

Therefore an electronic separation of 370 cm^{-1} attributed to the ground state ${}^2\Delta$ of the NiF molecule is justified.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH BIACETYL MONOXIME

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BIACETYL MONOXIME (BAM) has been reported as a photometric reagent for palladium¹, rhenium², molybdenum³, cobalt⁴, copper and nickel⁵. Literature survey shows that this compound has never been used as an analytical reagent for iron. However, as early as 1926, Taylor *et al.*⁶ reported that BAM forms a blue coloured water soluble complex with iron(II) in the presence of dilute sodium hydroxide which can be extracted into benzene and the colouration of the aqueous solution was unstable and completely destroyed on heating. In the course of our investigation we found that sodium hydroxide concentration should be critically maintained and it has a marked effect on the colour, intensity and extractibility of the complex. Thus BAM was not considered as a suitable reagent for iron. However, we found that when sodium hydroxide was replaced with ammonia, or methylamine in the presence of ascorbic acid as an anti-oxidant, a red coloured solution resulted whose intensity increased with rise in temperature. This iron complex could not be extracted into benzene. In this paper the characteristics and properties of iron(II)-BAM complex in the presence of ascorbic acid in ammonia or methylamine medium is described and a sensitive photometric method for determining iron in microgram level is proposed.

Procedure

To an aliquot of the solution containing 50 to 175 μg $(\text{NH}_3)/22$ to 80 μg (methyl amine) of iron(II) was added 2 ml of ascorbic acid (0.1 M) followed by 2.5 ml of BAM solution (0.1 M) and 5 ml of ammonia ($\sim 7\text{M}$) or 3 ml of methyl amine (40%). The solution was heated to 80–85° C for 5–10 min, cooled and the volume made up to 25 ml with distilled water. Absorbance was measured at 505 nm with NH_3 or 510 nm with methyl amine against a reagent blank.

Results and Discussion

A pH study of the complexation of BAM with iron(II) showed that the red complex gives a constant absorbance above pH 9.0 in ammonia or methyl amine medium. Excess of the amine did not effect the intensity of the colour.

The complexation between iron(II) and BAM in ammonia or methyl amine solution is slow and takes about 3 hours to reach equilibrium at room temperature ($27 \pm 1^\circ\text{C}$). The rate of the reaction can be increased by heating. A time-temperature study was made with solution containing 2.5 ml of 0.1 M reagent and 100 μg of iron(II). At various time intervals, the solutions were removed from the water bath, cooled and diluted to 25 ml with water and the absorbance was measured from 325 to 600 nm against water as reference. The results showed that the complex exhibited maximum absorbance at 495–515 nm with ammonia and 510 nm with methylamine after 5 min heating at 80–85° C. The colour produced in the reaction was stable for more than 10 hours. These conditions were therefore chosen for subsequent work. Reagent blanks prepared in a similar way did not show any absorption at 495–515 nm.

During the complexation between BAM and iron(II) which requires ammonia or methylamine, it is probable that the primary step is the reaction between the carbonyl group of BAM and amine resulting in the formation of an 'imine-oxime' compound.

Anti-oxidant

The red colour of the complex diminished in intensity on exposure to air but was stable on adding ascorbic acid. Several anti-oxidants were tested (sodium sulphite, hydroxylamine hydrochloride, hydrazine hydrochloride, sodium nitrite and ascorbic acid). Only ascorbic acid gave reproducible results.

Composition of the complex

The mole ratio method and the method of continuous variation were employed to determine the composition of the complex. These two methods showed conclusively that the complex contained one atom of iron to two molecules of the reagent. However, for complete complexation 5 and 10 fold excess of BAM is required in the methylamine and ammoniacal media respectively.

TABLE I
Characteristics of iron(II) complexes

Complex	λ_{\max} (nm)	ϵ (l/mol/cm)	Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	Validity of Beer's Law ($\mu\text{g}/\text{ml}$)	Optimal Concn. ($\mu\text{g}/\text{ml}$)
Fe(II)-BAM (NH_3)	495-515	5,050	0.011	0.0-20.0	2.0-7.0
Fe(II)-BAM (Methyl amine)	510	13,000	0.0045	0.0-9.0	0.9-3.25

TABLE II
Analyses of alloy samples

Sample	% Fe Present	% Fe Found
Sample A Co 20.5%, Cu 20.3%, Ni 24.4%, Zn 1.6%, Cr 5.4%, Mn 8.0%	5.30	5.19
Sample B Co 15.3%, Cu 10.3%, Ni 24.6%, Zn 15.3%, Cr 5.8%, Mn 13.0%, Al 5.4%	10.30	10.10

Beer's law, sensitivity, optimal concentration range are summarized in Table I. The standard deviation⁷ of the proposed method is 0.018 for 3 μg of iron per ml in a series of 10 determinations.

Effect of diverse ions

Of all the diverse ions studied, the following ions did not interfere (500 ppm) while working with 3 ppm of iron ($\pm 3\%$ error): sodium potassium, bromide, chloride, iodide, nitrate, oxalate, pyrophosphate, sulphate, tartrate and fluoride. Owing to the presence of excess ammonia or methylamine for the development of colour, most of the common ions precipitate, when present in high concentrations. Cobalt (10 ppm), nickel (5 ppm), and copper (5 ppm) do not interfere.

Analytical applications

The technique was applied to the determination of iron in two alloy samples. Table II summarizes the results. Iron was separated from interfering metal ions by extraction with methyl isobutyl ketone (MIBK) and benzene as proposed by Jackson and Philips⁸. It was quantitatively re-extracted with 10% ascorbic acid solution.

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A PROTEROZOIC STROMATOLITE FROM EAST AFRICA

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THE stratigraphic sequence of the Bukoban System (Late Proterozoic) in Tanzania and the Malagarasian in Burundi have been subjects of debate¹⁻³. Correlation of litho-units is rendered difficult because different units of the Bukoban are disconnected, and there is no established stratigraphic marker. It is difficult to distinguish the limestone members of the Ilagala Dolomitic Limestone and the older Kigonero Flags. The limestone members contain stromatolites. A systematic study of stratigraphically well recognized groups of stromatolites may contribute to solve the correlation problems.

Halligan¹ reports stromatolites from Bukoban rocks in north-western Tanzania. He refers them to similar forms described by Cahen⁴ from the Groupe de la Lindi of Zaire which Cahen called *Cryptozoon* or *Collenia*. Bertrand-Sarfati⁵ reports stromatolites from the Upper Precambrian of the Congo Basin and she correlates them with forms from Mauretania, the Haggat Massif and the Bushimai of Kasai. Gunatilaka¹ mentions stromatolites in association with