 μL of ethanol and the extraction recovery was high and then decreased by increasing the volume of ethanol. It is clear that by increasing the volume of ethanol, the solubility of

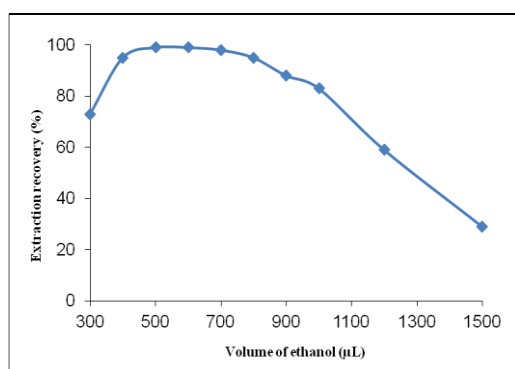


Fig. 4. Effect of the volume of disperser solvent (ethanol) on the extraction recovery of manganese by DLLME. Extraction conditions: water sample volume, 5.0 mL; extraction solvent (CHCl_3), 100 μL ; PAN concentration, $4.0 \times 10^{-4} \text{ mol L}^{-1}$; concentration of manganese, 50 $\mu\text{g L}^{-1}$; $\text{pH} = 10.0$.

the complex in water increases. Therefore, the extraction recovery decreases. Thus, 500 μL of ethanol was selected as the optimum volume in order to achieve a better and more stable cloudy solution.

Effect of Extraction Time

Extraction time is one of the most important factors in most extraction procedures. In DLLME, the extraction time is defined as the interval of time between injecting the mixture of disperser and extraction solvent, and starting centrifugation. The effect of extraction time was examined in the range of 0-45 min under constant experimental conditions. The results showed that the extraction time has no significant effect on the extraction efficiency. It was revealed that after the formation of the cloudy solution, the surface area between the extraction solvent and the aqueous phase is essentially infinitely large. Thereby, transfer of Mn-PAN complex from the aqueous phase to the extraction solvent is fast. This is one of the considerable advantages demonstrated by the DLLME technique, i.e., short extraction time.

Effect of Buffer Concentration

The influence of buffer amounts was studied by maintaining the other experimental variables constant. The results showed that above $0.5 \times 10^{-3} \text{ mol L}^{-1}$ of buffer solution, no obvious variation of the extraction yield took place. Thus, $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of buffer solution was chosen as the optimal to achieve higher buffering capacity.

Effect of Salt

For investigating the influence of ionic strength on the performance of DLLME, experiments were carried out by adding different amounts of NaCl ($0.0 - 1.0 \text{ mol L}^{-1}$). The other experimental conditions were kept constant. The results showed that the ionic strength has no appreciable effect upon extraction efficiency up to 1.0 mol L^{-1} of NaCl. These observations showed the possibility of using this method to separation of manganese from highly saline solutions.

Effect of Other Ions

The effects of common ions in natural water samples on the recovery of manganese were studied. In these experiments, 5.0 mL of solutions containing 50 ng mL^{-1} of manganese and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation of more than 5% in the extraction

recovery of the sample. The results (Table 1) indicate that the Mn (II) recoveries are almost quantitative in the presence of interfering ions.

Table 1. Effect of foreign ions on the preconcentration and determination of manganese.

Ion	Ion/Mn(II) (w/w)	Recovery (%)
Li ⁺	1000	96.4
Na ⁺	1000	101.5
Cu ²⁺	500	98.7
Ni ²⁺	500	95.8
Al ³⁺	500	99.3
Zn ²⁺	500	104.2
Pb ²⁺	250	103.7
Cd ²⁺	250	97.5
Co ²⁺	100	99.5
Cr ³⁺	100	102.6
Fe ²⁺	50	104.3
NO ₃ ⁻	1000	100.9
Cl ⁻	500	96.6
SO ₄ ²⁻	250	95.8

Figures of Merit

Table 2 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, repeatability, and enrichment factor. The calibration graph was linear within the range of 10-200 ng mL⁻¹ of manganese. The limit of detection, defined as C_L = 3S_B / m (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the

calibration graph, respectively), was 3.0 ng mL⁻¹. The relative standard deviation (RSD) for ten replicate measurements of 50 ng mL⁻¹ Mn (II) was 3.3 %. The enrichment factor was 50.

Application to Samples

The proposed DLLME-FAAS methodology was applied to the determination of Mn in several water samples. Water samples (i.e. tap water, sea water, river water and mineral water) were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and aliquots of water (5.0 mL) were subjected to DLLME. According to the results, the concentration of manganese in the analyzed water samples was below the LOD of the method. Moreover, the robustness of the proposed method was checked by performing recovery test on a synthetic sample (no certified reference material was available). Each type of water was spiked with variable amounts of Mn (II) to assess matrix effects. The results are shown in Table 3.

Table 2. Analytical characteristics of the proposed method.

Parameter	Analytical feature
Linear range (ng mL ⁻¹)	10-200
Limit of detection (ng mL ⁻¹) (n =10)	3.0
Repeatability (RSD, %) (n =10)	3.3
Enrichment factor	50

Table 3. Determination of Mn (II) in different water samples.

Sample	Mn ²⁺ spiked (ng mL ⁻¹)	Mn ²⁺ detected (ng mL ⁻¹)	Recovery (%)
Tap water	0.00	n.d. ^a	—
(From the drinking water system of Tehran, Iran)	0.10	0.098 (3.6) ^b	98
	0.20	0.198 (3.5)	99
Sea water	0.00	n.d.	—
(Caspian sea water, Iran)	0.10	0.102 (3.7)	102
	0.20	0.192 (3.8)	96
River water	0.00	n.d.	—
(Ziarat River, Gorgan, Iran)	0.10	0.101 (3.6)	101
	0.20	0.190 (3.5)	95
Mineral water	0.00	n.d.	—
(From Abali mineral water, Tehran, Iran)	0.10	0.097 (3.4)	97
	0.20	0.206 (3.5)	103

^a Not detected; ^b RSD of three replicate experiments

Table 4. Comparison of the present method with other methods for pre-concentration and determination of manganese(II).

Method	LOD ng mL ⁻¹	RSD (%)	EF	Reference
CPE-FAAS	2.9	1.3	17	19
CPE-FAAS	5.0	—	20	20
DLLME-UV-Vis	4.0	3.8	5.9	28
CPE-FAAS	33	—	96	29
SPE-UV-Vis	17	—	60	30
DLLME-FAAS	3.0	3.3	50	Present work

The relative recoveries of manganese from the mentioned water samples at various spiking levels were between 95.0 and 103.0 %. These results demonstrated that the matrices of these water samples had little effect on DLLME of manganese.

Comparison with other methods

A comparison of the present method with other reported methods for manganese preconcentration and determination is given in Table 4. The present method has low LOD, good enrichment factor and good RSD and these characteristics are comparable or even better than most of the other methods named in Table 4. All these results indicate that the present method is a reproducible, simple, and low-cost technique that can be used for the preconcentration and determination of manganese (II) in real samples.

CONCLUSION

Dispersive liquid-liquid microextraction combined with flame atomic absorption spectrometry allows tackling the determination of manganese in natural waters in a simple way. The method is efficient, rapid and economical. High preconcentration factor was obtained easily through this method and a detection limit at the sub ng mL⁻¹ level was achieved with only 5.0 mL of sample. In this method preparation time, as well as consumption of toxic organic solvents was minimized without affecting the sensitivity of the method.

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ОПРЕДЕЛЯНЕ НА СЛЕДИ ОТ МАНГАН ВЪВ ВОДНИ ПРОБИ ЧРЕЗ ПЛАМЪКОВА АТОМНО-АБСОРБЦИОННА СПЕКТРОФОТОМЕТРИЯ СЛЕД ДИСПЕРСИОННА ТЕЧНО-ТЕЧНА МИКРО-ЕКСТРАКЦИЯ

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(Резюме)

Дисперсионната течна-течна микро-екстракция е комбинирана с чрез пламъкова атомно-абсорбционна спектрофотометрия за определянето на манган във водни проби. Използвани са 1-(2-пиридиазо)-2-нафтол (PAN), хлороформ и етанол като хелатни агенти, екстрагент и диспергиращ разтворител. По този екстракционен метод смес от 500 μL етанол и 100 μL хлороформ (екстрагент) се инжектира бързо във водна проба, съдържаща манганови йони и $4 \times 10^{-4} \text{ mol L}^{-1}$ 1-(2-пиридиазо)-2-нафтол (PAN) (хелатообразуващ агент). Получава се мътна дисперсия. След центрофугиране (5 мин. при 4000 об./мин.) става утаяване на капки от дисперсията в конична епруветка ($70 \pm 2 \mu\text{L}$). Утаената фаза се отделя с помощта на микро-спринцовка и се разрежда до 100 μl д етанол. Тази система за въвеждане микро-проби се използва за анализ на разредени разтвори в чрез пламъкова атомно-абсорбционна спектрофотометрия. Оптимизирани са някои ефективни параметри на екстрагента и типът на диспергиращия разтворител и техния, времето за екстракция, солевият ефект, рН и концентрацията на хелатообразуващия агент. При оптималните условия факторът на обогатяване (EF) е 50 и е получен от водна проба само от 5 mL. Калибрационната линия е права в интервала 10–200 ng mL^{-1} с граница на откриване 50 ng mL^{-1} манган и 3.3 %. Методът е приложен успешно за екстракцията и определянето на манган в проби от някои природни води.