

SIMULTANEOUS DETERMINATION OF IRON(III) AND VANADIUM(V) WITH *N*-PHENYLCINNAMOHYDROXAMIC ACID AND THIOCYANATE BY EXTRACTION-SPECTROPHOTOMETRY

B. S. CHANDRAVANSHI*, ABIY YENESEW and ZERIHUN KEBEDE

Analytical Services and Research Unit, Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa (Ethiopia)

(Received 30th July 1984)

SUMMARY

N-Phenylcinnamohydroxamic acid (PCHA) reacts with iron(III) and vanadium(V) in the presence of thiocyanate to form water-insoluble orange and green complexes, respectively. The iron(III)-PCHA and vanadium(V)-PCHA-thiocyanate complexes can be quantitatively extracted into toluene and other common organic solvents at pH 1.5-2.0. The absorption spectra and composition of both complexes are described. The effects of foreign ions and of experimental variables on the extraction and determination of the two metal ions are studied. A simple, selective method is described for the simultaneous determination of iron(III) and vanadium(V) by extraction-spectrophotometry; absorbances are measured at 440 and 580 nm. Mixtures can be determined over the range 10^{-4} - 10^{-5} M in each metal. The method was applied successfully to the analysis of standard steels for iron and vanadium.

N-Phenylcinnamohydroxamic acid (PCHA) has been used for the determination of several metal ions [1-11], including the extraction-spectrophotometric determination of iron(III) [8, 9] and vanadium(V) [1, 10]. Successive extraction and spectrophotometric determination of these two metal ions have been reported [8, 9], but not their simultaneous determination, probably because of the very different conditions needed for the extraction of iron(III) and vanadium(V). Further study of the reactions of PCHA with these two metal ions under different conditions has led to the method for their simultaneous determination described below. In this procedure, *N*-phenylcinnamohydroxamic acid is used with thiocyanate for extraction and spectrophotometry. The method is simple, sensitive and selective, and does not need rigid control of experimental variables. The method compares well with earlier procedures for this purpose [12-14] and can be applied to the determination of iron and vanadium in alloy steels and complex mixtures.

EXPERIMENTAL

Apparatus and reagents

A Beckman Model 24 u.v.-visible spectrophotometer with 1-cm quartz cells and a Beckman Chem Mate pH meter were used. Analytical-grade reagents were used unless otherwise specified. Distilled water was used throughout.

Standard solutions of iron(III) and vanadium(V) were prepared from iron(III) nitrate nonahydrate and ammonium metavanadate, respectively, in water acidified with nitric acid; the solutions were standardized conventionally. An aqueous 0.50 M solution of ammonium thiocyanate was standardized by Volhard's method. Solutions of foreign ions (10 mg ml^{-1}) were acidified if necessary to prevent hydrolysis. The pH of solutions was adjusted with hydrochloric acid or ammonia (Spectrosol). Toluene and other solvents were redistilled.

The *N*-phenylcinnamohydroxamic acid (PCHA) was prepared as described previously [7]. A 0.005 M solution of PCHA in toluene was used.

Procedures

Preparation of sample solution. The steel sample (0.1 g) was heated gently in a 400-ml beaker with 10 ml of concentrated nitric acid until 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 solution was filtered through Whatman No. 42 filter paper to remove silicic acid and hydrated tungstic acid, the precipitate being 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 this solution were used.

Extraction of iron and vanadium. A solution containing 25–175 μg of iron(III) or vanadium(V) or both was mixed with 5 ml of 0.50 M ammonium thiocyanate and diluted to 25 ml with water, and the pH was adjusted to 1.5–2.0 with 1 M hydrochloric acid or 1 M ammonia solution. After quantitative transference to a 100-ml separatory funnel, the solution was extracted with 10 ml of the 0.005 M PCHA solution in toluene by vigorous shaking for 2–3 min. After phase separation, the organic phase was dried over anhydrous sodium sulphate (2 g), transferred quantitatively with toluene to a 25-ml volumetric flask and diluted to volume with toluene. The absorbance was measured after 40 min at 440 nm for iron(III), at 580 nm for vanadium(V), and at 440 and 580 nm for the simultaneous determination of the two metal ions, against the reagent blank.

For calibration, 0–2.5 ml of standard solutions of each metal ion ($50 \mu\text{g ml}^{-1}$) were taken through the procedure.

RESULTS AND DISCUSSION

Solvent for extraction and absorption spectra

Benzene, toluene, *o*-xylene, chlorobenzene, *o*-dichlorobenzene, chloroform, and carbon tetrachloride were found to extract both the complexes from the aqueous phase. Toluene was the most suitable solvent, giving quantitative extraction readily, and providing higher sensitivities for the colour reactions than the other solvents. The absorption spectra of the individual complexes were similar in all the nonpolar organic solvents but there were some variations in absorbances.

The absorption spectra are shown in Fig. 1. The reagent, PCHA, showed strong absorption only below 400 nm, with an absorbance maximum at 365 nm (π - π^* transition). Thus a reagent blank is necessary for precise measurements at <500 nm. The iron(III)-PCHA complex showed strong absorption bands at 440 and 375 nm; the spectrum was identical regardless of the presence or absence of thiocyanate, which proves that thiocyanate is not involved in the complex formation with iron(III). The vanadium(V)-PCHA complex showed strong absorbance at 380 nm and weak broad absorbance band around 475 nm in the absence of thiocyanate. In the presence of ethanol, a clearer absorption band appeared at 450 nm, possibly because of esterification [15]. When thiocyanate was added, the absorption bands at 380 and 450 nm were shifted to 373 and 430 nm, respectively, with an increase in intensity, and a new intense band appeared at 580 nm, indicating the formation of a mixed ligand complex. This spectrum was not affected by ethanol, suggesting the absence of a hydroxyl group in this complex. Probably the hydroxyl group in the vanadium(V)-PCHA complex is replaced by thiocyanate.

Composition of complexes

The compositions of iron(III)-PCHA and vanadium(V)-SCN-PCHA complexes were examined by the mole ratio [16] and continuous variations [17] methods and by a simple spectrophotometric method [18]. Both the mole ratio and Job's methods showed that the stoichiometric ratio of iron(III) to PCHA was 1:3 and the ratio of vanadium(V) to PCHA was 1:2 in the complexes; thiocyanate was kept at a constant concentration throughout these tests. To determine the stoichiometric ratio of vanadium(V) to thiocyanate in the mixed ligand complex, a series of solutions was prepared in which the

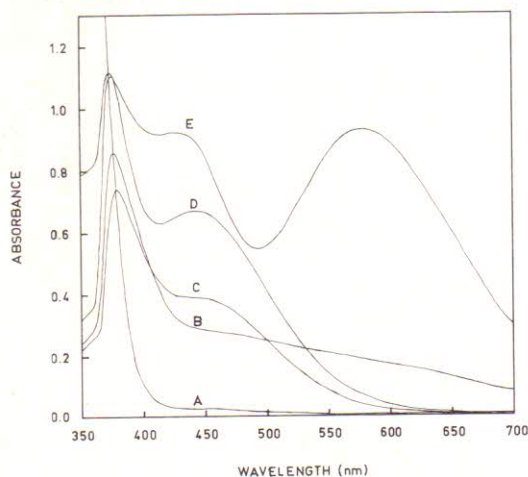


Fig. 1. Absorption spectra in toluene: (A) 2×10^{-3} M PCHA; (B) 8×10^{-5} M V(V)-PCHA; (C) 8×10^{-5} M V(V)-PCHA-ethanol; (D) 8×10^{-5} M Fe(III)-PCHA; (E) 1.2×10^{-4} M V(V)-SCN-PCHA (measured against reagent blank).