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Reverse flow injection spectrophotometric determination of iron(III) using norfloxacin

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Abstract

A reversed flow injection colorimetric procedure for determining iron(III) at the μg level was proposed. It is based on the reaction between iron(III) with norfloxacin (NRF) in 0.07 mol 1^{-1} ammonium sulfate solution, resulting in an intense yellow complex with a suitable absorption at 435 nm. Optimum conditions for determining iron(III) were investigated by univariate method. The method involved injection of a 150 μ l of 0.04% w/v colorimetric reagent solution into a merged streams of sample and/or standard solution containing iron(III) and 0.07 mol 1^{-1} ammonium sulfate in sulfuric acid (pH 3.5) solution which was then passed through a single bead string reactor. Subsequently the absorbance as peak height was monitored at 435 nm. Beer's law obeyed over the range of 0.2–1.4 μ g ml⁻¹ iron(III). The method has been applied to the determination of total iron in water samples digested with HNO₃-H₂O₂ (1:9 v/v). Detection limit (3 σ) was 0.01 μ g ml⁻¹ the sample through of 86 h⁻¹ and the coefficient of variation of 1.77% (n = 12) for 1 μ g ml⁻¹ Fe(III) were achieved with the recovery of the spiked Fe(III) of 92.6–99.8%.

Keywords: Iron(III); Reverse flow injection spectrophotometric; Norfloxacin (NRF)

1. Introduction

In recent years, numerous compounds that are widely used in pharmacology as therapeutic agents have been proposed as ligands for complexation of iron(III) for determining, this element spectrophotometrically. For example, the use of hydro-

xyurea [1] and 2-thiobarbituric acid [2] as complexing agents for iron(III) determination. Salicylic acid and some of its derivatives such as acetyl salicylic acid and salicylamide have also been reported for iron(III) determination by spectrophotometry after formation of a mixed-ligand iron(III)—salicylate purpurin complex [3]. Iron(III) has recently been determined spectophotometrically through complexation with norfloxacin (NRF) in ammonium sulfate—sulfuric acid media and subsequent measurement of the yellow 1:2 complex at 377 nm [4]. However, conventional

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spectrophotometric methods have some limitation, such as interference and relatively long analysis time. Hence, most analytical methods including spectrophotometric methods are based on flow injection analysis (FIA). Flow injection method for the determination of iron(III) in water using NRF as complexing agent is not yet available in the literature.

This paper describes a reverse flow injection (rFI) spectrophotometric procedure for determining total iron(III) in natural water samples using NRF as a chromogenic agent.

Normally, FIA, first used by Ruzicka and Hansen, is the technique in which a small volume of sample solution is injected into a reagent carrier stream flowing through a narrow bore tube to a detector such as a visible spectrophotometer where the derivative is measured [5]. Many innovations have been made since in modifying and applying this technique [6,7]. Johnson and Petty [8] was the first who described the technique in which a small volume of reagent solution is injected into a sample and carrier streams. This technique was named reverse flow injection analysis (rFIA) to contrast it with the normal technique, normal flow injection analysis (nFIA). In rFIA only small volumes of reagent are used and, also, because the determinant concentration in the reagent bolus increases with increasing dispersion, the determination is carried out with only slight dilution [8,9]. It is clear that, in this case, the sample (such as a water sample) is plentiful and inexpensive. Therefore, rFIA is very suitable for using expensive reagents.

2. Experimental

2.1. Solutions and reagents

Double distilled, deionized water was used throughout. All the chemicals used were of analytical reagent grade unless specified otherwise. Stock solution of 100 µg ml⁻¹ Fe(III) was prepared by dissolving a 8.6340 g of ammonium ferric sulfate dodecahydrate (Fluka) in water, acidifying with 2.00 ml of concentrated sulfuric acid (BDH) and making up to 1000 ml with 0.07

mol 1⁻¹ ammonium sulfate (Carlo Erba) solution. Solutions of lower concentrations of Fe(III) were obtained by appropriate, accurate dilution of this solution with 0.07 mol 1⁻¹ ammonium sulfate solution. Standard 0.04% w/v of NRF was prepared by dissolving a 0.1000 g of NRF in the minimum volume of 0.05 mol 1⁻¹ sulfuric acid. The pH of solution was adjusted to 3.5 with 0.10 mol 1⁻¹ ammonia and made up to 250 ml with 0.07 mol 1⁻¹ ammonium sulfate solution. A 0.07 mol 1⁻¹ ammonium sulfate solution was prepared by dissolving 9.2498 g of ammonium sulfate in 1000 ml of water.

2.2. Instrumentation

2.2.1. Flow manifold

The rFI system was used with a double-channel manifold as shown in Fig. 1. An EYELA peristaltic pump MP-3A (Tokyo Rikakikel Co., Limited, Japan) composed of tygon tubing with 1.02 mm internal diameter was used for propelling the standard and/or samples solution containing iron(III) which was then merged with a stream of 0.07 mol 1^{-1} (NH₄)₂SO₄ in H₂SO₄ with the same flow rate. The stream line was connected to a homemade, low-cost injection valve with two injection loops, where appropriate volume of the reagent solution (NRF) was injected using a 1 ml disposable syringe (Dong Bang Medical Supplied Corp.) stored in the loop and subsequently introduced into the FI system. The sample or standard stream containing the injected reagent flowing from the injection valve were passed through a mixing reactor consisting of a single string of glass beads (3.0 mm diameter) in a column of silicone tubing 3.2 mm i.d., 12.00 cm long. The yellow Fe(III)-(NRF)2 complex was passed through a flow-through cell (Hellma; 1 cm, Suprasil I window, type 178, 711-GS) in a spectrophotometer (Pve Unicam, SP6) connected to a chart recorder, Servograph Rec.51 (Radiometer, Copenhagen) for continuous monitoring at 435 nm. All connection tubing were of TPFE (1.02 mm i.d.)

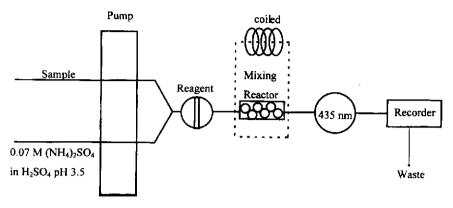


Fig. 1. Reverse FI manifold for iron(III) determination.

2.2.2. Procedure

2.2.2.1. Sample pretreatments. Natural water samples were collected in 1000 ml polyethylene bottles from Kuang River around the Northern Industrial Estate, Lamphun Province without treated with concentrated nitric acid and analysed immediately after digestion. The water samples were filtered through number 41 Whatman filter paper then 100.00 ml of each filtered water sample were accurately transfered into a 250 ml round bottom flask, 10.00 ml of a mixture consisting of HNO₃ and H_2O_2 (1:9 v/v). The samples were digested by heating under reflux until complete digestion was obtained (for about 1.5 h). After standing them to cool to room temperature the samples were transferred into each separated 100 ml volumetric flask and made up to the mark with deionized distilled water mixed well which were subsequently analyzed by both FAAS and rFIA.

2.2.2.2. Procedure for rFIA. Using the experimental setup as shown in Fig. 1, 150 μ l of the 0.04% w/v of NRF reagent solution was injected via a home-made injection valve into the merged streams of sample and/or standard solution containing Fe(III) and 0.07 mol 1⁻¹ (NH₄)₂SO₄ in H₂SO₄ solutions flowing with the same flow rate of 6.0 ml min⁻¹. The reagent was then mixed with the merged steams containing the sample 0.07 mol 1⁻¹ (NH₄)₂SO₄ in H₂SO₄ which was then passed through a single bead string reactor (sbsr) where the complexation reaction was taken place. The

resulting yellow Fe(III)-(NRF)₂ complex was subsequently monitored at 435 nm.

3. Results and discussion

3.1. Reverse FIA

The present work was undertaken development of a rFIA procedure for Fe(III) determination based on the complexation between Fe(III) and NRF, [1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)quinoline-3-carboxylic acid] in an ammonium sulfate (0.1 mol 1⁻¹) and sulfuric acid solution (pH 3.0) resulting in a soluble 1:2 Fe(III)–NRF complex having an absorption maximum at 377 nm which was adopted from the reported batchwise method [4].

As mentioned earlier, the term 'rFIA' was first used by Johnson and Petty [8] for describing the technique in which a small volumes of reagents were injected into a flowing stream of sample solution. In general the dispersion for a FIA system increases with the reaction tube length, tube diameter and flow rate and it is inversely proportional to the sample injection volume. The dispersion in nFIA are typically in the range 3–10 [6]. Increasing dispersion in nFIA leds to a decrease in analyte concentration and hence, it also reduce the sensitivity. On the other hand, in the rFIA, the relationship between dispersion and sensitivity are also reversed. When the reagent are injected into the sample stream the amount of

sample in the zone of the reagent increase as the dispersion increases, resulting in well-formed peaks as shown in Fig. 2. rFIA is undoubtedly the most convenient procedure for the monitoring of Fe(III) and other trace metals in water samples because the water sample (generally abundants) is used as carrier and selective reagent is injected for determining each analyte, then saving an important amount of expensive reagent.

3.2. Optimization of the FI system

Optimization of the FI and the chemical conditions were carried out by univariate method in which the initial parameters were selected and fixed by random while a variable was modified. The influence of pH, NRF concentration, (NH₄)₂SO₄ concentration, temperature, flow rate, reaction tube diameter and length, geometry of the mixing reactor and injection volume on the sensitivity and sampling were investigated.

3.2.1. Selection of wavelength

As reported in the literature, the shapes of the signals obtained for nFIA and rFIA are fundamentally different. Double peaks, which are undesirable in most applications, being more prevalent in rFIA [9–14]. The rFIA signal for Fe(III)–NRF complex, well defined single peaks were obtained with high reagent peaks. In order to obtained the required sensitivity for trace Fe(III) determination by rFIA care should be taken for the selection of wavelength. Since in rFIA the blank peak is usually far more higher that obtained by normal FIA (nFIA) method. It was

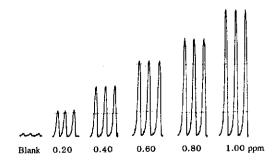


Fig. 2. Reverse FIA signals for Fe(III) determination.

found that the blank responses (B) decreased rapidly from the wavelength of 370 up to 435 nm and remained constant from wavelength 435–470 nm, and that the sample peaks or signals (S) decreased with increasing in wavelength. To overcome the high blank problem, the signal to blank ratio (S/B) was used instead of peak height. Therefore, in this case the absorption spectrum was obtained by plotting S/B versus wavelength and the analytical wavelength was 435 nm although the reported maximum absorption of the complex was at 377 nm [4], because at 435 nm the greatest S/B value was obtained and hence the greatest sensitivity.

3.2.2. Effect of pH on colour development

The complex formed by the reaction between 1 µg ml⁻¹ Fe(III) and NRF was studied at various pH values (pH 2.5–4.5) and different wavelengths (370–450 nm). After calculation of the S/B values which were then plotted against various wavelengths. Results are shown in Fig. 3. It was evident that the absorption maximum of such a complex studied was pH independent over the pH range of 2.5–4.5. As can be seen in Fig. 4, at pH values below and above 3.5 the S/B values decrease significantly. Hence, pH 3.5 was chosen as optimum.

3.2.3. Effect of NRF concentration

An amount of the reagent (NRF) greater than required by stoichiometry (NRF = 1:2) [4] is needed for complete colour development. The concentrations of NRF in the concentration range studied (0.02-0.10% w/v) were sufficient for color development, the higher concentration (0.12% w/v)

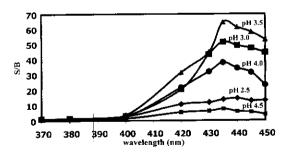


Fig. 3. Effect of pH on FIA signals and signal to blank ratio.

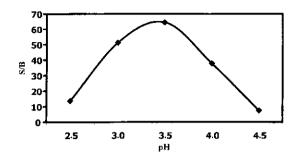


Fig. 4. Effect of pH on the FIA signals and the signal to blank ratio at 435 nm.

NRF) gave rise to the repression of the S/B value (see Fig. 5). Therefore, the concentration of 0.04% w/v NRF was selected as optimum because it exhibited the greated S/B value measured at 435 nm.

3.2.4. Effect of ammonium sulfate concentration on the complex formation of Fe(III)-NRF complex

Ammonium sulfate concentrations could more or less affect the formation of Fe(III)-NRF complex. So it is necessary to investigate to find out the optimum ammonium sulfate concentration to achieve the best selectivity and sensitivity of the method. Effect of ammonium sulfate concentrations over the range of 0-0.10 mol 1⁻¹ were examined for determining 0.2-1.0 µg ml⁻¹ Fe(III) in standard Fe(III) solutions. Linear relationship between peak height (or S/B) and various Fe(III) concentrations at each ammonium sulfate concen-

tration was obtained with the regression equations among which the regression equation at 0.07 mol 1^{-1} (NH₄)₂SO₄ was y = 67.70x - 1.27 ($r^2 = 0.9988$) showing the greatest sensitivity (defines as slopes of calibration curve). The sensitivity increased with increasing in (NH₄)₂SO₄ concentration up to 0.07 mol 1^{-1} further increase in (NH₄)₂SO₄ concentration gave rise to decrease in sensitivity. The (NH₄)₂SO₄ concentration of 0.07 mol 1^{-1} was chosen as suitable because it provided reasonable sensitivity and r^2 value.

3.2.5. Effect of temperature

Temperature over the range $15.0-27.0\,^{\circ}\mathrm{C}$ did not affect the slope of calibration curve over the range $0.2-1.0\,\mu\mathrm{g}\,\mathrm{ml}^{-1}$ Fe(III) (68.60, 69.10, 69.90, 69.90 mV and 70.40 at 15.0, 20.0, 25.0, 30.0 and 37.0 °C, respectively) indicating that the procedure could be carried out at room temperature.

3.2.6. Effect of flow rate

The flow rate of the reagent and carrier streams were varied from 3.0 to 10.0 ml min⁻¹, the flow rates of both streams are the same (6.0 ml min⁻¹). A high flow rate leads to a shorter time required for each sample passing through the FI system, poor reproducibility and a high rate of sample and carrier reagent consumption. At low flow rate, the dispersion was large and the residence time was long giving rise to low sampling rate. Therefore, as

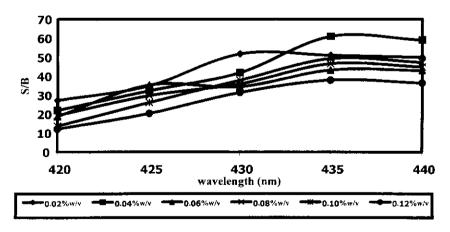


Fig. 5. Effect of NRF concentration on the F1 response of Fe(III)-NRF complex and signal to blank ratio at 435 nm.

a compromise the flow rate of 6.0 ml min⁻¹ was selected for the subsequent investigations.

3.2.7. Effect of reaction tube diameter and length

Effect of reaction tubing diameter was studied by varying the reaction tubing diameter from 0.76-1.52 mm i.d. It was found that the tubing diameter showed slightly effect on the sensitivity for Fe(III) determination. The sensitivity increased with increasing in tubing diameter up to 1.02 mm i.d. (slope = 63.80 mV) further increase in tubing diameter up to 1.52 mm id the sensitivity decrease (slope = 62.23 mV). However, differences in sensitivity lined between 0.11-2.64%. The sample throughput decreased with increasing in tubing diameter. Therefore, as a compromise between sensitivity (slope = 63.80 mV) with a reasonable sample throughput ($75 h^{-1}$) a 1.02 mm i.d. tubing was selected for further investigation.

Effect of reaction tube length was studied by varying the tubing length from 25.00 to 100.00 cm. It was clear that the sensitivity increased with increasing in sensitivity up to the tubing length of 50.00 cm (slope = 63.80 mV) further increase in tubing length led to the reduction of sensitivity. However, the effect is very small (less than 1.0%) and the sample throughput lined between 75 and $100 \, h^{-1}$. Therefore, a 50.00 cm tubing length was chosen as suitable reaction tube for further experiments.

3.2.8. Effect of geometry of the mixing reactor

The mixing reactor in the FI manifold is the position where the physical or chemical changes are taking place. So it is necessary to examine the optimum geometry of the mixing reactor in order to achieve the required sensitivity. Initially, the mixing tubing size (i.e. internal diameter and length) was optimized for making a coiled, serpentine, and a knitted reactors. The optimum mixing tubing was found to be 1.02 mm i.d. and 50.00 cm in length. It can be seen from Table 1 that among the six different configurations of mixing reactors studied most reactors provide nearly the same sensitivity because their slopes of calibration curves are in the range of 63.80-64.50 mV with the exception of sbsr which provides the greatest sensitivity (slope = 65.60 mV). By com-

Table 1
Effect of various types of mixing reactor

Linear regression equation	
y = 64.03x - 0.55	0.9981
y = 64.44x - 0.81	0.9984
y = 63.83x - 0.48	0.9971
y = 64.29x - 0.51	0.9986
y = 64.46x - 0.73	0.9982
y = 65.59x - 0.21	0.9974
	y = 64.03x - 0.55 $y = 64.44x - 0.81$ $y = 63.83x - 0.48$ $y = 64.29x - 0.51$ $y = 64.46x - 0.73$

paring the difference in slopes between each configuration of the reactors with the normal coiled reactor, there are slightly differences (about less them 1–3%) among the shapes of mixing reactors. This indicates that all types of mixing reactors studied can be used as well as the normal coiled reactor because the reaction rate between the chelating reagent (NRF) and Fe(III) is very fast with the sampling rate of 86 h⁻¹. However, the geometry of the mixing reactor chosen in this work was sbsr since it provided the greatest sensitivity (defines as slope of calibration curve) with a reasonable correlation coefficient as shown in Table 1.

3.2.9. Effect of injection volume

The injected reagent should be sufficient for complete color development in rFIA. Therefore, it is very important to optimize the injection volume. A 150 µl, 0.04% w/v NRF is chosen as optimum.

3.2.10. Calibration curve

Using the proposed rFI manifold for Fe(III) determination under the optimum conditions, the linear calibration curve over the range of 0.2-1.4 µg ml⁻¹ Fe(III) was established which can be expressed by the regression equation y = 64.25x + 0.01 ($r^2 = 0.997$) where y represents the peak height in mV and x is Fe(III) concentration in µg ml⁻¹ after subtraction of blank.

3.2.11. Interferences

Effects of some possible interfering ions on the determination of 1.2 μg ml⁻¹ Fe(III) were studied for the maximum w/w ratio of interfering ions to Fe(III) up to 100:1. The tolerance value (defines as the foreign-ion concentration causing an error

Table 2 Summary of the interferences of some ions on the FI responses obtained from 1.2 μg ml⁻¹ Fe(III)

Interfering ion	Tolerable concentration ratio (µg ml ⁻¹) of ion/Fe(III) ^a			
Cu, Na, NO3	100			
Cd, Mn	50			
F-	25			
Zn, Cl-	20			

The concentration of an ion is considered to be interfering when causing a relative error of more than $\pm 10\%$ with respect ot the signal of Fe(III) alone.

smaller than $\pm 10\%$ for determining the analyte of interest) for the ions studied are listed in Table 2. The presence of greater than 20:1 w/w of Zn:Fe(III), and Cl⁻:Fe(III), and 25:1 w/w of F⁻ leads to the reduction of FI signal probably owing to the complex formation of Zn(II) with NRF which does not absorbed at the working wavelength and less Fe(III)-NRF complex is formed. The presence of greater than 50:1 w/w of Cd:Fe(III) and Mn:Fe(III) results in the enhancement of FI signals, probably due to the formation of complexes with NRF which absorb at the same or very near to the working wavelength. Among the interfering cations and anions studied Cl⁻ and exhibited rater serious effect on Fe(III) determination. They led to the depression of Fe(III)-NRF signal of more than 10% when the interfering ion/Fe(III) were exceeded 25 and 20, respectively. When compared with other interferences studied, however, the concentration of both F and Cl in water sample is very low. Therefore, the concentration of F and Cl are so low that they do not interfere Fe(III) determination based on NRF. In addition, the formation constant of NRF with Fe(III) is large (4.0×10^8) [4].

3.2.12. Reproducibility, accuracy, detection limit and sampling rate

The reproducibility obtainable for the proposed method was 1.77% after 12-replicate determinations of 1.0 µg ml⁻¹ Fe(III) solutions. The accuracy expressed in term of percentage recovery was studied by spiking various amounts of Fe(III) standard solution (0.4, 0.6 and 0.8 µg ml⁻¹) into

the water samples collected from Kuang River around the Northern Industrial Estate of Thailand. The percentage recoveries of the spiked Fe(III) were ranging from 92.6 to 99.8. The recovery of the spiked Fe(III) is not so good depending on the sample matrices because we spiked standard Fe(III) into the real samples collected from different sites. The detection limits (3σ) for Fe(III) was 0.01 µg ml⁻¹ and the sampling rate was found to be 86 h⁻¹

3.2.13. Determination of Total Fe in natural water samples

The recommended method has been applied to the determination of total Fe in natural water samples collected from Kuang River around the Northern Industrial Estate in Lamphun after digesting the water samples with HNO₃: H_2O_2 (1:9 v/v) and heating under reflux. The results obtained were compared favorably with those obtained by FAAS as shown in Table 3. The accuracy was found to be high verified by the student t-test because the calculated student t-value (0.43) was less than the theoretical one (2.36) (n = 7) at a confident level of 95% indicating that results obtained by both rFIA and FAAS are in excellent agreement under identical experimental conditions.

Table 3

Determination of trace amount of total Fe in natural water samples collected from Kuang River around the Northern Industrial Estate in Lamphun

Sample numbers	FIA	AAS	Di
K1	0.7780	0.7786	0.0006
K2	0.9981	0.9882	0.0001
K3	0.8402	0.8385	-0.0017
K4	0.6582	0.6588	0.0006
K5	0.4356	0.4492	0.0136
K6	0.3967	0.3893	-0.0074
K7	0.2831	0.2845	0.0014
D			1.029×10^{-3}
S.D.			6.297×10^{-3}
T			0.43

Table 4
Optimization of chemical and FIA conditions

Variable	Studied range	Optimum value	
Wavelength (nm)	370-470	435	
рН	2.5-4.5	3.5	
NRF concentration (% w/v)	0.02 - 0.14	0.04	
(NH ₄) ₂ SO ₄ concentration (mol 1 ⁻¹)	0-0.10	0.07	
Temperature (°C)	15.0-37.0	Room temp.	
Flow rate (ml min 1)	3.0 - 10.0	6.0	
Mixing tubing diameter (mm i.d.)	0.76-1.52	1.02	
Mixing tubing length (cm)	25.00-125.00	50.00	
Mixing reactor geometry	Coiled, surpentine, knitted, straight line, sbsr	All types of reactors	
Injection volume (µl)	100-250	150	

4. Conclusions

A rFIA procedure for Fe(III) determination based on complexation with NRF has been developed in which a small volume of NRF was injected into the sample stream and the resulting 1:2 complex of Fe(III)–(NRF)₂ was measured at 435 nm. Optimum conditions for determining Fe(III) were investigated. It was found that effects of most parameters studied (concentration of (NH₄)₂SO₄, temperature, flow rate, reaction tube diameter and length, geometry of mixing reactor and injection volume) on the sensitivity for Fe(III) determination are very slight (not more than 2%) except pH and NRF concentration exhibited larger effect on the S/B ratio.

The optimum conditions for Fe(III) determination were shown in Table 4. Calibration curve over range 0.2-1.4 µg ml⁻¹ Fe(III) was established with a regression equation y = 64.25x + 0.01 (n = 7) and the correlation coefficient of 0.9997. The method was very sensitive as little as $0.01 \mu g ml^{-1}$ Fe(III) could be determined. The RSD of 1.77% (n = 12) for 1 µg ml⁻¹ Fe(III) and the sample throughput of 86 h⁻¹ were obtained. The recovery of the added Fe(III) was 92.6-99.8%. The proposed method has been applied to the determination of natural samples collected from Kuang River. Results were listed in Table 3. It was seen that results obtained by the recommended method were is good agreement with those obtained by AAS verified by t-test. The method in simple, inexpensive accurate and reproducible which is suitable for the monitoring of both cations and anions in the water samples.

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