Flow Injection Spectrophotometric Determination of Iron (II) in pharmaceuticals with 1 -(2- Benzoimidazolyl -Azo) - 2- Hydroxy - 3 Naphthoic Acid .

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Abstract

Iron (II) was determined spectrophotometrically by flow injection analysis with 1- (2- benzoimidazoly l - azo) hydroxy - 3- naphthoic acid (BIAHNA). The system involves injection 100 ul of iron (II) solution into ethanolic - BIAHNA carrier solution adjusted to pH 4.0 to form the complex in 120 cm coil reaction . Beer's law is obeyed in the range 0.05 - 2.5 ppm iron (II) at maximum absorption 625 nm, with relative standard deviation 0.56 -4.02%, relative error + 0.08 - 4.40% and detection limit 0.01 ppm. Analysis can be done at a rate of upto 78 sample per hour. Interferences of 24 cations and anions were studied and the method is applied to the determination of iron (II) in pharmaceuticals.

Introduction

Iron (II) is an essential element for humans. Adeficiency of iron (II) in the body is usually cured by adminstration of pharmaceuticals containing iron (II) to the anemic patient (1).

Consequently, a continuous assay of iron in these drugs given to humans is quite important (1) .

Iron is also important industrially as a content in soda-lime silica glass(2) , and in water treatment since ferrous ion is used to reduce chlorate concentrations (3).

The underlying theory of flow injection analysis (FIA) a technique which finds application in automation of chemical analysis, has been discussed (4) and applications of the technique have been described in a series of papers by (4).

FIA based on the injection of a liquid sample into a continuous stream of reagent or carrier appears to hold considerable promise for trace level determinations. The technique is capable of manipulating small sample volumes. In addition, the sample can be carried through various stages of physical and chemical processing whithout contact with the laboratory environmental thus reducing the possibilities for contamination (5).

FIA has increasingly been used in various fields, owing to its high sample throughput, cost effective performance and versatility (7).

BIAHNA was used for flow injection spectrophotometric determintion of Nickel (6).

In this paper we have examined the FIA spectrophotometric determination of iron (II) in pharmaceuticals through complex formation with BIAHNA as a new reagent.

Experimental

Apparatus:

Fig. 1 shows a schematic diagram of FIA system used for the determination of iron (II).

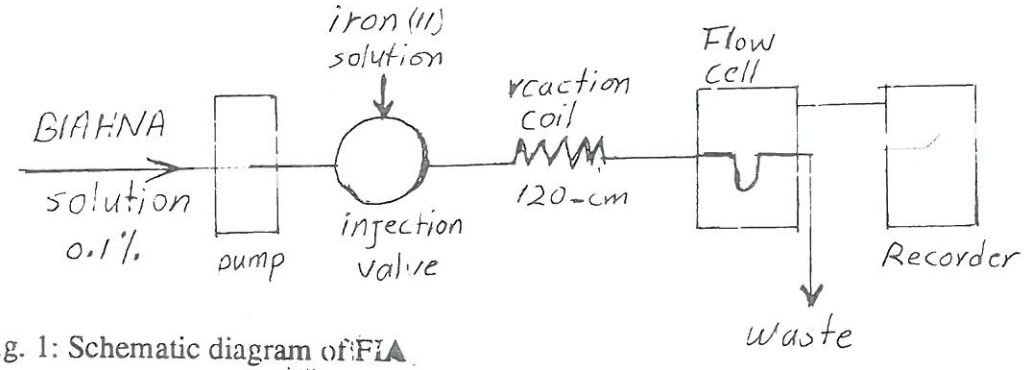

Fig. 1: Schematic diagram of FIA

A peristallic pump (Waston - Mor low 501 Z) was used to propel BIAHNA solution with steady flow rate. The injection valve was a 4 - way loop valve (Taylor Sevomex Type SV 220) with different sample loops. The complex formed was detected by UV/visible spectrotometer 4050 (LKB Biochrom Ul trospec II) with a flow cell of 1 mm flow path made of quartz (Pye Unicam UV 681435). The signals were recorded. Manifold Telfon tubing of 1 mm i.d. were used , and Philips PW - 9420 pH - meter was used.

Reagents;

All chemicals used were of analytical grad. Standard iron (II) solution (100 ppm): A . 0.7027 gm of ammonium ferrous sulphate ($NH_4)_2Fe\ SO_4.\ 6H_2\ 0$ was dissolved in water containing 2.5 ml of conc. $H_2\ S0_4$ and dilute with water with water to 1 liter ina standard volumetric flask. BIAHNA solution (0.1%): A 0.5 gm of the reagent (8) was dissolved in 96% ethanol and diluted to the mark in 500 ml standard volumetric flask.

Ammonium hydroxid solution: 0.04 m.

Recommended procedure:

The spectrophotometer of the FIA system was set at 625 nm , the carrier styeam (0.1% solution of BIAHNA adjusted to pH 4.0) was

pumped through with a flow rate 2 ml min^{-1} , and the absorbance was set to zero. A sample of 100 ul) was injected by the injection valve. The sample and the reagent were mixed in 120 - cm coil, and the peak height of the complex was recorded .

Results and Discussion

Optimization of experimental conditions:

Optimum reaction conditions between iron (II) and BIAHNA were examined by batch method. BIAHNA reacts with iron (II) to form wine - red complex with a maximum absorption of 625 nm . The chelate is best formed at pH 2.8 - 3.5, and pH 3.0 was selected in the subsequent measurements. 0.1% BIAHNA solution was used as a carrier stream. The composition of the complex in ethanolic solution was found to be 1:2 iron (II)/ reagent by Jobs method and mole ratio. The complex was formed immediately and was found to be stable for about 6 hr (7).

Optimization of flow system:

The effect of sample volume , flow rate and reaction coil were studied to obtain a constant and maximum peak height as follow:

a - Sample volume : Different sample volumes (40,80,100, 120,160) ul of iron (II) solution were used . A 100 ul sample volume gave maximum peak height as shown in Fig. 2.

b - Flow rate : Different flow rates (0.5, 1.0, 1.5, 2.0, 2.5 , 3.0, 4.0 and 5.0) ml min^{-1} were used. The optimum flow rate was found to be 2.0 ml min^{-1} as shown in Fig. 3.

c- Reaction coil : Different coil reaction of 1 mm i.d. (40, 80, 120, 160, 200) cm were used . The optimum coil length was found to be 120 - cm to form the complex as shown in Fig. 4.

Effect of pH:

Under the optimum conditions mentioned above the effect of pH of the carrier stream (0.1% BIAHNA solution) was studied. Fig. 5 shows that pH 4.0 is the optimum pH for determination of iron (II) by FIA system .

Clibration graph:

Under the optimum conditions. The calibration graph (absorbance as peak height in cm against concentration of iron (II) solution) was linear in the range of 0.05 - 2.5 Mg. ml^{-1} (0.05 - 2.5 ppm) of iron (II) , with the following least square regression equation

$$A = 1.2761 + 3.024\ [Fe^{2+}]$$

with correlation coefficient of 0.9731. The lower detection limit was 0.01 ppm.

Precision and Accuracy:

Under the optimum conditions, the precision and accuracy of FIA for determination of iron (II) were checked. Table (1) shows the relative standard deviation (RSD) and relative error percentage fromtriplicate injection of each concentrations (Fig.6).

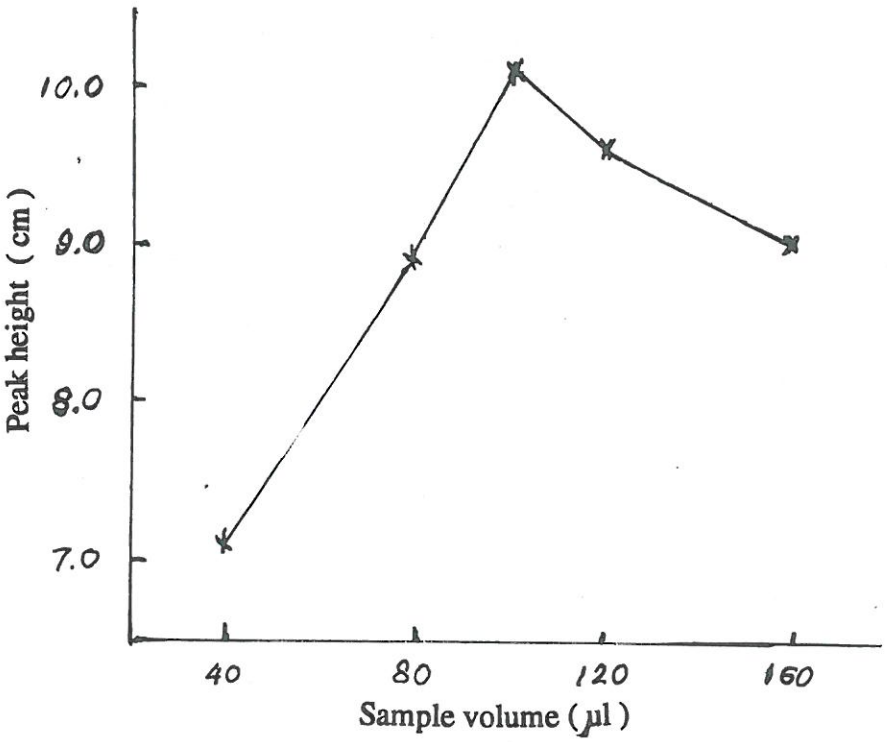

Fig.(2) : Effect of sample volume of iron (II) solution on the peak height .

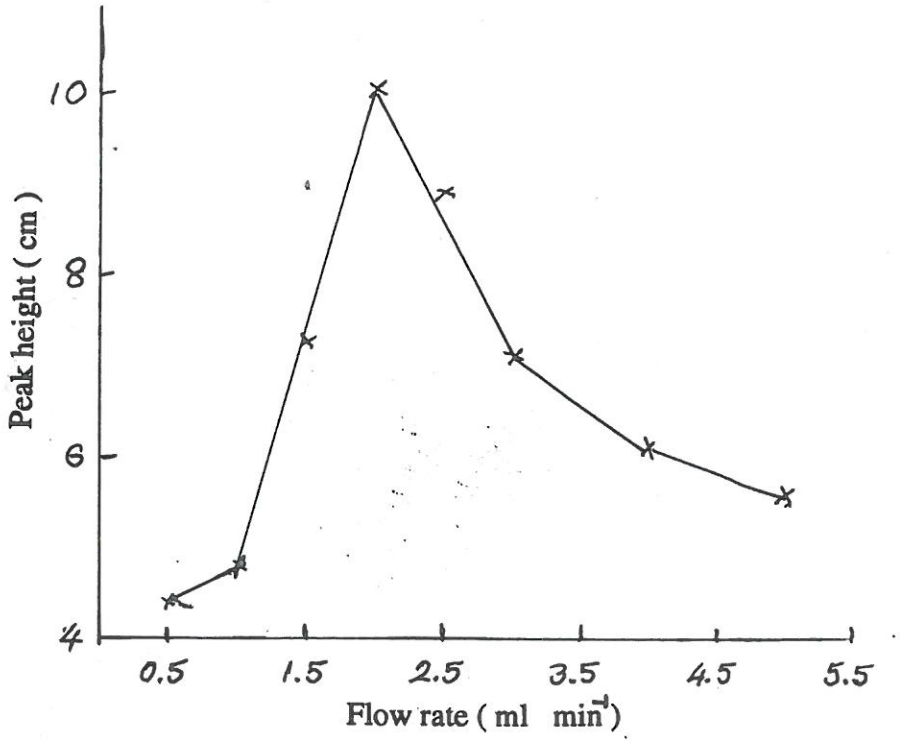

Fig.(3): Effect of flow rate on the peak height.

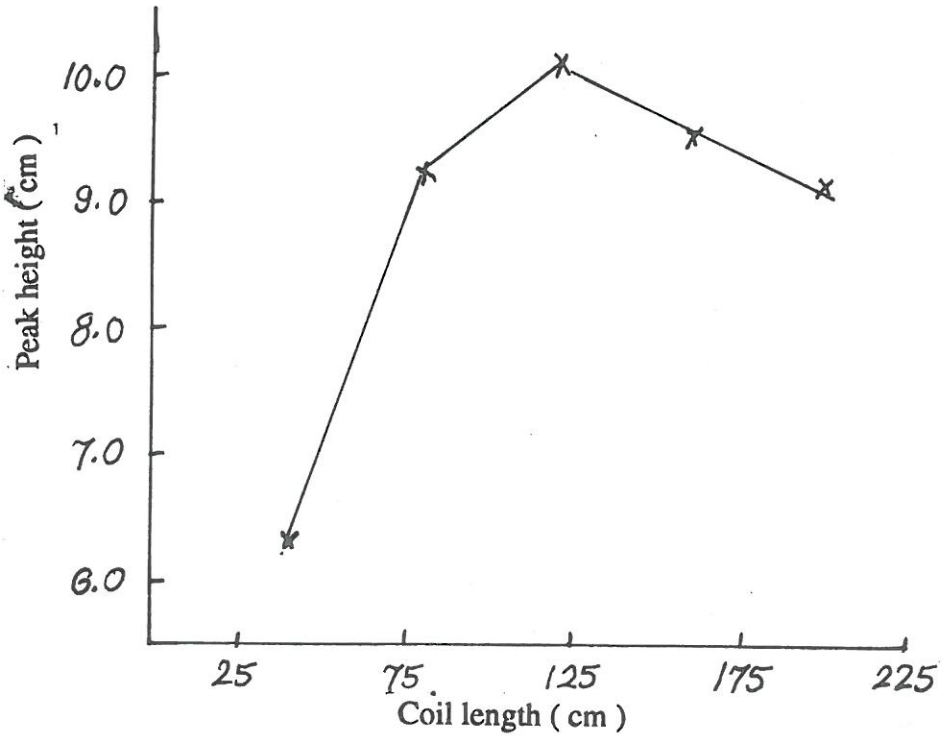

Fig.(4): Effect of coil length on the peak height .

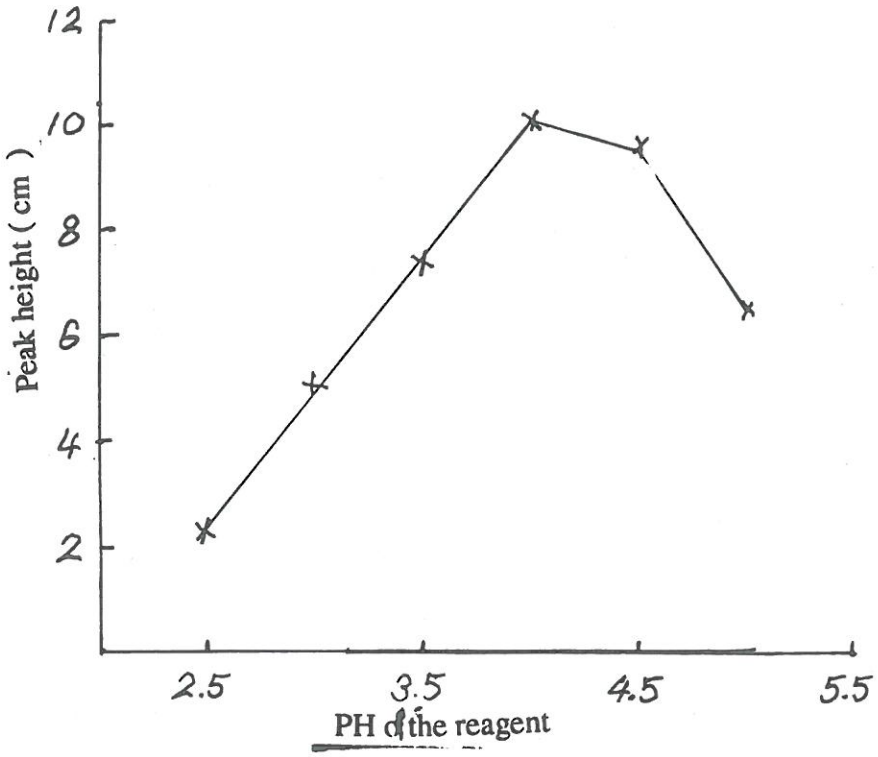

Fig.(5) : Effect of PH of the BIAHNA reagent on the peak height.

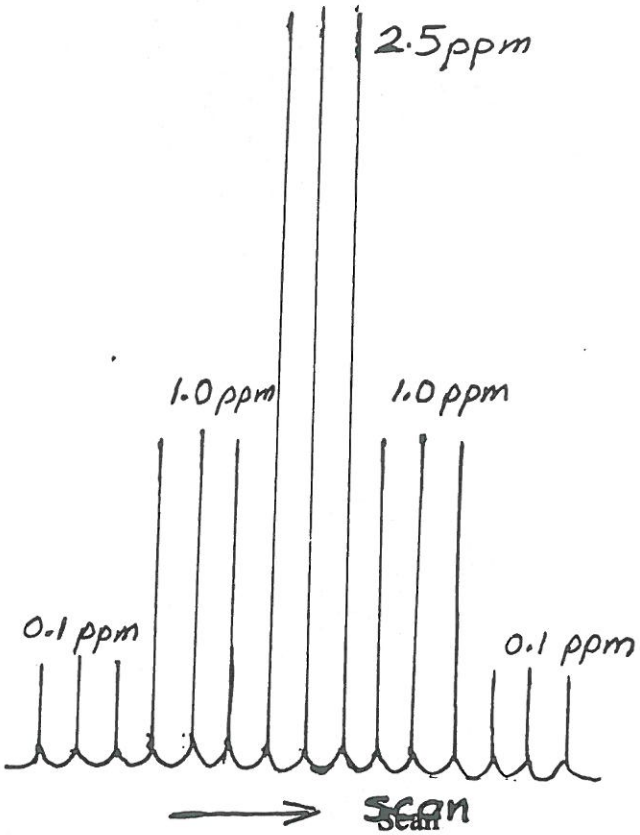

Fig.(6) : Peak heights obtained from the injection of triplicate standards (0.1, 1.0 and 2.5) ppm of iron (II) solutions under the optimum conditions.

Table (1): Precision and accuracy of the method

Amount of iron (II) taken (μg)	RSD%	Relative error%
2.5	4.02	0.00
25	1.28	-2.0
62.5	0.56	+0.08

INTERFERENCES:

In order to study the interferences of a diverse range of differention , synthetic solution containing 62.5 ppm of iron (II) and various amounts of the interferences were measured. Table (2) shows the maximum allowable concentration ot the interfering ions that cause errors less than + 5%.

Determination of iron (II) in pharmaceuticals:

To examine the validity of this new flow injection method, different pharmaceuticals (Table 3) were examined. The tablets are first powdered finely in a morter, then 5.5 ml of conc. $H_2 S0_4$ was added, and completed to 100 ul in a volumetric flask. Shake the solution gently and filter it (1) . The concentration of iron (II) that is prepared either by dissolving one tablet or capsul in 100 ml distilled water or taking 5 ml of the syrup is very high, so diluted iron (II) solutions were prepared by further dilutions in the range of 0.05-2.5 ppm. By applying the recommended procedure for the determination of iron (II) by flow injection method using the accurate volumes of the pharmaceutical solutions containing 0.05 - 2.5 ppm iron (II), good results were obtained as shown in Table 4.

Conclusion:

The iron (II) content in different materials has been determined by spectrophotmetric method in conjugation with FIA (10 - 14).

The proposed method is rapid, simple, precise :and accurate with ahigh sample through put (78 sample/h). The time requried for preparation is short and the reagent consumption is relatively low. The detection limit of iron (II) by this method is lower than that reported previos studies (11, 14). Furthermore the reagent is a new reagent and it has been used only for flow injection spectrophotmetric detemination of nickel (6).

Table (2): Effect of interfering ions on the determination of 62.5 µg of iron (II) in a final volume 25 ml.

Interfering ions	Amount added (µg)	Error%
I ron (III)	4.0	+2.43
Nickel(II)	2.5	+3.65
Mercury (II)	25	+5..0
Lead (II)	250	+2.22
Zinc (II)	100	+4.81
Cobalt(II)	5.0	+1.21
Silver(I)	250	+4.68
Manganese (II)	2.5	+4.34
Copper (II)	3.0	+4.16
Chrom (III)	2.0	+3.57
Calcium (II)	2250	+4.88
Magnesium (II)	2250	+4.11
Sulphate	1000	+1.72
Bicarbonate	2500	- 5.0
Bromide	10000	- 4.05
Iodate	500	+4.38
Nitrite	2500	+4.97
Chloride	5000	+4.41
Carbonate	1250	-2.94
Phosphate	500	+4.28
Persulphate	500	+4.41
Acetate	1000	- 4.36
Iodide	2500	- 4.34
Thiosulphate	250	+ 4.57

Table (3): Some Pharmaceuticals used in the present work.

Pharmaceutical	Notes
1- Ferrosam (tab.)	each tablet contains 200mg ferrous fumarate.
2- Hemavit (cap.	each capsule contains 160 mg ferrous fumarate+50 mg ascorbic acid.
3- Prenavital (caps.)	each capsule contains 4-5 mg ferrous sulphate.
4. Multisamavit (caps.9)	each capsule contains 10mg ferrous sulphate.
5- Ferrous Gluconate (syrup)	each 5 ml contains 300 mg ferrous gluconate.

The source of 1 - 4 is the state enterprise for drugs industry and medical applicances, Samarra- Iraq, the source of 5 is Lomapharm, Fed. Rep. of Germany.

Table (4): Determination of iron (II) in some pharmaceuticals.

Pharmaceuticals	Iron(II) taken	Iron(2) found	Error%
1- Ferrosam (tab.)	2.5 37.5 62.5	2.5 38.0 63.5	0.00 +1.3 +2.4
2- Hemavit (caps.)	2.5 37.5 62.5	2.5 36.0 64.0	0.00 -4.0 +3.20
3 -Prenavital caps.)	2.5 37.5 62.5	2.5 37.25 64.75	0.00 -0.66 +4.40
4- Multisamavit (caps).	2.5 37.5 62.5	2.5 36.25 62.25	0.00 -3.33 -0.40
5 - Ferrous Gluconate (syrup).	2.5 37.5 62.5	2.5 37.0 63.5	0.00 -1.33 +1.60

Results are average of three injections.

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التقدير المطيافي الضوئي للحديد الثنائي في المواد الصيدلانية بطريقة الحقن الجرياني باستعمال 1- (2 - بنزوايميد ازوليل - ازو) - 2 - هيدروكسي - 3 - حامض النفثويك .

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الخلاصة :

لقد تم استعمال تقنية الحقن الجرياني لتقدير الحديد الثنائي معتمدة على التقدير المطيافي الضوئي لمعقد الحديد الثنائي مع الكاشف العضوي 1- (2 -بنزوايميد ازوليل - ازو) -2 - هيدروكسي - 3 - حامض النفثويك (BIAHNA. تتضمن الطريقة حقن 100mL من محلول الحديد الثنائي الى محلول التيار الحامل (محلول BIAHNAالايثانولي) و المثبت عند PH 4.0لتكوين المعقد في ملف تفاعل طوله C.M120 . ينطبق قانون بير ضمن المدى 0.05-2.5PPM من الحديد الثنائي عند اعلى طول موجي 625 nm. وبانحراف قياسي نسبي 0.56 -4.02%، وخطأ نسبي 0.08 - 4.4%، وأقل حد للكشف 0.01 ppm . وتم اجراء التحليلات بمعدل 78 عينة لكل ساعة . وتم ايضا دراسة تداخل 24 ايونا موجبا على تقدير الحديد الثنائي وامكن تطبيق الطريقة لتقدير الحديد الثنائي في المواد الصيدلانية .