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DETERMINATION OF IRON(III) WITH N-PHENYLCINNAMOHYDROXAMIC ACID AND SODIUM AZIDE BY EXTRACTION AND SPECTROPHOTOMETRY

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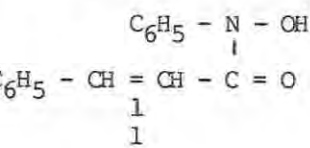
ABSTRACT: N-Phenylcinnamohydroxamic acid(PCHA) was found to react with iron(III) in the presence of azide to form an orange coloured ternary complex having a composition of 1:2:2 ($Fe:N_3^-$:PCHA). The complex was found to be stable and quantitatively extractable into ethylacetate from 0.1 - 0.9M hydrochloric acid solutions allowing reproducible and reliable spectrophotometric determination of iron. The effects of foreign ions and of experimental variables on the extraction and determination of iron(III) have been studied. On the basis of these studies a simple, precise, sensitive, and highly selective method has been developed for the determination of iron(III) by extraction and spectrophotometry. The method has been applied successfully for the determination of iron in blood and steel samples.

INTRODUCTION

N-Phenylcinnamohydroxamic acid (PCHA), 1, has been used for the extraction and spectrophotometric determination of iron(III) as a binary complex (1-3). However, titanium(IV), zirconium(IV), vanadium(V), molybdenum(VI), and tungsten(VI), which are commonly associated with iron in ores and alloys, interfere and require prior separation. The introduction of a third component (an auxiliary ligand) into a binary complex (simple complex) leads to the formation of a ternary system (mixed ligand complex) with advantageous properties(4) and allows higher sensitivity and selectivity of determination to be achieved. Hence, the extraction of iron(III) from aqueous sodium azide medium with PCHA has been studied in detail to improve the selectivity of the method by the formation of ternary complex. The present investigation has resulted in the development of a simple, precise, sensitive, and highly selective method for the determination of iron(III) as a ternary complex with PCHA and azide by solvent extraction and



spectrophotometry. The method has been found to be applicable to the analysis of steel and blood samples for iron without prior separation. The method has also been found to be more sensitive and selective than the earlier methods based on formation of ternary complexes of iron(III) with azide and other reagents (5,6).

EXPERIMENTAL

Apparatus and Reagents

A Beckman Model 24 UV-Vis spectrophotometer equipped with 1-cm matched quartz cells was used for absorbance measurements. A Beckman Chem Mate pH meter was used for the measurements of pH.

A standard solution of iron(III) was prepared by dissolving 4.0402g $Fe(NO_3)_3.9H_2O$ (BDH, AnalaR) in 100 ml of 1:5 (v/v) nitric acid and diluted to 1.0 litre with water. The solution was standardized volumetrically (7). A working solution was prepared by diluting a suitable aliquot of the standard solution to a known volume with water. N-Phenylcinnamohydroxamic acid was prepared by the reported method(8). A 0.005 M solution of PCHA in twice distilled ethylacetate was used for the extraction work. A 2.0 M solution was prepared by dissolving sodium azide (Hopkins and williams, AnalaR) in water. Solutions of foreign ions were prepared by dissolving known quantities of reagent grade salts in water to give 10 mg ml^{-1} of the ion in question. The solutions were acidified wherever necessary to prevent hydrolysis. Purified and redistilled solvents were used. All the other chemicals used were of analytical reagent grade.

Preparation of Sample Solutions

A measured amount of the blood sample (2 ml) was heated in a 250 ml Kjeldahl flask with 10 ml of a mixture of nitric, sulphuric, and perchloric acids in the ratio of 3:1:1(9) and evaporated to almost dryness. The residue was dissolved in 50 ml of acidified (hydrochloric acid) water by heating. The solution was transferred quantitatively into a 100 ml volumetric flask and diluted to volume with water. Suitable aliquots of the sample solution were taken for the analysis.

A weighed quantity of the steel sample (0.1g) was heated gently in a 400 ml beaker with 10 ml of concentrated nitric acid until the brisk reaction ceased, 5-10 ml of aqua regia was added and the solution was evaporated to near dryness to expel nitrogen oxides.The residue was dissolved in 50 ml of slightly acidified (hydrochloric acid) water by heating. The undissolved silicic acid and hydrated tungstic acid were filtered off and washed several times with hot water. The filtrate and washings were diluted to volume in a 500 ml volumetric flask with water. Suitable aliquots of the sample solution were taken for the analysis.

General Procedure

An aliquot of the solution containing 25-175 µg of iron (III)

was transferred into a 100 ml separatory funnel and 5 ml of 2M sodium azide solution was added to it. The acidity and volume of the aqueous phase were adjusted to 0.4-0.6 M and 10 ml with concentrated hydrochloric acid and water, respectively. A 10 ml aliquot of 0.005 M PCHA solution in ethylacetate was added to the funnel, the mixture was shaken vigorously for two minutes, and the funnel was allowed to stand to separate the two phases. The organic phase was collected in a 25 ml volumetric flask after drying over anhydrous sodium sulphate and diluted to volume with ethylacetate. The absorbance of the orange coloured extract was measured at 447 nm against the reagent blank.

For calibration, 0.50, 0.75, 1.00, 1.25, and 1.50 ml of the standard solution (100µg Fe ml^{-1}) were used through the procedure.

RESULTS AND DISCUSSION

Absorption Spectra

Several water-immscible organic solvents such as benzene, toluene, xylenes, chlorobenzene, chloroform, carbon tetrachloride, ethylacetate, amylacetate, and amylalcohol were found to extract the Fe(III) - N_3^- - PCHA complex from the aqueous phase. The absorption spectrum of the complex in the visible region was found to be similar in all the solvents. However, slight variations in the intensity of the absorption bands were noticed. Ethylacetate was found to be the most suitable solvent because the quantitative extraction of the complex was readily accomplised in it. It was also preferred due to the higher solubility of PCHA in it than in other solvents and due to its relatively lower toxicity.

The absorption spectra of PCHA and the Fe(III) - N_3^- - PCHA complex in ethylacetate have been determined in the visible region under different reaction conditions. The spectrum of PCHA showed negligible absorption in the region 700-500 nm, slight increasing absorption in the region 500-400 nm, and strong absorption beyond 400 nm (2,3). Thus a reagent blank is necessary for the precise measurements of absorbance at wavelenghts shorter than 500 nm.

The spectrum of the red coloured Fe(III) - N_3^- binary complex in aqueous solution showed an absorption band at 460 nm(10). However, the binary complex was found to be not extractable into the organic solvents. It was only the ternary Fe(III) - N_3^- - PCHA complex that was found to be completely extractable into the organic solvents. The spectrum of the ternary complex showed an intense and sharp absorption band (ε = 11500) at 375 nm and a relatively weak and broad absorption band (ε = 7500) at 447 nm which are due to Π-Π^* and charge transfer (L→M) electronic transitions, respectively. Although the absorption band at 375 nm was more intense the less intense absorption band at 447 nm was selected for the quantitative determination because of the strong absorption of the reagent at shorter wavelengths.

The position of the absorption band of the ternary complex extracted in to ethyl acetate was found to be unaffected by the changes in the concentrations of the constituents and hydrochloric acid in a wide range indicating the extraction of a single complex

species under each condition.

It has also been found that iron(III) cannot be extracted from aqueous solution in the absence of azide by the ethylacetate solution of PCHA. Iron(III) forms binary complex with PCHA when the later is introduced as an ethanolic solution which can subsequently be extracted into ethylacetate and other water-immiscible organic solvent as reported in literature (1-3).

Effect of Variables

The optimum acidity range of the aqueous phase for the complete extraction of iron(III) was found to be 0.1 - 0.9 M with respect to hydrochloric acid. At higher acidity the degree of extraction of the metal ion decreases due to the protonation of the ligands resulting in an incomplete formation of the ternary complex while at lower acidity the complex formation is retarded due to hydrolysis of the metal ion resulting in an incomplete extraction of iron(III). The optimum concentration range of azide in the aqueous phase for the complete extraction of iron(III) was found to be 0.5 - 2.0 M. At lower concentrations of azide the formation of iron(III) mixed ligand complex is incomplete while at higher concentrations of azide water soluble binary iron(III) - azide complex becomes more stable (11), resulting in an incomplete extraction of iron(III) under both conditions. A 25 - fold molar excess of PCHA was found to be necessary for the complete extraction of iron(III) from the aqueous phase. The necessity of the higher concentraction of PCHA for the complete extraction of iron(III) from azide medium indicates the greater stability of iron(III) - azide complex in the aqueous phase, i.e. azide is not easily replaceable by PCHA. A large excess of the reagent upto 100 - fold molar excess had no adverse effect on the extraction of iron(III) as a ternary complex.

The wavelength of maximum absorption and absorbance value of the coloured extract of the Fe(III) - N_3^- - PCHA complex was found to be not affected by the change in ionic strength of the aqueous phase between 0.1 and 1.0 M with respect to potassium nitrate. Variation in temperature of the aqueous phase between 20° and 40° C did not produce any change in the absorbance value of the coloured extract of the complex. It has also been found that the volume of the aqueous phase can be varied from 10 to 25 ml with respect to a fixed volume of 10 ml of the organic phase without any variation in the absorbance value or extraction efficiency of the system. However, more repetitive extractions were found to be necessary for the complete extraction of iron(III) from the larger volumes of the aqueous phase. It has been found that the order of addition of reagents has no effect on the characteristics of the coloured system. The iron(III) ternary complex was completely extracted into ethylacetate within two minutes. The absorbance value of the ethylacetate extract of the complex remained constant for at least seven days at $20^\circ \pm 2^\circ$ C.

Thus the method is free from the rigid control of experimental variables.

Photometric Characteristics of the Complex

The molar absorptivity, photometric sensitivity (12), the concentration range obeyed by Beer's law, and the optimum concentration range for the photometric determination evaluated from Ringboms plot (13) are summarized in Table 1. These results indicate that the method is sensitive and it can be applied for the determination of traces of iron.

Table 1. Photometric characteristics of the complex

λ_{max}	447 nm
ε	7500 l mole^{-1} cm^{-1}
Sensitivity	0.0074µg Fe cm^{-2}
Concentration range from Beer's law plot	0.5 - 9.0 ppm Fe
Optimum concentration range from Rigbom's plot	0.8 - 8.0 ppm Fe

Precision

The precision of the method was evaluated from ten independent analyses made on samples each containing 4 ppm of iron. The relative standard deviation was found to be 0.30%. These results indicate that the method is highly precise and gives reproducible results.

Composition of the Complex

The composition of the Fe(III) - N_3^- -PCHA ternary complex was determined by the continuous variations (14) and slope ratio (15) methods.

To determine the stoichiometric ratio of iron(III) to PCHA by the continuous variations method a series of solutions was prepared in which the mole-fractions of iron(III) and PCHA were varied between 0 and 1 at constant total concentration. The concentration of azide, the ionic strength, and the acidity were kept constant under optimum conditions throughout the series. The absorbance of the solutions of different composition was measured according to general procedure and plotted against the mole fraction of iron(III). The maximum obsorbance was found at the mole-fraction of 0.33 which indicated the stoichiometric ratio of iron(III) to PCHA to be 1:2 in the ternary complex.

To determine the stoichiometric ratio of iron(III) to PCHA by the slope ratio method a series of solutions was prepared in which the concentrations of iron(III) and azide, the ionic strength, and the acidity were kept constant and the concentration of PCHA was varied. The complex was extracted and the absorbance of the solutions of different composition was measured according to general procedure. The quantity log D_M was plotted against log [PCHA] (where D_M = concentration of iron in organic phase/ (total concentration of iron - concentration of iron in organic phase). The curve obtained gave a slope of 2.1 which indicated the

stoichiometric ratio of iron(III) to PCHA to be 1:2 in the ternary complex.

The stoichiometric ratio of iron(III) to azide was also determined by the slope ratio method. A series of solutions was prepared in which the concentrations of iron(III) and PCHA, the ionic strength, and the acidity were kept constant and the concentration of azide was varied. The complex was extracted by the general procedure and absorbance of the solutions of different composition was measured at 447 nm against the reagent blank. The quantity log D_M was plotted against log $[N_3^-]$. A straight line was obtained with a slope 1.98 which indicated the stoichiometric ratio of iron(III) to azide to be 1:2 in the ternary complex.

Thus the stoichiometric ratio of iron(III) to PCHA was found to be 1:2 by both the continuous variations and slope ratio methods while the stoichiometric ratio of iron(III) to azide was also found to be 1:2 by the slope ratio method in the ternary complex. Hence the overall composition of the Fe(III)-N_3^- -PCHA ternary complex is 1:2:2 (Fe:PCHA:N_3^-). Since the ternary complex is readily extractable into non-polar organic solvents it must be a electroneutral species. Therefore the formula of the ternary complex would be $Fe(N_3)_2L.HL$ where L^- and HL denote the anion and neutral molecule of PCHA, respectively.

Effect of Foreign Ions

The effects of foreign ions on the extraction and determination of iron(III) with PCHA and azide have been studied by adding known quantities of a desired ion to the solution containing 100 μg of iron(III). Extraction and determination of iron(III) was made according to the general procedure. The tolerance limit of foreign ions taken as concentration (ppm) which cause an error less than 2% are given in Table 2.

Titanium(IV) and vanadium(V) react with the reagents to form yellow and reddish violet coloured complexes, respectively, extractable into ethylacetate. Both complexes absorb strongly at 447 nm and so interfere. However, these interferences were overcome by masking titanium(IV) with fluoride and vanadium(V) with hydrogen peroxide(16).

The results given in Table 2 clearly indicate that almost all common ions which are normally associated with iron in ores, alloys, steels, and biological samples do not interfere in the determination of iron(III) with PCHA and azide. Hence the method is highly selective and can be applied for the determination of iron in diverse samples.

Application of the Method

In order to test the reliability of the newly developed method, it has been applied to the analysis of blood and steel samples for

Table 2. Tolerance limit of foreign ions in iron determination
Iron concentration = 4 ppm, $[N_3^-]$ = 1.0 M, [HCl] = 0.5 M.

Ion	Tolerance	Ion	Tolerance	Ion	Tolerance
Na^+	2000	Sn^{2+}	120	WO_4^{2-}	40
K^+	2000	Sn^{4+}	120	*Ti^{4+}	40
Li^+	2000	Bi^{3+}	400	Zr^{4+}	320
Ca^{2+}	1000	AsO_4^{3-}	400	**VO_2^+	40
Sr^{2+}	1000	SbO_4^{3-}	400	NH_4^+	2000
Ba^{2+}	1000	Ce^{4+}	400	Cl^-	2000
Mg^{2+}	1000	UO_2^{2+}	400	NO_3^-	2000
Be^{2+}	800	Th^{4+}	200	SO_4^{2-}	2000
Al^{3+}	400	Cr^{3+}	400	F^-	3000
La^{3+}	400	Mn^{2+}	400	AcO^-	400
Tl^+	400	Co^{2+}	400	Borax	400
Zn^{2+}	800	Ni^{2+}	400	HPO_4^{2-}	400
Cd^{2+}	800	Cu^{2+}	60	Citrate	40
Hg^{2+}	800	MoO_4^{2-}	400	Oxalate	40
		Tartarate	320		

*Masked by fluoride (3000 ppm).
**Masked by H_2O_2 (2 ml of 30%).

iron. The samples were decomposed and iron was determined according to the general procedure described above.

The iron content of the blood sample from an adult man was determined by the proposed method and also by 2,2' -bipyridyl (17,18) method for comparison. The results obtained by both the methods were essentially the same (Table 3), and fall within the range of iron content in whole blood reported for an adult man (19). Hence the proposed method is reliable and applicable for the determination of iron in biosamples.

Table 3. Determination of iron in blood

Method	Iron found* (mg/100 ml)	RSD (%)
Proposed method	77.24	0.30
2,2'-Bipyridyl method	77.41	0.35

Table 4. Determination of iron in BCS steels

BCS Steel No.	Iron certified (%)	Iron found*(%)
64a	83.45	83.89
241/1	65.87	65.25

*Average of triplicate analyses.

The iron content of two British Chemical Standard (BCS) steel samples was determined by the proposed method. The results of the analysis are given in Table 4. The experimental values are in good agreement with the certified values indicating the accuracy of the method.

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