

## SPECTROPHOTOMETRIC STUDIES ON FERROUS COMPLEXES OF QUINOLINE- AND PYRIDINE-CARBOXYLIC ACIDS. PART III. FERROUS DIPICOLINIC ACID AND FERROUS QUINOLINIC ACID SYSTEMS

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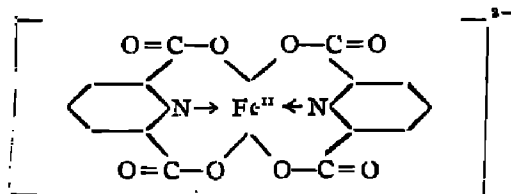
Highly soluble coloured ferrous complexes of dipicolinic and quinolinic acids have been studied by spectrophotometric method. The ferrous complexes of some other pyridine di- and tri-carboxylic acids with a carboxyl group in the  $\alpha$ -position to the nitrogen atom have also been studied in a qualitative manner.

Ferrous dipicolinic acid complex shows its maximum colour intensity between  $pH$  5 and 7 and the  $\lambda_{max}$  at  $480 m\mu$ . The intensity of colour, however, decreases in the presence of KCN or pyridine. The colour system obeys Beer's law, and its composition is given by  $1 Fe^{II} : 2$  acid, with an instability constant,  $1.85 \times 10^{-7}$ .

The soluble coloured complex of ferrous quinolinic acid has been found to give its maximum colour intensity between  $pH$  5.7 and 7.0 with  $\lambda_{max}$  at  $420 m\mu$ , and the colour is intensified with the addition of KCN, and to some extent with pyridine. The  $\lambda_{max}$  for cyanide-containing system lies at  $440 m\mu$ . The colour system with or without the cyanide obeys Beer's law under specified conditions. The composition of the complex is represented by  $1 Fe^{II} : 3$  acid with an instability constant of  $3.47 \times 10^{-11}$ .

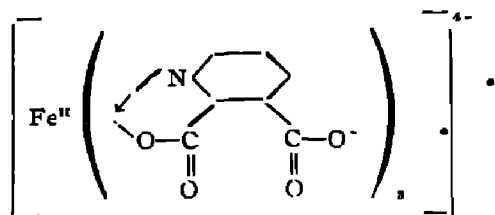
In the previous papers (Parts I and II, this *Journal*, 1958, 35, 297, 493) the formation of ferrous complexes with quinaldinic acid and picolinic acid has been studied by the spectrophotometric method. The results of studying the ferrous complexes of dipicolinic acid and quinolinic acid and also of other pyridine di- and tri-carboxylic acids with at least one carboxyl group at the 2-position to the nitrogen atom of the pyridine ring, are reported in the present communication.

The composition of ferrous dipicolinic acid (pyridine-2:6-dicarboxylic acid) complex from spectrophotometric measurements, following Job's method, is given by  $1 Fe : 2$  acid. The complex may therefore be represented by the following configuration, where the acid molecule behaves as a tridentate ligand.



The value of the instability constant of the complex was found to be  $1.85 \times 10^{-7}$ .

Quinolinic acid (pyridine-2:3 dicarboxylic acid) was found by Job's method to combine with ferrous ion yielding a complex of the composition  $1 Fe : 3$  acid. It can therefore possess an octahedral configuration as shown below :



Each acid molecule here behaves as a bidentate ligand with one of its carboxyl group remaining free. The value of the instability constant for the quinolinate complex was found to be  $3.47 \times 10^{-11}$ .

Pyridine-2:4- and 2:5-dicarboxylic acids and pyridine-2:4:6-, -2:3:6- and -2:4:5-tricarboxylic acids have all been found to furnish yellow to red ferrous complexes. Like ferrous quinaldinate and picolinate, the colour of the ferrous complexes of all the above mentioned pyridine carboxylic acids, with the exception of those of dipicolinic acid (2:6) and collidinic acid (2:4:6), is highly intensified by the addition of potassium cyanide solution and also to a considerable extent by pyridine. As in the case of picolinic acid, the part played by potassium cyanide in intensifying the colour of the soluble ferrous complex possibly lies in the formation of a cyano complex in which a molecule of the pyridine di- or tri-carboxylic acid in their coloured complexes is replaced by an equivalent number of cyanogen groups. They, thus, form anionic complexes, the colour intensity of which increases with an increasing amount of KCN and then finally reaches to a constant maximum value. In all these cases the absorption maximum remains practically unaltered.

It is, however, of striking interest to note that in the cases of dipicolinic acid and collidinic acid, the colour of the ferrous complex, in contrast to the behaviour of the ferrous complexes of other pyridine carboxylic acids, is considerably reduced in intensity by the addition of an excess of potassium cyanide.

#### EXPERIMENTAL

A Unicam SP 600 spectrophotometer and a Cambridge Bench Type  $p_H$  meter were used in this work. The reagents used were all of guaranteed quality.

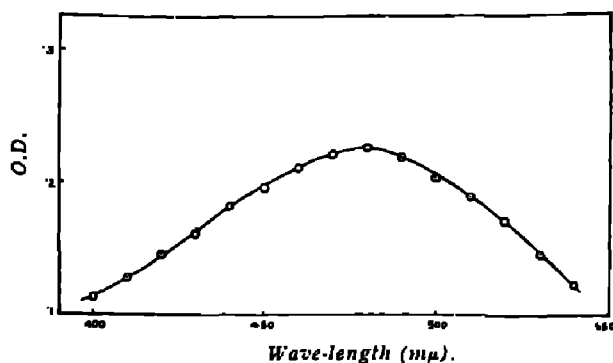
Dipicolinic, quino'inic, collidinic and pyridine-2:3:6-tricarboxylic acids were prepared by the permanganate oxidation of 2:6-dimethylpyridine, quinoline, collidine, and quinaldinic acid respectively (Ladenburg and Roth, *Ber.*, 1885, 18, 52; Königs, *Ber.*, 1879, 12, 983; Voigt, *Annalen*, 1885, 228, 31; Miller, *Ber.*, 1891, 24, 1916). Lutidinic and isocinchomeric acids were prepared by the permanganate oxidation of a mixture of 2:4- and 2:5-dimethylpyridine and then by subsequent separation of the two acids (Banerjee and Ray, *this Journal*, 1957, 34, 208). Pyridine-2:4:5-tricarboxylic acid was prepared by the oxidation of berberine with nitric acid (Weidel, *Ber.*, 1879, 12, 410).

*Ferrous Dipicolinic Acid System*

With dipicolinic acid iron (II) forms a highly soluble yellow coloured complex with its absorption maximum lying in the region of 480  $m\mu$ . The optimum  $p_H$  for the maximum colour formation ranges between 5 and 7. Unlike picolinic or quinaldinic acid and some other pyridine carboxylic acids, the colour intensity of the dipicolinic acid complex diminishes with the addition of potassium cyanide or pyridine. The maximum colour formation also requires some time, at least a period of 30 minutes at  $p_H$  6.4 and above. The colour is quite stable and remains unchanged for 24 hours at room temperature. At least one and half times the theoretical quantity of dipicolinic acid is required for the maximum development of colour. The coloured complex obeys Beer's law and the sensitivity is given by 0.044 $\gamma$ Fe/ $cm^2$  (Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York, 1950, p. 47).

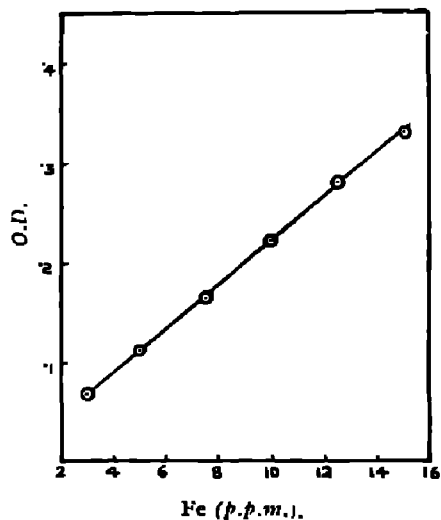
*Wave-length of Absorption Maximum ( $\lambda_{max}$ ).*—The same procedure, as described before (cf. Part I, *loc. cit.*), was followed. The reagent and the Fe<sup>II</sup> blank separately showed practically no absorption within the range of measurement. Fig. 1 shows the optical density values of the coloured complex at different wave-lengths. It should be noted that all measurements were made after one hour since the time of mixing the solution, when the colour was fully developed. From Fig. 1, it can be concluded that  $\lambda_{max}$  for ferrous dipicolinic acid system lies at 480  $m\mu$ .

FIG. 1



Ferric nitrate (50 p.p.m.) 10 c.c.  
 NH<sub>4</sub>OH.HCl (5%) 5 c.c.  
 Dipicolinic acid (0.25%) 10 c.c.  
 Total volume, 50 c.c.  
 Cell used, 1 cm.  $p_H$ , 6.

FIG. 2

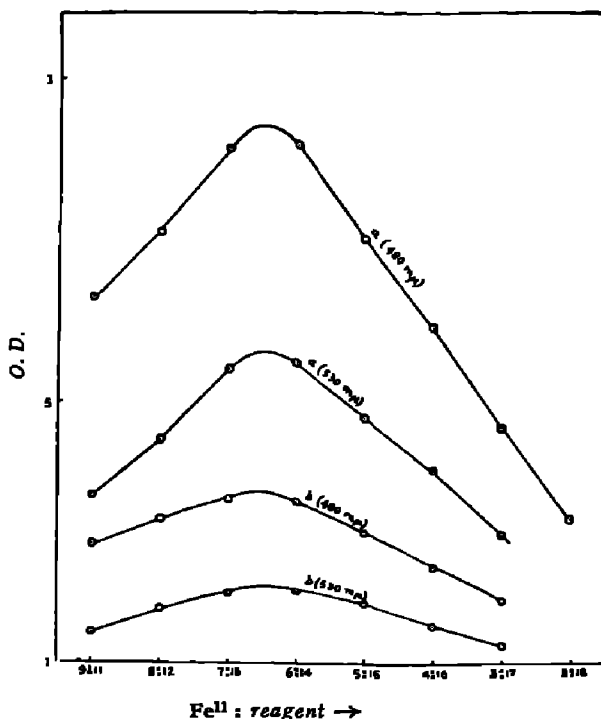


Ferric nitrate (50 p.p.m. Fe),  $x$  c.c.  
 NH<sub>4</sub>OH.HCl (5%) 5 c.c.  
 Dipicolinic acid (0.25%) 10 c.c.  
 Total vol., 50 c.c.  
 Cell used, 1 cm. 480  $m\mu$ .  $p_H$ , 6.

*Beer's Law.*—The coloured complex obeys Beer's law. This is evident from the optical density values shown in Fig 2.

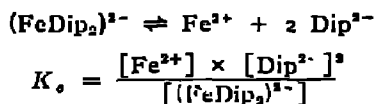
*Composition of the Coloured Complex of Ferrous Iron and Dipicolinic Acid.*—The composition of the coloured complex was determined by Job's method at  $p_H$  5.99 as in the case of ferrous picolinic acid system. The results of measurements are shown in Fig. 3 (a, b). It is clear that the composition of the complex is represented by 1 Fe : 2 acid.

FIG. 3



- (a) Ferrous amm. sulphate (0.005M) containing  $\text{NH}_4\text{OH} \cdot \text{HCl}$  (1%),  $x$  c.c. Dipicolinic acid (0.005M),  $y$  c.c.  $\text{KNO}_3$  (1M), 10 c.c. (added to maintain constant ionic strength). Buffer (5.99  $p_H$ ), 18 c.c. Total volume, 50 c.c. Cell used, 2 cm.  
 (b) Ferrous amm. sulphate (0.002M) containing  $\text{NH}_4\text{OH} \cdot \text{HCl}$  (1%),  $x$  c.c. Dipicolinic acid (0.002M),  $y$  c.c. All the other conditions are exactly the same as for (a).

*Instability Constant of the Coloured Complex.*—The instability constant of the coloured complex can be derived as in the previous cases from its dissociation in solution according to the equation :



where  $\text{H}_2\text{Dip}$  = one molecule of dipicolinic acid. The values of  $\text{Dip}^{2-}$  and  $K_s$  are calculated as in the case of the quinaldinic acid complex.

$$K_c = \frac{[\text{Fe}^{2+}]}{[(\text{FeDip}_2)^{2-}]} \times \frac{K_{a_1} \{[\text{Dip}_2] - 2[(\text{FeDip}_2)^{2-}]\}^2}{\{K_{a_1} + [\text{H}^+]\}^2} \quad \dots \quad (1)$$

The symbols have the same significance as in previous parts.  $K_{a_1}$ , the dissociation constant of  $(\text{HDip})^-$ , was determined at  $30^\circ$ , following the method suggested by Bjerrum. ("Metal-amine Formation in Aqueous Solutions", P. Haase and Son, Copenhagen, 1941).

#### *Dissociation Constant of Dipicolinic Acid*

The method of its determination consists in the titration of a solution of dipicolinic acid with a standard (carbonate free) alkali and noting the  $p_H$  values of the solution after each addition of the latter.

The dissociation of a dicarboxylic acid may be represented as follows:

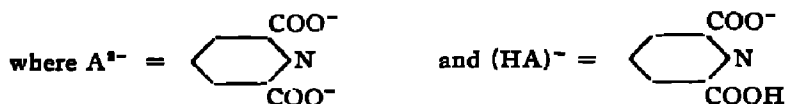


where  $\text{H}_2\text{A}$  represents a molecule of the dicarboxylic acid. Now for the successive acid dissociation constants we get

$$K_{a_1} = \frac{[\text{HA}^-] \times [\text{H}^+]}{[\text{H}_2\text{A}]} \quad \dots \quad \dots \quad (4)$$

and

$$K_{a_2} = \frac{[\text{A}^{2-}] \times [\text{H}^+]}{[\text{HA}^-]} \quad \dots \quad \dots \quad (5)$$



Let  $B$  be the total molar concentration of dipicolinic acid taken, so that

$$B = B_0 + B_1 + B_2 \quad \dots \quad \dots \quad (6)$$

where  $B_0$ ,  $B_1$  and  $B_2$  are the respective molar concentration of  $\text{Dip}^{2-}$ ,  $\text{HDip}^-$  and  $\text{H}_2\text{Dip}$ ; and let  $P$  be the molar concentration of the alkali added. Then from the measurements of the  $p_H$  of the solution we get,

$$2B - 2B_2 - B_1 - \text{H}^+ = P - \text{OH}^- \quad \dots \quad \dots \quad (7)$$

(Acid neutralised)      (Alkali used up)

which on transposition gives

$$2B_2 + B_1 = 2B - P - \text{H}^+ + \text{OH}^- \quad \dots \quad \dots \quad (8)$$

As it is a case of stepwise dissociation, where the amount of acid neutralised is assumed to be less than  $B$ , the process (2) may be regarded as still incomplete, and so the amount of  $B_0$  formed is negligibly small and can be ignored. Then from the equation (6) we get,

$$B = B_1 + B_2 \quad \dots \quad \dots \quad (9)$$

Substituting this value of B in (7) we get,

$$B_1 = P + H^+ - OH^- \quad \dots \quad \dots \quad (10)$$

and hence,

$$B_2 = B - P - H^+ + OH^- \quad \dots \quad \dots \quad (11)$$

So, 
$$K_{a_1} = \frac{B_1 \times [H^+]}{B_2} = \frac{[P + H^+ - OH^-] \times [H^+]}{[B - P - H^+ + OH^-]} \quad \dots \quad (12)$$

Again, when the acid neutralised is more than B, process (2) can then be regarded as complete, and so  $B_2$  may be taken as negligibly small. Then from (6) we get

$$B = B_0 + B_1 \quad \dots \quad \dots \quad (13)$$

and from (7) we get

$$B_1 = 2B - P - H^+ + OH^-$$

Hence,

$$B_0 = P - B + H^+ - OH^- \quad \dots \quad \dots \quad (14)$$

Therefore,

$$K_{a_1} = \frac{B_0 \times [H^+]}{B_1} = \frac{[P - B + H^+ - OH^-] \times [H^+]}{[2B - P - H^+ + OH^-]} \quad \dots \quad (15)$$

The formation curves for these systems were obtained by plotting  $\bar{\eta}$  against  $p_x$  values for each separate observations; where  $\bar{\eta}$  = average number of hydrogen ions bound to a fully dissociated ligand anion, *i.e.*,

$$\begin{aligned} \bar{\eta} &= \frac{\text{Total No. of } H^+ \text{ bound}}{\text{Total No. of ligand molecules present}} \\ &= \frac{2B_2 + B_1}{B} \end{aligned}$$

It will be clear from equations (4) and (5) that when  $\bar{\eta} = 0.5$  and  $1.5$  respectively,  $K_{a_1}$  and  $K_{a_2}$  become equal to the corresponding  $[H^+]$  value. Hence, by plotting the value of  $\bar{\eta}$  against  $p_x$ , the values of  $K_{a_1}$  and  $K_{a_2}$  can be readily obtained.

The results of measurements are recorded in Table I, and the  $\bar{\eta}/p_x$  curve is plotted in Fig. 4.

TABLE I

Acid taken = 150 c.c. of 0.004M. Alkali = 0.0999N-NaOH. Temp. = 30°.

B (conc. of the acid in moles/litre).	Alkali added.	$2B_2 + B_1 + H^+$ .	$p_x$ .	$\frac{2B_2 + B_1}{B} = \bar{\eta}$ .
0.00397	1 c.c.	0.00728	2.66	1.28
0.00395	2	0.00658	2.78	1.24
0.003922	3	0.00588	2.93	1.20
0.003896	4	0.00519	3.10	1.13
0.003872	5	0.00454	3.41	1.07
0.003847	6	0.00385	3.91	0.96
0.003822	7	0.00319	4.39	0.82
0.003797	8	0.00255	4.73	0.67
0.003774	9	0.00189	5.01	0.499
0.003751	10	0.00126	5.32	0.33
0.003727	11	0.000634	5.78	0.17

From Fig. 4,  $K_a$ , corresponding to  $\bar{\eta} = 0.5$  was found to be  $1 \times 10^{-5}$ . As the instability constant of ferrous dipicolinic acid complex had to be determined at about  $p_H$  6 it was assumed that the process (2) for the dissociation of the acid might be regarded as complete. Therefore the value  $K_a$ , only was necessary for the calculation of the instability constant of the ferrous dipicolinic acid complex.

FIG. 4

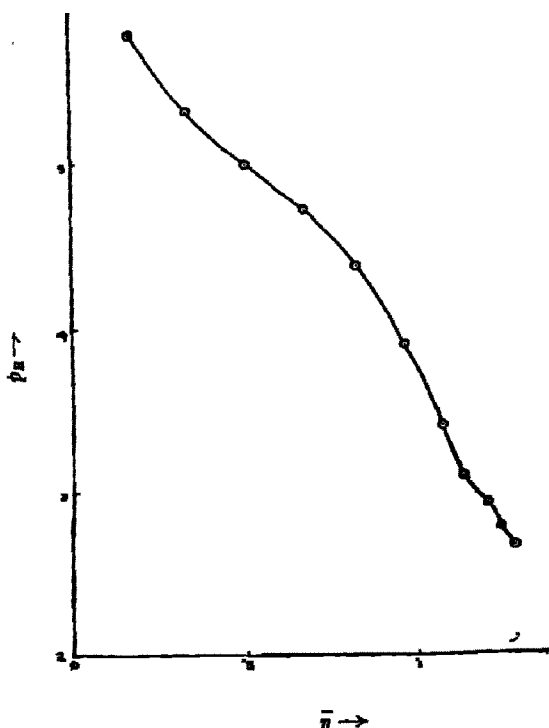


Table II (A, B) records the measured optical density values of the coloured complex in equilibrium.

TABLE II

A. Ferrous amm. sulphate (0.002M) containing  $\text{NH}_2\text{OH.HCl}$  (1%) =  $x$  c.c.  
 Dipicolinic acid (0.005M) =  $y$  c.c.  $\text{KNO}_3$  (1 M) soln. = 10 c.c.  
 Buffer = 18 c.c. ( $p_H$  5.99). Cell = 2 cm. 480 m $\mu$ .

Dipicolinic acid (c.c.)	...	1	2	3(a)	4	5(b)	6	7(c)	8(d)	9
Fe soln. (c.c.)	...	9	8	7	6	5	4	3	2	1
O.D.	...	0.040	0.072	0.118	0.176	0.223	0.229	0.184	0.124	0.070

B. Ferrous amm. sulphate (0.002M) containing  $\text{NH}_2\text{OH.HCl}$  (1%) =  $x$  c.c.

Dipicolinic acid (0.004M) =  $y$  c.c. All the other conditions are exactly the same as in A.

Dipicolinic acid (c.c.)	...	4	6(e)	8	10(f)	12	14(g)	16
Fe soln. (c.c.)	...	16	14	12	10	8	6	4
O.D.	...	0.172	0.279	0.411	0.525	0.476	0.378	0.240

From equation (1)  $K_a$  was calculated for a, b, c, d, e, f, g. The results are recorded in Table III.

TABLE III

$$K_{a_1} = 1 \times 10^{-5}. \quad [H^+] = 0.1023 \times 10^{-3}.$$

No.	[Dip <sub>2</sub> ].	[FeDip <sub>2</sub> ].	[Fe <sup>2+</sup> ]. <sup>a</sup>	K <sub>s</sub> .
a	$3.00 \times 10^{-4}$	$4.76 \times 10^{-5}$	$2.32 \times 10^{-4}$	$1.68 \times 10^{-7}$
b	$5.00 \times 10^{-4}$	$8.99 \times 10^{-5}$	$1.10 \times 10^{-4}$	$1.03 \times 10^{-7}$
c	$7.00 \times 10^{-4}$	$7.42 \times 10^{-5}$	$4.58 \times 10^{-5}$	$1.55 \times 10^{-7}$
d	$8.00 \times 10^{-4}$	$5.00 \times 10^{-5}$	$3.00 \times 10^{-5}$	$2.42 \times 10^{-7}$
e	$4.80 \times 10^{-4}$	$1.13 \times 10^{-4}$	$4.47 \times 10^{-4}$	$2.10 \times 10^{-7}$
f	$8.00 \times 10^{-4}$	$1.12 \times 10^{-4}$	$1.88 \times 10^{-4}$	$1.03 \times 10^{-7}$
g	$1.12 \times 10^{-3}$	$1.52 \times 10^{-4}$	$8.80 \times 10^{-5}$	$3.18 \times 10^{-7}$

Hence K<sub>s</sub> (mean) =  $1.85 \times 10^{-7}$

#### Ferrous Quinolinic Acid System

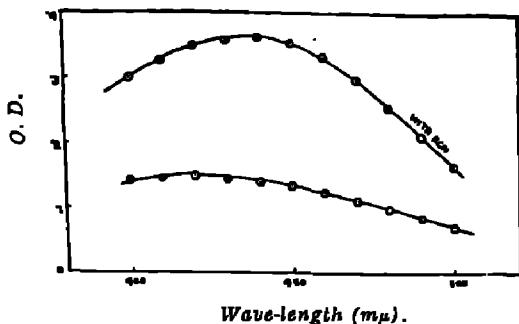
With quinolinic acid iron (II), as already stated, forms a highly soluble coloured complex. The colour is intensified with the addition of potassium cyanide or pyridine as is the case with ferrous picolinic acid and quinaldinic acid complexes. It resembles particularly the picolinic acid complex in this respect. There is, however, one difference namely, that it takes some time for the maximum colour development at a  $p_H$  higher than 6, or with a high concentration of KCN or pyridine. When optical densities were measured after the same interval of time for different solutions, a region of maximum intensification was observed with a moderate concentration of KCN. The  $\lambda_{max}$  of the simple ferrous quinolinic acid complex lies between 410 m $\mu$  and 430 m $\mu$ , and that of the cyanide-containing system at a somewhat higher value of 440 m $\mu$ . As in the case of picolinic acid, with the addition of a large excess of pyridine the  $\lambda_{max}$  shifts towards the ultraviolet region. The sensitivity of the simple coloured system is given by 0.066 $\gamma$  (Sandell, *loc. cit.*) and that of the cyanide-containing system by 0.028 $\gamma$  Fe/cm<sup>2</sup>. At least six times the theoretically required amount of the reagent is necessary for the maximum colour development. For the cyanide-containing system, as large as 100 moles of the latter for each mole of iron present are required for the maximum colour formation. The optimum  $p_H$  for colour formation lies between 5.7 and 7.0.

At about  $p_H$  8, the colour of the simple ferrous quinolinic acid system is somewhat weaker and assumes a reddish tint. At a higher  $p_H$  turbidity sets in. The colour system with or without the potassium cyanide under specified conditions obeys Beer's law and is quite stable at room temperature for 24 hours.

*Wave-length of Absorption Maximum.*—The same procedure as in the case of ferrous quinaldinic acid system was followed. The reagent blank (without iron) showed negligible absorption at about 420 m $\mu$ . Fig. 5 shows the optical density values of the coloured complex at different wave-lengths with or without KCN. It should be noted that in this case all measurements were made after one hour since the time of mixing the solutions. During this period it was found necessary to shake the mixture repeatedly to facilitate the development of colour. The mixture was found to show a strong tendency for bubble formation. Care had therefore to be taken to eliminate these before making the measurements. From Fig. 5 it can be concluded that  $\lambda_{max}$  for the simple ferrous quinolinic acid system lies between 410 and 430 m $\mu$  and that of the cyanide-containing system at 440 m $\mu$ .

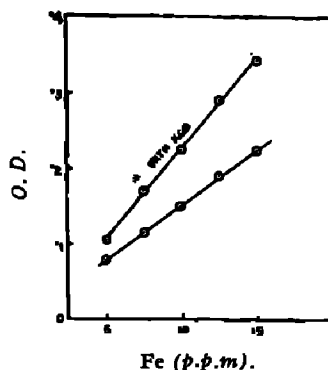


FIG. 5



Wave-length ( $m\mu$ ).  
 Ferric nitrate (50 p.p.m. Fe), 10 c.c.  
 $NH_2OH.HCl$  (5%), 5 c.c. Quinolinic acid (0.4%),  
 10 c.c. KCN (2%), 15 c.c.  
 Total vol., 50 c.c. Cell, 1 cm.  
 $p_H$ , 6.0 (without KCN) and  $p_H$ , 6.6 (with KCN).

FIG. 6

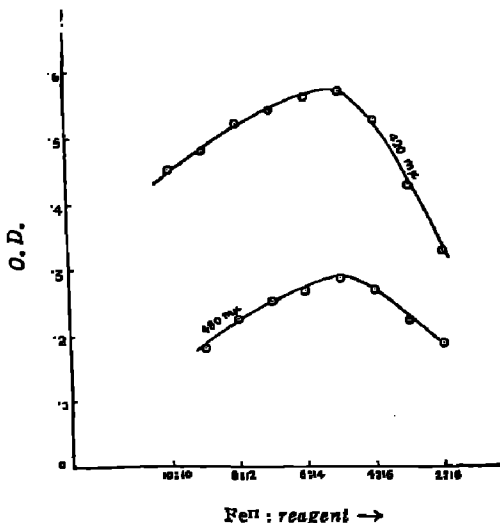


Fe ( $p.p.m.$ ).  
 Ferric nitrate (50 p.p.m. Fe),  $x$  c.c.  
 $NH_2OH.HCl$  (5%), 5 c.c. Quinolinic acid (0.4%),  
 10 c.c. Total vol., 50 c.c. Cell, 1 cm. KCN (2%),  
 15 c.c.  $p_H$ , 6.5 (with or without KCN).  
 $m\mu$ , 420 (without KCN) and 440 (with KCN).

**Beer's Law.**—The coloured complex with or without cyanide obeys Beer's law in the  $p_H$  range of 5.7 to 7.0. Fig. 6 gives a graphical representation of the optical density values for Beer's law.

**Composition of the Coloured Complex of  $Fe^{II}$  and Quinolinic Acid.**—The composition of the coloured complex was determined spectrophotometrically by Job's method at  $p_H$  5.99 as before. The values of measurements are represented in Fig. 7. It is thus clear that the composition of the coloured complex is given by 1 Fe : 3 acid.

FIG. 7



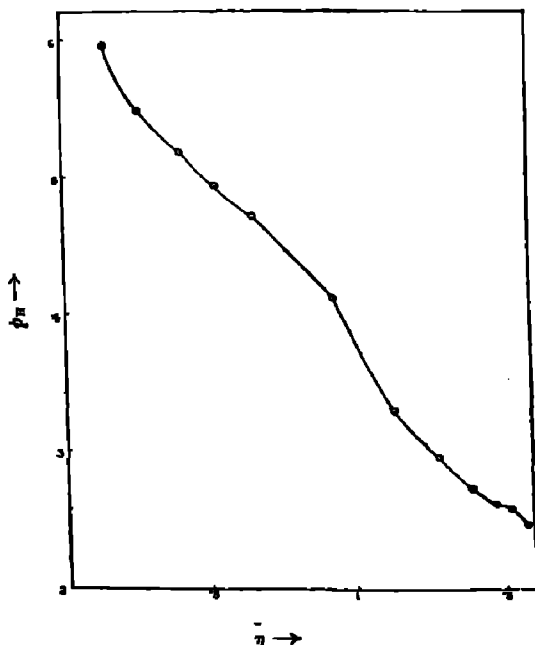
Fe<sup>II</sup> : reagent →  
 Ferrous ammu. sulphate (0.005 M) containing  $NH_2OH.HCl$  (1%),  $x$  c.c.  
 Quinolinic acid (0.005 M),  $y$  c.c.  $KNO_3$  (1 M) 10 c.c. Buffer (5.99  $p_H$ ), 18 c.c.  
 Total volume, 50 c.c. Cell, 1 cm.

*Instability Constant of the Coloured Complex.*—The instability constant of the coloured complex can be derived as in the previous cases. The value of  $K_c$  was calculated as in the case of picolinic acid (Part I, *loc. cit.*) from the equation :

$$K_c = \frac{[\text{Fe}^{2+}]}{[(\text{FeQui}_2)^{4-}]} \times \frac{K_a^3 \{[\text{Qui}] - 3 [(\text{FeQui}_2)^{4-}]\}^2}{\{K_a + [\text{H}^+]\}^3} \quad \dots (16)$$

where  $\text{H}_2\text{Qui}$  = one molecule of quinolinic acid and the other symbols have the same significance as before (Part I, *loc. cit.*).  $[\text{Fe}^{2+}]$  is the concentration of free ferrous ion,  $[\text{Qui}]$  = concentration of the total quinolinic acid taken and  $[(\text{FeQui}_2)^{4-}]$  is that of the complex ion formed as calculated from the observed optical density. The dissociation constants of the acid,  $K_a$ , and  $K_a$ , were determined at about  $30^\circ$  by a set of experiments similar to that made in the case of dipicolinic acid. The experimental results are recorded in Table IV and the  $\bar{\eta}/\rho_m$  curve is represented by Fig. 8.

FIG. 8



From Fig. 8,  $K_a$  and  $K_a$ , were obtained from the values of  $\bar{\eta} = 1.5$  and  $0.5$  respectively as  $2.5 \times 10^{-3}$  and  $1.04 \times 10^{-5}$ . As in the case of dipicolinic acid, the value  $K_a$  only was necessary for the calculation of the instability constant of the ferrous quinolinic acid complex.

Table V (A, B) record the measured optical density values of the coloured complex in equilibrium.

TABLE IV

Quinolinic acid taken = 150 c.c. of 0.01M. Alkali = 0.0999N-NaOH. Temp. = 30°

B (conc. of the acid in moles/litre).	Alkali added.	$aB_2 + B_1 + H^+$ .	$pH$ .	$\frac{2B_2 + B_1}{B} = \bar{n}$ .
0.009933	1 c.c.	0.019206	2.46	1.58
0.009804	3	0.017648	2.58	1.53
0.009740	4	0.016880	2.61	1.48
0.009616	6	0.015300	2.73	1.38
0.009434	9	0.013214	2.96	1.28
0.009260	12	0.011120	3.30	1.14
0.009036	16	0.008443	4.12	0.93
0.008824	20	0.005898	4.71	0.67
0.008722	22	0.004674	4.93	0.54
0.008622	24	0.003474	5.18	0.42
0.008523	26	0.002346	5.47	0.37
0.008428	28	0.001146	5.95	0.14

TABLE V

A. Ferrous amm. sulphate (0.001M) containing  $NH_4OH.HCl$  (1%) =  $x$  c.c. Quinolinic acid (0.005M) =  $y$  c.c.  $KNO_3$  (1M) soln. = 10 c.c. Buffer ( $pH$  5.99) = 18 c.c. Cell, 2 cm.

Quinolinic acid (c.c.)	...	1	2	3	4(a)	5(b)	6(c)	7(d)	8	9
Fe soln. (c.c.)	...	9	8	7	6	5	4	3	2	1
O.D. (420 $m\mu$ )	...	0.033	0.070	0.095	0.122	0.144	0.123	0.120	0.097	0.041

B. Ferrous amm. sulphate (0.001M) containing  $NH_4OH.HCl$  (1%) =  $x$  c.c. Quinolinic acid (0.004M) =  $y$  c.c. Other conditions are the same as in A.

Quinolinic acid (c.c.)	...	6	8	10(e)	12(f)	14	16 (g)
Fe soln. (c.c.)	...	14	12	10	8	6	4
O. D. (420 $m\mu$ )	...	0.167	0.195	0.212	0.195	0.168	0.132

From equation (16)  $K_s$  was calculated for a,b,c,d,e,f,g. The results are recorded in Table VI.

TABLE VI

$$K_s = 1.04 \times 10^{-5}. [H^+] = 0.1023 \times 10^{-2}.$$

No.	$[Qui]_0$ .	$[FeQui]_0$ .	$[Fe^{II}]_0$ .	$K_s$ .
a	$4.00 \times 10^{-4}$	$7.28 \times 10^{-5}$	$1.67 \times 10^{-4}$	$1.04 \times 10^{-11}$
b	$5.00 \times 10^{-4}$	$8.60 \times 10^{-5}$	$1.14 \times 10^{-4}$	$1.42 \times 10^{-11}$
c	$6.00 \times 10^{-4}$	$7.34 \times 10^{-5}$	$8.66 \times 10^{-5}$	$4.88 \times 10^{-11}$
d	$7.00 \times 10^{-4}$	$7.16 \times 10^{-5}$	$4.84 \times 10^{-5}$	$5.84 \times 10^{-11}$
e	$8.00 \times 10^{-4}$	$1.27 \times 10^{-4}$	$7.30 \times 10^{-5}$	$3.20 \times 10^{-11}$
f	$9.60 \times 10^{-4}$	$1.16 \times 10^{-4}$	$4.40 \times 10^{-5}$	$6.58 \times 10^{-11}$
g	$1.28 \times 10^{-3}$	$7.88 \times 10^{-5}$	$1.20 \times 10^{-5}$	$1.31 \times 10^{-11}$

Hence,  $K_s$  (mean) =  $3.47 \times 10^{-11}$ .

#### Coloured Systems of Ferrous Complexes with Some Other Pyridine Carboxylic Acids (Di and Tri)

Two other pyridine dicarboxylic acids with -COOH group in the  $\alpha$ -position, namely, lutidinic (2:4) and isocinchomeric (2:5) acids have been found, as already

stated, to give an intense yellow colour with ferrous ion with  $\lambda_{\max}$  in the range of 410 m $\mu$  to 440 m $\mu$ . The optimum  $p_H$  for maximum colour development lies at or about 6 for both. The colour of the ferrous complex of both the acids is intensified by the addition of KCN and pyridine. The sensitivity for both the coloured complexes was found to be almost equal and is given by 0.166  $\gamma$  Fe/cm<sup>2</sup> without KCN and 0.070  $\gamma$  Fe/cm<sup>2</sup> with KCN.

The yellow to red ferrous complexes formed in solution by the three pyridine tricarboxylic acids, viz., collidinic acid (2:4:6), berberonic acid (2:4:5) and the 2:3:6-acid, show an absorption maximum at 525 m $\mu$  for collidinic acid, and at 410 m $\mu$ —420 m $\mu$  for pyridine 2:3:6-tricarboxylic acid. The colour of berberonic acid ferrous complex is developed only in strong solutions. This acid has therefore little value for the colorimetric test of iron. The optimum  $p_H$  for colour development for these tricarboxylic acids also lies at or about 6. Sensitivity for ferrous collidinic acid complex is given by 0.052  $\gamma$  Fe/cm<sup>2</sup>. It behaves like ferrous dipicolinic acid complex towards KCN and pyridine, which decrease its colour intensity in solution. Pyridine-2:3:6-tricarboxylic acid ferrous complex, on the other hand, behaves like quinolinic acid with its colour being intensified by the addition of KCN or pyridine. The sensitivity of the coloured complex is 0.09  $\gamma$  Fe/cm<sup>2</sup> without KCN and 0.03  $\gamma$  Fe/cm<sup>2</sup> with KCN.

#### CONCLUSION

Table VII summarises the optimum conditions for colour development as also the sensitivity of coloured ferrous complexes of the quinoline carboxylic acid and of all the pyridine carboxylic acids studied in this series of communication. The instability constants of the coloured complexes have also been furnished for cases specially studied.

TABLE VII  
 $p_H = 6$  (in all cases)

Acid.	$\lambda_{\max}$ .	Sensitivity* in $\gamma/cm^2$ (Fe).		Instability constant.
		Without KCN.	With KCN.	
Quinaldinic	500-515 m $\mu$	0.036	0.0096	$3.63 \times 10^{-8}$
Picolinic	440	0.056	0.0280	$5.07 \times 10^{-12}$
Dipicolinic	480	0.044	Diminishes	$1.85 \times 10^{-7}$
Quinolinic	420-440	0.066	0.0280	$3.47 \times 10^{-11}$
Lutidinic	410-440	0.166	0.070	...
Isocinchomeric	410-440	0.166	0.0700	...
Collidinic	525	0.052	Diminishes	...
Pyridine-2:3:6-tricarboxylic	410-420	0.090	0.0300	...

\* Sandell, *loc. cit.*

The coloured ferrous complexes of the pyridine carboxylic acids with the exception of those of dipicolinic and collidinic acids show their maximum absorption practically in the same region of the visible spectrum, viz., 410-440 m $\mu$ . The absorption is shifted somewhat to the longer wave-length region in the cases of dipicolinic and collidinic acids, resembling that of quinaldinic acid. Of all the

acids, quinaldinic acid serves as the most sensitive reagent for ferrous iron, particularly with KCN. Their relative sensitivity and stability can be represented as follows in an increasing order :

*Sensitivity* (without KCN) : Lutidinic = isocinchomeric < pyridine-2:3:6 (acid) < quinolinic < picolinic < collidinic < dipicolinic < quinaldinic acid.

*Stability* : Quinaldinic < dipicolinic < quinolinic < picolinic acid.

For colorimetric analysis of iron, quinaldinic acid may therefore be regarded as a very useful reagent. The only drawback is that, on account of its high instability constant, a very large excess (25 times the theoretical amount) of the reagent is required for the purpose of estimation. While dipicolinic acid, which comes next in order of sensitivity when used without KCN, cannot be used in presence of KCN, and hence loses its usefulness as a colorimetric reagent. From a consideration of both sensitivity and stability, picolinic acid may also be regarded as a quite useful reagent for the estimation of iron, next in importance to quinaldinic acid. So far as the interference by foreign ions in the case of these two reagents is concerned, there is very little to choose between them (Rây and Bose, *Z. anal. Chem.*, 1933, 95, 400; Majumdar and Sen- this *Journal*, 1950, 27, 245; *Anal. Chim. Acta*, 1953, 8, 369).

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