2, 6-Diacetylpyridine Bis(benzoyl hydrazone) and 2, 6-Diacetylpyridine Bis(2-hydroxybenzoyl hydrazone) as Spectrophotometric Reagents for Determinations of Iron(III) and Vanadium(V)
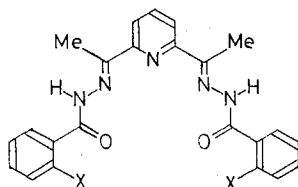
Yoshihiro Sasaki*

The syntheses, characteristics and analytical applications of 2,6-diacetylpyridine bis(benzoyl hydrazone) (DADBH) and 2,6-diacetylpyiidine bis(2-hydroxybenzoyl hydrazone) (DADSH) are studied. Both reagents are compared to determine iron and vanadium. A method for determination of vanadium using DADBH is proposed. The reagent reacts with vanadium(V) at the pH range of 2.6–4.0 to produce a yellow complex ($\lambda_{max}=335$ nm, $\varepsilon=2.74\times10^4$ l mol^{-1} cm^{-1}) in dimethylformamide-water (2:8 v/v). DADSH is tested to determine iron. The reagent produces a yellow complex of iron(III) ($\lambda_{max}=336$ nm, $\varepsilon=2.77\times10^4$ l mol^{-1} cm^{-1}, pH 2–3.5) in dimethylformamide-water (1:1 v/v). The sensitivities of the methods described are high, but the selectivities of them are low.

Since the hydrazones are available reagents for detection and determination of metal ions, analytical appliactions of various types of hydrazones have been tested. Recently, the heterocyclic hydrazones of 2,2'-dipyridyl ketone have been found to be high-sensitive or high-selective spectrophotometric reagents for the determinations of cobalt(II), palladium(II), zinc(II), cadmium(II) and iron(II).[1-5] The hydrazones possessing –N=C–C=N–NH–CX– group (X: O or S) have been described as colorimetric or fluorimetric reagents for the determinations of vanadium(V), rhenium(VII), aluminium(III) and gallium(III).[6-9] Bis(4-hydroxybenozyl hydra-

X = H : 2,6-DIACETYLPYRIDINE BIS(BENZOYL
        HYDRAZONE) (DADBH)
X = OH: 2,6-DIACETYLPYRIDINE BIS(2-HYDROXY-
        BENZOYL HYDRAZONE) (DADSH)

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zones) and bis(2-hydroxybenzoyl hydrazones) of glyoxals have been investigated to determine calcium(II), cadmium(II) and bismuth(III) spectrophotometrically or fluorometrically.[10,11]

In this paper, the preparations and properties of 2,6-diacetylpyridine bis(benozyl hydrzaone) (DADBH) and 2,6-diacetylpyridine bis(2-hydroxybenzoyl hydrazone) (DADSH) are described and spectrophotometric determinations of iron(III) and vanadium(V) with the reagents are studied.

EXPERIMENTAL

2,6-Diacetylpyridine Bis(2-hydroxybenzoyl hydrazone) (DADSH). 2,6-Diacetylpyridine (2.5 g) and 2-hydroxybenzoyl hydrazide (4.7 g) were mixed in ethanol and the mixture was refluxed for 3 h. The white DADSH was separated by filtration and washed with hot ethanol. mp > 300°C (dec). UV (dimethylformamide (dmf)) λ_{max} 322 nm (ε 35000). Fluorescence (dmf) λ_{ex} 352; λ_{em} 494 nm. IR (Nujol) 3170 (OH), 1655, 1640 cm^{-1}. Found: C, 63.73; H, 5.06; N, 15.72%. Calcd for $C_{23}H_{21}N_5O_4$: C, 63.73; H, 5.35; N, 16.16%.

2,6-Diacetylpyridine Bis(benzoyl hydrazone) (DADBH). The compound was prepared by mixing 2,6-diacetylpyridine (2 g) and benozyl hydrazide (3.2 g) according to the method described above. mp 239°C. UV (dmf) λ_{max} 315 nm (ε 33000). IR (Nujol) 3180 (NH), 1680, 1665 cm^{-1}. MS m/z 399 (M$^+$). Found: C, 68.86; H, 5.33; N, 17.31%. Calcd for $C_{23}H_{21}N_5O_2$: C, 69.15; H, 5.30; N, 17.54%.

DADSH and DADBH solutions were prepared by dissolving the reagents in dmf ($\approx 10^{-3}$ M (1 M = 1 mol/l)). Standard solutions of iron(III) (2.10×10^{-2} M) and vanadium(V) (9.60×10^{-3} M) were prepared from ferric nitrate nonahydrate (1 M hydrochloric acid) and ammonium metavanadate (0.3 M sulfuric acid) and were standardized by EDTA and redox titrations, respectively. Absorbances and absorption spectra were measured with a Hitachi 323 automatic recording spectrophotometer and a Shimazu Model UV 180 spectrophotometer. A Toa Electronic HA-15A digital pH meter was used for pH measurements.

Determination of Iron with DADSH (Method I). Transfer the sample solution, previously adjusted to pH ≈ 1.5 (not more than 30 μg of iron), by pipette into a 10 ml calibrated flask. Add 5 ml of the $\approx 2 \times 10^{-4}$ M DADSH solution and mix the solution thoroughly. Dilute with distilled water to ca. 9 ml and allow the solution to stand for 20 min. Add 0.5 ml of the 4 M hydrochloric acid solution and dilute with distilled water to the mark. Measure the absorbance at 340 nm against the reagent blank.

Determination of Vanadium with DADBH (Method II). Transfer the sample solution, previously adjusted to pH ≈ 2.5 (not more than 30 μg of vanadium), by pipette into a 10 ml calibrated flask. Add 2 ml of the $\approx 10^{-3}$ M DADBH solution and mix the solution thoroughly. Dilute with distilled water to ca. 9 ml and allow the solution to stand for 20 min. Add 0.5 ml of the 4 M hydrochloric acid solution and dilute with distilled water to the mark. Measure the absorbance at 340 nm

against the reagent blank.

RESULTS AND DISCUSSION

Analytical Properties of the Reagents. The solubilities of DADSH in organic solvents were very low. The solubility in dmf was 1.4 g l^{-1}. On the other hand, DADBH was soluble in organic solvents such as dmf and chloroform.

The characteristics of the absorption spectra of the reagents in dmf-water (1:1 v/v) were as follows. λ_{max} of DADSH: 300 nm (ε 7400, pH 0.4–1.6), 321 nm (ε 35700, pH 5.6), 307 nm (ε 28400) and 355 nm (ε 22200) (pH 9.6); λ_{max} of DADBH: no absorption maximum in the wavelength range of more than 300 nm (pH 1.3), 300 nm (ε 19400, pH 4.1), 313 nm (ε 27200, pH 5.7–9.3), 320 nm (ε 20500) and 365 nm (ε 9500) (pH 12.5).

The spectrophotometric method was used for the determination of the acid ionization constants in 0.1 M KCl dmf-water (1:1 v/v) solution. The pK_a values of DADSH were 2.7 (pK_{a1}), 6.6 (pK_{a2}) and 7.7 (pK_{a3}). The pK_{a1} value may be that of the protonated pyridine nitrogen atom, and the pK_{a2} and pK_{a3} values those
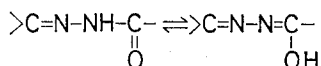
$$\text{>C=N-NH-C-} \rightleftharpoons \text{>C=N-N=C-}$$
$$\quad\quad\quad \overset{||}{O} \quad\quad\quad\quad\quad \overset{|}{OH}$$

Table I Spectral properties of some metal complexes with DADSH in dmf-water (1:1 v/v) or isoamyl alcohol

Metal Ion	pH	λ_{max} (nm)	ε ($\times 10^4$) (1 mol^{-1} cm^{-1})
Fe^{3+} a)	2.0–3.5	336	2.77
		(340)	(2.65)
Fe^{2+}	3.4	352	1.85
V^{5+} a)	3.0–4.5	336	2.54
		(340)	(2.46)
V^{+4}	3.6	359	2.44
Sn^{2+}	2.5–3.2	348	1.06
Pb^{2+}	3.7	356	1.73
Zr^{4+}	2.9	366	1.70
Bi^{3+}	3.1	350	2.14
Zn^{2+} b)	11	340	2.70
Cd^{2+} b)	0.04 M NaOH	315	3.30
		340	3.08
Ca^{2+} b)	0.04 M NaOH	303	2.82
		386	1.79
Sr^{2+} b)	0.04 M NaOH	379	0.73
Ba^{2+} b)	0.04 M NaOH	378	0.38

a) Measured in 0.2 M hydrochloric acid solutions.
b) Extracted into isoamyl alcohol.

Table II   Spectral properties of some metal complexes with DADBH in dmf-water (2:8 v/v) or chloroform

Metal Ion	pH	λ_{max} (nm)	ε ($\times 10^4$) (1 mol^{-1} cm^{-1})
Fe^{3+} [a]	2.0–3.2	300	2.85
V^{5+} [a]	2.6–4.0	335	2.74
		(340)	(2.73)
Ti^{4+}	2.7–3.2	342	1.87
Pb^{2+} [b]	4.2	348	0.60
Zr^{4+} [b]	2.9	355	0.50
Bi^{3+} [b]	3.1	329	1.71
Zn^{2+} [c]	11	340	2.59
		390	1.12
Cd^{2+} [c]	0.03 M KOH	343	4.58
		412	1.12
Mg^{2+} [c]	0.03 M KOH	352	1.55
Ca^{2+} [c]	0.03 M KOH	343	3.21
		391	1.14
Sr^{2+} [c]	0.03 M KOH	342	1.26
Ba^{2+} [c]	0.03 M KOH	348	0.46

a) Measured in 0.2 M hydrochloric acid solutions.
b) dmf-water (1:1 v/v).
c) Extracted into chloroform.

of the hydroxyl groups.   The pK_a values of DADBH were 4.2 (pK_{a1}) and 9.0 (pK_{a2}). The pK_a values may be caused by deprotonation of the pyridine nitrogen atom and deprotonation of hydroxyl group due to the ketone-enol tautomerism, respectively. These reagents did not be hydrolysed at any pH.

DADSH and DADBH reacted with many metal ions to give yellow complexes. The characteristics of some complexes in solutions are shown in Tables I and II. Copper(II), nickel(II), manganese(II), cobalt(II) and molybdenum(VI) also formed yellow complexes in the pH range of 4–6.

Study of Iron(III) and Vanadium(V) Complexes with DADSH and DADBH.   The absorption spectra of iron(III) and vanadium(V) complexes with DADSH and DADBH are shown in Figs. 1 and 2, respectively.   The spectra exhibited blue shifts by the addition of hydrochloric acid.   Since the addition of the acid gave rise to the constant spectra of the reagents and the lowest blank-values, the absorbances were measured in 0.2 M hydrochloric acid solutions.   The iron(III) and vanadium(V) complexes formed were stable in the acidic solutions for at least 2.5 h.   Figure 3 shows the relationship between pH, at which the complex-formation reactions take place, and the absorbances of the DADSH and DADBH systems.   In the iron-(III)-DADSH system, a maximum constant absorbance was obtained in the pH range of 2.0–3.5.   The optimum pH for the vanadium(V)-DADBH system was 2.6–4.0.
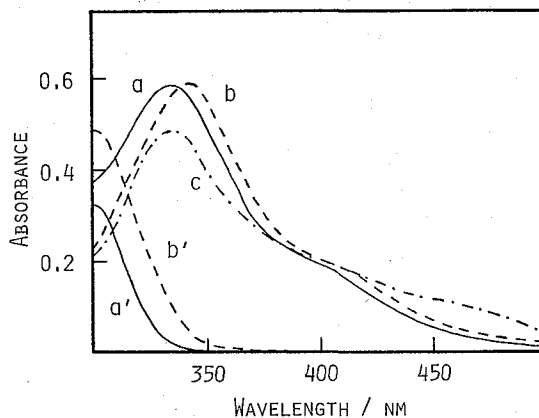
Fig. 1.   Absorption spectra of Fe(III)–DADSH and V(V)–DADSH
complexes in dmf-water (1:1 v/v).
$[Fe^{3+}]=2.10\times10^{-5}$ M, $[V^{5+}]=1.92\times10^{-5}$ M,
$[DADSH]=4.10\times10^{-5}$ M   a: Fe(III) complex, pH=3.4*)
b: Fe(III) complex, pH=2.9   c: V(V) complex, pH=3.6*)
a′ and b′: Reagent blanks of a and b, respectively
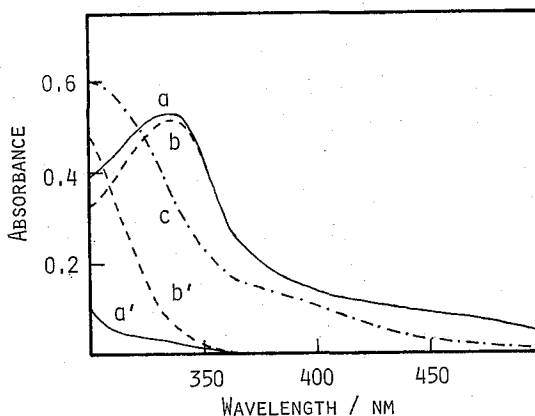*) Measured in 0.2 M hydrochloric acid solutions.

Fig. 2.   Absorption spectra of Fe(III)–DADBH and V(V)–DADBH
complexes in dmf-water (2:8 v/v).
$[Fe^{3+}]=2.10\times10^{-5}$ M, $[V^{5+}]=1.92\times10^{-5}$ M,
$[DADBH]=2.14\times10^{-4}$M   a: V(V) complex, pH=2.7*)
b: V(V) complex, pH=2.7   c: Fe(III) complex, pH=2.6*)
a′ and b′: Reagent blanks of a and b, respectively
*) Measured in 0.2 M hydrochloric acid solutions.

In order to determine the compositions and the apparent stability constants of
the DADSH and the DADBH complexes, continuous-variation and molar-ratio
methods were carried out.   Figure 4 shows the results of the continuous-variation
method.   The straight lines in the figure display the changes of absorbances in the
ideal systems, where it is assumed that the iron(III) and vandaium(V) complexes
with the stoichiometric ratio of metal to lignad of 1:1 are formed and the stability
constants of the complexes are very lrage.   In the vanadium(V)-DADBH system,
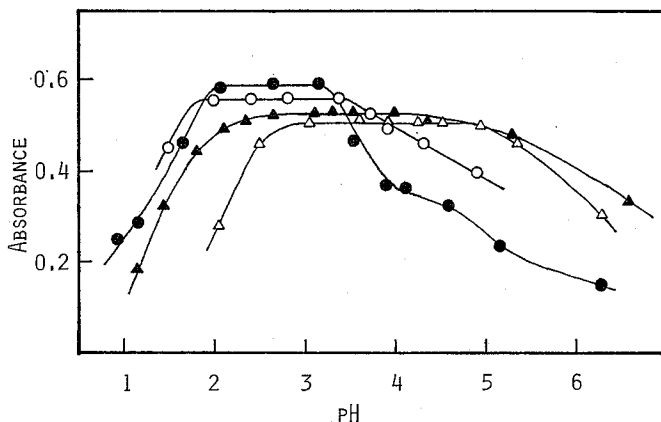
Fig. 3. Influence of pH on absorbances of Fe^{3+}- and V^{5+}-DADSH systems in dmf-water (1:1 v/v)[*], and of Fe^{3+}- and V^{5+}-DADBH systems in dmf-water (2:8 v/v)[*].

$[Fe^{3+}]=2.10\times10^{-5}$ M, $[V^{5+}]=1.92\times10^{-5}$ M

○: Fe^{3+}-DADSH system, 340 nm △: V^{5+}-DADSH system, 340 nm

●: Fe^{3+}-DADBH system, 300 nm ▲: V^{5+}-DADBH system, 340 nm

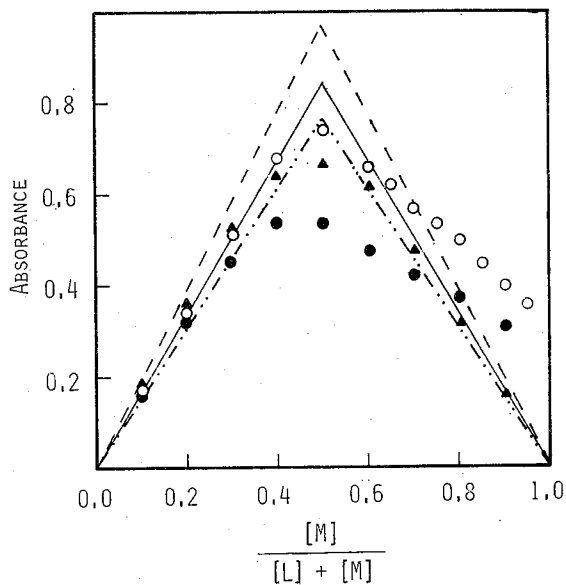[*] Measured in 0.2 M hydrochloric acid solutions.

Fig. 4. Continuous variation method.

Solvent: dmf-water (1:1 v/v)[*]

○, ———: Fe^{3+}-DADSH system,

  $[Fe^{3+}]+[DADSH]=6.36\times10^{-5}$ M, pH=2.5, 340 nm

▲, - - - : V^{5+}-DADBH system,

  $[V^{5+}]+[DADBH]=7.67\times10^{-5}$ M, pH=3.2, 340 nm

●, —·—: Fe^{3+}-DADBH ststem,

  $[Fe^{3+}]+[DADBH]=6.36\times10^{-5}$ M, pH=2.5, 305 nm

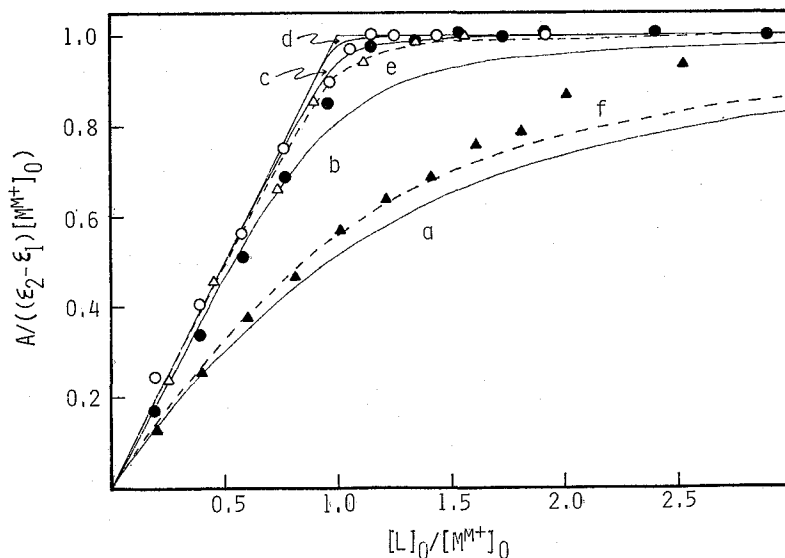[*] Measured in 0.2 M hydrochloric acid solutions.

Fig. 5. Molar-ratio method.
Solvent: dmf-water (1:1 v/v) containing 0.1 M KCl*⁾
○: Fe^{3+}-DADSH system (20°C),   △: V^{5+}-DADSH system (20°C)
●: Fe^{3+}-DADBH system (25°C),   ▲: V^{5+}-DADBH system (25°C)
K' values of correlation curves between $[L]_0/[M^{m+}]_0$ and $A/((\varepsilon_2-\varepsilon_1) [M^{m+}]_0)$
Fe^{3+} systems, a: 10^5, b: 10^5, c: 10^7, d: 10^8, $[Fe^{3+}]=12.10 \times 10^{-5}$ M
V^{5+} systems, e: 5×10^6, f: 1.5×10^5, $[V^{5+}]=1.92 \times 10^{-5}$ M
*⁾ Measured in 0.2 M hydrochloric acid solutions.

a complex with the ratio of 1:1 is seen to be formed. The vanadium(V)-DADSH system also showed the similar result of the continuous-variation method. The behaviors of the iron(III) systems are more complicated, ascribed mainly to form iron(III)-chloro complexes and different types of iron(III) complexes with DADSH and DADBH. However, the formations of DADSH- and DADBH-iron(III) complexes with the metal to ligand ratio of 1:1 are concluded under the condition that large amounts of the reagents exist.

Figure 5 shows the results of the molar-ratio method, where ε_1 and ε_2 represent the molar absorption coefficients of the protonated ligands, LH^+, and the formed complexes, respectively, and $[M^{m+}]_0$ the initial concentration of the metal ions. The results of the vanadium(V)-DADSH and the iron(III) systems indicate that the stoichiometric ratio of metal to ligand is 1:1 for the complexes formed in the systems. On the basis of the data, the apparent stability constants of the vanadium(V) complexes can be estimated, which are defined as

$$K' = \frac{[ML^{(m-n)+}]}{([M^{m+}]_0-[ML^{(m-n)+}]) ([L]_0-[ML^{(m-n)+}])} , \qquad (1)$$

where m-n and $[L]_0$ represent the number of charge of the complexes formed and the initial concentration of the ligands, and the activity coefficients are assumed to fall into constant values under the condition that $[M^{m+}]_0$ and $[L]_0$ are of the order

of 10^{-5} M in the 0.1 M KCl solutions. If the stability constants of the complexes are represented by

$$M^{m+} + L^{n-} \rightleftharpoons ML^{(m-n)+} , \quad K = \frac{[ML^{(m-n)+}]}{[M^{m+}][L^{n-}]} , \tag{2}$$

the correlation between K and K' is written as

$$K = h \times K' ,$$
$$h = (K_{a1}K_{a2}\cdots K_{an+1})^{-1} a_H^{n+1} + (K_{a2}\cdots K_{an+1})^{-1} a_H^n + \cdots + K_{an+1}^{-1} a_H + 1 , \tag{3}$$

where K_{ai} is the acid ionization constant of the ligands.

$$K_{a1} = \frac{[L] a_H}{[LH^+]} ,$$
$$K_{ai} = \frac{[L^{(i-1)-}] a_H}{[L^{(i-2)-}]} \qquad (i = 2, 3, \cdots, n+1) \tag{4}$$

Correlation curves between $[L]_0/[M^{m+}]_0$ and $A/((\varepsilon_a - \varepsilon_1)[M^{m+}]_0)$ $(=[ML^{(m-n)+}]/[M^{m+}]_0)$ are also shown in Fig. 5. The experimental data of the iron(III) systems were inconsistent with the calculated curves, suggesting that the iron(III) systems possess another reaction profile. The values of K' of the DADSH- and DADBH-vanadium(V) systems were 5.0×10^6 l mol^{-1} (20°C) and 1.5×10^5 l mol^{-1} (25°C), respectively. The difference of the K' values in the vanadium(V) systems may be due to that of the pK_a values of the reagents. If the formation of [VO$_2$L] is assumed in the vanadium(V) systems, we obtain by using the pK_a values of DADSH and DADBH and the pH values (3.4 for the DADSH system and 3.7 for the DADBH system), at which the complex-formation reactions occured, that $K \approx 6 \times 10^{16}$ l^3 mol^{-3} for the vanadium(V)-DADSH complex and $K \approx 3 \times 10^{18}$ l^3 mol^{-3} for the vanadium-(V)-DADBH complex.[12]

The Fundamental Study of the Determinations of Iron with DADSH and Vanadium with DADBH. The absorbances at 340 nm were used for the determinations of iron and vanadium. The relatoinship between the absorbances and the concentrations of hydrochloric acid in the solutions measured was investigated. As shown in Fig. 6, the addition of the acid gave rise to constant and low blank-values, but it led also to the decrease of the absorbance of the iron(III)-DADSH system. The pH values of 0.2 M hydrochloric acid solutions were 1.3 for the iron(III)-DADSH system and 0.9 for the vanadium(V)-DADBH system. The influence of the concentrations of DADSH and DADBH were studied. Constant absorbances were obtained in the DADSH concentration of more than 2.6×10^{-5} M for 11.8 μg of iron and in the DADBH concentration of more than 6×10^{-5} M for 10.0 μg of vanadium.

Calibration curves were prepared according to the procedures for the determinations of iron and vanadium. The curves obey Beer's law up to 35 μg iron and vanadium. The molar absorption coefficients, Sandell's sensitivities and the relative errors of the methods are as follows. For iron-DADSH system; 2.65×10^4 l mol^{-1} cm^{-1}, 2.1×10^{-3} μg cm^{-2}, 0.22%. For vanadium-DADBH system; 2.73×10^4 l mol^{-1}
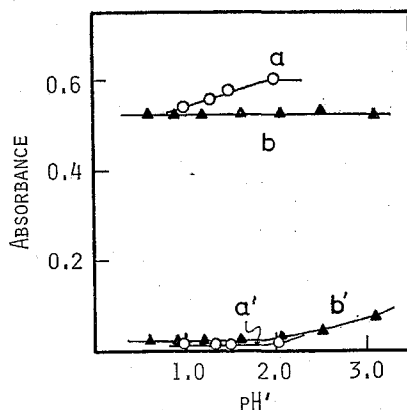
Fig. 6.　Relationship between absorbances of Fe^{3+}-DADSH and
　　　　V^{5+}-DADBH systems, and pH of hydrochloric acid
　　　　solutions measured.
a: Fe^{3+}-DADSH system, $[Fe^{3+}]=2.10\times10^{-5}$ M, $[DADSH]=4.47\times10^{-5}$ M,
　dmf-water (1:1 v/v)
b: V^{5+}-DADBH system, $[V^{5+}]=1.92\times10^{-5}$ M, $[DADBH]=2.14\times10^{-4}$ M,
　dmf-water (2:8 v/v)
a' and b': Reagent blanks of a and b, respectively

cm^{-1}, 1.9×10^{-3} μg cm^{-2}, 0.3%.

For the determination of 10.0 μg of vanadium by the method (II), the diverse ions can be tolerated at the levels given in Table III. The limiting value was taken as that value which caused an error of not more than 2.5% in absorbance. For the determination of 11.8 μg of iron by the method (I), Al^{3+}, Cr^{3+}, Zn^{2+}, and Cd^{2+}, are tolerated at the levels of 500, 100, 10 and 5 ppm, respectively.

The sensitivety of the method for the determination of vanadium described in this study is higher than that of pyridine-2-acetoaldehyde salicyloylhydrazone method.[6] However, the present method is rather poor in selectivity as shown in Table

Table III　Tolerance limits of diverse ions

Diverse Ion	Torerance limit
K^+, Ca^{2+}, Na^+, NH_4^+, Mg^{2+}, Ba^{2+}, Sr^{2+}, NO_3^-, Cl^-, Br^-, SCN^-, SO_4^{2-}, ClO_4^-	>1000 ppm
Al^{3+}	500 ppm
Cr^{3+}	250 ppm
Ni^{2+}, Pb^{2+}, I^-	100 ppm
Tartrate, NO_2^-	50 ppm
Citrate, F^-, Mo^{6+}	25 ppm
Cd^{2+}, Zn^{2+}, Cu^{2+}, $S_2O_3^{2-}$	10 ppm
Mn_2^+, Sn^{4+}	5 ppm
Ag^+, Bi^{3+}	2.5 ppm
W^{6+}	1 ppm
Co^{2+}, Sn^{2+}, Ti^{4+}, Zr^{4+}, Fe^{3+}, EDTA	<1 ppm

Vanadium taken: 10.0 μg.

III. In order to obtain high selectivity, the separation methods such as chromatography and solvent extraction should be utilized. DADSH seems to have an ability reacting with various metal ions. Therefore, the selectivity in the determination of iron with DADSH is presumably low.

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(12) In these cases, the equilibrium reactions would be represented as

$$2H^+ + L^- + VO_3^- \rightleftharpoons [VO_2L] + H_2O, \qquad K = \frac{[VO_2L]}{a_H^2[L^-][VO_3^-]}.$$
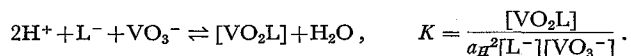
In order to estimate accurate K values, the pH values measured in this study should be corrected.