

Selective preconcentration, separation and speciation of ferric iron in different 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. This compound reacts with Fe(III) in the range of pH 3–6 to produce a red complex (2:3 mol ratio of Fe(III)/HBDAP) soluble in chloroform. The investigation included a study of the characteristics that are essential for solvent extraction and for spectrophotometric determination and speciation of iron. A highly sensitive, selective and rapid spectrophotometric method is described for the determination of trace amounts of iron(III) by HBDAP. The complex obeys Beer's law from 0.056 to 1.68 mg l⁻¹ with an optimum range. The detection limit (taken as three times the standard deviation of the reagent blank) is $\sim 1.23 \times 10^{-7}$ M Fe(III) and the limit of quantitation (taken as ten times the standard deviation of the reagent blank) is about 4.11×10^{-7} M Fe(III). A single extraction gave a good separation of iron(III) from iron(II). Good separation of Fe(III) from Ni(II), Fe(II), Co(II), Cd(II), Mn(II), Zn(II), Pb(II) was also achieved at pH 3–5. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is very important to determine trace of iron in water for environmental protection, hydrogeology and some chemical processes [1]. A number of methods for determination of iron based on extraction of iron complex into an organic phase following spectrophotometric measurements of

the complex have been used. Among them acetylacetone, benzoate, chloride, cupferron, 4,7-diphenyl phenanthroline, 8-quinolinol, thiocyanate, dibenzoylmethane, dithizone methods are well known examples for a long time [2,3]. These methods were not satisfactory, however, because many other metals were coextracted. The most frequently used method in these methods is phenanthroline method. Three molecules of phenanthroline react each atom of ferrous iron to form an orange–red complex [3]. The quantitative

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extraction of iron(III) has been investigated with synthesized macrocyclic schiff base containing bisphenol A subunits, the colored iron(III) schiff base complex can be used for the extraction spectrophotometry of iron(III) [4]. The study of the selective extraction of iron(III) by silica immobilized 5-formyl-3-arylazo-salicylic acid derivatives has been investigated, the process of selective extraction of iron(III), in presence of an interfering ion, by these phases was also studied by both column and batch equilibrium techniques in order to identify the possible type of interference in iron(III) extraction [5]. Hexaacetatocalix(6)arene has been used for the solvent extraction of iron(III), the metal from the organic phase was stripped with HCl and determined spectrophotometrically as its thiocyanate complex at 480 nm [6]. Liquid liquid extraction separation of iron(III) with 2-ethyl hexyl phosphonic acid, mono 2-ethyl hexyl ester (PC-88A) in toluene has been studied. From the extracted complex species in the organic phase iron(III) was stripped with HNO_3 , H_2SO_4 , HCl and later determined spectrophotometrically by thiocyanate method [7]. Selective preconcentration of iron in beverages and water samples using 2,4,6-tri-2-pyridinyl-1,3,5-triazine-tetraphenylborate-naphthalene adsorbent has been reported [8]. Iron is quantitatively retained on this adsorbent in the pH range 3.3–7.0 and at a flow rate of $1\text{--}8\text{ ml min}^{-1}$. The solid mass consisting of the metal complex along with naphthalene is dissolved from the column with DMF. The absorbance is measured with a spectrophotometer against the reagent blank. Effect of halophenols on the extraction of Fe(III) with 8-quinolinol in carbon tetrachloride has been studied. The phenols greatly enhance the extraction of Fe(III) with 8-quinolinol [9]. An organic solvent soluble mem-

brane filter (MF) is proposed for the simple and rapid preconcentration with subsequent spectrophotometric determination of trace levels of iron(II) in water. Iron(II) is collected on a nitrocellulose membrane filter as ion associate of an anionic complex, which is formed by iron(II) and ferrozine and cation surfactant. The ion pair compound and the MF can be dissolved in small volumes of 2-ethoxyethanol and the absorbance of the resulting solution is measured at 560 nm against blank [10].

In this work we propose a method which can be used determination of iron (III) and also for preconcentration and speciation of iron(III). *N,N'*-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane was used as a new extractant. A number of parameters have been evaluated. The developed method was tested in the determination of iron in soil, ore and natural water samples. The method may also be employed for the speciation and separation of iron in various natural waters.

2. Experimental

2.1. 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. Sodium perchlorate was added to give a constant ionic strength of 0.1 M.

HBDAP (shown in Fig. 1) was prepared by refluxing two 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 on cooling the yellow Schiff base solid appeared. The EtOH was removed by rotary evaporation and the solid recrystallized from hot EtOH. About 10 mmol of the Schiff base obtained was then dissolved in 100 ml of ethanol and 2 g (52 mmol) of sodium borohydride added in two portions in order to reduce the schiff base into amino phenol form. The mixture was stirred for 2 h, and $\sim 40\text{ ml}$ of double-distilled water was added to this. The product precipitated was filtered out, and recryst-

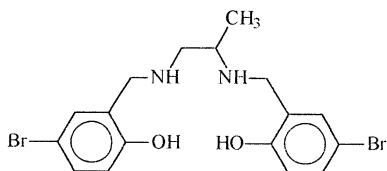


Fig. 1. Structure of *N,N'*-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane (HBDAP).

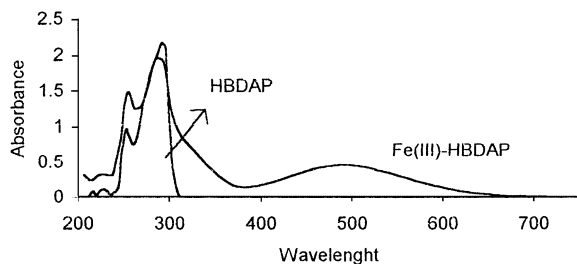


Fig. 2. The absorption spectra of the ligand (HBDAP) and iron(III)-HBDAP complex.

tallized 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.

2.2. Extraction method

Aqueous solutions containing 10^{-4} – 10^{-5} M Fe(III) chloride in appropriate buffer were shaken with equal volumes (15 ml/15 ml) chloroform solution of HBDAP (10^{-3} – 10^{-2} M) in a mechanical shaker at 25 °C. Sodium perchlorate was added to give a constant ionic strength of 0.1 M. 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. After phase separation the concentration of metal ion in aqueous phase was measured by AAS, the absorbance of organic phase was measured against reagent blank at 500 nm using a spectrophotometer.

2.3. Analysis of ore and soil samples

About 500 mg of a magnetite, arseno pyrite samples obtained from Balıkesir, Turkey and lead ore sample obtained from Çanakkale, Turkey, was dissolved in a mixture of 40 ml of HCl (1 + 1) and 10 ml of HNO₃ (1 + 2) by heating and stirring on a hot plate. The solution was cooled, filtered, and diluted to 250 ml with distilled water

in a standard flask. An aliquot of this solution was analyzed by the general procedure. Soil 1 sample was obtained from Balıkesir; Turkey and soil 2 sample was obtained from Çanakkale, Turkey. About 1 g of soil was slurred with 2 ml water in a 250 ml long stem beaker. Distilled HNO₃ (40 ml) was added and the mixture was heated at 70 °C for 2 h. The mixture was cooled, and 5 ml 30% H₂O₂ was added dropwise. Heating was continued for 1 h with intermittent stirring by gentle swirling of the beaker. The cooled contents were filtered and washed and diluted to 250 ml with distilled water in a standard flask. An aliquot of this solution was analyzed by the general procedure.

2.4. Analysis of water

The seawater was obtained from The Marmara Sea and tap and underground water samples was obtained from Balıkesir, Turkey. The determine of Fe(III), 100 ml of water samples was extracted with 20 ml of 10^{-3} M HBDAP in chloroform at pH 3.75 for 30 min and analyzed by general procedure. For the determining the total iron, 100 ml water samples was added to 2 ml of conc. HNO₃ and heated to boiling until volume 25 ml. Cool to room temperature. Fe(II) is oxidized to Fe(III) by boiling after adding HNO₃. After cooling to room temperature and after pH adjustment, analyzed by the general procedure.

3. Results and discussion

3.1. The effect of pH on the absorbance of iron(III) complex

The absorption spectra of the ligand (HBDAP) and iron-HBDAP complex are shown in Fig. 2. As seen, the spectra of iron-HBDAP complex has two maxima, one of which overlaps with the maximum of ligand at 285 nm. The other maximum appears at 500 nm at which the ligand has no absorbance. So wavelength 500 nm has been used in all subsequent measurements of absorbance.

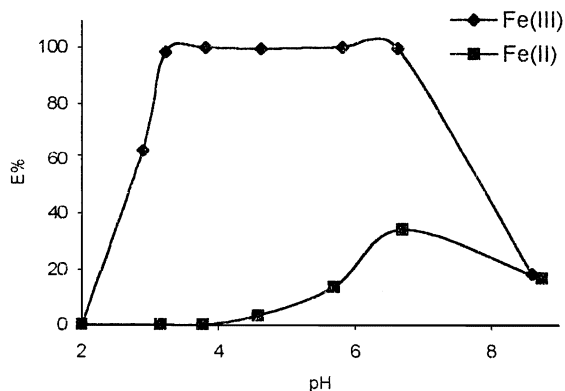


Fig. 3. The effect of pH on the extraction of iron(II) and iron(III) ions.

Table 1

The effect of Fe(II) ion concentration on the absorbance of iron(III) solutions

Amount added; Fe(II) (ppm)	Average absorbance
–	0.4528
5.585	0.4576
11.17	0.4553
33.51	0.4492
44.68	0.4512

The extraction curves for iron(II) and iron(III) as a function of the equilibrium pH are shown in Fig. 3. The extraction of Fe(III)–HBDAP complex increased greatly from pH 2 up to 3, remains constant between ~ 3 and 6.5 and then gradually decreased. Although iron(III) in aqueous solutions is precipitated at $\text{pH} > 3$, this precipitate is dissolved according to the complexation reaction

(Eq. (1)) after adding the complexing agent in organic phase and it was not observed any precipitate after extraction in aqueous media. Iron(II) extraction with HBDAP was poor and no quantitative extraction of iron(II) was attained in the pH range 3–9. Iron(III) was extracted at the pH 3.75, at which iron(II) was not extracted as shown in Fig. 3. In order to prevent the oxidation of Fe(II) to Fe(III), 10 ml of 10% hydroxylamine hydrochloride solution was added into the aqueous phase during the extraction. Solutions consisting of 10^{-4} M Fe(III) and various concentration range of Fe(II) were extracted in the presence of 0.1 M NaClO_4 at pH 3.75. Table 1 shows that the absorbances of the solutions do not vary with the concentration of Fe(II).

4. Composition of the extracted species

In order to confirm the stoichiometry of the Fe(III)–HBDAP complex spectrophotometric measurements were performed by using the Job and the slope–ratio method [11].

In Job's method the concentration of iron in the aqueous phase and HBDAP in the organic phase are varied so that their sum is equal to 1×10^{-4} M. The pH was kept at a value of 3.75 by a acetate buffer solution and the ionic strength was kept at 0.1 M by adding NaClO_4 . Results are shown in Fig. 4. The maximum absorbance value corresponds to a molar ratio $[\text{Fe}^{3+}]_w/[\text{H}_2\text{L}]_o$ of 2/3 which supports a Fe_2L_3 stoichiometry.

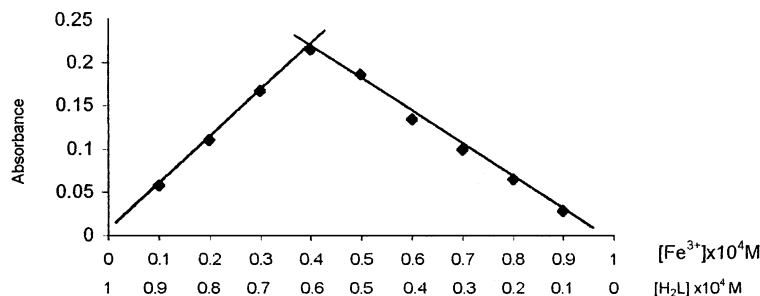


Fig. 4. Iron(III) complex stoichiometry determination in the extraction with HBDAP by spectrophotometric measurements at 500 nm (Job's method).

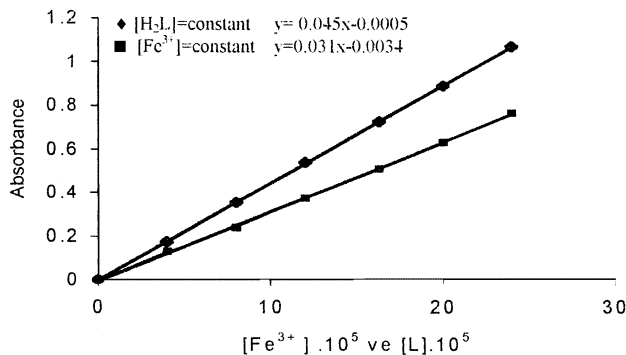
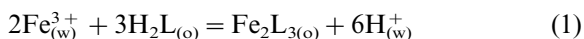


Fig. 5. Iron(III) complex stoichiometry determination in the extraction with HBDAP by spectrophotometric measurements at 500 nm (Slope ratio method).

The slope ratio method leads to similar results. It consists of two series of experiments: in the first series $[H_2L]_o$ is kept constant at 1×10^{-3} M while $[Fe^{3+}]_w$ is varied from 4×10^{-5} – 24×10^{-5} M keeping constant the pH and the ionic strength as in Job's method; in the second series $[Fe^{3+}]_w$ is kept 1×10^{-3} M while $[H_2L]_o$ is varied. Two absorbance straight lines are obtained as shown in Fig. 5. The slope ratio of both lines is equal to 2/3 which suggests again that the complex stoichiometry can be taken Fe_2L_3 .

The extraction process may be represented by the equation:



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 Fe_2L_3 is given by:

$$K_{ext} = \frac{[Fe_2L_3]_o [H^+]_w^6}{[Fe^{3+}]_w^2 [H_2L]_o^3} \quad (2)$$

$[Fe^{3+}]_w$ in Eq. (2) is the concentration of Fe(III) in the aqueous phase after extraction equilibrium is established as far as K_{sp} is concerned, Fe(III) concentration can be 2.25×10^{-7} mol l^{-1} at the extraction pH 3.75, whereas the experimental value of unextracted $[Fe^{3+}]$ from initial concentration of 10^{-4} mol l^{-1} after extraction is 1.43×10^{-7} mol l^{-1} showing that the complexation causes the dissolving of $Fe(OH)_3$. The metal distribution ratio (D) and the extraction constant are related by:

$$\log D = \log K_{ext} + 6pH + \log[Fe^{3+}]_w + \log 2 + 3 \log[H_2L]_o. \quad (3)$$

According to Eq. (3), a plot of $\log D - \log[Fe^{3+}]_w$ against $\log[H_2L]_o$ at constant pH 3.07 will give a straight line of slope is three and intercept $\log K_{ext} + 6pH + \log 2$; hence, from the graph (shown in Fig. 6) the extraction constant ($-\log K_{ext}$) has been calculated as 7.17. Additionally, $-\log K_{ex}$ values were calculated by using nine other different extraction data obtained at different pHs between 2 and 3. The results obtained confirmed the value of $-\log K_{ex}$ given above.

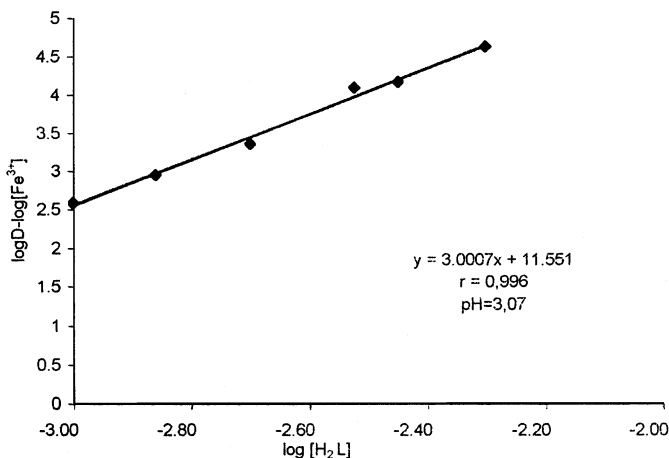


Fig. 6. Graphical calculation of the extraction constant.

Table 2
Effect of foreign ions on the determination 5.59 mg l⁻¹ of Fe(III)

Ion	Amount added (mg l ⁻¹)	Fe ³⁺ found (mg l ⁻¹)	Error%
None	–	5.59	0
Zn ²⁺	1000	5.70	1.97
Na ⁺	1000	5.60	0.18
NH ₄ ⁺	1000	5.76	3.04
I ⁻	1000	5.69	1.79
SCN ⁻	1000	5.61	0.36
K ⁺	1000	5.59	0
NO ₃ ⁻	1000	5.59	0
Cl ⁻	1000	5.59	0
Ba ²⁺	1000	5.62	0.54
Mg ²⁺	1000	5.56	-0.54
Br ⁻	1000	5.73	2.50
Ca ²⁺	1000	5.58	-0.18
SO ₄ ²⁻	1000	5.48	-1.97
Cd ²⁺	1000	5.70	1.97
Pb ²⁺	1000	5.45	-2.50
Ni ²⁺	1000	5.66	1.25
Co ²⁺	1000	5.67	1.43
CO ₃ ²⁻	1000	5.72	2.33
Mn ²⁺	1000	5.65	1.07
Al ³⁺	1000	5.69	1.79
Cr ³⁺	80	5.55	-0.72
F ⁻	40	5.59	0
C ₄ H ₄ O ₆ ²⁻	40	5.34	-4.47
Citrate ion	15	5.54	-0.89
Cu ²⁺	2	5.89	5.37
EDTA	1	5.49	-1.79

4.1. Effect of foreign ions

A 15 ml solution containing 5.585 mg l⁻¹ Fe(III) and various amounts of foreign ions was treated as described in the procedure. The results are given in Table 2. 2 mg l⁻¹ concentration of Cu(II) interfered to the absorbance of the complexes seen in the Table. The interference from Cu(II) was eliminated by using excess thiourea. The interference from Cr(III) was observed after 80 mg l⁻¹, the interference from F⁻ and tartarate ion were observed after 40 mg l⁻¹ and the interference from citrate ion were observed after 15 mg l⁻¹. The other ions listed in Table 1 did not interfere in the amounts up to 1000 mg with an error < 5%. The interference from EDTA is observed because of the fact that EDTA in the

solution hinders the complexation of Fe(III) with HBDAP by forming quantitatively Fe(III)–EDTA complex.

4.2. Separation of Fe(III) from other metal ions

The separation of the metal ions based on the pH adjustment was assisted by the observation that some of the metals were quantitatively extracted at certain pH values at which others were extracted minimally or not at all. The extracted amount of Fe(III) slightly increases up to pH 3, then the extraction is almost quantitative between pH 3 and 6.5. Whereas the extraction of Cu(II) occurs quantitatively between in the pH range of 3.5–10, that of other cations (Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and Pb(II)) is found to be quantitative in the pH range 8–10. These results show that it was possible to predict the separability of Fe(III) from other metal ions. The degree of separation was determined in terms of 'separation factor', S_f defined as the ratio of D_1 for the desired metal ion M_1 to D_2 for the contaminant metal ion M_2 .

$$S_f = D_1/D_2 = \frac{M_{1(\text{org})}/M_{1(\text{aq})}}{M_{2(\text{org})}/M_{2(\text{aq})}} \quad (4)$$

At certain pH values, Fe(III) is quantitatively extracted with 0.01 M HBDAP in chloroform alone from a synthetic mixture of Fe(III) and other metal ions (Table 3). All of these separations are based upon the magnitude of the separation factor (S_f). Only those separations indicating a large separation factor ($S_f = \infty$) was preferred while selecting optimum conditions for separations. The separation of Fe(III) is possible at pH 3–5 from Ni(II), Fe(II), Co(II), Cd(II), Mn(II), Zn(II), Pb(II). Furthermore the separation of Fe(III) from Cu(II) is difficult because of the separation factor is small. This separation factor can be increased in the presence of thiourea, then Cu(II) is not extracted while Fe(III) is quantitatively extracted in organic phase.

4.3. Determination of Fe(III)

The applicability of the HBDAP as a spectrophotometrically for Fe(III) was studied in the

range of 5×10^{-6} – 24×10^{-5} M buffered Fe(III) 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 conditions extraction was completed. The calibration graph obtained was a straight line passing through the origin over the range of mentioned above. The effective molar absorption coefficient at 500 nm was $9000 \text{ mol l}^{-1} \text{ cm}^{-1}$. The complex obeys Beer's law from 0.056 to 1.68 mg l^{-1} with an optimum range. The precision of the method was determined for eleven different samples, each containing 2.7×10^{-5} M of solution. The mean value of a Fe(III) was 2.709×10^{-5} M Fe(III) with a relative standard deviation of 0.41%. In addition, 30 replicate analysis of the same test solution containing 2×10^{-5} M Fe(III) using the general procedure gave a mean value of 2.08×10^{-5} M Fe(III) with a relative standard deviation of 0.13%. The detection limit [12] (taken as three times the standard deviation of the reagent blank) is $\sim 1.23 \times 10^{-7}$ M Fe(III) and the limit of quan-

titation (taken as ten times the standard deviation of the reagent blank) is $\sim 4.11 \times 10^{-7}$ M Fe(III).

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.

4.4. Analysis of the samples

The method was extended for the separation, speciation and determination of iron(III) from real samples. The proposed method was applied for the analysis of different samples containing iron (Tables 4 and 5). The obtained results from ore and soil samples which were compared with those obtained by FAAS, and results for Fe(II) and Fe(III) speciation results obtained from water samples which were compared with those obtained by 1,10 phenanthroline spectrophotometric method [3] indicate that the proposed procedures provide very good precisions. In different ores and soil and natural water samples, no ion has an interference. The results of six replicate determi-

Table 3
The separation factor for the separation of Fe(III) from other metals

Metal ion	pH 3.23	pH 3.82	pH 4.63	pH 5.72	pH 6.63
Cu(II)	70	82.75	13.55	10.2	3.72
Ni(II)	240.9	4174.4	365.6	371	350
Fe(II)	4717	26 507	1572	586	13.1
Co(II)	615.2	∞	21 822	956	263
Mn(II)	114	13 153	928.3	897	336.2
Zn(II)	∞	∞	7465	6984	1718
Pb(II)	49.9	24 040	611 468	568 561	2258
Cd(II)		8299	2036	1564	6.76

Table 4
Determination of iron in soil and ore samples

Sample	Extraction		FAAS	
	Average	Standard deviation (F)	Average	Standard deviation (F)
Pb ore (g g^{-1})	0.12	0.03	0.12	0.02
Arseno Pirit (g g^{-1})	0.367	0.002	0.36	0.01
Magnetite (g g^{-1})	0.66	0.02	0.66	0.05
Soil 1 (mg g^{-1})	20.4	0.5	21.0	0.7
Soil 2 (mg g^{-1})	9.2	0.5	9.2	0.3

Table 5
Determination and speciation of iron in natural waters

Sample	Extraction		1,10 Phenantroline	
	Fe(III)	Fe(II)	Fe(III)	Fe(II)
Sea water (mg l ⁻¹)	83.9 ± 5.2	7.3 ± 3.2	82.1 ± 4.9	6.3 ± 3.4
Tap water (mg l ⁻¹)	50.1 ± 6.6	13.2 ± 3.3	55 ± 5	9.7 ± 2.5
Underground water (mg l ⁻¹)	64.2 ± 0.9	19.5 ± 2.3	64 ± 1	19.1 ± 2.3

nations of iron in ore and soil samples are tabulated in Table 4. Because of ore and soil samples are dissolved in mixture of HNO₃ and HCl, the speciation of iron in this samples are not achieved. For determination of total iron in water samples, sample boiled with conc. HNO₃ until volume 25 ml. As a result Fe(II) is oxidized to Fe(III). Total iron was extracted and then analyzed by the general procedure. To determine Fe(III) in the same water sample, ~100 ml sample was extracted and analyzed by the general procedure. The amount of Fe(II) was calculated by subtracting Fe(III) from total iron. The results of the determination of Fe(II) and Fe(III) in water samples shows in Table 5.

5. Conclusions

The proposed method is simple, rapid and selective. Mutual separation and speciation of iron(II) and iron(III) was attained at pH 3.75. The coloured iron(III)–HBDAP complex can be used for the extraction spectrophotometry of iron(III). The performances of the method described here allows the determination of iron in most of water samples.

The Fe(II) concentration is usually measured using 1,10 phenanthroline method. This method directly determines the iron(II) concentration which contains too low trace concentration in water samples. The Fe(III) concentration is determined as Fe(II) after reducing Fe(III) to Fe(II), and hence total iron concentration is obtained. In this method dissolved or total concentration of Fe(II) as low as 10 mg l⁻¹ can be determined with a spectrophotometer using cells with a 5 cm or

longer light path. The proposed method has the advantage that it determines directly the iron(III) concentration which is contained at higher concentration in water samples. Therefore the Fe(II) concentration in water samples can be calculated from the difference between Fe(III) concentration before and after oxidizing the sample. Therefore, it is possible to state that the speciation of Fe(III) and Fe(II) in aqueous solution can be carried out by using this procedure. It is possible to determine the concentration of Fe(II) even if it is < 10 µg l⁻¹ after oxidizing to Fe(III). As a result, it can be concluded that proposed method enhances sensitivity, improve the detection limit and precision in terms of Fe(III). Concentration of HBDAP (10⁻³ M) required for the analysis much less as compared with reagents like 8-hydroxyquinoline, acetylacetone and thenoyltrifluoroacetone [7]. Extraction is difficult with dithizone as Fe(III) oxidizes the reagent and does not form a complex.

The separation of Fe(III) is possible at pH 3–5 from Ni(II), Fe(II), Co(II), Cd(II), Mn(II), Zn(II), and Pb(II), so that these ions can not interfere on the iron determination by HBDAP method. In phenanthroline method, an accepted method for determination of iron in water samples, chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess 5 mg l⁻¹, and nickel in excess 2 mg l⁻¹ cause interferences. Additionally bismuth, cadmium, mercury, molybdate and silver precipitate phenanthroline [3]. However in proposed method only a limited number of ions have been found to interfere the determination. Selective preconcentration and speciation of iron in different samples may be used as an alternative application.

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