Fluorometric Determination of Aluminium(III) and Cadmium(II) by Solvent Extraction of the Ternary Complex Composed of Metal Ion, 8-Hydroxy-5-quinolinesulfonic Acid, and Methyltrioctylammonium Ion

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A fluorometric micro determination of aluminium(III) and cadmium(II) using the formation of metal–8-hydroxy-5-quinolinesulfonic acid–capriquat (methyltrioctylammonium) ternary complex is described. These complexes are easily extracted into chloroform phase and the extract emits a strong fluorescence. Spectra of aluminium(III) and cadmium(II) ternary complexes have the excitation maximum at 396 nm and 400 nm, and emission maximum at 501 nm and 524 nm, respectively. Fluorescence intensity of the aluminium(III) and cadmium(II) ternary complexes extracted into chloroform showed the constant and maximum values in the pH range of aqueous phase from 5.3 to 8.5 and 8.1 to 8.5, respectively. The calibration curves for aluminium(III) and cadmium(II) show good proportionality in the concentration range from 0.5 to 5.0 and 1.0 to 50.0 μg, respectively. The relative standard deviation observed with four measurements was found to be 1.8% for 0.5 μg of aluminium(III) and 1.1% for 10.0 μg of cadmium(II). The effect of diverse ions is studied and a 25-fold amount of Cu(II), Ni(II), Fe(II), Fe(III) in weight gave errors, however, the interferences were easily eliminated by the addition of appropriate masking agent. In the determination of cadmium(II), an equal amount of Co(II), Ni(II), Mn(II), Fe(III) and twice amount of Al(III) gave negative errors, however, the interference of Fe(III) and Al(III) were also eliminated as above.

It has been recognized that the 8-hydroxy-5-quinolinesulfonic acid (abbreviated as H_2qs), which is well known as a derivative of oxine, forms several water soluble complexes with many metal ions, which emit strong fluorescence around 520 nm. Cadmium(II)[1] and magnesium(II),[2] were determined fluorometrically in aqueous phase by using H_2qs as the chelating agent. Kina *et al.*[3] reported that the fluorescence intensity of some metal complex is enhanced in the presence of surfactant.

We reported the photometric determination of iron(III),[4] cobalt(II),[5] and zinc(II)[6] employing the ion-pair extraction of metal–H_2qs chelate anion with Zephiramine (benzyldimethyltetradecylammonium chloride) cation. Cadmium(II) was also determined spectrophotometrically with H_2qs after separation as an ion-pair of tetraiodocadmate(II) anion with Capriquat (methyltrioctylammonium chloride, abbreviated as Cq^+-Cl^-) cation. We also reported the fluorometric determination of zinc(II) by using the formation of zinc(II)–H_2qs–Cq ternary complex.[8]

In the present paper, the fluorometric micro determination of aluminium(III) and cadmium(II) was described. The fluorescence intensity of the ternary complex composed of aluminium(III)–, as well as cadmium(II)–H_2qs–Cq in chloroform phase is proportional to the amount of metal ion in the aqueous phase.

Experimental

Reagents. *Standard Solution of Aluminium(III) and Cadmium(II)*: Aluminium(III) and cadmium(II) standard solution (Wako Pure Chemicals Co., for atomic absorption use, 1000 ppm) was applied and diluted with water as required.

1 mM H_2qs Solution:† The solution was prepared by dissolving 0.2252 g of H_2qs (Wako Pure Chemicals Co.) with 1 dm^3 of water.

7 mM Capriquat–Chloroform Solution: The solution was prepared by dissolving Dotite Capriquat (methyltrioctylammonium chloride, Dojindo Laboratories) in chloroform.

Buffer Solutions: Acetate, borate, and acetic acid–ammonia buffer solutions were prepared and adjusted to the appropriate pH values.

Organic solvents used in this study were all of analytical reagent grade. All the solutions were prepared with once deionized and then twice distilled water.

Apparatus. Fluorescence intensity was measured with a Shimadzu Digital Spectrofluorophotometer, Model RF-510, equipped with a Shimadzu recorder, U-125MU. Fused quartz cells, 10 mm × 10 mm × 45 mm, were used throughout the study.

Procedure. *Determination of Aluminium(III)*: To a sample solution containing (0.1—5.0)μg of aluminium(III) are added a 7-ml portion of 1 mM H_2qs solution and a 10-ml portion of the buffer solution (pH 6.5). The mixture is diluted to 50 ml with water and shaken with 10 ml of 6 mM Capriquat–chloroform solution for 3 min and then allowed to stand for 30 min. The organic layer is transferred into a beaker containing anhydrous sodium sulfate to remove the remaining water. Then, the fluorescence intensity of the extract is measured at 396 nm (excitation) and 501 nm (emission).

Determination of Cadmium(II): To a sample solution containing (1.0—50.0) μg of cadmium are added 8 ml of 1 mM H_2qs solution and 10 ml of borate buffer solution (pH 8.3). The mixture is diluted to 50 ml with water and shaken with 10 ml of 7 mM Capriquat–chloroform solution for 3 min and then allowed to stand for 30 min. Organic layer is separated and fluorescence intensity is measured at 400 nm (excitation) and 524 nm (emission).

Results and Discussion

Fluorescence Spectra. The fluorescence spectra of the organic extract obtained by the above procedure are given in Fig. 1. The aluminium(III)–H_2qs–Capriquat ternary complex in chloroform exhibited the excitation maximum at 396 nm and the fluorescence emission maximum at 501 nm, whereas the cadmium(II) complex showed at 400 nm and at 524 nm, respectively.

† 1 M = 1 mol dm^{-3}.

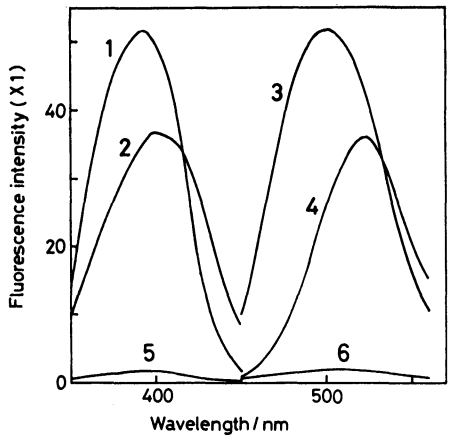

Fig. 1. Excitation and emission spectra.
Excitation spectrum of ternary complex: 1: Al(III) (λ_{Em}=501 nm), 2: Cd(II) (λ_{Em}=524 nm). Emission spectrum of ternary complex: 3: Al(III) (λ_{Ex}=396 nm), 4: Cd(II) (λ_{Ex}=400 nm), 5: excitation spectrum of reagent blank (λ_{Em}=501 nm), 6: emission spectrum of reagent blank (λ_{Ex}=524 nm).

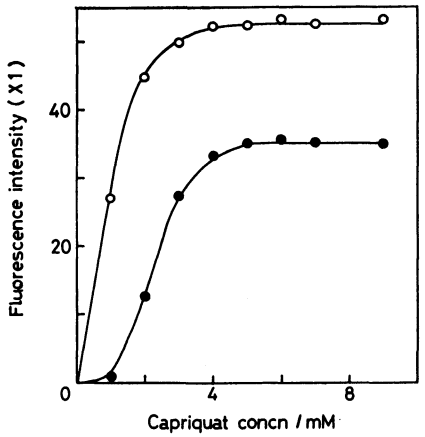

Fig. 2. Effect of Capriquat amount on the fluorescence intensity of chloroform extract.
—○—: Al(III) 5 μg/50 ml; $[H_2qs]_w$=0.2 mM; pH=7.7; λ_{Ex}=396 nm; λ_{Em}=501 nm. —●—: Cd(II) 50 μg/50 ml; $[H_2qs]_w$=0.2 mM; pH=8.3; λ_{Ex}=400 nm; λ_{Em}=524 nm.

An ion-pair of H_2qs–Capriquat was also extracted into chloroform, but showed a very weak fluorescence.

Effect of Capriquat Concentration. Effect of the Capriquat concentration on the fluorescence intensity is shown in Fig. 2. Capriquat–chloroform solutions of the various concentrations were added to the solution containing 5.0 μg of aluminium or 50.0 μg of cadmium with an excess amount of H_2qs at the optimum pH, and after extraction, the fluorescence intensity of the extract was measured. It was found that the fluorescence intensity shows a constant value for more than 4 mM of Capriquat for aluminium and 5 mM for cadmium. Thus, the concentration of Capriquat was adjusted to 6 mM for aluminium and 7 mM for cadmium.

Effect of H_2qs Amount. The effect of H_2qs concentration on the fluorescence intensity is shown in Fig. 3. The fluorescence intensity was found to be almost

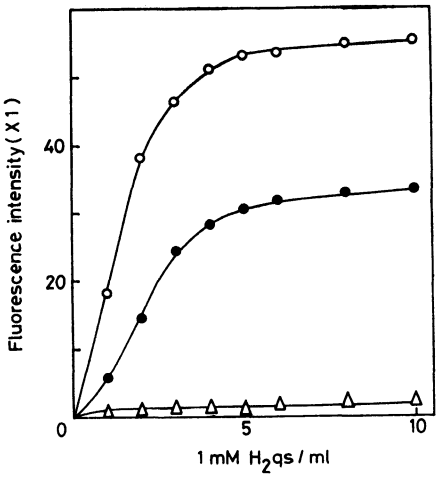

Fig. 3. Effect of H_2qs concentration on the fluorescence intensity of chloroform extract.
—○—: Al(III) 5 μg/50 ml; $[CqCl]_0$=6 mM; pH=7.7. —●—: Cd(II) 50 μg/50 ml; $[CqCl]_0$=8 mM; pH=8.3. —△—: Reagent blank.

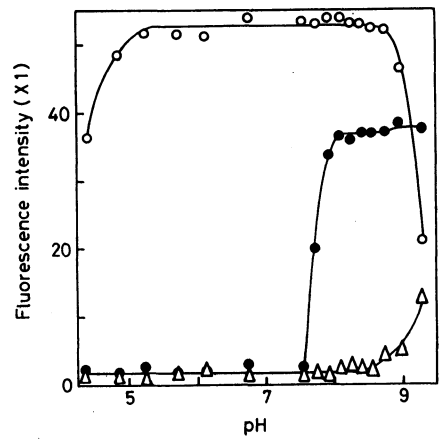

Fig. 4. Effect of pH on the fluorescence intensity o chloroform extract.
—○—: Al(III) 5 μg/50 ml; $[H_2qs]_w$=0.16 mM; $[CqCl]_0$=7 mM. —●—: Cd(II) 50 μg/50 ml; $[H_2qs]_w$=0.16 mM; $[CqCl]_0$=7 mM. —△—: Reagent blank.

Table 1. Selection of organic solvent

Organic solvent	Fluorescence intensity of ternary complex				Separation speed
	Al(III)[a]	Blank	Cd(II)[b]	Blank	
Chloroform	55.4	2.0	35.4	2.2	Fast
1,2-Dichloroethane	35.1	1.2	28.3	1.5	Fast
IBMK	28.9	1.3	31.5	1.4	Slow
Benzene	28.8	3.0	33.6	3.4	Slow
Xylene	24.3	3.5	33.2	3.6	Slow

a) Al(III) taken: 5.0 μg. b) Cd(II) taken: 50.0 μg.

constant, when more than 5 ml and 6 ml of 1 mM H_2qs solution were employed for aluminium(III) and cadmium(II), respectively. Therefore, the amount of H_2qs was kept to 7 ml for aluminium and 8 ml for cadmium.

TABLE 2. EFFECT OF DIVERSE IONS

Ion	M^{n+} added as	M^{n+} added (μg)	Al^{3+} found[a] (μg)	M^{n+} added (μg)	Cd^{2+} found[b] (μg)
Al^{3+}	$AlCl_3$	—	—	20	10.0[g]
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	500	1.01	1000	9.5
Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	5	0.99	20	10.4
Ca^{2+}	$CaCl_2$	500	0.97	1000	10.2
Cd^{2+}	$CdCl_2$	100	0.97	—	—
Co^{2+}	$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	5	0.90	10	8.6
Cr^{3+}	$CrCl_3 \cdot 6H_2O$	10	1.01	250	10.3
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	25	1.00[c]	10	9.5
Fe^{2+}	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	25	0.96[d]	20	9.8[d]
Fe^{3+}	$FeCl_3$	25	0.98[e]	10	7.6
Hg^{2+}	$HgSO_4$	100	1.02	100	10.0
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	500	1.05	250	10.2
Mn^{2+}	$MnSO_4 \cdot 4H_2O$	500	1.05	10	8.8
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	25	0.95[d]	10	8.1
Pb^{2+}	$Pb(NO_3)_2$	500	1.05	50	9.7
Sr^{2+}	$Sr(NO_3)_2$	500	0.98	1000	9.9
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	5	1.02[f]	10	25.7

a) Al(III) taken: 1.00 μg. b) Cd(II) taken: 10.0 μg. c) With thiourea. d) With ascorbic acid and phen. f) pH 5.3. g) With tiron.

Effect of pH. Effect of the pH of aqueous layer was examined. As shown in Fig. 4, the fluorescence intensity is constant over the pH range from 5.3 to 8.5 for aluminium(III) and from 8.1 to 8.5 for cadmium(II), while the observed blank value is very low. Thus, the pH was kept to 6.5 by 0.2 M acetic acid and 0.2 M ammonia for aluminium and to 8.3 by borate buffer for cadmium.

Organic Solvents. The effect of the various organic solvents on the fluorescence intensity was studied and the results were shown in Table 1. Benzene and xylene gave high blank value. Chloroform, 1,2-dichloroethane, and IBMK (isobutyl methyl ketone) gave low blank value, but the separation speed of IBMK was slow. Chloroform is adopted as the best organic slovent, because it shows the highest fluorescence intensity and the good separation was rapidly attained for both aluminium(III) and cadmium(II) complexes.

Effect of Shaking and Standing Time. A stable and constant fluorescence intensity of the extract was found with a shaking time longer than 1 min for both aluminium(III) and cadmium(II), so the shaking time was kept to 3 min. The optimum standing time was found to be 30 min for the both metal ions.

Calibration Curves. The calibration curves for aluminium(III) and cadmium(II) were obtained by the above procedures. A good proportionality between the fluorescence intensity and the concentration was observed in the concentration range from 0.1 to 2.0 μg for aluminium(III) and from 1.0 to 10.0 μg for cadmium-(II). At higher concentrations the calibration curve deviated slightly from the linearity, but the determination was feasible up to 5.0 μg for aluminium(III) and 30.0 μg for cadmium(II). The relative standard deviation observed with four measurements was found to be 1.8% for 5 μg of aluminium and 1.1% for 10.0 μg of cadmium.

Effect of Diverse Ions. The effect of sixteen cations on the determination of aluminium(III) and cadmium-(II) was studied. The results are summarized in Table 2. In the determination of 1.0 μg of aluminium(III), a 5-fold amount of cobalt(II) and 25-fold amount of copper(II), nickel(II), iron(II), and iron(III) reduced the fluorescence intensity, whereas a 5-fold amount of zinc(II) gave a positive error. However, the interferences were eliminated by the addition of thiourea for copper(II), together with 1,10-phenanthroline for nickel(II) and iron(II), and ascorbic acid with 1,10-phenanthroline for iron(III). The interference of zinc-(II) was eliminated by adjusting the pH to 5.3.

In the determination of 10.0 μg of cadmium(II), an equal amount in weight of cobalt(II), nickel(II), manganese(II), and iron(III) and a twice amount of iron(II) gave the negative errors, whereas an equal amount of zinc(II) and a twice amount of aluminium-(III) gave the positive errors. The interferences were eliminated, however, by the addition of 1,10-phenanthroline for iron(II) and tiron for aluminium(III).

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