

Thermometric Titration of Copper and Zinc in Copper-Based Alloys with Triethylenetetramine

Toshiaki HATTORI*, Hideshi ARAI**, Shunitz TANAKA** and Hitoshi YOSHIDA**

*Research Center for Chemometrics, Toyohashi University of Technology, Toyohashi 441, Japan

**Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

The thermometric titration of copper(II) ions with triethylenetetramine was investigated. The apparent enthalpy change of the titration reaction varied over a wide range, even from exothermic to endothermic, depending on the reaction conditions, such as pH of sample and titrant solutions, species of buffer and coexistence of auxiliary reagent. In acetate buffer solution, this reaction was endothermic, and copper(II) ions could be titrated with error less than 0.5% of RSD even in the presence of other heavy metal ions. Furthermore, the sequential titration of copper(II) and zinc(II) ions was possible with error less than 0.7% of RSD when tartrate was added as an auxiliary reagent to get sharp end points. The methods were applied to the analysis of four samples of copper-based alloy. The analytical results agreed closely with those obtained by the JIS (Japanese Industrial Standard) method based on electrogravimetry.

Keywords Thermometric titration, copper, zinc, triethylenetetramine, copper-based alloy, sequential titration, sharp end point

Thermometric titration is one of the rapid and simple analytical methods. It is based on the measurement of enthalpy change (ΔH) of the chemical system. Since most chemical reactions are accompanied by an enthalpy change, this method is applicable to many kinds of reactions. And thermometric titration is hardly affected by the properties of the sample solution, such as optical clarity, viscosity and dielectric constant, which frequently cause large errors in the other methods. Therefore, the method can be widely applied. We previously reported the determination of calcium ions and magnesium ions with EDTA¹ and anionic surfactants with metal-phen complexes.^{2,3}

For the thermometric titration of heavy metal ions, sodium diethyldithiocarbamate (DDTC) is a useful reagent. We have demonstrated in a previous paper that the simultaneous determination of copper(II) and cadmium (II) in one sample could readily be carried out.⁴ However, DDTC reacts with many metal ions to form the precipitates, sometimes by the coprecipitation phenomena, so the method yield poor results. Triethylenetetramine (Trien) is a selective reagent for copper(II) ion⁵⁻⁷, and it will be suitable reagent for sequential titration because it forms soluble complexes in water, even though the enthalpy changes for the complex formation of metals with Trien are smaller than those of the corresponding metal-DDTC chelates. We have also developed some methods to obtain well-defined end points on the thermometric titration.^{1-4,8} To achieve the clarification of the end point and the simultaneous thermometric determination of metal ions, it is necessary to give the adequate consideration

to the enthalpy changes of the reactions which may be related to sample species, titrant and auxiliary reagents.

In this work we investigated the optimum conditions for the thermometric titration of copper(II) ion with Trien, and for the sequential titration of copper(II) and zinc(II) ions with Trien in the presence of auxiliary reagents. The method established was applied to the determination of copper and zinc in copper-based alloys.

Experimental

Apparatus

The details of the differential thermometric titration apparatus used in this study were described previously.¹

Reagents

Commercially available Trien (Reagent grade, Wako Pure Chemical Ind., Osaka, Japan) was used after purification according to Reilly and Sheldon⁵ to obtain Trien sulfate. Two 0.5 M Trien solutions were prepared by dissolving the sulfate in distilled water, adding sodium hydroxide solution until the pH was 6.0 for single titration of copper(II) ion and 8.0 for sequential titration of copper(II) and zinc(II) ions. The Trien solution was standardized with a standard solution of copper(II) ions by thermometric titration. The 0.1 M standard solutions of copper(II) and zinc(II) were prepared by dissolving the pure metals (99.999% for copper, Mitsuwa Pure Chemicals, Osaka, Japan) (99.995% for zinc(II), Wako Pure Chemical Ind.) in

nitric acid. Other reagents used were of guaranteed reagent grade.

Procedure

Preparation of sample solution. The sample alloy is immersed into 2% acetic acid and then is gently stirred for a few minutes. The alloy is washed with distilled water three times, and finally with ethylalcohol two times. The dried alloy is kept in a desiccator containing silica gel. An accurately weighed amount of the alloy (1–2 g) is transferred into a covered 100-ml tall beaker and 20–40 ml of mixed acid (nitric acid:sulfuric acid:distilled water=7:10:40) is added. The solution is gently heated to dissolve the alloy. After the solution is evaporated to near dryness without a covered glass, it is dissolved in 50 ml of distilled water including a small amount of acetic acid. The pH of the solution is adjusted to 4–5 by addition of sodium hydroxide solution, and then the volume is diluted to 250 ml with distilled water. If insoluble material appears during such handling, it is filtered off.

Determination of copper(II) ion (procedure 1). One burette of thermometric titration apparatus is filled with 0.5 M Trien of pH 6.0, and another burette is filled with distilled water as a reference. A 10 ml portion of sample solution is taken in a 100-ml Dewar flask. Ten milliliters of 2 M acetic buffer solution are added, and the solution is diluted to 50 ml with distilled water. In the reference Dewar flask, 50 ml of distilled water are taken. The two flasks are set in the titration apparatus. The solutions are simultaneously titrated at the rate of 0.1 ml min⁻¹ by using twin burettes after the temperature has been equilibrated. The end point of the titration is simply determined graphically from the intersection obtained by extrapolation of the successive periods of the titration curve.

Sequential determination of copper(II) and zinc(II) ion (Procedure 2). This procedure is quite similar to procedure 1, except for using Trien solution of pH 8.0 as the titrant. The 10 ml of sample solution are taken in a 100-ml Dewar flask. Ten milliliters of 2 M sodium tartrate and 10 ml of 0.1 M borax buffer solution (pH 9.5) are added, and the solution is diluted to 50 ml with distilled water.

Results and Discussion

Titration of copper(II) ion

Copper(II) ion was titrated with Trien in various pH-buffer solutions. As shown in Fig. 1, their titration curves have a clear end point in the region from pH 5 to pH 10. However, the shape of the titration curve significantly changes with pH-buffer solutions. The apparent heat change of the titration reaction is endothermic in acetate buffer solution (Fig. 1 (A)), but exothermic in TEA (triethanolamine) buffer solution (Fig. 1 (B); 1, 2) and ammonia buffer solution (Fig. 1 (B); 3, 4). The results are summarized in Table 1.

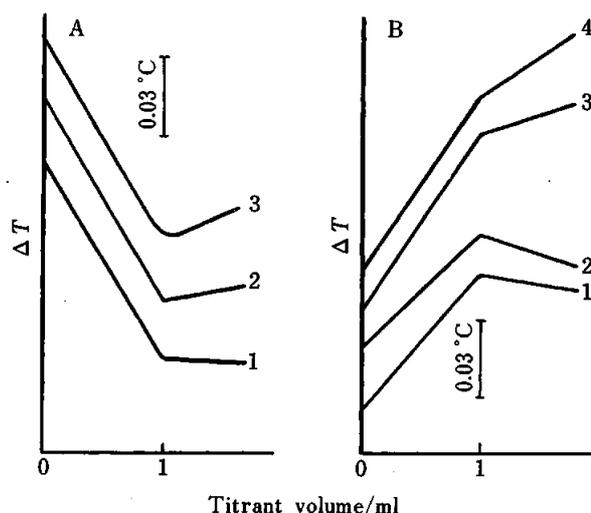


Fig. 1 Titration curves of 10⁻² M Cu²⁺ with 0.5 M Trien (pH 6.0) in various buffer solutions. (A) 0.2 M acetate: 1, pH 6.0; 2, pH 5.0; 3, pH 4.5. (B) 0.2 M TEA: 1, pH 7.0; 2, pH 8.0. 0.2 M ammonia: 3, pH 9.0; 4, pH 10.0.

Table 1 Titration of copper(II)

	Taken/ mg	Found/ mg	Error, %	RSD ^a , %
pH 5.0 ^b	6.35	6.34	-0.2	0.3
	12.71	12.7 ₁	0.0	0.3
	31.77	31.8 ₃	+0.2	0.2
	63.54	63.6 ₆	+0.2	0.1
	127.1	127.1	0.0	0.1
pH 8.0 ^c	31.77	31.8 ₃	+0.2	0.4
pH 10.0 ^d	31.77	31.7 ₄	-0.1	0.2

- a. Five runs.
b. Acetate buffer.
c. TEA buffer.
d. Ammonia buffer.

The titration reaction consists of five processes as follows (The charges of all chemicals are disregarded as a matter of convenience. The symbol ΔH represents enthalpy change).

(1) Complexation of copper(II) ion with Trien,



(2) Dissociation of copper(II)-buffer complex,



(3) Dissociation of H_m-Trien,



(4) Protonation of buffer,



(5) Dilutions of all chemicals, ΔH_5 .

Thereby the total apparent enthalpy change is;

$$\Delta H_{\text{obs}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5.$$

The heat change ΔH_1 of process (1), that is, of the reaction between copper(II) ion and Trien, is $-90.2 \text{ kJ mol}^{-1}$ from ref. 9. At a given pH 6.0 of titrant, ΔH_3 of the total dissociation calculated from ref. 10 is $124.4 \text{ kJ mol}^{-1}$.

ΔH_2 and ΔH_4 in a particular sample solution can be calculated from thermodynamic data. The interaction between acetic acid and copper(II) ion is weak. Therefore, the ΔH_2 of the total dissociation for copper(II)-acetate complexes is 6.6 kJ mol^{-1} for copper(II) ion at pH 5.0, as calculated in ref. 11. The ΔH_4 of total protonation of acetate ions (ref. 12) for protons (2.78 mol) derived from the dissociation of 1 mol of Trien at pH 6.0 is 1.2 kJ . As ΔH_5 of dilution of all chemicals is negligible, the apparent enthalpy change of the titration in the acetate buffer ΔH_{obs} is 42.0 kJ mol^{-1} . This value indicates that the titration reaction is endothermic, it agreed approximately with the real titration result (Fig. 1 (A); 2).

On the other hand, the ΔH_2 of the total dissociation of copper(II)-ammine complexes is 91.6 kJ mol^{-1} for copper(II) ion, and the ΔH_4 of the total protonation for ammonia (ref. 13) is -144.8 kJ for protons derived from dissociation of Trien. As the ΔH_5 is similarly negligible, the apparent enthalpy change of the titration in the ammonia buffer is $-19.0 \text{ kJ mol}^{-1}$, which supports the conclusion that the titration reaction in ammonia buffer solution is exothermic (Fig. 1 (B); 3, 4).

For the selective determination of copper(II) ion, acetate buffer solution is favorable because most heavy metal ions are not allowed to react with Trien at the low pH. The results in acetate buffer in the presence of

diverse ions are summarized in Table 2. The ions in the molar ratios given in Table 2 do not interfere with the determination of copper(II) within such low RSD as 0.5% except for Hg^{2+} , Ni^{2+} and Fe^{3+} , where these ions even in the concentration ratios given in the Table 2 strongly interfere with the accurate determination of copper(II). The presence of 0.1 M sodium tartrate enables the titration of copper(II) within RSD 0.5% in the presence of nickel(II) in the molar ratio $[\text{Ni(II)}]/[\text{Cu(II)}]=0.5$.

Sequential titration of copper(II) and zinc(II) ions

The simultaneous determination of copper(II) and zinc(II) ions was investigated by the thermometric titration. Since the formation constant of complexes of zinc(II) ions with Trien is lower than that of copper(II) ions, the titration at high pH is suitable to react zinc(II) ion quantitatively with Trien. At high pH, however, the formation of the hydroxide may occur. To inhibit the formation of the hydroxide, and make the each end-point for the thermometric titration clear, the use of an auxiliary reagent was investigated. Among the buffer and auxiliary reagents tried, borate-tartrate solution gave the best results. The sequential titration curves of copper(II) and zinc(II) ions are shown in Fig. 2.

The conditional stability constants of copper(II)-Trien and zinc(II)-Trien at pH 9.5 are $\log K'_{\text{Cu}}=11.1$, $\log K'_{\text{Zn}}=6.2$ in 0.2 M ammonia buffer, respectively, and $\log K'_{\text{Cu}}=17.1$, $\log K'_{\text{Zn}}=9.3$ in 0.4 M tartrate buffer, respectively (refs. 9,13,14). The difference of the free energy of the two reactions is enough large to titrate sequentially in both buffer solutions. In ammonia buffer, the apparent enthalpy changes of both copper(II) ions and zinc(II) ions with Trien are exothermic (curve 1). However in the borate-tartrate solution (curve 2), the apparent enthalpy change of copper(II) ions with Trien is exothermic, and that of zinc(II) ions is

Table 2 Effect of diverse cations on the determination of copper(II)

Cations	Added as	[Ion]/ [Cu ²⁺]	Found ^a / mg	Error, %
Ag ⁺	AgNO ₃	10	31.8 ₉	+0.4
Co ²⁺	Co(NO ₃) ₂	10	31.8 ₇	+0.3
Zn ²⁺	Zn(NO ₃) ₂	10	31.8 ₀	+0.1
Cd ²⁺	Cd(NO ₃) ₂	10	31.6 ₅	-0.4
Mn ²⁺	MnSO ₄	10	31.7 ₁	-0.2
Pb ²⁺	Pb(NO ₃) ₂	10	31.8 ₉	+0.4
Hg ²⁺ ^b	Hg(NO ₃) ₂	5	31.9 ₂	+0.5
Ni ²⁺ ^c	Ni(NO ₃) ₂	0.5	31.8 ₀	+0.1
Fe ²⁺	FeSO ₄ (NH ₄) ₂ SO ₄	10	31.8 ₃	+0.2
Fe ³⁺ ^c	Fe(NO ₃) ₃	5	31.7 ₇	0.0
Al ³⁺	Al(NO ₃) ₃	10	31.7 ₁	-0.2
Ca ²⁺	Ca(NO ₃) ₂	100	31.7 ₇	0.0
Mg ²⁺	Mg(NO ₃) ₂	100	31.8 ₀	+0.1
Sr ²⁺	Sr(NO ₃) ₂	100	31.8 ₀	+0.1
Ba ²⁺	BaCl ₂	100	31.7 ₄	-0.1

Cu²⁺: 31.77 mg in acetate buffer (pH 5.0).

a. Mean value of three runs.

b. Sodium chloride (0.1 M) was added.

c. Sodium tartrate (0.1 M) was added.

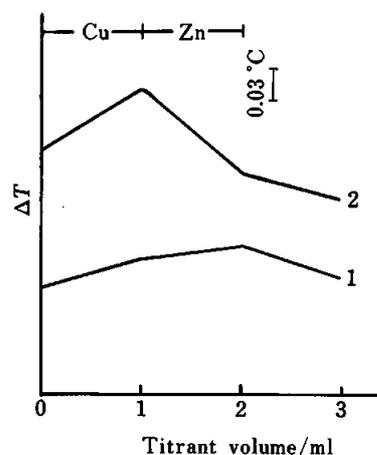


Fig. 2 Sequential titration curves of $10^{-2} \text{ M Cu}^{2+}$ and Zn^{2+} . 1: 0.5 M Trien (pH 10.0) as titrant; 0.2 M ammonia buffer solution (pH 9.5). 2: 0.5 M Trien (pH 8.0) as titrant; 0.02 M borate buffer solution (pH 9.5) in presence of 0.4 M sodium tartrate.

Table 3 Titration of copper(II) and zinc(II)

Cu:Zn	Cu ²⁺			Zn ²⁺		
	Taken/mg	Found ^a /mg	Error,%	Taken/mg	Found ^a /mg	Error,%
1:1	15.90	15.9 ₄	+0.3	16.57	16.5 ₃	-0.2
1:2	15.90	15.9 ₄	+0.3	33.14	33.2 ₃	+0.3
1:3	15.90	15.9 ₆	+0.4	66.28	66.2 ₅	-0.1
2:1	31.81	31.7 ₄	-0.2	16.57	16.4 ₇	-0.6
2:3	31.81	32.0 ₃	+0.7	66.28	66.6 ₇	+0.6
4:1	63.61	63.9 ₂	+0.5	16.57	16.5 ₅	-0.1

a. Mean value of five runs.

Table 4 Determination of copper-based alloys

	JIS method ^a		Cu,%	Present method		
	Cu,%	Zn,%		RSD ^b ,%	Zn,%	RSD ^b ,%
Cu-Be ^c	97.8	—	97.6	0.3	—	—
P-Bronze ^c	93.8	—	93.5	0.7	—	—
Brass 1 ^d	65.1	34.7	65.1	0.4	34.5	0.5
Brass 2 ^d	58.9	37.0	58.7	0.5	37.2	0.7

a. JIS H 1012 (for analysis of copper-based alloy); JIS H 1211 (for analysis of brass). b. Five runs. c. Procedure 1. d. Procedure 2.

endothermic, because the enthalpy change of formation between zinc(II) ions and Trien is small. The first endpoint in the borate-tartrate solution is sharper than that in the ammonia buffer solution. The results of sequential titration in the borate-tartrate solution are summarized in Table 3. The relative standard deviations of the sequential titration were all less than 0.7%.

Determination of copper and zinc in copper-based alloys

Copper and zinc in a rod of Copper Beryllium (Cu-Be), a sheet of Phosphor Bronze (P-Bronze), a screw of Brass (Brass 1) and a nut of Brass (Brass 2) were determined by this method. The single thermometric titration of copper(II) ion (procedure 1) was used for the analysis of the Copper Beryllium and Phosphor Bronze. The results of determination are summarized in Table 4. The certified values of constituents in Copper Beryllium are 98% copper and 2% Beryllium. The certified values of Phosphor Bronze are 94% copper, 6% tin and 0.02–0.4% Phosphor. For analysis of Phosphor Bronze, the filtration was necessary after adjustment of pH of sample solution because the hydroxide of tin precipitated. These values agreed with the data obtained by electrogravimetry based on JIS method and certified values.

The sequential thermometric titration of copper(II) and zinc(II) ions (procedure 2) was used for the analysis of the two brass samples. During the dissolution with mixed acid, a white powder precipitated in the sample solution prepared from the nut of brass (Brass 2). The precipitate was regarded as lead sulfate, and filtration was required. The estimated values of copper and zinc in the two brasses agreed also with those obtained by the JIS method, as shown in Table 4.

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