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# Extractive Spectrophotometric Determination of Chromium(III) with 1-(2-Pyridylazo)-2-naphthol

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**Synopsis.** 1-(2-Pyridylazo)-2-naphthol reacts with chromium(III), on heating at 80—90 °C for 35 min, at a pH of 3.2—3.7 in presence of acetate buffer. The reddish-brown chelate, extracted into 1-butanol, has two absorption maxima at 555 and 600 nm of equal intensity. The complex obeys Beer's law in the range 0.3—2.0 μg/ml, has molar absorptivity $1.28\times10^4$ at 555 nm.

1-(2-Pyridylazo)-2-naphthol, PAN, finds considerable application[1,2] as colorimetric reagent for determination of a number of metal ions. PAN has been found to be selective at lower pH values; hence a detailed investigation of chromium(III) has been carried out. This simple, sensitive and selective method is applied for the determination of chromium content in an alloy steel sample.

## Experimental

*Apparatus and Reagents.* A CΦ4 quartz spectrophotometer with 10 mm quartz cells was used for the absorption measurements. The absorption spectra was recorded on a Perkin-Elmer recording spectrophotometer, Type 402. A cambridge pH meter was used for all pH measurements.

Stock solution of Cr(III) containing 2 mg/ml of chromium was prepared from chromium(III) nitrate (J. T. Baker) and standardized[3] volumetrically. Experimental solutions were obtained by appropriate dilution of stock solution.

*1-(2-Pyridylazo)-2-naphthol.* 0.1% solution of 1-(2-pyridylazo)-2-naphthol (PAN) was prepared in methyl alcohol.

Buffer solution of pH 3.5 was prepared from 0.2 M sodium acetate and 0.2 M acetic acid.

*General Procedure.* An aliquot of chromium(III) solution containing <20 μg of chromium was taken, to which were added 5 ml of sodium acetate-acetic acid buffer, pH 3.5, and 1 ml of 0.1% PAN. The contents were shaken thoroughly, made to 15 ml and heated in a boiling water bath for 35 min, allowed to cool, made to 25 ml, and extracted in a separating funnel with 10 ml of butanol for 20 s. After separation of layers, organic phase was collected in a 10 ml volumetric flask containing 1 g of anhydrous sodium sulfate and absorbance of reddish-brown chelate was measured at 555 nm against the reagent blank prepared under similar conditions.

## Results and Discussion

*Effect of pH.* pH was varied from 0.5 to 7, and absorbance was found to be maximum (Fig. 1) in the pH range 3.2—3.7. Hence all studies were carried out at pH 3.5. Sodium acetate-acetic acid buffer was found to be the most suitable one.

*Effect of Reagent Concentration.* Reagent (0.1% PAN) concentration was varied from 0.1 to 5 ml with 13 μg of Cr(III) per 10 ml. Absorbance was found to be constant with amounts greater than 0.5 ml, hence 1 ml of reagent was used in all studies.

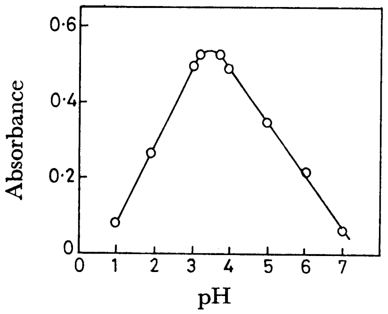

Fig. 1. Effect of pH.
[Chromium] = $3.95\times10^{-4}$ M.

*Effect of Heating and Stability.* Reaction of chromium(III) with PAN was too slow at room temperature to be observed, probably due to inertness of $[Cr(H_2O)_6]^{3+}$. However, complexation resulted on heating the reactants to a temperature of 80—90 °C. The time of heating was varied from 5 min to 120 min and stable colour was formed from 30 min onwards. Hence reactants were heated for 35 min in all studies. The complex was found to be stable for more than 48 hr.

*Choice of Solvent and Period of Equilibration.* Various solvents, such as benzene, xylene, carbon tetrachloride, butanol, chloroform, butyl acetate were tried for extraction of the complex, but the complex was extracted only into chloroform and 1-butanol. As absorbance was found to be greater in 1-butanol than in chloroform, 1-butanol has been selected as suitable solvent.

Period of shaking for extraction of the complex into 1-butanol was varied from 5 s to 180 s, and the absorbance was found to be constant over this period. Hence, a period of 20 s was chosen for extraction.

*Absorption Spectra.* Absorption spectra of Cr(III)-PAN chelate, extracted into butanol after heating for 35 min at pH 3.5 was recorded against a reagent blank prepared under similar conditions. The complex showed (Fig. 2) two absorption maxima at 555 and 600 nm, both of equal intensity. Hence, absorbance measurements can be carried out at 555 or 600 nm. The present studies were carried out at 555 nm.

*Composition of the Complex.* Composition of the complex was determined by Job's continuous variation method which gave a ratio of 1 : 2, metal-to-ligand, and the ratio was verified by mole ratio method.

*Beer's Law.* Beer's law was obeyed in the concentration range of 0.3 to 2.0 μg/ml of Cr(III). Molar absorptivity was $1.28\times10^4$ and Sandell's sensitivity was 0.004 μg of Cr(III) per cm$^2$.

*Effect of Diverse Ions.* Interference of about 46 ions in determination of 13 μg of Cr(III) per 10 ml was

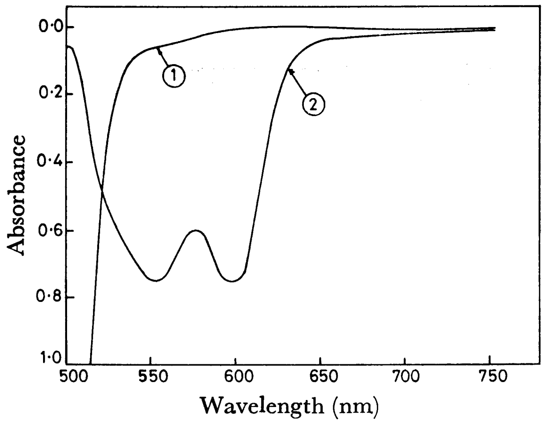

Fig. 2. Absorption spectrum of chromium(III)-PAN complex.
(1): Absorption spectrum of PAN *vs.* solvent,
(2): absorption spectrum of Cr(III)-PAN complex *vs.* reagent blank.
[Cr (III)] $= 1.25 \times 10^{-4}$ M, [PAN] $= 2.50 \times 10^{-4}$ M.

studied, setting the tolerance limit for interfering ions to cause an error of $\pm 2\%$ in chromium recovery. Of the interfering ions, Fe(III), Cu(II), Co(II), Ga(III), In(III), and Tl(III) caused positive error, while $CN^-$ and EDTA gave negative error. Interference due to Fe(III), was eliminated by prior extraction with mesityloxide[4] and those of Cu(II), Co(II), Ca(III), In(III), and Tl(III) was overcome by extracting their PAN complexes into chloroform before heating. The tolerance of some of the metal ions was due to decomposition of their chelates with PAN on heating. Most of the cations, associated with chromium, such as manganese, iron, cobalt, nickel, copper, titanium, zirconium, vanadium, niobium, tantalum, molybdenum and tungsten were tolerated, some of them in manyfold concentrations. The effect of foreign ions is shown in Table 1.

TABLE 1. EFFECT OF DIVERSE IONS
Amount of Cr(III) taken: 13 μg/10 ml, pH=3.5

| Foreign ion added | Tolerance limit μg |
|---|---|
| Ag(I), Mn(II), Pb(II), Fe(III)[a], $F^-$, $Cl^-$, $Br^-$, $I^-$, oxalate | 5000 |
| Sr(II), Ba(II), Ca(II), Mg(II), Zr(IV), Nb(V), $AsO_4^{3-}$, $ReO_4^-$, $TeO_3^{2-}$, $SeO_3^{2-}$, $SO_4^{2-}$ | 2000 |
| Ge(IV), Ta(V), $PO_4^{3-}$, malonate | 1000 |
| Be(II), Bi(III) | 500 |
| Cd(II), Sb(III), Ti(IV), Zn(II) | 200 |
| Ni(II)[b], Cu(II)[c], Ga(III)[c], In(III)[c], Tl(III)[c], $VO_3^-$, $MO_7O_{24}^{6-}$, $WO_4^-$ | 50 |

a) Extracted with mesityl oxide. b) Masked with DMG.
c) Extracted as PAN complex before heating.

*Precision and Accuracy.* Relative standard deviation and relative error, calculated from ten repeat determinations with 1.3 μg of Cr(III) per ml, were found to be $\pm 1.25\%$ and $\pm 0.80\%$ respectively.

*Application to the Analysis of Stainless Steel.* 0.5 g of austenitic stainless steel (Bureau of Analysed Samples, Newham Hall, U. K., No. 332) was dissolved in 10 ml of 1 : 4 $H_2SO_4$ and diluted to 250 ml. Four ml of this solution was acidified with HCl to 3.5 M, transferred to a 100 ml separating funnel and iron was removed by extraction with 10 ml of mesityl oxide.[4] The aqueous layer was evaporated to dryness and made up to 100 ml. An aliquot of this solution was taken, adjusted to pH 3.5, and to it were added 1 ml of PAN, 1 ml of 0.5% DMG and 5 ml of acetate buffer (pH 3.5). The contents were heated for 35 min, transferred after cooling to a separating funnel, and chromium complex extracted with 10 ml of 1-butanol. Absorbance of the organic phase was measured at 555 nm. From duplicate analysis, recovery of chromium was found to be 12.50% and 12.60%, compared to the theoretical value of 12.8%. Other constituents of the alloy are Si–0.44%, S–0.02%, P–0.015%, Mn–0.800%, Ni–12.40% and rest iron.

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