

SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH BIACETYL OXIME THIOSEMICARBAZONE

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A spectrophotometric method is described for the determination of the ferrous ion, based on the reaction of the latter with biacetyl oxime thiosemicarbazone under the formation of a red-coloured complex. The method requires a high excess of the reagent. With the optimum concentration of perchloric acid (0.05M), 1.2 µg Fe can be determined in 10 ml solution, after a preceding reduction of the possibly present ferric ion by ascorbic acid.

Biacetyl oxime thiosemicarbazone (H_2L) has been described as a reagent suitable for the determination of manganese¹ and oxygen². During the study of the stability of complexes of H_2L with transition metals in aqueous-ethanolic solutions, ferrous ions were established³ to form intensely red solutions, with the absorption maximum at 507 nm ($6250 \text{ l cm}^{-1} \text{ mol}^{-1}$). This red complex is formed in a strongly acidic medium and in the absence of air. In the presence of an excess of a reducing agent (*e.g.* ascorbic acid), the red colour is stable even in the presence of air; otherwise the complex is oxidized and the solutions turn brown. The high value of molar absorption coefficient together with the time stability of the ferrous complex in a solution suggest the possibility of an analytical application.

EXPERIMENTAL AND RESULTS

Chemicals and apparatus. The absorbances of solutions of the complex studied were measured on a spectrophotometer Spekol (Zeiss, Jena) with an amplifier ZV, in 1 cm cells at the wavelength of 507 nm. The blank reference solution was of the same composition, not containing, however, the ferrous salt. The pH values were measured on a pH-meter Precision OP-205 (Radelkis, Budapest); the glass electrode was calibrated by using standard solutions of NBS. Standard solutions of the ferrous salt were prepared by dissolving ferrous sulfate in solutions of various concentrations of perchloric acid and ascorbic acid. Solutions of metal salts for studying the effect of interfering ions were prepared from the corresponding nitrates or sulfates. All the chemicals mentioned were p.a. purity. $4 \cdot 10^{-2} \text{ M}$ stock solution of biacetyl oxime thiosemicarbazone in 96% (W/W) ethanol was kept in a refrigerator; the synthesis of the reagent has been described by Horvorka and Holzbecher⁴. All the studied solutions of the ferrous complex contained 40% (W/W) ethanol.

Study of Reaction Conditions

The absorbance of solutions of the ferrous complex of biacetyl oxime thiosemicarbazone was studied in 0.01M-HClO₄ in the presence of 2% ascorbic acid, with the total concentration of the ferrous salt $4.0 \cdot 10^{-5}$ mol/l and that of H₂L $2.0 \cdot 10^{-3}$ to $4.0 \cdot 10^{-2}$ mol/l. The maximum absorbance of the solutions was attained at $c_{H_2L} = 2 \cdot 10^{-2}$ mol/l. The absorbance increased in the dependence on time, from 0.192 (15 minutes) through 0.205 (60 minutes) to 0.220 (120 minutes). With the concentration of ascorbic acid less than 1%, the complex is unstable and the solutions turn brown during 10 minutes. When the concentrations 1 to 20% are used, the coloration is stable and its time development depends on the concentration of perchloric acid and on the period of standing of the mixture of the ferrous salt with ascorbic acid before the reagent is added. The effect of the concentration of perchloric acid on the formation of the ferrous complex was studied under the conditions given in Table I; in the medium of 0.25M-HClO₄ the solution was turbid from the beginning. The effect of the standing period of the mixtures of the ferrous salt with ascorbic acid of various concentrations on the complex formation is apparent from Table II. Identical results were obtained with mixtures heated on a water bath up to 50°C for 5–10 minutes and then cooled before adding the reagent. The effect of the concentration of the reagent on the complex formation under the optimum conditions follows from Table III. The interfering effect of some cations was followed at $c_{HClO_4} = 0.05M$, $c_{Fe} = 4.0 \cdot 10^{-5}M$, $c_{H_2L} = 2.0 \cdot 10^{-2}M$ and in the presence of 1% ascorbic acid in the mixture studied. The absorbances were measured after a standing period of 30 minutes. The results are represented on Fig. 1.

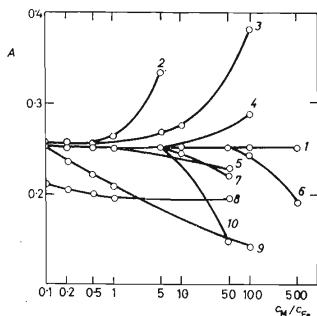


FIG. 1

Effect of Foreign Ions on the Absorbance of the Ferrous Complex

$4 \cdot 10^{-5}M\text{-Fe}^{2+}$, $2 \cdot 10^{-2}M\text{-H}_2\text{L}$, $5 \cdot 10^{-2}M\text{-HClO}_4$, 1% ascorbic acid, $\lambda = 507$ nm, absorbances measured after 30 minutes standing period of the mixtures. 1 Mn, Zn, Ba, Ca, Sr, Mg, Th; 2 Co; 3 Ni; 4 Sc; 5 Bi; 6 Cd; 7 Al; 8 Cu; 9 Ag; 10 Pb.

TABLE I

Dependence of the Formation of the Ferrous Complex on Time for Various Concentrations of Perchloric Acid ($4 \cdot 10^{-5} \text{M-Fe}^{2+}$, $2 \cdot 10^{-2} \text{M-H}_2\text{L}$, 2% Ascorbic Acid; λ 507 nm)

c_{HClO_4} mol/l	Absorbance, min					
	start	15	30	60	120	240
0.01	0.145	0.147	0.163	0.175	0.240	0.250
0.05	0.225	0.255	0.255	0.254	0.255	0.255
0.08	0.265	0.280	0.292	0.290	^a	^a
0.1	0.285	0.288	0.294	0.290	^a	^a

^a The solution is slightly turbid.

TABLE II

Dependence of the Formation of the Ferrous Complex on the Standing Period of the Mixture of the Ferrous Salt with Various Amounts of Ascorbic Acid Before the Addition of the Reagent ($4 \cdot 10^{-5} \text{M-Fe}^{2+}$, $5 \cdot 10^{-2} \text{M-HClO}_4$, $4 \cdot 10^{-2} \text{M-H}_2\text{L}$)

Standing period min	% ascorbic acid in the mixture	Absorbance (min) after the addition of H_2L				
		5	15	30	60	120
0	0.2	0.170	0.190	—	0.215	0.227
	1	0.205	0.216	0.223	0.230	0.245
	2	0.216	0.225	0.236	0.244	0.248
	4	0.232	0.242	0.244	0.252	0.252
30	0.2	0.152	0.224	0.245	0.245	0.250
	1	0.225	0.232	0.238	0.245	0.248
	2	0.234	0.242	0.244	0.244	0.248
	4	0.240	0.247	0.255	0.250	0.250
60	0.2	0.198	0.210	0.220	0.250	0.250
	1	0.220	0.229	0.250	0.250	0.250
	2	0.231	0.230	0.250	0.260	0.250
	4	0.242	0.242	0.250	0.260	—
120	0.2	0.238	0.248	0.250	0.255	0.255
	1	0.250	0.250	—	0.255	0.255
	2	0.250	0.265	—	0.260	0.255
	4	0.255	0.255	0.250	0.250	0.255

Calibration and Analytical Procedures

2 ml of the studied solution of the ferrous salt or of the sample analyzed, containing 1–20 $\mu\text{g Fe}$ in 0.25M-HClO₄ and 5% ascorbic acid, are transferred in a 10 ml flask. 5 ml of alcoholic solution of $4 \cdot 10^{-2}\text{M-H}_2\text{L}$ are added and the solution is brought to volume with water. The mixture is allowed to stand for 30 minutes and its absorbance is then measured in 1 cm cells at the wavelength of 507 nm against a blank solution of the same composition, but not containing the ferrous salt. The solution of the standard as well as that of the sample in 0.25M-HClO₄ and 5% ascorbic acid must be prepared at least 1 hour before mixing with the reagent.

Reproducibility of Iron Determination and Detection Limit

The reproducibility of the determination of iron in the absence of foreign ions by using the procedure described was examined in the range of validity of the Lambert-Beer law (1–20 $\mu\text{g Fe}/10\text{ ml}$). The absorbance measurements of nine different samples were repeated five times, always with freshly prepared solutions. The standard deviation was calculated by the linear regression method⁵ from the relation

$$s = [(y_i - Y_i)^2 / (n - 2)]^{1/2},$$

suitable for spectrophotometric determinations of trace contents⁶. Here y_i represent the absorbances corresponding to the given x_i values ($\mu\text{g Fe}$), while the Y_i values were calculated from the regression equation. The estimate of the standard deviation is $s = 7.5 \cdot 10^{-3}$.

The detection limit for the determination of iron by the method studied is 1.2 $\mu\text{g Fe}/10\text{ ml}$, as calculated from the relation⁵ $x_{\text{lim}} = \bar{x}_0 + 3s_0$ (\bar{x}_0 is the mean value, calculated from four measurements of absorbances of the blank experiment, and s_0 is the standard deviation for the blank experiment).

CONCLUSION

The studied spectrophotometric method for the determination of bivalent iron with biacetyl oxime thiosemicarbazone is very sensitive (detection limit 0.12 $\mu\text{g Fe}/\text{ml}$,

TABLE III

Dependence of the Absorbance on the Concentration of the Reagent Under the Optimum Conditions ($4 \cdot 10^{-5}\text{M-Fe}^{2+}$, 2% Ascorbic Acid, $5 \cdot 10^{-2}\text{M-HClO}_4$, λ 507 nm)

$c_{\text{H}_2\text{L}} \cdot 10^2$ mol/l	Absorbance, min			
	start	15	30	60
1.2	0.221	0.230	0.240	0.245
1.6	0.225	0.250	0.250	0.249
2.0	0.230	0.255	0.255	0.255
2.4	0.250	0.258	0.250	0.255
3.0	0.255	0.260	0.261	0.260
4.0	0.255	0.260	0.255	0.260

sensitivity according to Sandell 43 ng/cm²). The reagent can be compared, in that respect, with 2,2'-dipyridyl, 1,10-phenanthroline and its derivatives, chromazurol S, quercetin, etc. The advantage of the method is the low pH value, at which the determination of iron can be carried out, the disadvantage is the dependence of absorbance on the concentration of perchloric acid and the possibility of precipitation of the reagent at too low pH values ($\geq 0.1M-HClO_4$, Table I). The method is not interfered (Fig. 1) by an excess of the ions Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Zn^{2+} , and Th^{4+} (500 : 1), Cd^{2+} (50 : 1), Sc^{3+} (5 : 1); the ions Bi^{3+} , Co^{2+} , Ni^{2+} , and particularly Cu^{2+} , Ag^{2+} , and also Hg^{2+} , precipitating with the reagent, interfere.

A high excess of the reagent is necessary to attain the maximum absorbance of the ferrous complex in the range of the used low concentrations of iron. To explain this fact it must be taken into consideration that the reaction of ferrous salt with the reagent studied does not occur instantaneously (Table III); the high concentration of the free reagent affects favourably the complex formation rate.

The explanation of the observed high value of the absorption coefficient can be, according to Král⁷, based on the assumption that the most intensely colored complexes of bivalent iron (and also of some other transition metal ions) with ligands like 2,2'-bipyridyl, 1,10-phenanthroline, 8-hydroxyquinoline are formed only after the formation of noncentrosymmetric units, where usually one or three ligand molecules join the central atom; regarding the structure proposed for complexes of biacetyl oxime thiosemicarbazone with some bivalent metals⁸ both possibilities have to be considered, but the formation of 1 : 1 complex is more probable in acid solution.

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