Development of a Flow-Injection with Spectrophotometric Method for Total Iron in Water Samples

Su Örneklerinde Toplam Demir Tayini için Spektrofotometrik Akış Enjeksiyon Yöntemi Geliştirilmesi

Research Article

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ABSTRACT

A simple spectrophotometric flow-injection method is reported for the highly sensitive and fast determination of iron(III) and total iron. The method is based on the formation of iron(III)- (1-nitroso-2-naphthol-3,6 sulphonate) (NRS) complex. The optimum conditions for the reaction of iron(III) with NRS is studied. And the complex is selectively monitored at λ_{max}370 nm. With the reagent carrier solvent used was 5×10^{-4} M 1-nitroso-2-naphthol-3,6 sulphonate in 0.1 M acetic acid-acetate buffer solution at pH 4.0. Parameters affect simultaneously for the determination of iron(III) and interfering ions were tested. Relative standard deviation for five consecutive injections of 70 μg.L^{-1} iron(III) was 1.46% and for 5 μg.L^{-1} iron(III), it was 3.12%. The calibration graph was linear in the iron(III) concentration range 0.1-100 μg.L^{-1} and the limit of detection was 0.05 μg.L^{-1} for a 20 μL injection volume. The precision and accuracy of the method were checked by analysis of certified reference material and AAS method. The method was successfully applied to determine trace amounts of iron(III) and total iron in river and sea water samples.

Key Words
Flow-Injection Analysis, Iron, Spectrophotometric Determination, 1-Nitroso-2-naphthol-3,6 sulphonate.

ÖZ

Demir(III) ve toplam demirin oldukça hassas ve hızlı tayin edilmesi için basit bir spektrofotometrik akış enjeksiyon yöntemi geliştirilmiştir. Yöntem, demir(III) ile 1-nitrozo-2-naftol-3,6 sülfonat (NRS) reaktifi arasında oluşan gelen kompleksin oluşumuna dayanmaktadır. Demir(III) ile NRS tepkmesi için optimum koşullar belirlenmiş ve kompleks λ_{max}370 nm'de spesifik absorpsiyon dalga boyuna sahip olduğu görülmüştür. Hareketli faz olarak pH 4.0'de 0.1 M asetik asit-asetat tampon çözeltisinde 5×10^{-4} M derişimde l-nitrozo-2-naftol-3,6 sülfonat tuzu kullanılmıştır. Demir(III) tayininde kullanılan parametreler ve girişim yapan iyonlar test edildi. Peş peşe yapılan 70 μg.L^{-1} derişimdeki demir(III) enjeksiyonu için bağıl standart sapma %1.46 ve 5 μg L^{-1} derişimdeki demir(III) için ise elde edilen bağıl standart sapma %3.12 olarak belirlendi. Doğrusal çalışma bölgesinin 0.1-100 μg.L^{-1} demir(III) derişim aralığında olduğu belirlendi ve 20 μL enjeksiyon hacmi için tayin sınırı 0.05 μg.L^{-1} olarak bulundu. Yöntemin kesinliği ve doğruluğu, standart referans madde ve AAS yöntemi ile analiz edilerek test edildi. Yöntem, nehir ve deniz suyu numunelerinde demir(III) ve toplam demirin eser miktarlarını belirlemek için başarıyla uygulanmıştır.

Anahtar Kelimeler
Akış-Enjeksiyon Analizi, Demir, Spektrofotometrik Tayin, l-Nitrozo-2-naftol-3,6 sülfonat.

INTRODUCTION

Iron is considered as an essential mineral because it is needed to make part of our blood cells. Iron is the most abundant transition metal in the living system and serves more biological roles than any other metal. Iron, a vital element in the environment and biology, is widely distributed in nature [1]. Iron is one of the most important elements in metabolic processes, being indispensable for plants and animals and therefore it is extensively distributed in environmental and biological materials. Owing to the active role of iron in aquatic redox processes, the determination of the two oxidation states of his element, Fe(II) and Fe(III), is great importance for estimating properties relevant to biological or geochemistry, such as the solubility, photochemistry and colloidal chemistry of the element [2,3]. UV-visible spectrophotometry, atomic absorption spectrometry, inductively coupled plasma-mass spectrometry, cathodic stripping voltametry, fluorimetry and ion chromatography [4-9] have been used for determination of iron.

The association of FIA with UV-vis spectrophotometry is the most effective and suitable approach for routine analysis, mainly owing to its simplicity, low instrumental and operation cost high analysis rate and robustness. For this reason, it has been widely applied to the flow-injection determination of iron in several sample matrices [10-13]. Iron has been selectively determined in flow-injection systems by forming complexes with chelating agents which often show a suitable absorption at a characteristic wavelength [14-16]. A number of other chelating agents that have been reported for the spectrophotometric and/or flow-injection spectrophotometric determination of iron(III) and total iron include norfloxacin [17], 3-aminophtalhydrazide [18], 8-hydroxy-quinoline [19], SCN⁻ [20]. Flow-injection analyses (FIA), especially for spectrophotometric determination of metallic ions, have gained much interest in recent years because of their simplicity, high reproducibility and possibility of coupling different detection systems.

In our previous studies [21-23] simple flow-injection analysis methods was developed for the selective and sensitive determination of iron(II), iron(III) and total iron in sea and river water samples by using different complexing agents. In the present study, an ultra-sensitive and highly selective, simple and economic flow-injection spectrophotometric procedure using 1-nitroso-2-naphthol-3,6 sulphonate (Nitroso R-salt) (NRS) has been described for the determination of iron(III) and total iron. The reagent of the 1-nitroso-2-naphthol-3,6 sulphonate was used for the determination of iron [24,25]. The developed method is based on the detection of change in the composition of the between iron and NRS reaction. The advantages of the proposed method are simple, ultra-sensitive and inexpensive. In the procedure, the NRS in the reagent carrier solution, selectively reacts with iron(III) forming a complex with absorption maxima at 370 nm. The chemical structure of NRS is shown Figure 1.

This paper describes a rapid, selective and sensitive spectrophotometric FI method for direct determination of iron(III) at low $\mu g.L^{-1}$ levels in environmental samples. The reagent complexes with iron(III) to show absorption in the UV-vis region of the spectrum. Total iron was determined after oxidation of iron(II) to iron(III) with hydrogen peroxide. The effect of various parameters were investigated and the method was applied to the determination iron species in different water samples.
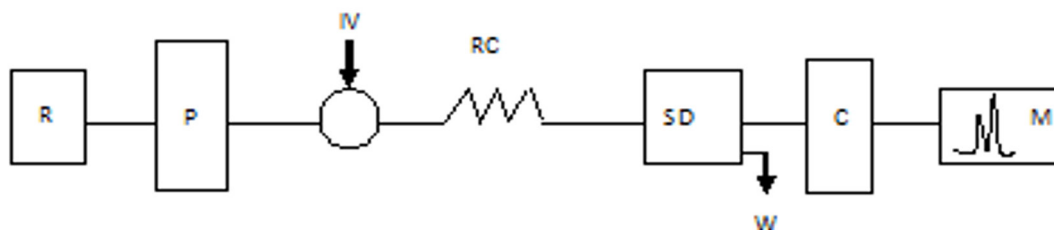
EXPERIMENTAL

Reagent and Chemicals
All chemicals used were of analytical reagent grade or the highest purity available. Double distilled deionized water was used throughout this
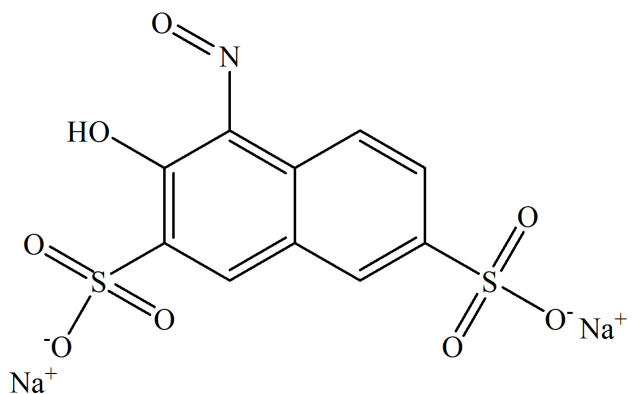
Figure 1. The chemical structure of 1-nitroso-2-naphthol-3,6 sulphonate (NRS).

Figure 2. Schematic diagram of the flow-injection system used for spectrophotometric determination of iron(III). R; reagent carrier solution, P, Peristaltic pump, IV; Rheodyne sample injection valve, RC; reaction coil, SD; spectrophotometric detector, W; waste, C; computer, M; monitor.

study. Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$ followed by washing with concentrated HNO_3, and were rinsed several times with high-purity deionized water. Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottles containing 1 mL of concentrated HNO_3.

Standard iron(II) and iron(III) stock solutions (5×10^{-3} M Fe(II) and Fe(III)) were prepared by dissolving $FeNH_4(SO_4)_2 \times 12H_2O$ and $Fe(NH_4)_2(SO_4)_2 \times 6H_2O$ in water and were standardized by titration with EDTA. Standard solutions of iron(II) and iron(III) were daily prepared by several dilutions of the stock solution with double deionized water. Certified reference material Zn/Al/Cu 43XZ3F (consisting of 0.085% iron) was provided by MBH Analytical Ltd. (UK).

A stock solution of the NRS (5×10^{-3} M) was prepared by dissolving requisite amount of the NRS (Aldrich) in deionized water.

Hydrogen peroxide and standard solution of other metal ions all of them from Merck (Darmstadt, Germany). Different concentrations of the metal solution were prepared with double distilled water.

Iron(III) ion react with NRS in aqueous medium. Metal-$(NRS)_n$ complexes were prepared by mixing 1 mL of 1×10^{-4} M standard solution of each metal cation suitable volume of 1×10^{-4} M NRS in double deionized water. Reagent carrier solution was composed of NRS in 0.1 M HAc/Ac^- buffer (pH: 4.0) prepared using acetic acid and sodium acetate.

Apparatus

UV-Visible spectra of metal-$(NRS)_n$ complexes

were taken with a UV-visible spectrophotometer (GBC Cintra 20, Australia). The pH measurements were made with a Jenway 3040 Model digital pH-meter.

In the FIA system, The absorbance of the iron-NRS complexes were measured with a UV-Visible spectrophotometer (λ_{max}: 370 nm) equipped with a peristaltic pump (ISMATEC; IPC, Switzerland) 0.50 mm i.d. PFTE tubing was used to propel the samples and reagent solutions. Samples were injected into the carrier stream Rheodyne injection valve that can be adjusted in the range of 5-50 µL sample loops and connected to a computer that incorporated with a PC1000 software program.

Flame atomic absorption spectrophotometer (ATI UNICAM 929) was also employed (the measuring conditions were as follows: UNICAM hollow cathode lamp, 10 cm 1-slot burner, air-acetylene flame (fuel gas flow-rate 1.50 L.min^{-1}), 0.2 nm spectral bandwidth, and 7 mm burner height. The wavelength and the lamp current of iron was respectively 248 nm and 5 mA) for the determination of iron content of water samples in reference to the FIA method.

General Procedure

The FIA system used is simple and shown schematically in Figure 2. The sample solution was introduced into the reagent carrier solution by the Rhodyne injection valve. NRS and iron(III) were reacted completely on 70 cm reaction coil (RC) resulting in a iron(III)-NRS complex and then passed through the flow through cell using to measure the absorbance at 370 nm. The signal was recorded as a peak, the height of which was proportional to the iron(III) concentration in the sample, and was used for all measurements. In

order to reproducibility, five replicate injections per sample were made. Total iron was determined by oxidizing the whole sample iron(II) to iron(III) in the procedure described [21].

Sample Preparation Procedures

Sea water (Black Sea, Samsun, Turkey) and stream water (River Mert, Samsun) samples were collected in prewashed polyethylene bottles. Samples were filtered (a cellulose nitrate membrane of pore size 0.45 µm Millipore Filter (Millford, MA) before use. Samples were stored at 4°C until analysis. Analyses were performed with the least possible delay. Before the analysis, 1 mL of 1 mL of H_2O_2 (10% w/w) was added to a 9 mL each sample for complete oxidation of iron(II) to iron(III) [22]. Then 20 µL of each sample solution was used for the determination of iron(III), as in the procedure described above.

A sample of the standard metal alloy was prepared according to procedure previously reported [23]. The volume of 10 mL of this solution was treated with H_2O_2 (10 mass%) for iron(II) oxidation. After the oxidation step, 20 µL of this solution was used for the determination of total iron.

RESULTS and DISCUSSION

### Spectrophotometric Studies of the-Metal-NRS Complexes

The reaction between iron and NRS using Job's method was investigated. The stoichiometry of the complex is Fe(III)-NRS= 1:3 (Figure 3). The pH factor is important for iron(III)-NRS complex formation. The absorbance (peak height) of iron(III)-NRS complex was studied by changing pH in the range of 2.0 to 7.0. The pH values were adjusted with the buffer solutions. As a consequence, the most suitable pH value of 4.0 was determined. Absorption spectra's those correspond to solutions of 5×10^{-5} M of iron(III)-complex measured against all the other metal-NRS complexes tested are shown in Figure 4. The molar absorptivity at λ_{max}: 370 nm is 4.86×10^4 $L.mol^{-1}.cm^{-1}$.

Iron(III) subsequently reacted with NRS at pH 4.0 and formed iron(III)-NRS complex. Iron(III)-NRS complex showed sharp absorption maximum at λ_{max}: 370 nm. At this wavelength, 4, 1-nitroso-2-naphthol-3,6 sulphonate has no absorption. The NRS complexes of all the metal ions with the anions tested show a negligible absorption. As can be seen, a large number of ions have no significant effect on the determination of iron(III). For tested metal ions whose tolerance limit has been studied, their tolerance ratios are given in Table 1.

Optimization of the Method

Various chemical variables of FIA system were optimized by use of the unvaried method at a fixed iron(III) concentration of $50 \mu g.L^{-1}$. The parameters of ionic strength and temperature was not taken into consideration in the study. Different molar excesses of NRS were added to a fixed metal ion concentration and absorbencies were measured according to the standard procedure. The NRS concentration was varied from 1×10^{-6} M to 1×10^3
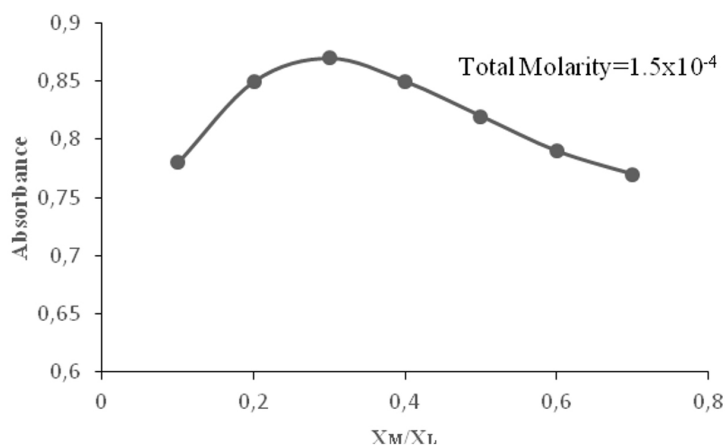
Figure 3. Composition of Fe(III)-NRS complex by Job's method.
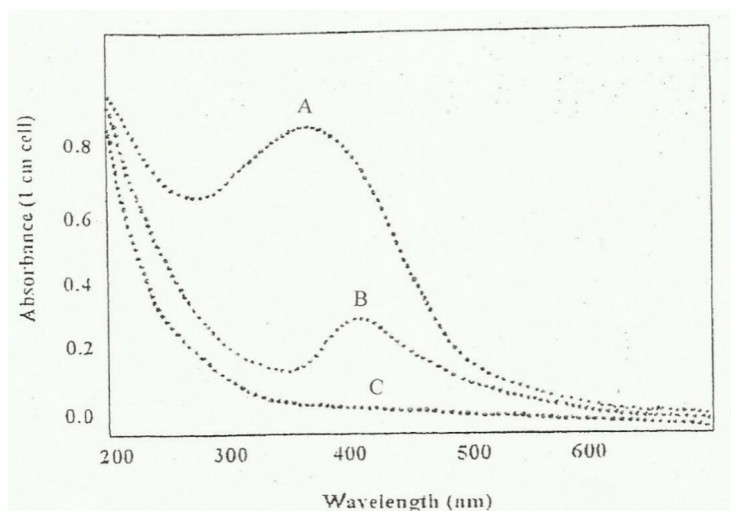
Figure 4. Absorption spectra of 5 x 10^{-5} M NRS and M-NRS complexes, A) Fe(III)-NRS, B) Fe(II)-NRS, C) NRS and M-NRS (M: Cr(III), Al(III), Cu(II), Co(II), Cd(II), Mn(II), K(I), Na(I), Ag(I), Ca(II), Mg(II), Ba(II), Hg(II).

M. The peak height was found to increase with increasing the NRS concentration up to 1x10^{-5} M and no noticeable increase was found at higher concentrations. Therefore, 5x10^{-4} M NRS reagent carrier solution was chosen as optimum because a wide linear range of the calibration curve, especially at low levels of iron(III) was obtained.

For all subsequent measurements, the concentration of the NRS fixed 5x10^{-4} M, the pH of the carrier solution was varied from 3.0 to 5.0. The interference effect of the iron(II) were found to increase with increasing pH up to 4.0 and remain constant at higher pH. Also, the peak heights were found to increase with increasing pH up to 4.0, remain constant to 4.0 and decreased slightly above that. The experiments showed that maximum complex formation was achieved at pH values between 3.0 and 5.0. The pH of the reagent carrier solution was adjusted to 4.0 to obtain maximum peak height and minimum iron(II) interference in the analysis.

The developed method, the effect of sample volume, mixing coil length and flow-rate was studied at the preferred concentration of the NRS and pH, has been optimized. The sample volume was varied from 5-50 µL. The peak height was decreased by decreasing sample size, and the peaks were broadened with increasing sample size due to sample zone dispersion. A sample injection volume of 20 µL was selected as a compromise between sensitivity and sample throughput rate.

The reaction coil (RC) was examined to guarantee a sufficient mixing between the NRS and the sample or standard by using PTFE tubing's (0.5 mm i.d.) at different lengths ranging between 10 and 100 cm. The peak height was increased with increasing mixing coil length from 10-50 cm. The peak height was decreased for lower concentrations and broadened for higher concentrations at longer coil lengths. A mixing coil length 70 cm was decided convenient for better peak height and shape.

The flow-rate was varied from 0.5 to 1.5 mL.min^{-1}. The peak height decreased by increasing flow-rate. Taking into consideration of the stability of the pump, peak shape and sampling time, the flow-rate of the reagent carrier solution was adjusted 0.8 mL.min^{-1}.

Analytical Performance
The developed analytical method was validated by evaluating the linear dynamic range, precision, accuracy, limit of detection (LOD) and limit of quantification (LOQ) by applying the calibration curve method. Under the preferred experimental conditions, a linear calibration graph was obtained for 0.1-100 µg.L^{-1} iron(III) with a regression coefficient of 0.9992. The limit of detection (blank signal plus three times the standard deviation of the blank) was 0.05 µg.L^{-1} and regression equation $Y = 0.8821 + 75.5182C$, where Y is the peak height (cm) and C is concentration in µg.L^{-1}. The precision of the method was investigated by five repetitive injections of 70 and 5 µg.L^{-1} of iron(III) and the

relative standard deviations were 1.46 and 3.12%, respectively. The sample throughput of the proposed method was almost 40 ± 5 h^{-1}.

Interference Studies

The interference effects of many metal ions and anions by standard addition on the determination of 50 μg.L^{-1} iron(III) at fixed concentration were examined. The results summarized in Table 1. The tolerable concentration of each diverse ion was taken as a highest concentration causing an error of $\pm$ 3%. Most of the ions examined did not interfere with the determination of 50 μg.L^{-1} iron(III). The major interference was found from iron(II) at the amounts of 10 mg.L^{-1} (Table 1). The proposed method can be successful applied for the determination of iron(III) and total iron.

Table 1. Tolerance limits of foreign ions on the determination of iron(III) ion of 50 μg.L^{-1} iron(III) ion.

Tolerance limit (μg.L^{-1})	Foreign ions
$\leq$ 50000	Cr(III), Al(III), Cd(II), Mn(II), K(I), Na(I), Ag(I), Ca(II), Mg(II), Ba(II), Co(II), Cu(II), Hg(II), CN$^-$, NO$_3^-$, NO$_2^-$, SO$_4^{2-}$, CO$_3^{2-}$, Cl$^-$, Br$^-$, PO$_4^{3-}$, NH$_4^+$, SCN$^-$
$\leq$ 300	Fe(II)

Applications

To evaluate the applicability of the proposed flow-injwction method, it was applied to the determination of iron(III) in river and sea water samples, and iron processing solutions. The samples collected from different sources were filtered and directly injected into the flow line by using calibration curve method. The analytical results obtained by the proposed method are in good agreement with the certified values as is shown in Table 2. The values obtained from the calibration curve as shown in Table 3. Atomic absorption measurements taken in water samples are also given for comparison (Table 3). Statistical analysis of the results by F- and t- tests showed no significant difference between the accuracy and precision of the proposed and reference method. The results for iron(III) in water samples were also in goog agreement with results obtained by the AAS. The results are given in Table 3. The accuracy of the method was confirmed by analysing Zn/Al/Cu 43XZ3 F standard reference material. The results obtained were in good agreement with the certified iron concentration (Table 2). Some reported procedures for iron determination are presented in the Table 4.

CONCLUSIONS

A new, simple, ultra-sensitive, and inexpensive flow-injection spectrophotometric procedure based on the NRS has been developed for the determination of iron(III) and total iron in a wide concentration range without employing any further care. The proposed method allows to measure iron concentrations directly in the

Table 2. Determination of total iron in standard reference material (SRM).

SRM	Certified (μg)	[a]Found (μg)	[a]Recovery (%)	[b]RSD%
Zn/Al/Cu 43XZ3 F	0.083	0.086 (0.02)	101.25$\pm$0.34	3.61

[a]Mean of three determinations with 95% confidence level (X$\pm$ ts/(n$^{1/2}$)
[b]Relative standard deviation.

Table 3. Determination of iron(III) and total iron in river and sea water samples.

Samples[1]	Iron(III)[2] (μg.L^{-1})	Total iron [2] (μg.L^{-1})			
	Found[3]	Found[3]	AAS	F-test[4]	t-test[5]
Organized industry water	74.34 (0.18)	81.17 (0.14)	83.11 (0.15)	1.6	2.1
Baruthane sea water	47.51 (0.18)	54.26 (0.04)	55.97 (0.20)	1.8	1.9
Mert river water	38.33 (0.24)	42.33 (0.02)	43.76 (0.09)	2.3	1.7

(1)Samples were collected at Samsun, Turkey.
(2)Values in parenthesis are the relative standard deviations for n= 5 with confidence level of 95%.
(3)The results found using the calibration graph.
(4)Tabulated value F for (4,4) degrees of freedom at P= 0.95 is 6.39.
(5) Tabulated value t for 4 degrees of freedom at P= 0.95 is 2.78.

Table 4. Comparison of selected reagents for the proposed FIA method and some reported procedures for iron determination.

Reagent	Limit of detection ($\mu g.L^{-1}$)	Linear range ($\mu g.L^{-1}$)	Reference
Norfloxacin	10	2-14	[17]
3-Aminophtalhydrazide	1.2	7.2-18.2	[18]
8-Hydroxy-quinoline	2.5	1-12	[19]
SCN$^-$	0.3	5.6-44.8	[20]
1-Nitroso-2-naphthol-3,6 sulphonate	0.05	0.1-100	Present work

sample without a matrix separation step. The method could be useful for application to various matrix in process control and in environmental monitoring. The method was successfully applied to the determination of iron in different types of water samples including river, sea and industry waste water samples. In addition to the simplicity of the method, the reagent used is commercially available and does not have a risk of serious toxicity, thus enhancing the potential applicability of the method for iron analysis in real samples, having good recovery, sensitivity, selectivity and rapidity.

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