

TABLE 1 — STABILITY CONSTANTS OF PAHA CHELATES

| Stability constant | Metal ion        |                  |                  |                  |                  |                  |
|--------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                    | Cu <sup>2+</sup> | Ni <sup>2+</sup> | Zn <sup>2+</sup> | Co <sup>2+</sup> | Mn <sup>2+</sup> | Cd <sup>2+</sup> |
| Log K <sub>1</sub> | 7.20             | 7.05             | 5.63             | 4.03             | 3.86             | 4.02             |
| Log K <sub>2</sub> | 6.09             | 4.12             | 4.96             | 3.62             | 3.60             | 3.55             |

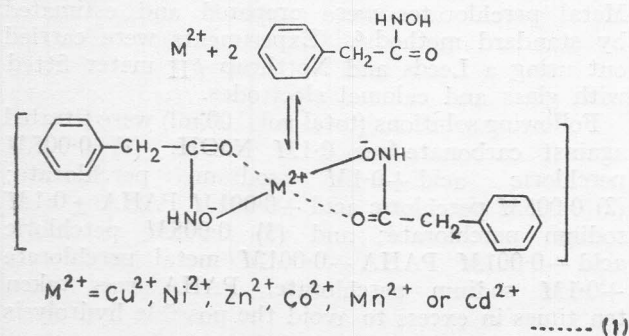
of the metal ions. Purified nitrogen gas was bubbled through the reaction mixture to remove dissolved oxygen.

The  $pK_a$  of PAHA was determined by the potentiometric method and was found to be  $9.25 \pm 0.03$  which is in close agreement with the value 9.19 reported earlier<sup>7</sup>.  $\bar{n}$  and  $pL$  values in the presence of metal ions were evaluated by Irving-Rossotti method<sup>4</sup>. The thermodynamic stability constants were calculated<sup>8</sup> from the formation curves by (i) the solution of simultaneous equations of the type  $\bar{n} + (\bar{n}-1)K_1 + (\bar{n}-2)K_1K_2[L]^2 = 0$  and (ii) correction-term method. The stability constants thus obtained by these two methods agree quite well and the average values are reported in Table 1.

Stability constants of other hydroxamic acid chelates are usually determined in aqueous-dioxane medium because of their insolubility in water. In the present work aqueous medium was found to be suitable as PAHA complexes are sufficiently soluble in water.

The highest  $\bar{n}$  value obtained for Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup> and Cd<sup>2+</sup> lies between 1.5 and 2.00 indicating ligand-metal ratio of 2:1. But in the case of Cu<sup>2+</sup> and Zn<sup>2+</sup> the highest  $\bar{n}$  value obtained was between 2.5 and 3.0. Considering that the tendency of Cu<sup>2+</sup> and Zn<sup>2+</sup> is to form tetra-coordinated complexes it may be assumed that Cu<sup>2+</sup> and Zn<sup>2+</sup> also form 2:1 complexes with the bidentate PAHA. This assumption gains support from the observation that for Cu<sup>2+</sup> and Zn<sup>2+</sup> insoluble precipitates are invariably formed before the end point is reached. The insoluble precipitates may be due to the formation of hydroxo-complexes which are responsible for the  $\bar{n}$  values above 2.0. That other structurally similar hydroxamic acids form 2:1 complexes is an additional point in favour of the above assumption.

pH was found to decrease when neutral metal perchlorate solution was added to a solution of the potassium salt of PAHA indicating that the oxygen of OH group is involved in the complex formation. The formation equilibrium of PAHA chelates can in general be represented by Eq. (1).



The greater solubility of the PAHA complexes in aqueous medium compared to those of BHA may be due to the greater ionic character of the PAHA complexes. In the BHA chelates the electron density of metal-oxygen bond is greatly delocalized by spreading over to the phenyl ring. In PAHA chelates the electron delocalization is restricted to five-membered chelate rings by the  $-\text{CH}_2-$  group intervening the carbonyl and phenyl ring. This makes the PAHA complexes relatively more ionic than BHA complexes.

The greater solubility and the high stability, especially that of Ni<sup>2+</sup>, show that PAHA could be used as an analytical reagent for the metal ions studied. The stability constants were found to follow the order  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$  which is in accordance with the Irving-William order.

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#### Influence of Citrate, Mandelate & Succinate on Titanium(IV)-Gallic Acid System

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Citrate and mandelate, but not succinate, form mixed complexes with titanium and gallic acid. The continuous variation experiments in the presence of constant concentration of these auxiliary ligands confirm that hydrolysis and polymerization of free metal ion is not responsible for the drag of  $X_{\text{max}}$  to higher values. The shift of the dragged  $X_{\text{max}}$  to lower values appears to be due to mixed complex formation with the auxiliary ligand.

EARLIER studies<sup>1,2</sup> have shown that auxiliary ligands (AL) like oxalate (OX) and tartrate (Tart) form mixed complexes with Ti (IV) and gallate (GA) in a wide range of acidity. This note

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describes similar spectrophotometric studies on the same system with citrate (Cit), mandelate (Mand) and succinate (Succ) as auxiliary ligands.

Considerable bathochromic and hyperchromic effects are observed on addition of Cit and Mand to Ti-GA mixtures at 1.87*N* acidity and *pH* 1.0 (e.g. curves 2, 3, 5 and 6 in Fig. 1). Also, only ternary mixtures exhibit  $\lambda_{\max}$  around 360 nm (the spectra were corrected for the absorption of Ti-GA and Ti-AL binary mixtures). These results show the formation of mixed complexes as in the case of OX and Tart, reported earlier<sup>1</sup>. The continuous variation method, varying Ti and GA continuously and keeping constant concentration of Cit/Mand<sup>3</sup>, indicated a composition of 1:1 (with respect to Ti and GA) in the mixed com-

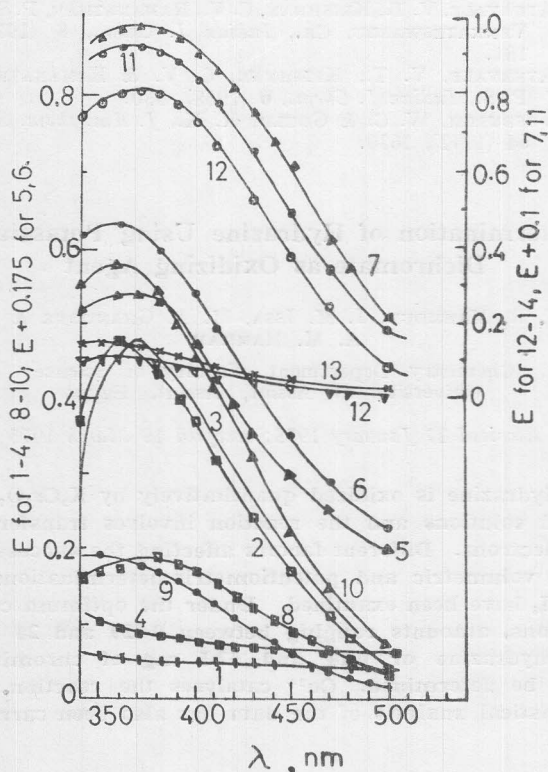


Fig. 1 — Spectra of Ti-GA-AL systems

| Curve | Acidity/ <i>pH</i> | $C_{Ti} \times 10^3 M$ | $C_{GA} \times 10^3 M$ | $C_{AL} \times 10^3 M$ |
|-------|--------------------|------------------------|------------------------|------------------------|
| 1     | 1.87 <i>N</i>      | 5.0                    | 25.0                   | —                      |
| 2     | 1.87 <i>N</i>      | 5.0                    | 25.0                   | 7.5 (Cit)              |
| 3     | 1.87 <i>N</i>      | 5.0                    | 25.0                   | 7.5 (Mand)             |
| 4     | 1.0                | 2.0                    | 10.0                   | —                      |
| 5     | 1.0                | 2.0                    | 10.0                   | 8.0 (Cit)              |
| 6     | 1.0                | 2.0                    | 10.0                   | 10.0 (Mand)            |
| 7     | 4.0                | 0.05                   | 0.8                    | —                      |
| 8     | 4.0                | 0.05                   | 0.8                    | 0.32 (Cit)             |
| 9     | 4.0                | 0.05                   | 0.8                    | 4.0 (Mand)             |
| 10    | 4.0                | 0.05                   | 0.8                    | 300.0 (Succ)           |
| 11    | 5.5                | 0.05                   | 0.8                    | —                      |
| 12    | 5.5                | 0.05                   | 0.8                    | 20.0 (Cit)             |
| 13    | 5.5                | 0.05                   | 0.8                    | 30.0 (Mand)            |
| 14    | 5.5                | 0.05                   | 0.8                    | 200.0 (Succ)           |

5 cm cells were used in expts 1-6.

TABLE 1 — RESULTS OF CONTINUOUS VARIATION METHOD IN EQUIMOLAR SOLUTIONS

| Sl No.                 | $C_{Ti} + C_{GA} \times 10^2 M$ | $C_{AL} \times 10^2 M$ | $X_{\max}$ |
|------------------------|---------------------------------|------------------------|------------|
| ACIDITY, 1.87 <i>N</i> |                                 |                        |            |
| 1                      | 2.5                             | —                      | 0.50       |
| 2                      | 2.5                             | 38 (Mand)              | 0.50       |
| 3                      | 2.5                             | 38 (Cit)               | 0.50       |
| 4                      | 2.5                             | 15 × $C_{Ti}$ (Mand)   | 0.33       |
| 5                      | 2.5                             | 15 × $C_{Ti}$ (Cit)    | 0.33       |
| <i>pH</i> = 1.0        |                                 |                        |            |
| 6                      | 1.0                             | —                      | 0.50       |
| 7                      | 1.0                             | 30 (Mand)              | 0.50       |
| 8                      | 1.0                             | 30 (Cit)               | 0.50       |
| <i>pH</i> = 4.0        |                                 |                        |            |
| 9                      | 0.05                            | —                      | 0.80       |
| 10                     | 0.05                            | 20 (Succ)              | 0.80       |
| 11                     | 0.05                            | 2.0 (Mand)             | 0.50       |
| 12                     | 0.05                            | 0.3 (Cit)              | 0.50       |
| <i>pH</i> = 5.5        |                                 |                        |            |
| 13                     | 0.025                           | —                      | 0.75       |
| 14                     | 0.025                           | 25 (Succ)              | 0.75       |
| 15                     | 0.025                           | 2.0 (Mand)             | 0.50       |
| 16                     | 0.025                           | 2.0 (Cit)              | 0.60       |

$\lambda_{\max} = 370$  nm; 5 cm cells were used in expts 1-8.

plexes at the two acidities (2, 3, 7 and 8 in Table 1). Modified Bent and French method<sup>4</sup>, varying  $C_{AL}$  (analysis of curves 1-4 in Fig. 2) showed the presence of one mole of AL per mole of the mixed complex from the limiting slope. The 1:1:1 composition of the mixed complexes at 1.87*N* acidity was further confirmed from the  $X_{\max}$  of 0.33 (4 and 5 in Table 1) obtained, when the modified continuous variation method<sup>5</sup> was applied. In this the  $C_{AL}$  is a constant multiple of  $C_{Ti}$  in all metal-ligand mixtures.

*E* values of ternary mixtures increase continuously with  $C_{Cit/Mand}$  at 1.87*N* acidity, while those at *pH* 1.0 pass through a maximum (curves 1-4 in Fig. 2). Increase of *E* values represents the increased formation of mixed complexes. Based on a treatment reported earlier<sup>1</sup>, it is concluded that the ratio of Cit/Mand to Ti in the colourless binary complexes, forming simultaneously, is 1 and >1 at the two acidities respectively.

There is no indication of mixed complex formation in the case of Succ.

At *pH* values 4.0 and 5.5 *E*, values of ternary mixtures decrease with increase of  $C_{AL}$ , the magnitude of decrease being very much lower in the case of Succ (curves 5-10 in Fig. 2). A comparison of the nature of spectra of ternary and binary systems reveals the formation of coloured mixed complexes in the case of Cit and Mand but not Succ (from the superimposability) though Succ forms colourless complexes with Ti.

From the shift of  $X_{\max}$  values to 0.5 and not beyond with increase of  $C_{Mand}$  (at *pH* 4.0 and 5.5) and  $C_{Cit}$  (at *pH* 4.0) in the continuous variation experiments (11, 12 and 15 in Table 1), the composition

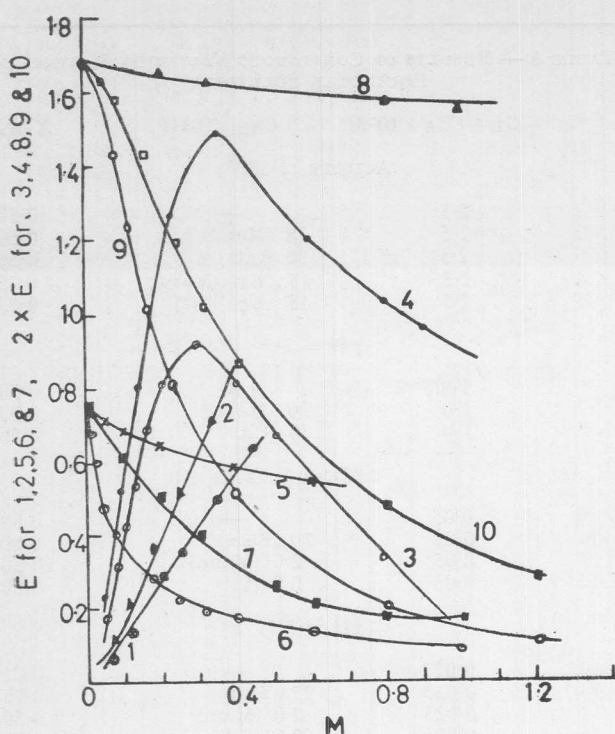


Fig. 2 — Effect of AL on Ti-GA system

| Curve | Acidity/pH | $C_{Ti} \times 10^3 M$ | $C_{GA} \times 10^3 M$ | AL   |
|-------|------------|------------------------|------------------------|------|
| 1     | 1.87N      | 5.0                    | 25.0                   | Cit  |
| 2     | 1.87N      | 5.0                    | 25.0                   | Mand |
| 3     | 1.0        | 2.0                    | 10.0                   | Cit  |
| 4     | 1.0        | 2.0                    | 10.0                   | Mand |
| 5     | 4.0        | 0.05                   | 0.8                    | Succ |
| 6     | 4.0        | 0.05                   | 0.8                    | Cit  |
| 7     | 4.0        | 0.05                   | 0.8                    | Mand |
| 8     | 5.5        | 0.05                   | 0.8                    | Succ |
| 9     | 5.5        | 0.05                   | 0.8                    | Cit  |
| 10    | 5.5        | 0.05                   | 0.8                    | Mand |

5 cm cells were used in expts 1-4

with respect to Ti and GA in the mixed complexes was inferred to be 1 : 1 as in the case of tartrate reported earlier<sup>2</sup>. The  $X_{max}$  of 0.60 in the case of Cit at pH 5.5 may be due to the formation of a mixed complex to a lesser extent and the binary 1 : 3 complex of Ti and GA existing simultaneously to a significant extent, than in the case of Mand. Modified Bent and French method cannot be applied at these acidities to arrive at the composition with respect to AL.

The results of continuous variation method in the presence of Succ, which does not form mixed complexes, are of interest. The  $X_{max}$  values of 0.80 and 0.75 at pH 4.0 and 5.5 respectively in the Ti-GA binary system are not shifted even in the presence of large amounts of Succ (9, 10, 13 and 14 in Table 1). This is expected as per Gould and Vosburg<sup>6</sup>. The  $X_{max}$  values expected for the 1:2 and 1:3 complexes forming at these pH values are 0.67 and 0.75. From a comparison of results of continuous variation method in the presence of different AL, it is con-

cluded that dragged  $X_{max}$  is shifted from that obtained in the binary system, when mixed complex formation occurs with the AL. Since Succ is able to hold Ti in solution at pH 4.0 and still the  $X_{max}$  is at a higher value, the drag of  $X_{max}$  cannot be attributed to hydrolysis and polymerization of free metal ion. As mentioned earlier, this is attributed to the simultaneous presence of lower complexes<sup>2</sup>.

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#### Determination of Hydrazine Using Potassium Dichromate as Oxidizing Agent

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Hydrazine is oxidized quantitatively by  $K_2Cr_2O_7$  in acid solutions and the reaction involves transfer of 4 electrons. Different factors affecting the success of the volumetric and potentiometric determinations of  $N_2H_4$  have been examined. Under the optimum conditions, amounts ranging between 0.029 and 24 mg of hydrazine or 0.14 and 52.5 mg of chromium can be determined.  $Cu^{2+}$  catalyses the reaction. A statistical analysis of the data has also been carried out.

VARIOUS methods have been employed for the determination of hydrazine using different oxidizing agents<sup>1-5</sup>. Recently, Gopala Rao and Krishna Rao<sup>6</sup> investigated the reaction between Cr(VI) and  $N_2H_4$  in the presence of phosphoric acid.

It has been observed by us that hydrazine is oxidized quantitatively by potassium dichromate in HCl medium and this reaction has been utilized for the volumetric and potentiometric determination of hydrazine.

Hydrazine, sodium thiosulphate and potassium dichromate solutions were obtained by dissolving the AR products in doubly distilled water. Solutions of hydrazine and sodium thiosulphate were standardized by recommended procedures<sup>7</sup>.  $CuSO_4$  (0.25M), KI (10%) and HCl (10M) solutions were prepared by dissolving CP products in doubly distilled water. Starch solution used as indicator was prepared according to the method described by Vogel<sup>7</sup>.