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INSTRUMENTATION, METHODOLOGY,
AND TECHNICAL DEVELOPMENTS

Preconcentration and Determination of Manganese in Water Samples Using *N*,*N′*-*bis*(2-Hydroxy-5-bromo-benzyl)1,2 Diaminopropane

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ABSTRACT

The synthesis and analytical applications of *N*,*N′*-*bis*(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane (HBDAP) are described. The investigation includes a study of the characteristics that are essential for solvent extraction and for spectrophotometric determination and preconcentration of manganese. The organic phase loaded with Mn(II) from aqueous phase was stripped in one stage by using different mineral acid solutions. It was found that stripping efficiency was quantitative in case of HNO_3. A highly sensitive, selective and rapid spectrophotometric method is described for the determination of trace amounts of manganese(II) by HBDAP. This compound reacts with manganese(II) in the range of pH 7–10 to produce a brownish complex (2:3 mol ratio of Mn(II)/HBDAP) soluble in chloroform. The complex obeys Beer's law from 0.12 to $13.2\,\mathrm{mg\,L^{-1}}$ with an optimum range. The relative standard deviations were % 0.02 (10 samples, each containing $3.2\,\mathrm{mg\,L^{-1}}$ Mn(II)). The precision was determined from 30 results obtained for $2.75\,\mathrm{mg\,L^{-1}}$ Mn(II); the mean value of a Mn(II) was $2.77\,\mathrm{mg\,L^{-1}}$ with a standard deviation of $0.018\,\mathrm{mg\,L^{-1}}$ Mn(II).

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Key Words: Manganese(II) determination; Spectrophotometry; Solvent extraction; Preconcentration, *N*,*N*′-*bis*(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane.

INTRODUCTION

The presence of manganese in water is generally not a health problem. In fact, small concentrations are essential to human health. Water with manganese has a metallic or medicinal taste. Tea or green leafy vegetables may become very dark when prepared with such water. High levels of manganese (i.e. levels greater than the current drinking water standards of 0.05 mg/L) may cause brown or black stains on porcelain fixtures and laundry. Manganese at this concentration should be treated.[1]

Manganese is an important trace element, which is essential to organisms and plants for the functioning of several enzymes, and is also an essential micro nutrient for the functioning of the brain nervous system and normal bone growth.[2] The oxidation of Mn(II) to Mn(VII),[3] thenoyltrifluroacetone,[4] 8-aminoquinoline,[5] and schiff bases,[6] because of low sensitivity, are not considered to be useful for trace analysis. Formaldoxime[7] is a superior reagent compared to the heterocyclic azo dye reagents[8–10] with respect to cost, simplicity and rapidity of the method. However, Fe, Ni and Co interfere.

A literature survey has shown that various solvent extraction methods for separating and preconcentrating manganese have been reported, such as macrocyclic crown ethers,[11] 3-(2-hydroxyphenyl)-2-mercaptopropenoic acid,[12] 4-isopropyltropolone,[13] di-(2-ethlyhexyl) phosphoric acid,[14] alkyl substituted β-diketones,[15] 2-(2-benzoxazolyl)malonaldehyde and 2-(2-benzoxazolyl)cyanoacetaldehyde,[16] o-phenanthroline and eosin[17] etc. Solvent extraction separation of Mn(II) with Cynex 302 into toluene has been studied and the thus separated manganese was stripped into HCl for its spectrophotometric determination by formaldoxime from binary mixtures, alloys and pharmaceutical samples.[18] A highly sensitive method for the rapid determination of dissolved Mn(II) and total dissolvable Mn in seawater has been developed. The method uses on-line concentration of Mn(II) onto 8-hydroxyquinoline immobilized onto a vinyl polymer gel. The Mn(II) is then eluted from the gel by acid and its concentration has been determined by spectrophotometric detection of the malachite green formed from the reaction of leucomalachite green and potassium periodate with Mn(II) acting as a catalyst.[19] Acyclic and macrocyclic Schiff bases containing bisphenol A subunits were synthesized and the effect of ligand atoms on the liquid–liquid extraction of manganese(II) has been studied. The phenol groups in the Schiff base moiety led to a large increase in the percent extraction of transition metal ions.[20] A chelating poly(dithiocarbamate) resin (PDTC) with macroreticular support is characterized as effective collector for traces of manganese from natural waters.[21] A rapid method has been described for the quantitative extraction of milligram amounts of Mn(II) with 2-propanol into chloroform.[22] Solvent extraction of divalent manganese from sulphate solutions was carried out using the sodium salt of Cyanex 272. Extraction of metal ions increased with increasing equilibrium pH and extractant concentration.[23]

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Solid phase extraction method was used for preconcentration of Mn(II) in drinking water samples. Flame atomic absorption spectrometric determination of Mn after separation/preconcentration by sorbing 8-hydroxiquinoline (oxine) complex of analytes on the Diaion HP-20 column has been established.[24]

The synthesis and the application of HBDAP as a new extractant to the preconcentration and determination of manganese at trace levels in water samples is reported here. Very high preconcentration factors could be achieved using this ligand by solvent extraction method for the determination of manganese in water samples.

EXPERIMENTAL

Reagents and Apparatus

All the reagents were of analytical grade and were used without further purification. Adjustment of pH was made with acetic acid, phosphoric acid, boric acid and their potassium salts. Potassium chloride was added to give a constant ionic strength of 0.1 M.

HBDAP (Fig. 1) was prepared by refluxing 2 equiv. of 5-bromo-2-hydroxybenzaldehyde (40 mmol) with 1 equiv. (20 mmol) of 1,2-diaminopropane in 100 mL of ethanol for 4 h. The solution turned bright yellow and the yellow Schiff base solid appeared on cooling. EtOH was removed by rotary evaporation and the solid recrystallized from hot EtOH. About 10 mmol of the Schiff base was dissolved in 100 mL of ethanol and 2 g (52 mmol) of sodium borohydride added in two portions. The mixture was stirred for 2 h, and about 40 mL of double-distilled water was added. The precipitate was filtered out and recrystallized from hot ethanol. The structure of the compound was confirmed by FT-IR and NMR spectrometry.

A 929 Unicam AAS Spectrometer was used and measurements carried out using an air-acetylene flame. Absorbance measurements were made using a Cary 1-E UV-Vis Spectrophotometer with 1.0 cm quartz cells. A pH meter (Metrohm 691 pH Meter) was also used.

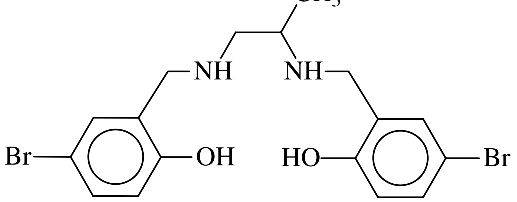

Figure 1. Structure of *N,N′-bis*(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane (HBDAP).

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Extraction Method

Aqueous solutions containing 10^{-5}–10^{-4} M Mn(II) chloride in appropriate buffer were shaken with equal volumes (15 mL/15 mL) of the chloroform solution of HBDAP (10^{-4}–10^{-3} M) in a mechanical shaker at 25°C. In most cases distribution equilibrium was attained in less than 15 min and a shaking time of 30 min was sufficient to obtain reproducible results. Potassium chloride was added to give a constant ionic strength of 0.1 M. After agitation, the solutions were allowed to stand for 10 min. The manganese concentration of the aqueous phase was determined by FAAS, and that of the organic phase from the difference by considering the mass balance. The pH of the aqueous phase was recorded as equilibrium pH. The absorption of the organic phase after extraction equilibrium had been established was measured spectrophotometrically at 494 nm.

Preconcentration Procedure

Extraction of the aqueous phase (100 mL) containing 17.6 μg Mn(II), a 30 mL portion of the organic phase (10^{-3} M HBDAP in chloroform) was stripped with 15 mL of aqueous acid solutions, including HCl, H_2SO_4, and HNO_3. The amount of manganese in aqueous phase was determined by FAAS after stripping the organic phase, and then the recovery percentage (R%) was calculated.

Analysis of Water

The seawater was obtained from The Marmara Sea and tap water, underground water and wastewater samples were obtained from Balıkesir, Türkiye. Stored samples had been acidified with 4 mL of 6 M HCl/L of sample. 100 mL water samples was added to 2 mL of conc. HNO_3 and heated to boiling. For determining Mn(II), 100 mL of water sample was extracted with 20 mL of 10^{-3} M HBDAP in chloroform at pH 8.01 for 30 min and then organic phase was analyzed by spectrophotometric procedure. In addition to the procedure above, 20 mL of organic phase was stripped with 10 mL of 10% HNO_3. Stripped aqueous phase was analyzed with standard addition method by FAAS. The data obtained by these two procedure were compared with each other.

RESULTS AND DISCUSSION

Spectrophotometric Determination of Mn(II)

The Effect of pH on the Extraction of Mn(II) and Absorbance of Manganese(II) Complex

Figure 2 shows the effect of pH on the extraction of Mn(II) into chloroform with HBDAP: the manganese extraction is quantitative within the pH range 8–10.

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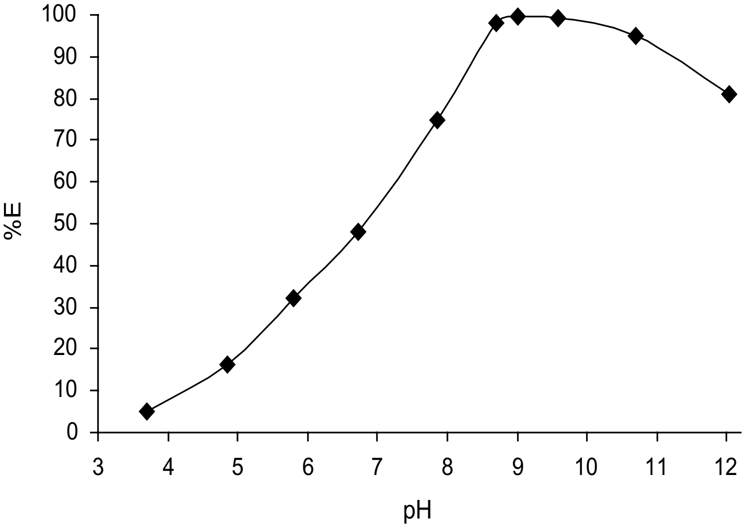

Figure 2. Effect of pH on the extraction of Mn(II).

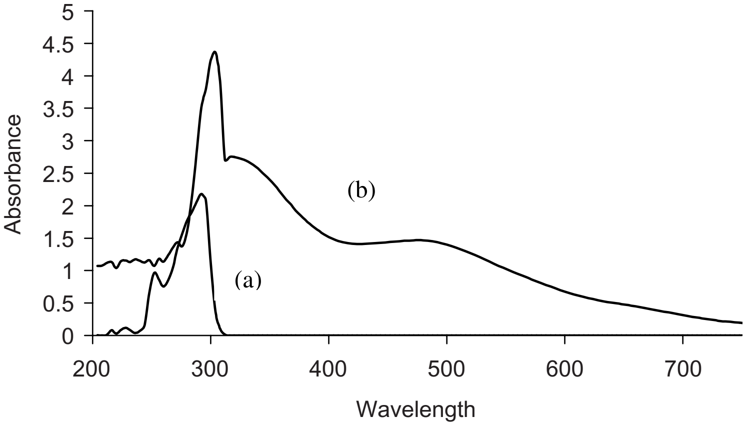

Figure 3. The absorption spectra of the ligand (HBDAP) (a) and manganese(II)-HBDAP (b) complex.

The absorption spectra of the ligand (HBDAP) and manganese-HBDAP complex are shown in Fig. 3. As seen, the spectra of manganese-HBDAP complex have two maxima, one of which overlaps with the maximum of ligand at 285 nm. The other maximum appears at 494 nm at which the ligand has no absorbance. So wavelength 494 nm has been used in all subsequent measurements of absorbance.

The absorbance of Mn(II)-HBDAP complex increases greatly from pH 7 up to 9, remains constant between about 9 and 11 and then gradually decreases. So, it was concluded that extraction of manganese(II) with HBDAP was quantitative in the pH range 9–10 (Fig. 4).

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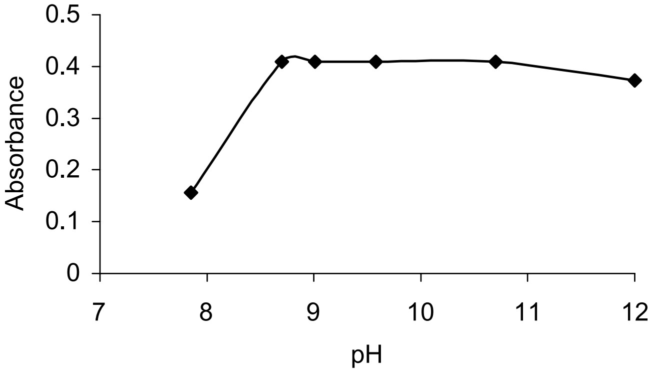

Figure 4. The effect of pH on the absorbance of manganese(II) complex.

Composition of the Extracted Species

In order to confirm the stoichiometry of the Mn(II)-HBDAP complex, spectrophotometric measurements were performed by using Job and slope-ratio methods.[25]

In Job's method the concentration of manganese in the aqueous phase and HBDAP in the organic phase are varied so that their sum is equal to $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$. The pH was kept at a value of 8.01 by a borate buffer solution and the ionic strength was kept constant at 0.1 M by adding a solution of KCl. The absorbance of the manganese complex in the organic phase, which develops a brown color was measured at $\lambda = 494\,\mathrm{nm}$. Results are shown in Fig. 5. The maximum absorbance value corresponds to a molar ratio $[\mathrm{Mn^{2+}}]_w/[\mathrm{H_2L}]_o$ of 2/3 which confirms the assumption of a $Mn_2H_2L_3$ stoichiometry.

The slope ratio method leads to similar results. It consists of two series of experiments: in the first series $[\mathrm{H_2L}]_o$ is kept constant at $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ while $[\mathrm{Mn^{2+}}]_w$ is varied from 4×10^{-5}–$24 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ keeping the pH constant and the ionic strength as in Job's method; in the second series $[\mathrm{Mn^{2+}}]_w$ is kept $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ while $[\mathrm{H_2L}]_o$ is varied from 4×10^{-5}–$24 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$. Two absorbance straight lines are obtained as shown in Fig. 6. The slope ratio of both lines is equal to 1.5 which suggests again that the complex stoichiometry can be taken as $Mn_2H_2L_3$.

According to the discussions above, the extraction process may be represented by the Eq. (1):

$$2\mathrm{Mn^{2+}_{(w)}} + 3\mathrm{H_2L_{(o)}} \rightleftarrows \mathrm{Mn_2H_2L_{3\,(o)}} + 4\mathrm{H^{+}_{(w)}} \tag{1}$$

where H_2L represents the extractant reagent and subscripts (w) and (o) denote the aqueous and organic phases, respectively. The extraction constant of the species $Mn_2H_2L_3$ is then given by the Eq. (2):

$$K_{\mathrm{ext}} = \frac{[\mathrm{Mn_2H_2L_3}]_o\,[\mathrm{H^+}]_w^4}{[\mathrm{Mn^{2+}}]_w^2\,[\mathrm{H_2L}]_o^3} \tag{2}$$

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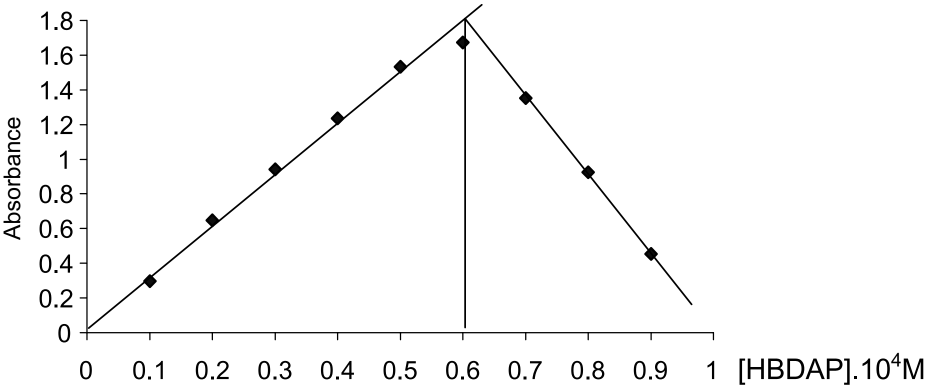

Figure 5. Manganese complex stoichiometry determination in the extraction with HBDAP by spectrophotometric measurements at 494 nm (Job's method).

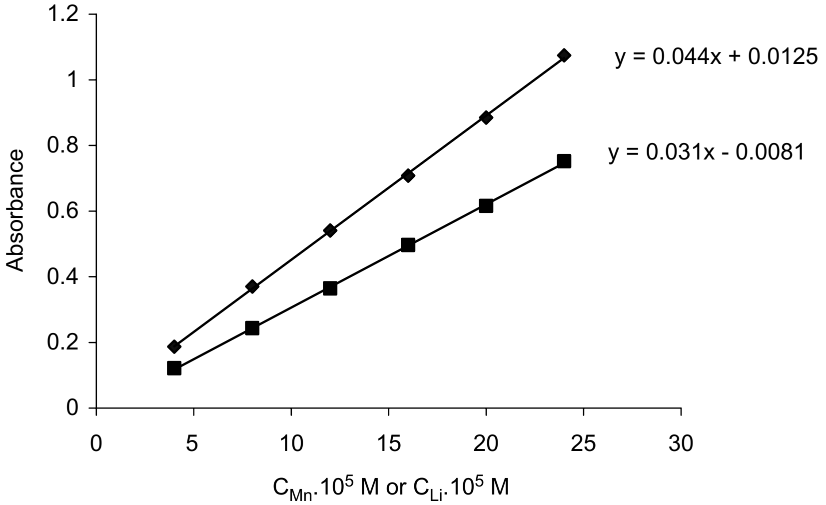

Figure 6. Manganese complex stoichiometry determination in the extraction with HBDAP by spectrophotometric measurements at 494 nm (Slope ratio method).

The metal distribution ratio (D) and the extraction constant are related by the Eq. (3):

$$\log D = \log K_{\mathrm{ext}} + 4\mathrm{pH} + \log[\mathrm{Mn}^{2+}] + \log 2 + 3\log[\mathrm{H_2L}]_{\mathrm{o}} \quad (3)$$

According to Eq. (3) a plot of $\log D$–$\log[\mathrm{Mn}^{2+}]$ against $\log[\mathrm{H_2L}]_{\mathrm{o}}$ at constant pH will give a straight line of slope is three and intercept $\log K_{\mathrm{ext}} + 4\mathrm{pH} + \log 2$; hence, from the graph (shown in Fig. 7) the extraction constant ($-\log K_{\mathrm{ext}}$) has been calculated as 18.7. Additionaly, $-\log K_{\mathrm{ex}}$ values were calculated by using 9 other different extraction data obtained at different pHs between 6.5 and 7.2. The results obtained confirmed the value of $-\log K_{\mathrm{ex}}$ given above.

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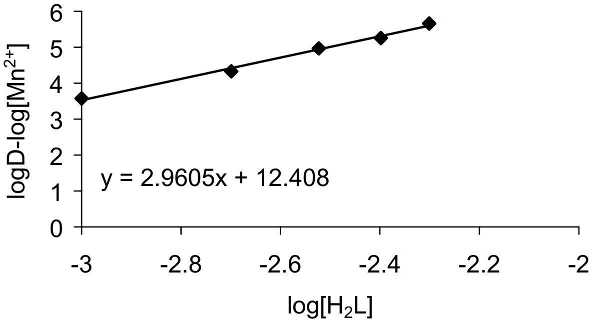

Figure 7. Graphical calculation of the extraction constant. The equation of the straight line is $y = 2.9605 \times + 12.408$.

Determination of Mn(II)

The applicability of the HBDAP as a spectrophotometrically determination method for Mn(II) was studied in the range of 5×10^{-6}–24×10^{-5} M buffered Mn(II) solutions. The concentration of HBDAP in chloroform was 10^{-3} M. The effective molar absorption was calculated from the data obtained by the measurements of organic phase absorbance at the condition extraction was completed. The calibration graph obtained was a straight line passing through the origin over the range of mentioned above ($r^2 = 0.9995$). The effective molar absorption coefficient at 494 nm was $8.95 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$. The complex was found to obey Beer's law from 0.12 to 13.2 mg L^{-1} with an optimum range. The relative standard deviations were calculated as % 0.02 (10 samples, each containing 3.2 mg L^{-1} Mn(II)). The precision was determined from 30 results obtained for 2.75 mg L^{-1} Mn(II); the mean value of a Mn(II) was 2.77 mg L^{-1} with a standard deviation of 0.018 mg L^{-1} Mn(II).

There were no measurable changes in the absorbance of the extracts even after standing for 5 days in a glass-stoppered tube at room temperature.

The molar absorptivity coefficient found for Mn(II)-HBDAP complex seems to be lower than formaldoxime and higher than other manganese chelating reagents as seen in Table 1. The developed procedure is more sensitive and more easy to apply than persulfate method which is accepted as a standard method for determination of Mn(II). In this method water samples are boiled with H_2O_2 and persulfate ion in order to oxidize Mn(II) ion to MnO_4^-. In the suggested method Mn(II) can directly be determined without need any pretreatment.

Effect of Foreign Ions

A 15 mL solution containing 6.59 mg L^{-1} Mn(II) and various amounts of foreign ions was treated as described in the procedure. The results are given in Table 2. 1 mg L^{-1} concentration of Cr(III) and Cd(II) interfered to the absorbance of the complexes as seen in the Table 2. The interference from Al(III) was observed

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Table 1. Comparison of reagents for the spectrophotometric determination of manganese.

Reagent	λ_{max} (nm)	ε ($mol^{-1}\,L\,cm^{-1}$) $\times 10^3$	Solvent
Persulfate	525	2.3	Water
1,6-*bis*{2-hydroxy-5-[2-(4-hydroxyphenyl)propane]-2-yl}2,5-diazahegza-1,5-dien	435	5.4	Nitrobenzene
Formaldoxime	455	12	Toluene
HBDAP	494	8.98	$CHCl_3$

Table 2. Effect of foreign ions on the determination 6.59 mg L^{-1} of Mn(II).

Ion	Amount added (mg/L)	Found Mn^{2+} (mg/L)	Error %
None	–	6.59	0
F^-	1000	6.86	4.1
$C_4H_4O_6^{2-}$	1000	6.76	2.6
Na^+	1000	6.59	0
Ba^{2+}	1000	6.76	2.54
Mg^{2+}	1000	6.87	4.2
Citrate ion	1000	6.70	1.7
K^+	1000	6.59	0
NO_3^-	1000	6.59	0
Cl^-	1000	6.59	0
NH_4^+	1000	6.81	3.3
Br^-	1000	6.70	1.7
Ca^{2+}	1000	6.87	4.2
SO_4^{2-}	1000	6.75	2.43
I^-	1000	6.75	2.43
SCN^-	1000	6.59	0
Zn^{2+}	300	6.59	0.045
CO_3^{2-}	100	6.46	−1.97
Pb^{2+}	80	6.48	−1.63
Ni^{2+}	50	6.54	−0.8
Cu^{2+}	50	6.32	−4.12
Fe^{3+}	50	6.57	−0.38
Co^{2+}	10	6.76	2.54
Al^{3+}	5	6.58	0.13
EDTA	5	6.70	−1.7
Cr^{3+}	1	5.50	16.6
Cd^{2+}	1	6.04	8.3

after 5 mg L^{-1} and the interference from Co^{2+} was observed after 10 mgL^{-1}. The interferences from Cu(II), Fe(III) and Ni(II) were observed after 50 mg L^{-1}, the interference from Pb(II) was observed after 80 mg L^{-1}, from carbonate ion after 100 mg/L and the interference from zinc(II) was observed after 300 mg/L.

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The other ions listed in Table 2 did not interfere in amounts up to 1000 mgL^{-1} with an error below 5%.

As can be seen, the interferences from different ions occurs at relatively high concentrations of ions, which are usually too high to be found in water samples. The method was applied to the determination of manganese(II) in the real water samples containing manganese. The results of the six replicate determinations of manganese in water samples are tabulated in Table 3.

Preconcentration of Mn(II) and Determination with FAAS

The effect of various acids on the stripping of the aqueous solution containing 0.176 ppm Mn(II) has been given in Table 4 for the preconcentration purpose. The highest recovery values, almost quantitatively have been obtained with 3% HCl and 10% HNO_3. The proposed procedure has also been applied to the wastewater samples obtained from different plants. As can be seen from the data given in Table 3, it has been concluded that the amount of Mn(II) can be determined by using FAAS after the proposed preconcentration procedure.

By following the proposed procedure, the effect of various ions on the preconcentration of Mn(II) and on the determination by FAAS was investigated. For the determination by FAAS of 55 μg of Mn(II) in 100 mL, no interference was caused by 1000 mg/L of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{-2}, Ba^{2+}, CO_3^{2-}, I^-, F^-, NH_4^+, tartrate ion, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+} and SCN.

Table 3. The results of manganese(II) amounts in water samples by spectrophotometric and preconcentration methods.

	Spectrophotometricically		FAAS after preconcentration	
Samples	Average (ppm)	Standard deviation (ppm)	Average (ppm)	Standard deviation (ppm)
Drink water	0.0353	0.008	0.0363	0.002
Sulphuric acid plant	1.563	0.001	1.558	0.019
Leather plant	0.138	0.002	0.151	0.0038
Hot spring water	0.013	0.002	0.015	0.002
Sea water	0.188	0.01	0.179	0.03
Boric acid plant	2.12	0.03	2.142	0.04

Table 4. The effect of acids on stripping.

	HCl			H_2SO_4			HNO_3		
% Acid	3%	5%	10%	5%	10%	20%	5%	10%	20%
Found μg	17.6	17.25	17.07	16.19	9.5	7.74	17.26	17.6	16.01
%R	99.5	98	97	92	54	44	98.07	100	90.97

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The interferences was observed after 100 ppm Al^{3+}, 100 ppm Cr^{3+} and 250 ppm of Fe^{3+}.

CONCLUSIONS

The results indicate that HBDAP in organic phase extracts efficiently manganese(II) in aqueous phase containing $0.1\,mol\,L^{-1}$ KCl in the pH range about 8–10 at 25°C. The extraction mechanism corresponds to a cation exchange, in which a complex of stoichiometric formula ($Mn_2H_2L_3$) is formed in the organic phase liberating at the same time 4 mol H^+ ions in the aqueous phase. Extraction constant has been calculated as $\log K_{ex} = -18.7 \pm 0.03$.

The effective molar absorption coefficient found for HBDAP seems to be higher than persulphate method as a standard method proposed for the determination of manganese. The suggested procedure has also some additional advantages. The proposed method may be interfered only by a few ions at higher concentrations and it has a high precision and a low standard deviation. A preconcentration process has been proposed for the determination of Mn(II) in water samples which contain so low concentrations of Mn(II) that they cannot be measured directly by FAAS. It has been shown that the extraction of aqueous phase containing Mn(II) with organic phase containing HBDAP and then stripping the organic phase with 10% HNO_3 give a solution Mn(II) which can directly be analyzed by FAAS. In this determination procedure, the foreign ions in the solution has been found not to interfere the absorbances. As a result it can be concluded that the proposed procedure can satisfactorily be considered as an alternative application for determination of Mn(II) spectrophotometrically and for preconcentration of Mn(II) before FAAS measurements in various samples. The obtained results from water samples by developed spectrophotometrical method which was compared with those obtained by FAAS using standard addition method after back extraction with 10% HNO_3 of organic phase, indicate that the proposed procedures provide very good precision (Table 3).

ABBREVIATIONS

AAS	Atomic absorption spectroscopy
EtOH	Ethyl alcohol
FAAS	Flame atomic absorption spectroscopy
FT-IR	Fourier transformed infra-red spectroscopy
HBDAP	*N*,*N′*-*bis*(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane
NMR	Nuclear magnetic resonance spectroscopy
PDTC	Poly(dithiocarbamate)

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REFERENCES

1. (http:/h2osparc.wq.ncsu.edu/index.html).
2. Schwarz, K. In *Clinical Chemistry and Chemical Technology of Metals*; Brown, S.S. Ed.; Elsevier: Amsterdam, 1977; 3–22.
3. Sandell, E.B.; Onishi, H. *Photometric Determination of Traces of Metals, General Aspects*, 4th Ed., Part I; Wiley: New York, 1978; 246–260.
4. Onishi, H.; Toita, Y. Spectrophotometric determination of manganese with thenoyltrifluor-acetone. Talanta **1964**, *11* (9), 1357–1364.
5. Gustin, V.K.; Sweet, T.R. Determination of small amounts of manganese by oxidation of 8-aminoquinoline, extraction, and spectrophotometry. Anal. Chem. **1964**, *36*, 1674–1676.
6. Cimerman, Z.; Galic, N.; Bosner, B. The schiff bases of saliscylaldehyde and aminopyridines as highly sensitive analytical reagents. Analytica Chimica Acta **1997**, *343*, 145–153.
7. Marczenko, Z. *Spectrophotometric Determination of Elements*, Ellis Horwood: Chichester, 1976; 307–592.
8. Donaldson, E.M.; Inman, W.R. Determination of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals with pan. Talanta **1966**, *13* (3), 489–497.
9. Abe, S.; Sone, T.; Fujii, K.; Endo, M. Liquid liquid extraction of transition metal ions with macrocyclic Schiff bases containing phenol or thiohene subunits. Analytica Chimica Acta **1993**, *274*, 141–146.
10. Klotz, I.M.; Loh Ming, W.C.; Stability constants for some metal chelates of pyridine-2-azo-*p*-dimethylaniline. J. Am. Chem. Soc. **1953**, *75*, 4159–4162.
11. Chadwick, R.B.; McDowell, W.J.; Baes, C.F. The synergistic solvent extraction of manganese by macrocyclic crown ethers in combination with didodecylnaphthalene sulfonic acid: effect of macrocycle substituents. Separation Science and Technology **1988**, *23* (12–13), 1311–1324.
12. Izoquierdo, A.; Gine, M.; Compano, R. Solvent extraction of titanium and manganese with 3-(2-hydroxyphenyl)-2-mercaptopropenoic acid. J. Inorg. Nucl. Chem. **1981**, *43*, 617–618.
13. Sekine, T.; Ninomiya, I.; Tebakari, M.; Noro, J. Solvent extraction of several divalent metal ions with 4-isopropyltropolone into chloroform in the absence and presence of trioctylphosphine oxide. Bull. Chem. Soc. Jpn. **1997**, *70*, 1385–1392.
14. Devi, N.B.; Nathsarma, K.C.; Chakravortty, V. Separation of divalent manganese and cobalt ions from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272. Hydrometallurgy **2000**, *54*, 117–131.
15. Koshimura, H.; Okubo, T. Solvent extraction of metals by alkyl-substituted-diketones. Anal. Chim. Acta **1970**, *49* (1), 67–75.
16. Karadjova, I.; Arpadjan, S.; Mandjukov, P.; Deligeorgiev, T. Solvent extraction of cadmium, cobalt, copper, iron, manganese, nickel and zinc into isobutyl

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methyl ketone with 2-(2-benzoxazolyl)malonaldehyde and 2-(2-benzoxazolyl)-cyanoacetaldehyde. Extraction-atomic absorption spectrometric determination of trace elements of the metals in molybdates. Analyst **1990**, *115*, 1539–1541.

17. Rauf, M.A.; Ikram, M.I.; Ahmad, M. Spectrometric studies of ternary complexes of vanadyl, manganese and iron with *o*-phenanthroline and eosin. J. Trace Microprobe Techn. **2002**, *20* (2), 171–180.
18. Argekar, A.P.; Shetly, A.K. Extraction of manganese(II) with bis(2,4,4-trimethylpently) monothiophosphinic acid and its spectrophotometric determination with formaldoxime. Analytical Sciences **1997**, *13*, 131–135.
19. Resing, J.A.; Mottl, M.J. Determination of manganese in seawater using flow injection analysis with on-line preconcentration and spectrophotometric detection. Anal. Chem. **1992**, *64*, 2682–2687.
20. Abe, S.; Fujii, K.; Sone, T. Liquid-liquid extraction of manganese(II), copper(II) and zinc(II) with acyclic and macrocyclic Schiff bases containing bisphenol A subunits. Analytica Chimica Acta **1994**, *293* (3), 325–330.
21. Yebra-Biurrun, M.C.; Garcia-Dopazo, M.C.; Bermejo-Barrera, A.; Bermejo-Barrera, M.P. Preconcentration of trace amounts of manganese from natural waters by means of a macroreticular poly(dithiocarbamate) resin. Talanta **1992**, *39* (6), 671–674.
22. Argekar, A.P.; Turel, Z.R. Solvent extraction of Mn(II) with 2-propionyl, 1-naphthol oxime-2-propanox into chloroform. J. Radioanal. Nucl. Chem. Letters **1985**, *96* (1), 41–50.
23. Devi N.B.; Nathsarma K.C.; Chakravortty, V. Extraction and separation of Mn(II) and Zn(II) from sulphate solutions by sodium salt of Cyanex 272. Hydrometallurgy **1997**, *45*, 169–179.
24. Armağan, F.; Soylak, M.; Elçi, L.; Doğan, M. Solid phase extraction of some metal ions on Diaiom-20 resin prior to flame atomic absorption spectrometric analysis. J. Trace Microprobe Techn. **2002**, *20* (4), 15–27.
25. Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 6th Ed.; A Harcourt Brace College Publisher, 1992; 583.

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