MICRODETERMINATION OF IRON IN ORGANO IRON COMPOUNDS AND IRON DRUGS[+]

التقدير المايكروغرامي للحديد في مركبات الحديد العضوية والأدوية الحاوية على الحديد

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Abstract:

A microgram amount of Organo iron and iron containing drug were decomposed using Schoniger flask combustion technique using a Pyrex- glass spiral as a sample holder. A 10mg of solid sodium sulphite was mixed with the weighed sample before the combustion step , 10ml of 5N- hydrochloric acid was used as absorbent solution, and 1ml of 20% perchloric acid was added to the resulting solution prior to the boiling step. The iron content was finally determined using atomic absorption spectrophotometer at wave length (248.3nm) with the help of a calibration graph prepared from standard solutions of ferric chloride. The percentage error were ranging from – 0.28 to + 0.35%, and the percent standard deviation was (0.869).

المستخلص:

تم تعيين كميات ضئيلة (مايكروغرامية) من الحديد في المركبات العضوية والدوائية بطرقة تحليلية بسيطة وسهلة. تعتمد الطريقة على تحويل المركبات العضوية الحاوية على الحديد إلى مركبات لا عضوية باستخدام طريقة الحرق في دورق الأوكسجين وباستخدام حامل نموذج حلزوني الشكل مصنوع من الزجاج المقاوم للحرارة. تم مزج 10ملغم من كبريتيت الصوديوم الصلب مع النموذج الموزون المعد للتحليل قبل عملية الاحتراق، كما وأستخدم 10 مل من محلول حامض الهيدروكلوريك بتركيز (5N) كمحلول ماص. وأضيف إلى المحلول الناتج مللي لتر واحد من حامض البيروكلوريك بتركيز(20%) قبيل خطوة الغليان. أخيرا تم تقدير محتوى الحديد في النموذج باستخدام مطياف الامتصاص الذري عند طول موجي (248.3nm) نانوميتر، وذلك بمساعدة منحى معيار تم تحضيره مسبقاً من مجموعة محاليل قياسية لكلوريد الحديديك. كانت نسبة الخطأ تتراوح بين 0.28-إلى 0.35%+ ، والانحراف القياسي النسبي (0.869).

Introduction:

Various methods for the determination of iron in iron containing organic compounds have been described in the literature. These include gravimetric [1-5], titrimetric [6-9] spectrophotometric [10-13], atomic absorption spectrometric [14] and polarography [15-17]. The object of the present paper was to evaluate atomic absorption spectrometric method for the determination of iron in iron drug containing compounds. The method is based on the conversion of iron in Organo iron compounds such as ferrosam and hemavit to ferric chloride using oxygen flask schőnigr [1,2] combustion method as shown in following general reaction, followed by atomic absorption spectrometric determination of iron produced at a wave length of 248.3nm. [3,4]

$$C_xH_yFe + 3HCl + O_2 \xrightarrow{HClO_4} FeCl_3 + xCO_2 + (y+3)H_2O$$

MATERIALS AND METHODS

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Reagents:

All the reagents used were of analytical reagent grade except where otherwise mentioned

1- 5N and 1N hydrochloric acid solutions.
2- 1N sulphuric acid solution
3- 1N nitric acid solution.
4- 100 ppm ferric chloride solution:
   Prepared by dissolving 0.1210 g of solid $FeCl_3.6H_2O$ in 250 ml of 1N and/or 5N hydrochloric acid solution.
5- 100 ppm ferric sulphate solution:
   Prepared by dissolving 0.17900 g of solid $Fe_2(SO_4)_3$ in 250 ml of 1N sulphuric acid solution.
6- 100 ppm ferric nitrate solution:
   Prepared by dissolving 0.1808 g of solid $Fe(NO_3)_3.9H_2O$ in 250 ml of 1N nitric acid solution.
7- All the iron containing drugs (tablets) were provided from the state company for drug industries, Samarra-IRAQ (SDI), with exception of ferric acetylacetonate complex which was prepared according to the following reaction:

$$\mathbf{3CH_3CO.CH_2COCH_3 + Fe^{3+} \longrightarrow [Fe(acac)_3]}$$

Ferrocene was supplied from the BDH Company.

Apparatus:

Microgram balance, Mettler AG CH-8606.

Glass wares (pipettes, burettes, conical flasks, volumetric flasks 10 ml….etc).

A simple closed flask combustion assembly [1,2] has been constructed from 500 ml Erlenmeyer flask (Fig 1). Pyrex glass spiral as simple clamping (Fig 2)

The present work was carried out on Atomic Absorption Spectrophotometer Perken Elmer Model 503, with a condition of a wave length of 248.3 nm with continuous current of 30 mA, slit setting 3 (0.2 nm) and iron hallow cathode lamp as the light source.

Calibration Graph:

A calibration graph was constructed between increasing amounts of standard solutions (ranged between 0.5 to 5 ppm of ferric chloride in 5N hydrochloric acid) and corresponding absorbance (Fig 3).

Recommended Procedure:

The weighed sample (3-10 mg) was mixed with 10 mg of solid sodium sulphite [3,4] and then wrapped in a Schoniger technique. A Pyrex – glass spiral holder [3] was used, and 10 ml of 5N hydrochloric acid as absorbent solution as initial volume was used.

After the combustion process was completed, the resulting solution was shaken well for about 10 minutes until the fumes was completely disappeared. Then the sample holder rinsed out with 5N hydrochloric acid solution. The resulting solution was boiled gently on a hot plate for 10 minutes with 1ml of 20% perchloric acid - to ensure that all iron would be present as Fe(III) [3] - together with the Pyrex–glass spiral holder immersed in the solution and rinsed out with about 30ml of the same acid solution and the boiling was continued till the solution volume was reduced to 20-25 ml The solution was then left to cool down and transferred quantitatively to a 100-ml volumetric flask, completed to the mark with 5N hydrochloric acid. Finally the atomic absorption of Fe(III) was measured using atomic absorption spectrometry at wave length (248.3nm) and the content of iron was determined with the aid of a calibration graph prepared from various concentrations of ferric chloride dissolved in 5N- hydrochloric acid solution.

The percentage of iron in the sample was calculated by applying the following relationship.

$$\% \mathbf{Fe} = \mathbf{(X / W)\ 100}$$

X :amount of iron present in the sample in mg/ml as deduced from the calibration graph.

W : weight of the sample in mg/ml.

Results and discussion:

A Pyrex-glass spiral was used for the decomposition of Organo iron compounds as a sample holder, instead of a platinum gauze due to the alloy formation between iron and platinum [3,8]. Iron form difficulty soluble oxides after closed flask decomposition [3,18] and it was found necessary to mix the sample with a flux prior to the combustion step. Sodium sulphite was found to be the best flux, which could bring about quantitative decomposition of Organo iron compounds.

After combustion, the oxidation process was completed and the iron oxides formed were dissolved completely in 5N hydrochloric acid and it was accomplished through addition of perchloric acid and boiling of the absorbing medium [3,4].
Plotting of the recorded atomic absorbance versus increasing iron concentration (introduced as ferric chloride dissolved in 5N hydrochloric acid solution) gave the calibration graph shown in (Fig 3) which was linear up to 5ppm (as described in the catalogue of the apparatus used).

The recommended procedure was used to find out the recovery of iron in the ferrocene, by using different absorbents, such as 1N hydrochloric acid, 1N sulphuric acid, 1N nitric acid and 5N hydrochloric acid in order to find the optimum absorption of solution.

The results obtained are illustrated in Table (1) which indicate that correct values could be obtained using 5N hydrochloric acid as absorbent. The deviation in the results from the calculated values on using 1N hydrochloric, sulphuric and nitric acids was attributed to the anionic interferences [19-23].

Analytical Application:

Analysis of a variety of organic compounds gave satisfactory results (Table 2).The average absolute error for all the results was +0.234, the maximum error did not exceed +0.62. The relative standard deviation for the determination of some organo iron compounds and drugs are given in (Table 3).

Conclusion:

It was shown that atomic absorption spectrophotometric method for the micro determination of iron in Organo iron compounds and drug containing iron, was simple, sensitive, accurate and rapid (one determination require not more than 40 minutes including the weighing step).

This method can be applied to a wide range of organoiron compounds and drug, and it can also be applied to many other elements in organic compounds.

Table 1: Effect of the absorbing medium on the recovery of iron. Determination of iron in Ferrocene.

Sample wt. (mg)	%of Iron Calc.	Found in 1N HCl	Found in 1N H2SO4 (a)	Found in 1N HNO3 (b)	Found in 5N HCl	Error %
5.110		20.87	-	-	-	-9.15
5.985		19.00	-	-	-	-11.02
7.885	30.02	22.83	-	-	-	-7.19
8.580		23.69	-	-	-	-6.33
7.275		-	12.82	-	-	-17.20
7.885	30.02	-	15.20	-	-	-14.82
10.345		-	13.73	-	-	-16.29
4.960		-	-	23.52	-	-6.50
5.595		-	-	12.50	-	-17.52
6.585	30.02	-	-	20.75	-	-9.27
9.400		-	-	13.82	-	-16.20
6. 175		-	-	-	30.23	+0.21
7.915		-	-	-	30.32	+0.30
8.390	30.02	-	-	-	29.80	-0.22
9.485		-	-	-	29.87	-0.15

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a = a standard solution of ferric sulphate were used for calibration graph.

b = a standard solution of ferric nitrate were used for the calibration graph.

Table 2: Results for the analysis of some Organo iron compounds and Organo iron drugs

Drug Tablet

Name of the Compound or drug	Average wt. of tablet (mg)	Sample weight (mg)	% of Iron Calc.	% of Iron Found	Error %
Ferrocene		*5.065*		*29.61*	*-0.41*
(Dicyclopenta-		*6.175*		*30. 23*	*+0.21*
dienyl iron)		**7.915**	**30.02**	**30.32**	**+0.30**
		8.410		*29.80*	*-0.22*
		9.485		*29.87*	*-0,15*
Ferric acetyl		*5.300*		*15.71*	*-0.09*
Acetonate		*6.825*	*15.80*	*15.52*	*-0.28*
		7.505		**15.53**	**-0.27**
		9.165		**16.15**	**+0.35**
Ferrosam*		**10.455**		**13.38**	**-0.20**
	484.144	**11.155**	**13.58**	**13.74**	**+0.16**
		11.245		**13.63**	**+0.05**
		13.245		**13.08**	**-0.50**
Fersoline**		**6.790**		**6.63**	**-0.15**
		7.000		**6.43**	**-0.35**
	553.45	**8.160**		**6.74**	**-0.04**
		9.150	**6.78**	**7.10**	**+0.32**
		9.260		**6.83**	**+0.05**
		10.580		**7.09**	**+0.31**
		12.690		**6.69**	**-0.09**
		13.750		**6.54**	**-0.24**
Hemavit***		**6.460**		**15.10**	**+0.62**
	363.186	**10.510**	**14.48**	**14.75**	**+0.27**
		11.850		**14.53**	**+0.05**
		15.360		**14.65**	**+0.17**

* Each tablet contains 200mg of ferrous fumarate.

** Each tablet contains 300 mg of ferrous gluconate.

*** Each capsule contains 160 mg of ferrous fumarate.

Table 3: Precision of the AAS method for the determination of iron in Ferrocene.

Number of measurement	*% of iron found (X)*	*Deviation* $X - \bar{X}$	*Variation* $(X - \bar{X})^2$
1	**29.81**	**0.21**	**0.0231**
2	**30.23**	**0.21**	**0.0231**
3	**30.31**	**0.29**	**0.0841**
4	**29.77**	**0.25**	**0.0625**
5	**29.87**	**0.15**	**0.0225**
6	**29.68**	**0.34**	**0.1156**

X = 179.67

The average percentage of iron found $\bar{X}$ = 29.945

$(X - \bar{X})^2 = 0.3309$

$$\textbf{Standard deviation } S = \left[\frac{(X - \bar{X})^2}{n-1}\right]^{1/2} = \left[\frac{0.3309}{5}\right]^{1/2} = 0.06618$$

$$\% \text{ Standard deviation } = \frac{S}{\bar{X}} \; 100 = \frac{0.06618}{29.945} \; 100 = 0.222007$$

. The % standard deviation of Ferrosam, Hemavit,and Fersoline are (2.02), (1.66), and (1,58) respectively

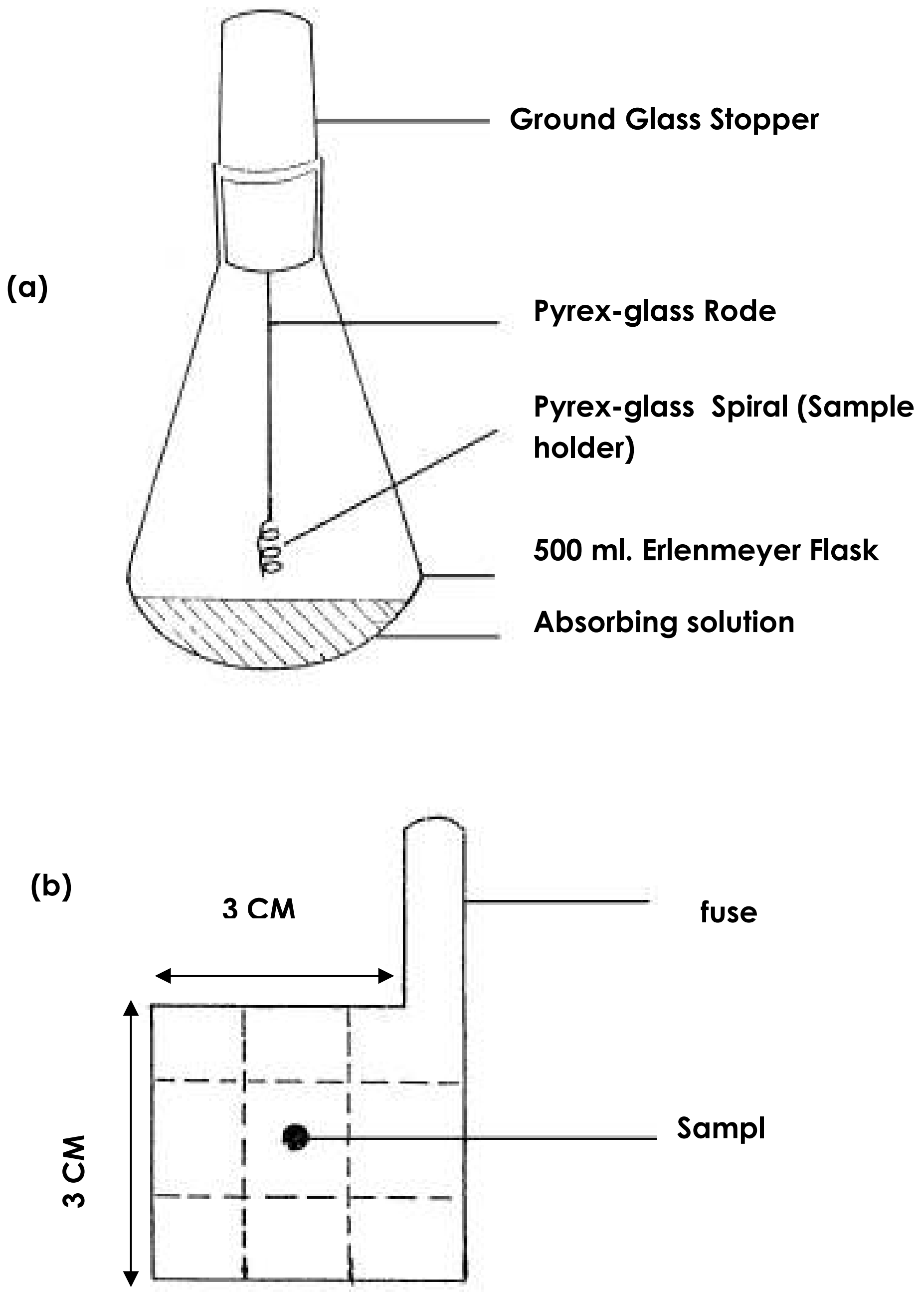

Fig. 1: Schoniger Technique
(a) Erlenmeyer Flask with a Pyrex Glass Spiral Sample Holder
(b) Ashless Filter Paper with Folded Lines Indicated.

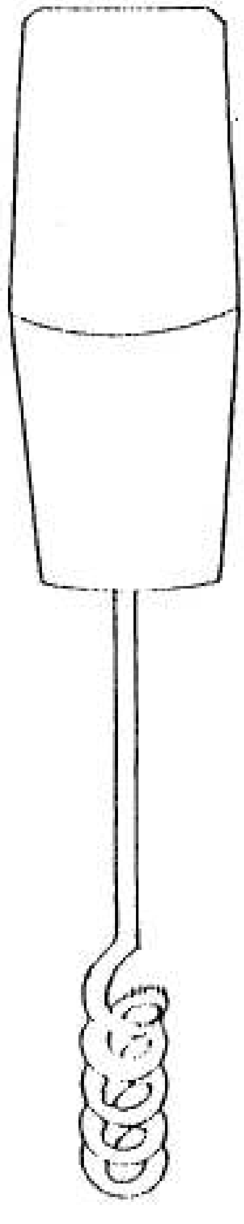

Fig. 2: Pyrex-glass Spiral Sample Holder

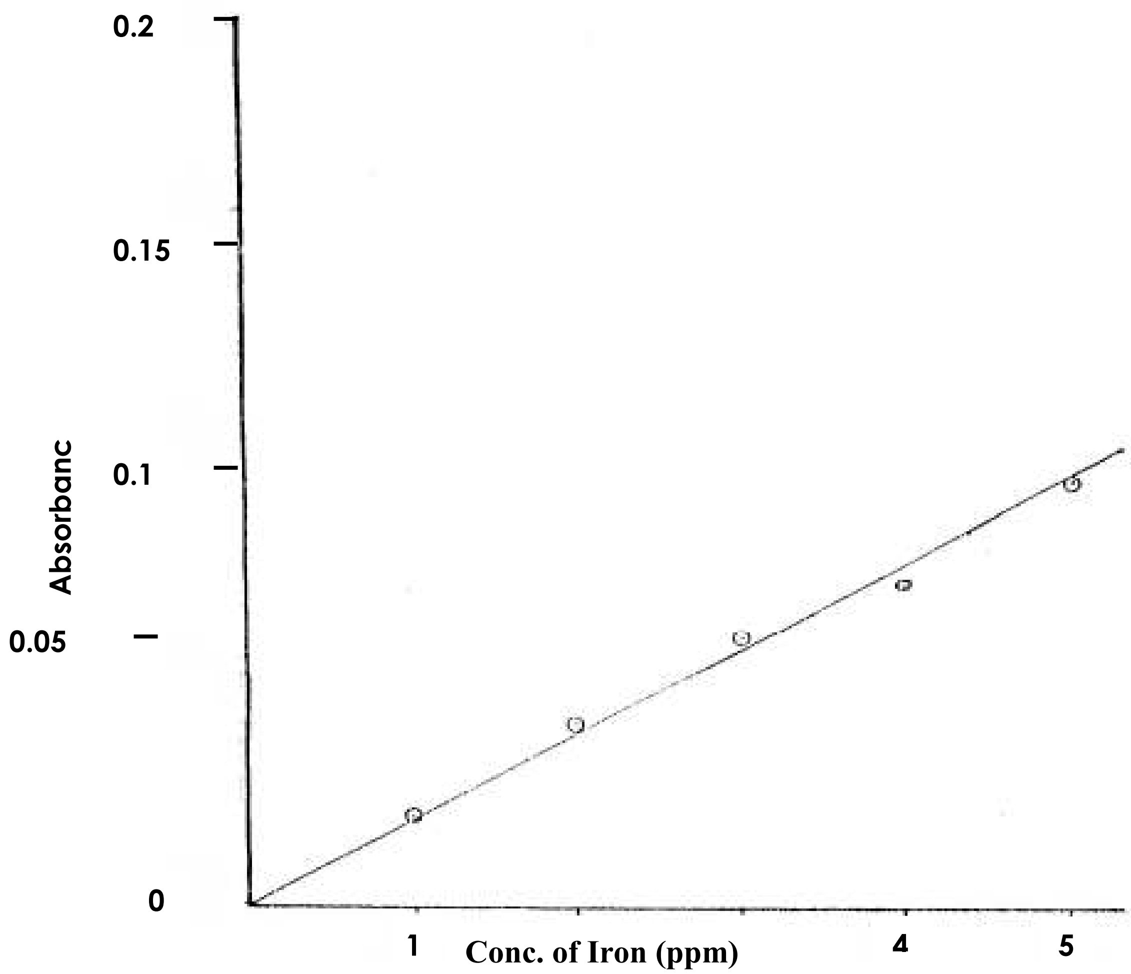

Fig.3: Calibration Graph for Iron

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