

TABLE I
The System : $\text{Zn Fe}_x \text{Sm}_{(2-x)} \text{O}_4$

No.	Composition	Molecular Weight	Colour	Density	Phases present
1.	$\text{Zn Fe}_{1.6} \text{Sm}_{0.4} \text{O}_4$	278.74	Blackish Brown	5.67	Gahnite $a=8.560 \text{ \AA}$
2.	$\text{Zn Fe}_{1.2} \text{Sm}_{0.8} \text{O}_4$	316.58	Blackish Brown	5.98	Gahnite $a=8.620 \text{ \AA}$
3.	$\text{Zn Fe}_{0.8} \text{Sm}_{1.2} \text{O}_4$	354.42	Slate Colour	6.29	Gahnite + Samario- Gahnite $a=8.790 \text{ \AA}$
4.	$\text{Zn Fe}_{0.4} \text{Sm}_{1.6} \text{O}_4$	392.26	Greenish Brown	6.60	Samario-Gahnite $a=8.980 \text{ \AA}$
5.	$\text{Zn Sm}_2 \text{O}_4$	430.10	Yellowish White	6.84	Samario-Gahnite $a=9.234 \text{ \AA}$

TABLE II
X-ray data of $\text{Zn Sm}_2 \text{O}_4$

I I ₀	d in Å	hkl
20	3.194	220
30	3.051	300, 221
100	2.781	311
10	2.655	222
10	2.471	321
10	2.325	400
10	2.154	331
10	2.047	420
20	1.914	422
10	1.863	500, 430
15	1.798	511, 333
10	1.681	521
20	1.668	440
10	1.595	433, 530
10	1.544	600, 442
10	1.222	642
10	1.176	731, 553
10	1.151	800
10	1.129	733
10	1.081	822
10	1.068	555, 751
10	1.033	840

Fe^{3+} and Sm^{3+} ions in all the mentioned compositions.

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A NEW VANADYL (IV) THIOCYANATE METHOD FOR THE SPECTROPHOTO- METRIC DETERMINATION OF VANADIUM (IV)

SANTINI *et al.*¹ carried out the spectrophotometric determination of vanadium based on the absorption properties of the blue vanadyl ion. Furman and Garner² have reported the complexes of vanadium (IV) and vanadium (III) with thiocyanate in aqueous medium.

In the present investigation the extraction behaviour of vanadyl thiocyanate complex with 8 : 3 *n*-butanol and ethyl acetate has been studied. This method has the advantages in that (1) 2–20 mg. of vanadium can be estimated rapidly, and (2) tolerance to interference by common anions and larger reagent concentrations (50 to 100 fold).

The extraction is quantitative and rapid (equilibration time is less than 30 sec) within the pH range of 0.5 to 2.5. Measurements are made at 730 nm at which wavelength the complex has maximum absorption. The other reagents have negligible absorption at this wavelength. For maximum intensity of colour, which is stable for more than

48 hours, a 50-fold excess of the reagent is used. Beer's law is obeyed from 2 to 20 mg of vanadium (IV) in 100 ml of solution. It is interesting to note that the extraction with the solvent mixture is greater than the sum of the extractions with either of the solvents individually. The first extraction will collect 95% of the total amount of vanadium (IV).

Reagents.—A 4% solution of sodium thiocyanate (B.D.H. AnalaR) is prepared.

Vanadium(IV) solution is prepared by reducing 50 ml of approximately 0.1 N sodium vanadate solution, mixed with 20 ml of 5 N sulphuric acid, with sulphur dioxide and standardised by the method of Dikshitulu and Gopala Rao¹.

All other reagents employed are of analytical reagent quality.

Procedure.—The sample solution containing 2 to 20 mg of vanadium (IV) is taken into a 150 ml separatory funnel, 2.5 to 25.0 ml of the reagent added and the pH adjusted to 0.5 to 2.5 with either dilute acid or alkali using a pH meter. The solution is shaken with 45 ml of the solvent mixture of *n*-butanol and ethyl acetate (8 : 3 v/v). The aqueous layer is collected after the two layers separate and the non-aqueous layer is run off into a 150 ml beaker. The aqueous layer is washed again with the solvent mixture. The non-aqueous extracts, collected in the beaker, are dried over anhydrous sodium sulphate and transferred to a 100 ml volumetric flask and the solution is made up to the mark. The optical density is then measured against the solvent blank at 730 nm using Hilger UVISPEK spectrophotometer using 1 cm glass cells.

Interferences.—100-fold excess of chloride, sulphate, nitrate, and perchlorate, and equal amount of phosphate do not interfere. Chromium (III) interferes, but the interference can be overcome by increasing the reagent concentration by 1½ times. Ce(III) precipitates out under the conditions of the experiment. Fe(III), Mo(VI), Ni(II), and Cu(II) interfere.

The authors gratefully acknowledge the award of a Junior Research Fellowship to one of them (K. V. B.) by the University Grants Commission, India.

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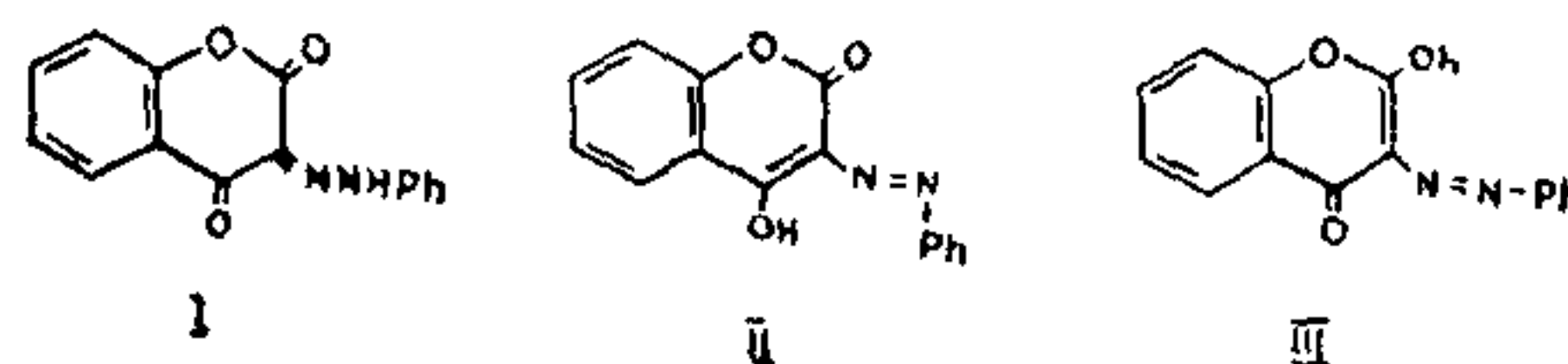
Waltair, India, March 17, 1973.

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COMPLEX FORMATION WITH 3-PHENYLAZO-4-HYDROXY COUMARIN

THE report^{1,2} on the complex formation of 3-phenyl-4 : 5 : 7-trihydroxy coumarin with various metal ions turned our attention to a study on the chelating capacity of 3-phenylazo-4-hydroxy coumarin. Although this compound was first made in 1945 by Huebner and Link³, and its derivatives were later on used as important intermediates in the synthesis of the antibiotic Novobiocin and its analogues⁴⁻⁷, very little is known regarding the binding capacity of this interesting ligand with metal ions. Moreover, since three tautomeric structures (I, II & III) are possible with this ligand theoretically⁸, it has been considered that a study of the spectral data of these metal complexes may provide an explanation as to which tautomeric form predominates under a particular set of experimental conditions.

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The reaction of this ligand, prepared by earlier reported procedures, with Ag(I), Tl(I), Cu(II), Mg(II), Mn(II), Al(III) and Th(IV) yielded the corresponding complexes. The general method of preparation consisted of mixing the equimolar quantities of the respective metal ions (in aqueous solution) and the ligand in methanol at room temperature. The products, obtained in good yield, were crystallised from dioxane and dried over calcium chloride *in vacuo*. The compounds were stable, non-volatile, soluble in non-polar solvents and non-conductors in dioxane and methanol solutions.

Gravimetric determinations on these complexes based on standard procedures indicated that the metal to ligand ratio is 1 : 1 in the case of silver and thallium, 1 : 2 in the case of copper, manganese and magnesium, 1 : 3 with aluminium and 1 : 4 with thorium. These results are also well in agreement with the analytical data presented in Table I.

Spectral Data.—The ultraviolet spectrum of the ligand consists of two bands at 246 nm and 420 nm. The former is attributable to the α , β -unsaturated

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