

Sensing of Iron Ions by Solid Phase Spectrophotometry

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ABSTRACT: *A new sensitive and selective spectrophotometric method for the determination of iron using a PVC membrane containing bathophenanthroline and dioctylphthalate as the solid phase extraction medium is investigated. Fe(II) in an aqueous sample solution is trapped on the membrane with an anion species, picrate ion and forms a complex with bathophenanthroline. The absorbance of the red-orange membrane is measured at 540 nm using a spectrophotometer. The influence of type and concentration of counter ion, temperature of analyte solution, time, pH and amount of reducing agent on the absorbance is investigated. The detectable limit of iron in a sample solution is in the range of 5×10^{-5} - 1×10^{-2} M. The effect of various cationic interferences on determination of iron is also studied.*

KEY WORDS: *Iron, Bathophenanthroline, Solid phase spectrophotometry*

INTRODUCTION

In filtered samples of oxygenated surface waters, iron concentrations seldom reach 1 mg/L. Iron in water can cause staining of laundry and porcelain. In water samples iron may occur in true solution, in a colloidal state that may be peptized by organic matter, in inorganic or organic iron complexes, or in relatively coarse suspended particles [1]. The most common methods for its determination are atomic absorption spectrometry [2] and spectrophotometric methods [3]. But their sensitivity is usually insufficient, therefore a preconcentration and matrix elimination step is required.

The most widely used techniques for the separation and preconcentration of trace amounts of iron are liquid-liquid extraction (LLE) [4-9], cation exchange resins [10] and solid phase extraction [11-19].

Solid phase extraction (SPE) is an attractive technique that reduces solvent usage, disposal costs and extraction time for sample preparation [12]. In SPE, water sample passes through a cartridge or a flat disk containing an adsorbent that retains the analytes. After that, the analytes are eluted using a suitable solvent [11-19].

An interesting type of SPE is solid phase spectropho-

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tometry which directly measure the analytes by spectrophotometry using a solid phase medium such as a poly (vinyl chloride) (PVC) membrane, instead of an organic solvent in the liquid-liquid extraction. A method using a solid phase as the extraction medium possesses many advantages over liquid-liquid extraction in spectrophotometry which is recently described [20].

Among application of the solid phase spectrophotometry, methods for determination of copper (I), (II) [20-22], selenium (IV) [23], vanadium (IV), (V) [24], cobalt (II) [25], zinc [26, 27], ascorbic acid [28], drugs in pharmaceutical preparations [29, 30] and cationic surfactants in water samples [31] are reported.

The aim of this study is to develop a solid phase spectrometry method for the determination of trace amounts of iron using a PVC membrane containing a chelating agent, bathophenanthroline, which possesses a high reactivity and selectivity to the iron (II) [30]. The influence of type and concentration of counter ion, temperature of sample solution, contact time, pH and amount of reducing agent on the color intensity of membrane are investigated.

EXPERIMENTAL

Reagents and instruments

Polyvinyl chloride (PVC) (high molecular weight) is obtained from Fluka Co. Dioctylphthalate (DOP), tetrahydrofuran (THF), picric acid and $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ all were obtained from Merck Co. Reagent-grade bathophenanthroline (Merck) is used as received. Analytical-grade potassium chloride, potassium bromide, sodium perchlorate, sodium nitrate, sodium acetate, potassium thiocyanate, hydroxylamine hydrochloride and other reagents (all from Merck) are used without any further purification.

The membrane absorbance is measured using a UV-Vis spectrophotometer (Shimadzu model 2100). A model 691 digital Metrohm pH meter equipped with a combined glass-calomel electrode is used. A stainless steel flat petri dish with a diameter of 6 cm is used for PVC membrane preparation.

Preparation of PVC membranes

Samples of 5.8, 287 and 540 mg of bathophenanthro-

line, PVC and DOP, as a plasticizer, are placed in a 25 mL beaker, respectively, and 10 mL of tetrahydrofuran (THF) is then added to the mixture. After stirring until the membrane feed has completely dissolved, the solution is cast in a flat petri dish with a diameter of 6 cm and stores until the THF has evaporated. The membrane obtained is colorless and flexible. The membrane is cut into 20x5 mm pieces (with 0.3 mm thickness).

Measurements

A 5 mL aliquot of aqueous sample solution containing iron is placed in a 30 mL beaker, and then 4 mg hydroxylaminehydrochloride, 5 mL acetate buffer solution (pH = 5), 5 mL of 0.01 M picric acid solution and 5 mL distilled water are each added. A sheet of PVC membrane is put into the solution and stirred for 10 min with magnetic stirrer. The membrane removed from the solution is rinsed with a small amount of deionized water, and wiped to remove any water droplets. The membrane is then put on a glass plate and the absorbance of the colored membrane is measured at 540 nm using the spectrophotometer. The same procedure is also carried out with 5 mL of deionized water instead of the iron solution as a blank test. To obtain an accurate absorbance of the membrane for the iron sample the absorbance value of the membrane of the blank test, is subtracted from that for the sample containing iron. The iron concentration is calculated from a calibration graph.

RESULTS AND DISCUSSION

Principle of the method

The assumed coloring model of the PVC membrane is shown in Fig. 1. The Fe(II) in aqueous solution produces coordinate bonds with the nitrogen atoms of bathophenanthroline (L) at the PVC membrane surface to form a positive-charged complex ion (FeL_3^{2+}) which, in turn forms an ion pair with a picrate ion (Pic^-), i.e. a neutral complex ($\text{FeL}_3 \cdot 2\text{Pic}$). The color of the PVC membrane changes from colorless to red and the color intensity of the membrane depends on the concentration of complex, i.e. Fe(II). Consequently, from the color intensity of the membrane, Fe(II) in a sample solution can be determined with a calibration graph using a spectrophotometer.

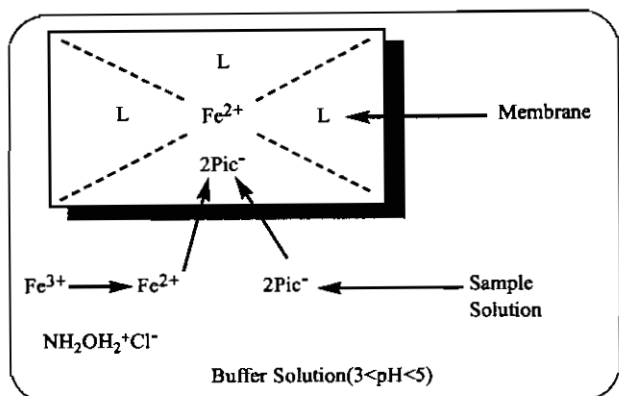


Fig. 1: Extraction profile of Fe(II) into the PVC membrane containing bathophenanthroline

Absorption spectra

The UV-Vis absorption spectra for a PVC membrane containing the Fe(II)-bathophenanthroline complex is shown in Fig. 2. The maximum absorption wavelength of the colored membrane is 540 nm.

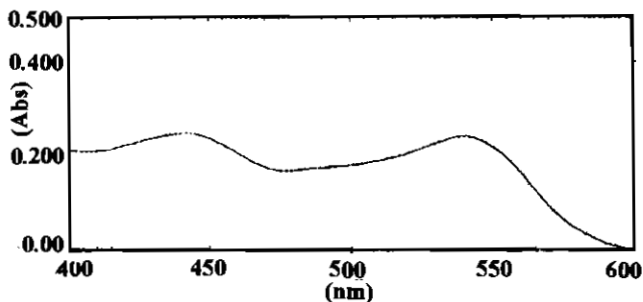


Fig. 2: Absorption spectra of colored PVC membrane. Solution containing 2.5×10^{-4} M Fe(II) (absorption at 440 nm is related to picric acid).

Effect of type and amount of anion species and amount of reducing agent

The effect of anion species that form ion pairs with the Fe(II)-bathophenanthroline complex ion (FeL_3^{2+}) is discussed. Picrate, perchlorate, bromide, chloride and nitrate are tested as counterions. In each case, different concentrations of counterion (from 0.01 to 1×10^{-5} M) are studied. The results are shown in Fig. 3.

The use of picrate ion give the highest absorbance and the color intensity of the membrane is low when using a hydrophilic ion such as chloride or bromide. It is recognized that the solubility of Fe(II)-bathophenanthroline complex in the extracting solvent, DOP, in the membrane increase by using a hydrophobic ion as a pairing ion. Fig.

4 shows that maximum membrane absorbance occurs at 4 mg of hydroxylamine hydrochloride. This amount of reducing agent is used in later experiments. Increasing the concentration of hydroxylamine hydrochloride causes the initial sharp increase of absorbance (Fig. 4). This is followed by its gradual decreases. Such increase in absorbance could be due to the increase of Fe(II) concentration. Decrease of absorbance may be related to complex formation of Fe(II) with hydroxylamine hydrochloride. As a result adsorption of Fe(II) to the surface of membrane which causes color formation is avoided.

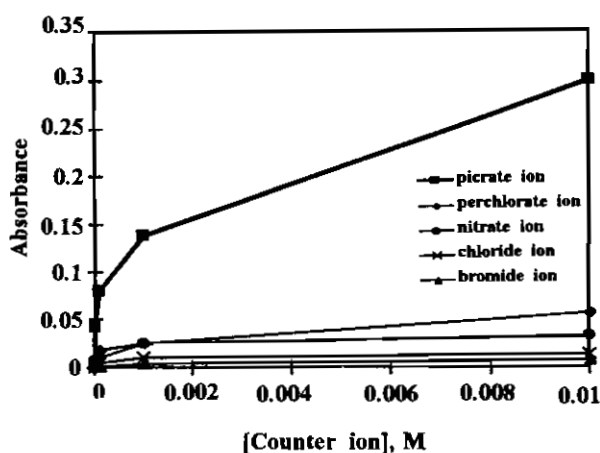


Fig. 3: Effect of type and concentration of counter ion on absorbance. $[\text{Fe(II)}] = 2.5 \times 10^{-4}$ M, HAHC = 4 mg, $t = 10$ min, $T = 25^\circ\text{C}$, $\text{pH} = 5$.

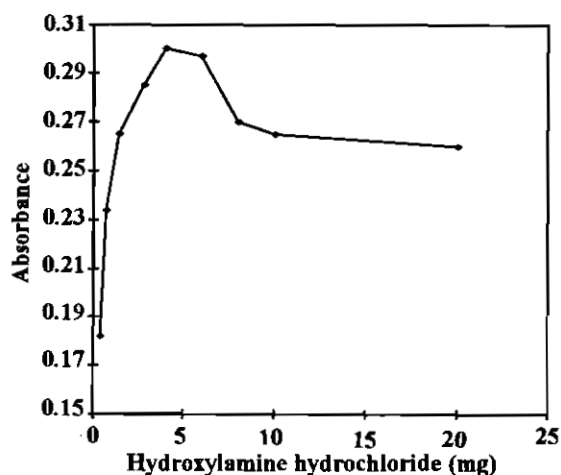


Fig. 4: Effect of the amount of Hydroxylamine hydrochloride on absorbance. Conditions: $[\text{Fe(II)}] = 2.5 \times 10^{-4}$ M, $t = 10$ min, $T = 25^\circ\text{C}$, $\text{pH} = 5$, $[\text{Picric acid}] = 0.01$ M.

Effect of temperature and time

Fig. 5 shows the relationship between the temperature and membrane absorbance with an iron concentration of 2.5×10^{-4} M. The membrane absorbance increases by rising temperature. At high temperatures (more than 50°C), the contraction of the membrane based on the elution of the extracting solvent, DOP, from the PVC membrane medium is observed. Fig. 6 shows that the membrane absorbance increases with time. At 40°C , the membrane absorbance become constant when the iron solution, containing a membrane is stirred for more than 50 min.

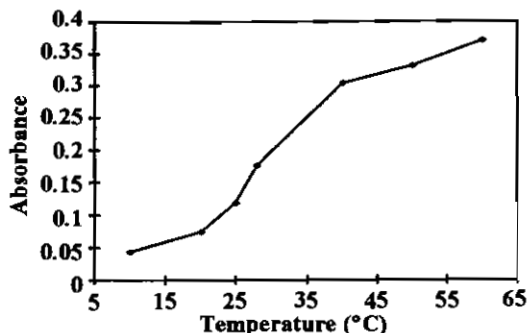


Fig. 5: Effect of the temperature on absorbance. Conditions: $[\text{Fe(II)}] = 2.5 \times 10^{-4}$ M, $t = 10$ min, $\text{pH} = 5$, $[\text{Picric acid}] = 0.01$ M, HAHC = 4 mg

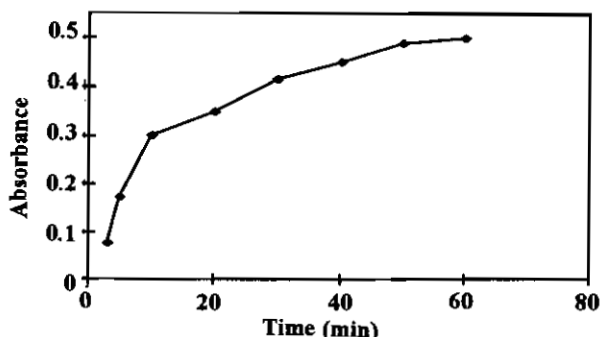


Fig. 6: Effect of time on absorbance. Conditions: $[\text{Fe(II)}] = 2.5 \times 10^{-4}$ M, $T = 40^\circ\text{C}$, $\text{pH} = 5$, $[\text{Picric acid}] = 0.01$ M, HAHC = 4 mg.

Effect of pH

The changes in the membrane absorbance by stirring for 10 min with a 2.5×10^{-4} M iron solution versus the pH of the sample solution is shown in Fig. 7. The membrane absorbance depended on pH of solution which is nearly constant in the range of 3-5.5. It seems when the pH is less than 3, a competition between H^+ and Fe(II) for com-

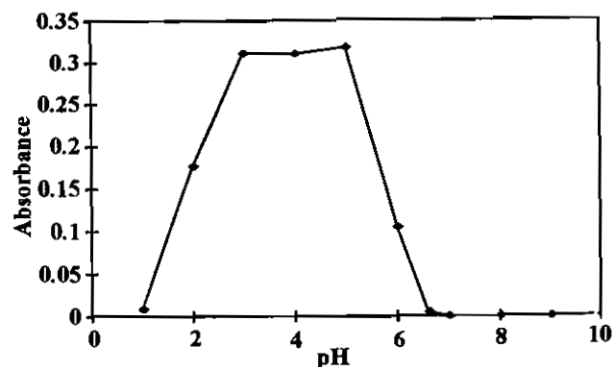


Fig. 7: Effect of the pH of solution on absorbance. Conditions: $[\text{Fe(II)}] = 2.5 \times 10^{-4}$ M, $t = 10$ min, $T = 40^\circ\text{C}$, $[\text{Picric acid}] = 0.01$ M, HAHC = 4 mg.

plexing with bathophenanthroline, decreases the absorbance. In pH values higher than 5.5 competition between OH^- and ligand causes the membrane absorbance decreases. In this study, a buffer solution of pH 5 is adopted.

Analytical performance

Fig. 8 shows the calibration curve for measuring Fe(II) solutions with this method. It is shown that a linear relation between absorbance and concentration is obtained with a correlation coefficient of 0.9975. Definition of detection limit for solid phase spectrometry is similar to ion selective electrodes [20].

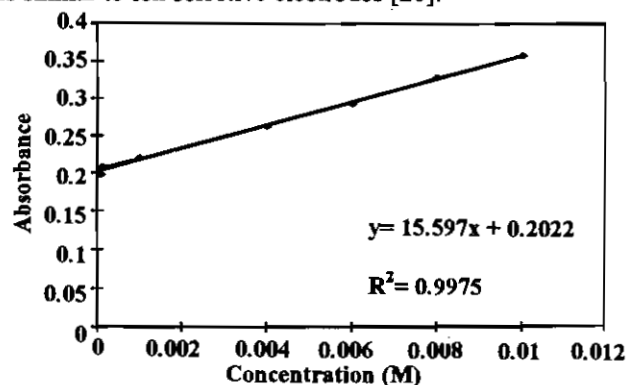


Fig. 8: Calibration curve ($\text{pH} = 5$, Other Conditions as Fig. 7).

The detection limit of a measurement made with an ion selective electrode is defined according to IUPAC as the intersection of two extrapolated segments of the calibrated graph [33]. The limit of detection using extrapolation is 3×10^{-5} M and detectable concentration of iron in a

Table 1: Iron determination in binary mixtures

Cation	Tolerance limit*	Salt	% Recovery
Li ⁺	100	LiNO ₃	99.3
Na ⁺	100	NaNO ₃	98.3
K ⁺	100	KCl	101.3
Be ²⁺	10	Be(NO ₃) ₂ .4H ₂ O	102.0
Mg ²⁺	100	Mg(NO ₃) ₂ .6H ₂ O	98.0
Ca ²⁺	100	CaCl ₂ .2H ₂ O	100.0
Sr ²⁺	100	Sr(NO ₃) ₂	100.6
Ba ²⁺	100	Ba(NO ₃) ₂	98.3
Cu ²⁺	10	CuCl ₂	98.0
Ni ²⁺	10	Ni(NO ₃) ₂ .6H ₂ O	101.9
Cd ²⁺	20	Cd(NO ₃) ₂ .4H ₂ O	100.0
Hg ²⁺	20	HgCl ₂	102.0

* Tolerance limit: mg of interfering ion / mg of Fe

Table 2: Determination of iron in water samples

Water sample	Fe conc. (M) (ICP) ^c	Added (M)	Founded (M)
Mazadaran river	$<9 \times 10^{-7}$	1×10^{-4}	$(1.09 \pm 0.30a) \times 10^{-4}$
Tarbiat Modarres well	$<9 \times 10^{-7}$	1×10^{-4}	$(1.08 \pm 0.16) \times 10^{-4}$
Alisadr spring	$<9 \times 10^{-7}$	1×10^{-4}	$(1.14 \pm 0.12) \times 10^{-4}$
Tehran tap water	$<9 \times 10^{-7}$	1×10^{-4}	$(1.03 \pm 0.28) \times 10^{-4}$
Distilled water	-	1×10^{-4}	$(9.90 \pm 0.21) \times 10^{-4}$
Acidic water 1 ^b	$(2.8 \pm 0.03) \times 10^{-4}$	-	$(2.40 \pm 0.33) \times 10^{-4}$
Acidic water 2 ^b	$(7.29 \pm 0.05) \times 10^{-3}$	-	$(7.37 \pm 0.04) \times 10^{-4}$

^a standard deviation based on three replicate analysis.

^b Acidic water samples were obtained from Water & Waste Water Organization of Tehran.

^c Inductively coupled plasma (ICP) analysis were performed in Atomic Energy Organization of Iran

sample solution is in the range of 1×10^{-2} to 5×10^{-5} M. In order to investigate the selective separation and determination of Fe(III) ion from its binary mixtures with diverse metal ions, the recommended procedure is followed for solution containing Fe(III) and other cations. A relative error of twice the standard deviation of the measurements (i.e. 3% concentration is considered tolerable).

The results are summarized in Table 1. It shows that the Fe(III) ions in the binary mixtures are determined by the PVC membrane, even in the presence of up to about 100 order of weight of the diverse ions. In the case of Be²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Hg²⁺, thiocyanate is used as precipitating agent (for Cu²⁺) and masking agent (for other

ions), because these ions make stable complexes with bathophenanthroline that are colorless and can fill the active sites of membrane. In order to get rid of Cu²⁺ as well as other interferences ions, hydroxylamine hydrochloride is initially added to a solution of Fe(III) and other ions. This causes the formation of Cu(I) and Fe(II) thereby. As much as 100 times to weight of the copper, potassium thiocyanate is added to the solution. This causes the precipitation of Cu(I) as a yellowish-brown solid. The precipitate is filtered and washed with 5 ml of distilled water. To those filtrate, the buffer and picric acid solutions are added. This is followed in accordance to the procedure given in the experimental section. It is evident that Hg²⁺, Ni²⁺, Cd²⁺ and Be²⁺ neither form a precipitate in the presence of thiocyanate nor do they cause any interference.

To assess the applicability of the method to real samples it is applied to the determination of iron in different water samples. For this purpose, firstly the real samples are passed through cellulose acetate membrane filter (0.45 μ m pore size). Then 20 mL of chosen samples are used to measure the amount of iron as mentioned in experimental section. As seen (Table 2), the results of three analysis of each sample obtained by the proposed method and amount of added or ICP are in satisfactory agreement. To study the reversibility of the system, two colored membranes are placed in both the buffer (pH = 3.5) and distilled water. No significant color changes are observed. Indication the irreversibility of the color change. Moreover, the study of the membrane absorbance / time, showed no color change of the membrane in one month period.

CONCLUSION

By using a new type of solid phase spectrophotometry based on a PVC membrane containing bathophenanthroline as the extracting medium, iron in the range of 5×10^{-5} to 1×10^{-2} M (i.e. 2.8 to 560 ppm) can be determined. The colored membrane can be kept for a few months without any color change. It is expected that the proposed sensing method will be widely applied in the determination of iron in a variety of aqueous samples, industrial wastewaters, etc. Lack of requiring expensive and / or toxic solvents may considered as advantages of

this method over the LLE-spectrophotometric determination. Its sensitivity is comparable to those of spectrophotometric methods. However due to lower cost of the equipments involved, one may carry out several experiments simultaneously. At the same time this provides higher speeds of measurements. Nevertheless, the sensitivity of this method is lower than those of attained atomic absorption / or emission spectrometry. The availability of equipments makes this method suitable for in situ measurements.

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