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Chemical Analysis of Mixtures of Metals by a Logarithmic Extrapolation Method

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Decomposition of the ternary molybdophosphoric acid of titanium(IV), vanadium(V), zirconium(IV) and niobium(V) by complexing agents such as oxalate, citrate or tartrate was found from a kinetic study to be of first-order with respect to each metal ion. The half lives and activation energies of decomposition were also examined. From the results chemical analysis of mixtures of the metals was studied by a logarithmic extrapolation method, utilizing the difference in decomposition rate. Metals in binary systems such as Zr–Nb, V–Zr, Nb–V, Ti–V and Ti–Nb could be determined simultaneously within a relative error of ±5%. Determination of 0.01∼0.2 mg of vanadium was carried out in the presence of titanium (0.1 mg), zirconium (0.5 mg), niobium (0.5 mg) and other diverse ions. Iron(III), aluminum, germanium(IV) and iodide interfered with the determination.

Spectrophotometric determination of titanium(IV), vanadium(V), zirconium(IV) and niobium(V) utilizing their chelate compounds, ternary heteropoly acids and peroxy compounds has been widely used.[1–5] The heteropoly acid method is sensitive in the determination of each metal, but can not be applied to mixtures of these metals because of their mutual interference.

For the chemical analysis of mixtures of these metals, the authors reported on a simultaneous determination of titanium(IV) and vanadium (V), based on the different rate of decomposition of each ternary molybdophosphoric acid in hydrochloric acid solution, without tedious separation procedure.[6] However, the method has the disadvantage that zirconium(IV) and niobium(V) should not be present since they form a precipitate.

The logarithmic extrapolation method has also been used for the analysis of mixtures of two components because of its simplicity and convenience.[7–10] Tanaka *et al.* used this method in the analysis of mixtures of some heavy metals, utilizing different rates of ligand substitution reactions.[11]

A method has been proposed for the simultaneous determination of two of the metal ions, titanium(IV), vanadium(V), zirconium(IV) and niobium(V) by the logarithmic extrapolation technique. This method is based on the different rates of decomposition of the ternary molybdophosphate of metal ions by complexing agents such as citrate, oxalate or tartrate. The kinetics of decomposition was examined by spectrophotometry, and a mixture of the four metal ions was analyzed in the presence of diverse ions.

General Considerations

The logarithmic extrapolation method[12–14] has been applied. After the faster reacting component(A) has reacted completely, the amount of the slower reacting component(B) at the initial time is determined by extrapolating the first-order plots to zero time, the amount of the former at the initial time being estimated by extrapolating logarithm of the difference between the

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total absorbance and the absorbance due to B to zero time. The procedure is as follows.

Logarithm of the net absorbance, log E_t, is plotted against time, E_t being obtained by subtracting the blank absorbance from that of the sample solution containing A and B. With the lapse of time diagram (I) gives first a curve, then a straight line when the ratio of rate constants for A and B is large enough. The straight line in (I) is extrapolated (line II) to zero time, to give an intercept of log $E_{B,0}$, logarithm of the absorbance due to initial B. Next, logarithm of the difference in absorbance, obtained by subtracting the absorbance in (II) from that in (I), is plotted against time. The intercept at zero time is log $E_{A,0}$, logarithm of the absorbance due to initial A (diagram III). The concentrations of A and B are calculated from $E_{A,0}$, and $E_{B,0}$ with the aid of calibration curves.

Experimental

Reagent. All the chemicals were of analytical reagent grade. Water was deionized and distilled. The solutions prepared were 0.1 M potassium dihydrogen phosphate, 0.2 M sodium molybdate dihydrate, 0.1 mg metal ion per ml (Ti, V, Zr and Nb) and 0.25 M complexing agent solution (ammonium oxalate monohydrate, sodium citrate dihydrate and sodium tartrate dihydrate).

Apparatus. Spectrophotometric measurements were made on a Hitachi Recorder QPD_{53} and a spectrophotometer Model 139, with 1 cm and 5.3 cm quartz cells. A pH meter, Toa Electronics Ltd., Model HA-5A was used.

Experimental Procedure. One ml phosphate solution was added to 10 ml molybdate solution in a 100 ml beaker, to which was then added a sample solution containing metal ions. The solution was diluted to *ca.* 40 ml with water, the pH being adjusted to 1.5 with 0.5 M sulfuric acid, and made up to 50 ml with water. The mixture was set aside for 2 hr and then 40 ml of the solution was transferred to a 50 ml cell. To this was added 10 ml of complexing agent solution, and the change in transmittance of the solution was recorded at 400 nm as a function of time. A blank solution containing phosphate and molybdate was treated in the same manner. All the experiments were carried out at 20±0.2 °C unless otherwise mentioned.

Results and Discussion

Molar Extinction Coefficients. The absorption spectra of the ternary molybdophosphoric acids and the reagent blank give peaks in the ultraviolet range.[15] Hence, all the absorbances were measured at 400 nm where the absorbance of the reagent blank was considerably low. The molar extinction coefficients of the ternary molybdophosphoric acids were kinetically determined. Figure 1 shows plots of log E_t *vs.* time t, which correspond to the decomposition of ternary molybdophosphoric acids by the complexing agent in 1 cm cells. The linear plots show that the decomposition follows the first-order rate law under the given conditions. The molar extinction coefficients of each ternary molybdophosphoric acid were estimated from the extrapolated intercept to time zero (log E_0). They were 1.57×10^3, 2.67×10^3, 1.28×10^3 and 1.52×10^3 for molybdotitanophosphoric, molybdovanadophosphoric, molybdozirconophosphoric and molybdoniobiophosphoric acid, respectively. Beer's law holds up to the concentration of 1 mg/50 ml of each metal at 400 nm.

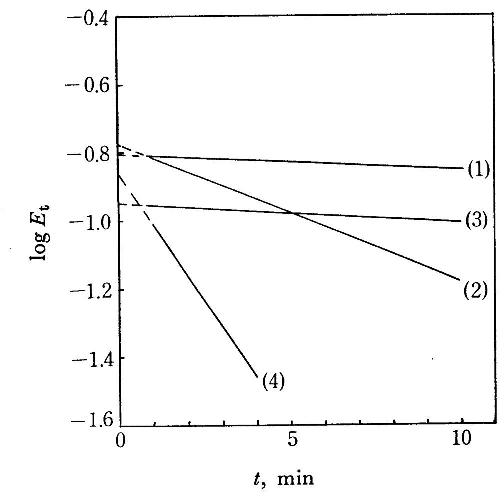

Fig. 1. Determination of E_0 for each metal.
(1) Ti(IV) 0.24 mg/50 ml (0.05 M citrate)
(2) V(V) 0.16 mg/50 ml (0.05 M citrate)
(3) Zr(IV) 0.40 mg/50 ml (0.50 M citrate)
(4) Nb(V) 0.40 mg/50 ml (0.05 M tartrate)
Cell length: 1 cm, temperature: 20 °C

On the other hand, the absorbance of the reagent blank was approximately 1.0 at 400 nm under the given conditions, but it decreased after the addition of a complexing agent to the solution and finally reached a constant value of 0.01 after 1 min. It is clear that molybdophosphoric acid itself decomposes completely within 1 min.

Half Life. In order to predict the possibility of the simultaneous determination of these metals in their binary mixtures, it is necessary to know the half life of the decomposition of each ternary molybdophosphoric acid by the complexing agent. It can be obtained from the plot of log E_t *vs.* t required for the decomposition. The results are given in Table 1. The half lives decreased in the order V>Ti>Zr>Nb for oxalate system and Ti>Zr>V>Nb for citrate or tartrate system. The following conclusions can be drawn: (1) Of these metals vanadium gives the longest half life for the oxalate system, in good accordance with the previous results,[6,16] where molybdo-

TABLE 1. VALUES OF HALF LIFE
Concentration of complexing agent: 0.05 M, wavelength: 400 nm, cell length: 5.3 cm, temperature: 20 °C

Metal	Half life (min)		
	Oxalate	Citrate	Tartrate
Ti[a]	1.50	70.0	66.0
V[a]	9.60	9.60	11.6
Zr[b]	0.83	49.0	20.0
Nb[b]	0.80	0.27	2.0

a) 0.08 mg taken b) 0.4 mg taken

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Table 2. Values of the Arrhenius activation energy (E_A)

Concentration of complexing agent: 0.05 M, wavelength: 400 nm, cell length: 5.3 cm

Metal	E_A kcal mol^{-1}		
	Oxalate	Citrate	Tartrate
Ti[a]	4.4	17.5	14.9
V[a]	16.3	15.4	17.9
Zr[b]	17.0	16.9	15.8
Nb[b]	7.5	13.9	14.4

a) 0.08 mg taken b) 0.4 mg taken

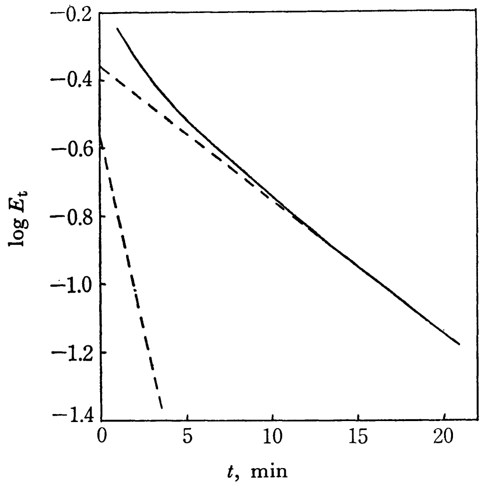

Fig. 2. Decomposition curve of mixture of Zr(0.5 mg) and Nb(0.5 mg) with tartrate.

Solid line: experimental data, dashed line: extrapolated data, tartrate: 0.05 M, cell length: 5.3 cm, temperature: 20 °C.

vanadophosphoric acid is the most inert in aqueous solution. (2) For citrate and tartrate systems, the half lives of quadrivalent metal ions (Ti,Zr) are longer than those of quinquevalent metal ions (V, Nb).

Activation Energy. Influence of temperature on the decomposition rate was examined at 15, 20, 25, and 30 °C. Straight Arrhenius plots gave the activation energies summarized in Table 2. They indicate that the activation energies for decomposition by oxalate are 4.4 kcal mol^{-1} and 7.5 kcal mol^{-1} for molybdotitanophosphoric and molybdoniobiophosphoric acids, respectively, and 13.9~17.9 kcal mol^{-1} for the other decomposition systems.

Simultaneous Determination of Two Metal Ions. In order to carry out the extrapolation method successfully, the ratio of the decomposition rate constants of the ternary molybdophosphoric acids in the mixture, k_A/k_B, should be greater than 4 for the case in which the ratio of initial concentration of two metals $[A]_0/[B]_0$ is equal to unity.[9] Pairs of metals in which the differential kinetic determination seems possible were chosen from Table 1, and simultaneous determination of the metal ions was examined. The result for a mixture of zirconium and niobium is given in Fig. 2. From plots of log E_t *vs.* t, the concentrations of zirconium and niobium were determined from the intercepts obtained by extrapolation (Table 3). Synthetic samples of Zr–Nb, V–Zr, Nb–V, Ti–V, and Ti–Nb have been successfully analyzed within a relative error of ±5%.

Table 3. Analysis of binary mixtures

Concentration of complexing agent: 0.05 M, wavelength: 400 nm, cell length: 5.3 cm, temperature: 20 °C

Mixture	Taken(mg)		Found(mg)		Complexing agent used
Zr–V	0.500	0.100	0.500	0.100	Oxalate
Nb–V	0.500	0.100	0.481	0.100	Oxalate
Nb–V	0.500	0.050	0.480	0.049	Oxalate
Ti–V	0.100	0.100	0.097	0.099	Oxalate
Ti–V	0.200	0.050	0.198	0.049	Oxalate
Ti–Nb	0.100	0.500	0.099	0.488	Tartrate
Zr–Nb	0.500	0.500	0.498	0.501	Tartrate
Zr–Nb	0.100	0.500	0.099	0.505	Tartrate
Ti–Zr[a]	0.200	0.500	0.203	0.365	Tartrate
Ti–Zr[a]	0.100	0.100	0.101	0.083	Tartrate

a) Temperature 25 °C

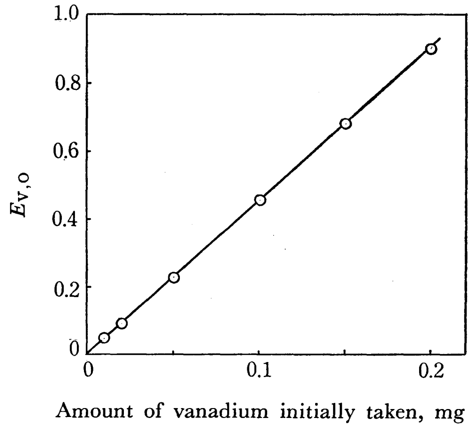

Fig. 3. Determination of V in the presence of Ti(0.1 mg), Zr(0.5 mg) and Nb(0.5 mg).

Oxalate: 0.05 M, cell length: 5.3 cm, temperature: 20 °C.

An attempt was made to analyze a mixture of titanium and zirconium using tartrate at 25 °C. Titanium was determined in the mixture but not zirconium (Table 3).

Determination of Vanadium in the Presence of Titanium, Zirconium and Niobium. We see from Table 1 that vanadium can be determined in the presence of titanium, zirconium and niobium by using oxalate as complexing agent, since the half life of molybdovanadophosphoric acid is more than six times greater than those of the other metals. Analysis of 0.01~0.2 mg of vanadium in the presence of titanium (0.1 mg), zirconium(0.5 mg) and niobium(0.5 mg) was examined at 20 °C. The plot of absorbance $E_{V,0}$, *vs.* the amount of vanadium gives a straight line (Fig. 3). The present method can be applied to the determination of vanadium in the presence of the other three metals.

Diverse Ions. The effect of diverse ions on the determination of 0.1 mg of vanadium was examined in the presence of titanium (0.1 mg), zirconium (0.5 mg) and niobium (0.5 mg). Five mg of Co(II), Ni(II), Mn(II), Cu(II), Cr(VI) and 0.1 mg of Si(IV), As(V) and W(VI) gave no interference, but 0.05 mg of Ge(IV) and 5 mg of iodide interfered with determination. Iron(III) and aluminum should not be present because of the formation of precipitate, and calcium for that of its oxalate.