September, 1992] © *1992 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *65*, *2537—2539 (1992)* 2537

Extractive Separation of Trace Amounts of Cu^{II}, Fe^{III}, and Ga^{III} from Al^{III} on the Basis of HSAB Rule

Hiroshi Kawamoto, Tohru Nishimura, Kin-ichi Tsunoda, and Hideo Akaiwa*
Department of Applied Chemistry, Faculty of Engineering,
Gunma University, Kiryu, Gunma 376

(Received April 10, 1992)

Synopsis. The design of a separation scheme for Cu^{II}, Fe^{III}, and Ga^{III} from Al^{III} by chelate extraction was proposed on the basis of the HSAB rule. Among the various chelating agents, 8-quinolinol was estimated to be the most effective for separation. This prediction was confirmed through experiments.

In previous work the authors introduced a new dual parameter scale, strength (S_A) and soft (σ_A) factors of a metal ion (M^{z+}), into the HSAB rule¹⁾ which was successfully applied to the design of a separation shceme of In^{III} from Ga^{III} by chelate extraction; thus, the most effective chelating agent could be predicted on the basis of the HSAB rule.²⁾ This approach was extended to group separations of Cu^{II}, Fe^{III}, and Ga^{III} from Al^{III} (matrix) by a single chelate extraction; the proposed method was confirmed to be applicable to practical analysis through experiments.

Experimental

Reagents. 8-Quinolinol was obtained from Wako Pure Chemicals, and used without further purification. *o*-Xylene and all the other chemicals used were of guaranteed grade. Deionized water was used throughout.

Apparatus. A Shimadzu Model ICPS-1000III ICP atomic emission spectrometer equipped with a plasma torch was used. A Horiba Model pH meter F-16 and Iwaki KM type shaker were also used.

Extraction Curves. Twenty cubic centimeters of an aqueous solution containing trace amounts of Al^{III}, Cu^{II}, Fe^{III}, or Ga^{III}, whose pH was preliminarily adjusted by adding the monochloroacetic acid–sodium monochloroacetate buffer, was placed in a separating funnel. An equal volume of *o*-xylene solution containing 5.0×10^{-3} mol dm^{-3} 8-quinolinol was added; the mixture was then shaken vigorously for 30 min. After the phases were allowed to separate, the pH of the aqueous phase was measured. To the organic phase 1 mol dm^{-3} nitric acid was added; a metal ion was back-extracted into the aqueous phase, which was applied to inductively coupled plasma atomic emission spectrometry (ICP-AES) in order to determine metal ions. All experiments were carried out at room temperature (ca. 293 K).

Analysis of Commercial Alum. Twenty grams of commercial alum (guaranteed grade $K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$ from Kanto Chemical Co., Int.) was dissolved in water, and made up to 1 dm³. Then, 5.00 cm³ of the sample solution and 15 cm³ of the monochloroacetic acid–sodium monochloroacetate buffer solution (pH 2.9) were mixed. The buffer solution was preliminarily shaken with a 5.0×10^{-3} mol dm^{-3} 8-quinolinol solution to remove any impurities. Then, Cu^{II}, Fe^{III}, and Ga^{III} of the aqueous phase were separated from Al^{III} by shaking 20 cm³ of an *o*-xylene solution containing 5.0×10^{-3} mol dm^{-3} 8-quinolinol for 30 min. After trace metal ions were back-extracted into 5.00 cm³ of 1 mol dm^{-3} nitric acid, the aqueous phase was applied to ICP-AES.

Results and Discussion

Extraction constants for metal chelate (K_{ex}) were rationalized by the HSAB rule:¹⁾

$$\log K_{ex} + zpK_a = S_A S_B + \sigma_A \sigma_B, \tag{1}$$

where pK_a, subscripts A and B, indicate the acid dissociation exponent of the chelating agent, the Lewis acid and the base, respectively. S_A and σ_A are defined by the following equations:

$$S_A = -\frac{2\Delta S_h{}^\circ}{2.30R} \tag{2}$$

and

$$\sigma_A = \frac{\Delta H_f{}^\circ}{2.30RT}. \tag{3}$$

Here, $\Delta S_h{}^\circ$, R, $\Delta H_f{}^\circ$, and T denote the hydration entropy of a metal ion, the gas constant, the heat of formation of an aqueous metal ion, and the absolute temperature, respectively. The extraction of a metal ion with a chelating agent (HR) is assumed to proceed according to

$$M^{z+} + zHR_{org} = MR_{z,org} + zH^+, \tag{4}$$

where the subscript org denotes the organic phase. Here, the extraction constant is defined as

$$K_{ex}{}^M = \frac{[MR_z]_{org}[H^+]^z}{[M^{z+}][HR]_{org}{}^z}. \tag{5}$$

In the absence of an auxiliary ligand in the aqueous phase, the distribution ratio of a metal M (D^M) is represented as D^M=$[MR_z]_{org}\{[M^{z+})|(MOH^{z-1}]+\cdots\}^{-1}$= $[MR_z]_{org}[M^{z+})^{-1}\alpha_{M(OH)}{}^{-1}$, where $\alpha_{M(OH)}$ is a side-reaction coefficient, and by introducing D^M into Eq. 5, the following is derived:

$$\log D^M\alpha_{M(OH)} = \log K_{ex}{}^M + z\log\,[HR]_{org} + z\text{pH}. \tag{6}$$

Although several side-reactions caused by the distribution of a chelating agent may be taken into consideration, only hydrolysis was considered in the present approximate approach because of a lack of quantitative data. Since the value of log $\alpha_{Al(OH)}$ nearly equals zero below pH 4,³⁾ the pH of an aqueous phase for the extraction of Cu^{II}, Fe^{III}, and Ga^{III} is adjusted to 3.0, and $[HR]_{org}$=5.0×10^{-3} mol dm^{-3} is adopted tentatively. Since $\log k_{ex}{}^M$+zpK_a=S_AS_B+$\sigma_A\sigma_B$, the following equation can be derived from Eq. 6:

$$\log D^{\mathrm{M}}\alpha_{\mathrm{M(OH)}} = S_{\mathrm{A}}S_{\mathrm{B}} + \sigma_{\mathrm{A}}\sigma_{\mathrm{B}} - zpK_{\mathrm{a}} + z\log[\mathrm{HR}]_{\mathrm{org}} + z\mathrm{pH}. \quad (7)$$

For the quantitative extraction of a metal ion, $\log D^{\mathrm{M}}$ should exceed 2; Eq. 7 is therefore rewritten as

$$\sigma_{\mathrm{A}}\sigma_{\mathrm{B}} \geqq 2 + \log\alpha_{\mathrm{M(OH)}} + zpK_{\mathrm{a}} - z\log[\mathrm{HR}]_{\mathrm{org}} - z\mathrm{pH} - S_{\mathrm{A}}S_{B} = Y^{\mathrm{M}}. \quad (8)$$

On the other hand, since $\log D^{\mathrm{Al}}$ should be below -2 to maintain 99% amounts of $\mathrm{Al^{III}}$ in the aqueous phase, the following equation can be obtained:

$$\sigma_{\mathrm{Al}}\sigma_{\mathrm{B}} \leqq -2 + 3pK_{\mathrm{a}} - 3\log[\mathrm{HR}]_{\mathrm{org}} - 3\mathrm{pH} - S_{\mathrm{Al}}S_{\mathrm{B}} = Y^{\mathrm{Al}}. \quad (9)$$

Here, $\log\alpha_{\mathrm{Al(OH)}}=0$ is assumed. Now, S_{A} and σ_{A} for metal ions can be calculated from the reported data[4,5] and are listed in Table 1. The pK_{a} and $\log\alpha_{\mathrm{M(OH)}}$ are given in the literature;[3] S_{B} and σ_{B} were calculated by the authors in a previous paper.[1] Thus, the feasibility of a quantitative separation can be evaluated by using Eqs. 8 and 9. The results of the calculations are given in Table 2, where 8-quinolinol, TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione), STTA (1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-butene-2-one) and dithizone (3-mercapto-1,5-diphenylformazan) are adopted as typical chelating agents. As can be seen in Table 2, only 8-quinolinol satisfies the condition expressed by Eqs. 8 and 9. The above predictions were confirmed through experiments.

As can be seen in Fig. 1, the quantitative separation of $\mathrm{Cu^{II}}$ from $\mathrm{Al^{III}}$ can be performed at pH=3.0. Strictly speaking, the extraction of $\mathrm{Fe^{III}}$ and $\mathrm{Ga^{III}}$ is not quantitative enough, probably because of side-reactions caused by the distribution of 8-quinolinol. However, since the per cent extractions for these ions exceed 95%, the above approximation in which only hydrolysis is considered seems to be reasonable.

The above separation scheme was applied to the determination of trace amounts of $\mathrm{Cu^{II}}$, $\mathrm{Fe^{III}}$, and $\mathrm{Ga^{III}}$ in high-purity alum. Since a large amount of $\mathrm{Al^{III}}$ interferes with the determination of trace metals, $\mathrm{Al^{III}}$ should be removed from the sample solution before ICP-AES is applied. Analytical results are given in Table 3. The values obtained by the calibration curve method were in good agreement with those found by the standard addition method. In conclusion, the present method

Table 1. Values of S_{A} and σ_{A}

$\mathrm{M^{z+}}$	S_{A}	σ_{A}
$\mathrm{Cu^{II}}$	31.9	11.2
$\mathrm{Fe^{III}}$	55.1	−8.32
$\mathrm{Ca^{III}}$	59.6	−36.8
$\mathrm{Al^{III}}$	54.7	−91.5

Table 2. Values of $\sigma_{\mathrm{A}}\sigma_{\mathrm{B}}$ and Y^{M}

$\mathrm{M^{z+}}$	Chelating agent	$\sigma_{\mathrm{A}}\sigma_{\mathrm{B}}$	Y^{M}	Remarks
$\mathrm{Cu^{II}}$	TTA	1.1	3.1	
	STTA	3.2	0.5	a)
	8-Quinolinol	1.5	0.1	a)
	Dithizone	4.9	−5.1	a)
$\mathrm{Fe^{III}}$	TTA	−0.8	1.8	
	STTA	−2.4	−1.7	
	8-Quinolinol	−1.1	−5.0	a)
	Dithizone	−3.7	−11.6	a)
$\mathrm{Ca^{III}}$	TTA	−3.7	0.0	
	STTA	−10.6	−3.3	
	8-Quinolinol	−4.9	−8.2	a)
	Dithizone	−16.2	−14.0	
$\mathrm{Al^{III}}$	TTA	−9.2	−2.5	b)
	STTA	−26.3	−6.0	b)
	8-Quinolinol	−12.2	−9.2	b)
	Dithizone	−40.3	−15.8	b)

a) Eq. 8 is satisfield. b) Eq. 9 is satisfied.

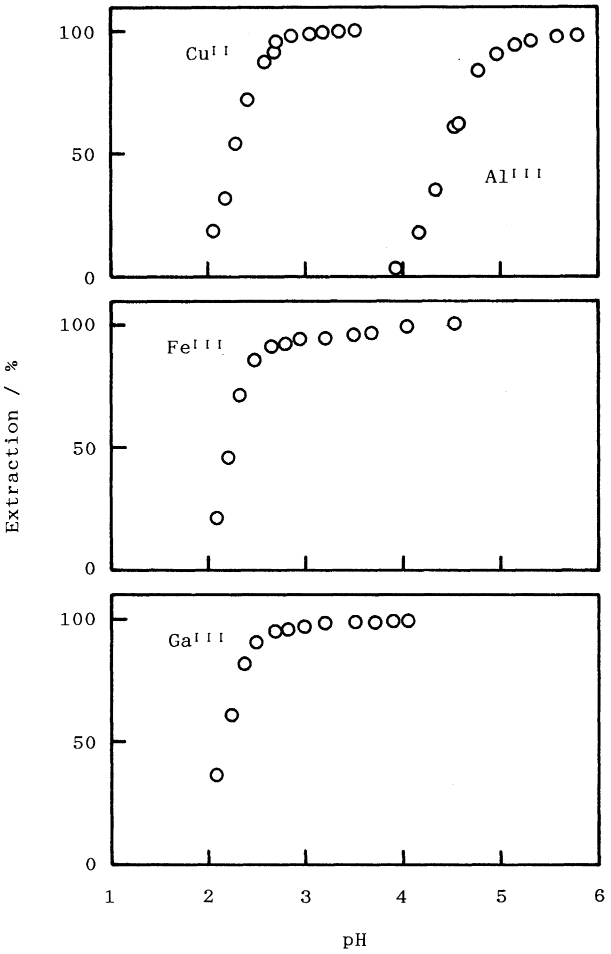

Fig. 1. Extraction curves. $[\mathrm{HR}]_{\mathrm{org}}=5.0\times10^{-3}\ \mathrm{mol\ dm^{-3}}$.

Table 3. Analytical Results for Alum

	C.C.M.[a)]	S.A.M.[b)]
	$\mu\mathrm{g\ g^{-1}}$	$\mu\mathrm{g\ g^{-1}}$
$\mathrm{Cu^{II}}$	1.1±0.1	0.92
$\mathrm{Fe^{III}}$	2.6±0.1	2.4
$\mathrm{Ca^{III}}$	3.2±0.3	3.2

a) Calibration curve method; an average of seven determinations. b) Standard addition method.

will be applicable to the determination of Cu^{II}, Fe^{III}, and Ga^{III} in high-purity aluminium, and the above approach may be effective for the separation of other trace metals.

References

1) H. Kawamoto and H. Akaiwa, *Chem. Lett.*, **1990**, 1451.

2) H. Kawamoto, T. Nishimura, K. Tsunoda, and H. Akaiwa, *Chem. Lett.*, **1991**, 1747.

3) A. Ringbom (translated by N. Tanaka and H. Sugi), "Saku Keisei Hannoh (Complexation in Analytical Chemistry)," Sangyou Tosho, Tokyo (1965), p. 329.

4) N. Nakasuka, "Saku Keisei Hannoh (Complex formation Reaction)," ed by Jpn. Soc. Anal. Chem., Maruzen, Tokyo (1974), p. 519.

5) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, New York (1952).