

DEVELOPMENT OF FLOW INJECTION ANALYSIS SYSTEM FOR DETERMINATION OF IRON(II) AND TOTAL IRON IN GROUND WATER

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Abstract

A reversed flow injection spectrophotometric determination of iron(II) and total iron has been carried out. It is based on the reaction between iron(II) and 4-(2-pyridylazo)-resorcinol (PAR) in acetate buffer pH 9.0 yielding a yellowish-orange coloured complex with an absorption maximum at 714 nm. The 50 μl of 5×10^{-4} mol L⁻¹ PAR solution was injected into a continuous flowing stream of 0.01 M HCl with an appropriate flow rate of 0.9 ml min⁻¹. Then, it was merged with sample solution and acetate buffer flowing at the rate of 2.2 and 2.4 ml min⁻¹, respectively, and the sample zone was detected by spectrophotometer. The optimum conditions of this system were determined. Two linear calibration curves over the concentration range 0.05-3.00 mg L⁻¹ of iron(II) and iron(III) solutions were obtained with the regression equations $A=0.176C+0.0128$ ($r^2=0.9988$) and $A=0.1116C + 0.0018$ ($r^2=0.9966$), respectively. A detection limit (defined as 2σ) was 0.012 mg L⁻¹ with a sample throughput of 180 samples h⁻¹. The relative standard deviation was 0.21% ($n = 15$) at the 3.00 mg L⁻¹ Fe (II). The proposed method was successfully applied to the determination of iron (II) and total iron in groundwater. Analytical results obtained by the proposed method were in good agreement with those obtained by reference methods.

Keywords : Flow injection analysis, PAR, Iron

Introduction

Trace metal ions play important roles in life. Thus, the determination of these in environmental samples is becoming increasingly importance. Nowadays, many people depend daily on groundwater for their drinking water. However, the contamination may increase as toxins damped on the ground. Drinking contaminated groundwater can have serious health effects. Iron is one of the most important elements because it is as significant factor in the evaluation of water quality and its reactivity also drive numerous chemical processes in natural waters.

Among the colorimetric reagents for determining metal ions including iron spectrophotometrically, 4-(2-pyridylazo resorcinol) (PAR) is one of the most interesting colorimetric reagents because it is water-soluble and forms soluble complexes with a large number of metal ions. Selectivity for certain metal ion can be achieved by changing pH of the reaction solution. These complexes have large molar absorptivities(10^4) at about 500 nm (Jezorek 1979) and exhibit high sensitivity for spectrophotometric detection. A variety of methods for the

determination of iron have been developed including spectrophotometry (Yotsuyanagi 1972) (Bobrowska-Grzesik 1996) (Youssef El Sayed 1996), titrimetry (Kochana 1992), chromatography (Divjak 1998), potentiometry (Hassan 1994) and atomic spectrophotometric method (Uzun 2001) (Kendüzler 2002) (Tewari 2000). These methods provide good accuracy and sensitivity, but are generally time consuming, require large volume of sample and reagent and also require expensive instrumental equipment. Flow injection analysis (FIA) technique is recognized as a versatile and valuable tool that is capable of analyzing multiple samples automatically and quickly (Ruzicka 1975) than batch analysis. FIA techniques have been reported based on spectrophotometric (Rocha 2001) (Themelis 2001) and chemiluminescence (Qin 1998) methods to the determination of iron in alloy and pharmaceutical preparations (Rocha 2001) (Themelis 2001) and water (Qin 1998). The spectrophotometric detection is widely used in FIA due to the low cost of instrumentation, the simplicity of procedures, as well as their speed, precision, and accuracy. In the present work, a very simple, rapid and sensitive reversed flow injection analysis (rFIA) spectrophotometric method has been described for the determination of iron (II) and total iron in groundwater using the reaction between PAR and Fe (II). The rFIA system was capable directly determination of Fe (II) followed by the determination of the total iron concentrations after the reduction of Fe (III) to Fe(II) by ascorbic acid.

Experimental

1. Reagents and solutions

All chemical reagents were of analytical-reagent grade and were used without further purification. All aqueous solutions were prepared by distilled water.

A standard stock solution of 1000 mg L⁻¹ iron (II) and iron (III) were prepared by dissolving accurately weighed amount of ferrous sulphate heptahydrate (Merck) and ammonium ferric sulfate (Fluka) in 1000 ml of water containing 10 ml of concentrated sulfuric acid. Working solutions were prepared by the stepwise dilution of the stock solution with distilled water.

A 5×10^{-3} mol L⁻¹ 4-(2-Pyridylazo) resorcinol (PAR) (Fluka) solution was obtained by dissolving its sodium salt in water. Universal buffer solutions containing borate, citric acid and phosphate with the pH adjusted with in the range between 7 and 11 were prepared.

2. Apparatus

All UV-Vis spectra were recorded by means of a diode-array spectrometer (Specord S10, Perkin Elmer, Germany). The reversed flow injection system used in this work (Fig.1) consists of two pumps (FIAS300 Perkin Elmer, Germany). One pump delivered carrier stream, buffer solution and sample solution at a fixed flow rate. The other pump was used to delivered PAR solution. The PAR solution was injected by a six-way injection valve into the carrier stream (HCl). PTFE tubing was used as flow lines and reaction coil in the system. All the signals were detected by UV-Vis spectrometer (Lamda2S, Perkin Elmer, Germany) and the signals were recorded using a personal computer.

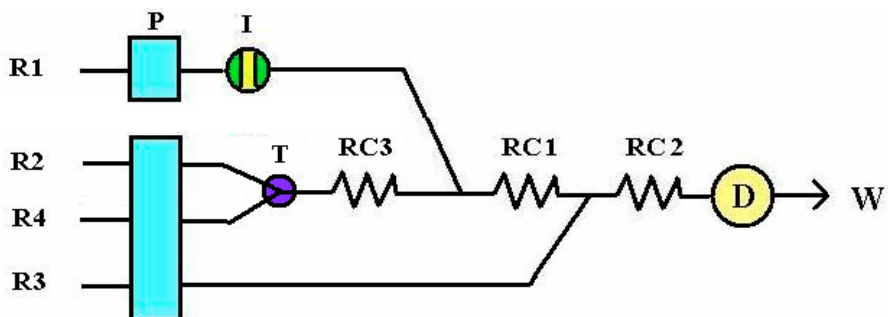


Figure 1 schematic diagram of reversed flow injection analysis for the determination of iron(II) and total iron. A, HCl; B, sample; C, ascorbic acid; D, buffer; P, peristaltic pump; I, injection valve; SV,selecting valve; RC1,RC2, and RC3, reaction coil 1, 2 and 3, respectively; D,detector; W,waste.

Results and Discussion

1. Absorption spectrum

The absorption spectra of PAR and iron (II)-PAR complex were shown in Fig. 2, it can be seen that PAR exhibits an absorption maximum at 412 nm whereas the complex shows two absorption maximum at 495 and 714 nm, respectively. Analytical wavelength chosen was at 714 nm due to no absorption peak of PAR found at this wavelength.

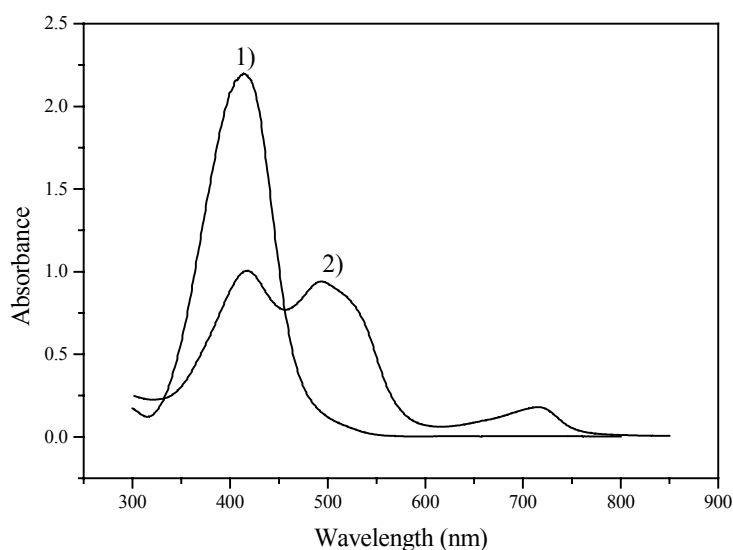


Figure 2 The absorption spectra of 1) PAR and 2) iron (II)-PAR complex in buffer solution pH 9

2. Optimisation of the reversed FIA system

The operational conditions of the rFIA system and chemical variables were optimized in a univariant way in order to obtain the high signal and the best reproducibility. The system operates via two distinct parts with the first being used for determination of Fe (II) and the other for the determination of total iron.

2.1 Chemical parameter optimization

The iron (II) solution reacts with PAR in buffer solution giving a yellowish-orange coloured complex. Therefore, the effects of carrier stream and PAR concentration and buffer were studied with the respect to the following preliminary conditions in Table 1. The effect of carrier stream (HCl) concentration was studied over the range 0.01 to 0.50 mol L⁻¹. A 0.01 mol L⁻¹ HCl concentration was found to be suitable for this determination. The detail study of this parameter is shown in fig 3. The PAR concentration was varied from 5.0×10^{-5} to 9×10^{-4} mol L⁻¹ (see Fig. 4) and a 5×10^{-4} mol L⁻¹ PAR concentration was chosen for this system. The buffer pH was tested within the range 7-11 as shown in Fig. 5. The results obtained clearly demonstrated that at pH 9 a good sensitivity was obtained. Therefore, this pH was selected as optimum parameter. Ascorbic acid is responsible for reduction of Fe (III) to Fe (II), the concentration was evaluated over the range 1-3 % which 1 % giving the best results as seen from Fig. 6.

Table 1 Preliminary Conditions for determination of Fe (II) and Fe (III) with PAR solutions in rFIA system

Parameters	Used values
Wavelength (nm)	714
reagent volume (μl)	100
Concentration of HCl (mol L ⁻¹)	0.01-0.50
Concentration of PAR solution (mol L ⁻¹)	5.0×10^{-5} - 9.0×10^{-4}
pH of buffer solution	7-11
Flow rate (ml min⁻¹)	
HCl	1.2
buffer	1.2
sample	1.2
ascorbic acid	0.4
Reaction coil Length (mm) (id 0.7mm)	
RC1	100
RC2	200
RC3	500

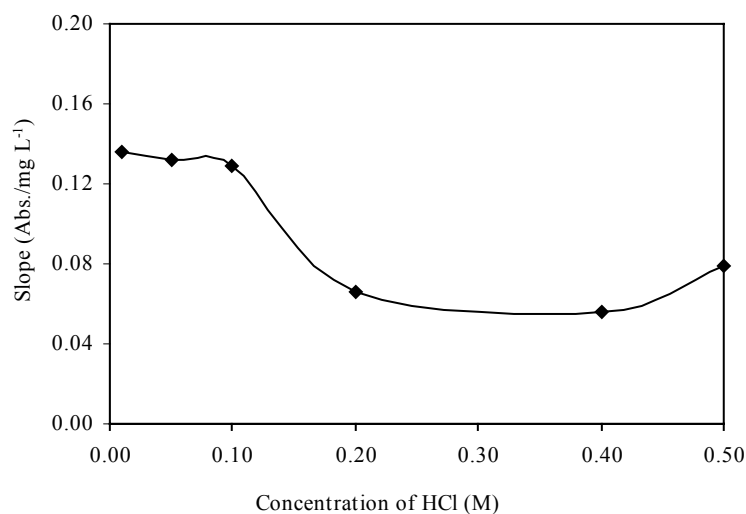


Figure 3 The effect of carrier stream (HCl) concentration on the signal for the determination of Fe(II) and total Fe.

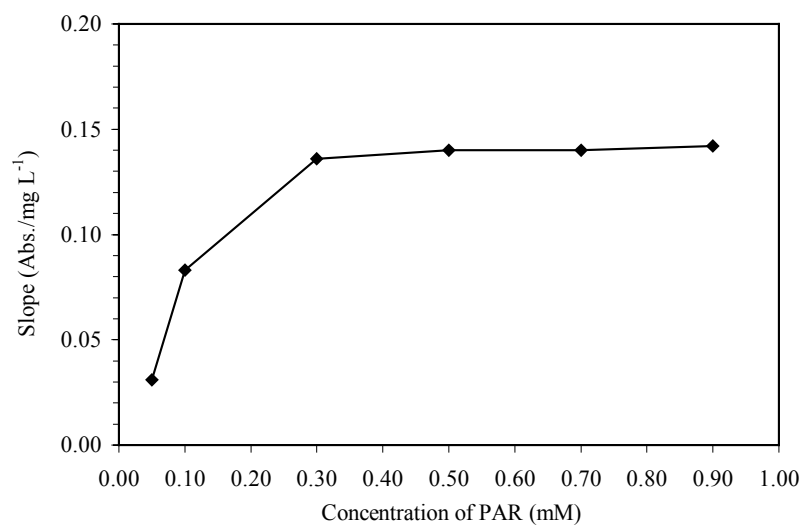


Figure 4 The variation of absorbance with respect to concentration of PAR solution.

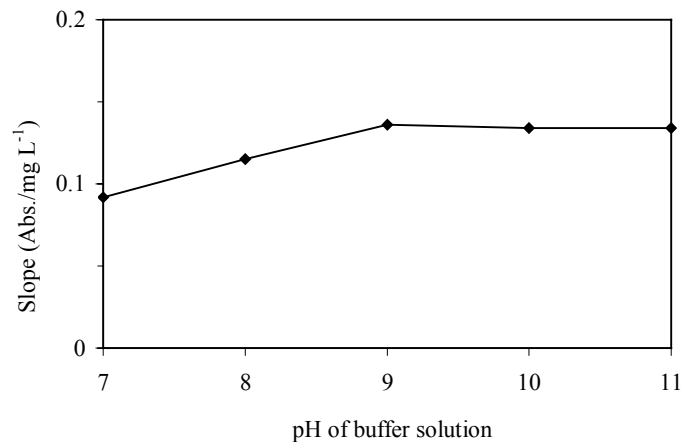


Figure 5 The influence of pH on the signal for the determination of Fe(II) and total Fe.

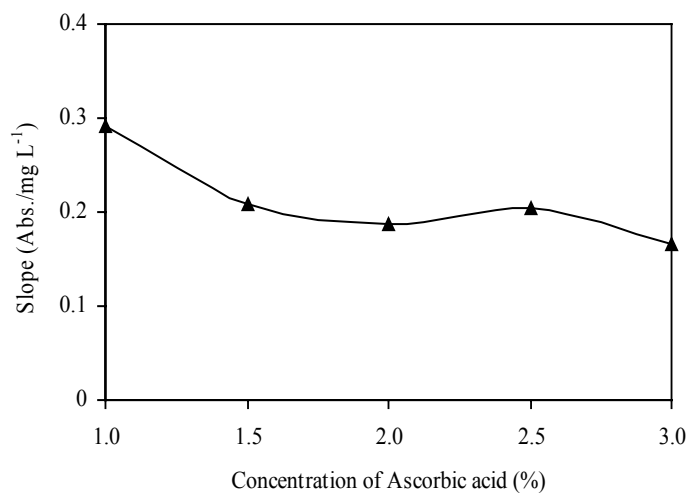


Figure 6 The effect of ascorbic acid concentration on the signal for the determination of Fe(II) and total Fe.

2.2. Flow injection variable optimization

Flow injection variables were studied under the above optimum chemical parameters. The flow rates of the various streams are very important because of the effect on the dispersion and penetration of the reaction zones as well as the precision of the method. The experimental results shown that the stream rate of sample, HCl

and buffer solutions were 2.2, 0.9 and 0.4 ml min⁻¹, respectively, for good precision and sensitivity of the determination.

The reagent solution injection volume was varied from 50 to 200 µl by changing the length of loop in the injection valve. The results indicated that the absorbance increased with an increase in injection volume. However, when the injection volume exceeds 100 µl leading to the distortions of the absorption signals, due to dispersion of solution occurs in the tubing. A volume of 50 µl was used as an optimum volume for subsequent experiments.

The influence of reaction coils was investigated in terms of coil length and internal diameter. The size must be suitable to allow minimal dispersion but provides sufficient sample volume to be determined. The lengths of reaction coils were varied between 100 and 700 mm with the internal diameter between 0.5 and 1.0 mm. Lengths of 100 and 500 mm and diameters of 0.7 and 1.0 mm were chosen for the optimum reaction coil, for RC2 and RC3 in Fig.1, respectively. Evaluation of the parameter of the reduction coil revealed that a length of 500 mm and an internal diameter 1.0 mm gave an optimum reduction of Fe (III) to Fe (II).

2.3 Analytical features

In the rFIA procedure, the two calibration curves for Fe (II) and Fe(III) were obtained under the conditions described above. The results showed that a good linear relationship was observed over the range 0.05-3.0 mg ml⁻¹ Fe (II) and Fe (III) and the equations are $A = 0.176C + 0.0128$ $r^2 = 0.9988$ and $A=0.1116C + 0.0018$ $r^2 = 0.9966$ for Fe(II) and Fe(III), respectively. The accuracy of the proposed rFIA method was evaluated and validated by determining the recoveries of the added varying concentrations of standard Fe (II) and Fe (III) species in the real sample. The results displayed in Table 2 shows very good recoveries and that this system is suitable for determination of Fe (II) and total iron species. The detection limit (2σ) found for the rFIA procedure was 0.012 mg L⁻¹ Fe (II), with a sample throughput of 180 samples h⁻¹. The relative standard deviation was 0.21% at the 3.00 mg L⁻¹ Fe (II).

Table 2 Recovery results

Sample	Found (mg l ⁻¹)		Added (mg l ⁻¹)		Total (mg l ⁻¹)		Recovery (%)	
	Fe (II)	Fe (III)	Fe (II)	Fe (III)	Fe (II)	Fe (III)	Fe (II)	Fe (III)
1	0.395	0.239	0.50	0.5	0.895	0.710	100.45	96.07
2	0.395	0.239	1.00	1.00	1.356	1.168	97.20	94.27
3	0.395	0.239	2.00	2.00	2.266	2.174	94.61	97.09

N = 5

2.4 Interference study

The effect of potential interfering metal ions (Pb²⁺, Cd²⁺, Zn²⁺ and Cu²⁺) in the determination of 1.00 mg L⁻¹ iron (II) was investigated. The levels of tolerated concentrations of foreign ions were considered as maximum concentration found to cause changes in signal, of less than 5%, compared with the signal for iron (II)

alone. The results are listed in Table 3. The higher concentrations of foreign ions than those listed in table 3 caused negative interferences in determination of iron (II), because of reagent consumption by side reactions. Thus, it can be concluded that the lower of foreign ions than those listed in table 3 do not interfere with the proposed method for determining in ground water samples.

Table 3 Tolerance limits of interfering ions

Species	Tolerable conc. (mg l ⁻¹)
Pb ²⁺	50
Cd ²⁺	50
Zn ²⁺	25
Cu ²⁺	2

2.5 Analytical Application

Water samples from the different selected sites of groundwater around the Naresuan University were analyzed by the proposed flow system. The accuracy was evaluated by comparing the results obtained for the same water samples by atomic absorption spectrometry and the standard method. The results are shown in Table 4, which was proved with *t*-test at 95% confidence level. The difference between the results obtained by the proposed method and the reference method were statistically not significant. Thus, the proposed method can be successfully applied to water samples.

Table 4 Determination of iron(II) and total iron in ground water compared with standard method

samples	Iron(II) found (mg l ⁻¹)		Total iron found (mg l ⁻¹)	
	rFIA	Standard method* (FIA)	rFIA	Standard method (AAS)
S1	0.034	0.036	0.048	0.047
S2	0.118	0.115	0.122	0.144
S3	0.241	0.229	0.616	0.657
S4	0.184	0.161	0.232	0.287
S5	0.109	0.119	0.151	0.171
S6	0.063	0.046	0.052	0.065
S7	0.031	0.180	0.371	0.415
S8	0.145	0.159	0.235	0.259
S9	0.068	0.061	0.072	0.081

* determination using 1,10-phenanthroline

Conclusions

The proposed method enabled to determine the Fe (II) and total iron in groundwater. It presents a very simple, good reproducibility and sample throughput. This method offers a linear detection range from 0.05 to 3.00 mg L⁻¹ and a detection limit of 0.012 mg L⁻¹. It was successfully applied to the determination of Fe (II) and

total iron without any sample pretreatments. The results given by the proposed method were in good agreement with those obtained by the reference methods.

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