

## NEW OXIDATIVE ELECTROPHILIC COUPLING REACTIONS AND THEIR APPLICATION TO SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) IN ENVIRONMENTAL WATERS, SOILS AND INDUSTRIAL EFFLUENT SAMPLES

UDC 546.723 : 535.243

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**Abstract.** *New oxidative electrophilic coupling reagents, 2-amino-2',5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2'-fluorobenzophenone (MFB) are exploited for the determination of trace concentrations of iron(III) in environmental water and soil samples.*

*The methods were based on oxidation of the electrophilic coupling reagents, 2-amino-2',5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2'-fluorobenzophenone (MFB) by iron(III) and coupling with phenoxazine (PNZ) in acidic medium to yield red color derivative having an absorbance maximum at 520 nm, which is stable up to 12 h. Beer's law are obeyed for iron in the concentration ranges 0.31-1.2121  $\mu\text{g mL}^{-1}$  and 0.42-1.41  $\mu\text{g mL}^{-1}$ , respectively. The optimum reaction conditions and other important analytical parameters were established. Interference due to various non-target ions was also investigated. The developed methods were applied to the analysis of iron(III) in various matrices. The performance of developed methods were evaluated in terms of Student's t-test and variance ratio F-test that indicate the significance of developed methods over reported method.*

**Key words:** *spectrophotometry, iron(III), phenoxazines, environmental samples, soil*

### 1. INTRODUCTION

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%. Elemental iron is rarely found in nature, as the iron ions  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  readily combine with oxygen- and sulfur-containing compounds to form oxides, hydroxides, carbonates, and sulfides in the form of an ore. Iron is most commonly found in nature in the form of its oxides (1,2) [1].

The principal minerals of iron are the oxides (hematite and magnetite), hydroxide (limonite and goethite), carbonate (siderite) and sulfide (pyrite) [2].

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Received June 20<sup>th</sup>, 2012, accepted February 27<sup>th</sup>, 2013.

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Iron can exist in aquatic systems (natural waters and their sediments) in several oxidation states: metallic iron (iron metal), ferrous iron (Fe II), and ferric iron (Fe III). The oxidation state in which iron exists in a particular aquatic system, and the redox reactions (chemical oxidation reduction reactions) in which it participates, depends on the presence or absence of dissolved oxygen (DO) [3].

Iron is an essential nutrient in the human diet. In the body, it is complexed with hemoglobin, which carries oxygen from the lungs to the cells of the body, and plays an equally essential role in respiratory enzymes such as cytochromes, which allows us to use oxygen. Iron deficiency is the most common cause of diseases mainly during infancy, pregnancy and adolescence. When the dietary intake is deficient in iron, a condition called anemia results [4, 5].

The determination of iron(III) has obtained particular attention being widely distributed in nature and one of the most important elements in geochemical, environmental and biological systems. Its geochemical, environmental and biological effectiveness is influenced by its chemical properties and the degree of complex formation, that is, continuous analyses are necessary for monitoring purposes and process control. Therefore, there is an increasing need of a simple and selective method for analysis of iron speciation in environmental (like water, soil and sediment) samples [6, 7].

Several methods have been employed to determine iron in biological specimens and/or pharmaceutical formulations including flow injection [4, 5, 8-11], isotope dilution high-resolution ICPMS [12], flame atomic absorption spectrometry [13, 14], high-performance liquid chromatography, HPLC [15], cathodic stripping voltammetry [16, 17]. However, Most of these techniques involve expensive instrumental set up, lengthy treatments and hence lack the simplicity needed for routine analysis.

In addition, there are many methods have employed various ligands followed by extracting the formed complexes for the determination iron(II) such as, O-phenanthroline [18], 5-nitro-6-amino-10-phenanthroline [19], 2,2-dipyridine [20], 5-bromo-salicylaldehyde thiosemicarbazone (5-BAST) [21], whereas, for the determination of iron(III), ligands like, piroxicam [22], thiocyanate and EDTA [23] have been used.

Thiocyanate is considered to be the famous reagent, which forms series of complexes with iron(III) depending on the concentration of thiocyanate [24]. However, it suffers from a number of disadvantages. For example, optical densities of ferric thiocyanate solutions depend upon the conditions used from the reaction (temperature, acidity, excess of reagent); the solutions may suffer from measure of fading and do not completely follow the Beer –Lambert's law [25].

In addition to those ligands mentioned above, common colorimetric reagents for the determination of either iron(II) or iron(III) in water, have been used such as 1,10-phenanthroline [26], 4,7-biphenyl-1,10-phenanthroline [27], ferrocyanide [28], thioglycollic acid [29]. With these chromogenic agents several steps are required for determination of iron and the methods are not rapid [30].

Moreover, there are visible spectrophotometry amongst the optical methods seems to be the most appropriate analytical approach for the determination of iron, as it provides sensitive, precise and accurate measurements of suitable analytes, and offers practical and economical advantages over other methods. However, some of the recently proposed spectrophotometric methods [31] for the determination of iron [32-39] are less sensitive and less selective.

The survey of the literature revealed that no attempts have been made to develop a non-kinetic or non-catalytic spectrophotometric method for the determination of iron(III) using oxidative electrophilic coupling reaction between phenoxazine as chromogen and 2-amino-2',5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2'-fluorobenzophenone (MFB) as an electrophilic coupling reagents.

These deficiencies encouraged the authors to develop facile, sensitive, accurate, inexpensive, reliable and cost-effective methods for the determination of trace amounts of iron in different matrices.

The present work is based on exploiting oxidative coupling reactions between phenoxazine as chromogen and 2-amino-2',5-dichlorobenzophenone (MCB) and 2-amino-5-chloro-2'-fluorobenzophenone (MFB) as an electrophilic coupling reagents to yield red derivative, which have been applied for the determination of iron(III) and total iron after oxidation of iron(II) in environmental waters, soils and industrial effluent samples.

## 2. EXPERIMENTAL

### 2.1. Materials and solutions

All solutions used were prepared from analytical grade chemicals unless specified otherwise. The reagents were used without further purification. Phenoxazine (PNZ), 2-amino-2',5-dichlorobenzophenone (MCB) and 2-amino-5-chloro-2'-fluorobenzophenone (MFB) were obtained from Aldrich.

Stock solution ( $1000 \mu\text{g mL}^{-1}$ ) of iron(III) was prepared by dissolving known quantity of ferric ammonium sulfate in 100 mL of distilled water. Solutions of required strength as needed in the analyses were prepared by diluting the stock solution with distilled water.

Fresh solutions of 0.025% (w/v) PNZ were prepared by dissolving 25 mg of each sample separately in 100 mL distilled ethyl alcohol. The 0.05% (w/v) solutions of MCB and MFB were prepared by dissolving 50 mg of the samples individually in 100 mL of distilled ethyl alcohol.

### 2.2. Apparatus

Specord 50 UV-Vis spectrophotometer with 1.0 cm silica quartz matched cell (Jasco, Tokyo, Japan) was used for measuring the absorbance.

### 2.3. General procedures

To a series of 25 mL calibrated flasks, 1.0 mL of 0.05% (w/v) MCB or MFB reagent an aliquots of standard solutions of iron(III), 2.0 mL of 0.025% (w/v) PNZ and 1.0 mL of 2 N hydrochloric acid were added. The contents were mixed thoroughly and allowed for 5 min to complete the reaction. The resultant red colored solutions in the standard flasks were made up to the volume with distilled water. Absorbance was measured at 520 nm with 1.0-cm quartz cell against the corresponding reagent blank, which was prepared similarly except for the addition of iron(III). The optical characteristics for determination of iron(III) with PNZ using MCB and MFB are shown in Table 1.

**Table 1** Spectral data for determination of iron(III) using MCB / MFB as electrophilic coupling agents and PNZ as chromogens

Parameters	PNZ	
	MCB	MFB
Color	Red	Red
$\mu_{\max}$ (nm)	520	520
Stability (h)	12	12
Beer's law ( $\mu\text{g mL}^{-1}$ )	0.31-1.21	0.42-1.41
Recommended ion concentration ( $\mu\text{g mL}^{-1}$ )	0.50	0.70
Molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ ) $\times 10^4$	2.65	2.12
Sand ell's sensitivity ( $\mu\text{g cm}^{-2}$ ) $\times 10^{-3}$	2.30	3.05
Regression equation <sup>a</sup> :		
Slope (a)	0.103	0.191
Intercept (b)	0.005	0.081
Correlation coefficient	0.9951	0.9992
Reaction time (min)	5	5
RSD% (n=7)	0.31	0.56
LOD ( $\mu\text{g mL}^{-1}$ )	0.025	0.028
LOQ ( $\mu\text{g mL}^{-1}$ )	0.085	0.091

<sup>a</sup> Regression curve:  $y = ax + b$ , where x is the concentration of iron(VI) in  $\mu\text{g mL}^{-1}$  and y is absorbance

### 3. RESULTS AND DISCUSSION

#### 3.1. Reaction mechanism

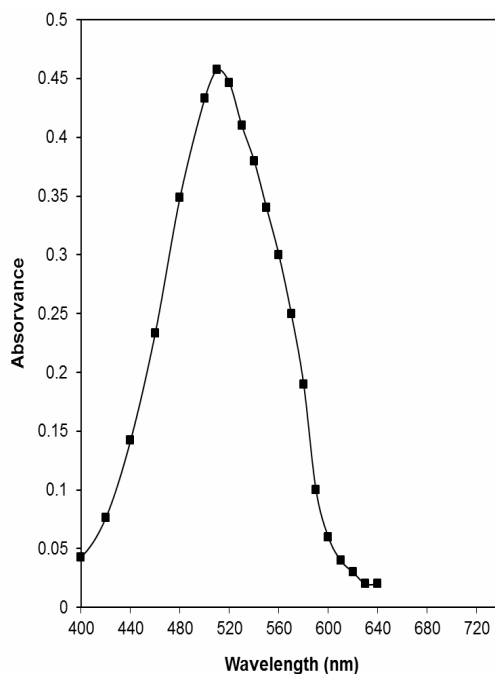
The chemical reactions in the spectrophotometric study, involved the reduction of iron(III) by MCB or MFB and the latter's subsequent oxidative coupling with PNZ in an acidic medium to form a red product. The factors affecting the color development, reproducibility, sensitivity and adherence to Beer's Law were investigated by optimizing the analytical variables.

#### 3.2. Optimization of factors affecting the absorbance

##### 3.2.1. Absorption spectra of colored derivatives

In order to have minimum interferences and best sensitivity, it was necessary to identify optimum wavelength for iron(III) determination in the developed methods.

This wavelength must be specific for the quantitative and specific monitoring of the (MCB)/(MFB) -Iron(III)-PNZ over the range 300–800 nm with a Specord 50-UV-vis spectrophotometer. Wavelengths of 520 nm were found optimum to get best results, shown in Figure 1.



**Fig. 1** Absorption spectrum for the reaction product formed between an electrophilic coupling, 2-amino-2',5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2'-fluorobenzophenone (MFB) and phenoxazine (PNZ) in the presence iron(III) in acidic medium.

Under the optimized conditions, although the color developed almost instantaneously, but 5 min were allowed to have maximum and constant absorbance in both the methods. The red color derivative was stable up to 12 h. The absorbance varied by  $\pm 2\%$  within a day. The color development was influenced by temperature in the range of 20-35 °C and the best results were obtained in this temperature range. At higher temperature the absorbance values decreased; which indicates the dissociation of color on prolonged heating.

### 3.2.2. Effect of reagents and acid concentration

The effect of PNZ reagent at 0.025% (w/v) solution in the range of 0.10-10.0 mL was studied to find the volume needed to get maximum color intensity. The results indicated that 1.0-3.0 mL of the solution was necessary. Hence, 2.0 mL of 0.025% (w/v) solution in a 25mL standard flask was taken. Maximum intensity of the red color was achieved in hydrochloric acid medium. Preliminary investigations showed that hydrochloric acid was better than sulfuric, phosphoric or acetic acid. Maximum intensity of the red color was achieved in the range of 0.5-2.0 mL of 1M HCl. Therefore, 1.0 mL of 1M HCl in 25 mL was used for getting best results. Similarly, the amount of MCB or MFB) for constant and maximum color development was investigated. It was found that 1.0-3.0 mL of the solution was necessary. Hence, 2.0 mL of 0.05% (w/v) MCB or MFB was selected to get reproducible results.

Experiments were carried out to optimize temperature and time of the reaction. It was found that maximum color intensity developed within 5 min at room temperature and

remained almost stable for about 12 h. Increase in reaction temperature decreased the intensity of red color. Hence, 5 min reaction was selected for the routine analysis.

### 3.2.3. Order of addition of reactants

During the investigation it was observed that the sequence of addition of reactants was also important as it influenced the intensity and the stability of the color of the product to a great extent. The sequences (i) PNZ-HCl-Iron(III)- (MCB) or (MFB) and (ii) Iron(III)-HCl- PNZ(MCB) or (MFB) gave less intense and unstable color. While, more intense and stable red color was obtained with sequence (iii) (MCB) or (MFB) -Iron(III)-PNZ-HCl. This was expected as the reaction (i) and (ii) produced radical cation while, in (iii) electrophilic reaction was involved.

### 3.2.4. Linearity, accuracy and precision

The spectrophotometric methods were further evaluated under the optimum conditions with regard to linearity, accuracy, and precision, molar absorptivity and Sandell's sensitivity.

The linearity of the spectrophotometric methods for the determination of iron(III) were evaluated under the optimum conditions. The regression calibration equation obtained under optimum conditions for Fe(III), PNZ and MCB was:  $Y = -0.005 + 0.103X$ ;  $r = 0.9951$  and  $n = 7$ . Where, Y is the absorbance and X the iron(III) concentration in  $\mu\text{gL}^{-1}$ . The calibration curve was linear over the range  $0.31\text{--}1.21 \mu\text{gL}^{-1}$  MCB and  $0.42\text{--}1.41 \mu\text{gL}^{-1}$  MFB. The molar absorptivity was  $2.65 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$  for PNZ - (MCB) complex and Sandell's sensitivity was  $0.0023 \text{ mgcm}^{-2}$ .

The accuracy of the methods was evaluated by taking real environmental samples like lake, well, and tap waters and soil samples and the results were compared with standard spectrophotometric method results. The results obtained in the developed spectrophotometric methods compared very well with those from the standard method [40]. The % R.S.D. was found to be  $< 0.93$  ( $n = 7$ ). Under the condition established for iron(III), the limit of detection (LOD) and the quantification (LOQ) of iron(III) were determined by employing the equation [41]:

$$\text{LOD} = 3\alpha/b$$

and

$$\text{LOQ} = 10\alpha/b$$

where  $\alpha$  is the deviation ( $n=7$ ) of the blank and b is the slope of the calibration plot.

The value of LOD and LOQ of the developed procedure were found  $0.025$  and  $0.085 \mu\text{g mL}^{-1}$ , respectively.

To further confirm the validity and accuracy of the developed methods, recovery tests were performed by standard addition method. Each test was repeated seven times. The results presented in Table 1 indicate very good recoveries and non-interference from commonly encountered constituents normally present in the environmental samples.

### 3.2.5. Effect of diverse ions

In order to evaluate the selectivity of the developed methods for analysis of iron(III) in various samples, the interference from foreign ions commonly present in water and soil was studied by adding known amounts of foreign species to a solution containing  $0.5 \mu\text{g mL}^{-1}$  of iron(III) by developed method. The tolerance limit for various ions is defined as the concentration of added ion causing less than  $\pm 3\%$  relative error for the iron(III)

determination. The effects of possible interference and the maximum tolerable concentration are given in the Table 2.

**Table 2** Effect of diverse species in the determination of 0.50  $\mu\text{g mL}^{-1}$  of iron(III) using proposed PNZ / MCB method

Foreign ions	Tolerance limit ( $\mu\text{g mL}^{-1}$ )
$\text{Bi}^{3+}$ , $\text{Ba}^{2+}$ , $\text{Ti}^{4+}$ , EDTA, $\text{Br}^-$ , citrate, tartarate, oxalate	1000
$\text{Na}^+$ , $\text{Mg}^{2+}$ , $\text{Al}^{3+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{K}^+$ , $\text{Hg}^{2+}$ , $\text{Ni}^{2+}$ , $\text{CH}_3\text{COO}^-$	100
$\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{SO}_4^{2-}$ , $\text{NH}_4^+$ , $\text{Co}^{2+}$ , $\text{Cu}^{2+}$ , $\text{PO}_4^{3-}$	50
Chloramine-T, Chloramine-B, $\text{IO}_3^-$ , $\text{IO}_4^-$ , $\text{BrO}_3^-$	0.2

### 3.3. Applications

#### 3.3.1. Preparation and analysis of water samples

Lake water, tap water, well water, ground water, sewage water, treated industrial effluent samples were collected in polyethylene containers cleaned with nitric acid and then filtered through Whatman No. 41 filter paper. Filtered samples were stored at 4 °C until analyzed. Before the analysis, 1.0 mL of  $\text{H}_2\text{O}_2$  (10% w/w) was added to 9.0 mL of each sample for the complete oxidation of iron(II) to iron(III). A set of experiments was conducted to check the validity of the method. The possibility of using our methods for the analysis of these samples was tested by determining the recovery of known amounts of iron(III) added to the samples. Recoveries were between 92.0 and 108.0% indicating that there is no serious interference in water samples. The results are shown in Table 3.

**Table 3** Determination of iron(III) in different environmental samples by proposed PNZ / MCB method

Sample	Iron(III) added ( $\mu\text{g mL}^{-1}$ )	Developed method				Reference method [40]	
		Iron(III) recovered ( $\mu\text{g mL}^{-1}$ )	Recovery (%) $\pm$ RSD <sup>a</sup>	<i>t</i> -value <sup>b</sup>	<i>F</i> -value <sup>c</sup>	Iron(III) recovered ( $\mu\text{g mL}^{-1}$ )	Recovery (%) $\pm$ RSD <sup>a</sup>
Lake water	0.50	0.51	102.0 $\pm$ 0.59	2.62	3.42	0.48	96.0 $\pm$ 0.40
	1.00	1.08	108.0 $\pm$ 0.25	1.50	2.36	1.05	105.0 $\pm$ 0.31
Tap water	0.50	0.48	96.0 $\pm$ 0.50	2.23	3.20	0.51	102.0 $\pm$ 0.59
	1.00	0.98	98.0 $\pm$ 1.20	1.52	2.94	1.08	108.0 $\pm$ 0.25
Well water	0.50	0.46	92.0 $\pm$ 0.54	1.74	4.56	0.48	98.3 $\pm$ 0.37
	1.00	0.99	99.0 $\pm$ 0.75	1.23	2.60	0.98	99.3 $\pm$ 0.57
Ground water	0.50	0.47	94.0 $\pm$ 0.34	1.56	3.98	0.48	100.8 $\pm$ 0.61
	1.00	1.05	105.0 $\pm$ 0.83	1.69	3.44	1.05	102.6 $\pm$ 0.78
Sewage water	0.50	0.48	96.0 $\pm$ 0.40	2.23	3.20	0.47	94.0 $\pm$ 0.34
	1.00	1.05	105.0 $\pm$ 0.31	1.52	2.94	1.05	105.0 $\pm$ 0.83
Treated industrial effluent	0.50	0.51	102.0 $\pm$ 0.65	1.23	4.44	0.51	96.6 $\pm$ 0.57
	1.00	1.08	108.0 $\pm$ 0.53	1.29	3.64	1.04	97.3 $\pm$ 0.21
Soil	0.50	0.51	102.0 $\pm$ 0.68	1.56	3.98	0.46	92.0 $\pm$ 0.54
	1.00	1.04	104.0 $\pm$ 0.52	1.69	3.44	0.99	99.0 $\pm$ 0.75

<sup>a</sup> Average of seven determinations, RSD - relative standard deviation

<sup>b</sup> Tabulated *t*-value at 95% confidence level is 2.18

<sup>c</sup> Tabulated *F*-value at 95% confidence level is 6.32

### 3.3.2. Preparation and analysis of soil sample [42]

Soil samples (0.5 g each) were slurred with 2.0 mL water in a 250-mL long stem beaker. Distilled HNO<sub>3</sub> (40 mL) was added and the mixture was heated at 70 °C for 2 h; the mixture was cooled and 5 mL of 30% H<sub>2</sub>O<sub>2</sub> was added drop wise. Heating was continued for 1h 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. As we could not find iron(III) in the soil sample, recovery test was conducted by adding different known amounts of iron(III) to fixed volume of test solution. Recoveries are close to 100% and the results are shown in Table 3. The result is the clear indication that there is no serious interference in soil samples by using proposed method.

## 4. CONCLUSION

The red colored derivatives formed under the above mentioned conditions can be regarded as oxidative coupling reactions between 2-amino-2',5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2'-fluorobenzophenone (MFB) and phenoxazine (PNZ) in the presence iron(III) in the acidic medium. The experiments indicated that developed methods has several remarkable analytical advantages with respect their high selectivity and sensitivity which allowed the determination of up to 0.31 µmL<sup>-1</sup> MCB and 0.42 µmL<sup>-1</sup>, simplicity, rapidity, reproducibility, precision, instantaneous color development, and its stability up to 12 h. Moreover, the developed methods do not involve elaborated cleanup procedure as required by the other methods, besides being less time consuming.

These methods have been successfully applied for the determination of iron(III) and total iron after oxidation of iron(II) in a variety of real samples. The results obtained by the developed methods were compared with the standard method by calculating the relative standard deviations. These results are comparable with standard procedures which indicate the validity of the methods.

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## **NOVA OKSIDATIVNA ELEKTROFILNA KUPLOVANJA I NJIHOVA PRIMENA ZA SPEKTROFOTOMETRIJSKO ODREĐIVANJE GVOŽĐA U VODAMA, ZEMLJIŠTU I INDUSTRIJSKIM OTPADNIM UZORCIMA**

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*Razvijena je i validirana metoda određivanja tragova jona gvožđa(III) u uzorcima vode i zemljišta pomoću oksidacionih elektrofilnih kuplujućih reagenasa, 2-amino-2',5-dihlorbenzofenona (MCB) ili 2-amino-5-hlor-2'-fluorbenzofenona (MFB).*

*Metode su zasnovane na reakciji oksidacije elektrofilnih kuplujućih reagenasa, 2-amino-2',5-dihlorbenzofenona (MCB) ili 2-amino-5-hlor-2'-fluorbenzofenona (MFB) jonima gvožđa(III), nakon čega sledi kuplovanje sa fenoksazinom (PNZ) u kiseloj sredini, pri čemu se dobiva proizvod crvene boje, koja je stabilna do 12 h, sa maksimumom absorbance na 520 nm. Beer-ov zakon važi u oblasti koncentracija gvožđa 0,31-1,2121  $\mu\text{g mL}^{-1}$  i 0,42-1,41  $\mu\text{g mL}^{-1}$ , redom za ove dve metode. Optimizovani su uslovi reakcije i ispitana je mogućnost inetrferencije sa ostalim, neciljnim jonima. Ova metoda se može primeniti za analizu gvožđa(III) u različitim uzorcima. Rezultati Studentovog *t*-testa kao i *F*-testa ukazuju na prednosti razvijene metode u odnosu na prethodno publikovane.*

*Ključne reči: spektrofotometrija, gvožđe(III), fenoksazini, realni uzorci, zemljište*