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(N, N, $\bar{N}$, $\bar{N}$ -Tetramethyl-p-phenylenediamine dihydrochloride) as a New Analytical Reagent for Spectrophotometric Determination of Iron(III).

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ABSTRACT

A new reagent N, N, $\bar{N}$, $\bar{N}$ - Tetramethyl-p- phenylenediamine dihydrochloride (TMPDA-2HCl) was described for the determination of Iron (III) spectrophotometrically. Beer's Law was obeyed between (0.4- 2.4 ppm) Iron(III). Optimum conditions were : pH(2-3) , $\lambda max = 560nm$, 2ml (0.001M) reagent freshly prepared for final 25ml solution containing 10 to 60 μg [i .e. 0.4 - 2.4 ppm Fe(III)] , colour developes after 10 minutes and remains stable for three hours .

Best straight line drawn by the method of least square gave correlation coefficient of (0.999) between (0 - 2 ppm). At lower limit of Fe(III) determination (0.4 ppm) ,maximum error did not exceed 5% in the presence of accumulative interfering ions with coefficient of variation of 1.8 %. These values , for 2 ppm Fe(III) ,were less than 4 % and 0.34 % respectively. Average extinction coefficient was about (1.5×10^4 $L.mol^{-1}$. cm^{-1}) . The stoichiometry of the complex [Fe(III) - R] was 1 : 1 .

Interferences of 27 ions were studied for their tolerance levels. Only few ions interfered seriously which were Cu^{2+},Ag^{+} ,Zn^{2+},Sn^{2+},$C_2O_4^{2-}$, and F^{-}.

INTRODUCTION

Iron(III)has been determined by reagents such as thiocyanate , Tiron (1) (Sodium -1,2-dihydroxybenzen - 3,4-disulphonate) and ammoniumdiisopropyldithio-phosphate (2) . Recently two new reagents have been described for the determination of total iron [Iron(II) + Iron(III)] . The first reagent was 3,4-dihydroxyphenylacetic acid (3) and the second (4) was 3 , 4 - Dihydroxybenzaldehyde.

The present work studies the use of N,N,$\bar{N}$,$\bar{N}$-Tettramethyl-p-phenylenediaminedihydrochloride (TMPDA-2HCl) as a reagent for the determination of Iron(III) . To the anthers knowledge and up to the most recent available review in 1992(5) ,this reagent has not been used for the determination of Iron(III) .

Experimental :

Chemicals : Both Analar and General purpose reagents were used from (Fluka , BDH and Ricdel de Hein) without further purifications . Ordinary distilled water prepared in all glass still and stored in polyethylene containers, was used .

Stock Solutions : 100ppm Fe(III) , was prepared from ammonium ferric sulphate . An appropriate amount of the salt was dissolved in little water containing a drop of concentrated H_2SO_4 to prevent hydrolysis and completed to the mark with distilled water .This solution was standardized gravimetrically (6) . A set of at least eight standards between 0 to 4 ppm Fe(III) were prepared by serial dilutions from another standard of 20 ppm which itself was prepared from the stock solution , each time a calibration curve was needed.

The reagent N,N,$\bar{N}$,$\bar{N}$ -Tetramethyl-p-phenylenediamine dihydrochloride (TMPDA-2HCL) 10^{-3} M . Solution was prepared in distilled water fresh every day.

Equipments :

The spectrum of the complex was taken using a double beam UV-Vis scanning spectrophotometer (Perkin Elmer Hitachi 200) .

All other absorbance measurements were taken on a single beam spectronic - 20 (From Milton - Roy Company USA) . Measurements of pH were taken using model(PW 9420 Philips) pH - meter equipped with a combined glass electrode .

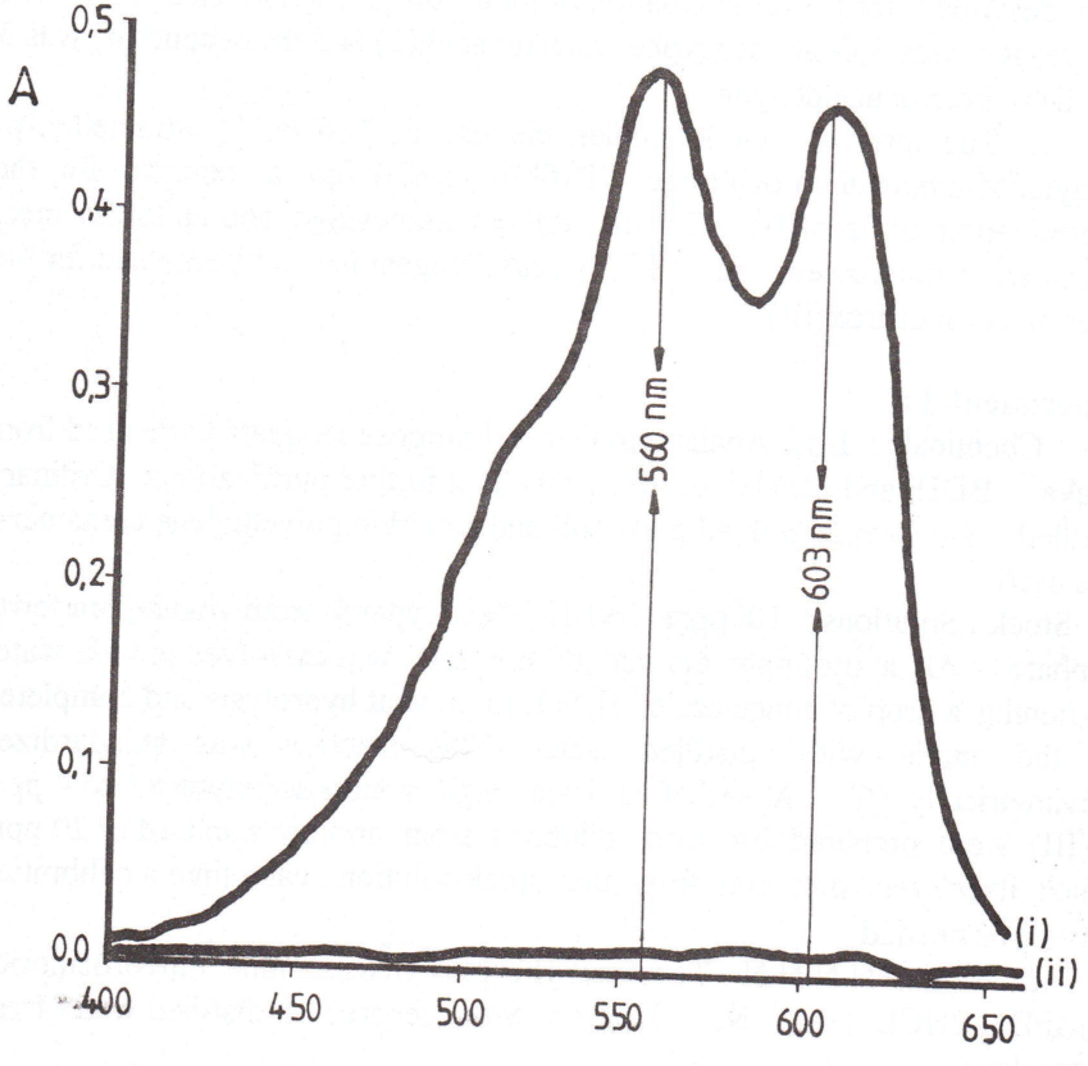

Fig. 1
The Absorption Spectra for the Complex [Fe(III)-R] Against the Blank (i) and the Blank Against D Water (ii)

Procedure :

Two mls of the reagent (TMPDA- 2HCL) with a suitable volume of Fe(III) standards or samples to give final concentration between (0.4 - 2.4 ppm) Fe(III) are taken in a 25ml capacity volumetric flask . The pH is adjusted with 0.02 M HCl so that the final solution will have pH between (2-3) . To avoid the tedious pH adjustment , it is possible instead to add 0.1 ml standard 0.02 M HCl , then the volume is completed to the mark . The blank is prepared in the same way containing no Fe(III) . The absorbance should be read after 10 min against the blank at room temperature at the wave length of 560 nm .

Draw the usual calibration curve [A vs. ppm Fe(III)] and measure the sample concentrations . For better accuracy , use the method of least - square (7) applying the equation $y = a + bx$ for concentrations around 2 ppm and the equation $y = bx$ close to 0.4 ppm .

RESULTS AND DISCUSSION

The Absorption Spectra :

The spectra of the complex [Fe(III) with the reagent TMPDA - 2HCl] against the blank and of the blank against distilled water are shown in Fig -1 . The spectrum of the complex showed two distinct maxima , first was at 560 nm , which was also chosen for all subsequent measurements , while the second was at 610 nm and has slightly lower sensitivity.

It is also clear from this figure that the blank has almost zero absorbance at the working wave length which is quite useful since this does not contribute in reducing sensitivity of the method

At these two maxima Fe(II) has two very small peaks on the negative side showing no significant effect and no possibility for direct determination of total iron.

pH Optimization :

Preliminary experiments showed that the complex is formed at low pH , at the pH of the prepared iron solution which was between 2.23 - 2.83. Fig 2 shows that at pH values lower than 2 and higher than 3 , the absorbance declines sharply while it remained constant between 2-3 at both low and high concentrations of Fe(III) . To avoid extensive pH adjustments , it was found that the addition 0.1ml of standard of 0.02M HCl was sufficient for all

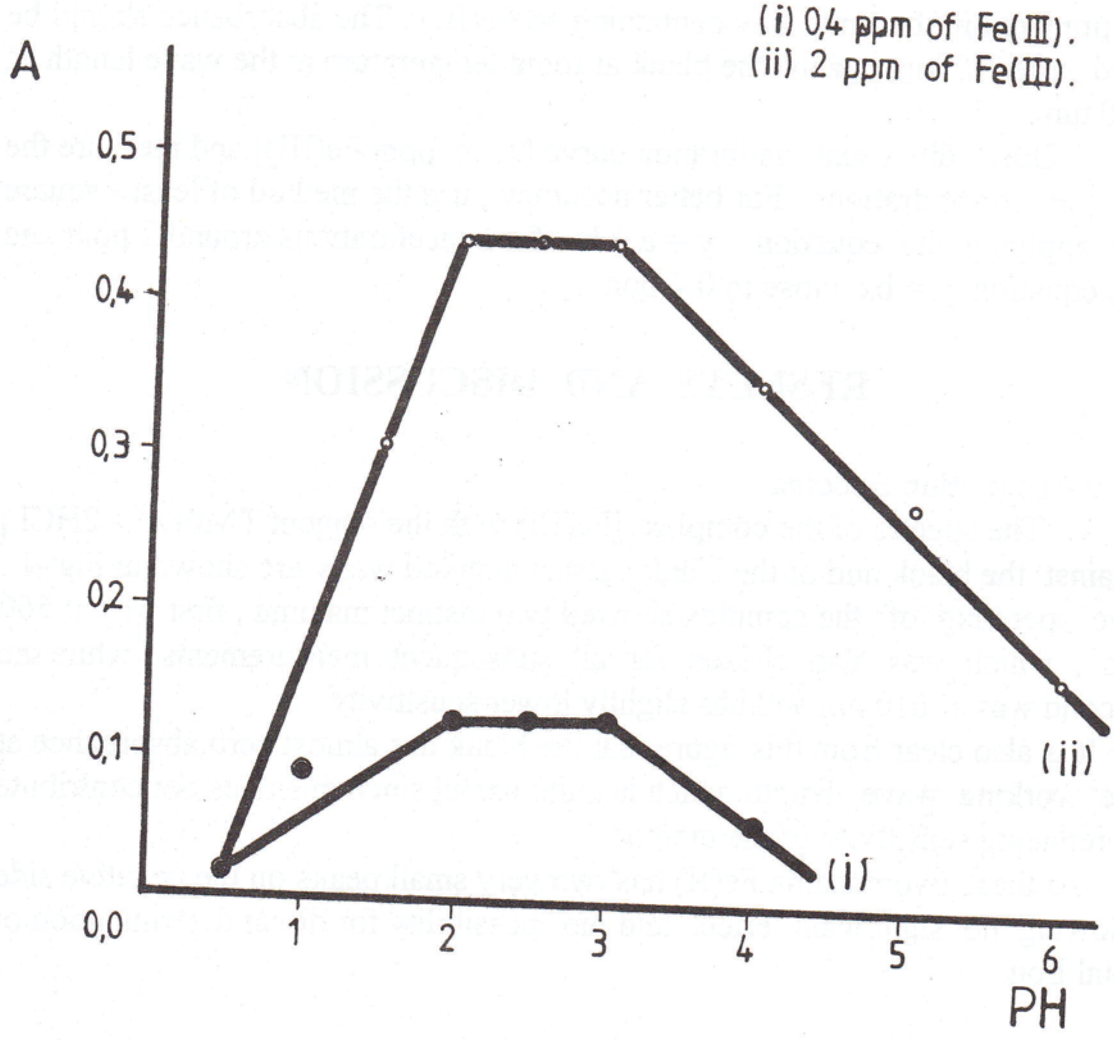

Fig. 2
The Effect of pH Optimization

solutions to maintain pH between 2.2-2.8 in the final 25ml solution without a need to a buffer solution .

Optimization of the Reagent Quantity:

Volumes between 0.1-2ml of the 10^{-3} M reagent were tested for the final 25ml solution . Best sensitivity was obtained when 2 mls of the reagent were present.

Stability Studies:

Both the reagent and the complex were tested for their stabilities as shown in Fig-3. It is shown that the complex formation is complete after ten minutes at (Room.Temperature) and remained stable for at least three hours . This is quite suitable for most applications .

The reagent , however , shows more instability particularly after 40 minutes from its preparation .But, comparing results obtained for the determination of a known quantity of Fe(III) , using both fresh and old reagents under identical conditions, showed no significant difference in their absorbances when the reagent is only 24 hrs .old and only 5% lower after three days .It was also found that this loss in sensitivity has not been associated with loss in accuracy providing that the same reagent was used for all standards and samples at the same time . However , it was preferred to use freshly prepared reagent each time.

Stoichiometry of the Fe(III) - Complex :

The two well - known methods namely , the mole ratio and continuous variation , were used to determine the structure of the complex and the results are shown in Fig 4 (a , b) . In the 1st - method , number of moles of the reagent were kept constant but number of moles of Fe(III) ion were changed . In the 2nd - method , however , number of moles of both reagent and Fe(III) were changed keeping total number of moles always the same .

Conclusions from both figures gave the same Fe(III) / R mole ratio of (1:1) , accordingly the structure given in Fig.(5) is proposed.

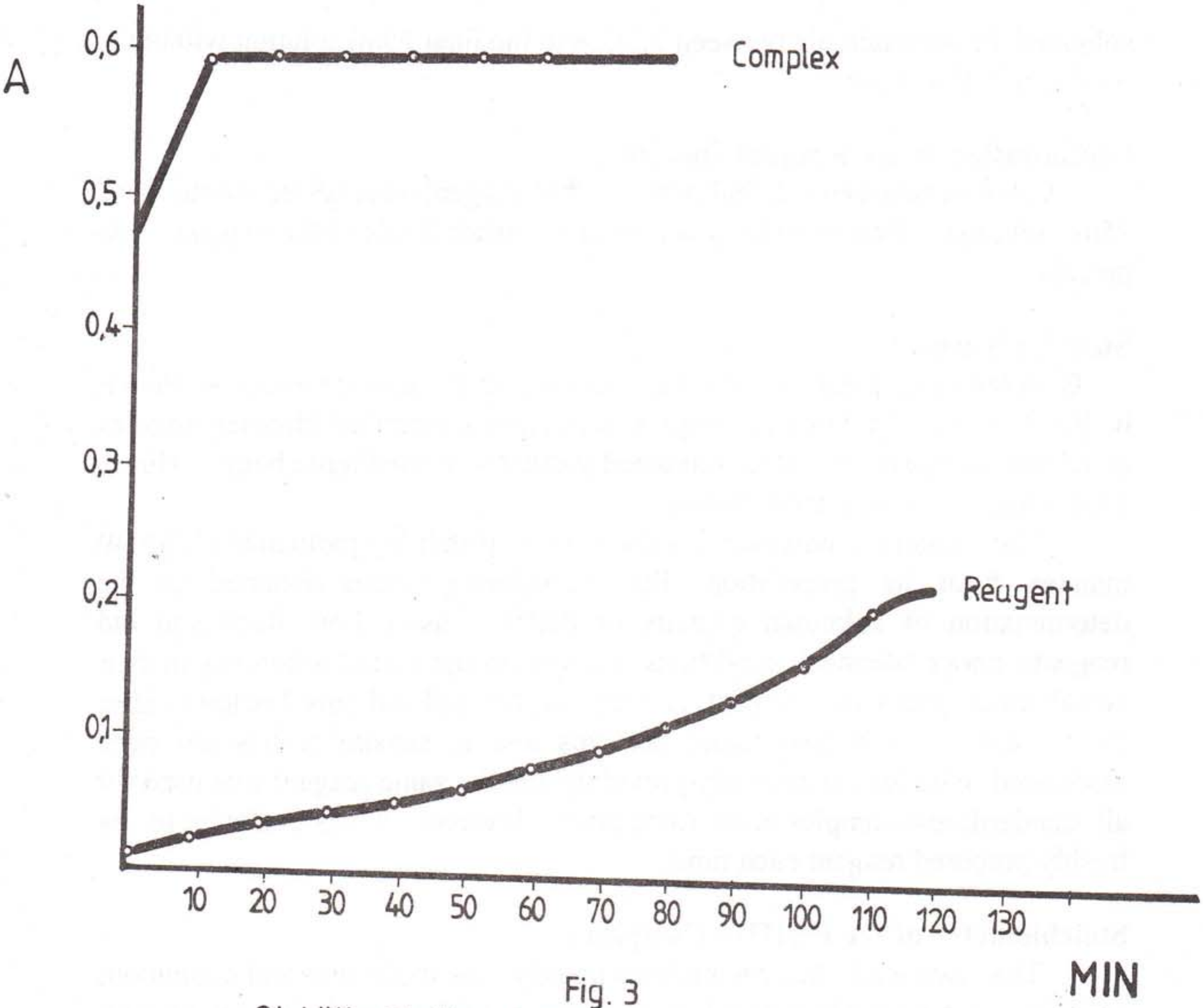

Fig. 3
Stability Studies of the Complex and the Reagent with Time.

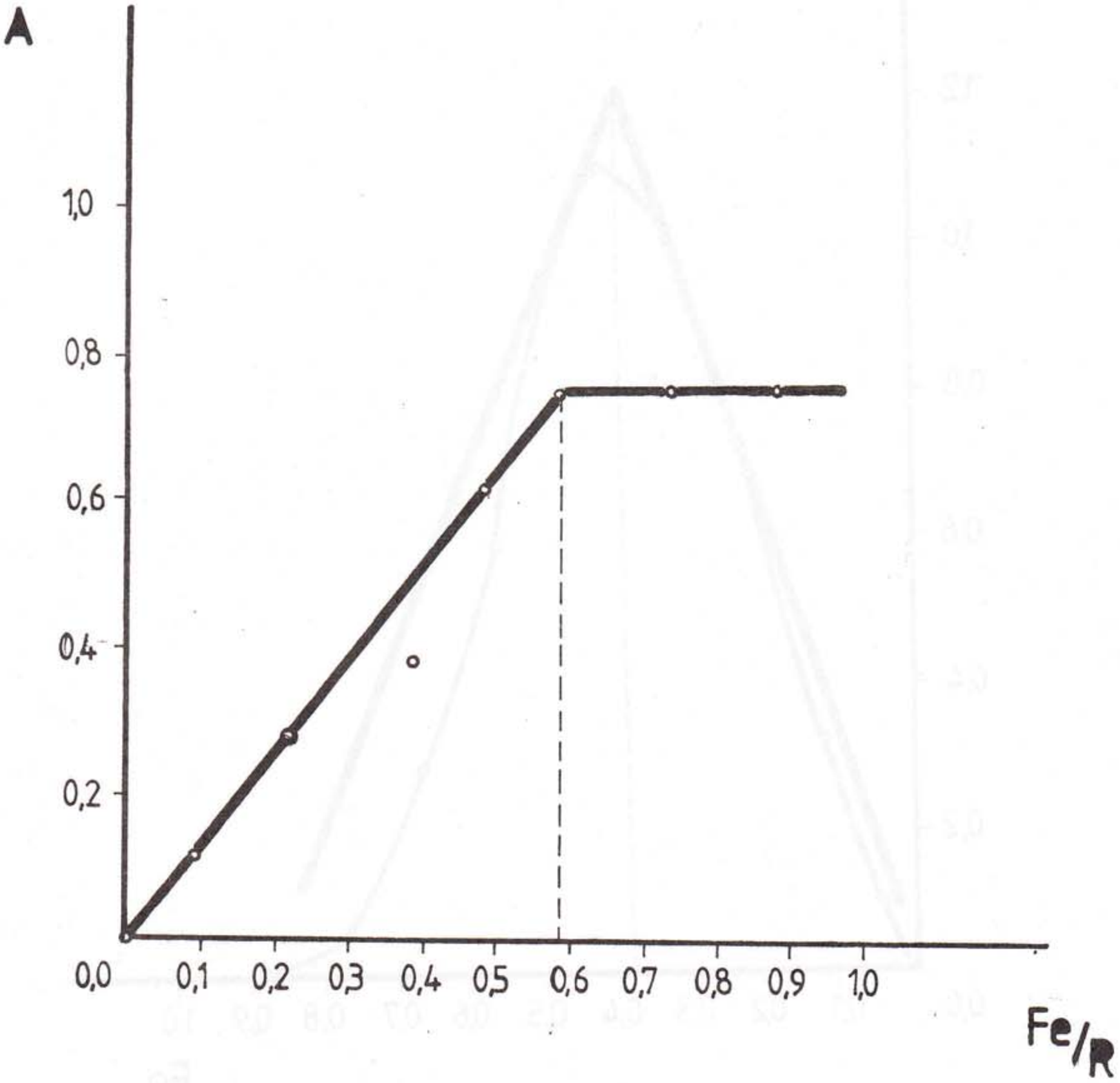

Fig. 4a
Stoichiometry of the Complex Fe(III).R.. (a) Mole Ratio Metbod

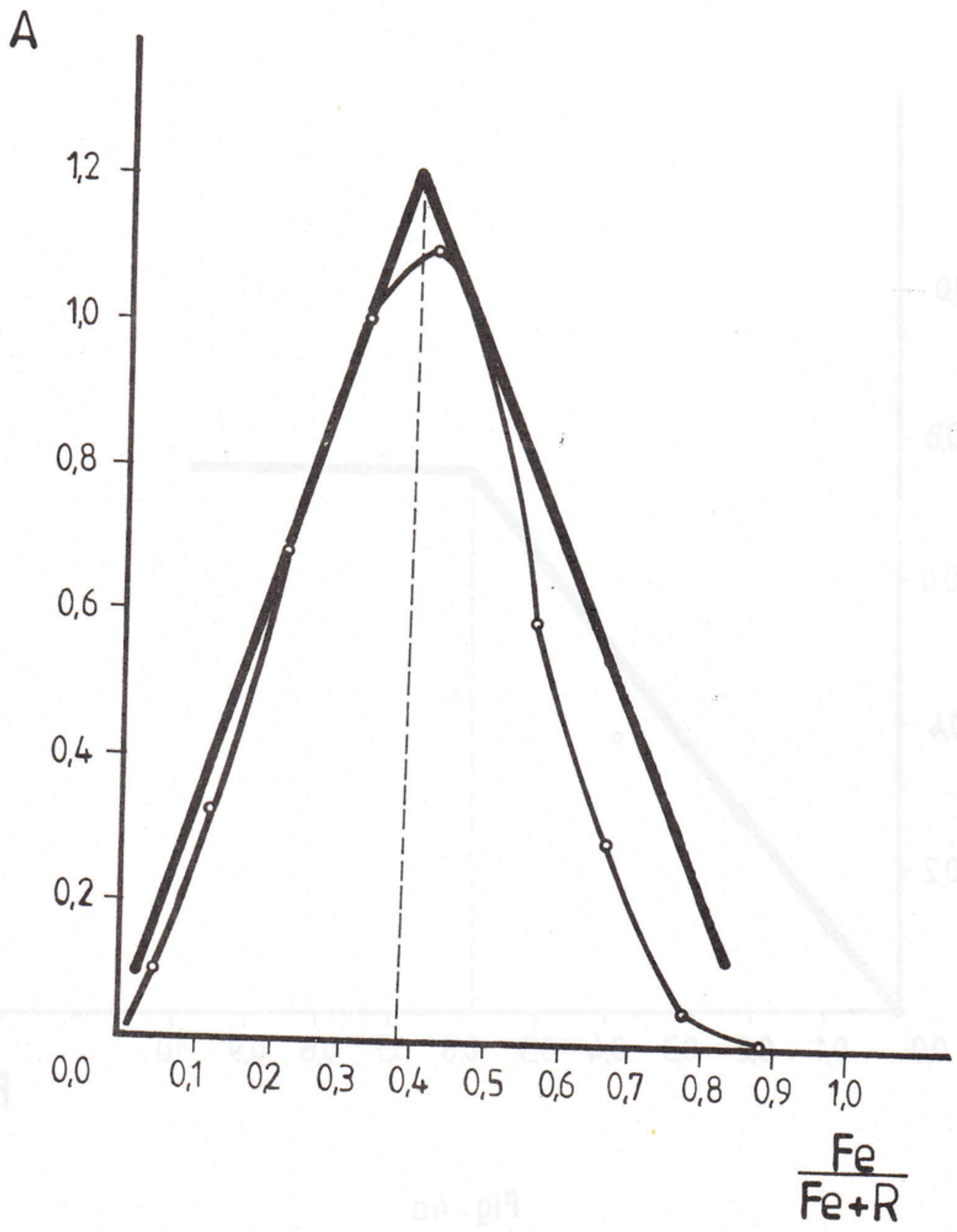

Fig. 4b

(6) Continuous Variation Method.

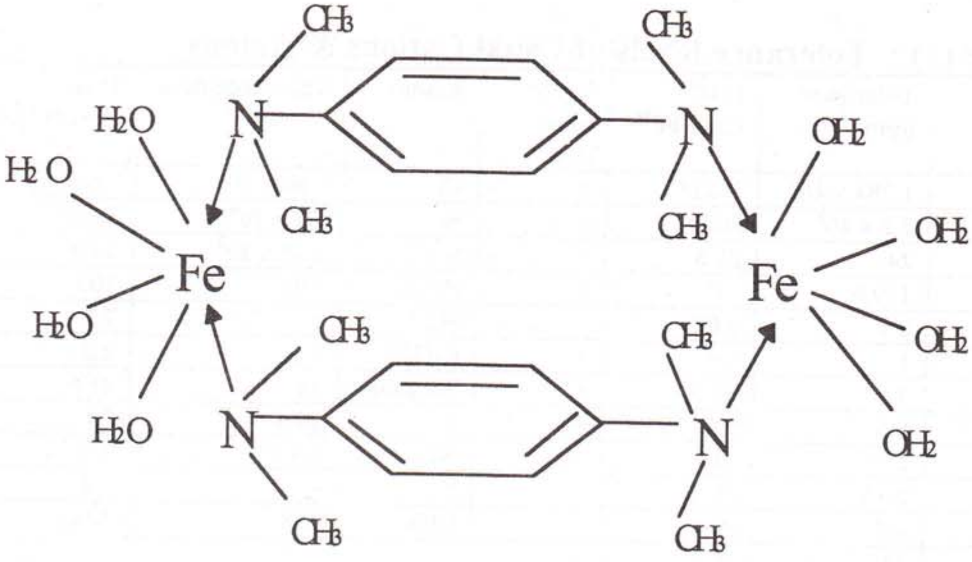

Fig.(5) : The proposed structure of the complex Fe(III) -TMPDA

Interferences :

To a solution of 1.12 ppm Fe(III) , a suitable salt of the metal to be studied was added in successive portions until deviation in absorbance compared to zero interference , has been observed . Table -1 shows the tolerance levels of the common cations and anions studied . The table indicates reasonable selectivity of the reagent towards Fe(III) . Except few cations and aniouns , such as Cu^{2+}, Ag^{+}, Zn^{2+}, Sn^{2+}, $C_2O_4^{2-}$ and F^- showed strong interferences , all other ions gave quite reasonable tolerance levels . Thus a broad field of applications of the method would be possible .

The mechanism of interferences may differ from one ion to another . The cations Cu^{2+}, Ag^{+}, Zn^{2+} , Cd^{2+} , Ni^{2+} ,. . . etc will interfere perhaps through the formation of complexes with the reagent therefore positive errors encountered . All other interferences are expected with any method of Fe(III) determination and not because of nonselectivity of the reagrnt. Fluoride interference, for instance, is quite natural since it forms a strong complex with Fe(III) of the form (FeF_6^{3-}) . Sn^{2+}, on the other hand, interferes through the reduction of Fe(III) to Fe(II) while some anions such as PO_4^{3-} form insoluble salts with iron(III), these interferences gave negative deviations . Fortunately the strong acidic condition of the present method minimizes the formation of insoluble salts between Iron(III) and anions such as PO_4^{3-} ,CO_3^{2-}, HCO_3^{-} , SO_4^{2-} , $C_2O_4^{2-}$ and tartarate,thus lowering the

Table (1) : Tolerance levels of Usual Cations & Anions

Cation	Tolerance ppm	Fold = Cat / Fe^{3+}	Error ditec-tion	Anions	Tolerance ppm	Fold = Anion / Fe^{3+}	Error Diтection
Na^+	1.784×10^4	16218	+	Cl^-	4.84×10^3	4400	-
K^+	2.2×10^3	2000	+	Br^-	6.2×10^4	16218	+
NH_4^+	24	21.8	+	SO_4^{2-}	2.68×10^3	2436	+
Ni^{2+}	119.6	17	+	HCO_3^-	120	109	-
Cu^{2+}	0.1	0.09	+	PO_4^{3-}	8	7.2	-
Zn^{2+}	1	0.9	+	$C_2O_4^{2-}$	2.6	2.3	-
Co^{2+}	96	87.2	+	Taratrate	48	43.6	-
Cd^{2+}	6.5	5.9	+	CHO_2^-	26.4	24	+
Pb^{2+}	240	218	+	NO_3^-	2.4×10^3	2181	+
Ca^{2+}	28.8	26.1	+	F^-	4	3.6	-
Fe^{2+}	10^6	90.9	+	ClO_3^-	258	234.5	+
Cr^{3+}	33.3	30.2	+				
Al^{3+}	9.7	8.8	+				
Ag^+	0.5	0.45	+				
Sn^{2+}	2.7	2.4	-				
Hg^{2+}	147	133.6	-				

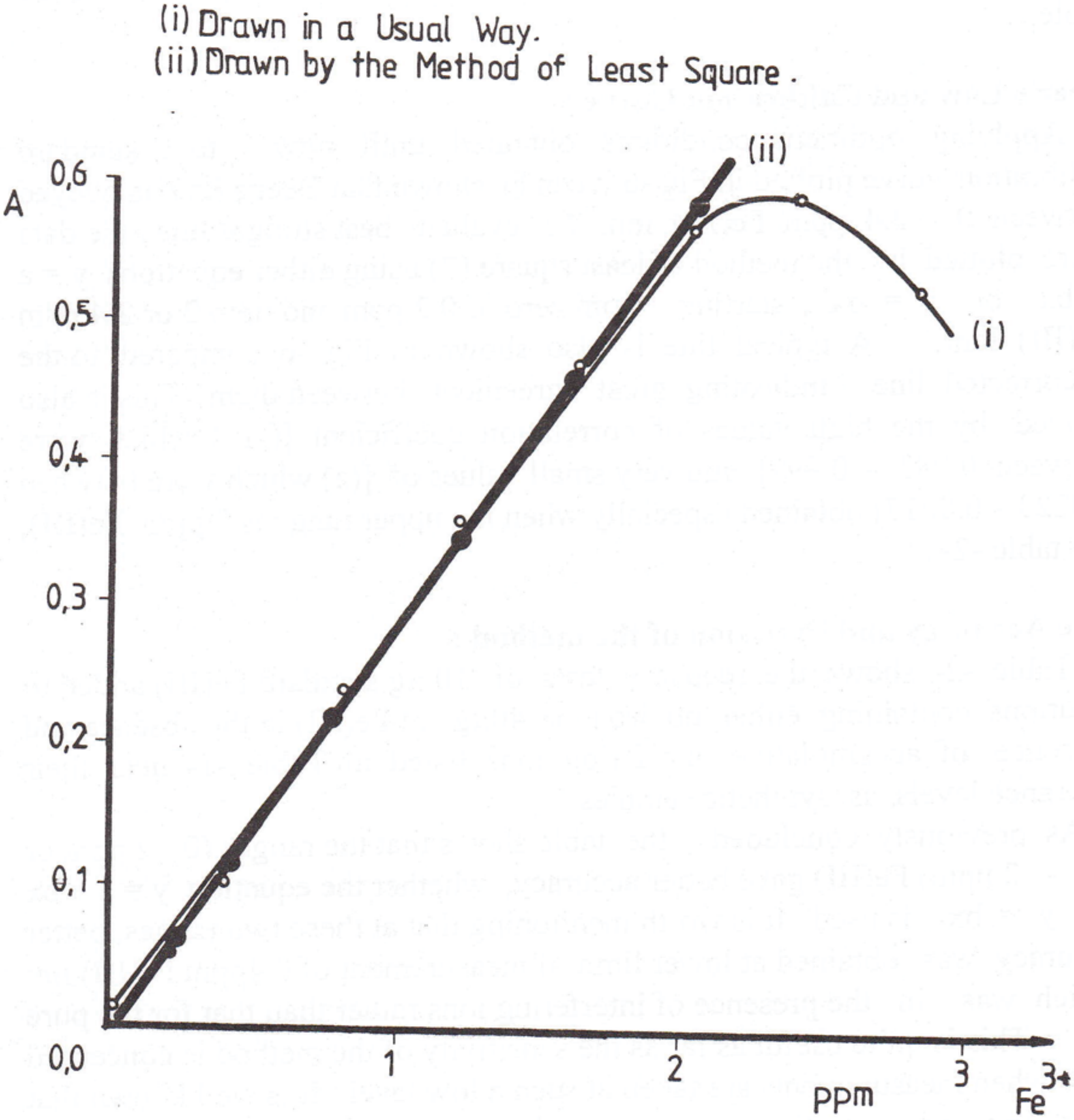

Fig . 6
The Application of Beer's Law

interferences of most of them to a reasonable level as it is clear from the table.

Beer's Law and Calibration Curve :

Applying optimum conditions obtained until now to a standard calibration curve plotted in Fig -6 it can be shown that Beer's Law is obeyed between 0 - 2.4 ppm Fe(III) ion. To evaluate best straight line , the data were plotted by the method of least square (7) using either equations $y = a + bx$ or $y = bx$, starting from zero or 0.2 ppm and upto 2 or 2.4 ppm Fe(III) ion. A typical line is also shown in Fig -6 compared to the uncorrected line , indicating great agreement between them . This is also proved by the high values of correlation coefficient [(r) which were between 0.983 - 0.999] and very small values of [(a) which were between 0.0223 - 0.0017] obtained especially when the upper range is 2 ppm Fe(III), see table -2- .

The Accuracy and Precision of the method :

Table -2- shows the recovery tests of 10 μg standard Fe(III) added to solutions containing either no iron or 40μg of Fe(III) in the absence and presence of accumulative interfering ions listed in Table -1- near their tolerance levels as synthetic samples .

As previously concluded , the table shows that the ranges (0 - 2 ppm or 0.2 - 2 ppm) Fe(III) gave better accuracy, whether the equation $y = a + bx$ or $y = bx$ is used . It is worth mentioning that at these two ranges, better accuracy was obtained at lower limit of measurement of 0.4ppm Fe(III) ion which was in the presence of interfering ions rather than that for the pure ion . This is quite useful as far as the sensitivity of the method is concerned and when measurements are taken at such a low level . It is well known that , at low concentrations any method loses its accuracy because of interferences . But here, apparently, there is some compensation effect , meaning that, the large negative error encountered in the measurement of the pure ion was compensated for by a large positive error caused by interferences. Such compensation is not rare in analytical chemistry .

The precision of the method was tested at two concentration levels by measuring absobances of eleven replicates at 0.4 ppm and 2 ppm Fe(III) . The absorbance readings at 0.4 ppm were 0.110 , 0.112 , 0.113 , 0.115 , 0.109, 0.111 , 0.113 , 0.110 , 0.115 , 0.112 and 0.110 , the calculated coefficient of variation (c.v) was 1.8 % . At 2 ppm level , the absorbances

Table 2 : Evaluation of the method of the calibration drawn by least Square Procedure

						Eq. y = a + bx			Eq. y = bx		
Range	**a**	**r**	**µg Fe(III) present**	**µg Total Fe(III) present**	**Interference**	**µg Fe(III) Found**	**Recovery %**	**Error %**	**µg Fe(III) Found**	**Recovery %**	**Error %**
(0 - 2)	0.0017	0.9958	Zero	10	Zero	8.9	89	-11	8.99	89.9	-10.1
ppm			Zero	10	Present	9.5	9.5	-5	9.59	95.9	-4.1
			40	50	Zero	49.3	98.6	-1.4	49.2	98.4	-1.6
			40	50	Present	48.3	96.6	-3.4	48.2	96.4	-3.6
(0.2-2)	0.0046	0.9989	Zero	10	Zero	9.3	93	-7	8.99	89.9	-10.1
ppm			Zero	10	Precent	9.85	98.5	-1.5	9.59	95.9	-4.1
			40	50	Zero	49	98	-2	49.2	98.4	-1.6
			40	50	Precent	48.3	96.6	-3.4	48.2	96.4	-3.6
(0-2.4)	0.0181	0.9878	Zero	10	Zero	8.3	83	-17	9.59	95.9	-4.1
ppm			Zero	10	Present	8.93	89.3	-10.7	9.59	95.9	-4.1
			40	50	Zero	52.9	105.8	+5.8	52.5	105	+5
			40	50	Present	51	102	+2	48.2	96.4	-3.6
(0.2-4)	0.0223	0.9831	Zero	10	Zero	7.9	79	-21	9.59	95.9	-4.1
ppm			Zero	10	Present	8.6	86.1	-13.4	9.59	95.9	-4.1
			40	50	Zero	53	106	+6	52.5	105	+5
			40	50	Present	51.6	103.2	+3.2	48.2	96.4	-3.6

were 0.581 , 0.586 , 0.583 , 0.584 , 0.586 , 0.582 , 0.580 , 0.583 ,0.585 , 0.581 and 0.583 gving the (c.v) of 0.34 % .

The sensitivity of the method calculated from Beer's Law showed that average $\varepsilon = 1.5 \times 10^4$ $L.mol^{-1} . cm^{-1}$ indicating a high sensitivity of the method so that 0.4 ppm Fe(III) is quite easy to determine .

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N, N, N̄, N̄- TETRAMETHYL-p-PHENYLENEDIAMINE DIHYDROCHLORIDE وەك ناسەرەوەیەکی تازە بۆ دیاری کردنی ئایۆنی ئاسنیك بەڕێگەی شەبەنگی بینراو .

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کورتەی توێژینەوە

توێژینەوە کرا دەربارەی ناسەرەوەی

N̄,N̄,N,N-TETRAMETHYL-p-PHENYLENEDIAMINE DIHYDROCHLORIDE

بۆ دیاری کردنی ئایۆنی ئاسنیك بەڕێگەی شەبەنگی بینراو . یاسای بیر لامبەرت دەگونجێ بۆ پەیتی 0.4 - 2.4 ppm لە ئاسنیك ، ئەمیش لە بارودۆخێکی نموونەی دا : λmax = 560nm ، (pH=2-3) ، 2ml لە ناسەرەوەکە بە پەیتی 0.001 M. دەمودەست ئامادە کرابێ بۆقەبارەی (25ml) کۆتایی لەگیراوەکە کە بڕی ئاسنیك لەناویا لە نێوان (10 - 60 µg) دایە ، بەواتا (0.4 -2.4 ppm FeIII)و ، ڕەنگەکەی دەگاتە بەرزترین ئاستی پێکهاتنی لە ماوەی 10 خولەك دا ، وەبەلایەنی کەمەوە بە جێگیری بۆ ماوەی (3) کاژێر دەمێنێتەوە .

باشترین هێڵی ڕاست کە کێشرابێ بە ڕێگەی (Least Square) بەهای هاوکۆلکەی پێکەوەلکانی (Correlation Coefficient) یەکسانەبە (0.999) وەلە نێوان (0 - 2 ppm)دا . لە کەمترین پەیتی دیاریکراوی ئاسندا (0.4 ppm) وەبوونی ئایۆنەکانی دیکە لە گیراوەکەدا بەرزترین ڕادەی هەڵە کەمتر بوو لە 5 % ، هاوکۆلکەی گۆڕان (Coefficient of Variation) بریتی بوو لە 1.8 % ، هەمان نرخ بۆ پەیتی 2ppm لە ئاسنیك کەمتر بوو لە 4 % و 0.34 % یەك لەدوای یەك .

تێکڕای هاوکۆلکەی مژینی مۆلی (Molar Extinction Coefficient) نزیکەی (1.5 X 10^{4} L mol^{-1} cm $^{-1}$) بوو ، هەروەها لەم بارودۆخەدا پێکهاتنی ئاوێتە ئالۆزەکە (Fe III -- R) بەڕێژەی (1:1) بوو .

توێژینەوە کرا بۆ زانینی بەرزترین توانای تێکەڵ بوونی (27) کاتایون و ئەنایون لە ناو گیراوەکەدا تەنها چەند ئایۆنێك زۆر کاریگەر بوون کە ئەمانەن :

$Cu^{2+}, Ag^{+}, Zn^{2+}, Sn^{2+}, C_2O_4^{2-}, F^{-}$

N,N,N̄,N̄-TETRAMETHYL-p-PHENYLENEDIAMINE DIHYDROCHLORIDE

ككاشف جديد لتقدير آيون الحديد الثلاثي بالطيف المرئي

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الخلاصة

لقد تم التوصل الى وصف كاشف جديد لتقدير الحديد الثلاثى بالطيف المرئى وهو _ _ N,N,N,N-TERAMETHYL -p-PHENYLENEDIAMINE DIHYDROCHLORIDE (TMPDA-2HCl) وتم تطبيق قانون بير لامبرت بين(0.4 - 2.4ppm FeIII). الظروف المثلىكانت كالاتي: pH(2 - 3),λmax=560nm. 2mls من الكاشف بتركيز (0.001M) محضر حديثا للحجم النهائى (25ml) من المحلول ويحتوى بين (0.4 - 2.4ppm) أى (10-60µg FeIII) واللون يصل اعلى تكون خلال عشرة دقائق ويبقى مستقرا لمدة ثلاث ساعات على الاقل .أحسن خط مستقيم مرسوم بطريقة المربعات الدنيا (Least- Square) أعطى معامل الارتباط (r = 0,999) . وعند التركيز الادنى لتقدير الحديد (0.4ppm FeIII) وبحضور الأيونات المتداخلة مجتمعة لم يصل الحد الاعلى للخطأ 5% ومعامل التغاير (1.8 %) . هذه القيم فى تركيز (2ppm FeIII) كانت أقل من 4% , 0.34% على التوالى .معدل معامل الانطفاء (Extinction Coefficient) كان $(1.5 \times 10^4\ L\ mol^{-1} . cm^{-1})$ وتركيب المعقد فى هذه الظروف كان (1:1) حديد ثلاثى R الكاشف. تمت دراسة (27) آيون لمعرفة الحد الاعلى للتداخل وكانت من بينهم عدد قليل ذو تداخل فعال وهم الأيونات $Cu^{2+}, Ag^{+}, Zn^{2+}, Sn^{2+}, C_2O_4^{2-}, F^{-}$

Caption of the Figures

Fig - 1 :-

The Absorption Spectra for the Complex [Fe(III) - R] Against the Blank (i) and the Blank Against D . Water (ii) .

Fig - 2 :-

The Effect of pH Optimization .
(i) 0.4 ppm of Fe(III) .
(ii) 2 ppm of Fe(III) .

Fig - 3 :-

Stability Studies of the Complex and the Reagent with Time .

Fig - 4 :-

Stoichiometry of the Complex Fe(III)-R.
(a) Mole Ratio Method .
(b) Continuous Variation Method .

Fig - 5:-

The Proposed Structure of the Complex Fe(III) -TMPDA

Fig - 6 :-

The Application of Beer's Law .
(i) Drawn in the Usual Way .
(ii) Drawn by the method of Least Square .