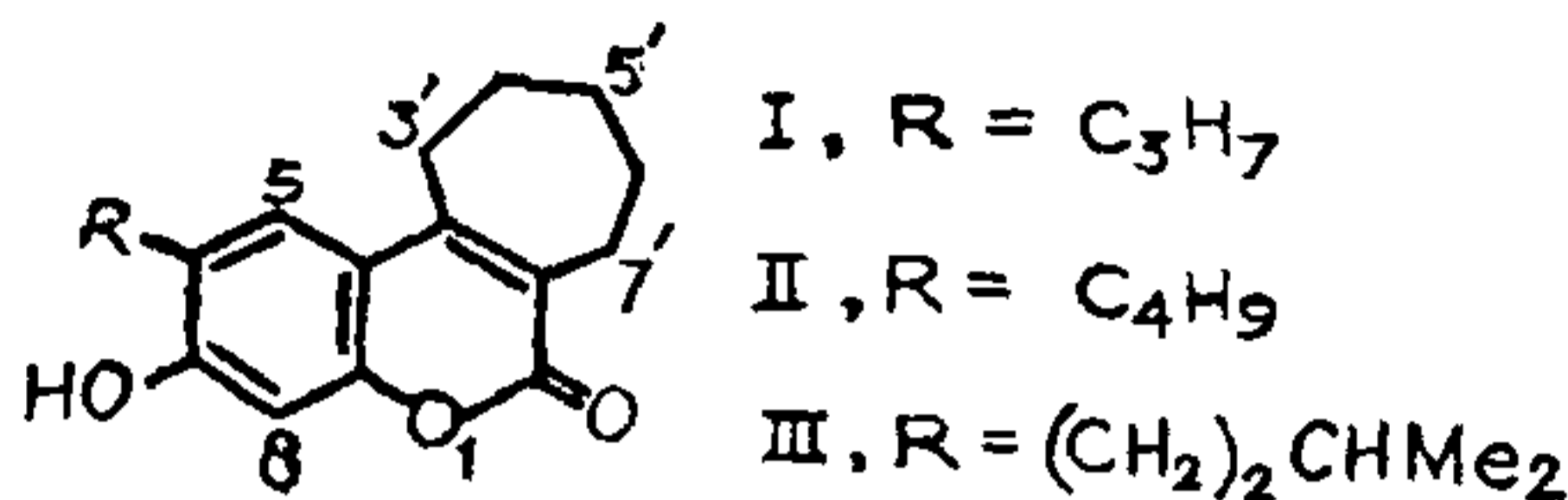


TABLE I  
Toxicity of hydroxycoumarin compounds against black rat (*Rattus rattus*)  
No. of Rats used : 10



Compound No.	Conc. of the compound in the bait (%)	Average body weight (gms)	Mortality %	Kill period Range			Average bait intake gm/rat/day	Mg of poison/kg body wt. reqd. Av.
				Av.	Min.	Max.		
I, R	0.25	156	10	32	25	35	10	5208
„	0.50	150	20	25	20	30	7	6225
„	1.00	158	30	25	20	28	5	7881
„	2.00	160	50	20	17	27	5	12772
II, R	0.25	140	20	30	26	32	9	4911
„	0.50	185	20	30	25	30	8	6648
„	1.00	180	40	25	20	30	5	8593
„	2.00	175	50	20	18	25	5	11428
III, R	0.25	155	10	31	26	36	9	4734
„	0.50	149	20	25	21	31	7	5989
„	1.00	160	30	25	21	28	5	7968
„	2.00	168	50	20	18	25	5	12227

compounds were found to be more or less identical in their toxicity.

In a study of the structure-activity relationship in this class of 7 hydroxycoumarin derivatives, it appears that the length of the side chain does not play a significant role in its toxicity. The structural changes in the other parts of the molecule to increase the toxicity are in progress.

The authors are thankful to the Principal, D.N. College, Meerut and the Director, Indian Grain Storage Institute, Hapur, for providing the necessary laboratory facilities. Thanks are also due to Dr. Nitya Anand, Director, C.D.R.I., Lucknow, for the spectral data. Mrs. Veena is grateful to CSIR, New Delhi, for financial assistance.

Indian Grain Storage Institute,  
Hapur (U.P.),  
November 19, 1977.

K. K. ARORA.  
VELNA.\*  
O. P. MALIK.\*

\* Department of Chemistry, D.N. College, Meerut (U.P.).

- Hesse, G. and Urbanck, F., *Chem. Ber.*, 1958, **91**, 2733.
- Dobme, A.R.L., Cox, F. H. and Ellis Miller, *J. Am. Chem. Soc.*, 1926, **48**, 1688.

#### FORMATION CONSTANTS OF SOME BIVALENT METAL CHELATES OF 2-HYDROXY-1-NAPHTHALIDENE-2', 5'-DIMETHOXYANILINE

In continuation of our earlier work on the determination of stability constants of various Schiff bases of 2-hydroxy-1-naphthaldehyde, a structurally similar ligand has been selected to study the behaviour of some divalent metal ions with this ligand.

In the present communication, the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-2', 5'-dimethoxyaniline with some bivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti.<sup>1</sup>

#### Experimental

A Corning Model 12, precision research pH meter with a wide range glass electrode and a calomel reference electrode was used for the pH measurements. The smallest scale division on the expanded scale is 0.005 pH unit.

The ligand, 2-hydroxy-1-naphthalidene-2', 5'-dimethoxyaniline was synthesised and repeatedly crystallised to get an analytically pure sample (Observed m.p. 148°C). The chemicals used were of B.D.H. analytical grade. The medium of titration was a

dioxan-water mixture containing 75% (v/v) of dioxan which was purified by the method of Vogel.<sup>2</sup> Sodium perchlorate was added to maintain a constant ionic strength (0.1M). The titrations were carried out at  $25 \pm 0.1^\circ \text{C}$  in a nitrogen atmosphere.

The following solutions were titrated potentiometrically against standard carbonate-free sodium hydroxide solution (1.03 M), keeping the total volume as 40 ml.

(i) 5 ml of (0.16 M)  $\text{HClO}_4$  + 5 ml of (0.64 M)  $\text{NaClO}_4$  + 30 ml of dioxan.

(ii) 5 ml of (0.16 M)  $\text{HClO}_4$  + 5 ml of (0.64 M)  $\text{NaClO}_4$  + a requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution + 30 ml of dioxan.

(iii) 5 ml of (0.64 M)  $\text{NaClO}_4$  + 5 ml of (0.008 M) metal salt solution in (0.16 M)  $\text{HClO}_4$  + a requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution + 30 ml of dioxan.

The experimental method of Irving and Rossotti<sup>1</sup> was applied to determine the values of  $\bar{n}$  and pL.

#### Results and Discussion

In the ligand it is the chelated phenolic 'OH' group which takes part in the complex formation and the proton is replaced from it by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, Y, the number of dissociable protons attached to each ligand molecule is one.

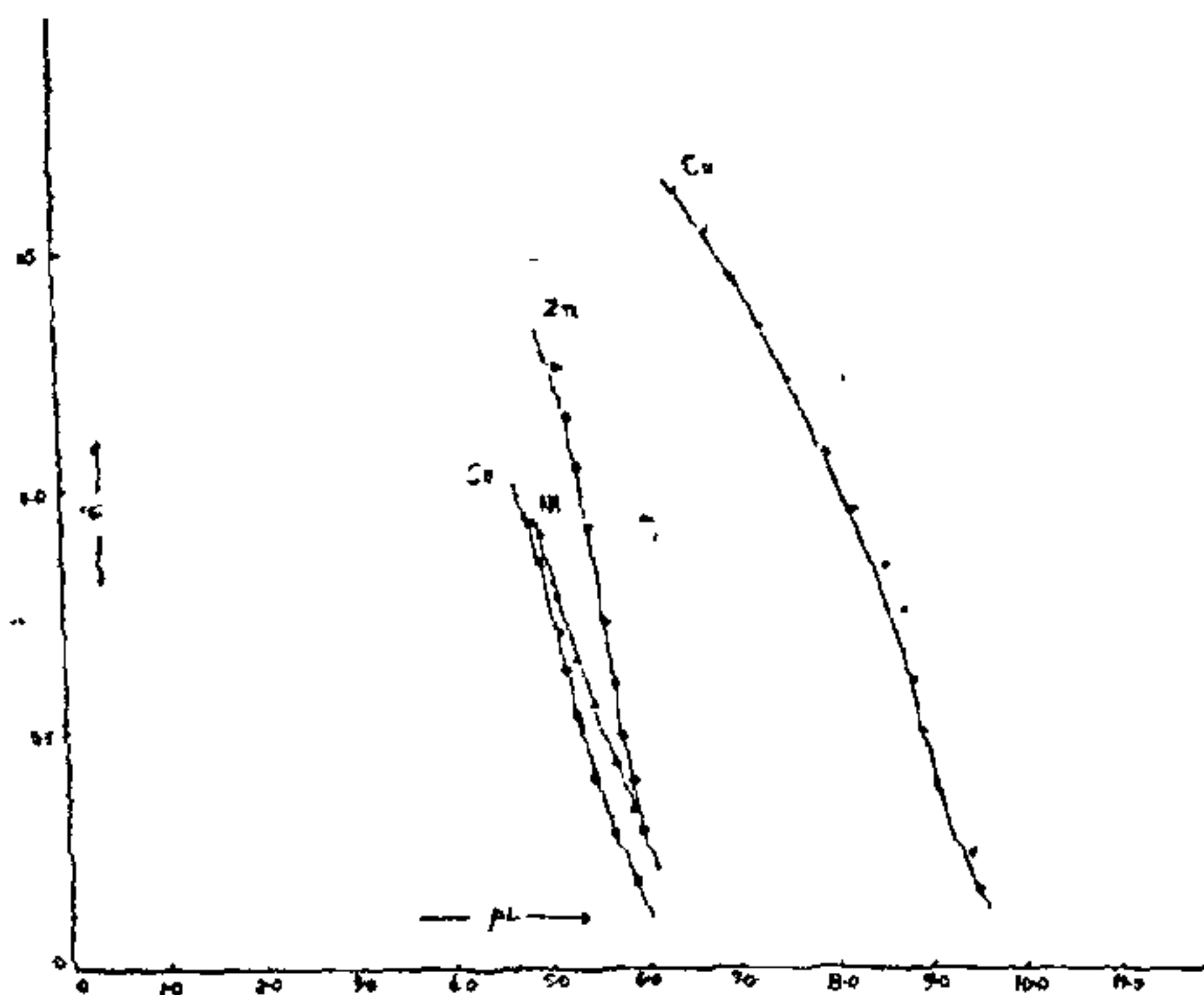


FIG. 1. Metal-ligand systems of 2-Hydroxy-1-Naphthalidene-2', 5'-Dimethoxyaniline. Formation curves.

The  $\bar{n}$  vs. pL plots (Fig. 1) indicate the formation of 1:1 complexes for all four metal ions.  $\text{Cu}^{2+}$  forms 1:2 complexes as well while  $\text{Zn}^{2+}$  shows a tendency to form 1:2 complexes.  $\log K_1$  and  $\log K_2$  values were determined by the half integral method. The values

so obtained agree well with those evaluated from the straight line plots of  $\log \bar{n}/(1 - \bar{n})$  against pL (Fig. 2). The most representative values are recorded in Table I.

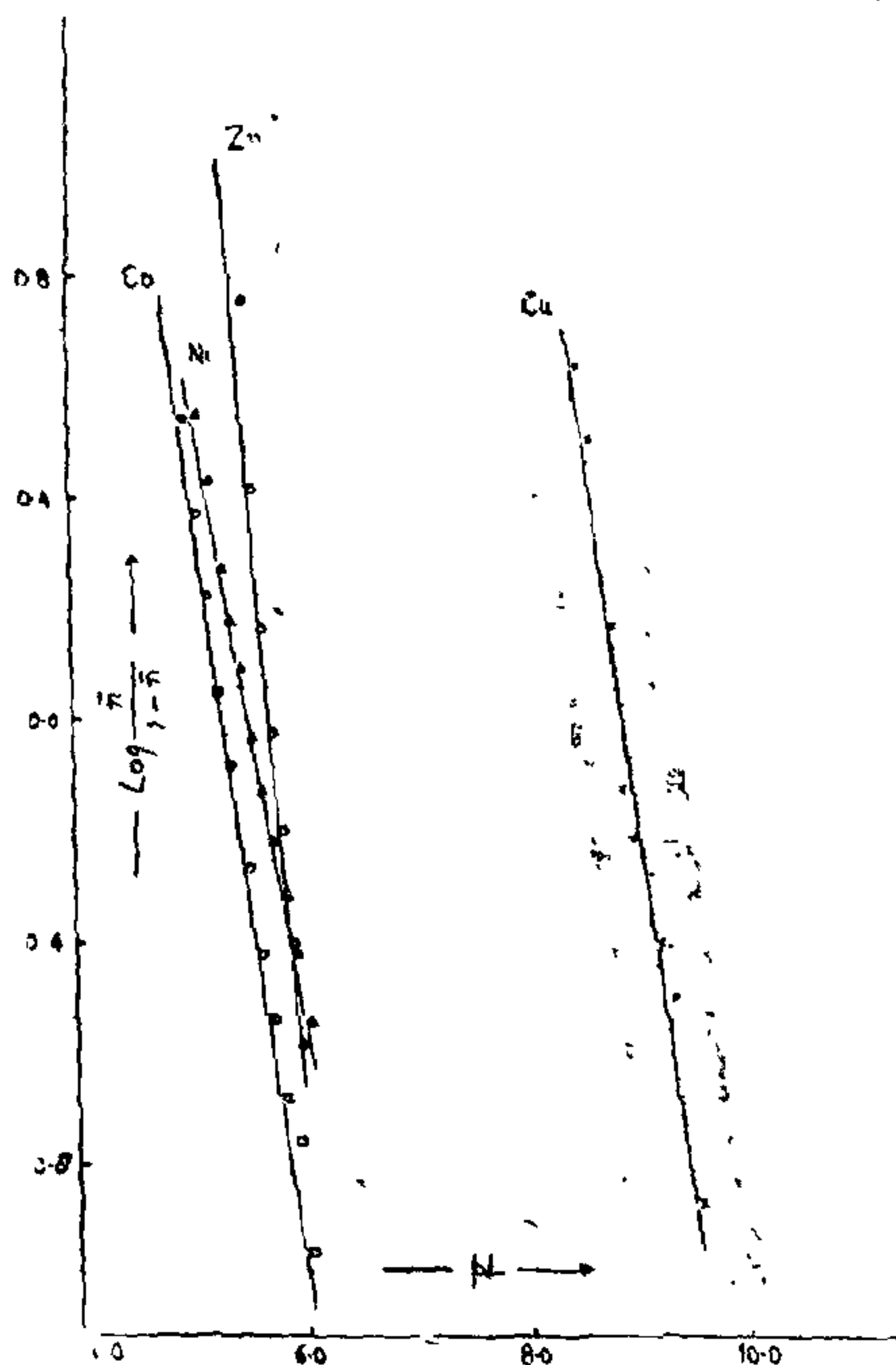


FIG. 2. 2-Hydroxy-1-Naphthalidene-2',5'-Dimethoxyaniline.

TABLE I

Stepwise stability constants of various complexes

Cations	$t = 25^\circ \text{C}$				
	$\text{H}^+$	$\text{Cu}^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Zn}^{2+}$
$\log K_1$	9.66	8.95	5.60	5.39	5.80
$\log K_2$	2.20	6.90	..	..	..

Regarding the order of stability of the metal chelates it would be relevant to mention here that in their attempt to place zinc in the Irving and Williams order<sup>3</sup> Murakami *et al.*<sup>4</sup> studied the metal complexes of catechol derivatives for the bivalent transition metal series and found the stability order to follow the sequence:



This order has also been observed in the present study. Johnston and Freiser<sup>5</sup> attribute the lower

value of nickel to steric hindrance which prevents the formation of a square planar structure.

The authors wish to thank Dr. D. G. Vartak, B.A.R.C., Bombay and Dr. R. A. Kulkarni Principal, Ramnarain Ruia College, Bombay, for their valuable suggestions and continuous encouragement.

Department of Chemistry, M. S. MAYADEO,  
Ramnarain Ruia College, S. H. HUSSAIN,  
Matunga, Bombay-400 019,  
December 16, 1977.

1. Irving, H. M. and Rossotti, H. S., *J. Chem. Soc.*, 1954, p. 2904.
2. Vogel, A. I., *A Text Book of Practical Organic Chemistry*, III Edition, Longmans, p. 177.
3. Irving, H. and Williams, R. J. P., *J. Chem. Soc.*, 1953, p. 3192.
4. Murakami, Y., Nakamura, K. and Tokunaga, M., *Bull. Chem. Soc. Japan*, 1963, 36, 669.
5. Johnston, W. D. and Frieser, H., *Analytica Chim. Acta*, 1954, 11, 302.

#### DETERMINATION OF MICRO AMOUNTS OF BROMATE COLORIMETRICALLY USING RESACETOPHENONE OXIME—AN INDIRECT METHOD

It is reported that ferric iron reacts quantitatively with resacetophenone oxime in slightly acidic solutions giving a purple colored soluble complex of considerable stability<sup>1-3</sup>. The reactivity between ferrous iron and potassium bromate coupled with the fact mentioned above is employed to develop a colorimetric procedure for the determination of micro-amounts of bromate. The results obtained are presented in this communication. Since thiocyanate reacts with ferric iron giving deep red colour, the studies are also repeated with thiocyanate for the purpose of comparison. The results obtained with the oxime as well as thiocyanate are presented in Fig. 1.

The standard deviation, molar absorptivity and Sandell sensitivity<sup>4</sup> are  $9.3 \times 10^{-3}$ ,  $9.5 \times 10^{12}$  lit. mole<sup>-1</sup> cm<sup>-1</sup>,  $5.9 \times 10^{-2}$   $\mu$  gm/cm<sup>2</sup>;  $5.1 \times 10^{-3}$ ,  $2.1 \times 10^{13}$  lit. mole<sup>-1</sup> cm<sup>-1</sup>,  $2.6 \times 10^{-2}$   $\mu$  gm/cm<sup>2</sup> respectively for the oximate and thiocyanate complexes. Even though satisfactory results are obtained with thiocyanate, the method employing the resacetophenone oxime is preferred in view of the fact that iron(III) forms complexes of different composition depending upon thiocyanate concentration<sup>5</sup>.

#### Reagents

Resacetophenone oxime is prepared by the standard procedure<sup>6,7</sup>. All other chemicals used are of A.R. Grade.

#### Recommended Procedure

2.5 ml of iron(II) solution (0.1 M) in sulphuric acid (0.03 M) is pipetted out into each of 25 ml volumetric flasks containing different aliquots of bromate solution (0.05 mg/ml). About 20 to 30 minutes are allowed to make sure that the oxidation of iron(II) is complete. Then 2.5 ml of the oxime solution (0.1 M) is added to each of the flasks and the contents are made up to the mark. Absorbances of the solutions are measured at 500 nm using water as blank.

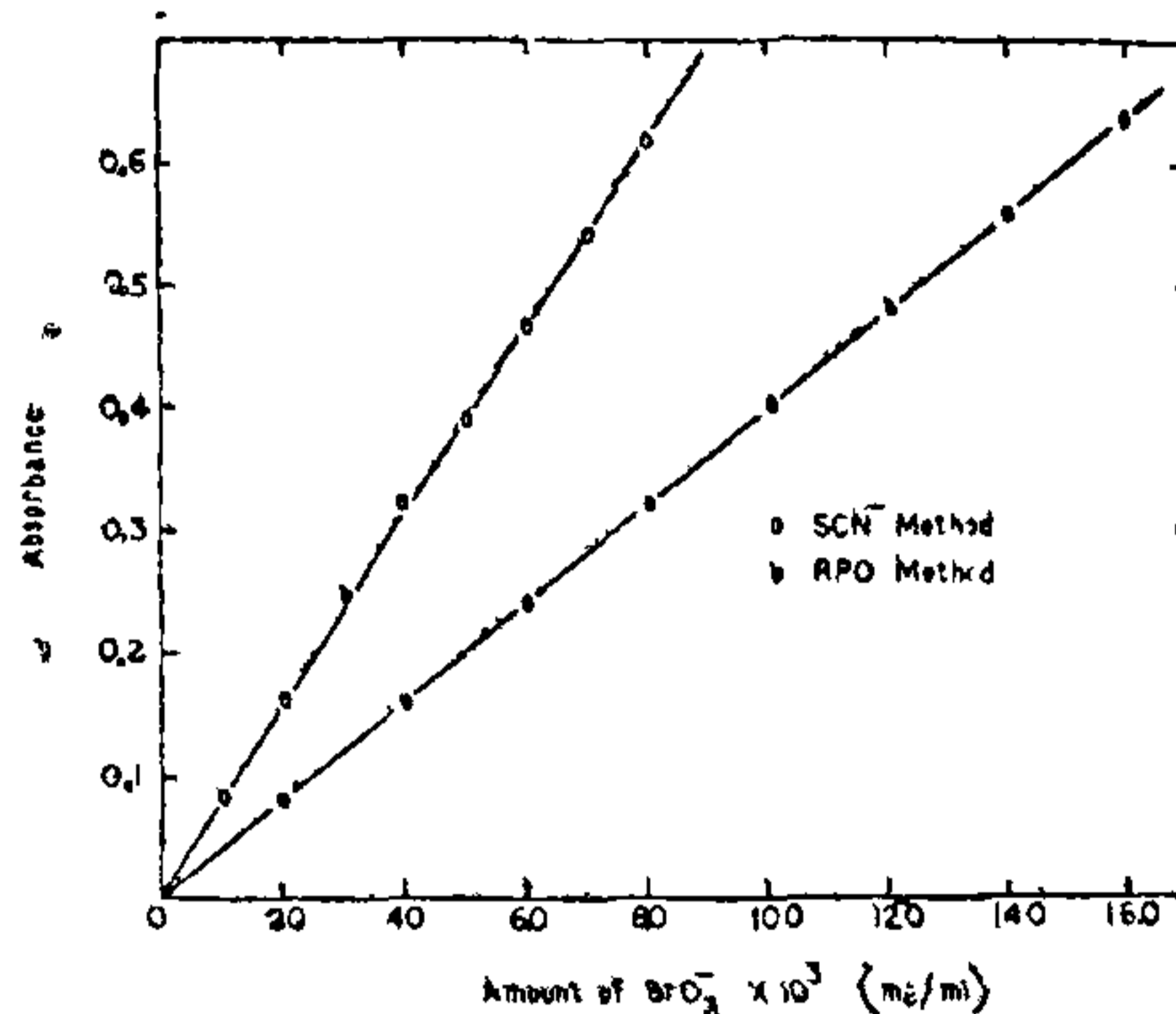


FIG. 1

Similar procedure is adopted for ferric thiocyanate method. The acid concentration is maintained at 0.08 M. Absorbance measurements are however carried out at 450 nm.

#### Effect of Acidity

In the oximate method, the color intensity decreases with the increase of acid concentration. Lower acid concentrations though improved the color intensity, are undesirable since minimum acidity is required to suppress hydrolysis and to facilitate the oxidation of iron(II). Hence the optimum overall concentration is to be maintained at 0.003 M.

#### Interferences

Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> nitrate, chloride, bromide did not interfere even when present in large excess.

The method is simple and rapid compared to the colorimetric methods reported in literature<sup>8</sup> for the determination of bromate employing organic reagents, such as methyl orange, phenol red, fluorescein, etc. Reagents like methyl orange, methyl red suffer from the drawback that they are acid-base sensitive. The other reagents are either less sensitive or suffer from other defects (*loc. cit.*).

Moreover, the present method is very sensitive since the redox reaction involved between iron(II) and bromate is a multi-electron process.