

TABLE 1—EQUILIBRIUM AND FORMATION CONSTANTS OF Cu(II) MIXED LIGAND COMPLEXES, [Cu(II)-PA-L].

	L		
	Glycine	α -Alanine	Phenylalanine
$-\log K'$	2.13 ± 0.10	2.36 ± 0.10	1.55 ± 0.06
$-\log K''$	2.81 ± 0.12	1.04 ± 0.11	2.23 ± 0.12
$\log K_{MAL}$	7.47 ± 0.10	7.50 ± 0.10	7.50 ± 0.06
$\log \beta_{MAL}$	16.07 ± 0.12	16.10 ± 0.11	16.10 ± 0.12

$$T_A = [HA] + [A^-] + [CuA^+] + [CuAL] \quad \dots (3)$$

$$T_L = [HL] + [L^-] + [CuAL] \quad \dots (4)$$

where T_M , T_A and T_L represent the total concentrations of the metal, and primary and secondary ligands species respectively and T_{OH} is the concentration of the base added to the reaction mixture during titration. Since $T_M = T_A = T_L$ and $T_{OH} = mT_M$, it follows from the above equations that,

$$a[Cu^{2+}]^2 + b[Cu^{2+}] - c = 0 \quad \dots (5)$$

where, $a = K_{MA} \cdot k_1/[H^+]$, $b = x + y$, $c = \{(2-m)T_M - [H^+] + [OH^-]\}xy$, $x = 1 + k'_1[H^+]$ and $y = 1 + k'_1/[H^+]$.

k_1 represents the dissociation constant of picolinic acid and k'_1 that of α -amino acid; K_{MA} = formation constant of 1:1 Cu(II)-picolinic acid binary complex (8.60)⁴.

The equilibrium concentration of free metal ion present in the reaction mixture was determined by solving Eq. (5). The concentrations of other species involved in the equilibrium relations were then calculated using above relations and also the values of equilibrium constants K' and K'' of the reactions (i) and (ii) respectively.

Stability of 1:1:1 mixed ligand complexes—The stability constants of ternary complexes in these systems may be determined by the expression:

$$K_{MAL} = \frac{[CuAL]}{[CuA^+][L^-]} = \frac{K'}{k'_1} \quad \dots (6)$$

Further, the over-all stability constant of the mixed ligand complexes may be calculated by the relation:

$$\beta_{MAL} = \frac{[CuAL]}{[Cu^{2+}][A^-][L^-]} = \frac{K''}{k_1 k'_1} \quad \dots (7)$$

The values of formation constants of the ternary complexes are listed in Table 1.

Constant values of the equilibrium and stability constants have been obtained at all points of the titration curves before the precipitation occurs at about $m=2$ in all these systems. The data given in Table 1 reveal that the values of $\log \beta_{MAL}$ for each of these mixed ligand complexes is higher than the mean of $\log K_{MA2}$ (16.00)⁴ and $\log K_{ML2}$ (Gly = 14.83; Ala = 15.37; Phe = 14.90)⁵⁻⁷. The reason for this extra stabilization is the electrostatic ligand effect which promotes the formation of the mixed complex.

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Paper Chromatographic Separation of Iron Valences via Their Anthranilates & Their Photometric Estimation as Pyridine Adducts

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Quantitative separation of iron valences via their anthranilates by paper chromatography has been achieved with large ΔR_f values. The anthranilates of iron form synergistic adducts with pyridine, which are extractable into inert solvents like benzene, toluene and carbon tetrachloride. Both these adducts, when extracted into benzene, show sharp absorption maxima at 390 nm. The extraction of ferric complex is quantitative whereas the extraction of ferrous is not. The ferrous complex is also unstable and is therefore oxidised to ferric before estimation.

A number of studies report the chromatographic separation of iron valences in their simple ionic forms¹⁻⁹, but only a few report complexation before chromatographic separation¹⁰⁻¹². Complexation widens the difference in the physicochemical properties of the valences enabling easy and better separations.

Dinsel and Sweet¹³ have reported the separation of ferrous and ferric anthranilates at pH 4.5 by differential extraction with *n*-pentanol, followed by photometric estimation. In their work (i) only oxygen-containing solvents (not inert solvents like benzene, toluene, carbon tetrachloride etc.) could extract ferric anthranilate, whereas neither type could extract ferrous anthranilate; (ii) minimum quantities handled in their estimation for ferric complex were about 50 μ g; and (iii) the absorption spectrum obtained for ferric complex was far from satisfactory; in fact it exhibited no more than a plateau between 420 and 500 nm.

By adapting their anthranilate reactions to paper chromatographic separation, it has been possible to handle much lower quantities of the order of 10 μ g. In addition, we have also found that in the presence of pyridine, both ferrous and ferric anthranilates form adducts, which can be extracted not only by oxygen containing solvents but also by inert solvents like benzene, toluene, carbon tetrachloride, chloroform, etc. The benzene extract of ferric complex exhibits a well-defined peak at 390 nm with higher ϵ value ($\epsilon = 1988$), indicative of greater

sensitivity than that obtained by the previous workers¹³ ($\epsilon = 1302$).

Approximately decimolar solutions of the ions freshly prepared by dissolving analytical grade ferrous and ferric ammonium sulphates in deionised and deoxygenated water acidulated with H_2SO_4 were used for analysis.

A saturated solution of anthranilic acid was prepared by dissolving recrystallized anthranilic acid (25g) in water (300 ml) containing a 10% solution (75 ml) of NaOH. The solution was then diluted to 500 ml and the pH adjusted to 4.5 with dil. sulphuric acid¹³. The solution was allowed to stand for about 10 min and the supernatant liquid decanted and stored in a brown bottle.

Ferric anthranilate on the chromatogram was detected by its red colour. Further confirmation was done by spraying with a 2M acidic solution of potassium thiocyanate¹⁴.

Ferrous anthranilate when sprayed with 2% aq. solution of bipyridyl (pH 3) also developed a red colour¹⁴.

Rutter's technique¹⁵ of circular paper chromatography was adopted using 12 cm circles of Whatman No. 1 chromatographic paper. The spotting sequence was as follows: Anthranilic acid (20 μ l) was spotted at the centre of the circle followed by the ferrous and ferric ions (individually or in admixture), and finally with the complexing agent. The spot was dried at each step. The complexation was instantaneous and quantitative¹³. The complexed ions were then eluted with alcohols, ketones, esters and other oxygen-containing solvents (vide Table 1).

Photometric estimation—To an aliquot of the sample, anthranilic acid (20 ml, pH 4.5) was added followed by pyridine (4 ml) and the solution diluted to 30 ml. After standing for 2 min, the complex was extracted with benzene (7 ml) and the benzene extract dried over anhyd. sodium sulphate. The extract was transferred to 10 ml standard flask,

and the volume made up to the mark with benzene. The absorbance at 390 nm was measured with Beckman model B spectrophotometer using 1 cm matched quartz cell.

In the case of ferrous complex, 2 ml of a 10% aqueous solution of hydroxylammonium chloride was added during complexation to suppress the possible oxidation of ferrous to ferric state.

The chromatograms were cut out for the ions, and the complexes were extracted with dil. H_2SO_4 ; complexation and extraction were followed as described above. The ferrous ion has to be oxidised by hydrogen peroxide to ferric as otherwise the extraction of the ferrous complex into benzene is not usually complete. This also obviates the error due to slow oxidation to ferric state. The absorbances of the extracts were measured at 390 nm.

Table 1 shows that with higher alcohols, ketones, esters, nitrobenzene and dioxan, the separation is clean and thorough with $\Delta R_f \approx 1.0$. The migration of the ferric complex, $Fe(An)_2OH.H_2O$ (An = anthranilate), is due to the possible displacement of the water molecule by the oxygen-containing solvents¹³ and their consequent solubilization. Ferrous anthranilate being coordinatively an unsaturated complex, is supposed to contain two water molecules similar to other divalent metal anthranilates¹⁶. Though the ferrous complex has two coordinated water molecules, their displacement does not happen due to stronger co-ordination than in the ferric complex¹⁶⁻¹⁸. However if the solvent is more strongly co-ordinating, like pyridine and formamide, the co-ordinated water molecules of the ferrous complex are displaced, leading to solubilization and migration. The lower alcohols are not suitable for quantitative separation as they lead to the weakening of ferric anthranilate bond¹⁸ with the result that Fe(III) diffuses out. The ferrous and ferric complexes are quite stable in many solvent systems wherein a quantitative separation of the two valences have been obtained.

The photometric estimation suggested by Dinsel and Sweet¹³ has been improved to give greater sensitivity via the formation of a synergistic adduct with pyridine¹⁹. When excess pyridine (4 ml for 30 ml of aqueous phase) was added to the ferric anthranilate complex, an orange red complex was obtained which was extractable in benzene with 4 ml of pyridine the ferric complex exhibited maximum absorbance at 390 nm. Pyridine evidently displaces the co-ordinated water molecule to yield an adduct of composition $Fe(An)_2OH.Py$. The consequent lessening of polarity leads to solubilization by benzene. The absorption spectrum of the adduct shows a sharp absorption peak with appreciable ϵ ($\epsilon = 1988$ at λ_{max} 390 nm). The adduct formation was complete and the extraction was quantitative and the complex was stable for more than 24 hr.

The ferrous anthranilate gives with pyridine a golden yellow complex which can also be extracted into benzene. This shows a well-defined absorption peak also at 390 nm similar to the ferric adduct. However, the ferrous complex is stable only for 15 min even in presence of hydroxylammonium chloride and its extraction is not quantitative. Hence,

TABLE 1—PAPER CHROMATOGRAPHIC SEPARATION OF IRON VALENCES VIA THEIR ANTHRANILATES

Eluent	R_f		Estimated (μ g) ^c	
	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
Methanol	Zero	1.0 ^d		
Ethanol	do	1.0 ^d		
Isopropanol	do	1.0 ^d		
Isobutanol	do	1.0	10.09	9.92
Isoamyl alcohol	do	1.0	10.03	9.98
Ketones ^a	do	1.0	9.92-10.07	9.96-10.04
Esters ^b	do	1.0	9.95-10.06	9.91-10.08
Nitrobenzene	do	1.0	10.01	9.91
Dioxan	do	1.0	9.95	10.05
Pyridine	1.0 ^d	1.0		
Formamide	1.0 ^d	1.0		

(a) Acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and acetophenone.

(b) Methyl acetate, ethyl acetate, *n*-butyl acetate, isoamyl acetate and vinyl acetate.

(c) Quantity spotted : 10 μ g each of Fe²⁺ and Fe³⁺; average of 3 to 4 estimations

(d) Diffused

it was oxidised to ferric before extraction and analysis.

Elements such as Co, Ni, Cr, Mn, Cu, Pb, Hg, Zn, which are usually associated with iron, do not interfere in this estimation. Co and Ni give purple and bluish green adducts, but they do not show any absorption at 390 nm.

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1-Hydroxy-2-acetonaphthone Oxime as Amperometric Reagent for Copper & Nickel†

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Copper (0.25-5 mg) is titrated against the oxime in the presence of sodium acetate-acetic acid buffer of pH 4.5 at an applied potential of -0.4 V (vs SCE) and nickel (0.25-3 mg) is titrated in the presence of ammonium chloride-ammonia buffer of pH 8.5 at an applied potential of -1.4 V (vs SCE). L-shaped curves are obtained in both the cases. The effect of elements commonly associated with these metals in their ores and alloys has been studied. Determination of copper and nickel in a binary solution is also reported. The method has been applied for the analysis of copper and nickel in constantan and german silver.

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SEVERAL 1,2-dioximes and certain other oximes find use as titrants in the amperometric titration of nickel and several other metals, notably palladium, cobalt and copper¹. Resacetophenone oxime² and 2-hydroxy-1-acetonaphthone oxime³ have been successfully employed for the determination of copper and nickel in a binary solution. We have successfully employed an isomer of the latter as an amperometric titrant for copper and nickel. An alcoholic solution of the reagent is more stable than that of the corresponding 2-hydroxy isomer.

All chemicals used were of AR grade. Solutions of copper and nickel were standardised by the iodometric^{4a} and dimethylglyoxime^{4b} methods respectively.

1-Hydroxy-2-acetonaphthone oxime was prepared from 1-hydroxy-2-acetonaphthone⁵ by the usual procedure of oxime preparation⁶. It was recrystallised from rectified spirit and dried *in vacuo*. A stock solution (0.025 M) of the reagent was prepared in rectified spirit. Solutions of various metal ions used for the study of the effect of foreign ions were prepared such that each ml contained 5 mg of the metal.

Sodium acetate (2M) and acetic acid (2M) buffer (pH 4.5) acted as the supporting electrolyte for copper while ammonium chloride (0.5 M) and ammonia (0.5M) buffer acted as the supporting electrolyte for nickel.

Lange's polarometer model III coupled with multiplex galvanometer type MGF-2, a modified Lingane type H-cell and the d.m.e. (Toshniwal, India) were used for amperometric titration. The drop time of d.m.e. was maintained at about 3 sec in all the studies. An Elico pH meter model Li-10 was used for pH measurements. The reproducibility of the instrument was ± 0.05 pH units.

Determination of copper—To measured volumes of standard copper (II) solution (0.25-5 mg of copper) were added sodium acetate (5 ml), acetic acid (5 ml) Triton-X-100 solution (1 ml, 1%) and rectified spirit (10 ml) and the total volume was made up to 75 ml. The solution was deoxygenated by bubbling purified hydrogen gas for 20 min. The voltage was fixed at -0.4V (vs SCE) and the solution titrated against standard oxime solution (0.025M). After each addition of the reagent from the microburette, hydrogen gas was passed into the solution to ensure thorough mixing and then corresponding current readings were noted from the galvanometer. The current readings were corrected for volume changes. An L-shaped curve was obtained. The end point corresponded to 1:2 (metal : reagent) stoichiometry.

The method developed was successfully employed for the determination of copper in brass, gun-metal, Devarda's alloy and chalcopyrites. The results are recorded in Table 1. Only Fe(III) out of several associated elements (nickel, cobalt, zinc, manganese, cadmium, aluminium, arsenic, selenium and tellurium) interfered in the determination of copper. Its interference was eliminated by masking with fluoride. Five determinations of 1.012 mg of copper gave a