Acid-Base Property and Metal Chelate Formation of 4-(2-Pyridylazo)-resorcinol[*]

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4-(2-Pyridylazo)-resorcinol (PAR) has recently been suggested as a water-soluble metal indicator for the EDTA-titration of lead and other metal cations in place of 1-(2-pyridylazo)-2-naphthol (PAN)[1]. The latter forms a colloidal suspension when dissolved in water in the pH range 2 to 13[2], and this fact is one of the disadvantages of the reagent in aqueous systems. The use of PAR as a color reagent in colorimetric analysis[3] and as a metal indicator in precipitation titration[4] and in chelatometric titration[5] has been proposed, all of which is based on the formation of stable colored chelates of PAR with various heavy metals such as lead, cobalt and uranium.

The present paper concerns the acid dissociation of PAR, its chelate formation with some metal cations in aqueous solutions, the stability constant of copper(II)-PAR chelate and the comparison between PAR and PAN as analytical reagent.

The absorption spectra of PAR in aqueous

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[1] P. Wehber, *Z. anal. Chem.*, **158**, 10 (1957); **167**, 186 (1958).

[2] B. F. Pease and W. B. Williams, *Anal. Chem.*, **31**, 1044 (1959).

[3] F. H. Pollard, P. Hanson and W. J. Geary, *Anal. Chim. Acta*, **20**, 26 (1959).

[4] R. Püschel, E. Lassner and R. Scharf, *Z. anal. Chem.*, **163**, 104, 344 (1958); **165**, 401 (1959).

[5] E. J. Langmyhr and H. Kristiansen, *Anal. Chim. Acta*, **20**, 524 (1959).

solution at various pH values have been examined, the acid dissociation constants determined by pH-titration and colorimetric method. The composition of the metal chelates of PAR with tervalent iron, bivalent cobalt, nickel, copper, zinc, cadmium, mercury and lead has been determined with the aid of the continuous variation method⁶⁾ and the stability constant of copper(II)-PAR chelate determined potentiometrically by pH-titration; its utility in chelatometric analysis was discussed.

Experimental

The PAR used in this study was a sample for test supplied by Dojin Pharmaceutical Laboratories, Kumamoto, Japan.

Found: C, 61.4; H, 4.5; N, 18.7; Calcd. for $C_{11}H_9O_2N_3$: C, 61.1; H, 4.2; N, 19.5⁷⁾.

PAR in free acid form is readily soluble in an aqueous alkaline solution. Solubility in water at 10°C was found to be only 5 mg./100 ml.

4-Benzeneazoresorcinol was kindly given by Dr. Yoshio Matsunaga in our laboratory.

A solution of 10^{-2} M potassium hydroxide was prepared by direct dissolution of metallic potassium (E. Merck) in deionized water in a current of nitrogen, and standardized against $1.007_4\times10^{-2}$ M hydrochloric acid. The standard solution of the

Fig. 1. Absorption spectra of PAR.
5×10^{-5} M: 1 cm. silica cell (Cary)

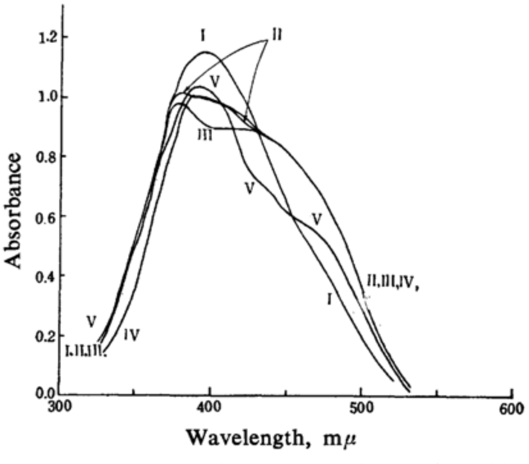

Fig. 1a. Absorption spectra of PAR in acid solutions.

I: 4.7 N HNO_3
II: 3.2 N HNO_3
III: 1.6 N HNO_3
IV: 0.1 N HNO_3
V: pH 3, acetate buffer (0.1 M KNO_3)

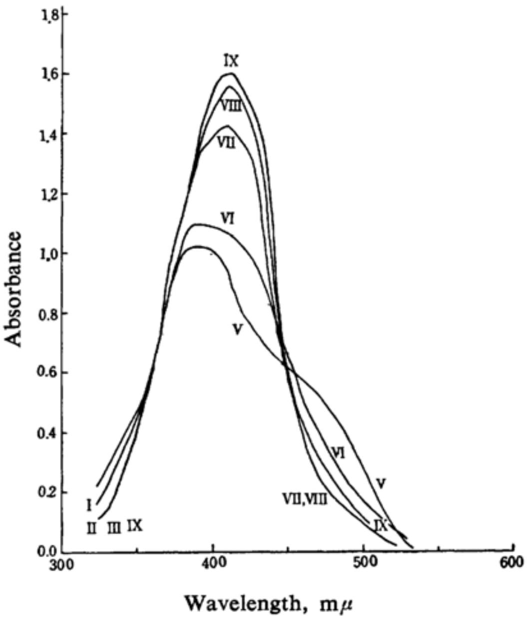

Fig. 1b. Absorption spectra of PAR in neutral solutions.

V: pH 3, acetate buffer
VI: pH 5, acetate buffer
VII: pH 7, phosphate buffer
VIII: pH 9, borax buffer
IX: pH 11, 0.001 N NaOH
(0.1 M KNO_3)

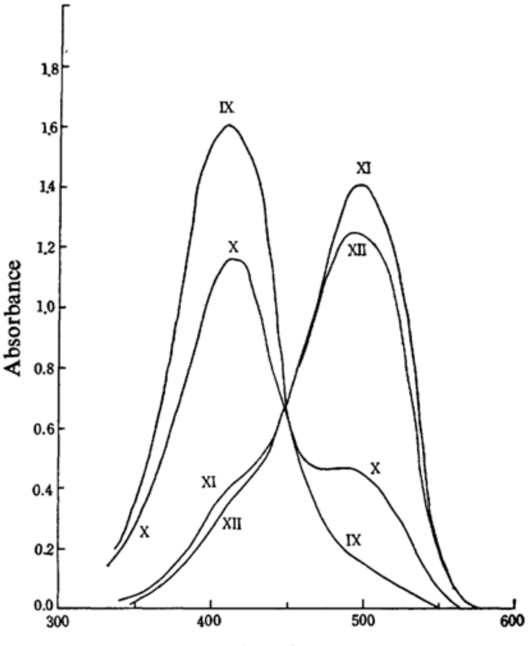

Fig. 1c. Absorption spectra of PAR in alkaline solutions.

IX: 0.001 N NaOH
X: 0.01 N NaOH
(0.1 M KNO_3)
XI: 0.1 N NaOH
XII: 1 N NaOH

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6) Y. Shibata, T. Inouye and Y. Nakatsuka, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **42**, 983 (1921); R. Tsuchida, This Bulletin, **10**, 27 (1933). Cf. P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

7) Elementary analysis was performed by Mr. Shozo Masuda in our department. The PAR might contain some impurities (cf. Refs. 2 and 3). The purity of the PAR calculated from the content of nitrogen 18.7/19.5=0.96, agreed with that (0.94) determined by photometric titration with a copper nitrate solution.

acid was prepared by passing a known amount of potassium chloride solution through a column of cation-exchange resin in H-form (Diaion SK #1, analytical grade).

All the other chemicals were of reagent grade, and all metal salts were used as nitrates. Acetate, phosphate and borax buffer, nitric acid, potassium hydroxide and sodium hydroxide solution were used to control the pH. By photometric titrations[7a] with 1.00×10^{-4} M copper nitrate solution, the PAR solutions were standardized after suitable dilution whenever necessary.

The absorption spectra were measured by a Cary Model 11 and a Shimadzu QB-50 spectrophotometer and the colorimetric measurements were done by a Hirama IIb filter electrophotometer. For pH-titrations and pH measurements a Denkishiki DG pH meter equipped with a glass and a calomel electrode was used; the measurements were carried out in a thermostat regulated at 25±0.2°C by circulating water from another large thermostat. During titration the solution was stirred magnetically and bubbled with nitrogen gas through a capillary.

Results and Discussion

Acid Dissociation of PAR.—The absorption spectra of aqueous solutions of PAR depend on the pH values as shown in Fig. 1. The spectra in acid solutions have somewhat complicated aspects which may be caused by the presence of pyridinium form or azo-protonated forms as in case of PAN[2] and some azobenzene derivatives[8]. It can be suggested that an undissociated form a, two kinds of the dissociated forms b and c, and one-protonated form d exist in neutral and alkaline solutions. As the degree of acid dissociation of *o*-hydroxyl group may be lower than that of *p*-hydroxyl group through an intramolecular hydrogen bond formation, the absorption maxima at 390, 410 and 490 mμ can be assigned to a, b and c, respectively, and the broad shoulder from 400 to 470 mμ to d. The existence of these dissociation stages in neutral and alkaline solutions can be supported by similar study on 4-benzeneazoresorcinol. As shown in Fig. 2, in the neutral solution the spectrum has a doublet of 375 and 410 mμ (Curve I)[9]. In the weakly alkaline solutions the absorption maximum shifts to 430 mμ (Curves II and III) and in the more alkaline solution the maximum further shifts to 475 mμ and shows a shoulder at 390 mμ (Curve IV). These properties are analogous to those of PAR.

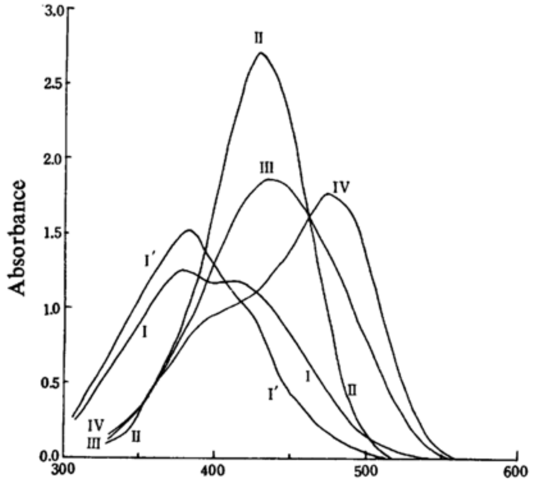
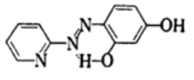


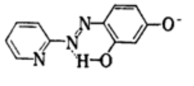
Fig. 2. Absorption spectra of benzeneazoresorcinol.

7×10^{-5} M: 1 cm. silica cell (Cary)

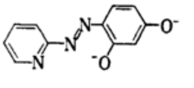
I: 8% ethanol
I': 95% ethanol
II: 4×10^{-4} M borax in 8% ethanol
III: 3×10^{-2} M NaOH in 8% ethanol
IV: 0.7 M NaOH in 8% ethanol



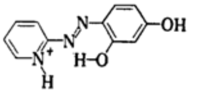
(a)



(b)



(c)



(d)

Determination of Acid Dissociation Constants of PAR.—From the pH dependency of the spectra the acid dissociation constants of PAR k_{a_1} and k_{a_2} defined by Eqs. 1 and 2 are estimated as about 10^{-6} and 10^{-12}, respectively.

$$k_{a_1}=\frac{[C_{11}H_8O_2N_3^-]\,[H^+]}{[C_{11}H_9O_2N_3]} \qquad (1)$$

$$k_{a_2}=\frac{[C_{11}H_7O_2N_3^{2-}]\,[H^+]}{[C_{11}H_8O_2N_3^-]} \qquad (2)$$

In order to obtain more accurate values 100 ml. of 4.72×10^{-5} M PAR solution was titrated with 1.085×10^{-2} M potassium hydroxide solution at 25°C (Fig. 3). One proton caused by the first dissociation was neutralized and k_{a_1} was calculated as 1.48×10^{-6} ($pk_{a_1}=-\log k_{a_1}=5.83$) according to the following equation:

[7a] T. Iwamoto, *Japan Analyst* (*Bunseki Kagaku*), **10**, 189 (1961).

[8] M. T. Rogers, T. W. Campbell, R. W. Maatmann, *J. Am. Chem. Soc.*, 73, 5122 (1951).

[9] The absorption spectrum of 4-benzeneazoresorcinol in an ethanolic solution taken from the late Dr. F. Iimura's unpublished results shows also a singlet maximum at 375 mμ. The splitting may be elucidated in terms of solvent effect.

$$k_{a_1}=\frac{[H^+](aC+[H^+]-[OH^-])}{C-(aC+[H^+]-[OH^-])} \qquad (3)$$

where C stands for the total concentration of PAR and a moles of base added per mole of the acid. Another proton caused by the second dissociation was not liberated under these conditions because of the low value of the second dissociation constant k_{a_2}, as foreseen by the absorption spectra measurements. Then it was approximately determined from absorption measurements of aqueous PAR solutions in the range of pH between 10 and 13.8 with a filter electrophotometer using the filters transparent in the vicinity of 420 and 485 mμ. From the curves in Fig. 4, pk_{a_2} was estimated as 12.5 ($k_{a_2}=3.2\times10^{-13}$).

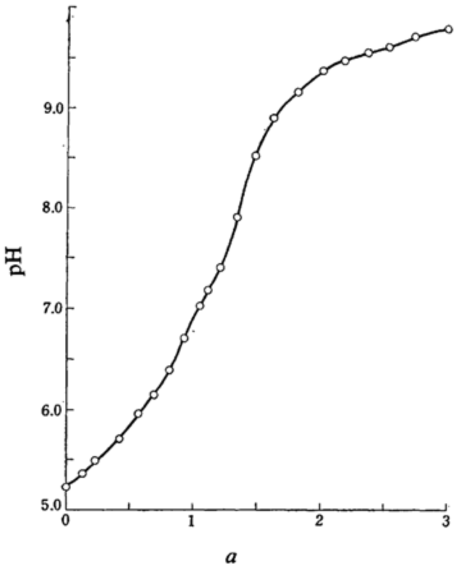


Fig. 3. pH-Titration of PAR free acid. 100 ml. of 5×10^{-5} M PAR solution with 0.01 N KOH solution.
a: moles of base added per mole of acid

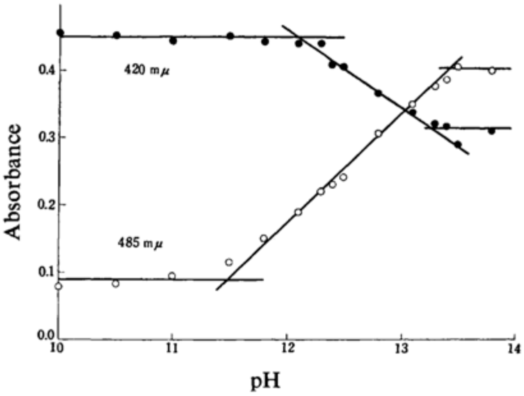


Fig. 4. Absorbance vs. pH of PAR solutions. 5×10^{-6} M PAR, 2 cm glass cell.
Full circle, at 420 mμ; open circle, at 485 mμ

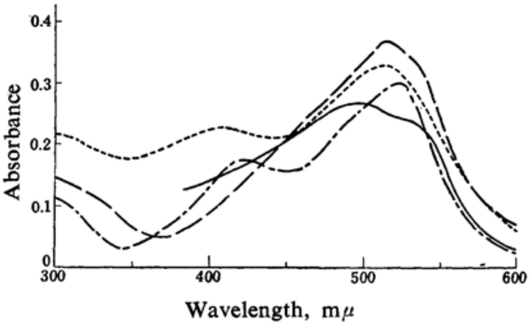


Fig. 5. Absorption spectra of metal-PAR chelates.

—— Fe(PAR)$_2$: 0.6×10^{-5} M pH 4
— — Co(PAR)$_2$: 0.8×10^{-5} M pH 4
—·— Cu(PAR): 1.0×10^{-5} M pH 4
---- Pb(PAR): 1.0×10^{-5} M pH 10
1 cm. silica cell (Shimadzu)

TABLE I. COMPOSITIONS AND MOLAR EXTINCTION COEFFICIENTS OF METAL-PAR CHELATES

Metal	Composition	pH	ε at 517 mμ
Fe(III)	1 : 2	4.0	4.2×10^4
Co(II)	1 : 2	4.0	4.2×10^4
Ni(II)	1 : 2	4.0	2.2×10^4
Cu(II)	1 : 1	4.0	3.0×10^4
	1 : 1	10.0	3.2×10^4
Zn(II)	1 : 1	10.0	—
Cd(II)	1 : 1	10.0	—
Hg(II)	1 : 1	10.0	—
Pb(II)	1 : 1	10.0	3.8×10^4

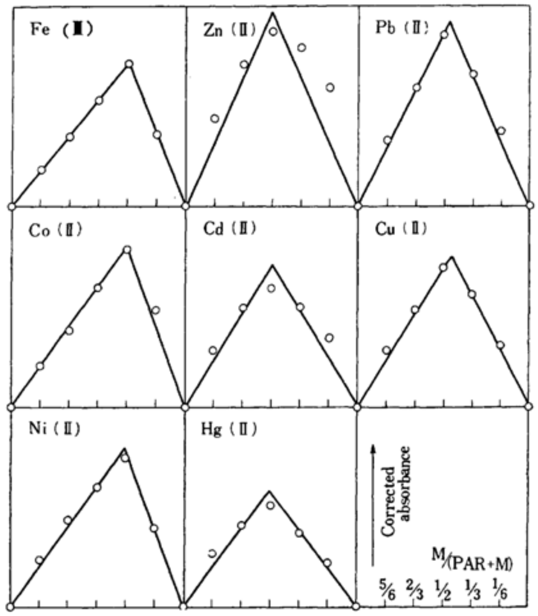
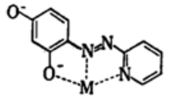


Fig. 6. Graphical determination of the composition of metal-PAR chelates.

Compositions of PAR Chelates of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II).—Wehber[1] and Pollard et al.[3] reported the coloration of the chelates of PAR with various kinds of metals in aqueous solutions. In Fig. 5 are shown a few examples of absorption spectra measured by the present author. The composition of these chelates in aqueous solutions was determined by means of the continuous variation method using the filter photometer with a 517 mμ filter. The results and the molar extinction coefficients of the chelates are given in Table I. In Fig. 6, data are shown graphically. From these data PAR may be considered to act as terdentate ligand having three donor atoms in a plane [10]:



The details of the structure of metal-PAR chelare are now under investigation.

Stability Constant of Copper(II)-PAR Chelate.—In the presence of copper(II)-EDTA chelate, PAR may be applied as a metal indicator to the titration of metal cations which neither form colored chelates with PAR nor react with PAR rapidly and reversibly. To compare the function of the Cu-PAR indicator system with that of Cu-PAN[11], the stability constant of copper(II)-PAR chelate was determined by pH-titration. One hundred ml. of solution containing 4.72×10^{-6} mol. of PAR and the equimolar amount of copper nitrate was titrated with the above-mentioned potassium hydroxide solution. The titration curve shown in Fig. 7 exhibits a marked inflection at $a\simeq2$. Acid dissociation and chelate formation of PAR are as follows:

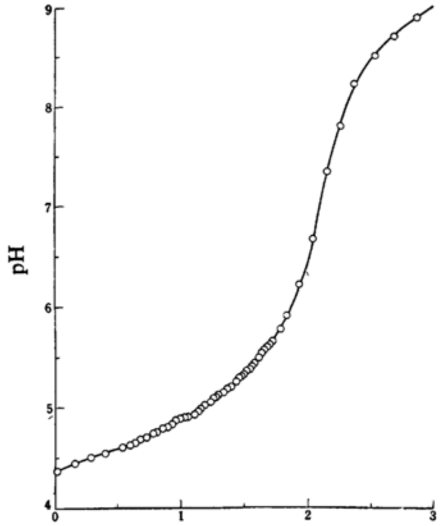


Fig. 7. Titration curve of copper(II)-PAR chelate.
5×10^{-5} M Cu-PAR solution 100 ml. with 0.01 M KOH solution
$\mu=0.1$ M KNO_3, 25°C
a: moles of base added per mole of chelate

$$H_2D=H^++HD^- \qquad (pk_{a_1}=5.83) \tag{4}$$

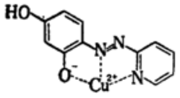
$$HD^-=H^++D^{2-} \qquad (pk_{a_2}=12.5) \tag{5}$$

$$Cu^{2+}+D^{2-}=CuD^{12)} \tag{6}$$

$$Cu^{2+}+H_2D=2H^++CuD \tag{6'}$$

$$CuD+H^+=HCuD^+ \tag{7}$$

where H_2D is PAR in undissociated form, HD^- in b form (p. 607) and $HCuD^+$ is one-protonated form of Cu-PAR chelate that may exist in considerably low pH region:



The equilibrium constant for Eq. 6, $k=[CuD]/[Cu^{2+}][D^{2-}]$, gives the stability constant of copper(II)-PAR chelate provided that the activity coefficient of each species is maintained constant. If $k_a'=[H^+][CuD]/[HCuD^+]$ is postulated as the acid dissociation constant for the process reverse to Eq. 7, Eq. 8 gives the relation between k, k_{a_1}, k_{a_2} and the concentration of D^{2-} throughout the titration under the experimental conditions:

$$\begin{aligned} k[D^{2-}]^2([H^+]^2/k_{a_1}k_{a_2}+[H^+]/k_{a_2}) \\ -[D^{2-}][H^+]^2/k_{a_1}k_{a_2} \\ =(a-1)+[H^+]-[OH^-] \end{aligned} \tag{8}$$

where C stands for the total concentration of PAR (=that of Cu^{2+}) and a the moles of base added per mole of PAR.

With the assumption that at adjacent plots of the measurements in the buffer region of the titration curve the value of $[D^{2-}]$ is the same, k was calculated to be 5×10^{11} as the mean value from thirty sets of simultaneous equations derived from Eq. 8. k_a', which can be considered as the second dissociation constant of a hypothetical dibasic acid H_2CuD^{2+},

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[10] Y. Muto, This Bulletin, **31**, 1017 (1958); F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 2733 (1957); F. Lions and H. A. Goodwin, ibid., **81**, 6415 (1959).

[11] H. Flaschka and H. Abdine, *Z. anal. Chem.*, **152**, 77 (1956); *Chemist-Analyst*, **45**, 2 (1956).

[12] It is not necessary for CuD to be neutral in charge, for PAR is considered as a terdentate ligand and the coordination requirement of copper(II) atom will be fulfilled by another unidentate anion (e. g. nitrate ion) in the solution.

was determined graphically[13] to be 5×10^{-6} from the titration data.

Analytical Aspects of PAR

Cu-PAR Indicator in EDTA-Titrations.—Pease and Williams[2] have determined the stability constant of copper(II)-PAN chelate to be approximately 10^{16}. This value is considerably greater than that of PAR chelate, 5×10^{11}. Comparing the value for PAN chelate with that for copper(II)-EDTA chelate, 2×10^{18}, they have concluded "this is one reason that the copper(II)-PAN indicator may be successfully used in complexometric titrations of metals with EDTA".

According to Flaschka-Khalafallah's error-equation in visual end-point determination in chelatometric titration, Eq. 9[14], however, it may be concluded that Δp, the deviation of end-point (metal-combined indicator/free indicator$=1/9$) from equivalence-point, for the above-mentioned copper(II)-EDTA-PAN system is to be $+0.04$, i. e., the theoretical error is $+4\%$ when C_M and C_I were put as 10^{-3} and 10^{-6}, respectively.

$$\Delta p=(9rC_M-0.01C_I-1/9k)/C_M \qquad (9)$$

where C_M: total concentration of metal,
C_I: total concentration of indicator,
k : stability constant of metal-indicator complex,
K : stability constant of metal-complexan, and $r=k/K$.

The error obtained here is contrary to Cheng's observation[15]. To make the error below 0.5%, the stability constant of metal-indicator complex must be below 10^{15}. The value for Cu-PAR satisfies such a requirement. In regards to the relationship of the stability of copper(II)-indicator to that of copper(II)-EDTA, it may be concluded that PAR is a more accurate indicator than PAN provided that the stability constant of Cu-PAN is reliable. Nevertheless, for the practical applications as a titration indicator no remarkable difference between them, except the higher solubility of PAR in water, has yet been found out.

PAR as a Detection Reagent for Heavy Metals.—It must be mentioned that the high absorbancy in the visible region and the water-solubility of PAR chelates favor the detection of heavy metals and very high sensitivity can be achieved. For example, the identification limit of copper(II) in ordinary spot test was found to be 0.01 μg in 0.04 ml. test solution, i. e., limit of dilution is $1:2.5\times10^{-7}$, and that in resin spot test using a few grains of cation-exchange resin Dowex 50W-X8 in H-form as a collector of copper(II)-PAR chelate to be 0.0005 μg ($1:1.3\times10^{-8}$)[16].

Summary

Acid dissociation stages of analytical reagent 4-(2-pyridylazo)-resorcinol (PAR) and metal chelate formation of PAR were investigated by absorption measurements and pH-titrations. The first acid dissociation constant was determined as 1.48×10^{-6} ($pk_{a_1}=5.83$) and the second as 3.2×10^{-13} ($pk_{a_2}=12.5$) at 25°C. PAR forms 1:2 chelate with Fe(III), Co(II) and Ni(II), and forms 1:1 chelate with Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II). The stability constant of copper(II)-PAR chelate was determined as 5×10^{11} at 25°C. Some analytical aspects of PAR were also discussed.

The author wishes to thank Dr. Eiiti Minami, Professor Emeritus, for his interst in this work and Mr. Kunihiko Mizumachi, Lecturer in Rikkio University, for his ardent encouragement and advice in the calculation of the chelate stability constant. He also thanks Dojin Pharmaceutical Laboratories for the gift of the sample of PAR.

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[13] S. Glasstone, "An Introduction to Electrochemistry", Van Nostrand Co., New York (1956), p. 401.

[14] H. Flaschka and S. Khalafallah, *Z. anal. Chem.*, 156, 401 (1957).

[15] K. L. Cheng, *Anal. Chem.*, 30, 243 (1958).

[16] M. Fujimoto and T. Iwamoto, unpublished results to be reported in detail together with the data for PAN.