

hydrate with ester) with the corresponding aldehyde in ethanol heated over a water bath for 3 h<sup>7</sup>. Crystals obtained on cooling were further purified by recrystallization from petroleum ether-acetone. Purity was checked by TLC, elemental analysis, and IR and PMR studies.

4-Hydroxybenzylidenesalicyloylhydrazine (m.p. 231°C) showed the colour change in crystalline form from white to yellow on exposure to sunlight for 5 min and reversal to the original colour thermally in the dark or on keeping in the dark at 25°C for a week. The cycle could be repeated several times without any fatigue in the molecule. The compound did not show any colour change when exposed to UV light (365 nm). When either of the OH groups was replaced or substituted by the -OCH<sub>3</sub> group, the photochromic property of the compound was lost.

Photochromism among *N*-salicylideneanilines has been attributed to the existence of intramolecular hydrogen bonding between the phenolic proton and the imine nitrogen leading to intramolecular hydrogen transfer followed by *cis-trans* isomerization yielding photochromic coloured species on excitation<sup>5</sup>. Compounds with an *ortho* group other than OH have also shown photochromic behaviour<sup>8,9</sup>, and the photochromism involves an intramolecular proton shift from a suitable *ortho* group to the nitrogen of the >C=N leading to quinoid-type structure.

In the present case 2-hydroxybenzylidenesalicyloylhydrazine did not show observable colour change on irradiation (UV, sunlight) in the solid state whereas 4-hydroxybenzylidenesalicyloylhydrazine is photochromic in the solid state (sunlight). The observation, indicates that *ortho* groups that are able to shift their proton intramolecularly to the azomethine nitrogen are not essential for photochromism in this series of compounds. Further investigations of the mechanism of photochromism in this series of compounds are under progress.

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### EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF IRON IN STEELS AND HAEMATITE ORE USING THIOCYANATE AND CHLORPROMAZINE

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MANY methods have been reported for the spectrophotometric determination of iron in steel, ores, rocks and minerals<sup>1</sup>. However, these methods are not well suited for simple and selective determination of iron because of complicated procedures or chemical interferences. The thiocyanate method is applicable in routine analysis, but it has serious shortcomings such as the formation of more than one product with iron(III), [Fe(SCN)<sub>n</sub>]<sup>+3-n</sup>, n=1...6, depending on the concentration of thiocyanate. In the work described here chlorpromazine (CPZ) was chosen as a reagent to establish a new, simple, rapid and selective extraction and spectrophotometric determination of microamounts of iron in haematite and steels.

A Beckman Model DB, UV-VIS spectrophotometer with 1 cm matched silica cells was used for absorbance measurements. Stock solution of iron(III) was prepared by dissolving iron(III) ammonium sulphate (AnalaR, BDH) in double-distilled water with a few drops of sulphuric acid. This stock solution was standardized gravimetrically<sup>2</sup> and used after appropriate dilutions as and when required. 0.05 M CPZ solution in chloroform, and ammonium thiocyanate, 25% w/v in water, were also prepared.

Various aliquots of iron solution containing



1–27.5  $\mu\text{g}$  of metal were transferred into a series of separatory funnels. Two ml of 10 M  $\text{H}_2\text{SO}_4$  and 5 ml of 25% ammonium thiocyanate were added and the solutions were diluted to 20 ml with distilled water. Ten ml of 0.05 M CPZ in chloroform was added and the mixture was equilibrated. The chloroform layer was collected in a 10-ml standard flask and the absorbance of each extract at 480 nm was measured against a similarly prepared reagent blank. A calibration graph was drawn and was subsequently used in sample determination.

CPZ reacts with iron(III)-thiocyanate in acidic medium to form a yellow ion-association complex which can be extracted into chloroform. This extract shows  $\lambda_{\text{max}}$  of 480 nm. A study of the possibility of extraction of the ion-association complex from hydrochloric, sulphuric, acetic, perchloric and nitric acid media was carried out. There was no complex formation in nitric, acetic and perchloric acid media. Sulphuric acid and hydrochloric acid were found to be suitable for the formation and extraction of the ion-association complex, offering rapidity, sensitivity and stability of the colour reaction between iron and thiocyanate. A 0.1–1.2 M HCl or 0.2–2.5 M  $\text{H}_2\text{SO}_4$  concentration was found to be essential for getting a clear yellow extract of the complex. Below this level of acidity the organic extract becomes turbid after a few minutes of extraction.

The effects of the amounts of reagents added on the extraction of iron were studied. The results indicated that for between 2 and 10 ml of 25% ammonium thiocyanate the absorbance of the extract had a constant maximum absorbance at 480 nm. Similarly, for 5 to 10 ml of 0.5% CPZ in chloroform, the organic extract showed constant absorbance.

An equilibration time of 1 to 2 min was sufficient for maximum recovery of iron into chloroform. Shaking the mixture for up to 10 min did not alter the colour intensity of the complex. Changing the volume of the aqueous phase from 10 ml to 50 ml did not affect the absorbance of the organic extract. Of the various solvents, viz. benzene, toluene, chloroform, dichloromethane and carbon tetrachloride, investigated for extraction of the iron-association complex, chloroform was found to be the best for complete extraction of the complex. The colour of the extract remained stable for at least 72 h at room temperature (28°C).

Beer's law was obeyed over a range of 0.05 to 3 ppm of iron, with an optimum concentration range, evaluated from Ringbom's plot, of 0.1–2.75 ppm of

iron. The Sandell sensitivity of the ion-pair complex was found to be 0.019  $\mu\text{g}$  iron  $\text{cm}^{-2}$ . At 480 nm the molar absorptivity is  $2.9 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ . The precision of the method calculated from relative standard deviation of 10 measurements is found to be  $\pm 1.5\%$ .

The probable stoichiometry of the complex was investigated by the Job's method of continuous variation and the equilibrium shift method. Job's method indicated a ratio of 1:1 for iron to CPZ, and the ratio of thiocyanate to iron, from the equilibrium shift method, was 4:1. Hence the ratio Fe:SCN:CPZ in the extracted ion-pair is 1:4:1.

The effect of presence of several extraneous cations and anions on the extraction of the ion-pair of iron was tested by adding different amounts of foreign ions to a fixed amount of iron. The colour was developed and extracted, and absorbance was measured following the general procedure described above. Cations of alkali and alkaline earth metals did not interfere. Among the transition metals, Mo(VI), Nb(V), Re(VII), Co(II) and Ti(IV) interfered seriously. However, interference due to Nb(V) was reduced by masking it with NaF during extraction, while that due to Re(VII) was reduced by its pre-extraction with tetraphenylarsonium ion. Molybdenum must be separated before extraction. Among the anions,  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  at up to 5000 ppm had no effect on the absorbance, and phosphate did not cause interference. Thiosulphate and  $\text{I}^-$  interfered.

To ascertain the validity of the proposed method, standard steel samples H. No. 6-4828 58 Cr V<sub>4</sub> and H. No. 7-2034 15 C DV<sub>6</sub> were analysed. The result showed values of 96.7 and 96.1% against the certified values of 96.78 and 96.292 respectively. Haematite ore analysis by the proposed method indicated a value of 63.1%, as against the certified value of 63.56%.

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