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Spectrophotometric determination of iron through measurement of permittance of the copper-ethylenediaminetetraacetate absorbing system

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ABSTRACT

A new analytical method has been proposed for spectrophotometric determination of iron through measurement of permittance of the copper(II)-ethylenediaminetetraacetate, $[Cu(II)\text{-}EDTA]^{-2}$ absorbing system. In this method, Fe^{3+} solution buffered at pH 1.15 was treated with measured and excess of ethylenediaminetetraacetic acid (EDTA) and the surplus EDTA was used for generation of $[Cu(II)\text{-}EDTA]^{-2}$ system. Permittance of the absorbing system measured at 722nm was observed directly proportional to the concentration of iron. At pH 1.15, the average value of the permittance coefficient was investigated as 0.5168 $lit.g^{-1}cm^{-1}$ for quantitative determination of iron in the range of 1.0mg to 10.0mg. The effects of some important variables on the determination of iron based on proposed method were studied. Efficacy of this method was further tested for determination of iron in Livogen-Z, Ferium-xt and Orofer-xT tablets. The average accuracy was found good, which was evaluated by comparison of results obtained with those claimed by the manufacturer. The metal cations such as aluminum, barium, calcium, cadmium, lead, magnesium, manganese, zinc, and copper do not interfere in determination of iron.

KEYWORDS

Absorbing system;
Clearance;
Permittance;
Permittance coefficient;
Iron analyte;
$[Fe(III)\text{-}EDTA]^{1-}$ chelate;
$[Cu(II)\text{-}EDTA]^{2-}$ chelate;
Test solutions;
True blank;
Reagent blank.

INTRODUCTION

Iron, the most abundant element in the earth's crust (5.6 % by mass), is immensely important both in human civilization and in living systems[1]. Iron is so widely diffused in nature, in both divalent and trivalent oxidation states combined as ferrous and ferric compounds[2]. The ferrous iron has light green color while the ferric iron is in yellow color, but ferric iron produces the red-colored complex with thiocynate solution while ferrous iron yields no coloration[3]. Iron plays an important role in biological processes. In living systems iron is an essential constituent of numerous biomolecules. The body of a healthy human adult contains about 4 to 5 g of iron, 65% of which is present in hemoglobin and muscle hemoglobin[1,4] that is myoglobin[5] . Ferrous iron is the central structural unit of hemoglobin and myoglobin, performing the function of binding of molecular oxygen through transferring an electron by self oxidation to ferric iron[5]. For the deficiency of iron, the ferrous iron

(generally in the form of ferrous ascorbate or ferrous fumarate) being used for medical purposes and can be taken internally without danger.

The disodium salt of ethylenediaminetetraacetic acid, EDTA has found considerable use as a standard reagent for determination of numerous metals by photometric titration. Sweeter and Bricker have reported good photometric titration of ferric iron with EDTA by using salicylic acid as indicator for ferric ions[6]. The information of stability/formation constant (log K_f) of $[Fe\text{-}EDTA]^{1-}$ and $[Cu\text{-}EDTA]^{2-}$ chelates and their absorption spectra are the parameters utilized by Underwood for simultaneous determination of iron and copper in a single photometric titration[7]. Although detection of the exact end point by graphical means is tedious and time consuming route yet photometric titration methods are consistently used, since the presence of other substances absorbing at the same wavelength does not necessarily cause the interference, in as much as only the change in absorbance is significant[8].

The log K_f value[9,10] of EDTA complexes of iron and copper are reported as 24.23 and 18.70 respectively, these values are sufficiently larger indicates both chelates are have satisfactorily stability; however, $[Fe(III)\text{-}EDTA]^{1-}$ is more stable than $[Cu(II)\text{-}EDTA]^{2-}$. The wide difference in these stability constants permits for iron to react with EDTA first in presence of copper consequently, copper ions functioning as an indicator[7] in iron titration as well as allows for simultaneous[7] determination of both metals in a single photometric titration. The same concept of difference in log K_f values of $[Fe(III)\text{-}EDTA]^{1-}$ and $[Cu(II)\text{-}EDTA]^{2-}$ complex was exercised for spectrophotometric determination of iron through taking the advantage of copper ion as an indicator for determination of surplus EDTA.

In this method, the sample solution of Fe^{3+} buffered with chloroacetic acid was treated first with measured and excess of EDTA reagent; after quantitative chelation of Fe^{3+} as $[Fe(III)\text{-}EDTA]^{1-}$ the surplus EDTA was utilized for generation of $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system via adding measured quantity of Cu^{2+} solution. The solution with greater concentration of Fe^{3+} left the smaller amount of surplus EDTA (for generation of absorbing system) and vice a versa. As a result, the color intensity of $[Cu(II)\text{-}EDTA]^{2-}$ chelate was observed inversely proportional to the concentration of iron. Consequently, permittance[11] of the absorbing system was found directly proportional to the concentration of iron. Thus, the absorbance quenching[11] action of iron analyte on to the $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system was worked out in alternative manner for determination of iron.

EXPERIMENTAL

Apparatus

(1) Shimadzu UV-Visible spectrophotometer (Model UV-1800) was used with the quartz cuvettes for measurement of % transmittance. The software UV Probe version 2.33 was used for obtaining the absorption curves.

(2) Equip-tronics pH-meter with combined glass and calomel electrode (Model EQ-610) was used to check the pH of test solutions.

Reagents and chemicals

All chemicals used were analytical reagent grade and were used without further purification.

(a) 2.0 L. 0.0179M Fe^{3+} solution [viz. 1.0 mg ml^{-1} of iron] was prepared by dissolving 17.270 g. of $FeNH_4(SO_4)_2.12H_2O$ in minimum quantity of conc. HNO_3, followed by dilution with distilled water containing sufficient HNO_3 to make the final solution in 0.5M HNO_3. This solution of Fe^{3+} was standardized against standard EDTA solution using chloroacetate buffer and salicylic acid in acetone as an indicator.

(b) 4.0 L. 0.05M EDTA solution was prepared by dissolving 74.448 g. of disodium dihydrogen ethylenediaminetetraacetate dihydrate, $Na_2H_2EDTA.2H_2O$ in distilled water.

(c) 4.0 L.0.05M $Cu(NO_3)_2$ solution was prepared by dissolving 48.320 g. of $Cu(NO_3)_2.3H_2O$ in distilled water. The solutions of EDTA and $Cu(NO_3)_2$ are termed here as absorbing system reagents.

(d) 2.0 L. 1.0 M $CH_2ClCOOH$ solution was prepared by dissolving 189.0 g. of monochloroacetic acid in distilled water. The solution of chloroacetate was used as buffer.

(e) 4.0 Liter 0.5M HNO_3 solution was prepared by diluting 128.0 ml of conc. HNO_3 with distilled water.

(f) The iron tablets, Livogen-z (contains 50mg of elemental iron) manufactured by Merck India Ltd., Ferium-xt and Orofer-xT (both tablet contains 100mg of elemental iron) manufactured by Emcure Pharmaceuticals Ltd. were used for determination of iron.

Method for determination of iron

The method proposed for determination of iron was tested primarily with the standard solution of Fe^{3+}. The test solutions (TS) of iron in the range of 0.001g to 0.010 g were prepared by adding 1.0ml, 2.0ml to 10.0ml aliquots of 1.0 mg ml^{-1} Fe^{3+} solution sequentially into 50ml graduated flasks each containing 5.0ml of 1.0 M $CH_2ClCOOH$ as a buffer solution. To equalize the proton ions concentration, 9.0ml, 8.0ml to 0.0ml aliquots of 0.5M HNO_3 were also added in descending order into these volumetric flasks numbered as 2 to 11. After addition of 5.0ml of 0.05M EDTA solution reaction mixture in the flask were shaken thoroughly for quantitative chelation of Fe^{3+} with EDTA and 5.0ml of 0.05M $Cu(NO_3)_2$ solution was added for utilization of the surplus EDTA and generation of $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system. The reaction mixtures were further diluted up to the mark with distilled water. Excluding only Fe^{3+} solution, the reagent blank (RB) solution[11] was prepared in flask No.1 with 10.0ml 0.5M HNO_3. The true blank (TB) or reference solution[11] was also prepared in the similar way using 14.0ml of 1.0 mg ml^{-1} Fe^{3+} solution. The added 5.0ml of 0.05M EDTA was completed utilized for chelation of the iron present in this flask, therefore, $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system was not generated in TB solution, so act as a reference. The visible absorption spectrum of $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system (viz. RB solution) was obtained against the TB solution, and a wavelength 722nm was selected for measurement. The %T of RB as well as each TS was measured at 722nm against TB as a reference. The %T of the RB was used for obtaining the clearance[11] value of test solutions. The graph of logarithm of clearance viz. permittance[11] against the concentration of Fe^{3+} was used for determination of iron. An analogous method was employed for quantitation of iron in Livogen-z, Ferium-xt and Orofer-xt tablets.

RESULT AND DISCUSSION

The hexadentate chelating reagent, ethylenediaminetetraacetic acid gives remarkably stable chelates with Fe^{3+} and Cu^{2+} in one-to-one stoichiometry[12]. Reilley and Schmid[13] showed the minimum pH needed for satisfactorily chelation of various cations with EDTA. The strongly acidic pH (in the range of 1-2) can be accepted by the trivalent metal cation for complexation with EDTA. Therefore, the quantitative chelation of Fe^{3+}

TABLE 1 : Effect of concentration of reagents on permittance and permittance coefficient; results obtained in quantitative determination of iron at 50ml dilution with different volume of absorbing system's reagents

Iron (g)	5.0ml		6.0ml		7.0ml		8.0ml	
	Pr	Pr. Coeff.	Pr	Pr. Coeff.	Pr	Pr. Coeff.	Pr	Pr. Coeff.
0.000	0.0000	---	0.0000	---	0.0000	---	0.0000	---
0.001	0.0103	0.5153	0.0102	0.5114	0.0102	0.5117	0.0103	0.5136
0.002	0.0204	0.5108	0.0205	0.5121	0.0206	0.5148	0.0204	0.5096
0.003	0.0307	0.5125	0.0310	0.5160	0.0307	0.5118	0.0309	0.5143
0.004	0.0415	0.5183	0.0409	0.5116	0.0414	0.5177	0.0409	0.5117
0.005	0.0515	0.5152	0.0518	0.5179	0.0515	0.5146	0.0517	0.5171
0.006	0.0614	0.5117	0.0614	0.5119	0.0617	0.5145	0.0624	0.5202
0.007	0.0722	0.5154	0.0727	0.5191	0.0724	0.5172	0.0722	0.5158
0.008	0.0836	0.5225	0.0833	0.5206	0.0835	0.5220	0.0836	0.5222
0.009	0.0939	0.5216	0.0941	0.5225	0.0941	0.5227	0.0939	0.5217
0.010	0.1048	0.5241	0.1048	0.5239	0.1045	0.5227	0.1044	0.5222
Average value:		0.51674	--	0.51669	--	0.51697	--	0.51684

TABLE 2 : Effect of final dilution of test solutions; results obtained in quantitative determination of iron in the range of 1.0mg to 10.0mg using 5.0ml of 0.05M EDTA and 5.0ml of 0.05M $Cu(NO_3)_2$ reagents at different dilutions

Iron (g)	25ml dilution			50ml dilution			100ml dilution		
	Pr.	Pro. Const.	Pr. Coeff.	Pr.	Pro. Const.	Pr. Coeff.	Pr.	Pro. Const.	Pr. Coeff.
0.000	0.0000	---	---	0.0000	---	---	0.0000	---	---
0.001	0.0206	20.62	0.5155	0.0103	10.31	0.5153	0.0052	5.17	0.5172
0.002	0.0413	20.65	0.5163	0.0205	10.25	0.5124	0.0103	5.14	0.5142
0.003	0.0619	20.64	0.5160	0.0309	10.31	0.5154	0.0155	5.16	0.5163
0.004	0.0826	20.65	0.5161	0.0415	10.37	0.5183	0.0207	5.17	0.5171
0.005	0.1030	20.59	0.5148	0.0513	10.26	0.5129	0.0258	5.16	0.5163
0.006	0.1237	20.61	0.5152	0.0615	10.25	0.5127	0.0309	5.15	0.5148
0.007	0.1445	20.64	0.5160	0.0722	10.31	0.5154	0.0362	5.18	0.5178
0.008	0.1653	20.67	0.5166	0.0831	10.39	0.5196	0.0415	5.19	0.5192
0.009	0.1863	20.70	0.5175	0.0941	10.46	0.5230	0.0466	5.18	0.5180
0.010	0.2081	20.81	0.5202	0.1048	10.48	0.5241	0.0520	5.20	0.5202
Average:		20.656	0.51641		10.338	0.51691		5.171	0.51712

with EDTA can be attainable at pH 1-1.5. Wagreich and Harrow[14] also showed that, EDTA has enormous nucleophilic capability to chelate the cupric ion over a broad pH range and the stability of $[Cu(II)\text{-}EDTA]^{2-}$ chelate is not much affected by the pH of solution. Even at acidic pH the reaction of Cu^{2+} with EDTA results with generation of intensely blue colored $[Cu(II)\text{-}EDTA]^{2-}$ chelate; which was employed as the absorbing system at 745nm for spectrophotometric determination of copper[6]. The earlier study[15] of quantitative determination of bismuth was carried out at pH 1.0-1.25 via generating the $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system and the same absorbing system was exploited here for spectrophotometric determination of iron.

Determination of surplus EDTA

The formation constant ($\log K_f$) value[9,10] of $[Fe(III)\text{-}EDTA]^{1-}$ and $[Cu(II)\text{-}EDTA]^{2-}$ chelates are reported 24.23 and 18.70 respectively, which indicates that both chelates have enough stability but iron chelate is much more stable than copper chelate. The sufficient difference (about 5.53) in these $\log K_f$ values permits to utilized surplus EDTA in the test solution for generation of $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system, without disturbing the stability of iron chelate. Furthermore, copper chelate exhibits maximum absorption in the visible region where other species in the test solution exhibits nil absorption.

Effect of $[H^+]$ on the linearity

The stability of $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system is not much affected by small change in pH of the solution[14]. But variable concentration of proton in test solutions affects the ionization of EDTA that reflects an adverse effect on the analytical performance of the method. Because variable aliquots (1.0ml to 10.0ml) of the standard solution of iron (having concentration 1.0mg ml^{-1} prepared in 0.5M HNO_3) used for preparation test solutions, those carry the different concentration of proton. Consequently, the solution of 0.5M HNO_3 was added in descending order (from 9.0ml to 0.0ml) for compensation of effect of the H^+ ions on the ionization of EDTA. The proposed method involves the measurement of permittance of test solution (TS) in comparison with permittance of the reagent blank (RB) solution, so excluding only the sample, the composition of both solutions was kept essentially identical. Moreover, addition of buffer species ensures quantitative chelation of both metals through nullification of the effect of protons released from EDTA during complexation reactions.

Selection of the wavelength for measurement

In the proposed method, the quantitative determination of iron was carried through measurement of permittance[11] of $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system. The optical density of absorbing system indicates the concentration of surplus EDTA in test solution. Therefore, for attending the greater sensitivity, it was necessary to carry out measurement at the wavelength to which absorbing system shows absorption maxima (λmax). For this purpose, the visible absorption curve of $[Cu(II)\text{-}EDTA]^{2-}$ chelate (viz. RB solution) was obtained against the TB solution as a reference, both were prepared as described in the method. The spectrum study showed that, $[Cu(II)\text{-}EDTA]^{2-}$ chelate in chloroacetic acid and nitric acid medium exhibits absorption maxima at 722nm. Therefore, measurement of %T was carried out at 722nm to which all other species are transparent, except the free Cu^{2+} ions have little absorbancy at this wavelength. Therefore, equivalent amount of it also added in TB or reference solution for compensating the background absorbance of unused Cu^{2+} ions. Though the concentration of unused/free Cu^{2+} ions was not identical in all test solutions, but that does not much affect the analytical linearity of permittance versus concentration of iron. Only Cu^{2+} ions have slight absorbancy at 722nm, therefore, other blank solution (copper blank) was also prepared simply by diluting with distilled water (to 50.0ml) the experimental volume of cupric nitrate, nitric acid and chloroacetic acid solutions. The absorption spectrum of the RB solution when obtained against copper blank, then also absorbing system proved its absorption maxima at 722nm. The results obtained against true blank do not differ significantly from those obtained against copper blank. So, all the measurements were carried out using free copper ions solution as a blank or reference.

Analytical performance of the method

The test solutions of iron prepared as mentioned in method confirms that, at the measured and excess con-

centration of EDTA, the optical density of [Cu(II)-EDTA]$^{2-}$ system was directly proportional to the concentration of surplus EDTA and inversely proportional to the concentration of iron. Because, the extent of chelation reaction that occurred between Fe^{3+} and excess of EDTA is governed by only the concentration of Fe^{3+}. Therefore, the concentration of surplus EDTA left after complexation of Fe^{3+} was inversely proportional to the concentration of iron and hence permittance[11] of test solutions was observed directly proportional to the concentration of iron. After measurement of %T at 722nm of [Cu(II)-EDTA]$^{2-}$ absorbing system (each TS and RB) against TB as a reference, the clearance of test solution was calculated[11] and the logarithm of clearance (permittance) of the absorbing system was determined by using following eq. (1). It was observed that, permittance of the test solution is linear function of concentration of iron and was dependent only on the concentration of iron. Therefore, the linearity of permittance against the concentration of iron was used for construction of calibration curve. With 1.0cm optical path of the absorbing system the proportionality constant determined for determination of iron.

Permittance and permittance coefficient

The permittance[11] (Pr) of the test solution was calculated by using following eq. (1)

$$Pr = \log \frac{\%T_{TS}}{\%T_{RB}} \quad (1)$$

In this equation, $\%T_{TS}$ and $\%T_{RB}$ designates the percent transmittance of the test solution and reagent blank solution respectively, measured against the same reference solution. The relationship between permittance (Pr) of test solution and concentration (c) of quencher analyte[11] in it was reported in earlier study[15] and was used here for determination of proportionality constant/ permittance coefficient (a′) of 1.0cm path length (b) absorbing system. Eq. (2).

$$a' = \frac{Pr}{bc} \text{ (concentration of quencher analyte in g } L^{-1}) \quad (2)$$

In this experiment, the quantitative determination of iron in the range of 1.0mg to 10.0mg was carried out at 722nm by using different volumes (5.0ml, 6.0ml, 7.0ml and 8.0ml) of the absorbing system's reagents. The copper blank solution used as a reference for these measurements. Permittance value of the test solutions was observed directly proportional to the concentration of iron (TABLE 1) and even if the concentration of reagents was altered, the permittance is constant for a fixed concentration of iron. Similarly to earlier the study[15] in this experiment it is observed that, at a fixed wavelength, permittance is dependent only on concentration of the analyte and is independent on the concentration of absorbing system's reagents. At 722nm, the permittance coefficient at every different concentration of Fe^{3+} as well as the volume of reagents is also nearly constant.

The values of permittance (TABLE 1) are little bit more at higher concentration of iron because, the yellow color intensity of ferric-EDTA chelate fades the blue color intensity copper-EDTA chelate (have low concentration at higher concentration of iron) through generating the green color to test solution. This effect also increases value of the permittance coefficient corresponding more, so the average value of permittance coefficient was considered for determination of analyte. In these determinations (TABLE 1) the average value of permittance coefficient was found equal to 0.5168 lit.g^{-1}cm^{-1} and which was for determination concentration of the stock solution of iron (1.0 mg ml^{-1}) from which the test solutions were prepared.

Magnitude of permittance and permittance coefficient

The concentration/volume of reagents does not affect the permittance as well as permittance coefficient (TABLE 1) but dilution (of the test solutions) factor shows pronounced effect on permittance. This study was carried out through quantitative determination of iron in the range of 1.0mg to 10.0mg (with the 5.0ml volume of the reagents) at the 25ml, 50ml and 100ml final dilution of test solutions. The result of these assay (TABLE 2), elucidates that, the value proportionality constant [calculated with eq. (2)] was observed decreasing with increase in final dilution volume of test solutions. This is because, the number of absorbing species per unit path length in the solution decreases with dilution. For result reported in TABLE 2, the average proportionality constants are 20.656 at 25.0ml, 10.338 at 50ml and 5.171at 100ml final dilution. From this it is clear that, when dilution volume of test solutions is doubled, the proportionality constant was decrease

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TABLE 3 : Results obtained at 722 nm in the quantitative determination of iron in Livogen-Z, Ferium-xt and Orofer-xT tablets, permittance coefficient values are compared for determination concentration of sample

Volume of 0.05M EDTA and 0.05M $Cu(NO_3)_2$	Iron sample analyzed	Observed permittance coefficient ($lit.g^{-1}cm^{-1}$)	Conc. of iron solution found ($mg\ ml^{-1}$)	Error in %
5.0 ml each	1.0mg ml^{-1} Fe^{3+}	0.51674	1.0000	0.00
	2 Livogen-Z	0.51673	0.9999	0.01
	1 Ferium-xt	0.51697	1.0005	0.05
	1 Orofer-xT	0.51666	0.9998	0.02
6.0 ml each	1.0mg ml^{-1} Fe^{3+}	0.51669	1.0000	0.00
	2 Livogen-Z	0.51691	1.0004	0.04
	1 Ferium-xt	0.51673	1.0001	0.01
	1 Orofer-xT	0.51696	1.0005	0.05
7.0 ml each	1.0mg ml^{-1} Fe^{3+}	0.51697	1.0000	0.00
	2 Livogen-Z	0.51697	1.0000	0.00
	1 Ferium-xt	0.51683	0.9999	0.01
	1 Orofer-xT	0.51678	0.9996	0.04

nearly equal to half but at one liter dilution is permittance coefficient (measured in $lit.g.^{-1}cm^{-1}$) was observed unchanged.

The second important factor which affects the magnitude of permittance and permittance coefficient is the wavelength selected for measurement. The wavelength determines the extent of absorption and hence the readings of %T; consequently, execute the marked effect on the values of these two parameters. The $[Cu(II)\text{-}EDTA]^{2-}$ absorbing system in chloroacetic acid and nitric acid medium was showed the λmax at 722nm. Along with λmax wavelength, when same test solutions were measured at other wavelengths that generates the different values for permittance and permittance coefficient. That means the magnitude of permittance and also permittance coefficient (a′) is absolutely administrated by the wavelength selected for analysis. The magnitude of both of these parameters was observed maximum at system's λmax wavelength. Therefore, for achieving the greater sensitivity for the method, measurements were carried out at the absorption maxima (722nm) of the absorbing system.

Determination of iron in iron tablets

The proposed method was applied for determination of iron in Livogen-z, Ferium-xt and Orofer-xT tablets. The sample (two tablets of Livogen-z, one tablet of Ferium-xt, or one tablet of Orofer-xT) was heated with 15ml of conc. HCl followed by addition of 5ml of conc. HNO_3. The organic matter was destroyed by treatment with 5-6ml of 70% perchloric acid. (WARNING: Boiling perchloric acid can result in serious explosions). The solution was slowly heated in fuming hood

TABLE 4 : Effect of cations on determination of iron, results obtained in the determination of iron from 1.0mg to 10.0mg, the value permittance coefficient was determined at 722nm in absence and in presence of different concentration of cations

Cation added as interference	Amount added (mg)	Observed permittance coefficient ($lit.g^{-1}cm^{-1}$)	Conc. of iron solution found ($mg\ ml^{-1}$)	Error in %
Standard	0.00	0.51690	1.0000	0.00
Aluminum	10.0	0.51696	1.0002	0.02
	20.0	0.51695	1.0001	0.01
	30.0	0.51690	1.0000	0.00
	40.0	0.51697	0.9994	0.06
Barium	10.0	0.51679	0.9998	0.02
	20.0	0.51705	1.0003	0.03
	30.0	0.51684	0.9999	0.01
	40.0	0.51683	0.9998	0.02
Calcium	10.0	0.51683	0.9998	0.02
	20.0	0.51696	1.0002	0.02
	30.0	0.51663	0.9995	0.05
	40.0	0.51700	1.0002	0.02
Cadmium	10.0	0.51676	0.9997	0.03
	20.0	0.51704	1.0003	0.03
	30.0	0.51683	0.9998	0.02
	40.0	0.51688	0.9999	0.01
Lead	10.0	0.51689	0.9999	0.01
	20.0	0.51695	1.0001	0.01
	30.0	0.51677	0.9997	0.03
	40.0	0.51704	1.0003	0.03
Magnesium	10.0	0.51676	0.9997	0.03
	20.0	0.51704	1.0003	0.03
	30.0	0.51683	0.9998	0.02
	40.0	0.51688	0.9999	0.01
Manganese	10.0	0.51696	1.0002	0.02
	20.0	0.51695	1.0001	0.01
	30.0	0.51690	1.0000	0.00
	40.0	0.51677	0.9997	0.03
Zinc	10.0	0.51683	0.9998	0.02
	20.0	0.51680	0.9998	0.02
	30.0	0.51690	1.0001	0.01
	40.0	0.51687	0.9999	0.01

for about 20-25 minutes; at this stage maximum of the acid fumes were ceased. With the addition of 10ml of distilled water, the sample solution was again boiled for 10 minutes. The solution was cooled and diluted nearly to 90ml with distilled water. With drop wise addition of conc. HNO_3, the pH of sample solution was adjusted equal to pH (=0.48) of standard solution containing 1.0mg ml^{-1} iron. The sample solution was filtered after dilution to 100ml and the amount of iron was determined by the recommended method. The results of this determination are represented in TABLE 3.

The iron tablets contain ferrous iron generally in the form of ferrous ascorbate or ferrous fumarate. When the tablets were digested with these acids, the ferrous iron gets oxidized to ferric iron. The concentration of iron in the sample solutions of tablet (two tablets of Livogen-z, one tablet of Ferium-xt, or one tablet of Orofer-xT) at 100ml dilution is 1.0mg ml^{-1}. Therefore, 1.0ml to 10.0ml of sample aliquots were tested for determination of iron in the range of 1.0mg to10.0mg and the value of the permittance coefficient thus obtained was used for determination of concentration of iron in stock solution of iron tablets. That is, the accuracy of method was studied with permittance coefficient; values obtained in the sample analysis are compared with those obtained in the analysis of standard Fe^{3+} solution of same strength and same pH.

Interferences in the determination of iron

The type of interference can be predicted form the formation constant[9, 10] of the EDTA chelates of the metal cations. Therefore, the interfering cations can be classified into two groups. The first group is composed of those cations whose EDTA chelates in acidic medium are sufficiently stable comparative to iron chelate. The EDTA chelate of Bi^{3+} is nearly stable as Fe^{3+} chelate, accordingly Bi^{3+} is the serious interfering cation in determination of iron. The second type of interfering ions includes those cations which do not compete with iron but with copper for the EDTA. These are the cations which forms more stable chelate than copper chelate. At such strongly acidic pH 1.15, no any divalent metal forms more stable chelate than copper chelate. The cations whose EDTA chelate is less stable than copper chelate, particularly the aluminum, barium, calcium, cadmium, lead, magnesium, manganese, zinc and as well the copper does not interferes in iron determination. The interference study of copper was not carried out in this experiment because that was added in excess for generation of absorbing system. The interference study was carried out by adding 10mg, 20mg, 30mg or 40mg of these metal cations separately in to the test solutions containing 1.0mg to 10.0mg of iron. The interfering cation of same concentration was also added in true blank solution but not in the reagent blank solution. The result of the interference study is reported in TABLE 4, in the form of permittance coefficient. The values of permittance coefficient in absence (only with standard 1.0mg ml^{-1} Fe^{3+}) and in presence (with standard 1.0mg ml^{-1} Fe^{3+} plus the added cation) of interference are observed nearly same. At pH 1.15, all of these metal cations up to 40mg do not interfere in the determination of iron. When the added metal cations interfere in the determination which increases the %T reading of test solutions, consequently that raises the values of permittance as well permittance coefficient. The concentration of added cation when reaches in excess, that increases the optical density of the test solutions with respect to regent blank solution. Hence, the %T readings were observed decreased and that decreases the values of permittance and permittance coefficient. In the previous literature[6,7] the inferences study was also completed.

CONCLUSIONS

The method described here for determination iron is based on the measurement of concentration of surplus EDTA through generating the $[Cu\text{-}EDTA]^{-2}$ absorbing system. The absorbing system was found excellent (for determination of iron) because of its formation and stability at strongly acidic pH 1.15 to which quantitatively chelation of trivalent Fe^{3+} was attained. At this pH, many divalent metal cations (TABLE 5) do complexed by EDTA, this makes the process selective. The sufficient difference in the stability constant of $[Fe\text{-}EDTA]^{-1}$ chelate and $[Cu\text{-}EDTA]^{-2}$ chelate, the stability of iron-EDTA chelate is not affected because of the addition of relative larger amount of Cu^{2+} ions. For the same reason that, copper ions does not interferes in the determination iron. The linearity between permittance and the concentration of iron was main-

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tained even at low concentration (1.0mg) of iron. The lower concentration of iron (less than 1.0 mg) is not determined in this experiment, but it is possible through increasing the sensitivity[15] of the method by decreasing the volume/concentration of reagents; since permittance and permittance coefficient are not preside over the concentration of reagents. The proposed method is very simple, easy to execute and which proved to be a better method as compared to other methods involve the step of preconcentration of analyte. The sensitive of the method practiced here was found up to 1.0mg of iron, when determined with 5.0ml of 0.05M EDTA and 5.0ml of 0.1M $Cu(NO_3)_2$ and produces the reproducible results with good accuracy. The method also found excellent over the photometric titration of iron with EDTA since, the graphical method of determination of exact end point is tedious and time consuming process. When the proportionality constant at specific dilution (or permittance coefficient) is determined for standard solutions of known concentration, in this method the concentration analyte can be determined directly with eq. (1) reported in earlier study[15]. The proposed method also neglects a step of standardization of reagents, since it involves the measurement of permittance of TS with respect to RB. Excluding only the analyte, the composition of the reagent blank must be identical in every respect to test solutions. This is the only care have to be taken for the good linearity. The results reported in the TABLE 4 showed that the method is excellent for the determination of iron in iron tablets.

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