



# Utility of solid-phase spectrophotometry for determination of dissolved iron(II) and iron(III) using 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline

Alaa S. Amin<sup>a,\*</sup>, Ayman A. Gouda<sup>b</sup>

<sup>a</sup> Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

<sup>b</sup> Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt

## ARTICLE INFO

### Article history:

Received 13 April 2008

Received in revised form 17 May 2008

Accepted 20 May 2008

Available online 7 July 2008

### Keywords:

Iron determination

Quinoxaline azo dyes

Solid-phase spectrophotometry

Water analysis

## ABSTRACT

A new simple, very sensitive, selective and accurate procedure for the determination of trace amounts of iron(II) by solid-phase spectrophotometry (SPS) has been developed. The procedure is based on fixation of iron(II) as 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline on a styrene-divinylbenzene anion-exchange resin. The absorbance of resin sorbed iron(II) complex is measured directly at 743 and 830 nm. Iron(III) was determined by difference measurements after reduction of iron(III) to iron(II) with hydroxylamine hydrochloride. Calibration is linear over the range 1.0–20  $\mu\text{g L}^{-1}$  of Fe(II) with relative standard deviation (R.S.D.) of 1.65% ( $n = 10.0$ ). The detection and quantification limits for 100 mL sample system are 280 and 950  $\text{ng L}^{-1}$  using 0.5 g of the exchanger. The molar absorptivity and Sandell sensitivity are also calculated and found to be  $2.86 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.0196 \text{ ng cm}^{-2}$ , respectively. The proposed procedure has been successfully applied to determine iron(II) and iron(III) in tap, mineral and well water samples.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Iron is widely distributed in nature and is one of the most important elements in environmental and biological effectiveness influenced by its chemical properties, such as valence, solubility, and the degree of complex formation. The determination of iron(II) and iron(III) in aqueous solution is of great importance to evaluate the redox environment of natural waters. There is an increasing need for a highly sensitive method for analysis of iron speciation in environmental and biomedical studies [1]. The simultaneous determination of iron(II) and iron(III) has obtained particular attention [2–5].

Spectrophotometric determination of iron in different oxidation states in water has been reported [6–11]. For the determination of iron in  $\mu\text{g L}^{-1}$  levels in natural waters, an appropriate preconcentration process is usually required [12]. This process is time consuming and the proportion of iron(II) and iron(III) may be altered by atmospheric oxygen in the course of analysis.

Solid-phase spectrophotometry (SPS) combines the preconcentration of the species of interest on a solid matrix, usually an

ion-exchanger, with the aid of complexing agent and subsequent measurement of the absorbance of the complex in the solid phase. This provides an increase in selectivity and sensitivity with respect to conventional spectrophotometric method [13–18].

Many reagents are suggested for determination of iron by solid-phase spectrophotometry: 1,10-phenanthroline [19,20], bathophenanthroline [21], ferrozine [22,23], thioglycolic acid [24] and thiocyanic acid [25]. Some methods using these reagents are of low sensitivity and selectivity. 1,10-Phenanthroline is one of the most useful reagents for determining iron(II) and has been used to the determination of iron(II) and iron(III) [20], but Cu(II) and Zn(II) interfere.

2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline (DCHNAQ) is one of the quinoxaline reagents [26,27], it has been successfully used for spectrophotometric determination of gold(III) [26], scandium(III) [27], mercury(II) [28], vanadium(V) [29] and ruthenium(III) [18]. The goal of the present work is intended to study the possibilities of using DCHNAQ as a reagent for the determination of trace iron(II) and iron(III) by SPS. The optimum conditions have been established. Iron(II) reacts with DCHNAQ to give a coloured complex, which is easily sorbed on an anion-exchange resin and provides the basis for a relatively simple, accurate and rapid spectrophotometric method of iron(II) at  $\mu\text{g L}^{-1}$  level, without a previous preconcentration step. The proposed method is free from many

\* Corresponding author at: Faculty of Community, Department of Medical Science, Umm Al-Qura University, Makkah 1234, Saudi Arabia.

E-mail address: [asamin2002@hotmail.com](mailto:asamin2002@hotmail.com) (A.S. Amin).

interferences and has been applied to the determination of iron(II) and iron(III) in tap, mineral and well water samples.

## 2. Experimental

### 2.1. Apparatus

A PerkinElmer Lambda 12 UV–vis spectrophotometer with a 5.0 mm quartz cell was used for all spectral measurements. An Orion research model 601A/digital ionalyzer pH meter was used for checking the pH of buffer solutions of pH values ranging from 2.5 to 12.0, prepared as recommended previously [28].

### 2.2. Reagent

Analytical reagent grade chemicals and doubly distilled water were used throughout. 2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline used in the present investigation was prepared according to the procedure described previously [24]. A 0.0826 g of DCHNAQ was dissolved in 100 mL of absolute ethanol (826 mg L<sup>-1</sup>).

Iron(III) standard stock solution, 1000 mg L<sup>-1</sup>, was prepared by dissolving 4.3175 g of Fe(NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O in 20 mL of 1:1 HCl and diluted to 500 mL with water. Iron(II) stock solution, 1000 mg L<sup>-1</sup>, was prepared by dissolving 3.511 g of iron(II) ammonium sulphate hexahydrate in 50 mL of 1.0 M HCl and diluted to volume in a 500 mL calibrated flask. The working standard solutions were prepared freshly by dilution with water.

Hydroxylamine hydrochloride, 10% solution, was prepared by dissolving 10.0 g of hydroxylamine hydrochloride in 100 mL water. The solution was freshly prepared every day. Styrene-divinylbenzene anion exchange resin was used in the chloride form. The resin was soaked in alcohol for 12.0 h, then treated with 2.0 M HCl for 6.0 h, finally with distilled water until the washing was free from chloride. It was dried at 40 °C and stored in a brown reagent bottle.

### 2.3. Absorbance measurements

The absorbance of DCHNAQ–Fe<sup>2+</sup> complex sorbed on the resin was measured in a 5.0 mm cell at 743 and 830 nm against a 5.0 mm cell packed with resin equilibrated with blank solution. The net absorbance ( $A_c$ ) for the complex was obtained using the equation [30]:

$$A_c = A_{743} - A_{830}$$

where  $A_{743} = A_{s743} - A_{b743}$  and  $A_{830} = A_{s830} - A_{b830}$  and  $A_{sxxx}$  and  $A_{bxxx}$  are the absorbances of the sample and the blank (cell packed with resin equilibrated with blank solution), respectively at the indicated wavelength. When the absorbance was measured at two different wavelengths, one corresponding to absorption maximum of the complex (743 nm) and the other in a region where the complex absorbs very low (830 nm), the absorbance difference,  $A_{743} - A_{830}$ , could be assumed to be constant under the similar packing conditions.

### 2.4. General procedure

For the determination of total iron in a 100 mL sample containing 0.1–20.0 µg of total iron (II and III), 2.0 mL of 10% hydroxylamine hydrochloride solution, 2.0 mL of 826 mg L<sup>-1</sup> DCHNAQ solution, 10.0 mL acetate buffer solution of pH 3.54 and 0.5 g of styrene-divinylbenzene resin were added. The mixture was stirred for 20 min. The coloured resin was collected and transferred to 5.0 mm

quartz cell with the aid of a dropping pipette. A blank solution containing all reagents except iron was prepared and treated in the same way as the sample. The absorbance difference between sample and blank was measured after 5.0 min as described in Section 2.3.

For the determination of iron(II) in a 100 mL water sample containing 0.1–20 µg of iron(II), the same procedure was used but without the addition of 2.0 mL of 10% hydroxylamine HCl.

## 3. Results and discussion

### 3.1. Absorbance spectra

Iron(II) forms a deep red complex with DCHNAQ at the optimum conditions. Fig. 1 shows the absorption spectra of Fe<sup>2+</sup>–DCHNAQ complex fixed on an anion-exchange resin and in solutions. The absorption maximum of Fe<sup>2+</sup>–DCHNAQ complex is at 727 nm in solution, whereas it shifted to bathochromic direction at 743 nm in the solid phase. It is evident that the sensitivity increases when the complex is sorbed on the resin.

Investigations were carried out to establish the most favourable conditions to give a highly colour intensity and to achieve maximum colour development in the quantitative determination of iron. The influence of each of the following variables on the complexation reaction was tested.

### 3.2. Effect of pH

The optimum pH for the formation and fixation of the complex species was in the range 2.86–4.28 using different types of buffer solutions (universal, acetate, phosphate and thiel [28]). Acetate buffer solution was used to maintain the optimum one which give highest absorbance value in addition to the stability of the colour fixed species, so, all subsequent studies were performed at pH 3.54. Moreover, 10 mL of pH 3.54 acetate buffer solution was selected for 100 mL sample volume.

### 3.3. Effect of reagent concentration

The absorbance increases with DCHNAQ concentration increase. Maximum and constant absorbance was achieved with 1.5–2.5 mL

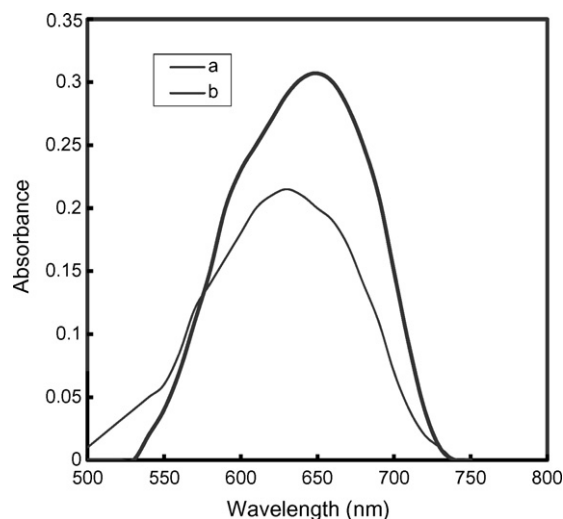


Fig. 1. Absorption spectra of Fe<sup>2+</sup>–DCHNAQ complex: (a) in solution:  $C_{Fe^{2+}} = 2.0 \text{ mg L}^{-1}$ ,  $C_{DCHNAQ} = 413 \text{ mg L}^{-1}$ , pH 3.54, 10 mm path length; (b) on the resin:  $C_{Fe^{2+}} = 12 \text{ } \mu\text{g L}^{-1}$ ,  $C_{DCHNAQ} = 165.2 \text{ mg L}^{-1}$ , pH 3.54, 0.5 g resin, 5 mm optical path length.

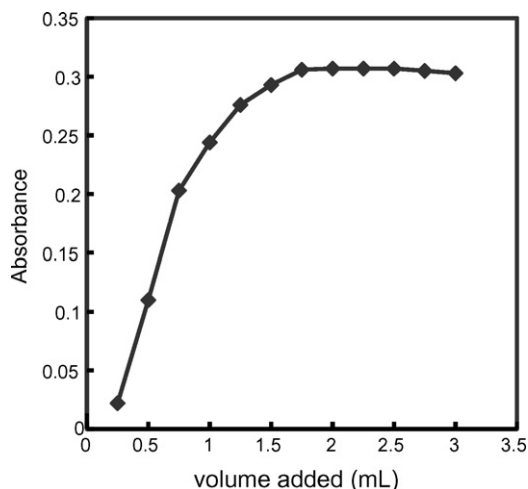


Fig. 2. Effect of  $826 \text{ mg L}^{-1}$  DCHNAQ volume on the complexation of  $12 \text{ } \mu\text{g L}^{-1}$  in sorbed form.

of  $826 \text{ mg L}^{-1}$ . Therefore, 2.0 mL was selected as the optimum volume (Fig. 2).

#### 3.4. Effect of time

The effect of stirring time on colour intensity was investigated. The rate of equilibration was not influenced by the rate of reduction of iron(III) to iron(II). The colour development was complete within 15.0 min (Fig. 3). A stirring time of 20 min was chosen to keep the analysis time. The absorbance of ion-exchange resin phase became stable after ion-exchange resin was transferred into cell for 5.0 min and had no change for 6.0 h.

#### 3.5. Effect of resin

The use of a large amount of resin lowered the absorbance as usual. Only the amount required filling the cell and to facilitate handling (i.e. 0.5 g) was used for all studies. Constant absorbance was obtained by adding 10% hydroxylamine HCl solution, in the range 0.5–4.0 mL, for the reduction of iron(II), 2.0 mL of 10% hydroxylamine HCl solution were employed.

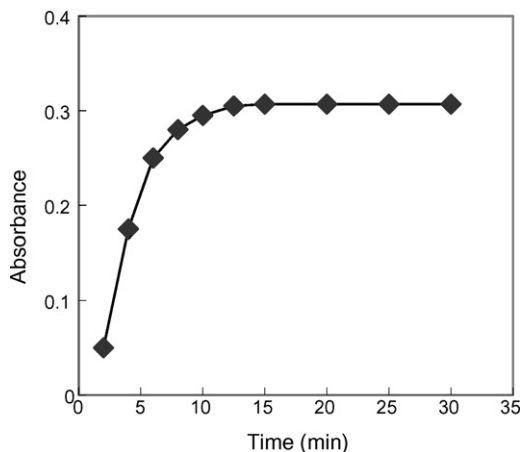


Fig. 3. Dependence of colour development in solid phase on stirring time, conditions:  $12 \text{ } \mu\text{g L}^{-1}$  of  $\text{Fe}^{2+}$ ,  $165.2 \text{ mg L}^{-1}$  DCHNAQ, pH 3.54, 0.5 g resin for 100 mL sample.

#### 3.6. Composition of the complex

The nature of the complex species fixed on the resin was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of DCHNAQ to  $\text{Fe}^{2+}$ , obtained by varying the DCHNAQ concentration, showed inflection at molar ratio 2.0, indicating presence of two DCHNAQ molecules in the fixed complex. Moreover, the Job method showed a ratio of DCHNAQ to iron(II) = 2.0. Consequently, the results indicated that the stoichiometric ratio was 2:1 [DCHNAQ:iron(II)]. The conditional formation constant ( $\log K$ ), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 7.88, whereas the true constant was 8.00.

#### 3.7. Analytical data

The calibration graph for iron(II) ions was linear in the concentration range  $1.0\text{--}20 \text{ } \mu\text{g L}^{-1}$  for 100 mL volumes with  $r^2$  of 0.9992 using 0.5 g of resin. The regression equation may be expressed by

$$A = 0.003 + 5.12 \times 10^{-3}C, \quad r = 0.9996$$

where  $C$  is the concentration of iron in the sample solution in  $\mu\text{g L}^{-1}$ . The molar absorptivity, and Sandell sensitivity of the complex sorbed on the resin from 100 mL sample volume are recorded in Table 1.

Reproducibility was measured for a series of 10 independent determinations containing  $12.0 \text{ } \mu\text{g L}^{-1}$  of iron(II) in 100 mL sample using 0.5 g of the exchanger. The relative standard deviation was 1.65%.

The sensitivity expressed as molar absorptivity of the proposed method is compared in Table 2 with those of published spectrophotometric methods. The higher sensitivity of the proposed method is notable, greater even than that of the SPS [43] that used 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulphonic acid. Also, the proposed method is more sensitive than other method [19–25], that based on solid-phase spectrophotometry (Table 2).

The standard deviation ( $s$ ) of the  $A_{\text{blank}}$ , the background absorbance measured for the blank, calculated as the average of 10 determinations and expressed as  $s$  units was 0.006. The IUPAC detection limit ( $K=3.0$ ) [30] and the quantification limit ( $K=10$ ) [31] were calculated for 100 mL sample (Table 1).

Table 1  
Analytical parameters

Parameter	Value
pH	3.54
Amount of exchanger (g)	0.5
Optimum DCHNAQ concentration ( $\text{mg L}^{-1}$ )	165.2
Optimum hydroxylamine concentration (%)	0.2
Stirring time (min)	20
Beer's law limit ( $\mu\text{g L}^{-1}$ )	1.0–20
Ringbom optimum range ( $\mu\text{g L}^{-1}$ )	2.5–18
Molar absorptivity ( $\times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$ )	2.86
Sandell sensitivity ( $\text{ng cm}^{-2}$ )	0.0196
Detection limit ( $\text{ng L}^{-1}$ )	280
Quantification limit ( $\text{ng L}^{-1}$ )	950
Regression equation <sup>a</sup>	
Slope ( $b$ )	$5.12 \times 10^{-3}$
Intercept ( $a$ )	0.003
Correlation coefficient ( $r$ )	0.9996
R.S.D. (%)	1.65

<sup>a</sup>  $A = a + bC$ , where  $C$  is the concentration of iron in  $\mu\text{g L}^{-1}$ .

**Table 2**  
Comparison of the sensitivity of the methods for spectrophotometric determination of iron

Reagent	$\lambda_{\max}$ (nm)	$\epsilon$ ( $\times 10^{-4}$ L mol $^{-1}$ cm $^{-1}$ )	Reference
Ferrozine	562	2.79	[34]
2,4,6-Tri(2'-pyridyl)-1,3,5-triazine	595	2.15	[35]
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	558	7.10	[36]
Azid-tetrahydrofuran	396	1.53	[37]
Thiocyanate-benzyltriethylammonium	476	2.79	[38]
Pyrocatechol violet-CTAB	595	6.55	[39]
2,4,6-Tris(2'-pyridyl)-1,3,5-triazine-picrate	600	22.0	[40]
Morin-Triton X-100	418	6.15	[41]
1-Nitroso-2-naphthol-Tween 80	446	1.69	[42]
Di-2-pyridylketone salicyloyl hydrazone	375	1.26	[9]
1-(5-Bromo-2-pyridylazo)-2-naphthol-6-sulphoric acid-SPS	765	47.7	[43]
DCHNAQ	743	286	This work

### 3.8. Effect of diverse ions

A systematic study of the effect of foreign ions on the determination of iron(II) was undertaken for a maximum W/W ratio value [foreign ion to iron(II)] of 18,000. Tolerance is defined as the foreign ion concentration causing an error smaller than  $\pm 3.0\%$  in the determination of the analysis. The tolerance values for the ions studied are recorded in Table 3. The proposed method offers better selectivity than that proposed in other SPS methods [19–25].

In order to apply the method to determine iron in natural water samples, the interference from species commonly found in water was studied. The interference was negative for  $F^-$  and positive for other ions. Negative interference is due to decomposition of the formed complex with iron(II), whereas positive interference is due to formation of another complex with the examined ions with excess of DCHNAQ.

The most serious interference in the determination of iron in natural water due to their relatively high concentrations, were from  $Ca^{2+}$ ,  $Mg^{2+}$  and  $SO_4^{2-}$ . However, the interference level can be reduced by diluting the sample, taking into account the sensitivity of the proposed method, without reducing the accuracy and whilst maintaining the simplicity and short duration of analysis.

### 3.9. Analytical applications

The proposed method has been applied to the determination of iron(II) and iron(III) in water samples using the standard

**Table 3**  
Effect of diverse ions on the determination of  $12 \mu\text{g L}^{-1}$  of iron

Foreign ions	Tolerance limit ( $\mu\text{g L}^{-1}$ )
$Na^+$ , $K^+$ , $Li^+$	18,000
$NO_3^-$ , $CH_3COO^-$	13,500
$Cl^-$ , $ClO_4^-$	11,000
$SO_4^{2-}$ , $PO_4^{3-}$	9,000
$S_2O_3^{2-}$ , $SiO_3^{2-}$	7,500
$Ca^{2+}$ , $Mg^{2+}$ , $Si^{2+}$	6,000
Benzoate, citrate	5,000
Succinate, borate	3,750
$Cu^{2+}$ , $Co^{2+}$ , $Ni^{2+}$	2,500
$Pd^{2+}$ , $Pt^{4+}$	1,800
$Zn^{2+}$ , $Cd^{2+}$	1,100
$Mo^{6+}$ , $W^{6+}$	800
$Zr^{4+}$ , $VO_2^+$	500
$Be^{2+}$ , $Sc^{3+}$	300
$La^{3+}$ , $Sm^{3+}$ , $Gd^{3+}$	250
$Al^{3+}$ , $Pb^{2+}$	200
$F^-$	100

addition method. Sensitivity was modified by matrix effect and this fact can be evaluated from the ratio of the slope of the standard addition calibration graph. The ratios were 1.4 for tap water, 1.6 for river Nile water, 0.8 for mineral water and 1.1 for well water samples. The mean value (six determinations) of the iron found in the analysis for 100 mL sample system (taking into account the dilution factor) was  $43.20 \pm 0.006 \mu\text{g L}^{-1}$  for tap water,  $140.5 \pm 0.010 \mu\text{g L}^{-1}$  for river Nile water,  $7.103 \pm 0.005 \mu\text{g L}^{-1}$

**Table 4**  
Determination of iron(II) and iron(III) in water samples

Sample	Added		Proposed method <sup>a</sup> ( $\mu\text{g L}^{-1}$ )				ICP-AES method <sup>a</sup> [32] ( $\mu\text{g L}^{-1}$ )	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	<i>t</i> -value <sup>b</sup>	<i>F</i> -test <sup>b</sup>	Fe(II)	Fe(III)
Tap water	–	–	14.5	28.7	1.17	2.78	14.7	28.5
	2.0	4.0	16.6	32.6	1.29	3.13	16.6	32.5
	4.0	8.0	18.6	36.7	1.56	–	18.7	36.6
	6.0	12.0	20.5	40.5	–	3.27	20.6	40.5
Well water	–	–	46.3	94.2	1.34	3.46	46.5	94.0
	3.0	5.0	49.3	99.3	1.08	–	49.4	99.1
	6.0	10.0	52.4	104.3	–	2.71	52.4	104.2
	9.0	15.0	55.4	109.3	1.20	2.93	55.4	109.2
Mineral water	–	–	2.8	4.3	1.44	3.69	2.8	4.4
	4.0	6.0	6.7	10.4	–	3.25	6.8	10.4
	8.0	12.0	10.8	16.4	1.32	–	10.9	16.3
	12.0	18.0	14.9	22.3	1.26	3.07	14.8	22.3
Well water	–	–	36.2	78.9	–	2.85	36.3	79.0
	2.5	5.0	38.8	83.8	1.40	3.73	38.8	84.0
	5.0	10.0	41.3	88.9	1.52	–	41.2	88.9
	7.5	15.0	43.7	94.0	–	3.56	43.8	93.9

<sup>a</sup> Average of six determinations.

<sup>b</sup> Theoretical values for *t*- and *F*-values at 95% confidence level for five degrees of freedom are 2.57 and 5.05, respectively.

for mineral water and  $115.10 \pm 0.012 \mu\text{g L}^{-1}$  for well water samples.

In order to check the absolute accuracy of the proposed method, a recovery study was carried out on the water samples mentioned above using a competitive method. For this, different amounts of reference iron(II) material were added to water sample and the percentage recovery was determined. Table 4 showed the results obtained for all water samples. These results confirm the validity of the proposed method.

The performance of the proposed method was assessed by calculation of the *t*-value (for accuracy) and *F*-test (for precision) compared with ICP-AES method [32]. The mean values were obtained in a Student's *t*- and *F*-tests at 95% confidence limits for five degrees of freedom [33]. The results showed that the calculated values (Table 4) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other methods. Also, there is no need for extraction or heating in the present method.

#### 4. Conclusion

The proposed method permits the simultaneous determination of trace amounts of iron(II) and iron(III) by solid-phase spectrophotometry using DCHNAQ as complexing agent. Solid-phase spectrophotometry combines the preconcentration of the species of interest on a solid matrix and subsequent measurements of the absorbance of the complex in the solid phase. This provides an increase in selectivity and sensitivity with respect to conventional spectrophotometric method without requiring expensive and sophisticated instrumentation such as ICP, ETAAS. The method is highly sensitive, selective, simple and economical for the determination of iron(II). The proposed method has been applied to the determination of iron in natural water samples with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

#### References

- [1] K. Hirayama, N. Unohara, *Anal. Chem.* 60 (1988) 2573.
- [2] J. Tamarit, V. Irazusta, A. Moreno-Cermeño, J. Ros, *Anal. Biochem.* 351 (2006) 149.
- [3] X.-P. Yan, M.J. Hendry, R. Kerrich, *Anal. Chem.* 72 (2000) 1879.
- [4] S. Oszałdowski, D. Marchut, *Anal. Chim. Acta* 540 (2005) 207.
- [5] G. Absalan, M. Nekoeinia, *Anal. Chim. Acta* 531 (2005) 293.
- [6] W. Ruengsitagoon, *Talanta* 74 (2008) 1236.
- [7] M. Hasani, A. Rezaei, H. Abdollahi, *Spectrochim. Acta (A)* 68 (2007) 414.
- [8] P.K. Tarafder, R. Thakur, *Microchem. J.* 80 (2005) 39.
- [9] M.C.C. Areias, L.H.S. Avila-Terra, I. Gaubeur, M.E.V. Suarez-Iha, *Spect. Lett.* 34 (2001) 289.
- [10] M.J. Almendral, A. Alonso, M.J. Porras, M.A. Garci, Y. Curto, *Microchim. Acta* 147 (2004) 117.
- [11] M.A. Akl, Y. Mori, K. Sawada, *Anal. Sci.* 22 (2006) 1169.
- [12] R.B. Willis, D. Sangster, *Anal. Chem.* 48 (1976) 59.
- [13] F.C. Garcia, R. Checa, R. Avidad, L.F. Capitan-Vallvey, *Talanta* 42 (1995) 711.
- [14] K. Yoshimura, S. Ohashi, *Talanta* 25 (1978) 103.
- [15] L.S.G. Teixeira, F.R.P. Rocha, *Talanta* 71 (2007) 1507.
- [16] M.C. Valencia, J. Garcia, L.F. Capitan-Vallvey, *Anal. Lett.* 23 (1990) 1095.
- [17] A.S. Amin, *Anal. Chim. Acta* 437 (2001) 265.
- [18] A.S. Amin, *Spectrochim. Acta (A)* 58 (2002) 1831.
- [19] Z. Zhao, H. Liu, *Huaxue Shiji* 13 (1991) 123.
- [20] S. Nigo, K. Yoshimura, T. Tarutani, *Talanta* 28 (1981) 669.
- [21] K. Ohzeki, Y. Satoh, Y. Kawamura, T. Kambara, *Bull. Chem. Soc. Jpn.* 56 (1983) 2618.
- [22] S. Li, W. Gao, *Talanta* 31 (1984) 844.
- [23] M.L. Fernandez-de Cordova, A. Ruiz-Medina, A. Diaz, *Fres. J. Anal. Chem.* 357 (1997) 44.
- [24] Y. Liu, X. Qu, B. Guo, J. Li, *Fenxi Ceshi Xuebao* 16 (1997) 35.
- [25] R. Ga, Y. Liu, *Fenxi Huaxue* 24 (1996) 1309.
- [26] A.S. Amin, S. Shakra, A.A. Abdalla, *Bull. Chem. Soc. Jpn.* 67 (1994) 1286.
- [27] A.S. Amin, *J. Saudi Chem. Soc.* 3 (2000) 129.
- [28] A.S. Amin, G.O. El-Sayed, *Monatshefte* 132 (2001) 587.
- [29] A.S. Amin, *Spectrochim. Acta (A)* 59 (2003) 1025.
- [30] IUPAC, *Spectrochim. Acta (B)* 33 (1978) 242.
- [31] Analytical Methods Committee, *Analyst* 112 (1987) 199.
- [32] M.G.D. Tamba, R. Falciani, T.D. Lopez, A.G. Coedo, *Analyst* 119 (1994) 2081.
- [33] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, 3rd edn., Ellis Horwood, Chichester, 1993.
- [34] M.V. Dawson, S.J. Lyle, *Talanta* 37 (1990) 1189.
- [35] G.S.R. Krishnamurti, P.M. Huang, *Talanta* 37 (1990) 745.
- [36] J. Miura, *Analyst* 114 (1989) 1323.
- [37] C.J. Chacarolli, J.F. Andrade, O.M. Guimaraes, V.R. Balbo, C.S. Venezuela, F.S. Teruel, *Anal. Chim. Acta* 411 (2000) 217.
- [38] K.C. Bayan, H.K. Das, *Talanta* 35 (1988) 57.
- [39] M.T.M. Zaki, W.H. Mahmoud, A.Y. El-Sayed, *Talanta* 35 (1988) 253.
- [40] M.I. Toral, A.B. Barrera, *Talanta* 36 (1989) 1069.
- [41] M.T.M. Zaki, A.M. El-Atrash, W.H. Mahmoud, A.Y. El-Sayed, *Analyst* 113 (1988) 937.
- [42] J. Yun, H. Choi, *Talanta* 52 (2000) 893.
- [43] J. Chen, J. Lin, *Anal. Lett.* 34 (2001) 2169.